

RESEARCH PAPER

A VARIABLE-ORDER TIME-FRACTIONAL DERIVATIVE MODEL FOR CHLORIDE IONS SUB-DIFFUSION IN CONCRETE STRUCTURES

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Abstract

This study proposes a new variable-order fractional diffusion equation model to describe the coupled chloride diffusion-binding processes in reinforced concrete, in which the order of fractional derivative term is a variable function instead of a constant in the standard fractional model. The concentration influence coefficient k is introduced to capture the effect of concentration dependency on chloride transport due to the chloride binding behavior. The two parameters in the proposed model can be determined directly by a statistical analysis of measurement data. Four test cases illustrate that the proposed variable-order fractional derivative model agrees significantly better with experimental data than the most commonly used traditional model governed by the classical Fick's second law, especially when a large concentration coefficient k is involved. That proposed model is also verified by accurately predicting chloride concentration profiles in a period of 200 days.

MSC 2010: 74H15, 74S20, 76R50, 81T80

Key Words and Phrases: variable-order fractional derivative, sub-diffusion, time dependence, concrete, chloride ions, chloride binding, concentration dependence

1. Introduction

Durability of reinforced concrete structures exposed to various chloride-rich environments highly depends on their resistance to chloride ions penetration. Once the chloride concentration on rebar surface inside concrete crosses over the threshold level, a chloride-induced reinforcement corrosion occurs [9]. To evaluate the chloride pollution on concrete structures, a reliable and accurate model of chloride penetration in concrete is highly demanded by civil engineering communities.

Although there exist many complicated transport mechanisms [3], diffusion is in general predominant [33] in the saturated concrete. In traditional models, chloride ions diffusion is often considered to obey Fick's laws. These models are commonly used for chloride penetration because of its easily-obtained error-function solutions [8, 4, 1, 20]. The measurement of chloride diffusivity is a major task in predicting the chloride profiles in concrete to examine the accuracy and applicability of diffusion equation models. However, many experiments and field observations illustrate that the diffusion coefficient is not of a constant, but a time-dependent parameter decreasing with concrete age [34, 28, 36]. Such phenomena, are usually termed as anomalous diffusion, do not follow the Fick's second law and exhibit significant time-dependent feature.

To be more precise, it is in essence a sub-diffusion process, in which chloride ions diffuse slower than in the normal diffusion [22, 18]. A few anomalous diffusion models, such as the modified time-dependent coefficient model [36, 17], have since been developed to remedy the incapability of the traditional normal diffusion model.

Moreover, interactions between chloride ions in the pore solution and solid phase of cement matrix form the Friedel's salt [32] and present a typical concentration dependency [33, 11, 10, 42] and are quite difficult to be described by the traditional models. Although the Nernst-Planck flux equation model [13, 12, 2] can well depict such diffusion processes with clear physical significance, its complicated expressions and many parameters severely impede its applicability. It is highly desired to develop a simple model with fewer parameters that can effectively describe such chloride ions diffusion processes in concrete.

The time-fractional diffusion equations have extensively been used to depict anomalous diffusion processes in literature, such as Wyss [37], Nigmatullin [23], Mainardi [19], etc. The fractional diffusion equation is in fact an integral-differential equation and can effectively describe the memory properties. In particular, the time-fractional derivative has been considered a powerful tool to model sub-diffusion processes [41, 27, 15].

However, the chloride transport in saturated concrete is a quite complicated diffusion-binding process and characterizes time and concentration dependency, which is quite difficult to be described only by a constant-order fractional diffusion equation model [5, 24]. For example, when the parameter m , which relates to the cementitious material in concrete in the power law time-dependent coefficient diffusion model [36], is very small (close to zero), the fractional derivative order of corresponding time-fractional diffusion equation becomes extremely close to 1 [40]. The fractional model now reduces to the normal diffusion model governed by Fick's second law. In these cases, we found that the constant-order time-fractional diffusion model is not suitable to describe the time- and concentration-dependent chloride ions diffusion processes [40].

This study makes the first attempt to extend the variable-order time fractional derivative diffusion equation to model chloride ions diffusion in concrete. In our variable-order fractional diffusion model, the fractional derivative order is a function of time or concentration to characterize the time or concentration-dependent feature of chloride transport processes.

2. Mathematical physics models

2.1. Error function solution model to Fick's second law

The most commonly used chloride transport predictive model is the Fick's second law, which can be written as

$$\frac{\partial C(x, t)}{\partial t} = D_a \frac{\partial^2 C(x, t)}{\partial x^2}, \quad 0 < x < +\infty, \quad t > 0, \quad (2.1)$$

where the chloride ions diffuse from the concrete surface into the semi-infinite medium, $C(x, t)$ is the chloride concentration (percent concrete) at depth x after time t , and D_a represents the apparent chloride diffusion coefficient (m^2/s) and can be determined by fitting experimental or field measurement data, reflecting the average diffusivity during the period of exposure. Because of the effect of densification during hardening, the chloride ingress rate has significantly been overestimated. To overcome this obvious defect, D_a is often replaced by the time-dependent functions in the recent proposed models [36].

The empirical model equation (2.1) has the analytical solution in terms of error-function (ERFC model) as follows

$$C(x, t) = C_s \operatorname{erfc}\left(\frac{x}{2\sqrt{D_a t}}\right), \quad (2.2)$$

where $C_s = C(0, t)$ is the boundary value expressed as a surface chloride content (percent concrete), and $\operatorname{erfc}()$ denotes the complementary error function. Because of easy-to-use merit of its simple analytical solution,

the model equation (2.1) is comprehensively used for predicting chloride profiles in concrete. However, as shown in [35], the prediction with this model does not agree well with the measured profiles.

2.2. Chloride binding

As chloride ions penetrate through concrete, interactions occur between chloride ions and cement matrix, thereby leading to the effective removal of free chloride ions from the pore solution systems. A proportion of chloride ions is bound to the solid phase in concrete. This chloride binding process is very complicated and influenced by various factors [16, 38, 21], which is generally simplified by the binding adsorption isotherms. In this study, we choose the following Langmuir isotherm in the modeling

$$C_b = \frac{\alpha C_f}{1 + \beta C_f}, \quad (2.3)$$

where C_b (mol/m³ of concrete) and C_f (mol/m³ of pore solution) are the bound and the free chloride concentrations, respectively, and α and β the constants. As shown in Fig. 1, the slope of the isotherm curve gradually approaches zero with the increasing free chloride concentration. This indicates no more free chloride is bound to the absorption sites, and then the chloride transport retreats from a coupled diffusion-binding process to the diffusion-dominant process.

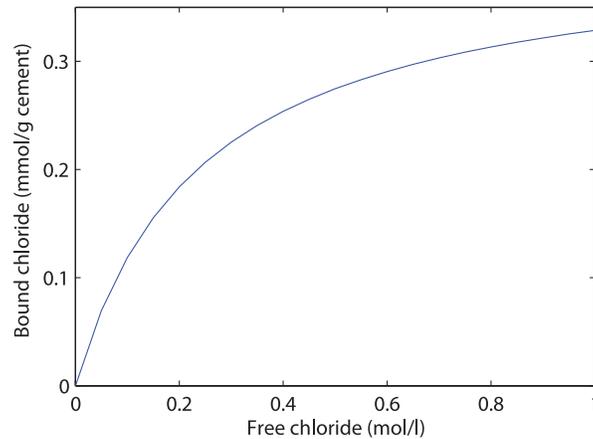


Fig. 1. The schematic diagram of Langmuir adsorption isotherm of Eq.(2.3) with fitted parameters $\alpha = 1.67, \beta = 4.08$ in [26].

Combining the principle of mass conservation with the Langmuir absorption isotherm (see Eq.(2.3)), the chloride diffusion under non-steady state conditions can be described by a modified form of Fick's second law as follows [26]

$$\left(1 + \frac{\alpha}{\omega_e(1 + \beta C_f)^2}\right) \frac{\partial C_f(x, t)}{\partial t} = D_c \frac{\partial^2 C_f(x, t)}{\partial x^2}, \quad 0 < x < +\infty, \quad t > 0, \quad (2.4)$$

where D_c denotes the chloride diffusion coefficient (m^2/s), and ω_e is the evaporable water content (m^3 evaporable water/ m^3 concrete).

Since the coefficients α and β characterizing the chloride binding behavior are evaluated by data fitting, a large amount of measurement is required for different concrete samples under diverse environmental conditions. In addition, accurate parameters D_c and ω_e are highly demanded in this model. Eq.(2.4) is a highly non-linear equation hard to be accurately solved. These disadvantages make this model less attractive in the practice.

2.3. Variable-order time-fractional diffusion model

2.3.1. Constant and variable-order fractional derivative operators. Fractional derivative implies the derivative of arbitrary real-valued order. In recent decades, growing attention has been paid to theory and applications of fractional calculus [22, 39]. In this study, we employ the Caputo definition of fractional derivative, which has clear physical meanings and is widely used in practical engineering problems [25]. Its definition can be stated as follows

$$\frac{d^p f(t)}{dt^p} = \frac{1}{\Gamma(n-p)} \int_0^t \frac{f^{(n)}(\tau)}{(t-\tau)^{p+1-n}} d\tau, \quad n-1 < p \leq n, \quad (2.5)$$

where p is the derivative order and n an integer, $\Gamma(\cdot)$ denotes the Gamma function and can be expressed by $\Gamma(z) = \int_0^\infty e^{-t} t^{z-1} dt$, ($\text{Re}(z) > 0$).

The definition of variable-order Caputo fractional derivative is straightforward and is written as [7]

$$\frac{d^{p(t)} f(t)}{dt^{p(t)}} = \frac{1}{\Gamma(n-p(t))} \int_0^t \frac{f^{(n)}(\tau)}{(t-\tau)^{p(t)+1-n}} d\tau, \quad n-1 < p(t) \leq n, \quad (2.6)$$

where $p(t)$ is a function with respect to variable t [29].

2.3.2. Constant and variable-order time-fractional diffusion equations. Although the ERFC model mentioned in Section 2.1 has the advantage of engineering friendliness, i.e. the simplicity in performing the predictions, it has a few obvious drawbacks: (1) this model cannot depict the time dependence of chloride diffusion in concrete, (2) the concentration dependency of chloride binding behaviors cannot be described with a constant apparent diffusion coefficient, (3) the coincidence between predicted and

measured profiles is missing. To overcome these shortcomings and deficiencies in the traditional ERFM model, it is highly desired to develop a simple and efficient model to describe chloride ions diffusion in concrete.

Fractional derivative has been found a power mathematical tool in characterizing non-local and history-dependent process such as anomalous diffusion in complex media. The fractional diffusion equations have attracted great attention in recent decades. The commonly used constant order time-fractional diffusion (COFD) equation is expressed as

$$\frac{\partial^p C_f(x, t)}{\partial t^p} = K \frac{\partial^2 C_f(x, t)}{\partial x^2}, \quad 0 < x < +\infty, \quad t > 0, \quad (2.7)$$

where $0 < p < 1$ is the order of time-fractional derivative, K denotes a generalized diffusion coefficient, and $C_f(x, t)$ represents the free chloride concentration at (x, t) in the pore system.

The chloride ingress into concrete is not only a pure diffusion process, but also the coupled chemical and physical binding interaction with the cement matrix. The binding properties can be defined by the binding absorption isotherms as described by Langmuir isotherm shown in Eq.(2.3). Then, the chloride diffusion equation can be rewritten by revising Eq.(2.4)

$$\frac{\partial C_f(x, t)}{\partial t} = D^* \frac{\partial^2 C_f(x, t)}{\partial x^2}, \quad D^* = \frac{D_c}{1 + \frac{\alpha}{\omega_e(1+\beta C_f)^2}}. \quad (2.8)$$

As shown in the above Eq.(2.8), the coupled diffusion-binding interactions lead the chloride penetration through concrete to a concentration-dependent anomalous diffusion which no longer obeys the Fick's second law.

According to the binding isotherm Eq.(2.3), most free chloride ions at low concentration level in the pore solution are changed into the bound formation and vice versa. With the increasing concentration, the chloride binding capacity in the cement matrix will gradually decay and D^* increases until a relatively stable level. Then, the Eq.(2.8) will be reduced to normal diffusion equation with a constant D^* .

As mentioned in Section 2.2, the non-linear diffusion model, i.e., Eqs.(2.3) and (2.8), encounter certain disadvantages in the engineering applications. Meanwhile, although the time-fractional derivative has the merit of describing time dependence property, the constant-order time-fractional diffusion model cannot well characterize the concentration dependency of chloride ions diffusion processes in concrete. Therefore, this paper proposes the following variable-order time-fractional diffusion (VOFD) equation to describe

the complex concentration-dependent chloride diffusion process

$$\frac{\partial^{p(C_f)} C_f(x, t)}{\partial t^{p(C_f)}} = D_\alpha \frac{\partial^2 C_f(x, t)}{\partial x^2}, \quad 0 < x < +\infty, \quad t > 0, \quad (2.9)$$

where $0 < p(C_f) < 1$ is the variable order of time-fractional derivative.

It is well-known that mean square displacement (MSD) is an important and easy-to-implement statistical tool to characterize different types of diffusions [30]. The MSD of constant-order fractional diffusion equation can be expressed as $\langle x^2(t) \rangle \propto t^p$, where $H = p/2 \in (0, 1)$ is the Hurst exponent. $H = 0.5$ denotes the normal diffusion process following the Fick's second law. Otherwise, $0 < H < 0.5$ represents sub-diffusion process and $0.5 < H < 1$ means super-diffusion process, respectively. Here, it is interesting to note that the power law time-dependent coefficient diffusion model [36] and the COFD model (see the Eq.(2.7)) have almost identical diffusion tendencies due to their same MSD behaviors [40]. According to the features of coupled chloride diffusion-binding behavior, the variable function $p(C_f)$ increases with the gradually increasing free chloride concentration level until the upper limit of sub-diffusion $p = 2$, $H = 1$. In addition, the concentration-dependent diffusion coefficient D^* in Eq.(2.8) with the variation form of the second power enables us to evaluate the variable function $p(C_f)$ by

$$p(C_f) = 1 - k \left(\frac{C_s - C_f}{C_s} \right), \quad 0 < k < 1, \quad (2.10)$$

where C_s is the free chloride concentration at the exposed surface (mol/l of pore solution), and k denotes the dimensionless concentration influence coefficient and represents the degree of influence of concentration dependence arising from the chloride binding behaviors. The larger k implies the higher chloride binding capacity and vice versa.

The main work in the foregoing variable-order time-fractional diffusion model is the determination of parameters D_α and k . Because the analytical solution of Eq.(2.9) is not available in most cases, we employ finite difference method to get its numerical solution. The numerical discretization schemes are briefly introduced in Appendix, and for more details please refer to [30],[43] and [31].

3. Results and discussions

To investigate the applicability and reliability of the proposed VOFD (see the Eq.(2.9)) model, two benchmark experiments [14, 12] will be used to validate the predicted chloride profiles produced by the present VOFD model.

3.1. Example 1

Loser et al. [14] investigated the chloride resistance of concretes of four different binders, i.e. CEM I, CEM II, CEM III and CEM I+V. Here, CEM I is the ordinary Portland cement(OPC), CEM II and CEM III are industrially mixed binders containing 80-94% OPC and 6-20% limestone powder for CEM II and 35-64% OPC and 36-65% slag for CEM III, respectively. V represents a low CaO fly ash (V). The measured experimental data of free chloride content after the samples exposed for 50 days immersion, mixtures with water-binder ratio of 0.45 will be used in this study. For more details of these experiments please refer to [14]. We examine the traditional ERFC (Eq.(2.2)), the present VOFD and the COFD (Eq.(2.7)) models of chloride ingress in saturated concrete against these experimental data. The parameters in these three different models are obtained (see Table 1) via the least square fitting of measurement data to describe the chloride profiles, respectively.

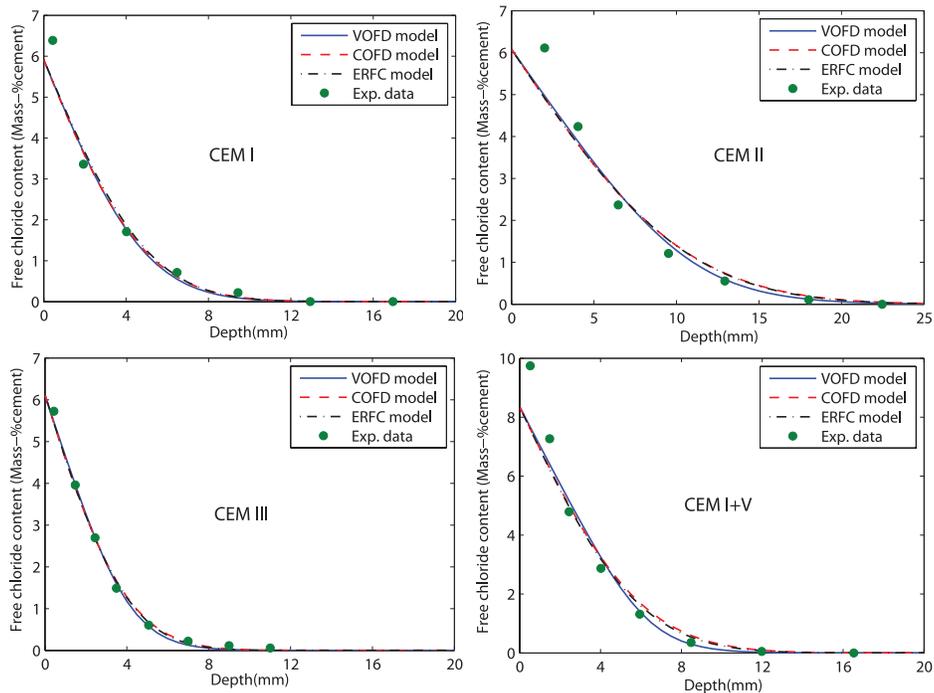


Fig. 2. Experimental data in [14] and predicted chloride profiles by VOFD model, COFD model and ERFC model, respectively, for four different types of binder.

TABLE 1. Model parameters determined in VOFD, COFD and ERFC models, respectively

Cement Type	VOFD Model		COFD Model		ERFC Model
	k	$D_\alpha(\text{m}^2/\text{s}^p(\text{C}_i))$	p	$K(\text{m}^2/\text{s}^p)$	$D_a(\text{m}^2/\text{s})$
CEM I	0.06	0.17	0.96	0.18	0.16
CEM II	0.47	1.73	1.00	0.70	0.69
CEM III	0.35	0.20	0.98	0.11	0.10
CEM I+V	0.87	1.21	0.99	0.22	0.21

As shown in Fig. 2, the predicted chloride profile of the COFD model appears very close to that of the ERFC model. This is because the parameter p in COFD model approximately approaches to 1 and also, as illustrated in Table 1, the value of K and D_a is almost the same in all four different concretes. The COFD model, therefore, can be reduced to ERFC model, at least in these cases. Also, we can observe from these figures that the VOFD and ERFC models have the same diffusion tendency when the depth is not so large. However, the predicted profiles vary as the value of depth further increases, e.g. when the depth is larger than 7.5 mm in CEM II. Here, the point corresponding to the location at which the difference occurs is defined as the “cross point”, for example, the point at 7.5 mm depth in CEM II. From the exposed surface to the cross point, the chloride content is relatively larger, and the chloride transport is a diffusion-dominated process. Over the cross point, the chloride content is decreasing to a lower level, and the chloride ions penetrate through concrete governed by a coupled diffusion-binding mechanism, in which a proportion of free chloride in the pore solution is bound to the cement matrix. The chloride binding leads to a significant decrease of free chloride concentration after the cross point. Then, the velocities of chloride ions diffusion will be slowed down at these low concentration areas. It is obvious that the ERFC model is not capable of describing these concentration-dependent diffusion processes, but our VOFD model performs better as shown in Fig. 2. In addition, the mean square errors between different models and the experimental data are obtained. As shown in Table 2, the VOFD model has the minimal mean square error for all the four different concrete. Therefore, it is testified again that the present VOFD model is a more reliable and effective model to describe chloride ions diffusion in concrete.

Table 1 shows the parameter values obtained by fitting the experimental data. The small concentration influence coefficient k results in almost no difference observed for the profiles (e.g. CEM I and CEM III in Fig. 2) between the ERFC and the VOFD models. Moreover, when the parameter

TABLE 2. Mean square errors of three different models

Cement Type	VOFD Model	COFD Model	ERFC Model
CEM I	0.1425	0.1427	0.1443
CEM II	0.1958	0.2272	0.2292
CEM III	0.0134	0.0175	0.0193
CEM I+V	0.6722	0.7443	0.7416

D_α keeps the same level in different concretes as shown in Table 1, e.g. 0.17/0.20 for CEM I/III, the relatively larger k , e.g. 0.35/0.06 for CEM III/I, indicates a stronger chloride binding capacity and chloride resistance for the particular concrete, e.g. CEM III here. This can be testified by the observed chloride penetration depths (as shown in Fig. 2, 8 mm for CEM III compared to 12 mm for CEM I). On the other hand, when k is large (e.g. 0.47 for CEM II and 0.87 for CEM I+V), the differences are significantly observed after an apparent cross point (see the Fig. 2). As a result, the larger k and smaller D in the present VOFD model illustrate the stronger chloride resistance and vice versa. In the end, the shorter chloride penetration depth (12 mm for CEM I+V than 22 mm for CEM II) also proves that the supplementary fly ash can effectively improve the chloride binding capacity.

3.2. Example 2

Khitab et al. [12] obtained a series of experimental results of chloride profiles in the saturated concrete samples based on the CEM-I-type cement with water-cement ratio of 0.4. For more details of these experiments please refer to [12]. In this study, we will use these measurement data to validate our proposed VOFD model by predicting concentration profiles. According to the least square fitting of measured experimental data of concrete samples exposed for 100 days, the parameters k and D_α in the VOFD model, p and K in the COFD model and D_a in the ERFC model can be determined, respectively. In the end, the obtained model parameters $k = 0.81$, $D_\alpha = 2.21$, $p = 1$, $K = 0.31$ and $D_a = 0.31$ in the corresponding model will be further used for predicting the chloride profiles in these samples exposed for 200 days. Because the fractional order p equals to 1 in this example, the COFD model reduces to the ERFC model. Thus, the COFD model curve is omitted in the Figs. 3 and 4.

Compared with the measured experimental data, the diffusion profiles of the VOFD and ERFC models are displayed in Fig. 3. The VOFD model has a significantly better agreement with experimental data than the ERFC model in the whole given depth range. Due to the relatively large concentration influence coefficient $k = 0.81$, the sharp differences are

observed between these two models after a cross point at the depth of about 8 mm. Moreover, over the cross point, the VOFD model has a much higher accuracy because it characterizes the feature of concentration dependence during chloride penetration in concrete. In contrast, the ERFC has no such capacity of describing this complicated diffusion-binding process.

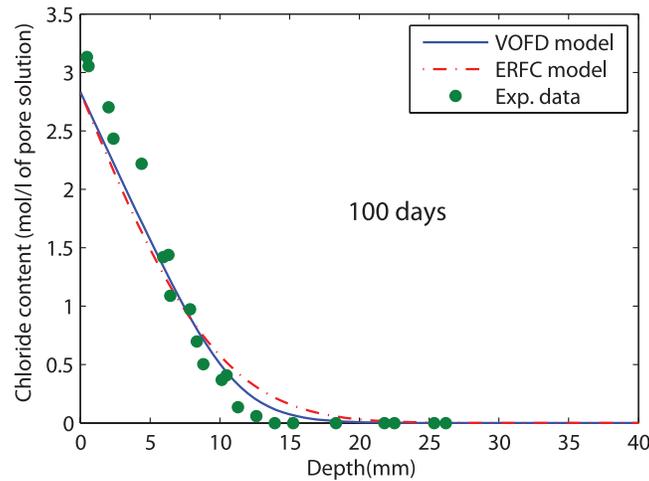


Fig. 3. Comparison of VOFD model, ERFC model and experimental data[12] of the concrete samples exposed for 100 days.

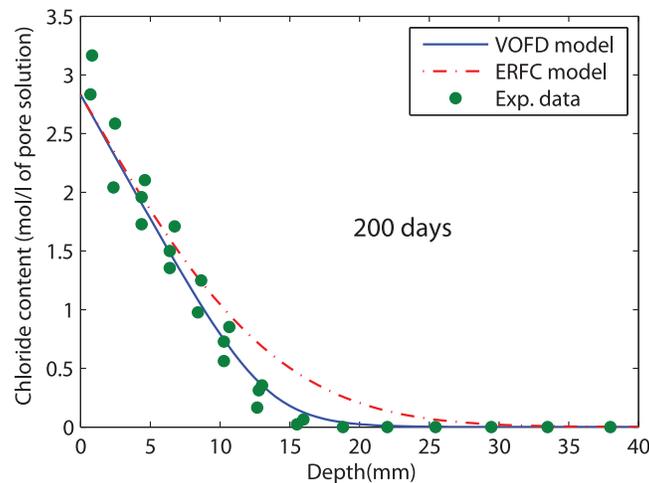


Fig. 4. Predicted 200-day chloride profiles by VOFD model and ERFC model, respectively, with the fitted model parameters determined at 100 days.

Fig. 3 shows that by using the model parameters obtained by fitting the 100-day experimental results, the VOFD and ERFC models predict chloride profiles of concrete exposed for 200 days. As shown in Fig. 3, we can see no coincidence between the ERFC model and the measured data. The chloride ingress is significantly overestimated by the ERFC model with the constant apparent diffusion coefficient D_a . This means that this empirical model can not depict the time dependence of chloride diffusion processes due to the effect of densification of concrete during hardening. On the other hand, the time-fractional derivative reflects the property of time dependence. Combining the concentration-dependent variable function $p(C_f)$ of derivative order (see Eq.(2.10)), the VOFD model may be quite effective to describe this complicated chloride transport process in concrete. As shown in Fig. 3, the profile by the VOFD model is in very good agreement with the experimental data.

4. Conclusions

This study proposes a variable-order time-fractional derivative diffusion model to describe chloride ions diffusion processes in concrete. Like the ERFC model, the proposed model of the chloride ingress remains phenomenological and does not interpret the specific interactions occurred in concrete. However, the present time-fractional derivative model is capable of describing the time dependence of chloride transport by the variable-order time-fractional derivative. In particular, the concentration-dependent chloride diffusion-binding behavior can be well depicted by the derivative order of a variable function $p(C_f)$.

The VOFD model has only two parameters: concentration influence coefficient k and generalized diffusion coefficient D_α , which can be obtained straightforward by using the least square fitting technique. The parameter k represents the degree of concentration influence of chloride transport due to the chloride binding behavior, and the larger k indicates the stronger resistance to chloride ingress. It should be pointed out that the applicability and reliability of the VOFD model for chloride transport in concrete need to be further investigated in comparison with more experimental data.

Appendix

To introduce the numerical scheme clearly, some notations are given as follows: Δx is the spatial grid size, Δt the time step, $C(x_i, t_j) = C_i^j$ denotes the chloride concentration at $x_i = i\Delta x$, $i = 0, 1, 2, \dots, M$, $M = x_R/\Delta x$ and $t_j = j\Delta t$, $j = 0, 1, 2, \dots, x_R$ represents the fictitious right boundary. One point noted here is that $x_R \gg T$, where T is the cover thickness of rebars in concrete and indicates the fictitious gradient boundary condition $C(x_{M-1}, t) = C(x_M, t)$ in the deep concrete for numerical computation.

In this study, finite element method is used to discretize the variable-order time-fractional derivative term

$$\begin{aligned} \frac{\partial^{p(C)} C(x, t_{j+1})}{\partial t^{p(C)}} &= \frac{1}{\Gamma(1-p^{j+1})} \int_0^{t_{j+1}} \frac{\partial C(x, \tau)}{\partial \tau} \frac{1}{(t_{j+1}-\tau)^{p^{j+1}}} d\tau \\ &= \frac{1}{\Gamma(1-p^{j+1})} \sum_{k=0}^j \int_{k\Delta t}^{(k+1)\Delta t} \frac{\partial C(x, \tau)}{\partial \tau} \frac{1}{(t_{j+1}-\tau)^{p^{j+1}}} d\tau \\ &\approx \frac{1}{\Gamma(1-p^{j+1})} \sum_{k=0}^j \int_{k\Delta t}^{(k+1)\Delta t} \frac{\partial C(x, \tau_k)}{\partial \tau} \frac{1}{(t_{j+1}-\tau)^{p^{j+1}}} d\tau, \quad (\text{A.11}) \end{aligned}$$

where $\partial C(x, \tau_k)/\partial \tau$ is approximated by the forward finite difference scheme

$$\frac{\partial C(x, \tau_k)}{\partial \tau} = \frac{C(x, \tau_{k+1}) - C(x, \tau_k)}{\tau} + o(\tau), \quad (\text{A.12})$$

Thus,

$$\begin{aligned} \frac{\partial^{p(C)} C(x_i, t_{j+1})}{\partial t^{p(C)}} &\approx \frac{1}{\Gamma(1-p_i^{j+1})} \sum_{k=0}^j \frac{C(x_i, t_{k+1}) - C(x_i, t_k)}{\Delta t} \int_{k\Delta t}^{(k+1)\Delta t} \frac{1}{(t_{j+1}-\tau)^{p_i^{j+1}}} d\tau, \\ &= \frac{1}{\Gamma(1-p_i^{j+1})} \sum_{k=0}^j \frac{C(x_i, t_{j-k+1}) - C(x_i, t_{j-k})}{\Delta t} \int_{k\Delta t}^{(k+1)\Delta t} \frac{1}{(t_{j+1}-\tau)^{p_i^{j+1}}} d\tau, \\ &= \begin{cases} \frac{(\Delta t)^{-p_i^{j+1}}}{\Gamma(2-p_i^{j+1})} (C_i^{j+1} - C_i^j) \\ + \frac{(\Delta t)^{-p_i^{j+1}}}{\Gamma(2-p_i^{j+1})} \sum_{k=1}^j (C_i^{j-k+1} - C_i^{j-k}) [(k+1)^{1-p_i^{j+1}} - k^{1-p_i^{j+1}}], & j \geq 1, \\ \frac{(k\Delta t)^{-p_i^{j+1}}}{\Gamma(2-p_i^{j+1})} (C_i^1 - C_i^0), & j = 0, \end{cases} \\ &= \begin{cases} a_i^{j+1} (C_i^{j+1} - C_i^j) + a_i^{j+1} \sum_{k=1}^j b_k^{i,j+1} (C_i^{j+1} - C_i^j), & j \geq 1, \\ a_i^1 (C_i^1 - C_i^0), & j = 0, \end{cases} \quad (\text{A.13}) \end{aligned}$$

where $a_i^{j+1} = \frac{(\Delta t)^{-p_i^{j+1}}}{\Gamma(2-p_i^{j+1})}$, $b_k^{i,j+1} = [(k+1)^{1-p_i^{j+1}} - k^{1-p_i^{j+1}}]$, $k = 0, 1, 2, \dots, j$, $C^0 = C(x, t = 0)$. It is interesting to note that the discretization of variable-order time-fractional derivative term is different from the integer-order derivative in that all the past data before the unknown instance are required to evaluate the current solution. The discretization reflects the history dependency of the fractional derivative. The spatial derivative term in Eq.(2.9) can be approximated with central difference scheme

$$\frac{\partial^2 C(x_i, t_j)}{\partial x^2} = \frac{C_{i+1}^j + C_i^j + C_{i-1}^j}{(\Delta t)^2} + o(x^2). \quad (\text{A.14})$$

According to the implicit finite difference scheme, substituting Eq.(A.13) and (A.14) into Eq.(2.9) produces

$$\frac{\partial^{p(C)} C_f}{\partial t^{p(C)}} = D_\alpha \frac{\partial^2 C_f(x, t)}{\partial x^2}, \tag{A.15}$$

then

$$D_\alpha \frac{C_{i+1}^j + C_i^j + C_{i-1}^j}{(\Delta t)^2} = \begin{cases} a_i^{j+1}(C_i^{j+1} - C_i^j) + a_i^{j+1} \sum_{k=1}^j b_k^{i,j+1}(C_i^{j+1} - C_i^j), & j \geq 1 \\ a_i^1(C_i^1 - C_i^0), & j = 0 \end{cases} \tag{A.16}$$

Changing the sequence of variables in the above equation, we have

$$\begin{aligned} & \frac{D_\alpha}{(\Delta x)^2} C_{i-1}^{j+1} - (a_i^{j+1} + \frac{2D_\alpha}{(\Delta x)^2}) C_i^{j+1} + \frac{D_\alpha}{(\Delta x)^2} C_{i+1}^{j+1} \\ &= \begin{cases} -a_i^{j+1} C_i^j + a_i^{j+1} (\sum_{k=1}^j b_k^{i,j+1} (C_i^{j+1} - C_i^j)), & j \geq 1, \\ -a_i^1 C_i^0, & j = 0. \end{cases} \end{aligned} \tag{A.17}$$

Then, we can obtain the numerical solution of Eq.(2.9).

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