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Transport properties of high-volume fly ash concrete: Capillary water sorption, water sorption under vacuum and gas permeability

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ABSTRACT

Studying concrete's resistance to carbonation-induced corrosion usually involves exposing the material to CO_2 for quite some time. To estimate the performance of high-volume fly ash (HVFA) concrete more quickly, two key properties governing this process can be studied, namely water penetrability and gas permeability. With respect to HVFA mixtures optimized for usage in an environment exposed to carbonation with wetting and drying, we adopted the latter approach. This paper presents a full assessment of concrete mixtures with varying fly ash amounts. A 50% fly ash mixture by mass with a binder content of 400 kg/m^3 and a water-to-binder ratio of 0.4 had a lower capillary water uptake (−32.6%), water sorption under vacuum (−10.7%) and gas permeability (−78.9%) than a proper reference normally used in this environment. The fly ash applied had an excellent quality regarding loss on ignition (3.5%) and fineness (19% retained on a 45 μm sieve).

1. Introduction

As fly ash, a by-product from coal-fired electricity production, offers both important economical and environmental benefits [1], its use as a partial cement replacement in concrete has become common practice. Since the end of the 20th century, the importance of the latter benefit has become even more evident. In order to reduce greenhouse gas emissions, more efforts were demanded from the concrete industry on the subject of replacing more cement with by-products of other industries. After all, the production of cement is one of the primary sources of CO_2 emissions, which are held responsible for global warming. In 2002, a report indicated that 5% of the global anthropogenic CO_2 emissions were at the expense of the cement industry [2]. Because of the large application of this building material worldwide, even small reductions in greenhouse gas emissions per ton of cement produced can make a big difference [3].

In 1986, Malhorta introduced the concept of high-volume fly ash concrete (HVFA concrete). It is defined as a concrete in which at least 50% of the binder material consists of fly ash. Its use has been proven successful in various, mostly non-steel reinforced concrete building applications [4].

However, a clear environmental benefit for steel reinforced HVFA concrete only exists if the material is as strong and durable as the more traditional concrete mixtures. Durability assessment usually requires an exposure of the concrete to the deterioration processes present in its natural environment. Given this kind of approach, evaluation of the resistance to carbonation-induced corrosion takes some time. For instance, the European standard NBN B15-100 offers a methodology for validation of fitness to allow use of type II additions, such as fly ash, in concrete. According to this standard, the procedure provided for conditioning and carbonation testing takes 133 days [5]. Logically, many concrete technologists prefer representative testing methods with quicker results. Therefore, a somewhat different approach was adopted in this research. By studying the parameters that influence the deterioration process instead of the process itself, a faster understanding of the concrete's durability is possible. With respect to carbonation-induced corrosion, the accessibility to water and the permeability to air are very relevant parameters to be studied [6].

This paper presents the capillary water sorption, the water sorption under vacuum, and the gas permeability of concrete with various amounts of the cement (0%, 35%, 50% and 67%) replaced by fly ash on a mass basis. Differences between both transport mechanisms were evaluated. The concrete's gas permeability was also linked to the amount of water absorbed and related to the relative humidity of the concrete environment.

2. Materials and methods

2.1. Materials

In total, nine mixtures were tested for capillary water sorption, water sorption under vacuum and gas permeability: three

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reference mixtures (F0-1, F0-2, and F0-3), one mixture with 35% (F35), four mixtures with 50% (F50-1, F50-2, F50-3, and F50-4) and one mixture with 67% (F67) of the cement replaced by fly ash. Table 1 gives an overview of the concrete mixture proportions, the water-to-binder ratio (*W*/*B*), the applied dosage of polycarboxylic ether-based superplasticizer (SP), the slump and the compressive strength class according to NBN EN 206-1 [7]. Note that some of the HVFA mixtures (F50-2, F50-3, and F50-4) did not really need the SP dosage applied (2.5 ml/kg B), given their high slump class (S5). However, no signs of segregation were visually observed.

The three reference mixtures differ in cement content (350 kg/m^3 versus 400 kg/m^3), water-to-cement ratio *W*/*C* (0.5 versus 0.4) and the type of cement used (C(I) = CEM I 52.5 N versus C(HSR) = CEM I 52.5 N HSR, according to NBN EN 197-1 [8]). All of them meet the limits mentioned in NBN EN 206-1 for use in an XC4 concrete environment, the most critical exposure class for carbonation-induced corrosion involving cyclic wetting and drying of the material. In accordance with the European standard, the *W*/*C* is not higher than 0.5, the minimum cement content is higher than 300 kg/m^3 and the compressive strength class exceeds C30/37 [7]. It is noted that the latter criterion is supplementary. Its fulfillment only counts as an indication that the composition is not in violation with the other two criteria [9].

Since manufacturers are being encouraged to use as little cement as possible for economic and environmental reasons (see Section 1), mixture F0-1 is probably more representative for a concrete to be used in an XC4 environment. The other references (F0-2, and F0-3) were made to evaluate the impact of varying cement replacement levels, when the total amount of binder (cement + fly ash) and the water-to-binder ratio (*W*/*B*) were kept constant at 400 kg/m^3 and 0.4, respectively.

The four mixtures with a fly ash content of 50% differ in *W*/*B* (0.5 versus 0.4), type of cement (C(I) versus C(HSR)) and type of fly ash (FA(1) versus FA(2)). Table 2 presents the chemical and physical characteristics of both cements and fly ashes.

After concrete manufacturing, all cast specimens were stored in a climate chamber with a temperature of 20 ± 2 °C and a relative humidity of 95 ± 5%. Demoulding took place the next day after which the specimens were kept in the same climate chamber until the appropriate testing age (28 and 91 days) was reached. The experiments after 91 days of curing were mainly executed to evaluate the impact of the slow pozzolanic fly ash reaction.

2.2. Water penetrability

The amount of water penetrating the concrete differs with the prevailing transport mechanism, the saturation degree and the exposure time of the material. Two scenarios were evaluated experimentally and compared with each other.

Table 2
Chemical and physical characteristics of the cement and fly ash types. The densities and specific surfaces (*) for C(I) and C(HSR) were provided by the cement manufacturer. The theoretical mineralogical composition (**) of the cement clinker was derived from the chemical analysis using the Bogue equations.

%	C(I)	C(HSR)	FA(1)	FA(2)
LOI	2.1	0.9	5.2	3.5
45 μm fineness	–	–	29	19
Density (kg/m^2)	3120*	3220*	2094	2074
Specific surface (m^2/kg)	390*	410*	230	352
CaO	63.12	64.10	2.47	2.51
SiO_2	18.73	21.10	49.34	53.06
Al_2O_3	4.94	3.80	24.55	23.96
Fe_2O_3	3.99	5.00	6.23	6.50
SO_3	3.07	2.50	–	–
MgO	1.02	1.00	1.73	1.79
K_2O	0.77	0.57	3.84	3.32
Na_2O	0.41	0.15	0.52	1.08
C_3S^{**}	66.90	60.72	–	–
C_2S^{**}	3.31	14.78	–	–
C_3A^{**}	6.35	1.62	–	–
C_4AF^{**}	12.13	15.20	–	–

2.2.1. Capillary water sorption

When a non-saturated concrete element is in contact with water at one side and absorbed water evaporation is possible from the other side, a permanent flowing regime through capillary sorption is established [10]. As poor water drainage is sometimes a problem around buildings and structures, the motivation for evaluating this phenomenon is clear. Capillary sorption of concrete containing different amounts of fly ash was evaluated using a test method similar to the one described in the Belgian Standard NBN B15-217 [11]. At the age of 28 and 91 days, three 150 mm on a side cubes (*n* = 3) of each mixture were removed from the climate chamber and oven dried to constant mass (<0.1% mass change within 24 h) at 40 °C. Usually, this takes about 14 days. Note that this 40 °C is only slightly different from the drying temperature (50 °C) prescribed in ASTM C 1585 – 04^e [12]. After weighing the oven dry specimens, they were put on rods in a water bath in such a way that they were immersed for no more than 5 mm. To obtain unidirectional flow, the sides adjoining the inflow face were covered with a self-adhesive tape. The experiment was carried out in a climate chamber with a constant temperature of 20 ± 2 °C and a relative humidity of 60 ± 5%. For each concrete mixture, the capillary water uptake per unit area after 1 day and 14 days was calculated. In addition to this traditional capillary sorption experiment, the specimens were afterwards dried again at 105 °C, whereupon the test was repeated. By adopting the latter drying procedure, all capillary and gel water is eventually removed from the concrete [10].

Table 1
Mixture proportions, water-to-binder ratio (*W*/*B*), the applied dosage of polycarboxylic ether-based superplasticizer (SP), the slump and the compressive strength class of the nine tested concrete compositions.

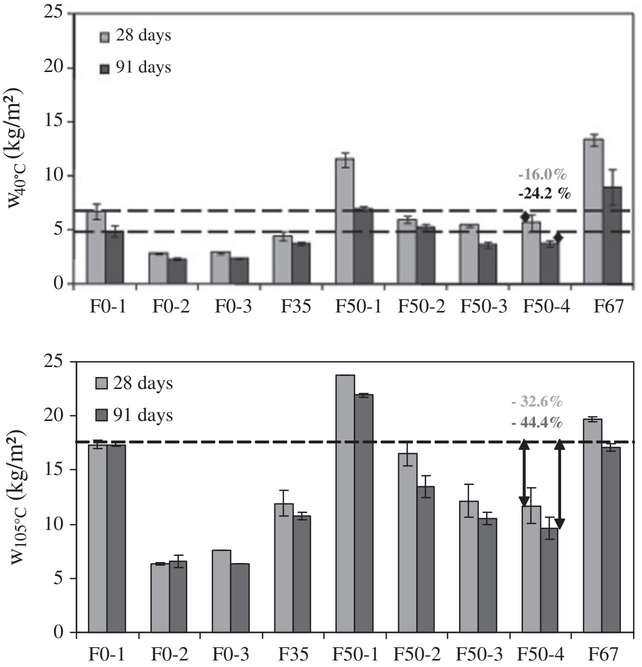
Mix	F0-1	F0-2	F0-3	F35	F50-1	F50-2	F50-3	F50-4	F67
Sand 0/4 (kg/m^3)	791	686	686	668	620	660	660	660	652
Agg. 2/8 (kg/m^3)	425	451	451	437	405	432	432	432	432
Agg. 8/16 (kg/m^3)	618	694	694	678	628	668	668	668	660
Water (kg/m^3)	175	160	160	160	200	160	160	160	160
C(I) (kg/m^3)	350	400	0	260	200	200	0	200	132
C(HSR) (kg/m^3)	0	0	400	0	0	0	200	0	0
FA(1) (kg/m^3)	0	0	0	140	200	200	200	0	268
FA(2) (kg/m^3)	0	0	0	0	0	0	0	200	0
W/*B* (–)	0.5	0.4	0.4	0.4	0.5	0.4	0.4	0.4	0.4
SP (ml/kg B)	0.0	1.9	2.5	1.9	0.0	2.5	2.5	2.5	1.9
Slump (–)	S1	S1	S4	S1	S5	S5	S5	S5	S2
Strength class (–)	C35/45	C50/60	C50/60	C35/45	C16/20	C25/30	C25/30	C35/45	C16/20

Drying at 105 °C is sometimes subject to criticism as the method may induce pore collapse and a modification of the stoichiometry and density of the C–S–H [13,14]. However, in the literature, the same drying temperature has been applied successfully to measure the total porosity of concrete by means of hydrostatic weighing after vacuum saturation. This porosity seems to be only slightly higher in comparison with the one deduced from experimental water vapour desorption isotherms [15]. Compared to total porosities calculated from phase assemblage of the present hydrates, the measured porosities through hydrostatic weighing and oven drying at 110 °C are also only slightly higher [16]. Nevertheless, it needs to be noted that in addition to total porosity, pore connectivity and size are equally important for the transport properties of concrete.

However, when comparing the amount of water absorbed after both drying at 40 °C and 105 °C, it can be seen that an adequate comparison between mixtures is still possible after pre-drying at the higher temperature (see Section 3.2.1, Fig. 1).

2.2.2. Water sorption under vacuum

In laboratories, concrete's accessibility to water can be evaluated in different ways. For instance, it is possible to measure the amount of water absorbed under vacuum. Vacuum saturation tests were performed for all nine compositions on cylindrical concrete specimens with a diameter of 100 mm and a thickness of 50 mm. At the age of 28 and 91 days, three cores were drilled out of three cast concrete cubes with a 150 mm side. By equally dividing these cores into three, nine specimens ($n = 9$) were eventually obtained. All cylinders were first dried in a ventilated oven at 105 °C to constant mass (<0.1% mass change within 24 h). The whole drying procedure is in correspondence with the one described in ASTM C 642 – 06 [17]. After measuring the oven dry masses (m_d), the specimens were put in a tank where a vacuum with a residual pressure of 2.7 kPa was created for 2.5 h. Then, water was introduced at a rate of 50 mm/h until complete submersion of the samples. Since the 100 mm diameter cylinders were standing on their side to minimize contact with the bottom of the tank, this takes about two hours. Subsequently, air pressure was restored and the samples were kept under water for 24 h. A similar vacuum saturation technique is mentioned in ASTM C 1202 – 05 [18]. The procedure described here is in accordance with the Belgian Standard NBN B05-201 [19] and allows the calculation of a permeable porosity φ (%) using Eq. (1).



FA/B (%)	0			35	**50**				67
W/B (-)	0.5	0.4	0.4	0.4	0.5	0.4	0.4	**0.4**	0.4
B (kg/m³)	350	400	400	400	400	400	400	**400**	400
C	(I)	(I)	(HSR)	(I)	(I)	(I)	(HSR)	**(I)**	(I)
FA	-	-	-	(1)	(1)	(1)	(1)	**(2)**	(1)

Fig. 1. Influence of the concrete composition on $w_{40\,°C}$ (kg/m^2) and $w_{105\,°C}$ (kg/m^2), the capillary water uptake per unit area (including stdv) after both preparatory drying at 40 °C and 105 °C followed by a 14 days sorption test ($n = 3$).

$$\varphi = 100 \times \frac{m_s - m_d}{m_s - m_l} \tag{1}$$

Within this formula, m_l and m_s stand for the mass under water and the water saturated mass after vacuum saturation, respectively. The result counts as an estimation of the total permeable porosity. In the literature, similar hydrostatic weighing techniques have been used successfully to measure this porosity [15,16]. All methods require oven drying at an elevated temperature ranging from 105 °C to 110 °C and were published in test method recommendations [20] and national standards [19,21].

To evaluate the water sorption under vacuum of the tested concrete mixtures, both the water uptake per unit area (kg/m^2) and the total permeable porosity resulting from Eq. (1) were calculated.

2.3. Gas permeability

It is known that less oxygen penetrates the concrete at a higher water saturation degree [22,23]. Therefore, it is valuable to express the gas permeability of concrete as a function of its water content. Per concrete mixture, two 400 × 400 × 100 mm concrete slabs were cast and conditioned as described in Section 2.1. At the ages of 28 and 91 days three cylindrical specimens ($n = 3$) with a diameter of 150 mm and a thickness of 50 mm were drilled out of the center of the slabs. Subsequently, the specimens were subjected to the test procedure (Table 3) originally developed by Boel [23]. First, the specimens were stored in a ventilated oven at 80 °C for 10 days, whereafter they were vacuum saturated in accordance with the

Table 3
Experimental procedure to express concrete's apparent gas permeability k_a in function of its saturation degree [23].

Day	Instruction	Measurement
0	Drying at 80 °C	
10	Removing from oven	
	Vacuum saturation according to Section 2.2.2	
11	Weighing	m_s
	Hydrostatic weighing	m_l
	Covering cylinders' mantles with aluminium foil	
	Weighing	
	Drying at 80 °C	
12	Covering cylinders completely with aluminium foil	
	Drying at 80 °C	
13	Removing from oven	
	Storing in climate room (20 °C and 60% RH)	
14	Weighing	m_{S1}
	First gas permeability test	k_{a1}
	Drying at 80 °C	
17	Covering cylinders completely with aluminium foil	
	Drying at 80 °C	
18	Removing from oven	
	Storing in climate room (20 °C and 60% RH)	
19	Weighing	m_{S2}
	Second gas permeability test	k_{a2}
	Drying at 105 °C	
24	Removing from oven	
	Storing in climate room (20 °C and 60% RH)	
25	Weighing	m_{S3}
	Third gas permeability test	k_{a3}

method described in Section 2.2.2. Then, the cylinders were dried in three steps, successively at 80 °C (step 1, step 2) and 105 °C (step 3), until all capillary and gel water was removed. After each drying phase, the flow rate Q (ml/s) and the corresponding apparent oxygen permeability k_a was measured using the 'cembureau' permeameter mentioned in RILEM TC 116-PCD [24]. The weighing of the samples at each drying step made it possible to calculate the total permeable porosity φ (%) (1) and its saturation degree S_x (2).

$$S_x = 100 \times \frac{m_{Sx} - m_{S3}}{m_s - m_{S3}} \tag{2}$$

In this equation m_{Sx}, m_s and m_{S3} correspond with the mass at drying step x (1, 2 or 3), the water saturated mass after vacuum saturation and the completely dry mass at drying step 3, respectively.

The actual oxygen permeation tests were executed at 2 bar pressure. Before each measurement, a certain waiting period (± half hour) was required to obtain a steady gas flow rate Q (ml/s) through the three cylindrical specimens. The apparent oxygen permeability k_a of each mixture was calculated by means of Eq. (3) [23], without performing a Klinkenberg correction [25].

$$k_a = \frac{2Q}{A}\frac{\mu LP}{(P^2 - P_a^2)} \tag{3}$$

The other parameters in Eq. (3) are: the cross-sectional area A of the specimen (m^2), the thickness L of the specimen (m), the dynamic viscosity μ of the fluid (2.02×10^{-5} N s m^{-2} for O_2 at 20 °C), the atmospheric pressure P_a (bar) and the absolute inlet pressure P (2 bar).

By using Eqs. (2) and (3) together, gas permeability can be expressed as a function of the saturation degree. For comparison between mixtures, mainly the gas permeabilities of completely dry samples (S_{S3}) were considered.

Complete drying (e.g. at 105 °C) can result in shrinkage cracking which modifies the pore structure leading to artificially high porosity and permeability values. The shrinkage cracking that occurs as a result of drying does not, however, falsify the results of the gas permeability measurement on the ranking of different mixtures, but the results of such an evaluation are specific to the treatment of the samples to achieve equilibrium [26,27]. Given this limited influence, the same pre-drying temperature was also applied for measuring the permeable porosity with a vacuum saturation test [26]. This is in correspondence with the experimental procedure described in Section 2.2.2.

3. Results and discussion

3.1. Concrete mixtures

Since an equivalent performance approach was adopted for evaluating fly ash concrete, the minimum binder content and maximum W/B ratio replace the limiting values regarding cement content and W/C ratio, respectively. As can be seen in Table 1, mixture F35 with a lower W/B ratio (0.4 instead of 0.5) and a higher binder amount (400 kg/m^3 instead of 350 kg/m^3) meets the indicative strength class for an XC4 environment (C30/37). With the same binder content and W/B ratio, a 50% fly ash replacement only results in a higher strength class (C35/45) when C(I) is used in combination with FA(2) (mixture F50-4). Based solely on its mechanical performance, concrete F50-4 is the most promising HVFA mixture.

3.2. Water penetrability

3.2.1. Capillary water sorption

As mentioned in Section 2.2.1, the choice of the preparatory drying procedure and test method was justified with literature findings [10,13–16]. Fig. 1 shows the 14 days capillary water sorption per unit area after preparatory drying at 40 °C ($w_{40\,°C}$) and 105 °C ($w_{105\,°C}$) for each mixture after both 28 and 91 days of curing. Error bars indicate the standard deviations on the individual values (stdv). When comparing the impact of subsequently drying at 40 °C and 105 °C, it is noted that the differences between mixtures remain more or less the same, although the rankings change slightly. Even a rather good linear correlation (R^2: 0.80) was found between $w_{40\,°C}$ and $w_{105\,°C}$. This indicates that it is justified to compare equally dry mixtures with each other after drying at 105 °C. It supports the still frequent use of this temperature by many researchers [10,13–16]. Comparison of the $w_{105\,°C}$ values resulted in the following findings.

Compared to the reference mixtures with the same binder content (F0-2, and F0-3), mixtures where cement has been partially replaced with fly ash, have a higher capillary water uptake. However, in comparison with F0-1, a more representative OPC concrete composition for an XC4 environment (see Section 2.1), mixtures F35, F50-3 and F50-4 have a significantly lower value for $w_{105\,°C}$. The same goes for mixture F50-2, but only after 91 days of curing and when evaluated after drying at 105 °C.

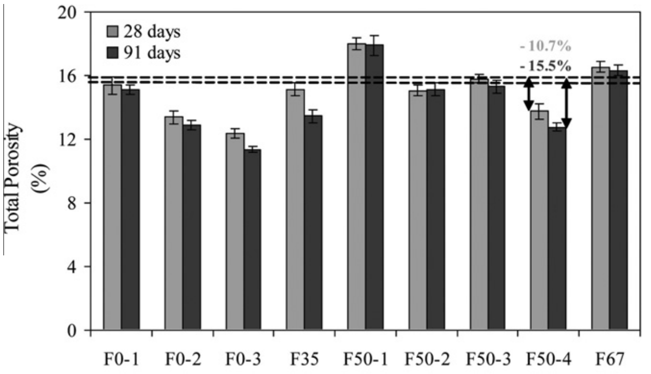
The exact cause for the significant lower water uptake of the C(HSR) based fly ash mixture F50-3 compared to HVFA composition F50-2, cannot be given. According to Zingg et al., the higher C_3A content of C(I) is responsible for a higher adsorption of the polycarboxylate type superplasticizer [28]. As a consequence, the dispersion of the cement particles can be less. This may result in a less homogeneous microstructure and a different permeability. However, this hypothesis would implicate that the concrete mixtures F50-2 and F50-3 must have a somewhat different consistency when applying the same SP dosage. As can be seen in Table 1, this was not the case since both concrete compositions belong to the same slump class (S5). Further research on this matter is therefore imperative.

Of all of the 50% fly ash mixtures, F50-4 with incorporation of fly ash FA(2) gives the lowest values. After 28 and 91 days of curing, the mean decrease compared to F0-1 for $w_{105\,°C}$ amounts to 32.6% and 44.4% respectively. For drying at 40 °C, these decreases were 16.0% and 24.2%, respectively.

3.2.2. Water sorption under vacuum

As discussed in Section 2.2.2, hydrostatic weighing techniques similar to the method applied here for porosity measurements are accepted in the literature [15,16,19–21]. Fig. 2 presents the total permeable porosities φ (%) of the nine tested concrete compositions at ages of 28 and 91 days. The values obtained are more or less proportional to the capillary water uptake per unit area $w_{105\,°C}$ (Fig. 1). An R^2 value of 0.82 exists between the two parameters (Fig. 3). As the parameter φ is a measure for the absorbed amount of water, this kind of relation was expected. However, some differences were observed.

- No pronounced differences seem to exist between the porosities measured after 28 and 91 days of curing (Fig. 2) for different fly ash mixtures (F50-1, F50-2, F50-3, F67). In correspondence with the capillary sorption test, a significant decrease should be noted, since the slow pozzolanic reaction of fly ash normally results in additional hydration products and a finer, less accessible pore structure with time [4]. However, this is not the case.
- In contrast with their $w_{105\,°C}$ values (Fig. 1), the total permeable porosity of mixture F50-3 with 50% cement C(HSR) and 50% fly ash FA(1) is slightly higher than the one measured for F50-2 (Fig. 2).
- The C(HSR) based reference F0-3 is characterised by a lower total porosity compared to reference F0-2 (Fig. 2), despite the higher $w_{105\,°C}$ value after 28 days (Fig. 1).



FA/B (%)	0			35	**50**				67
W/B (-)	0.5	0.4	0.4	0.4	0.5	0.4	0.4	**0.4**	0.4
B (kg/m³)	350	400	400	400	400	400	400	**400**	400
C	(I)	(I)	(HSR)	(I)	(I)	(I)	(HSR)	**(I)**	(I)
FA	-	-	-	(1)	(1)	(1)	(1)	**(2)**	(1)

Fig. 2. Influence of the concrete composition on the total permeable porosity (including stdv) compared to F0-1 after preparatory drying at 105 °C ($n = 9$).

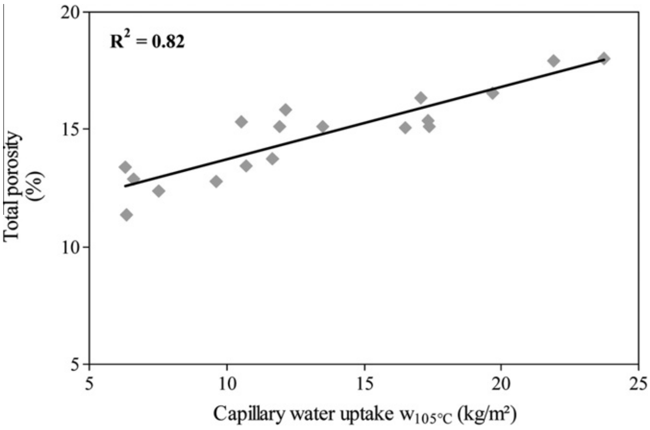
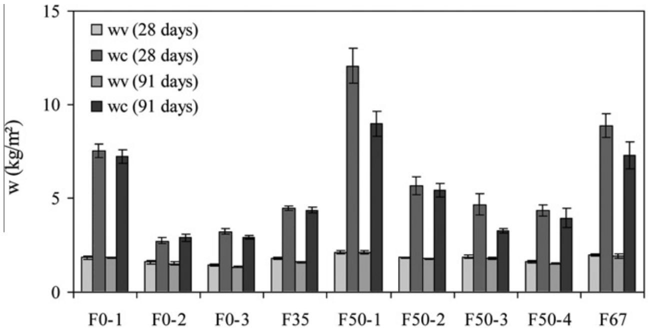


Fig. 3. Pronounced linear correlation (R^2: 0.82) between the total permeable porosity φ (%) and total water uptake $w_{105\,°C}$ (kg/m^2) after a 14 days capillary sorption test for all 9 mixtures after both 28 and 91 days of curing.

- In comparison with F0-1, the more representative reference for an XC4 environment (see Section 2.1), the mixtures (F35, F50-2, and F50-4) are characterised by similar or lower porosities. Of all fly ash containing mixtures, mixture F50-4 performs best. After 28 and 91 days of curing, a porosity decrease of respectively 10.7% and 15.5% was noted, which is even higher than for mixture F35.

As can be seen in Fig. 4, the water uptake per contact area after a 24 h vacuum saturation (w_v) test is significantly less than after 24 h of unidirectional capillary sorption (w_c). This is mainly due to the fact that the volume/exposed surface area ratios for the vacuum specimens are lower than for the sorption samples. Splitting the vacuum specimens directly after determining the mass under water (m_l) and the water saturated mass (m_s), showed that the fracture surfaces of the samples were already completely wet after 24 h. This was not the case for the sorption samples that were also split. As they were not totally saturated yet, they could achieve a higher water uptake within the same time span.

Note that both a capillary sorption test and a water sorption test under vacuum simulate different forms of exposure to water. It is up to the concrete technologist to evaluate which technique is more representative for each situation in practice.



FA/B (%)	0			35	50				67
W/B (-)	0.5	0.4	0.4	0.4	0.5	0.4	0.4	0.4	0.4
B (kg/m³)	350	400	400	400	400	400	400	400	400
C	(I)	(I)	(HSR)	(I)	(I)	(I)	(HSR)	(I)	(I)
FA	-	-	-	(1)	(1)	(1)	(1)	(2)	(1)

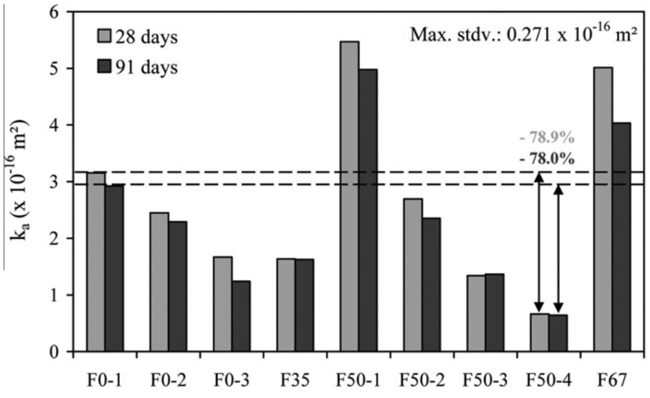
Fig. 4. The mass gain per contact area (kg/m^2) after vacuum saturation (w_v) is significantly lower than after a 24 h capillary sorption test (w_c) for all concrete compositions.

3.3. Gas permeability

3.3.1. Gas permeability in dry state

Regarding the apparent gas permeability k_a, results obtained from the completely dry specimens of each concrete mixture were compared after both 28 and 91 days of curing (Fig. 5). Since the 'cembureau' apparatus normally measures the gas permeability of three cylindrical specimens at the same time, a standard deviation on the individual values cannot be calculated. However, the gas permeability of an individual concrete cylinder can be determined if two of the three specimen cells are detached from the experimental setup. As this strategy prolonges the duration of the test considerably, it was only adopted for F0-2 and F35 at both curing ages. The maximum measured standard deviation on the individual values (max. stdv) amounted to 0.271×10^{-16} m^2.

Comparison between mixtures leads to the following conclusions (Fig. 5). Compared to the more representative OPC concrete for an XC4 environment F0-1 (see Section 2.1), most of the fly ash containing mixtures (F35, F50-2, F50-3, and F50-4) are less permeable to oxygen. F50-4 gives k_a values that are 78.9% and



FA/B (%)	0			35	**50**				67
W/B (-)	0.5	0.4	0.4	0.4	0.5	0.4	0.4	**0.4**	0.4
B (kg/m³)	350	400	400	400	400	400	400	**400**	400
C	(I)	(I)	(HSR)	(I)	(I)	(I)	(HSR)	**(I)**	(I)
FA	-	-	-	(1)	(1)	(1)	(1)	**(2)**	(1)

Fig. 5. Influence of the concrete composition on the apparent gas permeability k_a ($\times 10^{-16}$ m^2) measured at 2 bar pressure ($n = 3$) in comparison with F0-1.

78.0% lower after 28 and 91 days, respectively. In comparison with the C(HSR) based reference (F0-3), mixture F50-3 shows a lower gas permeability after 28 days. This is not true for the C(I) based mixtures (F0-2 versus F50-2). With a *W*/*B* ratio of 0.4, a cement replacement level of 50% (F50-2) results in a higher gas permeability. When only 35% of the binder consists of fly ash (F35), this is not the case.

Note that similar trends between mixtures analogous to F0-2, F35, F50-2 and F67, were observed when performing the experiment after preparatory drying at 60 °C [6]. This indicates that a drying temperature of 105 °C still enables an adequate comparison between concrete compositions.

3.3.2. Gas permeability in relation with its permeable porosity and saturation degree

With a higher porosity, gases can penetrate the concrete more easily. By plotting the obtained k_a values of each mixture as a function of its permeable porosity φ after 28 and 91 days, this hypothesis is confirmed (Fig. 6). A pronounced linear relation exists between the two parameters for both OPC concrete and fly ash containing concrete, i.e. R^2 values amount to 0.94 and 0.93, respectively. In comparison with OPC concrete, the same decrease in porosity for fly ash concrete results in a higher reduction of the gas permeability. It indicates that pores open to the concrete surface are less connected when additional hydration products are present due to the pozzolanic fly ash reaction. It is to be noted that the linear relation for OPC and fly ash concrete is only valid within a certain total permeable porosity range. Concrete with a low porosity is never completely inaccessible to oxygen.

Since reinforced concrete used in structures is seldom completely dry, it is better to look at the gas permeability as a function of the concrete's saturation degree. As the k_a value per concrete mixture and curing age was measured at three different saturation degrees, it is possible to plot the square root of the gas permeability k_a as a function of the concrete's dryness (%), the complement of its saturation degree (100 – *S*). This results in a pronounced linear correlation for all concrete mixtures after both 28 days (Fig. 7a) and 91 days (Fig. 7b) of curing. Except for composition F67 after 91 days, all R^2 values exceed 0.90.

Concrete's saturation degree highly depends on its environmental conditions. Literature shows that it is possible to calculate the equilibrium mass water content for a given temperature and relative humidity from a dynamic vapour sorption test (Dynamic Vapour Sorption, Surface Measurement Systems, London, UK) on cementitious pastes. The use of pastes is justified because the presence of aggregates in concrete does not influence the isotherms. This can be explained by the fact that the micro- and mesopores, where the moisture equilibrium processes described by the isotherms take place, are much smaller than the paste aggregate interface inhomogenities and the typical voids present in this zone [15]. Two pure cement pastes (100% C(I), *W*/*B* ratio = 0.5, cfr. F0-1; 100% C(I), *W*/*B* ratio = 0.4, cfr. F0-2) and a paste in which 50% of the cement was replaced with FA(1) (cfr. F50-2), have been subjected to such an experiment at the age of 4 months. A more detailed description of the applied test method and the results can be found in De Belie et al. [29]. The adsorption and desorption isotherms for pastes corresponding with F0-1, F0-2 and F50-2 are included in this article and shown in Fig. 8. It can be seen that HVFA composition F50-2 is characterised by a reduced saturation at intermediate relative RHs in comparison with the OPC pastes. This may indicate that the HVFA composition is more accessible to gases and thus more susceptible to carbonation for a RH range of 60 ± 5%. This is the humidity condition which is normally applied for evaluation of carbonation resistance conforming to NBN B15-100 [5]. It is also worth noting that the hysteresis is considerably less for the HVFA paste than for the pure cement pastes.

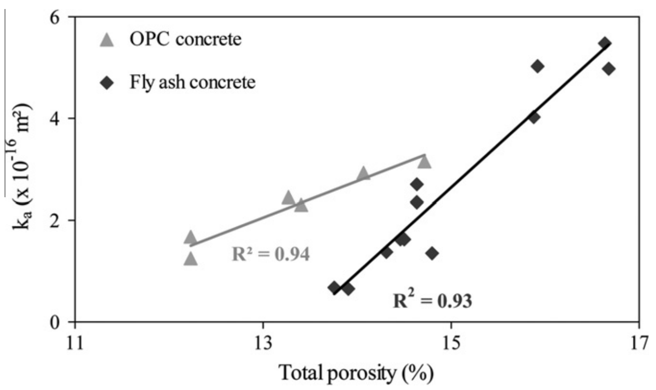


Fig. 6. Pronounced linear relation between the apparent gas permeability k_a ($\times 10^{-16}$ m^2) and the total porosity φ (%) for both OPC concrete (F0-1, F0-2, F0-3) and fly ash concrete (F35, F50-1, F50-2, F50-3, F50-4, F67) with R^2 values of respectively 0.94 and 0.93.

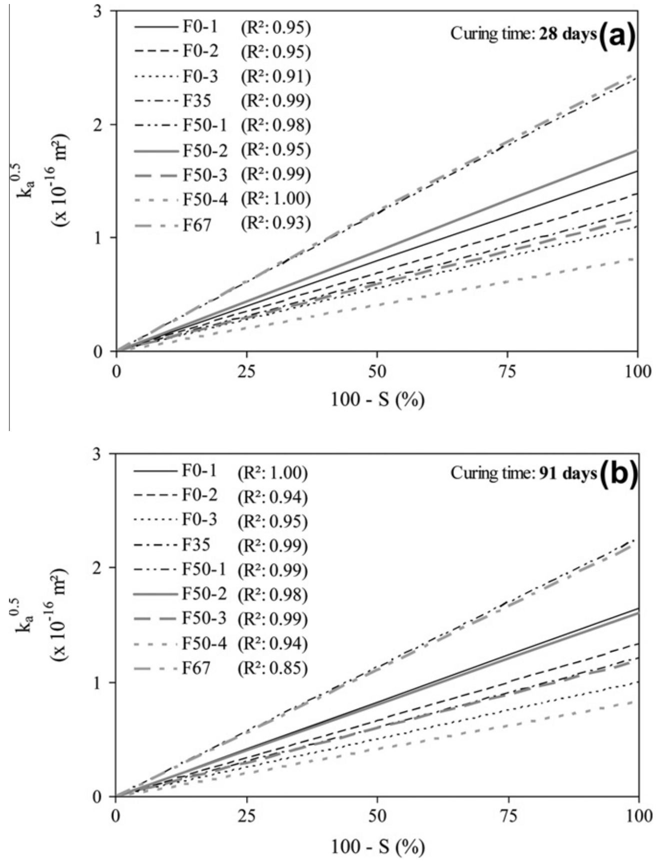


Fig. 7. The square root of the apparent gas permeability k_a ($\times 10^{-16}$ m^2) as a function of 100% minus the saturation degree S (%) gives a pronounced linear correlation for all concrete mixtures after both 28 days (a) and 91 days (b) of curing.

3.4. Overall performance of HVFA concrete

As results of both water penetrability and gas permeability tests show, it is possible to design a HVFA mixture that performs analogously or even better than an OPC concrete representative for an environment exposed to carbonation with cyclic wetting and drying (XC4). Apart from the higher binder content (400 kg/m^3 instead

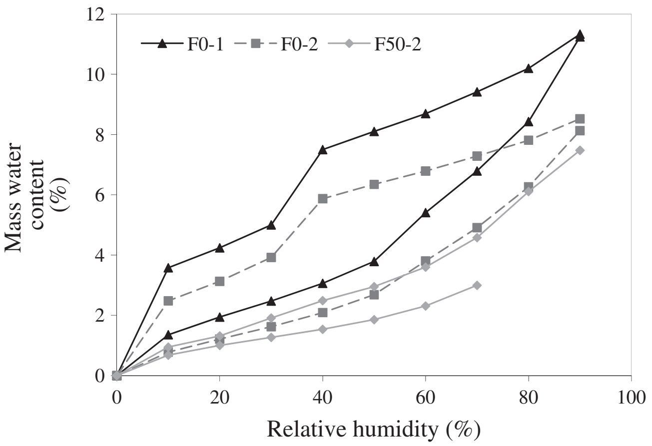


Fig. 8. The adsorption and desorption isotherms for cementitious pastes corresponding with F0-1, F0-2 and F50-2 indicate a reduced saturation at intermediate RHs for HVFA composition F50-2 at the age of 4 months.

of 350 kg/m^2) and the lower *W*/*B* ratio (0.4 instead of 0.5), special attention needs to be paid to the properties of the fly ash. With respect to a fly ash percentage of 50%, clear differences were observed for the mixtures containing FA(1) and FA(2). As can be seen in Table 2, both fly ashes approximately meet the requirements regarding loss on ignition ($\leqslant$5%, Class A) and the 45 μm fineness ($\leqslant$40%, Class N) mentioned in NBN EN 450-1 + A1 [30]. The first parameter stands for the potential mass loss after heating for 1 h at 950 °C. The second parameter corresponds with the amount of material remaining on a 45 μm sieve. The incorporation of FA(2), with a lower 45 μm fineness compared to FA(1) (19% instead of 29%) and a higher specific surface (352 m^2/kg instead of 230 m^2/kg), results in concrete with a significantly lower water penetrability and gas permeability. However, it is expected that all HVFA mixtures will perform better at later age (after 1 or 2 years) even when the fly ash is coarser.

Since high quality HVFA mixtures mostly require a higher binder content and a lower *W*/*B* ratio, the environmental benefit does not simply equal the cement replacement level applied. The 200 kg/m^3 cement content of mixture F50-4 needs to be compared with the amount used in its proper reference concrete. Since mixture F0-1 corresponds best with the concrete type for an XC4 environment according to NBN EN 206-1 [7], 350 kg/m^3 counts as the reference cement content. From this point of view, the cement reduction is only 43% when HVFA concrete is applied. As the HVFA mixture requires addition of superplasticizer, this also needs to be taken into consideration when assessing the actual environmental benefit of the material. A correct environmental evaluation would require a life cycle assessment approach. This methodology is currently being studied at the Magnel Laboratory for Concrete Research.

4. Conclusions

HVFA mixtures with a total binder content of 400 kg/m^3 (50% cement CEM I 52.5 N, 50% fly ash) and a *W*/*B* ratio of 0.4 can be significantly less accessible to water and gases (CO_2, and O_2) than the OPC concrete normally used in an XC4 environment if the 45 μm fineness (19%) of the fly ash is far below the limiting values mentioned in NBN EN 450-1 + A1 [30]:

(1) For 28 and 91 days curing periods followed by preparatory drying at 105 °C, capillary water sorption after 14 days for F50-4 is 32.6% and 44.4% lower than the value obtained for the reference. Differences between all mixtures regarding permeable porosity, a measure related to the total water content after vacuum saturation, are less pronounced. Nevertheless, a more or less linear correlation was found between the capillary water uptake and this porosity.

(2) In comparison with its reference, the HVFA mixture was characterised by a 78.9% and 78.0% lower apparent gas permeability k_a at the ages of 28 and 91 days, respectively. For both OPC and fly ash concrete, a pronounced linear correlation exists between this gas permeability measured at 2 bar pressure and the total permeable porosity. Plotting the square root of k_a as a function of the concrete's dryness, gives a pronounced linear correlation and makes it possible to calculate the gas permeability corresponding with the saturation degree of the concrete in equilibrium with the environment.

(3) Given the higher binder content (400 kg/m^3 instead of 350 kg/m^3) and the lower *W*/*B* ratio of this high quality 50% fly ash mixture compared to the reference, the cement replacement level is only 43%. Moreover, the additional environmental impact of superplasticizers needs to be taken into account along with a complete life cycle analysis to obtain a correct environmental score for this 'green' concrete type.

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