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PARAMETER ESTIMATION METHODOLOGY FOR THE HALL DIFFUSION MODEL IN REINFORCED CONCRETE SAMPLES

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ABSTRACT

This article presents a methodology for fitting the parameters of the chloride-ion Hall's diffusion coefficient in re-inforced concrete samples exposed to aggressive marine environments. The methodology aims to minimize the mean square error (MSE) between experimental and simulated chloride-ion concentration profiles, based on Fick's second law coupled with Hall's empirical diffusion equation and appropriate initial and boundary value condi-tions (IBVP). This minimization problem is formulated as a nonlinear dynamic optimization problem (NDOP) and solved using the Levenberg-Marquardt algorithm, with constraints set on each parameter to ensure they fall within a specific range. The numerical solution of the IBVP, which is also part of the NDOP constraints, is achieved through a spatial finite element semi-discretization, combined with an explicit Runge-Kutta RK(4) scheme for temporal approximation at each time step. The estimated MSE for the fitted diffusion coefficient pa-rameters was on the order of 10^{-5}, and the relative error between experimental and predicted concentration values was less than 1%. The consistency and accuracy of the numerical results demonstrate that the model effectively explains the diffusion behavior of chloride ions in reinforced concrete exposed to aggressive marine conditions, with a composition like that reported by Anzola E. et al. in [6]. Furthermore, the average value of the predicted diffusion coefficient can be compared with the reference threshold value reported in the literature [4], supporting the potential of this methodology for determining the service life of this specific material con-figuration.

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RESUMEN

Este artículo presenta una metodología para el ajuste de los parámetros del coeficiente de difusión de iones cloruro según el modelo empírico de Hall en muestras de concreto reforzado expuestas a ambientes marinos agresivos. El objetivo de la metodología es minimizar el error cuadrático medio (ECM) entre los perfiles de concentración de iones cloruro obtenidos experimentalmente y aquellos simulados, utilizando la segunda ley de Fick acoplada con la ecuación empírica de difusión de Hall y condiciones iniciales y de contorno apropiadas (problema de valores iniciales y de frontera, IBVP por sus siglas en inglés). Este problema de minimización se formula como un problema de optimización dinámica no lineal (NDOP) y se resuelve mediante el algoritmo de Levenberg-Marquardt, imponiendo restricciones sobre cada parámetro para garantizar que se encuentren dentro de un rango específico. La solución numérica del IBVP, que también forma parte de las restricciones del NDOP, se logra mediante una semi-discretización espacial con elementos finitos, combinada con un esquema explícito de Runge-Kutta RK(4) para la aproximación temporal en cada paso de tiempo. El ECM estimado para los parámetros ajustados del coeficiente de difusión fue del orden de 10^{-5}, y el error relativo entre los valores de concentración experimentales y los predichos fue menor al 1%. La consistencia y precisión de los resultados numéricos demuestran que el modelo explica eficazmente el comportamiento difusivo de los iones cloruro en concreto reforzado expuesto a condiciones marinas agresivas, con una composición similar a la reportada por Anzola E. et al. en [6]. Además, el valor promedio del coeficiente de difusión predicho puede compararse con el valor umbral de referencia reportado en la literatura [4], lo que respalda el potencial de esta metodología para la determinación de la vida útil de esta configuración específica de material.

PALABRAS CLAVE: Optimización dinámica no lineal, coeficiente de difusión de Hall, muestras de hormigón armado.

1. INTRODUCTION

The "economy-durability" ratio, combined with the properties of reinforced concrete, makes it a widely used material in marine constructions today. However, the negative effect of the composition of marine environments on the structure of the concrete is still a big concern worldwide [11]. In particular, the corrosion of metal embedded into the reinforced concrete induced by chloride diffusion is one of the important issues [10, 12, 7].

Predicting the chloride transport mechanism into the concrete structure is essential to enlarging the material performance in marine environments [20]. Concrete is a porous material. Therefore, chlorides transport in concrete involves the diffusion of chloride ions into the pore solution, as well as physical and chemical interactions with the pore surfaces in the cement matrix [18].

For an effective maintenance plan in a specific marine environment, it is crucial to understand the chloride ion diffusion mechanism and the resulting chloride concentration profile within the concrete, even more so than the chemical reactions occurring at the metal surface [14]. The primary objective is to minimize ion penetration into the concrete structure and thereby extend the material's service life [24].

The analysis of actual chloride profiles in reinforced concrete requires substantial investment and long-term monitoring. This process involves testing concrete samples with specific water-cement ratios under marine environmental conditions. However, chloride diffusion is generally a slow process, influenced by the porosity and resistance of the material matrix [25, 5, 18]. Given the time-consuming nature of this approach, mathematical models and simulations offer a more efficient alternative for predicting chloride concentration profiles and the durability of reinforced concrete under similar environmental conditions [2].

The change in concentration gradient due to diffusion is typically modeled using Fick's second law, and the chloride ion diffusion coefficient D (m^2/s) is often estimated experimentally through regression analysis of concentration profiles C (in ppm) [26]. A key limitation of this approach is the assumption that the diffusion coefficient D remains constant, which contradicts experimental evidence showing that diffusional resistance is concentration dependent. In the context of porous adsorption media with nonlinear isotherms, a functional relationship between the diffusion coefficient and concentration has been established [22]. To address this, Morón et al. in [15] propose a model to estimate the durability of reinforced concrete structures in marine environments, which evaluates four nonlinear empirical equations for the diffusion coefficient:

- Langmuir's Model

$$D(C) = k_1 \left(\frac{C}{1 + k_2 C} \right); \tag{1.1}$$

- Temkin's Model

$$D(C) = k_1 \ln(k_2 C); \tag{1.2}$$

- Gilliland's Model

$$D(C) = k_1 \exp(k_2 C); \tag{1.3}$$

- Hall's Model

$$D(C) = k_1 \left(\frac{1 + k_2 C}{1 + k_3 C} \right); \tag{1.4}$$

where the k_i, $i = 1, 2, 3$, are specific rate constants fitting to the concentration profiles measured in cores extracted from reinforced concrete samples that were exposed to an aggressive marine environment. The authors noticed some important issues: the quality of the concrete and external agents have a strong influence on the chloride ion diffusion coefficient, more than the concentration rate within the concrete. However, Hall's model provided a better fit for the results in 70% of cases with lower mean squared error. On the other hand, the parameters in Hall's model match the constant coefficient D_0 with lower chloride ion concentrations, and with the highest diffusion coefficient $D = \frac{k_1 k_2}{k_3}$, when concentrations are higher. In addition, the parameters k_2 and k_3 are related to the ion's presence and mobility, respectively [15].

A 3-years experimental study by Anzola et al. [6] showed chloride concentration profiles in prismatic rein-forced concrete samples exposed to an aggressive marine environment. To simulate this response and contribute to the estimation of the service life of future civil constructions with characteristics like these reinforced concrete samples, in conditions of an aggressive marine environment, in this work a fitted version of Hall equation (1.4) based on a dynamic optimization problem of the mean square error (MSE) between the experimental and simulated concentrations is presented. Here, Fick's second law coupled with (1.4) and appropriate initial and boundary conditions are part of the constraints for the dynamic optimization problem. Furthermore, it predicts the concentrations using a numerical model based on a nonlinear finite element discretization in the spatial coordinate and the Runge-Kutta (R4) scheme for the time step advance.

The following sections present the mathematical and numerical ion diffusion model into the material porous matrix, the dynamic optimization problem with its constrainers, and the numerical results with their validation according to the experimental date reported by Anzola et al. in [6]. Finally, the last section shows concluding remarks.

2. MATERIALS AND METHODS

2.1. Mathematical model

As mentioned before, reinforced concrete samples were subjected to an aggressive marine environment, with one side of the cross-section exposed to the environment while another side was isolated. The mathematical model considers a one-dimensional diffusion of the chloride ion in the longitudinal direction ($L > 0$). If the reference coordinate system is placed on the exposed face at $x = 0$, then the isolated face will correspond to $x = L$.

The ion concentration is described in terms of a positive function $C(x, t)$ defined at all $(x, t) \in [0, L]\times[0, T]$. Therefore, the model should satisfy the following initial and boundary conditions (IBVP):

$$\frac{\partial C}{\partial t}(x,t) = \frac{\partial}{\partial x}\left(D(C(x,t))\frac{\partial C}{\partial x}(x,t)\right), \quad \forall\,(x,t) \in (0,L)\times(0,T]; \tag{2.1}$$

$$C(x,0) = 0, \quad \forall\, x \in (0,L]; \tag{2.2}$$

$$C(0,t) = C_s(t), \quad \forall\, t \in (0,T]; \tag{2.3}$$

$$\frac{\partial C}{\partial x}(L,t) = 0, \quad \forall\, t \in (0,T]. \tag{2.4}$$

Equation (2.1) is the Fick's second law, and the diffusion coefficient $D(C(x,t))$ is given by the Hall's model:

$$D(C(x,t)) = k_1\left(\frac{1 + k_2C(x,t)}{1 + k_3C(x,t)}\right). \tag{2.5}$$

Initial condition (2.2) represents the concentration of the reinforced concrete samples when exposed to the marine environment, at the instant when the experimental measurement starts ($t = 0$). The boundary condition (2.3) refers to the side expose to the environment ($x = 0$), where concentration is described by function $C_s(t)$, $\forall\, t \in (0, T]$. We assume that $C_s(0) = 0$ to ensure compatibility and continuity in initial and boundary conditions. Finally, the boundary condition (2.4) indicates that the flow of chlorides in the isolated cross-section ($x = L$) is zero.

2.2. Numerical model

The mathematical model (2.1)-(2.4) is a non-homogenous initial boundary value problem (IBVP) for the Fick's second law coupled whin Hall's diffusion coefficient D on an interval $[0, L]$, with either Dirichlet and

Neumann conditions on $x = 0$ and on $x = L$, respectability [19]. Furthermore, the relation (2.5) between the Hall's diffusion coefficient D and the concentration $C(x,t)$ is non-linear. For solution approximate of the IBVP, we propose a numerical approach by using finite element semi-discretization in the x-coordinate and a Runge-Kutta RK(4) scheme for time discretization.

2.2.1. Variational formulation

The spatial semi-discretization of the IBVP (2.1)-(2.4) by the finite element method is based on an equivalent variational formulation [3]. However, for this purpose it is convenient to homogenize the Dirichlet-type boundary condition (on $x = L$) by introducing the suitable change:

$$\bar{C}(x,t) = C(x,t) - \frac{(x-L)^2}{L^2} C_s(t) \tag{2.6}$$

Therefore, the IBVP (2.1)-(2.4) in terms of $\bar{C}$ is:

$$\frac{\partial \bar{C}}{\partial t}(x,t) = \frac{\partial}{\partial x}\left(D(\bar{C}(x,t)) \frac{\partial \bar{C}}{\partial x}(x,t) \right) + F(\bar{C}, x, t), \quad \forall\, (x,t) \in (0,L) \times (0,T]; \tag{2.7}$$

$$\bar{C}(x,0) = \bar{C}^0(x), \quad \forall\, x \in (0,L]; \tag{2.8}$$

$$\bar{C}(0,t) = 0, \quad \forall\, t \in (0,T]; \tag{2.9}$$

$$\frac{\partial \bar{C}}{\partial x}(L,t) = 0, \quad \forall\, t \in (0,T], \tag{2.10}$$

where

$$F(\bar{C}, x, t) = \left(\frac{2C_s(t)}{L^2} \right) \frac{\partial}{\partial x}\left(D(\bar{C})(x-L) \right) - \frac{(x-L)^2}{L^2} \frac{dC_s}{dt}(t) \tag{2.11}$$

and

$$\bar{C}^0(x) = \left(\frac{C_s(0)}{L^2} \right) (x-L)^2 \tag{2.12}$$

Variational formulation for (2.7)-(2.10) lead to the Proposition 2.1..

Proposition 2.1.. *Let V be the infinite-dimensional set formed by all continuous functions in the interval $[0,L]$ that vanish on the boundary $x = 0$. Then, the IBVP (2.7)-(2.10) is equivalent to the variational problem: find the function $t \mapsto \bar{C}(t) \in V$, $\forall\, t \in [0,T]$,such as:*

$$(d_t \bar{C}(t), v) + a(\bar{C}(t), v) + b(\bar{C}(t), v) = \ell(v,t); \quad \forall\, v \in V, \tag{2.13}$$

$$(\bar{C}(0), v) = (\bar{C}^0, v); \quad \forall\, v \in V, \tag{2.14}$$

where

$$(d_t\bar{C}(t),v) = \int_0^L \frac{\partial \bar{C}}{\partial t}(x,t)v(x)\,dx \tag{2.15}$$

$$a(\bar{C}(t),v) = \int_0^L D(\bar{C}(x,t))\frac{\partial \bar{C}}{\partial x}(x,t)\frac{dv}{dx}(x)\,dx \tag{2.16}$$

$$b(\bar{C}(t),v) = \left(\frac{2C_s(t)}{L^2}\right)\int_0^L D(\bar{C}(x,t))(x-L)\frac{dv}{dx}(x)\,dx \tag{2.17}$$

$$\ell(v,t) = -\frac{1}{L^2}\frac{dC_s}{dt}(t)\int_0^L (x-L)^2 v(x)\,dx \tag{2.18}$$

$$(\bar{C}^0,v) = \left(\frac{C_s(0)}{L^2}\right)\int_0^L (x-L)^2 v(x)\,dx \tag{2.19}$$

Proof. The technique employed to prove this proposition is standard in the theory and practice of the finite element method. For further details, the reader is referred to [8, 9]. □

2.2.2. Variational formulation semi-discretization

Following the methodology presented in references [19], [8] and [9], we consider a partition of the interval $[0,L]$ according to the longitudinal discretization of the samples into M pieces $I_j = [x_j, x_{j+1}]$ of length $h_j = x_{j+1} - x_j$ where $j = 1, \ldots, M$. Each sub-interval I_j is called a finite element.
If $h = \max\limits_{1\le j\le M}(h_j)$, the partition represents a mesh of finite elements I_j and nodes x_j, which we will denote by $\mathcal{T}_h$, where $h > 0$ is known as the mesh size. Now, for simplicity, we introduce the finite-dimensional vector space:

$$X_h^1 = \{v \in \mathcal{C}^0(0,L);\ \ v|_{I_j} \in \mathbb{P}_1(I_j),\ \forall\, I_j \in \mathcal{T}_h\}, \tag{2.20}$$

that is the space of globally continuous functions that are polynomials of degree 1 on the single elements ($\mathbb{P}_1(I_j)$) of the mesh $\mathcal{T}_h$. Moreover, we define

$$V_h = \{v_h \in X_h^1;\ \ v_h(0) = 0\} \tag{2.21}$$

that is, in fact, a discrete subset of V and it is called a finite-element space generated by basis functions $\{\varphi_j\}_{j=1}^{M+1}$ that link each node x_j in the mesh, such as $\varphi_j|_{I_j} \in \mathbb{P}_1(I_j)$.
The semi-discretization of (2.13)-(2.14) can be expressed in terms of the approximating functions $t \mapsto \bar{C}_h(t) \in V_h$, instead of the original $t \mapsto \bar{C}(t) \in V$, for a fixed $t \in [0,T]$, and the test functions $v_h \in V_h$ instead of the test function $v \in V$. The next proposition expresses this semi-discretization approach.

Proposition 2.2. (Semi-discrete variational problem)**.** *Let* V_h *be the finite element space defined in* (2.21)*, and assume the initial condition* $\bar{C}^0 \in V_h$*. Suppose that the boundary function* $C_s(t)$ *and its time derivative* $\dfrac{dC_s}{dt}(t)$ *are continuous on* $[0,T]$*. Then, there exists a unique function* $t \mapsto \bar{C}_h(t) \in V_h$*, for all* $t \in [0,T]$*, such that:*

$$(d_t\bar{C}_h(t),v_h) + a(\bar{C}_h(t),v_h) + b(\bar{C}_h(t),v_h) = \ell(v_h,t);\quad \forall\, v_h \in V_h, \tag{2.22}$$

$$(\bar{C}_h(0),v_h) = (\bar{C}^0,v_h);\quad \forall\, v_h \in V_h, \tag{2.23}$$

Proof. The technical aspects of this proof are also standard; see [9]. A brief outline is as follows:

i) The semi-discrete variational formulation defines a nonlinear system of ordinary differential equations, posed on the finite-dimensional space V_h, of the form

$$M\frac{d\bar{\boldsymbol{C}}}{dt}(t) + A(\bar{\boldsymbol{C}}(t))\bar{\boldsymbol{C}}(t) + \boldsymbol{b}(\bar{\boldsymbol{C}}(t)) = \boldsymbol{\ell}(t), \quad \forall\, t \in (0, T],$$

where M is the mass matrix, $\bar{\boldsymbol{C}}(t)$ is the vector of coefficients associated with $\bar{C}_h(t)$, and the terms A, $\boldsymbol{b}$ and $\boldsymbol{\ell}$ are nonlinear but can be shown to be continuously differentiable in $\bar{\boldsymbol{C}}(t)$.

ii) By standard qualitative theory of ordinary differential equations (see [17] and [16]), the existence and uniqueness of a solution to the above system are guaranteed over a short time interval (i.e., a local solution).

iii) Then, under regularity assumptions on the coefficient $D(\bar{C})$ and the boundary function $C_s(t)$, the local solution can be extended globally over the interval $(0, T]$. With this, it follows that the semi-discrete variational problem admits a unique solution $\bar{C}_h(t)$ in V_h for all $t \in [0, T]$.

□

Since $V_h = \text{gen}(\{\varphi_j\}_{j=1}^{M+1})$, then in Proposition 2 we can take

$$\bar{C}_h(t) = \sum_{j=1}^{M+1} \bar{C}_j(t)\varphi_j. \tag{2.24}$$

Furthermore, following Galerkin's method, the arbitrary test function v_h is chosen to be the same as the basis functions [23]; i.e $v_h \equiv \varphi_i$. Now, the discrete variational formulation (2.22)-(2.23) is equivalent to a nonlinear ordinary differential equations system, with initial conditions (IVP's): find $\{\bar{C}_j(t)\}_{j=1}^{M+1}$ for all fixed $t \in (0, T]$ and each $i = 1, \ldots M+1$:

$$\sum_{j=1}^{M+1} m_{ij}\frac{d\bar{C}_j}{dt}(t) + \sum_{j=1}^{M+1} a_{ij}(t)\bar{C}_j(t) + b_i(t) = \ell_i(t); \tag{2.25}$$

$$\sum_{j=1}^{M+1} m_{ij}\bar{C}_j(0) = \bar{C}_i^0, \tag{2.26}$$

where

$$m_{ij} = \int_0^L \varphi_j(x)\varphi_i(x)\,dx; \tag{2.27}$$

$$a_{ij}(t) = \int_0^L D\Big(\sum_{j=1}^{M+1} \bar{C}_j(t)\varphi_j(x)\Big)\frac{d\varphi_j}{dx}(x)\frac{d\varphi_i}{dx}(x)\,dx; \tag{2.28}$$

$$b_i(t) = \left(\frac{C_s(t)}{L^2}\right)\int_0^L D\Big(\sum_{j=1}^{M+1} \bar{C}_j(t)\varphi_j(x)\Big)(x-L)\frac{d\varphi_i}{dx}(x)\,dx; \tag{2.29}$$

$$\ell_i(t) = -\frac{1}{L^2}\frac{dC_s}{dt}(t)\int_0^L (x-L)^2\varphi_i(x)\,dx, \tag{2.30}$$

$$\bar{C}_i^0 = \left(\frac{C_s(0)}{L^2}\right)\int_0^L (x-L)^2\varphi_i(x)\,dx, \tag{2.31}$$

with

$$D\Bigg(\sum_{j=1}^{M+1}\bar{C}_j(t)\varphi_j(x)\Bigg) = \frac{k_1\left[L^2 + k_2L^2\displaystyle\sum_{j=1}^{M+1}\bar{C}_j(t)\varphi_j(x) + k_2(x-L)^2C_s(t)\right]}{L^2 + k_3L^2\displaystyle\sum_{j=1}^{M+1}\bar{C}_j(t)\varphi_j(x) + k_3(x-L)^2C_s(t)} \tag{2.32}$$

For implement the numerical approach, the IVP's (2.25)-(2.26) can be expressed in a compact vector form by introducing the unknown column vector $\bar{\boldsymbol{C}}(t) = (\bar{C}_1(t), \ldots, \bar{C}_{M+1}(t))^\top \in \mathbb{R}^{(M+1)\times 1}$ and the notations: for $i, j = 1, \ldots, M+1$

$$a_{ij}(\bar{\boldsymbol{C}}(t)) \equiv a_{ij}(t); \quad b_i(\bar{\boldsymbol{C}}(t)) \equiv b_i(t) \quad \text{and} \quad \ell_i(\bar{\boldsymbol{C}}(t)) \equiv \ell_i(t).$$

The new form of the IVP's is now expressed as: given $M = [m_{ij}] \in \mathbb{R}^{(M+1)\times(M+1)}$, $t \mapsto A(\bar{\boldsymbol{C}}(t)) = [a_{ij}(\bar{\boldsymbol{C}}(t))] \in \mathbb{R}^{(M+1)\times(M+1)}$, $t \mapsto \boldsymbol{b}(\bar{\boldsymbol{C}}(t)) = [b_i(\bar{\boldsymbol{C}}(t))] \in \mathbb{R}^{(M+1)\times 1}$, $t \mapsto \boldsymbol{\ell}(t) = [\ell_i(t)] \in \mathbb{R}^{(M+1)\times 1}$ and $\bar{\boldsymbol{C}}^0 = [\bar{C}_i^0] \in \mathbb{R}^{(M+1)\times 1}$, find $t \mapsto \bar{\boldsymbol{C}}(t)$ such as:

$$M\frac{d\bar{\boldsymbol{C}}}{dt}(t) + A(\bar{\boldsymbol{C}}(t))\bar{\boldsymbol{C}}(t) + \boldsymbol{b}(\bar{\boldsymbol{C}}(t)) = \boldsymbol{\ell}(t); \quad \forall\, t \in (0, T] \tag{2.33}$$

$$M\bar{\boldsymbol{C}}(0) = \bar{\boldsymbol{C}}^0 \tag{2.34}$$

Matrices M, $A(\bar{\boldsymbol{C}}(t))$ and vectors $\boldsymbol{b}(\bar{\boldsymbol{C}}(t))$ and $\boldsymbol{\ell}(t)$ are built using the element-by-element contribution assembly strategy on the mesh $\mathcal{T}_h$, and considering the properties for the basis functions $\{\varphi_j\}_{j=1}^{M+1}$: $\varphi_j(x_i) = \delta_{ij}$ para $1 \leq i, j \leq M+1$. Furthermore, for the nonlinear integrands involved in the definition of the terms a_{ij} and b_i, an appropriate Gauss quadrature formula is used [8].

2.3. Fitting diffusion model parameters

In this section we consider a partition of the time interval $[0, T]$ into N discrete times: $t_0, t_1, \ldots, t_{n-1}, t_n, \ldots, t_{N-1}, t_N$, coinciding with the sampling times when the experimental chloride-ion concentration was measured and such that: $t_0 < t_1 < \cdots < t_{n-1} < t_n < \cdots < t_{N-1} < t_N$. Here t_0 and t_N are the initial and final sampling times, respectively.

Now, let $C_{exp}(x_j, t_n)$ be the experimental chloride-ion concentration in the j-th cross-section x_j of a reinforced concrete sample represented by interval $[0, L]$ and in the n-th discrete time t_n. The Hall's model parameters k_1, k_2 and k_3 in (2.32) are fitted by the minimization of the mean squared error (MSE) between C_exp and the simulated concentration $C(x_j, t_n; k_1, k_2, k_3)$ from the numerical solution of the VIP's (2.33)-(2.34) in each discrete space-time point (x_j, t_n) expressed by (from expression (2.6)):

$$C(x_j, t_n; k_1, k_2, k_3) = \bar{C}(x_j, t_n; k_1, k_2, k_3) + \frac{(x_j - L)^2}{L^2}C_s(t_n).$$

Parameters k_1, k_2 and k_3 in this minimization problem vary in ranges that are physically admissible and have already been reported in the reviewed literature (see for example [1] and [2]).

The non-linear dynamic optimization problem in the fitting procedure is:

$$\min_{k_1,k_2,k_3} \quad \frac{1}{((M+1)\times N)} \sum_{n=1}^{N} \sum_{j=1}^{M+1} |C_{exp}(x_j,t_n) - C(x_j,t_n;k_1,k_2,k_3)|^2, \tag{2.35}$$

$$\text{s.t.} \quad k_\ell^L \leq k_\ell \leq k_\ell^U, \quad \ell \in \{1,2,3\}, \tag{2.36}$$

$$\text{and the model (2.33)-(2.34)}, \tag{2.37}$$

where k_ℓ^L and k_ℓ^U denote the admissible lower and upper bounds for the ℓ-th parameter k_ℓ.

The non-linear dynamic optimization problem (2.35)-(2.37) is solved numerically using the Levenberg-Marquardt approximation algorithm. The Levenberg-Marquardt algorithm was selected for solving the nonlinear dynamic optimization problem due to its robustness and efficiency in handling least-squares minimization tasks involving nonlinear models with a moderate number of parameters. In this study, the objective function corresponds to the mean square error (MSE) between simulated and experimental chloride-ion concentrations, which exhibits a smooth structure favorable for this algorithm. The Levenberg-Marquardt method effectively combines the rapid local convergence of the Gauss-Newton approach with the stability of gradient descent, offering a practical balance between speed and robustness [21]. Moreover, this algorithm has demonstrated reliable performance in related nonlinear identification problems involving physical parameter estimation, as reported in [21], where it was used to model the dynamic behavior of photovoltaic modules. These features make it particularly suitable for the parameter fitting task within the chloride diffusion model under consideration.

On the other hand, the model (2.33)-(2.34) is solved numerically using a Runge-Kutta RK(4) time discretization proposed by Larson M.G., & Bengzon F. in [13], in each discrete time t_n.

The consistency of this methodology with the sampling of experimental data has also been considered. Here, the spatial and temporal discretization follows the sub-intervals defined by the j-th depth x_j in the reinforced concrete sample, and the times t_n reported by Anzola, E. et al. in [6] during their experimental measurements.

2.3.1. Optimization algorithm for parameter fitting

The following algorithm outlines the procedure associated with the previously presented methodology for the optimal estimation of the Hall diffusion model parameters (k_1, k_2, and k_3), based on the nonlinear dynamic optimization problem (2.35)–(2.37) and its solution using the Levenberg–Marquardt (LM) algorithm.

Algorithm 1 Fitting Hall's Diffusion Parameters via Levenberg–Marquardt Algorithm

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Require: Experimental data $C_{\text{exp}}(x_j, t_n)$, initial guess $\boldsymbol{k}^{(0)} = (k_1^{(0)}, k_2^{(0)}, k_3^{(0)})$, parameter bounds $k_\ell^L$, $k_\ell^U$, convergence tolerance $\varepsilon$
Ensure: Optimal parameters $\boldsymbol{k}^* = (k_1^*, k_2^*, k_3^*)$
 1: Initialize iteration counter $m \leftarrow 0$
 2: Set $\boldsymbol{k}^{(m)} \leftarrow \boldsymbol{k}^{(0)}$, choose damping parameter $\lambda > 0$
 3: repeat
 4:     Solve the semi-discrete PDE system (2.33)–(2.34) using RK(4) for current $\boldsymbol{k}^{(m)}$
 5:     Compute model predictions $C(x_j, t_n; \boldsymbol{k}^{(m)})$
 6:     Compute residuals: $r_{j,n}^{(m)} = C_{\text{exp}}(x_j, t_n) - C(x_j, t_n; \boldsymbol{k}^{(m)})$
 7:     Form residual vector $\boldsymbol{r}^{(m)}$
 8:     Estimate Jacobian matrix $J^{(m)} = \frac{\partial \boldsymbol{r}}{\partial \boldsymbol{k}}$
 9:     Compute parameter update using:
            $$\delta\boldsymbol{k}^{(m)} = \left[(J^{(m)})^\top J^{(m)} + \lambda I\right]^{-1} (J^{(m)})^\top \boldsymbol{r}^{(m)}$$
10:     Update parameters: $\boldsymbol{k}^{(m+1)} \leftarrow \boldsymbol{k}^{(m)} + \delta\boldsymbol{k}^{(m)}$
11:     Project each $k_\ell^{(m+1)}$ to satisfy bounds $k_\ell^L \le k_\ell^{(m+1)} \le k_\ell^U$
12:     Update $\lambda$ based on error decrease (e.g., decrease if MSE improves, increase otherwise)
13:     Increment iteration counter $m \leftarrow m + 1$
14: until $\|\delta\boldsymbol{k}^{(m)}\|_2 < \varepsilon$ or maximum iterations reached
15: return $\boldsymbol{k}^* \leftarrow \boldsymbol{k}^{(m)}$
```

The LM algorithm described in Algorithm 1 aims to determine the optimal values of the Hall's model parameters k_1, k_2, and k_3 by minimizing the mean squared error (MSE) between experimental data and the numerical solution of the chloride diffusion model. Below is a step-by-step explanation of the algorithm:

- **Initialization (Lines 1–2):** The algorithm starts from an initial guess $\boldsymbol{k}^{(0)} = (k_1^{(0)}, k_2^{(0)}, k_3^{(0)})$ and a damping parameter λ. Bounds for each parameter ensure the solution remains within physically admissible ranges.
- **Numerical solution (Line 4):** For the current parameter estimate $\boldsymbol{k}^{(m)}$, the semi-discrete system (2.33)–(2.34) is solved numerically using a Runge–Kutta RK(4) scheme. This provides the approximate solution $\bar{C}(x_j, t_n)$.
- **Reconstruction of total concentration (Line 5):** The original concentration $C(x_j, t_n; \boldsymbol{k}^{(m)})$ is reconstructed using:

  $$C(x_j, t_n; \boldsymbol{k}^{(m)}) = \bar{C}(x_j, t_n; \boldsymbol{k}^{(m)}) + \frac{(x_j - L)^2}{L^2} C_s(t_n).$$

- **Residual computation (Lines 6–7):** The residuals are defined as:

  $$r_{j,n}^{(m)} = C_{\text{exp}}(x_j, t_n) - C(x_j, t_n; \boldsymbol{k}^{(m)}),$$

and are collected into a residual vector $\boldsymbol{r}^{(m)}$.

- **Jacobian estimation (Line 8):** The Jacobian matrix $J^{(m)}$ is estimated as:

$$J^{(m)} = \left[\frac{\partial \boldsymbol{r}^{(m)}}{\partial k_1}, \frac{\partial \boldsymbol{r}^{(m)}}{\partial k_2}, \frac{\partial \boldsymbol{r}^{(m)}}{\partial k_3} \right],$$

  using finite difference or analytical methods.

- **LM update (Lines 9–10):** The parameter update is computed using:

$$\delta \boldsymbol{k}^{(m)} = \left[(J^{(m)})^\top J^{(m)} + \lambda I \right]^{-1} (J^{(m)})^\top \boldsymbol{r}^{(m)};$$

  I represents the identity matrix, and the new estimate is:

$$\boldsymbol{k}^{(m+1)} = \boldsymbol{k}^{(m)} + \delta \boldsymbol{k}^{(m)}.$$

- **Parameter projection (Line 11):** The components of $\boldsymbol{k}^{(m+1)}$ are clipped to satisfy the bounds in (2.36).

- **Damping Adjustment (Line 12):** If the MSE decreases, λ is reduced; otherwise, it is increased to enhance stability.

- **Stopping criterion (Line 13):** The iteration stops when:

$$\|\delta \boldsymbol{k}^{(m)}\|_2 < \varepsilon,$$

  where $\|\cdot\|_2$ denotes the Euclidean vector norm, and $\varepsilon > 0$ is a predefined tolerance.

- **Final output (Line 14):** The optimal parameters are returned:

$$\boldsymbol{k}^* = (k_1^*, k_2^*, k_3^*).$$

This algorithm integrates a robust optimization strategy with a time-dependent nonlinear diffusion model. It ensures a physically consistent fit of the model parameters to the experimental chloride concentration data, effectively combining numerical simulation with inverse modeling.

3. RESULTS

The reinforced concrete samples and experimental conditions of reference are described as follows [6]: prismatic shape of 15×15×30 cm^3; water-cement ratio (Portland I type): 0.45; embedded A-400 steel structure (see [4]). The environmental parameters and atmospheric pollutants average of the marine environment to which these reinforced concrete samples were exposed for 3 years ($t = 1$ year; $t = 2$ years and $t = 3$ years) are: temperature of 20.45°C; relative humidity of 89.00%; precipitation of 105.00 mm; 35.88 mg/m^2×day of chlorides; 20.96 mg/m^2×day of SO$_2$ and 396.43 ppm (parts per million) of CO$_2$.

The experimental chloride concentration profiles were measured every year in each slice of 15×15×15 cm^3 extracted from the test samples at the following depths: 0.5 cm, 1cm, 2cm, 3cm, 3.5cm and 4cm. The

Depth	$t_1 = 1$	$t_2 = 2$	$t_3 = 3$
$x_1 = 0.5$	3332	7915	11625
$x_2 = 1.0$	2448	2446	3617
$x_3 = 2.0$	1088	1500	1507
$x_4 = 3.0$	272	503	663
$x_5 = 3.5$	68	374	525
$x_6 = 4.0$	0	330	242

Table 1: Experimental chloride concentration profiles from cores (C_{exp}).

concentration on the exposed face $C_s(t > 0)$ remained constant and equal to the average of the values reported each year in [6]: 3528.9 ppm. After titration of each sample, the authors report the experimental data, in parts per million (ppm), as shown in Table 1 for one of these samples that we selected.

The initial guess for the iterative fitting process using the experimental data (Table 1), were: $k_1^{(0)} = 0.1000 \times 10^{-8}$, $k_2^{(0)} = 0.3000 \times 10^{-3}$, $k_3^{(0)} = 0.4000 \times 10^{-3}$, according to Morón, O. et al. in [15]. After running the non-linear dynamical optimization problem (2.35)-(2.37), the fitted parameters were reported: $k_1^* = 0.8432 \times 10^{-7}$, $k_2^* = 0.9000 \times 10^{-3}$, $k_3^* = 1.2000 \times 10^{-3}$, for a fit accuracy that yields the MSE$= 5.3160 \times 10^{-5}$.

The percentage relative error in the induced Euclidean matrix norm

$$\left(\frac{||C_{exp} - C||_2}{||C_{exp}||_2}\right) \times 100,$$

was 0.220%, where C_{exp} and C were the matrix of concentrations extracted from Table 1 and Table 2 respectively. This result suggested that the IBVP (2.7)-(2.10) can predict the concentration profile for the reinforced concrete samples and the reference experimental conditions.

Depth	$t_1 = 1$	$t_2 = 2$	$t_3 = 3$
$x_1 = 0.5$	3332	7916	11627
$x_2 = 1.0$	2448	2444	3611
$x_3 = 2.0$	1088	1497	1507
$x_4 = 3.0$	272	505	663
$x_5 = 3.5$	68	378	550
$x_6 = 4.0$	0	343	261

Table 2: Estimated chloride concentration profiles from cores (C).

The estimated values of the diffusion coefficient in a sample are reported in Table 3. The average value of the diffusion coefficient ($0.73614\times10^{-7}\text{cm}^2/\text{s}$) is above the reference threshold value ($0.50000\times10^{-9}\text{cm}^2/\text{s}$) reported in [4]. This result suggests that the service life of any structure with similar composition to the sample and subjected to the same marine environment conditions reported by Anzola, E. et al. in [6], could be even shorter than that expected for a 3cm thick cement lining [1].

Depth	$t_1 = 1$	$t_2 = 2$	$t_3 = 3$
$x_1 = 0.5$	0.6746×10^{-7}	0.6525×10^{-7}	0.6465×10^{-7}
$x_2 = 1.0$	0.6859×10^{-7}	0.6860×10^{-7}	0.6719×10^{-7}
$x_3 = 2.0$	0.7238×10^{-7}	0.7077×10^{-7}	0.7075×10^{-7}
$x_4 = 3.0$	0.7913×10^{-7}	0.7639×10^{-7}	0.7498×10^{-7}
$x_5 = 3.5$	0.8273×10^{-7}	0.7779×10^{-7}	0.7617×10^{-7}
$x_6 = 4.0$	0.8432×10^{-7}	0.7834×10^{-7}	0.7958×10^{-7}

Table 3: Estimated values of the diffusion coefficient ($D(C)$).

4. CONCLUSIONS

This article presents a methodology to fit the specific speeds k_1, k_2 and k_3 for the chloride-ion Hall's diffusion coefficient in reinforced concrete samples exposed to aggressive marine conditions, using a non-linear dynamic optimization problem (NDOP) that minimizes the mean square error (MSE) between the experimental concentration values reported in the literature, and the simulated chloride concentration by the one dimensional Fick's second law coupled with the Hall's empirical equation, initial and boundary value conditions (IBVP). The methodology proposed a spatial and time discretization for the IBVP, using a finite element and Runge-Kutta RK(4) approaches respectively, to evaluate concentrations in reinforced concrete samples exposed to three years of aggressive marine environment. With the finite element semi-discretization, the IBVP result in a system of initial value problems (IVP's) for concentrations at each depth during exposure time to the marine environment. The IVP's and the range values for the three specific velocities of Hall's empirical equation were the constraints for the NDOP. Next, the Levenberg-Marquardt algorithm led to accurately solve the NDOP. Regarding the precision of the methodology, the relative percentage error between the experimental and estimated concentrations was less than 1%, and the order of the MSE for the fitted parameters was 10^{-5}, suggesting that the proposed model and the estimating methodology could accurately predict the ion-concentration profile and the service life of any civil construction structure with similar composition and subjected to aggressive marine conditions reported in [6].

While the results demonstrate the accuracy and robustness of the proposed methodology, some limitations should be acknowledged. These include the assumption of homogeneous material properties, the restriction to diffusion-only mechanisms, and the absence of uncertainty quantification or validation under diverse environmental conditions. However, these limitations open opportunities for future research to extend the model with coupled multi-physics phenomena, incorporate stochastic analysis, and explore broader datasets to enhance generalizability and predictive power.

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