# **Salt Attack, Durability and Service Life of Concrete Structures**



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**Abstract** The chapter in this book presents concepts on the durability of concrete structures directly relating to deterioration due to the attack of chloride and sulfate salts. The matter becomes necessary due to the aggressive conditions that the structure may be exposed to. In the case of sulfates, these can be present in soils, acid rain, sewage and the sea. Marine environments, on the other hand, are mainly responsible for the penetration of chlorides in concrete, another situation is the free chloride that can be present in the concrete mass and react when in large quantities. We covered the operation of chloride attack and sulfate attack, the calculation models and related life prediction and some recent studies to understand the behavior of buildings in the long term. This study becomes relevant for understanding the deterioration mechanisms that compromise durability.

**Keywords** Sulphate attack · Chloride ion · Durability · Service life · Concrete structures

# **1 Introduction**

A reinforced concrete structure, in addition to mechanical resistance, must have adequate durability, which consists of resisting the environmental actions of the environment where it is inserted, during the period of its useful life.

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J. M. P. Q. Delgado (ed.), *Building Pathology, Durability and Service Life*, Building Pathology and Rehabilitation 12, [https://doi.org/10.1007/978-3-030-47302-0\\_3](https://doi.org/10.1007/978-3-030-47302-0_3)

According to the American Concrete Institute [\(2001\)](#page-13-0), the durability of concrete can be defined as the ability to resist any deterioration process, for example, the action of weather, chemical agents and abrasion.

Thus, it is stated that knowing the durability and useful life of the structures is of paramount importance to prevent pathological manifestations and to understand the behavior of buildings in the long term (Medeiros et al. [2011\)](#page-14-0).

Environmental conditions can accelerate the deterioration of a reinforced concrete structure due to its level of aggressiveness. Some of these regions are industrial environments, marine regions and cities with high levels of air pollution. Among the various deterioration agents existing in these environments are the action of sulfates, which causes the deterioration of concrete, and chloride ions, which cause the corrosion of reinforcement.

According to Alexander and Beushausen [\(2019\)](#page-13-1) corrosion occurs due to a reaction that leads to the loss of the protective oxide layer of the steel. The presence of chlorides is one of the causes of the corrosion process in reinforced concrete structures; the structure will be exposed to the action of chlorides in marine environments mainly (Aguiar [2014\)](#page-13-2).

The speed of entry of aggressive agents such as sulfates and chlorides depends on the present amount of these agents, on the permeability of the concrete and on the humidity (Aguiar [2014\)](#page-13-2). As it are talking about the entrance of external agents in the concrete, the concrete covering has a fundamental role in the useful life of the structure, being as important the quality of the material as the depth of this layer (Alexander and Beushausen [2019\)](#page-13-1). Figure [1](#page-1-0) illustrates these important elements in the concrete cover layer.

The prediction of the useful life given through calculation models is of fundamental importance for professionals in the area of concrete structures to understand the mechanisms of deterioration. This modeling foreseeing corrosion according to Félix et al. [\(2018\)](#page-13-3) happens in two stages, the initiation and the propagation.

<span id="page-1-0"></span>

The FIB Bulletin [\(2006\)](#page-13-4) presents deterioration prediction models, such as carbonation and chloride ingress. Lifetime designs are usually based on the period of onset of corrosion, according to authors Alexander and Beushausen [\(2019\)](#page-13-1).

## **2 Sulfate Action**

#### *2.1 General Concepts*

According Costa [\(2004\)](#page-13-5), among the various salts that produce harmful effects on concrete, sulfates stand out, which may have an internal or external origin to concrete. The sources of internal sulfates are the various additions present in clinker and cement (Skalny et al. [2002\)](#page-15-0), whereas the external sources can be water in the soil, acid rain, sewage, and sea, among others.

The degradation of the concrete due to the attack of sulfates can manifest itself through the expansion and cracking of the concrete or through the loss of mass and strength. When in solution, the magnesium, calcium, potassium, sodium and ammonium sulfates can react with the hydrated cement paste and the consequence is the breakdown of the concrete after some time.

The most well-known means of sulfates attack on concrete are reactions with the hydration products of aluminates producing secondary ettringite and reactions with calcium hydroxide producing gypsum (Costa [2004\)](#page-13-5).

According to Mehta and Monteiro [\(2008\)](#page-14-1) the intensity and the process of attack of sulfates varies with the concentration of the ion and the composition of the cement paste. High levels of  $C_3A$  and calcium hydroxide in the Portland cement paste increase its susceptibility to attack by sulfates (Lee and Lee [2007\)](#page-14-2). In addition to  $C_3$ A, the relationship between  $C_3$ S/C<sub>2</sub>S silicates also has an influence on the resistance of cements to attack by sulfates, and the higher this relationship, the greater the susceptibility to attack by sulfates (Al-Amoudi [2002\)](#page-13-6).

According to Lee and Lee [\(2007\)](#page-14-2),  $C_3S$  hydration produces 61% C–S–H and 39% CH, while  $C_2S$  hydration produces 82% C–S–H and 18% CH. Considering that the strength of the hardened cement paste is reduced when in the presence of CH, it is expected that cements containing a greater amount of  $C_2S$  will be more resistant in environments rich in sulfates.

The main types of sulfates that attack the cement paste are calcium  $(CaSO<sub>4</sub>)$ , sodium  $(Na_2SO_4)$  and magnesium  $(MgSO_4)$  sulfates, in an increasing order of aggressiveness.

Due to its low solubility in water,  $CaSO<sub>4</sub>$  is considered the least aggressive sulfate to the cement paste, however there are studies that consider that the high alkalinity of the cement increases the solubility of these ions, allowing the attack to the cement paste (Drimalas et al. [2011\)](#page-13-7). In Eq. [1,](#page-3-0) the reaction of  $CaSO<sub>4</sub>$  with  $C<sub>3</sub>A$  is presented to form the secondary ettringite, causing the expansion and cracking of the cement paste.

<span id="page-3-0"></span>
$$
3(CaSO2 \cdot 2H2O) + 4CaO \cdot Al2O3 \cdot 19H2O + 17H2O
$$
  
\n
$$
\rightarrow 3CaO \cdot Al2O3 \cdot 3CaSO4 \cdot 32H2O
$$
 (1)

The  $Na<sub>2</sub>SO<sub>4</sub>$  can react with CH forming gypsum, as indicated in Eq. [2,](#page-3-1) and with the aluminate phases forming ettringite, as presented in Eqs. [3](#page-3-2) and [4](#page-3-3) (Drimalas et al. [2011;](#page-13-7) Piasta et al. [2014\)](#page-14-3).

<span id="page-3-2"></span><span id="page-3-1"></span>
$$
Ca(OH)2 + Na2SO4 · H2O \rightarrow CaSO4 · H2O \downarrow +2NaOH
$$
 (2)

$$
2Na_2SO_4 + 3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O + 2Ca(OH)_2 + 2H_2O
$$
  
\n
$$
\rightarrow 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O + 2NaO
$$
 (3)

<span id="page-3-3"></span>
$$
3Na_2SO_4 + 2(4CaO \cdot Al_2O_3 \cdot 19H_2O) + 14H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O + 2[A(OH)_3]6NaOH
$$
 (4)

The  $MgSO<sub>4</sub>$ , due to its high solubility in water, is the type of sulfate that produces the greatest deterioration of the cement paste and can react with all cement hydration products.  $MgSO_4$  can generate the decomposition of the C–S–H phase of the cement paste, forming expansive compounds, producing brucite  $(Mg(OH)_2)$  and hydrated magnesium silicate (M–S–H) (Liu et al. [2013\)](#page-14-4). As an example of the possible reactions of  $MgSO<sub>4</sub>$  with the hydrated cement paste compounds, in Eq. [5](#page-3-4) the reaction with ettringite is presented and in Eq. [6](#page-3-5) the reaction with C–S–H.

<span id="page-3-5"></span><span id="page-3-4"></span>
$$
(CaO)3Al2O3 \cdot CaSO4 \cdot 12H2O + 2MgSO4 + 2Ca(OH)2 + 20H2O
$$
  
\n
$$
\rightarrow (CaO)3Al2O3 \cdot 3CaSO4 \cdot 32H2O + 2Mg(OH)2 \downarrow
$$
  
\n
$$
xMg2+ + xSO42- + xCaO \cdot SiO2 \cdot aq + 3xH2O
$$
  
\n
$$
\rightarrow xCaSO4 \cdot 2H2O + xMg(OH)2 + SiO2 \cdot aq
$$
 (6)

Due to the low solubility of  $Mg(OH)_2$ , it precipitates in all reactions of magnesium sulfate with calcium hydroxide or any other phase of the cement paste that contains calcium. The more compacted layer of brucite can slow up the attack forward at first. However, the pH of the solution tends to decrease with the release of  $Mg^{2+}$  ions and the acidity of the solution tends to accelerate the dissociation of calcium ions from the phases present in e cement paste, promoting an increase in gypsum formation. With this, there is a depletion of  $Ca(OH)_2$  in the medium and the decalcification of C–S–H begins to occur, which is converted to M–S–H, which does not have any type of binding properties with the other phases of the concrete (Drimalas et al. [2011;](#page-13-7) Piasta et al. [2014\)](#page-14-3).

#### *2.2 Durability Models*

Models that simulate the attack mechanisms are important to understand how the reactions occur, being able to quantitatively predict the products of these deleterious reactions in the concrete.

Lorente et al. [\(2011\)](#page-14-5) analyze the results of the transfer sulfate sodium and magnesium in the pores of concrete comparing models the migration of the magnetic field and natural diffusion. In the first, it was based on the principle that sulfate is an ionic species, so an electric field was used to induce migration and reactions (inspired by classic chloride migration models), while in diffusion, which occurs naturally, starting from a more concentrated (external) to less concentrated (internal) region, sulfate reacts with the cementitious matrix. The tests proved that in the migration, the penetration depth of the sulfate is greater with  $MgSO<sub>4</sub>$ , while in the diffusion, the reaction products are greater when  $Na<sup>+</sup>$  is the counter-ion. This can be explained due to the kinetics of brucite formation slower than the sulfate penetration time under an electric field.

The ion diffusion mechanism in concrete can be modeled using Fick's second law. Of the existing models, the authors Sun et al. [\(2013\)](#page-15-1) innovate in order to consider the effect of the evolution of sulfate ion diffusion related to the immersion time and concentration of sulfate ions, whose damage evolution has been proven through ultrasonic measurements. A numerical method was used to solve the nonlinear parabolic differential equation that describes the diffusion by sulfate ions, later with experiments to validate the model. It was then obtained functions that describe the evolution of the damage induced by the sulfate that significantly accelerates the penetration of sulfate ions when the concentration of sulfate is high and/or immersion time is greater.

Campos et al. [\(2016\)](#page-13-8) proposed a kinetic model with the objective of predicting the evolution and distribution of the internal sulfate attack on conventional concrete and dams, considering two pyrrhotite oxidants, usually contained in contaminated aggregates, which in the presence of water and oxygen react and can form expansive products. The models were validated through measurements in real dams. It was found that, while in conventional concrete, oxygen is the main oxidant, with exponential kinetic evolution over time, in concrete in dams,  $Fe<sup>3+</sup>$  is the main oxidant, with kinetic evolution in the form of "S". The fact can be explained by the pH of the aggregates, which determines the main oxidant of pyrrhotite (oxygen:  $pH > 4$  and  $Fe<sup>3+</sup>: pH < 4$ ). In conventional concrete, aggregates are surrounded by cement paste, becoming alkaline. While in the case of dams, larger aggregates are not influenced by the structure's pH, remaining acidic.

Most of the existing mechanical models of external diffusion sulfate attack, applied even at the structural level, do not consider the varying humidity conditions. Cefis and Comi [\(2017\)](#page-13-9) developed a model that simulates the mechanical effects of expansion in partially saturated conditions, considering that the effect of formation of ettringite, based on results obtained by simplified diffusion models, implies the

formation of chemicals accounted for by the amount of aluminates that cause volumetric deformation in the concrete. Chemical and mechanical damage describe the formation of micro-cracks that decrease the elastic properties of concrete.

Feng et al. [\(2018\)](#page-13-10) developed a model microstructural linear elastic finite element that calculates the force driving the growth expanding the phase aft external attack sulfate in cement paste, which, although it has a wide range of compositions, is governed the mostly by the stage of formation of etringita. Crystallization pressure and stress fields are tracked in the microstructure on a micrometer scale. The damage initially caused by the expansion, in addition to causing damage to the physical properties, that is, the linear elastic properties in the microstructure; they also cause rheological changes in the progressive reactions that will attack the innermost region of the concrete, through mechanisms based on the concentration of sulfate ions and changes in the pH in the aqueous solution within the porous structure.

It is observed when soluble carbonates are present, confirming reductions in pH of the pore solution, which usually accompanies the input sulfates, there is a destabilizing significantly from calcium monosulfoaluminate, becoming spontaneously AFt without adding extra sulfate. Therefore, the progress of phase transformations and expansion of the surface into the porous material is dictated by the input rate of fronts of concentration of sulfate ions and pH, which are not essentially coincident.

The behavior within the first  $100 \mu m$  surface provide information on the concentration of sulfate, concentration of carbonate and pH on the microstructure and a substantial material expansion.

#### *2.3 Studies Carried Out*

Studies were carried out using 3 types of Brazilian cements, designated CP-II F 32, CP-IV and CP-V, subjected to attack by 3 types of sulfates,  $CaSO<sub>4</sub>$ ,  $Na<sub>2</sub>SO<sub>4</sub>$  and  $MgSO<sub>4</sub>$ , for 5 months, with a concentration of 10% in relation to the body of water. A high concentration was chosen to accelerate the degradation of the cement. For the study, mortar specimens were used in the mix 1:3, with a ratio of w/c 0.5. Table [1](#page-5-0) shows the composition of the cements used, with CP-IV cement considered resistant to sulfates.

	$Al_2O_3$ (%)	$SiO2$ (%)	$Fe2O3$ (%)	CaO $(\% )$
$CP-III$ $F32$	4.25	18.62	2.88	61.03
CP-IV	9.79	28.99	4.07	45.45
$CP-V$	4.30	18.96	2.95	60.76

<span id="page-5-0"></span>**Table 1** Chemical composition of cements

*Source* Schiavini [\(2018\)](#page-14-6)



<span id="page-6-0"></span>**Fig. 2** SEM images of CP-IV

In Fig. [2,](#page-6-0) it is possible to observe the SEM images of the CP-IV cement after the 5 months of attack of the different types of sulfates, comparing with a sample free of attack.

Figure [2a](#page-6-0) represents the image of the microstructure of the reference CP-IV, where it is possible to observe C–S–H formations, a fact confirmed by the high presence of Ca and Si indicated in the EDS. In Fig. [2b](#page-6-0), which represents the image of CP-IV that suffered  $CaSO<sub>4</sub>$  attack, in addition to C–S–H it is also possible to observe the formation of ettringite. The sample subjected to the attack of  $Na<sub>2</sub>SO<sub>4</sub>$  is represented in Fig. [2c](#page-6-0) where the formation of Portlandite is observed, and it is not possible to evidence the attack by sulfates. The 2D image represents the sample subjected to the attack of  $MgSO_4$  where it is possible to observe the formation of monosulfate and brucite, however in the formation of monosulfate, according to EDS results, Ca was replaced by Mg. The results presented above indicate the greater aggressiveness of MgSO4 when compared with other types of sulfates, even in a sulfate-resistant cement.

It is also possible to check the resistance of the 3 types of cements against MgSO4 attack, as illustrated in Fig. [3.](#page-7-0)

In Fig. [3a](#page-7-0), which is an image of the CP-II F32 cement, it is possible to observe the formation of ettringite and the EDS indicates a small presence of Mg. The CP-IV cement is represented in Fig. [3b](#page-7-0) and, as mentioned above, presents the formation of monosulfate and brucite. CP-V cement is illustrated in Fig. [3c](#page-7-0) where it is possible



**Fig. 3** SEM image of the MgSO4 attack on different types of cement

<span id="page-7-1"></span><span id="page-7-0"></span>

<b>Table 2</b> Sulfate concentration in cement		CaSO <sub>4</sub>	Na <sub>2</sub> SO <sub>4</sub>	MgSO <sub>4</sub>
samples	$CP$ -II $F32$	0.50	1.23	1.81
	CP-IV	0.41	0.82	1.40
	$CP-V$	0.56	0.98	1.47

*Source* Schiavini [\(2018\)](#page-14-6)

to observe the formation of monosulfate with a large amount of Mg, according to an analysis by EDS.

In addition to the SEM images, the amounts of sulfates that penetrated the samples were also determined using the APHA Method  $4500$ —SO<sub>4</sub><sup>2–</sup>, from ASTM, as shown in Table [2.](#page-7-1)

By the sulfate concentrations determined in the mortar samples, it is possible to observe that MgSO4 presents greater aggressiveness and that CP-IV has the highest resistance to attack by the 3 types of sulfates used.

In addition to the laboratory experiment, a study was also carried out on a 18 year-old construction work on a sewage treatment plant that used CP-IV cement, sulfate resistance, with an  $w/c = 0.45$  ratio with a compressive strength of 42 MPa (Mazer et al. [2019\)](#page-14-7).

According Rheinheimer and Khoe [\(2013\)](#page-14-8), the sewage from this sewage treatment plant has a sulfate concentration less than 200 mg/L and according to NBR 12.655 (ABNT [2006\)](#page-13-11) this condition represents a moderate aggressiveness, however the average sulfate content found in analysis of 4 samples was 7.84%, at a depth of up to 5 cm and a porosity of 12.76%, determined by mercury intrusion (Mazer et al. [2019\)](#page-14-7).

#### **3 Chloride Action**

#### *3.1 General Concepts*

The action of aggressive agents on reinforced concrete causes its degradation, which, according to Johnson [\(1969\)](#page-14-9) and Martin-Pérez et al. [\(2000\)](#page-14-10), has as its main symptoms cracks, disintegration and stains. According to Martin-Pérez et al. [\(2000\)](#page-14-10) reinforcement corrosion due to the action of chloride ions is a major cause of degradation of reinforced concrete structures.

This corrosion is the result of an electrochemical process, accompanied by anodic and cathodic reactions. According to Mehta [\(1982\)](#page-14-11) the reactions that occur due to the action of the chloride ions are presented in Eqs. [7](#page-8-0) and [8:](#page-8-1)

• Anodic reaction involving Cl<sup>−</sup> ions

$$
\text{Fe} + 2\text{Cl}^- \to \text{FeCl}_2 \to \text{Fe}^{++} + 2\text{Cl}^- + 2e^- \tag{7}
$$

• Cathodic reaction

<span id="page-8-1"></span><span id="page-8-0"></span>
$$
\frac{1}{2}O_2 + H_2O + 2e^- \to 2(OH)^-
$$
 (8)

The corrosion of reinforcement in environments subjected to the action of chlorides has been studied by several authors, among which, Otieno et al. [\(2016\)](#page-14-12) studied the phenomenon in a laboratory and natural environment considering the parameters of covering, crack opening and concrete quality, it is not possible to infer the results in the natural environment from the laboratory results. Bouteiller et al. [\(2016\)](#page-13-12), on the other hand, verified the influence of temperature and relative humidity, verifying that higher temperatures and relative humidity in 80% showed higher corrosion rates of the reinforcement.

Several studies (Castro-Borges et al. [2013;](#page-13-13) Kuosa et al. [2013;](#page-14-13) Medeiros-Junior et al. [2015\)](#page-14-14) demonstrate that the main factors influencing the chloride penetration in concrete are the type of cement, the chloride diffusion coefficient, the water/cement ratio, the curing of concrete, the surface concentration of chlorides, the exposure conditions, the relative humidity, and the ambient temperature. Pradelle et al. [\(2017\)](#page-14-15) performed a sensitivity analysis on some models and observed that the thickness of the reinforcement covering and the concentration of chlorides had a greater influence on the useful life of the structures than the chloride diffusion coefficient.

Considering the influence of the marine aggressiveness zone, Zhu et al. [\(2016\)](#page-15-2) analyzed, for 28 years, beams subjected to the action of saline fog and observed that after 1 year of exposure, the concentration of chlorides near the reinforcement was higher than the limit established by RILEM and that these beams showed loss of rigidity and load capacity due to the cracking and corrosion process of the reinforcement over time. Valipour et al. [\(2014\)](#page-15-3) evaluated reinforced concrete specimens exposed to tidal and splash zones for 650 days and found that the corrosion rate was higher in the splash zone than in the tidal zone.

Once the chloride ions have penetrated the concrete structures, they can be found in two different forms: combined with the cement hydration compounds physically or chemically, or free in the concrete pores, the latter being the ones that act in the process corrosion resistance.

Determination of the content of free chloride ions in concrete is not common because the carbonation process can release combined chloride ions (Kropp and Hilsdorf [1995\)](#page-14-16), thus it is common to establish models for predicting useful life based on the amount of total chloride ions in the concrete. However, Mohammed and Hamada [\(2003\)](#page-14-17) established relationships between the total amount of chloride ions and the amount of free chloride ions for different types of Japanese cements, among which are mentioned: common Portland cement (OPC), moderate heat cement hydration (MH), the initial high strength cement (HES), and a cement with a high content of  $C_3A$  (AL). For all cements surveyed, the authors found linear relationships between the amounts of total and free chloride ions, as indicated in the equations below:

$$
OPC: C_t = 1.1597C_f \quad R^2 = 0.94 \tag{9}
$$

$$
HES: C_t = 1.1390C_f \quad R^2 = 0.97 \tag{10}
$$

$$
MH: C_t = 1.1266C_f \quad R^2 = 0.87 \tag{11}
$$

$$
AL: C_t = 1.4821C_f \quad R^2 = 0.98 \tag{12}
$$

where  $C_t$  corresponds to the total amount of chloride ions and  $C_f$  is the amount of free chloride ions in the concrete. In the expressions above, it is observed that cement with a high  $C_3$ A content has a lower  $C_f/C_t$  ratio, indicating a better ability of Chloride ions to combine with hydrated cement compounds, in particular aluminate compounds.

The ability to combine Chloride ions in concrete depends mainly on the amount of C<sub>3</sub>A, for the formation of Friedel's Salt (3CaO·Al<sub>2</sub>O<sub>3</sub>·CaCl<sub>2</sub>·10H<sub>2</sub>O) (Kropp and Hilsdorf [1995\)](#page-14-16).

Many of the models used to determinate the chloride penetration profile in concrete structures is based on Fick's laws (Andrade et al. [1997;](#page-13-14) Liang and Lin [2003;](#page-14-18) Sun et al. [2012;](#page-15-4) Petcherdchoo [2013\)](#page-14-19). Some of those models consider the diffusion coefficient as constant in time. However, this argument is not valid for concrete because studies show variations in the chloride diffusion coefficient according to the penetration depth, the degree of cement hydration, with the surface concentration of chlorides,

with the temperature, and with the pH of the concrete (Mazer [2010;](#page-14-20) Nogueira and Leonel [2013;](#page-14-21) Safehian and Ramezanianpour [2013\)](#page-14-22).

In the search for a better model of the chloride penetration profile, some studies (Val and Trapper [2008;](#page-15-5) Bastidas-Arteaga et al. [2011;](#page-13-15) Andrade et al. [2013\)](#page-13-16) have shown deterministic or probabilistic models for describing the transport mechanism of chlorides in concrete. In this context, the chaos theory is a good option for developing the concrete technology. Another option is the use of fractals as a way to model the diffusion process. The flexibility of fuzzy logic is also a good feature to work with subjective and qualitative parameters.

Thus, the models with applications in the concrete technology that contains a mathematical approach using fuzzy logic, chaos theory and fractals, are few and recent (Anoop et al. [2002;](#page-13-17) Altmann et al. [2012;](#page-13-18) Anoop and Raghuprasad [2012;](#page-13-19) Mazer et al. [2017\)](#page-14-23).

#### *3.2 Durability Models*

The durability models existing for determining the useful life of concrete due to chloride penetration are mostly based on the 2nd Fick's Law, indicated in Eq. [13.](#page-10-0)

<span id="page-10-1"></span><span id="page-10-0"></span>
$$
\frac{\partial C}{\partial t} = D_a \frac{\partial^2 C}{\partial x^2} \tag{13}
$$

where ∂C/∂t represents the change in concentration over time; Da is the apparent diffusion coefficient, in cm<sup>2</sup>/s and  $\partial^2 C/\partial x^2$  is the mass flow gradient. It is also possible to observe that the chloride diffusion coefficient is constant.

Some existing models are presented below. Saetta et al. [\(1993\)](#page-14-24) developed a model that uses environmental parameters in its formulation, presented in Eq. [14.](#page-10-1)

$$
\frac{\partial C_t}{\partial t} = -div[D_a \cdot \nabla C_t] + \frac{C_t}{\alpha} \frac{\partial \omega}{\partial t}
$$
(14)

where  $C_t$  is the total chloride ion concentration in kg/m<sup>3</sup>;  $D_a$  is the apparent diffusion coefficient in m<sup>2</sup>/s;  $\alpha$  is a capacity factor; and  $\omega$  represents the amount of water.

This model considers, in addition to the diffusion coefficient of chlorides as a function of time, environmental parameters such as temperature and relative humidity, which are implicit in the parameters  $D_a$  and  $\omega$ , given by:

$$
\omega = \omega_{sat} h \left( 1.16h^3 - 1.05h^2 - 0.11h + 1 \right) \tag{15}
$$

$$
D_a = \frac{D_i}{\alpha} \tag{16}
$$

where  $\omega_{\text{sat}}$  is the amount of evaporable water from the concrete; h is the relative humidity; and  $D_i$  represents the diffusion coefficient admitted as the base coefficient, given by:

$$
D_i = D_{i,ref} f_1(T) f_2(t_e) f_3(h)
$$
\n(17)

where  $D_{i,ref}$  representing the diffusion coefficient evaluated for a temperature T = 23 °C, relative humidity h = 100% and degree of hydration of the cement at 28 days. The functions  $f_1, f_2$  and  $f_3$  consider the influence of temperature T, maturation time t and relative humidity h, respectively.

The synergistic effect of the  $CO<sub>2</sub>$  action, chloride and sulfate ions was modeled by Liang and Lin [\(2003\)](#page-14-18), considering the unidimensional action of aggressive agents. The proposed model is given by:

$$
\frac{\partial C}{\partial t} = D_s \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} - K_T C \tag{18}
$$

with initial and boundary conditions:

$$
C(x, 0) = C_i, C(0, t) = C_s \text{ and } C(L, t) = C_f \tag{19}
$$

where C is the concentration of chemical corrosive;  $C_i$ ,  $C_s$  and  $C_f$  are the initial concentration of contaminants in the concrete, on the concrete surface and at the interface between the concrete and the reinforcement;  $D<sub>s</sub>$  represents the diffusion coefficient;  $\nu$  is the average speed of water in the pore structure of concrete;  $K_T$  is the first order decay constant at temperature  $T$ ; L is the thickness of the reinforcement covering; x is the depth; and t is the time.

For the case of the existence of only Chloride ions, this model comes down to 2nd Fick's Law.

Anoop et al. [\(2002\)](#page-13-17) applied the concepts of Fuzzy Logic to consider the effects of environmental factors in the initiation and propagation of corrosion by chloride ions in reinforced concrete elements. Initially, the authors applied the concepts of Fuzzy Sets to environmental characteristics such as temperature, relative humidity and degree of wetting and drying, defining an Environmental Aggression Factor (EAF). After a first stage of modeling, the authors define the concrete class and the water/cement ratio, according to current regulations, and it is then possible to determine the minimum thickness of the reinforcement covering. To determine the time required for corrosion to start, the authors apply the 2nd Fick's Law:

$$
t_i = \frac{d^2}{4D} \left[ erf^{-1} \left( \frac{c_s - c_r}{c_s} \right) \right]^{-2} \tag{20}
$$

where d is the thickness of the chloride ion free coating; D is the Chloride Diffusion coefficient, in cm<sup>2</sup>/s; erf is Gauss's error function;  $c_s$  represents the surface concentration of chloride ions; and  $c_r$  is the critical concentration of chloride ions.

#### *3.3 Studies Carried Out*

Guzzo [\(2018\)](#page-13-20) evaluated the depth of chloride penetration and the concentration of chlorides in a conventional concrete with 25 MPa of compressive strength and in a Reactive Powder Concrete (RPC) with 174 MPa of strength, exposed for 24 months to a 5% chloride solution in relation to body of water. The author observed a concentration of total chlorides of 0.86% in conventional concrete and 0.88% in RPC, in relation to the cement mass. In a first analysis it is believed that there are no differences between the two types of concrete, however in conventional concrete, the penetration of chlorides reached a depth of 4.83 mm and in RPC it was 1.41 mm.

Mazer [\(2010\)](#page-14-20) analyzed the influence of temperature and the region of exposure on the penetration of chlorides in conventional concretes with 30 MPa of compressive strength. The author evaluated the temperatures of 15, 20, 25 and 30  $^{\circ}$ C, in the regions of submerged exposure, level variation and atmospheric zone, at the ages of 6, 12 and 18 months. The author observed that the increase in the ambient temperature leads to an increase in the chloride diffusion coefficient. It was also observed that the wetting and drying cycle of the region of water level variation influenced the concentration of chlorides in the region. In addition, the penetration rate from 6 months to 12 months was higher than the penetration rate from 12 to 18 months.

### **4 Conclusions**

The approach explored in this work provides a perspective for understanding the mechanisms of concrete deterioration through aggressive sulfate and chloride environments. The phenomena are complex, depending on several factors such as temperature, pH, degree of hydration of the cement compounds, time, types of reagents involved, concrete coverage, concrete permeability. In this sense, it was proven that the mathematical models mentioned here are essential to try to understand the mechanisms of diffusion and reaction over time. Although it recognizes a remarkable advance in the understanding of the durability and useful life of concrete structures, many studies should be done to improve the methodologies of investigation and understanding of these phenomena. Most of the models that are used to estimate the penetration of aggressive agents and to predict durability and useful life are based on Fick's Laws, often considering the diffusion coefficients of aggressive agents constant over time (although they are variable), and still disregarding the use of other important variables. Therefore, it is admitted the importance of developing improved methodologies to represent the nature, diffusion and reaction of aggressive agents in the most realistic way possible, consecutive deteriorations from the first reaction that gave rise to disintegration, in a quantitative and qualitative way.

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