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## Capillary imbibition depth in particle-bed 3D printing – Physical frame and one-dimensional experiments

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1           **Capillary imbibition depth in particle-bed 3D printing –**  
2           **physical frame and one-dimensional experiments**

3  
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8  
9  
10   **Abstract**

11   This paper deals with the control of the net geometry of a printed object in the case  
12   of powder-bed or particle bed binding technologies. We first measure and compare  
13   water penetration in one-dimensional experiments for various powder-beds. Our  
14   results, despite the simplicity of the experimental set-up, show a feature that has not  
15   been reported in literature so far, namely the fact that water penetration depth is not  
16   finite but is fully uncontrolled on longer time scales. We discuss the physical origin of  
17   this feature and the reasons why it is hidden by other aspects in most papers or  
18   applications. We finally show that water penetration depth can be controlled by a  
19   dispersed organic water thickener. Our results suggest the formation of a non-  
20   Newtonian fluid between the binder grains, which allows, in turn, for the control of  
21   the naturally uncontrolled capillary-driven water penetration in the powder-bed.

22

23 **Keywords:** Powder-bed; 3D Printing; Penetration; Cement; Plaster; Thickeners

24

## 25 **1. Introduction**

26 Digital fabrication with concrete emerged at the end of the 20<sup>th</sup> century [1,2]  
27 and has since received widespread attention [3–9]. This technology integrates  
28 computer-aided design with automated production processes in the production of  
29 construction objects [3]. Additive Manufacturing (AM) is a class of Digital fabrication  
30 that consists in manufacturing layer-by-layer cement-based materials [5,6]. Various  
31 AM techniques exist as classified in [10], including particle-bed binding, material  
32 extrusion, and material jetting. Particle-bed binding adopts selective powder  
33 activation by liquid jetting to bind the particle bed layer-by-layer [6,11–16]. After  
34 printing, the unreacted particles [6] are removed to retrieve the printed object. This  
35 technology allows for the processing of real three dimensional complex shapes with  
36 a high resolution of the order of the constitutive powder size.

37 From a material point of view, two particle-bed binding technologies are  
38 currently developed. The first solution (sand-bed 3D printing) uses an inert sand  
39 particles bed and a liquid binder made of cement or plaster and water [11]. The  
40 second solution (powder-bed 3D printing) consists in spraying a solvent (water) on a  
41 reactive powder made of a binder (cement, plaster) and potentially a sand [17,18].

42 Dimensional accuracy is, similarly to other digital processing technologies, one  
43 of the main concerns of powder bed 3D printing techniques. While the printing  
44 accuracy is influenced by the size of the particles, it is mainly driven by the behavior  
45 (at contact and during penetration) of the droplets of water deposited or projected  
46 at the surface of the reactive binder. Besides, the process may also be kept under  
47 control by the competition of the imbibition and the setting kinetics.

48 In the current work, we study the penetration of water in various powder-beds.  
49 In pure cement powder-bed and pure plaster powder-bed, we show that capillary-  
50 driven water penetration is fully uncontrolled and is therefore not expected to be  
51 directly compatible with industrial 3D printing applications. Our results suggest that

52 the use of water thickeners dispersed in a given powder-bed for a given water  
53 droplet allows for the control of the naturally uncontrolled capillary-driven liquid  
54 water penetration through the progressive formation of a non-Newtonian fluid  
55 between the powder grains.

56

## 57 **2. Background and research significance**

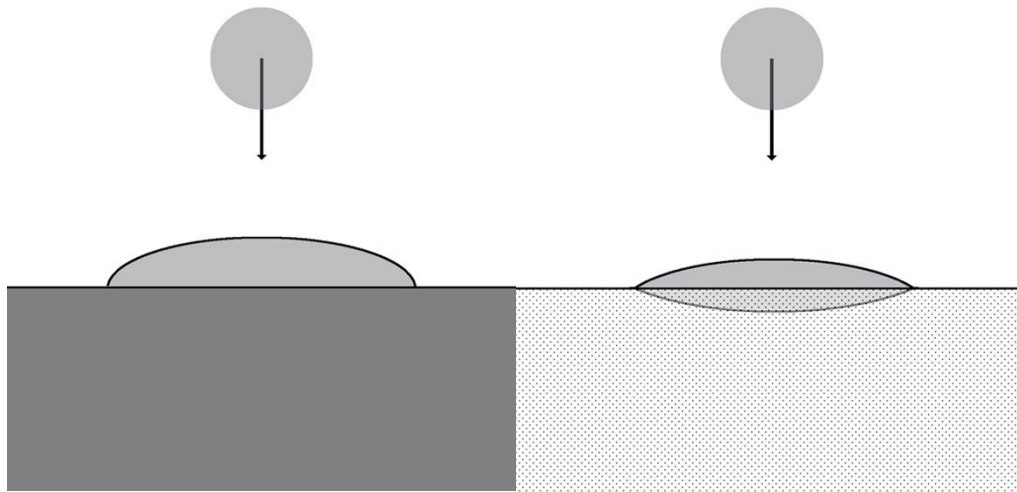
58 When a water droplet of diameter  $d$ , volumic mass  $\rho$  and surface tension  $\gamma$  hits  
59 a solid non-permeable surface, the droplet either splashes or coats the surface. In  
60 very rare and specific conditions, it might bounce off [19]. Typical water spraying  
61 systems result in droplet velocities  $V$  of the order of 1 m/s. If the droplet kinetic  
62 energy density, of order  $\rho V^2$ , is much higher than capillary pressure of order  $\gamma/d$ , the  
63 droplet splashes when hitting the surface. For typical values of surface tension  
64 around  $\gamma \approx 0.05$  Pa.m, this is expected to only happen for sprayed droplets larger  
65 than 1 mm. As a consequence, most spraying devices in powder bed printing will  
66 deliver droplets that do coat the surface and do not splash. Obviously, devices  
67 delivering a low velocity constant stream (or jet) of liquid (*i.e.* not spraying) will also  
68 coat the surface as long as the local liquid pressure does not reach the cohesion limit  
69 of the powder bed.

70 The surface of the powder bed is however permeable and the coating process is  
71 driven therefore by the competition between the droplet (or liquid stream) viscous  
72 spreading as usually described by Tanner's law [20] and capillary imbibition (see Fig.  
73 1).

74 The two features in Fig. 1 despite their major influence on the geometric  
75 accuracy of the printing process have not been studied in details in the case of  
76 cement or plaster powder beds, where both spreading/coating and imbibition on  
77 medium to long time scales are expected to potentially compete with hydration and  
78 vary with the physical properties of the particles bed.

79 We choose here to decorrelate the two above features for the sake of simplicity  
80 and choose to focus this study on capillary imbibition only using the simple one-

81 dimensional experiments described in the next section.



82

83 **Fig. 1.** Coating of a surface by a non-splashing liquid droplet. (Left) non permeable  
84 surface – coating only (right) permeable surface – coating and imbibition occur  
85 simultaneously.

86

87 From a practical point of view, for a robust and repeatable geometry control of  
88 powder bed binding techniques, the liquid projected or deposited on the surface of  
89 the powder bed is expected (and assumed) to diffuse inside the powder over a well-  
90 controlled length [6,11,17,21]. In literature, process parameters such as droplet mass,  
91 pressure, particle layer thickness, particle composition and packing properties  
92 [6,18,22,23] were all reported to play an essential role in geometry control.

93 From a theoretical point of view, the liquid penetration length is driven by the  
94 capillary diffusion of a Newtonian liquid in a porous particle bed. Within this frame,  
95 the liquid is expected to be free to diffuse in the dry powder under the effect of  
96 capillary suction [6,11,24]. Most powder beds contain powders with binder particles  
97 around 10 micrometers. As a consequence, the typical powder bed pore size  $r$  is  
98 expected to be of the order of the size of the constitutive particles, namely around  
99 10 micrometers. This suggests that the capillary suction is around  $\gamma/d$ , namely  
100 around  $10^4$  Pa. This pressure is far higher than any gravity induced stress at the level  
101 of one powder layer. With hydrostatic pressure  $\rho gH$  around  $10^2$  Pa for centimetric  
102 layers, hydrostatic pressure influence on short time scales imbibition can therefore

103 be neglected.

104 Please note that, within the present study, any external pressure applied to the  
105 liquid, such as the one induced by applying a liquid jet, will be neglected. This  
106 assumption holds true as long as the liquid external pressure stays lower than  
107 capillary suction, namely  $10^4$  Pa.

108

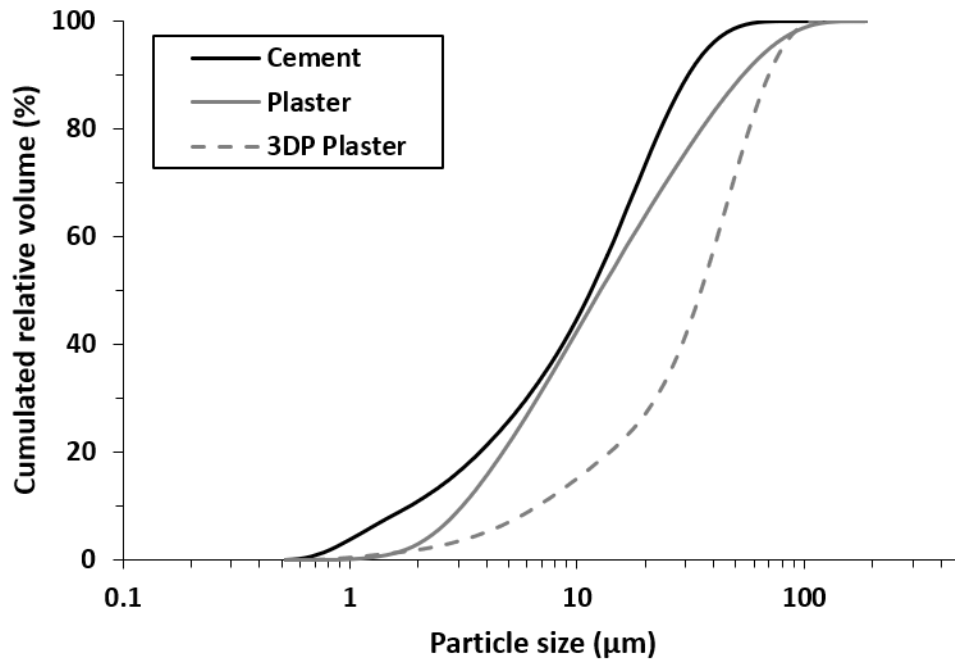
## 109 **2. Materials and methods**

### 110 **2.1. Powder characterization**

111 Three powders are used in this study: a CEM I Cement (Lagerdorf, Lafarge) with  
112 a density of  $3150 \text{ kg/m}^3$ ; a plaster (Molda 3 Normal, Formula Saint-Gobain) with a  
113 density of  $2630 \text{ kg/m}^3$ ; and a 3D printing plaster powder (3DP Plaster) obtained from  
114 a printer manufacturer (PXL Core, Z-Corp) with a density of  $2530 \text{ kg/m}^3$ . The main  
115 components of the 3D printing plaster powder are calcium sulfate hemihydrate (80%-  
116 90% by weight), vinyl polymer and carbohydrate [25]. The particle size distribution of  
117 each powder was measured with a laser particle size analyzer (Malvern Mastersizer S)  
118 after dispersion in isopropanol (see **Fig. 2**Erreur ! Source du renvoi introuvable.). The  
119 median particle sizes of the cement powder, the plaster powder and the 3DP Plaster  
120 powder are around  $11.5 \mu\text{m}$ ,  $12.5 \mu\text{m}$  and  $35 \mu\text{m}$ , respectively.

121 A hydroxy ethoxy methoxy cellulose (HEMC) was used as a water thickener in  
122 the cement powder bed system. The HEMC is used in powder form. The constitutive  
123 macro-molecules have a molar mass of  $370,000 \text{ g/mol}$  and a density of  $1200 \text{ kg/m}^3$ .  
124 The radius of HEMC in dilute regime was measured to be around  $39 \text{ nm}$  using  
125 Dynamic Light Scattering [26]. The polymer overlapping concentration  $c^*$  of HEMC is  
126 around 0.3%. More details about this polymer can be found in a previous work  
127 where this polymer is noted as HEMC A [26]. The mass ratio of HEMC to cement  
128 ranges from 0% to 8%. For the preparation of the powder-bed containing both  
129 cement powder and HEMC, dry cement powder and the HEMC powder were mixed  
130 for 30 minutes in a planetary mixer to achieve homogeneity.

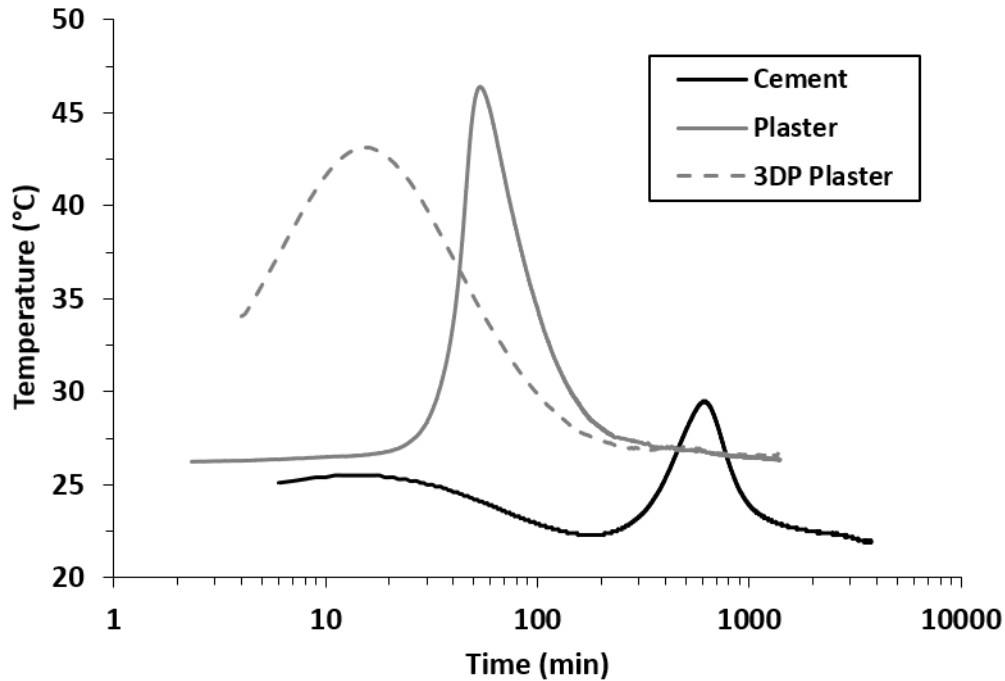
131



132  
 133 **Fig. 2.** Cumulative particle size distribution of the cement powder and the plaster  
 134 powder used in this study.

135  
 136 The packing fraction of the powder-beds (*i.e.*, the volume of solid by unit of  
 137 total volume) was assessed by measuring the mass of powder in a reference  
 138 container. The measured packing fractions of cement (with or without HEMC), plaster,  
 139 and 3DP plaster powders were all  $40 \pm 2\%$ . Packing density was checked before each  
 140 experiment after preparation of the powder bed.

141 In order to assess the potential water consumption induced by ongoing  
 142 chemical reactions, a thermocouple was embedded in sealed plastic containers (5.2  
 143 cm in diameter and 7.0 cm in height). The containers were filled with fresh cement  
 144 paste (water-to-powder mass ratio  $w/p = 0.4$ ), plaster paste ( $w/p = 0.6$ ) and 3D  
 145 printing plaster paste ( $w/p = 0.6$ ). A distinct temperature increase, which denotes the  
 146 onset of the acceleration period [27], was recorded after 2 min, 20 min and 200 min  
 147 for 3D printing plaster paste, plaster paste, and cement paste, respectively. A peak in  
 148 temperature was then measured at 15 min, 60 min, and 600 min for 3D printing  
 149 plaster paste, plaster paste, and cement paste, respectively (see **Fig. 3**).



151

152 **Fig. 3.** Temperature variation during hydration as a function of time for the three  
 153 binders studied here.

154

## 155 2.2. Liquid characterization

156 In order to assess the viscosity of the interstitial solution formed upon  
 157 penetration into the cement powder mixed with HEMC, solutions with different  
 158 HEMC dosages were independently prepared. HEMC dry powders were slowly added  
 159 to a beaker containing deionized water. A magnetic stirrer was used to disperse the  
 160 solution for 24 h. A C-VOR Bohlin stress-controlled rheometer with serrated parallel  
 161 plates (diameter = 40 mm, gap = 0.5 mm) was then used to assess the rheological  
 162 properties of the solutions. An increasing shear rate ramp from  $0.01 \text{ s}^{-1}$  to  $100 \text{ s}^{-1}$  was  
 163 applied for 1000 s (with a logarithmic distribution of shear rates) followed by a  
 164 decreasing shear rate ramp for 1000 s. Only the decreasing ramps are analyzed in the  
 165 following.

166 Typical rheological measurements of these solutions are plotted in **Fig. 4 (a)**. For  
 167 solutions with HEMC concentration lower than 2%, a Newtonian behavior was  
 168 systematically measured. We noted that the solution behavior gradually switches to  
 169 a shear-thinning behavior at high shear rates as the HEMC concentration becomes

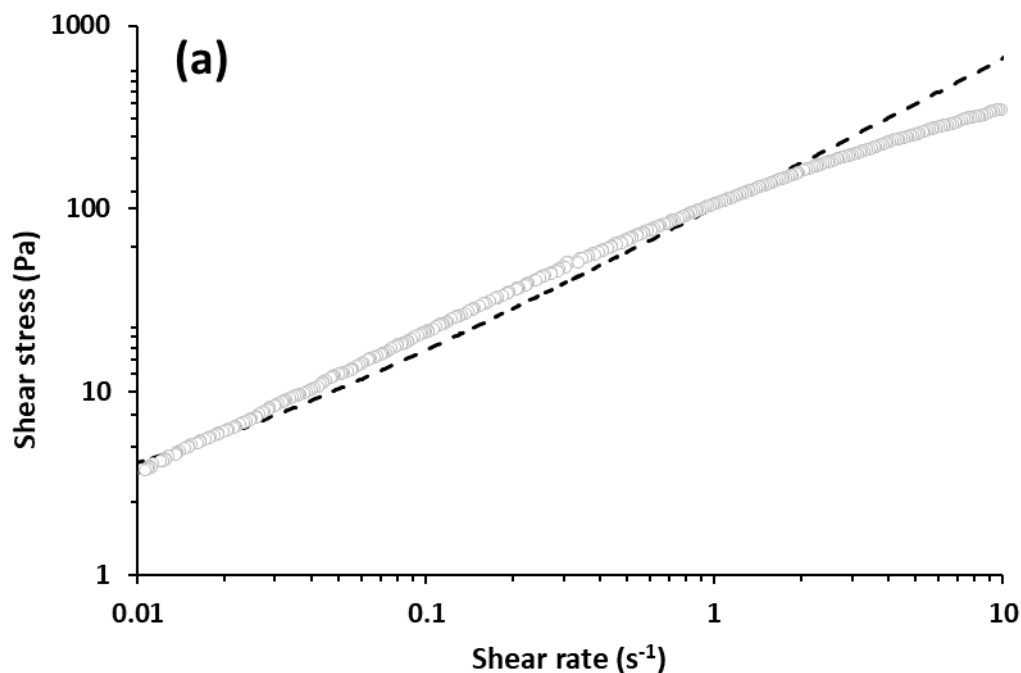


170 higher than the overlapping concentration  $c^*$  given above. For solutions with HEMC  
171 concentrations higher than 4%, a yield stress fluid behavior was measured. It finds its  
172 origin in the formation of an entangled polymer network above a second critical  
173 concentration noted  $c^{**}$  [28,29]. The yield stress of these HEMC solutions is  
174 extrapolated from a Herschel–Bulkley model fitting at low shear rates (see **Fig. 4 (a)**).

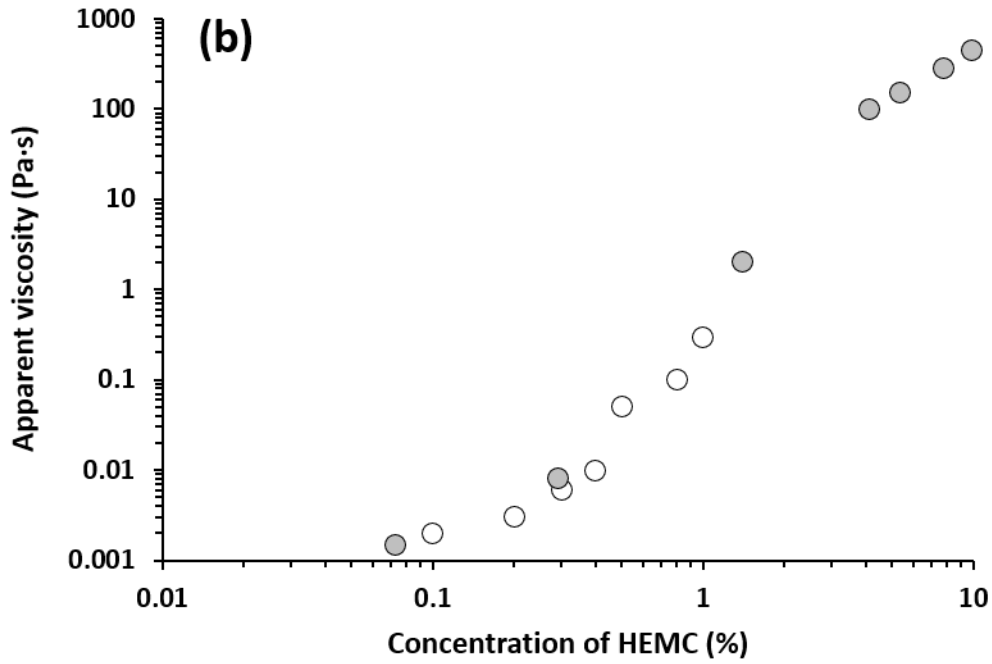
175 The apparent viscosity of the solutions (*i.e.*, the ratio between the shear stress  
176 and the shear rate) is plotted at a shear rate of  $1 \text{ s}^{-1}$  in **Fig. 4 (b)**. The viscosity  
177 increases sharply from  $1 \text{ mPa}\cdot\text{s}$  to several thousands of  $\text{Pa}\cdot\text{s}$  as the HEMC  
178 concentration increases from 0% to 10% (see **Fig. 4 (b)**).

179 We then plot in **Fig. 4 (c)** the yield stress as a function of HEMC concentration.  
180 In the range of dosages studied in this work, the yield stress of the solutions  
181 increases gradually up to 30 Pa.

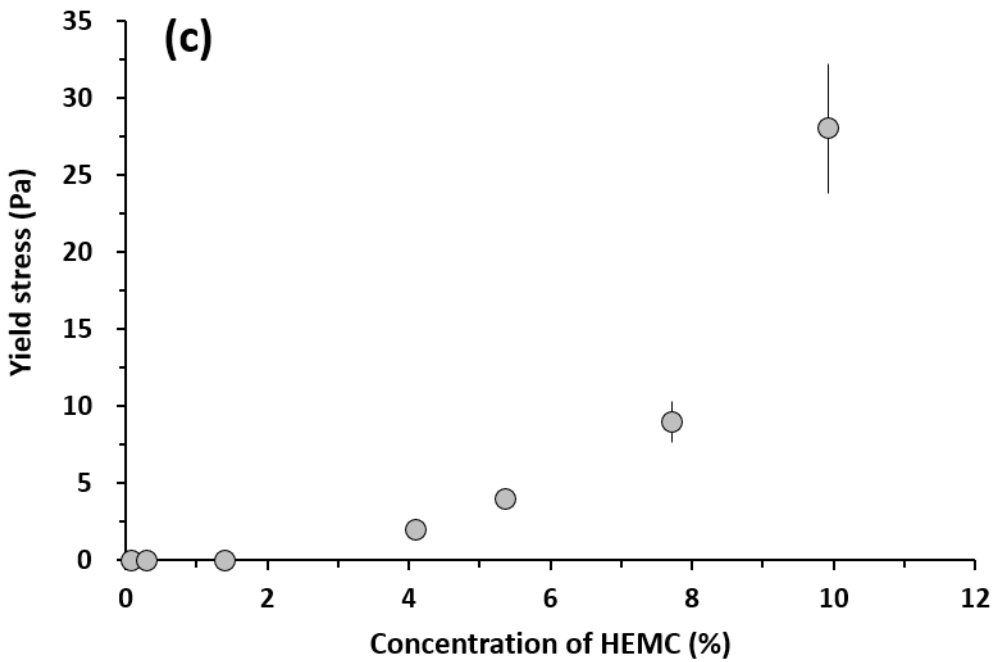
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183



184



185

186 **Fig. 4.** Rheological properties for solutions with different HEMC concentrations: (a)  
 187 Shear stress as a function of shear rate for a solution of 4% HEMC in water (circles).  
 188 The dash line is the Herschel–Bulkley model fit used to extrapolate yield stress; (b)  
 189 Apparent viscosity at 1 s<sup>-1</sup> as a function of HEMC concentration (white circles are  
 190 results from a previous study [26]); (c) Yield stress as a function of HEMC  
 191 concentration.

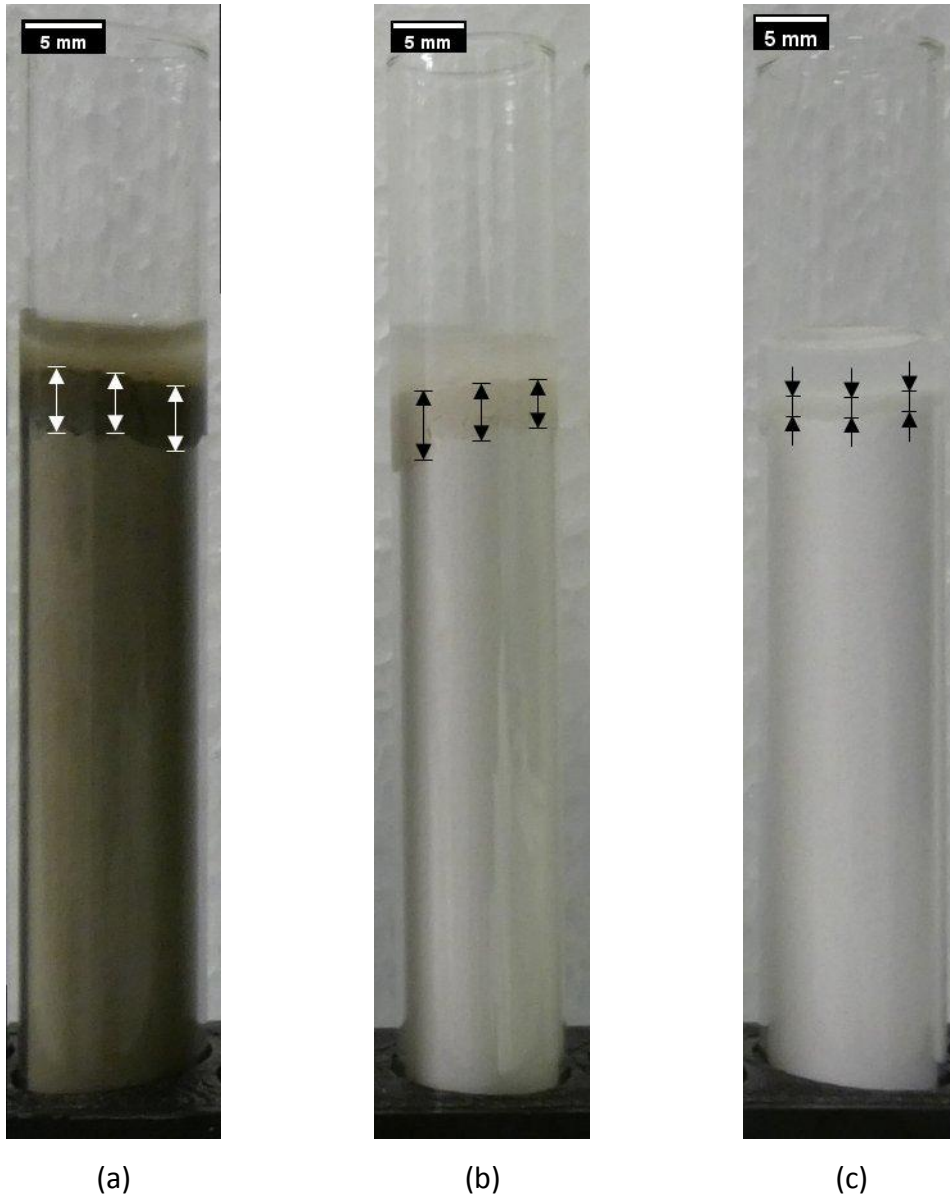
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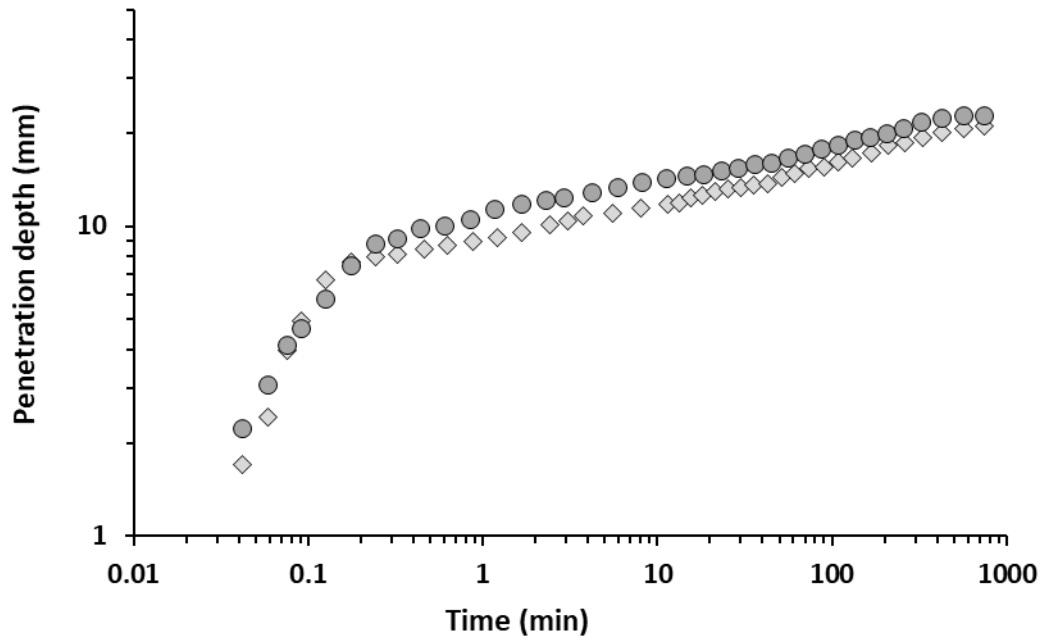
### 194 **2.3. One-dimensional water penetration measurements**

195 As discussed in the background section, a one-dimensional penetration experiment  
196 was designed to assess liquid penetration in the powder bed. The powder was  
197 packed into glass tubes with an inner diameter of 10.5 mm and a height of 10 cm.  
198 The bottom of the tubes was cut off by a wire cutter and sealed with filter paper. This  
199 allows air to escape from the bottom during liquid penetration. The tubes were filled  
200 up to 7 cm and gently vibrated to obtain both a flat top-surface of the bed and to  
201 achieve the packing fraction mentioned in **section 2.1**. Then, 0.4 mL of distilled water  
202 was added within 1 second on the top-surface of powder-bed using a high-  
203 performance micro-pipette (see **Fig. 5**). The tubes were then sealed to avoid any  
204 evaporation. The above amount of water corresponds theoretically to a water layer  
205 of thickness around 5 mm before penetration. A digital camera was then used to  
206 record the penetration depth of the liquid. Comparing the water level above the  
207 surface and the penetration depth in the powder bed and accounting for the porosity  
208 to be filled by water, we concluded that wall effects are negligible in our experiments  
209 (results not shown here). Some penetration fronts were noted to be non horizontal,  
210 which may be due to the heterogeneity of the pore size distribution. The penetration  
211 depths of the liquid reported in this work were therefore computed by averaging  
212 three measurements, *i.e.*, left, middle, and right of each tube picture at each  
213 recording time (see arrows in **Fig. 5**). We moreover checked the repeatability of our  
214 measurements (see **Fig. 6**). All measurements were carried out at room temperature  
215 ( $22 \pm 1^\circ\text{C}$ ).

216



217 **Fig. 5.** One-dimension measurement of water penetration in powder-beds: (a)  
218 cement powder; (b) plaster powder; (c) 3DP plaster powder. The arrows stand for the  
219 depth of the liquid that has penetrated in powder-bed. Note: the images shown here  
220 were taken 30 s to 1 min after water addition.  
221



222

223 *Fig. 6. Repetition of the one-dimensional measurement for pure cement powder-bed*  
 224 *with a solid volume fraction of 40% and a 0.4 ml water addition.*

225

### 226 **3. Penetration of water in plaster powder bed and cement powder bed**

#### 227 **3.1. Experimental results**

228 We first show in **Fig. 7** the measured water penetration depth as a function of time  
 229 for plaster powder-bed, cement powder-bed and commercial 3DP Plaster powder-  
 230 bed. The water penetration depths in plaster and cement powders show similar  
 231 trends. They initially increase with the square root of time for around 1 min and slow  
 232 down sharply afterward. The transition occurs for a penetration depth around 7 mm.  
 233 This depth corresponds to the so-called “saturation penetration depth” computed by  
 234 assuming that the initial water on top of the sample has fully penetrated and has  
 235 saturated the porosity of the powder bed (see the fine dash line in **Fig. 7**). It means  
 236 that, as soon the available water has fully filled the available porosity, the initial fast  
 237 penetration regime ends.

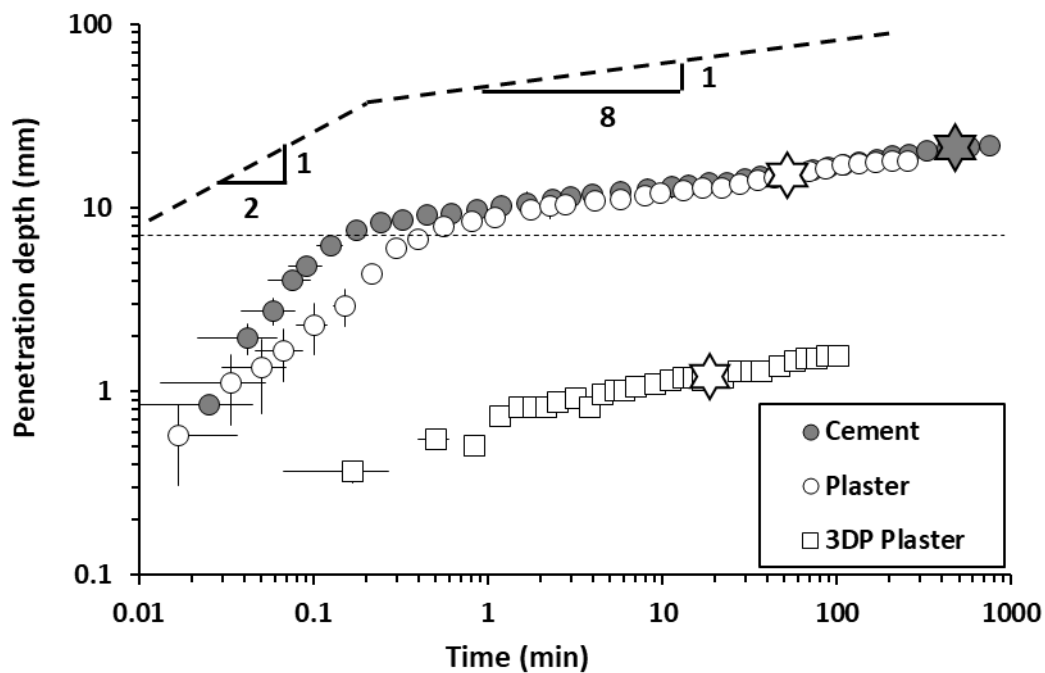
238 However, capillary imbibition does not stop when water has fully invaded the  
 239 porosity. The interesting feature to be kept in mind from **Fig. 7** is that, after the initial  
 240 fast penetration of around 7 mm in one minute, water penetration depth more than

241 doubles over the following 100 minutes. This evolution scales with the power  $1/8^{\text{th}}$  of  
242 time as indicated in **Fig. 7** (this observation will be studied in a further study). As a  
243 consequence, the liquid saturation in the powder bed porosity drops down from 100%  
244 at 1 minute to 50% at 100 minutes.

245 We then note that hydration onset does not affect water penetration kinetics (Cf.  
246 star symbols in **Fig. 7**). However, around the time of the hydration peak of plaster and  
247 cement from **Fig. 3**, the water penetration front gradually vanishes preventing any  
248 further measurements (see **Fig. 7**).

249 Finally, we note that water penetration depth in the commercial 3DP plaster  
250 powder is far lower than the ones measured in the two other types of powder  
251 despite the fact that all powder beds have the same packing fraction and therefore  
252 porosity.

253



254

255 **Fig. 7.** Water penetration depth in powder-beds as a function of time. The dash lines  
256 stand for the scaling relationship between penetration depth and time. The fine  
257 horizontal dash line stands for the saturated penetration depth (Cf. text for definition),  
258 and the stars on each curve stand for the time of hydration peak.

259

260 **3.2. Discussion**

261

262 **3.2.1 Saturated penetration**

263 According to Washburn's law, as long there exists a reservoir of water above the  
264 surface, water penetration depth  $h_s$  can be written as [30]:

$$h_s = \sqrt{\frac{k_0 P_{cap} t}{2\mu}} \quad (1)$$

265 where  $\mu$  is the liquid viscosity. The permeability  $k_0$  of the porous medium, can be  
266 estimated using the Kozeny-Carman formula  $k_0 = \frac{\omega^3}{45(1-\omega)^2} r^2$ , where  $\omega$  is the  
267 porosity and  $r$  is, as above, the pore radius [31,32].  $P_{cap}$  is the capillary pressure  
268 already discussed above and is of the order of  $\gamma/r$ . It can be noted from **Eq. (1)** that  
269 water penetration depth in the powder-bed is expected to scale with the square root  
270 of time. Interestingly, this is the case for both the plaster powder-bed and the  
271 cement powder-bed, but not for the commercial 3DP Plaster powder (see **Fig. 7**).

272

273 **3.2.2 Unsaturated penetration**

274

275 When there is no water left above the surface, the saturated powder is expected  
276 to desaturate progressively as water penetration goes on. As a decrease in saturation  
277 leads to a decrease in the liquid relative permeability [33], water penetration kinetics  
278 is expected to slow down (see **Fig. 7**). This decrease in permeability, and therefore  
279 the slowing down of the water penetration velocity under the constant capillary  
280 pressure, will go on. This decrease is expected to stop when the liquid saturation in  
281 the porosity reaches a critical saturation level, below which the liquid network in the  
282 porosity is expected to disconnect [34]. At this latter stage, water displacement may  
283 only occur through vapor transfers, which are orders of magnitude slower. Typical  
284 values for this critical saturation level are of the order of 5%. This suggests that, on  
285 long time-scales, water may travel over distances 20 times longer than the saturation  
286 depth discussed in the previous section.

287 This long time-scales propagation of water may be a major issue if the onset of  
288 the hydration reaction is slow. Indeed, during the dormant period, this long-range  
289 water propagation may bring the water saturation level below the amount required  
290 for proper cement hydration.

291 However, this feature has not been, up to the authors' knowledge, ever  
292 discussed, reported or even measured in the cement-based literature so far.  
293 Propagation depth of water is always assumed to be a finite value and it is always  
294 assumed that there is locally enough water for the binder hydration when it occurs.

295 A first reason could be hydration itself. Even if the onset of hydration does not  
296 affect the unsaturated propagation of water as shown in **Fig. 7.**, the hydration peak is  
297 expected to consume enough water locally to bring saturation below the critical  
298 saturation level defined above and stop any further water propagation. If this  
299 happens not too long after the end of the saturated propagation regime, the water  
300 propagation length could then appear as finite and constant.

301 However, particle bed printing is, more than often, carried out, on non-  
302 accelerated systems where the hydration peak only occurs after several hours. In  
303 these cases, another explanation could be found in the lower permeabilities of the  
304 powder beds used in real printing when compared to the pure powder beds studied  
305 here. If we consider that 50% of the powder volume is often substituted by sand, we  
306 can expect the packing fraction of the bed to increase from the measured value of 40%  
307 (see section 2.1.) up to 70%. The porosity would, in turn, drop from 60% to 30% and  
308 the permeability would scale down by a factor 5 according to the analytical approach  
309 proposed by Perrot *et al.* [35,36]. As a consequence, the "fast" saturated penetration  
310 regime would then last 5 times longer (*i.e.* of the order of ten minutes) and the  
311 further unsaturated water penetration length before the hydration peak would then  
312 become much shorter. The penetration depth would then be finite and well-  
313 controlled and there would locally be enough water for the binder hydration.

314 Such a feature would however prevent from powder printing based on pure  
315 powders (*i.e.* without any coarser particles allowing for a decrease in porosity and  
316 permeability). Nevertheless, several authors in literature have carried out some



317 powders printing on pure metakaolin powders without encountering any specific  
318 issues regarding the activation liquor penetration depth [16]. However, while these  
319 activation liquors (sodium silicates or potassium silicates) have similar surface  
320 tension values as water, they have viscosities one or two orders of magnitudes higher.  
321 Once again, as the penetration kinetics of this high viscosity liquid is slower, it  
322 becomes easier to reach a finite and well-controlled liquid penetration by ending it  
323 with a chemical reaction.

324

## 325 **4. Penetration of water in powder-beds containing thickeners**

### 326 **4.1. Experimental results**

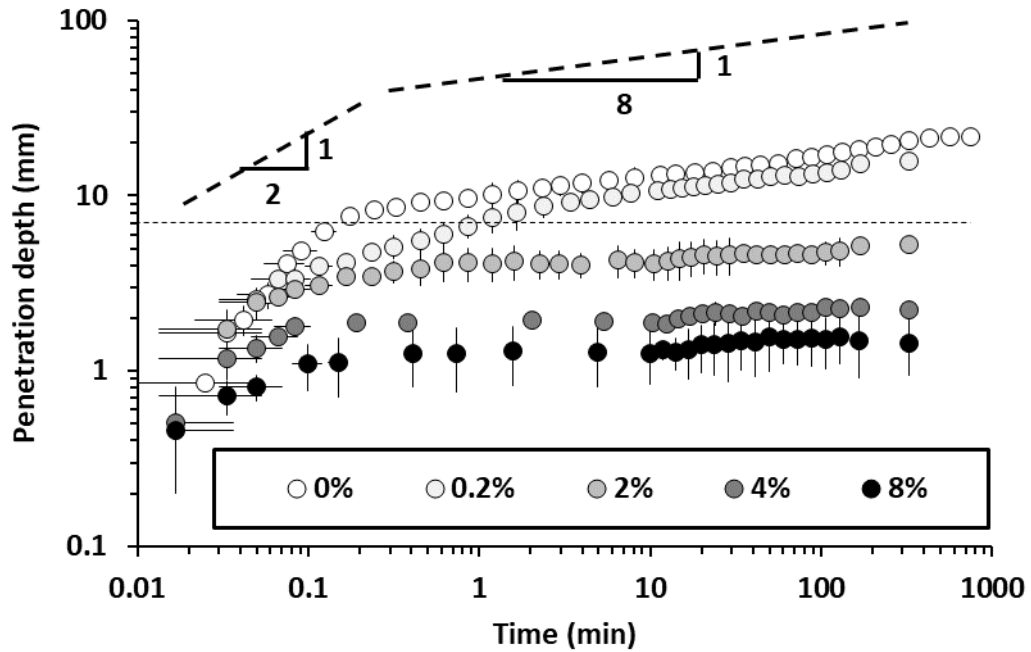
327 We plot in **Fig. 8** the measured water penetration depth as a function of time  
328 for various HEMC dosages.

329 For dosages lower than around 1%, the curves are similar to the ones obtained  
330 previously on powder beds not containing any HEMCs with a saturated penetration  
331 regime followed by an unsaturated penetration regime. The water penetration depth  
332 kinetics are however slower (Cf. the 0.2% HEMC dosage curve in **Fig. 8**)

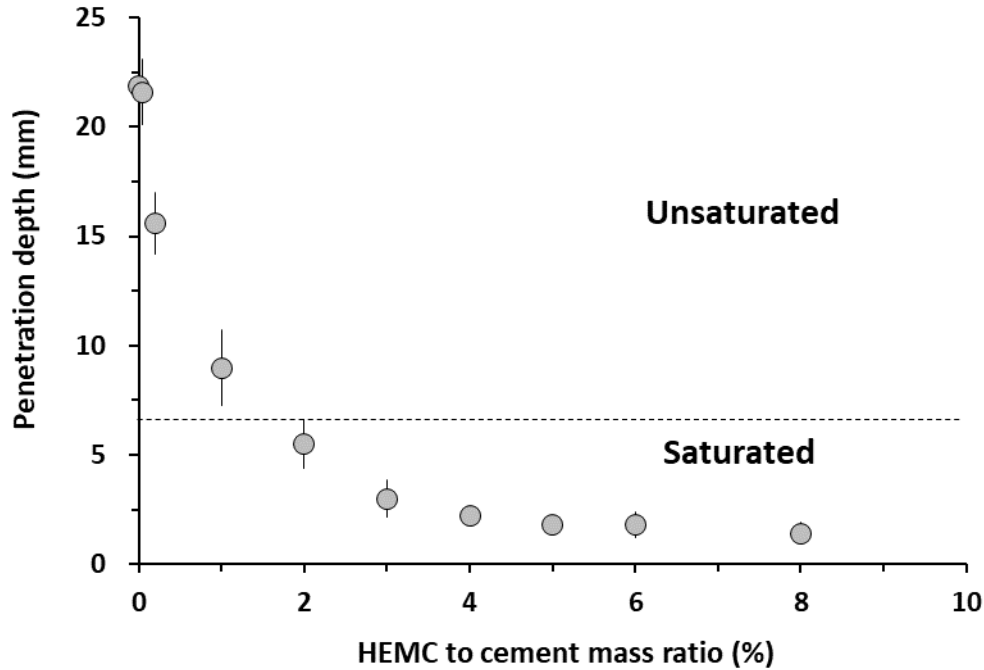
333 For dosages higher than around 1%, the water penetration depth follows a  
334 different trend than the one measured previously. In a first saturated penetration  
335 regime, the penetration depth increases quickly and then stops. On longer time  
336 scales, water penetration depth barely changes. The time and penetration depth at  
337 which penetration stops both decrease with increasing HEMC dosage. It can  
338 moreover be noted that, for these dosages, some residual water on top of the  
339 surface can be visually assessed. This result is in contrast with the idea that water  
340 continuously propagates in the sample under the effect of capillary suction. This, in  
341 turn, suggest that something able to compete with capillary forces prevents the  
342 water from moving. As a consequence, the water penetration depth becomes finite  
343 and is correlated to the thickener's dosage as shown in **Fig. 9**.

344 We suggest, in the following, that the dissolution in the penetrating liquid of the  
345 thickener dispersed in the powder bed is able to provide the penetrating water with

346 a yield stress, which, in turn, is able to prevent the water from propagating despite  
347 capillary suction.  
348



349  
350 **Fig. 8.** Penetration depth as a function of time for powder-bed containing different  
351 HEMC dosages. The numbers in the legend stand for the mass ratios of HEMC to  
352 cement, the bold dash lines stand for the scaling relationship between penetration  
353 depth and time, and the fine dash line stands for the saturated penetration depth  
354 after which the system is unsaturated.  
355



356

357 **Fig. 9.** Penetration depth after 200 minutes as a function of HEMC content in the  
 358 cement powder bed. The dash line stands for the water penetration depth, above  
 359 which the system becomes unsaturated.

360

#### 361 4.2. Discussion

362 We assume in a first step that the HEMC gets fully dissolved in the penetrating  
 363 water upon contact. This assumption allows for the computation of the HEMC  
 364 concentration as a function of penetration depth. In the saturated penetration  
 365 regime, the concentration is expected to be constant and proportional to the HEMC  
 366 dosage in the powder bed while, in the unsaturated penetration regime, this  
 367 concentration is expected to increase with penetration depth. Indeed, the total  
 368 amount of water in the powder bed stays constant while the depth of the invaded  
 369 porous zone and the potentially dissolved HEMC amount both increase.

370 Let us first focus on the saturated penetration regime that applies to all the  
 371 highest dosages of HEMC in **Fig. 8** and **Fig. 9**. According to the analytical frame of  
 372 Pierre et al [11,37], a yield stress fluid penetration in a powder bed is expected to  
 373 stop at a depth  $H$  where the capillary pressure gradient  $\nabla P/H$  equilibrates the stress  
 374 gradient  $\tau_c/d_p$  [11].  $d_p$  is the particle diameter and  $\tau_c$  is the yield stress of the

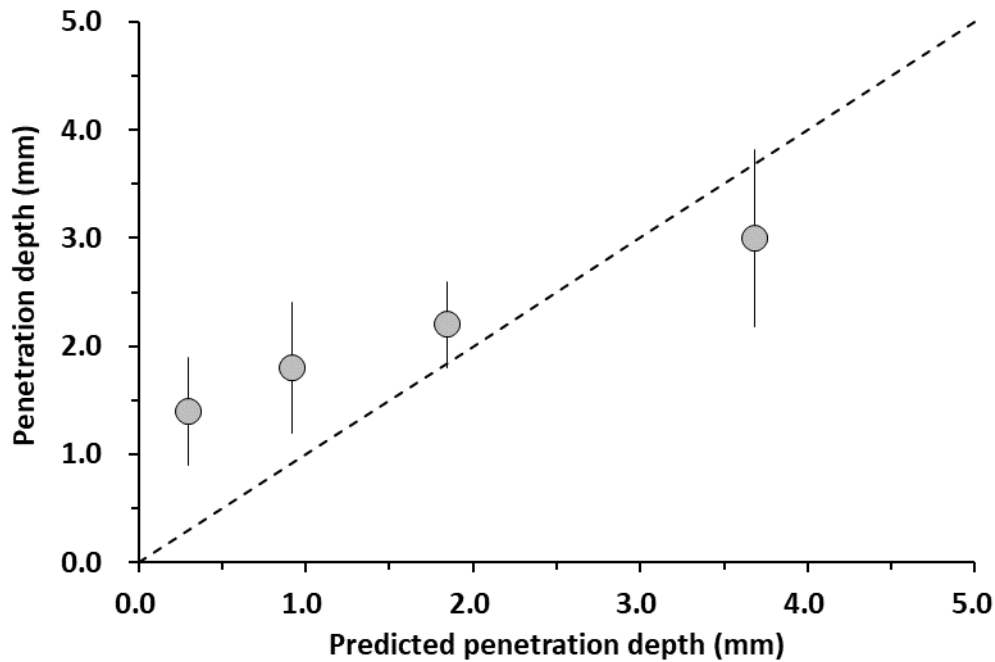
375 penetrating fluid. Therefore, the penetration depth of a yield stress fluid in a powder-  
376 bed is expected to scale as [11]:

$$H = \frac{d_p P_{cap}}{\alpha + 6\kappa(1 - \omega)/\omega} \cdot \frac{1}{\tau_c} \quad (2)$$

377 where  $\kappa$  captures the fraction of the powder grains surface area where the fluid is  
378 sheared. It is assumed to be equal to 1 when penetration is homogeneous.  $\alpha$  is a  
379 dimensionless geometrical fitting parameter reported to equal 5.5 in [10].

380 We plot the penetration depth measured here as a function of the predicted  
381 penetration depth according to **Eq. (2)** in **Fig. 10**. To do so, we use the yield stress  
382 values from **Fig. 4 (c)**. The predicted penetration depth is in rather good agreement  
383 with the measured one. This suggests that, at first order, one can consider that all  
384 HEMC particles are immediately dissolved in the penetrating liquid [38,39] and that  
385 the influence of HEC on the capillary suction is neglectable. It could however be  
386 objected that the higher penetration depths (compared to predicted ones) measured  
387 at lower dosages in **Fig. 10** are the traces of a delay in the dissolution the thickener  
388 while the lower penetration depth measured at the highest dosage suggests that the  
389 thickener dissolution is not complete. It can however be inferred that, for a system  
390 that stays saturated, penetration depth scales at first order with the inverse of the  
391 yield stress of the penetrating fluid. We suggest that this feature explains the lower  
392 penetration depth measured in the case of the commercial plaster in **Fig. 7**. Total  
393 Organic Carbon (TOC) measurements carried out on this powder revealed the  
394 presence of a high amount of organic compound (results not shown here) that we  
395 suggest to be the signal for a thickener addition.

396



397

398 **Fig. 10.** Experimental penetration depth for HEMC concentration above 3% and  
 399 predicted penetration depth (see Eq. (2)). The black dash line stands for  $y = x$ .

400

401 For the powder beds that reach the unsaturated regime, the resulting HEMC  
 402 effective dosage in the penetrating liquid is expected to be proportional to the  
 403 penetration depth leading to a progressive change in the penetrating liquid  
 404 rheological properties. For the lowest HEMC dosages, it is unlikely that they develop  
 405 a yield stress fluid on the time scale of the experiment (*e.g.*, the case of HEMC  
 406 dosage of 0.2% in Fig. 8). Consequently, the unsaturated penetration process follows  
 407 the same steps as the one described for powder beds not containing any thickeners.  
 408 It can however be expected that the penetration process is slowed down by the  
 409 higher viscosity of the penetrating fluid resulting from the dissolution of the  
 410 thickener. For higher HEMC dosages in the unsaturated regime, we suggest that,  
 411 similarly to saturated regimes, the unsaturated penetration process stops as soon as  
 412 a yield stress fluid is formed and balances the capillary-driven force as shown in Eq.  
 413 (2).

414

415 **5. Shape control: morphology of liquid penetration zone**

416 According to the above results and discussion, water penetration depth is  
417 naturally uncontrolled. It can however be controlled by dispersing a thickener into  
418 the powder bed. This means that the extent of the penetration zone during printing  
419 becomes tunable at will depending on the dosage of thickener in the powder bed. In  
420 practice, this dosage shall therefore be chosen so that there remains enough water  
421 in the porosity to fully hydrate the reactive powder in the penetrated zone. To  
422 illustrate this situation, we carry out the following experiments similarly to the ones  
423 from [16].

424 Water droplets of 20  $\mu\text{L}$  (diameter around 3 mm) are deposited on the powder-  
425 bed surface using an ultra-high-performance micropipette. After penetration and  
426 setting, the resulting hardened zones in the bed are extracted from the unreacted  
427 powder using a sieve with a mesh size of 200  $\mu\text{m}$ . This last step is carried out 12 h  
428 after the droplet deposition.

429 It can be noted that the typical penetration time of the droplets is around 1 min  
430 (visual observation), whereas, in this period, the water evaporation ratio (*i.e.* the  
431 ratio between evaporated water mass and droplet mass) always stays lower than 2%  
432 (data not shown here).

433 We show in **Fig. 11** the morphology of the resulting granules after setting and  
434 hardening as a function of CE dosage. It can be seen in **Fig. 11** that, the cement  
435 powder containing none or the lowest HEMC dosage (*i.e.*, the granule with 0.2%  
436 dosage of HEMC), the morphology of the hardened objects extracted from the  
437 unreacted powder is uncontrolled. The resulting object has a typical size far lower  
438 than the water penetration depth expected from the one-dimensional  
439 measurements of the previous sections (*i.e.*, the translucent cylinder in **Fig. 11**). We  
440 suggest that the slow unsaturated penetration regime shown in **Fig. 8** brings the  
441 water-to-cement ratio in most of the samples below the value required for hydration  
442 and grains binding.

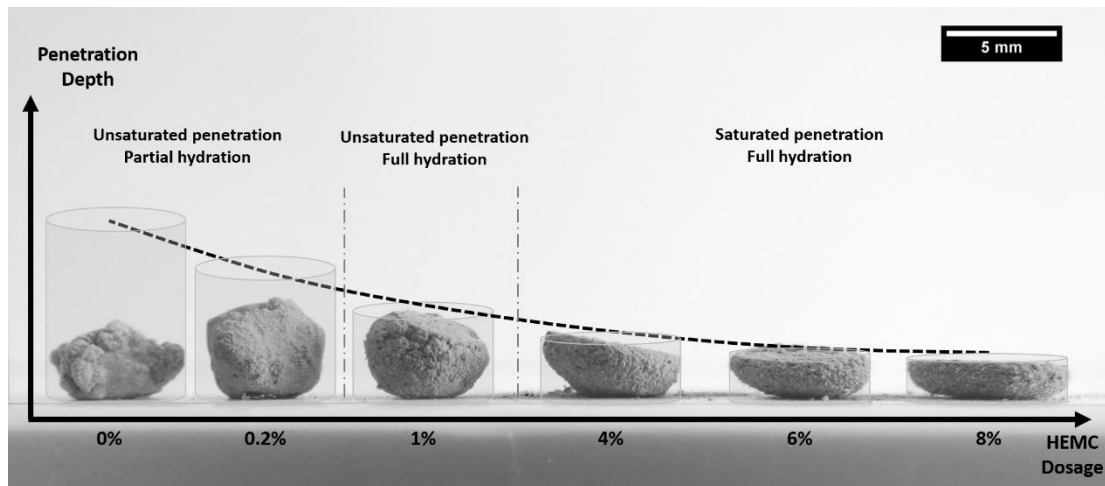
443 Although one could print in this regime with a bit of experience and practice, it  
444 has to be noted that, in such conditions, recycling of the powder surrounding the  
445 printed object shall become an issue. Indeed, in this regime, the porosity of the

446 powder surrounding the extracted object will contain some water. It is expected  
447 therefore to be partially hydrated even though this hydration was not sufficient to  
448 bind the cement grains.

449 In the case of the cement powder containing 1 % dosage of HEMC in **Fig. 11**, it  
450 can be expected from the previous sections of this paper that unsaturated  
451 penetration occurs for a short period of time. It however stops as soon as a yield  
452 stress fluid appears due to the thickener dissolution and balances the capillary  
453 pressure. Therefore, the saturation level stays high enough to allow for proper  
454 hydration and binding of the cement grains. However, printing objects in this regime  
455 would potentially raise the issue of printing rate and productivity. Indeed, the above  
456 regime involves a slow unsaturated penetration process as shown in **Fig. 8**. The final  
457 shape, although controllable, will only be reached after a couple hours.

458 For the cement powder containing 4%, 6%, and 8% HEMC in **Fig. 11**, the shape of  
459 the granules that formed during liquid penetration is the one of regular disks. The  
460 influence of the coating (or spreading of the droplet) not studied in this work can  
461 clearly be seen. The thickness of these disks decreases with increasing HEMC dosage  
462 in the powder-bed. In this thickener dosage range, the penetration zone is expected  
463 to be saturated with liquid and hydration allows for the binding of the cement grains.  
464 The shape of the hardened granules can therefore be well-controlled. There  
465 however exists a risk of having an excess of water at the top of the powder bed if the  
466 deposition rate of water above the bed is not adequately chosen.

467



468

469 **Fig. 11.** *The morphology of the liquid penetrated area after hardening. The HEMC*  
 470 *dosage is the mass ratio between HEMC and cement. The dash line stands for the*  
 471 *expected stabilized penetration depth and the transparent cylinders stand for the*  
 472 *expected stabilized penetration area.*

473

## 474 6. Conclusions

475 In this paper, we studied the physics behind net geometry control in the case of  
 476 powder-based printing technologies.

477 We have measured one-dimensional water penetration as a function of time in  
 478 simple experiments on various powder beds. Our results showed that water  
 479 penetration goes through different penetration regimes. Initially, water saturates  
 480 the powder bed and water penetration depth increases with the square root of time.  
 481 This first regime is followed by an unsaturated penetration regime where  
 482 penetration drastically slows down. Despite this slowing down, it was shown that  
 483 water penetration does not stop when the porosity of the powder bed gets  
 484 saturated as usually assumed. This results, on the typical time scale of cement  
 485 setting, into an invaded porous zone larger than expected where the porosity is only  
 486 partially saturated. It may, in turn, result into a loss of control of the resulting  
 487 printed object geometry and into a poor hydration of the binder. Analysis and  
 488 extrapolation have however suggested that this feature matters mostly when  
 489 injecting a pure powder bed (i.e. with low packing properties and therefore high



490 porosity) with a low viscosity liquid.

491 In such cases, our second set of experiments has shown that dispersing a  
492 thickener inside the powder bed allows for a better control of the printed object net  
493 geometry and hydration. As water propagates into the powder under the effect of  
494 capillary suction, the thickener dissolves into the liquid and modifies its rheological  
495 behavior. Our results suggested that this may lead, for sufficient thickener dosages,  
496 to the formation of a yield stress fluid between the powder grains. This yield stress is  
497 then able to compete with capillary suction. Even at low thickener dosages, a yield  
498 stress eventually develops as the desaturation of the powder bed increases the  
499 effective thickener concentration. The formation of this non-Newtonian fluid  
500 between the powder grains allows, in turn, for the control of the naturally  
501 uncontrolled capillary-driven liquid penetration of the powder-bed.

502

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