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# A performance based approach for durability of concrete exposed to carbonation

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Carbonation is a widespread degradation of concrete and may be coupled with more severe degradations. In order to change from prescriptive requirements to performance based specifications for durability, through the equivalent performance concept, it is necessary to find relevant performance tests and indicators. Concrete mixtures of the reported study were designed complying with required binder contents and water–cement ratios to investigate the effects of binder composition, aggregate type and curing conditions. Early drying severely affected performances, as well as cement replacement by low-calcium fly ash. Aggregates had indirect effects on actual water content and curing. Porosity, gas permeability and chloride diffusivity were found as unreliable indicators for carbonation, since they only characterise compactness of concrete. An accelerated carbonation test is proposed as a performance test, as it is sensitive enough and results were consistent with natural carbonation in the studied exposure conditions. Another indicator, based on chloride diffusivity/initial CaO content ratio, could provide useful data for given aggregate mixes and curing conditions, as it takes into account compactness of concrete and chemical reactivity of binder.

*Keywords:* Durability; Carbonation; Equivalent performance concept; Accelerated test

## 1. Introduction

Corrosion of steel reinforcement is one of the major causes of degradation of concrete structures. Initiation of corrosion may be due to ingress of chloride ions or carbonation. Carbonation results in a drop of pH of surface concrete, then corrosion of steel bars is likely to occur because they are not passivated anymore. Although carbonation is often considered as less severe than chloride ingress, it is much more widespread, because it involves carbon dioxide (CO<sub>2</sub>) from air. Furthermore, carbonation coupled with chloride ingress reduces durability of concrete exposed to de-icing salts and marine environments, because carbon-

ation accelerates chloride ingress [1]. Besides, ductility of concrete would decrease with an increase in the degree of carbonation [2]. Therefore carbonation has to be taken into account for designing most of concrete mixtures.

Carbonation is the result of a chemical reaction between carbon dioxide and concrete hydrates, such as portlandite Ca(OH)<sub>2</sub> and calcium silicate hydrates (CSH), producing calcite CaCO<sub>3</sub> and water. The mechanism of degradation is now well known and models [3–6] describe the propagation of the dissolution front, mainly in Portland cement pastes or concrete. But the recent development of performance based specifications for durability of concrete show the need for relevant indicators that might be applied to all kinds of binders and would be relatively easy to assess [7–9]. Most of the experimental studies have dealt with the effect of compactness through variations in water–cement ratio, as it is a major parameter as far as durability of

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concrete is concerned. However, in construction practice, concrete mixtures are often designed from the maximum water/binder ratio complying with standards and varying other parameters such as aggregate and binder types.

As the assessment of life time of a concrete structure from a given concrete mixture is still difficult, standards on concrete often rely on prescriptive specifications, assuming that they will result in appropriate durability. In the new European Standard EN 206-1 [10] on performance, production and conformity of concrete, exposure classes are defined. XC exposure classes deal with carbonation. For each exposure class, minimum binder content and maximum water–binder ratio are specified. Minimum strength is also mentioned, and in French standard maximum mineral admixtures contents are also defined. However, the new European standard allows performance based specifications through the *equivalent performance concept* [10–12]. Equivalent performance has to be shown through a comparison with a reference concrete mixture, which complies with prescriptive requirements for a given exposure. The comparison may be done through durability tests, provided that they give reliable ranking of performances of concrete exposed to a given degradation, such as carbonation. This study is part of a project aimed at designing a methodology to implement the *equivalent performance concept* to every exposure class. This study deals with reference concrete mixtures, as they are not defined in the standard. The purpose is to investigate the variability of performances of concrete mixtures which comply with prescriptive requirements, i.e. threshold values of standard, in order to provide data to choose reference concrete mixtures, taking into account the effect of mineral admixtures, aggregate types and curing conditions. The experimental study includes assessment of durability indicators and mercury intrusion porosimetry on hardened concrete before degradation, accelerated carbonation test and natural carbonation, in order to find performance indicators of concrete exposed to carbonation.

## 2. Experimental program

### 2.1. Materials, mixture proportions and curing

In European standard EN 206-1 [10], XC exposure classes classifies the environmental conditions from low (XC1) to high (XC4) risk of carbonation, depending on carbon dioxide concentration and saturation degree of concrete. Only two sets of prescriptive specifications are defined in the French standard NF EN 206-1. The two levels of minimum strength of concrete (C20/25 and C25/30), maximum water–binder ratio (0.65 and 0.60) and minimum binder content (260 and 280 kg/m<sup>3</sup>) respectively correspond to XC1–XC2 and XC3–XC4 exposure classes. Two series of five and three concrete mixtures have been designed, keeping these values constant, and varying binder and aggregates types. Two binders were used, namely: Portland cement CEM I 52.5 N and another binder made of 70%

Table 1  
Properties of cementitious materials

|                                | Cement CEM I 52,5 N                 | Fly ash |
|--------------------------------|-------------------------------------|---------|
|                                | Blaine surface (cm <sup>2</sup> /g) | 3440    |
| Mean diameter (µm)             | –                                   | 24      |
| Clinker (%)                    | 98.0                                | –       |
| CaO                            | 63.77                               | 2.2     |
| SiO <sub>2</sub>               | 20.21                               | 52.5    |
| Al <sub>2</sub> O <sub>3</sub> | 4.18                                | 27.9    |
| Fe <sub>2</sub> O <sub>3</sub> | 2.22                                | 5.6     |
| SO <sub>3</sub>                | 2.76                                | 0.6     |

Portland cement (C) and 30% fly ash (FA). Properties of cement and fly ash are given in Table 1. Portland cement was substituted by fly ash (FA) according to the maximum FA/(C + FA) ratio allowed by the standard. Two aggregates mixtures were chosen to take into account the possible effects of aggregate type on interfacial transition zone, and effects of grading of aggregates on compactness of concrete. Boulonnais sand and gravel are crushed dense limestone aggregates. They have been used in other laboratory studies [13] and the main feature of the sand is a high proportion of fine elements (6.7% below 63 µm). The other type is the sea aggregates which are washed and have a relatively high porosity in terms of Water absorption, as shown in Table 2. The design of the mixtures was performed by the Faury method, adjusting the mixture curve (including cement and admixture) with a reference granulometric curve [14]. The second aggregate mix made of sea aggregates lacks fine elements between 63 and 315 µm. Fine siliceous sand (0/1 mm) was used in B8 concrete mixture to compare the effect of mineral admixture (fly ash) and grading of aggregates.

Two batches of each concrete were made and cast in 70 × 70 × 280 mm<sup>3</sup> moulds for accelerated carbonation test and Ø 110 × 220 mm moulds for other tests. After 24 h of sealed curing, the first set of specimens was cured under water for 28 days and will be referred to as “24 h – Water”. The second set of specimens was sealed cured until concrete reached 50% of the minimum 28-day characteristic strength from standard NF EN 206-1, which is 20 MPa for XC1–XC2 classes and 25 MPa for XC3–XC4 classes. Then they were cured in a room at a constant temperature of 20 °C and a constant relative humidity of 50% RH for 28 days. They will be referred to as “50%”.

Table 2  
Properties of aggregates

|                              | Boulonnais aggregates |         | Sea aggregates |         | Fine sand |
|------------------------------|-----------------------|---------|----------------|---------|-----------|
|                              | Sand                  | Gravels | Sand           | Gravels |           |
|                              |                       |         |                |         |           |
| Passing <125 µm (%)          | 15.7                  | 0.5     | 2.6            | 0.1     | 7.1       |
| Water absorption (%)         | 0.8                   | 0.7     | 0.6            | 2.1     | 0.2       |
| Density (kg/m <sup>3</sup> ) | 2650                  | 2670    | 2580           | 2600    | 2650      |

## 2.2. Experimental procedures

The same set of durability tests was performed on the 16 previously described materials. The tests were carried on three samples from the same batch after 28 days, except the mercury intrusion porosimetry test, which was done on two samples after 90 days.

Compression tests were carried out just after sealed curing and also after 28 days. The experimental program included assessment of three so-called general durability indicators [8], namely: water porosity, gas permeability and chloride diffusivity. Water porosity was measured according to the AFPC-AFREM procedure [15]. Gas permeability was measured according to the AFPC-AFREM procedure at a relative pressure of 1.0 bar to assess apparent permeability, and between 2.0 and 4.0 bar to assess permeability by Klinkenberg approach [16]. Chloride diffusivity was assessed from a steady state migration test called LMDC test [17]. This migration test consists in accelerating a chloride diffusion test by a constant electrical field. The effective chloride diffusion coefficient is assessed from the chloride ion flux in the cathodic cell in steady state.

Accelerated carbonation test was done according to the AFPC-AFREM procedure in a carbonation chamber at 20 °C and 65% RH with 50% CO<sub>2</sub>. The main result of the accelerated carbonation test is carbonated depth. This was assessed by a colorimetric method based on the drop of pH at the carbonation front [18]. A phenolphthalein solution was sprayed on cross sections of prismatic 70 × 70 × 280 mm<sup>3</sup> samples, at 7, 14, 21, 28, and 56 days. Carbonated material is not coloured by phenolphthalein. Specimens from the same batch were kept after 28 days at a constant temperature of 20 °C and relative humidity of 50% RH to measure natural carbonation after one year, according to the AFPC-AFREM procedure.

## 3. Results and discussion

### 3.1. General durability indicators

The ingress of aggressive ions or molecules into saturated or dry concrete is governed by several transport mechanisms. Diffusion often prevails, as transport is due to concentration gradients between porous net and environment of concrete. Permeability characterises the ease with which a fluid will pass through a material under a pressure difference [7]. As far as carbonation is concerned, the main transport mechanism would be diffusion. Gas permeability has already been assessed as an indicator of potential durability [8,19]. Because of gas transport, carbon dioxide flows into concrete to react with hydration products, and oxygen flows through surface concrete to corrode steel reinforcement. One of the objectives of the study is to identify relevant indicators by comparing durability indicators with carbonation rates. Compressive strength and porosity may be regarded as general indicators for poten-

tial durability. Each result (Table 4) is a mean value, from free tests on different samples.

A characteristic strength of 20 MPa was required for B1, B2, B3, B4 and B5 concrete mixtures, according to specifications for XC1–XC2 classes, and a 25-MPa characteristic strength was required for B6, B7 and B8 concrete mixtures, for XC3–XC4 classes. Twenty-eight-day compressive strengths were from 50% (B8) to 139% (B1) higher than required. As concrete mixtures complied with maximum water/binder ratios and minimum binder contents, this result may seem surprising. However in European standard EN 206-1 the values for strength are related to CEM I 32.5, but according to French standard NF EN 206-1 CEM I 42.5 or 52.5 has to be used to take into account mineral admixtures, such as fly ash, in assessment of equivalent binder content (equal to cement +  $k \times$  admixture). Moreover, the highest strengths were measured on concrete including crushed limestone aggregates (B1, B2, B6, and B7). The sand contains 7% of fine elements (<63 μm), which are not taken into account in binder content. So fine element content (Table 3) could partly explain this difference. The difference in compressive strength of concrete mixtures including crushed limestone or sea aggregates may also come from compactness of concrete mixtures and actual water/binder ratio. Effective water content ( $W_{\text{eff}}$ ) differs from added water by water which is absorbed by aggregates. This is assessed from WA24 (water which is absorbed after 24 h in standardized conditions), given for each type of sand or gravel. Sea gravel is more porous and has a WA24 of 2%, instead of 0.7% for limestone gravel. But during batching and curing, gravels may not absorb so much water, so the real water content of paste is higher for concrete made of sea gravels and strength is lower.

As the two sands have very different contents of fine elements, the corresponding volumes of paste are different. So porosity of paste would be a more reliable indicator to compare the two sets of concrete mixtures. Volume of paste has been defined as  $W_{\text{eff}}$  + volume of fine elements (<125 μm) (Table 3). If it is assumed that the porosity of concrete is the porosity of paste, porosity of concrete/volume of paste ratios give porosity of paste (Table 4).

$$\text{Porosity}_{\text{paste}} = \frac{\text{Porosity}_{\text{Concrete}}}{\text{Volume of paste}} \quad (1)$$

Porosity/volume of paste ratios are consistent with strengths. They are closely linked to aggregate type, and the significant differences are consistent with what was assumed about real water content of paste to explain differences in strengths. Use of fine sand in B5 concrete mixture results in reduction of concrete porosity and porosity of paste, especially for dry curing (“50%”).

The type of curing seems to have a significant effect, especially on gas permeability as shown in Table 4. This does not only come from curing conditions but also from configuration of samples for durability tests. Compressive strengths of studied concrete mixtures are significantly

Table 3  
Mixture proportions

| Exposure classes (kg/m <sup>3</sup> )          | XC1, XC2 |       |       |       |       | XC3, XC4 |       |       |
|------------------------------------------------|----------|-------|-------|-------|-------|----------|-------|-------|
|                                                | B1       | B2    | B3    | B4    | B5    | B6       | B7    | B8    |
| Boulonnais gravel 12/20                        | 541      | 561   |       |       |       | 541      | 561   |       |
| Sea gravel 10/20                               |          |       | 553   | 553   | 553   |          |       | 553   |
| Boulonnais 4/12                                | 416      | 432   |       |       |       | 416      | 432   |       |
| Sea Gravel 4/12                                |          |       | 446   | 425   | 452   |          |       | 446   |
| Boulonnais sand 0/4                            | 992      | 915   |       |       |       | 980      | 900   |       |
| Sea sand 0/4                                   |          |       | 819   | 880   | 712   |          |       | 805   |
| Fine sand 0/1                                  |          |       |       |       |       |          |       | 144   |
| Cement CEM I 52,5 N                            | 260      | 207   | 207   | 260   | 260   | 280      | 223   | 223   |
| Fly ash (FA) Cordemais ( $k = 0,6$ )           |          | 89    | 89    |       |       |          | 95    | 95    |
| Weff.                                          | 163.8    | 163.8 | 163.8 | 163.8 | 163.8 | 162.4    | 162.4 | 162.4 |
| WRA (Glenium 27)                               | 3.82     | 3.65  | 0.97  | 0.50  | 0.60  | 3.67     | 2.98  | 1.69  |
| Equivalent binder content ( $C + k \cdot FA$ ) | 260      | 260   | 260   | 260   | 260   | 280      | 280   | 280   |
| $W_{eff}/(C + k \cdot FA)$                     | 0.63     | 0.63  | 0.63  | 0.63  | 0.63  | 0.58     | 0.58  | 0.58  |
| FA/(C + FA)                                    | 0        | 0.30  | 0.30  | 0     | 0     | 0        | 0.30  | 0.30  |
| Fine elements (<125 $\mu$ m)                   | 447      | 468   | 317   | 283   | 289   | 465      | 488   | 339   |
| Volume of paste (L/m <sup>3</sup> )            | 318      | 328   | 271   | 256   | 258   | 322      | 340   | 284   |

Table 4  
Durability indicators

|    | Strength, 28 days (MPa) |      | Water porosity (%) |      | Porosity/ volume of paste (%) |      | Intrinsic permeability ( $10^{-17}$ m <sup>2</sup> ) |      | Chloride diffusivity ( $10^{-12}$ m <sup>2</sup> /s) |      |
|----|-------------------------|------|--------------------|------|-------------------------------|------|------------------------------------------------------|------|------------------------------------------------------|------|
|    | 24 h Water              | 50%  | 24 h Water         | 50%  | 24 h Water                    | 50%  | 24 h Water                                           | 50%  | 24 h Water                                           | 50%  |
|    | B1                      | 47.8 | 36.2               | 12.7 | 14.4                          | 40.0 | 45.2                                                 | 2.6  | 9.8                                                  | 1.94 |
| B2 | 40.0                    | 31.2 | 13.7               | 15.0 | 41.6                          | 45.6 | 3.1                                                  | 21.3 | 1.93                                                 | 1.80 |
| B3 | 35.4                    | 25.3 | 14.1               | 17.3 | 52.1                          | 63.7 | 4.4                                                  | 20.2 | 1.90                                                 | 1.81 |
| B4 | 37.8                    | 31.3 | 13.6               | 17.3 | 52.9                          | 67.4 | 4.3                                                  | 17.3 | 1.80                                                 | 1.77 |
| B5 | 37.7                    | 29.4 | 13.2               | 15.4 | 51.1                          | 59.7 | 3.9                                                  | 18.7 | 1.82                                                 | 1.71 |
| B6 | 52.1                    | 38.6 | 14.2               | 13.9 | 44.0                          | 43.2 | 6.5                                                  | 10.2 | 1.43                                                 | 1.63 |
| B7 | 52.7                    | 38.8 | 14.2               | 15.7 | 41.8                          | 46.3 | 3.1                                                  | 8.1  | 1.46                                                 | 1.28 |
| B8 | 37.5                    | 32.5 | 15.1               | 15.9 | 53.1                          | 56.2 | 4.2                                                  | 12.5 | 1.49                                                 | 1.80 |

higher than required characteristic strengths. So strength at the end of sealed curing is less than 50% of measured 28-day compressive strength. It actually ranged from 22% (B1 50%) to 31% (B8 50%). So because of drying, hydration rate of surface concrete of “50%” samples is relatively low and this explains the increase in transport properties, such as gas permeability. Finally, for the “50%” curing condition, the stronger concrete undergoes the worst curing conditions. This discrepancy between required and actual compressive strength and its consequences on real curing is also to be kept in mind to analyze results from carbonation tests. But configuration of samples and testing device may be taken into account to explain effects of curing conditions on gas permeability. This was assessed on cylindrical Ø 110 × 50 mm specimens sawed from Ø 110 × 220 mm samples; as gas flux is transverse, it may flow through surface concrete layer which is likely to be more permeable for the “50%” curing condition because of early drying. In real atmospheric conditions, air or gas gets into concrete from the surface, so configuration and effect of curing conditions on durability may be different.

### 3.2. Mercury intrusion porosimetry

In order to better understand results from measures of global properties, mercury intrusion porosimetry (MIP) tests have been carried out. Pore size distribution curves and quantitative results, such as porosities, median and average pore diameters may be useful to analyze properties of concrete [20,21]. Quantitative results are mean values from tests on two 10-g specimens from the same cylindrical Ø 110 × 220 mm sample of sound concrete.

MIP tests were carried out on B6 concrete samples after 28 days and 90 days, to investigate the effect of curing condition, as shown in Fig. 1. The porous mode which appeared clearly at 28 days for “50%” curing tended to decrease, but it could still be observed after 90 days and it had an influence on median pore diameter.

In Fig. 2, compressive strength is plotted against macroporosity, which is defined as porosity for pore diameters exceeding 50 nm. Compressive strength decreases with an increase in porosity, which is to be linked to Water/Binder ratio of paste.

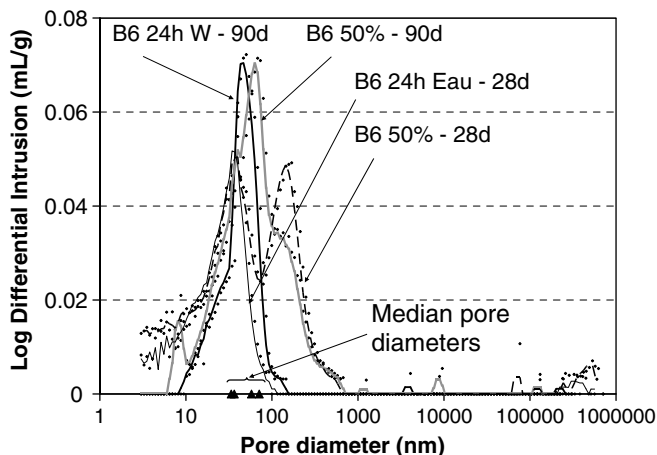


Fig. 1. Pore size distribution of B6 concrete mixture.

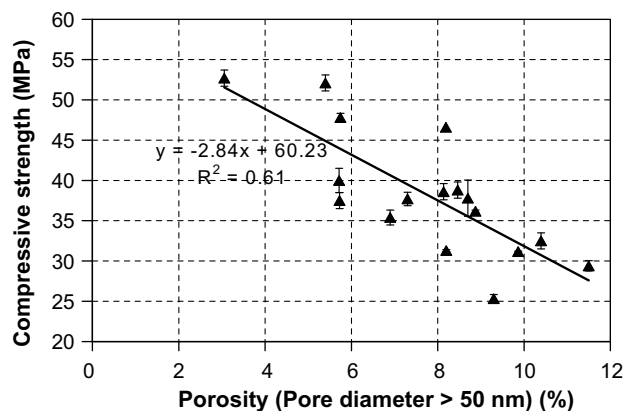


Fig. 2. Compressive strength and macroporosity.

The average pore diameter is assessed from the ratio of the total intruded volume of mercury and the total pore surface area. This is based on the assumption that the pores are cylindrical and open at the ends. Median pore diameter is defined as the pore diameter at which 50% of the total volume of intruded mercury is intruded; a parameter that is mainly affected by the number of large pores. So it is better to use the median pore diameter to correlate with permeability. In Fig. 3, intrinsic permeability is plotted against median pore diameter. Equations can be found in the literature to link porosity and permeability, through MIP and other data. From the results of the study, median pore diameter seems to be a relevant parameter as far as gas permeability is concerned. However, MIP results do not account for carbonation behaviour, which has to be deduced from specific tests or more reliable indicators.

### 3.3. Accelerated carbonation test

Twenty-eight-day carbonated depths and standard deviations are given in Fig. 4. In spite of the dispersion of some results, significant differences can be observed. Most of carbonation depths ranged from 4 to 12 mm, whereas water/

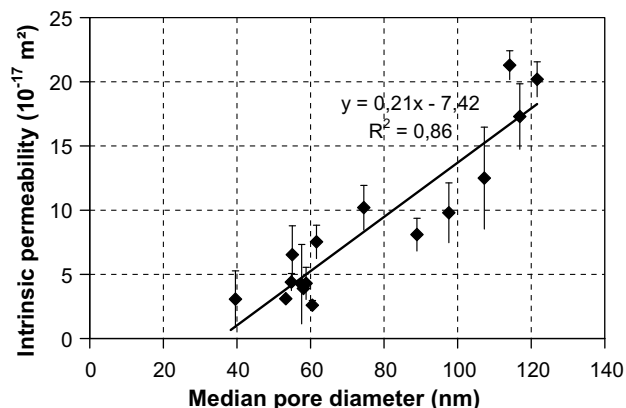


Fig. 3. Intrinsic permeability and median pore diameter.

binder ratio and binder content were kept constant. So the accelerated carbonation test is interesting in a performance based approach, as it is sensitive [21,24].

Effects of composition parameters and curing conditions appear on the results of the accelerated test. “Dry” cured (“50%”) concrete generally had higher carbonation depths than concrete cured under water, except B8 50% concrete. It should be noted that this result may not be relevant, as it is not consistent with other properties of the same material (Table 4), results for B3 concrete (Fig. 3), which had the same binder and aggregates, and natural carbonation.

Water/binder ratio had not systematically the expected effect on carbonation, as B1, B4 and B5 concrete mixtures ( $W/B = 0.63$ ) showed lower carbonated depths than B6, B7, and B8 concrete mixtures ( $W/B = 0.58$ ). But the difference between the two  $W/B$  ratios is relatively low and the difference between the water contents of, respectively, 163.8 and 162.4  $L/m^3$  is even lower (0.9%), as binder content also varied. So the accelerated test might not have been sensitive enough to show the difference, which also occurred for other properties, such as porosity and gas permeability. The effect of fly ash is clear and has already been reported [22]. From concrete mixtures made of the same aggregates with the same  $W/B$  ratio, a negative effect of fly ash may be deduced. In case of use of fly ash, a lower portlandite content in concrete may come from a lower lime content in binder or from the consumption of portlandite by pozzolanic reaction. From other experimental studies [22,25], the last explanation would be wrong. The effects of aggregates are more difficult to analyze. Moreover, the test may not have been sensitive enough to draw conclusions. Paste of sea aggregates concrete mixtures had higher actual  $W/B$  ratio than limestone aggregates concrete mixtures, but “50%” curing lead to better curing for sea aggregates concrete mixtures. As far as water cured concrete is concerned, from B1/B4, B2/B3 and B7/B8 concrete mixtures, it may be deduced that the crushed limestone aggregates lead to better resistance against carbonation. This may also come from the quality of the interfacial transition zone between paste and aggregates or from density of the mix, as sea aggregates mix lacks fine elements. In B5

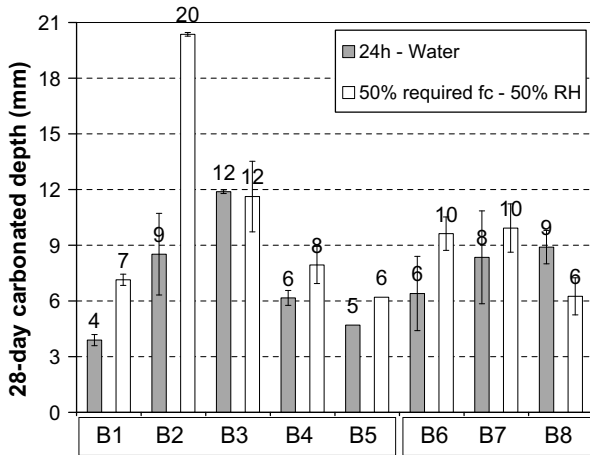


Fig. 4. 28-day carbonated depths, from AFPC-AFREM accelerated test.

concrete mixture, fine sand was added and the concrete mixture seemed to have a better behavior than B4.

As the study was also aimed at investigating relevance of commonly used durability indicators about carbonation, 28-day carbonation depth is plotted against porosity, chloride diffusivity, and gas permeability in Figs. 5–7.

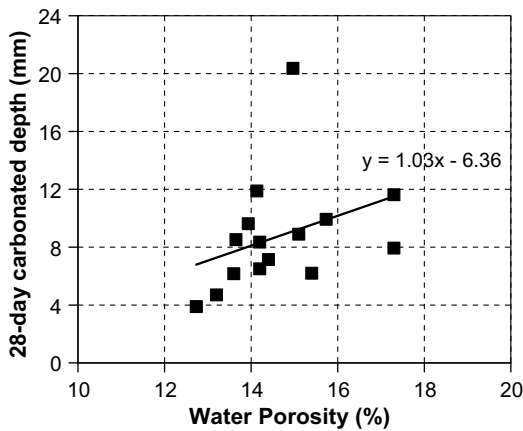


Fig. 5. Carbonated depth and porosity.

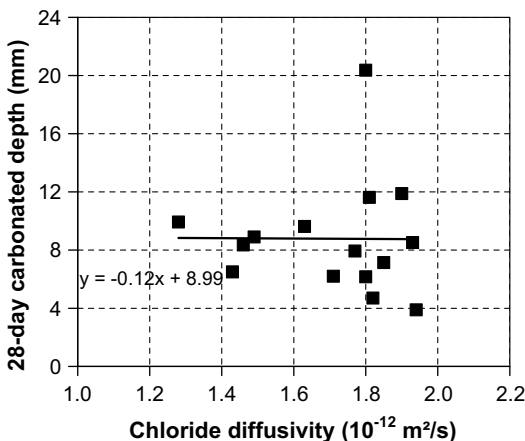


Fig. 6. Carbonated depth and chloride diffusivity.

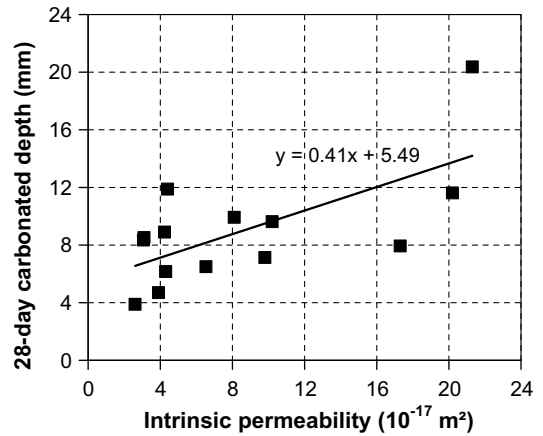


Fig. 7. Carbonated depth and intrinsic permeability.

The highest sensitivity is shown with gas permeability, but no good correlation between global properties and carbonation may be deduced from these results. For instance, the same porosity can be associated with very different carbonation rates. This has already been reported in other studies [23]. Gas permeability is not based on the real transport mechanism of CO<sub>2</sub> through concrete, but the test has emphasized the properties of the surface concrete layer exposed to early drying, which is also the first layer exposed to carbonation. This could explain previous attempts to use gas permeability as an indicator for carbonation behaviour [19]. The three indicators deal with compactness and properties of the porous net of concrete, but they do not take into account chemical reactivity of binder and carbonatable content. Initial CaO content could provide a first assessment of carbonatable content, to be used in a more reliable indicator of performance of concrete exposed to carbonation (Fig. 9). CaO contents of concrete mixtures given in Table 6 were calculated from CaO content of cement and fly ash (Table 1), and used in chloride diffusivity/CaO ratio. This indicator is linked to carbonation rate, calculated from a linear regression on carbonation depths vs. square root of time curves, as shown in Fig. 8.

The last indicator seems to give a better assessment of performances of concrete exposed to the accelerated car-

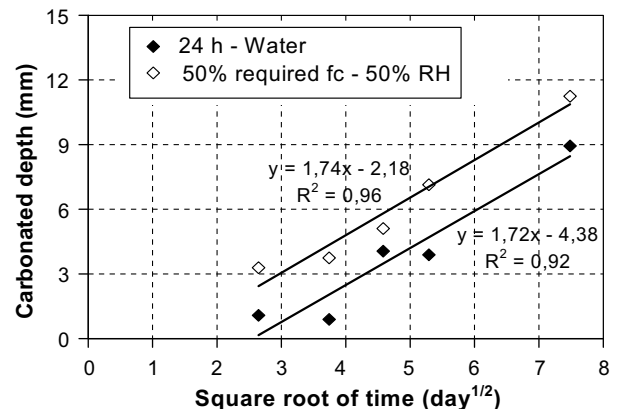


Fig. 8. B1 concrete mixture, carbonated depth vs. square root of time.

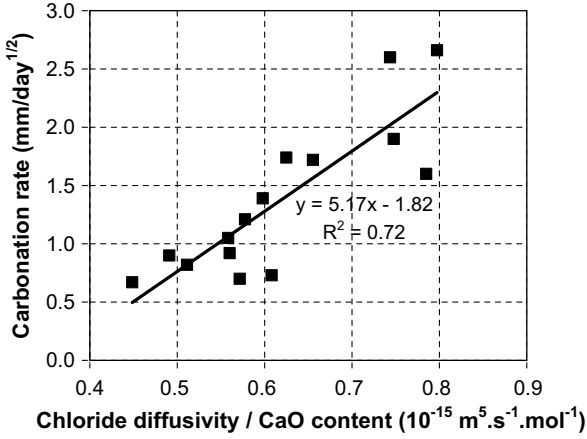


Fig. 9. Carbonation rate and potential durability indicator.

bonation test, but Fig. 9 also reveals several behaviours. So it must be detailed to take into account curing conditions and the effect of aggregates (Figs. 10 and 11). If a set of concrete mixtures is made of the same aggregates and undergoes the same curing conditions, the indicator seems reliable enough to be used in a comparative way. This is

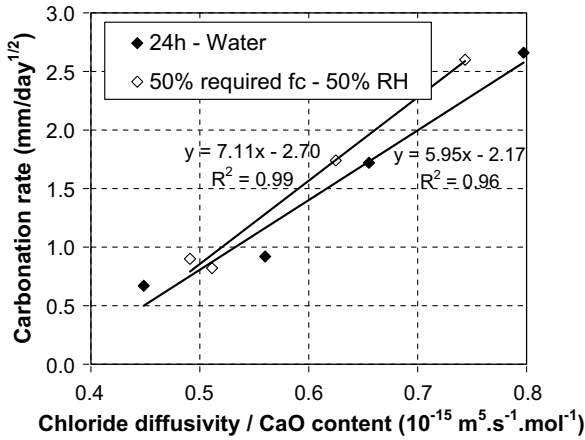


Fig. 10. Chloride diffusivity/CaO content using Boulonnais aggregates.

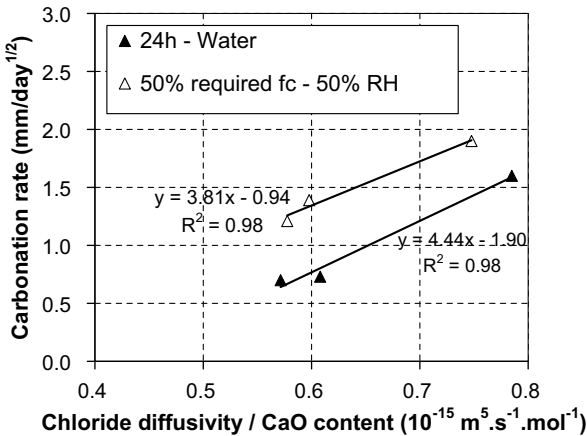


Fig. 11. Chloride diffusivity/CaO content using sea aggregates.

consistent with previous results. Assié et al. [24] found a strong correlation between carbonation rate and chloride diffusivity, for concrete mixtures that had the same initial CaO content.

The indicator does not take into account relative humidity and saturation degree, which could account for differences between materials resulting from the two studied curing conditions. From the results, initial CaO content would be a relevant assessment of the proportion of carbonatable material. It has been shown that carbon dioxide actually reacts with portlandite, but also with CSH and not hydrated  $C_2S$  and  $C_3S$ . The rates of the various carbonation reactions are not the same, but the global rate would not be sensitive to the exact proportions and rates [4].

Furthermore the relevance of the indicator can be confirmed by models aimed at assessing the rate of carbonation of concrete under accelerated test. One of these models [3,4] is based on a description of the physico-chemical processes and gives, after simplifying assumptions, the evolution of the carbonation front with time  $x_c$ , through an expression of the form:

$$x_c = \sqrt{\frac{2D_{e,CO_2}^c [CO_2]^0}{[Ca(OH)_2]^0 + 2[CSH]^0 + 3[C_3S]^0 + 3[C_2S]^0} t} \quad (1)$$

$D_{e,CO_2}^c$  is the effective  $CO_2$  diffusivity of carbonated concrete,  $D_{e,CO_2}^c$  is the concentration of  $CO_2$  in surrounding atmosphere and the denominator is the total molar concentration of CaO, in carbonatable materials.  $D_{e,CO_2}^c$  is computed from porosity of the paste and ambient relative humidity [3]. Saturation degree and properties of porous net are assumed to be steady in time in the carbonated layer, so hydration and production of water and all the effects of carbonation on diffusivity are not comprehensively described. Recent models include more accurate descriptions of these phenomena and mechanisms of carbonation of the different phases [5,6].

### 3.4. Natural carbonation

From 28 days after batching, one  $70 \times 70 \times 280 \text{ mm}^3$  specimen from the same batch was stored in laboratory at  $20^\circ\text{C}$  and 50% of relative humidity, to assess carbonation depth after one year. The carbonation depths from the two tests (laboratory conditions and accelerated test) are given in Table 5 and plotted on Fig. 12. Photographs of cross-sections of naturally carbonated specimens are given in Fig. 13. Natural carbonation results show the same trends as the accelerated test. Classifications of performances from the two tests were consistent for given aggregate type and curing conditions. The accelerated test tends to emphasize differences, for given curing conditions. The laboratory exposure conditions are severe as far as carbonation is concerned, as experimental studies [4,18] have shown that the rate of carbonation is maximum at a relative humidity between 50% and 60%. Moreover, compressive strength of the concrete specimens of the “50%”



Table 5  
Carbonated depths from natural carbonation and accelerated test

| Curing          | Classification of performances |    | Carbonated depth (mm) |             | Classification of performances |    | Carbonated depth (mm) |             |
|-----------------|--------------------------------|----|-----------------------|-------------|--------------------------------|----|-----------------------|-------------|
|                 | Boulonnais aggregates          |    | Natural               | Accelerated | Sea aggregates                 |    | Natural               | Accelerated |
| 24 h – water    | 1                              | B1 | 1.2                   | 3.9         | 1                              | B5 | 2.4                   | 4.7         |
|                 | 2                              | B6 | 2.1                   | 6.5         | 2                              | B4 | 3.3                   | 6.2         |
|                 | 3                              | B2 | 2.1                   | 8.5         | 3                              | B8 | 3.3                   | 8.9         |
|                 | 4                              | B7 | 3                     | 8.4         | 4                              | B3 | 3.4                   | 11.9        |
| 50% fc – 50% RH | 5                              | B6 | 9.5                   | 9.6         | 5                              | B5 | 9.1                   | 6.2         |
|                 | 6                              | B1 | 10.9                  | 7.1         | 6                              | B4 | 9.2                   | 7.9         |
|                 | 7                              | B7 | 11.6                  | 9.9         | 7                              | B8 | 12.1                  | 6.3         |
|                 | 8                              | B2 | 13.7                  | 20.4        | 8                              | B3 | 12.8                  | 11.6        |

Table 6  
Carbonation rate and diffusivity-CaO content indicator

|    | CaO content ( $10^3 \text{ mol/m}^3$ ) | Chloride diffusivity/initial CaO content ( $10^{-15} \text{ m}^5 \text{ mol}^{-1} \text{ s}^{-1}$ ) |      | Carbonation rate ( $\text{mm/day}^{1/2}$ ) |      |
|----|----------------------------------------|-----------------------------------------------------------------------------------------------------|------|--------------------------------------------|------|
|    |                                        | 24 h Water                                                                                          | 50%  | 24 h Water                                 | 50%  |
| B1 | 2.96                                   | 0.66                                                                                                | 0.62 | 1.72                                       | 1.74 |
| B2 | 2.42                                   | 0.80                                                                                                | 0.74 | 2.66                                       | 2.60 |
| B3 | 2.42                                   | 0.78                                                                                                | 0.75 | 1.60                                       | 1.90 |
| B4 | 2.96                                   | 0.61                                                                                                | 0.60 | 0.73                                       | 1.39 |
| B5 | 2.96                                   | 0.61                                                                                                | 0.58 | –                                          | 1.21 |
| B6 | 3.19                                   | 0.45                                                                                                | 0.51 | 0.67                                       | 0.82 |
| B7 | 2.61                                   | 0.56                                                                                                | 0.49 | 0.92                                       | 0.90 |
| B8 | 2.61                                   | 0.57                                                                                                | 0.69 | 0.70                                       | –    |

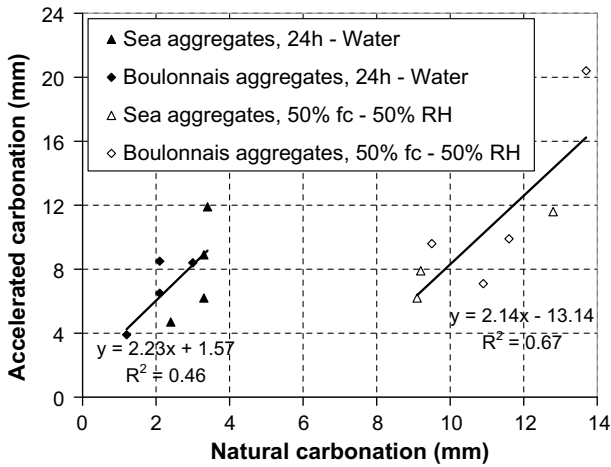


Fig. 12. Natural and accelerated carbonation depths.

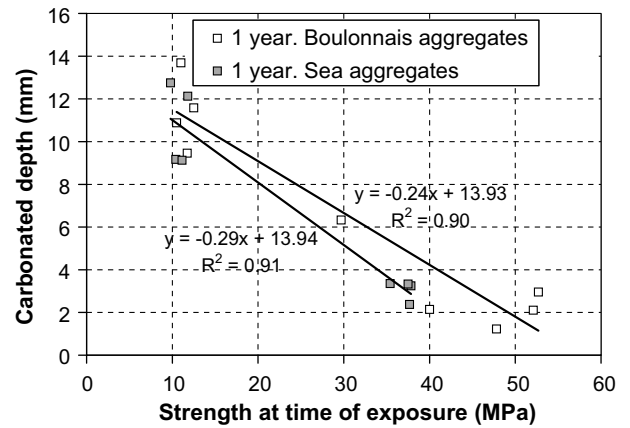


Fig. 14. Naturally carbonated depth and Compressive strength at time of exposure.



Fig. 13. 1-year natural carbonation fronts of B1, B2, B3, B4, B5, B6, B7, B8 concrete samples. First row: 50% curing conditions. Second row: 24 h - Water curing conditions.

series after sealed curing was only from 22% to 31% of the 28-day compressive strength measured on water cured specimens. Therefore it was less than 50% of the actual compressive strength. Fig. 14 shows a good correlation between “naturally” carbonated depth and compressive strength at time when concrete is exposed to desiccation and CO<sub>2</sub> from air [26].

#### 4. Conclusions

The *Equivalent performance concept* defined in European standard EN 206-1 on specification of concrete allows qualifying a concrete mixture which does not comply with prescriptive specifications, provided that its test performance is at least as good as a mixture which complies with limiting values from standards. In this context, the main objective of the study was to find a performance based indicator to assess potential durability of concrete exposed to carbonation, to be used to compare potential durability of different concrete mixtures.

Carbonated depth was assessed on concrete prisms after 12 months at 50% RH in the laboratory and after 28 days of accelerated test at 65% RH and 50% CO<sub>2</sub>. For a given aggregate type and curing conditions, the results from the two tests are consistent. Results from other study comparing outdoor carbonation with accelerated test also showed general consistency between the two series of results [13]. So the accelerated test can give reliable information on potential durability in a short term. Therefore carbonated depth from this test may be used as an indicator to show equivalent performance.

The studied concrete mixtures of the study complied with the same prescriptive specifications (Eq. binder content and water/eq. binder ratio), so they could be used as reference concrete mixtures. However they showed quite different potential durability. This variation in performances has to be taken into account in the definition of the reference concrete mixture. A satisfactory level of potential durability has to be ensured, for instance by defining higher minimum Eq. binder content and lower maximum water/eq. binder ratio for the reference concrete mixture.

General indicators for potential durability, such as water porosity, gas permeability, chloride diffusion were not reliable to assess resistance of concrete to carbonation. However they also showed the influence of curing. End of curing at 50% of specified 28-day strength is often deemed satisfactory. But if actual 28-day strength is higher than specified strength, these curing conditions can be more severe than expected.

This study is part of a project aimed at designing methods to implement the *equivalent performance concept*. For each exposure (chloride penetration, leaching, sulphate attacks, etc.), performance based tests and reliable indicators have to be found. The objective of the methodology is to take into account exposure and potential durability to qualify innovative concrete mixtures.

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