CARBONATION OF BLENDED CEMENT CONCRETES AFTER 12 YEARS OF NATURAL EXPOSURE

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Abstract
In urban environments, the durability of reinforced concrete structures is limited by carbonation-induced corrosion. To prevent steel corrosion, the selection of a proper concrete in terms of type of binder, water/binder ratio and curing time, is of fundamental importance. At this aim the knowledge of the resistance to carbonation in the exposure environment is required. Usually carbonation is evaluated from accelerated tests, however natural exposure tests are needed to validate short-term tests and make reliable predictions of the behaviour in a real environment. This paper reports the carbonation of concretes with different binders, water/binder ratios and curing, exposed for more than twelve years outdoor in Milan in sheltered conditions. Concretes with Portland cement exhibited a higher carbonation in comparison with concretes with limestone and pozzolanic cements. Curing seemed to be less effective than the type of binder and the water/binder ratio.

Highlights
The natural carbonation was evaluated on different types of concrete.
The type of binder strongly affected the carbonation.
Curing time showed a lower influence than the type of binder and water/binder ratio.
Natural and accelerated carbonation coefficients showed good correlation.

Keywords
Blended cement, curing, carbonation, service life, sheltered conditions

1. Introduction
The exposure of reinforced concrete (RC) structures to urban environments may lead to corrosion of steel reinforcement induced by carbonation [1]. To prevent the steel corrosion it is of fundamental importance to choose a suitable combination between the type of concrete, i.e. type of binder, water/binder ratio and curing time, and the construction details, e.g. the concrete cover thickness [2]. In the simplified prescriptive approach proposed in the European standards, i.e. EN 206 and Eurocode 2 [3,4], requirements on the concrete composition and the concrete cover thickness are provided as a function of the exposure class in order to guarantee a service life of the order of 50 years. In particular, the limiting values for concrete composition and properties in relation to exposure classes recommended in the EN 206 refer to the use of any type of common cement conforming to EN 197-1. Dealing with carbonation, this seems to suggest that the resistance to carbonation is comparable for concrete mixes made with different types of binder.
In the literature several studies investigated the effect of concrete characteristics, i.e. type of concrete and curing time, on the resistance to carbonation under natural exposure conditions. In the study of Sanjuán et al. [5] concretes made with CEM I 42.5R and CEM I 52.5N, with the addition of fly ash and silica fume, and with water/binder ratios between 0.33 and 0.69, were exposed in laboratory for about 10 months. Concretes made with Portland cement without additions showed

the higher resistance to natural carbonation. On concretes made with a water/binder ratio of 0.47 and replacing the Portland cement with 10%, 20%, 30% of natural pozzolan, exposed in the laboratory environment for six months, the resistance to natural carbonation decreased with increasing the natural pozzolan replacement [6]. After two years of exposure in sheltered and unsheltered conditions, the resistance to carbonation of concretes produced with two different water/binder ratios (0.40 and 0.65) and nine different cements (Portland, limestone, ground granulated blast-furnace slag, fly ash and microsilica, in various amounts) was higher on concrete made with Portland cement in comparison with concretes made with blended cements [7]. In different natural exposure conditions, representing moderate, less severe and severe carbonation-induced corrosion exposures, concretes containing 100% Portland cement, 35% fly ash and 50% ground granulated blast-furnace slag, showed that in blended cements concrete the carbonation resistance was lower than in Portland concretes [8].The study carried out by Ribeiro et al. [9], where concretes prepared with Portland cement and different replacement levels of cement with fly ash, ground granulated blast-furnace slag, or both additions were exposed for 10 years to a natural environment not sheltered from rain, confirmed these results. Exposure of 45 different concrete mixtures for a period of 5 years in five natural significantly different locations showed that the carbonation resistance of concretes with fly ash and pozzolan is comparable and much lower than that of concrete with slag [10].

As far as the impact of curing is concerned, the study carried out by Parrott [11] on concretes made with Portland cement indicated that further curing beyond 3 days was not of significant influence on long-term natural carbonation. In the research carried out by Wang [12] that investigated both Portland cement and blended cements to make concretes with different water/binder ratios, a small reduction in carbonation depth, after 2 years of exposure, was observed when the curing was increased from 3 to 7 days. A higher reduction was observed increasing the curing from 3 to 28 days. Ikotun's results showed that a slight increase in carbonation resistance was achieved increasing the curing from 7 to 28 days, regardless the type of binder [8].

As it can be observed, the currently available literature on natural carbonation are not only limited in number, but they also have an exposure duration often significantly lower in comparison with the expected service lives of RC structures. This may be critical to fully understand the impact of concrete quality in hindering the penetration of carbonation.

In a definitely higher number, the resistance to carbonation of concretes made with different binders has been investigated through accelerated tests that are characterized by a duration of the order of months and also by a CO_2 concentration significantly higher than that in atmosphere [13-16]. The results of accelerated tests, although they allow a first screening of the performances of different types of concrete, cannot be directly used to design the service life of a RC structure, since they do not take into account the real exposure conditions (such as, for instance, the actual relative humidity, temperature, wetting event) and the curing. Correlations between accelerated and natural tests are, then, needed to predict the behaviour in a real environment. Neves et al. [17] analyzed 90 cores – 65 taken from sheltered elements and 25 from unsheltered elements - from 21 viaducts, with an age between 4 and 32 years. According to them the correlation between the natural carbonation, measured on the cores, and the accelerated carbonation, measured through an accelerated carbonation test on the non-carbonated inner part of the same cores, was poor. In the study of Sanjuán et al. [5] the carbonation depth of concretes made with Portland cement and fly ash binder with a water/cement ratio ranging from 0.33 and 0.69, exposed to natural condition (i.e. 0.03% CO_2) was 40 and 5 times lower than those of specimens respectively exposed to 100% and 5% CO_2. According to Durán-Herrera [18] the accelerated carbonation coefficient was between 2 and 2.5 times those obtained for the natural exposure, depending on the type of concrete. A wider range of variability (with values lower than 2 and values higher than 12) of the ratio between the accelerated and the natural carbonation coefficient was determined in the study of Rozière et al [14]. Although almost all the studies highlighted that a good relationship between accelerated and natural carbonation can be established, a general relationship between them cannot be assessed, since it is

strongly affected by the exposure conditions, as for instance the outdoor conditions, and the CO_2 concentration in the accelerated tests [19]. The recent models for the service life design, as for instance the one developed by the International Federation of Concrete, *fib*, propose to evaluate the concrete behaviour under natural exposure conditions from the results of an accelerated test by modifying them through a series of corrective factors [20]. In a previous study, results of field inspection of 30-year-old buildings were compared to the service life modelled through the *fib* Model Code [21-22]. Although some design parameters, e.g. the inverse resistance to carbonation, or model coefficients, e.g. the exponent f_e or b_w, had higher influence than others on the modelled carbonation depth, it was found that no single parameter had a predominant role. Hence, the reliability of the corrective factors still needs to be assessed through results of carbonation tests in natural environment.

An experimental study was carried out to evaluate the carbonation under natural exposure conditions of concretes made with Portland cement and several supplementary cementing materials (SCMs), i.e. limestone, fly ash, natural pozzolan and ground granulated blast-furnace slag, water/binder ratios ranging from 0.42 to 0.61, and cured for 1, 7 and 28 days. This paper reports the results obtained on the different concretes exposed for more than twelve years in outdoor sheltered conditions and compares them with other properties of hardened concrete, e.g. compressive strength and accelerated carbonation. Experimental data were then used to evaluate the service life that can be achieved in a sheltered environment, to better understand the differences among concretes made with different binders and to validate the limiting values provided in the European standards.

2. Materials and methods

A Portland cement CEM I 52.5R (PC), according to EN 197-1 standard, and five blended cements were used. Blended cements were obtained by replacing part of the cement with SCMs, in particular with 15% and 30% of ground limestone (15LI and 30LI), 30% of fly ash of class F (FA), 30% of natural pozzolan (PZ) and 70% of ground granulated blast-furnace slag (GGBS). Table 1 reports the chemical compositions and the specific surface area of PC and the different SCMs.

Concretes were cast with three different water/binder ratios, equal to 0.42, 0.46 and 0.61, and two different binder dosages, equal to 300 and 350 kg/m^3. Crushed limestone aggregate with maximum size of 16 mm was used, and an acrylic superplasticizer was added to the mixtures in order to achieve a class of consistence *S4* according to EN 206 standard. Table 2 summarizes the concrete mixes and the slump. Each concrete is indicated with a label that reports the type of cement, the water/binder ratio and the binder content, for instance PC-0.61-300 indicates a concrete made with Portland cement, water/binder ratio of 0.61 and a binder content of 300 kg/m^3.

After pre-wetting the interior of the concrete mixer, the aggregates and the cementitious materials were introduced and mixed for about 30 s to homogenize the materials. Then, the water was added and mixed for about 3 min. Concrete was poured into molds on a vibrating table with a vibration time useful to fully compact it. The molds were covered with a plastic sheet and stored in laboratory at 20°C. After 24 hours the specimens were demolded and curing continued at 20°C and 95% relative humidity in a curing chamber where temperature was controlled through sensors placed inside.

Compressive strength was measured after 1, 7 and 28 days of curing on 100 mm cubic specimens and results are reported in Table 3 [23,24]. Sorption was evaluated on cylindrical specimens, cured 28 days, with diameter of 100 mm and height of 50 mm. After reaching a constant dry-mass, the lateral surface of the specimens was masked with epoxy. Then specimens were placed in a tray such that their bottom surfaces up to a height of 2 mm were in contact with water. After different time intervals up to 24 h, the specimens were weighed to determine mass gain. Results obtained on PC-0.42-350 and LI concretes can be found in [23,24] and are reported, together with those related to the other concretes, in Table 3.

Carbonation was evaluated on 100 mm cubic specimens cured 1, 7 and 28 days, exposed outside in natural conditions, sheltered from rain and sun - on the roof of the Department of Chemistry,

Materials and Chemical Engineering of Politecnico di Milano – according to the exposure chamber indicated in EN 12390-10 (one specimen for each combination of type of concrete and curing time). Milan climate can be classified as *cfa* according to the Köppen climate classification, i.e. a humid subtropical climate characterized by hot and humid summers, and cold to mild winters. In particular the average annual temperature is around 13°C, with minimum and maximum average monthly values around -1°C and 30°C. The annual rainfall is about 1000 mm, whilst the average annual relative humidity is around 75% with minimum and maximum average monthly values around 70% and 85%.

Four faces of the cubes were masked with epoxy, so that carbonation was allowed to penetrate only from two opposite faces (the cast and a mould surface). During exposure, the unmasked faces were oriented vertically. After different exposure times (within 5 years of exposure), a 20 mm core was drilled and the average value of carbonation depths was measured, on the mould surfaces, with the phenolphthalein test. After about 12.5-13 years of exposure, the specimens were split, the carbonation depth of the fracture surface was measured on points spaced 10 mm from each other (in some specimens the fracture surface was limited due to the presence of the previous cores and carbonation depth was measured on, at least, three points) and the average value was determined. The average carbonation depths, d, measured after different exposure times, t, were interpolated, with the least squares method, to obtain the natural carbonation coefficient, k_{nat}:

$$d = k_{nat} \cdot \sqrt{t} \quad (1)$$

Accelerated carbonation tests in accordance with the procedure proposed in the *fib* Model Code (T = 20°C, R.H. = 65% and CO_2 = 2%) had also been carried out on the same concretes, moist cured 1, 7 and 28 days and results are reported in Table 3 [23,24].

3. Results

Figure 1 shows, as an example, the trend with time of the carbonation depth on concretes with 15% of limestone, moist cured for 7 days and exposed in an outdoor sheltered environment. An increase of the carbonation depth can be observed increasing the time of exposure, as well as increasing the water/binder ratio; a significant effect of the binder content was not observed. After almost 13 years of exposure, values of the order of 14 mm were measured on the concrete made with water/binder ratio of 0.61, between 5-7 mm on the concretes made with water/binder ratio of 0.46 and around 2.5 mm on the concrete with water/binder ratio of 0.42.

Carbonation depths were fitted through the relationship (1) to determine the carbonation coefficient k_{nat}, and the fitting lines are also reported in Figure 1. Figure 2 shows the carbonation coefficient as a function of the water/binder ratio and the curing time for all concretes (the effect of the binder content was neglected). For each type of binder, the carbonation coefficient and the water/cement ratio were fitted through an exponential relationship (in the interpolation values obtained on GGBS-0.46-300 concrete were not considered). The good relationship observed for each type of cement at each curing time indicates that the carbonation coefficient increased, with increasing the water/binder ratio. For instance, for 15LI concretes, 7-day cured, the carbonation coefficient increased from 0.88 to 3.87 mm/year$^{0.5}$ when the water/binder ratio increased from 0.42 to 0.61 (Figure 2b). Figure 2 also shows the role of the type of binder on the carbonation coefficient. The PC concretes showed the lower carbonation coefficient. For instance, for 7-day cured concretes, the carbonation coefficient varied between 0.86 to 2.12 mm/year$^{0.5}$ when the *w/b* ratio varied between 0.61 to 0.46. These values were slightly lower than those evaluated on 15LI concretes. A higher carbonation coefficient in comparison with PC concretes can be observed on concretes made with PZ, FA, GGBS and 30LI. For instance the carbonation coefficient of 7-day cured concretes made with *w/b* ratio of 0.61 was 1.7, 2.21, 1.63 and 1.88 mm/year$^{0.5}$ respectively for FA, PZ, GGBS and 30LI. A similar behaviour can be observed also at the other curing times.

4. Discussion

The role of concrete characteristics on the carbonation coefficient in sheltered natural environment, mainly the type of binder and the curing time, will be discussed. Then, a comparison with other properties of the hardened concrete, i.e. the compressive strength and the accelerated carbonation coefficient, will be carried out. Finally, on the basis of the experimental results, the impact of the concrete characteristics on the service life of a reinforced concrete structure will be evaluated, by means of a probabilistic approach. Although a sheltered exposure environment is not the most aggressive one, in relation to carbonation-induced corrosion, each RC element needs to be designed to withstand the environmental actions. This implies on one hand to avoid the occurrence of a pre-defined limit state during the service life, and on the other hand to select a suitable combination of concrete composition and concrete cover thickness, without being conservative if unnecessary.

4.1 Mix proportions and curing
Results presented in the previous section well reflected the effect of the water/binder ratio, indicating that an increase of the water/binder ratio led, as expected, to an increase of the carbonation coefficient. Furthermore, it seems that the carbonation coefficient was more affected by the *w/b* ratio when SCMs were used.
Results previously presented also highlighted a different impact of the type of binder on the carbonation coefficient. To better investigate this impact, Figure 3 shows the ratio between the carbonation coefficient measured on the concretes made with SCMs and the carbonation coefficient measured on PC concretes, k_{SCMs}/k_{PC}, at equal water/binder ratio, binder dosage and curing (results obtained on GGBS-0.46-300 concretes can be considered, as previously observed, as anomalous data). At each curing time, the k_{SCMs}/k_{PC} ratio was always higher than 1 (15LI-0.42-350 concrete, cured 7 days, was an exception), indicating that the use of blended cement led to an increase of the carbonation coefficient. A doubling, and for some water/binder ratios even more, of the carbonation coefficient can be observed for PZ, 30LI, FA and GGBS. 15LI showed, at the different curing times, a lower carbonation coefficient in comparison with the other blended cements; however, compared to PC the carbonation coefficient was 1.5 times higher.
These results are in agreement with data reported in the literature, showing a lower carbonation coefficient of concretes made with Portland cement in comparison with concretes with pozzolanic and hydraulic binders, i.e. natural pozzolan, fly ash and ground granulated blast-furnace slag and limestone binders. In particular, in the study of Lye et al. [25] based on a literature review, for concretes made with 70% GGBS and exposed in sheltered conditions (range of temperature: 20-30°C, range of relative humidity: 50-75%), the mean relative change of carbonation depth of GGBS concrete relative to reference PC concrete was around 100%, which corresponds to a double of the carbonation coefficient in comparison to PC concrete, being similar to results obtained in this work. For concretes with 30% FA, in accordance to another review of Lye et al. [26], the mean relative change of carbonation depth of FA concrete relative to reference PC concrete was slightly lower than 100%, whilst in this work the carbonation coefficient was also three times higher than that of PC concrete.
In limestone concretes, the limestone mainly acts as an inert constituent and, hence, the porosity is higher in comparison with a Portland cement concrete and increases, increasing the limestone content [24]. Sorption, defined as the absorption of water in the capillary pores due to the capillary action, clearly confirmed the higher porosity of limestone concretes in comparison with Portland concretes (Table 3). In pozzolanic and hydraulic binders, on one hand, the pozzolanic reaction consumes the calcium hydroxide, that is no longer available for the carbonation reaction, leading to a faster penetration of carbon dioxide; on the other hand, the pozzolanic reaction leads to the refinement of the microstructure of capillary pores which can contribute to hinder the penetration of carbonation. The sorptivity coefficients of 28-day cured PZ, FA and GGBS concretes were almost comparable to each other and, at least for concretes with water/binder ratio of 0.42 and binder content of 350 kg/m^3, also similar to that of PC concrete. Conversely, they were clearly lower than those showed by LI concretes. Hence, although a reduction of the capillary porosity occurred, it is

reasonable to assume that the reduction of the calcium hydroxide weights more in determining the carbonation coefficient. Further insights on this issue can be provided analysing the effect of curing. Figure 4 shows, for all the concretes, the ratio between the carbonation coefficient measured on the concretes cured 1 (Figure 4a) and 28 days (Figure 4b) and the carbonation coefficient measured on 7-day cured concretes, at equal water/binder ratio and binder dosage. The comparison between concretes cured 1 and 7 days shows for all the concretes, except those with pozzolanic additions, a value slightly higher than 1, indicating that the carbonation coefficient decreased increasing the curing from 1 to 7 days. A further decrease of the carbonation coefficient can be observed increasing the curing from 7 to 28 days. Surprisingly the Portland concretes experienced the highest decrease (a ratio around 0.5 was evaluated), whilst the decrease of concretes with pozzolanic and hydraulic binders was limited (with a ratio between 0.8 and 0.9). Comparable results can be obtained analysing the effect of curing on the accelerated carbonation coefficient, suggesting that a further hydration of concrete, that would have limited the effect of curing, during the outside exposure did not occur. Conversely, a more pronounced effect of curing can be observed on compressive strength in particular for concrete with pozzolanic and hydraulic binders (Table 3). These results confirmed that, although on pozzolanic and hydraulic binders there is a combined effect of the decrease of amount of calcium hydroxide and of the refinement of the pore microstructure both due to the pozzolanic reaction, that cannot be easily distinguished, the consumption of calcium hydroxide appears to be stronger than the reduction of the capillary porosity.

An attempt to quantify the effect of curing was carried out, by means of determining a corrective curing coefficient, K_c, evaluated, in agreement to the relationship proposed in the *fib* Model Code for Service Life Design [20], as:

$$K_c = \left({t_c}/{7} \right)^{b_c} \qquad (2)$$

Where t_c is the curing time and b_c is an exponent. Figure 5 shows the curing coefficient as a function of the curing time, regardless the water/binder ratio and the binder content. Of course, at a curing time equal to 7, the curing coefficient is 1. At the other curing times, a high variability can be observed, in agreement with that observed also in the *fib* Model Code. The average curing coefficients evaluated after different curing times were interpolated, with the least squares method, to obtain the exponent b_c and a value of -0.1 was determined. A similar value of K_c, equal to -0.15, was evaluated also considering the results obtained through accelerated tests. This value is different with the average value, equal to -0.567, proposed in the *fib* Model Code, which indicates a more significant effect of the curing.

4.2 Correlation with hardened properties of concrete
The carbonation coefficient in a natural environment is often estimated from other hardened concrete properties that are usually easily measured, such as the compressive strength. Hence, the correlation between these two parameters was explored and is shown in Figure 6. In general, concretes with a higher compressive strength showed also a lower carbonation coefficient, hence a higher resistance to carbonation. Despite the high variability, exponential correlations between compressive strength and carbonation coefficient were determined for each curing time, regardless the type of cement (values of R^2 higher than 0.65 for each curing time were determined). Indeed, the high variability of results hided the effect of the type of cement on these correlations. These results suggest that both these properties of hardened concrete are mainly governed by the capillary porosity of the cement paste. The existence of a correlation between strength and carbonation coefficient, often evaluated through accelerated tests, is expected. However, some Authors determined a linear relationship [7,14,27], whilst others an exponential relationship [28,29], and a

general consensus is still lacking, due also to the different test procedures used to evaluate the carbonation.

Usually the actual behaviour of concrete in a certain exposure condition is evaluated from accelerated tests. At this regard, Figure 7 shows the relationship between the accelerated carbonation coefficient obtained through accelerated tests (Table 3), k_{acc}, and the carbonation coefficient measured on specimens exposed outside sheltered from rain, k_{nat}, for the different types of concrete at the different curing times. The accelerated carbonation coefficient is about one order of magnitude higher than the natural carbonation coefficient. For instance the carbonation coefficient measured on 15LI-0.46-300 concrete, cured 7 days, increased from about 2.2 mm/year$^{0.5}$ when specimens were exposed outside in sheltered conditions to around 12 mm/year$^{0.5}$ when specimens were exposed to an environment with 2% of carbon dioxide. Despite the variability of data, a good correlation can be determined between k_{acc} and k_{nat}, slightly dependent on the type of cement. This dependence on the type of binder might be due to a different way of exchange moisture with the atmosphere, impacting the carbonation rate. This confirms that the carbonation coefficient can be estimated from results of an accelerated test provided that corrective factors, that take into account the actual exposure conditions, are determined.

Figure 8 shows the environmental factor as a function of the curing time and the type of binder, evaluated as the ratio between the natural and the accelerated carbonation coefficient. This factor takes into account the different carbon dioxide concentration between the urban environment and the accelerated test and the different relative humidity and temperature that in the accelerated test were fixed to respectively 65% and 20°C and that in the real environment varied in time. Since sheltered exposure conditions were considered, this factor does not take into consideration the variation of concrete humidity due to rain. A quite high variability of the environmental factor can be observed that slightly increases increasing the curing time. Neglecting the effect of the type of binder, even if some slight influence was observed, and curing time, it can be estimated that the environmental factor is between 0.06 and 0.25, with an average value of 0.15, which is similar to the theoretical ratio of carbonation rates (i.e. the square root of the ratio between $CO_{2,acc}$ and $CO_{2,nat}$) suggesting that the main parameter that affects the environmental factor in sheltered conditions is the carbon dioxide concentration.

4.3 Impact of concrete characteristics on the service life

Results presented in the previous sections highlighted that concrete characteristics have an impact on the concrete carbonation. This means that the service life can be significantly different using concretes made with different binders. To evaluate the service life that can be guaranteed with the binders employed in this study, starting from data obtained in natural conditions, and to verify the requirements provided in the European standards, a probabilistic approach for the evaluation of service life was applied, considering simplified models both for the initiation and the propagation periods. For structures exposed to carbonation induced corrosion, the initiation time can be defined as the time required for carbonation to reach the depth of the outermost steel bars, whilst the propagation period can be defined as the time required to consume the steel bars of an amount that leads to the cracking of the concrete cover. In particular, for the initiation period, the probability of failure, p_f, was evaluated as the probability that the initiation limit state function, g, reaches negative values:

$$p_f = P\{g < 0\} = P\{x - k_{nat} \cdot \sqrt{t_i} < 0\} \quad (3)$$

where x is the concrete cover thickness, k_{nat} is the carbonation coefficient and t_i is the initiation time. For the propagation period, the probability of failure was evaluated through the following limit state equation:

$$p_f = P\{g < 0\} = P\{P_{lim} - v_{corr} \cdot t_p < 0\} \quad (4)$$

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where P_{lim} is the limit penetration of corrosion, v_{corr} is the corrosion rate and t_p the propagation time. In order to apply these equations to a RC element exposed in outdoor sheltered environment, reliable values for the involved parameters need to be defined. In the determination of the parameters the prescriptions provided in the European standards, in relation to an exposure class XC3, were considered. The carbonation coefficient was, then, evaluated for concretes made with a water/cement ratio of 0.55. In particular, it was considered that k_{nat} were described by a normal distribution, with a mean value determined, for each type of binder considered in this work, from data reported in Figure 2 and with a standard deviation equal to 20% of the mean value. A mean concrete cover thickness of 25 mm was taken into account, in agreement with the prescriptions of the European standards for the exposure class XC3, with a standard deviation of 6 mm, assuming that precautions were taken at the construction site. As far as the propagation period is concerned, it was assumed that it was independent from the type of binder, since reliable values of the corrosion rate for the different types of binder are still lacking in the literature [30]. The corrosion rate was described through a beta distribution function, characterized by a mean value and a standard deviation respectively of 2 and 0.4 µm/year and upper and lower limits of 5 and 0.5 µm/year, in agreement with literature data for outdoor sheltered environment [1,30]. Finally, P_{lim} was described by means of a normal distribution with a mean value and a standard deviation respectively equal to 100 and 30 µm. Table 4 summarizes the values selected for the different parameters.

Figure 9 shows the probability of failure as a function of the initiation and propagation times evaluated solving the limit state equations through a Montecarlo method (the lines in grey scale refer to the initiation time for the different types of binder, whilst the green line refers to the propagation time). The probability of failure, i.e. the probability of reaching the limit state, increased increasing the time. Assuming a target probability, P_0, equal to 10% (horizontal line in Figure 9), the initiation time varied from about 13 years for 30LI, to 16-18 years for PZ, FA and GGBS, to 34 years for 15LI and to values even higher than 100 years for PC. The duration of the propagation period can be estimated for all the concretes made with different binders, assuming a target probability of 10%, around 30 years.

From results shown in Figure 9, the service life was evaluated for each time of binder, by summing the cumulative distribution functions of the initiation and of the propagation periods (Figure 10). The service life that can be guaranteed with the different binders can be estimated after the definition of the target probability of failure. Assuming P_0 equal to 10%, i.e. considering that the cracking of concrete cover occurs in the 10% of the structure, the service life varied from values around 50-60 years for 30LI, FA, PZ and GGBS, to values around 80 years for 15LI and to values even higher than 100 years for PC. Increasing the target probability, for instance considering a P_0 equal to 50%, that means to evaluate the mean service life, values of the order of 80 years can be reached even with the less performant binder.

These simulations suggest that, at least for the exposure class XC3, indications provided in the European standards are suitable to guarantee a service life of 50 years with all the types of binder considered in this work, although they behaved differently in relation to carbonation. These results are in disagreement with Lye et al. [25,26] that made a literary review on the carbonation of GGBS and FA concretes, exposed outdoor in sheltered conditions. They concluded that the prescribed values of the Standards for XC3 exposure may need to be reconsidered for these types of concrete, since extrapolated carbonation depths at 50 years higher than 25 mm were determined considering concretes with water/binder ratio of 0.55.

Finally, according to the simulation, the use of a Portland cement, of class 52.5R, seemed to be excessive, indicating that a correct durability design should be aimed not only to guarantee a pre-defined service life, but also to avoid the oversizing, that in this case would lead to higher costs also in terms of sustainability. No considerations can be done for the other exposure classes, in particular the XC4 that is for RC elements exposed in unsheltered conditions and is the most aggressive class.

5. Conclusions

Natural carbonation was studied on 24 concretes made with Portland cement and different supplementary cementitious materials in different proportions, i.e. 15 and 30% limestone, 30% fly ash, 30% natural pozzolan and 70% ground granulated blast-furnace slag, three water/binder ratios, cured 1, 7 and 28 days and exposed for more than 12 years in sheltered conditions. On the basis of the experimental results and their analysis, the following conclusions can be drawn:

- Concretes made with Portland cement exhibited the lowest carbonation coefficient for each water/binder ratio and each curing time. The carbonation coefficient of concretes made with 30% pozzolan, 30% limestone, 30% fly ash and 70% ground granulated blast-furnace slag was more than doubled in comparison with Portland concretes. 15% limestone concretes carbonation coefficient was 1.5 times higher than Portland concretes. In pozzolanic and hydraulic concretes, the behaviour in relation to the carbonation was mainly governed by the consumption of calcium hydroxide no more available for the carbonation reaction. Conversely, in limestone concretes, the behaviour depended to the increase of porosity, due to the presence of limestone that mainly acts as an inert constituent.
- A decrease of the carbonation coefficient was observed increasing the curing from 1 to 28 days and increasing the curing time was less effective in concretes made with pozzolanic or hydraulic binder than with Portland cement.
- The carbonation coefficient and compressive strength were well correlated through an exponential relationship, suggesting that the two parameters are mainly governed by the capillary pores.
- A good relationship was determined between the accelerated and the natural carbonation coefficient, which was slightly affected by the type of cement, whilst the influence of the water/binder ratio and the curing time can be neglected. The average ratio between the natural and the accelerated carbonation coefficient was around 0.15.
- The prescriptions provided in the European standards, in terms of water/binder ratio and concrete cover thickness, allowed to guarantee, with a probability of failure of 10%, a service life of, at least, 50 years in a sheltered environment with all the binders employed in this study.

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Table 1 Main chemical components and specific surface area, σ, of Portland cement and supplementary cementitious materials.

	CaO (%)	SiO_2 (%)	Al_2O_3 (%)	SO_3 (%)	Fe_2O_3 (%)	MgO (%)	K_2O (%)	Na_2O (%)	Mn_2O_3 (%)	TiO_2 (%)	Cl^- (%)	σ (cm^2/g)
PC	63.5	20.5	5.28	3.29	2.84	1.53	1.0	0.29	0.07	0.24	0.01	5340
LI	43.8	15.8	1.98	0.27	0.80	1.10	0.6	0.06	0.05	0.11	-	6102
FA	2.92	52.9	33.2	0.73	5.23	1.06	1.2	0.72	0.04	1.17	-	5437
PZ	4.49	54.6	21.1	0.14	4.4	1.19	7.0	3.52	0.15	0.55	0.01	4606
GGBS	41.7	33.9	13.0	2.10	0.37	6.62	0.3	0.45	0.24	0.54	0.257	5624

Table 2 Mix proportion and slump of concrete mixes.

Series	PC (%)	Label	w/b	Water (kg/m³)	Binder (kg/m³)	Cement (kg/m³)	Aggregates (kg/m³)	Slump (mm)
PC	100	PC-0.61-300	0.61	183	300	300	1857	200
		PC-0.46-300	0.46	138	300	300	1979	185
		PC-0.46-350	0.46	161	350	350	1868	190
		PC-0.42-350	0.42	147	350	350	1913	180
15LI	85	15LI-0.61-300	0.61	183	300	255	1857	180
		15LI-0.46-300	0.46	138	300	255	1979	170
		15LI-0.46-350	0.46	161	350	297.5	1868	205
		15LI-0.42-350	0.42	147	350	297.5	1913	175
30LI	70	30LI-0.61-300	0.61	183	300	210	1857	210
		30LI-0.46-300	0.46	138	300	210	1979	170
		30LI-0.46-350	0.46	161	350	245	1868	165
		30LI-0.42-350	0.42	147	350	245	1913	165
FA	70	FA-0.61-300	0.61	183	300	210	1857	170
		FA-0.46-300	0.46	138	300	210	1979	200
		FA-0.46-350	0.46	161	350	245	1868	150
		FA-0.42-350	0.42	147	350	245	1913	200
PZ	70	PZ-0.61-300	0.61	183	300	210	1857	160
		PZ-0.46-300	0.46	138	300	210	1979	210
		PZ-0.46-350	0.46	161	350	245	1868	210
		PZ-0.42-350	0.42	147	350	245	1913	185
GGBS	30	GGBS-0.61-300	0.61	183	300	90	1857	210
		GGBS-0.46-300	0.46	138	300	90	1979	200
		GGBS-0.46-350	0.46	161	350	105	1868	200
		GGBS-0.42-350	0.42	147	350	105	1913	200

Table 3 Results of compressive strength, $f_{c,cube}$, accelerated carbonation coefficient, k_{acc} and sorptivity, S, for concrete mixes [23,24].

Series	Label	$f_{c,cube,1}$ MPa	$f_{c,cube,7}$ MPa	$f_{c,cube,28}$ MPa	$k_{acc,1}$ mm/year$^{0.5}$	$k_{acc,7}$ mm/year$^{0.5}$	$k_{acc,28}$ mm/year$^{0.5}$	S kg/m^2·h$^{0.5}$
PC	PC-0.61-300	23	45	59	30.6	21.2	18.4	-
	PC-0.46-300	28	62	87	15.9	12.8	3.9	-
	PC-0.46-350	47	76	80	19.2	12.9	4.6	-
	PC-0.42-350	50	83	87	-	7.3	-	0.34
15LI	15LI-0.61-300	20	38	45	32.2	26.6	22.2	1.29
	15LI-0.46-300	35	60	75	18	11.8	8.5	0.56
	15LI-0.46-350	42	65	68	17.9	12.1	7.8	0.69
	15LI-0.42-350	50	68	83	-	11.2	-	0.46
30LI	30LI-0.61-300	19	31	37	40.4	34.6	27.4	1.48
	30LI-0.46-300	35	47	61	29.2	20.7	16.8	0.65
	30LI-0.46-350	35	49	57	24.3	23.2	16.1	0.89
	30LI-0.42-350	42	57	67	-	12.3	-	0.67
FA	FA-0.61-300	20	30	44	29.9	30.9	21.9	0.94
	FA-0.46-300	35	52	76	27.2	24.9	18.7	0.41
	FA-0.46-350	32	52	75	24	22.5	8.9	0.5
	FA-0.42-350	49	66	81	-	13.2	-	0.29
PZ	PZ-0.61-300	20	35	43	34.6	32.7	25.3	0.96
	PZ-0.46-300	37	54	70	23.1	18.3	11.0	0.51
	PZ-0.46-350	37	55	69	22.1	16.6	13.8	0.51
	PZ-0.42-350	37	54	73	-	13.4	-	0.46
GGBS	GGBS-0.61-300	8	35	45	29	25	24	0.99
	GGBS-0.46-300	13	46	55	32.4	24	22.7	0.49
	GGBS-0.46-350	16	59	55	18.5	16.7	13.5	0.38
	GGBS-0.42-350	24	76	83	-	13.4		0.30

Table 4 Values of the selected parameters and types probability density function distribution, PDF, (BetaD = beta distribution; ND = normal distribution) used as inputs in the limit state equations (m = mean value, σ = standard deviation).

Parameter	Unit	PDF	Options	m	σ
k_{nat}	mm/year$^{0.5}$	ND	PC	1.6	0.32
			15LI	2.8	0.56
			30LI	4.6	0.92
			FA	4	0.8
			PZ	4.1	0.82
			GGBS	3.9	0.78
X	Mm	ND	All	25	6
v_{corr}	μm/year	BetaD $(0.5<v_{corr}<5)$	All	2	0.4
P_{lim}	μm	ND	All	100	30

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