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CORROSION INHIBITORS' EFFECT ON DESIGN SERVICE LIFE OF RC STRUCTURES

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ABSTRACT

The implementation of new data regarding the performance of corrosion inhibitors is applied through a performance-based method approved by recent European standards for the probabilistic calculus of service life of reinforced concrete structures. A set of concrete compositions was mixed in order to experimentally obtain strength – compressive – and durability properties – carbonation and chloride diffusion and together with the available results concerning the performance of two types of corrosion inhibitors three scenarios were defined for each concrete composition: i) plain concrete; ii) concrete with added admixture inhibitor and iii) concrete with surface applied migration inhibitor. The probabilistic calculus of service life for each scenario was carried out using modeling equations in which the concrete properties were changed in view of the inhibitors' performance characteristics. The results show that there is a significant improvement in the design service life when this is modeled considering the effect of corrosion inhibitors.

Keywords: carbonation, chlorides, corrosion inhibitors, design service life, durability, performance-based method, probabilistic calculus, reinforced concrete corrosion.

1. INTRODUCTION

Durability of RC structures as regards corrosion is at the present time of significant concern. The corrosion of steel reinforcement is the main cause of deterioration of these structures and depends on the surrounding environment. The environmental agents that take part in corrosion are carbon dioxide (CO_2) and chloride ions (Cl^-).

Both these agents in a certain extent and beyond the concrete cover depth, acting differently with regard to chemical reaction, might destroy the steel passive layer (depassivation) – initiation period[1]. However, corrosion itself will only begin if there is substantial electrical potential difference in the steel reinforcement along with the presence of sufficient moisture and oxygen in the surrounding concrete – propagation period [1].

The corrosion in steel develops in two distinct regions: the anode, where the passive layer is destroyed and steel is dissolved; and the cathode, where hydroxide ions are formed due to the combination of oxygen, water and the electrons that pass through the steel coming from the anode.

Concerning the durability design of RC structures, for decades, deem-to-satisfy definitions for new structures [2-6] and the same prescriptive method combined with traditional repair techniques [7] were preconized. Today's state-of-the-art includes additionally techniques than can be either alternative or complementary to traditional repair, which include, from the concept of repair to that of protection electrochemical methods, surface protective coatings or chemical corrosion inhibitors [8].

In the particular case of chemical corrosion inhibitors, conceived to slow down the process of corrosion (acting mainly on the propagation period), for the repair of RC structures, these are an alternative measure either:

- combined with traditional repair techniques, allowing a multi-barrier strategy, added as an admixture to fresh concrete, hereafter designated AACI, or applied on repaired hardened concrete surfaces, acting as a migrating corrosion inhibitor, hereafter designated MCI

  or
- as a sole measure, applied on hardened existing concrete surfaces, acting as a migrating corrosion inhibitor (MCI).

For design engineers there is the need of having reliable information regarding the performance of the involved materials in each of the techniques that might constitute part or the whole of a solution concerning durability. The aim of this article is, therefore, to present a study where the performance of concrete is quantified in terms of service life, as regards corrosion of steel reinforcement, with and without the presence of corrosion inhibitors. It is not intended to study herein the chemical nature of corrosion inhibitors nor their influence on specific concrete properties.

Probabilistic methods are becoming widely used for the design of both new and repaired structures [9,10]. Relevant research has been carried out in the past years concerning the performance of corrosion inhibitors in both carbonation and chloride presence environments [11-20]. With available probabilistic methods, some of which already preconized by national European standards [21,22] based on the guidelines of DuraCrete project [23], it is now possible to include the effect of corrosion inhibitors in the modeling equations that allow an estimate of the service life of RC structures.

In view of the previous, the purpose of the presented work is to analyze the influence of corrosion inhibitors properties on the design Service life of RC structures exposed to carbonation and chlorides environments. The implementation of the mathematical models used experimental data of 4 concrete mixes – 2 for carbonation diffusion and 2 for chloride migration – and additionally experimental data concerning the specific effect of corrosion inhibitors carried out by Andrade [24].

2. CORROSION INHIBITORS AND ENVIRONMENTAL CLASSIFICATION

One of the possible definitions of corrosion inhibitors is given by ISO 8044:1989 which states that this material is a chemical substance that, in a certain amount, decreases the corrosion rate without changing the concentration of any other corrosion agent [25].

Corrosion inhibitors are classified by Söylev and Richardson [25] according to their specific action:

i. Anodic inhibitors: act on the anode. Examples: calcium nitrite and sodium nitrite (inorganic compounds);
ii. Cathodic inhibitors: act on the oxygen reaction around cathodes. Examples: sodium hydroxide and sodium carbonate (inorganic compounds);
iii. Mixed inhibitors: act on both anodic and cathodic regions. Examples: aminoalcohols and aminocarboxylates (organic compounds).

The main property of these agents, taking into consideration why they have so far being produced, is to act in the propagation period, i.e., when corrosion starts. Some of these corrosion inhibitors have also the ability to act as pore blockers, acting in the initiation period.

Having into account the aforementioned, it is therefore important to clarify the environmental exposure classes established by the European standards, where corrosion is the main cause of deterioration of RC structures. This definition is done in the framework of the European homogenized standards EN 1992-1-1 [26] and EN 206-1 [27] since the modeling analysis is done for corrosion related exposure classes in Spain, with specific characteristics of this country’s environments [28].

Table 1 presents the definition of the exposure classes regarding corrosion of RC structures for all the countries that adopted European homogenized standards. **Figure 1** shows how these classes are associated with real microenvironments in bridges and buildings.

The present study will focus on the most aggressive exposure environments that include the ones showed in **Table 1** and **Fig. 1**.

Table 1 – Definition of corrosion environmental exposure classes: EHE 08 [21], EN 206-1 [27] and EN 1992-1-1 [26]

Environment type	Spanish Exposure classes	European Equivalent classes	Description of the environmental exposure classes
Carbonation	IIa	XC4	High humidity on a cyclic basis or concrete surfaces subject to water contact
	IIb	XC3	Moderately humid.
Chlorides	IIIa	XS1	Areas exposed to airborne salt but not in direct contact with sea water.
	IIIb	XS2	Permanently submerged elements.
	IIIc	XS3	Tidal, splash and spray zones.

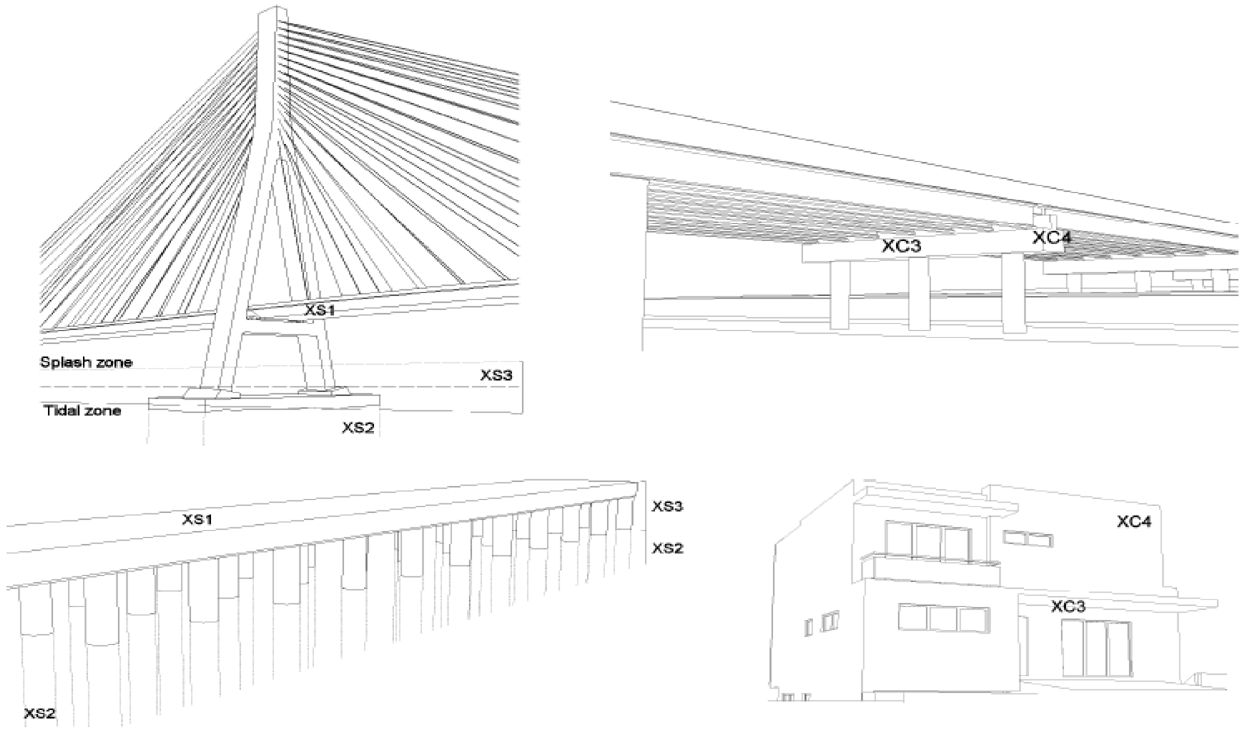

Fig. 1 – Exposure classes associated with microenvironments in different structures. Carbonation: viaduct and dwelling; Chlorides: bridge and quay.

For the five classes of **Table 1**, the calculus of the design service life was carried out based on the experimental information of materials properties from Tables 4 and 5 and considering both initiation and propagation periods. It is precisely on the propagation period that the modeling effect of corrosion inhibitors is to be understood.

All the equations, materials and environmental parameters used are those defined by the Spanish standard EHE 08 [21] and presented in the following sections for each environmental agent: carbon dioxide and chlorides.

3. DURABILITY MODELS FOR RC STRUCTURES – CORROSION

3.1 Carbonation

The equations used for the modeling of carbon dioxide diffusion are those defined, as previously mentioned, by Annex 9 of EHE 08 [21] which is one of the documents following the approach preconized by the harmonized European standards EN 206-1[27] and EN 1992-1-1 [26].

The modeling of the initiation period for carbonation corresponds to the study of CO_2 penetration into concrete. This action progresses through a diffusion process and is based on Fick's 1st law for the estimation of the carbonation depth over time, which is expressed by (Eq. (1)):

$$t_i = \left(\frac{c}{K_c} \right)^2 \tag{1}$$

where t_i (years) is the time until steel depassivation, c (mm) is the concrete cover of steel reinforcement. The parameter K_c (mm/year) is the carbonation coefficient that may be theoretically obtained by (Eq. (2)):

$$K_c = c_{env}\ c_{air}\ a\ f_{cm}{}^{b} \tag{2}$$

where c_{env} is the environment coefficient , c_{air} is the porosity coefficient and a and b are parameters defined as function of the binder type (**Table 2**). The variable f_{cm} is the mean concrete compressive strength in N/mm^2.

The propagation period is based on Faraday's law where the radius reduction factor of the steel reinforcement is obtained from the empirical equation (Eq. (3)) [21]

$$t_p = \frac{80}{\phi} \frac{c}{V_{corr}} \tag{3}$$

where t_p (years) is the time that mediates between steel depassivation and a certain loss of steel section, c (mm) is the concrete cover of steel reinforcement, ϕ (mm) is the diameter of steel reinforcement and V_{corr} (μm/year) the corrosion velocity depending on the exposure classes (**Table 3**).

Table 2 – Coefficients for carbonation modeling: Spanish standard EHE 08 [25] - Annex 9

Coefficients a and b			Coefficients c_{env} and c_{air}:			
Binder type	a	b	Environment	c_{env}	Occluded Air	c_{air}
OPC (ordinary Portland cement)	1800	-1.7	Protected from rain	1.0	< 4.5 %	1.0
OPC + 28% fly ash (FA)	360	-1.2	Exposed to rain	0.5	≥ 4.5 %	0.7
OPC + 9% silica fume (SF)	400	-1.2				
OPC + 65% blast-furnace slag (BS)	360	-1.2				

3.2 Chlorides

Within the same procedure, the initiation period resulting from chlorides action is based on Fick's 2nd law for diffusion. Although chlorides migration may also result from permeation and capillary absorption, this simplification is assumed. The Spanish standard EHE 08 [21] defines the following equations (Eq. (4) and Eq. (5)):

$$t_i = \left(\frac{c}{K_{Cl}}\right)^2 \tag{4}$$

$$K_{Cl} = \sqrt{D(t_0)\left(\frac{t_0}{t}\right)^n}\left(1 - \sqrt{\frac{C_{th} - C_b}{C_s - C_b}}\right) \tag{5}$$

where K_{Cl} can be defined as the global chloride diffusion coefficient, $D(t_0)$ = chloride diffusion coefficient at testing age t_0 (usually at 28 days = 0.0767 years NT Build 492 [30]), t = time over which diffusion takes place, C_{th} = chloride threshold content (% binder weight), C_s = chloride concentration at concrete surface (% binder wt) – see Eq. (6) and **Table 3**, C_b = initial chloride amount in the concrete mass (% binder weight) and n is the aging factor that depends on the binder type.

$$C_s\,(\%\,binder\ wt) = C_s\,(\%\,concrete\ wt)\frac{2300\ (kg/m^3)}{Binder\ \ dosage\ (kg/m^3)} \tag{6}$$

Placing Eq. (5) into Eq. (4) the initiation period may be calculated using the following expression:

$$t_i = \left[\left(\frac{1}{c}\left(1-\sqrt{\frac{C_{th}-C_b}{C_s-C_b}}\right)\right)^{-2}\frac{1}{12\ D(t_0)\ t_0^n}\right]^{\frac{1}{1-n}} \tag{7}$$

Similar to carbonation modeling, the estimation of Service Life in chloride environments may be carried out using experimental data of concrete mixes for new structures or using the results of *in situ* tests obtained from existing structures.

Moreover, given the available experimental results by Andrade [24], not only it is possible to account for the effect of the corrosion inhibitor in the propagation period t_p, by means of V_{corr} reduction, as it is also possible to account for an additional effect in the initiation period t_{i} through the increase of the chloride threshold C_{th}. According to the report by Andrade [24] it was verified an increase of the level of free chloride ions that breakdown the steel passive layer of the tested specimens before active corrosion, i.e., the end of the initiation period followed by the start of the propagation period.

The equation and variables for the estimation of the propagation period in chloride environments are the same as for carbonation exposure classes and presented above – Eq (3). However, it is worth mentioning that the type of corrosion in chloride environments is significantly different from the one induced by carbonation environments where corrosion is uniform. In chloride environments is common the development of pitting corrosion, which is non-uniform and more intensive and concentrated at different spots of steel cross-section. In Table 3, corrosion velocity V_{corr} adopted by the Spanish code EHE 08 [21] is expressively different for both environments. This code opted to consider values of corrosion velocity much higher for chloride exposure classes (10 to 25 times) when compared to values define for carbonation exposure classes. For simplification purposes, it is fair to consider that such differences in these values of uniform corrosion velocity regard intentionally the effect of pitting corrosion for classes XS1 and XS3 and might be therefore considered equivalent to non-uniform modeling.

Table 3 – Other modeling parameters according to each exposure class – EHE 08 [21] (Annex 9)

Environment type	Spanish Exposure classes	European Equivalent classes	V_{corr} (μm/year)	Cs (% concrete wt)	
Carbonation	IIa	XC4	3	-	
	IIb	XC3	2		
Chlorides	IIIa	XS1	20	Until 500 m 0.14	500 m – 5000 m 0.07
	IIIb	XS2	4	0.72	
	IIIc	XS3	50	0.50	

4. EXPERIMENTAL PROCEDURE

4.1 Introduction

The experimental work was carried out to evaluate the compressive strength and the durability properties of four concrete mixes studied in relation to the accelerated diffusion of CO_2 [28] and rapid chloride migration [29]. These concrete compositions were chosen in view of their suitability to the exposure classes according to EHE 08 [21].The tests results were to be included in the mathematical models of EHE 08 [21] (Annex 9) for estimating the service life of the studied compositions subjected to the mentioned exposure classes.

The determination of the compressive strength at the age of 28 days was carried out following the standard EN 12390-3. As for carbonation, tested samples with 100 mm diameter and 50 mm of thickness were subjected to an environment with 65% RH, 20 ºC and 5% of CO_2 air content for 14, 28, 42 and 56 days after a 28 days conditioning: 3 days curing in saturated environment and 25 days in 65% RH and 20 ºC. Based on the first Fick’s law and a linear regression, the accelerated carbonation coefficient k_{accel} is obtained and hence K_c, considering $k_{accel} \approx 7K_c$ [31].

Regarding chloride migration, the experimental procedure for the determination of the coefficient of migration followed the rapid non-steady state chloride test [29], which included cylindrical specimens with 100 mm diameter and 50 mm of thickness. Before being in a low pressure hermetic recipient and immersed in a solution of calcium hydroxide for vacuum treatment, the specimens were subjected to 14 days of drying at 20ºC and 50% of RH.

4.2 Concrete compositions

Each concrete composition included cements respecting the EN 197-1 [30]. In this standard the cements are characterized according to the proportion of clinker and other constituents (limestone filler, silica fume, fly ashes, pozzolans, blast furnace slag, etc.). The cement (binder) types used in the four concrete compositions studied, as well as the cement dosage and w/c ratio are shown in **Table 4**.

Table 4 – Studied concrete compositions and test results at the age of 28 days

Cement (binder) type	Constituents	Dosage kg/m^3	w/c	f_{cm} 1) MPa	k_{accel} 2) mm/√year	K 3) mm/√year	$D(t_0)$ 4) x10^{-12} m^2/s
CEM I (OPC)	>95% clinker	320	0.53	56.1	21.0	3.0	-
CEM II/B-L	20% L; >75% clinker	320	0.48	41.1	57.4	8.2	-
CEM III/A	60% BS; >35% clinker	340	0.45	54.8	-	-	2.3
CEM IV/B-V	40% FA; >55% clinker	340	0.45	52.1	-	-	6.4

L – limestone filler; BS – blast furnace slag; FA – fly ash

1) Cubic compressive strength. molds with 150 mm edge tested following EN 12390-1

2) It is assumed that carbonation depth x grows with square root of time t: $x=k\sqrt{t}$, hence $k_{accel}$is the slope of x vs $\sqrt{t}$ curve

3) Accelerated and 'Normal' carbonation coefficient. $k_{accel} \approx 7\,K$ based on Muntean et al. 2005 [31]

4) Chloride migration Coefficient following NT Build 492 [29]

4.3 Tests results

Test results concerning the experimental program are presented in **Table 4**, including: mean compressive strength f_{cm} value; accelerated coefficients of carbonation k_{accel} and the 'normal' coefficient of carbonation K_c and the coefficient of chloride migration $D(t_0)$.

5. SERVICE LIFE DESIGN EXAMPLES

5.1 Models input data

In order to analyze the effect of corrosion inhibitors on the design service life of RC structures, from the analytical point of view based on experimental data, several scenarios were tested as regards both mentioned environments: carbonation and chlorides.

The modeled properties with direct influence on the corrosion process that might be adjusted depending on the tested performance of the inhibitor type, following the definition of the Spanish standard EHE 08 [21] (Annex 9), are V_{corr} and C_{th}.

Table 5 shows the tests results of the chosen corrosion inhibitors obtained from the report of IETcc (Instituto Eduardo Torroja) by Andrade [24]. Of the two types of the chosen corrosion inhibitors: one is an admixture added to the concrete mass (AACI) and the other is a compound applied externally over the concrete surface of RC elements (MCI).

Table 5 – Experimental results of corrosion inhibitor admixtures tested by Andrade [24]
(Report requested by Quimilock, S.A.)

Inhibitor admixture type Commercial designation	Inhibitor admixture type	Inhibitor admixture proportion	Increase* in chloride threshold – C_{th}	Reduction* of corrosion velocity - V_{corr}
Mixed inhibitors Aminocarboxylates MCI 2005 ®	Added Admixture Corrosion Inhibitor AACI	0.60 l/m^3 concrete volume	54%	83%
Mixed inhibitors Aminocarboxylates MCI 2020 ®	Surface applied Migration Corrosion Inhibitor MCI	0.27 l/m^2 concrete surface	72%	46%

*in comparison with the reference concrete mix of the report by Andrade[24]

The definition of the concrete cover value, one of the main variables, was made in view of what is normal practice and following the deem-to-satisfy requirements of the Spanish standard EHE 08 [21] (Chapter 7). Accordingly, minimum cover is defined as the one that should be verified in any point of the steel reinforcement. In order to guarantee these minimum values, a nominal cover is preconized and defined in the design drawings (Eq. (8)).

$$c_{nom} = c_{\min} + \Delta c \qquad (8)$$

where c_{nom} is the nominal cover, c_{min} is the absolute minimum cover and Δc is the deviation as function of the quality control which in this case is defined as 10 mm, considering a standard level of quality control . **Table 6** presents the nominal cover values defined by EHE 08 [21].

Table 6 – Nominal cover c_{nom} required by EHE 08 [21] – Chapter 7 for each exposure class – mm (in)

Spanish Exposure classes	European Equivalent classes	Type of cement (binder)	Design target life t_g (25 MPa $\leq f_{ck} <$ 40 MPa)	
			50 years	100 years
IIa	XC4	CEM I (> 95% clinker)	20	30
		Other types of cement	25	35
IIb	XC3	CEM I (> 95% clinker)	25	35
		Other types of cement	30	40
IIIa	XS1	Clinker + 30%-70% BS* Clinker + 20%-40% FA* Clinker + 20% Pozz* Clinker + 6%-10% SF*	30	35
		Remaining cements	50	70
IIIb	XS2	Clinker + 30%-70% BS* Clinker + 20%-40% FA* Clinker + 20% Pozz* Clinker + 6%-10% SF*	35	40
		Remaining cements	45	**
IIIc	XS3	Clinker + 30%-70% BS* Clinker + 20%-40% FA* Clinker + 20% Pozz* Clinker + 6%-10% SF*	40	45
		Remaining cements	**	**

Notes: f_{ck} = 5% fractile of the concrete compressive strength; BS=blast furnace slag; FA=fly ash; Pozz=Pozzolans; SF= silica fume; *cement constituents according to EN 197-1 [30]; ** unsuited cover in view of concrete elements' execution.

For the implementation of the Service Life modeling, **Tables 7** and **8** – carbonation microenvironments: XC3 and XC4 – and **Tables 9** to **11** – chlorides microenvironments: XS1, XS2 and XS3 – present the values of the variables for each studied scenario, as regards the use of inhibitor:

i) Plain concrete – without corrosion inhibitor;
ii) Concrete with AACI (added admixture corrosion inhibitor);
iii) MCI (migrating corrosion inhibitor) applied over the concrete surface.

As presented in the previous chapter, four types of concrete were tested in order to quantify the durability properties as to CO_2 diffusion and chloride migration. Taking into account the aptness of the concrete mixes with regard to the Spanish deem-to-satisfy requirements, the compositions with CEM I and CEM II/B-L were designed for carbonation environments, while concrete compositions with CEM III/A and CEM IV/B-V were designed for chloride environments.

Considering carbonation classes, the variable that is changed in view of the presence of the corrosion inhibitors is the corrosion velocity V_{corr} (acting on the propagation period), which is reduced in accordance with **Table 5**. All corresponding variables are presented in **Tables 7** and **8**.

Table 7 – Carbonation class XC4 (exposed) – Calculus variables

Variables	Concrete		
	Plain	Corrosion Inhibitor (AACI)	Migrating Corrosion Inhibitor (MCI)
Corrosion Velocity, V_{corr}	**3.0** μm/yr	**0.51** μm/yr	**1.62** μm/yr
Cover, c (c_{nom})	25 mm		
Carbonation coeff., K_C	CEM I[**]: 1.5[*] mm/$\sqrt{yr}$		
	CEM II/B-L[***]: 4.1[*] mm/$\sqrt{yr}$		
Steel bar diameter, ϕ_0	8 mm		

[*] for RC elements exposed to rain the standard EHE 08[28] affects K_c with a reduction environment coefficient of 0.5

[**] CEM I – cement type according to EN 197-1[31]: >95% clinker content

[***] CEM II/B-L – cement type according to EN 197-1[31]: 20% limestone filler; > 75% clinker content

$V_{corr(AACI)} = (1-0.83)\ V_{corr(plain)} = 0.17\ V_{corr(plain)}$

$V_{corr(MCI)} = (1-0.46)\ V_{corr(plain)} = 0.54\ V_{corr(plain)}$

Table 8 – Carbonation class XC3 (protected) – Calculus variables

Variables	Concrete		
	Plain	Corrosion Inhibitor (AACI)	Migrating Corrosion Inhibitor (MCI)
Corrosion Velocity, V_{corr}	**2.0** μm/yr	**0.34** μm/yr	**1.08** μm/yr
Cover, c (c_{nom})	30 mm		
Carbonation coeff., K_C	CEM I: 3.0 mm/$\sqrt{yr}$		
	CEM II/B-L: 8.2 mm/$\sqrt{yr}$		
Steel bar diameter, ϕ_0	8 mm		

With respect to chlorides microenvironments, the values of all variables are shown in **Tables 9** to **11**. In this case, two variables are changed: the chloride threshold C_{th} (acting on the initiation period) and the corrosion velocity V_{corr} (acting on the propagation period) (**Table 5**). In the particular case of submerged elements – exposure class XS2 – the use of migration corrosion inhibitors (MCI) is not considered since it is not applicable on site.

Table 9 – Chlorides class XS1(aerial) – Calculus variables

Variables	Concrete		
	Plain	Corrosion Inhibitor (AACI)	Migrating Corrosion Inhibitor (MCI)
Chloride threshold, C_{th}	**0.4%** (binder wt)	**0.62%** (binder wt)	**0.69%** (binder wt)
Corrosion Velocity, V_{corr}	**20** μm/yr	**3.4** μm/yr	**10.8** μm/yr
Cover, c (c_{nom})	35 mm		
Migration coefficient, $D(t_0)$	CEM III/A: 2.3×10^{-12} m^2/s		
	CEM IV/B-V: 6.4×10^{-12} m^2/s		
Chloride surface amount, C_s	0.95% (binder wt)		
Initial chloride content, C_i	0% (binder wt)		
Aging factor, n	0.50		
Testing age of concrete, t_0	28 days		
Steel bar diameter, ϕ_0	8 mm		

[*] CEM III/A – cement type according to EN 197-1 [30]: 60% blast furnace slag; >35% clinker content

[**] CEM IV/B-V – cement type according to EN 197-1 [30]: 40% fly ash; > 55% clinker content

$C_{th(AACI)} = 1.54\ C_{th(plain)}$

$C_{thMCI)} = 1.72\ C_{th\ (plain)}$

$V_{corr(AACI)} = (1-0.83)\ V_{corr\ (plain)} = 0.17\ V_{corr\ (plain)}$

$V_{corr(MCI)} = (1-0.46)\ V_{corr\ (plain)} = 0.54\ V_{corr\ (plain)}$

Table 10 – Chlorides class XS2 (submerged) – Calculus variables

Variables	Concrete		
	Plain	Corrosion Inhibitor (AACI)	Migrating Corrosion Inhibitor (MCI)
Chloride threshold, C_{th}	**0.4%** (binder wt)	**0.62%** (binder wt)	**Not applicable**
Corrosion Velocity, V_{corr}	**4** μm/yr	**0.68** μm/yr	**Not applicable**
Cover, c (c_{nom})	40 mm		
Migration coefficient, $D(t_0)$	CEM III/A: 2.3×10^{-12} m^2/s		
	CEM IV/B-V: 6.4×10^{-12} m^2/s		
Chloride surface amount, C_s	4.87% (binder wt)		
Initial chloride content, C_i	0% (binder wt)		
Aging factor, n	0.50		
Testing age of concrete, t_0	28 days		
Steel bar diameter, ϕ_0	8 mm		

Table 11 – Chlorides class XS3 (tidal/splash) – Calculus variables

Variables	Concrete		
	Plain	Corrosion Inhibitor (AACI)	Migrating Corrosion Inhibitor (MCI)
Chloride threshold, C_{th}	**0.4%** (binder wt)	**0.62%** (binder wt)	**0.69%** (binder wt)
Corrosion Velocity, V_{corr}	**50** µm/yr	**8.5** µm/yr	**27** µm/yr
Cover, c (c_{nom})	45 mm		
Migration coefficient, $D(t_0)$	CEM III/A: 2.3x10^{-12} m^2/s		
	CEM IV/B-V: 6.4x10^{-12} m^2/s		
Chloride surface amount, C_s	3.38% (binder wt)		
Initial chloride content, C_i	0% (binder wt)		
Aging factor, n	0.50		
Testing age of concrete, t_0	28 days		
Steel bar diameter, ϕ_0	8 mm		

5.2 Probabilistic method implementation

The conceptual basis of a probabilistic-based approach is to ensure that the required performance is maintained throughout the intended life of the structure along with the optimization of the incurred service life costs [33]. This purpose is followed attempting a realistic assessment of the interrelation between design, durability, future maintenance and repair.

For the implementation of this method limits must be established. Accordingly, most European countries have adopted what the EN 1990–Eurocode 0 [34] establishes, i.e., a probability of failure of 6.7%.

Limit state function and variables' distribution laws

Eqs. (9) and (10) express the limit state function *g(x)* used for the implementation of the Monte Carlo method.

Carbonation modeling of design service life

$$g(x) = t_L - t_g = \left\{ \left(\frac{c}{K_c} \right)^2 + \frac{80}{\phi} \frac{c}{V_{corr}} \right\} - t_g \qquad (9)$$

Chloride modeling of design service life

$$g(x) = t_L - t_g = \left\{ \left[\left(\frac{1}{c} \left(1 - \sqrt{\frac{C_{th} - C_b}{C_s - C_b}} \right) \right)^{-2} \frac{1}{12\, D(t_0)\, t_0^n} \right]^{\frac{1}{1-n}} + \frac{80}{\phi} \frac{c}{V_{corr}} \right\} - t_g \qquad (10)$$

The probability of failure corresponds to the probability that the limit state function is negative:

$$P_f = P[g(x) < 0] \qquad (11)$$

The probabilistic analysis of service life distribution is carried out using the statistical parameters of the involved variables: mean values (**Tables 7** to **11**) and standard deviation with their distribution laws (**Table 12**). The mean values of each variable are based on the experimental tests results and the data of Andrade [24] and EHE 08 [21], while the values adopted for the standard deviation are based on [9,10,23,32].

The implementation of the cited method was carried out by means of the Monte Carlo method with 1 000 000 generated values for each random variable.

Table 12 – Standard deviation and Distribution laws of the variables

Exposure classes	Variable	Standard deviation	Distribution
All classes	c (c_{nom})	8 mm	Log-normal
	V_{corr}	0.20 μ	Log-normal
	ϕ_0	-	Deterministic
XC3 and XC4 (carbonation)	K_C	0.30μ	Log-normal
XS1, XS2 and XS3 (chlorides)	$D(t_0)$	0.20μ	Normal
	t_0	-	Deterministic
	C_{th}	0.12 μ	Normal
	C_S	0.20 μ	Normal

μ - mean value (**Tables 7** to **10**)

6. RESULTS AND DISCUSSION

The present discussion is carried out in light of the corrosion modeling presented by the current Spanish regulation EHE 08 [21] for reinforced concrete structures. As remarked before, the modeling equations present some simplifications that have relevant influence on the results and are worth to outline. These simplifications include the same equation for the propagation period (Eq. (3)), whether the environment is of uniform corrosion or pitting corrosion – though with significantly different values of corrosion velocity (Table 3), and the same corrosion velocity regardless the cement type.

In addition, considering recent data form Andrade [24], the variables that are directly affected by corrosion inhibitors – C_{th} and V_{corr} – are included in the equations defined for chlorides environment (Eqs. (7) and (10)), while for carbonation modeling only V_{corr} is taken into account (Eq. (3) – propagation) with no variable (inhibitor dependent) being defined for the initiation period. This means that for carbonation the modeling results might express less variation when considering the inhibitors.

Another important remark is related to fact that there is not yet significant evidence of the performance of corrosion inhibitors throughout time. The implementation of the modeling equations and the inhibitors' properties assumes that their performance of is kept constant with time both for the initiation period and the propagation period.

Based on the previous, the performance of the analyzed compositions is expressed in **Figs. 2** to **6** as result of the implementation of the probabilistic calculus using the modeling of EHE 08 [21].

The estimated design service life is represented by the probability of failure P_f in function of time. **Figs. 7** and **8** present the design service life results where P_f reached 6.7%, where the proportion of both initiation and propagation periods is also expressed. From **Figs. 2** to **8** it can be seen that there are significant differences for each composition if the effect of corrosion inhibitors is regarded. Considering the same level of probability of failure P_f, compared to concrete mixes without inhibitors, there is an increase in the design service life values for concrete compositions with AACI and MCI.

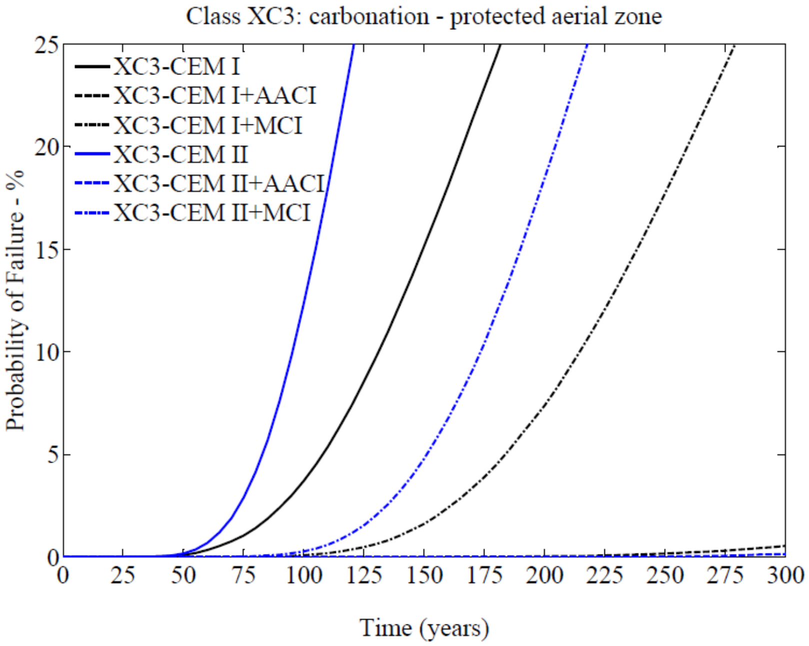

Fig. 2 – Probabilistic Service life results: exposure class XC3 – protected aerial zone

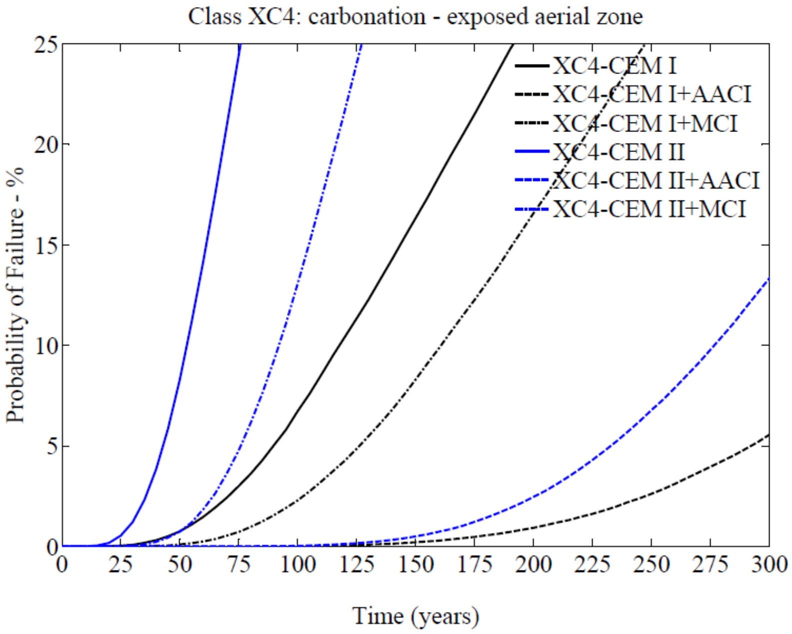

Fig. 3 – Probabilistic Service life results: exposure class XC4 – exposed aerial zone

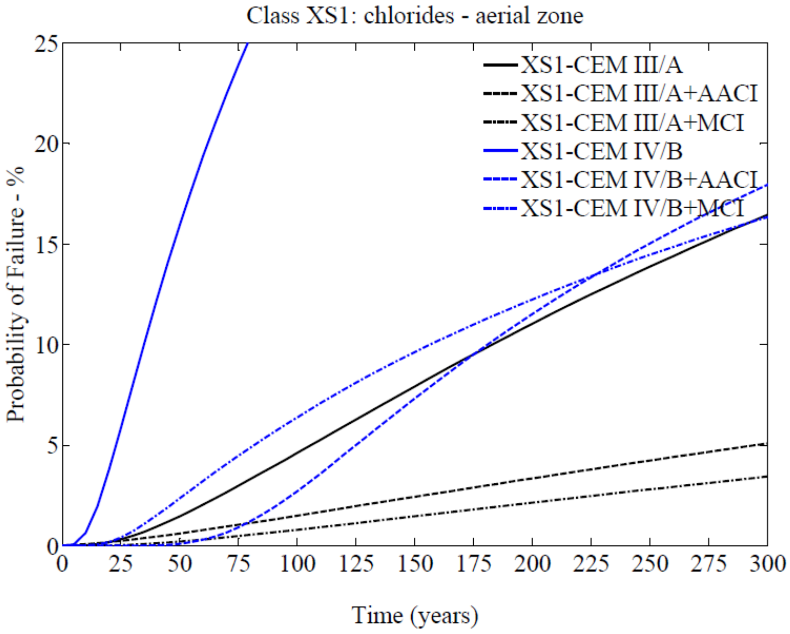

Fig. 4 – Probabilistic Service life results: exposure class XS1 – aerial zone

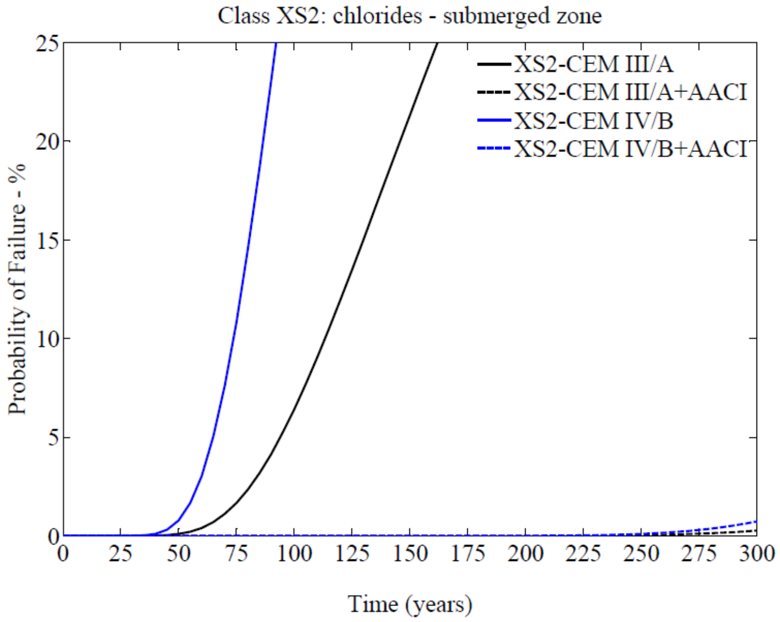

Fig. 5 – Probabilistic Service life results: exposure class XS2 – submerged zone

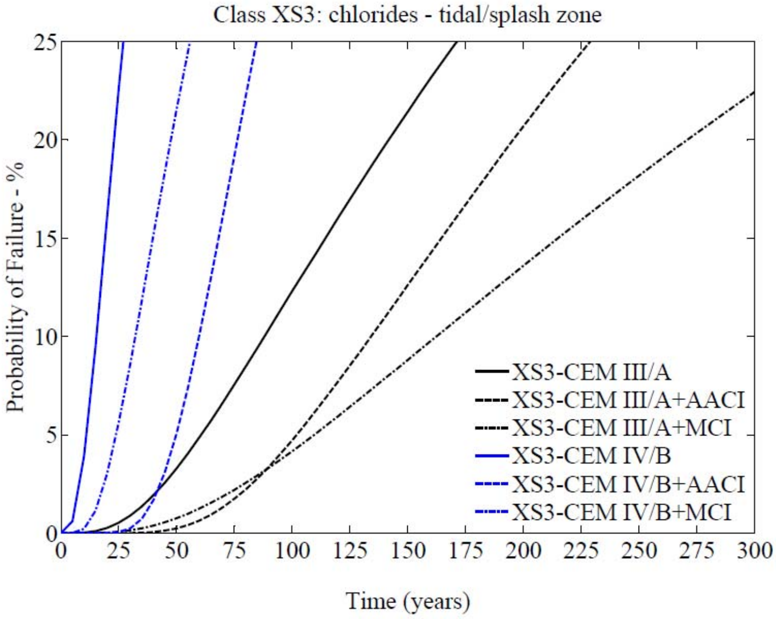

Fig. 6 – Probabilistic Service life results: exposure class XS3 – tidal/splash zone

Considering carbonation exposure classes XC3 (IIb) and XC4 (IIa), the results of design service life for compositions with AACI present enhanced performance when compared to plain concrete mixes and mixes with surface applied MCI (**Figs. 2** and **3**). This difference is of such scale for class XC3 that the curves representing the performance of concrete mixes with AACI show a modeling result above 300 years of design service life for both CEM I and CEM II/B-L (**Fig. 7**). This is explained by the fact that, as mentioned before, the modeling effect of the inhibitors in carbonation environments is considered only in the propagation period, since there is no available data so far as regards the influence in the initiation period (pore blocking action). The results shown in **Figs. 2**, **3** and **7** present performance differences consistent with the experimental results of the inhibitors analyzed (**Table 5**). It should be, however, highlighted that, concerning durability of RC structures, realistic service life values are not expected to exceed 100-120 years if up-to-date criteria are followed. Higher values should then be analyzed with wariness.

Concerning chlorides environment classes XS1 (IIIa), XS2 (IIIb) and XS3 (IIIc), the effect of corrosion inhibitors is modeled in both periods: initiation (Eq. (7)) – through change in C_{th} values – and propagation (Eq. (3)) – changing V_{corr} values. In any case it is evident that for classes XS1 (aerial) and XS3 (tidal) the initiation period is prevailing, while for class XS2 the propagation has the highest share of the complete service life. The improvement in the performance of the compositions where corrosion inhibitors are modeled is clear when these are compared with plain concrete performance (**Figs. 4** to **6**). It is also evident that compositions with the effect of AACI and MCI show close performance for both cement types – CEM III/A and CEM IV/B – for classes XS1 and XS3. Such similarity, in comparison with carbonation exposure classes, seems to result from a compensation given by the change in the variable C_{th} since for this parameter MCI inhibitor shows, in its turn, improved performance according to the referenced tests results (**Table 3**). In the particular case of RC submerged elements – exposure class XS2 – the analysis is made for plain concrete and concrete with AACI (MCI is not applicable) and it is possible to note (**Fig. 5**) that there is a huge difference for both cement types. This outstanding improvement is explained by the influence of the inhibitor AACI on the properties of the concrete that are directly related with the initiation period t_i. In other words, with AACI the initiation period becomes the larger share of contribution to the total design service life (**Fig. 8**). Accordingly, and taking into account the results of chlorides environments (**Fig. 8**) and specially those of tidal/splash exposure (class XS3), the contribution of the propagation period is almost negligible.

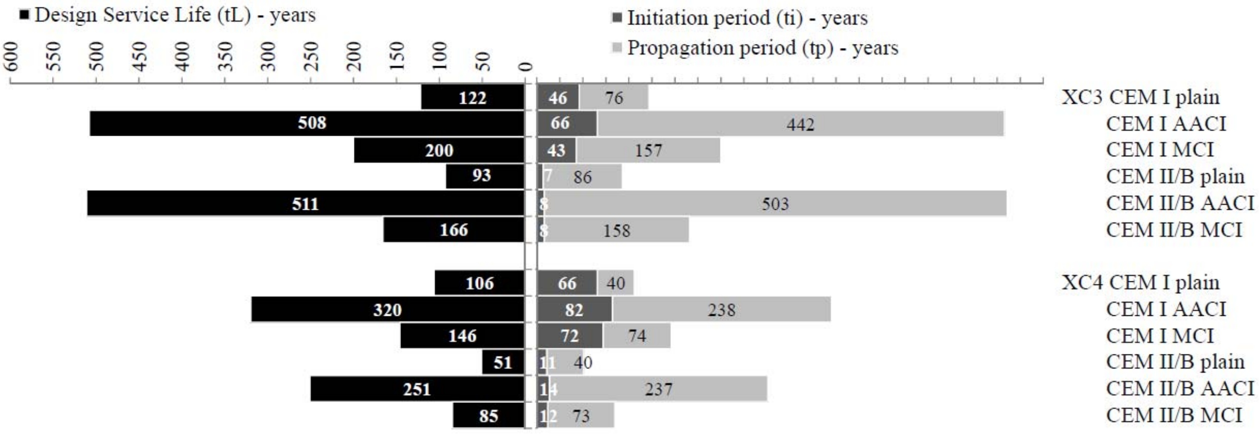

Fig. 7 – Design Service Life t_L, initiation period t_i and propagation period t_p for P_f=6.7%.

Exposure classes XC3 and XC4

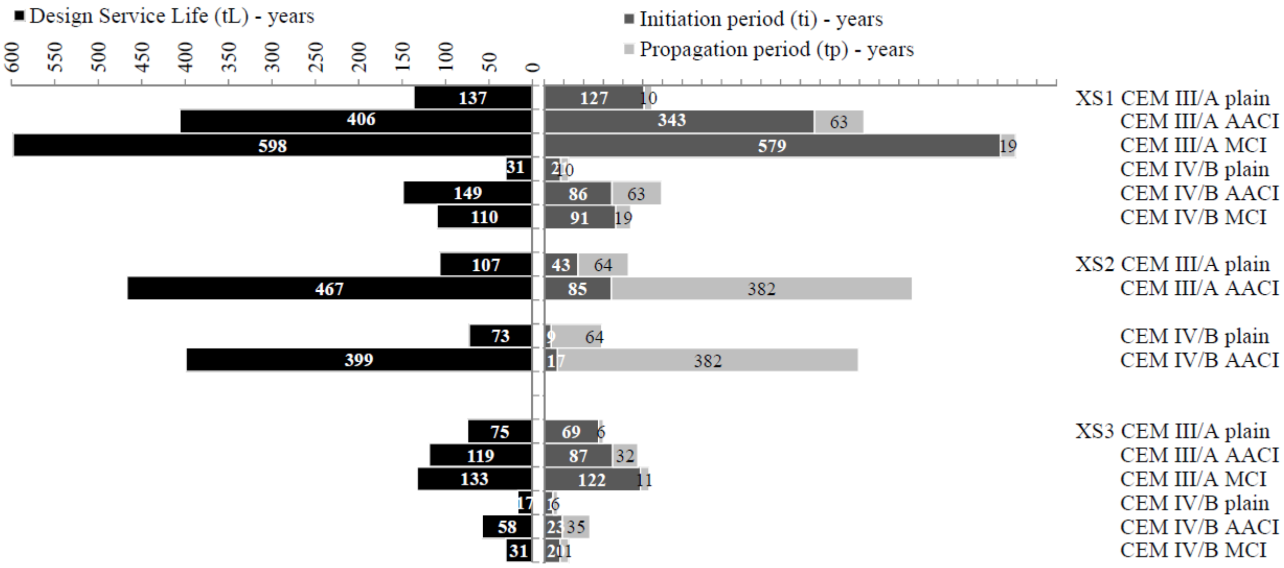

Fig. 8 – Design Service Life t_L, initiation period t_i and propagation period t_p for P_f=6.7%.

Exposure classes XS1, XS2 and XS3

7. CONCLUSIONS

The presented work refers to the implementation of design service life models taking into account the effect of corrosion inhibitors based on recent research [24] and on tested concrete mixes suited for RC structures in different environments. This analysis was developed based on equations and parameters of the European/Spanish standards and guidelines [21,23] considering corresponding environments and construction characteristics.

The overall conclusions are drawn bellow:

- All cases show an increase in the design service life values for the probability of failure P_f considering the influence of corrosion inhibitors;
- In carbonation environments – classes XC3 and XC4, compositions with AACI present outstanding performance in comparison with plain concrete mixes and with mixes with surface applied MCI. For all cases the propagation period has the largest share of the whole calculated design service life;
- As regards classes XS1, XS2 and XS3 – chlorides environments, both initiation and propagation periods are affected by the presence of corrosion inhibitors when modeling equations are implemented. This effect results from changing the values of C_{th} for the initiation part of the modeling and at the same time from changing the values of V_{corr}

for the propagation part. It is though noteworthy the effect of corrosion inhibitors for the submerged environment – class XS2 – where the propagation period is significantly higher than the initiation period.

Due to its specific surrounding conditions, submerged elements present very slow corrosion progress and therefore class XS2 might not constitute the main concern in RC structures. On the other hand, aerial and tidal environments are indeed the focus of the main problems as regards deterioration and it is in these cases that the use of corrosion inhibitors becomes important, especially if tidal/splash areas are considered.

- It appears that the use of AACI shows outstanding improvement when compared with RC elements without any corrosion inhibitor (plain) or even with migrating inhibitors (MCI). This difference comes mostly from the contribution on the initiation period – inhibition of diffusion of aggressive agents. However, the use of AACI is limited in the case of existing structures, since only in those cases where traditional repair works replacing contaminated concrete mass this product can be used. In those cases where the aim of owners and designers is the protection of contaminated existing structures with no intrusive intervention, MCI presents itself as the only adequate solution within this type of materials. Nevertheless, its action is in this case restricted to the propagation period.

NOTATION:

a = parameter defined by EHE 08 as function of binder type

b = parameter defined by EHE 08 as function of binder type

c = concrete cover which on the edge of steel passivation equals carbonation depth

c_{air} = porosity coefficient

C_b = initial chloride % by binder weight in concrete mass

c_{env} = environment coefficient

c_{min} = absolute minimum cover

c_{nom} = nominal cover (mean value)

C_S = chloride % by binder weight at concrete surface

C_{th} = chloride threshold % by binder weight

$D(t_0)$ = chloride diffusion coefficient

f_{cm} = mean concrete compressive strength

$g(x)$ = limit state function

k_{accel} = accelerated carbonation coefficient

K_c = carbonation coefficient

K_{Cl} = global chloride diffusion coefficient,

n = aging factor

P_f = probability of failure

t = time over which diffusion takes place

t_0 = testing age of non-steady state chloride migration test

t_g = target period for a given probability of failure

t_i = time until passivation - initiation period

t_L = design service life

t_p = time between steel passivation and a certain section loss - propagation period

V_{corr} = steel corrosion velocity

AACI = admixture added corrosion inhibitor

MCI = migrating corrosion inhibitor

Δc = deviation as function of the quality control

ϕ = diameter of steel reinforcement bars

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