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1 Impact of carbonation on unsaturated water 2 transport properties of cement-based materials

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16 **Abstract**

17 In unsaturated conditions, the durability of concrete structures is strongly dependent on the evolution
18 of the amount of free water within concrete porosity. Reliable durability assessment of concrete
19 structures in relation to their environment thus requires accurate unsaturated water transport
20 description as well as reliable input data. The effect of carbonation on water transport remains poorly
21 studied and data are lacking. It was then the purpose of this article to acquire all the data needed to
22 describe unsaturated water transport in carbonated cementitious materials (porosity, water retention
23 and unsaturated permeability). Four hardened pastes made with four different binders were
24 carbonated at 3% CO₂ to ensure representativeness with natural carbonation. Beyond the modification

25 of the water retention curve and porosity clogging, significant microcracking due to carbonation
26 shrinkage was observed. The consequence on permeability highlighted a competition between
27 porosity clogging and microcracking that was dependent on the initial mineralogical composition.

28 **Keywords:** waste management (E); cement paste (D); drying (A); permeability (C); microstructure (B)

29 **1. Introduction**

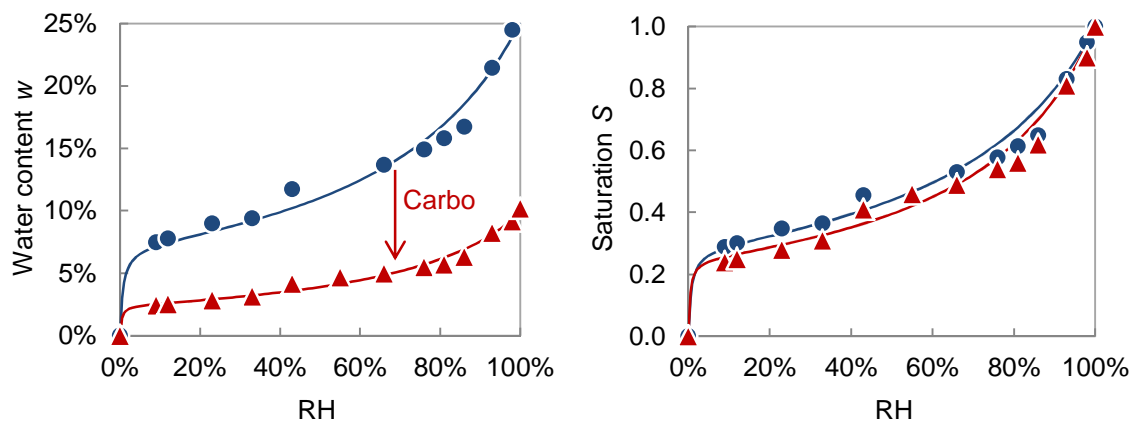
30 In unsaturated conditions, the durability of concrete structures is strongly dependent on the evolution
31 of the amount of free water within concrete porosity (the term “free water” means the water that can be
32 evaporated: it includes capillary and adsorbed water). This dependence is well illustrated by the
33 results of Tuutti [1] that show the strong evolution of the corrosion current (over several orders of
34 magnitude) of steel embedded in a carbonated mortar as a function of the external relative humidity
35 (RH). In a more general way water significantly influences concrete performances and durability
36 (shrinkage, creep, cracking, transport properties). Reliable durability assessment of concrete
37 structures in relation to their environment thus requires accurate unsaturated water transport
38 description. Many studies were published on this specific subject and a lot of data were acquired in the
39 laboratory using different cement-based materials taking care to avoid interaction with carbon dioxide
40 (CO_2). These results are of course very important but they are not fully relevant for durability appraisal
41 because they disregard the fact that concrete structures are being carbonated when exchanging water
42 with the environment.

43 Carbonation refers to the reaction between the calcium contained in concrete pore solution and
44 gaseous CO_2 . It leads to hydrates dissolution (mainly portlandite and C-S-H) and precipitation of
45 calcium carbonate (CaCO_3). Beyond the fall of the pore solution pH that triggers rebar depassivation
46 and corrosion, the precipitation of CaCO_3 generates porosity clogging: the reduction of which depends
47 on the cement type and water to cement ratio (w/c) [2-8]. The specific surface area is then significantly
48 decreased (around 50%) despite conflicting observations [9, 10].

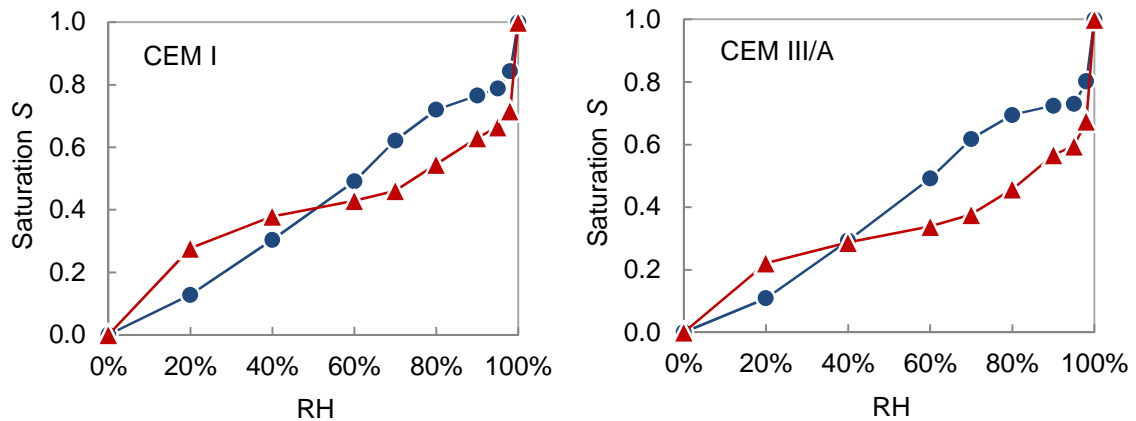
49 The pore size distribution is also altered. Litvan and Meyer [11] studied carbonated concrete samples
50 taken from a 20-year field exposure test (two concretes made with CEM I and CEM III). They found
51 that carbonation led to significant coarsening of the pore structure of the CEM III concrete whereas the
52 finer pores were affected for the CEM I one. Using pastes with different w/c (from 0.4 to 0.7) Ngala

53 and Page [5] found that carbonation (using 5% of CO₂) increased the proportion of capillary pores
 54 (pores larger than 30 nm) whatever the binder and water to binder ratio. More recently, Thiéry et al. [7]
 55 carbonated CEM I pastes with different w/c (using 50% of CO₂) and found that carbonation was
 56 capable of producing large capillary pores (larger than 100 nm) for w/c greater than 0.45. This could
 57 be just a consequence of the high CO₂ content used in this study because the authors noted that this
 58 phenomenon was reproduced using 10% of CO₂. Morandea [12, 13] conducted similar experiments
 59 using CEM I pastes with or without fly ash (using 10% of CO₂). The pore volume of the CEM I pastes
 60 was almost uniformly reduced over the whole pore size distribution whereas a significant coarsening
 61 was obtained for pastes containing fly ash.

62 The water retention curves (*i.e.* adsorption and desorption isotherms) are also transformed. Due to
 63 porosity clogging, the water retained at equilibrium is significantly reduced [2, 4, 14-16]. In addition,
 64 using CEM I pastes of different w/c Houst [14], Houst and Wittmann [4] ($\approx 90\%$ CO₂) and Thiéry et al.
 65 [7] (50% CO₂) showed that despite this reduction in water content (in percent by dry mass) the curves
 66 remained unchanged when they were expressed in saturation (Figure 1). This highlights the change in
 67 density induced by carbonation due to CO₂ fixation (1.60 and 2.03 g/cm³ for non- and carbonated
 68 pastes respectively as estimated using mercury intrusion porosimetry [14]). This also means that all
 69 the pores were impacted in the same manner by CaCO₃ precipitation. This is of course not consistent
 70 with the coarsening of the pore structure discussed above. This is also not consistent with the results
 71 of Hyvert [16] who obtained significant alteration of the water retention curve of CEM I and CEM III/A
 72 mortars (w/c = 0.5) after carbonation (50% CO₂) (Figure 2).



73 **Figure 1: Effect of carbonation on the desorption isotherm of a CEM I paste (w/c=0.4), redrawn**
 74 **after [14]. Key: ● non-carbonated paste, ▲ carbonated paste.**



75 **Figure 2: Effect of carbonation on the desorption isotherm of CEM I and CEM III/A mortars**
 76 **(w/c=0.5), redrawn after [16]. Key: ● non-carbonated paste, ▲ carbonated paste.**

77 The effect of carbonation on permeability is also controversial. Martin [17] used CO₂ in gas
 78 permeability tests and observed a reduction in permeability as a consequence of carbonation during
 79 the test. Using CEM I grouts, Dewaele et al. [9] obtained permeability decrease of several orders of
 80 magnitude after carbonation (by injection under pressure of CO₂-rich water). Claisse et al. [6]
 81 carbonated CEM I concretes (5% CO₂) and measured significant increase in the so-called
 82 impermeability index [18] indicating a fall in permeability. In the same way Song and Kwon [19]
 83 carbonated two CEM I concretes and found that the permeability coefficient of the carbonated
 84 concretes was three times less than that of the non-carbonated ones. These results are however not
 85 consistent with the observations of Borges et al. [20] who measured oxygen permeability on CEM I
 86 paste with or without slag (75% and 90%). The CEM I paste permeability values remained stable after
 87 carbonation (5% CO₂) whereas the pastes incorporating slag showed significant increase in
 88 permeability. Moreover Thiéry et al. [7] and Wang et al. [21] showed that for a high w/c CEM I concrete
 89 (0.84) the permeability (evaluated using inverse analysis) was increased after carbonation (by one
 90 order of magnitude).

91 In summary, there are not enough studies dealing with the effect of carbonation on water transport
 92 properties and the results are piecemeal and often conflicting. This might be due to differences in CO₂
 93 content, cement type or even mix composition. It is then the purpose of this article to study the effect
 94 of carbonation and to acquire all the data needed to describe unsaturated water transport in
 95 carbonated cement pastes; that is to say: porosity, water retention curve and unsaturated permeability
 96 (see section 2).

97 2. Theoretical framework

98 Water transport within concretes involves three mechanisms: (i) permeation of the liquid phase; (ii)
99 permeation of the gaseous phase (mix of vapour and dry air) and (iii) diffusion of vapour within the
100 gaseous phase (the transport of adsorbed water is not accounted for here). The description of these
101 phenomena results in a complex set of coupled differential equations [22-25]. The major disadvantage
102 of this approach is the great number of input data that are required and the experimental difficulty
103 related to their assessment.

104 Water transport is then usually described in a simplified way using a single equation as for liquid
105 permeation only (the two other motions are included). This approach was found to be valid (water
106 transport in the gaseous phase was found to be negligible compared liquid permeation) for weakly
107 permeable materials [24]: this was the case for a concrete with an intrinsic permeability equal to 1×10^{-21}
108 m^2 [26]. More recently, Thiéry et al. [27, 28] estimated the respective contribution of each motion for
109 three different concretes. They showed that this approach validity depends on the intrinsic permeability
110 and the RH-domain that is considered. For instance for a high-performance concrete with low
111 permeability ($\approx 2 \times 10^{-22} \text{m}^2$) the assumption appears to be valid between RH=20% and 100% whereas
112 for a low-strength concrete with high permeability ($\approx 4 \times 10^{-19} \text{m}^2$) the validity domain is limited to 65%-
113 100% RH.

114 To describe water transport in a simplified way, we have started using Darcy's law extended to
115 unsaturated flow [29] which allowed estimating the water flux \underline{j} :

$$\underline{j} = -\rho \frac{K_e}{\eta} \underline{\text{grad}}(P) \quad (1)$$

116 where P is the liquid pressure [Pa]; η and ρ the water viscosity [Pa·s] and density [kg/m^3] respectively.
117 K_e is the effective permeability that characterizes the resistance of the unsaturated concrete to water
118 flow (under a pressure gradient) [m^2]. It was expressed as the product ($K \times k_r$) in which K is the
119 intrinsic permeability [m^2] and k_r the relative permeability that accounts for the effect of desaturation
120 on the depercolation of the saturated porous network (ranges between 0 and 1). The mass
121 conservation equation then wrote:

$$\frac{\partial}{\partial t} (\rho \phi S) = -\text{div}(\underline{j}) = \text{div} \left[\rho \frac{K_e}{\eta} \underline{\text{grad}}(P) \right] \quad (2)$$

122 S is the saturation index [without unit], it describes how pores are filled with liquid water and ranges
 123 between 0 (dry state) and 1 (saturated state). ϕ is the concrete porosity (volume per volume) [without
 124 unit]. In isothermal conditions, assuming that water is incompressible and that a differentiable relation
 125 between saturation S and water pressure P exists (this relation is known as the capillary pressure
 126 curve) eq. (3) could be easily obtained:

$$\phi \left(\frac{\partial S}{\partial P} \right) \frac{\partial P}{\partial t} = \text{div} \left[\frac{K_e}{\eta} \underline{\text{grad}}(P) \right] - S \left(\frac{\partial \phi}{\partial t} \right) \quad (3)$$

127 The right-hand term $\left(S \frac{\partial \phi}{\partial t} \right)$ accounted for porosity reduction induced by carbonation and the pressure
 128 P was calculated using the so-called Kelvin-Laplace equation:

$$P(h) = -\rho \frac{RT}{M} \ln(h) \quad (4)$$

129 R is the universal gas constant [J/mol/K], T is the absolute temperature [K]. M is the liquid water molar
 130 mass [kg/mol] and h is the relative humidity. The description of water transport within concrete thus
 131 required the knowledge of only three physical parameters: the concrete porosity (ϕ), the effective
 132 permeability (K_e) and the left-hand term $\left(\frac{\partial S}{\partial P} \right)$ which was assessed using the water retention curve [30].
 133 It must be noted that for constant porosity, eq. (3) could be simplified to eq. (5) which was used to
 134 describe unsaturated water transport in the non-carbonates pastes (part 4.4.1).

$$\phi \left(\frac{\partial S}{\partial P} \right) \frac{\partial P}{\partial t} = \text{div} \left[\frac{K_e}{\eta} \underline{\text{grad}}(P) \right] \quad (5)$$

135 3. Materials and specimens

136 3.1. Materials

137 Four different hardened cement pastes with constant water to binder ratio (0.40) were used (Table 1).
 138 These binders were chosen because they are being used for R&D studies by the French Agency for
 139 radioactive waste management (Andra) and its partners. The low-pH mix was designed in the field of
 140 geological disposal to limit the chemical interaction between clay minerals and concrete structures [31,
 141 32]. The CEM I, CEM V/A and Low-pH mix were already studied in a previous work [33, 34] in which
 142 the water transport properties of the non-carbonated materials were characterized. The cement pastes
 143 CEM I, CEM III/A, CEM V/A and Low-pH blend (T1 from [32]) are respectively noted PI, PIII, PV and
 144 PBP in this study.

Table 1: Cement pastes composition.

Compound	CEM I	CEM III/A	CEM V/A	Low-pH blend (T1)
CEM I	100%	39%	56%	37.5%
Slag	-	61%	22%	-
Fly ash	-	-	22%	30%
Silica fume	-	-	-	32.5%
Superplasticizer Chryso® Fluid Optima 175	-	-	-	1% of binder (by mass)
Water to binder ratio	0.40	0.40	0.40	0.40

146

147 3.2. Specimens preparation

148 The pastes were prepared in twelve consecutive batches of 2 L (3 batches for each composition) over
 149 two days. The appropriate amounts of cement and water were mixed in a planetary mixer until
 150 homogenization of the fresh mix. The paste was then poured into polypropylene cylindrical moulds
 151 ($\varnothing 50 \times 100$ mm) and vibrated to remove entrapped air bubbles. The specimens were kept two weeks
 152 after casting in their sealed moulds before unmoulding. The specimens were then cured for four
 153 months in sealed containers immersed in specific curing solutions. The composition of the curing
 154 solutions of the PI, PIII and PV specimens was designed to prevent calcium and alkalis leaching. The
 155 pore solutions were expressed at high-pressure [35] from specimens kept in sealed moulds for 4
 156 months. The use of the device optimized by Cyr & Daidié [36] allowed retrieving several millilitres of
 157 solution, the composition of which was analyzed using ionic chromatography (Table 2).

158 Because the pore-solution of PBP was known to exhibit significant changes during the early months of
 159 hydration [32], a different protocol was chosen: several specimens were reduced into a rough powder
 160 and added to deionized water to generate the curing solution.

161

162 **Table 2: Ion chromatography results for the pore solutions of PI, PIII and PV.**

Cations (mmol/L)	PI	PIII	PV
Na ⁺	52	130	98
K ⁺	473	366	469
Ca ²⁺	2.5	2.3	2.0
pH	13.6	13.5	13.5

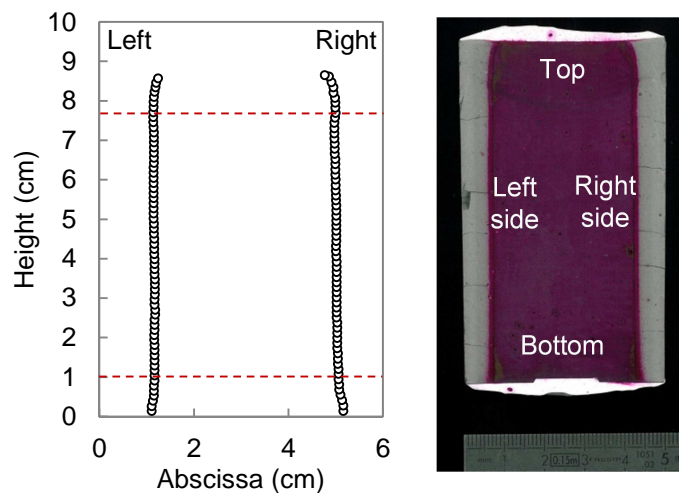
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164 The top and bottom parts of the samples that present different properties from the bulk [37-39] were
 165 cut off and discarded. The thickness of the parts to be removed was assessed by using accelerated

166 chemical degradation [40]. One specimen of each paste was immersed in ammonium nitrate solution
167 (6 mol/L). The leaching solution was stirred constantly but not renewed [41]. After one month, the
168 samples were withdrawn from the solution, sawn in two parts and sprayed with phenolphthalein
169 solution. Three zones could be observed (Figure 3):

- 170 • the central part where the degradation depth was constant versus height,
- 171 • the bottom part where the degradation depth was less due to sedimentation,
- 172 • the top part where the degradation depth was higher due to bleeding and sedimentation.

173 The removal of top and bottom ends (10 mm) was believed to yield homogeneous properties versus
174 height. 140 disks per paste (6 mm-thick) were sawn from the central part of the resulting specimens.
175 Most of these disks (110 per paste) were used for carbonation study and the remaining part was
176 dedicated to the non-carbonated pastes characterization.



177 **Figure 3: Degradation profile of PI sample after one month in ammonium nitrate (6M) at**
178 **ambient temperature.**

179 **3.3. Accelerated carbonation**

180 Accelerated carbonation was achieved using the device developed by Drouet [33]. It includes a
181 climatic chamber for environmental control and a specific system allowing an accurate regulation of
182 the CO₂ partial pressure. Prior to carbonation, the 440 disks were kept in the carbonation device
183 without CO₂ (25 ± 0.2 °C and 55 ± 1% RH) in order to reach a constant value of saturation that
184 promotes carbonation [3, 42-44]. One month later, the equilibrium was reached (constant mass
185 variation) and the carbonation test was started with a CO₂ content of 3.0 ± 0.2%. This value was

186 chosen to ensure representativeness of the mineralogical evolution compared to atmospheric
187 carbonation [45]. The carbonation progress was monitored in a simple way through mass variation.
188 The process was pursued until the complete carbonation state which was verified afterwards using X-
189 ray diffraction (XRD) and thermogravimetric analysis (TGA) (see section 5.1.).

190 **4. Methods**

191 **4.1. Mineralogical assemblage**

192 The mineralogical changes induced by carbonation were identified using a PANalytical X'Pert
193 diffractometer and Cu K α radiation ($\lambda = 1,54 \text{ \AA}$) (XRD). The solid samples surface was scanned
194 between 5 and 65°, with a step size of 0.017°. The use of the X'Celerator detector allowed the
195 acquisition time of the diffractograms to be around 20 minutes.

196 Thermogravimetric analysis experiments (TGA) were accomplished using a NETZSCH STA 409 PC
197 LUXX device to determine the amount of portlandite (CH) and calcium carbonate ($\bar{C}\bar{C}$). Following
198 current methodology [46] the samples were powdered ($120 \pm 0.1 \text{ mg}$) and tested at a constant heating
199 rate of 10°C/min up to 1150°C under N₂ flowrate (80 mL/min).

200 The C-S-H content was evaluated following the method proposed by Olson and Jennings [47] and the
201 water content at equilibrium with RH = 20% (input data for the estimation process) was obtained from
202 the water desorption isotherms.

203 ²⁹Si Magic Angle Spinning (MAS) Nuclear Magnetic Resonance (NMR) was used to probe the effect of
204 carbonation on the C-S-H structure as commonly done [45, 48-51]. We did not use ¹³C NMR because
205 it was found difficult to distinguish one calcium carbonate from the others [52]. The ²⁹Si MAS NMR
206 experiments were conducted following the current protocol of Brunet et al. [53]. Spectra were collected
207 using a Bruker 300WB NMR spectrometer operating at a Larmor frequency of 59.3 MHz (magnetic
208 field 7.05 T). Samples intended for MAS NMR analysis were powdered (around 100 mg sieved to
209 remove the particles larger than 100 μm) and packed in ZrO₂ 4mm (outer diameter) rotors. Sample
210 spinning frequency was 10,000 Hz and recycle delay was 2s. No differences in line shape were seen
211 for longer recycle delays (20s, 200s) and spin rate of 10 kHz was found to be sufficient to remove

212 paramagnetic effects (*i.e.* here spinning sidebands intensity minimized). Data were processed using
213 an in-house made software [53].

214 **4.2. Porosity**

215 Water porosity ϕ was obtained using oven-drying. The specimens were preliminarily saturated under
216 vacuum and water following the current standard used in France [54]. 80°C was chosen as the
217 reference temperature in order to enable comparison with a previous study focused on similar
218 materials [33] but supplementary tests were conducted at 105°C to enable comparison with literature.

219 The pore size distribution was investigated by mercury intrusion porosimetry (MIP) using a
220 Micrometrics Autopore IV. Samples were crushed into small parts (several millimetres), frozen by
221 immersion into liquid nitrogen, let to dry under vacuum for seven days and then tested at $20 \pm 2^\circ\text{C}$.
222 Two samples of each formulation were used.

223 **4.3. Water desorption isotherm**

224 The desorption isotherms were characterized using the desiccator method [55]. The non-carbonated
225 samples were tested just after the cure (after 4 months) whereas the carbonated ones were tested
226 after the cure (4 months) and carbonation (1 year). All the samples were resaturated before the test
227 (4 h under vacuum and then 20 h under water and vacuum). A set of specimens (from 3 to 6) of each
228 paste was inserted into a desiccator above a specific saturated salt solution to control the RH (Table
229 3). Thirteen different sample-sets were placed simultaneously into thirteen different desiccators
230 including different salt solutions. This procedure allowed reducing the test duration, but might have
231 resulted in increasing variability.

232 **Table 3 Saturated salt solutions used in the desiccator method [56-59].**

Saturated salt solution	Chemical formula	RH (20°C)
Calcium chloride	CaCl_2	$\approx 3\%$
Lithium chloride	LiCl	11%
Potassium acetate	$\text{C}_2\text{H}_3\text{KO}_2$	23%
Magnesium chloride	MgCl_2	33%
Potassium carbonate	K_2CO_3	43%
Magnesium nitrate	$\text{Mg}(\text{NO}_3)_2$	54%
Sodium bromide	NaBr	59%
Ammonium nitrate	NH_4NO_3	63%
Potassium iodide	KI	70%

Ammonium chloride	NH ₄ Cl	80%
Potassium nitrate	KNO ₃	92%
Potassium sulfate	K ₂ SO ₄	98%
Deionized water	H ₂ O	100%

233

234 The thirteen desiccators were put in an air-conditioned room ($20 \pm 2^\circ\text{C}$). At given times, the
 235 desiccators were opened and the samples weight was measured. The results (relative mass variation
 236 at equilibrium $(\frac{\Delta m}{m})(h)$ enabled the calculation of the water retention curves expressed in terms of
 237 water content $w(h)$ (ratio of the mass of water for the RH h to the dry mass) [60]:

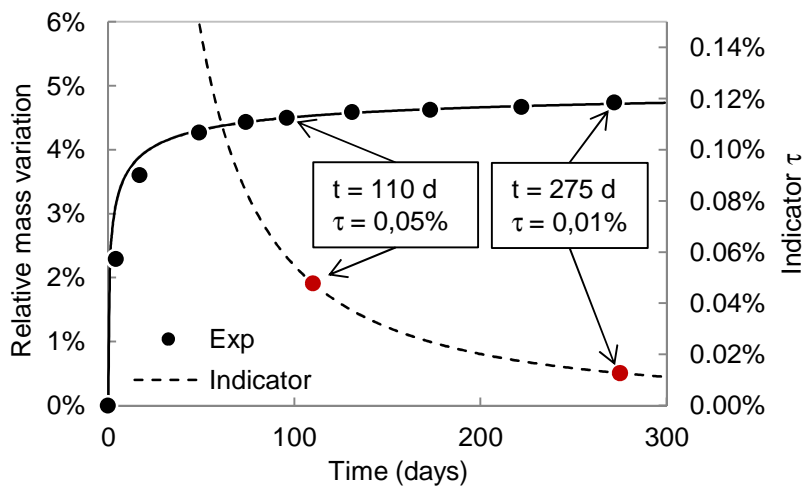
$$w(h) = \frac{d_{sat}}{d_{sat} - \phi} \left[\left(\frac{\Delta m}{m} \right) (h) + \frac{\phi}{d_{sat}} \right] \quad (6)$$

238 where d_{sat} is the specific gravity of the saturated paste. It was measured using the buoyancy method.

239 The deviation from equilibrium was characterised using an indicator τ defined as:

$$\tau(t) = \frac{\left(\frac{\Delta m}{m} \right)_{t+1} - \left(\frac{\Delta m}{m} \right)_t}{\left(\frac{\Delta m}{m} \right)_t} \quad (7)$$

240 where $(\frac{\Delta m}{m})_t$ and $(\frac{\Delta m}{m})_{t+1}$ are the relative mass variation measured at the times t and one day after
 241 respectively. Once the indicator τ became lower than 0.05%, the equilibrium was considered
 242 achieved. For instance, in the case of carbonated PI at 43% RH (Figure 4), the criterion was reached
 243 after 110 days. After 275 days, the indicator τ reached 0.01% (five time lower than the criterion) but
 244 the difference between the relative mass variations at 110 and 275 days remained very limited: about
 245 3.5% (relative value).



246

247 **Figure 4: Characterization of the desorption isotherm (carbonated PI at 20°C and 43% RH).**

248 Complementary tests were conducted using a sorption balance (SMS DVS Advantage) [10, 61]. This
249 device presents two major benefits: (i) a complete desorption isotherm could be obtained in about ten
250 days and (ii) it allowed testing some specific RH values that are difficult to achieve using saturated salt
251 solutions (especially RH lower than 30%). A few disks were crushed and then powdered (sieved to
252 remove the particles larger than 100 μm) in a CO_2 -free glove box. The powder was resaturated using
253 deionized water: a sample of about 50 mg was taken and introduced into the sorption balance. The
254 tests were performed at $25^\circ\text{C} \pm 0.1^\circ\text{C}$ and the RH was decreased by steps under the “dm/dt” mode
255 (the software automatically shifted from one RH step to another when equilibrium was considered to
256 be reached).

257 The specific surface area (S_S) was assessed using the well-known BET model [62, 63]:

$$w(h) = \frac{C w_m h}{(1-h)[1+(C-1)h]} \quad (8)$$

258 where C and w_m are the two BET parameters. C is related to the energy of the first layer and w_m
259 represents the water content needed to complete a monomolecular layer. The specific surface area
260 (S_S) was calculated using the BET monolayer parameters w_m following [64]:

$$S_S = N_A \frac{w_m A}{\rho V} \quad (9)$$

261 where N_A is Avogadro's number, V is the molar volume of water vapour and A is the surface occupied
262 by one molecule of liquid water obtained following [65, 66]:

$$A = 1.091 \frac{M}{N_A \rho} \quad (10)$$

263 **4.4. Permeability**

264 **4.4.1. Inverse analysis**

265 The intrinsic permeability (K) was fitted through numerical simulations to match experimental data [26,
266 67]. Here, initially saturated specimens ($\emptyset 50 \times 100$ mm) were submitted to 55% RH and 25°C in a
267 climatic chamber during 100 days. The finite-element code Cast3m¹ was used to solve eq. (3). The
268 relative permeability to liquid water k_r was evaluated using the Mualem-van Genuchten model [68,
269 69]. The water retention curves were fitted using the equation proposed by van Genuchten:

¹ <http://www-cast3m.cea.fr/changelang.php?lang=en>

$$w = w_{sat} \left[1 + \left(\frac{P}{P_0} \right)^{\frac{1}{1-m}} \right]^{-m} \quad (11)$$

270 where P_0 and m are the two positive parameters of the model and w_{sat} is the water content at
 271 saturation (RH = 100%). The relative permeability k_r was calculated using Mualem's model (the value
 272 of the parameters P_0 and m are the same as above) [69]:

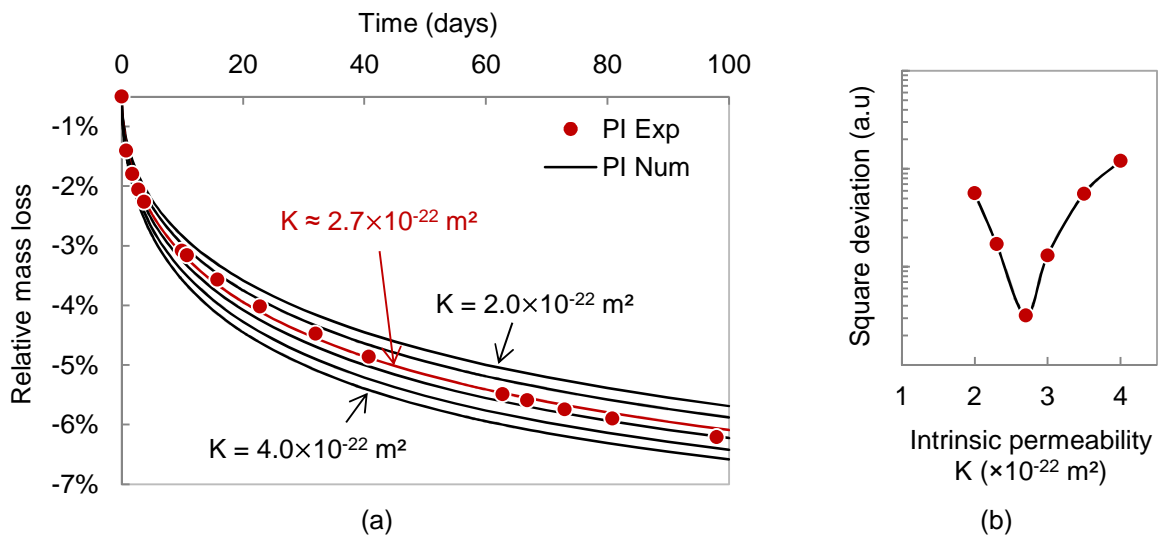
$$k_r = \left[1 + \left(\frac{P}{P_0} \right)^{\frac{1}{1-m}} \right]^{-mp} \left\{ 1 - \left(\frac{P}{P_0} \right)^{\frac{1}{1-m}} \left[1 + \left(\frac{P}{P_0} \right)^{\frac{1}{1-m}} \right]^{-m} \right\}^2 \quad (12)$$

273 where the exponent p is known as the pore-interaction factor (without unit) and embodies pore
 274 tortuosity. It was taken equal to +0.5 as suggested by Mualem [68], but p may be negative or positive
 275 [68].

276 The moisture capacity (the left-hand term $\phi \left(\frac{\partial S}{\partial P} \right)$ in eqs. 3 and 5) was then:

$$\phi \left(\frac{\partial S}{\partial P} \right) = \frac{m\phi}{(m-1)P_0} \left(\frac{P}{P_0} \right)^{\frac{1}{1-m}} \left[1 + \left(\frac{P}{P_0} \right)^{\frac{1}{1-m}} \right]^{-1-m} \quad (13)$$

277 The numerical restitution (solid line) of the experimental relative mass loss (circles) is illustrated on
 278 Figure 5 (a). The value of K is estimated by minimization of the quadratic difference between the
 279 computed and measured relative mass loss for each measuring time (Figure 5 b). The minimum
 280 yielded the value of the intrinsic permeability. In this example (non-carbonated PI), the optimal value of
 281 K was equal to $2.7 \times 10^{-22} \text{ m}^2$.

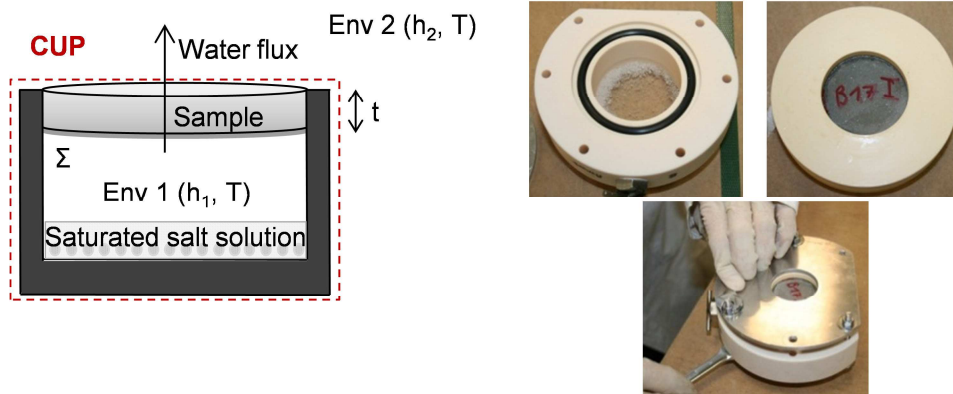


282 **Figure 5: (a) Numerical restitution of the relative mass loss as a function of the intrinsic**
 283 **permeability K (non-carbonated PI) and (b) Evolution of the quadratic deviation as a function of**
 284 **the intrinsic permeability K .**

285 Inverse analysis was used for non-carbonated specimens only. The carbonated ones were too small
 286 (the specimens dry too quickly and the mass loss is too low to yield appropriate results) and another
 287 approach had to be used to assess permeability.

288 4.4.2. Cup-method

289 The cup-method [70] is a direct way of determination of the effective permeability. In this experiment,
 290 disks do constitute a boundary separating two different environments (same temperature but two
 291 different RH: h_1 and h_2) through which water is transported (Figure 6)



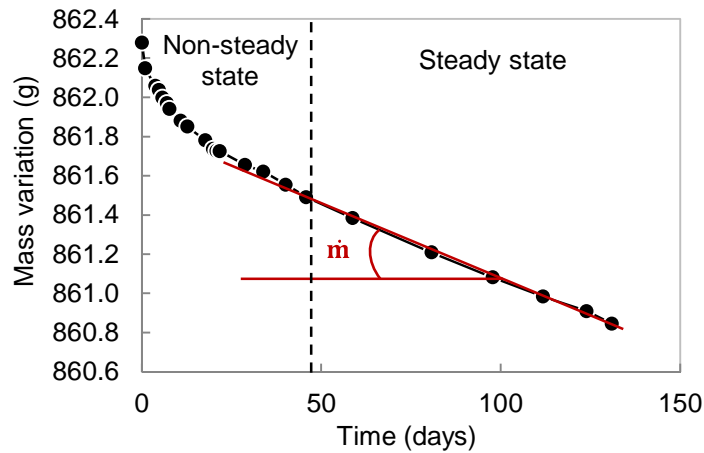
292

293 **Figure 6 : Sketch and photos of the cup-method set up.**

294 The permeability was assumed to be constant on the RH range $[h_1; h_2]$. In steady state, Darcy's law
 295 allows estimating the effective permeability K_e based on the mass loss measurement (Figure 7):

$$K_e = -\frac{\dot{m}\eta}{\rho\Sigma\frac{\Delta P}{t}} \quad \text{and} \quad \Delta P = -\rho\frac{RT}{M}\ln\left(\frac{h_1}{h_2}\right) \quad (14)$$

296 where \dot{m} is the mass loss time derivative [kg/s], Σ the disk cross sectional area [m²], t the thickness
 297 [m], ΔP the liquid pressure difference between the two environments (computed using eq.14) [Pa].



298

299 **Figure 7 : Cup mass evolution (PI disk) vs. time for a 64% (h_1) – 55% (h_2) RH range at 25°C**

300 An experimental set-up was implemented by adapting existing diffusion cells (Figure 6). In practice, h_1
 301 was controlled using a saturated salt solution whereas h_2 was controlled using a climatic chamber
 302 (which also allows controlling temperature). In this test, initially saturated samples are used to focus on
 303 the drying path (and h_1 was always greater than h_2). The cup-method is implemented on carbonated
 304 disks (due to the small specimen thickness) as well as non-carbonated ones to validate the method.

305 4.5. Cracking

306 Because cracks were observed on the disks surface after carbonation, some of them were
 307 impregnated with a fluid resin incorporating a fluorescent dye². The disks were observed in the light of
 308 a ultra-violet (UV) lamp. The resin-filled cracks could clearly be seen thanks to the dye fluorescence.
 309 Pictures were taken and then processed using a specific software³ in order to provide a cracking index
 310 (I_C) to compare qualitatively the pastes (grey-scale image processing). The cracking index was simply
 311 defined as the ratio of the number of pixels attributed to the cracks to the total number of pixels of the
 312 disk surface:

$$I_C = \frac{\text{Number of pixels attributed to the cracks}}{\text{Total number of pixels of the surface}} \quad (15)$$

² Struers EpoDye and EpoFix

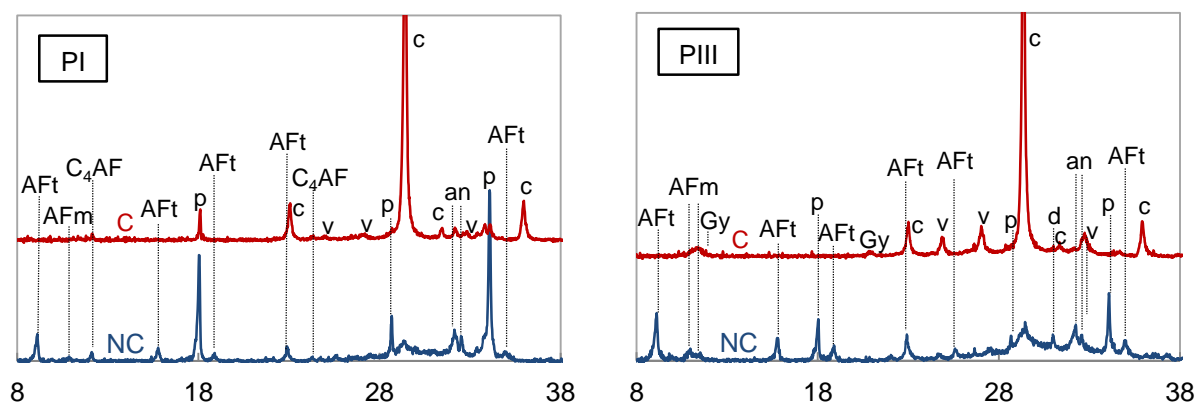
³ <http://imagej.nih.gov/ij/>

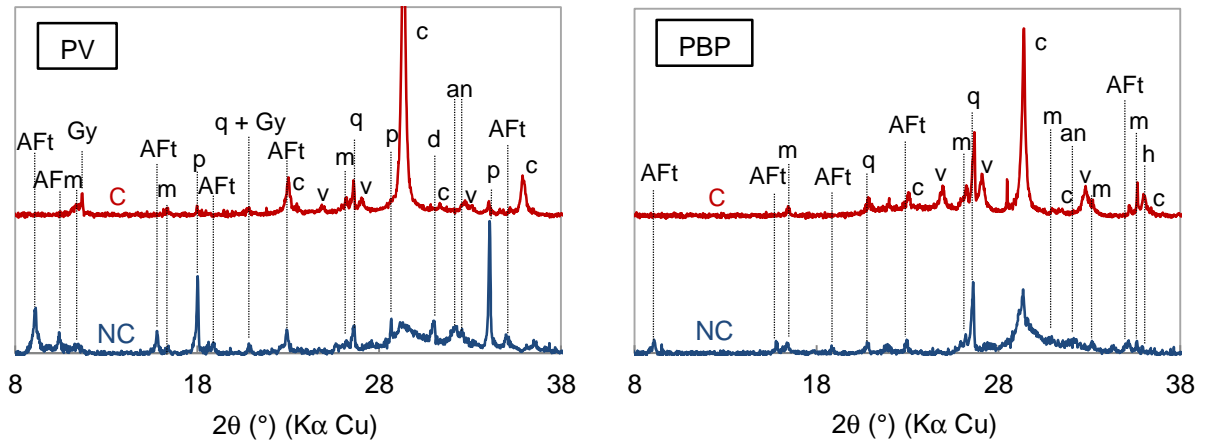
313 5. Results

314 5.1. Mineralogical changes

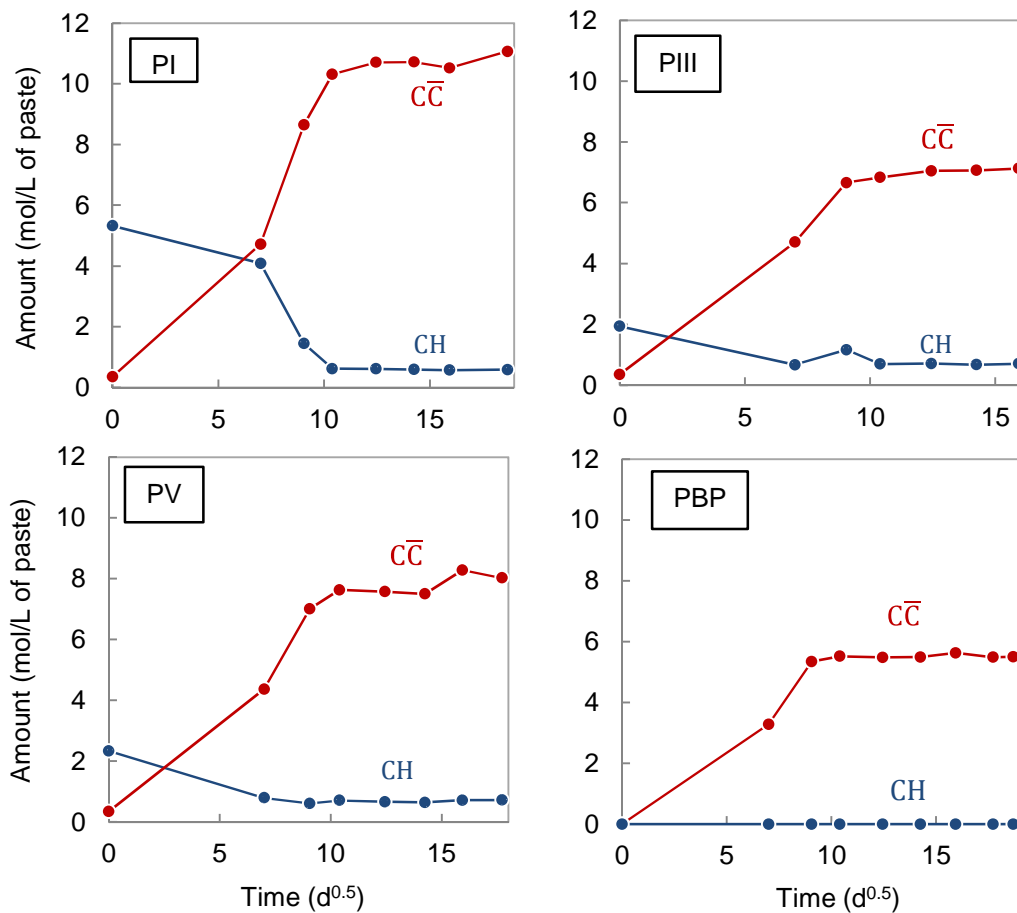
315 The usual mineralogical changes could be highlighted using XRD (Figure 8): dissolution of the main
316 hydrates (portlandite, AFt and AFm) and precipitation of calcium carbonate (calcite and vaterite, the
317 presence of aragonite was not identified). These evolutions were supported by the TGA data (Figure
318 9). 100 days were necessary to achieve a stabilized state of carbonation (constant concentration of
319 calcium carbonate). As it was expected, the amount of calcium carbonate increased with the initial
320 portlandite content. The remaining presence of portlandite was also observed after carbonation that
321 was attributed to the calcium carbonate formation around the portlandite crystal inhibiting their
322 dissolution [71-74].

323 Figure 10 presents the results obtained using ^{29}Si NMR. Q_0 represents isolated SiO_2 tetrahedra, Q_1
324 denotes chain end groups, Q_2 middle groups, Q_3 branching sites and Q_4 cross-linking ones [48]. Q_2^p
325 represents the bridging SiO_2 sites but other tetrahedra cannot be distinguished using ^{29}Si MAS NMR.
326 A more detailed analysis would be required to describe accurately the C-S-H structure [51]. ^{29}Si NMR
327 spectra showed that carbonation decreases the amount of anhydrous phases (Q_0) in agreement with
328 the XRD results. But above all this, the characteristic peaks of the C-S-H (Q_1 , Q_2^p and Q_2) drastically
329 decreased revealing significant decalcification of the C-S-H. The end result was close to a silicate
330 material ($Q_{3\text{ gel}}$ and $Q_{4\text{ gel}}$) which could possibly contain calcium (Ca-enriched silica gel with a low C/S
331 ratio).





332 **Figure 8: X-ray diagrams acquired for non-carbonated (NC) and carbonated (C) pastes PI, PIII,**
 333 **PV and PBP - AFt: ettringite, AFm: monosulfate, m: mullite, p: portlandite, q: quartz, Gy:**
 334 **gypsum, c: calcite, v: vaterite, a: aragonite, d: dolomite, an: anhydrous phases C₂S and C₃S, h:**
 335 **hematite.**



336 **Figure 9: Evolution of the amounts of portlandite (CH) and calcium carbonate (CC) as a function**
 337 **of carbonation time in PI, PIII, PV and PBP.**

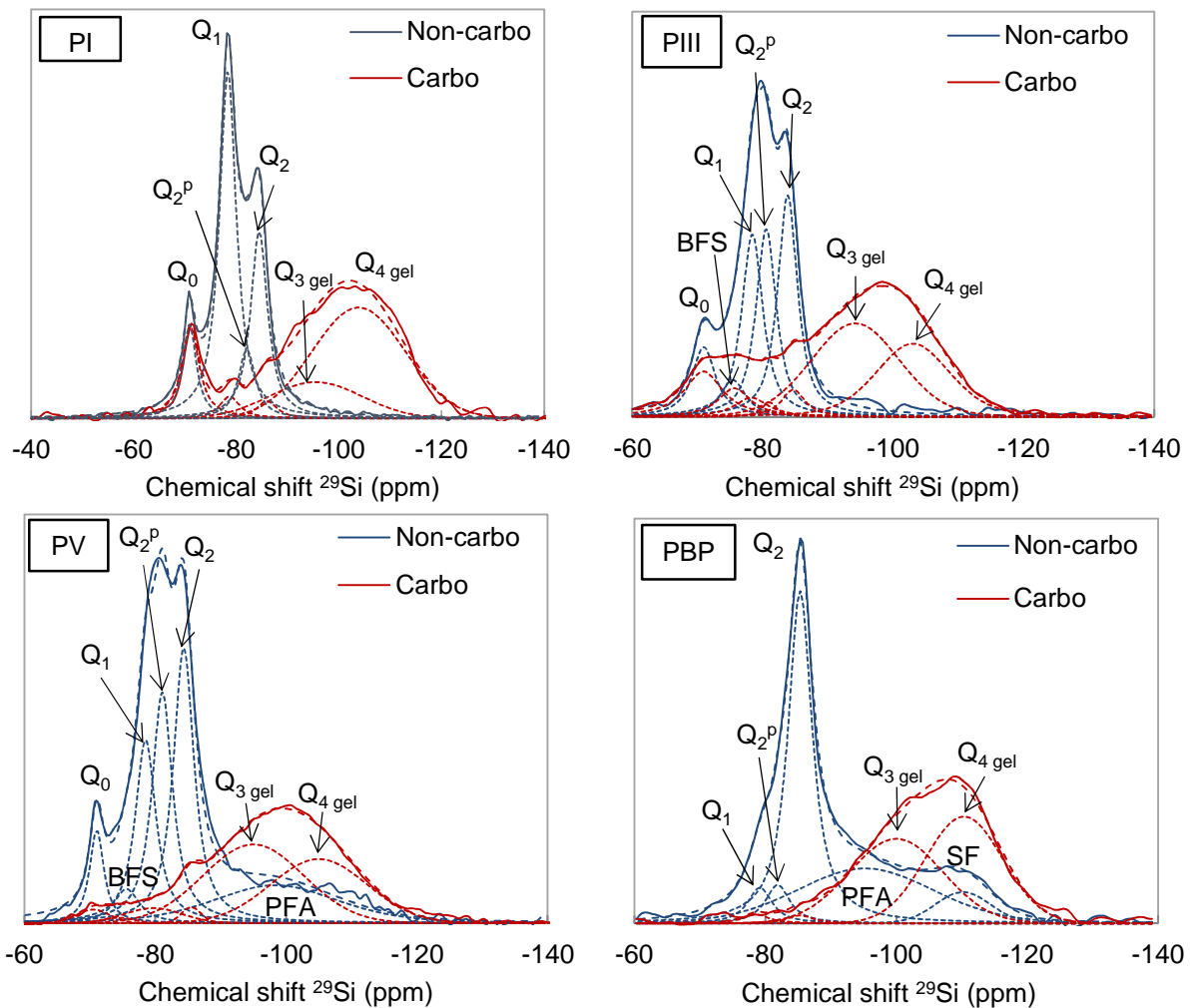


Figure 10: ^{29}Si MAS NMR spectra of PI, PIII, PV and PBP.

338

339 Many disks were cracked or even broken at the end of the carbonation campaign, regardless of the
 340 composition: more than 50% of the PI specimens and to a lesser extent PIII, PV and PBP (between
 341 25% and 40%). This was believed to be due to the combination of drying and carbonation shrinkage.
 342 Only the unbroken and non-cracked disks (as observed with the naked eyes) were used for further
 343 characterization.

344 5.2. Porosity

345 The precipitation of calcium carbonate led to the reduction of water porosity (Table 4). The fall of
 346 porosity was of the same order of magnitude of those obtained by Ngala and Page [5]. The porosity
 347 variation was directly related to clinker substitution by pozzolanic additions: the higher the initial
 348 portlandite content, the higher the fall of porosity (Figure 9 and Table 4).

349

Table 4: Porosity to water of the cement pastes.

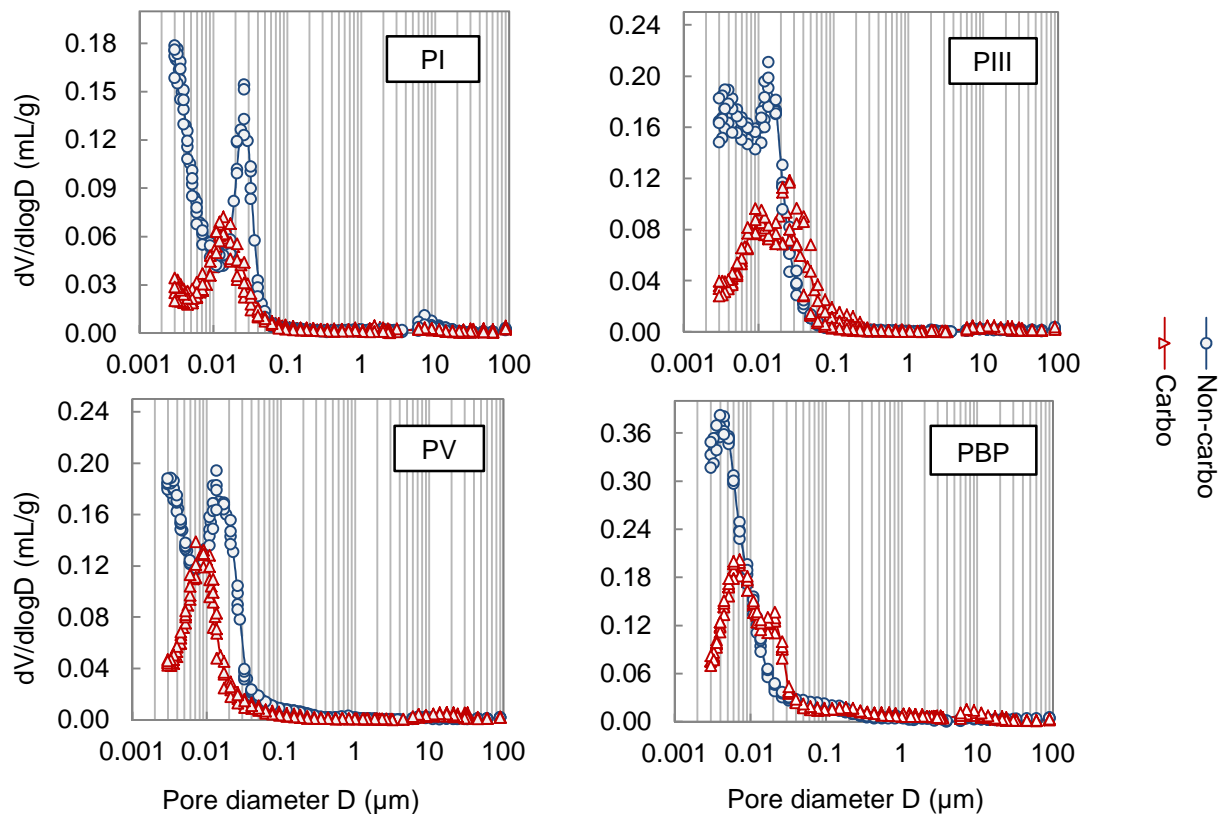
		PI	PIII	PV	PBP
Water content w_{sat}	Non-carbonated	22.1%	26.2%	25.2%	30.6%
	Carbonated	10.0%	14.8%	14.1%	20.0%
Porosity	Non-carbonated	36.3%	39.8%	36.9%	41.0%
	Carbonated	21.1%	29.3%	27.6%	35.5%
	Variation	-15.2%	-10.5%	-9.3%	-5.5%

351

352 Not only the total porosity was reduced but also the pore size distribution was modified (Figure 11).

353 The critical pore diameter decreased for PI and PV whereas a slight, but significant, coarsening of the

354 pore structure was observed for PIII and PBP.

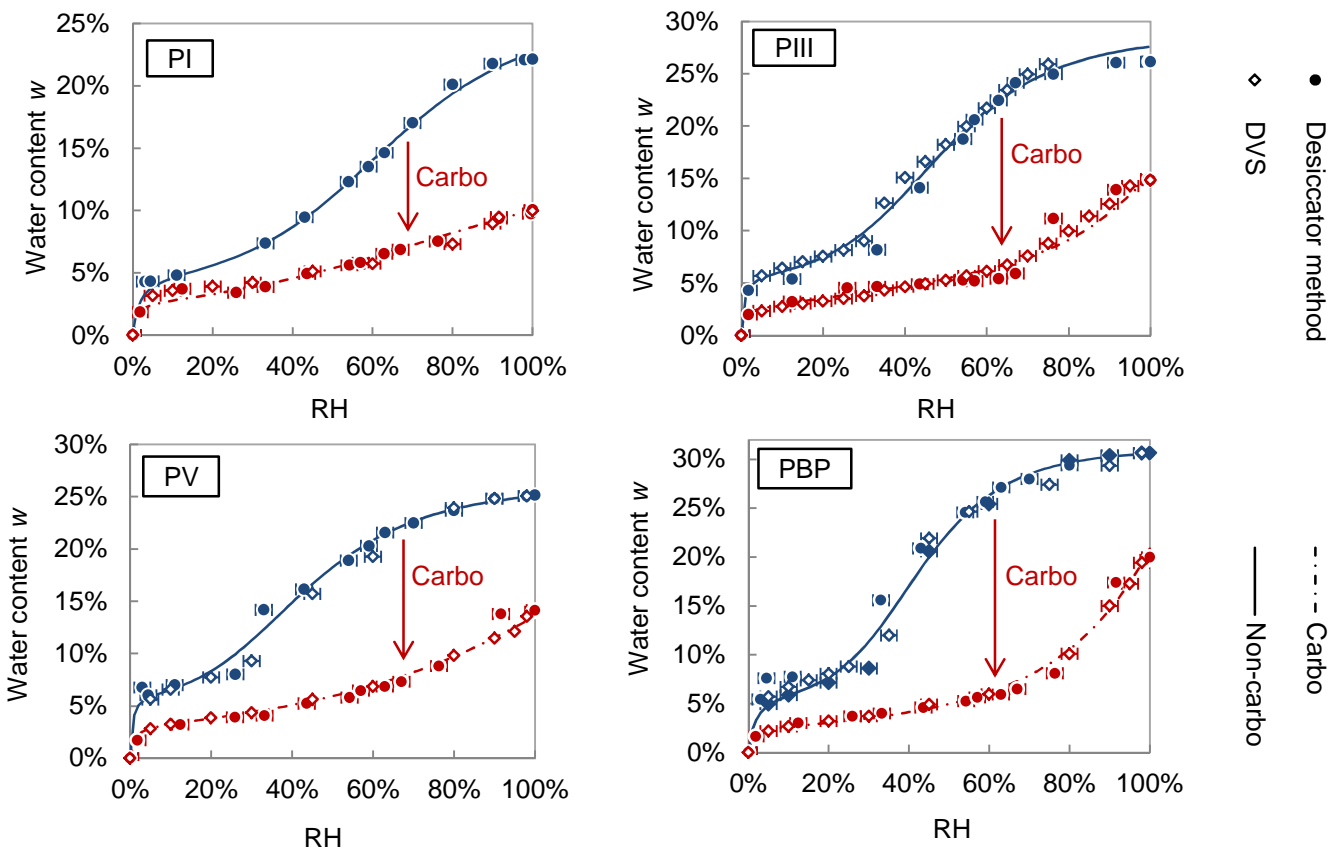


355 **Figure 11: Impact of carbonation on the pore size distribution (characterized by MIP two**
 356 **samples per formulation).**

357 5.3. Water desorption isotherm

358 Figure 12 presents the water desorption isotherms obtained using the desiccator method (filled circles)
 359 and the sorption balance (DVS, open diamonds). A satisfactory agreement between the two methods

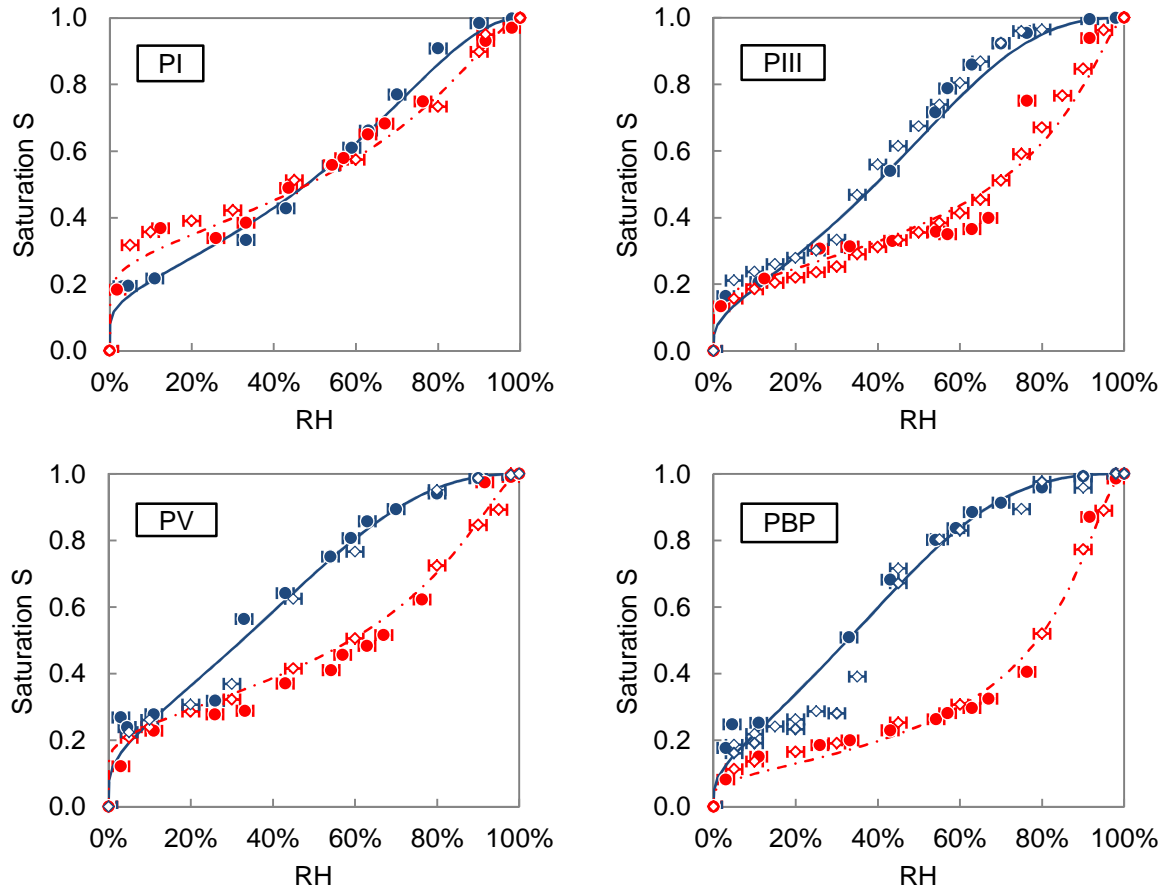
360 was then obtained for all the binders in the non- and carbonated states. Carbonation led to a
 361 significant drop of water content at equilibrium that was directly related to porosity clogging (Table 4).
 362 The desorption isotherms morphology was also altered as a consequence of the pore size distribution
 363 modification. This is patent when saturation is used to plot the water retention curves (Figure 13). As
 364 already beheld by Houst and Whittmann [4], the modifications of the CEM I paste curve appeared
 365 moderate and remained limited to low RH. Those of the blended pastes were more significant and
 366 appeared to be all the more significant as the amount of addition was high.



367 **Figure 12: Water retention curves of the hardened cement pastes (water content). The lines are**
 368 **guides for the eyes only.**

369 The van Genuchten parameters needed for the inverse analysis (pressure P_0 and exponent m) were
 370 evaluated; the results are presented on Figure 13 and the parameters are listed on Table 5.

371



372 **Figure 13: Water retention curves of the hardened cement pastes (saturation). The lines**
 373 **correspond to van Genuchten model (eq. 11).**

374 **Table 5: The van Genuchten parameters (P_0 in MPa and m without unit) obtained by**
 375 **capillary-pressure curve fitting.**

	PI		PIII		PV		PBP	
	P_0	m	P_0	m	P_0	m	P_0	m
Non-carbo	51.4	0.46	86.5	0.56	96.9	0.53	108.7	0.58
Carbo	26.8	0.33	14.9	0.34	20.8	0.34	14.9	0.43

376

377 Carbonation led to a reduction of the specific surface area (Table 6). Using the approach proposed by
 378 Olson and Jennings [47] together with the desorption isotherm (water content at 20% RH), the C-S-H
 379 content was estimated (

380 Table 7). It was then implicitly assumed that this approach remains valid for carbonated cementitious
 381 materials. It was found that ΔS_S increased with $\Delta C-S-H$ indicating C-S-H carbonation and partial
 382 dissolution.

383

Table 6: Impact of carbonation on the specific surface area (S_s).

S_s (m ² /g)	PI	PIII	PV	PBP
Non-carbonated	190	300	298	382
Carbonated	93	89	98	88
ΔS_s	-97	-211	-200	-294

384

385

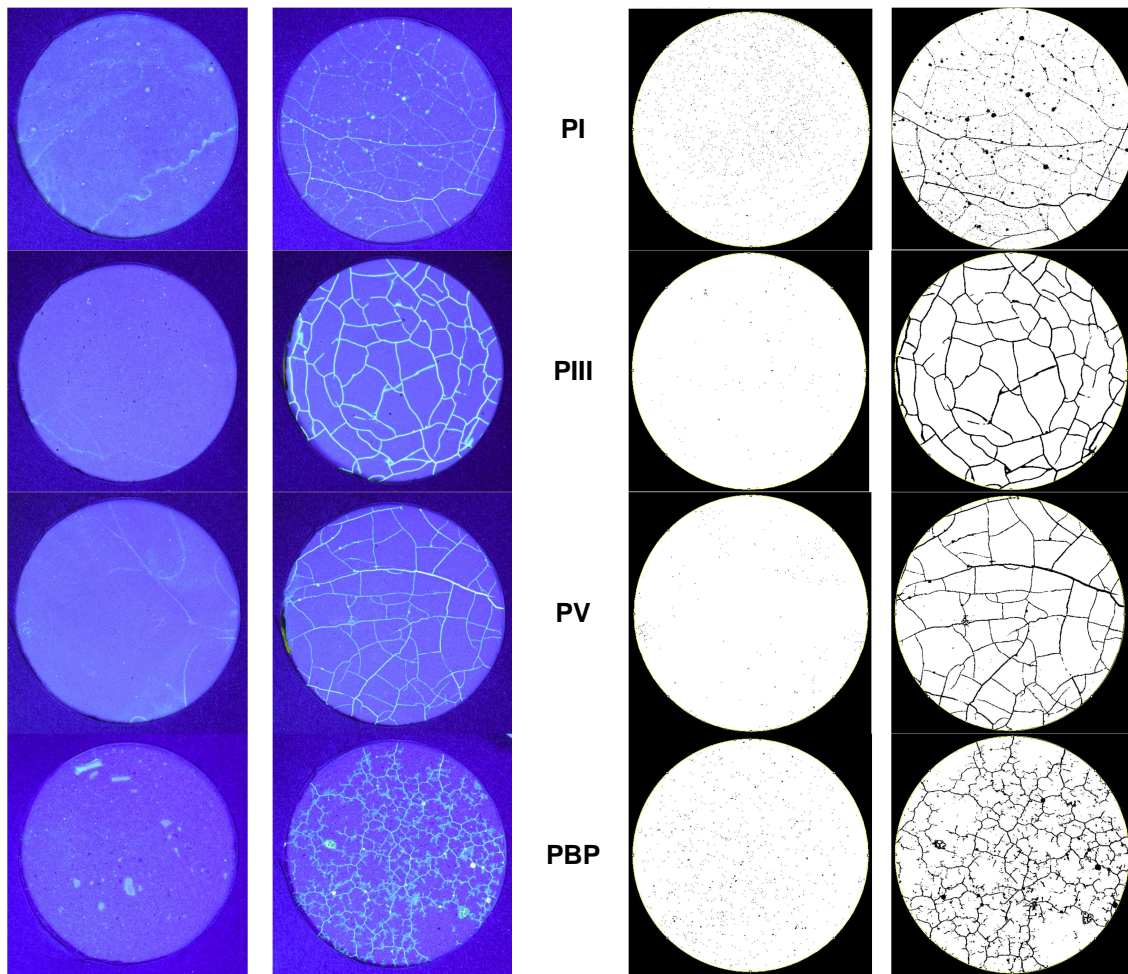
Table 7: Impact of carbonation on the C-S-H content.

C-S-H concentration (mol/L of paste)	PI	PIII	PV	PBP
Non-carbonated	5.2	6.5	6.5	7.6
Carbonated	3.7	3.3	3.9	2.6
Δ C-S-H	-1.4	-3.2	-2.5	-5.0

386

387 5.4. Cracking

388 Figure 14 presents the pictures of the non- and carbonated disks surface. The absence of cracks on
389 the non-carbonated disks could be noticed whereas the carbonated ones were more or less
390 significantly cracked depending on the considered binder. Although only the disks surface could be
391 observed, the resulting cracking pattern was believed to be representative of that of the bulk. The
392 image processing results are reported on Figure 14 (“thresholded” binary image) and in Table 8
393 (cracking index values). An average crack opening of 10-15 μ m was measured for all the binders.
394 Different values of the cracking index were found depending on the considered binder: PI presented
395 the lowest value and PBP the highest.



396 **Figure 14: Photos of the non- and carbonated impregnated disks under UV light (on the left)**
 397 **and result of the image processing (on the right)**

398 **Table 8: Cracking indices (I_c).**

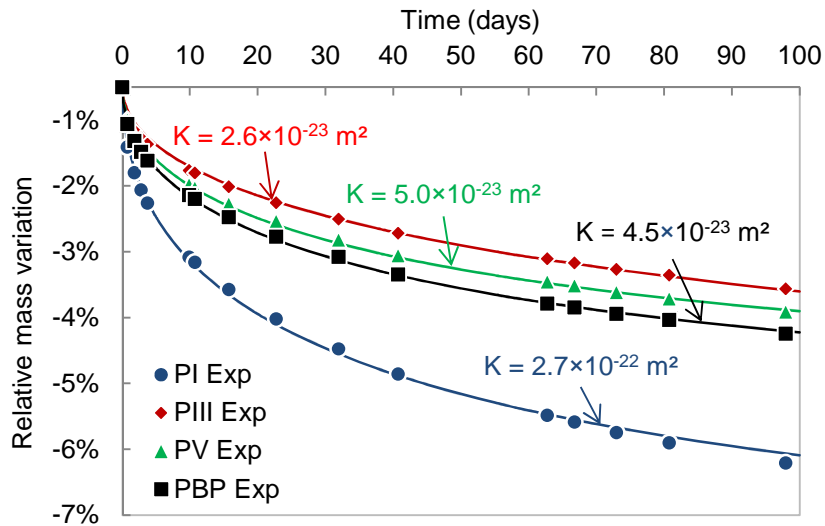
	PI	PIII	PV	PBP
I_c (%)	4%	9%	7%	10%

399

400 **5.5. Permeability**

401 **5.5.1. Inverse analysis**

402 The numerical restitution of the experimental drying kinetics of the $\varnothing 50 \times 100$ mm cylinders (55% RH
 403 and 25°C) is presented on Figure 15 (following the method presented in part 4.4.1). The obtained
 404 intrinsic permeability values are compiled in Table 9. These values are consistent with the pore size
 405 distributions: the finer the pore size distribution, the lower the permeability value.



406

407 **Figure 15: Numerical restitutions of the relative mass loss as a function of the intrinsic**
 408 **permeability (K) (PI, PIII, PV and PBP).**

409 **Table 9: Values of the intrinsic permeability (K) of non-carbonated paste.**

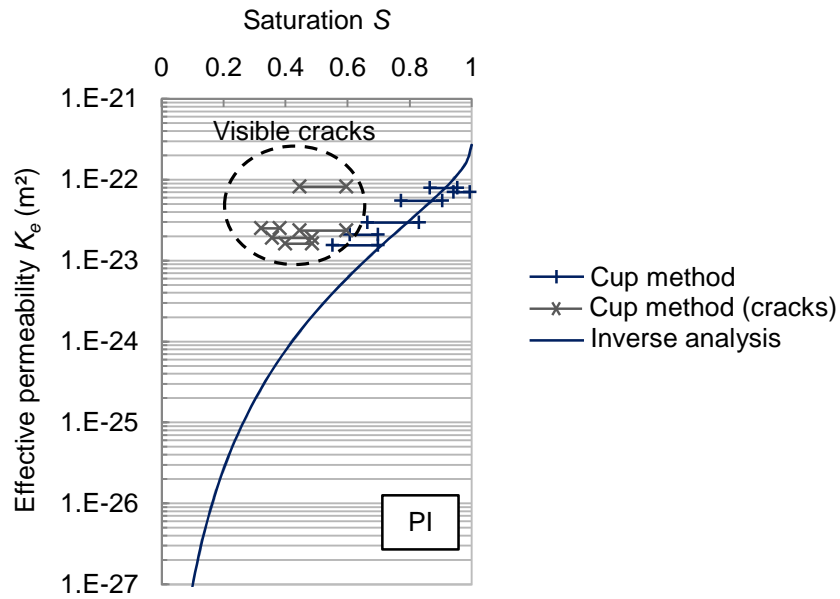
	PI	PIII	PV	PBP
K_{nc} ($\times 10^{-22}$ m ²)	2.70	0.26	0.50	0.45

410

411 5.5.2. Cup method

412 Firstly, the cup-method was applied on non-carbonated PI to compare with inverse analysis (Figure
 413 16). A good agreement between both methods was noticed: the two datasets presented the same
 414 order of magnitude and described a similar trend. A small difference could however be observed that
 415 could be due to:

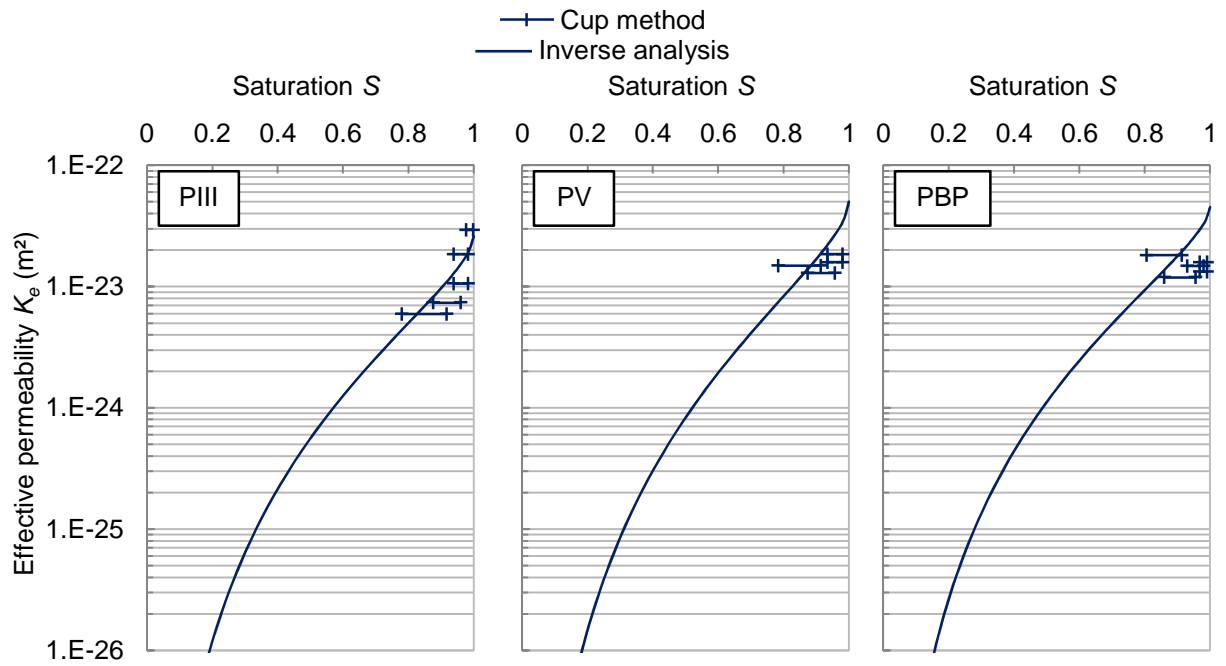
- 416 - the variability linked to the differences between the batches used for the two methods (the data
 417 required for inverse analysis were extracted from a previous study [33],
- 418 - uncertainties on the unsaturated properties (for instance water retention curve),
- 419 - the error on the relative permeability (k_r) assessed using Mualem's model and more specifically
 420 the value of the pore interaction factor p (eq. 12) [68, 75, 76].



421 **Figure 16: Effective permeability (K_e) evolution vs. saturation state (S), at 25°C, for non-**
 422 **carbonated PI.**

423 It was noticed that for RH lower than 40%, a permeability increase was obtained for the non-
 424 carbonated specimens. Cracks could be observed on the disk surface. They were believed to be due
 425 to restrained drying shrinkage. Beyond that, the authors think that the comparison was globally
 426 satisfactory and that the cup method is an efficient tool for unsaturated permeability evaluation. This
 427 statement could not however be generalized to the blended cements (Figure 17) for which the reliable
 428 permeability description was limited to a small range of saturation (around 0.8 to 1.0). This was due to
 429 their refined pore size distribution leading to flattened desorption isotherms at high RH (Figure 12). In
 430 the following sections, the permeability of non-carbonated blended cement pastes was then described
 431 using inverse analysis.

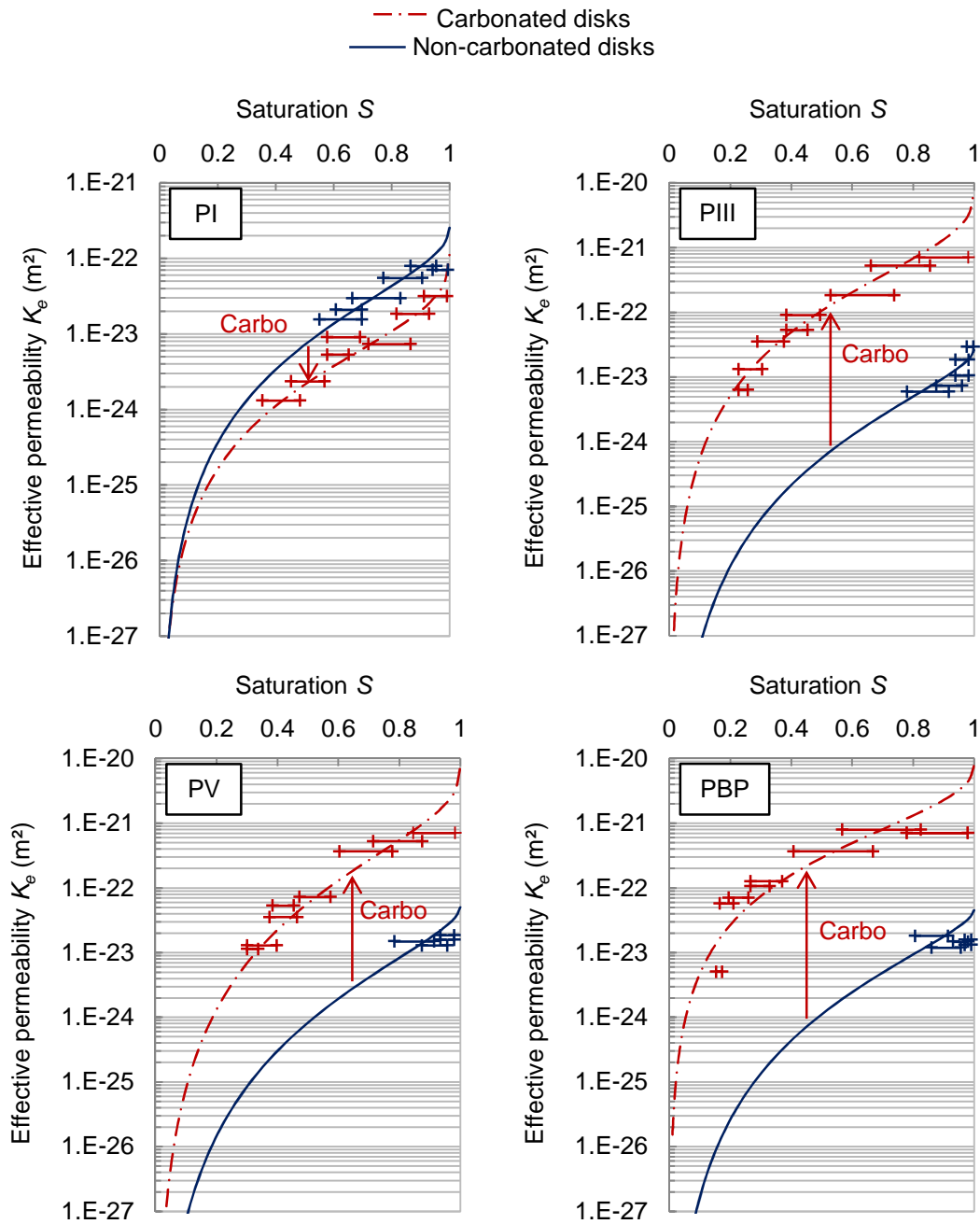
432



433 **Figure 17: Effective permeability (K_e) evolution vs. saturation state (S), at 25°C, for non-**
 434 **carbonated PIII, PV and PBP.**

435 The cup-method was applied to assess the unsaturated permeability of the carbonated pastes (Figure
 436 18). A decrease in the permeability of PI was observed subsequently to carbonation that is consistent
 437 with porosity clogging. On the opposite side, a significant increase of permeability was found for the
 438 blended cements despite the fall of porosity.

439



440 **Figure 18: Impact of carbonation on the effective permeability (K_e). The lines stand for the best**
 441 **fit using Mualem-van Genuchten model (with $p \neq 0.5$).**

442 Intrinsic permeability values of the carbonated pastes were assessed following eq. (16). This is the
 443 well-known Mualem-van Genuchten equation. It is the same as eq. (12) but it is expressed in terms of
 444 saturation instead of pressure. No restriction was imposed to the pore interaction factor value (the
 445 exponent p) to improve the fitting capacity [75-79]. The resulting p values were different from the
 446 default value (+0.5) proposed by Mualem [68]: they were all negative as it was already observed [75,
 447 76]. The corresponding values (pore interaction factor and intrinsic permeability) are compiled in

448 Table 10.

$$K_e = K_c^{exp} S^p [1 - (1 - S^{1/m})^m]^2 \quad (16)$$

449

450

Table 10: Intrinsic permeability value of the carbonated pastes.

	PI	PIII	PV	PBP
K_c^{exp} ($\times 10^{-22}$ m ²)	1.16	74.82	74.39	81.48
p	-3.31	-2.59	-1.83	-2.18

451

452 Two different explanations were explored to explain the significant permeability increase of the
453 blended cement pastes: (i) coarsening of the pore structure and formation of large pores and (ii)
454 microcracking. These points are discussed in the following section.

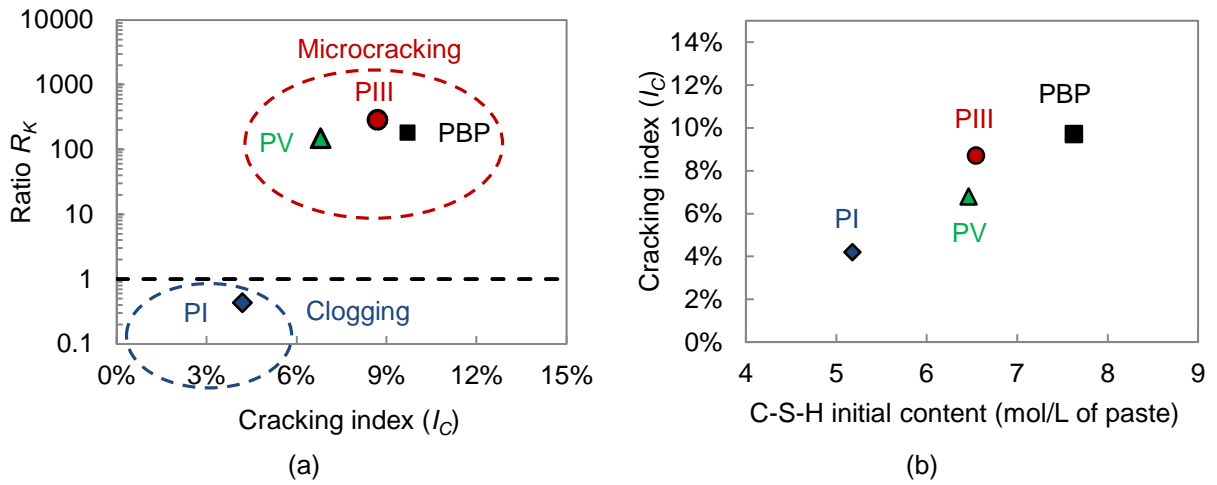
455 6. Discussion

456 The coarsening of the pore structure and formation of large pores could not be observed using MIP.
457 Microcracking was then believed to be the major cause of the permeability increase. This was
458 supported by the fact that the permeability of the carbonated disks increases with the cracking index
459 (I_c) as depicted on Figure 19 (a). R_K is the ratio of the intrinsic permeability of the carbonated paste
460 K_c^{exp} to the non-carbonated one K_{nc} (Table 11):

$$R_K = \frac{K_c^{exp}}{K_{nc}} \quad (17)$$

461 For $R_K \leq 1$ (PI), the high amount of calcium carbonates (due to the high initial portlandite content) led
462 to significant porosity clogging that prevailed over the effect of microcracking. On the contrary, for
463 $R_K \geq 1$ (PIII, PV and PBP), the effect of microcracking prevailed over porosity clogging. This fact was
464 directly related to the initial mineralogical composition of the pastes. C-S-H rich pastes (with low
465 portlandite) showed significant cracking after carbonation (Figure 19, b): the higher the initial C-S-H
466 content, the higher the cracking index (I_c). The authors believe that the cracking was induced by
467 C-S-H carbonation following the proposition of Swenson and Sereda [71]. The C-S-H decalcification
468 induced by carbonation and the subsequent polymerisation (increase of the main silica chain length)
469 generated shrinkage [80]. This carbonation shrinkage [42, 71, 81-83] eventually led to cracking as it

470 was already observed [20, 84, 85]. The substantial C-S-H decalcification observed for all the binders
 471 after complete carbonation using ^{29}Si NMR supported this assumption (Figure 10).



472 **Figure 19: Influence of cracking on permeability (a) and influence of C-S-H initial content on the**
 473 **cracking index (I_C).**

474 The dataset obtained was used to describe the effect of porosity clogging on permeability. A simple
 475 law derived from Kozeny-Carman model [86-89] was used:

$$K_c^{K-C} = K_{nc} \left(\frac{\phi_c}{\phi_{nc}} \right)^3 \left(\frac{1 - \phi_{nc}}{1 - \phi_c} \right)^2 \quad (18)$$

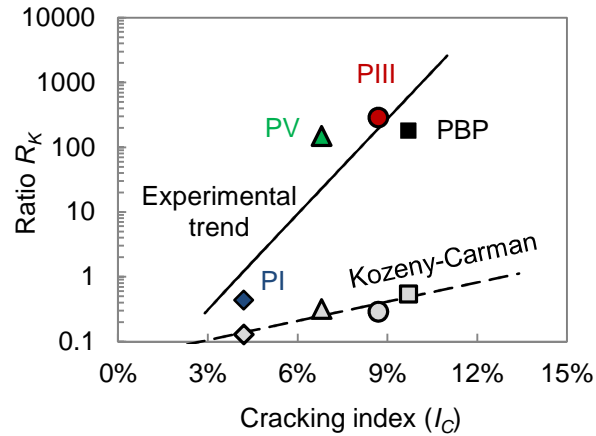
476 where K_{nc} , K_c^{K-C} , ϕ_c and ϕ_{nc} are the intrinsic permeability and water porosity values of the non- and
 477 carbonated pastes respectively. The ratio R_K was computed once again, but this time the permeability
 478 of the carbonated pastes was estimated using eq. (18) (K_c^{K-C} , Table 11). The results are depicted on
 479 Figure 20. For the PI paste the measured permeability was of the same order as the one obtained
 480 using eq. (18) but was three times higher. This suggested that the effect of porosity clogging was
 481 counterbalanced by microcracking. The results were however very different for the blended cements,
 482 the discrepancy between experimental and computed data increased with the cracking index (I_C). This
 483 suggested that in that specific case microcracking was the main cause of permeability increase and
 484 that clogging had negligible impact.

485

Table 11: Influence of clogging on permeability.

Permeability ($\times 10^{-22}$ m ²)	PI	PIII	PV	PBP
K_{nc}	2.70	0.26	0.50	0.45
K_c^{exp}	1.16	74.82	74.39	81.48
K_c^{K-C} (eq. 18)	0.35	0.08	0.16	0.24

487



488

489

Figure 20: Competition between porosity clogging and cracking.

490 Conclusion

491 The impact of carbonation on unsaturated water transport was addressed using four pastes made with
 492 different binders (three commercial cements and a low-pH blend). In the framework of a simplified
 493 approach for the description of unsaturated water transport, three physical parameters were
 494 characterised: porosity, water desorption isotherm and permeability. The samples were carbonated at
 495 a CO₂ content of 3% to ensure representativeness and mitigate cracking (as already observed at
 496 50%). The precipitation of calcium carbonate led to porosity reduction, the extent of which was related
 497 to the initial composition of the paste (portlandite and C-S-H contents). The water desorption curves
 498 were significantly altered by carbonation:

- 499 • a drop of water content was observed over all the RH range according to porosity clogging;
- 500 • the isotherms morphology was changed in relation to pore size distribution modification.

501 The cup-method test was a good alternative to inverse analysis for the assessment of the unsaturated
 502 permeability. The results highlighted a competition between two concomitant phenomena: porosity
 503 clogging and microcracking. A decrease of permeability after carbonation was observed for Portland

504 cement (CEM I): porosity clogging prevailed over microcracking. On the contrary and despite the fall of
505 porosity, significant permeability increase was obtained for the blended cements: microcracking
506 prevailed over clogging. Permeability was found to increase with cracking (digital image processing)
507 and more specifically with the initial C-S-H content. C-S-H decalcification revealed by ²⁹Si NMR was
508 believed to be the main cause of shrinkage resulting in cracking.

509 This study was only a first step; these tests should also be conducted using concretes. The presence
510 of aggregates might help mitigating the consequences of carbonation shrinkage and change the
511 cracking pattern (the cracks could be concentrated around the aggregates).

512 **Acknowledgments.**

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514 supply cements free of charge.

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