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Ph Turcry, K. Namoulniara, 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 https://hal.science/hal-02316861

Submitted on 20 Jul2022

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

9 Indicators of durability are nowadays key-parameters in the design of reinforced concrete structures. One way to guarantee durability is usually to design concrete 10 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.

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.

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

72 In order to answer this question, the long term efficiency of two standard water repellent agents were investigated in the present study. An experimental campaign 73 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.

82 2 Materials and experimental procedures

83 2.1 Water repellents

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

87 Silanes are a family of monomers molecules derived from different alkyl groups linked to each other by a silicone molecule (Figure 1). The waterproofing properties 88 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]

 $\begin{array}{cccc} R & & & & & \\ I & & & & \\ OR' & Si & OR' & & \\ & & & \\ & & & \\ & & & \\ OR' & & & \\ & & & \\ OR' & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & &$

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^2 (i.e. at 150 $g/m^2/coat$). To ensure a complete polymerization, the treated 106 specimens were conserved 14 days in room conditions before furthers 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)

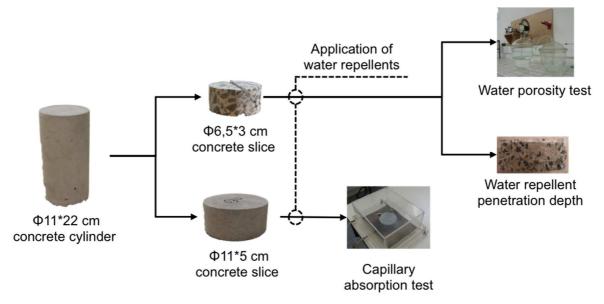
Constituents	Mass (kg)	
Portland limestone cement	275	
Water	222	
W/C	0.8	
Fine aggregates 0/4	729	
Coarse aggregates 6/10	1085	

117

118 Concrete cylinders (Φ 11x22 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±5% RH and 20°C during 7 days. This conservation was required to have 126 sufficiently dry surfaces before the application n of water repellent.

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

133 Figure 2: Summary diagram of the experimental procedure



134

135 2.3 Experimental procedures

To measure the penetration depths of the water repellents, the 30 mm thick slices were split into two parts then split areas were sprayed with water, according to the European standard [EN 1504, 2005]. The penetration depths were measured with a ruler and correspond to the thickness remained dry due to the hydrophobic effect of 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 form 145 three results for each study case.

Mercury intrusion porosimetry (MIP) was carried out with the Micrometrics Autopore III 9420 porosimeter, according to a procedure recommended by the AFPC-AFREM [Arliguie et al., 2008]. The test was performed on 15 mm side cubes sawn from the 30 mm thick slices. In the case of treated slices, these cubic samples contained the treated zone (determined previously with the penetration depth). Before mercury 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 until weight stabilization. They were cooled and then put in contact with water (Figure2). Specimens were regularly weighted during the test.

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

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

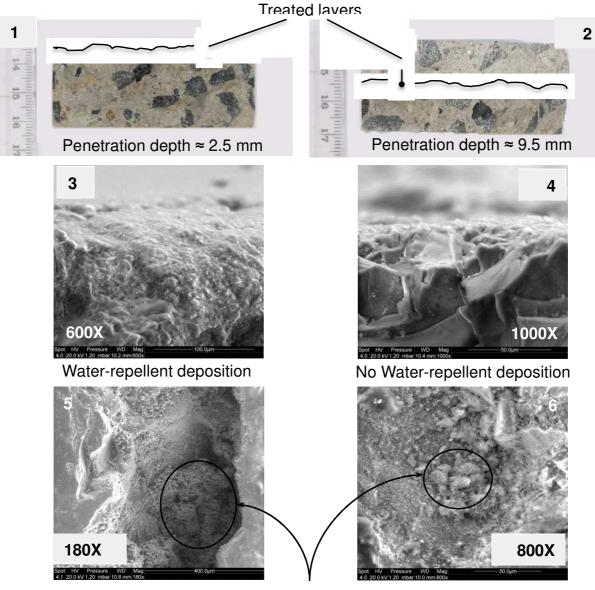
172 The absorption of a water repellent depends, on the one hand, on the chemical 173 nature (type of cement, nature of aggregates, temperature, pH), the physical 174 properties (i.e. porosity) and the water saturation degree of the concrete substrate, 175 and, on the other hand, on the application, 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.

The water repellent H1 is a siloxane solution in solvant phase. The siloxane molecule is itself a silane molecule partially hydrolyzed. When siloxane contacts the interstitial solution, a residual hydrolysis takes place very quickly causing the formation of polysiloxanes. These polymers create a hydrophobic barrier that reduces and even cancels the additional absorption of the product, which explains the lower penetration depth of H1. This assumption seems to be confirmed by SEM analyses. A thin film 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 the188 sample treated by H2 (image 4, Figure 3).

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

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

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



Agglomerated particles of water-repellent

3.2 Water porosities

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

Table 2: Measured penetration depths of water-repellent and water porosities of
 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	

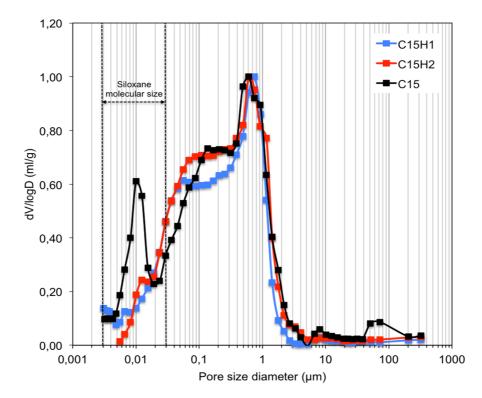
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The reference C15 concrete has the highest water porosity with 14,9%. As planned, with this high value, this concrete can be classified under the low durability category structure materials [AFGC, 2004]. The lowest porosities were determined on C15H1 and C15H2 concretes with 13,2% and 8,1%, respectively. Note that porosities of the treated specimens are inversely proportional to the penetration depth of water 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.

Although the treated layers have a hydrophobic behavior, the problem encountered in the determination of the water porosity can also be related to the reduction of the pores connectivity. Water repellent cover partially or totally the pore surfaces. This behavior occurs when the size of polymerized water repellent molecule is lower than the pores diameter. The siloxane molecular structure is close to polymerized molecule. We can assume that the pores diameter ranging from 3 to 30 nm (the size of siloxane molecules) in the case of C15H1 and between 0.4 and 30 nm in the case of C15H2 are no longer accessible to water. This hypothesis is confirmed by MIP curves shown in Figure 4. For the pore size distribution range from 5 to 19 nm and 3 to 19 nm respectively for the C15H1 and C15H2, the volume of mercury that has 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

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

244 3.3 Capillary water-absorption

Figure 5 gives the time-evolution of the specimen mass during the absorption test. The non-treated specimen has a classic kinetic of capillary absorption [Ollivier et al., 2008], with a linear evolution of the absorbed water mass per unit volume in function of the square root of time until saturation. This law does not apply to the water repellent concretes, particularly during the first four hours of capillary absorption, where the amount of absorbed water is lower than the one observed for the reference concrete. Capillary absorption curves of the treated concretes can bedivided 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°, revealing a low 257 wetting surface, with 92° and 122° 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 protects 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 kg/m³. 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.
- Phase II: The capillary absorption curves follow a conventional kinetics (similar to the reference concrete), indicating that water is in the untreated layer. However, the absorption kinetics are still lower. The repellent layer provides greater hydraulic resistivity thereby reducing the overall conductivity of the treated samples. This effect is greater when the depth of penetration increases (i.e. for C15H2).
- Phase III: This phase corresponds to the moment when the water reaches the upper face of the sample. Unlike the C15, C15H1 and C15H2 need about respectively 24 hours and 4 days to reach their maximum absorption. In the case of C15H1, the

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

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

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

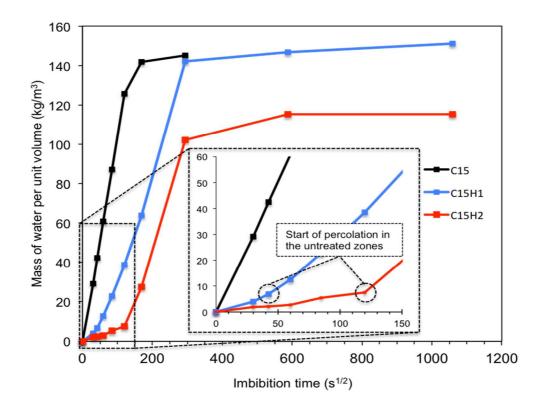
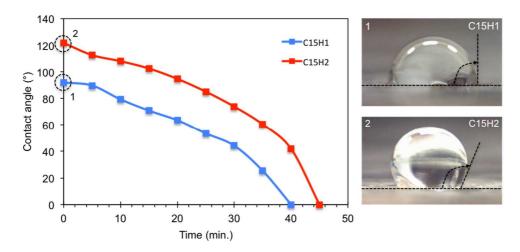


Figure 6: Contact angle as a function of time and water repellents used (H1 andH2) on C15 concrete



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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

Pore network models were used successfully to study a wide range of multiphase flows and to predict effective properties like permeability [Amiri et al., 2005]. In this work, we use a dynamic pore network model derived from generic "ball-and-stick" models [Blunt et al., 1992], [Leventis et al., 2000], [Valavanides, 2001], [Gielen, 2007] within which pore bodies and throats are represented by spheres and straight cylinders with circular cross-sections, respectively. These models only allow "piston type" motion, in which the invading wetting fluid advances in a connected front that occupies the bulk of the pore space. A detailed description of the model is available in [Lux & Anguy, 2012].

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

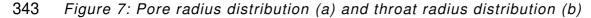
328 4.2 Construction of pore networks

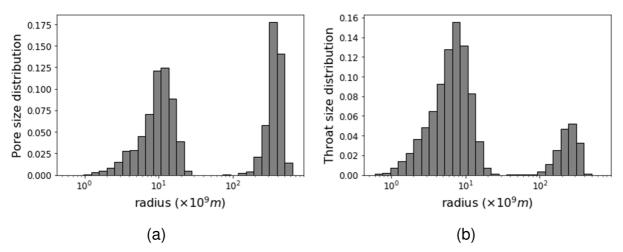
329 The pore size distribution for the reference network, which represents the untreated 330 sample, is partially based on the MIP results. The objective here is not to create a realistic pore network, which is a quite difficult task (see for instance [Tsakiroglou, 331 332 2000]), but to create a network 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_{ii} of a throat connecting two pores i and j of radii R_i and R_i respectively, is 337 uniformly distributed between min(R_i , R_i) and min(R_i , R_i)/2. Figure 7a and 7b show the 338 pore and throat radius distributions measured on a realization of a pore network 339 made of 10x25x10 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

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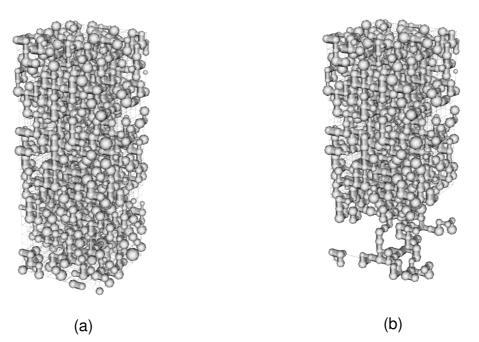


As shown in the previous section, the porosity of the concrete sample is reduced in the layer where the water repellent penetrates. The MIP curves show that the proportion of small pores is reduced in the treated samples. As said previously, it is likely that the smallest pores are entirely filled by the water repellent, what reduces the connectivity of the pore network and hence the porosity. If the water repellent 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 (Ferer 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.

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

Figure 8: A realization of a 10 x 25 x 10 pore network before (a) and after (b)
removing small pores in a layer of thickness equal to 30% of the total height of
the network.



4.3 Simulations of water capillary absorption

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

Water invades the network from the bottom (y=0), and air can escape from the opposed face (top). The other sides are impermeable to water and air. Initially, all pores are filled with air, except for the pores in contact with the water reservoir, which are half filled. The water pressure at the inlet is constant and fixed to a value close to the atmospheric pressure (100kPa) like in previous experiments, and the same applies for the air pressure at the outlet. Simulation ends when all air is trapped. Figure 9 shows different stages of the imbibition in a realization of a pore network with a treated layer thickness equal to 20% of the sample height. Figure 10 shows the evolution of the water saturation for each network versus the square root of time. Note that the water saturation stabilizes only after a very short time. This is due to the small dimensions of the studied network. What is important here is the relative difference between all numerical experiments.

394 Although air trapping is more important in the numerical simulations than in the experimental results, the general behavior is very similar. In the modified part of the 395 396 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.

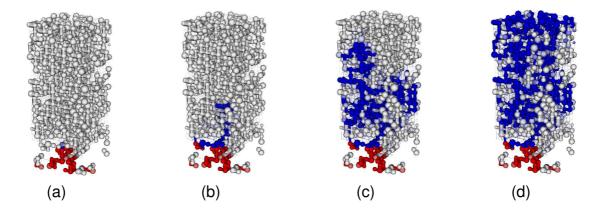
The reduction of the macroscopic capillary pressure, due to the fact that the
layer contains far fewer small pores than in the reference network.

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

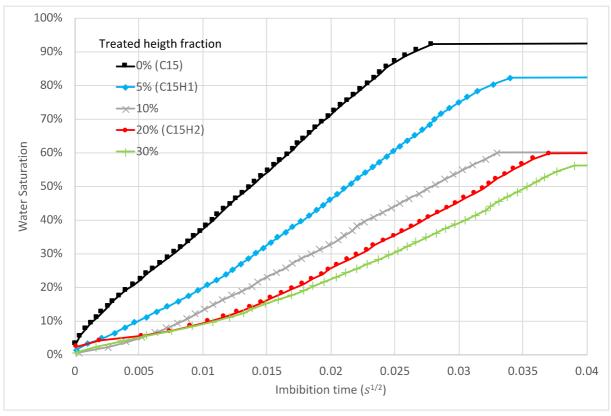
Figure 9: Visualization of the pore network at different stages of the imbibition:
(a) water begins to fill the unmodified part of the network, (b) final state in the
modified layer, (c) percolation and (d) final state.

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.



435 5 Conclusion

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

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

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

461 6 Acknowledgements

462 E. Conforto, research engineer (LaSIE UMR 7356 CNRS), is acknowledged for her463 support in the scanning microscopy investigations.

465 7 References

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