Advanced Modelling of Chloride Penetration in Concrete Considering Time- and Space-Dependent Diffusivity

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Abstract. For reinforced concrete structures, corrosion of reinforcing steel bars induced by chloride ions represents a recurring durability risk. Chloride ion diffusion is commonly described by Fick's laws, which are strictly applicable only when the diffusivity is assumed to be constant in both time and space. Under this assumption, the diffusion process and the associated exposure scenario can be greatly simplified. In this paper, a more comprehensive, non-constant, multifactorial diffusivity model is proposed, accounting for, among others, the effects of temperature, deformation, and damage. Given that the diffusivity varies in time and space, random numerical solutions are required. For this purpose, the Runge-Kutta method is implemented for both 1D and 2D models, and the results are plotted using Hermite polynomials. The boundary conditions relevant to this application are calibrated to solve the governing partial differential equations under randomly fluctuating diffusivity. The results demonstrate that traditional approaches significantly underestimate chloride concentrations at certain depths, particularly for long-term exposure scenarios.

Keywords: Diffusion model; corrosion; advanced analyses; structural engineering.

1 Introduction

One of the most relevant deterioration mechanisms of reinforced concrete (RC) structures is the corrosion of reinforcing steel bars caused by chloride ion diffusion. Chloride ions penetrate the concrete cementitious matrix from the external environment.

In general, structures located in aggressive environments, such as industrial areas and coastal zones up to about 4.0 km from the sea, are highly susceptible to this type of attack [10]. Several studies on real structures (e.g., bridges, offshore structures, etc.) have shown that proximity to the sea has a significant impact [11].

Once corrosion begins, it reduces the cross-sectional area of the steel bars, decreasing their resistance and ductility, with consequences for the structure's stability, load-bearing capacity, and public safety [3, 12, 13].

Figure 1 shows a real photo of two RC beams subjected to corrosions of the steel bars and concrete [1]. The purpose of these photos is only to help illustrate the risk associated with the occurrence of this phenomenon, which must be avoid in order to maintain and "build resilient infrastructure" in accordance with the 2030 Agenda for sustainable development [16].

Fig. 1. Real photo of the RC beams subjected to corrosions.

The chloride ions diffusion in concrete is a relatively simple process, since it is a non-linear process depending on the time and several other intrinsically phenomena, such as the capillary absorption and permeation of the water contenting chloride and other ions. The diffusion process is described by Fick's laws, where the diffusion coefficient (or diffusivity) is the key parameter to estimate the trend of the chloride concentration in concrete [17, 18].

In fact, credible papers put the attention on the correct estimation of the diffusivity in order to account for chemical and mechanical interactions, which can be distinguished in four different types as self-diffusivity, free diffusivity, diffusivity in saturated capillary pores, solid diffusivity [7].

The diffusivity is largely used as a constant value in a determinist way, usually dependent only on the water/cement (w/c) ratio, which can be considered as a reference and standard value. However, in this way, some important factors are not considered as the binding chloride, temperature, humidity, concrete aging, etc. (treated in this study). In [14, 19] some empirical and analytical models for predicting the chloride diffusivity are listed, where these factors are considered but, in many cases, separately to each

[1] These photos refer to the fire station building built in 1984 and located in the city of Penela, Portugal. The first author of this paper worked on this executive project during the years 2019-2020 to evaluate its stability and resistance for seismic retrofitting in the presence of a new construction built above [5].

other. Therefore, considering a unique formula where more factors are accounted for could be an innovative aspect to be studied.

These models make the diffusivity non-constant and highly non-linear. Therefore, the use of a constant diffusivity could be insufficient to represent more accurate and realistic chloride concentrations in concrete.

The correlation between diffusivity and temperature could be relevant when considering climate change, as highlighted by the intergovernmental panel on climate change (IPCC) [15], which may require the re-evaluation of many existing structures considering this factor as studied in [3].

Also, the representation in only one-direction (1D) can be very simplified not representing the real situations. For this, the focus of this paper is to quantify a more complete diffusivity, in order to include different factors that mainly account for the material characteristics and environmental variations in 1D and 2D models. These analyses are only possible by developing advanced methods as Runge-Kutta (RK) and Hermite polynomials (HPs). Therefore, the main purpose of this study is definitively to overpass the use of the constant diffusivity by considering external and internal factors.

2 Materials and Methods

Consider a structure near a coastal area that, for years, has been exposed to extreme conditions and a corrosion phenomenon. A chemical element that plays an important role for these processes is the chloride ion.

The total concentration of chloride ions, C, in direction i (x, y, z) and time, t, in a homogeneous and saturated concrete structural member is governed by the partial differential equation (PDE) called second Fick's law:

$$\frac{\partial \mathrm{C(i,t)}}{\partial \mathrm{t}} = \mathrm{D}\frac{\partial^2 \mathrm{C(i,t)}}{\partial \mathrm{i}^2} \tag{1}$$

where D is the diffusivity that can be expressed by using a relation accounting for many multi-factors as [1, 4]:

$$\mathrm{D} = \mathrm{f}_0(w/c)\mathrm{f}_1(\mathrm{C_b})\ \mathrm{f}_2(\mathrm{T})\ \mathrm{f}_3(\mathrm{t})\ \mathrm{f}_4(\varepsilon, \mathrm{d})\ \mathrm{f}_5(\mathrm{h}) \tag{2},$$

which each factor, f_0, f_1, f_2, f_3, f_4, and f_5 is correlated to the water-cement (w/c) ratio, binding chloride C_b, internal temperature T, time (or age) t, elasto-plastic axial deformation ε, concrete damage d, and internal humidity h, respectively.

Some factors are more common to be used as for instance T and h, whereas other ones are more difficult to be estimated as ε and d. In literature (among others [7, 8]) several analytical and experimental relations can be found, which are valid under some hypotheses to be known to control the model and to quantify the outputs. In this study, an

interesting and non-common aspect regards the approach in adopting a unique relation accounting for many factors simultaneously.

The total C value in Eq. (1) is divided in two parts: the free chloride dissolved in pore solution, C_f, and the mentioned C_b, where their correlation is defined by the well-known non-linear Langmuir isotherm [2] mainly depending on the evaporable water content, and characteristics of the material composition. In this sense, only C_f participates to the mechanical diffusion process being "free" to move and for this reason it is treated in this paper, whereas C_b is entrapped (i.e., "binding") between other ions hence it could be studied by chemical analyses.

Equation (1) can be solved analytically under specific conditions and considering D as constant parameter, or numerically in order to consider non-constant D. In particular, for $D \neq 1$, it is possible to use the explicit Runge-Kutta (RK) method to find the solutions and Hermite polynomials (HPs) to plot them [3].

The ordinary HPs in x (i.e., $H_n(x)$) and t (i.e., $H_n(t)$), described by the numerical series, generating functions, and identities functions, are, respectively:

$$\begin{cases} H_n(x) = n! \sum_{r=0}^{\frac{n}{2}} \frac{(2x)^{n-2r}(-1)^r}{(n-2r)!r!}, & \text{in x direction} \\ H_n(t) = n! \sum_{r=0}^{\frac{n}{2}} \frac{(2t)^{n-2r}(-1)^r}{(n-2r)!r!}, & \text{in time t} \end{cases} \tag{3}$$

$$\begin{cases} \sum_{n=0}^{\infty} \frac{p^n}{n!} H_n(x) = e^{2xp+p^2}, & \text{in x direction} \\ \sum_{n=0}^{\infty} \frac{p^n}{n!} H_n(t) = e^{2tp+p^2}, & \text{in time t} \end{cases} \tag{4}$$

$$\begin{cases} H_n(x) = (-1)^n e^{x^2} \frac{d^n}{dx^n}\left(e^{-x^2}\right), & \text{in x direction} \\ H_n(t) = (-1)^n e^{t^2} \frac{d^n}{dt^n}\left(e^{-t^2}\right), & \text{in time t} \end{cases} \tag{5}$$

where the indexes n, r, and p provide the order of the formulas and define their values (for more details see [6]). These HPs satisfy the orthogonality relation, i.e., $H_n(x)$ and other HPs of degree j, $H_j(x)$, are orthogonal in $L^2_\omega(\Lambda)$, where $\Lambda = (-\infty, +\infty)$ regards the weight function defined as $\omega(t) = e^{-x^2}$, and they satisfy the following formula:

$$\int_{-\infty}^{+\infty} \left[H_n(x) H_j(x) \omega(x)\right] dx = 2^n n! \sqrt{\pi} \delta_{n,j} \tag{6}$$

where $\delta_{n,j}$ is the Kronecker delta function under n and j subscripts. For instance, for $H_n(t)$ in t-domain, Eq. (6) assumes a similar form with x = t, whereas Eq. (6) is equal to zero when $n \neq j$.

In this study, to solve Eq. (1) analytically by considering a non-constant D, the initial and boundary conditions (i.c. and b.c., respectively) must be defined as:

$$\begin{aligned} &\text{i.c.:} \quad C(x_m, 0) = C_0, \quad \text{in } \Omega \\ &\text{b.c.:} \quad C(0, t_m) = C_s, \quad \text{at } \partial\Omega_1 \\ &\text{b.c.:} \quad C(q\, x_m, t_m) = C_0, \quad \text{at } \partial\Omega_2 \end{aligned} \tag{7}$$

where x_m and t_m are two variables related to the position and time of the chloride concentration, respectively, which must be pre-defined to not generate the arbitrary constants that represent the degrees of freedom during a mathematical integrating operation; for this Eq. (7) refers to a finite medium (see Fig. 2 (left)). The domains Ω, Ω_1, Ω_2 represent the concrete surface and its boundaries in a more general way.

The parameters C_0 and C_s are the inner chloride concentration already present in a concrete member during its manufacturing and the surface chloride concentration transported by wind, respectively.

Note that Eqs. (3)-(7) refer to a 1-dimensional (1D) model in a x direction, however it is possible to extend this model in a 2D by adding the polynomial $H_n(y)$ in y-direction, which can be estimated in analogue way to $H_n(x)$. Due to this similarity for brevity only some formulas are shown.

The parameter q in Eq. (7) quantifies the goodness of the approximated analysis with respect the "exact" one. The exact analysis can be obtained by Eq. (1) under a constant D, since in this way it is possible to find the closed-form analytical solution (i.e., the traditional common solution) of the semi-infinite medium shown in Fig. 2 (right) and used in [17]. The convergence between both analyses has been obtained by several interactions, and it was considered reached when the mean relative error in terms of chloride concentrations provides the minimum value (or an error < 5.0%, usually accepted in structural engineering). Finally, a liner q-D function is plotted providing thus an acceptable value of $q \approx 12.50$ (for more details see [1, 4]).

This q-parameter is also the key to pass from a traditional analysis with a constant diffusivity in 1D semi-infinite medium to an advanced analysis with non-constant diffusivity in 2D finite medium as shown in Fig. 2. Finding a defined q value appears useful for this purpose.

In Fig. 2 it is represented a 1D constant diffusivity (dashed line in right side) and a 2D non-constant and random diffusivity (left side). All parameters have been already explained.

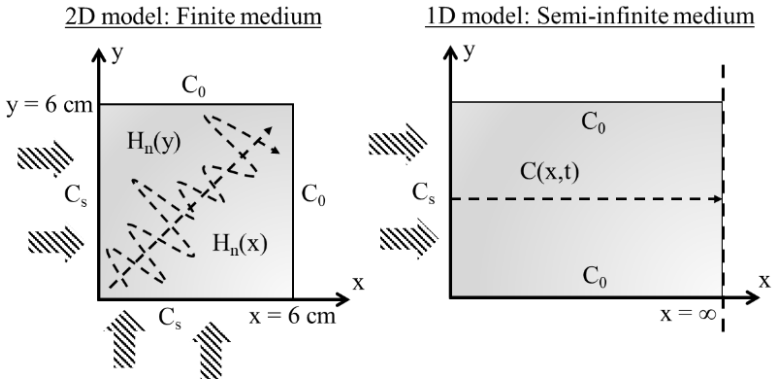


Fig. 2. General scheme of the chloride diffusion by analytical 1D and numerical 2D model.

Table 1 lists the main parameters used to carry out this study [7, 8].

Table 1. Used parameters for the analyses.

Parameter	Value
Inner chloride concentration, C_0	0.50 kg/m^3
Surface chloride concentration, C_s	1.15 kg/m^3
Reference factor, f_0 (for w/c = 0.50)	4.35 cm^2/year
Binding factor, $f_1(C_b)$	0.66
Temperature factor, f_2 (for T = 20.0 ºC)	0.84
Age factor, $f_3(t)$	1.28
Deformation and damage factor, $f_4(\varepsilon, d)$	1.0 – 8.92
Humidity factor, f_5 (for h = 60.0%)	0.13
Diffusivity, D	0.41 – 3.66 cm^2/year (Eq. (2))

Note that D parameter ranges between two limits due to the variability of the f_4 factor shown in [19], whereas the f_0 factor provides its physical meaning.

In the sequel the analyses and results are plotted and discussed.

3 Analyses and Results

Numerical analyses under the mentioned data are here developed and results are plotted in terms of chloride concentrations in a concrete element. Figure 3 shows the chloride concentration by exact analytical and numerical solutions for a constant D = 0.41 cm^2/year. Results during a period of t = 3.0 - 57.0 years and concrete depth x = 0 - 6.0 cm are shown.

Figure 3a) shows non-calibrated results (i.e., q = 1.0) whereas Fig. 3b) shows the calibrated results (q = 12.50) indicating a very good agreement. This comparison allows to understand well the weight of the q variation. It is also possible to see that the boundary conditions at x = 0 play an important role on the calibration since in the non-calibrated solution $C \neq C_s$, which is inconsistent to Eq. (7).

Note that the chloride concentration, obtained by the numerical approach, has been calculated considering the multi-factorial D (Eq. (2)) usually neglected.

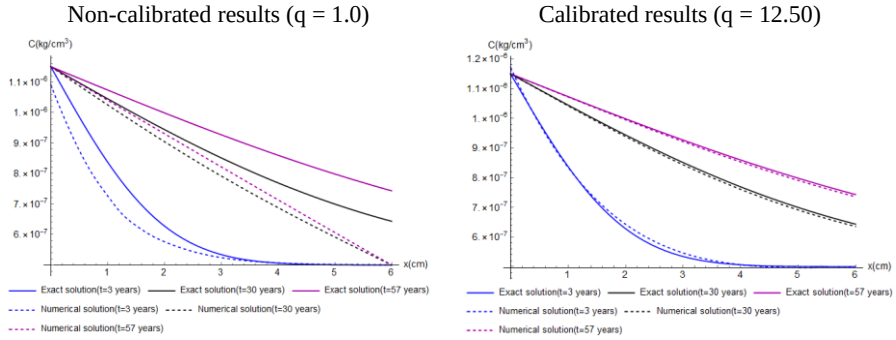


Fig. 3. Chloride concentrations by analytical and numerical solutions under a) non-calibrated q, and b) calibrated q value.

A finite number of random combinations in order to perform and to show the analysis has been chosen. Here, 3 combinations have been considered to represent 3 possible different cases by using the classical methods to develop general loadings [9]:

$$D(t) = \frac{D}{\alpha}\left[\sum_{i=1}^{N} \sin(\omega_i t + \phi_i) + \alpha\right] \qquad (8)$$

where ω_i is the circular frequency, ϕ_i is the random phase (ϕ_i = 0 - 2π), N and α are partial factors purely correlated to the D form, e.g., N = 10, α =10 allows to generate one or two peaks each year by simulating season peaks (winter and summer).

Figure 4 shows the generated amplitude of the diffusivity (constant and random lines in Fig. 4a)) that produce the chloride concentration curves shown in Fig. 4b). The constant values refer to the values shown in Table 1. The considered points are placed at 3.0 cm from the external surface of the concrete structural member. The period interval for the analysis is 0 - 60.0 years.

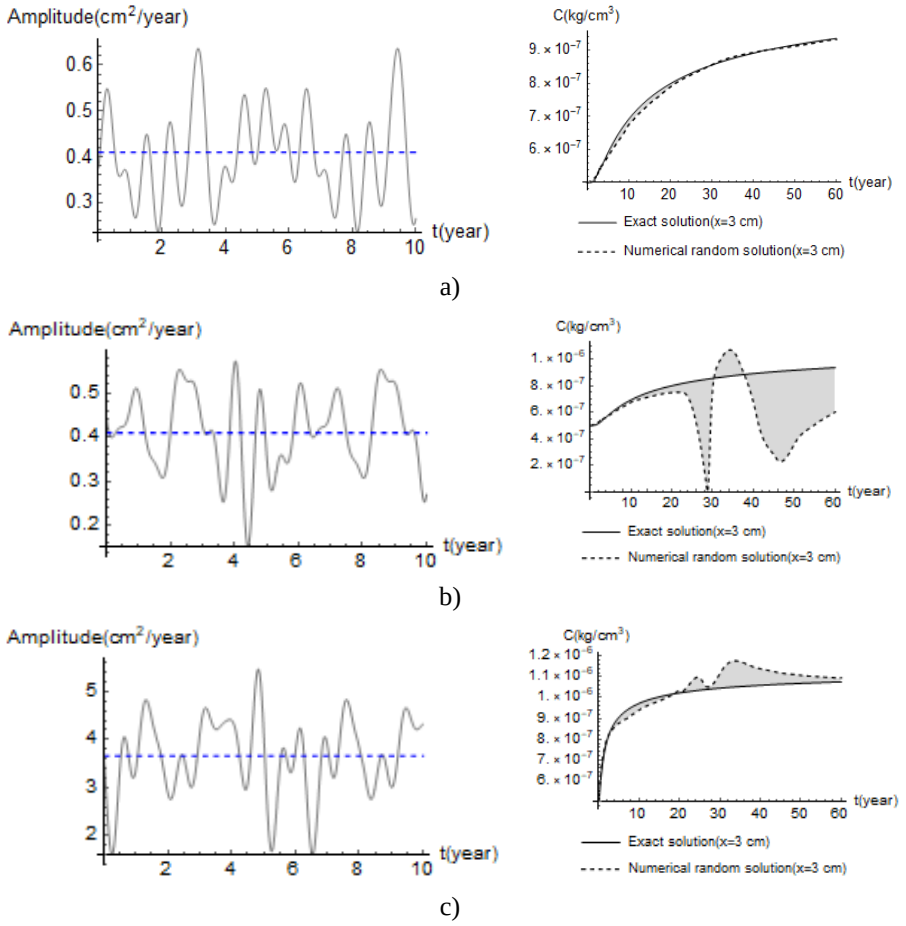


Fig. 4. Constant and random D amplitude (left side) and chloride ions concentrations (right side) for a) random 1, b) random 2, and c) random 3.

The chloride concentration by random D can be greater or lesser than the chloride concentration by constant one. The trend follows the principle that C increases with increasing D. When a diffusivity trend is composed by more points placed above the constant D, the chloride concentration by numerical solution is greater than the chloride concentration by exact solution and vice-versa. The solid grey area (in Fig. 4, right) represents the difference of the chloride concentration in concrete between two solutions. In this way, it is possible to quantify the possible over or under-estimation of concentration C.

The chloride concentration is plotted for a defined depth x. Considering that the proposed model is non-linear dynamic, it is possible that for the same depth x, the chloride concentration C decreases or increases in the time t, differently for the constant D, which always increases the concentration C monotonically. With this approach, it is

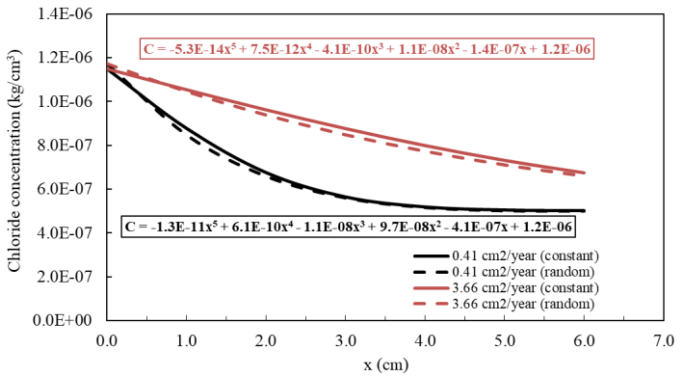
possible to model the random nature of the chloride ions flux in the cementitious matrix simulating real applications.

The values of the chloride concentration in Fig. 4c) are higher than those in Fig. 4a)-b) up to about 1.35. This is due to the different vales of D and the amplification of the f_4 factor, which accounts for the elastic deformation like a structure response under external loadings. This is an important aspect worth emphasizing is that chloride ion flux always occurs when structures support service loads; therefore, the effects of stress-strain states along the structure, including deformation and damage, must be considered in chloride penetration prediction models for more accurate assessments.

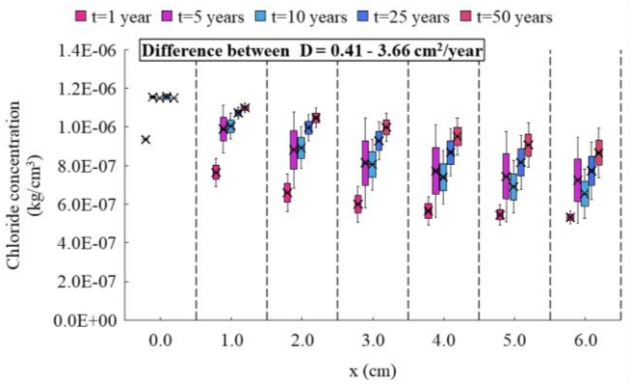
It is possible to note that relevant effects of the random D occur after a certain time (in general, t > 25.0 years). This could indicate that for large periods, the use of constant D bad estimates the scenarios in RC structures.

By Eq. (3), the cubic polynomial approximate solutions in time t, and fifth degree polynomial approximate solution in x direction are obtained. Figure 5a) shows the chloride concentration by analytical (solid lines) and numerical (dashed lines) solution for both limits of D. The approximated polynomials refer to trends similar to random 1 where the discrepancies are minimal, thus the relations in Fig. 5a) could be considered more reliable and useful for practical applications.

Figure 5b) shows the difference between both diffusivity limits for different years. The difference of the values are represented by using a box and whisker chart with a mean value indicated by "×". The upper extreme of the box chart refers to the chloride concentration obtained by D = 3.66 cm^2/year, whereas the lower extreme refers to 0.41 cm^2/year. In general, the boxes increase by increasing x-depth, however due to the randomness of the analysis this trend is not always verified.



a)



b)

Fig. 5. Chloride concentration in terms of a) polynomial trends (t = 4.0 years), and b) general variations.

Finally, as already mentioned, the analysis can be extended from 1D to 2D model with D = 3.66 cm^2/year for the period t = 1.0 – 50.0 years. The interpolation for 2D model is carried out before in one direction, x-axis, and then in other direction y-axis (or vice-versa), thus the chloride concentrations inside concrete are plotted.

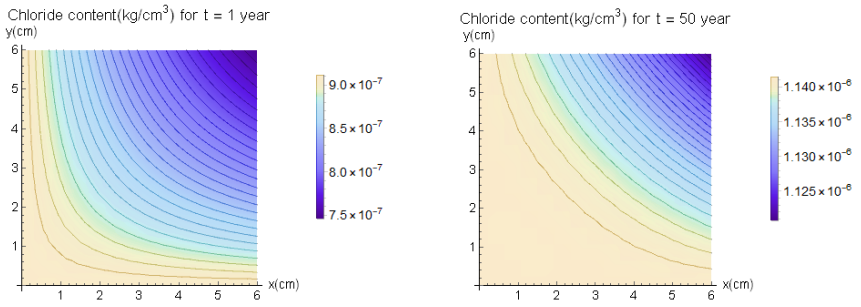


Fig. 6. 2D chloride concentrations by numerical random solutions for D = 3.66 cm^2/year at 1.0 - 50.0 years.

In analogue way for Fig. 4, for large time the effects of a random D more influence the chloride concentration as visible in Fig. 6. This is consistent to the physical real process, since the chloride concentration is a cumulative process that comes from different directions and not only from one direction are usually modelled. Actually, this is more evident in 2D model. The mean 2D/1D ratio by considering random and analytical model is about 1.25 (i.e., 1.14/0.90). This gap should quantify the poor approximation of the analytical model by using constant diffusivity in only one direction.

4 Conclusions

In this paper the chloride ions diffusion in RC members by considering non-constant multi-factorial diffusivity has been studied. For this, numerical solutions in 1D and 2D models have been developed by using explicit Runge-Kutta (RK) method to find the solutions and by Hermite polynomials (HPs) to plot them. Specific boundary conditions have been specified for this issue.

A more complete diffusivity D accounts for the w/c ratio, binding chloride, temperature, concrete age, concrete deformation, damage, and humidity. From literature, it appears that these factors are the most relevant to well quantify the diffusivity thus the chloride concentrations.

By using a non-constant random D, it is shown that the analytical solutions poor estimates the chloride concentration in RC structures for large period. In particular, the impact of the random D happens after a certain time. Due to the dynamism of the proposed model, it is possible that the chloride concentration C, at a certain depth x, decreases in the time t, whereas the total concentration C, in a RC element, increases. Also, the non-linearity of the random diffusivity D could provide low values in 1D model and high values in 2D model. These phenomena show the low reliability of the analytical solution using a constant D for predicting long scenario and instantaneous chloride concentrations.

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