

Research Article

Concentration Distribution of Chloride Ion under the Influence of the Convection-Diffusion Coupling

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The transfer process of chloride ion under the action of the convection-diffusion coupling was analyzed in order to predict the corrosion of reinforcement and the durability of structure more accurately. Considering the time-varying properties of diffusion coefficient and the space-time effect of the convection velocity, the differential equation for chloride ion transfer under the action of the convection-diffusion coupling was constructed. And then the chloride ion transfer model was validated by the existing experimental datum and the actual project datum. The results showed that when only diffusion was considered, the chlorine ion concentration increased with the time and decreased with the decay index of time. Under the action of the convection-diffusion coupling, at each point of coupling region, the chloride ion concentration first increased and then decreased and tended to stabilize, and the maximum appeared at the moment of convection velocity being 0; in the diffusion zone, the chloride ion concentration increased over time, and the chloride ion concentration of the same location increased with the depth of convection (in the later period), the velocity of convection (in the early period), and the chloride ion concentration of the surface.

1. Introduction

Chloride ion is the main factor affecting the durability of RC structures in subsea environment [1–6]. It can cause the corrosion of steel bars, diminish the bearing capacity of structures, and even influence the service life that cannot meet the design requirement [7, 8]. In the salt fog environment and splash zone, where the concrete structure is in an unsaturated state between water saturated and completely dry, the ion on the surface of concrete migrates into concrete by the diffusion of concentration and capillary absorption [9–11]. In the environment of pressure water, chloride ion transfers to internal parts mainly through convective motion caused by concentration diffusion and pressure infiltration [12]. It can be seen that the convection-diffusion coupling is the main approach of the transfer of chloride ion in concrete. Therefore, in order to improve the durability of concrete structure, studying the concentration distribution of chloride ion under the coupled action is of great significance.

Traditional research of the transmission of chloride ions in concrete considers only the diffusion effect, induces the

analytical solution of chloride concentration based on the partial differential equation of the Fick's second law [13–17], and modifies the equations according to the service environment [18–20]. Since the transmission mechanism of chloride ion is complex and the parameters for the partial differential equation are a lot, there is no accepted and precise analytical formula for chloride concentration. The methods adopted include empirical method, finite element method, difference method, and analytic method. DuraCrete [21] proposed an experience method which considers that within $0 \sim \Delta x$ (Δx is the total convection depth) the chloride ion convection is mainly caused by pore fluid flow while that outside this region is mainly caused by concentration diffusion. Jin et al. [9] adopted the method of finite difference to calculate the chloride ion concentration in the region of the convection-diffusion coupling. Based on the law of conservation of matter, Pan and Chen [22] deduced convection-diffusion equation of chlorine ion in unsaturated concrete, and the preliminary analysis for stability of the parameters in the model and finite element calculation has been carried out. Li [23] analyzed the migration of moisture in concrete under the

action of the pressure and established a theoretical model for chloride ion concentration in the unsaturated concrete, under the action of water flow rate, depth of penetration, and the convection-diffusion coupling. Xiang [24] distinguished the region of the convection-diffusion coupling and diffusion area and solved the equation of the convection-diffusion coupling by using the finite difference method. By assuming the initial boundary conditions and using traditional solutions, the questions of diffusion zone were answered. On this basis, Yue et al. [25] adopted the method of separation and substitution of variables, respectively, to solve the transfer of the chloride ion in the coupling and diffusion area. It is supposed that the speed of convection is constant and irrelevant to the position or time. The transfer of chloride ion in the concrete under the conditions of convection was obtained. Jia et al. [26] studied the transmission law of chloride ion in unsaturated concrete and steel structures by numerical simulation. Feng et al. [27] considered the difference of water transport between dry and wet cycles; a convection-diffusion equation for chloride ion transport in unsaturated concrete was derived. For the research above, the differential equations of the coupling of diffusion-convection are mostly the same, but the convection velocity is different. To simplify the calculation, the time-varying nature of diffusion coefficient was not considered in those researches.

With the consideration of a time-varying characteristic of diffusion coefficient, the differential equation for the transfer of chloride ion under the action of the convection-diffusion coupling was set up. The coupling zone and the diffusion zone were distinguished by the convection velocity. The numerical analysis with MATLAB was adopted to predict the concentration of chloride ion, and the influences of the parameters were analyzed.

2. The Differential Equation of Transfer of Chloride Ion under the Action of the Coupling of Chloride Ion

Because the depth of capillary absorption and penetration is limited, the convective region exists only within a certain depth beneath the surface of the concrete. DuraCrete [21] thought that the depth of influenced convection was 14 mm. Lei [28] concluded that the depth of a convection zone in an underground structure was approximately 5 mm to 10 mm. Within this depth, the chloride ion transferred into internal layer of the concrete under the action of the convection-diffusion coupling. If the depth was greater than this value, the transfer of the chloride ion was mainly under the influence of diffusion.

The one-dimensional equation of the transfer of chloride ion under the action of convection-diffusion is shown below [9, 25]:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left[D \frac{\partial C}{\partial x} - C(v_p + v_c) \right]. \quad (1)$$

In the expression, C value refers to the concentration of chlorine; D is the diffusion coefficient of chloride ion; x is the calculating depth of chloride ion. v_p and v_c refer to flow

velocity of pore fluid under the action of pressure permeability and capillary, respectively.

An initial condition is

$$C|_{t=0, x>0} = C_0. \quad (2)$$

Boundary conditions are

$$\begin{aligned} C|_{x=0} &= C_s, \\ C|_{x=\infty} &= C_0. \end{aligned} \quad (3)$$

In the expression, C_s is the concentration of free chlorine ion on the surface of the concrete; C_0 is the initial concentration of free chloride ion for the concrete.

2.1. The Diffusion Coefficient of Chloride Ion. In the transfer process of chloride ion, diffusion coefficient is very important [29, 30]. In the current research, diffusion coefficient is mainly considered in three situations.

(1) *Constant.* The diffusion coefficient is invariant during the whole service period; the expression is

$$D = 10^{-12.06+2.4W/B}. \quad (4)$$

In the expression, W/B is water-binder ratio.

(2) *Time-Varying.* The diffusion coefficient of chloride ion changes over time. It is generally believed that the law of change can be expressed by an exponential function [31, 32]:

$$D(t) = D_0 \left(\frac{t_0}{t} \right)^\alpha. \quad (5)$$

In the expression, $D(t)$ is the diffusion coefficient of time t ; t_0 is the test age of diffusion coefficient of the concrete, which is usually evaluated as 28 d. D_0 is the diffusion coefficient of time t_0 , according to type (4); α is the attenuation index of time.

(3) *Tend to Be Stable after Some Years.* After some years, the hydration of concrete is basically completed, and the change of the internal microstructure probably does not occur any longer. At this point, the diffusion coefficient of chloride ion tends to a stable value [32].

$$D(t) = \begin{cases} D_0 \left(\frac{t_0}{t} \right)^\alpha & t < t_k \\ D_0 \left(\frac{t_0}{t_k} \right)^\alpha & t \geq t_k. \end{cases} \quad (6)$$

In the expression, t_k is the time when diffusion coefficient tends to be stable.

2.2. Convection Velocity. Under the condition of convection, permeation rate of pore fluid caused by pressure or capillary action decreases gradually with increasing depth and reaches 0 when it gets to the depth of the convection. In order to simplify the calculation, it is assumed that the permeation rate of the pore fluid linearly decreases over time. v_{\max} refers

to the maximum rate, and the time spent before convection speed reaches zero is t_1 .

$$t_1 = \frac{2\Delta x}{v_{\max}}. \quad (7)$$

In the expression, Δx is the total depth of convection.

The depth of convection at time t :

$$x(t) = \frac{2t_1 - t}{2t_1} t \cdot v_{\max}. \quad (8)$$

The convection velocity under the effect of space and time:

$$v(x, t) = \begin{cases} \frac{\sqrt{t_1^2 - 2t_1x/v_{\max}}}{t_1} v_{\max} & 0 < x \leq x(t), t \leq t_1 \\ 0 & \text{other situations,} \end{cases} \quad (9)$$

where $v(x, t)$ is the convection velocity of the x point at the t time.

In conclusion, (1) becomes

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left[D_0 \left(\frac{t_0}{t} \right)^\alpha \frac{\partial C}{\partial x} - C \cdot v(x, t) \right]. \quad (10)$$

3. Model Verification

3.1. Verification with Existing Experimental Datum. Wang and Zhou [33] studied the transmission of chloride ion in concrete specimen in the seaside environment simulated by salt frog box. The size of the concrete specimen is 100 mm × 100 mm × 400 mm, and the load level was set to be 0, 0.3, and 0.5 of its strength. The transmission time was 35 d, 70 d, 120 d, and 180 d and the water cement ratio is set to be 0.38. α was 0.20. For C_s , with the consideration of its change over time, C_s stood at 0.25% at the time of 35 d and 70 d and reached 0.32% at 120 d and 240 d. The paper of Park et al. [34] took $v_{\max} = 2 \times 10^{-8}$ mm/s. Δx was 10 mm; C_0 was 0. When only diffusion and the convection-diffusion coupling were taken into account, the calculated results and experimental results are shown by Figure 1.

Figure 1 shows that when the time of erosion migration for chloride ion is short, such as 35 d, 70 d, 120 d, and 240 d, the curve under the action of diffusion overlapped the one of the coupling of diffusion-coupling. It illustrates that the effect of convection is not obvious at the moment; when it was eroded more than 5 a, the value of C value under the action of the convection-diffusion coupling is more than that when only convection was considered. Through Figures 1(a), 1(b), 1(c), and 1(d), it can be seen that the experimental value coincides well with the value under the influence of the convection-diffusion coupling. It illustrates that this model is suitable for initial migration simulation for chloride ion.

3.2. Engineering Measured Data. The paper of de Rinçon et al. [35] had taken specimen from a bridge (General Rafael

Urdaneta Bridge) by core pulling method in order to study the chloride ion distribution after 38 years. The pulling position is above the ocean surface. In this project, α was 0.50, C_s was 0.27%, v_{\max} was 2×10^{-8} mm/s, Δx was 10 mm, and C_0 was 0.11%. When the influence of only diffusion and the convection-diffusion coupling was considered, the calculated value and the measured data are shown in Figure 2.

Figure 2 plots the fact that when only the influence of diffusion was considered, the calculated value is less than the measured value. Under the action of the convection-diffusion coupling, the calculated value consisted well with the measured value. It shows that this model is suitable for the migration simulation of chloride ion when erosion has been carried out after a period of time.

Therefore, this model is suitable for simulating the whole process of chloride ion migration, accurate and practical.

4. The Engineering Application

4.1. Engineering Background. The service environment of the inside lining of subsea tunnels is similar to the atmospheric zone of the ocean, which is eroded by salt fog with the chloride ion permeated to the inside of the concrete mainly by diffusion and capillary action. Taking a subsea tunnel as an example, the design parameters were selected according to reference of Jin et al. [36]: for concrete C50, its water-binder ratio (W/B) is 0.32, and the thickness of protective cover is 60 mm. In the reference of CECS220 [37], α is 0.50, C_s is 0.225%, v_{\max} is $v_{\max} = 2 \times 10^{-8}$ mm/s, Δx is 10 mm, C_0 is 0, and t_k is 30 a.

4.2. The Concentration of the Chloride Ion. Figure 3 shows how the concentration of the chloride ion changed over time, when only the diffusion ($v_{\max} = 0$) and the convection-diffusion coupling ($v_{\max} = 2 \times 10^{-8}$ mm/s, $\Delta x = 10$ mm) were considered.

Figure 3 shows that only when the diffusion ($v_{\max} = 0$) was considered did C increase over time. If the convection-diffusion coupling was taken into account, the value of C value at every point ($x = 6$ mm was taken as an example) in the coupling area increased and then decreased over time and gradually came close to the value of C value when only the diffusion was considered, and the maximum value appeared at the point ($t_1 = 15.8$ a) when convection velocity became 0. For each point of the diffusion area ($x = 60$ mm, e.g.) C value increased over time, and at any time C value was greater than that when only the diffusion was considered. At the time of 100 a, in the depth of protective layer thickness ($x = 60$ mm), the concentration of the chloride ion did not reach the critical value of CECS220 [37] 0.065%. It shows that there was no corrosion at that moment, and structural durability was excellent.

4.3. Analysis of the Parameters

4.3.1. Influence of Diffusion Coefficient. When the influence of diffusion was considered, Figure 4 shows the concentration distribution of the chloride ion when the attenuation index

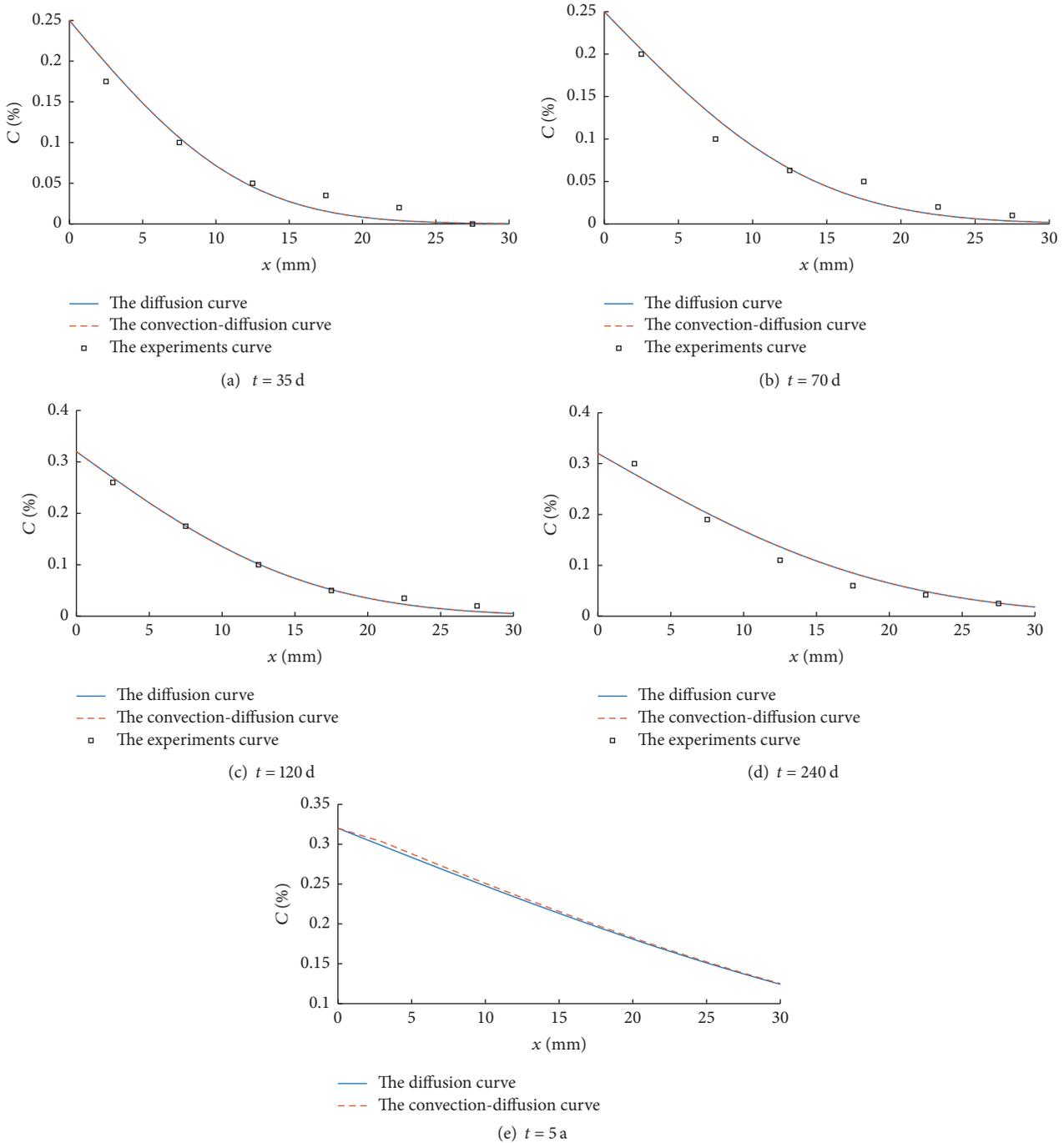


FIGURE 1: Result comparison between model calculation and experiment.

of time was 0 (when diffusion coefficient was constant), 0.3, 0.5, and 0.7, respectively. In order to analyze the situations of each point with C value changing over time, three values at the time of early ($t = 5$ a), medium ($t = 50$ a) ($t = 100$ a), and later were chosen.

Figure 4 depicts that, in all the cases, C value decreased with the increase of the distance and finally tended to the stable value (initial concentration of chloride ions). In circumstances with the same value of time and location, C value

decreased with α increasing. This is because the coefficient of diffusion decreased with α increasing. By the comparison between the cases of early, middle, and late time, it can be seen that, with the same α , C value in each point increased with the increase of service time; α impacted on C value significantly, and the longer the service time, the greater the impact.

Figure 5 shows the concentration distribution of chloride ion in four cases where the diffusion coefficient is constant ($\alpha = 0$), and diffusion coefficient tends to be stable after 30

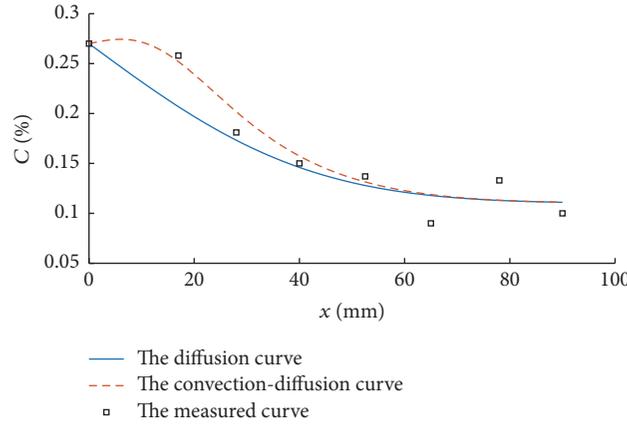


FIGURE 2: Result comparison between model calculation and the measured data.

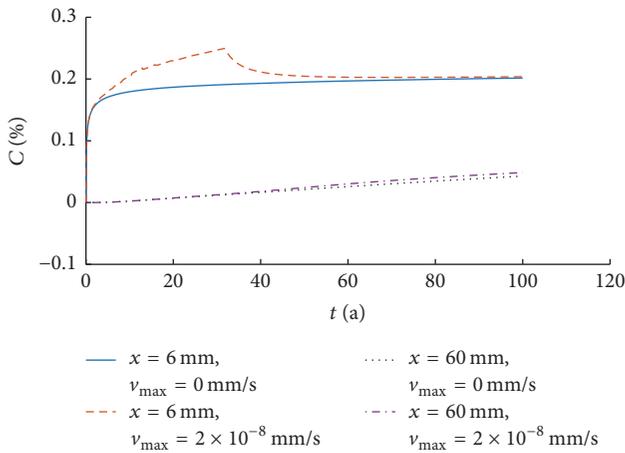


FIGURE 3: The trend of concentration of the chloride ion over time.

years ($t_k = 30$ a) and 40 years ($t_k = 40$ a) and time-varying ($t_k = +\infty$), respectively.

Figure 5 illustrates that t_k has little impact on C value. At the early stage, except in the situation that $\alpha = 0$, because in the other three cases diffusion coefficients were equal during the period of time $0 \sim 5$ a, the three curves coincided. At the mid time, because D was not equal between 30 a and 50 a, three curves slightly separated. In the late period, the three curves separated increasingly, but the difference was still small. At the same location, $C_{t=0} > C_{t=30} > C_{t=40} > C_{t=+\infty}$, which was the same order with diffusion coefficient being 100 a.

4.3.2. Influence Caused by the Depth of Convection. Figure 6 plots the concentration distribution of chloride ion with different depths of convection. Among them, $\Delta x = 0$ mm was the case only considering the diffusion.

Figure 6 illustrates that Δx has a great impact on C value. In the early period, C value decreased with the increase of distance in all situations and then tended to a constant value; in the middle period, with $\Delta x = 20, 30$ mm, C value first increased and then decreased with the increase of distance

and in the end tended to be a constant value. This is because, with $\Delta x = 20$ mm, the total time of convection was 63 a. At this point (50 a), the velocity is quite close to 0, the C value is large, and the effect of convection was obvious, which was consistent with the test results in document of Zhang et al. [38]. At the late period, when Δx was 30 mm, C value first increased and then decreased with the increase of distance and finally tended to be stable. This was because with $\Delta x = 30$ mm the total time of convection was 95 a. At this point (100 a), the velocity is quite close to 0, the C value is large, and the effect of convection was obvious. However in the situations with other convection depths, convection movement had already been off. C value decreases with the increase of the distance and finally tended to the stable value. At the same location, with the deeper the convection depth, C value became the bigger.

4.3.3. Influence of Convection Velocity. Figure 7 shows the concentration distribution of chloride ion with different velocities of convection.

Figure 7 shows that in the early period the velocity of convection has an effect on C ; for the condition with bigger velocities of convection ($v_{max} = 6 \times 10^{-8}$ mm/s), C value first increased and then decreased with the increase of distance and finally became stable. When convection velocity was smaller ($v_{max} = 0, 2, 4 \times 10^{-8}$ mm/s), C value decreases with the increase of distance and then finally tended to be stable. At the same location the bigger the convection velocity, the bigger the C value. At the middle period, all of the convection movement was off, and the smaller the convection speed was, the later the convection movement was off and nearer to 50 a. Therefore, the more obvious the convection effect, the bigger the C value. In the late period, convection velocity nearly did not have any impact on C value, and three curves almost overlapped. The value of C value decreased with the increase of distance and tended toward the stable value at the end.

4.3.4. The Effect of Concentration of Chloride Ion at Surface Level. Figure 8 shows the different concentration distribution C_s of chloride ion at surface level.

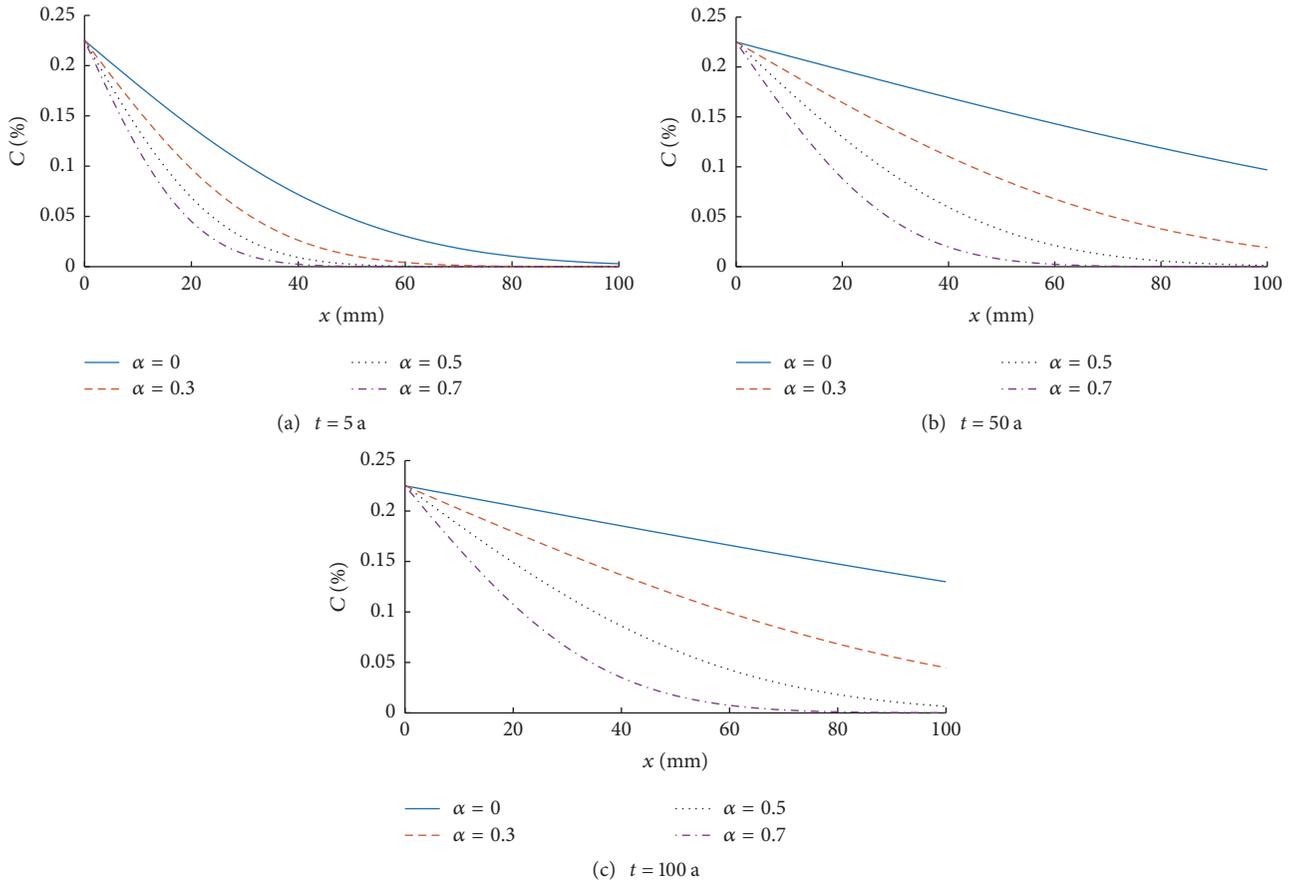


FIGURE 4: The effects on concentration of the chloride ion by α .

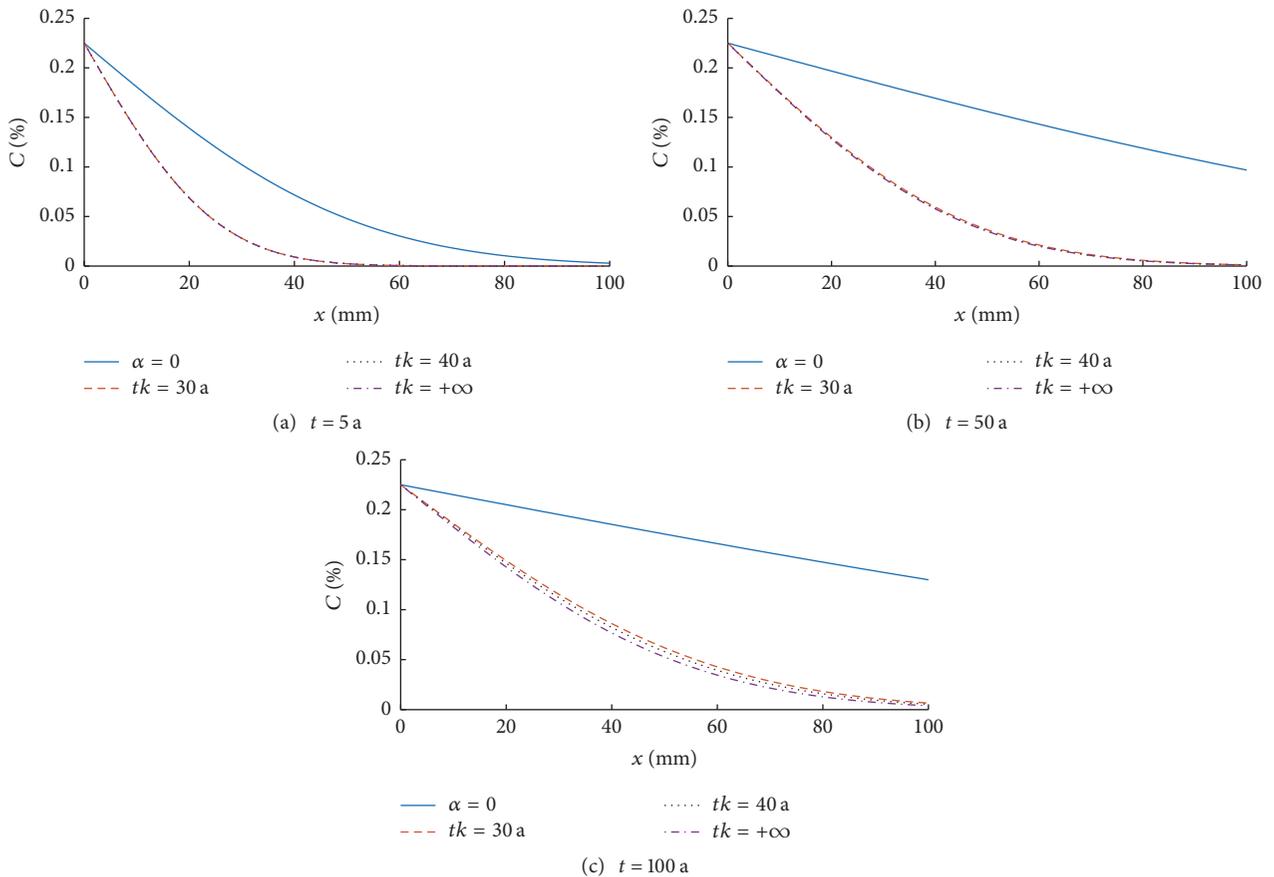


FIGURE 5: Impact on concentration of chloride ion caused by t_k .

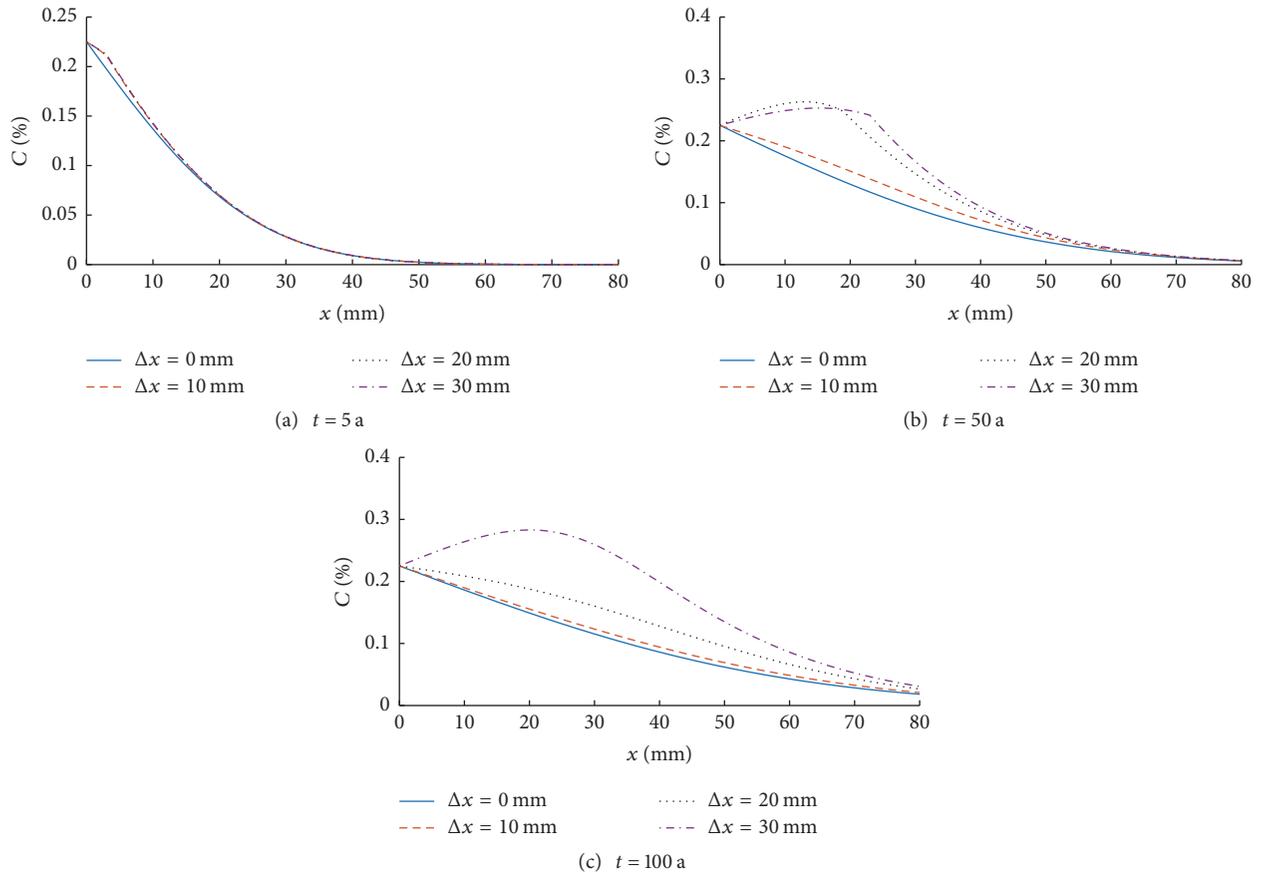


FIGURE 6: Influence caused by the depth of convection.

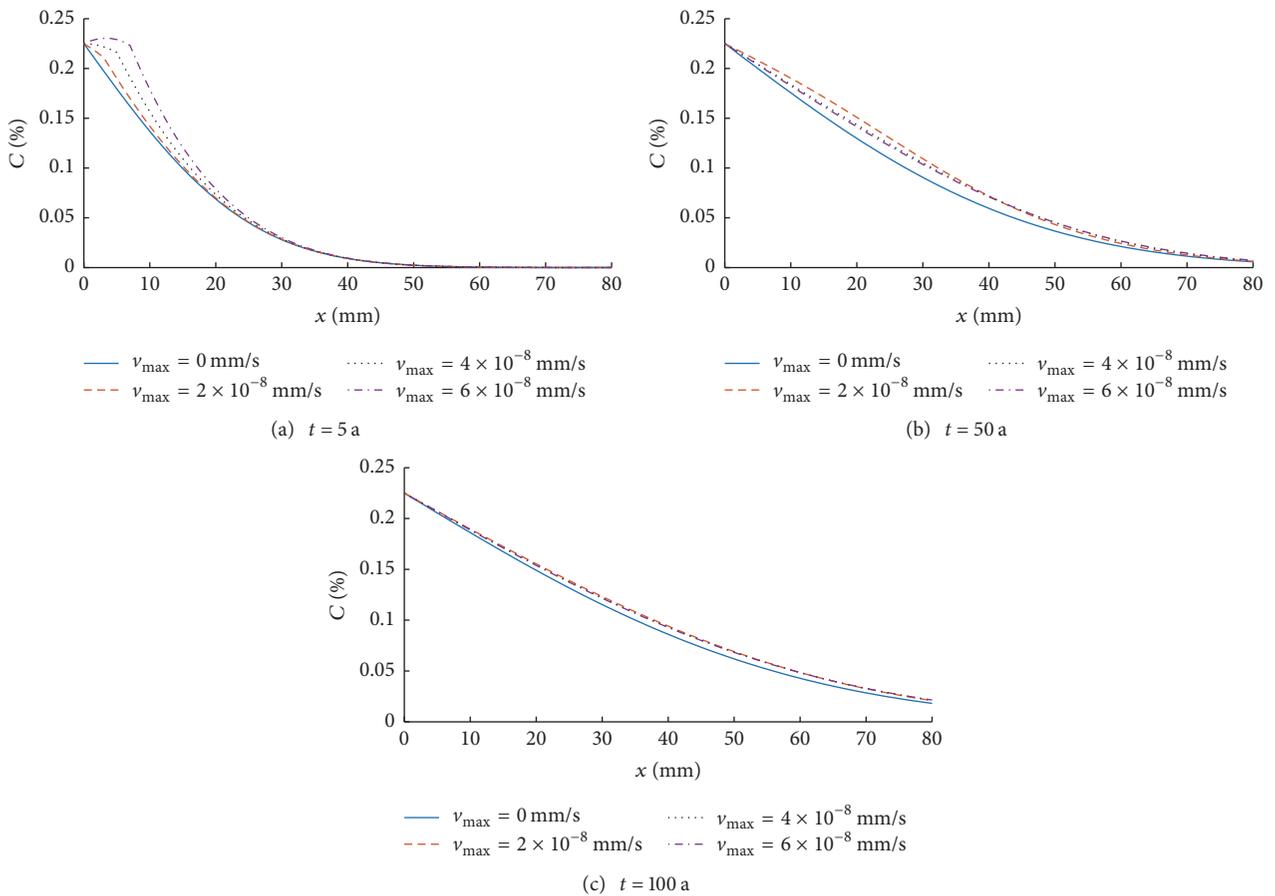


FIGURE 7: Influence of convection velocity.

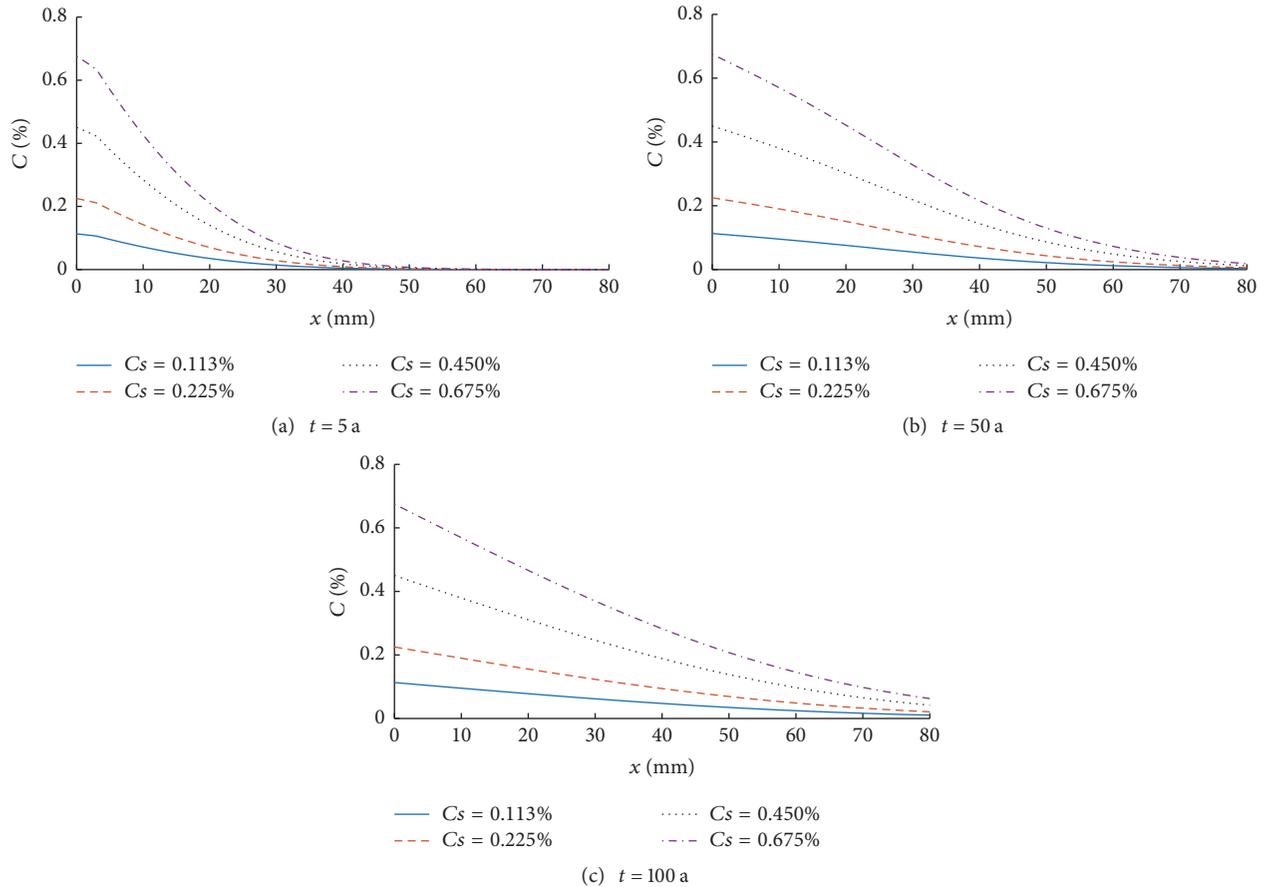


FIGURE 8: Effects on the concentration of chloride ion by C_s .

Figure 8 shows that C_s has a great impact on C value. At the same location, the value of C value increased with the increase of C_s ; in the cases with the same C_s , the value of C value at each point increased with the increase of service time.

5. Conclusions

The time-varying properties of the diffusion coefficients and the space and time effect of the convection velocity were discussed, the concentration of chloride ion under the action of the convection-diffusion coupling was calculated, the durability of the structure was evaluated, and the influence of the parameters was analyzed. The following conclusions have been drawn:

(1) If only diffusion was considered, at any time, C value decreased with the increase of distance and tended toward a constant value. At any location, C value increased over time.

(2) If time-varying of diffusion coefficient was taken into account, parameter t_k had almost no effect on C value, while parameter α noticeably influenced C value, the bigger α , the smaller C value. It can be seen that regardless of the time-varying characteristic of diffusion coefficient calculation of C value is conservative.

(3) Under the influence of the convection-diffusion coupling, in each point of the coupling zone, the C value first increased and then decreased with the increase of time and finally tended to be a constant value. The maximum value appeared at the point when the convection velocity is 0. For each point in the diffusion zone, the C value increased over time.

(4) Under the effect of the convection-diffusion coupling, the depth of the convection had a significant effect on C value. At the same location, with the deeper the convection, the C values become larger. Convection velocity only has impact on C value in the early period. In the late period, at the same point, with the greater velocity of convection, C values are the larger. The concentration of chloride ion at surface level has a great impact on C value, and at the same location C value increased with the increase of C_s .

(5) The influence of the section stress on the diffusion and convection has not been considered, which can be studied by means of experiment and numerical simulation in the further research.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

Acknowledgments

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