Carbonation Service Life modelling of RC structures for concrete with portland and blended cements.

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Abstract

The presented work aims at studying the modelling of long term performance of concrete compositions with different proportions of clinker as regards the diffusion of CO_2 in concrete – carbonation. The replacing constituents of clinker that will be part of the binder in each concrete composition are limestone filler and low calcium fly ash (FA). The used percentage of FA by weight of binder was of 50%. Concrete compositions were made following standard prescribed requirements to attain service lives of 50 and 100 years as regards concrete performance against reinforcing steel corrosion. Test results of compressive strength and carbonation depth are reported at different curing ages of 28, 90, 180 and 365 days. Carbonation results were used for the implementation of modelling equations in order to estimate the design service life regarding reinforcing steel corrosion. Two performance-based methods were used: safety factor method and probabilistic method, and their results compared with the traditional prescriptive approach. At the age of 28 days the composition with OPC is the only one that reaches the target periods of 50 or 100 years. For the probabilistic method, different curing age results were analysed. For the tested results at 90, 180 and 365 days of age the reliability of some of the compositions with blended cements is within the minimum required, although still far from the higher performance of concrete with OPC.

Keywords: concrete carbonation, design service life, durability, fly ash blended cement, reinforced concrete corrosion.

1. Introduction

There is a need to reduce the presence of clinker in commercialized cement, considering that each ton of produced clinker releases to the atmosphere nearly 800 kg of CO_2 . This has substantial effect on cement production costs and moreover on the environment.

Furthermore, after penetration by diffusion from the external environment, carbon dioxide (CO_2) reacts with the calcium hydroxide present in hydrated concrete forming calcium carbonate. This reaction, known as carbonation, lowers the alkalinity of the concrete breaking the passive layer around the steel reinforcement that prevents corrosion.

Important developments have been taking place considering the modelling of the service life of reinforced concrete (RC) structures as regards corrosion of steel reinforcement due to carbonation [1-8].

Based on reference documents [2,3,7] the Portuguese Standard NP EN 206-1 [9] for the design of concrete compositions includes two alternative specifications – prescriptive [10] and performance-based [11] – in view of environmental exposure.

The performance–based specification makes no restriction concerning concrete constituents and dosage. The criterion is related to the modelling lifetime result (service life) based on testing results of accelerated carbonation on concrete samples of the designed concrete composition. This means that there is some flexibility in using water/binder ratios different to those imposed by traditional prescriptive approach ratio or different dosage and types of cement, including those blended with supplementary cementitious materials such as fly ash (FA).

The use of FA blended cements in concrete has several environmental benefits, such as material recycling and energy saving. Recent works have been carried out focusing permeability and carbonation of high-

performance concrete and, despite some of the mentioned enhancements, increasing FA content leads to increasing carbonation [12; 13, 14, 15].

Regarding time effect, some authors showed that the high amount of hydroxides in concrete and therefore a high presence of alkali might not diminish the carbonation rate [16, 17]. As to blended cements (lower presence of hydroxides), it is worth to outline that the effect of time on concrete is related with the period that these blended cements need to develop their hydraulic and pozzolanic properties [18].

Considering design service periods of 50 and 100 years for different RC structures and the use of blended cements, doubts still remain whether the traditional design of concrete with prescribed composition is a viable way or if performance-based design may lead to more realistic estimates of RC durability. The article presents results that include strength and carbonation of prescribed concrete compositions with OPC, limestone cement (PC-L) and FA blended cement according the prescriptive specification LNEC E464 [10] for ages of 28, 90, 180 and 365 days. Additionally, modelling results of service life are presented based on the performance-based specification LNEC E465 [11] using carbonation testing values. Two performance-based methods were implemented for all ages: safety factor method and probabilistic method.

2. Definition of design service life

2.1 Prescriptive definition

The prescriptive methodology LNEC E464 [10] sets the limits of the concrete constituents (maximum w/c ratio, minimum cement dosage and cement type), the minimum compressive strength and the concrete cover thickness for a design working life of 50 years (target period) under the environmental exposures in issue – Eurocode 2 [19] defines and describes environmental exposure classes in view of the aggressive agent. For carbonation induced corrosion four classes are defined and described: XC1; XC2; XC3 and XC4 (Table 1).

Exposure class	Description	Informative examples where exposure classes may occur
XC1	Dry or permanently wet	Concrete inside buildings with low air humidity Concrete permanently submerged in water
XC2	Wet, rarely dry	Concrete surfaces subject to long-term water contact Many foundations
ХСЗ	Moderate humidity	Concrete inside buildings with moderate or high air humidity External concrete sheltered from rain
XC4	Cyclic wet and dry	Concrete surfaces subject to water contact, not within exposure class XC2

Table 1 – Environmental exposure classes for carbonation induced corrosion (Eurocode 2: EN 1992-1-1 [19])

The same prescribed limits of the concrete composition and 10 mm added to the 50 years concrete cover permit, according to this specification, a design working life of 100 years. The specification LNEC E465 [11], following the guidelines of Eurocode 2 [19], classifies the minimum durability concrete cover— $c_{min,dur}$ — for reinforced concrete structures according to structural classes with which structures' design working life and type are associated [20]. Table 2 presents the defined limits according to the Portuguese specification [10].

Table O Duagavinting limits fo	www.eucline.life_of_CO.ve	ana /I NEC E4C4 0004 [4C	11
Table $2 - Prescriptive limits to$	or working life of 50 ye	ais (lineo e464 2004 10	J))

Cement Type	CEM I (Re	ference): CE	EM II/A		CEM II/B: (CEM III/A		
Exposure Class	XC1	XC2	XC3	XC4	XC1	XC2	XC3	XC4
[minimum nominal cover [minimum durability concrete cover] (mm)*	25 [15]	35 [25]	35 [25]	40 [30]	25 [15]	35 [25]	35 [25]	40 [30]
Maximum w/c	0.65	0.65	0.60	0.60	0.65	0.65	0.55	0.55
Minimum cement dosage (kg/m ³)	240	240	280	280	260	260	300	300
Minimum strength class	C25/30	C25/30	C30/37	C30/37	C25/30	C25/30	C30/37	C30/37
	LC25/28	LC25/28	LC30/33	LC30/33	LC25/28	LC25/28	LC30/33	LC30/33

*c_{nom} = c_{min,dur} + 10 mm (EN 1992-1-1, NP EN 206-1)

2.2 Performance-based definition

There is a lack of understanding of the consequences associated with the prescriptive approach of the specification LNEC E464 [10], which means that there is lack of clear understanding of in-service durability performance of a structure at the design stage.

Therefore, specification LNEC E465 [11] has introduced a performance-based approach that involves a thoughtful and realistic assessment of the correlation between design, durability along with future maintenance and repair.

The basis of such an approach is to ensure that the required performance is maintained throughout the intended life of the structure along with the optimization of the inherent lifetime costs [21].

Following these performance-based specifications, the design of concrete compositions can be carried out through performance-based indicators as an alternative to the definition of the quantities of its constituents. In fact, since each composition has to be tested and its results analysed, there are no limits whatsoever for the constituents' type and quantity.

Having into account the typical deterioration model as regards corrosion of steel into concrete [21], in which two periods are clearly distinguished: *initiation period* – external agents penetrate into concrete up to the level of reinforcing steel and *propagation period* – onset of steel corrosion within the concrete, the performance-based approach criterion relies on the probability of a deterioration agent attaining a certain depth and/or quantity or the probability of its effect attaining a certain level of deterioration.

In either case this probability (of failure) cannot surpass the values associated with a so called limit state, defined in standards or codes. Table 3 shows the maximum values of probability of failure P_f and the corresponding maximum reliability index β established by both Eurocode 0 [23] and the Portuguese specification LNEC E465 [11] for three different reliability classes RC3 RC2, RC1 [23].

Since this probability P_f assumes extremely reduced values, it is common to define the probability of failure through the reliability index β (Eq. 1) [1, 24].

$$P_f = \Phi\left(-\beta\right) \tag{1}$$

The Ultimate Limit State (collapse) is not considered by the LNEC E465 [11] for corrosion deterioration, while the Eurocode 0 considers only the limit state associated to serviceability for reliability class RC2.

Reliability classes	ULS		SLS	
	Eurocode 0	LNEC E465	Eurocode 0	LNEC E465
RC1	3.3 / 5 x10 ⁻⁴	_	-	1.2 / 1.2x10 ⁻¹
RC2	3.8 / 7 x10 ⁻⁵	_	1.5 / 7 x10 ⁻²	1.5 / 7 x10 ⁻²
RC3	3.3 / 1 x10 ⁻⁵	_	-	2.0 / 2 x10 ⁻²

Table 3 – Minimum values of β / maximum values of P_f

ULS – ultimate limit state

SLS – serviceability limit state

In view of the previous, tests results are included in mathematical models in order to perform a lifetime estimation regarding the type of action—chlorides [24] or carbonation [25]. The following sections will present the existing service-life predictive models based on durability indicators for carbonation induced corrosion and the following criteria of acceptance or failure, in view of Portuguese standards [9,11].

2.2.1 Modelling of the initiation period for carbonation

The initiation period concerning the penetration of carbon dioxide is based on the model of CEB [3] which the specification LNEC 465 [11] adopted considering the Portuguese environment. This model expresses the diffusivity of hardened concrete and it relates the concrete carbonation with time as follows:

$$x = \sqrt{\frac{2 \times \Delta C}{R_{C65}}} t \sqrt{k_0 k_1 k_2} \left(\frac{t_0}{t}\right)^n$$
(2)

Where due to carbonation, steel depassivation starts when a depth *x* equals the concrete cover *c* of the reinforcing steel. R_{C65} ((kg/m³)/(m²/year)) defines the carbonation resistance obtained from the accelerated test [27].

$$R_{C65} = \frac{2 \times C_{accel} t_1}{X_1^2} = \frac{2 \times C_{accel}}{k^2}$$
(3)

where X_1 is the carbonation depth (m), t_1 is the time (years), C_{accel} is the carbon dioxide concentration (90x10⁻³ kg/m³).

 ΔC =0.7x10⁻³ kg/m³ (difference of carbon dioxide concentration between the exterior and the carbonation front), k_0 =3 is a constant value that accounts for the testing method and conditions [11,27] k_1 is the constant that accounts for the presence of relative humidity [11], k_2 is the constant that accounts for the curing influence: 1.0 for normalized cure and 0.25 for a 3 day period of curing [11], t_0 is the reference period = 1 year and *n* is the parameter that accounts for the wet/dry cycle influence in time [11]. Table 4 shows the values of parameters k_1 and *n* for all exposure classes.

Table 4 – Constant parameters k_1 and n for carbonation exposure classes [11]

Parameter	XC1	XC2	XC3	XC4
<i>k</i> ₁	1.00	0.20	0.77	0.41
п	0	0.183	0.02	0.085

The end of the initiation period corresponds to the depassivation due to carbonation and hence from Eq. (2) t becomes the initiation period t_i expressed as:

	$R_{acc} c^2$	<u>1</u> -2 <i>n</i>
$t_i =$	$\frac{1.4 \times 10^{-3} k_0 k_1 k_2 t_0^{2n}}{1.4 \times 10^{-3} k_0 k_1 k_2 t_0^{2n}}$	(4)

2.2.2 Modelling of the propagation period after carbonation

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The propagation period corresponds to the beginning of corrosion of steel reinforcement within the concrete. This causes the loss of section of steel bars which results into loss of strength of the steel reinforcement itself. Additionally, there is an increase of volume of the corrosion product around steel bars which leads to internal stresses against the surrounding concrete and consequent loss of bond between concrete and steel [28].

In either case cracks may easily develop. Moreover, the access of oxygen and moisture to the steel reinforcement is eased by the presence of these cracks, which may well increase the corrosion rate. The estimate of the propagation period depends on the definition of different levels of corrosion, established as limits, depending, in its turn, on crack width. Even though the modelling of the propagation is by some means difficult due to the complexity of the factors involved, it can be simplified by the quantification of the corrosion rate.

The following equations and definitions are proposed by the specification LNEC E465 [11] of the National Annex of the NP EN 206-1 [9]

Farady's law

 $\Delta r = 0.0115 \ I_{corr} \ t_p$

[29] where Δr (mm) is the reduction of the radius of the ordinary steel reinforcement, I_{corr} (μ A/cm²) is the corrosion rate, and t_p (years) is the propagation period.

Empirical equation for the estimate of the radius reduction causing first surface cracking

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$$\Delta r = \frac{1}{1000} \left(74.5 + 7.3 \frac{c}{\phi_0} - 17.4 f_{td} \right)$$
(6)

[30] where f_{td} (MPa) is the concrete tensile strength (obtained from the Brazilian test), with values of 3 and 4 MPa which can be considered in view of the compressive strength class [19] of each proposed concrete composition. Cover depth is represented by c (mm) and ϕ_0 (mm) is the initial diameter of ordinary reinforcement bar.

Influence of the corrosion type on steel section reduction

$$\phi_0 - \phi = \alpha \,\Delta r \tag{7}$$

being α = 2 for generalized corrosion (associated with carbonation).

Considering y (%) as the relative reduction of the steel reinforcement radius calculated from:

$$\frac{\phi_0 - \phi}{2} = \frac{y}{100} \phi_0 \tag{8}$$

The final equations resulting from the previous considerations are the following:

$$t_p = \frac{y \phi_0}{1.15 \,\alpha \, I_{corr}} \tag{9}$$

Where y(%) is obtained as follows:

,

$$y = \left(74.5 + 7.3\frac{c}{\phi_0} - 17.4f_{td}\right)\frac{0.2}{\phi_0}$$
(10)

The I_{corr} values used to obtain the propagation period depend on the different corrosion levels and on the exposure classes (Table 5).

Table 5 – I_{corr} for different corrosion levels and exposure classes XC [11]

Exposure classes	Corrosion levels	Corrosion current density <i>I_{corr}</i> (μΑ/cm ²)
XC1	Negligible	< 0.1
XC2	Low	0.1 – 0.5
XC3	Negligible	< 0.1
XC4	Low / Moderate	0.1 - 0.5 / 0.5 - 1

(5)

2.2.3 Partial safety factor method (semi-probabilistic)

The partial safety factor method of the performance-based specification [11] is based on Eq. (2) for the modelling of the initiation period. It includes a deterministic calculus using calibrated reduction factors (safety factors) in order to introduce the probabilistic nature of the problem (semi-probabilistic method).

The definition of the safety factors (table 6) by the referred specification is related to the different reliability levels and based on the assumption that the lifetime of a structure is represented by a Log-normal statistical distribution with a coefficient of variation (COV) of 0.5 [2].

Table 6 – Safety factor γ values for each reliability class [11]

Reliability class	Safety factor value
RC1	2.0
RC2	2.3
RC3	2.8

Before the reduction by means of the safety factors, in this particular case, the calculus of t_i is not fully deterministic since the concrete cover value is based on the $c_{\min,dur}$ which is considered a characteristic value instead of a mean value c_{nom} [7].

In the modelling equations, for the majority of the variables, mean values are used. However, for the concrete cover the deterministic calculus considers a characteristic value $c_{\min,dur}$ [7]. The initiation period obtained by a deterministic calculation is then divided by a safety factor γ associated with a required reliability level and added to the predefined minimum propagation periods [11].

In view of the referred definitions, the specification LNEC E465 [11] specifies different minimum propagation periods t_p for each exposure class and different minimum required target periods t_g (Table 7).

Considering that the requirement for service life design is t_L/t_g , it is finally possible to calculate the design service life t_L as:

$$t_L = \frac{t_i}{\gamma} + t_p \tag{11}$$

where t_i is the initiation period obtained from Eq. 4, γ is the safety factor according to Table 6 and t_p is the propagation period given in Table 7. With regard to the propagation modelling [11] establishes the estimated minimum propagation period for each environmental class and expected service lives of 50 and 100 years.

Target servisse life - t_g t_g = 50 years		$t_{g} = 100$ years
Exposure class	t _p estimated (years)	t_{ρ} estimated (years)
XC1	>100	>100
XC2	10	20
XC3	45	90
XC4	15 - dry region	20 - dry region
	5 - wet region	10 - wet region

2.2.4 Probabilistic method

The probabilistic analysis of lifetime distribution is carried out using the limit state function with respect to carbonation diffusion (Eq. 12) as well as the statistical parameters of the involved variables – mean and coefficient of variation (CoV) (Table 14). The mean values of each variable are based on the experimental program and LNEC E465 [11], while the values adopted for the standard deviation are based on [7] and [8].

As mentioned before, the concrete cover specified for a target period t_g of 100 years is obtained from the one specified for 50 years plus 10 mm. Equation (12) expresses the limit state function used for the implementation of the Monte Carlo method where λ represents the model uncertainty:

$$g(x) = t_L - t_g = \lambda \left\{ \left[\frac{R_{C65} c^2}{1.4 \times 10^{-3} k_0 k_1 k_2 t_0^{2n}} \right]^{\frac{1}{1-2n}} + \frac{y \phi_0}{1.15 \alpha I_{corr}} \right\} - t_g$$
(12)

Hence, the probability of failure may be expressed as the probability that the limit state function is negative:

$$P_f = P\left[g\left(x\right) < 0\right] \tag{13}$$

3. Experimental program

3.1 Introduction

The purpose of the experimental part of this study is to evaluate the properties of blended FA concrete compositions, in comparison to ordinary Portland cement (OPC, only clinker as binder) and PC–L (binder: clinker and limestone filler), concerning its durability as regards carbonation beyond 28 days of age. Cement types CEM I 42.5R (OPC) and CEM II/A-L 32.5N (PC–L) are the most commercialized cements in the Portuguese market.

Two sets of reference concrete compositions with cement of high clinker content were defined, complying with EN 197-1 [31] – CEM I 42.5R (OPC) and CEM II/A-L 32.5N (PC–L). Two others were defined with the same cement mixed with fly ashes (FA) in a proportion of 50% each of total binder. All compositions were designed in order to respect the prescribed limits of the specification E464 (2004) of NP EN 206-1 [9], namely the restriction to the use of no more than 50% of FA as binder.

The experimental work was carried out to evaluate the compressive strength and the durability properties of the mixes studied in relation to the accelerated diffusion of CO_2 [27] at 28, 90, 180 and 365 days.

3.2 Concrete compositions

The constituents and properties of the cement and fly ash used in this work are presented in table 8. Each composition set has three mixes varying in binder dosage: 330, 360 and 390 kg/m³ and in all cases the water/binder (w/b) ratio is 0.55. All compositions were defined with the same aggregates and with similar proportions which included two fine aggregates silica based and two limestone coarse aggregates (tables 9 and 10).

Table 8 – Portland cement OPC (CEM I 42.5R) and PC–L (CEM II/B-L 32.5N) and fly ash (FA). Constituents and properties – wt%.

		DC I	۲A
	OFC	FC-L	ГА
	(CEM I)	(CEM II/B-L)	
clinker (%)	95	60	-
lime filler (%)	-	35	-
Loss on ignition (%)	3.17	14.42	5.41
	10.45	15.04	50 13
$SIO_2(70)$	19.45	15.04	50.15

Al ₂ O ₃ (%)	4.17	3.33	22.20
Fe ₂ O ₃ (%)	3.51	2.96	9.74
CaO (%)	62.42	61.09	4.13
MgO (%)	2.20	1.30	1.44
CI (%)	0.03	0.03	
SO ₃ (%)	2.90	2.51	0.82
CaO free (%)	1.39	0.89	0.47
Density (g/cm ³)	3.11	2.99	2.46
Specifc surface area (cm ² /g)	4408	5491	3343
Compressive strength (MPa)			
2d	31.9	20.2	-
7d	45.5	30.9	-
28d	56.9	39.5	-

Table 9 – Concrete compositions with OPC (CEM I 42.5R) and PC-L (CEM II/B-L 32.5N) as binder – kg/m³

	I 330	I 360	I 390	II 330	II 360	II 390
Type of cement	CEM I	CEM I	CEM I	CEM II/B-L	CEM II/B-L	CEM II/B-L
Cement dosage	330	360	390	330	360	390
Fly ash dosage	-	-	-	-	-	-
sand 0.25-0.5 mm	260	240	220	260	240	220
sand 1-2 mm	580	550	520	580	550	520
gravel 8-10 mm	470	490	500	470	490	500
gravel 14-25 mm	530	530	540	530	530	540
w/b	0.55	0.55	0.55	0.55	0.55	0.55

I 330 - concrete composition with type of cement CEM I with 330 kg/m³ dosage

II 330 - concrete composition with type of cement CEM II/B-L with 330 kg/m³ dosage

1 Table 10 – Concrete compositions with 50% of FA as binder – kg/m³

	I 330 FA	I 360 FA	l 390 FA	II 330 FA	II 360 FA	II 390 FA
Type of cement	CEM I	CEM I	CEM I	CEM II/B-L	CEM II/B-L	CEM II/B-L
Cement dosage	165	180	195	165	180	195
Fly ash dosage	165	180	195	165	180	195
sand 0.25-0.5 mm	260	240	220	260	240	220
sand 1-2 mm	580	550	520	580	550	520
gravel 8-10 mm	470	490	500	470	490	500
gravel 14-25 mm	530	530	540	530	530	540
w/b	0.55	0.55	0.55	0.55	0.55	0.55

I 330 FA – concrete composition with 330 kg/m³ binder dosage: 165 kg/m³ CEM I and 165 kg/m³ FA

II 330 FA - concrete composition with 330 kg/m³ binder dosage: 165 kg/m³ CEM II/B-L and 165 kg/m³ FA

3.3 Preparation and conditioning of specimens

The determination of the compressive strength at the age of 28 days and the corresponding preconditioning were carried out following the standard EN 12390-3 [32]. The same procedure was followed for 90, 180 and 365 days.

As for carbonation, following the Portuguese specification LNEC E391 [27], testing samples were cylindrical with 100 mm diameter and 200 mm height. Before entering the carbonation chamber, samples were cured in water saturated environment until 14 days before their testing age (14, 76, 166 and 351 days) and then subjected to 50% RH and 20-25°C. The following accelerated carbonation environment was 65% RH, $20^{\circ}C$ and 5% of CO₂ air content. For each composition 1 sample was removed and had its carbonation depth analysed at four different dates, between 7 to 56 days after entering the carbonation chamber.

Table 11 resumes the conditioning and testing plan of the concrete compositions for all curing ages.

ag	e (days)	28 days	samples	90 days samples		180 days samples		365 days samples	
0			compositi	ions' mixing: s	amples pouring	g for compressi	ve and carbon	ation tests	
		carbonation samples	compressive samples	carbonation samples	compressive samples	carbonation samples	compressive samples	carbonation samples	compressive samples
14		wet cure.: 20°C; 100%RH dry cure: 20-25°C; 50%RH	wet cure: 20ºC; 100%RH	wet cure:					
28		carbonation test	compressive test	20ºC; 100%RH	wet cure: 20ºC;				
	28+7 ⁽¹⁾ 28+21 ⁽²⁾ 28+42 ⁽³⁾ 28+56 ⁽⁴⁾	1 st sample 2 nd sample 3 rd sample 4 th sample			100%RH	wet cure: 20ºC; 100%RH	wet cure:		
76			8	dry cure: 20-25ºC; 50%RH			20ºC; 100%RH	wet cure:	
90				carbonation test	compressive test			20⁼C; 100%RH	wet cure: 20ºC;
	$90+7^{(1)}$ $90+21^{(2)}$ $90+42^{(3)}$ $90+56^{(4)}$			1 st sample 2 nd sample 3 rd sample 4 th sample					100%RH
166					<u>=</u>	dry cure: 20-25ºC; 50%RH			
180						carbonation test	compressive test		
	$180+7^{(1)} \\ 180+21^{(2)} \\ 180+42^{(3)} \\ 180+56^{(4)}$					1 st sample 2 nd sample 3 rd sample 4 th sample			
351								dry cure: 20-25ºC; 50%RH	
365								carbonation test	compressive test
	$\begin{array}{r} 365{+}7^{(1)}\\ 365{+}21^{(2)}\\ 365{+}42^{(3)}\\ 365{+}56^{(4)} \end{array}$							1 st sample 2 nd sample 3 rd sample 4 th sample	

Table 11 – Testing plan for the different ages

 $^{(1)}$ varied between 7 and 14 days $^{(2)}$ varied between 21 and 28 days

⁽³⁾ varied between 35 and 42 days

⁽⁴⁾ varied between 42 and 56 days

4. Tests results

Although without a direct relation with durability, the concrete compressive strength is a reference parameter as regards the performance of a concrete composition. Therefore, tests were made in order to evaluate this property at different ages. Accordingly and as a parallel procedure, accelerated carbonation tests were carried out for the same compositions and same ages.

4.1 Compressive strength

The experimental campaign included concrete compositions subjected to compressive tests at the ages of 28, 90, 180 and 365 days. Fig. 1 presents the results of compressive strength f_c of all compositions: Portland cement I and II/B-L (Fig. 1a) and blended fly ash cement I+50%FA and II/B-L+50%FA (Fig. 1b). Fig. 1c and 1d present the compositions assembled by type of cement, in which each group includes the results of the three different dosages: 330, 360 and 390 kg/m³.



Fig. 1 – Compressive strength f_c at the ages of 28, 90, 180 and 365 days: **a**) and **b**) Each composition; **c**) and **d**) Set of composition by cement type

In view of the existing data [33] the results show that concrete mixes with Portland cement have higher values of compressive strength at early ages. Nevertheless, while composition with cement I (OPC) has the highest results for all ages, cement II/B-L (PC-L) presents the lowest vales for 180 and 90 days of age, even when compared to the blended cement mixes.

Concerning the age influence, Fig. 1a compared to 1b and 1c compared to 1d, clearly show that there is higher increase of the compressive strength for fly ash blended cement. In particular, concrete with binder II/B-L+FA shows similar strength at 90 days of age and 20% more compared to cement II/B-L (Fig. 1c and 1d).

4.2 Carbonation: Accelerated diffusion

As already mentioned, the durability parameter studied herein refers to the penetration by diffusion of carbon dioxide into the concrete samples. The test consists of placing several concrete samples in an environment chamber with accelerated carbonation – when compared to the amount of CO_2 present in the atmosphere.

After the established time in the chamber, each sample is removed, sliced in two halves and sprayed with phenolphthalein The result of carbonation depth corresponds to the thickness with no change of colour, while the remaining area (with change of colour) indicates pH>9. This method slightly underestimates the carbonation depth [34] since the reaction occurs for a pH<10-11. This associated error was simply assumed and the procedure and corresponding analysis were nevertheless carried out.

Fig.2 presents the accelerated carbonation results of each composition with OPC and PC-L (Fig. 2b, 2d, 2f, 2h) for the four ages. Between these two Portland cement concrete mixes, it is possible to distinguish lower CO_2 diffusion for OPC, which may be due to the higher presence of calcium hydroxide to be combined with carbon dioxide.

As to compositions with FA blended cement, higher carbonation depths are verified in relation to Portland cement (Fig. 2 and 3). However, the difference between OPC+FA and PC-L+FA is not as high, which is typical given the quantity of FA as binder (50%). Furthermore, it is observed in this case that there is evidently a higher scatter of results, better observed in Fig. 6.



Fig. 2 – Accelerated carbonation depth in time at the ages of 28, 90, 180 and 365 days. OPC (cement I): **a**), **c**), **e**) **g**) and PC-L (cement II/B-L): **b**), **d**), **f**) **h**)



Fig. 3 – Accelerated carbonation depth in time at the ages of 28, 90, 180 and 365 days. OPC (cement I) + 50%FA: **a**), **c**), **e**) **g**) and PC-L (cement II/B-L) + 50%FA: **b**), **d**), **f**) **h**)

Although with some variation [35], it is considered that carbonation depth grows with the square root of time: $x = k\sqrt{t}$ (14) This way it is possible to obtain the carbonation coefficient k represented by the slope of each regression. For CEM I (OPC) and CEM II/B-L (PC-L) at all studied ages, it is possible to distinguish the performance of each concrete composition. In the case of blended cement compositions this difference is not evident.



Fig. 4 – Carbonation coefficient, k: a) cements I and II/B-L; b) I+50%FA and II/B-L+50%FA.

Fig. 4 shows the results of carbonation coefficient *k*. Hence, in Fig. 4, *k* is much lower for the concrete mixes with cement I, as only binder, than the remaining. On the opposite, Fig. 4b shows that the worst results are those of concrete with II/B-L+50%FA. Compositions with II/B-L and I+50%FA have closer results between them. Nevertheless, and despite higher results' scatter, compositions with blended cement present higher development as to performance results with the age. From the four slopes of all regressions in Fig 4a and 4b, the least refers to concrete with cement I, which means that with this type of cement there is lower performance evolution with the age regarding CO_2 diffusion.

The Portuguese specification [11], as part of the National Annex of the Portuguese standard NP EN 206-1 [9], defines the carbonation resistance R_{C65} ((kg/m³)/(m²/year)) obtained from Eq. (3). The results of this property are shown in table 12 and they are to be included in the modelling equation for the service life estimation.

Concrete composition	28 days		90 days		180 days		365 days	
	k	R _{C65}	k	R _{C65}	k	R _{C65}	k	R _{C65}
I (OPC)	26	270	15	831	9	2286	8	2818
II/B-L (PC-L)	71	36	51	68	47	82	28	303
I + 50% FA	80	33	45	93	49	128	40	118
II/B-L + 50% FA	106	16	79	35	83	36	61	45

Table 12 – Results of carbonation diffusion k and carbonation resistance R_{C65}

k - mm/√year

R_{C65} - (kg/m³)/(m²/year)

4.3 Carbonation vs Compressive strength

The analysis of Fig. 5a shows that the compressive strength increases with age for concrete with cement type I and remains stable from 90 days onward for concrete with cement type II/B-L. As to the coefficient of carbonation, it decreases with increasing strength and age of concrete.





In Fig. 5b – FA concrete compositions – it is shown that, in general, both for cement type I as for type II/B-L the compressive strength increases with age, but there is overall a lower compressive strength and higher coefficient of carbonation when compared to compositions without fly ashes and of the same age. Additionally, for compositions with FA blended cements, carbonation coefficient decreases with increasing compressive strength and age of concrete.



Fig. 6 – *k* vs *f_c*: a) cement types I and II/B-L; b) I+50%FA and II/B-L+50%FA.

Fig. 6 presents charts of concrete carbonation coefficient versus compressive strength ($k \ge f_c$) for the analysed compositions with cement I and II/B-L with and without fly ashes.

Compositions without fly ashes (Fig. 6a) show a decrease of the carbonation coefficient with the increase of compressive strength. There is a clear difference (different slopes) but nevertheless continuity of behaviour between cement type II/B-L – with higher carbonation – and cement type I.

Regarding compositions with fly ashes (Fig. 6b), it is shown that those with cement type II/B-L present higher carbonation level. However, carbonation rate as function of compressive strength is of the same order (similar slopes).

5. Results of service life analysis

The estimation of the service life period using the Partial Safety Factor method has been carried out considering the exposure class XC4 for the target periods t_g of 50 and 100 years with a cover $c_{\min,dur}$ of respectively 30 and 40 mm.

For the probabilistic method, where all random variables have their distribution laws, the concrete cover values for the exposure class XC4 were taken as 40 (t_q =50 yrs) and 50 mm (t_q =100 yrs).

In both methods the analysis was based on an established assumption (LNEC E465 and EC0) that the performance limit is expressed as reliability inex $\beta \ge 1.5$ or probability of failure $P_f \le 7\%$.

5.1 Service life estimation based on tests results at 28 days of age

In the present recommendations and standards [2-4,7,11], the estimation of the service life of reinforced concrete structures regarding corrosion is based on tests results of concrete specimens at 28 days of age.

The next two subsections present the results of both performance-based methods – Partial Safety Factor; Probabilistic – as well as the corresponding discussion and comparison.

5.1.1 Partial safety factor method

Table 13 shows the results of design service life of RC structures included in exposure class XC4 based on the semi-probabilistic calculus using a safety factor of $\gamma = 2.3$ (Eq. 11 and table 6).

It can be seen that concrete composition with ordinary Portland cement – CEM I – has a performance far higher for carbonation wet/dry environment than the remaining tested compositions with a design (calculus) service life $t_L = 174$ years (184 years – dry region) for 50 years of target period and $t_L = 348$ years (358 years – dry region) for 100 years of target period.

All the other compositions present results that do not reach the required target lives of 50 and 100 years. Compositions with CEM II/B-L and CEM I+50%FA show results close to each other (similar performance), but still not attaining the target lives. The composition with lowest performance is II+50%FA, which includes cement type II/B-L and fly ashes (low quantity of clinker: \approx 30% + \approx 18% of limestone filler+ 50%FA). This concrete mix presents 11 years (humid region) and 21 years (dry region) of design service life for a target life of 50 years and 21 years (humid region) and 31 years (dry region) for t_a =100 years.

It should be noticed that with an equally defined propagation period t_p regardless the type of binder, the initiation period t_p assumes different contribution for the final design service life t_L . For CEM I composition it may be considered negligible, while for CEM II + 50%FA it is between half and 2/3 of the design service life.

In summary, according to the implemented modelling equations, the composition based on clinker as its only binder is the only one that fulfils the Portuguese standard requisites, surpassing both defined target lives of 50 and 100 years.

As to the design values of service life, having into account values over 300 years, some considerations on this matter are taken in subsection 5.1.3, since such high values are difficult to accept as realistic.

Composition	<i>R</i> _{C65}	Target p	period t _g =50) years; c _{min}	_{,dur} =30 mm	=30 mm Target period t_g =100 years; $c_{min,dur}$ =40 mm				
	(kg/m ³)/(m ² /year)	<i>t_p</i> years	t _{ic} years	t _i years	t <u>L</u> years	t _p years	<i>t_{ic}</i> years	t _i years	<i>t_L</i> years	
I	270	5	389	169	174	10	777	338	348	Humid
		15			184	20			358	Dry
II/B-L	36	5	34	15	20	10	68	30	40	Humid
		15			30	20			50	Dry
l + 50% FA	33	5	31	13	18	10	62	27	37	Humid
		15			28	20			47	Dry

Table 13 -	Design	sorvico I	lifo: nart	ial cafoty	factor	method_	class	XC4
	Design	SEIVICEI	me. part	iai Saiely	lacioi	methou-	U1222	AG4

II + 50% FA	16	5	13	6	11	10	26	11	21	Humid
		15			21	20			31	Dry

 t_{ρ} is the propagation period obtained from (Table 7). t_{ic} is the initiation period obtained from (4). $t_i = t_{ic}/\gamma$ is the design initiation period.

 $t_L = t_i + t_p$ is the design service life.

5.1.2 Probabilistic method

As mentioned before, the probabilistic method is based on the modelling equations and parameters defined in the specification LNEC E 465 [11]. However, the design service life results t_L are calculated considering the mean values of the random variables (Table 14) and their distribution laws according to existing references [4–7,20]. The coefficient of variation of the model uncertainty was assumed in view of what some authors considered [8].

The implementation of the probabilistic calculus for the design lifetime has been carried out by means of the Monte Carlo method with 100 000 generated values for each variable. The random variables of the limit state function have been considered with probability distribution functions according to various reference documents [5,6,36].

Variable	Mean value – μ	CoV	Distribution
Carbonation resistance, R_{C65}	Table 4 and 14	0.30	Normal
Cover, <i>c</i> (c _{nom})	40 mm (t _g =50 yrs) 50 mm (t _g =100 yrs)	0.25 0.20	Log-normal
Test parameter, k_0	3	-	Deterministic
RH parameter, k1	0.41 (Table 4)	-	Deterministic
Cure parameter, k_2	1.0	-	Deterministic
Wet/dry cycle parameter, n	0.085 (Table 4)	-	Deterministic
Corrosion current density, <i>I</i> corr	1.0 μA/cm ²	0.20	Normal
Tensile strength, f_{td}	3 MPa	0.25	Normal
Model uncertainty – Eqs (13) and (14)	1	0.15	Normal

Table 14 - Probabilistic variables for the calculus of the design service life - class XC4

Figure 7 shows the lifetime results obtained from the Monte Carlo simulation of all compositions for 50 years of target period. The results are presented in the form histograms – frequency of results – and their cumulative frequency. The latter represents the equivalent to the distribution function from which the service life in years is related with the probability of non-exceedance.

The peak value of Lifetime in years is significantly higher for CEM I (Fig. 7a) when compared to CEM II/B-L (Fig. 7b), CEM I+50%FA (Fig. 7c) and CEM II+50%FA (Fig. 7d). The latter presents the lowest lifetime peak value, being approximately half of those attained by CEM II/B-L and CEM I+50%FA.





Fig. 7 – Monte Carlo Lifetime results for t_q =50 years: frequency and cumulative.

As mentioned before the performance of each concrete composition is evaluated in view of their service life with a certain reliability level (or probability of failure). Figure 8 presents the development of the performance throughout time for both target periods of 50 and 100 years. It can be seen that only the composition with CEM I reaches (and surpasses) the minimum required reliability index $\beta = 1.5$, while for this level of performance the concrete mixes with CEM II/B-L and CEM I+50%FA do not go beyond approximately 20 and 40 years (see also table 15) for target periods of 50 and 100 years, respectively. Concrete composition with CEM II+50%FA only attains 12 and 19 years (table 15) for each target period.



Fig. 8 – Reliability Index throughout time for the different concrete compositions Minimum β required for Serviceability Limit State = 1.5 (class RC2)

From the results expressed in table 15 the binder based only on clinker (OPC – CEM I) presents values of design service life t_L = 212 years (t_g = 50 years) and t_L = 450 years (t_g = 100 years) subjected to carbonation exposure class XC4. Similarly to what is noted in the previous method (subsection 5.1.1), also in this method these values of design life are significantly high, raising questions to how close they are to reality.

Composition	<i>R</i> _{<i>C65</i>}	Target period <i>t_g</i> =50 years c _{min,dur} =40 mm	Target period <i>t_g=</i> 100 years c _{min,dur} =50 mm
	(kg/m ³)/(m ² /year)	t _L - years	<i>t</i> _L - years
CEM I	270	212	450
CEM II/B-L	36	23	42
CEM I + 50% FA	33	21	41
CEM II + 50% FA	16	12	19

Table 15 - Design service life: probabilistic method- class XC4

5.1.3 Discussion and comparison between Partial Safety Factor method and Probabilistic method

Both methods are compared and analysed based on the results summarized in table 16. Despite their differences, both performance-based methods show results with values beyond what it could be considered as realistic for the concrete composition with CEM I.

As regards durability related to corrosion of steel reinforcement, the Portuguese standards consider the possibility of designing structures for working lives of 50 or 100 years with or without major interventions. This means that it might be acceptable to design RC structures with such service lives or similar. However, it is questionable if these design values are realistic in case they go beyond 120-150 years.

So that a reasonable comparison can be carried out, it is important to summarize some of the differences associated with the statistical nature of these two methods. Although the safety factor method uses a deterministic calculus taking into account a probabilistic conversion through the introduction of a certain safety factor, it considers $c_{min,dur}$ as the input cover value in Eq. 12, which is a characteristic value, rather than a mean one. On the other hand, the probabilistic method considers the cover mean value (nominal cover c_{nom}) with coefficients of variation of 0.20 and 0.25, is adopted by different references [4,6].

Furthermore, it is important to outline two relevant differences: the safety factor method of the performancebased specification LNEC E465 [11] does not account for the model uncertainty and it sets the minimum propagation period values; on the other hand, the probabilistic calculus considers the model uncertainty through the coefficient λ and also the direct implementation of the mathematical expression of the propagation period (Eq. 13).

service life – carbonation exposure class XC4	Table 16 – Comparison of results between Partial Safety Factor	r method and Probabilistic method: Desi	gn
	service life – carbonation exposure class XC4		

	Target period te	g = 50 years		Target period $t_g = 100$ years			
	t _L - years		Ratio	<i>t</i> _L - ye	ars	Ratio	
Composition	PSF	Prob.	PSF / Prob.		Prob.	PSF / Prob.	
CEM I	174* (184**)	212	0.82 (0.87)	348 (358)	450	0.77 (0.80)	
CEM II/B-L	20 (30)	23	0.87 (1.30)	40 (50)	42	0.95 (1.19)	
CEM I + 50% FA	18 (28)	21	0.86 (1.33)	37 (47)	41	0.90 (1.15)	
CEM II + 50% FA	11 (21)	12	0.92 (1.75)	21 (31)	19	1.11 (1.63)	

* Dry region

** Humid region

Table 16 presents the results of predicted design service life concerning class XC4 for both methods and their ratio— safety factor/probabilistic approach, concerning dry and humid regions, for the propagation period, adopted in the partial safety factor method. There seems to be slightly better convergence of results for the target period of 100 years whose ratios vary from 0.77 to 1.63, while for 50 years the values vary from 0.86 to 1.75. However, it should be noticed that for low values of service life the pre-set propagation period t_p in the safety factor method may induce important differences since it increases its proportion in the design service life t_L .

The differences between the performance- based approaches may be explained by the following considerations:

- the safety factor values are obtained by using a log-normal distribution for the lifetime of structures and considering a coefficient of variation (COV) of 0.50 [2];
- the probabilistic method reflects the uncertainties associated with the models while the partial safety factor method [11] does not account these on the safety factor values;
- the safety factor method [11] uses a characteristic value— c_{min,dur}—of the concrete cover for the deterministic calculus of the design service life, while the probabilistic method uses a mean value (nominal—c_{nom}).

5.2 Probabilistic analysis with tests results at 90, 180 and 365 days of age

The use of performance-based approaches for the evaluation of concrete compositions is generally carried out with tests on specimens with 28 days of age.

Given the different behaviour of concrete with clinker as the only binder constituent compared with concrete mixes with supplementary cementitious materials, namely in what concerns ageing properties, a probabilistic analysis with specimens with longer ages – 90, 180 and 365 days – was carried out in order to check the evolution expressed by means of their reliability.

The analytical results are presented through the reliability index β calculated considering the experimental results of the studied mixes at the referred ages. The analytical results are expressed in Figure 9 and Table 17 for systems (composition + cover) designed for 50 years of target life t_g and in Figure 10 and Table 18 for 100 years of target life.

From Figure 9 it can be seen that for the concrete mix with CEM I there is little evolution – from $\beta = 2.85$ to 3.57 (Table 17) – of the reliability index for higher ages (Fig. 9a) and accordingly the variation of the ratio β/β_{28} is negligible Fig. 9b. Concrete mixes with CEM II/B-L and CEM I+50%FA show an apparent similar evolution although the ratio β/β_{28} is slightly higher for CEM I+50%FA, especially at 365 days of age. This composition even shows the highest ratio at 90 days of age. Concrete mix CEM II+50%FA presents the lowest β values and little evolution between 90, 180 and 365 days.



Fig. 9 – Performance at different ages for a target life t_g = 50 years

Table 17 – Performance by means of Reliability Index β at different ages for a target life t_g = 50 years

	CEM I C		CEM	CEM II/B-L CEM t I+5		+50%FA	CEM II/B	CEM II/B-L+50%FA	
Age	β	β/β_{28}	β	β/β_{28}	β	β/β_{28}	β	β/β_{28}^*	
28 days	2.85	1.00	0.38	1.00	0.25	1.00	-0.87	1.00	
90 days	3.37	1.18	1.32	3.46	1.75	7.03	0.34	2.39	
180 days	3.54	1.24	1.57	4.13	2.15	8.65	0.38	2.44	
365 days	3.57	1.25	2.94	7.70	2.05	8.26	0.71	2.81	

 β_{28} – reliability index at 28 days of age

* in this case: $Ratio = \frac{\beta - \beta_{28}}{|\beta_{28}|}$

For systems designed for a target period of 100 years (Figure 10a and Table 18) the performance level regarding the reliability index is close to what it is obtained for a target period of 50 years. The main difference is related with the ratio $\beta | \beta_{28}$, though, in fact, its values highly depend of the reliability index at the age of 28 days. CEM I+50%FA has a very low reliability index value for 28 days of age (β =0.04) that makes

the ratio $\beta \beta_{28}$ significantly high for each of the other ages and which is why this composition is clearly detached from the others in Figure 10b.

When the results and graphs are analysed it appears that CEM I has no significant evolution as regards the reliability index for specimens with 28, 90, 180 and 365 days. For the other compositions the major increase in the reliability is obtained at the age of 90 days, except for concrete mix CEM I +50%FA that still shows a significant increase from 180 to 365 days.



Fig. 10 – Performance at different ages for a target life t_g = 100 years

	CEM I		CEM II/B-L		CEM I+50%FA		CEM II/B-L+50%FA	
Age	β	β/β_{28}	β	β/β_{28}	β	eta / eta_{28}	β	eta / eta_{28}^{*}
28 days	2.86	1.00	0.20	1.00	0.04	1.00	-1.36	1.00
90 days	3.36	1.17	1.31	6.50	1.80	43.61	0.15	2.11
180 days	3.54	1.24	1.61	7.97	2.22	53.83	0.20	2.15
365 days	3.62	1.26	2.95	14.58	2.13	51.50	0.61	2.44

Table 18 – Performance by means of Reliability Index β at different ages for a target life t_g = 100 years

For tests results at 90, 180 and 365 days of age, the reliability performance with the calculation of the reliability index β shows that CEM I has values significantly above the required one (β =1.5) at all ages.

Concrete mix CEM II/B-L shows β values close to 1.5 for 90 and 180 days of age and a relevant increase for 365 days of age with β =2.9. CEM I+50%FA is also close to β =1.5 for 90 days of age and a slight increase and stagnation from 180 days of age on (β = 2.0 to 2.2). In the case of concrete mix CEM II+50%FA, this composition does not reach for any age the required reliability index, although there is a relevant evolution from 28 days to 90 days of testing age.

6. Conclusions

All compositions were designed to respect the prescribed requirements of the NP EN 206-1 [9] for RC structures with a working life (target period) of 50 and 100 years against steel corrosion due to carbonation environments.

In view of the NP EN 206-1 [9] for RC structures and the results obtained from the testing program, the service life analysis lead to the following conclusions:

- For tests results at 28 days of age only CEM I (only clinker as binder) reaches (and largely surpasses) the target periods of 50 and 100 years of the prescribed requirements. All other concrete compositions (limestone filler and FA blended cements) had service life results far from the target periods. This means that for the design of the blended compositions herein presented the approach through service life modelling (performance-based) does not meet the estimated target periods of the design based on prescription. As for both performance-based methods, there is globally fair convergence, except for the composition CEM II+50%FA with less than 35% of clinker by weight of binder;
- For the testing ages of 90, 180 and 365 days, the reliability performance of the blended compositions with at least 50% clinker (CEM II/B-L and CEM I+50%) were able to reach the requirements of the prescribed, although their performance is still far from that of CEM I.

Considering the studied concrete compositions and the carbonation environment it is possible to conclude that, in the presence of blended cement with high amount of limestone filler or low calcium FA, the two existing concrete design approaches – prescription method and performance-based method – do not seem to constitute an alternative to one another, since the modelling results of service life are very different from the prescribed target periods. This is a matter where there is still a need to carry out studies to allow a better understanding of this difference.

Regarding time effect, for the concrete compositions aged 90, 180 and 365 days, those with no less than 50% clinker by weight of binder were able to reach the required reliability performance for both target periods of 50 and 100 years. For the case of those with blended cement concrete this means better convergence between the two options of designing concrete compositions.

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