

Influence of the coupled time and concrete stress effects on instantaneous chloride diffusion coefficient

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HIGHLIGHTS

- A method for calculating the instantaneous chloride diffusion coefficient (D_{ins}) is proposed.
- D_{ins} is smaller than apparent chloride diffusion coefficient (D_a) at the same exposure time.
- The relative error between D_{ins} and D_a has both time and stress dependence.
- D_{ins} has both time and stress dependence and the age reduction factor manifests stress dependence.
- A theoretical model of chloride ion concentration is established based on the model of D_{ins} .

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ABSTRACT

Chloride ion penetration can cause corrosion of steel embedded in concrete in chloride-laden environment. Investigating the model of chloride diffusion is of vital importance to durability assessment and residual service life prediction of concrete structures. In this paper, firstly, a calculation method of instantaneous chloride diffusion coefficient (D_{ins}) is established based on the apparent chloride diffusion coefficient (D_a). Then, the existing experimental data in the literature are used for studying the influence of the coupled time and concrete stress effects on D_{ins} , and the theoretical model of D_{ins} is established. Finally, based on the established model of D_{ins} , a prediction model of chloride concentration is proposed and the model is validated by two sets of experimental data. By comparative study with experimental data, the results show that the calculation method of D_{ins} is reasonable and feasible, and D_{ins} is smaller than D_a at the same exposure time. Generally, the relative error between D_{ins} and D_a increases with the exposure time under the same tensile or compressive stress level, while at the same exposure time, it first increases and then decreases with increasing concrete tensile stress level, whereas it decreases with increasing concrete compressive stress level. It is found that D_{ins} has strong time and stress dependence. The computed results of the proposed chloride ion concentration model agree well with the experimental data.

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1. Introduction

In chloride-laden environment such as off-shore and coastal areas, chloride ion penetration is the main instigating factor of corrosion of steel reinforcement in concrete structures [1]. After chloride ions are transported to the surface of steel reinforcement, its concentration would accumulate with time. When the chloride concentration at certain locations along the steel reinforcement reaches a threshold level, the protective passivation layer on the surface of steel is destroyed locally and corrosion is initiated [2].

The corrosion of steel will induce spalling and splitting cracks in concrete cover, deteriorate the bond performance between steel and the surrounding concrete, and reduce the cross-sectional area and strength capacity of steel reinforcement. These will seriously shorten the service life of concrete structures [3].

The transport mechanism of chloride ions in concrete is complicated. The way that chloride ions penetrate into concrete mainly includes diffusion, permeation, capillary adsorption, migration, and convection [4–5]. The transport of chloride ions in concrete is closely related to the external environment and the physical and chemical properties of concrete, but in most cases, diffusion is considered to be the most important transport mode of chloride ions in concrete [6–7]. Generally, Fick's second law of diffusion is

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adopted to describe the diffusion process of chloride ions in concrete [7–9].

It should be noted that the chloride diffusion coefficient fitted by the error function solution of Fick's second law of diffusion is the apparent chloride diffusion coefficient (D_a) of concrete, which is the average chloride diffusion coefficient during a period of exposure time. This is to be distinguished from the chloride diffusion coefficient at a point of time which is called the instantaneous chloride diffusion coefficient (D_{ins}) [4,8–9]. Stanish and Thomas [8], and Zhang et al. [9] found that D_{ins} and D_a had different time dependence, and there could be a significant deviation in the long-term chloride concentration prediction or the residual service life prediction of concrete structures by using the time-dependent model of D_a . This is mainly due to the reason when D_a is used to estimate the service life of concrete structures, there is an inherent assumption that the conditions in service are identical to the conditions during testing. If this is not the case, then the D_a projected from the test results are invalid. It is noteworthy that D_a is a function of both the material properties of concrete and test conditions [8]. On the contrary, D_{ins} is only a property of the materials [4,8]. Therefore, it is very meaningful to quantify the difference between D_{ins} and D_a , and establish a time-dependent model of D_{ins} .

At present, some researchers have studied the variation of D_{ins} . Song et al. [4] pointed out that D_{ins} had different meanings from D_a , and the two manifested different time-dependence. Stanish and Thomas [8] proposed an analytical procedure for determining the D_{ins} as a function of time for a concrete using data from bulk diffusion tests. Zhang et al. [9] found that D_{ins} was smaller than D_a at the same exposure time, but the difference between D_{ins} and D_a decreased with increasing water/binder ratio of concrete. In addition, the incorporation of different mineral admixtures in concrete can also cause a change in the difference between D_{ins} and D_a . Based on Fick's second law of diffusion, Frederiksen et al. [10] established a relationship between D_{ins} and D_a , and found that D_{ins} could be approximated by a linear function of D_a . Obviously, the above research on D_{ins} had been limited to the effects of exposure time and mix proportions of concrete.

Since the concrete structure is subjected to various external loads such as imposed gravity load and wind load, during service life, the influence of concrete stress on chloride diffusion in concrete should be considered [11–14]. To the best knowledge of the authors, there has been no literature reporting the influence of concrete stress on D_{ins} , and the research on the influence of the coupled time and concrete stress effects on D_{ins} is severely inadequate. Therefore, it is necessary to bridge the research gap. In this paper, firstly, a calculation method of D_{ins} is established. Then, the influence of the coupled time and concrete stress effects on D_{ins} is investigated with reference to existing experimental data in the literature. Finally, a prediction model of chloride concentration is proposed based on the established theoretical model of D_{ins} .

2. Chloride diffusion model

Consider concrete in exposure to chloride-laden environment, under the action of concentration gradient, chloride ions will diffuse from the surface of concrete with high concentration to the inner of concrete with low concentration, and the whole process can be described by Fick's second law of diffusion [15–16], as given by Eq. (1).

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

where $C(x, t)$ is the chloride concentration at depth x and exposure time t ; and D is the chloride diffusion coefficient in concrete.

Theoretically, Eq. (1) is a partial differential equation that has no closed form solution, and it can only be solved by using numerical methods such as finite element or finite difference approach. However, by simplifying the problem and making some assumptions about the boundary conditions and the diffusion process, a closed form solution of Eq. (1) can be derived. Assume the diffusion of chloride ions in concrete can be regarded as diffusion in an one-dimensional semi-infinite medium, the chloride diffusion coefficient and the surface chloride concentration are both constant, the initial chloride concentration in concrete is zero, and concrete does not chemically combine with chloride ions. Then, an error function solution of Eq. (1) can be obtained, as written in Eq. (2) [17–19].

$$C(x, t) = C_s \left[1 - \operatorname{erf} \left(\frac{x}{2\sqrt{D_a t}} \right) \right] \quad (2)$$

where C_s is the surface chloride concentration; D_a is the apparent chloride diffusion coefficient; and erf is the error function.

3. Instantaneous chloride diffusion coefficient

3.1. Time-dependent characteristic of instantaneous chloride diffusion coefficient

In the diffusion process of chloride ions, on one hand, because of the continuous hydration of cement particles in concrete, the pores in concrete are constantly filled with new hydration gel products, and the pore size distribution of concrete shifts towards smaller aperture, thus the porosity of concrete reduces [20–21]. On the other hand, chloride ions can chemically bind with aluminates (C_3A) and ferrites (C_4AF) to form Friedel's salt and Kuzel's salt, respectively [22–23]. Moreover, the electrostatic forces between chloride ions and the surface of calcium silicate hydrates (C-S-H) can lead to the formation of physical bond. Therefore, the chloride diffusion coefficient in concrete will decrease with increasing concrete age.

The D_a obtained from Eq. (2) is not the chloride diffusion coefficient at a point of time during the period of exposure, but the average chloride diffusion coefficient from the time when the concrete structure is subjected to chloride ion penetration to the end of the whole exposure period [8,18]. Some researchers refer to the chloride diffusion coefficient at a point of time as D_{ins} , and adopted the following time-dependent empirical model for D_{ins} [4,8–9,18]:

$$D_{ins}(t') = D_{ins,ref} \left(\frac{t_{ref}}{t'} \right)^m \quad (3)$$

in which $D_{ins}(t')$ is the value of D_{ins} at concrete age t' ; $D_{ins,ref}$ is the value of D_{ins} at concrete age t_{ref} (generally, t_{ref} is taken as 28 days and the value of D_{ins} at the concrete age of 28 days is taken as $D_{ins,ref}$); and m is the age reduction factor.

The age reduction factor m is not a constant, and its value is affected by materials and age factors [9,16]. Zhang et al. [9] stated that the age reduction factor m was affected by blending with mineral admixtures, such as fly ash and silica fume. Mangat and Molloy [15] found that the age reduction factor m increased with the water/cement ratio of concrete. Mangat and Limbachiya [24] showed that the age reduction factor m was affected by concrete mix proportions and initial curing conditions of concrete. Petcherdchoo [25] pointed out that the age reduction factor m for concrete incorporating fly ash or a combination of fly ash and silica fume had obvious time-dependent characteristics.

3.2. Calculation of instantaneous chloride diffusion coefficient

Since $D_{ins,ref}$ and m are unknown parameters in Eq. (3), it is necessary to determine these two parameters before applying Eq. (3) to predict the value of D_{ins} . Theoretically, D_a is the average value of D_{ins} over the period of exposure. Stanish and Thomas [8] established the relationship between D_{ins} and D_a , as shown in Eq. (4), which has been adopted by a number of researchers such as Song et al. [4], Zhang et al. [9], Tang and Gulikers [26], and Petcherdchoo [27].

$$D_a = \frac{\int_{t_1}^{t_2} D_{ins,ref} \left(\frac{t_{ref}}{t'} \right)^m dt'}{t_2 - t_1} \quad (4)$$

where t_1 is the age at which concrete begins to suffer from chloride attack; and t_2 is the age of concrete at the end of chloride attack.

Since the value of D_{ins} decreases as the concrete age increases, it is well known from Eq. (4) that over the exposure period from t_1 to t_2 , there is a point of time t_{eff} at which $D_{ins}(t_{eff})$ is equal to D_a , as depicted in Fig. 1. From the figure, it is observed that the value of D_a obtained by using the Eq. (2) at time t_2 is obviously greater than $D_{ins}(t_2)$ at time t_2 . For any chloride ion exposure period, the time t_{eff} can always be found such that D_{ins} and D_a are equal, hence the time-dependent curve of D_a can be obtained, as shown in Fig. 2. Apparently, D_a is greater than D_{ins} at any fixed point of time during the whole exposure period of chloride diffusion.

Substituting $t' = t_{eff}$ into Eq. (3), Eq. (5) can be obtained. For the purpose of determining the time t_{eff} at which D_{ins} is equal to D_a , Eq. (4) can be further simplified, as shown in Eq. (6). In Eq. (6), if m is 0, it indicates that the chloride diffusion coefficient does not change with time. In this case, D_{ins} and D_a are equal at any time, that is, in Fig. 2, the projection of dashed line coincides with the solid line and is parallel to the time axis. Due to the continuous hydration of the cement particles in concrete, the chloride diffusion coefficient changes with time and it is not possible for m to be equal to 0 before the cement hydration is completed. If m is equal to 1, the self-blocking phenomenon will occur in concrete, the chloride diffusion coefficient decreases with time in a hyperbolic manner and the chloride ion concentration in concrete will not change with time [28]. This phenomenon only applies to the long-term prediction of chloride concentration considering the time-dependence of D_a [8].

$$D_a = D_{ins}(t_{eff}) = D_{ins,ref} \left(\frac{t_{ref}}{t_{eff}} \right)^m \quad (5)$$

$$D_a = \begin{cases} D_{ins,ref} t_{ref}^m \frac{t_2^{1-m} - t_1^{1-m}}{(1-m)(t_2 - t_1)} & (m \neq 0, 1) \\ D_{ins,ref} t_{ref}^m \frac{\ln\left(\frac{t_2}{t_1}\right)}{t_2 - t_1} & (m = 1) \end{cases} \quad (6)$$

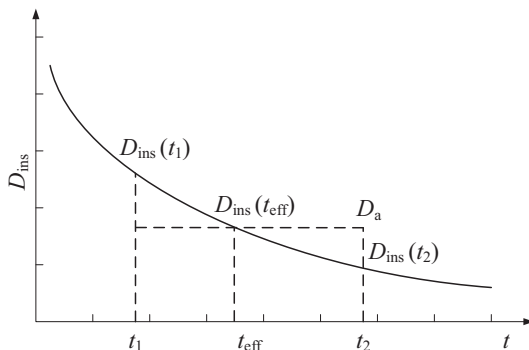


Fig. 1. Relationship between D_a and D_{ins} .

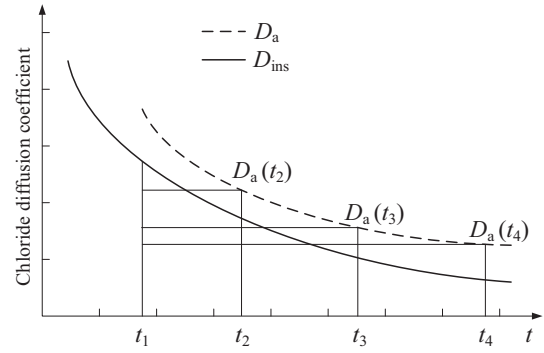


Fig. 2. Time-dependent characteristics of D_a .

Through Eq. (5) and Eq. (6), the time t_{eff} can be determined, as formulated in Eq. (7).

$$t_{eff} = \begin{cases} \left[\frac{(1-m)(t_2 - t_1)}{t_2^{1-m} - t_1^{1-m}} \right]^{1/m} & (m \neq 0, 1) \\ \frac{t_2 - t_1}{\ln\left(\frac{t_2}{t_1}\right)} & (m = 1) \end{cases} \quad (7)$$

Over the exposure period from t_1 to t_2 , if t_{eff} is determined, the following method can be adopted to obtain D_{ins} :

- (1) Assume an initial value of m .
- (2) In Eq. (7), the age at which concrete begins to suffer from chloride attack t_1 is taken as 28 days. Assume a designated concrete age (such as 84 d, 140 d, 196 d, 252 d) as the value of t_{eff} , since m has been assumed in step 1, t_2 can be obtained from Eq. (7).
- (3) Generally, the test of chloride ion penetration is conducted after the concrete specimens have been cured for 28 days. Therefore, the value of $D_a(t_2 - 28)$ should be calculated. Curve fitting is performed with respect to the variations of D_a at different exposure time to obtain $D_a(t_2 - 28)$. Then, the value of $D_{ins}(t_{eff})$ can be obtained by setting $D_{ins}(t_{eff}) = D_a(t_2 - 28)$.
- (4) Curve fitting by using Eq. (3) is performed with respect to $D_{ins}(t_{eff})$ at different time points t_{eff} obtained in step 3, and a new value of m can be determined.
- (5) Replace the original value of m in step 2 with the new value of m in step 4, and repeat steps 2 to 4 until the absolute error of the two m values among steps 4 and 2 is less than 0.01, then stop the iteration. By substituting the m value and the $D_{ins,ref}$ obtained in step 4 into Eq. (3), a time-dependent model of D_{ins} can be established.

The final value of m can be determined after three or four iterations of step 2 through step 4. The above method of calculating the D_{ins} can be automated using a computer programme.

4. Coupled time and concrete stress effects

4.1. Influence of the coupled time and tensile stress effects on D_{ins}

The experimental data from Wang [29] are employed to study the influence of the coupled time and concrete tensile stress effects on D_{ins} . In the test, the design strength grade of concrete was C50, and the water/cement ratio was 0.3. P.O.42.5 low alkali Portland cement conforming to the General Administration of Quality Supervision, Inspection and Quarantine of China (AQSIQC) standard GB 175-2007 [30] was adopted, in which alkali content was less than 0.6%. Mineral admixtures included grade I fly ash conforming to the AQSIQC standard GB/T 1596-2005 [31] and grade

S95 ground slag powder conforming to the AQSIQC standard GB/T 18046–2008 [32]. Coarse aggregate employed was gravel which was divided into two grades, including 5–16 mm and 10–25 mm. Fine aggregate employed was natural river sand, and the type “HT-HPC” polycarboxylate high performance water reducing agent was adopted. Mixing water was tap water. The mix proportions of concrete contained 343 kg/m³ of cement, 147 kg/m³ of water, 686 kg/m³ of sand, 1072 kg/m³ of gravel, 88.2 kg/m³ of fly ash, 58.8 kg/m³ of ground slag powder, and 4.9 kg/m³ of water reducing agent.

To study the effect of concrete stress on chloride diffusion in steam-cured concrete and ordinary concrete, Wang [29] designed two types of concrete specimens including steam-cured concrete specimens and ordinary concrete specimens. Each type of concrete specimen contained tensile stress specimens, compressive stress specimens, and non-stress specimens. The sizes of tensile and compressive stress specimens were 100 × 100 × 400 mm, and those of non-stress specimens were 150 × 150 × 150 mm.

This paper only uses the experimental data of ordinary concrete specimens for research. The tensile stress specimens were stressed at 0.3, 0.5 and 0.7 times of the concrete tensile strength, respectively. The ratio of tensile stress to concrete tensile strength is denoted as the tensile stress level δ_T . Under each tensile stress level, there were four groups of tensile stress specimens corresponded to different exposure times, and each group had one specimen. Therefore, there were 12 tensile stress specimens in total. The concentration of NaCl solution used in the test was 5%, and the exposure time of the four groups of tensile stress specimens under each tensile stress level was 56 days, 112 days, 168 days, and 224 days, respectively. Similarly, the non-stress specimens were also divided into 4 groups, and each group had one specimen, therefore, there were 4 non-stress specimens in total. The exposure time of the four groups of non-stress specimens was 56 days, 112 days, 168 days, and 224 days, respectively. The experimental data of tensile stress specimens and non-stress specimens can be found in Wang [29].

The values of C_s and D_a of tensile stress specimens and non-stress specimens can be obtained using Eq. (2) to perform the curve fitting on the experimental data, as shown in Table 1. It can be found that both C_s and D_a manifest time and tensile stress dependence. This is in line with the research findings by Wang et al. [21]

Table 1
Values of C_s (%) and D_a ($\times 10^{-11}$ m²/s) under different tensile stress levels.

Exposure time (d)	Tensile stress level δ_T							
	0		0.3		0.5		0.7	
	C_s	D_a	C_s	D_a	C_s	D_a	C_s	D_a
56	0.421	2.878	0.459	3.073	0.504	3.130	0.522	3.520
112	0.456	1.806	0.491	1.850	0.516	1.983	0.570	2.522
168	0.479	1.413	0.501	1.493	0.559	1.613	0.573	1.738
224	0.512	1.167	0.532	1.196	0.577	1.306	0.588	1.582

Table 2
Values of D_{ins} ($\times 10^{-11}$ m²/s) under different tensile stress levels.

Exposure time (d)	Concrete age (d)	Tensile stress level δ_T			
		0 D_{ins}	0.3 D_{ins}	0.5 D_{ins}	0.7 D_{ins}
—	28	4.524	4.896	4.822	5.201
56	84	1.428	1.480	1.622	1.943
112	140	0.815	0.829	0.953	1.200
168	196	0.584	0.586	0.696	0.903
224	252	0.461	0.458	0.557	0.738

and Xu et al. [33], who studied the effect of compressive stress on chloride diffusion and reported that both C_s and D_a were dependent on time and compressive stress.

Based on the values of D_a listed in Table 1, by using the proposed computation method of D_{ins} in Section 3, the values of D_{ins} at different exposure time (or concrete ages) and the age reduction factor m under different tensile stress levels can be determined, as listed in Table 2 and Table 3 respectively. It is evident from Table 2 that, similar to D_a , D_{ins} also manifests time and tensile stress dependence. Due to the continuous hydration of cement, the porosity of concrete decreases with concrete age, hence there is a tendency of D_{ins} to decrease with increasing exposure time. However, tensile stress can lead to extensional deformation and increase the porosity of concrete, hence there is a tendency of D_{ins} to increase with the concrete tensile stress level.

In order to quantitatively evaluate the difference between D_{ins} and D_a , the relative error Δ_D among the two coefficients is calculated as per Eq. (8), and is depicted in Fig. 3. In the figure, it is noted that D_{ins} is smaller than D_a , and the relative error Δ_D between D_{ins} and D_a ranges approximately from 45% to 65%. In general, Δ_D increases with the exposure time under the same tensile stress level, and increases first and then decreases with increasing tensile stress level at the same exposure time.

$$\Delta_D = (D_a - D_{ins})/D_a \times 100\% \quad (8)$$

The relationship between $D_{ins,ref}$ and tensile stress level should be established before the time and tensile stress dependent model of D_{ins} is proposed. The values of D_{ins} at concrete age of 28 days in Table 2 are taken as $D_{ins,ref}$ in Eq. (3). For brevity, it is denoted as $D_{ins,28}(\delta_T)$, or simply as $D_{ins,28}$. Further, the value of D_{ins} at concrete age of 28 days and tensile stress level of 0 is evaluated and denoted as $D_{ins,T0}$. The relationship between $D_{ins,28}(\delta_T)/D_{ins,T0}$ and tensile stress level is plotted in Fig. 4, and their correlation is determined

Table 3
Values of m under different tensile stress levels.

δ_T	0	0.3	0.5	0.7
m	1.05	1.09	0.99	0.90
R^2	0.9992	0.9993	0.9990	0.9990

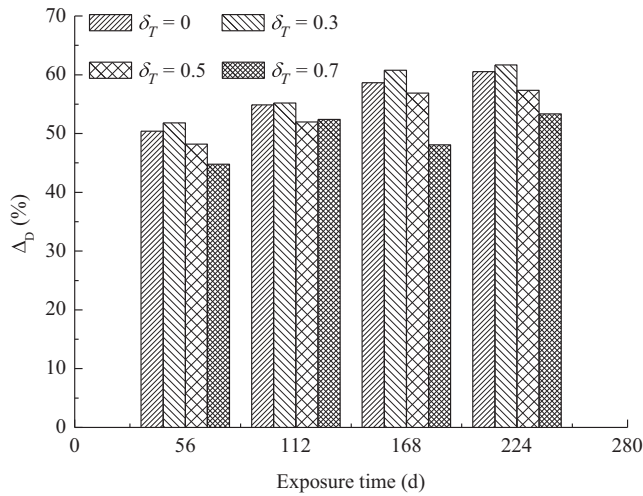


Fig. 3. Relative deviation between D_{ins} and D_a under tensile stress.

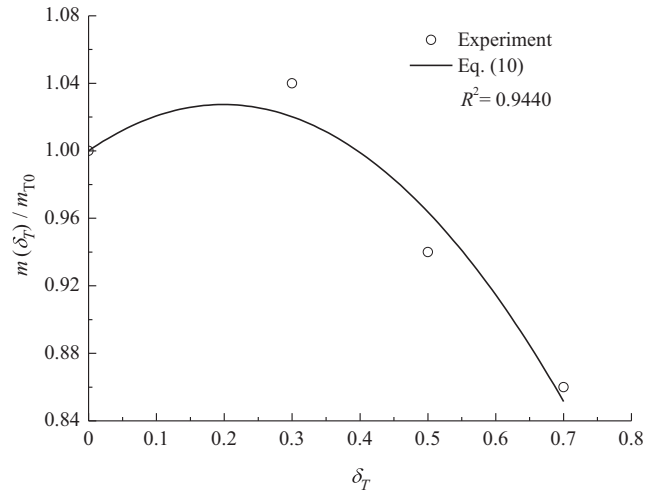


Fig. 5. Relationship between $m(\delta_T)/m_{T0}$ and tensile stress level.

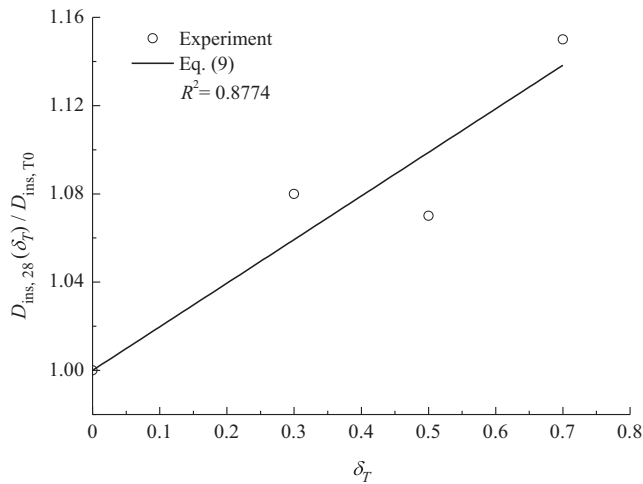


Fig. 4. Relationship between $D_{ins,28}(\delta_T)/D_{ins,T0}$ and tensile stress level.

by means of the linear regression method, which shows that $D_{ins,28}$ increases linearly with the tensile stress level. The resulting regression formula is given by Eq. (9).

From Table 3, it is also found that the age reduction factor m is a function of the tensile stress level. Basically, $m(\delta_T)$ first increases and then decreases with increasing tensile stress level. Denote m_{T0} to be the age reduction factor at tensile stress level of 0, the variation of $m(\delta_T)/m_{T0}$ with the tensile stress level is plotted in Fig. 5, and their correlation is determined by means of the linear regression method. The resulting regression formula is a quadratic polynomial as given by Eq. (10).

$$D_{ins,28}(\delta_T) = D_{ins,T0}(1 + 0.20\delta_T) \quad (9)$$

$$m(\delta_T) = m_{T0}(1 + 0.28\delta_T - 0.70\delta_T^2) \quad (10)$$

Substituting Eq. (9) and Eq. (10) into Eq. (3), the model of D_{ins} considering the influence of the coupled time and tensile stress effects can be obtained, as shown in Eq. (11). The linear part of Eq. (11), as replication of right side of Eq. (9), considers the effect of tensile stress on D_{ins} , while the exponential part of Eq. (11) considers the influence of the coupled time and tensile stress effects on D_{ins} .

$$D_{ins}(t') = D_{ins,T0}(1 + 0.20\delta_T) \left(\frac{t_{28}}{t'} \right)^{m_{T0}(1 + 0.28\delta_T - 0.70\delta_T^2)} \quad (11)$$

4.2. Influence of the coupled time and compressive stress effects on D_{ins}

In this section, the experimental data from Xu et al. [33] is adopted to study the influence of the coupled time and concrete compressive stress effects on D_{ins} . In the test, the water/cement ratio of concrete specimens was 0.57, and ordinary Portland cement (P.O. 42.5) conforming to the AQSIQC standard GB 175–2007 [30] was used. The fine aggregate was natural river sand with a fineness modulus of 2.40. The coarse aggregate was gravel with maximum size of 20 mm and apparent density of 2880 kg/m³. The mixing water was tap water. The mix proportions of concrete contained 360 kg/m³ of cement, 205 kg/m³ of water, 661 kg/m³ of sand, and 1174 kg/m³ of gravel. There were six groups of specimens subjected to different compressive stress levels δ_c (i.e. the ratio of compressive stress to concrete compressive strength), and each group had four specimens. The specimen size was 100 × 100 × 300 mm. The compressive stress levels applied to the six groups of specimens were 0, 0.1, 0.3, 0.4, 0.5, and 0.6, respectively. The number of drying-wetting cycles in 3.5% NaCl solution underwent by four specimens in each group was 25, 50, 75 and 100, respectively. Each drying-wetting cycle was 1 day, including 12 h of drying and 12 h of wetting. The experimental data of specimens can be found in Xu et al. [33]. The values of C_s and D_a under different compressive stress levels were reported in Xu et al. [33], and are tabulated in Table 4.

Based on the values of D_a listed in Table 4, by using the proposed computation method of D_{ins} in Section 3, the values of D_{ins} at different exposure time (or concrete ages) and the age reduction factor m under different compressive stress levels can be obtained, as shown in Table 5 and Table 6, respectively. From Table 5, it is found that D_{ins} is time-dependent and decreases with increasing exposure time. When the compressive stress level ranges from 0 to 0.3, concrete is in elastic stage, and the compressive stress reduces the porosity of concrete, so that the chloride diffusion coefficient decreases with the increase in compressive stress level, but it is not substantial [21,34], hence the D_{ins} in Table 5 changes slightly. When the compressive stress level is greater than 0.3, new micro-cracks are formed inside concrete [21,35]. If the decrease in volume of the pores inside concrete is less than the increase in volume of the micro-cracks formed under compressive

Table 4
Values of C_s (%) and D_a ($\times 10^{-11}$ m²/s) under different compressive stress levels.

Exposure time (d)	Compressive stress level δ_c									
	0		0.3		0.4		0.5		0.6	
	C_s	D_a	C_s	D_a	C_s	D_a	C_s	D_a	C_s	D_a
25	0.115	6.190	0.113	6.130	0.138	7.057	0.174	8.240	0.225	9.462
50	0.145	3.452	0.142	3.451	0.171	4.622	0.211	6.093	0.269	7.134
75	0.168	2.523	0.171	2.517	0.191	3.483	0.226	4.680	0.291	5.770
100	0.176	2.120	0.173	2.130	0.201	3.075	0.236	4.210	0.305	5.384

Table 5
Values of D_{ins} ($\times 10^{-11}$ m²/s) under different compressive stress levels.

Exposure time (d)	Concrete age (d)	Compressive stress level δ_c				
		0	0.3	0.4	0.5	0.6
		D_{ins}	D_{ins}	D_{ins}	D_{ins}	D_{ins}
—	28	8.764	8.502	8.774	9.632	10.761
25	53	2.694	2.695	3.951	5.346	6.539
50	78	1.273	1.297	2.336	3.598	4.674
75	103	0.791	0.816	1.700	2.845	3.824
100	128	0.556	0.579	1.352	2.404	3.311

Table 6
Values of m under different compressive stress levels.

δ_c	0	0.3	0.4	0.5	0.6
m	1.85	1.81	1.26	0.93	0.79
R^2	0.9991	0.9990	0.9975	0.9965	0.9966

stress, the chloride ion diffusion channel would enlarge, and the D_{ins} will increase with further increase in compressive stress level.

Comparing Table 4 and Table 5, it can be found that there is large difference between D_{ins} and D_a under the same compressive stress level, and the relative error Δ_D among the two coefficients can be calculated per Eq. (8), as depicted in Fig. 6. It can be observed from the figure that D_{ins} is smaller than D_a , and the relative error Δ_D ranges approximately from 30% to 75%. In general, Δ_D increases with the exposure time under the same compressive stress level, and decreases with increasing compressive stress level at the same exposure time.

To establish the time-dependent and compressive stress-dependent model of D_{ins} through Eq. (3), it is necessary to first establish the relationship between $D_{ins, ref}$ and concrete

compressive stress. The values of D_{ins} listed in Table 5 at concrete age of 28 days are taken as $D_{ins,ref}$ in Eq. (3). For brevity, it is denoted as $D_{ins,28}(\delta_c)$, or simply as $D_{ins,28}$. Further, the value of D_{ins} at concrete age of 28 days and compressive stress level of 0 is evaluated and denoted as $D_{ins,C0}$. The relationship between $D_{ins,28}(\delta_c)/D_{ins,C0}$ and compressive stress level is plotted in Fig. 7, and their correlation is determined by means of the linear regression method. The resulting regression formula is given by Eq. (12). Basically, $D_{ins,28}$ has a quadratic polynomial relationship with the compressive stress level, and it first decreases and then increases with increasing compressive stress level.

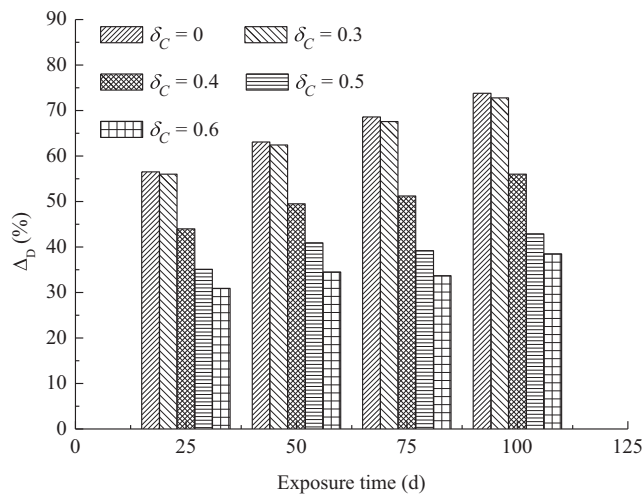
$$D_{ins,28}(\delta_c) = D_{ins,C0}(1 - 0.66\delta_c + 1.72\delta_c^2) \tag{12}$$


Fig. 6. Relative deviation between D_{ins} and D_a under compressive stress.

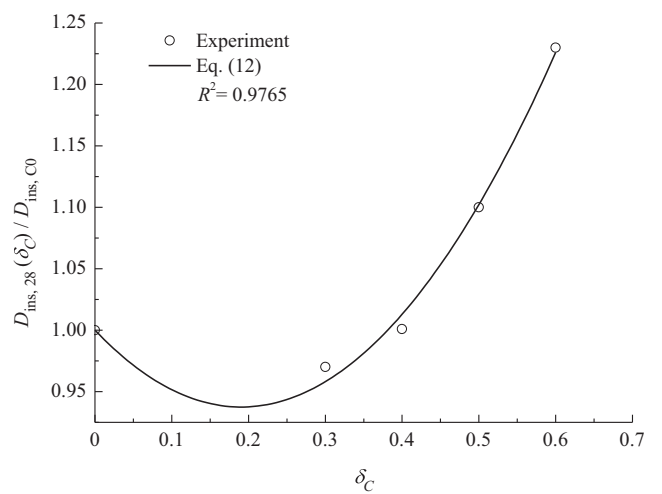


Fig. 7. Relationship between $D_{ins,28}(\delta_c)/D_{ins,C0}$ and compressive stress level.

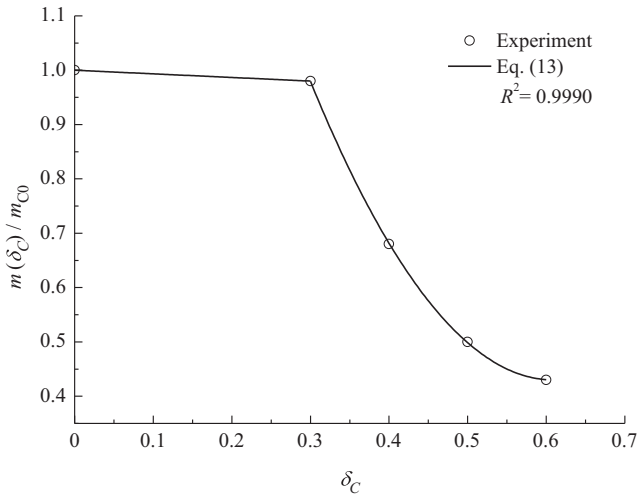


Fig. 8. Relationship between $m(\delta_c)/m_{C0}$ and compressive stress level.

It is also found from Table 6 that the age reduction factor m is a function of the compressive stress level. Basically, $m(\delta_c)$ decreases with increasing compressive stress level at variable rate. Denote m_{C0} to be the age reduction factor at compressive stress level of 0, the variation of $m(\delta_c)/m_{C0}$ with the compressive stress level is plotted in Fig. 8. In view of m changes slightly within the range of compressive stress level from 0 to 0.3, and changes rapidly when the compressive stress level is greater than 0.3, piecewise function is employed in the linear regression to determine the relationship between $m(\delta_c)$ and compressive stress level, as stated in Eq. (13).

$$m(\delta_c) = \begin{cases} m_{C0}(1 - 0.07\delta_c) & (0 \leq \delta_c \leq 0.3) \\ m_{C0}(2.56 - 7.01\delta_c + 5.75\delta_c^2) & (0.3 \leq \delta_c \leq 0.6) \end{cases} \quad (13)$$

Substituting Eq. (12) and Eq. (13) into Eq. (3), the model of D_{ins} considering the influence of the coupled time and compressive stress effects can be obtained, as shown in Eq. (14). The quadratic part in Eq. (14), as replication of right side of Eq. (12), considers the effect of compressive stress on D_{ins} , while the exponential part of Eq. (14) considers the influence of the coupled time and compressive stress effects on D_{ins} .

$$D_{ins}(t') = D_{ins,C0} (1 - 0.66\delta_c + 1.72\delta_c^2) \left(\frac{t_{28}}{t'} \right)^{m(\delta_c)} \quad (14)$$

5. Theoretical model of chloride concentration

On the basis of the formulations to account for the influence of the coupled exposure time and concrete stress effects on the D_{ins} as proposed in the last section, the theoretical model of chloride ion concentration is hereunder established, which is useful for durability design and residual service life prediction of concrete structures in chloride-laden environment.

Table 7
Values of C_s (%) and D_a ($\times 10^{-12}$ m²/s) under different tensile stress levels from Wang et al. [13].

Exposure time (d)	Tensile stress level δ_T					
	0		0.3		0.5	
	C_s	D_a	C_s	D_a	C_s	D_a
35	0.313	12.519	0.266	14.916	0.318	15.147
70	0.316	9.449	0.326	10.483	0.375	10.911
120	0.331	6.933	0.359	7.351	0.431	7.146
180	0.399	4.807	0.430	5.360	0.509	5.236

5.1. Theoretical model of chloride concentration under coupled time and tensile stress effects

Considering the influence of the coupled time and tensile stress effects, the model of D_{ins} is represented by Eq. (11). Let $t_1 = t_{28}$, $t_2 = t_{28} + t$, and substituting Eq. (11) into Eq. (4), the relationship among D_a , D_{ins} , δ_T and the exposure time can be obtained, as expressed in Eq. (15).

$$D_a = \frac{D_{ins,28}(\delta_T)}{1 - m(\delta_T)} \left[\left(1 + \frac{t_{28}}{t} \right)^{1-m(\delta_T)} - \left(\frac{t_{28}}{t} \right)^{1-m(\delta_T)} \right] \cdot \left(\frac{t_{28}}{t} \right)^{m(\delta_T)} \quad (15)$$

Subsequently, by substituting Eq. (15) into Eq. (2), the theoretical model of chloride ion concentration which considers the influence of the coupled exposure time and concrete tensile stress effects as given by Eq. (16) is established. It should be noted that δ_T in the expression is limited to 0.7, which corresponds to the upper limit of the range of tensile stress experimentally investigated by Wang [29].

$$C(x, t) = C_s \left[1 - \operatorname{erf} \left(\frac{x}{2 \sqrt{\frac{D_{ins,28}(\delta_T)}{1 - m(\delta_T)} \left[\left(1 + \frac{t_{28}}{t} \right)^{1-m(\delta_T)} - \left(\frac{t_{28}}{t} \right)^{1-m(\delta_T)} \right] \cdot \left(\frac{t_{28}}{t} \right)^{m(\delta_T)} \cdot t}} \right) \right] \quad (0 \leq \delta_T \leq 0.7) \quad (16)$$

5.2. Theoretical model of chloride concentration under the coupled time and compressive stress effects

Considering the influence of the coupled time and compressive stress effects, the model of D_{ins} is represented by Eq. (14). Let $t_1 = t_{28}$, $t_2 = t_{28} + t$, and substituting Eq. (14) into Eq. (4), the relationship among D_a , D_{ins} , δ_c and the exposure time can be obtained, as expressed in Eq. (17).

$$D_a = \frac{D_{ins,28}(\delta_c)}{1 - m(\delta_c)} \left[\left(1 + \frac{t_{28}}{t} \right)^{1-m(\delta_c)} - \left(\frac{t_{28}}{t} \right)^{1-m(\delta_c)} \right] \cdot \left(\frac{t_{28}}{t} \right)^{m(\delta_c)} \quad (17)$$

Subsequently, by substituting Eq. (17) into Eq. (2), the theoretical model of chloride ion concentration which considers the influence of the coupled exposure time and concrete compressive stress effects as given by Eq. (18) is established. It should be pointed out that δ_c in the expression is limited to 0.6, which corresponds to the upper limit of the range of compressive stress experimentally investigated by Xu et al. [33].

$$C(x, t) = C_s \left[1 - \operatorname{erf} \left(\frac{x}{2 \sqrt{\frac{D_{ins,28}(\delta_c)}{1 - m(\delta_c)} \left[\left(1 + \frac{t_{28}}{t} \right)^{1-m(\delta_c)} - \left(\frac{t_{28}}{t} \right)^{1-m(\delta_c)} \right] \cdot \left(\frac{t_{28}}{t} \right)^{m(\delta_c)} \cdot t}} \right) \right] \quad (0 \leq \delta_c \leq 0.6) \quad (18)$$

6. Model validation

In this section, the experimental data from Wang et al. [13] and Wang et al. [21] are utilised to validate the rationality of Eq. (16) and Eq. (18), respectively.

Wang et al. [13] studied the influence of mechanical load on chloride diffusion in concrete members in tidal zone and salt spray zone. For this purpose, 40 plain concrete beam specimens with size of $100 \times 100 \times 400$ mm were cast. There were 20 specimens in tidal zone and 20 specimens in salt spray zone respectively, and the specimens in each zone were divided into four groups according to the pre-defined exposure time for chloride penetration (35, 70, 120, and 180 days). The load levels applied to the four groups of specimens in each zone were 0, 0.3, and 0.5 times of concrete strength. For each specimen, five faces were sealed with epoxy while one rectangular face was left unsealed to allow chloride ion penetration from only one dimension. The experimental data from the specimens in tidal zone are employed to verify Eq. (16). The values of C_s and D_a under different tensile stress levels are reported in Wang et al. [13], as summarised in Table 7. In Eq. (16), $D_{ins,T0}$ and m_{T0} are unknown parameters which can be determined by way of the proposed computation method in Section 3 through the values of D_a under zero tensile stress level listed in Table 7. The values of $D_{ins,T0}$, m_{T0} , and t_{28} are 15.364×10^{-12} m²/s, 0.85, and 28 days respectively, and the values of C_s are listed in Table 7. Fig. 9 depicts the comparison between the computed results from Eq. (16) and the experimental data from Wang et al. [13]. It can be observed that the computed results agree well with the experimental data. The R^2 value ranges from 0.964 to 0.999, indicating the high accuracy and reliability of the proposed theoretical model.

Wang et al. [21] studied the influence of sustained compressive load on chloride diffusion in concrete. In the test, the specimens with size of $100 \times 100 \times 300$ mm were cast in laboratory at air temperature of $25 \pm 2^\circ\text{C}$. The compressive stress levels applied to the specimens were 0, 0.2, 0.3, 0.4, 0.5, and 0.7 times the concrete compressive strength. All the specimens were exposed to an alternate wetting-drying environment for undergoing four different configurations of exposure cycles (4, 8, 12, and 16 cycles respectively). Each cycle consisted of 1 week of immersion in 5% NaCl solution followed by 1 week of drying in a tank, therefore, the four exposure cycles corresponded to 56, 112, 168, and 224 days, respectively. In Eq. (18), the compressive stress level δ_c is limited to 0.6, and the experimental data of the specimens with compressive stress level of 0.3 were not given in Wang et al. [21], hence the experimental data of the specimens with compressive stress level of 0, 0.2, 0.4, and 0.5 are selected to verify Eq. (18). In the computation using Eq. (18), $D_{ins,C0}$ and m_{C0} are unknown parameters which can be determined by way of the proposed computation method in Section 3 through the values of D_a under zero compressive stress level listed in Table 8. The values of $D_{ins,C0}$, m_{C0} , and t_{28} are 2.296×10^{-11} m²/s, 0.53, and 28 days respectively, and the values of C_s are listed in Table 8. Comparison between the computed results from Eq. (18) and the experimental data is shown in Fig. 10. It can be observed from the figure that the computed results are consistent with the experimental data. Except when the compressive stress level is 0.5 and the exposure time is 224 days in Fig. 10 (d) where the R^2 value is 0.769, the other values of R^2 are between 0.904 and 0.996, which indicates that the proposed theoretical

Table 7
Values of C_s (%) and D_a ($\times 10^{-12}$ m²/s) under different tensile stress levels from Wang et al. [13].

Exposure time (d)	Tensile stress level δ_T					
	0		0.3		0.5	
	C_s	D_a	C_s	D_a	C_s	D_a
35	0.313	12.519	0.266	14.916	0.318	15.147
70	0.316	9.449	0.326	10.483	0.375	10.911
120	0.331	6.933	0.359	7.351	0.431	7.146
180	0.399	4.807	0.430	5.360	0.509	5.236

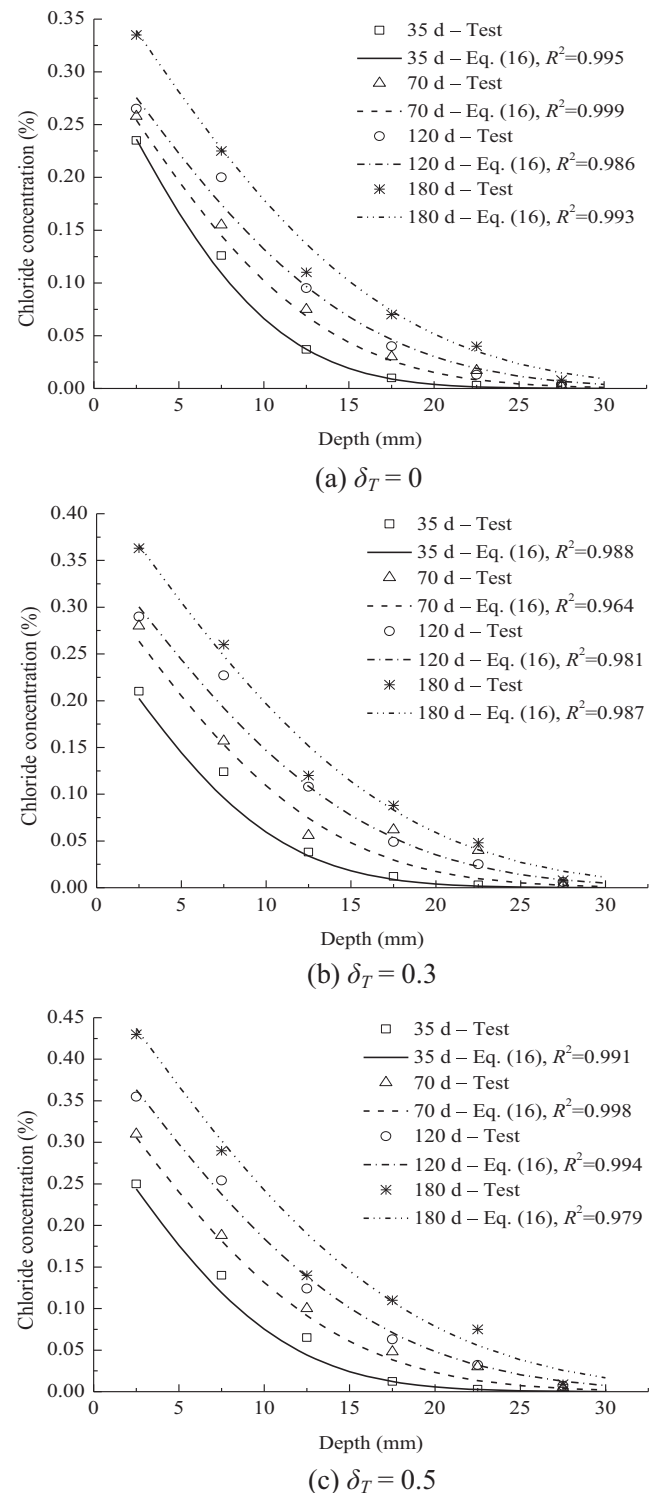


Fig. 9. Comparison between the computed results from Eq. (16) and the test data from Wang et al. [13].

model is accurate and reliable for predicting chloride ion concentration in concrete under compressive stress state.

It should be particularly pointed out that the derivation process in Section 3 allows the calculation of D_{ins} based on measured data of chloride ion concentration in concrete structures under loads. Laboratory and field measurements of chloride ion concentration in different exposure environment can be conducted, such that the time-dependent and stress-dependent models of D_{ins} corre-

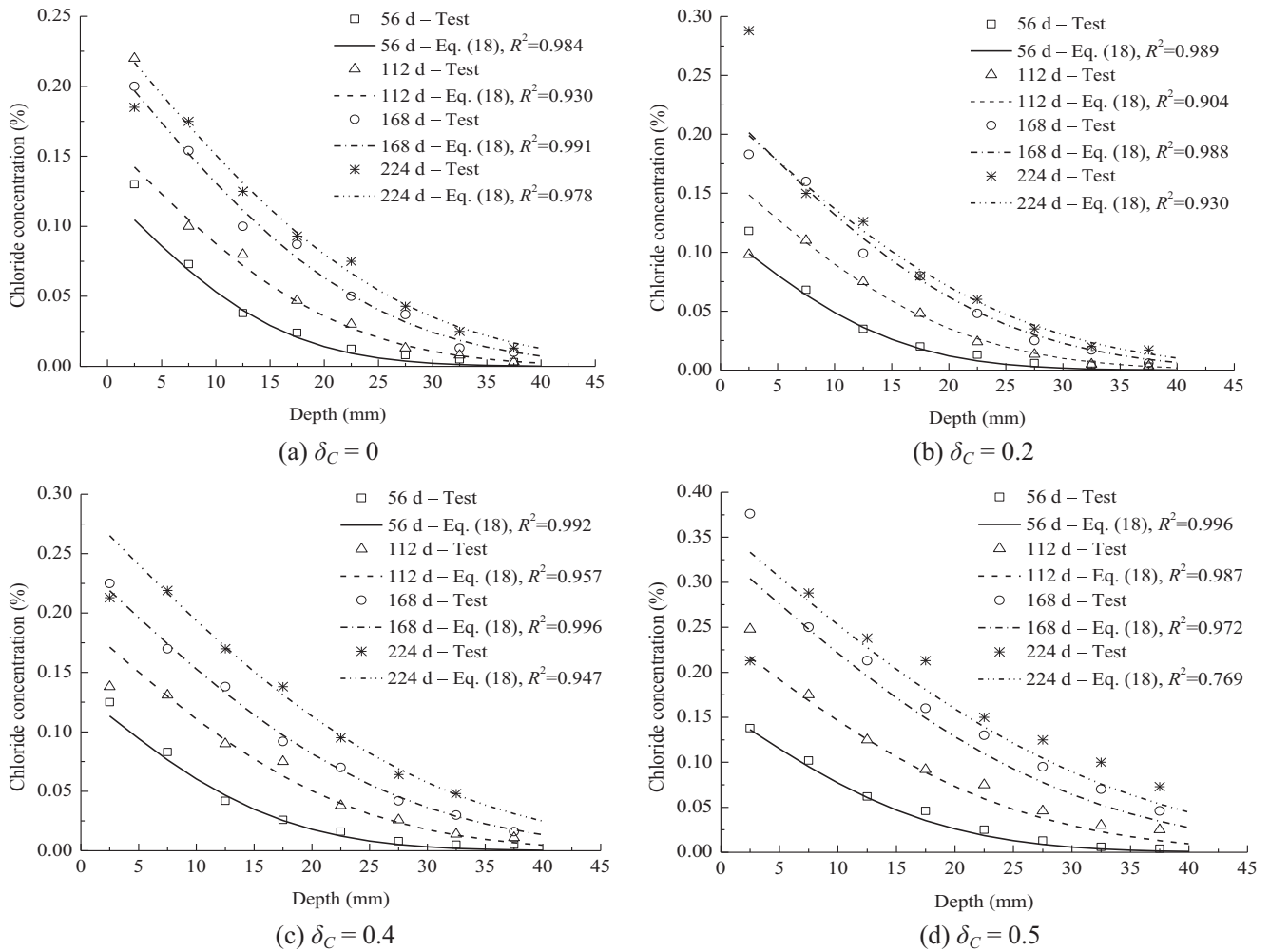


Fig. 10. Comparison between the computed results from Eq. (18) and the test data from Wang et al. [21].

spond to various materials and environmental conditions can be established. This enables calibration of the theoretical model of chloride ion concentration that considers the influence of the coupled exposure time and concrete stress effects, in order to develop universal prediction model of chloride ion concentration for durability design and service life prediction of concrete structures.

7. Conclusions

Based on the results obtained in this research, the following conclusions can be drawn:

- (1) A method for calculating the instantaneous chloride diffusion coefficient D_{ins} has been proposed, and a model of D_{ins} considering the influence of the coupled time and concrete stress effects has been established.
- (2) When concrete is subjected to tensile or compressive stress, D_{ins} is smaller than D_a at the same exposure time, and the relative errors between them are approximately in the range of 45% to 65% or 30% to 75%, respectively. Under the same concrete stress level, the relative error between D_{ins} and D_a increases with the exposure time. While at the same exposure time, the relative error first increases and then decreases with increasing tensile stress level, whereas it decreases with increasing compressive stress level.

- (3) It is noted that D_{ins} manifests both time and stress dependence. At the same exposure time, D_{ins} increases with increasing tensile stress level, and first decreases and then increases with increasing compressive stress level. Under the same tensile or compressive stress level, D_{ins} decreases with increasing exposure time. On the other hand, the age reduction factor m manifests stress dependence and can be expressed as a function of concrete stress level.
- (4) The theoretical model of chloride ion concentration considering the influence of the coupled exposure time and concrete stress effects has been established. The model is useful for durability design and residual service life prediction of concrete structures in chloride-laden environment. Further research to carry out additional laboratory experimentation and field measurements with different materials and at varying environmental conditions for possible extension and refinement of the model is recommended.

CRediT authorship contribution statement

J. Wang: Methodology, Validation, Formal analysis, Investigation, Writing - original draft. **P.-L. Ng:** Formal analysis, Investigation, Writing - review & editing. **H. Su:** Investigation. **J.-S. Du:** Conceptualization, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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