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Ph Turcry, K. Namouniara, P-Y. Mahieux, J. Lux, A. Aït-Mokhtar, Ph.  
Turcry

### ► To cite this version:

Ph Turcry, K. Namouniara, P-Y. Mahieux, J. Lux, A. Aït-Mokhtar, et al.. Efficiency of water repellent surface treatment: Experiments on low performance concrete and numerical investigation with pore network model. *Construction and Building Materials*, 2019, 227, pp.116638. 10.1016/j.conbuildmat.2019.08.019 . hal-02316861

**HAL Id: hal-02316861**

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Submitted on 20 Jul 2022

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1 Efficiency of water repellent surface treatment: Experiments on  
2 low performance concrete and numerical investigation with pore  
3 network model

4 K. Namouniara, P-Y. Mahieux\*, J. Lux, A. Aït-Mokhtar, Ph. Turcry  
5 Université de La Rochelle, LaSIE UMR CNRS 7356, Avenue Michel Crépeau, 17042  
6 La Rochelle, France  
7 \* Corresponding author: pierre-yves.mahieux@univ-lr.fr

8 **Abstract**

9 Indicators of durability are nowadays key-parameters in the design of reinforced  
10 concrete structures. One way to guarantee durability is usually to design concrete  
11 mixtures with low porosity and low transfer properties. An alternative or in addition to  
12 this performance-based approach is the use of treatments such as water repellent,  
13 applied on surface of both new and existing concrete structures. The aim of the  
14 present study is to evaluate the efficiency of two water repellents with respect to  
15 water capillary absorption. Both studied water repellents were applied on a concrete  
16 with relatively low mechanical performances (28-day compressive strength equal to  
17 20 MPa). Porosity, pore structure and capillary absorption kinetics were determined  
18 according to the AFREM recommendations [Arliquie et al., 2008] for both treated and  
19 non-treated concrete samples. The water repellents were found to significantly  
20 reduce the water absorption kinetics. However, this reduction was shown to be  
21 temporary. The surface treatments slow down the water transfer but when the water  
22 passes through the physical barrier, the kinetics capillary absorption becomes similar  
23 to that of non-treated concrete. A pore network model was used to support this  
24 explanation of the observed absorption kinetics and to model the effect of water-  
25 repellent.

26

## 27 1 Introduction

28 Corrosion due to aggressive agents such as chloride is the most frequent pathology  
29 of reinforced concrete structures [Costa, 2002], [Poupard et al., 2003]. Corroded  
30 structures need expensive repairs. Ollivier et al. pointed out that the United States of  
31 America should dedicate a budget of more than \$ 100 billion during ten years for  
32 repairs [Ollivier et al., 2008]. The use of mortar patches is a common method to  
33 repair of corroded structures [Canisius, 2004], [Soufi et al., 2016]. Alternative solution  
34 to avoid spending time and money in maintenance is to protect newly cast concrete  
35 structures with surface treatments, which limit the diffusion of aggressive agents  
36 through the concrete cover. The European standard EN 1504 defines three types of  
37 surface treatments [EN 1504, 2005]: coatings, impregnations and hydrophobic  
38 impregnations. Coatings produce a hydrophobic layer on the exposed concrete  
39 surface. Impregnations reduce the cover porosity by filling partially or completely  
40 capillary pores. Hydrophobic impregnations, also called water repellent agents, are  
41 surface treatments designed to protect concrete against water penetration. Their  
42 chemical components reduce surface tension and turn concrete into a hydrophobic  
43 material. Unlike coatings, no film forms on the cover surface and the concrete  
44 appearance remains unchanged: only the surfaces of capillary pores are coated with  
45 the hydrophobic substances.

46 Since the 1970's, many researches were conducted to evaluate the performance of  
47 repair products. Basheer et al. give an overview of the scientific studies conducted on  
48 the methods of assessment and performance of surface treatments [Basheer et al.,  
49 1997]. More recently, other works complete this literature review [Schueremans et  
50 al., 2007], [Medeiros, 2008 and 2009], [Pigino et al., 2012], [Pan et al., 2017].  
51 Surface treatments tend to improve the performance of concrete against the  
52 penetration of aggressive agents and service-life of concrete structures. Johansson  
53 shows that the penetration of chloride ions is reduced from 70% to 80% [Johansson,  
54 2006]. Medeiros shows that the diffusion coefficient of chloride is reduced by 80%,  
55 while the capillary absorption coefficient is reduced from 73% to 98% [Medeiros,  
56 2008]. Zhao et al. confirm that the dissolved ions cannot penetrate the porous  
57 network because the water penetrates only in vapor form [Zhao et al., 2005].  
58 Basheer et al. state that it is important to study the behavior of concrete treated in  
59 their environment and also for a long term period because it seems that the water

60 repellents are sensitive to climate conditions (UV attacks, freeze-thaw cycles, etc.)  
61 and their ability to protect the concrete can be reduced [Basheer et al., 1997].  
62 However, Schueremans et al. [Schueremans et al., 2007] show, through a study  
63 focused on the quality and quantity of water repellent agents, that it is possible to  
64 obtain good results in the long term with respect to the penetration of aggressive  
65 agents and thus in protection of reinforced concrete structures.

66 Putting aside the eventual degradation of water repellents, many studies agree that  
67 these protections are effective for reducing the transfer process and particularly the  
68 water absorption. One can, however, wonder how long the protective effects last,  
69 since only a small depth of the cover is usually impregnated by the hydrophobic  
70 treatment. Thus, one can wonder if protection remains efficient when aggressive  
71 agents have diffused beyond the treated depth.

72 In order to answer this question, the long term efficiency of two standard water  
73 repellent agents were investigated in the present study. An experimental campaign  
74 was carried out on a concrete with poor mechanical performances. This kind of  
75 concrete was chosen in order to reduce the time of the mass transfer phenomenon  
76 investigated in our laboratory work, namely water capillary absorption. Microstructure  
77 of treated and non-treated concrete specimens was also investigated. In parallel,  
78 numerical simulations based on a pore network model were also carried out in order  
79 to complete our investigation on the effects of the porous network connectivity  
80 reduction and the penetration depth on the capillary absorption.

81

## 82 2 Materials and experimental procedures

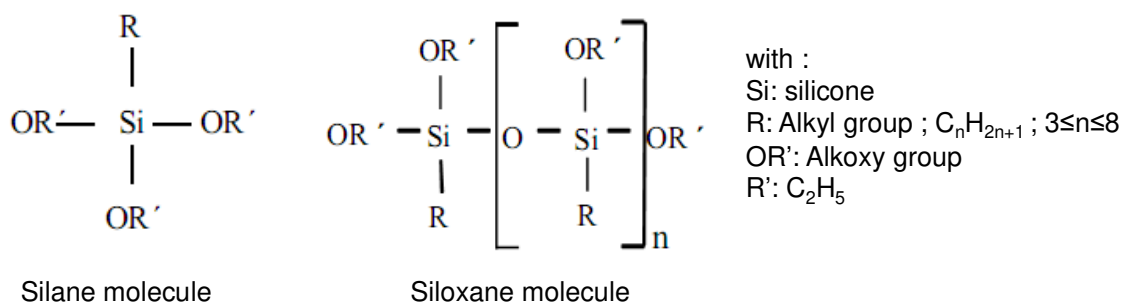
### 83 2.1 Water repellents

84 Two water repellents agents were studied: the first agent (denoted H1) is composed  
85 of siloxanes molecules, while the second one (denoted H2) is composed of silanes  
86 molecules.

87 Silanes are a family of monomers molecules derived from different alkyl groups  
88 linked to each other by a silicone molecule (Figure 1). The waterproofing properties  
89 of silanes come from a double chemical reaction (hydrolysis and condensation)  
90 between water repellent and concrete. Silanes molecules react with the interstitial  
91 water to form silanols groups (reaction in an alkaline solution at high pH value) and  
92 ethanol. Silanols groups then react with siliceous phases (aggregates and  
93 cementitious matrix) to form a hydrophobic layer on the surface of concrete pores  
94 (alkyl group). Generally, larger the molecule of the alkyl group is, better the  
95 repellency of the silane is. Silanes are volatile and some active components can  
96 evaporate during the application, especially if the operation does not take place  
97 under ideal conditions.

98 Siloxanes are oligomer molecules derived from partially hydrolyzed molecules of  
99 silanes. Siloxanes react with concrete silica to form a hydrophobic layer. In concrete  
100 pores, the reactions are identical to those described for the silane molecules, with a  
101 residual hydrolysis and polycondensation.

102 *Figure 1: Silane and siloxane molecule [Johansson, 2010]*



103 Water repellents were applied on the surface of the tested specimens (described in  
104 the following section) by paintbrush in two coats for an overall quantity equal to 300  
105 g/m<sup>2</sup> (i.e. at 150 g/m<sup>2</sup>/coat). To ensure a complete polymerization, the treated  
106 specimens were conserved 14 days in room conditions before further investigations.

## 107 2.2 Concrete

108 Experiments were carried out on a low performance concrete made with a Portland  
109 limestone cement CEMII/B-LL/32.5, with a 0/4 mm siliceous sand and a 6/10 mm  
110 diorite coarse aggregates. Concrete composition, given in table 1, has been  
111 investigated in previous research program [Tahlaïti, 2010], [Soufi et al., 2016]. Due to  
112 its high W/C ratio, this concrete has a relatively high porosity (table 2) and low  
113 mechanical performance (compressive strength equal to 20 MPa at 28 days), what  
114 makes it convenient for accelerating mass transfers and highlights in a reasonable  
115 time the impact of water repellent agents used.

116 *Table 1: composition of studied concrete (per cubic meter)*

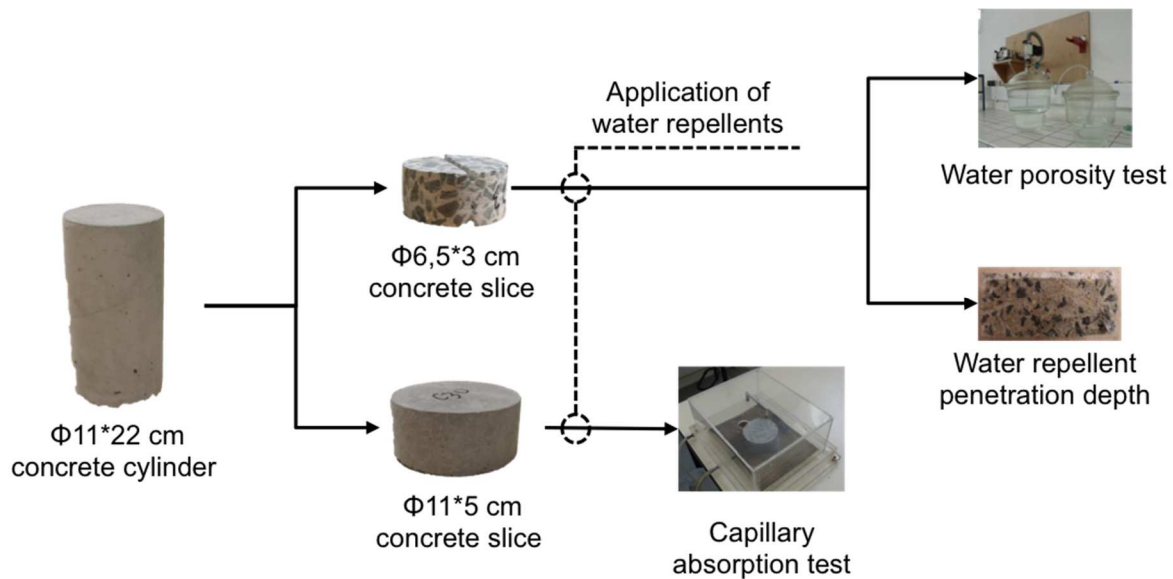
Constituents	Mass (kg)
Portland limestone cement	275
Water	222
W/C	0.8
Fine aggregates 0/4	729
Coarse aggregates 6/10	1085

117  
118 Concrete cylinders ( $\Phi 11 \times 22$  cm) were cast, demoulded at 1 day and conserved in  
119 water at 20°C during 21 days. After this curing period, some cylinders were cored  
120 and sawn to obtain slices with 65 mm in diameter and 30 mm in height. These  
121 specimens were used for porosity and water repellent penetration depths  
122 measurements. A second series of cylinders was sawn to obtain cylindrical  
123 specimens with 110 mm in diameter and 50 mm in height. The latter were used for  
124 capillary absorption tests. All the specimens were placed after sawing in a room at  
125  $75 \pm 5\%$  RH and 20°C during 7 days. This conservation was required to have  
126 sufficiently dry surfaces before the application of water repellent.

127 Among all the specimens, some of them (denoted C15) were non-treated and used  
128 as reference, others were treated with the water repellent H1 and H2 (denoted  
129 C15H1 and C15H2, respectively). Note that the water repellents were applied only on  
130 one sawn surface of the specimens (i.e. one plane circular surface). The  
131 experimental program is summarized in Figure 2.

132

133 *Figure 2: Summary diagram of the experimental procedure*



134

### 135 2.3 Experimental procedures

136 To measure the penetration depths of the water repellents, the 30 mm thick slices  
137 were split into two parts then split areas were sprayed with water, according to the  
138 European standard [EN 1504, 2005]. The penetration depths were measured with a  
139 ruler and correspond to the thickness remained dry due to the hydrophobic effect of  
140 water repellent.

141 The water porosities were assessed according to the French standard NF P 18-459  
142 [NF P 18-459, 2010]. Specimens were water-saturated during 24 hours under  
143 vacuum (around 2.5 kPa) and then oven-dried at 105°C. Volumes were determined  
144 by hydrostatic weighing. The average of water porosities values were calculated from  
145 three results for each study case.

146 Mercury intrusion porosimetry (MIP) was carried out with the Micrometrics Autopore  
147 III 9420 porosimeter, according to a procedure recommended by the AFPC-AFREM  
148 [Arliguie et al., 2008]. The test was performed on 15 mm side cubes sawn from the  
149 30 mm thick slices. In the case of treated slices, these cubic samples contained the  
150 treated zone (determined previously with the penetration depth). Before mercury  
151 intrusion, the cubic samples were dried during 7 days at 45°C in a ventilated oven.

152 Capillary water absorption tests were performed following the procedure proposed by  
153 the AFPC-AFREM [Arliguie et al., 2008]. The lateral faces of the 50 mm thick  
154 specimens were sealed with a resin coating to insure unidirectional transport from  
155 bottom to the top during absorption. Before testing, specimens were dried at 80°C

156 until weight stabilization. They were cooled and then put in contact with water (Figure  
157 2). Specimens were regularly weighted during the test.

158 A FEI/Philips Quanta 200 SEM was used to make images on non-polished layer  
159 samples in environmental conditions, in order to locate the water repellents and  
160 observe their microstructures.

## 161 3 Experimental results

### 162 3.1 Penetration depths

163 As shown in Figure 3, the average penetration depth of C15H1 is lower than the  
164 penetration depth of C15H2, with 2.5 and 9.5 mm average depths, respectively.

165 When applied on a concrete surface, the water repellent goes into the cement matrix  
166 by capillary suction. This absorption follows the classical Washburn law [Aït-Mokhtar  
167 et al., 2004] during 6 to 8 hours according to Gerdes et al. [Gerdes et al., 2001]. After  
168 that, the absorption slows down due to chemical reactions taking place in the porous  
169 network (hydrolysis and polycondensation, see section 2.1). Over time, these  
170 chemical reactions and the consecutive condensation prevent any additional  
171 penetration of water repellent.

172 The absorption of a water repellent depends, on the one hand, on the chemical  
173 nature (type of cement, nature of aggregates, temperature, pH), the physical  
174 properties (i.e. porosity) and the water saturation degree of the concrete substrate,  
175 and, on the other hand, on the application, the quantity and the quality of the water  
176 repellent agent. In this study, the main reason that can explain the difference  
177 between the penetration depths is the molecular structure of the studied products  
178 and the chemical reactions that occur during the absorption phase, since all other  
179 parameters remain constant.

180 The water repellent H1 is a siloxane solution in solvent phase. The siloxane molecule  
181 is itself a silane molecule partially hydrolyzed. When siloxane contacts the interstitial  
182 solution, a residual hydrolysis takes place very quickly causing the formation of  
183 polysiloxanes. These polymers create a hydrophobic barrier that reduces and even  
184 cancels the additional absorption of the product, which explains the lower penetration  
185 depth of H1. This assumption seems to be confirmed by SEM analyses. A thin film  
186 can be seen on the concrete surface (image 3, Figure 3) revealing the presence of



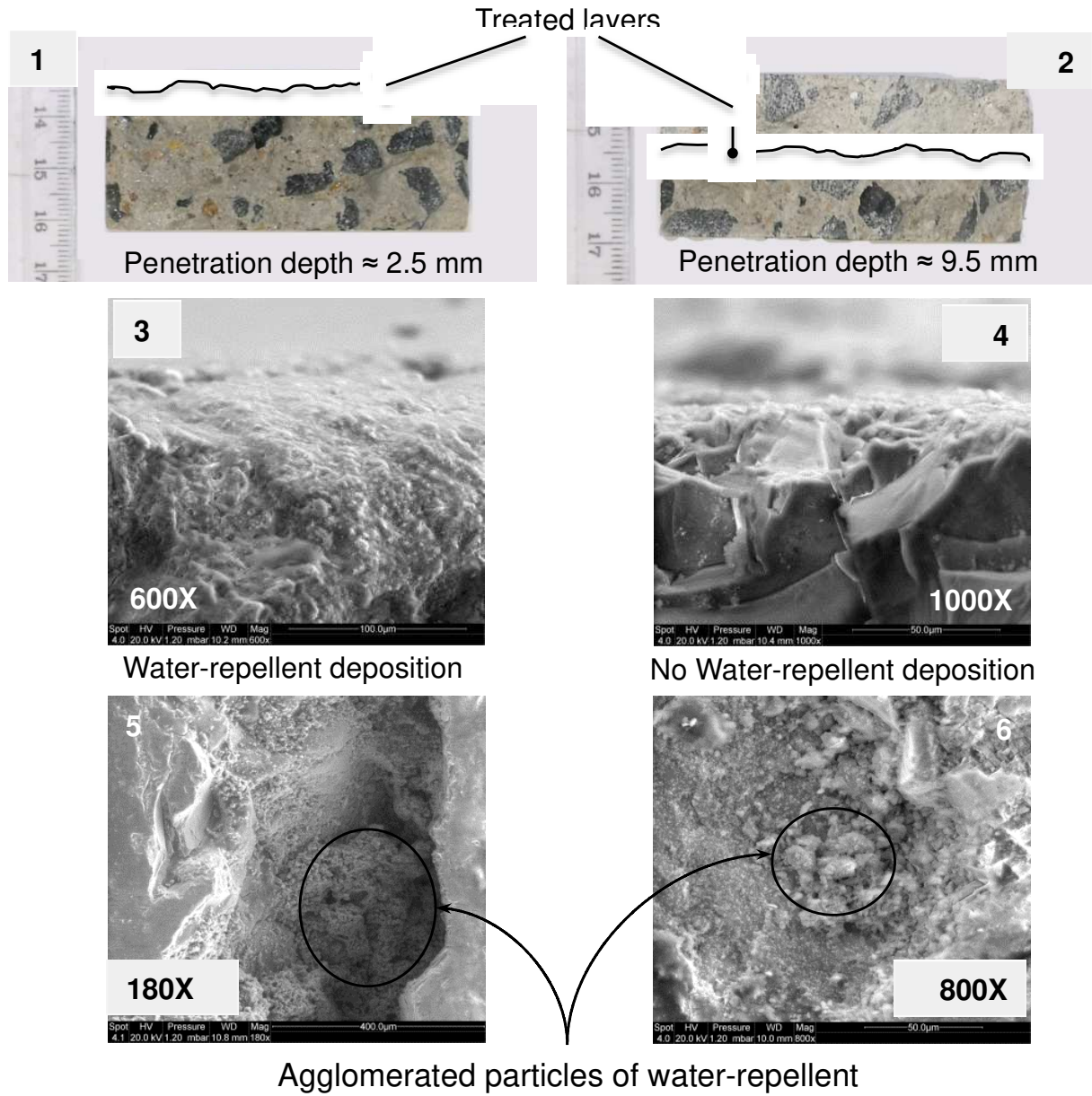
187 H1 repellent on the surface, while no film can be detected on the surface of the  
188 sample treated by H2 (image 4, Figure 3).

189 The water repellent H2 is a pure silane solution (99 % of actives substances). The  
190 time required for complete hydrolysis and poly-condensation is longer than that of  
191 H1. Furthermore, the smaller size of the H2 molecules allows the water repellent to  
192 penetrate the pores network inaccessible to the H1 siloxane molecules. The  
193 combination of these two parameters allows the H2 water repellent having a better  
194 penetration depth in comparison with H1.

195 In addition, images 5 and 6 in Figure 3 show that microstructures of water repellents  
196 after condensation are identical in both cases with agglomerated forms, partially  
197 distributed on the pores surface.

198

199 *Figure 3: Multi-scan approach of water repellents penetration (image 1 and 2:*  
200 *transversal sections, images 3 and 4: SEM scans of concretes surface, images 5*  
201 *and 6: SEM scans of the pores surface*



202

203

204 3.2 Water porosities

205 Table 2 gives penetration depths and water porosities obtained on the reference  
206 concrete C15, C15H1 and C15H2. Note that C15H1 and C15H2 samples are  
207 composed both of treated concrete and non-treated concrete layers, since the  
208 penetration depths are less than the smallest dimension of samples (30 mm).

209 *Table 2: Measured penetration depths of water-repellent and water porosities of*  
210 *C15, C15H1 and C15H2*

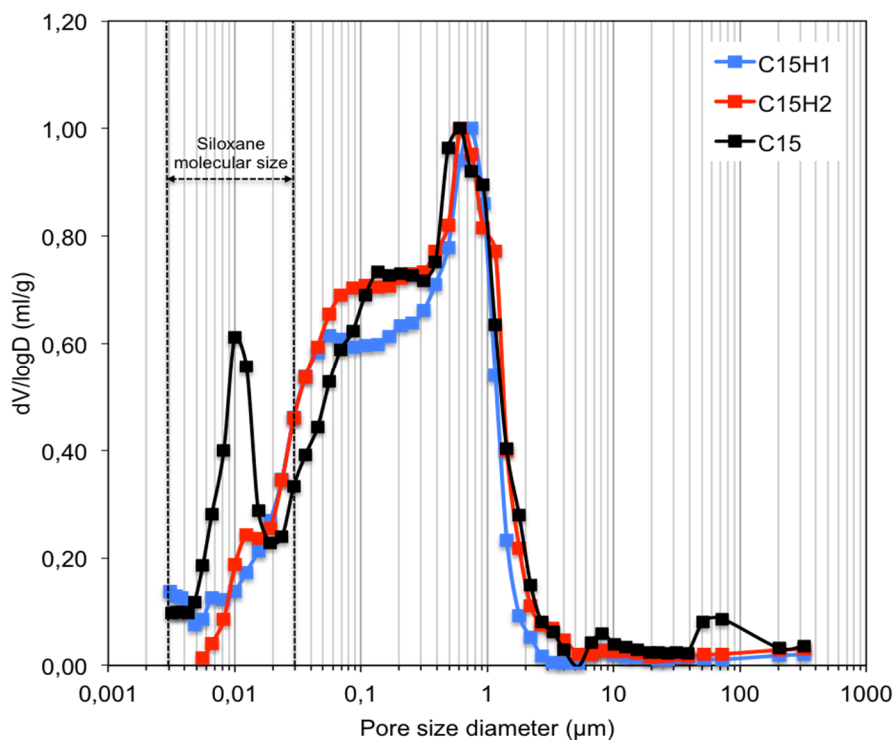
	Penetration depth (mm)	Water porosity (%)
C15	0	14.9 ± 0.5
C15H1	2.5 ± 0.5	13.2 ± 0.1
C15H2	9.5 ± 2.5	8.1 ± 0.5

211  
212 The reference C15 concrete has the highest water porosity with 14,9%. As planned,  
213 with this high value, this concrete can be classified under the low durability category  
214 structure materials [AFGC, 2004]. The lowest porosities were determined on C15H1  
215 and C15H2 concretes with 13,2% and 8,1%, respectively. Note that porosities of the  
216 treated specimens are inversely proportional to the penetration depth of water  
217 repellents. In view of these results, we can question the effectiveness of this method.  
218 Indeed, if we use the measured water porosities in the two treated samples as a  
219 basis for calculating the porosity in the treated layer, we found negative values, even  
220 when taking into account the measurement uncertainties. This can be explained by  
221 two things: first, it is possible that zones that are only partially filled by water repellent  
222 could not be detected visually. The boundary between the treated and untreated  
223 zone is probably more gradual than what is observed on the photographs. Secondly,  
224 it is likely that water will not be able to enter the porous network partially or totally  
225 treated with a water repellent, despite the vacuum imposed in the desiccator. The  
226 saturation time imposed during 24 hours was not sufficient to obtain a complete  
227 saturation of the treated layer.

228 Although the treated layers have a hydrophobic behavior, the problem encountered  
229 in the determination of the water porosity can also be related to the reduction of the  
230 pores connectivity. Water repellent cover partially or totally the pore surfaces. This  
231 behavior occurs when the size of polymerized water repellent molecule is lower than

232 the pores diameter. The siloxane molecular structure is close to polymerized  
233 molecule. We can assume that the pores diameter ranging from 3 to 30 nm (the size  
234 of siloxane molecules) in the case of C15H1 and between 0.4 and 30 nm in the case  
235 of C15H2 are no longer accessible to water. This hypothesis is confirmed by MIP  
236 curves shown in Figure 4. For the pore size distribution range from 5 to 19 nm and 3  
237 to 19 nm respectively for the C15H1 and C15H2, the volume of mercury that has  
238 penetrated the sample is really smaller than in the case of the reference concrete.

239 *Figure 4: Pores size distribution of C15, C15H1 and C15H2 concretes*



240  
241 Finally, it seems that the treated layers can be only very partially water-saturated.  
242 However, as shown in the following section, the water-absorption is sufficient to  
243 ensure a percolation through the treated layer.

### 244 3.3 Capillary water-absorption

245 Figure 5 gives the time-evolution of the specimen mass during the absorption test.  
246 The non-treated specimen has a classic kinetic of capillary absorption [Ollivier et al.,  
247 2008], with a linear evolution of the absorbed water mass per unit volume in function  
248 of the square root of time until saturation. This law does not apply to the water  
249 repellent concretes, particularly during the first four hours of capillary absorption,  
250 where the amount of absorbed water is lower than the one observed for the

251 reference concrete. Capillary absorption curves of the treated concretes can be  
252 divided into three parts, as follows:

253 Phase I: when the treated concrete sample is placed on capillary absorption test,  
254 water does not immediately penetrate the porous network because the external  
255 surface is hydrophobic, as shown by the capillary contact angle test (Figure 6). In  
256 both cases, the initial contact angle is clearly greater than  $90^\circ$ , revealing a low  
257 wetting surface, with  $92^\circ$  and  $122^\circ$  respectively for the C15H1 and C15H2. However,  
258 on the surface of treated samples, the hydrophobic effect is temporary, since the  
259 contact angle is not constant with time: it decreases quickly. In the best case, it takes  
260 up to 45 minutes for a drop of water to completely penetrate the material. In fact, the  
261 water repellent does not prevent the water vapor diffusion [Johansson et al., 2009]  
262 [EN 1504, 2005]. Under a moisture gradient, the water molecules will be adsorbed on  
263 the internal surface of the concrete pores and on the water repellent alkyl groups.  
264 Over time, it creates a continuous water film, which gradually reduces the effect of  
265 the water repellent and consequently increases capillary absorption.

266 This phenomenon is observed in both cases and corresponds to the significant  
267 change in the slope of the absorption curves. This change indicates the time required  
268 for the continuous film to form and it is sufficient to create a percolation through the  
269 untreated material. For the C15H1 and C15H2, it occurs after 45 minutes and 4  
270 hours, respectively. This second water repellent H2 protects much longer than the  
271 H1, although these two products only protect very temporarily. This latest  
272 observation is very remarkable and highlights the limit of these two water repellents  
273 for the protection of concrete structures. In addition, the required amount of water to  
274 ensure a percolation is similar in both cases, i.e. about  $10 \text{ kg/m}^3$ . This means that the  
275 water fills about 1% of the overall porosity. It is unlikely that this amount of water will  
276 fill the entire the porous network of the treated layer.

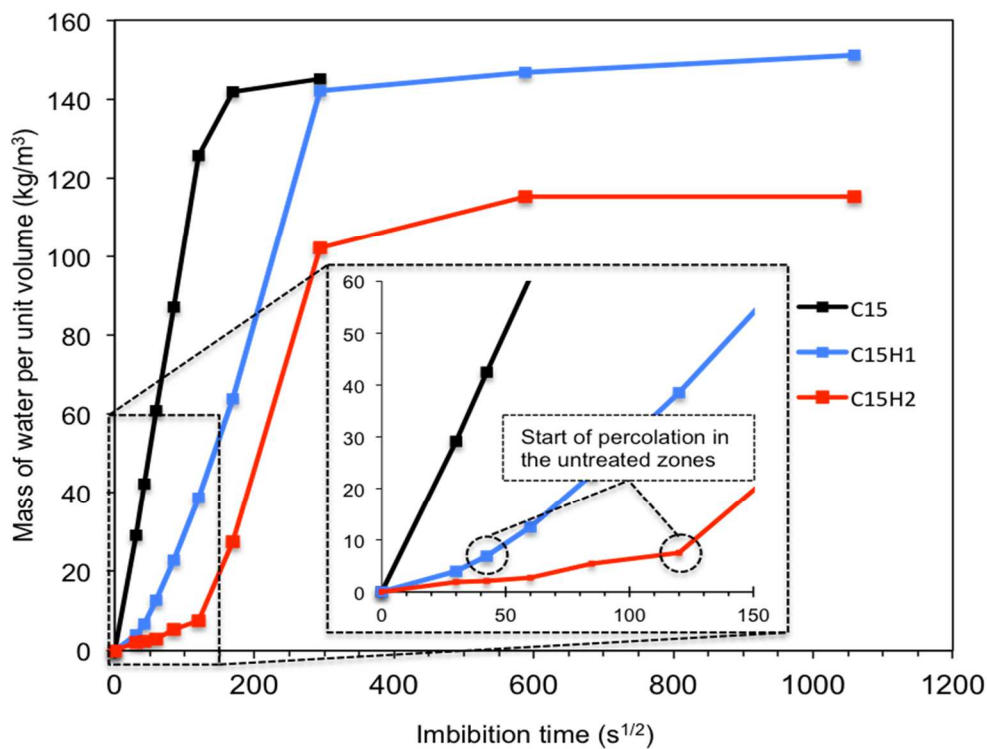
277 Phase II: The capillary absorption curves follow a conventional kinetics (similar to the  
278 reference concrete), indicating that water is in the untreated layer. However, the  
279 absorption kinetics are still lower. The repellent layer provides greater hydraulic  
280 resistivity thereby reducing the overall conductivity of the treated samples. This effect  
281 is greater when the depth of penetration increases (i.e. for C15H2).

282 Phase III: This phase corresponds to the moment when the water reaches the upper  
283 face of the sample. Unlike the C15, C15H1 and C15H2 need about respectively 24  
284 hours and 4 days to reach their maximum absorption. In the case of C15H1, the

285 amount of absorbed water is the same as the C15. The thin penetration depth of this  
286 water repellent is insufficient to observe a significant decrease of the total amount of  
287 water absorbed. However, we notice a significant decrease of water absorbed in the  
288 C15H2 sample.

289 Therefore, the water repellent increases the time required to reach the maximum  
290 absorption but not enough to protect over time the concrete structures against the  
291 aggressive agents. These results show that the effectiveness of water repellents  
292 depends mainly on the depth of penetration.

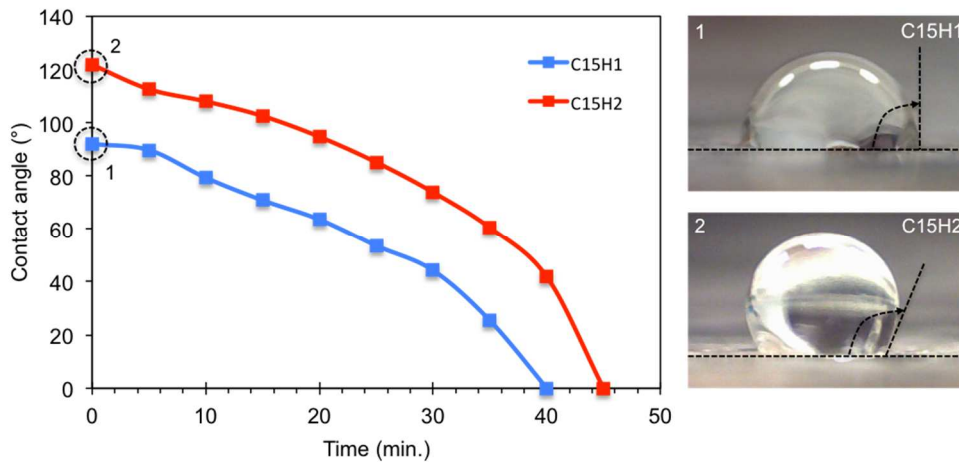
293 *Figure 5: Capillary absorption of C15, C15H1 and C15H2 concretes*



294

295

296 *Figure 6: Contact angle as a function of time and water repellents used (H1 and*  
297 *H2) on C15 concrete*



298

299 These results do not challenge the quality of the water repellents used, but rather  
300 their effectiveness to protect over time the concrete structures against the capillary  
301 absorption. In the literature, researchers focused their studies on concretes specially  
302 formulated for aggressive environments and have not highlighted this phenomenon.  
303 All are unanimous to say that these surface treatments have a real effect on the  
304 absorption and hence are effective to limit the transport of aggressive agents but  
305 none of them quantify the temporary effect of this maintenance system. For a  
306 predictive approach to sustainability maintenance by surface treatments, our results  
307 highlight the necessity to extend existing studies since it seems that this  
308 phenomenon observed on a low-quality concrete is also valid on all types of  
309 concrete.

## 310 4 Modeling of capillary absorption

311 In order to complete the experimental study, numerical simulations of capillary  
312 absorption using a pore network approach were carried out. This numerical approach  
313 aims at simulating the effects of the porous network connectivity reduction and the  
314 penetration depth on the capillary absorption.

### 315 4.1 Modeling principle

316 Pore network models were used successfully to study a wide range of multiphase  
317 flows and to predict effective properties like permeability [Amiri et al., 2005]. In this  
318 work, we use a dynamic pore network model derived from generic “ball-and-stick”  
319 models [Blunt et al., 1992], [Leventis et al., 2000], [Valavanides, 2001], [Gielen, 2007]

320 within which pore bodies and throats are represented by spheres and straight  
321 cylinders with circular cross-sections, respectively. These models only allow “piston  
322 type” motion, in which the invading wetting fluid advances in a connected front that  
323 occupies the bulk of the pore space. A detailed description of the model is available  
324 in [Lux & Anguy, 2012].

325 We consider 3D networks made of pores arranged on a regular cubic lattice and  
326 connected by throats. In this kind of networks, the coordination number (i.e. the  
327 number of throats connected to each pore) is 6.

## 328 4.2 Construction of pore networks

329 The pore size distribution for the reference network, which represents the untreated  
330 sample, is partially based on the MIP results. The objective here is not to create a  
331 realistic pore network, which is a quite difficult task (see for instance [Tsakiroglou,  
332 2000]), but to create a network with a correct range of pore sizes. We use two  
333 Gaussian distributions noted G1 and G2 in order to generate two distinct populations  
334 of pores. Table 3 summarizes the properties of the chosen distributions and their  
335 respective probability, as well as the prescribed minimum and maximum radii. The  
336 radius  $R_{ij}$  of a throat connecting two pores  $i$  and  $j$  of radii  $R_i$  and  $R_j$  respectively, is  
337 uniformly distributed between  $\min(R_i, R_j)$  and  $\min(R_i, R_j)/2$ . Figure 7a and 7b show the  
338 pore and throat radius distributions measured on a realization of a pore network  
339 made of  $10 \times 25 \times 10$  pores along  $x$ ,  $y$  and  $z$ -axes, respectively.

340 *Table 3: Pore size distributions for the reference network*

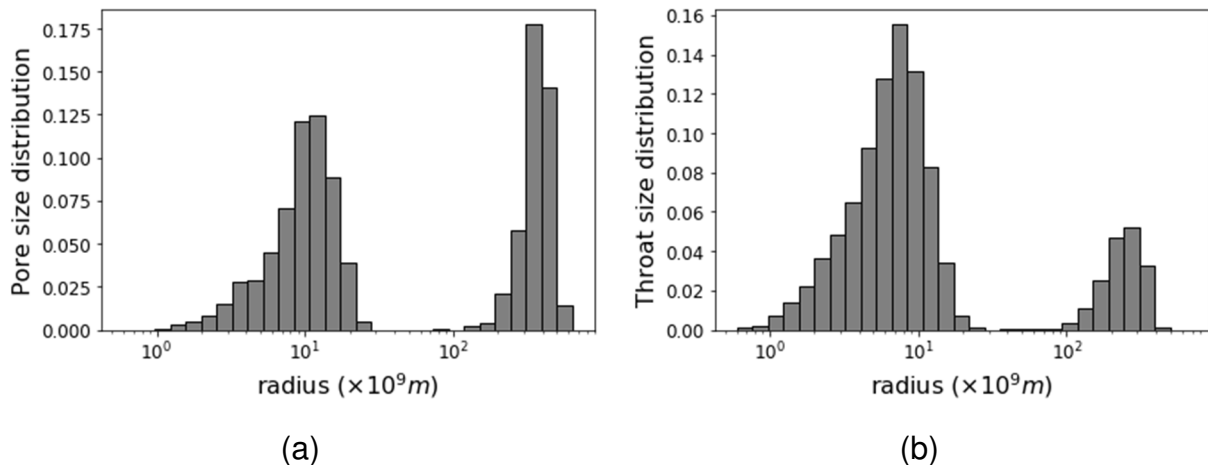
	Average radius (nm)	Standard deviation (nm)	Probability	Minimum radius	Maximum radius
G1	400	100	40%	1	1000
G2	10	5	60%	1	100

341

342



343 *Figure 7: Pore radius distribution (a) and throat radius distribution (b)*



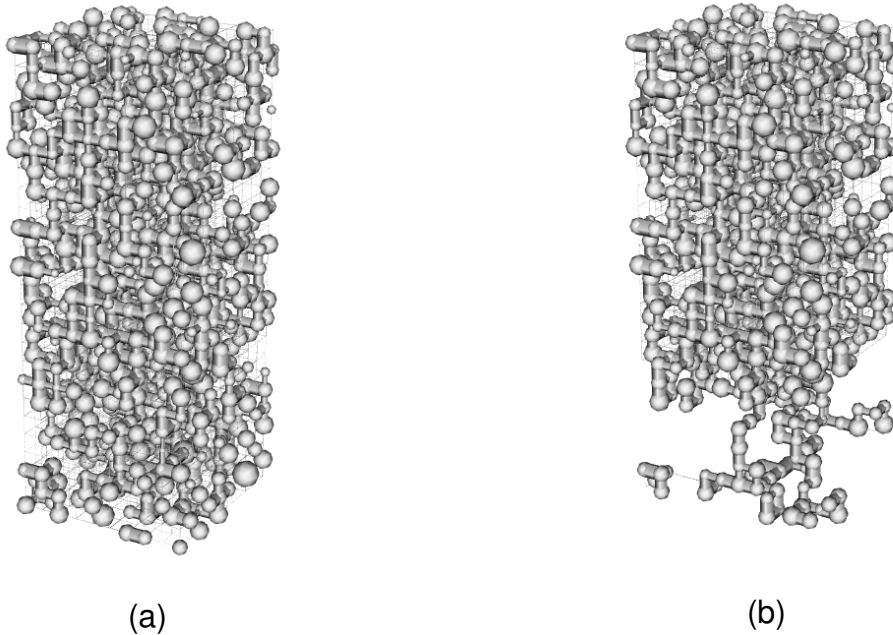
344 As shown in the previous section, the porosity of the concrete sample is reduced in  
345 the layer where the water repellent penetrates. The MIP curves show that the  
346 proportion of small pores is reduced in the treated samples. As said previously, it is  
347 likely that the smallest pores are entirely filled by the water repellent, what reduces  
348 the connectivity of the pore network and hence the porosity. If the water repellent  
349 enters other pores, there is no evidence that it modifies notably their radius.

350 In this work, we consider that water repellent enters preferentially into the smallest  
351 pores and fills them entirely. We use a simple invasion percolation algorithm is used  
352 in order to simulate the penetration of the water repellent into the network and the  
353 subsequent reduction of the porosity (Ferrer et al., 2003). This algorithm works as  
354 follows: the smallest pore located at the bottom surface is first marked as filled. Then,  
355 at each iteration, the algorithm looks at all neighbors of the currently filled pores and  
356 immediately fills the smallest of all the neighbors. As filled pores are non accessible  
357 to water, they are therefore deleted from the network. The algorithm stops when the  
358 porosity of the layer is lower or equal to the porosity objective, which is arbitrarily set  
359 to 1/3 of the initial network porosity. Note that connectivity checks are performed at  
360 each iteration to ensure that the deletion (i.e. filling) of an element does not lead to  
361 the creation of two disconnected networks. Thus, all the empty pores remain  
362 connected to the whole network and to the inlet (i.e. there is always at least one path  
363 that connects two pores in the network). The porosity objective in the layer being very  
364 small (around 5%), this constraint is necessary to avoid the disconnection of all the  
365 remaining pores from the inlet.

366

367 Figure 8 shows a realization of a network made of a  $10 \times 25 \times 10$  pores and the  
368 results of our algorithm for a layer height of 30% of the total network height. Note that  
369 the connectivity in the layer partially filled by the water repellent is drastically  
370 reduced.

371 *Figure 8: A realization of a  $10 \times 25 \times 10$  pore network before (a) and after (b)*  
372 *removing small pores in a layer of thickness equal to 30% of the total height of*  
373 *the network.*



#### 374 4.3 Simulations of water capillary absorption

375 Simulations of free imbibition are carried out on several realizations of network of  
376 size  $8.9 \times 22 \times 8.9 \mu\text{m}^3$  made of  $10 \times 25 \times 10$  pores. In order to study the influence of  
377 the layer thickness on the imbibition kinetics, the base network is modified using the  
378 aforementioned procedure to generate layers of thickness equal to 5%, 10%, 20%  
379 and 30% of the total height of the base network. Porosity is fixed to 15% in the base  
380 network and is reduced to approximately 5% in the layer where the water repellent  
381 penetrates.

382 Water invades the network from the bottom ( $y=0$ ), and air can escape from the  
383 opposed face (top). The other sides are impermeable to water and air. Initially, all  
384 pores are filled with air, except for the pores in contact with the water reservoir, which  
385 are half filled. The water pressure at the inlet is constant and fixed to a value close to  
386 the atmospheric pressure (100kPa) like in previous experiments, and the same  
387 applies for the air pressure at the outlet. Simulation ends when all air is trapped.

388 Figure 9 shows different stages of the imbibition in a realization of a pore network  
389 with a treated layer thickness equal to 20% of the sample height. Figure 10 shows  
390 the evolution of the water saturation for each network versus the square root of time.  
391 Note that the water saturation stabilizes only after a very short time. This is due to the  
392 small dimensions of the studied network. What is important here is the relative  
393 difference between all numerical experiments.

394 Although air trapping is more important in the numerical simulations than in the  
395 experimental results, the general behavior is very similar. In the modified part of the  
396 studied networks (treated layer), the imbibition kinetic is indeed far slower than for  
397 the reference network until the height of the water front exceeds the layer thickness.  
398 In a second part, the slope of the curves greatly increases and remains constant until  
399 the water front reaches the top of the network, which indicates that the imbibition  
400 follows a classical Washburn law. Note that the slopes of the first and second part  
401 are both smaller when the thickness of the treated layer increases.

402 The slow kinetic observed in the first part is the consequence of:

- 403 • The reduction of the macroscopic hydraulic conductivity in the layer, due to the  
404 lower porosity but also to the lower connectivity of the pore network.
- 405 • The reduction of the macroscopic capillary pressure, due to the fact that the  
406 layer contains far fewer small pores than in the reference network.

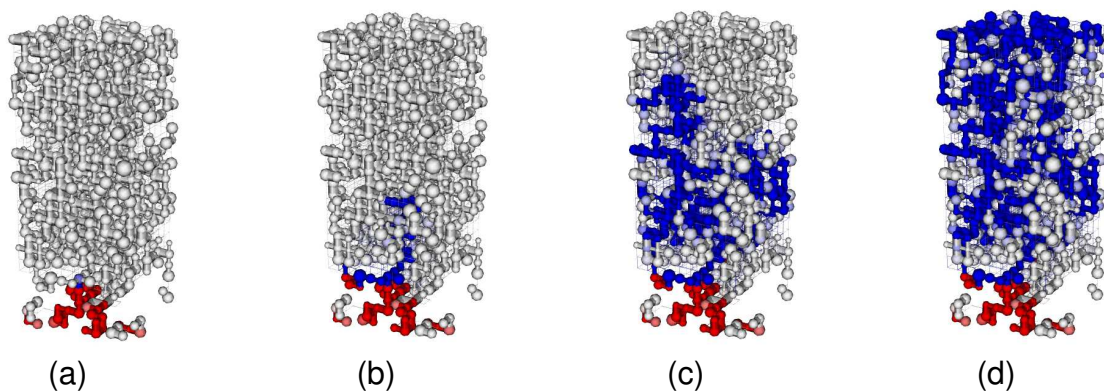
407 When the fluid enters the unmodified part of the network, i.e. the part where the  
408 water repellent has not penetrated, the capillary flow is only affected by the reduction  
409 of the hydraulic resistance in the layer, which explains that the imbibition kinetic  
410 becomes slower than in the reference network when the thickness of the hydrophobic  
411 layer increases. Note however that the flow pattern can be altered by the low  
412 connectivity in the layer. For example, Figure 8b shows a typical capillary fingering  
413 pattern, which partly explain the important trapping observed in the simulations.

414 Pore network simulations allow reproducing qualitatively the observed experimental  
415 behavior. It is a good indication that the observed kinetics may be partly explained by  
416 the filling of the smaller pores by the water repellent. However, one can notice that  
417 the experimental kinetics in the layer is slower than in simulations. This could be  
418 explained by other effects, which are not taken into account in the numerical  
419 simulations. In particular the contact angle is assumed to be zero and constant in  
420 simulations. Even if Figure 5 shows that the contact angle at the surface decreases  
421 quite quickly, we have no indication about the evolution of the wettability inside the

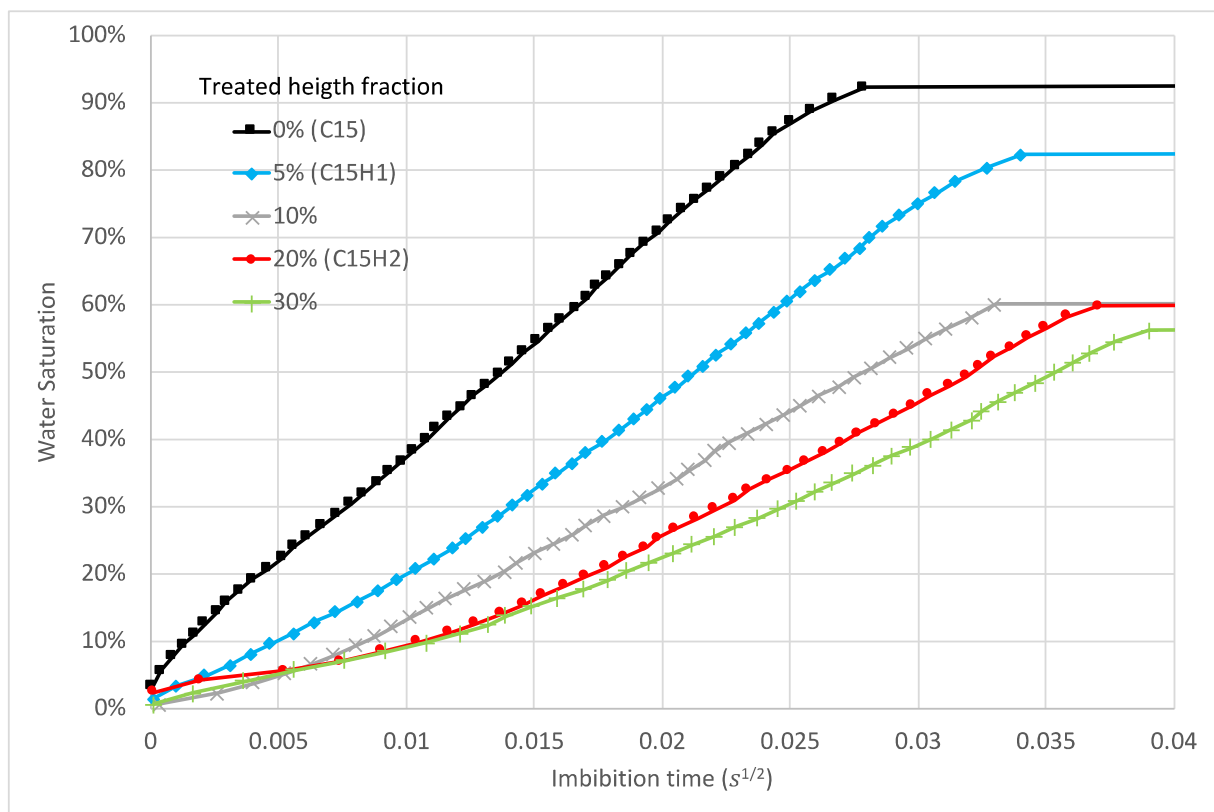
422 concrete sample. It is likely that the average contact angle is greater inside the  
423 treated layer than in the rest of the network, which decrease the capillary pressure  
424 inside the layer.

425 *Figure 9: Visualization of the pore network at different stages of the imbibition:*  
426 *(a) water begins to fill the unmodified part of the network, (b) final state in the*  
427 *modified layer, (c) percolation and (d) final state.*

428 *Empty pores are colored in white while filled pores are either colored in blue or*  
429 *in red. Red pores are located in the layer where the water repellent penetrates,*  
430 *while blue pores are located in the unmodified part of the network.*



431  
432 *Figure 10: Imbibition kinetics for different layer thicknesses expressed in*  
433 *percentage of the total height.*



434

## 435 5 Conclusion

436 In this paper, we have studied the effects of two water repellent agents on the water  
437 imbibition kinetics and on the microstructure of a relatively low performance concrete.  
438 Numerical simulations based on a pore network approach were also carried out to  
439 support our experimental findings. Based on our results, the following conclusions  
440 can be drawn:

- 441 • The water porosity of concrete samples is reduced in the treated layer by  
442 water repellent penetration. The internal face of concrete pores is coated with  
443 the hydrophobic water repellent, which fills primarily the smallest pores and  
444 reduces consequently the connectivity of porous network. This explains why it  
445 is difficult to access the global porosity of specimens treated with water  
446 repellent.
- 447 • The efficiency of the water repellents to reduce capillary absorption kinetics  
448 depends of their penetration depth.
- 449 • The repellent effect is quite limited in time. When water exceeds the limit of  
450 the treated layer, the absorption kinetics become quite similar to those of the  
451 non-treated concrete. The capillary absorption coefficient is however lower  
452 due to a lower hydraulic conductivity in the treated layer.
- 453 • Pore network simulations allow reproducing qualitatively the experimental  
454 behavior. This supports the fact that the observed kinetics may be partly  
455 explained by the filling of the smallest pores by the water repellent.

456 These results confirm the importance of an exhaustive preliminary study in view to  
457 protect a reinforced concrete structure in its environment. Particular attention must be  
458 paid to the perfectibility of water repellent against the water absorption kinetics in  
459 view to improve the efficiency and durability of these systems.

460

461 **6 Acknowledgements**

462 E. Conforto, research engineer (LaSIE UMR 7356 CNRS), is acknowledged for her  
463 support in the scanning microscopy investigations.

464

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