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Sensitivity analysis of chloride ingress models: Case of concretes immersed in seawater

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HIGHLIGHTS

- A reliability sensitivity analysis of chloride ingress models is performed.
- A framework is proposed to calculate a reliability service life for RC structures.
- The concrete cover thickness and the critical chloride content play a crucial role.
- To a lesser extent, the effective chloride diffusion coefficient is influential.
- The *Freundlich* description of chloride binding is difficult to use.

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ABSTRACT

Reinforced concrete structures exposed to a marine environment deteriorate as a result of chloride-induced corrosion of the steel rebars. A wide variety of models to predict chloride ingress in water-saturated concretes have already been developed to understand and predict the underlying transport processes. The majority of these models focus on the initiation period of chloride-induced corrosion in order to predict the service life of reinforced concrete structures. They require information on the concrete properties, the concrete cover thickness, the definition of corrosion initiation, etc. These models combine well-known mechanisms, *i.e.* diffusion of relevant ions, electrical interactions between ions, and interactions between these ions and the solid matrix. As the mechanisms to consider are well identified, the objective here is to perform a probabilistic analysis of some common models. A general framework is proposed to calculate a reliability service life for reinforced concrete structures under chloride attack in case of continuous immersion in seawater. Then a sensitivity analysis is performed in terms of the most relevant mechanisms and influencing input data. The results point out the crucial role of the concrete cover thickness, the critical chloride content and, to a lesser extent, the effective chloride diffusion coefficient. The difficulty to use the *Freundlich* isotherm for chloride binding is highlighted; it seems to be due to the non-linearity of the description which is still difficult to control.

1. Introduction

Nowadays, designers of reinforced concrete (RC) structures have to deal with service life issues related to degradations resulting from mechanical, chemical and environmental actions, as well as more general sustainability issues (reduction of the carbon footprint, limitation of the depletion of natural resources, etc.). To achieve this multi-criteria objective, the common approach [1,2] is based on requirements about mix-design parameters, thickness of concrete cover, etc., and thus does not provide an adequate guide for designers to develop innovative, environment-friendly and sustainable solutions. Considering environmental attacks, more flexible approaches based on performances to be achieved in terms of durability indicators (DIs) have been developed [3–5]. The authors consider predictive durability models consistent with these approaches, *i.e.* they use DIs as input data and they have a clear physical and chemical basis.

This present study deals in particular with the issue of chloride-induced corrosion [6] of the embedded steel rebars. This degradation mechanism can lead to a shortening of Service Life (SL) of RC

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structures (exposed to seawater or deicing salts). The simplest and most conservative approach to determine the SL of RC structures is to consider only the initiation period of steel corrosion. For this purpose, predictive models [7–14] take account of microstructure, transport (gas, water, ions) and chemical properties of concrete.

In this paper, only fully water-saturated concretes are considered, *i.e.* chloride ingress is limited to a coupled diffusion-binding process. This situation represents a theoretical case since major problems of chloride-induced corrosion are observed for RC structures subjected to wetting–drying cycles (tidal zone). Nevertheless, the assumption of chloride transport through fully water-saturated materials has shown its relevance in many cases (at least for high performance concretes). Furthermore, this approach has the advantage of simplicity given the limited number of involved input data.

To increase the relevance of the prediction for practice, durability models can be coupled with reliability tools [15–23]. In this way, they can integrate the uncertainties of measurements [24], the variability of cementitious materials properties and quality of execution (*e.g.* concrete cover thickness). The present study is carried out with this framework in mind.

The main objective of this paper is to perform a sensitivity analysis of predictive tools in terms of the most relevant mechanisms and influencing input data (choices of correlation, mean value and variability). This could help to define an effective strategy for the assessment of input data for durability models.

The paper is structured as follows. Firstly, chloride ingress models are presented. Different levels of refinement are proposed: diffusion of chloride ions only or multi-diffusion of major ions present in seawater and pore water, adsorption phenomena of ions on the solid matrix, buffering role of portlandite ($Ca(OH)_2$), etc. Four chloride ingress models are selected based on their simplicity and their acceptable computation time even if coupled with a probabilistic approach. Secondly, reliability approaches are introduced and the different tools used for sensitivity analysis are described in detail. Thereafter, a large range of cementitious materials are studied and the statistical distribution for each input data is presented. A methodology for a probabilistic SL prediction of RC structures immersed in seawater is provided. A comparative study of these four chloride ingress models is performed. Sensitivity analysis is then carried out, and the impacts of the mean and the standard deviation for each input data, as well as the correlation coefficients, are quantified.

2. Service life prediction models

2.1. From chloride ingress models...

This paper focuses on one-dimensional and engineering-friendly models predicting chloride ingress within water-saturated cementitious materials. Four mathematical models have been chosen from those already discussed in a previous paper [25]: Erf, MI1_Fre (Mono-ionic model + *Freundlich* isotherm), MS5_Fre (Multispecies model involving 5 ions + *Freundlich* isotherm) and MS8_K_act (Multispecies model involving 8 ions + *Kari* isotherms + equilibrium of the precipitation-dissolution reaction of $Ca(OH)_2$). Thanks to models which mostly use intrinsic input data and to their general level of refinement, chloride ingress can be predicted for any type of cementitious material, from the ordinary to the high performance material, with or without supplementary cementitious materials (SCMs) [12,26–28]. Table 1 provides an overview of the key features of each model.

At the most eight dissolved salts in seawater ions are considered: chloride (Cl^-), sodium (Na^+), potassium (K^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), sulfate (SO_4^{2-}), hydroxyl (OH^-) and hydrogen (H^+). These ions represent correspond to the principal ionic species present in seawater and, as well as in the concrete interstitial solution.

These four models differ in terms of description of transport: two of them consider only one single ion, *i.e.* chlorides (Erf and MI1_Fre), whereas the other two are multi-species (MS5_Fre and MS8_K_act). Single ion models are based on the assumption that chloride ingress is only controlled by diffusion (Fick's law) while multi-species models consider the diffusion of all considered ionic species as well as the electrical interactions between them. The simplified Nernst–Planck equation can model this coupled movement of ions:

$$J_i = -D_i\left[\frac{\partial c_i}{\partial x} + \frac{c_i z_i F}{RT}\frac{\partial \psi}{\partial x}\right] \quad (1)$$

where J_i, D_i, c_i and z_i are the molar flux (mol/m^2/s), the effective diffusion coefficient (m^2/s), the concentration (mol/m^3), the valence number (−) associated with each ion i, respectively. ψ is the local electrical potential (V) which arises in order to maintain electroneutrality in the pore solution. F is the Faraday constant (9.649×10^{-4} C/mol), R the ideal gas constant (8.314 J/mol/K), T the absolute temperature (K), and x the depth (m). In order to apply the Nernst–Planck equation, for all ions the effective diffusion coefficients are assumed to be proportional to each other [27,28]:

$$\frac{D_i}{D_i^0} = \frac{D_{Cl^-}}{D_{Cl^-}^0} = \phi\tau \quad (2)$$

where τ and ϕ are the tortuosity (−) and the porosity (−) of the cementitious materials, respectively. D_i^0 is the intrinsic diffusion coefficient in water related to ion i. Using Eq. (2), all the effective diffusion coefficients can be assessed from the knowledge of D_{Cl^-}.

The binding of ions onto the solid cementitious matrix is considered. This phenomenon is taken at equilibrium [14,29], thus all the relations are based on an explicit physically-based formula between free and bound ions. The adopted description relies on previously proposed theories of physical adsorption onto solid surfaces (mainly onto calcium silicate hydrates *C-S-H*). Three levels of refinement are developed (see Table 1): a linear function (model Erf), the *Freundlich* isotherm (MI1_Fre and MS5_Fre) and a

Table 1
Overview of studied physico-chemical models. s_{Cl} and c_{Cl^-} are the bound content and the free concentration of chloride ions.

Models	Species								Chloride binding isotherms	Buffer role of $Ca(OH)_2$
	Cl^-	Na^+	K^+	OH^-	H^+	Ca^{2+}	Mg^{2+}	SO_4^{2-}		
Erf	✓								Linear[a]: $s_{Cl} = Kc_{Cl^-}$	
MI1_Fre	✓								*Freundlich*[b]: $s_{Cl} = \mu c_{Cl^-}^{\gamma}$	
MS5_Fre	✓	✓	✓	✓	✓				*Freundlich*[b]: $s_{Cl} = \mu c_{Cl^-}^{\gamma}$	
MS8_K_act	✓	✓	✓	✓	✓	✓	✓	✓	*Kari*[c]	✓

[a] The linear isotherm is a one-parameter function (K).
[b] The *Freundlich* isotherm is a two parameter isotherm (μ and γ).
[c] More details available in Appendix A and in Kari et al. [10]. Only one parameter C_{ads} has to be assessed.