



# OPEN Numerical study on ion migration in concrete under the influence of salt solution

Xianyuan Chen<sup>1,4</sup>, Zhaocai Meng<sup>3,4</sup>, Xinjiang Zheng<sup>2</sup>✉ & Zirui Gao<sup>4</sup>

This study investigates the migration and distribution of sulfate and chloride ions in concrete, incorporating the time-dependent relationship between the concrete compaction process and ion migration. Based on Fick's second law, a modified model for sulfate ion migration in concrete is established. The findings reveal that the sulfate ion concentration within concrete increases with time but at a decreasing rate, with the compaction process significantly affecting this growth. The distribution of sulfate ions shows a decrease with increasing depth, and the difference between the modified model and the diffusion model amplifies over time. The external ion concentration has a minor impact on the distribution pattern but affects the internal ion concentration. Additionally, the study indicates that cracks initiate within 30 mm of the concrete surface and extend with time, leading to structural degradation. The pore compactness process has a limited effect on chloride ion content, which remains relatively stable before concrete deterioration.

**Keywords** Ion migration, Chemical attack, Sulfate ion, Chloride ion, Numerical simulation

Sulfate attack poses a significant threat to the durability of concrete structures. Sulfate ions migrate through the pores of concrete, then chemically react with the solid phase of the concrete to produce poorly soluble salt-type products. These minerals, characterized by their low solubility, absorb substantial amounts of water, leading to expansion and the generation of internal swelling stresses. When the expansion stress exceeds the tensile strength of the concrete, it results in concrete degradation. Consequently, the deterioration of concrete subjected to sulfate attack can be conceptualized as a superposition of damage processes, which may be investigated separately according to the principle of disproportionation. The migration of chloride ions is also influenced by the pore densification process in concrete due to sulfate ion attack, especially when both sulfate and chloride ions collectively attack the concrete. Current research primarily focuses on the process of concrete damage and degradation, with limited attention given to the impact of the pore densification process. The formation of salt minerals is an irreversible process, and the newly formed, poorly soluble minerals continuously precipitate within the concrete pores, progressively filling them over time. This process impedes the migration of  $\text{SO}_4^{2-}$  and affects the movement of chloride ions within the concrete. The process of concrete densification directly influences the timing and location of concrete damage and deterioration.

Marchand et al. investigated the transport of  $\text{SO}_4^{2-}$  in concrete and the influence of chemical reaction products on ion diffusion properties<sup>1</sup>. Gospodino V et al. analyzed the pore filling by chemical reaction products in concrete and its effect on the transport of sulfate ions<sup>2,3</sup>. Li and Wang developed a damage prediction model for concrete in sulfate environments, considering the interplay between damage and compaction processes<sup>4</sup>. These methods are based on research into concrete damage and compaction processes but do not account for the time dependence of the  $\text{SO}_4^{2-}$  migration process. Zuo and Sun studied the distribution law of  $\text{SO}_4^{2-}$  concentration in concrete using the finite difference method<sup>5</sup>. Wan and Zuo analyzed the distribution of  $\text{SO}_4^{2-}$  in concrete and the variation in ion consumption due to chemical reactions<sup>6</sup>. Gospodinov and Kazandjiev established a mathematical model for the transport of  $\text{SO}_4^{2-}$  that describes how chemical products influence the erosion process of sulfate ions<sup>7</sup>. This approach, centered on the study of the concrete damage mechanism, did not consider the concrete densification process resulting from sulfate ion attack nor the response of the  $\text{SO}_4^{2-}$  migration process to diffusion reactions. Liang and Wang considered the diffusion coefficient of sulfate ions as a function of water-to-ash ratio and erosion time but did not provide a mathematical model for analyzing sulfate ion migration within concrete<sup>8</sup>. Chen and Tang conducted indoor modeling experiments to examine ion

<sup>1</sup>Fuzhou Urban Greening Management Office, Fuzhou 350001, China. <sup>2</sup>Institute of Ocean Engineering, Shenzhen International Graduate School, Tsinghua University, Beijing, China. <sup>3</sup>Fuzhou Planning & Design Research Institute Group Co. Ltd., Fuzhou 350108, China. <sup>4</sup>Department of Civil Engineering, Shanghai Jiao Tong University, Shanghai 200240, China. ✉email: xinjiangzheng@tsinghua.edu.cn

distribution and degradation characteristics under the dual attack of  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$ . Jin and Sun analyzed the mutual effects of sulfate and chloride salt complex attack on ion migration within concrete<sup>10</sup>. Liu and Li studied the diffusion pattern of chloride ions affected by sulfate ions by investigating the chloride diffusion model under sulfate environments<sup>11</sup>.

Although previous studies have explored the migration of sulfate ions in concrete, the influence of chemical reaction products on ion diffusion properties, and the damage mechanisms of concrete under the combined action of sulfate and chloride ions, these studies have not adequately considered the time dependence of the sulfate ion migration process and the impact of the concrete pore densification process on ion transport. This paper investigates the pore densification process in concrete due to sulfate attack and analyzes the transport of  $\text{SO}_4^{2-}$  and chloride ions within the concrete. A model of sulfate ion transport inside concrete is established, taking into account the densification process and the time dependence of the ion transport process, based on Fick's second law. Additionally, a simplification analysis of chloride ion migration under the influence of sulfate ions is conducted. The models are validated using existing data. In an environment of sodium sulfate solution and chloride ion attack, the migration of sulfate and chloride ions through the densification process of concrete pores is simulated using COMSOL Multiphysics software. The distribution of sulfate and chloride ions within the concrete is analyzed over time and space.

## Analysis of ion transport mechanism in concrete

### Diffusion based on Fick's second law

The Fickian diffusion equation serves as the fundamental physical principle for describing the ion transport mechanism within the pore solution of concrete structures. By assuming that ion transport within concrete behaves as a one-dimensional diffusion problem in a semi-infinite medium, the concentration of ions can be readily determined using the Fick equation, as shown in Eq. (1).

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (1)$$

where  $C$  represents the ion concentration at a depth  $x$  within the concrete at time  $t$ , and  $D$  is the ion diffusion coefficient ( $\text{m}^2/\text{s}$ ).

### Sulfate ion transport equation with consideration of chemical reaction

Sulfate ions penetrate the concrete through its pores and react chemically with the solid phase of the concrete to form insoluble salts. This process involves both the demineralization reactions and the migration of ions through the concrete pores. Assuming that the volume of the concrete is not altered by sulfate ion attack and that the pores in the concrete do not interact with each other, the concentration of sulfate ions within the concrete can be derived based on the conservation of ion mass and Fick's second law, as presented in Eq. (2)<sup>12</sup>.

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial C}{\partial x} \right) + \frac{\partial}{\partial y} \left( D \frac{\partial C}{\partial y} \right) - kC \quad (2)$$

where  $k$  is the rate constant for the chemical reaction between sulfate ions and the concrete solid phase ( $\text{s}^{-1}$ ). The value of  $k$  is influenced by the surface area of the concrete pore that is in contact with sulfate ions.

### Effect of concrete porosity

Sulfate ions that have infiltrated the concrete react with the solid phases to form poorly soluble minerals, a process that is irreversible and intensifies over time<sup>11</sup>. To investigate the impact of reactants on the filling of concrete pores, it is assumed that the newly formed minerals are continuously adsorbed onto the walls of the concrete pores, thereby diminishing the pore cross-sectional area. As depicted in Fig. 1, the thickness of the adsorption layer is denoted as  $\delta(Z, t)$ , and  $R_0$  represents the average radius of the concrete pores. The thickness  $\delta(Z, t)$  is greatest in the vicinity of the contact surface, where sulfate ions react most promptly and thoroughly with the concrete solid phase, as well as with the reaction by-products.

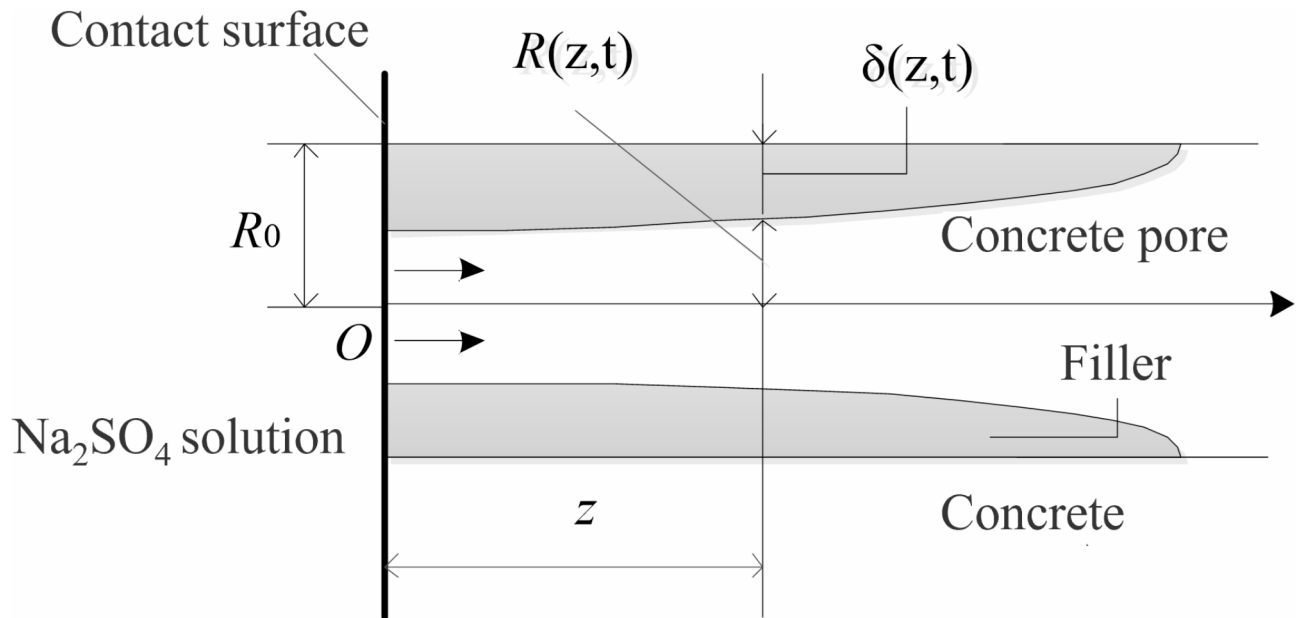
Considering that sulfate ions migrate through individual pores in the concrete without being influenced by the transport of sulfate ions from adjacent pores, the modified diffusion coefficient of sulfate ions during the process of concrete pore filling can be determined using Eq. (3)<sup>13</sup>.

$$D_{\text{eff}} = D \frac{F(z)}{F_0} \quad (3)$$

where  $z$  represents the migration distance of sulfate ions within the concrete pores, and  $F_0$  is the average cross-sectional area of the concrete pores at the initial time  $t=0$ .  $F(z)$  denotes the cross-sectional area of the pores at a depth  $z$  within the concrete at time  $t$ , which can be calculated using Eq. (4).

$$F(z) = \pi R(z, t)^2 = \pi [R_0 - \delta(z, t)]^2 \quad (4)$$

According to Eqs. (2) and (3), the equivalent diffusion coefficient of sulfate ions during the filling process of concrete pores can be obtained.



**Fig. 1.** Longitudinal cross-section of concrete pores.

$$D_{\text{eff}} = D_{28} \left[ 1 - \frac{\delta(z,t)}{R_0} \right]^2 \quad (5)$$

where,  $D_{28}$  is the diffusion coefficient of sulfate ions in concrete at 28 days,  $\delta(z,t)/R_0$  is the ratio between the adsorption layer on the concrete pore wall and the concrete pore radius, which is proportional to the quantity  $q$  ( $\text{kg}/\text{m}^3$ ) of intrusive sulfate ions consumed by the chemical reaction in the concrete.

$$\frac{\delta(z,t)}{R_0} = k_z q \quad (6)$$

where  $k_z$  is the correlation coefficient.

### The binding effect of concrete solid phase on chloride ions

Chloride ions within concrete are categorized into free and bound states. The energy of the concrete solid phase adsorbs a certain quantity of free chloride ions. In addition to physical adsorption, chloride ions can also react with tricalcium aluminate (C3A) to form Friedel's salt. There exists a relatively distinct proportional relationship between the free and total chloride ions in both ordinary and high-performance concretes, which ranges approximately from 0.77 to 0.89<sup>13</sup>.

### Modified ion transport equation

Based on the equivalent diffusion method, the equivalent diffusion coefficients of sulfate ions and chloride ions in concrete can be expressed as Eq. (7).

$$D_{i,\text{eff}} = K_0 D_{i,28} \quad (7)$$

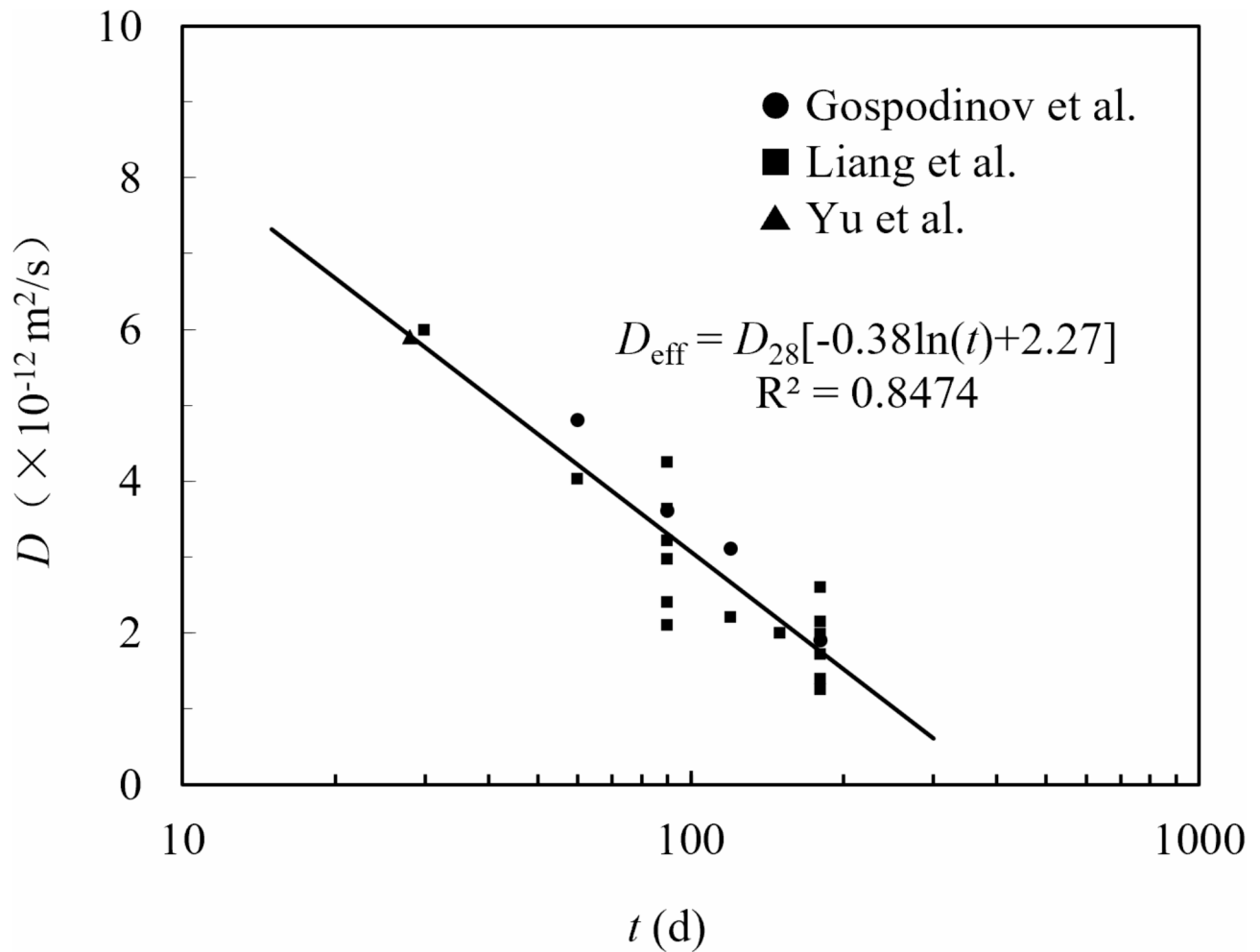
where  $K_0$  is the equivalent coefficient. When concrete is subjected to the simultaneous attack of sulfate and chloride ions, the densification process of pore filling within the concrete primarily occurs because the reaction products of sulfate ions with the concrete solid phase adsorb to the pore walls, thereby reducing the cross-sectional area of the concrete pores. The change in the ion diffusion coefficient is mainly attributed to the alteration of the concrete pore cross-sectional area. Consequently, the value of  $K_0$  can be determined through fitting based on the existing data of the sulfate ion diffusion coefficient as it varies with time.

Figure 2 shows the change of sulfate ion diffusion coefficient with time<sup>8,12,14</sup>. According to the data, the fitting Eq. (8) can be obtained.

$$K_0 = -0.38 \ln(t) + 2.27 \quad (8)$$

where  $t$  is the age of concrete (day). Equation (7) captures the temporal dependency of the diffusion coefficient changes for sulfate and chloride ions in concrete, which is influenced by the pore-filling process within the concrete.

According to Eqs. (4) and (6), we get



**Fig. 2.** Variation of the diffusion coefficient of sulfate ion with time.

$$K_0 = \left[ 1 - \frac{\delta(z, t)}{R_0} \right]^2 \quad (9)$$

$$k_z q = 1 - (K_0)^{1/2} \quad (10)$$

Equation (9) delineates the time-dependent nature of the concrete pore-filling process, while Eq. (10) formulates the relationship between the number of sulfate ions that have infiltrated the concrete and are consumed by the reaction as a function of time.

In conclusion, within the dense phase of concrete affected by sulfate ion intrusion, temperature variations are not taken into account. Concurrently, it is assumed that the pores are fully saturated, and ion migration occurs along individual concrete pores, independent of the influence from adjacent pores and the transport of sulfate ions within them. A modified equation for the migration of sulfate ions within concrete during the densification process has been provided.

$$\frac{\partial C}{\partial t} = \left[ \frac{\partial}{\partial x} \left( D_{i, \text{eff}} \frac{\partial C}{\partial x} \right) + \frac{\partial}{\partial y} \left( D_{i, \text{eff}} \frac{\partial C}{\partial y} \right) \right] - (K_0)^{1/2} k C \quad (11)$$

where  $(K_0)^{1/2}$  represents the relationship between the influence of chemical reaction rates. When  $i$  is a chloride ion, considering the adsorption effect of chloride ions on the concrete solid phase, the chloride ion diffusion coefficient should also be adjusted by multiplying it with a reduction factor of 0.85.

### Soundness of concrete

Soundness of concrete refers to the property of not exhibiting cracks, disintegration, or other flaws due to excessive volume change. This volume change is primarily caused by the hydration of crystalline magnesia, specifically periclase (MgO), present in cement. Measuring the soundness of concrete is crucial for ensuring the durability and performance of structures. Common methods for assessing concrete soundness include the ASTM

C151 autoclave expansion test (AET), water storage expansion test, Le Chatelier split ring test, and modified AET with a longer pre-autoclave curing period. Each method has its own advantages and disadvantages, and the choice of method depends on specific requirements and available resources<sup>15,16</sup>.

Description of the finite element model  
Model design

The COMSOL Multiphysics software was employed to develop a migration model for ions within the concrete protective layer, which is based on the modified ion migration equation for concrete. The model dimensions were set at 80 mm × 80 mm. Considering the significant fluctuations in ion concentration near the boundary where the concrete interfaces with the external solution, a finer mesh was applied in this region to mitigate the potential for aberrant ion concentration values at the boundary. The boundary and initial conditions for the model are as follows:

$$\begin{cases} t = 0 & 0 < x < L & C_i = C_{i,init} \\ t > 0 & x = 0 & C_i = C_{i,b}; \quad x = L & \frac{\partial C_i}{\partial x} = 0 \end{cases} \tag{12}$$

where, *L* is the thickness of the protective layer (that is, the width of the model).

Model environment and calculation parameters

When the external ion concentration is elevated, numerical comparison of the computed ion distribution is advantageous for analyzing the migration mechanism of ions during concrete pore filling and the distribution of ions within the concrete. To account for the influence of varying external sulfate ion concentrations, the ion concentrations at the boundary can be set to the sulfate ion concentrations found in 5% and 10% sodium sulfate solutions, which are approximately 350 mol/m<sup>3</sup> and 700 mol/m<sup>3</sup>, respectively. The chloride ion content at the model boundary can be assigned the upper limit of the chloride ion concentration observed in the salt content of the Nantong Binhai Region, which is roughly 250 mol/m<sup>3</sup>.

The calculation parameters are shown in Table 1.

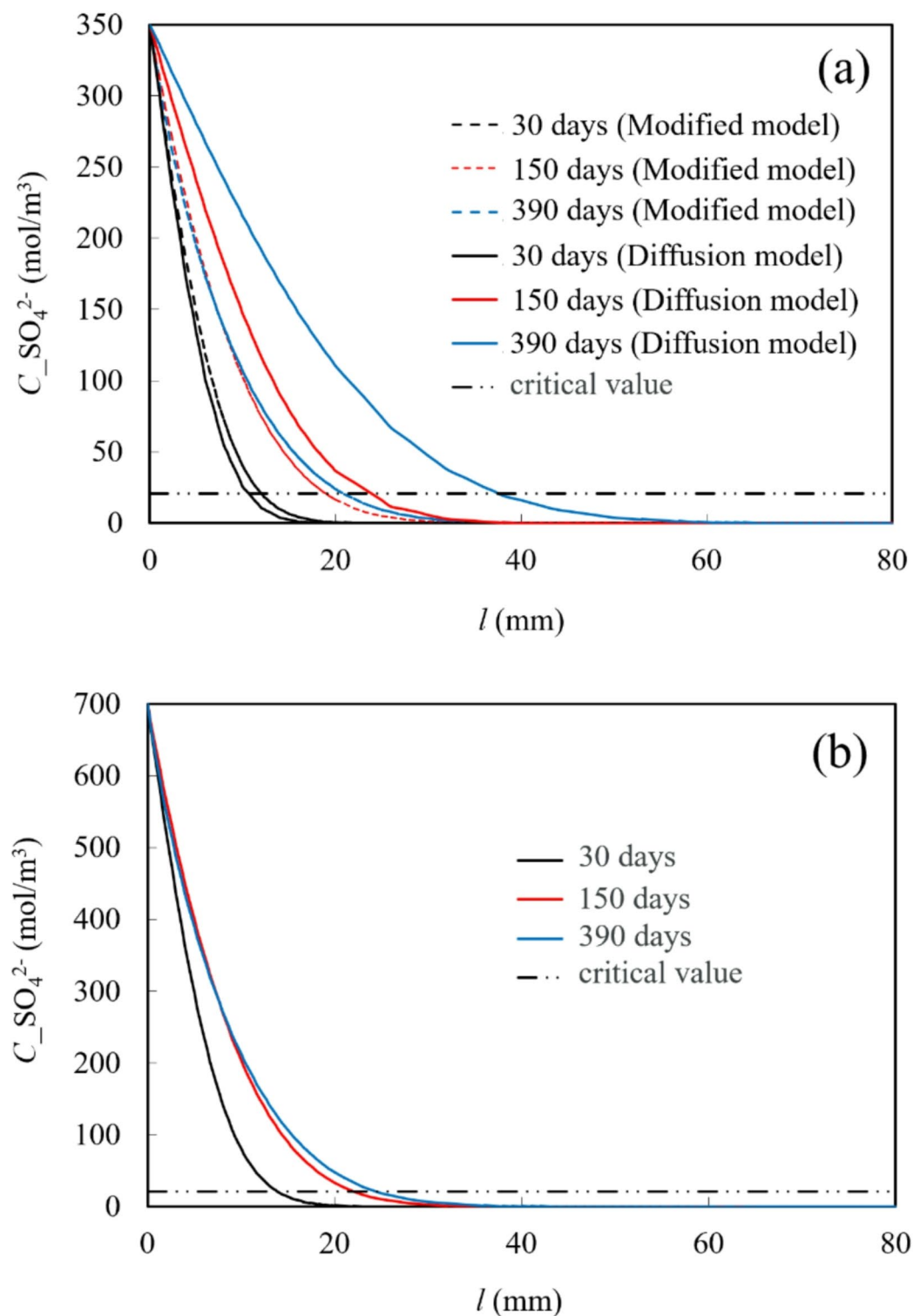
Results and analysis  
Distribution of sulfate ions over time and space

Figure 3(a) depicts the distribution of sulfate ions within concrete when the model boundary is exposed to a 5% sodium sulfate solution, without considering the concrete compaction process. Here, *C*<sub>SO<sub>4</sub><sup>2-</sup> represents the sulfate ion concentration, and *l* denotes the distance from the concrete surface. The figure illustrates that over time, the concentration of sulfate ions in concrete increases gradually, with a decelerating rate of increase. In the modified sulfate ion migration model, the rate of sulfate ion accumulation in concrete decreases sharply with increasing time. For instance, at a depth of 15 mm within the concrete, the sulfate ion concentration is 2.5 mol/m<sup>3</sup> after 30 days under the diffusion model. In comparison, after 150 days and 390 days, the concentrations reach 79.6 mol/m<sup>3</sup> and 158.5 mol/m<sup>3</sup>, respectively, representing increases of 31.8 times and 63.4 times. When the concrete pore filling process is considered, the sulfate ion concentrations at a depth of 15 mm after 30, 150, and 390 days are 6.6 mol/m<sup>3</sup>, 45.1 mol/m<sup>3</sup>, and 53.8 mol/m<sup>3</sup>, respectively. Compared to the 30-day mark, the ion content at 150 days and 390 days, increases by only 6.8 times and 8.2 times, respectively. This demonstrates that accounting for the concrete compaction process significantly affects the growth of sulfate ions over time. This is due to the fact that in the early stages of sulfate ion attack on concrete, as time progresses, the reaction between sulfate ions and the concrete solid phase generates more reaction products, which fill the concrete pores, refining the pore structure and reducing internal defects, thereby increasing concrete density and impeding sulfate ion migration. Simultaneously, the invading sulfate ions react biochemically with the concrete solid phase, diminishing the content of free sulfate ions within the concrete pores. The stage of concrete pore densification is beneficial in retarding the sulfate ion attack on concrete; however, with the increasing formation of poorly soluble salt-type minerals, the newly formed minerals can absorb a significant amount of water, leading to volume expansion that may result in concrete destruction if the expansion stress exceeds the concrete’s tensile strength.</sub>

The concentration of sulfate ions within concrete decreases progressively with increasing depth of ion penetration. In the initial stages of ion invasion, the ion distribution curves in concrete are similar under both models, but the discrepancy between them widens over time. For example, at 30 days, the sulfate ion distribution curves in concrete under the diffusion model and the modified model are nearly identical. At depths of 5 mm, 10 mm, and 15 mm in the concrete, the sulfate ion contents under the diffusion model are 241.0 mol/m<sup>3</sup>, 147.2 mol/m<sup>3</sup>, and 79.6 mol/m<sup>3</sup>, respectively, at 150 days, representing reductions of 0.61 times and 0.33 times

	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>
<i>D</i> <sub>28</sub> (m <sup>2</sup> /s)	5.90 × 10 <sup>-12</sup>	4.72 × 10 <sup>-11</sup>
<i>C</i> <sub>pinit</sub> (mol/m <sup>3</sup> )	0	0
<i>C</i> <sub>pb</sub> (mol/m <sup>3</sup> )	350	250
	700	

Table 1. The calculation parameters.



**Fig. 3.** Distribution of sulfate ion concentration in concrete.

at the 10 mm and 15 mm depths, respectively, compared to the 5 mm depth. At 390 days, the contents are 280.9 mol/m<sup>3</sup>, 215.7 mol/m<sup>3</sup>, and 158.5 mol/m<sup>3</sup>, respectively, with similar reduction rates. Under the modified ion transport model at 150 days, the sulfate ion contents are 200.0 mol/m<sup>3</sup>, 102.3 mol/m<sup>3</sup>, and 49.1 mol/m<sup>3</sup>, respectively, with reductions of 0.51 times and 0.25 times at the 10 mm and 15 mm depths, respectively, compared to the 5 mm depth. At 390 days, the contents are 194.9 mol/m<sup>3</sup>, 106.8 mol/m<sup>3</sup>, and 53.8 mol/m<sup>3</sup>, respectively, with reductions of 0.54 times and 0.28 times. This indicates that considering the concrete pore filling process has a minimal impact on the spatial distribution of sulfate ions in concrete but a significant effect



on their concentration. Within the same time period, the sulfate ion content in concrete that accounts for the densification process is substantially lower.

Figure 3(b) illustrates the distribution of sulfate ions within the modified sulfate ion migration model, assuming a boundary condition of a 10% sodium sulfate solution. The figure reveals that the temporal and spatial distribution pattern of sulfate ions in concrete is comparable to that observed when the boundary condition is a 5% sodium sulfate solution. This indicates that variations in the concentration of external sulfate ions do not influence the temporal and spatial distribution of sulfate ions within the concrete matrix. However, the concentration of sulfate ions within the concrete is significantly affected by the external ion concentration. Higher concentrations of external sulfate ions result in greater sulfate ion content within the concrete at equivalent time points and depths. As time progresses, the disparity in ion content increases, although the magnitude of this increase remains relatively consistent. For instance, at a depth of 15 mm in the concrete, the sulfate ion concentrations after 30, 150, and 390 days are 6.6 mol/m<sup>3</sup>, 45.1 mol/m<sup>3</sup>, and 53.8 mol/m<sup>3</sup>, respectively, when the boundary condition is a 5% sodium sulfate solution. In contrast, when the boundary condition is a 10% sodium sulfate solution, the concentrations are 13.4 mol/m<sup>3</sup>, 89.3 mol/m<sup>3</sup>, and 106.6 mol/m<sup>3</sup>, respectively, representing increases of 2.03 times, 1.98 times, and 2.36 times compared to the 5% solution conditions.

It is worth noting that the observed pronounced temporal concentration change in Fig. 3b, despite the negligible spatial distribution impact due to external sulfate concentrations, can be attributed to the nature of diffusion and the specific model conditions. The one-dimensional model focuses on the depth into the concrete, where the boundary condition (external sulfate concentration) directly influences the concentration gradient at the surface, driving the diffusion process. The time dependency of diffusion and the cumulative effect of continuous diffusion over time lead to significant differences in internal concentrations. Additionally, the interaction with pore filling, which is also time-dependent, further amplifies the differences in internal concentrations. While the model does show sensitivity to the initial boundary conditions, this is not necessarily an indication of oversensitivity but rather a natural consequence of the diffusion process and the specific conditions of the model.

### Durability of concrete under sulfate ion attack

Du and Li<sup>17</sup> have indicated that the corrosion resistance coefficient of concrete is typically 0.8. In this context, if the water-cement ratio of the concrete is 0.38, it can be inferred that the concrete structure's durability is compromised when the mass concentration of sulfate ions reaches 2.0 g/L. The corresponding molar concentration is 20.8 mol/m<sup>3</sup>. As depicted in Fig. 3, during the pore compaction phase of concrete, at depths greater than 30 mm, the sulfate ion concentration remains below the critical level even when exposed to an external concentration of 10% sodium sulfate solution. However, within the first 30 mm of the concrete, the sulfate ion concentration exceeds the critical value. Consequently, as the duration of ion attack increases, an increasing number of physical and chemical reaction products accumulate within the concrete pores within this 30-mm zone. These products exert pressure on the pore walls, ultimately generating an expansion stress that surpasses the concrete's tensile strength. This leads to the formation of cracks in the concrete, which propagate and cause the surface layer to spall off. Subsequently, sulfate ions at depths greater than 30 mm start to exceed the critical concentration, and concrete cracking extends beyond this depth, ultimately resulting in the degradation of the concrete structure.

### Distribution of sulfate ions at different depths of concrete

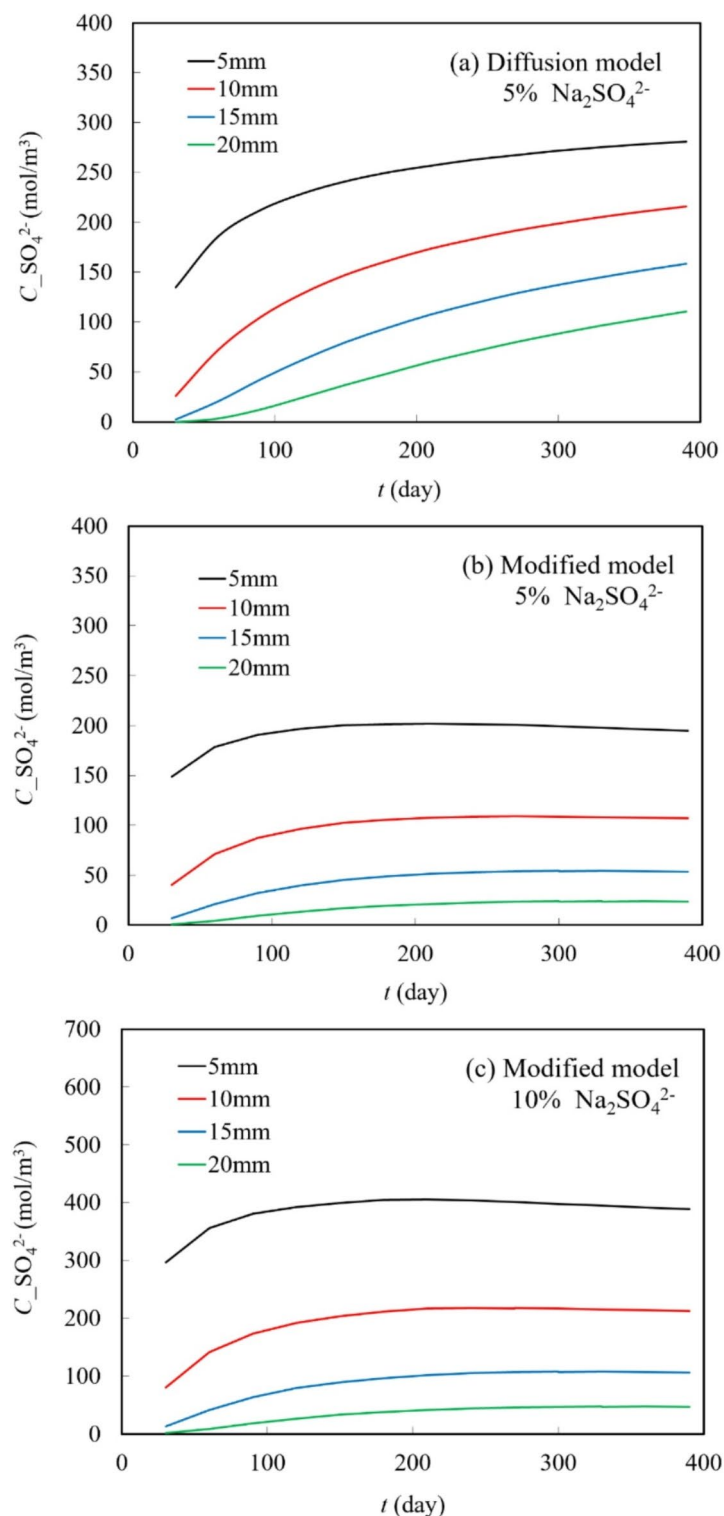
Figure 4 illustrates that accounting for the concrete pore densification process significantly influences the temporal distribution of sulfate ions at varying depths within the concrete, as compared to the diffusion model. When the concrete is exposed to a 10% sodium sulfate solution, the distribution of internal sulfate ions over time and space resembles that observed in a 5% sodium sulfate solution. During the pore compaction phase of concrete, the concentration of sulfate ions at different depths increases over time, although the rate of increase diminishes sharply. As time progresses to a certain point, the sulfate ion content at various depths within the concrete tends to stabilize, showing minimal change with further increases in time.

At a depth of 5 mm from the concrete surface, following an initial period of sulfate ion intrusion, there is a slight decline in the concentration of sulfate ions. This occurs because, as the duration of ion attack extends, the concrete solid phase on the surface undergoes chemical reactions or physical crystallization with sulfate ions, thereby filling the pores on the concrete surface. This results in a denser concrete surface and impedes the deeper penetration of sulfate ions. Concurrently, sulfate ions that have penetrated the surface layer continue to migrate to the deeper regions of the concrete, while the concentration of sulfate ions at the surface decreases significantly due to the initial compaction.

The surface layer of the concrete undergoes compaction first, and the insoluble salt minerals formed during this process absorb substantial amounts of water, leading to volume expansion. When the expansion stress exceeds the concrete's tensile strength, failure occurs. Consequently, under sulfate attack, the failure mode of concrete progresses from the surface inward, with cracking and degradation initiating at the surface. Once cracks form, external sulfate ions rapidly infiltrate the concrete through these pathways. The products of chemical reactions or physical crystallization further fill the pores or cracks, exacerbating cracking and damage, and thereby substantially reducing the service life of the concrete structure. Therefore, the impact of the concrete pore densification process on concrete durability warrants considerable attention.

### Distribution of chloride ions over time and space

Figure 5 depicts the distribution of chloride ions within concrete when the process of concrete pore densification is neglected.  $C_{Cl}$  represents the concentration of chloride ions, while  $l$  denotes the distance from the concrete surface. The figure clearly indicates that the consideration of the concrete pore compaction process significantly

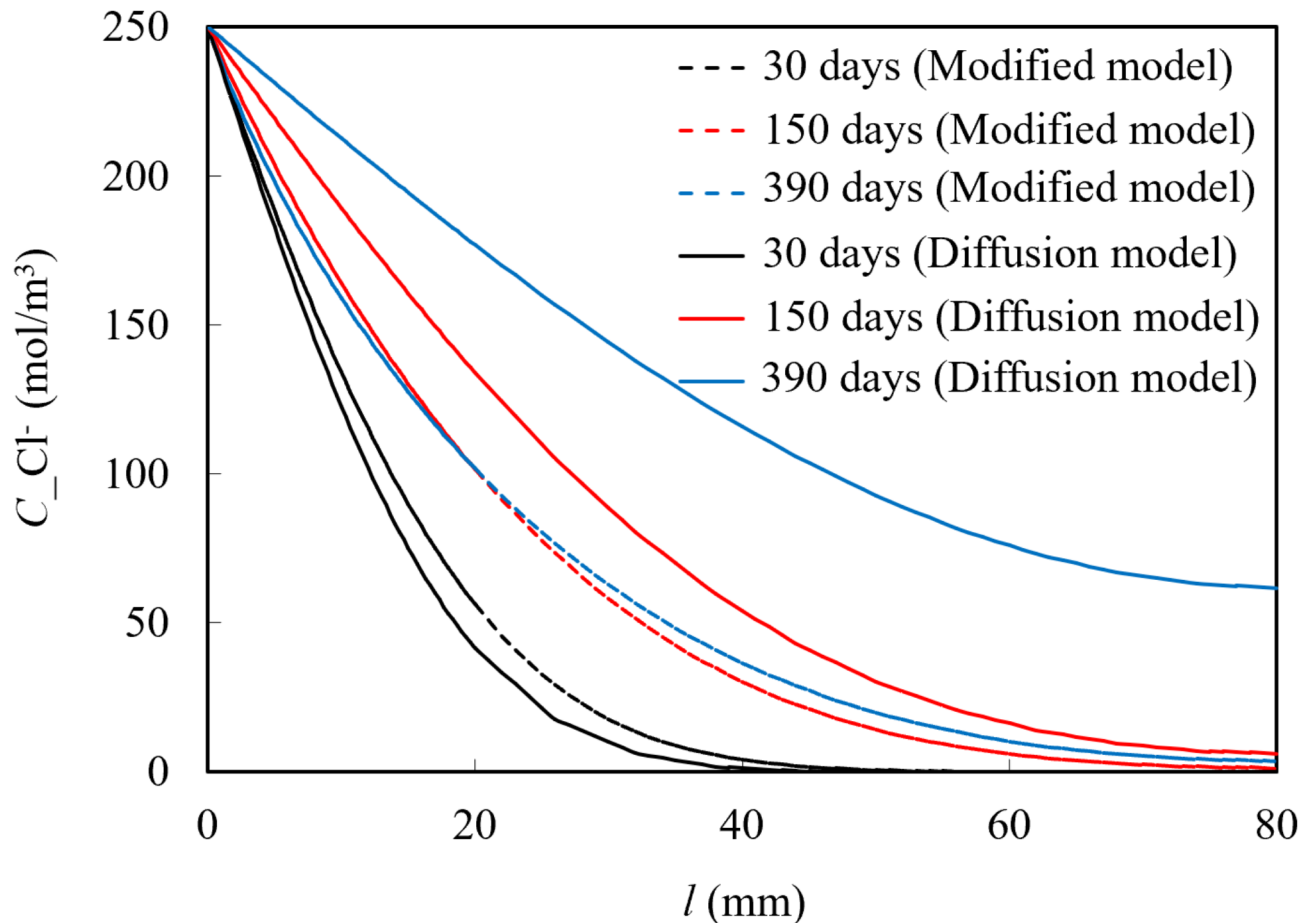


**Fig. 4.** Distribution of sulfate ions at different depths of concrete.

affects the chloride ion content within the concrete. During the pore-filling phase of concrete, the rate of increase in chloride ion content diminishes sharply over time. This reduction is attributed to the physical and chemical reaction products formed between sulfate ions and the solid phase of the concrete, which decrease the effective cross-sectional area of the concrete pores, thereby impeding the intrusion of chloride ions into the concrete's interior.

At a concrete age of 30 days, the chloride ion content in the concrete, as predicted by the modified model, exceeds that of the diffusion model. This discrepancy arises because the diffusion coefficient of chloride ions





**Fig. 5.** Distribution of chloride ion in concrete.

decreases progressively as the ion erosion process evolves. However, when the concrete age is less than 28 days, the actual diffusion coefficient of chloride ions in the modified model is greater than the apparent diffusion coefficient of chloride ions at 28 days, as used in the diffusion model. At 30 days, the concrete under the modified model, which accounts for the pore compaction process, has accumulated a higher chloride ion content compared to the diffusion model.

As the concrete age exceeds 28 days, the diffusion coefficient of chloride ions decreases abruptly due to the physical and chemical reaction products that fill the pores, resulting from the interaction between sulfate ions and the concrete solid phase. Consequently, the chloride ion content in the concrete, as predicted by the modified model, increases at a much slower rate.

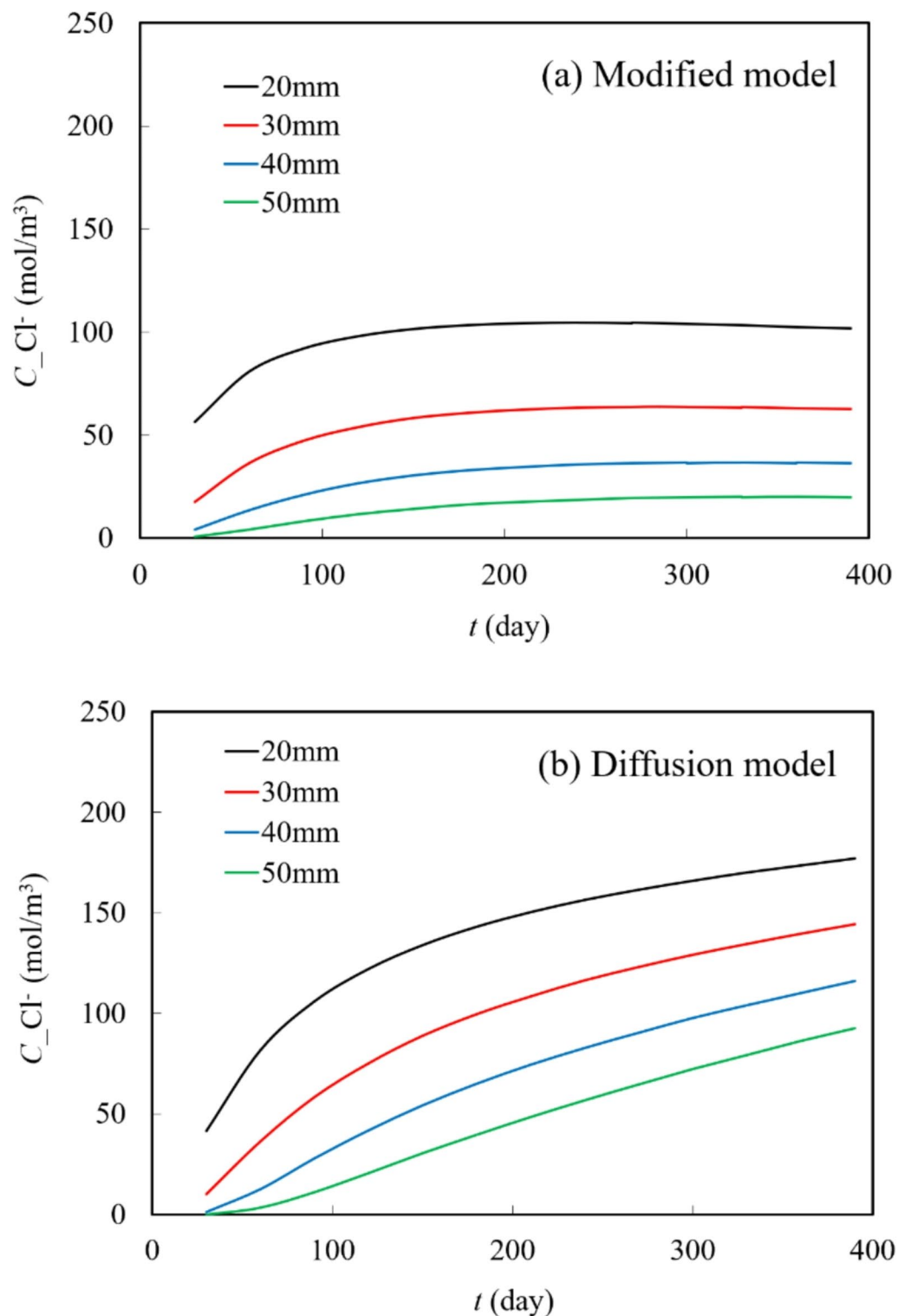
#### The distribution of chloride ions at different depths

Figure 6 demonstrates that, in contrast to the diffusion model, the influence of incorporating the concrete pore compaction process on the temporal distribution of chloride ions at various depths within the concrete is pronounced. Following a period of ion infiltration into the concrete, the chloride ion content at different depths, as predicted by the modified model, remains relatively stable over time.

#### Validation

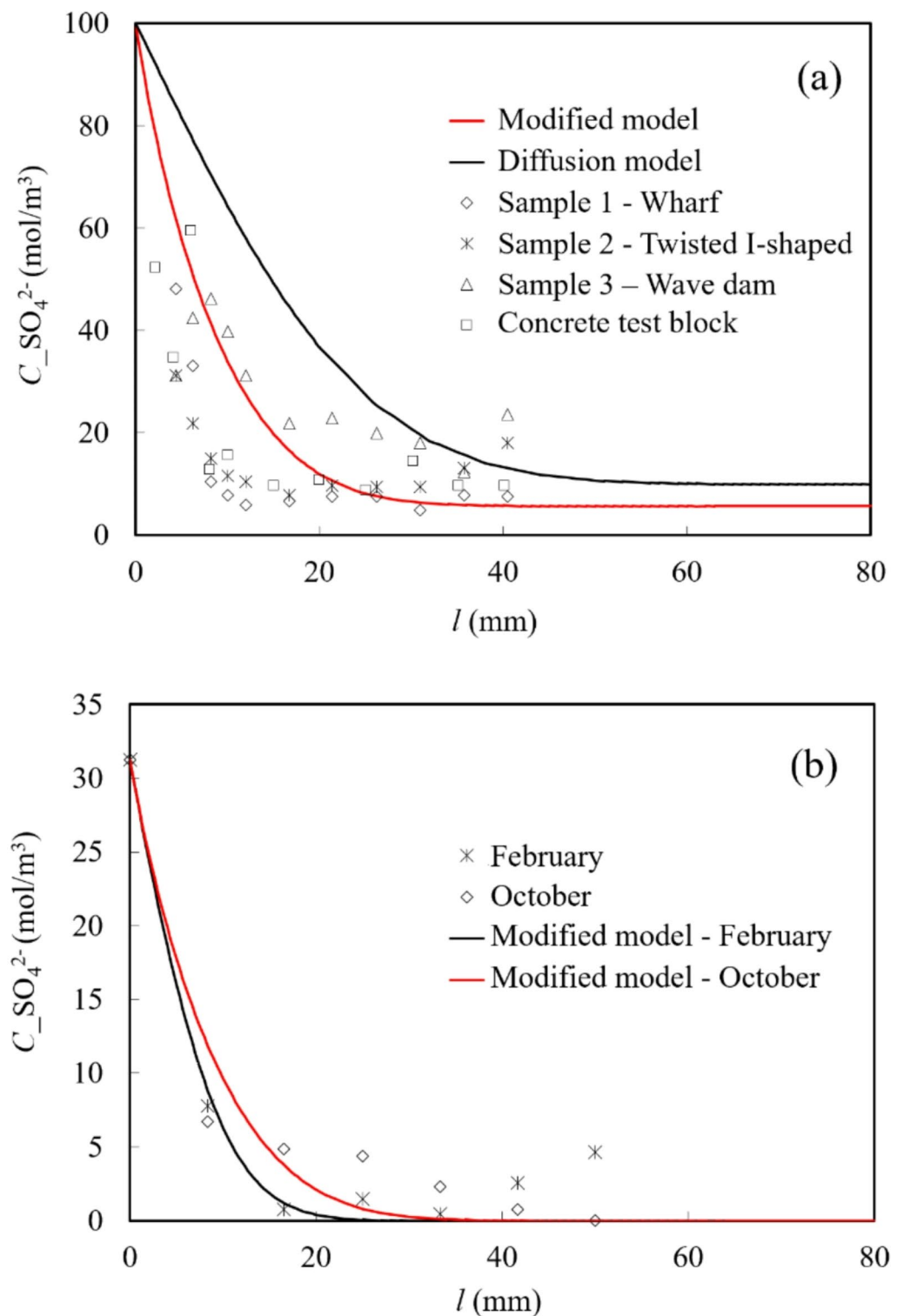
Ma et al.<sup>18</sup> subjected a concrete test block to exposure in the ocean spray zone for a period of 12 months. They collected samples from various structural elements, including a wharf, wave dam, and I-shaped concrete members, all of which had been exposed to the ocean spray environment for 12 months. Utilizing the spectrophotometer method, they measured the sulfate radical content within the concrete ions, and the findings are presented in Fig. 7(a). The sulfate ion concentration at the model's boundary was inferred from the measured concentration distribution curve, yielding an approximate value of 100 mol/m<sup>3</sup>. The initial sulfate ion concentration in the concrete was estimated to be around 10 mol/m<sup>3</sup>. Condor et al.<sup>19</sup> immersed concrete test blocks in a 3000 mg/L sulfate solution for 10 months, resulting in a sulfate ion concentration at the model boundary of approximately 31.3 mol/m<sup>3</sup>, as shown in Fig. 7(b). The results indicate a good agreement between the model's calculation outcomes and the actual measured data, thereby validating the model's accuracy.

Figure 7 shows that the model prediction agrees well with the experimental data as a whole, but there are some deviations under extreme ion concentration and long-term exposure, which may be due to the simplification of



**Fig. 6.** The distribution of chloride ions at different depths.

model assumptions, changes in concrete characteristics, environmental factors and long-term effects of chemical reactions. Although the specific bias is not known, its acceptability is usually judged by assessing relative error and prediction accuracy. Future studies need to optimize the model and include more influencing factors to improve the prediction accuracy. At present, the model is only used to predict the results in the range of normal ion concentrations, and the model is no longer suitable for the case of extreme ion concentrations.



**Fig. 7.** Comparison of calculated results and measured results of sulfate ion concentration.

## Conclusion

In this study, we have developed a model for sulfate ion migration in concrete based on Fick's second law, taking into account the time-dependent relationship between the concrete compaction process and ion migration. We have conducted a simplified analysis of chloride ion migration under the influence of sulfate ions and examined the distribution of sulfate and chloride ions in concrete over time and space during the pore compaction stage. The primary findings are as follows:

- (1) The concentration of sulfate ions within the concrete increases progressively over time, with a decreasing rate of increase. In the modified sulfate ion migration model, the growth rate of sulfate ions within the concrete decreases markedly as time progresses. The consideration of the concrete compaction process has a significant impact on the temporal growth of sulfate ion concentrations.
- (2) The sulfate ion concentration within the concrete diminishes as the depth of ion penetration increases. Early in the ion intrusion process, the amended model exhibits a sulfate ion distribution profile similar to that of the diffusion model, with the discrepancy between the two models widening over time. The consideration of the concrete pore-filling process has a negligible effect on the spatial distribution pattern of sulfate ions within the concrete but exerts a substantial influence on the sulfate ion concentration. Over the same period, the sulfate ion content within the concrete is significantly lower when the compaction process is taken into account.
- (3) Changes in external sulfate ion concentration have a minimal impact on the temporal and spatial distribution of sulfate ions within the concrete but do affect the internal sulfate ion concentration. Higher external ion concentrations result in greater sulfate ion content at the same time and depth within the concrete, with the disparity in ion content increasing over time, albeit with a modest rate of change.
- (4) As the duration of ionic attack increases, cracks initially form within the first 30 mm of the concrete and subsequently propagate to depths greater than 30 mm, ultimately leading to the degradation of the concrete structure. Accounting for the concrete pore compactness process has a limited effect on the chloride ion content within the concrete. Under the modified model, the chloride ion content in the concrete remains largely constant over time before the onset of concrete deterioration.

### Data availability

All data used during the study are available from the corresponding author by request.

Received: 11 December 2024; Accepted: 1 April 2025

Published online: 11 April 2025

### References

1. Marchand, J., Samson, E. & Maltais, Y. Theoretical analysis of the effect of weak sodium sulfate solutions on the durability of concrete. *Cem. Concr. Compos.* **24** (3), 317–329 (2002).
2. Gospodinov, P. N., Kazandjiev, R. & Mironova, M. The effect of sulfate ion diffusion on the structure of cement stone. *Cem. Concr. Compos.* **18** (6), 401–407 (1996).
3. Gospodinov, P. N. Numerical simulation of 3D sulfate ion diffusion and liquid push out of the material capillaries in cement composites. *Cem. Concr. Res.* **35** (3), 520–526 (2005).
4. Li, S. W., Wang, Y. F. & Wang, S. N. Research on the prediction model of the concrete damage in the sulfate aggressive environment. *J. Wuhan Univ. Technol.* **14**, 35–39 (2010).
5. Zuo, X. B. & Sun, W. Full process analysis of damage and failure of concrete subjected to external sulfate attack. *J. Chin. Ceramic Soc.* **37** (7), 1063–1067 (2009).
6. Wan, X. R. & Zuo, X. B. Numerical simulation of diffusion reaction of sulfate ion in concrete subjected to external sulfate attack. *Industrial Constr.* **40** (1), 843–843 (2010).
7. Gospodinov, P. N., Kazandjiev, R. F. & Partalin, T. A. Diffusion of sulfate ions into cement stone regarding simultaneous chemical reactions and effects. *Cem. Concr. Res.* **29** (10), 1591–1596 (1999).
8. Liang, Y. N., Wang, J. & Kong, H. X. Study of sulfate diffusion coefficient in concrete. *Concrete* **3**, 11–13 (2011).
9. Chen, X. B., Tang, M. X. & Ma, K. L. Underground concrete structure exposure to sulfate and chloride invading environment. *J. Cent. South. Univ. (Science Technology)*. **43** (7), 2803–2803 (2012).
10. Jin, Z. Q., Sun, W. & Zhang, Y. S. Study on damage of HPC under the corrosion of chloride and sulfate. *Industrial Constr.* **35** (1), 5–7 (2005).
11. Liu, R. G., Li, H. & Chen, Y. Research to the chloride diffusion impact of sulfate of marine concrete. *Concrete* **2012**(2), 18–20.
12. Gospodinov, P. N., Kazandjiev, R. F. & Partalin, T. A. Diffusion of sulfate ions into cement stone regarding simultaneous chemical reactions and resulting effects. *Cem. Concr. Res.* **29** (10), 1591–1596 (1999).
13. Gospodinov, P., Kazandjiev, R. & Mironova, M. The effect of sulfate ion diffusion on the structure of cement stone. *Cem. Concr. Compos.* **18** (6), 401–407 (1996).
14. Kabira, H., Hootona, R. D. & Popoff, N. J. Evaluation of cement soundness using the ASTM C151 autoclave expansion test. *Cem. Concr. Res.* **136**, 106159 (2020).
15. Arong, Shigeyuki, M., Harunobu, I. & Yiliguqi Utilization of Svm in the soundness evaluation of reinforced concrete slab Bridge. *J. JSCE*. **8**, 59–70 (2020).
16. Yu, Y., Zhang, Y. X. & Khennane, A. Numerical modelling of degradation of cement-based materials under leaching and external sulfate attack. *Comput. Struct.* **158**, 1–14 (2015).
17. Du, Y. J. & Li, Y. T. Preliminary study on the prediction of service life of high performance concrete in sulphate erosion resistance. *J. Northwest. F Univ. (Natural Sci. Edition)*. **12**, 100–102 (2004).
18. Ma, Z. M., Zhao, T. J. & Wang, P. Experimental study of sulfate corrosion of concrete in marine environment. *China Concrete Cem. Prod.* (10), 5–8. (2013).
19. Condor, J., Asghari, K. & Unatrakarn, D. Experimental results of diffusion coefficient of sulfate ions in cement type 10 and class G. *Energy Procedia*. **4**, 5267–5274 (2011).

### Acknowledgements

The authors gratefully acknowledged Fuzhou University.

### Author contributions

Xianyuan Chen: Investigation, Writing-Original draft; Zhaocai Meng: Writing – review & editing; Xinjiang Zheng: Validation; Project administration. Zirui Gao: Data curation.

## Declarations

### Competing interests

The authors declare no competing interests.

### Additional information

**Correspondence** and requests for materials should be addressed to X.Z.

**Reprints and permissions information** is available at [www.nature.com/reprints](http://www.nature.com/reprints).

**Publisher's note** Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

**Open Access** This article is licensed under a Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International License, which permits any non-commercial use, sharing, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if you modified the licensed material. You do not have permission under this licence to share adapted material derived from this article or parts of it. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by-nc-nd/4.0/>.

© The Author(s) 2025