Research Article

Chloride Penetration in Coastal Concrete Structures: Field Investigation and Model Development

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Field measurements of 42 in-service reinforced concrete bridges in coastal environments of Southeast China, covering a wide range of service year, span length, and concrete mixture, were carried out to investigate the chloride penetration. 323 sets of chloride measurement data were collected in total and then analyzed to optimize the parameters involved in the common chloride diffusion model derived based on Fick’s second law. A modified chloride diffusion model was then proposed, taking into consideration a range of influencing factors including ambient temperature, relative humidity, stress state, carbon dioxide, chloride binding, and ageing. Verification of the modified model with field measurement data was performed. The sensitivity of the chloride diffusion to variations of each parameter was discussed in detail eventually.

1. Introduction

Chloride-induced corrosion of reinforcing steel is the main issue affecting the durability of reinforced concrete (RC) structures in coastal environments [1, 2]. Corrosion of rebars usually requires repair or replacement of RC elements, resulting in huge maintenance cost, out of service time, and waste of materials and energy [3–5]. The maintenance cost of concrete bridges in developed countries, such as the United States, Canada, Japan, Australia, and the United Kingdom, has accounted for 0.01% to 0.1% of the gross domestic product in recent years [6]. Growing attention has been paid to accurate predictions of the chloride penetration in concrete worldwide.

The penetration of chloride ions in concrete is a complicated process, and diffusion is generally regarded as the primary transport mechanism in present service life calculations [7]. Collepardi [8] was the first who studied the diffusion characteristics of chloride ions in concrete based on Fick’s second law. Noteworthy, the prediction accuracy of Collepardi’s model was found imperfect in practical applications due to oversimplified assumptions. A comprehensive literature survey has revealed that chloride diffusion in concrete is influenced by a number of factors. Quantitative characterizations and mathematical descriptions regarding the effects of these factors on chloride diffusion are available. The impact of temperature on the chloride diffusion has been normally formulated by using the well-known Arrhenius law. Based on a series of experimental measurements, Mangat and Molloy [9] found a decreasing trend of chloride diffusion as elapse of time, and they used a power function to describe the ageing effect; i.e., the chloride diffusion coefficient decreases with age. Chloride binding capacity is another important parameter influencing the chloride penetration. The binding behaviour can be physical (mainly by calcium silicate hydrates) and/or chemical (mainly by aluminate phases) [6]. Different types of chloride binding isotherms including linear, Langmuir, Freundlich, and BET were recognized depending on the concrete mixture and particularly on the chloride concentration [10]. Changes of water-cement ratio (0.35–0.5) and replacement of ordinary Portland cement by pozzolans (i.e.,
5% silica fume, 5% metakaolin, or 10% natural zeolite) led to substantial differences in chloride diffusion, as investigated by Tadayon et al. [11]. The rate of chloride diffusion can decrease by a factor of 20 when the internal relative humidity of concrete decreases from 100% to 80%. The S-shaped relationship and Gaussian function were reported enabling to describe the moisture-dependent chloride diffusion [12, 13].

It should be noted that most previous models/equations were put forward based on the data from laboratory tests and that the aforementioned studies only considered a single variable in the analysis of chloride diffusion. As a matter of fact, the chloride diffusion in concrete depends on environmental conditions, as well as on a variety of other factors among which the time dependency of chloride diffusion is of uttermost importance. Software called Life-365 considering various influencing factors was developed to predict the service life and life-cycle cost of reinforced concrete exposed to chloride-laden environments [14]. The team from the DuraCrete project launched a chloride diffusion model that includes an ageing factor, an environmental factor, and a curing factor [15]. The model by Ababneh [16] combined the effects of chloride binding, moisture capacity, and moisture diffusion coefficient. Wang et al. [17] highlighted the importance of stress state in chloride transport. They investigated the chloride diffusion in concrete under different stress states and then proposed chloride diffusion equations considering a series of factors such as stress level, age, temperature, and relative humidity. The strong interrelationships between carbonation, aggregate shape, chloride binding, and diffusion have recently been formulated [18–20]. Nguyen et al. [21] reported a chloride ingress model considering the temperature, age, moisture content, and chloride concentration. All factors that change the microstructure and internal moisture condition will inevitably alter the chloride penetration [22]. The different models aforementioned will be further discussed afterwards.

The chloride ion concentration of the concrete surface, when exposed to the marine environment, is a function of exposure time [23]. Song et al. [24] and Pack et al. [25] proposed a logarithmic function to characterize the time-dependent characteristics of the surface chloride concentration. A square root function was adopted by Petcherdchoo [26] for the same purpose. The time-dependence of concrete surface chloride content was affected by the water-cement ratio and chloride concentration of the ambient environment [27, 28]. In present service life calculations, e.g., Life-365 [14] and DuraCrete [15], the surface chloride concentration $C_s$ of concrete (when exposed for a relatively long-term period to stable environment including atmospheric, tidal, and submerged) is set as a constant.

Up to date, the data from field exposure tests or on-site measurements regarding chloride penetration remain limited. Calibrations, validations, or modifications of the laboratory-based model with data from field investigations have been of prime interest for a reliable service life prediction. In this study, 42 coastal concrete bridges with different ages, span lengths, and concrete mixtures in Fujian province of Southeast China were investigated. The chloride concentration at different depths of these concrete bridges was sampled and measured. In total, 323 sets of data were collected, with which the existing chloride diffusion models were evaluated and compared. A modified chloride diffusion model for the concrete structures in the marine environment is then proposed after verifications with field data. A detailed discussion regarding sensitivity analysis of chloride diffusion to changes of each influencing parameter is carried out subsequently.

2. Field Investigations of Chloride Penetration

2.1. General Information of the Coastal Concrete Bridges.

Fujian province is located along the coast of Southeast China with a broad coastline whose climate is typically as high temperature and high humidity. A total of 42 in-service concrete bridges from four cities, as shown in Figure 1(a), in Fujian coastal areas were selected for investigation. Table 1 gives the information of the concrete bridges. Ordinary Portland cement was the essential binder for all concretes. The water-cement ratio was similarly in the range of 0.42–0.46. All concretes were exposed to the atmospheric marine condition. The construction details of these bridges were provided by the China Bridge Management System (CBMS) and the Fujian Highway Administrative Bureau. The age distribution of these bridges is shown in Figure 1(b). More than 60% of the bridges are in the range of 11–30 years old. The oldest age is 51 years, while the youngest is only 5 years. The selected bridges cover a wide range of coastlines and service years and can therefore representatively reflect the chloride penetration process in concrete structures serving in the coastal environment. The climate over the past 20 years has been recorded for the four cities under study. Annual changes of the average values of the ambient temperature $T$ and humidity RH of the concrete bridges in Ningle city (as a representative) are given in Figures 1(c) and 1(d), respectively. Note that the four cities exhibit slightly different $T$ values (around 2°C maximum) and different RH values (around 1.5% maximum).

2.2. Sample Collection and Chloride Content Measurement.

Concrete samples were drilled from the bottom of the bridge decks or piers on-site, following the sampling procedure specified in China Technical Specification for Test of Chloride Ion Content in Concrete (JGJ/T322-2013) [29]. Powder samples were obtained by grinding the concretes at the depth from 2.5 mm to 50 mm. The powder samples were taken at intervals of 5 mm for the first 30 mm and of 10 mm for the depth 35–50 mm. Then, the powder samples were sieved through a 0.16 mm mesh screen and dried in an oven at the temperature of 105 ± 5°C for 2 hours before cooling down to room temperature in a desiccator. The chloride content of the concrete powder samples was measured by the ion chromatography. The procedure in detail is described as follows:

1) A 1000 mg/l of chloride solution was diluted by deionized water into 2, 4, 6, 8, 10, and 15 mg/l solutions. The diluted solutions were then processed.
with the ion chromatography method to get the calibration curves for chloride content measurement as shown in Figure 2.

(2) Concrete powder sample of 200 mg was dissolved in deionized water for two hours. Then the solution was filtered by a slow speed quantitative filtration paper and rinsed with deionized water.

(3) A small amount of the solution sample was collected and tested with the silver nitrate until no pre-

(4) These solutions were processed in the chromatography apparatus to determine the chloride content. A total of 323 sets of concrete powder samples were investigated based on the above procedures. The results were expressed in terms of mass percentage (i.e., the mass percentage of the chloride ions in concrete).

2.3. Data Analysis. The diffusion of chloride ions in concrete can be accelerated when the ambient temperature and humidity are high [30]. The exposure site of the selected concrete bridges in this study can be regarded under a typical high-temperature and high humidity environment. The average annual humidity is about 80%, and the average annual temperature is about 20°C with a maximum temperature over 35°C. For concrete structures in the atmospheric environment, chloride penetration is affected by capillary absorption in the surface concrete and diffusion is the primary mechanism of chloride transport in the internal concrete [31]. Figure 3 shows the typical chloride profile in the bridges. The chloride concentration generally decreases along the depth, and the peak concentration of chlorides appears at a certain depth near the surface.
phenomenon is ascribed to the capillary absorption effect on the surface as well as the precipitation of chloride crystals.

By using Fick’s 2nd law of diffusion to fit the chloride profile, i.e., depths from 7.5 mm to 45 mm as given in Figure 3, the surface chloride concentration $C_s$ is calculated to be about 0.10% (with correlation coefficient $R^2 = 0.737$). Note that the convection zone was not taken into consideration in curve fitting of the chloride profile. However, physically speaking, the fitted $C_s$ value is applicable to the real marine circumstance because all influencing factors, which may not be considered but hidden behind the $C_s$ value, were already involved in the chloride profile (depths 7.5–45 mm). The thickness of the concrete cover is approximated as 27.5 mm. Note that according to the ACI Guide to Durable Concrete (ACI 201R-16) [32] and the Chinese Code for Design of Concrete Structures (GB 50010-2010) [33], the limit of the chloride content in prestressed concrete is 0.06%, while the limits are 0.08% and 0.10% as specified in ACI 201R-16 and GB 50010-2010, respectively, for reinforced concrete under coastal conditions. Referring to the above standard specifications, the chloride contents of all the selected bridges in the decks have significantly exceeded the limit. Moreover, the chloride contents of all the bridge piers have exceeded the threshold value as regulated in ACI 201R-16, and five bridges have exceeded the limit beyond the specification in the Chinese code. Hence, the chloride contents in the bridges under the coastal environment are considered detrimental in terms of reinforcement corrosion. In this regard, intensive attention should be paid, and effective actions are immediately required to avoid structural failure of these bridges.

3. Modified Chloride Diffusion Model

3.1. Evaluation of the Existing Chloride Diffusion Models.

Six models of chloride diffusion from the literature are evaluated against the measurement data from 42 coastal concrete bridges. These models include the Collepardi model [8], the Life-365 model [14], the DuraCrete model [15], the Ababneh model [16], the Nguyen model [21] and the Wang model [17]. The model expression and corresponding parameter descriptions are given in Table 2.

Validations of the six models were carried out based on a series of regression analyses. The results of the surface chloride concentration and chloride diffusion coefficient in different models are provided in Table 3. As can be seen, the surface chloride concentrations from different models are similar with a narrow range from 0.095% to 0.101%. On the contrary, the fitted chloride diffusion coefficients show significant differences, which can be related to the different factors introduced in each model. In all cases, the correlation coefficients ($R^2$) are in the range from 0.737 to 0.841, which is in an acceptable agreement, with the Collepardi model being the smallest $R^2$ value of 0.737. Another interesting observation can be ascribed to the Nguyen model, which corresponds to a significantly higher chloride diffusion coefficient than that of other models.

For a further analysis, the mean absolute errors (MAEs), standard deviations (SDs), and coefficients of variation (CVs) of the above models are calculated and compared. As shown in Table 4, all the models show a CV larger than 11%, with the greatest CV of 15.537% from the Collepardi model. Conceivably, based on the test results from the 42 coastal concrete bridges, the Collepardi model may result in the largest discrepancy among these models when it is used for the estimation of the chloride concentration in marine concrete bridges.

Comparisons of the above models with on-site measurement data are shown in Figure 4. Note that 95% of the data points of the Collepardi model falls within the range of ±35%, while 95% of the data points of the Life-365 model, and the DuraCrete model falls within the range of ±30%. For the rest of the models (Ababneh, Nguyen, and Wang), 95% of their respective data points fall within the range of ±25%, i.e., within the two linear relationships $y = (1 ± 0.25)x$. Therefore, based on the on-site measurement data, the latter three models exhibit a better capability in chloride diffusion predictions.
Table 2: Chloride diffusion models from different reports.

| Model          | Model expression                                                                 | Parameter descriptions                                                                 |
|----------------|----------------------------------------------------------------------------------|----------------------------------------------------------------------------------------|
| Collepardi [8] | $C_x = C_s [1 - \text{erf}(x/2\sqrt{Dt})]$                                      | $C_s$ is the chloride concentration at a depth of $x$ (mm) when the concrete age equals $t$ (s); $C_s$ is the surface chloride concentration; $D$ is the chloride diffusion coefficient; erf is the error function |
| Life-365 [14] | $D(t) = D_{ref} (t_{ref}/t)^m \exp[(U/R)((1/T_{ref}) - (1/T))]$                | $D(t)$ is the chloride diffusion coefficient at time $t$; $D_{ref}$ is the diffusion coefficient at a reference time $t_{ref}$ ($= 28$ days); $U$ is the activation energy of the diffusion process; $R$ is the gas constant; $T$ is the absolute temperature. $m$ is the constant (depending on mix proportions) |
| DuraCrete [15] | $D(t) = D_0 (t_0/t)^m k_e k_c$                                                  | $k_e$ is the environment factor; $k_c$ is the curing factor; $D_0$ is the diffusion coefficient at a reference time $t_0$; $f_1$ accounts for effects of water-cement (w/c) ratio and curing time ($t_0$) on the chloride diffusion coefficient; $f_2(g_i)$ accounts for effects of the composite action of aggregates and cement paste on the chloride diffusion coefficient; $f_3(H)$ accounts for the effect of relative humidity on the chloride diffusion coefficient; $f_4(T)$ accounts for the effect of temperature on the chloride diffusion coefficient; $f_5(C_f)$ accounts for the effect of chloride concentration on the chloride diffusion coefficient |
| Ababneh [16]  | $D_{Cl} = f_1(w/c,t_0)f_2(g_i)f_3(H)f_4(T)f_5(C_f)$                              | $D_{Cl,ref}$ is the reference diffusion coefficient measured at standard conditions; $f_1(T)$ takes into account the effect of temperature; $f_2(t_0)$ considers the effect of concrete age; $f_3(w/c)$ accounts for the effect of moisture content; $f_4(C_f)$ considers the effect of chloride concentration |
| Nguyen [21]   | $D_x = D_{Cl,ref} f_1(T) f_2(t) f_3(W) f_4(C_f)$                                  | $D_{cl,ref}(w/c, t_0)$ is defined as a reference chloride diffusion coefficient, accounting for the effect of w/c ratio and curing time ($t_0$); $f_2(t)$ accounts for the influence of concrete age ($t$); $f_3(W)$ considers the effect of temperature; $f_4(C_f)$ accounts for the effect of relative humidity; $f_5(C_{Cl})$ accounts for the dependence of chloride diffusion coefficient on the chloride concentration; $f_6(\lambda_{so})$ accounts for the influence of external loads |

Table 3: Results of regression analysis with different chloride diffusion models.

| Chloride diffusion model | Chloride diffusion coefficient ($D_i$) ($10^{-11}$ m²/s) | Surface chloride concentration ($C_s$) (%) | Coefficient of determination ($R^2$) |
|-------------------------|----------------------------------------------------------|-------------------------------------------|-------------------------------------|
| Collepardi [8]          | 0.394                                                    | 0.095                                     | 0.737                               |
| Life-365 [14]           | 1.047                                                    | 0.096                                     | 0.786                               |
| DuraCrete [15]          | 0.497                                                    | 0.097                                     | 0.797                               |
| Ababneh [16]            | 7.891                                                    | 0.101                                     | 0.841                               |
| Nguyen [21]             | 44.60                                                   | 0.101                                     | 0.836                               |
| Wang [17]               | 3.187                                                    | 0.098                                     | 0.830                               |

Table 4: Accuracy of different models for predicting chloride diffusion in marine concrete bridges.

| Model          | Average | Mean absolute error (MAE) (%) | Standard deviation (SD) | Coefficient of variation (CV) |
|----------------|---------|-------------------------------|-------------------------|------------------------------|
| Collepardi [8] | 1.013   | 11.355                        | 0.157                   | 15.537                       |
| Life-365 [14]  | 1.014   | 10.189                        | 0.137                   | 13.558                       |
| DuraCrete [15] | 1.011   | 9.904                         | 0.134                   | 13.259                       |
| Ababneh [16]  | 1.009   | 8.820                         | 0.114                   | 11.294                       |
| Nguyen [21]   | 1.009   | 8.933                         | 0.117                   | 11.597                       |
| Wang [17]     | 1.008   | 8.892                         | 0.118                   | 11.657                       |
Figure 4: Continued.
3.2. Modified Chloride Diffusion Model for Coastal Structures.

Fick’s 2nd law is widely used nowadays to describe the chloride penetration in concrete [8]:

\[ \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}, \]

\[ C(x, t) = C_0 + (C_S - C_0) \left[ 1 - \text{erf} \left( \frac{x}{2\sqrt{D}t} \right) \right], \]

where \( C(x, t) \) is the chloride concentration at a depth of \( x \) (mm) when the concrete age equals \( t \) (s), \( C_0 \) is the initial chloride concentration, \( C_S \) is the surface chloride concentration, \( D \) is the chloride diffusion coefficient, and \( \text{erf} \) is the error function which can be expressed by

\[ \text{erf}(u) = \frac{2}{\sqrt{\pi}} \int_0^u e^{-t^2} dt. \]

It is assumed that the diffusion of chloride ions in concrete is one-dimensional in a semi-infinite uniform medium and the chloride diffusion is not constant. Fick’s 2nd law can be modified as

\[ \frac{\partial C(x, t)}{\partial t} = D(t, \eta) \frac{\partial^2 C(x, t)}{\partial x^2}, \]

where \( D(t, \eta) \) is the modified chloride diffusion coefficient and \( \eta \) is introduced representing various influencing parameters on chloride diffusion, which covers the effects of concrete characteristics, exposure condition, temperature, relative humidity, age, and stress state.

For the sake of simplification, the modified chloride diffusion coefficient is expressed as

\[ D(t, \eta) = D_1(t) \cdot f(\eta), \]

where \( D_1(t) \) and \( f(\eta) \) refer to the chloride diffusion coefficient (changing with hydration time \( t \)) and the correction factor (related to various influencing parameters), respectively.

Due to the continuous cement hydration, the pore structure inside concrete normally continues refining with age. The time-dependent chloride diffusion coefficient \( D_1(t) \) can be expressed as [34]

\[ D_1(t) = D_0 \left( \frac{t_0}{t} \right)^m, \]

where \( D_0 \) is the chloride diffusion coefficient at a reference age \( t_0 \) and \( m \) is the ageing factor.

Following the partial coefficient method, \( f(\eta) \) can be expressed as

\[ f(\eta) = q_e \cdot q_s \cdot q_k \cdot q_{\text{RH}}(\text{RH}) \cdot q_T(T), \]

where \( q_e \) is the chloride binding coefficient [35], \( q_s \) is the stress coefficient (being 0.8–0.9 under compression and 1.0–1.1 under tension [36]), \( q_k \) is the deterioration coefficient related to the aggressive environment [36], \( q_T \) is the coefficient related to carbon dioxide attack, and \( q_{\text{RH}}(\text{RH}) \) and \( q_T(T) \) account for the effect of temperature and relative humidity, respectively, on the chloride diffusion in concrete.

For carbon dioxide, its effect on chloride diffusion can be formulated as [37]

\[ q_e = \left( \frac{C}{C_1} \right)^a, \]
where $C$ and $C_1$ (i.e., 0.0476%) are the measured and standard carbon dioxide concentrations, respectively, and $a$ is the carbon dioxide concentration coefficient.

The effect of temperature on chloride diffusion can be described by the Arrhenius equation [16]:

$$q_T(T) = \exp \left[ \frac{U}{R} \left( \frac{1}{T_0} - \frac{1}{T} \right) \right],$$

(8)

where $U$ is the activation energy of the chloride diffusion (35000 J/mol), $R$ is the gas constant (8.314 J mol$^{-1}$ K$^{-1}$), and $T$ and $T_0$ ($T_0=296$ K) are the current and the reference absolute temperatures, respectively.

From the study of Saetta et al. [30], the effect of relative humidity on chloride diffusion is formulated as

$$q_{RH}(RH) = \left[ 1 + \left( \frac{1 - RH}{1 - RH_c} \right)^{4a} \right]^{-1},$$

(9)

where $RH$ and $RH_c$ are the measured relative humidity and the critical relative humidity, respectively. The $RH_c$ value is estimated as 75% for ordinary Portland cement concrete [30, 38].

By substituting equations (7) to (8) into equation (6), $f(\eta)$ can be obtained:

$$f(\eta) = q_e \cdot q_s \cdot \left( \frac{C}{C_1} \right)^a \cdot \left[ 1 + \left( \frac{1 - RH}{1 - RH_c} \right)^{4a} \right]^{-1} \cdot \exp \left[ \frac{U}{R} \left( \frac{1}{T_0} - \frac{1}{T} \right) \right].$$

(10)

By substituting equations (5) to (9) into equation (4), a modified chloride diffusion coefficient as shown in the following equation is then obtained for concrete structures in the coastal environment:

$$D(t, \eta) = q_e \cdot q_s \cdot q_k \cdot \left( \frac{C}{C_1} \right)^a \cdot \left[ 1 + \left( \frac{1 - RH}{1 - RH_c} \right)^{4a} \right]^{-1} \cdot \exp \left[ \frac{U}{R} \left( \frac{1}{T_0} - \frac{1}{T} \right) \right] \cdot D_0 \left( \frac{t_0}{T} \right)^m.$$  

(11)

Substituting equation (11) into equation (3), and assuming that the initial chloride concentration ($C_0$) inside the concrete is zero and the surface chloride concentration $C_s$ is constant, a modified chloride diffusion model is subsequently proposed and shown as follows:

$$C(x,t) = C_s \times \left[ 1 - \text{erf} \left( \frac{x}{2 \sqrt{D_0(t)f(\eta)t^{1-m}}} \right) \right].$$

(12)

where $D_0(t)$ is expressed as follows:

$$D_0(t) = \frac{m}{1-m}D_0.$$  

(13)

The proposed model, equation (12), has accounted for the influences of temperature, relative humidity, carbon dioxide, stress state, chloride binding, and the deterioration coefficient of the environment. Note that the influence of convection is neglected for simplicity in the proposed model. In order to determine the parameters in equation (12), regression analysis was implemented based on the on-site measurement data from the 42 in-service marine concrete bridges in Fujian province. The results are listed in Table 5.

Given that all bridges under investigation have been in service for more than 5 years; for the sake of a simplified calculation, the surface chloride concentration $C_s$ is assumed as a constant and set to be 0.0986% (Table 5). In this context, the modified chloride diffusion model for marine concrete structures can be established and is described in equations (14a) and (14b):

$$C(x,t) = 0.0986\% \times \left[ 1 - \text{erf} \left( \frac{x}{2 \sqrt{1.613 \times 10^{-10} (t_0^{0.693} f(\eta)t^{1-0.693})}} \right) \right].$$

(14a)

$$f(\eta) = 0.392 \cdot q_s \cdot 1.28 \cdot \left( \frac{C}{C_1} \right)^{0.512} \cdot \left[ 1 + \left( \frac{1 - RH}{1 - RH_c} \right)^{4a} \right]^{-1} \cdot \exp \left[ \frac{U}{R} \left( \frac{1}{T_0} - \frac{1}{T} \right) \right] \cdot D_0 \left( \frac{t_0}{T} \right)^m.$$  

(14b)

3.3. Validation of the Proposed Model. Validations of the proposed model with the 323 sets of chloride measurement data from 42 coastal concrete bridges were performed, and the results, based on regression analysis, are shown in Table 6. As can be seen, the correlation coefficient $R^2$ of the proposed model with field measurement data is 0.843, which is higher than that of the other models as shown in Table 3. Moreover, the $F$ value is 4686.338, which is greater than $F_{0.05}(4.323) = 5.650$, and the $P$ value is found to be approximately zero, indicating a strong agreement between the proposed model and the field measurement data.

Table 7 lists the distribution of prediction errors of the proposed model for the 42 coastal bridges. It can be seen...
that among all the 323 sampling points, 68.4% (221) of the prediction results falls within the range of 10% and 23.8% (77) of the prediction results is within the range 10–20%. Hence, in total, 92.2% of the prediction results has a relative error less than 20%, indicating an acceptable agreement between the prediction and the field measurement data.

Figure 5 compares the calculated chloride content from the proposed model and the measured data from field samples. The results of the regression analysis are given in Table 8. Note that all data points in Figure 5 fall within the range of ±20%. Therefore, the proposed model shows a better agreement with the field measurement data than other models (as indicated in Figure 4). The MAE of the proposed model is about 8.663% with an SD of 0.112, and the CV is 11.091%. Compared to those results shown in Table 4, the proposed model gives the smallest values of the MAE, SD, and CV, indicating a more reliable prediction than the other models.

To further validate the reliability of the proposed model, the filed measurement data from the Haimen Bridge that connects two cities in Guangdong province, i.e., Shenzhen and Shantou in the southeast of China, were collected and compared. Note that the environment and climate conditions of Shenzhen and Shantou are similar to those coastal cities in Fujian province, with the characteristics of high temperature and high relative humidity. The comparison between the field measurement data in the pier of Haimen Bridge and the calculated chloride concentrations by the proposed model is shown in Figure 6. A good agreement has been found. For the data points at the depth greater than 15 mm, the calculated results are slightly greater than the measured data. Such discrepancy is possibly caused by the different microstructures between the surface and the internal part of the concrete samples because the microstructure of the internal concrete mainly relies on cement hydration, while the surface concrete can additionally interact with the exposure environment.

4. Discussion

A modified chloride diffusion model (equations (14a) and (14b)) has been proposed. Based on regression analyses with field measurement data, the modified model has shown a better agreement than the existing models for predicting the chloride diffusion in coastal concrete structures. The modified model involves a series of influencing parameters including ambient temperature, humidity, stress state, age, and carbon dioxide. The sensitivity of chloride diffusion to variation of each parameter is discussed below, in order to further understand their role in service life prediction of the actual marine concrete structures.

4.1. Effect of Ambient Temperature. Five different ambient temperatures, i.e., 10°C, 15°C, 20°C, 25°C, and 30°C, are...
randomly selected to analyze the influence of ambient temperature on chloride diffusion. The other factors are kept as constant (relative humidity RH = 80%, CO₂ concentration \( C = 0.0467\% \), stress-state coefficient \( q_s = 1.0 \), age \( t = 25 \) years, chloride binding coefficient \( q_e = 0.392 \), and environmental coefficient \( q_K = 1.28 \)). The chloride concentrations at different depths under various ambient temperatures were calculated using equations (14a) and (14b). The results are shown in Figure 7. As can be seen, the chloride concentration increases with the increase of ambient temperature. The increase of chloride concentration is particularly obvious for a deeper depth. This observation clearly points to a significant effect of temperature on the steel corrosion initiation, which requires a threshold concentration of chlorides at the steel surface. Table 9 lists the on-site exposure condition of Baoan bridge and Xiaoyue bridge. The other factors of the two bridges are basically similar, while the ambient temperature of the Baoan bridge is higher than Xiaoyue bridge. Figure 8 shows the chloride profile of the two bridges. As indicated, the Baoan bridge with a higher ambient temperature shows a higher chloride concentration than the Xiaoyue bridge. This provides a further evidence for the temperature effect on chloride diffusion, i.e., higher temperature causes faster penetration of chlorides.

### 4.2. Effect of Ambient Humidity

Moisture is a prerequisite for the diffusion of chloride ions in concrete. In case the relative humidity in concrete is lower, the diffusion rate of chloride ions can be smaller \[28\]. In this study, considering the on-site weather condition of Fujian coastal area, five different relative humidity levels, i.e., 55%, 65%, 75%, 85%, and 95%, were adopted to investigate the influence of ambient humidity on chloride diffusion. The other factors are kept constant (ambient temperature \( T = 20°C \), stress-state coefficient \( q_s = 1.0 \), age \( t = 25 \) years, CO₂ concentration \( C = 0.0467\% \), chloride binding coefficient \( q_e = 0.392 \), and environmental coefficient \( q_K = 1.280 \)). The chloride concentration with depth at different ambient humidity was calculated using equations (14a) and (14b). The results are plotted in Figure 9. The chloride concentration increases with the increase of humidity, and the chloride profile looks very similar for relative humidity ranging from 85% to 95%. However, an obvious drop can be found when the relative humidity decreases from 85% to 75%. The reason hidden behind is attributed to the fact that a great number of the water-filled pores (which provide paths for chloride diffusion) become discontinuous when the ambient humidity is below 85% \[38\].

Table 10 provides the on-site condition of Xialou bridge and Hongsan Third bridge. The other factors of the two bridges are basically similar, while the relative humidity of Xialou bridge is higher. Figure 10 gives the chloride diffusion profile based on field measurement data from the two bridges, i.e., Xialou bridge and Hongsan Third bridge. As observed, the Xialou bridge with a higher ambient humidity has a higher chloride concentration than Hongsan Third bridge in all depths. Obviously, the field measurement data provide a solid evidence for the modified model to evaluate the effect of the ambient humidity on the chloride diffusion in coastal concrete structures.
4.3. Effect of Stress State. Different stress states including 0.90, 0.95, 1.00, 1.05, and 1.10 were studied in order to analyze its influence on chloride diffusion. The other factors are taken as fixed values (ambient temperature $T = 20^\circ$C, ambient humidity $\text{RH} = 80\%$, age $t = 25$ years, $\text{CO}_2$ concentration $C = 0.0467\%$, chloride binding coefficient $q_e = 0.392$, and environmental coefficient $q_K = 1.280$). The chloride concentration with depth under different stress states was calculated using equations (14a) and (14b). The results are shown in Figure 11. It can be seen that the

| Bridge | Age (years) | Temperature (°C) | Relative humidity (%) | $\text{CO}_2$ concentration (%) | Compressive strength (MPa) | Water-cement ratio |
|--------|-------------|-------------------|-----------------------|-------------------------------|---------------------------|--------------------|
| Baoan  | 7           | 21.3              | 77                    | 0.0476                        | 35.0                      | 0.45               |
| Xiaoyue| 7           | 18.8              | 79                    | 0.0452                        | 31.1                      | 0.45               |

Table 9: Field condition of the Baoan bridge and the Xiaoyue bridge.

Figure 8: Comparison of the chloride profile between Baoan bridge and Xiaoyue bridge.

Figure 9: Chloride profile vs. ambient humidity according to the proposed model (equations (14a) and (14b)).
chloride concentration increases with the increase of stress state, but the change of concentration with stress state is actually not obvious in these cases under study. Figure 12 shows the chloride profile of Yingqian bridge. k_"he chloride profiles are not very different for the concrete bridge under different stress states. k_"his agrees with the finding as indicated already in Figure 11.

4.4. Effect of Age. Five different ages were employed, i.e., 5, 15, 25, 35, and 45 years, in order to study the ageing effect on chloride diffusion. The other factors are fixed (ambient temperature \( T = 20°C \), ambient humidity \( \text{RH} = 80\% \), \( \text{CO}_2 \) concentration \( C = 0.0467\% \), stress-state coefficient \( q_s = 1.0 \), chloride binding coefficient \( q_e = 0.392 \), and environmental coefficient \( q_K = 1.280 \)). The chloride concentration with

| Bridge          | Age (years) | Temperature (°C) | Relative humidity (%) | \( \text{CO}_2 \) concentration (%) | Compressive strength (MPa) | Water-cement ratio |
|-----------------|-------------|------------------|-----------------------|-----------------------------------|----------------------------|--------------------|
| Xialou          | 19          | 19.4             | 82                    | 0.0465                            | 36.6                       | 0.45               |
| Hongsan Third   | 20          | 20.1             | 75                    | 0.0496                            | 27.2                       | 0.46               |

Table 10: Field condition of Xialou bridge and Hongsan Third bridge.

Figure 10: Comparison of the chloride profile between Xialou bridge and Hongsan Third bridge.

Figure 11: Chloride profile vs. stress state according to the proposed model (equations (14a) and (14b)).
depth at different ages was calculated using equations (14a) and (14b). The results are shown in Figure 13. As can be seen, the chloride concentration increases with the increase of age, especially in the first 15 years. With a further increase of the age (>15 years), the change of the chloride concentration becomes slower, which may be ascribed to the chloride binding effect in the concrete. With ongoing penetration, accumulation of chloride ions in concrete takes place until saturation of the chloride content attains. A higher chloride concentration will result in a slower diffusion process [38].

4.5. Effect of Carbon Dioxide. To what extent can the carbonation influence the chloride diffusion coefficient in marine concrete, a discussion is carried out. The CO₂ concentration was set as a variable, i.e., 0.0436%, 0.0456%, 0.0476%, 0.0496%, and 0.0516%. The other factors are fixed (ambient temperature \( T = 20^\circ\text{C}, \) ambient humidity RH = 80%, stress-state coefficient \( q_s = 1.0, \) chloride binding coefficient \( q_e = 0.392, \) environmental coefficient \( q_K = 1.280, \) and age \( t = 25 \) years). The chloride concentration with depth at different CO₂ concentrations was calculated using equations (14a) and (14b). The results are presented in Figure 14. It appears that the chloride concentration increases with a higher CO₂ concentration. Nevertheless, changes of the chloride concentration are insignificant for CO₂ concentration in the range 0.0436~0.0516%. Table 11 lists the on-site condition of Hongting Second bridge and Xialou bridge. The other factors of the two bridges are

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**Figure 12:** Comparison of chloride profile between two different bridges.

**Figure 13:** Chloride profile vs. age according to the proposed model (equations (14a) and (14b)).
basically similar except that the CO₂ concentration of Xialou bridge is higher. Figure 15 shows the chloride profiles of the two bridges, which are very similar. It is found that the difference in CO₂ concentration from 0.0465% to 0.0496% does not result in a significant difference in chloride penetration.

### 5. Conclusions

A broad range of field investigations on chloride penetration in 42 concrete bridges exposed to the coastal environment of four cities in the Southeast of China was conducted. Representative data from bridges, e.g., Baoan bridge, Xiaoyue

![Figure 14: Chloride profile vs. CO₂ concentration according to the proposed model (equations (14a) and (14b)).](image1)

![Table 11: Condition of the Hongting Second bridge and the Xialou bridge.](image2)

![Figure 15: Comparison of chloride profile between Hongting Second bridge and Xialou bridge.](image3)
bridge, Xialou bridge, Hongting Second bridge, and Hongshan Third bridge, were intensively analysed and compared. A modified chloride diffusion model well applicable for concrete structures in coastal environments has been proposed based on a series of mathematical descriptions, together with validations with 323 sets of field measurement data. The modified model takes the influencing factors into consideration including ambient temperature, carbon dioxide, relative humidity, stress state, chloride binding, and concrete age. Compared to the existing models, the modified model enables to reflect the complex coastal climate conditions and provides a better prediction of the long-term chloride diffusion coefficient in atmospheric concrete.

Temperature significantly affects the chloride diffusion in coastal concrete structures. The effect of ambient humidity on chloride diffusion becomes pronounced when the humidity lower than 85%. For a long-term exposure, the surface chloride concentration approaches to a constant value and the concrete ageing factor can be set as 0.69 for ordinary Portland cement concrete (with a water-cement ratio of 0.42–0.46) when serving in the atmospheric marine environment.

The data and associated findings, along with the modified model, presented in this work are based on concrete structures exposed to the marine environment of Fujian province of China. Extension of the modified model to make it applicable to other marine environment is in progress. The results will be reported in a separate paper in the future.

Data Availability

The data used to support the findings of this study are included within the article. Any additional data related to the paper may be acquired from the corresponding author upon request.

Conflicts of Interest

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

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