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

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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.

Keywords: Chloride, Concrete, Durability, Modeling, Reliability, Sensitivity analysis

Highlights

- A reliability sensitivity analysis of chloride ingress models is performed.
- A framework is proposed to calculate a reliability service life for RC structures.

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- 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.

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 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, 25–28]. Table 1 provides an overview of the key features of each model.

[Table 1 about here.]

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/m²/s), the effective diffusion coefficient (m²/s), the concentration (mol/m³), 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]:

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

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 competitive multi-species adsorption named *Kari* model (MS8_K_act), described in more detail in Appendix A and in Kari *et al.* [10]. These CBIs implicitly consider chemical binding (see methods of assessment in Section 4). Indeed, as their parameters are generally determined using inverse analysis of measured chloride profiles (total content and free concentration of ions Cl^-), the authors consider that both chemical and physical binding are reflected in the fitted parameters. The chosen formulas are not able to take account for aging and/or kinetic effects. Firstly, the authors are indeed not convinced that the descriptions of aging and kinetic effects available in the literature are enough consolidated. Since those descriptions are mostly empirical, their introduction in the present approach would have led to inconsistencies with physically-based relationships which are preferred. Secondly, the determination of the statistical distribution for the parameters representing these phenomena would have been difficult. Nevertheless, it is reasonable to consider that the variability which is introduced for the binding parameters encompasses those aging and/or kinetics phenomena.

The *pH*-buffering role of portlandite $\text{Ca}(\text{OH})_2$ is only introduced in case of the model MS8_K_act, assuming that the content of $\text{Ca}(\text{OH})_2$ is high enough to ensure its equilibrium with the pore solution anytime and anywhere. It leads to the following relationship:

$$\text{Ca}(\text{OH})_2 \Leftrightarrow \text{Ca}^{2+} + 2 \text{OH}^- \quad K_p = c_{\text{Ca}^{2+}} c_{\text{OH}^-}^2 \quad (3)$$

where $c_{\text{Ca}^{2+}}$ and c_{OH^-} are the free concentration (mol/m^3) of calcium and hydroxyl ions, respectively. K_p is the equilibrium constant of the dissolution-precipitation reaction of portlandite which depends on the ambient temperature.

This set of equations is complemented by molar conservative equations. For each ionic species, a balance equation is written:

$$\frac{\partial n_i}{\partial t} = -\vec{\nabla} \cdot \vec{J}_i \quad (4)$$

where t is the time (s) and n_i is the molar content of the ionic species i (mol/m^3 of concrete).

For the three models MI1_Fre, MS5_Fre and MS8_K_act, the set of equations (transport and binding) is solved by a finite-element code named *Bil* implemented in C language (<http://perso.lcpc.fr/dangla.patrick/bil/index.html>).

For the Erf model, an analytical formula is available:

$$c_{\text{Cl}^-} = c_{\text{Cl}^-}^0 + (c_{\text{Cl}^-}^{\text{ext}} - c_{\text{Cl}^-}^0) \left(1 - \text{erf} \left(\frac{x}{2 \sqrt{\frac{D_{\text{Cl}^-}}{\phi + K} t}} \right) \right) \quad (5)$$

where $c_{\text{Cl}^-}^0$ and $c_{\text{Cl}^-}^{\text{ext}}$ are the initial and boundary free chloride concentration (mol/m^3), respectively, erf is the error function.

2.2. . . . towards service life prediction

In this paper, SL prediction of RC structures corresponds to the initiation period of chloride-induced corrosion, *i.e.* the time required for the depassivation of the first layer of steel bars. Numerous parameters can influence the depassivation [30, 31]: steel surface condition, binder properties, characteristics of the concrete/steel interface [32] and environmental factors.

Hausmann [33] introduced the notion of a critical chloride content required for the depassivation of steel rebars. The DuraCrete project [23] mentioned that the critical chloride content is defined as “the amount at which a depassivation of the steel surface and iron dissolution begins, irrespective of whether it leads to visible corrosion damage on the concrete surface”. This definition is chosen here for its simplicity. As mentioned by Angst *et al.* [30], the critical chloride content can be expressed in different ways: a total chloride content, a free chloride concentration or a ratio between the free chloride and hydroxyl concentrations $\frac{c_{\text{Cl}^-}}{c_{\text{OH}^-}}$. Glass and Buenfeld [31] discussed the relevance of a threshold level based on a free chloride concentration by pointing out that bound chlorides present a corrosion risk and that the resistance of concrete against chloride is not only related to the presence of hydroxyl ions but also to many other species. Moreover, it remains difficult to accurately measure free chloride and pH within concrete. In view of the critics regarding the involvement of free chloride in the definition of the threshold level of chloride-induced corrosion, the authors have chosen the expression of total chloride content n_{th} (subscript *th* refers to threshold), besides as used many times in the literature [23, 30, 31, 34–39].

Therefore, the critical depth x_{th} is defined as the depth with respect to the exposed concrete surface at which n_{th} is reached. This depth is compared to the concrete cover thickness e to assess the SL.

3. Reliability approaches

3.1. Principles of the reliability approaches

Reliability approaches aim to determine the time-dependent failure probability $P_f(t)$ as a function of the model input data which are considered as random variables. Lemaire *et al.* [40] define the concepts used in the present research:

- A random vector $\vec{X}$ among input data of the models. According to the choice of model, $\vec{X}$ corresponds to:

$$\begin{aligned}\vec{X}_{Erf} &= [e \ n_{th} \ \phi \ D_{Cl^-} \ K] \\ \vec{X}_{M11_Fre} &= [e \ n_{th} \ \phi \ D_{Cl^-} \ \mu \ \gamma] \\ \vec{X}_{MS5_Fre} &= [e \ n_{th} \ \phi \ D_{Cl^-} \ \mu \ \gamma \ c_{Na^+}^0 \ c_{K^+}^0] \\ \vec{X}_{MS8_K_act} &= [e \ n_{th} \ \phi \ D_{Cl^-} \ C_{ads} \ c_{Na^+}^0 \ c_{K^+}^0 \ c_{OH^-}^0]\end{aligned}\tag{6}$$

where ϕ and D_{Cl^-} are the porosity (-) and the effective chloride diffusion coefficient (m^2/s), respectively. K , (μ, γ) or C_{ads} are the parameters of CBIs. $c_{Na^+}^0$, $c_{K^+}^0$ and $c_{OH^-}^0$ are the initial concentrations of sodium, potassium and hydroxyl ions in the pore solution, respectively. Probability distribution (type, mean value and standard deviation) and linear correlation coefficients are necessary.

- A failure scenario defined by a limit state function G :

$$G(\vec{X}, t) = e - x_{th}(\vec{X}, t)\tag{7}$$

This function G defines three states: if $x_{th} < e$, it represents the safety domain; if $x_{th} = e$, it equals the limit state and if $x_{th} > e$, it represents the failure domain.

- The failure probability is defined as:

$$P_f(t) = P(G(\vec{X}, t) \leq 0) = \int_{G(\vec{X}, t) \leq 0} f_X(\vec{x}) d\vec{x}\tag{8}$$

where f_X is the joint probability density function of the random vector $\vec{X}$.

Direct calculation of $P_f(t)$ presents many difficulties. Firstly, the failure domain $G(\vec{X}, t) \leq 0$ is not explicitly known for three of the four studied chloride ingress models (except for the model Erf) since the limit state function G is calculated using a finite-volume code. Secondly, for correlated random variables, the joint probability density function f_X cannot be determined using the probability density functions f_{X_i} of each input data X_i and the correlation coefficients between the input data.

In this paper, different calculation techniques [40] are used to assess P_f by means of numerical tools:

- *First Order Reliability Method (FORM)*: The calculations are performed in the standardized Gaussian space, *i.e.* the physical $\vec{X}$ is converted to a vector $\vec{U}$ of centered, standard and uncorrelated Gaussian variables using the Nataf transformation [40]. FORM solves the optimization problem of the distance β (hereafter named the reliability index) from the origin (mean value point in the physical space) to the limit-state surface. The design point P^* belongs to the limit-state surface such as $\beta = |OP^*|$. In this paper, only positive values for β are considered, which means that the mean value point belongs to the safety domain. An approximated value of P_f is thus deduced from β :

$$P_f \simeq \Phi(-\beta)\tag{9}$$

where Φ is the cumulative distribution function of the centered and reduced normal law. This leads to approximate the limit state surface by the hyperplane tangent to the limit state surface at the point P^* .

- *First Order Reliability Method coupled with a Response Surface Method (FORM-RSM)* [41, 42]: The limit state function $G(\vec{X}, t)$ is approximated by a polynomial function $\bar{G}$ of degree two without crossed terms. Coefficients of $\bar{G}$ are determined to minimize the approximation error around the design point P^* . They are assessed using least square minimizations for a number of appropriate vectors $\vec{X}$. In this paper, as proposed by Bucher [43], these vectors are chosen according to a “star” experimental design.
- *Importance Sampling Monte Carlo simulations (MCIS)*: This method is used in order to validate the two previous simplified reliability approaches, FORM and FORM-RSM. This is based on a sampling concentrated around the design point P^* . In this paper, 10 000 simulations were performed. In comparison with crude Monte Carlo simulations, MCIS is more efficient and limits the number of drawings. Nevertheless, if the design point P^* determined by the First Order Reliability Method (FORM) is not correct, the results obtained by Monte Carlo simulations performed around this point do not allow to fairly evaluate the failure probability P_f . In addition to the P_f value, MCIS provide an estimation of the variability of this value. If this is too large, 10 000 supplementary simulations are performed until obtaining a satisfactory variability. The accuracy of this method can be estimated by the P_f due to the calculation method.

Each of these methods is independently applied for each time of calculation in order to express reliability information according to time. This approach is satisfactory [44] since the failure function G continuously decreases over time and the random vector $\vec{X}$ remains time-independent (no aging effect or kinetics are taken into account).

The reliability calculations are solved using two toolboxes ReliabTbx [45] (FORM-RSM calculations) and FERUM [46] (MCIS and FORM calculations) implemented in MATLAB® language environment.

In the following the authors will not reason in terms of failure probability P_f but in terms of reliability index β by considering its evolution as a function of the time. On the whole, they will use the expression “ β –” to address results relative to the reliability index (*e.g.* beta-curves, beta-value, etc.).

The final objective is to calculate a reliability service life (SL), which means the identification of a threshold value for β . It corresponds to the criterion for the end of service life (β_{lim}). β_{lim} must be chosen independent of the material and structural parameters, as well as of the boundary conditions. Previous studies in the literature [16, 20, 45, 47, 48] consider a time-independent value. In contrast, the authors have adopted a function of time in agreement with the annex C of EN 1990 [49]. Thus, β_{lim}^τ is determined at time τ using the following relation:

$$\Phi(\beta_{lim}^\tau) = [\Phi(1.5)]^{\frac{\tau}{50}} \quad (10)$$

In a systematic way, the reliability SL T_{SL} is defined as the time when $\beta(T_{SL}) = \beta_{lim}^{T_{SL}}$. Using Eq. (10), β_{lim} is equal to 1.5, 1.304 and 1.024 (corresponding to failure prob-

abilities 7, 10 and 16 %, respectively) at 50, 100 and 120 years, respectively . In comparison, the previous studies performed by Deby *et al.* [16] and Muigay *et al.* [20] are consistent with this approach since they consider $\beta_{lim} = 1.5$ for a targeted service life of 50 years.

3.2. Sensitivity analysis

Previously different sensitivity analyses [22, 45, 50–54] have been previously performed on predictive durability models. Nevertheless, in case of chloride ingress models, some limitations are observed: the variability of input data is not considered, no comparison of models has been performed and a limited number of cementitious materials have been tested.

In this paper, a sensitivity analysis is carried out in the framework of the reliability approach, in order to improve our comprehension of the studied models, the major mechanisms and the significance of each input data. This is accomplished at the reliability SL T_{SL} and based on two sensitivity indicators.

Firstly, the direction cosine α_i represents the global influence of the random variable U_i over the limit-state, and thus the response of the reliability model:

$$\alpha_i = - \frac{\partial \beta(T_{SL})}{\partial u_i} \bigg|_{\vec{U}^*} \quad (11)$$

where u_i and $\vec{U}^*$ are the realization of U_i and the vector of the design point coordinates in the standardized Gaussian space, respectively. In practice, the direction cosine informs on the global influence of the associated input data on the reliability calculation, without making a distinction between its mean value and its standard deviation. By definition, α_i checks the following equality : $\sum \alpha_i^2 = 1$. Consequently, the interpretation of results is simplified using α_i^2 due to the normalization of the contribution of each individual input data.

Secondly, to achieve a more comprehensive approach, the influence of the values for the mean value and standard deviation can be studied separately using the elasticity coefficients. The elasticity ε_{p_i} with respect to the reliability parameter p_i of the random variable X_i is defined as:

$$\varepsilon_{p_i} = \frac{p_i}{\beta(T_{SL})} \frac{\partial \beta(T_{SL})}{\partial p_i} \bigg|_{U^*} \quad (12)$$

Regarding the mean value, if the elasticity ε_{m_i} of variable X_i is close to zero, this signifies that a variation of the mean value does not influence the reliability result, and thus an approximated value can be chosen. Thus, the analysis of ε_{m_i} responds quantitatively to the need to limit expensive experimental tests by pointing out input data for which only the order of magnitude is necessary. In contrast, a high value for ε_{m_i} implies that the associated mechanism related to the variable X_i plays a significant role in durability prediction.

The elasticity ε_{σ_i} with respect to the standard deviation of X_i can be interpreted as follows. If ε_{σ_i} is close to zero, the variable X_i can be considered as deterministic compared to the other variables. In contrast, if its value is high, it is necessary to limit the scatter of the associated variable X_i in order to achieve the expected long-term durability performance.

4. Studied materials

Concretes and mortars [55–58] ranging from low-grade to high-performance materials, and with or without supplementary cementitious materials, are studied (see Table 2).

[Table 2 about here.]

All materials have already been characterized from the point of view of the microstructure, transport and chemical properties. The type of the probabilistic distribution (including deterministic input data), mean value, and the coefficient of variation are presented in Table 2 and explained in the following.

For the concrete cover thickness, the critical content of chloride, the porosity and the effective chloride diffusion coefficient, the authors have selected probabilistic distributions previously proposed in the literature [16, 23, 37, 59]. Due to a lack of literature data, for the parameters μ , K and C_{ads} of the *Freundlich*, linear and *Kari* isotherms, respectively, as well as for the initial concentrations of alkali (K^+ and Na^+) and hydroxyl ions, a log-normal distribution with a coefficient of variation equal to 20 % is systematically chosen. As the parameter γ of the *Freundlich* isotherm is defined between 0 and 1, a normal distribution with a coefficient of variation equal to 20 % and truncated in the range [0 1] is used. Other initial ion concentrations (Cl^- , SO_4^{2-} , Mg^{2+} , Ca^{2+} and H^+) are considered deterministic to simplify the calculations. Moreover, ion concentrations in seawater (*i.e.* the boundary conditions) are chosen deterministic since the seawater in contact with the concrete specimens can be seen as an infinite reservoir with constant chemical composition.

The mean or deterministic values of the input data are presented in Table 2. The porosity ϕ is determined by hydrostatic weighing according to the French Standard NF P18-459 and the effective chloride diffusion coefficient D_{Cl^-} is calibrated by inverse analysis carried out on total chloride contents (tcc) profiles [25]. For all materials (except concretes M75SF and M120SF), these tcc profiles are the results of a diffusion test performed in the laboratory on water-saturated samples [26, 28, 55, 57, 58]. In case of the two high performance concretes M75SF and M120SF, they are assessed on concrete specimens placed in a tidal zone [56]. The *Freundlich* parameters (see Table 2) are calibrated for the concretes M25, BO and M30FA on experimental tcc and free chloride concentration (fcc) profiles [26] (note that the difference between tcc and fcc profiles enables to assess the binding). In case of the other studied materials, the *Freundlich* parameters are only assessed by numerical inverse analysis of experimental tcc profiles [25] (due to a lack of more complete experimental data). For the linear and *Kari* isotherms, the mean values of K and C_{ads} are calibrated using a least-square method and ensuring that the obtained CBI is the closest as possible to the *Freundlich* isotherm constructed using the mean values of μ and γ . The aim is to keep a consistent description between the studied CBI models. Finally, boundary and initial conditions have to be specified. Ion concentrations for a seawater with a salinity equal to 35 g/L [60] are chosen as boundary conditions. For the initial concentration of the pore solution, experimental values previously published in the literature are used [61, 62].

The threshold total chloride content n_{th} involves numerous influencing parameters which lead to a high random nature. Values proposed by Polder [37] are chosen: a

log-normal distribution with a mean value equal to 0.5 % of mass of binder and a high coefficient of variation equal to 44 %. This choice is more conservative than the distributions proposed in the DuraCrete project [23] and the fib model code [39].

According to EN 1992-1-1 [1], it is common to prescribe a concrete cover thickness of 0.05 m. For comparison purpose this value is selected whatever the studied material. A classical statistical distribution is used for the concrete cover depth e , *i.e.* a log-normal law with a coefficient of variation equal to 20% [16, 23]. For a mean value of 0.05 m, this corresponds to a standard deviation of 0.01 m.

5. Results

In this section, the vector $\vec{X}$ of independent random variables as defined in Eq. (6) is considered. The correlation effects between ϕ , D_{Cl^-} and CBI parameters will be investigated in Section 5.4.

5.1. Validation of the probabilistic approach

Probabilistic calculations need to be verified. The models used in the present paper are classified in the following ascending order of approximation: MCIS, FORM and FORM-RSM. Thus, as soon as the MCIS model is verified, it will be used to check the two other models.

For each determined failure probability P_f as calculated by MCIS, an estimation of its coefficient of variation (c_v) is calculated as provided by Lemaire [40]. Whatever the considered models, the studied materials or the calculation time, it has been verified that c_v remains less than 3 % (for 10000 simulations). This confirms the relevance of the calculations provided by MCIS.

β -values determined by FORM and FORM-RSM are checked using MCIS results and Eq. (7) (to convert P_f into β). For concretes M75SF, M120SF and Mo2, the three calculation methods, MCIS, FORM and FORM-RSM are compared in Fig. 1 which shows a qualitative consistency with each other.

[Figure 1 about here.]

The coefficient of determination R^2 [63] can be used to assess quantitatively the accuracy of approximated β -curves (FORM or FORM-RSM) with respect to MCIS. If the value of R^2 is close to 1, an approximated β -curve is satisfactory. In case of unsatisfactory results using FORM-RSM ($R^2 < 0.98$), calculations of the reliability index using FORM are considered. This strategy enables to limit the computation time.

5.2. Service life prediction

Fig. 2 illustrates β -curves for M75SF, M120SF and Mo2.

[Figure 2 about here.]

The four chloride ingress models, Erf, MI1_Fre, MS5_Fre and MS8_K_act are compared. β_{lim} according to EN 1990 [49] is illustrated in black dotted lines in order to determine the reliability SL (see method described in Section 3.1). The determined β -curves are clearly different according to the considered chloride ingress model.

A first point of explanation relies on the number of probabilized input data. Indeed, the addition of input data as random variables increases the level of uncertainty and leads to a logical reduction in the calculated β -values. An example can perfectly illustrate this effect. Let's consider the models Erf and MI1_Fre which differ in terms of CBI but are similar regarding the description of ion transport. The *Freundlich* isotherm (used in model MI1_Fre) can transform into a linear one (thus corresponding to the model Erf) if the value of parameter γ is close to 1 (see concretes M75SF and M120SF). Therefore for the same material, predicted tcc profiles are similar. Nevertheless, a minimal difference exists between the β -curves. Since the model MI1_Fre considers two variables for the description of the CBI instead of one for Erf, MI1_Fre leads to lower β -values.

Moreover, discrepancies can be explained by physical and chemical considerations. Models MI1_Fre and MS5_Fre adopt the same CBI (*Freundlich* isotherm) but differ in terms of transport description. A multi-species transport (MS5_Fre) modeling means a concerted movement of ions, *i.e.* ions with a high diffusion coefficient (OH^- and H^+) are slowed down; in contrast, transport of ions with a low diffusion coefficient (Na^+ , K^+ and Cl^-) are accelerated. Thus, chloride ingress is accelerated by using model MS5_Fre in comparison with model MI1_Fre [14] and β -values for the multi-species model are reduced in comparison with the mono-ionic model.

The interpretation of results obtained with model MS8_K_act remains tricky since it differs from other models both in CBI and transport descriptions. The resulting concerted movement of the main eight ions dissolved in seawater leads to chloride diffusion similar to the case of single ion diffusion. But, as detailed by Pradelle *et al.* [25], the competitive ion adsorption on the solid matrix corresponding to model MS8_K_act leads to an unusual shape of the CBI. For high fcc the content of bound chloride ions falls drastically illustrating a severe competitive adsorption between ions. This has a direct impact on the shape of the simulated tcc profiles (see the presence of a bell shape in the vicinity of the surface for instance [25]).

Considering the methodology described in Section 3.1, the reliability SL T_{SL} is assessed. Table 3 resumes the results obtained for the different studied models and materials.

[Table 3 about here.]

Furthermore, the deterministic SL using the mean value of the vector $\vec{X}$ (*i.e.* SL corresponds to $\beta = 0$) and the expected SL according to the performance-based approach (Perf.) are reported. The performance-based approach used by Baroghel *et al.* [64] to assess the SL relies on durability performances to be achieved in terms of durability indicators (DIs) which can be easily assessed in laboratory by means of direct measurements. Regarding chloride ingress, Baroghel *et al.* consider the porosity and the apparent diffusion coefficient as DIs (see Table 2). The choice of an apparent diffusion coefficient is justified by the facility to measure it with respect to the effective diffusion coefficient. The advantage of the apparent diffusion coefficient is also its capacity to encompass both transport phenomena and binding effects.

Deterministic SL values based on mean values are logically higher than those obtained with probabilistic calculations due to the consideration of uncertainties. Deterministic T_{SL} is in general classified in the following increasing order for a given con-

crete: MS5_Fre, MS8_K_act, MI1_Fre and Erf. The ranking of reliability T_{SL} is slightly different: MS5_Fre, MI1_Fre, MS8_K_act and Erf. This discrepancy emphasizes the role of the number of input data considered as random variables (6 for MI1_Fre and 8 for MS8_K_act). On the whole, these results are consistent with the previous analysis of the ranking of β -curves (see Fig. 2).

Whatever the considered model, a ranking of predicted (deterministic or reliability) T_{SL} can also be determined for the six studied concretes (increasing order): M25, BO, M30FA, C1, M75SF and M120SF. Even if this ranking is consistent with the performance-based approach, predicted values are shorter. There are two plausible explanations:

- in the framework of the performed calculations of reliability T_{SL} , the description of the initiation of corrosion is skewed by significant uncertainties due to a lack of scientific knowledge on the actual extent of the dispersions of input data. This leads to arbitrarily fixing of the scattering of some variables. Furthermore, the description of the initiation of corrosion, based on a single parameter n_{th} , is clearly not relevant for SL calculations and might lead to underestimation due to the chosen high variability (standard deviation of 44 %).
- in case of reliability T_{SL} calculations, since a threshold reliability index β_{lim} as a function of time is chosen, it leads to a reduced T_{SL} in comparison with previous studies using a fixed threshold, whatever the targeted service life [16, 20, 45].

Moreover, a conservative approach has been assumed in this paper since the propagation period of corrosion is not taken into account in the calculation of T_{SL} . This is an acknowledged shortfall (also present in the performance-based approach) since, during a part of the propagation period, damages remain limited and RC structures continue to be functional for their intended use. This should be taken into account when comparing the present study and observations carried out on real RC structures made of the same materials.

In spite of abnormally low T_{SL} calculated for most of the studied materials, the simulations remain relevant from a strict concrete point of view and for the purpose of a sensitivity analysis.

5.3. Reliability sensitivity analysis

The reliability sensitivity analysis is only carried out at T_{SL} . This is relevant in view of the fact that durability models are used to predict T_{SL} and that designers want to know the most influencing input data in terms of mean value and variability of the studied input data for this specific value. Firstly, a global analysis is performed using the direction cosines α . Thereafter, a more precise analysis is carried out using the elasticities with respect to the mean and the standard deviation.

5.3.1. Direction cosines α

Fig. 3 illustrates the square of the direction cosines α^2 obtained for each set of statistical input data in case of the four studied models.

[Figure 3 about here.]

Considering each predictive model and each input data X_i , no clear trend is observed between the different cementitious materials (see that the variability of α^2 is illustrated by a high coefficient of variation around 20 %). Similarly, no clear influence of the level of modeling refinement can be found. Thus the following sensitivity analysis will be valid whatever the model and the concrete.

Globally, the comparison of the various input data reveals that a maximum for α^2 is obtained for the concrete cover thickness e (60-70 % on average) and the critical chloride content n_{th} (20-30 % on average). Nevertheless, no conclusion can be drawn to distinguish between e and n_{th} , the most influencing input data since in some cases α^2 values are of the same order of magnitude, or even $\alpha^2(n_{th})$ can be higher than $\alpha^2(e)$.

Among the other input data linked to the concrete properties, only α^2 related to the effective chloride diffusion coefficient D_{Cl^-} and the power coefficient γ of the *Freundlich* isotherm are significantly different from 0. As a whole, it confirms that D_{Cl^-} is a key input data among the concrete properties.

Now let's have a look more specifically at the influencing role of the CBI parameters. K and C_{ads} (used in models Erf and MS8_K_act, respectively) represent the slope of the CBI (the *Kari* model is almost linear [25]). Their α^2 values are close to 0. Regarding the models MI1_Fre and MS5_Fre, the chosen *Freundlich* description corresponds to a two-parameter CBI, *i.e.* μ is linked to the slope from the origin while γ expresses the non-linear nature of the CBI. $\alpha^2(\gamma)$ is higher than α^2 values associated with the other input data characterizing chloride binding. As the *Freundlich* description remains empirical, such results are difficult to interpret with physical or chemical arguments. Nonetheless, it seems to correspond to the chosen significant variability of parameter γ which is based on a previous study performed by the present authors [25]. Due to several numerical calibrations of CBI parameters performed for a large panel of concretes, the authors have indeed shown that γ is randomly distributed between 0.2 and 1.0 with no clear ranking according to the kind of concrete. It confirms the difficulty to use this parameter for a consistent description of the CBI.

Also other input data related to concrete properties exist and are considered as random variables, *i.e.* the porosity, and the initial alkali and hydroxyl concentrations. Their α^2 values are close to 0. Therefore, no advanced knowledge of these input data (*e.g.* mechanical pore solution extraction in order to determine initial alkali and hydroxyl concentrations) is required to accurately predict T_{SL} .

A comparative study with results previously published in the literature can now be conducted. In general, sensitivity analyses were performed in case of analytical chloride ingress models (derived from the error function) [22, 52, 54], except the paper of Conciatori *et al.* [51] (multi-species model STADIUM®). The results of these papers are consistent with each other: the concrete cover thickness and the critical chloride content are the key input data to predict the SL of RC structures immersed in seawater. Let's note that Saassouh and Lounis [22] consider a low standard deviation (20 %) for the critical chloride content, and thus find a limited impact on the SL prediction.

For the input data linked to the concrete properties, the most influencing input data is the apparent chloride diffusion coefficient which encompasses both transport phenomena and binding effects. By comparison, regarding the chloride ingress models studied in the present paper, the effective chloride diffusion coefficient D_{Cl^-} is a key input data among the studied concrete properties whereas the influence of the binding

parameters seems to be limited.

5.3.2. Elasticity with respect to the mean value ϵ_m

The comparison between elasticities with respect to the mean value of each input data X_i is shown in Fig. 4.

[Figure 4 about here.]

As mentioned in the previous section dealing with direction cosines, for each input data X_i , no clear trend appears with respect to the studied concretes and the kind of model. Nevertheless, some discussions remain common to the four studied chloride ingress models.

The elasticity of the concrete cover thickness $\epsilon_m(e)$ is between 1.4 and 3.6. A clear distinction between $\epsilon_m(e)$ and $\epsilon_m(n_{th})$ is noticed ($\epsilon_m(n_{th})$ is between 0.3 and 1.7). This confirms the crucial role of these two input data in the calculation of β .

As a second step, a focus on the input data related to solely the concrete properties can be made. $\epsilon_m(D_{Cl-})$ is between 0.5 and 1.5 which represents the same order of magnitude as $\epsilon_m(n_{th})$. This reinforces the idea that chloride ingress is mainly controlled by transport phenomena. $\epsilon_m(\phi)$ is negligible whatever the type of concrete and model suggesting that an approximated value can be chosen for this parameter. This is in line with the principle of an *a priori* assessment based on models or the use of approximated relationships. For instance usual relationships between compressive strength and porosity [65] could be useful.

Furthermore, Fig. 4 allows an analysis of the influence of the CBI descriptions. Considering the input data linked to the slope of the CBI (K , μ and C_{ads}), the elasticities with respect to the mean stay in the same order of magnitude (between 0.01 and 0.3). Like for the porosity, these low values of ϵ_m indicate a limited influence of these input data and allow to consider as assessment of first order. Among others, two methods for determination of K , μ and C_{ads} seem possible. On the one hand, the analytical formula proposed by Baroghel-Bouny *et al.* [26] can be used, where the binding capacity is directly related to the content of *C-S-H*, residual aluminates C_3A and C_4AF . On the other hand, values proposed by Pradelle *et al.* [25] for a large range of cementitious materials can be employed. Note that in the specific case of the *Freundlich* description, most weight is observed on the parameter γ ($\epsilon_m(\gamma)$ is between 0.088 and 0.85). This confirms the observation made in Section 5.3.1 based on the analysis of the direction cosines.

Considering the two multi-species models (MS5_Fre and MS8_K_act), ϵ_m values for the initial concentrations of alkali and hydroxyl ions are close to 0. Initial concentrations of these ions can thus be determined using approximate hydration models or assessed using analogies with similar concretes since the low level of accuracy for these methods does not impair the ability of the used chloride ingress models to predict T_{SL} . This statement confirms *a posteriori* the choice made in Section 4 to consider initial ion concentrations by comparison with similar concretes.

5.3.3. Elasticity with respect to the standard deviation ϵ_σ

The elasticities $\epsilon_\sigma(X_i)$ with respect to the standard deviation of each input data X_i are illustrated in Fig. 5.

[Figure 5 about here.]

As described in the previous discussion about the direction cosines and the elasticities with respect to the mean values, ε_σ seems to be independent of the type of concrete and/or used model. Again, the standard deviations of e and n_{th} play a crucial role in the assessment of β : the mean value of $\varepsilon_\sigma(e)$ and $\varepsilon_\sigma(n_{th})$ are in the range of 0.65 and 0.4, respectively.

The influence of the standard deviation of the other input data is weak in comparison to those of e and n_{th} . In case of input data linked to transport properties, D_{Cl^-} and ϕ , ε_σ values are close to 0. ϕ can thus be considered as deterministic. Regarding D_{Cl^-} , the calculated results highlight a weak influence of its standard deviation; it suggests not to pursue an exact determination of its statistical distribution and the one chosen in the present paper seems relevant (log-normal and 10 % as a coefficient of variation).

Let us focus now on input data describing the interactions between the chloride ions and the solid matrix. In spite of arbitrarily high coefficients of variation (20 %), all ε_σ related to the input data representing the slope of CBI (K , C_{ads} and μ) are negligible, which encourages not to go further in the determination of their statistical distributions as well. In case of the models MI1_Fre and MS5_Fre, the most significant variable in terms of ε_σ is γ . Globally, its influence seems even higher than D_{Cl^-} but lower than e and n_{th} . This highlights again that the chosen important variability of this input data has an impact on the calculated β , *i.e.* an essential role among the input data linked to the concrete properties.

ε_σ values for initial alkali and hydroxyl ions have been determined; they are close to 0. These three concentrations can then be defined as deterministic. Such results confirm the arbitrary hypothesis to define their statistical distribution as log-normal with a coefficient of variation of 20 %. This choice seems not to influence the SL prediction.

5.4. Influence of the correlation

The possible influence of some correlation coefficients is evaluated in this section. This is relevant because it is likely that DIs and main properties of concrete are correlated [66]. For this purpose, the following strategy is adopted. In case of models Erf and MI1_Fre, results in terms of β -curves and direction cosines are compared according to two scenarios: the vector $\vec{X}$ is an independent random vector (scenario called “Independent”) or the correlation coefficients $r(\phi, D_{Cl^-}) = 0.7$, $r(\phi, CBI) = -0.7$ and $r(D_{Cl^-}, CBI) = -0.7$ are introduced (scenario called “ $r(\phi, D_{Cl^-}, CBI)$ ”). CBI means the parameters K or μ of the linear and *Freundlich* isotherms, depending on the considered model. Due to a lack of experimental data, the authors have arbitrarily chosen for a correlation coefficient of 0.7 since this value is sufficiently high to potentially influence the reliability calculation. A negative sign for the correlation coefficient means that the influence of the variables is opposite.

Whatever the considered scenarios (independent or with correlations), almost identical β -curves are determined (see Fig. 2). Thus, taking into account the correlation coefficient among D_{Cl^-} , ϕ and CBI does not modify the reliability T_{SL} prediction.

It is however possible that the introduced correlation coefficients modify the sensitivity analysis conclusions. To simply discuss this issue, the comparison between an

independent and a correlated vector $\vec{X}$ in terms of direction cosines is performed in Fig. 6.

[Figure 6 about here.]

Remarks for the models Erf and MI1_Fre can be pointed out. Unexpectedly, all the input data can be impacted by the introduced correlations, and not only those which are correlated. Nevertheless, in most cases, these changes do not modify the relative influence of each input data. Whatever the scenario, the concrete cover thickness and the critical chloride content remain to be the key input data. Globally, for other input data, the orders of magnitude for α_i^2 remain much lower than those of e and n_{th} .

The authors recall that in case of independent variables, $\alpha^2(\phi)$ is close to 0 and $\alpha^2(D_{Cl^-})$ is low but not negligible. The introduction of correlation conducts to an increase of the weight of ϕ to reach that of D_{Cl^-} . Dealing with the CBI parameters, α^2 values evolves as follows : $\alpha^2(\gamma)$ is significantly different from 0, but still remaining well below $\alpha^2(e)$ and $\alpha^2(n_{th})$; $\alpha^2(K)$ and $\alpha^2(\mu)$ values (already low for independent variables) decreases for the scenario $r(\phi, D_{Cl^-}, CBI)$.

This discussion globally highlights the weak effect of correlations on the sensitivity analysis. Nevertheless, this study remains limited and does not allow global conclusions to be drawn.

6. Conclusions

A sensitivity analysis of chloride ingress models for RC structures immersed in seawater has been performed in the framework of a reliability approach, *i.e.* the variabilities of the input data are taken into account. A methodology for a probabilistic service life (SL) prediction has been presented.

Once the adopted reliability approach has been verified, the authors have estimated the SL of a set of concretes and mortars, and compared the results with deterministic calculations and the values obtained by the performance approach based on the use of durability indicators. The calculated reliability SL T_{SL} is shorter than the one assessed by using the performance-based approach of durability. This is partly due to the definition of β_{lim} , as a time-dependent function. Two biases in the methodology have also been identified: the standard deviation of the concrete cover has been chosen quite high as well as the one of the chloride threshold for corrosion initiation. Moreover, the chosen conservative modeling does not consider the propagation of corrosion. These elements represent perspectives to improve the methodology to calculate T_{SL} .

A sensitivity analysis has been performed using three different indicators: the direction coefficients, the elasticities with respect to the mean value and the standard deviation. The following conclusions are drawn:

- The study confirms that the key input data to predict the SL of RC structures immersed in seawater are clearly the concrete cover thickness and the critical chloride content. It is thus important to define with enough accuracy the mean value and the coefficient of variation of these input data since the determination of the reliability index β mainly depends on these two input data.

- The mean value of the effective chloride diffusion coefficient has a similar influence than the critical chloride content, which confirms the key role of diffusion phenomena in the chloride ingress process in comparison to binding capacity of the matrix. Nevertheless, even if the studied concretes belong to a broad range, the role of binding characteristics could be stronger if concretes blended with a very high content of supplementary cementitious materials were considered.
- In contrast, approximated values can be chosen for the porosity, input data related to the slope from the origin of the CBI (for instance coefficient μ for *Freundlich* description) and the initial concentrations of alkali and hydroxyl ions. They can be determined by analogy with similar materials or by using easy-to-use analytical formula or models. However, regarding the initial concentrations within the concrete, the conclusions will have to be confirmed for materials which intrinsically contain a high content of chloride ions, *e.g.* concretes mixed with cement containing blast furnace slag. The importance of the initial chloride concentration may prove not to be negligible.
- The elasticities with respect to the standard deviation indicate that the porosity, the initial concentration of alkali and hydroxyl ions within the concrete can be considered as deterministic. For other input data, the effective chloride diffusion coefficient and input data linked to the slope of CBIs, approximate statistical distributions are adequate.
- The practical use of the *Freundlich* description of the concrete binding isotherm turns out to be complex due to the high level of uncertainty which still relies on the power coefficient and the relative weight of this input data in the assessment of SL. Thus, the use of a *Freundlich* description, as a global approximation of physical and chemical interactions between ions and solid matrix, will generate too high uncertainties in the durability prediction of RC structures as long as its scattering cannot be sufficiently controlled. This leads to consider a single parameter CBI as the most relevant way to address chloride binding modeling in order to make a better management of uncertainty possible.
- The last part of the present paper has dealt with the introduction of correlation coefficients between the porosity, the effective chloride diffusion coefficient and the slope of the chloride binding isotherm. The authors have observed no significant influence of correlation effects on reliability SL predictions. Adding correlations between input data just seems to modify the influence of input data but in a moderate way. More investigations are however needed to confirm these results.

These conclusions can be summarized as follows: the concrete cover depth, the critical chloride content and the effective chloride diffusion coefficient are crucial parameters. This may lead to consider a simple model based on Fick's second law for the description of chloride penetration in immersed concrete. Nevertheless, it is necessary to bear in mind that only chloride content profiles are probably not sufficient to predict SL because, as recalled in the paper and even if not yet really well established, the propagation of corrosion is certainly highly controlled by the presence of other species like

hydroxyl and alkali ions. This consideration simply points out the benefits of more sophisticated models than those based on the mono-diffusion Fick approach.

In the literature, chloride ingress models developed for saturated conditions are often used for high performance concretes placed in tidal zone. It would be interesting to expand the conclusions of the present study for these kinds of concrete which remain closely saturated.

All these conclusions allow a deeper understanding of chloride ingress models since a robust framework has been proposed for reliability service life calculations. The sensitivity analysis quantifies the influence of each input data (mean, standard deviation and correlation coefficient) and enables to identify the input data which necessitate a thorough management of their uncertainties. This finally allows to propose relevant and robust tools to predict SL but also a strategy to limit expensive experimental tests, necessary to determine input data.

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A. Description of ion adsorption onto *C-S-H*

Table 4 summarizes the considered equations describing the competitive adsorption onto solid matrix.

[Table 4 about here.]

The authors add the hypothesis that the capacity of solid matrix to adsorb is constant for all ions. Constants of adsorption reaction are assumed to be equal to those of adsorption reactions onto *C-S-H*. Such hypothesis is also used by other authors [10, 67]. Thus, analytical relationships (see Eq. (13) and Eq. (14)) between the content of bound ions and the free concentration of ions can be written. First, let us note D as:

$$D = 1 + K_{OH}c_{OH^-} + (K_{Ca} + K_{CaSO_4}c_{SO_4^{2-}} + K_{CaCl}c_{Cl^-})\frac{c_{Ca^{2+}}}{c_{H^+}} + \frac{K_{Na}c_{Na^+} + K_Kc_{K^+}}{c_{H^+}} + K_{Cl}c_{Cl^-} \quad (13)$$

Analytical relationships are then:

$$\begin{cases} s_{OH} = C_{ads} \frac{K_{OH}c_{OH^-}}{D} \\ s_{Cl} = C_{ads} \frac{(K_{CaCl}\frac{c_{Ca^{2+}}}{c_{H^+}} + K_{Cl})c_{Cl^-}}{D} \\ s_{Ca} = C_{ads} \frac{(K_{Ca} + K_{CaSO_4}c_{SO_4^{2-}} + K_{CaCl}c_{Cl^-})c_{Ca^{2+}}}{D c_{H^+}} \\ s_{SO_4} = C_{ads} \frac{K_{CaSO_4}c_{SO_4^{2-}}c_{Ca^{2+}}}{D c_{H^+}} \\ s_{Na} = C_{ads} \frac{K_{Na}c_{Na^+}}{D c_{H^+}} \\ s_K = C_{ads} \frac{K_Kc_{K^+}}{D c_{H^+}} \end{cases} \quad (14)$$

where the parameter C_{ads} has to be calibrated. s_{OH} , s_{Cl} , s_{Ca} , s_{SO_4} , s_{Na} and s_K are the bound content (mol/m^3) of hydroxyl, chloride, calcium, sulfate, sodium, and potassium ions, respectively.

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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 $\text{Ca}(\text{OH})_2$
	Cl^-	Na^+	K^+	OH^-	H^+	Ca^{2+}	Mg^{2+}	SO_4^{2-}		
Erf	✓								Linear ^a : $s_{\text{Cl}} = Kc_{\text{Cl}^-}$	
MI1_Fre	✓								Freundlich ^b : $s_{\text{Cl}} = \mu c_{\text{Cl}^-}^\gamma$	
MS5_Fre	✓	✓	✓	✓	✓				Freundlich ^b : $s_{\text{Cl}} = \mu c_{\text{Cl}^-}^\gamma$	
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.

Table 2: Main characteristics of the studied concretes [55, 57, 58]. Regarding the statistical distributions, LN, Tr. N and D mean log-normal distribution, truncated normal distribution and deterministic, respectively.

Concretes // Mortars		Statistical law	Mean Value						Coefficient of variation	
			M25	M30FA	M75SF	M120SF	BO	C1		
Content (kg/m ³)	Gravel (G) (min/max grain size (mm))		1007 (5/20)	986 (4/20)	1044 (5/20)	991 (5/20)	1192 (4/20)	825 (3/8)	- -	- -
	Sand (S) (min/max grain size (mm))		899 (0/5)	879 (0/5)	877 (0/5)	820 (0/5)	744 (0/5)	695 (0/4)	1365 (0/4)	1253 (0/4)
	Cement (C)		230	223	360	470	353	560	618	682 ^a
	Fly ash (FA)		0	95	0	0	0	0	0	0
	Silica fume (SF)		0	0	22	57	0	0	0	0
	Water (W)		193	166	136	124	172	224	264	267
	Super-plasticisers (SP)		0	1.1	12	15.6	0	0	7.72	10.22
	Retarder (R)		0	1.4	0	0	0	0	2.5	3.3
Content (% by mass of clinker)			2.5	2.5	2.5	2.5	4.3	6	1.5	24.7
			14	14	14	14	6.9	9	14	9.7
Water-to-binder ratio (W/B)			0.84	0.52	0.36	0.23	0.49	0.40	0.43	0.39
Average 28-day cylinder compressive strength (MPa)			22.2	58.6	85.5	127.5	48.5	49.5	76.1	70.7
Apparent chloride diffusion coefficient D_{app} (10 ⁻¹² m ² /s)			10.0 ^b	1.7 ^b	0.79 ^b	0.04 ^b	5.45 ^b	-	-	-
Average water porosity ϕ (-) (age ^c)		LN	0.159 (90 d)	0.137 (90 d)	0.084 (45 d)	0.074 (45 d)	0.124 (90 d)	0.159 (28 d)	0.192 (1 y)	0.220 (1 y)
Effective chloride diffusion coefficient D_{Cl^-} (10 ⁻¹² m ² /s) (age)		LN	8.062 ^d (90 d)	0.374 ^d (90 d)	0.153 ^e (2 y)	0.029 ^e (2 -4 y)	1.422 ^d (84 d)	0.345 ^d (180 d)	2.405 ^d (6 m)	0.105 ^d (4 m)
<i>Freundlich</i>		LN	0.303 ^f	0.373 ^f	0.403 ^g	0.237 ^g	0.908 ^f	2.677 ^g	16.36 ^g	11.25 ^g
<i>Linear</i>		Tr. N	0.948 ^f	0.952 ^f	1 ^g	1 ^g	0.797 ^f	0.510 ^g	0.404 ^g	0.430 ^g
<i>Kari</i>		LN	0.222	0.280	0.403	0.237	0.270	0.144	0.471	0.378
		LN	347.15	438.23	639.10	375.85	424.26	230.26	807.35	1476.37
Initial concentration of the pore solution mol/m ³)	Cl^-	D	0	0	0	0	0	1	0.5	2
	K^+	LN	$\approx 93^h$	$\approx 93^h$	$\approx 170^h$	$\approx 170^h$	$\approx 93^h$	156	272	362
	Na^+	LN	$\approx 64^h$	$\approx 64^h$	$\approx 38^h$	$\approx 38^h$	$\approx 64^h$	23	100	94
	SO_4^{2-}	LN	$\approx 1^i$	$\approx 1^i$	$\approx 1^i$	$\approx 1^i$	$\approx 1^i$	$\approx 1^i$	$\approx 1^i$	$\approx 4^i$
	Mg^{2+}	D	$\approx 0^j$	$\approx 0^j$	$\approx 0^j$	$\approx 0^j$	$\approx 0^j$	$\approx 0^j$	$\approx 0^j$	$\approx 0^j$
	OH^-	D / LN ^k	These three last concentrations are determined using the electro-neutrality condition and the self-ionization equation of water. In case of model MS8_K_act, the equilibrium of the dissolution-precipitation reaction of $Ca(OH)_2$ is also considered.							- / 20 %
	H^+	D								-
	Ca^{2+}	D								-
Boundary condition		D	Immersion in seawater (salinity: 35 g/L) ^l							-

^a The cement is composed of 55 % clinker, 22 % fly ash and 22 % ground-granulated blast-furnace slag.

^b Values were determined by a non-steady state migration test.

^c For the water porosity experiments, the specimens were cured in water during the time specified in brackets.

^d Values were determined by inverse analysis on a total chloride content profile (concrete specimens immersed in a NaCl solution). More details are available in Pradelle *et al.* [25].

^e Values were determined by inverse analysis on a total chloride content profile (concrete specimens *in-situ* in a tidal zone).

More details are available in Pradelle *et al.* [25].

^f Parameters were calibrated directly on CBI experimentally determined using the profile method [26].

^g Parameters were calibrated by inverse analysis on a total chloride content using the methodology developed in [25].

^h Experimental data are not available. Values for a normal (named CO) and a high performance (named CH) cement pastes studied by Baroghel-Bouny [61] are chosen.

ⁱ Values for ordinary and high performance (including silica fume) cement pastes obtained by Codina [62] are chosen.

^j Because of a lack of available data, initial magnesium concentration is assumed to be equal to 0.

^k Initial hydroxyl concentration is a random variable only in the case of model MS8_K_act.

^l In seawater, the concentrations of Cl^- , Na^+ , K^+ , Mg^{2+} and Ca^{2+} ions are equal to 19.7, 11.1, 0.41, 1.31 and 0.44 g/L, respectively.

Table 3: Determination of the service life for the studied concretes and mortars, considering the four studied chloride ingress models and the performance-based approach [4].

Models		Erf		M11-Fre		MS5-Fre		MS8-K _{act}		Performance-based approach (Perf.)
		Determ.	Reliab.	Determ.	Reliab.	Determ.	Reliab.	Determ.	Reliab.	
Concretes	M25	335 d	55 d	308 d	43 d	245 d	35 d	304 d	52 d	∅ ^b
	M30FA	23 y	6 y	21 y	5 y	16.5 y	4y	20 y	6 y	< 30 y
	M75SF	76.5 y	27 y	84.5 y	21 y	61 y	15 y	69 y	23 y	120 y
	M120SF	677 y	> 120 y ^a	4013 y	> 120 y ^a	3017 y	> 120 y ^a	590 y	> 120 y ^a	120 y
	BO	7.5 y	2y	7 y	1 y	5 y	357 d	6.5 y	1 y	50-100 y
	C1	66 y	13 y	55 y	10 y	41 y	7 y	64.5 y	12 y	∅ ^b
Mortars	Mo1	5 y	1 y	4 y	269 d	4 y	284 d	6.5 y	1 y	- ^c
	Mo2	199 y	86 y	134 y	51 y	96 y	32 y	158.5 y	69 y	- ^c

^a For M120SF, the reliability SL T_{SL} cannot be determined but is significantly higher than 120 years.

^b Porosity of M25 and C1 is too high to apply the performance-based approach.

^c Performance-based approach cannot be applied in case of mortars.

Table 4: The equilibrium constants K for physical adsorption onto C-S-H [10].

Reaction equations	K
$\equiv SiOH + OH^- \Leftrightarrow \equiv SiO^- + H_2O$	$K_{OH} = 10^{-12.70}$
$\equiv SiOH + Ca^{2+} \Leftrightarrow \equiv SiOCa^+ + H^+$	$K_{Ca} = 10^{-9.40}$
$\equiv SiOH + Ca^{2+} + Cl^- \Leftrightarrow \equiv SiOCaCl + H^+$	$K_{Ca} = 10^{-6.00}$
$\equiv SiOH + Ca^{2+} + SO_4^{2-} \Leftrightarrow \equiv SiOCaSO_4^- + H^+$	$K_{CaSO_4} = 10^{-8.90}$
$\equiv SiOH + Na^+ \Leftrightarrow \equiv SiONa + H^+$	$K_{Na} = 10^{-13.64}$
$\equiv SiOH + K^+ \Leftrightarrow \equiv SiOK + H^+$	$K_K = 10^{-13.64}$
$\equiv SiOH + Cl^- \Leftrightarrow \equiv SiOHCl^-$	$K_{Cl} = 10^{-0.35}$