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Research Article

Model for Sulfate Diffusion Depth in Concrete under Complex Aggressive Environments and Its Experimental Verification

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Sulfate attack is one of the most important factors that lead to the performance deterioration of concrete materials. The progress of the sulfate diffusion depth in concrete is an important index that quantitatively characterizes the rate of concrete damage, cracking, and spalling due to sulfate attacks. The progress of the diffusion depth of concrete to sulfate attack is systematically investigated in this paper by both theoretical and experimental study. A newly time-varying model of the diffusion depth is developed, which has comprehensively considered a mass of parameter of complex environments for the first time. On this basis, a method is further proposed for effectively predicting the residual life of in-service concrete structures subject to sulfate attack. Integrating the data from the self-designed high-temperature dry-wet accelerated corrosion test and a large amount of experimental data reported in the existing literatures, the effectiveness and accuracy of the time-varying model of the diffusion depth by sulfates are finally verified.

1. Introduction

Concrete is currently the most widely used building material in the world. However, because concrete structures are inevitably exposed to various natural aggressive environments that are full of chemically aggressive mediums (e.g., sulfates and carbon dioxide), the service life of concrete structures is significantly reduced. Sulfates are the most aggressive and destructive medium and also one of the main factors affecting the durability of concrete [1]. The mechanism of the deterioration of concrete by sulfates involves the transport characteristics of sulfate ion diffusion into concrete and chemical reactions with the cement hydration products. This causes the cracking and spalling of concrete [1, 2] and the loss of concrete strength, among others. Recently, the deterioration mechanism of concrete attacked by sulfates has been extensively studied. From a macroscopic point of view, sulfate ions enter concrete through diffusion, permeation, and capillary adsorption [1]. Then, the sulfate ions chemically react with the cement hydration products of concrete to generate expansive products (e.g., ettringite) [3–6]. The expansive products continuously fill the internal pores of concrete, thus expanding the concrete and gradually generating expansion stress with the progress of the chemical reaction. When the magnitude of the stress exceeds the tensile strength of concrete, the concrete will crack. With the deterioration, several layered deterioration zones are generated from the outside to the inside of concrete [7–9]. The sulfate-induced damaged concrete section can thus be divided into three layers from the exposure surface to the core, that is, the degraded layer where concrete cracks due to the expansion stress, the compacted layer where the internal pores of concrete are continuously filled with the expansive products, and the undamaged layer where no sulfate ion enters. Hereafter, the total thickness of the degraded and compacted layers is so called the sulfate diffusion depth. From the mechanism perspective, the rate of diffusion reaction, depth of sulfate diffusion, and expansion stress due to the generation of the expansive products are the main important indexes that are used to quantitatively characterize the concrete degradation mechanism by sulfates and identify the layered deterioration zones. They are significantly affected by both the external sulfate environment and concrete composition (e.g., concentration [10, 11], temperature [12, 13],

degradation methods of sulfate solution, such as dry-wet cycle and soaking [14], and content of tricalcium aluminate (C_3A) in cement [15, 16]). Therefore, some experimental studies and theoretical analyses have been conducted to elucidate the mechanism of concrete degradation by sulfates mainly from the perspectives of diffusion reaction of sulfate ions, diffusion depth, and expansion stress of concrete, to develop the relevant prediction models, which can generally be divided into mechanism [17–21] and empirical models [22–26].

As aforementioned, with the process of the diffusion reaction of sulfates in concrete, the sulfate diffusion depth increases and the expansive product forms and accumulates, leading to the generation of the concrete expansion stress and finally the cracking of concrete, which in turn will affect diffusion reaction properties of sulfate in concrete. Therefore, the progress of sulfate diffusion depth is an important bridge that connects the transport characteristics of sulfates with the expansive cracking of concrete. It is also an important index that shows the degree of concrete degradation by sulfates and quantitatively characterizes the rates and processes of concrete damage, cracking, and spalling. The establishment of a time-varying model of sulfate diffusion depth is the basis for both the design of concrete structures against sulfate attack and the improvement of structure durability. As described in the second section of this paper, some relevant studies are still conducted, but the results are relatively inconclusive. Regarding this aspect, the mechanism analysis and experimental study were combined, and the progress of concrete degradation depth by sulfates was systematically studied in this paper, which has comprehensively considered a mass of parameter of complex environments for the first time.

2. Existing Prediction Models for Sulfate-Induced Concrete Diffusion Depth

Some models have already been established for the prediction of sulfate diffusion depth. These models can be generally divided into empirical and mechanism models that help to better understand the process of sulfate attacks. Although there are some limitations, these models were used as the research foundation of this study. Therefore, firstly it is necessary to briefly introduce and analyze these models.

2.1. Empirical Models. Atkinson et al. [24] soaked concrete samples with a C_3A content of 8% completely in a mixture of sodium sulfate and magnesium sulfate (0.19 mol/L), and the sulfate diffusion depth was measured to be 42 mm after five years of degradation. Based on the regression analysis of a series of data, Atkinson et al. proposed an empirical model for the prediction of diffusion depth as follows:

$$X = \frac{4.2}{5} \cdot \frac{C_{C_3A}}{8} \cdot \frac{\left(Mg^{2+} + SO_4{}^{2-}\right)}{0.19} \cdot t, \quad (1)$$

where X is the diffusion depth (cm), C_{C_3A} is the content of C_3A in cement (%), Mg^{2+} or $SO_4{}^{2-}$ is the concentration of the aggressive solution (mol/L), and t is the time (year).

Atkinson's model assumed the existence of a linear relationship between diffusion depth and time and that the rate of diffusion is a constant. The model considered the effect of both the concentration of the external solution and the C_3A content of the concrete on the diffusion depth but neglected an important factor, the porosity of concrete which mainly depends on the water/cement ratio of concrete. The porosity of concrete mainly affects the transport rate of sulfates and generally can be quantified by introducing the diffusion coefficient, an important factor in predicting sulfate diffusion depth in later models.

Shuman and Rogers (1989) [25] thus modified Atkinson's model by introducing the diffusion coefficient D as follows:

$$X = 1.86 \times 10^6 C_{C_3A} \left(Mg^{2+} + SO_4{}^{2-}\right) D_0 \cdot t, \quad (2)$$

where D_0 is the initial diffusion coefficient of the sulfates in the concrete. The model considered the effect of the diffusion coefficient or in fact the porosity of concrete; however, the diffusion coefficient was considered as a constant, 3.4×10^{-11} m^2/s, which was irrational based on the present understanding that the pores of concrete would be gradually blocked with the increase in the reaction products, thus affecting the transport and diffusion of sulfate ions. The accuracy of the model has not been experimentally verified and cannot be universally applied.

Skalny et al. (2002) [26] experimentally investigated the degradation of concrete with different C_3A contents (9~13%) in different sodium sulfate solutions (500~33,800 g/L) and proposed the following prediction model of diffusion depth based on the four-year period experimental data:

$$X = \left[0.11S^{0.45}\right] \cdot \left[0.143t^{0.33}\right] \cdot \left[0.204e^{0.145C_3A}\right], \quad (3)$$

where S is the concentration of the sulfate solution (g/L), t is the time of immersion (days), and C_{C3A} is the C_3A content in the cement (%). Clearly, Skalny's model improved the linear relationships among the diffusion depth, time, and concentration of external solution; however, the model also failed to reveal the effect of water/cement ratio or diffusion coefficient on the rate of diffusion and did not consider the relationships between diffusion depth and diffusion reaction.

2.2. Mechanism Models. As for the pure mechanism models, Li et al. (2010) [20] proposed a theoretical model for the prediction of diffusion depth by theoretical derivation using Fick's first law:

$$X = \sqrt{\frac{2D_0C_St}{a}}, \quad (4)$$

where D_0 is the initial diffusion coefficient of the sulfates in the concrete, C_S is the concentration of the sulfates on the concrete surface, t is the degradation time, and a is the capacity of the concrete to absorb sulfates. In this model, parameter a is a relatively abstract concept that reveals the capacity of concrete to consume sulfate media, and the correctness of the model is difficult to verify and has never been experimentally verified directly.

Considering the problem of diffusion reaction, Lee et al. (2013) [21] derived a model similar to Li's model also using Fick's first law as follows:

$$X = \sqrt{\frac{2D_0Ct}{C_{C_3A}}}, \tag{5}$$

where C is the concentration of the sulfate solution.

As shown by a comparison between Li's and Lee's models, the latter model mainly considered the content of C_3A, while the former model mainly considered the capacity of concrete to consume sulfate media. Therefore, these two models are essentially the same, only in different manifestations. However, because it is relatively easy to determine the content of C_3A in the latter case, Lee's model is more acceptable. The problem is that Lee's model has never been experimentally verified.

As shown by the analysis of the above models, the existing prediction models for the depth of concrete degradation by sulfates are not perfect, and one of their major defects is that they did not consider the effect of the diffusion characteristics of the sulfates in concrete or the time-varying feature of their diffusion characteristics on the development of diffusion depth, not to mention that some of them have not been experimentally verified to prove their correctness.

3. A Time-Varying Model for Sulfate Diffusion Depth

3.1. Time-Varying Model for Sulfate Diffusion Depth Dominated by Diffusion. Although sulfate ions can enter into concrete by many methods such as permeation, capillary adsorption, and diffusion [1] in reality, diffusion is the main method of transportation. Thus, existing extensive experimental and theoretical studies on the transport of sulfates in concrete are based on Fick's law of diffusion. Based on this background and the following rational assumptions, in this study, the time-varying characteristics of sulfate diffusion depth dominated by diffusion are firstly derived:

(1) In a pure immersed aggressive environment, the sulfate ions enter into concrete mainly by diffusion. Thus, the diffusion of sulfate ions in the pores of concrete obeys Fick's law of diffusion [28], and supposing at the point of time t, in seconds (s) or days (d), the diffusion depth of SO_4^{2-} is x, in meter (m), the concentration of sulfate ions passing through a unit area S (m^2) of the concrete section is $C(x)$, mol/m^3, and the mass is $M(x)$, mol, the following relation is derived:

$$M(x) = -D_e \cdot S \cdot \frac{\partial C(x)}{\partial x} dt, \tag{6}$$

where D_e is the effective diffusion coefficient of the sulfates in concrete, generally an order of magnitude of 10^{-10} ~10^{-14} m^2/s [29], and the value of D_e is related to the degradation process, temperature, and so forth; the minus sign shows that sulfates diffuse into the direction of lower concentration.

(2) In (6), $\partial C(x)/\partial x$ is the distribution gradient of the concentration of sulfate ions with the change of depth, because the concentration of sulfate ions in concrete shows a curved distribution (see the experimental results of Section 4). Generally, it is difficult to directly express the distribution gradient by an accurate explicit equation. However, according to the study by Tixier and Mobasher [19], the effect of simplifying the curved distribution of the concentration of sulfate ions into a linear distribution on the accuracy of analysis can be neglected. Therefore, in this study, the concentration of sulfates was assumed to have a linear distribution with the change of depth, as shown in Figure 1 where x is the diffusion depth; thus:

$$\frac{\partial C(x)}{\partial x} = -\frac{C_S - C_0}{x}, \tag{7}$$

where C_S is the concentration of the sulfates on concrete surface, and C_0 is the initial concentration of the sulfates in the concrete.

(3) Ettringite is the primary product of concrete degraded by sulfates that leads to cracking of concrete and is generated by reactions of unhydrated/hydrated C_3A and calcium sulfoaluminate with sulfates, in which the equation equilibrium of the chemical reaction can expressed by [19]

$$\mathrm{CA} + q\overline{S} + nH \longrightarrow C_6A\overline{S_3}H_{32}, \tag{8}$$

where CA represents the calcium aluminates, $\overline{S}$ is the concentration of the SO_4^{2-}, q is the weighted mean stoichiometric number of the overall reaction, $C_6A\overline{S_3}H_{32}$ is the ettringite, H denotes the water that takes part in the reaction, and n is the stoichiometric coefficient of the water.

Suppose that the diffusion amount of a unit volume of sulfate ions at time dt is chemically absorbed by all the calcium aluminates of concrete within the range dx when sulfate ions enter into concrete; the law of conservation of mass can be expressed as follows:

$$C_{\mathrm{CA}} \cdot S \cdot dx = -qD_e \cdot S \cdot \frac{\partial C}{\partial x} dt, \tag{9}$$

where C_{CA} is the molar concentration of calcium aluminates.

Combining (7) and (9), the following relationship can be obtained:

$$C_{\mathrm{CA}} \cdot x \cdot dx = qD_e (C_S - C_0)\, dt. \tag{10}$$

Integrating both sides of (10) within the sulfate diffusion depth X yields

$$\int_0^X C_{\mathrm{CA}} \cdot x \cdot dx = q \int_0^t D_e (C_S - C_0)\, dt. \tag{11}$$

Expanding and rearranging the integrals of (11), the sulfate diffusion depth X can be expressed as follows:

$$X = \sqrt{\frac{2D_e (C_S - C_0) \cdot q}{C_{\mathrm{CA}}}} \cdot \sqrt{t}. \tag{12}$$

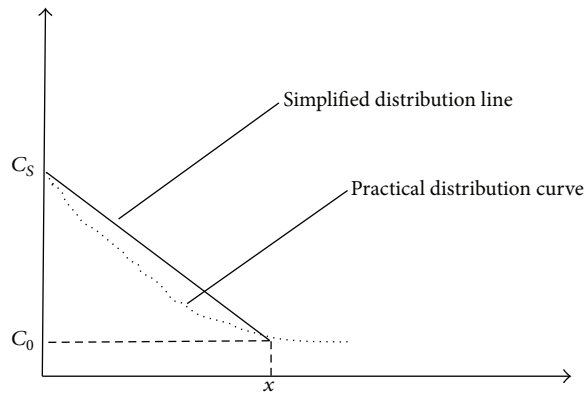

Figure 1: Schematic diagram of the simplified distribution of the concentration of sulfate ions.

As can be seen in (12), sulfate diffusion depth is a complex variable and depends on the following parameters: the effective diffusion coefficient D_e, the concentration of the sulfates on the concrete surface C_S, the concentration of the sulfates initially existing in the concrete C_0, the weighted mean stoichiometric number of the chemical reaction q, the concentration of calcium aluminates C_{CA}, and the degradation time t.

Moreover, it should be noted that the effective diffusion coefficient D_e heavily depends on the porosity or the pore structure of concrete and changes as the variation of the porosity of concrete due to the sulfate attack; the sulfate diffusion depth model has in fact indirectly considered the effect of the porosity of concrete by introducing the effective diffusion coefficient D_e into the model.

3.2. Time-Varying Model of Sulfate Diffusion Depth in Complex Environments. The sulfate diffusion depth model of (12) is derived in a pure immersed aggressive environment; however, the practical environment of sulfate degradation is more complex. Consequently, (12) is further derived in this section to properly consider the time-varying characteristics of the diffusion coefficient, concentration, and temperature of sulfate solution.

3.2.1. Effect of the Time-Varying Characteristics of the Diffusion Coefficient on Diffusion Depth. The diffusion coefficient D_e reflects the diffusion rate of the sulfate ions in concrete material and closely related to the number and structure of the internal pores of concrete. In the above diffusion equation, D_e is assumed to be a constant, which is inconsistent with that of a practical situation, as the actual diffusion coefficient will differ significantly from the initial diffusion coefficient after the permeation and chemical reaction of sulfates [30].

Tumidajski et al. applied Fick's law of diffusion to the fitting of experimental data and obtained an effective diffusion coefficient considering the time-varying characteristics as follows [31]:

$$D_e = 2.217 \times 10^{-7} \cdot t^{-0.76}, \tag{13}$$

where the unit of day is used for time in the regression analysis.

Tumidajski's effective diffusion coefficient is the result of the fitting based on a specific environment and cannot be extended to other aggressive environments; however, based on Tumidajski's idea, in this study, the effective diffusion coefficient D_e defined by (14) is accepted to develop the diffusion depth to consider the time-varying characteristics:

$$D_e = D_0 \left(\frac{1}{t}\right)^m, \tag{14}$$

where D_0 is the initial diffusion coefficient of the sulfates in concrete, that is, the diffusion coefficient corresponding to $t = 0$; m is the attenuation coefficient of the diffusivity with time, which is generally related to the water/cement ratio of concrete, and so forth.

Although the initial diffusion coefficient D_0 is of important material parameter that quantifies the ability of concrete to resist the sulfate attack, it is actually hardly possible to obtain the initial diffusion coefficient D_0 directly by test as no diffusion occurs. Thus, the time-dependent effective diffusion coefficient D_e given by (14) is recalculated using another referenced diffusion coefficient $D_{e,0}$ corresponding to any point of time $t_0 > 0$, instead of D_0.

Thus, with (14), it is easy to get

$$D_{e,0} = D_0 \left(\frac{1}{t_0}\right)^m. \tag{15}$$

Dividing (14) to (15), the following equation is derived:

$$\frac{D_e}{D_{e,0}} = \left(\frac{t_0}{t}\right)^m. \tag{16}$$

Therefore, the effective diffusion coefficient D_e can be expressed by

$$D_e = D_{e,0} \left(\frac{t_0}{t}\right)^m. \tag{17}$$

Substituting (17) into (12), a time-varying model of diffusion depth is developed:

$$X = \sqrt{\frac{2D_{e,0} t_0^m (C_S - C_0) q}{C_{CA}}} \cdot \sqrt{t^{1-m}}. \tag{18}$$

3.2.2. Effect of Aggressive Environment Parameters on Diffusion Depth. Existing studies indicate that, among the aggressive environment parameters, the concentration of solution, temperature [10–13], and mode of degradation (e.g., dry-wet cycle, half soaking, and continuous full soaking) [14] significantly affect the rate of diffusion depth. C_S of Model (18) depends on the concentration of sulfate solution and thus has directly revealed the effect of the concentration of solution on diffusion depth. The change of temperature significantly affects the effective diffusion coefficient $D_{e,0}$ as shown by the formula of $D_{e,0}(T) = D_{eT} \exp[U(1/T_0 - 1/T)]$ [32] (where D_{eT} is defined as the effective diffusion coefficient measured at a reference point of time at temperature T_0,

mm^2/s, and U is the activation energy bisected by the gas constant, KJ/mol).

To evaluate the effect of the accelerated degradation modes on diffusion depth, Atkinson and Hearne [33] studied the correlation of concrete performance deterioration between the two following modes: (1) soaked in sulfate solution on a long-term basis and (2) dry-wet cycle. It was found that the performance of concrete in the two degradation systems could be equated by an equivalent coefficient of 8. In other words, the rate of the performance deterioration of concrete caused by dry-wet cycle was eight times that of the concrete caused by pure soaking. Dry-wet cycle accelerated the effect of ionic crystallization on the microstructure of capillary pores, further changing the diffusion characteristics of sulfate ions and thus affecting diffusion depth. Therefore, based on the experiment conducted by Atkinson and Hearne, in this paper, the acceleration effect of dry-wet cycle on the rate of sulfate diffusion is simply equivalent to the amplification adjustment of the diffusion coefficient $D_{e,0}$ as follows: $D_{e,0} = \eta^2 D_{eT}$ (η^2 defined as the coefficient of influence of dry-wet cycle on the diffusion coefficient of concrete). Substituting it into (18), it yields

$$X = \eta\sqrt{\frac{2D_{e,0}t_0^m\left(C_S - C_0\right)q}{C_{\mathrm{CA}}}} \cdot \sqrt{t^{1-m}}. \tag{19}$$

Notably, (19) considers the effects of the time-varying characteristics of the diffusion coefficient and parameters of complex environments. Therefore, this model can be universally applied to a certain extent.

3.3. A Method for Evaluating the Diffusion Depth of In-Service Concrete Structures Attacked by Sulfates. For a specific aggressive environment, the model parameters, η, m, $D_{e,0}$, and so forth, are unique. Consequently, for any two given points of time t_1 and t_2, the two corresponding depths of sulfate diffusion, X_1 and X_2, can be calculated as follows:

$$X_1 = \eta\sqrt{\frac{2D_{e,0}t_0^m\left(C_S - C_0\right)q}{C_{\mathrm{CA}}}} \cdot \sqrt{{t_1}^{1-m}}, \tag{20a}$$

$$X_2 = \eta\sqrt{\frac{2D_{e,0}t_0^m\left(C_S - C_0\right)q}{C_{\mathrm{CA}}}} \cdot \sqrt{{t_2}^{1-m}}. \tag{20b}$$

Dividing (20b) by (20a), it yields

$$X_2 = \left(\frac{t_2}{t_1}\right)^{(1-m)/2} \cdot X_1 = \left(\frac{t_2}{t_1}\right)^{\beta} \cdot X_1, \tag{21}$$

where $\beta = (1 - m)/2$.

The attenuation coefficient of diffusivity m or β in a specific environment can be solved from (21) and given by

$$m = 1 - 2 \cdot \frac{\ln X_2 - \ln X_1}{\ln t_2 - \ln t_1}. \tag{22a}$$

Or

$$\beta = \frac{\ln X_2 - \ln X_1}{\ln t_2 - \ln t_1}. \tag{22b}$$

Thus, based on the two given diffusion depths by sulfate, X_1 and X_2, at any two points of time and substituting (22b) into (21), the diffusion depth X_t corresponding to any point of time t can be calculated by

$$X_t = \left(\frac{t}{t_1}\right)^{\beta} \cdot X_1. \tag{23}$$

Therefore, Model (19) has a great engineering significance that, for a concrete structure actually subjected to sulfate attack, if the diffusion depths (e.g., X_1 and X_2) at any two different points of time (e.g., t_1 and t_2) are first measured (actually, this information can be easily obtained by nondestructive testing such as ultrasonic testing method [34, 35]), the progress of the diffusion depth of in-service concrete structure at any future point of time can then be evaluated by (23), and hence the residual service life of the concrete structure can be assessed.

However, it is a fact that, similar to the derivation of (23), the diffusion depth of in-service concrete structure at any future point of time can also be obtained using Atkinson and Shuman's model, Skalny's model, and Li's or Lee's model and correspondingly rederived by (24), (25), and (26), respectively.

Based on Atkinson and Shuman's models, (24) is yielded:

$$X_t = \left(\frac{t}{t_1}\right) \cdot X_1. \tag{24}$$

Using Jambor's model, (25) is obtained:

$$X_t = \left(\frac{t}{t_1}\right)^{0.33} \cdot X_1. \tag{25}$$

And adopting Li's or Lee's model, (26) is developed:

$$X_t = \left(\frac{t}{t_1}\right)^{0.5} \cdot X_1. \tag{26}$$

It is self-evident from (24)–(26) that only one measured diffusion depth value at any point of time is needed to evaluate the progress of diffusion depth and hence (24)–(26) are probably more advantageous than (23). However, as aforementioned, a mass of parameter of sulfate aggressive environment has significantly affected the sulfate diffusion process, and thus a relatively major error cannot be avoided if the degradation information at one point of time is relied solely on to infer the overall development. Therefore, in this study, the degradation information at any two points of time is preferably used by the model (19) to predict diffusion depth, with greater advantages in terms of the rationality and accuracy of prediction that will be further demonstrated in the following model verification and comparison. Moreover, certain limitations are still present in the derivation by Atkinson and Shuman's model, Jambor's model, Lee's model, and so forth. The rationality of (24)–(26) is still in doubt.

4. Experimental Verification of the Time-Varying Model of Diffusion Depth

The above time-varying model of diffusion depth is a semitheoretical mechanism model, and in this section, the

Table 1: Mineral constituents and contents of cement.

Constituent	C_3S	C_2S	C_3A	C_4AF
Content (%)	59.10	15.99	8.74	12.71

Table 2: Concrete mix proportion.

Material	Water (kg/m^3)	Cement (kg/m^3)	Sand (kg/m^3)	Gravel (5~25 mm)
Dosage	200	417	638	1125
Proportion	0.48	1	1.53	2.70

self-designed test data and existing experimental data will be used to verify the rationality and correctness of the model, respectively.

4.1. Model Verification Based on the Self-Designed Test. In this part, the detailed information related to the design, process, and result of the test is first introduced, followed by model verification.

4.1.1. Design of Concrete Mix Proportion. In this paper, the cement used for the preparation of concrete is the Japanese Onoda PII52.5 pure Portland cement of which the mineral constituents are shown in Table 1. The water/cement ratio of the concrete is 0.48, and its design strength grade is C50. The mix proportion of concrete is shown in Table 2. The samples are cubes of 150 mm in side length, and they are watered and cured under standard conditions for 28 days. The 28-day average compressive strength of three samples is measured to be 56.1 MPa.

4.1.2. Experimental Scheme of Accelerated Sulfate Attack. Considerable statistical data indicate that the concrete structures on coastlines are frequently subject to sulfate attack, and the coastal environment with high-temperature dry-wet cycling climatic condition possesses the characteristics of a typical sulfate degradation environment. Therefore, in this study, the coastal high-temperature wet-dry cycling climatic environment is simulated by using the meteorological conditions of coastal regions. The high temperature is thus defined as 40°C, and a dry-wet cycling period is defined as 12 h. The specific parameters of the test environment are shown in Table 3. The degradation points of time were defined as follows: 0, 30, 60, 90, 120, and 150 days. All the samples were placed in a professionally designed climate-simulated corrosion test chamber, with an accurate control system and test instruments to ensure the cycling system of the set temperature and humidity.

4.1.3. Layered Test Method for Sulfate Ion Content. The concrete samples at different degradation periods are sampled to measure the distribution of sulfate ions as per the following specific operation procedure: (1) remove the core in the middle for sampling purpose from the samples at various degradation ages; (2) cut these cores into slices by layers and each layer of slice was 5 mm in thickness, corresponding to depths of 2.5, 7.5, and 12.5 mm, and gradually increased by 5 mm in succession; (3) grind these slices into powder for the chemical analysis of the sulfate ions in the concrete; and (4) determine the content distribution of the sulfate ions in the concrete in various degradation periods from the outside to the inside. The main steps are shown in the Methods for Chemical Analysis of Cement (ASTM C114-2010) [36].

Table 3: System of dry-wet cycling test.

Cycling process	Specific parameters
Soaking	Soaked in 7% sulfate solution for 9 h at 25°C
Drying at room temperature	Dried for 1 h at room temperature
Drying at high temperature	Dried for 1 h at 40°C
Natural cooling	Naturally cooled for 1 h

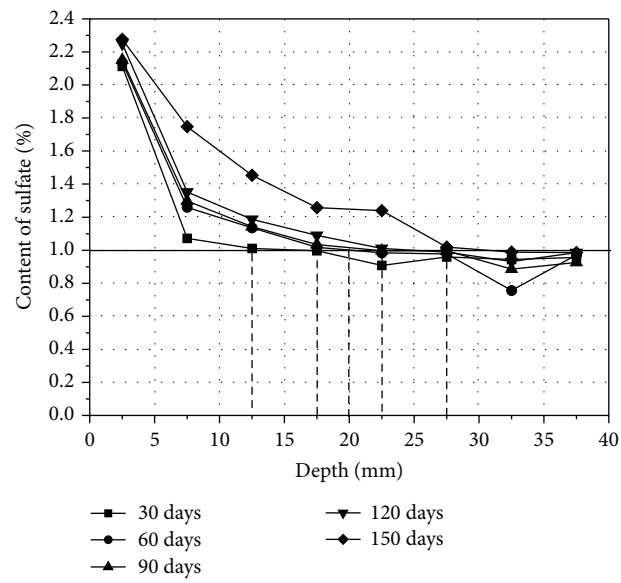

Figure 2: Distribution law of sulfate ions in concrete.

4.1.4. Experimental Results and Analysis. Figure 2 depicts the distribution law of sulfate ions at various depths of concrete at the same degradation age, and the vertical coordinate shows the measured concentration of the sulfate ions of the corroded layer including the initial concentration of sulfate ions present in the concrete itself. Figure 2 indicates that the transport of sulfate ions from the solution into the concrete is a gradual process and that the concrete close to the surface layer undergoes a relatively long period of degradation by sulfate ions and has a relatively high content of sulfate ions. Therefore, the concentration of sulfate ions in the first layer rapidly becomes saturated; the concrete at a relatively large depth has a relatively low content of sulfate ions.

The depth at which the concentration of sulfate ions in concrete reaches or slightly exceeds the initial concentration is defined as the diffusion depth as shown in Figure 2. At the point of time of 30 days during the degradation, the content

Table 4: Sulfate diffusion depth in concrete at various degradation times.

Degradation time (day)	30	60	90	120	150
Diffusion depth (mm)	12.5	17.5	20	22.5	27.5

of sulfate ions at 12.5 mm reached 1.031%, approximately equal to the initial concentration of sulfates of 1% initially contained in the concrete in this study. Therefore, the diffusion depth at a point of time of 30 days is 12.5 mm as shown in Figure 2. In the same way, the diffusion depths at a point of time of 60, 90, 120, and 150 days are measured to be 17.5, 20, 22.5, and 27.5 mm, respectively, as shown in Table 4.

4.1.5. Verification of the Time-Varying Model of Diffusion Depth

(1) Verification of Model (19). The concentration of sulfate ions on concrete surface C_S is approximately equal to the solution concentration of 7%, or 304.1 mol/m^3. The measured concentration of sulfate ions initially contained in the uncorroded concrete is ~1.0%; that is, the initial concentration C_0 is measured to be 1.0%, or 43.44 mol/m^3. The content of calcium aluminates is defined as the mass of C_3A in cement; that is, C_{CA} = 8.74%, or 134.98 mol/m^3. The weighted mean stoichiometric number of the chemical reaction q is 2.67 [27]. The referenced effective diffusion coefficient $D_{e,0}$ corresponding to the period of 30 days' degradation is used to calculate the diffusion depth, whose value was evaluated to be 1.28×10^{-12} m^2/s based on Fick' second law. Relying on the measured diffusion depth values at points of time 30 and 60 days as the two sample reference points of time, the attenuation coefficient of diffusivity with time m is calculated to be 0.029 using (22a) and (22b).

At present, the scientific quantification of the correlation between the deterioration rates of concrete attacked by sulfates under long-term immersion and dry-wet cycle conditions is still limited. This is because of the lack of systematic experimental studies on the degradation mechanism under these two conditions and that the equivalent relationship between the two degradation mechanisms is still unclear. Thus, the above parameters are substituted into Model (19) for the fitting approximation of the measured diffusion depths at various points of time, and the variation curve of the diffusion depth with time is obtained and plotted in Figure 3. The dry-wet cycle acceleration coefficient of the test is thus calculated to be $\eta = 3.41$ ($\eta^2 = 11.63$), with a fitting correlation coefficient of 0.978, indicating the high prediction accuracy of the model.

As the dry-wet cycle aggressive environment used in this study is more severe and complex than that reported in the literature [33] and the calculated dry-wet cycle acceleration coefficient is 11.63, greater than the value of 8 reported in the literature [33], it finally corroborated the rationality of Model (19).

(2) Data Verification of Model (23). The experimental data in this study were used to further verify Model (23). The measured diffusion depth values at points of time 30 and 60 days were introduced as the two sample reference points of time, and the parameter $\beta = 0.486$ is calculated using (22a) and (22b). Model (23) is used to predict the diffusion depths of the subsequent 90~150 days. The results are shown in Table 5 and Figure 4.

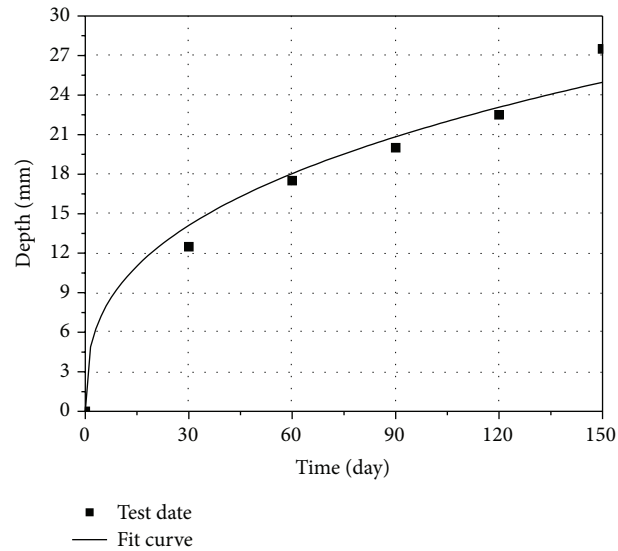

Figure 3: Prediction of Model (19) compared with the experimental results.

Table 5: Experimental and calculated values of diffusion depth.

Degradation time (d)	Measured diffusion depth (mm)	Calculated diffusion depth (mm)	Relative error
30	12.5	—	—
60	17.5	—	—
90	20	21.18	5.9%
120	22.5	24.32	8.1%
150	27.5	27.07	1.6%

As shown in Table 5 and Figure 4, Model (23) has a high accuracy in predicting the development trend of sulfate diffusion depth, with a mean relative error of 5.2%. It should be noted that the relative error (RE) defined as follows is utilized to assess all the model performance:

$$\mathrm{RE} = \frac{\sqrt{[\mathrm{Theo.}\,(X) - \mathrm{Exp.}\,(X)]^2}}{\mathrm{Exp.}\,(X)}, \tag{27}$$

where Theo.(X) and Exp.(X) are, respectively, the theoretical and experimental values of the diffusion depth X.

4.2. Model Verification Based on Existing Tests. Currently, some experimental data on the accelerated concrete degradation by sulfates are available. However, most of the existing literatures did not report the raw material composition and relevant parameters of the test; thus, only few data are available to further verify model (23).

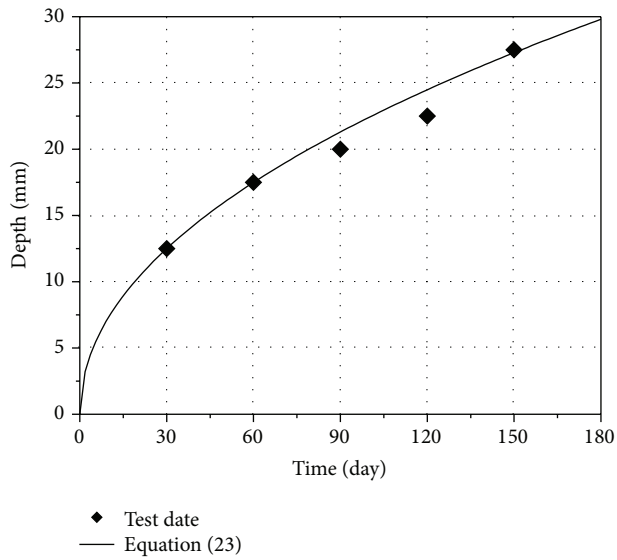

Figure 4: Prediction of Model (23) compared with the experimental results.

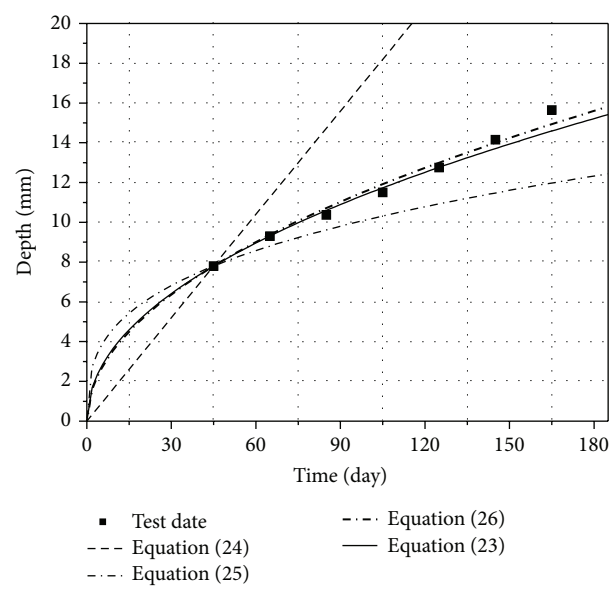

Figure 5: Comparisons of various predictions of diffusion depth with test.

In the literature [34], the effect of different sulfate solution pressures on the rate of degradation was studied in a pure aggressive environment. The diffusion depth was used as the evaluation index, and the sulfate diffusion depths at various degradation ages were obtained. These data will be used to further verify Models (23)–(26) in this section. Firstly, the sulfate diffusion depths measured on the 45th and 65th day in the literature [36] are used to determine the attenuation index β of Model (23) and β of 0.48 is obtained. Then, based on the diffusion depth value on the 45th day, (23)~(26) are used to predict the future development trend of diffusion depth. The results are shown in Figure 5 and Table 6.

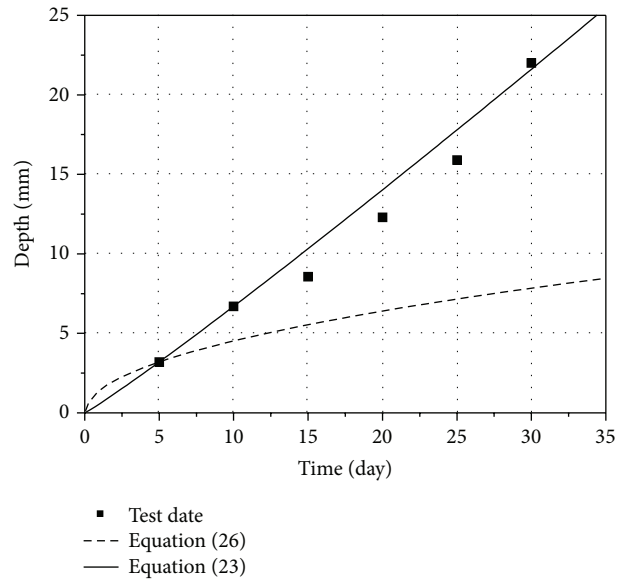

Figure 6: Accuracy comparison of Models (23) and (26) using experimental values reported in reference [27].

As shown in Table 6 and Figure 5, both Model (23) proposed in this study and Model (26) showed a very high accuracy in predicting the diffusion depth, while all the other models had significant errors, thus highly verifying the correctness of Model (23). However, notably Model (23) proposed in this study and Model (26) have an equal accuracy. This is because the attenuation index β of Model (23) of 0.48 is quite coincidentally approximate to the constant attenuation index 0.5 of Model (26). Thus, the fact that the accuracy of Model (26) is highly consistent with that of Model (23) in this case is a coincidence. This point will be further demonstrated by the verification comparison between Models (26) and (23) based on the experimental data reported in the literature [35].

In the literature [35], the concrete samples were placed under dry-wet cycle condition in sodium sulfate solution with 15% concentration. The samples were immersed for three days and dried for two days, and the concrete diffusion depth was measured at the end of each cycling period. The series of measured data are used to verify Models (26) and (23) again. The results are shown in Table 7 and Figure 6.

As shown in Table 7 and Figure 6, the model proposed in this study once again is highly consistent with the experimental data, while Model (26) shows a significant error in predicting the sulfate diffusion depth in this experimental environment. This is because significant differences are observed between the attenuation indexes obtained by these two models. The constant attenuation index β of 0.5 used by Model (26) fails to simulate the development trend of the sulfate diffusion depth in this experimental environment, while the attenuation index β of 1.07 calculated by (22a) and (22b) based on the measured diffusion depths on the fifth and tenth day can exactly reflect the actual situation.

In a word, the above substantial experimental verification finally concludes that the time-varying model of (23) for the prediction of concrete diffusion depth by sulfates has a very high accuracy and is of important engineering significance.

Table 6: Diffusion depth values calculated by various models (mm).

Time (day)	Solution pressure (MPa)	Test value (mm)	Equation (24)		Equation (25)		Equation (26)		Equation (23)	
			Calculated depth	Relative error %	Calculated depth	Relative error %	Calculated depth	Relative error %	Calculated depth	Relative error %
45	1.5	7.8	—	—	—	—	—	—	—	—
65		9.31	11.26	20.9	8.8	5.5	9.37	0.06	—	—
85		10.37	14.73	42	9.62	7.2	10.72	3.4	10.58	2.0
105		11.50	18.20	58.8	10.32	10.3	11.91	3.6	11.71	1.83
125		12.76	21.67	71	10.93	14.3	13	1.9	12.74	0.16
145		14.15	25.13	77.6	11.48	18.9	14	1.1	13.68	3.32
165		15.65	28.60	82.7	11.98	23.5	14.94	4.6	14.55	7.03
45	3.0	9.22	—	—	—	—	—	—	—	—
65		11.01	13.32	21	10.39	5.7	11.08	0.6	—	—
85		12.26	17.42	42	11.37	7.2	12.67	3.4	12.51	2.0
105		13.59	21.51	58	12.19	10.3	14.08	3.6	13.85	1.91
125		15.09	15.61	69.7	12.92	14.4	15.37	1.8	15.06	0.20
145		16.73	29.71	77.6	13.57	18.9	16.55	1.0	16.17	3.34
165		18.5	33.81	82.7	14.16	23.5	17.66	4.6	17.2	7.02

Table 7: Experimental [27] and calculated values of diffusion depth.

Time (day)	The text values of the diffusion depth (mm)	Equation (26)		Equation (23)	
		Calculated depth of attack (mm)	Relative error %	Calculated depth of attack (mm)	Relative error %
5	3.2	—	—	—	—
10	6.7	4.5	32.5	—	—
15	8.56	5.5	35.3	10.3	20.3
20	12.3	6.4	48	14	13.8
25	15.9	7.2	55	17.8	10.1
30	22.0	7.8	64.4	21.6	1.1

5. Conclusion

Sulfate attack is one of the important factors leading to the deterioration of material performance and durability reduction of concrete. In this paper, the progress of concrete diffusion depth induced by sulfates is studied comprehensively, and the following conclusions are drawn:

(1) A time-varying mechanism model is derived for the sulfate diffusion depth in concrete. Effects of the attenuation characteristics of concrete diffusion reaction, the temperature and concentration of sulfate solution, and the action of dry-wet cycle are comprehensively considered in the model derivation, and hence the model can be successfully employed to predict the progress of sulfate-induced diffusion depth in complex environments for the first time.

(2) On the basis of the above time-varying model, a theoretical system and methods for effectively predicting the diffusion depth of in-service concrete structures under deterioration by sulfates are proposed. In other words, if the sulfate diffusion depth values of an in-service concrete structure at any two points of time are known, the progress of the diffusion depth of the concrete structure can be accurately obtained. The model is simple, widely applicable, and does not require specific environment and material parameters in advance. It can predict the future progress of the diffusion depth based on the measured diffusion depth values at any two points of time only.

(3) After integrating the self-designed high-temperature dry-wet accelerated degradation experimental data and some experimental data reported in the existing literatures, the correctness and accuracy of the time-varying model for concrete degradation depth induced by sulfates and the diffusion depth prediction model based on any two reference points of time from various aspects and perspectives are verified.

Conflict of Interests

There is no conflict of interests related to this paper.

Acknowledgments

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