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1 Influence of carbonation on the microstructure and the gas 2 diffusivity of hardened cement pastes

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9 ABSTRACT

10 The influence of carbonation on the oxygen-effective diffusion coefficient (D_{e,O_2}) of hardened
11 cement pastes (HCP) is investigated in the scope of durability. Experiments are carried out on HCP
12 made with different binders (Portland cement, fly ash, slag, metakaolin binders) and water-to-
13 binder ratios at three relative humidity levels. At a given RH, the change in D_{e,O_2} due to carbonation
14 depends on the mix composition. However, in most of cases, D_{e,O_2} increases after carbonation,
15 despite the porosity clogging. This is explained by both the decrease in the water saturation
16 degree, especially at high RH, and the change in the pore size distribution. A good correlation is
17 found between the mean pore diameter and gas diffusivity before and after carbonation at low
18 water saturation degree ($R^2 > 0.84$ on a log-log scale). D_{e,O_2} is significantly less dependent on the
19 water saturation degree after carbonation.

20 **Key words:** Durability; effective diffusion coefficient; carbonation; water retention capacity; pore
21 size distribution.

22

23 1. INTRODUCTION

24 Carbonation is recognized as a significant cause of corrosion in concrete reinforcement
25 [1][2]. This physicochemical process causes diverse chemo-mechanical changes in the cement
26 paste, especially changes in the microstructure and chemistry of the cementitious matrix [3][4].

27 The first mechanism controlling concrete carbonation is the gaseous CO_2 diffusion process
28 by which CO_2 moves through the gas-filled pores. This phenomena is governed by an effective-

29 diffusion coefficient, which is a durability indicator of concrete, a quality parameter indicating the
30 level of gas tightness of cementitious materials, and a relevant input parameter for service life
31 prediction models of concrete in a real environment [5][6][7]. Previous works [8][9] show that
32 transport properties of cementitious materials are highly dependent on the degree of water
33 saturation. Hence, the determination of transport properties at various hydric states is of high
34 importance. On the other hand, carbonation causes numerous changes in the cement paste
35 microstructure [4][10]. It should be noted that, in the literature, experimental data on the effect of
36 carbonation on gas diffusivity are lacking compared to investigations on other transport
37 phenomena such as chloride diffusion and water transfer [11][12][13]. The microstructure of the
38 hardened cement paste (HCP) determines the transport properties of concrete to a high extent,
39 since HCP is the component that contributes for the greatest part of the concrete porosity [14][15].
40 Therefore, in the present work, diffusion tests are carried out on HCP samples, employing an
41 experimental setup from our previous works [9]. The latter uses atmospheric oxygen as the
42 diffusing gas and allows for the determination of oxygen diffusivity under different hygrometric
43 conditions. Admittedly, major differences exist between O_2 and CO_2 gases: their solubility in fluids,
44 their molecular size, etc. Nevertheless, it is possible to obtain a good prediction of CO_2 diffusivity
45 by means of values of O_2 diffusivity [16][17]. Plus, the CO_2 -effective diffusion coefficient of partially
46 water saturated cementitious materials cannot be measured using gaseous CO_2 since it chemically
47 reacts with the calcium-bearing phases of the materials and changes their microstructure.

48 The second mechanism controlling the carbonation progress of concrete is the CO_2 -binding
49 capacity of its hardened cement paste. This property is directly related to the amount of the
50 calcium-bearing phases that could dissolve and react to result in the formation of calcite. The
51 amount of carbonatable compounds influences the rate of carbonation: a higher amount of
52 carbonatable compounds hinders the carbonation depth progress [5]. Note that the amount of
53 bound CO_2 varies with the different humidity levels in each exposure site: the pastes exposed to
54 the higher humidity (unsheltered from rain) are those fixing a higher amount of CO_2 [18].

55 The partial replacement of cement with alternative powders entails a considerable
56 environmental impact. However, the use of these additions, also called Supplementary
57 Cementitious Materials (SCMs) should not adversely affect the behavior of the material. SCMs can

58 be classified into pozzolanic, hydraulic or inert substances. There are great differences in the
 59 respective contribution of each SCM's type to the hydration reaction of the cement and,
 60 consequently, to the HCP microstructure. Therefore, it is important for the carbonation resistance of
 61 cementitious materials to know what role an optional additive plays in the microstructure of the
 62 material.

63 In the present work, the oxygen-effective diffusion coefficient of six different HCPs
 64 blended with fly ash, slag, limestone and metakaolin additions is determined after 90 days
 65 hydration in the non-carbonated state and after carbonation under 1% CO₂ concentration by
 66 volume.

67 The influence of the degree of water saturation is assessed at both states after a preconditioning at
 68 three relative humidity levels: 55%, 95% and 33%. The microstructural changes, phase
 69 assemblage and CO₂-binding capacity of the tested HCPs are investigated using water porosity,
 70 mercury intrusion porosimetry (MIP), and XRD and TGA techniques, respectively. The carbonation
 71 resistance is deduced from this work's results using a deterministic model from the literature. The
 72 carbonation performance of the six HCPs is compared to experimental results after exposing the
 73 HCPs to carbonation in a room regulated at 50%RH.

74 2. MATERIALS AND METHODS

75 2.1 Cement pastes mixtures

76 With the aim of testing the most widely used binders, six types of cement pastes, including
 77 blended cements, are tested. Two cement types are used to prepare the samples. The oxide
 78 composition of the raw materials is given in Table 1. The cement pastes mix compositions are
 79 shown in Table 2. Note that the water-per-binder ratio W/B is expressed in mass and the
 80 replacement percentage of the additions is expressed in relation to the total amount of additions
 81 plus ordinary Portland cement (i.e. CEM I according to European nomination). Only binary systems
 82 are investigated. Note that in the case of limestone, the EN 197-1 standard accepts 35% of
 83 replacement at the most [19]. Therefore, it was decided to increase the limestone content to 40%
 84 to evaluate the consequences of such a high value.

Material	Constituent (%)									
	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	K ₂ O	Na ₂ O	SO ₃	TiO ₂	LOI

CEMI 52.5 N	64.1	20.1	5.2	3.3	0.8	0.76	0.28	3.0		1.8
CEMI 52.5 N PM	60.86	19.27	4.59	3.25	2.01	0.97	0.19	2.88		1.99
Fly ash	5.08	83.45				1.66	1.4	0.58		<5
Slag	43.7	37.4	10.8	0.5	6.5	0.36	0.49	0.1	0.6	<1.5
Metakaolin	0.2	55	40	1.4	0.1	0.4	0.4	-	1.5	1

Table 1: Oxide composition of the raw materials

Mix name	W/B	Cement type	Addition type	Addition content (wt%)	Air content (vol%)
PC6	0.60	CEM I 52.5 N	-	0	0.2
FA6	0.60	CEM I 52.5 N	FA	30	0.1
SL6	0.60	CEM I 52.5 N	Slag	60	0.7
LS6	0.60	CEM I 52.5 N	Limestone	40	1.0
SL35	0.35	CEM I 52.5 N PM	Slag	50	0.1
MK45	0.45	CEM I 52.5 N	MK	20	0.1

Table 2: Mix design of the tested cement pastes

2.2 Preparation of the HCPs samples

The cement pastes are prepared using a waring blender until homogenization of the fresh mix. The pastes are poured in cylindrical molds (diameter 4 cm; height 10 cm) and vibrated to remove entrapped air bubbles. The molds are rotated for 24h in order to avoid the sedimentation of solid particles. The mixes are then demolded and stored in a 100% RH room at ambient temperature for 90 days. Note that the hydration duration is a very important parameter when studying pastes containing pozzolanic additions such as fly ash. After 90 days, it is supposed that the portlandite content of such a paste will only slightly change over a further hydration duration, since most of the pozzolanic hydration reactions have already taken place [20][21][22]. For each mix, 6 molds are prepared. The air content of each mold is determined through the density measurements of the fresh paste. Cylinders with the lowest air content are used for the diffusion tests (Table 2).

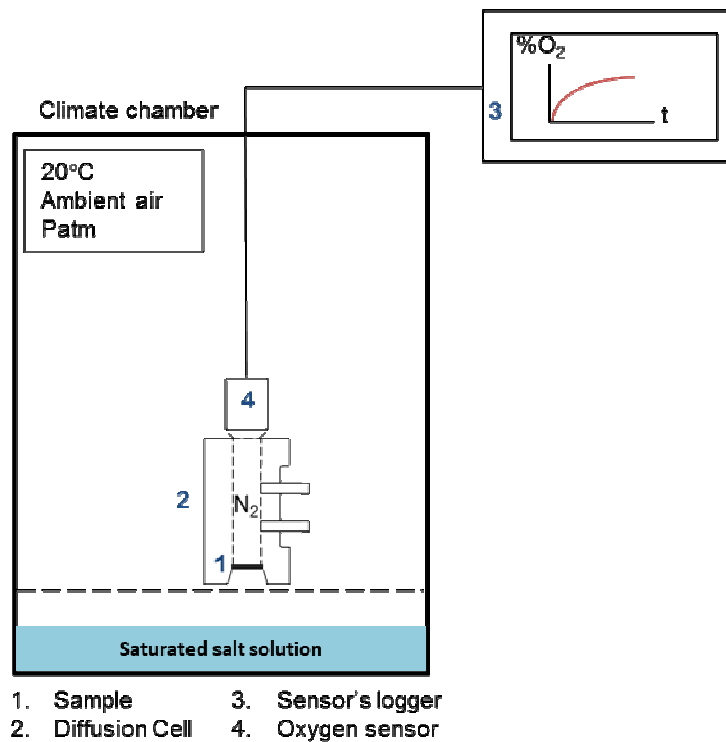
For each HCP mix, two cylinders are used for the diffusion tests before carbonation and two in the carbonated state. From these cylinders, thin samples of 2.5 mm are sawed using a precision saw. Testing thin samples is convenient since they carbonate and reach water equilibrium in a

101 reasonable amount of time (3 to 5 weeks). First, 60 discs are used to be tested in the non-
102 carbonated state. These discs are placed directly in climate chambers equilibrated at three
103 different relative humidity levels (33% 55% and 93%). The hygrometry is maintained at a constant
104 level by means of saturated salt solutions, and soda lime was added in the climate chambers in
105 order to avoid the carbonation of the samples during preconditioning. The CO₂ concentration inside
106 these chambers did not exceed 10 ppm (using a sensor with a detection limit of 75 ppm). In
107 parallel, 60 discs from the six paste mixtures are tested in the carbonated state. Carbonation of the
108 tested samples is achieved using accelerated carbonation in an environment-controlled climate
109 chamber equipped with a system that allows for an accurate regulation of the CO₂ partial pressure
110 and temperature. Prior to carbonation, the 60 discs are kept in a room regulated at 55% relative
111 humidity for a month in order to reach a constant degree of water saturation that promotes
112 carbonation. Afterwards, they are placed in the carbonation chamber with a CO₂ content of $1 \pm$
113 0.2% for six weeks and 55%RH. This value (1% CO₂ by volume) is chosen to ensure the
114 representativeness of the mineralogical evolution compared to atmospheric carbonation [23], to
115 avoid cracking of cement pastes after carbonation [24] and to carbonate the samples in a
116 reasonable amount of time. The temperature at each conditioning step is 20°C. The carbonation
117 progress is monitored in a simple way through a phenolphthalein solution: the colorlessness of the
118 phenolphthalein indicator test was the termination criterion. This procedure is chosen to examine
119 samples with the same or comparable progress of carbonation. The oxygen-effective diffusion
120 coefficient is also determined for carbonated samples at three relative humidity levels. Note that in
121 order to test the carbonated HCP at 93% RH, all the discs are first water saturated under vacuum
122 for 48h and placed in a climate chamber at 93%RH until mass equilibrium is reached. The reason
123 behind water saturating these samples is to test all the HCPs in the desorption state only. After all
124 diffusion tests are performed, the samples are dried in the oven at 105°C to reach their dry mass,
125 which allows for the determination of their degree of water saturation at the three relative
126 humidities chosen.

127 *2.3 Oxygen-effective diffusion coefficient*

128 The oxygen-effective diffusion coefficient is measured using an experimental setup developed
129 during our previous works [9]. The test method relies on the accumulation of gaseous oxygen

130 inside a diffusion cell called a “downstream chamber”. The tested specimens are discs with a
 131 diameter of 4 cm and a thickness of 2.5 mm. This experimental setup contains no upstream
 132 chamber: one face of the tested specimen is in contact with the ambient air of the climate chamber
 133 (volume of 40 L), i.e. at an O₂ concentration of around 20% by volume, and the other face is in
 134 contact with the inside volume of the cell (68ml). The absence of the O₂ bottle is of relevance from
 135 a practical point of view. The volume of the climatic chamber is much larger than the volume of the
 136 downstream cell, so the oxygen concentration in the climatic chamber is constant over the test
 137 duration. At the beginning of the test, the downstream chamber is flushed with nitrogen for 20s to
 138 reach an O₂ concentration lower than 0.3%. The experimental setup (Figure 1) is then placed
 139 inside a temperature and relative humidity-controlled climate chamber (also called an “upstream
 140 chamber”).



141 Figure 1: Schematic description of the setup of the determination of the oxygen-effective diffusion
 142 coefficient

143 By means of saturated salt solutions, the relative humidity inside the climate chamber is set at
 144 the same relative humidity as the one used for the pre-conditioning of the tested samples during

145 the diffusion test. The relative humidity level is monitored inside the climate chamber by means of
146 a sensor during the test period and found to vary slightly (2% to 5% at the most).

147 Oxygen diffuses successively from the ambient air through the sample into the cell initially filled
148 with nitrogen. Oxygen concentration is monitored inside the cell by an oxygen gas sensor. This
149 sensor allows for continuous readings of the oxygen concentration. All measurements are carried
150 out at 20°C and 1 atm. The oxygen-effective diffusion coefficient is determined by minimizing the
151 residue between the experimental and numerical accumulation curve. The numerical accumulation
152 curve is obtained by solving Fick's second law of diffusion with a finite volume solver in python
153 called fipy, version 3.1.3 [25]. More details about the experimental setup and data analysis are
154 given in [9].

155 *2.4 Microstructure characterization techniques*

156 Water porosity (ϕ) is obtained using hydrostatic weighting and oven-drying the HCP samples at
157 105°C. The specimens are preliminarily water-saturated under vacuum for 48h following the
158 current standard used in France [26]. The pore size distribution of the samples is determined using
159 mercury intrusion porosimetry (MIP). The degree of water saturation of the tested samples at 33%,
160 55% and 93% RH is calculated using equation (1), where m is the mass of the sample at moisture
161 equilibrium, m_0 the dried mass, and m_{sat} the saturated mass. The saturated mass of the 2.5 mm
162 thick samples is determined via water soaking under the vacuum for 48h. The dry mass is obtained
163 after drying the samples in the oven at 105°C for 3 days.

164

$$S_r = \frac{m - m_0}{m_{sat} - m_0} \quad (1)$$

165 Changes in the pore structure characteristics of the paste samples after exposure to 1% CO₂ are
166 assessed using mercury intrusion porosimetry. MIP provides information about the connectivity of
167 the pores and reveals information about pore geometry [27]. This technique is based on the
168 Laplace equation [28], which relates the pressure applied to the pore diameter. This diameter
169 actually corresponds to the entry diameter of the pore. The tested samples are small blocks of a
170 typical size of a few mm to 1 cm. These samples are cored out from the hardened cement paste

171 discs and pre-dried at 45°C for 24h. Note that the smallest pores (gel pores) are only partly
 172 measured by this technique. Thus, the water porosity is certainly higher [29].

173 Note that these tests are carried out right after sawing the thin cement pastes under water (and
 174 pre-drying at 45°C for MIP test) in order to avoid carbonation of the discs. After carbonation, when
 175 the pH-indicator becomes colorless over the 3mm thickness samples, water porosity, pore size
 176 distribution and degree of water saturation are determined on the carbonated discs. MIP test is run
 177 on one specimen only while the other tests are carried out on three replicates.

178 2.5 Mineralogical changes

179 Before and after carbonation of the HCP, one complete disc of each mix at both states is grinded
 180 and sieved completely using a sieve of 63 µm, and then 30 mg of this powder is used for the TGA
 181 and XRD tests. Only one test is run for each mix.

182 The mineralogical changes induced by carbonation are identified using TGA and XRD techniques.
 183 The degree of carbonation (D_oC) is determined using TGA. D_oC is defined as the CO₂-bound with
 184 respect to the total theoretical maximum binding capacity MBC (equation 4). TGA (Mettler TGA-
 185 DSC 3+) is used to quantify all carbonates polymorphs. Around 30 mg of the powder sample is
 186 placed in the device and heated from 30 to 1000°C at 10°C/min under a small nitrogen flow (20
 187 mL/min). The temperature of the carbonates' decomposition is assumed to range from 550 to
 188 1000°C [30]. Previous work of Radha et al [31] shows that the decomposition temperature of all
 189 carbonates polymorphs is around 800°C. The samples' degree of carbonation D_oC is determined
 190 based on the amount of anhydrous cement using equations 3 and 2:

$$191 \quad D_{o}C = \frac{BC}{MBC} \quad (2)$$

$$192 \quad B_{-CO2} = \frac{m_{CO2}^{550-1000^{\circ}}}{m_{Oxyde}^{1000^{\circ}} + m_{CO2}^0 + m_{H2O}^0} \quad (3)$$

$$MBC = \sum \frac{\text{carbonatable cationic oxide}}{M(\text{carbonatable cationic oxide})} * M_{CO2} - SO3 * \frac{M_{CO2}}{M_{SO3}} \quad (4)$$

193 Where B_{-CO2} is the bound CO₂, $m_{CO2}^{550-1000^{\circ}}$ is the mass loss that corresponds to the decarbonation
 194 of CaCO₃, m_{CO2}^0 , and m_{H2O}^0 are, respectively, the CO₂ and water amount present in the raw
 195 materials (cement and mineral additions used). MBC is the maximum amount of CO₂ that could be
 196 present in the sample if all CaO (except the one coming from CaCO₃ present in the raw materials,

197 and the one introduced in the mix LS6 as an additive) was carbonated. This value could be
 198 approximately inferred by the quantity of its main carbonatable cationic oxides such as CaO, MgO,
 199 SO₃, etc.

200 The amount of SO₃ is deduced in the calculation of the maximum degree of carbonation because
 201 in the presence of an excess of sulfate anions, calcium cations react with sulfate anions to form
 202 gypsum at room temperature even when the system is buffered by atmospheric CO₂.

203 The X-ray diffraction (XRD) is used to identify the nature and amount of the different calcium
 204 carbonate polymorphs. XRD tests were carried out with a Philips/PANalytical X'Pert Pro-MPD
 205 Powder Diffractometer with an X'Celerator detector of an incident CuK α radiation beam by 40 kV
 206 and 40 mA to a rotation sample. The specimens are scanned for 40 minutes from 2 θ = 5 to 65° by
 207 a step of 0.25° without protection from CO₂ and in a dry environment (RH~40%).

208 The carbonation depths of the six HCPs are measured directly by means of phenolphthalein
 209 solution after exposing side-sealed discs of 3 cm thickness and 4 cm diameter to natural
 210 carbonation in a relative humidity controlled room at 50%. The carbonation depth is measured
 211 once a month for six months. Note that the samples were preconditioned for one week in a climate
 212 chamber with soda lime prior exposure to carbonation.

213 3. RESULTS

214 3.1 Changes in the chemical composition

215 The amount of portlandite, calcite and other hydration products such as C-S-H and ettringite is
 216 estimated before and after the carbonation test. The recorded mass losses during TGA are
 217 expressed in the percentage relative to the residual mass of the sample at 1000°C.

	Before carbonation (g /100g)			After carbonation (g /100g)		
	30-350	350-550	550-950	30-350	350-550	550-950
Temperature range (°C)	30-350	350-550	550-950	30-350	350-550	550-950
Released component	H ₂ O	H ₂ O	CO ₂	H ₂ O	H ₂ O	CO ₂
Main cement phases [30]	C-S-H, AFt & other hydrates	CH	CC	C-S-H, AFt & other hydrates	CH	CC
PC6	18.4	9.2	4.4	10.8	7.6	36.6
FA6	16.0	5.7	4.7	5.1	0.7	33.4

SL6	15.3	4.0	3.5	5.4	0.6	30.5
LS6	12.3	6.0	21.3	4.9	1.2	51.2
SL35	14.4	5.0	4.5	5.0	0.6	27.7
MK45	19.9	4.7	4.4	5.9	0.5	24.9

Table 3: TGA results before and after carbonation of the six HCP

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Table 3 presents the TGA results on the evolution of the content of bound water and CO₂ to portlandite (CH), (C-S-H), and calcium carbonate, respectively. The six HCP are tested before and after accelerated carbonation at 1%. The high content of calcium carbonate before the carbonation of the paste's LS6 corresponds to the unreacted limestone present in the initial mix, while the small amounts of calcium carbonate present in the other HCPs before carbonation are due to the initial CO₂ amount in cement (up to 2%) and to a slight carbonation of the paste during the preparation and conditioning in a CO₂-low concentration environment (10ppm). Results from Table 3 reveal that portlandite is still present only in the PC6 after carbonation, while it is consumed for blended systems.

228

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Even though the highest amount of calcium carbonate formed after carbonation is observed for PC6, the lowest consumptions of hydration products upon carbonation are observed for this HCP.

231

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Before carbonation (BC), results from Table 4 also reveal that a slight amount of calcite was formed during the preparation of the samples. The portlandite content of the blended cement pastes is remarkably lower than the portlandite content of PC6 because they contain less ordinary Portland cement (OPC) that can hydrate to form portlandite. Moreover, the reduced amount of portlandite formed is consumed by the pozzolanic reaction of fly ash, slag, and metakaolin.

	PC6		FA6		SL6		LS6		SL35		MK45	
	BC	C	BC	C	BC	C	BC	C	BC	C	BC	C
Calcite%	<2	9.2	<2	10.8	2.3	30	39.8	66.6	5.2	13.4	3.5	8.3
Portlandite%	18.0		7.8	4.8	5.4		8.5		4.0		6.0	
Ettringite%	<2		<2		<2		<2		<2		<2	
Vaterite%		77		57.3		57.8		13.7		56.7		78.1

Aragonite%		7.7		9		6.4				22.5		6.7
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236 Table 4: Estimation of the content of some crystal minerals before (BC) and after carbonation (C)
 237 based on the raw data from XRD analysis

238 Results from Table 4 show that for all HCPs the CaCO₃ polymorph predominantly formed after
 239 carbonation is the metastable vaterite (vaterite is the second most metastable CaCO₃ polymorph
 240 after amorphous calcium carbonate [31]). Calcite and aragonite formation also took place but to a
 241 much lesser extent.

242 Only the samples with limestone powder showed an exception, containing mainly calcite after
 243 carbonation. The presence of limestone seems to favor the further precipitation of calcite.
 244 According to [32], calcite precipitates preferentially on limestone particles as the latter acts as a
 245 nucleation surface for calcite.

246 3.2 Degree of carbonation

247 The amount of bound-CO₂ during the preparation and the conditioning of the six HCPs (B-
 248 CO₂ⁱⁿⁱ), and the bound CO₂ after the carbonation test (B-CO₂^f) are investigated using TGA analysis
 249 (cf Table 5). These values are used to calculate the carbonation degree, expressed as the bound
 250 CO₂ per maximum bound CO₂ (MBC). Note that the amount of limestone introduced initially during
 251 the preparation of the LS6 is deducted in the calculation of the initial and final degrees of
 252 carbonation in table 5 and not deducted in the results of table 3.

253 Table 5 shows results of the amount of CO₂ that disappeared due to the carbonation of
 254 portlandite in the HCPs. This value (CO₂^{CH}) is calculated according de equation 5.

$$CO_2^{CH} = \left(\frac{\Delta\%CH}{M_{H_2O}} M_{CO_2} \right) * \frac{1}{B_{-CO_2}^f} \quad (5)$$

255 $\Delta\%CH$ (Results taken from Table 3) corresponds to the variation of the amount of water in
 256 portlandite per unit mass of anhydrous cement before and after carbonation. $B_{-CO_2}^f$ is the total
 257 amount of bound-CO₂ after carbonation of the HCPs (results shown in Table 5) M_{CO_2} and M_{H_2O} are
 258 the molar masses of carbon dioxide and water respectively. Note that the small amount of CO₂
 259 present in the raw materials (<2%) is taken into consideration in these calculations.

260 The highest degree of carbonation is observed for PC6, even though the amount of bound CO₂
 261 by portlandite is the lowest comparing to other systems, which highlights the important carbonation
 262 of other phases (C-S-H, ettringite... c.f Table 3). In agreement with this results

263 Meanwhile the lowest degree of carbonation is observed for SL35 (Table 5). This could be
 264 explained by the low diffusivity of the SL35 (due to the low water-binder-ratio 0.35) and its high C-
 265 S-H content. Previous works in the literature show that the carbonation of C-S-H leads to the
 266 formation of calcium-enriched silica gel. Part of the calcium would remain trapped in this gel and
 267 would not participate in the formation of CaCO₃ [33].

268 Although the phenolphthalein solution was colorless for all the six HCP after the accelerated
 269 carbonation period, the degree of carbonation of these materials varies between 34.1% and
 270 68.4%. This result highlights the questionable reliability of the pH-indicator method to study the
 271 carbonation performance of cementitious materials. In agreement with this results, Omikrine-
 272 Metalssi et al [34] show that the carbonation continues even 1cm beyond the carbonation depth
 273 indicated by the phenolphthalein indicator. Andrade [35] also states that the DoC in the carbonated
 274 zone is not a direct function of the carbonation depth.

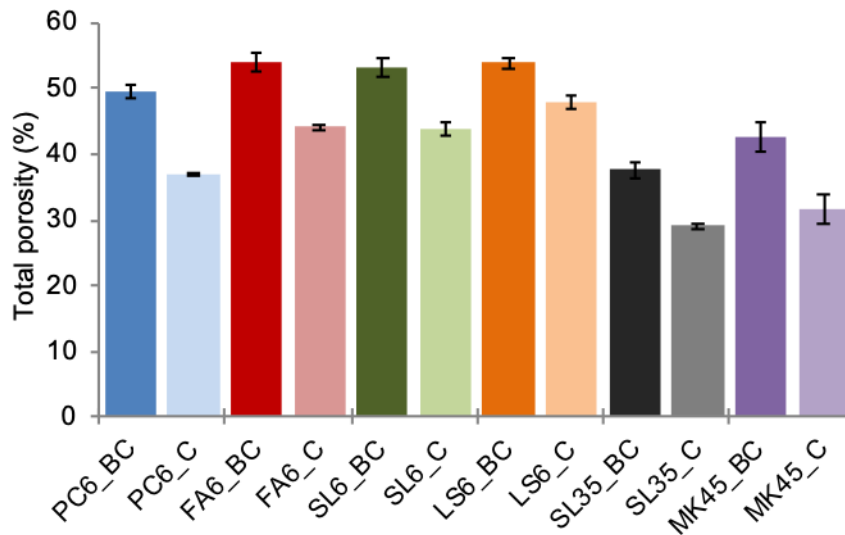
	MBC	B _{-CO₂} ⁱⁿⁱ	D _{oC} ⁱⁿⁱ	B _{-CO₂} ^f	D _{oC} ^f	CO ₂ fixed by portlandite / Total CO ₂	Amount of carbonatable compounds
	g _{CO₂} /100g anhydrous	g _{CO₂} /100g anhydrous	%	g _{CO₂} /100g anhydrous	%	%	mol/m ³
PC6	51.2	3.1	6.1	35.3	68.4	10.7	8686.1
FA6	37.6	2	5.3	24.3	64.7	36.6	4017.4
SL6	43.1	2	4.5	21.5	49.9	27.2	2087.4
LS6	30.5	0.4	1.3	17.1	56.1	22.9	2432.1
SL35	43.4	2.4	5.5	14.8	34.1	38.8	2465.4
MK45	41.5	3.2	7.6	20.8	50.2	41.2	4773.6

275 Table 5: Bound CO₂ values before (B_{-CO₂}ⁱⁿⁱ) and after carbonation (B_{-CO₂}^f); carbonation degrees of
 276 the tested material before (D_{oC}ⁱⁿⁱ) and after carbonation (D_{oC}^f); maximum CO₂-binding capacity
 277 (MBC), and the amount of carbonatable compounds of the six HCPs

278 Note that the amount of carbonatable compounds is deduced from the final bound-CO₂ by
 279 multiplying this value with the cement dosage and dividing by the molar mass of carbon dioxide.
 280 This property is a direct input parameter required by service life prediction models (equation (6)).

281 3.3 Porosity changes upon carbonation

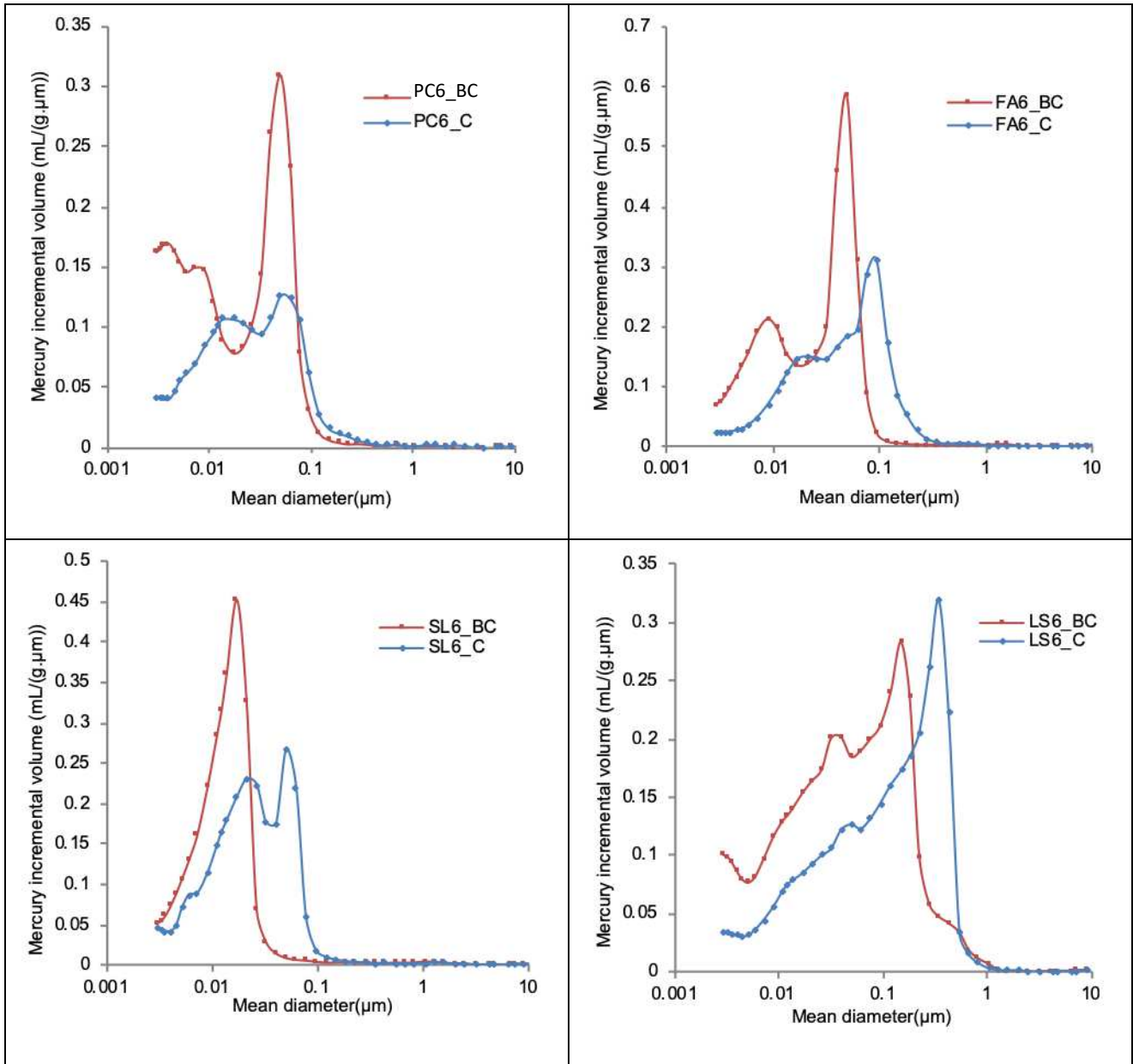
282 Figure 2 gives the porosities of the six HCPs before and after carbonation. The total water
283 porosity of the carbonated cement pastes is 6 to 12% smaller than the total porosity of HCPs
284 before carbonation. The carbonation of the hydrates phases in cement is known to cause an
285 increase in the solid phase volume.

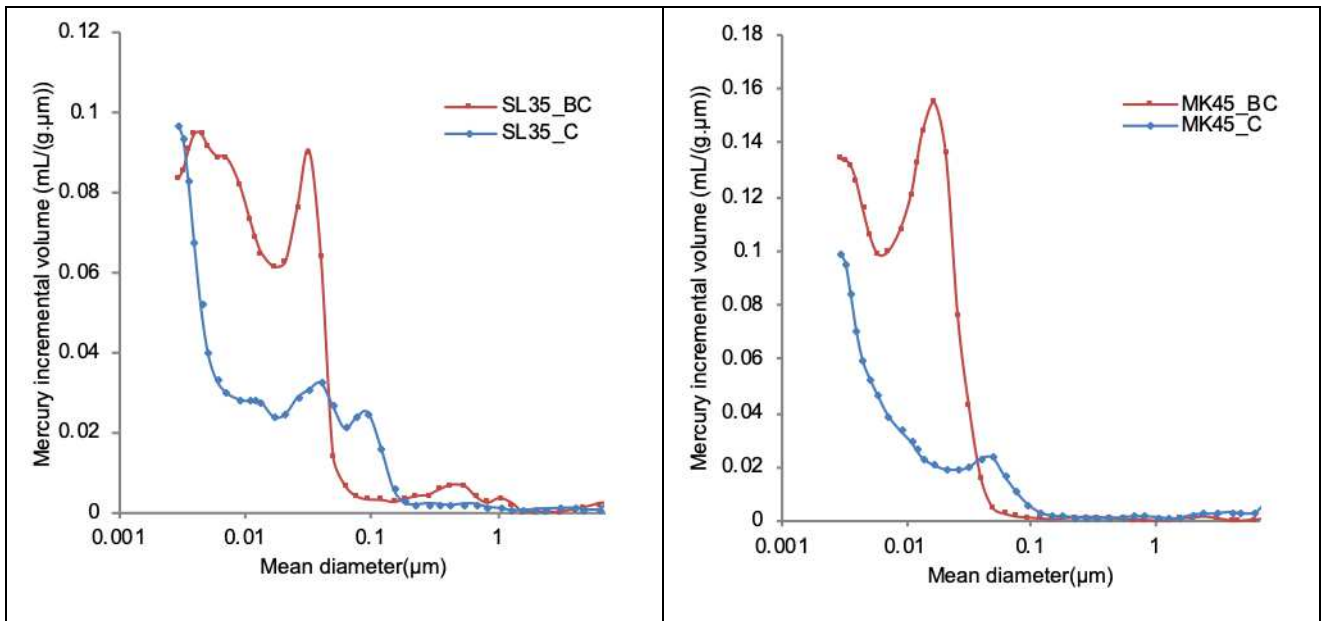


286
287 Figure 2 : Influence of carbonation on the water porosity of the six HCPs. BC: before carbonation
288 C: carbonated.

289 Although FA6, SL6, and MK45 contain a large amount of C-S-H, their total porosity decrease was
290 lower than PC6. This could be due to the smaller molar volume (change due to carbonation) of low
291 Ca/Si C-S-H in HCPs with pozzolanic additions, which generally causes a slight decrease in the
292 porosity [36]. The effect of carbonation on the six HCPs' pore size distribution (PSD) is investigated
293 by means of MIP (Figure 3). It is noted that for PC6 carbonation resulted in a reduction of the
294 amount of small pores ($d < 8$ nm) and a formation of a large amount of pores with a bigger diameter
295 than 20 nm. The carbonation of the paste FA6 even induced the disappearance of pores with a
296 small diameter < 10 nm and the formation of pores with a diameter of 200 nm. Note that this paste
297 pore size distribution goes from a bimodal distribution to a trimodal distribution upon carbonation.
298 This result is also observed for the pastes' SL6; the pore size distribution goes from a monomodal
299 distribution centered on pores with a diameter of 10 nm to a bimodal distribution of higher pore
300 diameter: 60 and 30 nm. A coarsening in the pore size distribution of LS6 is observed: carbonated
301 LS6 contains a lower number of small pores and a shift of the main mode to a bigger pore diameter

302 is observed. As for SL35, carbonation caused the formation of small pores with a diameter of
303 around 3 nm, the clogging of pores with a diameter of around 7 nm, and an increase in the pores
304 entry diameter. This result is also observed on MK45, where carbonation caused a clogging of
305 pores with a diameter of 20 nm and an appearance of a small amount of pores with a bigger
306 diameter of 40 nm after carbonation.





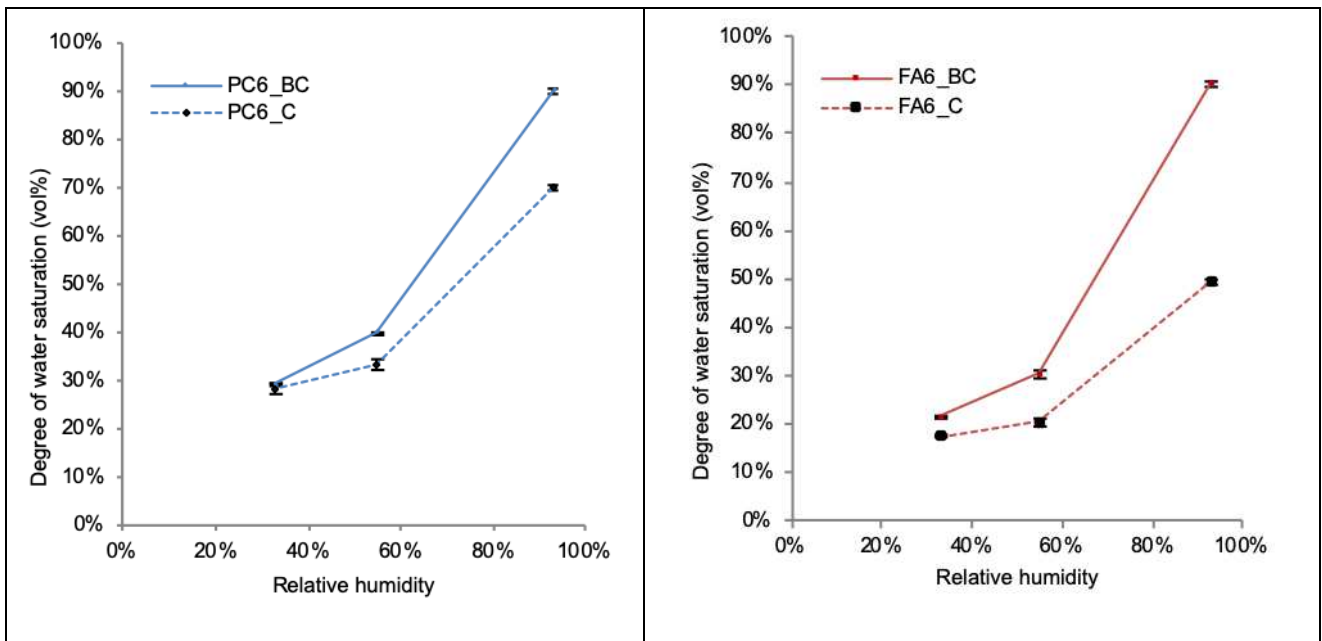
307 Figure 3 : MIP results on the PSD of the six HCPs before carbonation (BC) and after carbonation

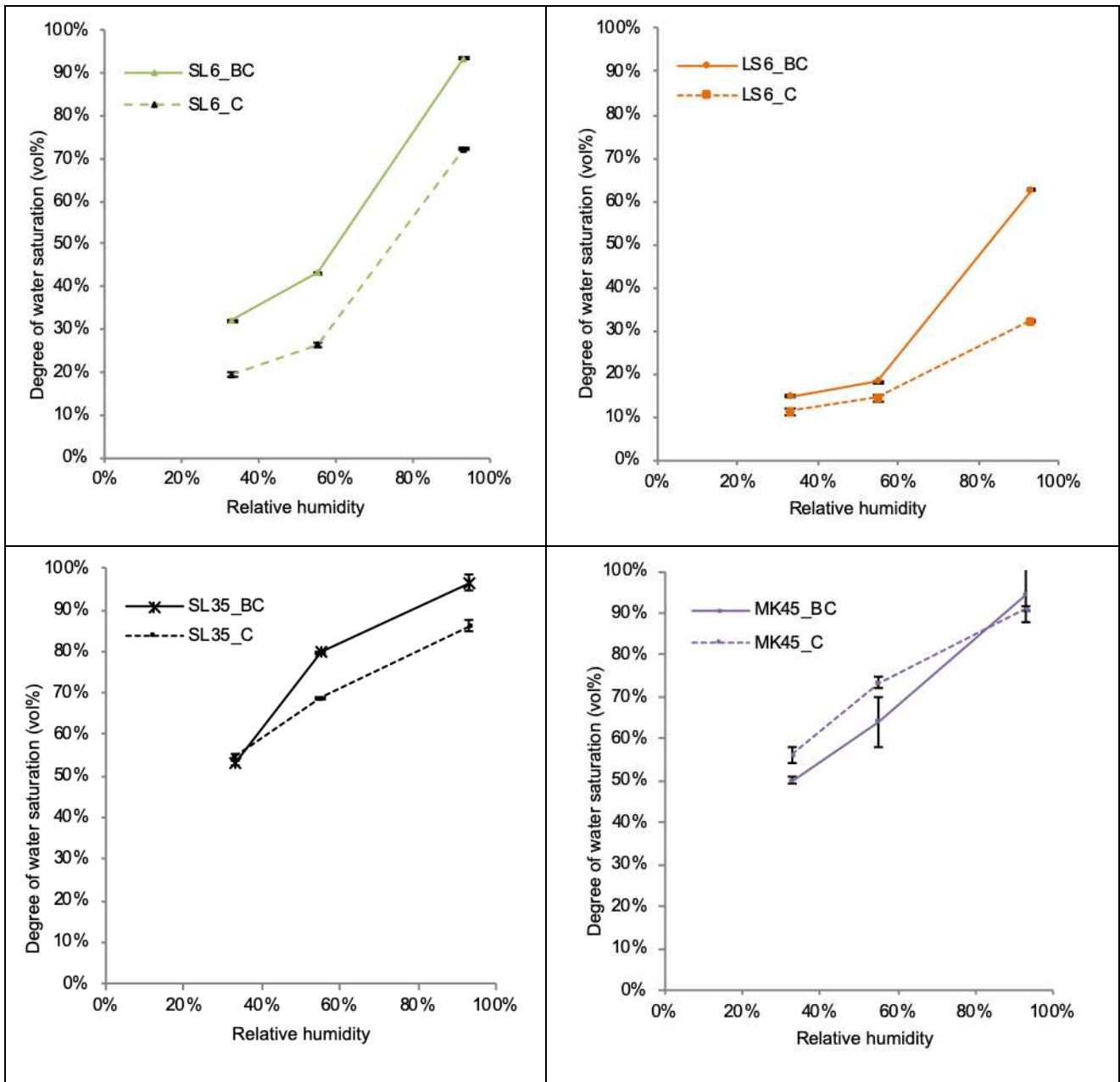
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(C)

309

3.4 Effect of carbonation on the water retention capacity



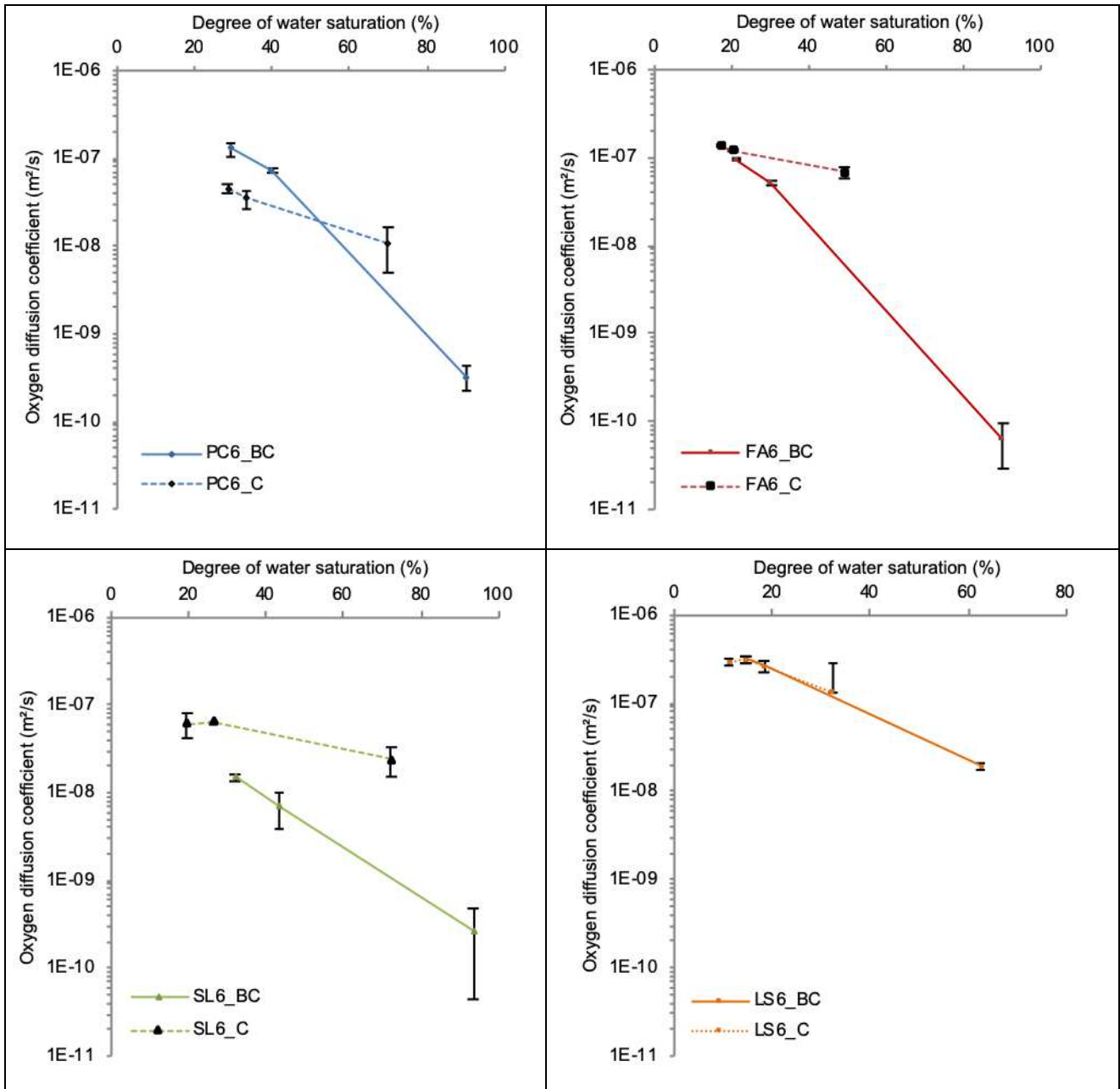


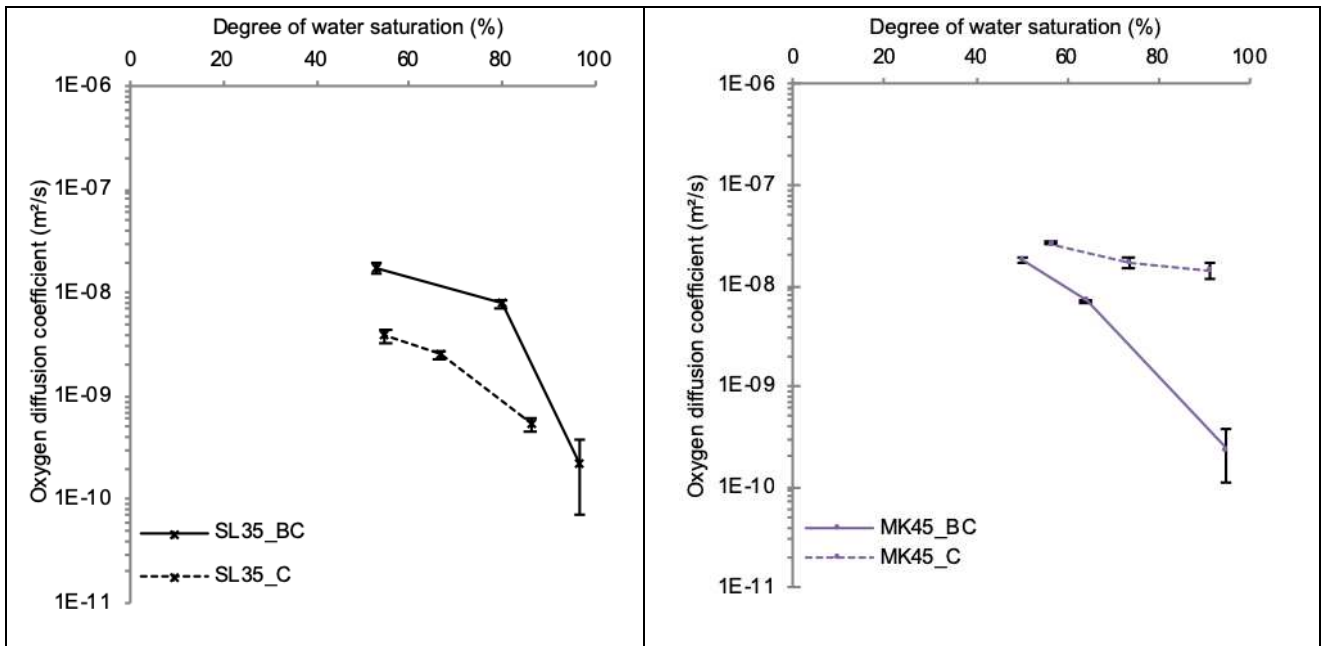
310 Figure 4: The degree of water saturation (vol%) of the tested HCPs before carbonation (BC) and
 311 after carbonation (C) at three relative humidity levels

312 Results shown in Figure 4 indicate that carbonation exerts a different effect on the water retention
 313 capacity of the hardened cement pastes. For pastes PC6, FA6, LS6 and SL35, the degree of water
 314 saturation at 33%RH only slightly changed; however, at 55% RH, carbonated samples are 3% to
 315 17% less water saturated and at 93% RH, carbonated samples are 11% to 41% less water
 316 saturated. As for SL6, carbonated samples are 20% less water saturated at almost all relative
 317 humidity levels; however, carbonated MK45s are 6% to 9% more water saturated than the non-
 318 carbonated samples at 33% and 55% RH, and only 3% less water saturated at 93% relative
 319 humidity. Note that the decrease in the water retention capacity upon carbonation is investigated in

320 the first desorption isotherm (from water saturated condition) and is more significant for blended
 321 cement pastes and appears to be all the more significant as the amount of additions and the water-
 322 per-binder ratio are high (SL6).

323 *3.5 Effect of carbonation on oxygen-effective diffusion coefficient*





324 Figure 5: Oxygen-effective diffusion coefficient of the tested HCPs before and after carbonation at
 325 three degrees of water saturation

326 The oxygen-effective diffusion coefficient depends both on the degrees of water saturation
 327 corresponding to the relative humidity of preconditioning and on the state of carbonation (Figure 5).
 328 PC6 pastes exhibit a decrease in the oxygen-effective diffusion coefficient by a factor of 3 at low
 329 and intermediate relative humidity upon carbonation, whereas an increase in D_{e,O_2} by a factor of 21
 330 at 93% RH is observed upon carbonation. The same is observed for SL35: D_{e,O_2} decreased by a
 331 factor of 5 and 3 at 33% and 55% RH, respectively, and increased by a factor of 2.5 at 93% RH.
 332 As for FA6 pastes, carbonation caused an increase in the D_{e,O_2} at all relative humidity levels by a
 333 factor of 1.5, 2.3 and 1000 at 33%, 55% and 93% RH, respectively. D_{e,O_2} also increased for SL6 by
 334 a factor of 4, 9 and 93 at 33%, 55% and 93% RH, respectively. For LS6, D_{e,O_2} is hardly influenced
 335 by carbonation at 33% and 55% RH while it increased by a factor of 7 at a high RH of 93%. Note
 336 that LS6 diffusivity before carbonation is the highest. Carbonated MK45 exhibits higher oxygen
 337 diffusivity at all RH levels. D_{e,O_2} increases by a factor of 1.5, 2.3 and 60 at 33%, 55% and 93% RH,
 338 respectively. Note that the oxygen-effective diffusion coefficient is highly dependent on the relative
 339 humidity of preconditioning for non-carbonated HCPs and only slightly dependent on the RH of
 340 carbonated HCPs.

341 **4. DISCUSSION**

342 *4.1 Microstructural changes upon carbonation*

343 The decrease in the total porosity given in the results (Figure 2) is also noticed by several authors
344 in the literature [37][11], either on-site [38][39] or under accelerated exposure conditions [40][41].
345 Pihlajavaara et al [42] and Tri et al [41] measured a decrease in the total porosity (clogging)
346 ranging from 10% to 15% on CEMI-based carbonate cement pastes ($0.3 < W/C < 0.8$). Figure 2
347 shows that the nature of the binder is involved in the variation of porosity; the highest porosity
348 change is found for PC6 (12%). In agreement with our findings, Hyvert [43] also found that the total
349 porosity variation is more important for CEMI (9.4%) materials than CEMIII (6%) materials. This
350 result could be directly linked to the nature and relative amount of the hydrates formed by
351 pozzolanic reactions that lower the amount of portlandite and that lower the Ca to Si ratio in C-S-H
352 phases, as the high content of C-S-H tends to maximize this drop in porosity [11]. Note that FA6
353 total porosity is 5 to 7% higher than the total porosity of PC6. This result was also obtained by
354 Papadakis et al [44] when testing mortar samples prepared with 30% fly ash, an increase in
355 porosity of 13% is found.

356 The pore size distribution is also strongly impacted by carbonation (cf. Figure 3). When the W/B is
357 high, which is the case of the HCPs PC6, SL6, and LS6, the carbonation caused a coarsening of
358 the PSD. However, for SL35 and MK45, carbonation resulted in the formation of both finer and
359 coarser pores. Johannesson and Utgenannt [45] also reported a redistribution of pore sizes upon
360 carbonation in Portland cement mortar samples. The authors predicted that well-carbonated mortar
361 has a significantly higher volume of pores in the pore size range of 2 to 7 nm. Those MIP results
362 are also consistent with the observations of Shah et al [10].

363 As a consequence of the variation in the pore size distribution and porosity of the HCPs upon
364 carbonation, the water retention capacity decreased notably (Figure 4). These results are
365 explained, together with the overall evolution of pore size distribution, by the consumption of the C-
366 S-H phase after carbonation and the increase of pore entry diameter. In agreement with our
367 results, it has been reported by Johannesson and Utgenannt [45] that the degree of water
368 saturation (obtained by desorption) for the non-carbonated mortars is higher (by 15%) when
369 compared with a well-carbonated sample, especially at 95% relative humidity. The reduction of
370 liquid saturation (S_l) is observed in spite of the reduction of total porosity (ϕ), which means that the

371 average volume content of water per unit volume of paste decreases but the pore entry diameter
372 tends to increase upon carbonation.

373 4.2 *Mineralogical changes*

374 Tables 3, 4, and 5 results show that after carbonation, portlandite is still present in carbonated PC6
375 (only 10% of bound-CO₂ was due to carbonation of portlandite) while it is highly consumed for
376 blended cement pastes. In agreement with our findings, Soja et al [37] determined a higher
377 portlandite consumption for blended cements with limestone with regards to OPC pastes after
378 exposure to natural carbonation, which is a rather encouraging result for predicting the natural
379 carbonation mechanisms from accelerated carbonation tests at 1% CO₂. MK45, which contains
380 20% metakaolin, also showed an almost complete depletion of portlandite (41% of the total bound-
381 CO₂ is due to portlandite carbonation Table 5) and a high consumption of C-S-H after carbonation
382 at 1% CO₂ (cf Table 3). The same conclusion is drawn by Machner et al [46], who noted that
383 carbonation caused an almost complete decomposition of the C-S-H phase and the consumption
384 of the portlandite after carbonation at 1% CO₂ of HCPs with 20% metakaolin. XRD results (Table 4)
385 show the formation of the three CaCO₃ polymorphs for all HCPs with a high amount of calcite for
386 LS6 and a predominant formation of vaterite for other HCP. The high formation of vaterite could be
387 explained by the carbonation of C-S-H phases. Indeed, Black et al [47][48] studied the carbonation
388 of synthetic C-S-H in which the initial Ca/Si ratio appeared to influence the crystalline carbonate
389 species formed. For Ca/Si ratios greater than 0.67, principally calcite and vaterite were observed
390 and for ratios below 0.50, aragonite was most prevalent. Thiery et al. [49] attributed the more
391 poorly crystallized and the more thermodynamically unstable forms of CaCO₃ to the carbonation of
392 the C-S-H phases.

393 4.3 *Oxygen-effective diffusion coefficient*

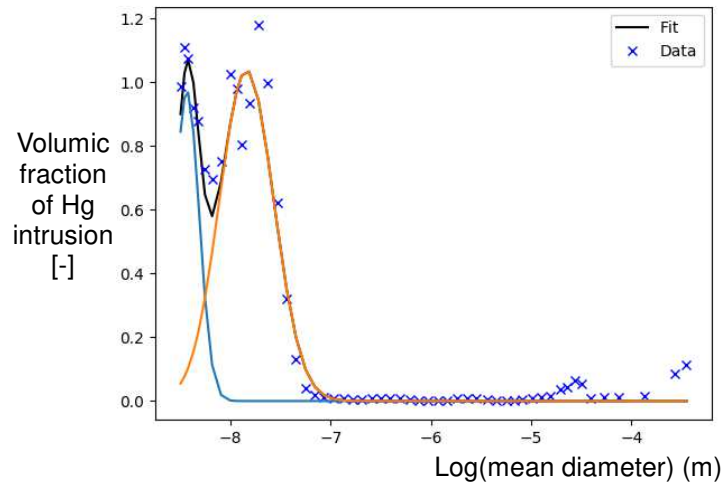
394 The pronounced reduction in the total porosity as a result of carbonation (precipitation of
395 calcium carbonates causes clogging of total porosity) of the six HCPs is expected to positively
396 affect the durability performance of the materials, thus reducing the oxygen-effective diffusion
397 coefficient. This is indeed observed for PC6, LS6 and SL35 at 33% and 55% RH. This reduction
398 could be explained by the fact that carbonation only slightly varied the degree of water saturation at

399 these two RH levels (3 to 8%). However, at a high relative humidity of 93%, the O₂-effective
400 diffusion coefficient for carbonated samples decreased notably by a factor that varies from 2.4
401 (SL35) to 10 (LS6). This result is a consequence of the decrease of the water retention capacity of
402 these HCPs after carbonation (cf. Figure 4). An increase in the diffusion coefficient is obtained after
403 the carbonation of FA6 and SL6 because of the low degree of water saturation of these samples
404 upon carbonation (cf. Figure 4). In agreement with our results, Dutzer et al [24] show an increase
405 in the gaseous helium diffusivity upon accelerated carbonation (3% CO₂ vol.) for blended cement
406 pastes, a result they attributed to the cracking induced carbonation.

407 However, D_{e,O₂} results of MK45 are inconsistent: although the degree of water saturation
408 slightly increased upon carbonation (Figure 4) and MIP results showed the formation of small
409 porosity for carbonated samples (Figure 3), the oxygen-effective diffusion coefficient increased at
410 all RH levels (factor up to 60 at 93% RH). This result could be explained by the slight increase of
411 the largest pore diameter, even if its volume fraction is lowered (Figure 3). Note that the oxygen-
412 effective diffusion coefficient of the six HCPs after carbonation is less dependent on the RH of
413 preconditioning compared to the non-carbonated state diffusivity. *Soja* et al [37] investigated the
414 influence of natural carbonation on the oxygen-effective diffusion coefficient on CEMI and
415 limestone blended cement pastes. Results show a lower oxygen-effective diffusion coefficient even
416 for limestone blended samples equilibrated at 70% RH. *Houst* et al [42] noted that the carbonation
417 of Portland cement paste samples caused a decrease in the diffusivity of CO₂ and O₂ at
418 intermediate RH. These microstructural modifications strongly modify the transfer properties in
419 cementitious materials, especially in terms of diffusion and permeability. However, we noticed that
420 this conclusion is only valid for PC6, LS6 and SL35 at low and intermediate relative humidity levels.
421 Our results on the variation of D_{e,O₂} upon carbonation for the six HCPs can be summarized as
422 follows: (i) for blended cement pastes with a W/B 0.45 and 0.6, an increase of the gas diffusivity is
423 observed at all RH levels, (ii) PC6 and SL35 show a decrease in the diffusion coefficient at 33%
424 and 55% RH and an increase in the D_{e,O₂} at 93% RH, (iii) for all HCP (but LS6), D_{e,O₂} is less
425 dependent on the RH in the carbonated state.

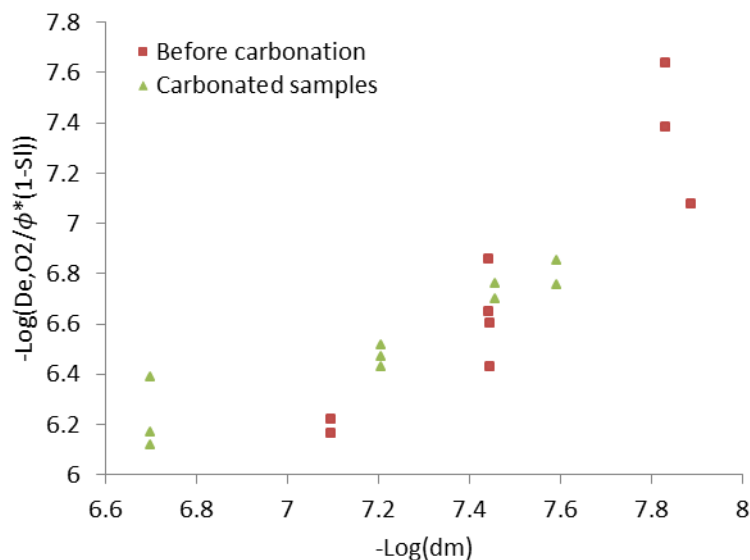
426 4.4 Gas-diffusivity versus mean pore diameter

427 Using an automatic tool that allows for the fitting of the data from the MIP analysis (Figure 3), the
428 mean pore diameter and its corresponding volumetric fraction is computed assuming that each
429 mode is of a normal distribution (Figure 6). This analysis is carried out for all HCPs before and after
430 carbonation. The number of modes of each MIP result is chosen in order to optimize the fit.



431 Figure 6: An example of MIP data automatically fitted

432 Using these results, a weighted arithmetic mean (the weight in the volumetric fraction of each
433 mode) diameter of each paste MIP data (Figure 3) is calculated and compared with the effective-
434 diffusion coefficients determined experimentally on samples with a saturation degree lower than
435 50%. The oxygen-effective diffusion coefficient is corrected by the total porosity (ϕ) and the degree
436 of water saturation (S_i) of the tested samples. This correction is made in order to consider that the
437 transport process is made only through the gas filled pores.



438

439 Figure 7: Oxygen-effective diffusion coefficient versus weighted mean pore diameter at different
440 of saturation degrees

441 Under the Knudsen diffusion assumption, the effective diffusion coefficient is directly proportional
442 to the mean pore diameter of the cementitious material when the mean pore diameter is lower than
443 the mean free path of oxygen molecules at atmospheric pressure and 20°C (i.e. $-\log(d_m) > 7$)
444 [50][51]. Indeed, Figure 7 shows that the oxygen-effective diffusion coefficient displays a somewhat
445 linear trend (in log-scale) with respect to the weighted mean pore diameter ($-\log(d_m) > 7$). For
446 carbonated and non-carbonated samples, the slope equals 0.9 ± 0.05 ($R^2 = 0.92$) and 1.6 ± 0.2 ($R^2 =$
447 0.84), respectively. These results show that the pore size distribution and the degree of water
448 saturation are appropriate material properties to consider in the modeling of the gas-diffusivity of
449 cementitious materials. Note that this result is consistent with previous findings in the literature [9]
450 carried out on HCPs hydrated at different durations.

451 4.5 Carbonation performance of different HCPs

452 The carbonation rate ($\text{mm/year}^{0.5}$) of the tested HCPs is calculated at 55% RH from the results
453 of oxygen gas diffusivity at the carbonated state (Figure 5) and TGA results of the amount of
454 carbonatable compounds (Table 5). Note that the amount of carbonatable compounds is the
455 product of the cement dosage in the paste by the CO_2 -binding capacity. This 55% relative humidity
456 is chosen since it is suggested that the most rapid carbonation of concrete occurs at a relative
457 humidity near 50% to 65%, which is also the recommended RH for natural carbonation tests by the
458 EN 12390-10 standard [19]. The carbonation depth (X_c) of these HCPs are calculated based on
459 the Papadakis deterministic model [5] (equation 6), where $[\text{CO}_2]_0$ is the ambient CO_2 concentration
460 ($400 \pm 25 \text{ ppm}$) converted to mol.m^{-3} , t is the carbonation exposure duration (s), D_{e,CO_2} the CO_2 -
461 effective diffusion coefficient in the carbonated layer, and carbonatable compounds (mol.m^{-3}). Note
462 that D_{e,CO_2} is calculated using Graham's law, which allows it to be deduced from the O_2 -effective
463 diffusion coefficient.

$$x_c = \sqrt{\frac{2 D_{e,\text{CO}_2} [\text{CO}_2]_0}{\text{Carbonatable compounds}} \cdot t} \quad (6)$$

464

465 SL35 results are not shown on Figure 8 because no sharp carbonation depth could be seen on
466 these samples even after 4 months of exposure.

HCP	Carbonation kinetics (mm/year ^{0.5})
PC6	1.7
FA6	4.6
SL6	4.7
LS6	9.6
SL35	1
MK45	1.6

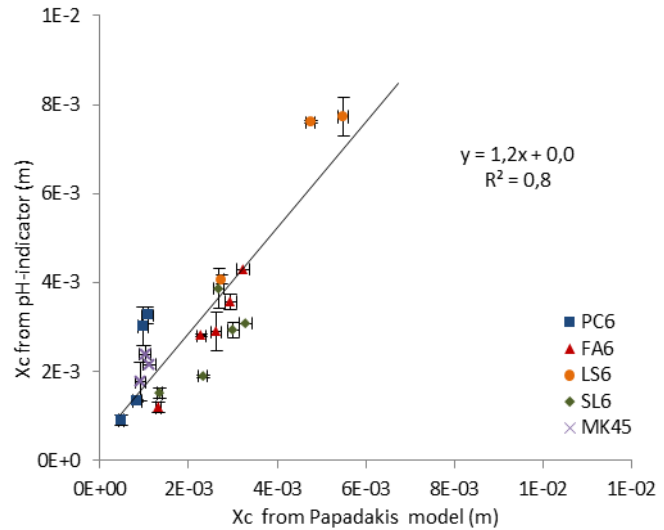


Table 6 : Carbonation kinetics calculated under natural carbonation (400 ppm) carbonation at 55% RH

Figure 8: HCPs' Xc determined with pH-indicator vs Xc predicted using Papadakis' model

467

468 Figure 8 shows that the carbonation depths obtained from Papadakis' model are correlated to
469 the carbonation depths measured experimentally using phenolphthalein solution. The horizontal
470 error bars are due to oxygen-effective diffusion coefficient variation within replicates, and the
471 vertical errors bars are a result of averaging 5 carbonation depth readings. The pH-indicator results
472 are slightly higher than Papadakis' model; this overestimation could be due to errors of averaging
473 or microcracks within the samples (that the model does not take into consideration).

474 As expected, PC6 and blended HCPs with low W/B ratios (SL35 and MK45 cf. Table 6)
475 present the highest carbonation resistance. These results are explained by the very low gas
476 diffusion coefficient of the SL35 and MK45 and PC6's high amount of carbonatable compounds.
477 Although PC6 contains the highest carbonatable compounds, SL35 and MK45 have a higher
478 carbonation resistance (i.e. lower carbonation kinetics). These results show that the carbonation
479 depth progression is mainly driven by the CO₂-effective diffusion coefficient of these pastes: the
480 gas-diffusivity of SL35 and MK45 is 10 and 2 times lower than for PC6, respectively. Therefore, the
481 low value of gas diffusivity can compensate for the low carbonatable compounds content. FA6,

482 containing 30% fly ash, showed low carbonation resistance (high carbonation kinetics of 4.6
483 mm/year^{0.5}). Fly ash is known to react with the calcium hydroxide CH formed during the hydration
484 of the cement to form calcium silicate hydrate C-S-H with a lower C/S ratio [36] than the C-S-H
485 phase in pure Portland cement. Indeed, various studies in the literature found increased
486 carbonation depths of concrete when adding fly ash. Morandea et al [52] reported that with
487 increasing clinker by fly ash (0%, 30%), the carbonation depth under accelerated carbonation (10%
488 CO₂, 63% RH) increases by a factor of 2. SL6 and SL35 with 60% and 50% slag replacement by
489 mass, respectively, contain a comparable amount of carbonatable compounds because of the
490 similar cement composition. In spite of that, SL6 carbonation resistance is almost 5 times higher
491 than SL35 (cf. Table 6). This is due to the low W/B ratio of SL35, which caused the oxygen-
492 effective diffusion coefficient of SL35 to be 26 times lower than SL6. In comparison to PC6, SL6,
493 which is cast at the same W/B (0.6), has a carbonation kinetic that is 2.8 times higher. This is
494 explained by the low carbonatable compounds of SL6 compared to PC6 (cf. Table 5). Furthermore,
495 HCPs containing slag have a C-S-H phase with a C/S ratio around 1.5 and below [53]. LS6
496 performed the worst concerning carbonation resistance. This is due to the high limestone
497 substitution level (40%), low carbonatable compounds, and high oxygen-effective diffusion
498 coefficient in both carbonated and non-carbonated states. The latter is due to the coarser pore
499 structure compared to pure Portland cement (PC6) (cf. Figure 3), which is characterized by larger,
500 interconnected pores. Such a pore structure promotes gaseous CO₂ transport. The high
501 carbonation kinetics of limestone cement pastes is also justified with the fact that calcite forms
502 preferentially on limestone particles, and less on portlandite and the C-S-H phases [32][54]. The
503 latter would prevent their further carbonation or slow it down considerably. Lollini et al [55] reported
504 that with a limestone content of 15%, no influence on the carbonation behaviour was observed, but
505 at 30%, a remarkable worsening of the carbonation resistance is observed (by 60% to 80%). The
506 MK45 carbonation rate is found to be comparable to that of PC6, although the latter is cast at a
507 W/B ratio of 0.6 and the MK45 W/B ratio is 0.45, and MK45 carbonatable compounds is twice
508 lower than PC6. Note that MK45 gas diffusivity is two times lower than PC6, which compensates
509 for the lower amount of carbonatable compounds in MK45 pastes. Bucher et al [56] investigated
510 the natural and accelerated carbonation (4% CO₂) of concrete specimen with a cement

511 replacement of 15 to 25% metakaolin cast at a water per binder ratio of 0.6. In this case, the
512 carbonation depth of concrete with metakaolin is found to be 2 to 4 times higher than the
513 carbonation depth of concrete specimen with CEMI: the higher the metakaolin content, the greater
514 the carbonation depth.

515 **CONCLUSIONS**

516 The results of this work allow drawing the following conclusions:

- 517 • Despite a porosity clogging, carbonation induces an increase in the oxygen-effective
518 diffusion coefficient for most of the tested HCPs at all relative humidity levels. Only the
519 Portland cement paste with W/B=0.6 and the slag paste with W/B=0.35 have a decreased
520 gas diffusivity at 33% and 55% RH after carbonation.
- 521 • The oxygen-effective diffusion coefficient variation upon carbonation at a given RH is
522 explained by changes in both the water retention capacity and the pore size distribution.
- 523 • For all HCPs, the oxygen-effective diffusion coefficient is less dependent on the relative
524 humidity of preconditioning after carbonation than before.
- 525 • The gas diffusion coefficient shows a good correlation with the mean pore diameter of the
526 tested HCPs (in log scale) when the degree of water saturation is lower than 50%. This
527 result is established for both carbonated and non-carbonated HCPs, which proves the
528 direct dependence of the gas diffusivity on the pore size distribution and degree of water
529 saturation of cementitious materials.
- 530 • Regarding the durability performance, the theoretical carbonation rate should be dominated
531 by the gas diffusivity, since, for the tested HCPs, the latter varies over two orders of
532 magnitude, while the amount of carbonatable compounds varies only by a factor of 4.
- 533 • Materials made with a combination of OPC, slag or metakaolin could behave as well as
534 material containing only OPC with respect to carbonation, providing a low gas diffusivity
535 which can be obtained by a W/B ratio carefully optimized. This could provide a real
536 opportunity to decrease the clinker content in concretes without impacting negatively the
537 durability performance related to carbonation. Further studies on the reinforcement

538 corrosion rate using this kind of mixtures must be carried out before definite conclusion can
539 be made.

540 **No conflict of interest**

541 The authors declare that they have no conflict of interest.

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