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# *In-situ* X-Ray tomographic monitoring of plaster setting

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## Abstract

The first real time monitoring of plaster hydration using X-Ray tomography is reported in this paper. Dissolution of hemihydrate particles and formation of a network of gypsum needles can be observed in 3D. A 3D quantitative analysis based on the microstructure evolution allows the determination of the degree of reaction. In particular, the size of hemihydrate particles is shown to have an influence both on the hydration kinetics and on the final microstructure of the set plaster. This work paves the way to the understanding of the relationship between microstructure evolution, chemical degree of reaction and mechanical strength development for material processed through a setting reaction.

## Keywords

Hydration (A), Kinetics (A), Microstructure (B), Particle size distribution (B), *in-situ* X-Ray tomography

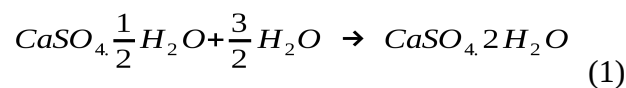
## 26 1. Introduction

27

28 Plaster is one of the most ancient materials used for construction in the world, with evidence of its  
29 use over several thousands of years (traces of gypsum in ancient Egypt are often considered as the  
30 first example of its use). Plaster is still largely used for dry wall due to its low cost, low toxicity, low  
31 embodied energy and also to its lightweight, sound absorption and fire resistance.

32 Its production starts from the calcination of gypsum, calcium sulfate dihydrate ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), at  
33 around 120-130°C. During calcination calcium sulfate dihydrate loses  $\frac{3}{4}$  of its crystallization water  
34 and turns into calcium sulfate hemihydrate ( $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ ) also referred to as plaster powder.  
35 Plaster is then prepared as a solid binder through a hydration reaction in water, with the dissolution  
36 of calcium sulfate hemihydrate (HH) and the precipitation of calcium sulfate dihydrate (DH), as  
37 shown in Eq. 1. “Plaster” usually refers to both the calcium sulfate hemihydrate and to the final set  
38 material, made of calcium sulfate dihydrate. It can be classified as a hydraulic binder and its  
39 hydration is usually considered as being well understood, involving only one chemical reaction and  
40 fully crystalline highly pure components.

41



43

44 The driving force for this hydration reaction is the higher solubility of HH in water as  
45 compared to DH. This phenomenon has been described first by Lavoisier and Le Chatelier back in  
46 1765 and 1887 respectively and is largely reviewed in the literature. Authors often consider three  
47 steps in the hydration of plaster: dissolution of calcium sulfate hemihydrate leading to a  
48 supersaturated solution with respect to gypsum, nucleation and growth of gypsum needles and final  
49 formation of a solid material by entanglement of gypsum needles with complete depletion of HH.

50 The water to plaster (W/P) ratio, *i.e.* the amount of water used to hydrate the HH powder, is always

51 well above the theoretical stoichiometric mass ratio of 0.186. This higher amount of water increases  
52 the fluidity of the paste, which becomes moldable. This also explains the high level of porosity in  
53 the final material obtained after complete drying of the excess water.

54

55 Monitoring and controlling the kinetics of the setting reaction are critical for industrial purposes and  
56 many studies can be found in the literature on the use of chemical additives to accelerate or to delay  
57 the setting time of plaster. During the setting process, the plaster evolves both from a chemical point  
58 of view (monitored by the degree of reaction) and from a mechanical point of view (from a liquid  
59 paste to a solid material). Therefore, both aspects have been thoroughly investigated. For instance,  
60 the monitoring of the hydration reaction can be carried out using a large number of techniques, the  
61 most popular being calorimetry [1] as the hydration reaction (Eq. 1) is exothermic. Additional  
62 methods are also used such as electrical conductimetry in diluted pastes [2], X-Ray diffraction [3]  
63 or nuclear magnetic resonance [4] to determine the rate of water consumed by the hydration  
64 reaction. Other analytical techniques can be used, such as differential thermal analysis or particle  
65 size analysis but they can only be implemented *ex-situ*; thus, they require to stop the reaction at  
66 different times, and demand one sample per studied time. Nevertheless, all these methods allow the  
67 determination of the degree of the hydration reaction.

68 On the other hand, the solidification of plaster can be monitored by the measurement of rheological  
69 and mechanical properties during setting, either with standard methods just like Vicat and Gilmore  
70 needles, knife setting time, or using rheometers. The evolution of the elastic modulus versus time  
71 can also be monitored by the measurement of ultrasound speed through the setting paste [5].

72 Some authors tried to link the degree of reaction and the development of strength, based on a  
73 description of the development of the microstructure at different times. Lewry and Williamson [1]  
74 suggested an evolution of the microstructure in three stages: firstly, development of a matrix of  
75 gypsum needles providing the initial strength, then relief of internal stresses caused by the built-up  
76 of pressure associated with needles growth and finally increase of strength due to water evaporation



77 after complete hydration.

78 The detailed description of the bonds formation between gypsum crystals is beyond the scope of our  
79 study, but it is admitted that the contact forces are highly dependent on the crystallographic  
80 orientation of the crystal faces in contact, as measured by atomic force microscopy [6,7].

81 The morphological description of the entanglement of gypsum crystals after hydration, as well as its  
82 structuring during the hydration phase, is critical as it directly controls the final strength of the  
83 material. The observation of the evolution of plaster microstructure with time is seldom described in  
84 the literature and mainly after having stopped the hydration at different times. The only study where  
85 the setting process has been monitored *in-situ* is, to the best of our knowledge, the work by Ridge  
86 [8] showing the growth of gypsum needles under an optical microscope. Lewry and Williamson  
87 carried out a *post-mortem* analysis based on scanning electron micrographies of fractured surfaces  
88 after having stopped the hydration at different stages. This allowed them to show the concomitant  
89 presence of partly solubilized HH particles and newly formed gypsum crystals [9]. This method is  
90 widely used to characterize the local organization of crystals due to its relative easiness and the high  
91 resolution one can reach. However, it is not possible to monitor *in-situ* the evolution of the  
92 microstructure during setting. Besides, the protocol used to stop the hydration might impact on the  
93 observed microstructure.

94 X-Ray tomography has a strong potential for the study of plaster hydration, the presence of water  
95 and solid ensuring a good contrast between the phases. Historically, the first scans of gypsum were  
96 acquired at high resolution using synchrotron source on a hydrated plaster [10]. Recent work was  
97 done on the *in-situ* mechanical loading of fully hydrated plaster in a X-Ray tomograph [11]. Only  
98 two studies deal with the use of X-Ray tomography during hydration of plaster [4,10]. In Bentz  
99 2002 [10], 3D scans showed the concomitant existence of gypsum crystals and HH particles, but  
100 without any quantitative analysis. In Song 2009 [4], 3D scans with a voxel size of 3  $\mu\text{m}$  of  
101 hydrating plaster were acquired after stopping the hydration reaction after 60 minutes. Pore volume  
102 distribution was analyzed but no specific analysis of the pore evolution with hydration time was

103 performed. One example of an *in-situ* monitoring of hydration was carried out on a cement paste  
104 [12]. The hydration was studied with X-Ray synchrotron tomography from 1 to 60 days, as the  
105 hydration kinetics is much slower than for gypsum. The resolution of the X-Ray device used in this  
106 study, even if as low as 0.7  $\mu\text{m}$ , was a limitation to monitor the cement hydration as the calcium  
107 silicate hydrates controlling the strength are nanosized.

108

109 3D volumes with a voxel size of a few micrometers can be acquired and reconstructed in about 3  
110 minutes on a lab scale apparatus thanks to recent development in microtomography. The present  
111 study focuses on the real time monitoring of plaster setting using X-Ray tomography, for the first  
112 time to the best of our knowledge. The volume of material studied here is sufficiently large to give  
113 an average behavior of the setting of a plaster paste, with a statistical number of HH particles  
114 dissolving and with fluidity typical of an industrial process. 3D quantitative volume analysis is  
115 reported and the influence of HH particle size on the setting process and on the final microstructure  
116 of plaster is investigated; the evolution of HH particle size versus hydration time is also examined.

117

## 118 2. Materials and methods

119

### 120 2.1. Plaster preparation

121

122 A beta calcium sulfate hemihydrate was used for this study, supplied in store retail, with purity  
123 above 96%. The hydration reaction was prepared using a W/P ratio of 0.72. In general, the powder  
124 was used as received. In order to understand the influence of the granulometry of the raw powder on  
125 the microstructure of the set plaster, some plaster samples were prepared with HH sieved powder  
126 (either between 63 and 40  $\mu\text{m}$  or below 40  $\mu\text{m}$ ).

127 The time when the HH powder was put in contact with water is referred to as the initial time in the  
128 paper. HH and tap water, stored at 23°C, were mixed by hand for 3 minutes. For X-Ray tomography

129 observation, the paste was injected with a syringe into a drinking straw with a diameter of 3 mm,  
130 directly mounted on the X-Ray tomograph. Knowing that surfaces of the setting paste were not  
131 observed, it was assumed that the bulk of the sample remained saturated with respect to water  
132 during the time period required for the complete acquisition (1 h 44 min). Setting time was  
133 separately characterized on the remaining paste, which was not injected into the straw, by the knife  
134 setting time method: setting time was then defined as the time after which a cut made in the paste  
135 with a blade remained opened.

136

## 137 2.2. X-Ray tomography – *in-situ* setting of the plaster

138

139 The internal observation of the microstructure evolution during the plaster setting was carried out  
140 by means of X-Ray tomography using a vtomex device (GE Phoenix|X-Ray GmbH) equipped with  
141 a 160 kV nano-focus tube, a tungsten transmitting target, and a 1920 x 1536 pixel Varian detector –  
142 see [13] for more details. The X-Ray tube produces a polychromatic conical beam. The experiments  
143 were performed at a voltage of 80 kV and a current of 280  $\mu\text{A}$ , with a voxel size of  $2.5 \mu\text{m}^3$ . Due to  
144 the fast changes during hydration, the acquisition parameters were optimized in order to reduce the  
145 scan time. A continuous rotation was used and the integration time was 333 ms for each of the 600  
146 projections acquired over  $360^\circ$ . These parameters resulted in measurement periods of 200 s for a  
147 complete scan. The first scan was acquired 13 minutes (800 s) after the initial time; these 800 s  
148 corresponded to the time needed to prepare the sample (600 s) and to perform the first acquisition  
149 (200 s). In total, plaster setting was monitored during 6200 s after the initial time. After this time  
150 period, no more modification in the microstructure could be noted. The sample was then dried  
151 outside of the tomograph at  $45^\circ\text{C}$  until constant weight was reached. It was re-scanned afterwards to  
152 observe the final set and dried microstructure. Because fast acquisition was no longer an issue, this  
153 last scan (denoted 24 h in the paper) was achieved with improved conditions *i.e.*, 900 projections  
154 and averaging of 3 images at each step angle.

155 For coding the absolute value of the attenuation coefficient of each voxel, 32 bits volumes were  
156 reconstructed from the projections. The reconstructed volumes were first subjected to a median  
157 filtering. Then, the different scans were spatially registered: each scan was aligned with respect to  
158 the previous one to better follow-up the evolution of the microstructure versus time.

159

### 160 2.3. X-Ray tomography – final microstructure

161

162 X-Ray tomography was also used to perform 3D analysis at very high resolution ( $0.4 \mu\text{m}^3$  per  
163 voxel) of the final microstructure of small pieces of plaster once set *ex-situ* ( $\sim 0.5 \times 0.5 \times 5 \text{ mm}$ ).  
164 Note that such a very small voxel size requires very much care in doing the tomographic  
165 acquisition. The tomograph used, different from the one used for the *in-situ* experiment, was  
166 designed by the company RX Solutions. This tomograph is equipped with a  $\text{LaB}_6$  emission tip for  
167 the X-Ray source, which ensures that the actual spot size is physically smaller than  $0.4 \mu\text{m}$ . The  
168 resolution is then not modified by geometric blur and that the voxel size is really close to  $0.4 \mu\text{m}^3$ .  
169 The Hamamatsu X-Ray source was operated with a  $\text{LaB}_6$  cathode at a voltage of 100 kV. The  
170 detector was a Hamamatsu CCD camera with a pixel size of  $12 \mu\text{m}$ . Each scan consisted of 900  
171 projections with an exposure time of 5 s and an averaging of 3 radiographs for each projection. The  
172 cone-beam XCT data were reconstructed by a filtered back projection Feldkamp-algorithm. The  
173 reconstructed data were processed and visualized with the public domain ImageJ / Fiji shareware  
174 [14,15].

175 High resolution tomography was also carried out after final hydration of HH powder sieved  
176 between 63 and  $40 \mu\text{m}$  and below  $40 \mu\text{m}$  to check for the differences in microstructure with the  
177 reference material, prepared from unsieved powder.

178

179

180

## 181 2.4. 3D volumes analysis and quantification

182

183 A quantitative analysis of the 3D volumes was also carried out. The analyzed volume was  $1.5 \text{ mm}^3$   
184 *i.e.*, sufficiently large to collect significant information about the setting process as it contained  
185 initially tens of thousands of HH particles larger than  $5 \mu\text{m}$ . The voxel gray values distribution in  
186 this volume was recorded at different times ranging from 800 s to 6200 s, as well as after the drying  
187 of the plaster; the corresponding histograms were computed. In parallel, the absolute value of the  
188 attenuation coefficient of the different phases present in the setting material were determined from  
189 specific regions using the volumes where they were the most present *i.e.*, on the first volume  
190 (acquired at 800 s) for HH particles and ionic solution and on the last volume (6200 s) for gypsum  
191 and trapped air.

192 In order to study the influence of the particle size of the HH reactant powder on dissolution kinetics,  
193 easy to recognize individual HH particles of different initial sizes were manually selected and the  
194 evolution of their thicknesses was followed with time. Note that HH particles were all connected at  
195 the first observation time, which complicated the quantitative image analysis since the morphology  
196 of the individual HH particles could not be measured easily. Therefore, their size was measured  
197 using a mathematical morphology operation named “granulometry” (see [16] for more details).

198 Also, about 70 HH particles ranging from below  $10 \mu\text{m}$  up to  $70 \mu\text{m}$  were manually selected and  
199 divided into 7 classes depending on their initial measurable thickness, referred to as  $T_{800}$  in this  
200 study. For each class, the average thickness over 10 particles was calculated and its evolution with  
201 hydration time was plotted.

202 A 3D rendering of HH particles in the initial paste and of large porosities after setting was also  
203 computed. A first algorithm was used to detect 3D clusters of connected voxels and to label each  
204 separate connected clusters. Morphological parameters of these labels were finally calculated  
205 (volume, position, ...).

206 Last but not least, granulometry measurement were performed on image acquired at  $2.5 \mu\text{m}^3$  to

207 assess the mesopore distribution. This method was also applied on high resolution images to  
208 measure the thicknesses of both gypsum phase and micropores.

209

## 210 3. Results

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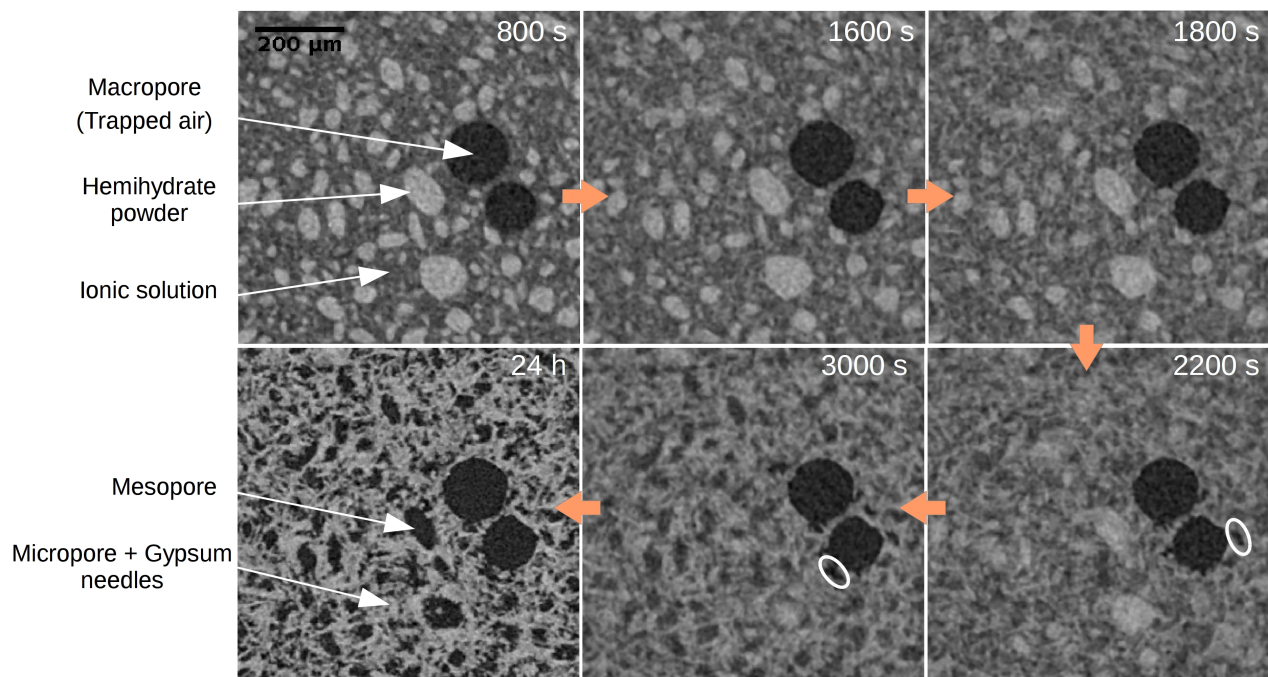
### 212 3.1. *In-situ* qualitative observation of microstructural evolutions during setting

213

214 The evolution of plaster microstructure during setting was first qualitatively observed. Figure 1  
215 shows a same tracked cross-section obtained from the reconstructed volumes at five different times  
216 and after complete setting and drying of the sample (indicated as 24 h). The quality of the  
217 reconstruction is obviously not perfect. This is because of the low signal to noise ratio due to the  
218 fast acquisition and also to the possible motion of the sample during the time required for a scan.

219 The microstructure of the sample is however rather clearly distinguishable from these images.

220 In the first picture scanned after 800 seconds (corresponding to the very first acquisition after the  
221 initial time), HH rounded particles are clearly visible in white, surrounded by a phase consisting of  
222 an ionic solution and gypsum crystals nuclei (in dark gray). The gypsum nuclei could not be imaged  
223 at such a resolution. Two large entrapped air bubbles, in black, can also be observed as frequently  
224 noted in set plaster [17]. The different morphologies and gray levels observed for the distinct phases  
225 (HH, ionic solution, gypsum and air) allowed us to monitor the evolution of each phase separately  
226 during the setting of the material.



228 Fig. 1. Microstructural changes during the setting of plaster. Reconstructed 2D slices extracted from  
 229 the 3D volumes acquired during the *in-situ* tomography experiments, between 800 and 3000  
 230 seconds. The last slice (24h) was obtained after drying at 45°C.

231

232

233 When considering the images shown in Figure 1 and the corresponding animated sequence  
 234 (Video\_1), modifications in the microstructure with setting time are evident. In particular, two  
 235 phenomena are observable:

- 236 - the progressive dissolution of HH particles, with a visible influence of their size, the largest  
 237 ones being the last ones to completely disappear,
- 238 - the formation of a network of gypsum needles inside the initial dark gray area i.e., inside the  
 239 ionic solution (in terms of contrast, this led to a bleaching of the plaster matrix).

240 Both phenomena occurred in parallel, leading to a decrease of the gray level in the initial HH grain  
 241 areas and to its increase in the zone initially occupied by the ionic solution. This indicates a clear  
 242 transport of matter from the HH particles towards the solidifying crystals inside the ionic solution.

243 The entrapped air bubbles seemed unaffected by the setting reaction, despite a global reduction in  
244 size that will be quantified hereafter. One can also note that the desaturation of pores from ionic  
245 solution into air could be observed in the tomographic images: at 2200 and 3000 seconds, the pores  
246 located close to air bubbles (surrounded by a circle in Figure 1) started to have a darker gray level.  
247 As water absorbs X-Ray more than air, its gray value is higher compared to air. Therefore, the  
248 darkening of these pores clearly showed that they began to be filled with air rather than water, this  
249 phenomenon initiating from entrapped air bubbles.

250 The final microstructure obtained after drying (last image of Figure 1), acquired with the same  
251 voxel size but with improved imaging conditions, was typical of set gypsum, with an entanglement  
252 of gypsum crystals (in white) and three levels of porosity (in black):

253 - spherical macropores of several hundreds of microns were due to air bubbles entrapped inside  
254 the setting paste.

255 - irregularly shaped mesopores of several tens of microns (see arrows in Figure 1) were left by  
256 the dissolution of large HH particles,

257 - micropores formed a percolating network in the space left between entangled gypsum crystals.

258 With these experimental setting conditions, gypsum crystals have a typical average length of 15  $\mu\text{m}$   
259 and lateral dimensions between 1 and 2  $\mu\text{m}$  [17]; therefore, they could not be individualized with  
260 the voxel size used here (2.5  $\mu\text{m}^3$ ). The comparison of the first and the final image highlights very  
261 clearly that the location of the final mesopores corresponded rather well to the position of initial  
262 large HH particles. Excepted for the air bubbles, the final microstructure (24 h) was nearly the exact  
263 negative of the initial one (800 s) in terms of attenuation coefficient.

264

265 Figure 2 shows the 3D rendering of a HH particle at 800 s and of the remaining mesoporosity after  
266 its complete dissolution. It confirmed that large HH particles led to the formation of mesoporosities.

267 Morphological measurements were performed from the segmented volumes (cropped around the  
268 HH particle and the resulting mesopore) to calculate the respective dimensions of each object. The



269 results are summarized in Table 1: the mesopore was smaller and occupied only 52% of the initial  
 270 HH particle volume, with an average uni-dimensional shrinkage of about 18%.  
 271 The same labeling measurements were performed separately on all trapped air bubbles. The results  
 272 showed a limited volume decrease of approximately 8% between the first and the last acquisition  
 273 and a negligible variation of the inter-bubble distance.

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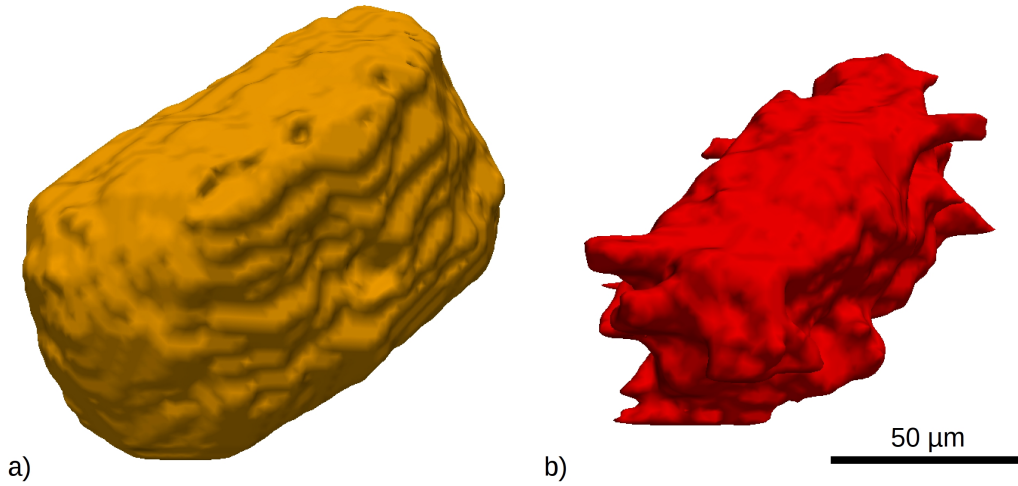
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283 Fig. 2. 3D rendering of a) HH particle (800 s), length = 123 μm b) Resulting mesopore after setting  
 284 and drying (24 h), length = 113 μm.

285

286

	Volume (μm <sup>3</sup> )	A (μm)	B (μm)	C (μm)
Hemihydrate particle (HH) at 800 s	566 844	123	74	60
Mesopore (P) at 24 h	296 437	113	55	47
P/HH ratio	0.52	0.92	0.74	0.78

287

288 Table 1. Morphological parameters of the HH particle shown in Figure 2a and of the resulting  
 289 mesoporosity (Figure 2b). A, B and C are the dimensions of the 3D objects in their three principal  
 290 axes.

291

292

293

## 294 3.2. *In-situ* quantitative analysis of *dissolution / precipitation kinetics*

295

### 296 3.2.1. Global analysis – “microstructural” degree of reaction

297

298 As observed in Figure 1, the distinct phases (HH, ionic solution, gypsum and air) showed different  
299 gray levels. Therefore, in addition to a phenomenological description of the microstructure  
300 evolution during hydration, a quantitative analysis was carried out using 3D volume analysis. The  
301 characteristic gray level of each phase was determined: a typical gray value of 0.05 corresponded to  
302 trapped air (macropores), 0.15 to the ionic solution at 800 s, 0.21 to the matrix of growing gypsum  
303 crystals surrounded by the ionic solution and 0.31 to initial HH particles. The histogram of the  
304 voxel gray values distribution of the whole volume was computed at different times (Figure 3). At  
305 the beginning of the setting reaction, two peaks could be noted, corresponding to ionic water  
306 solution and to HH particles. During setting, these two peaks merged into a single one, which arose  
307 from the contribution of both the ionic solution and the growing gypsum crystals. The separation of  
308 these two phases could not be achieved because of the limited spatial resolution and of the small  
309 difference between the gray values of gypsum crystals and of the ionic solution. The gray value of  
310 the gypsum peak tended to increase during the setting process. After drying, this single peak  
311 separated into two peaks: one for gypsum, and one for air. Please note that imaging conditions were  
312 improved for the 24 h scan (dried plaster).

313 A degree of setting reaction was computed from the evolution of the intensity of the two peaks  
314 highlighted by dashed lines in Figure 3 i.e., the HH peak on the one hand and the gypsum peak on  
315 the other hand (Figure 4). Due to the setting reaction (Eq. 1), the intensity of the peak corresponding  
316 to HH decreased with time while the intensity of the gypsum peak increased. The evolution rate was  
317 not constant: after a slow evolution until 1000 s, the rate increased up to around 1600 s for HH  
318 dissolution and around 1800 s for DH precipitation. After 2500 s, no significant variations were  
319 observed anymore.

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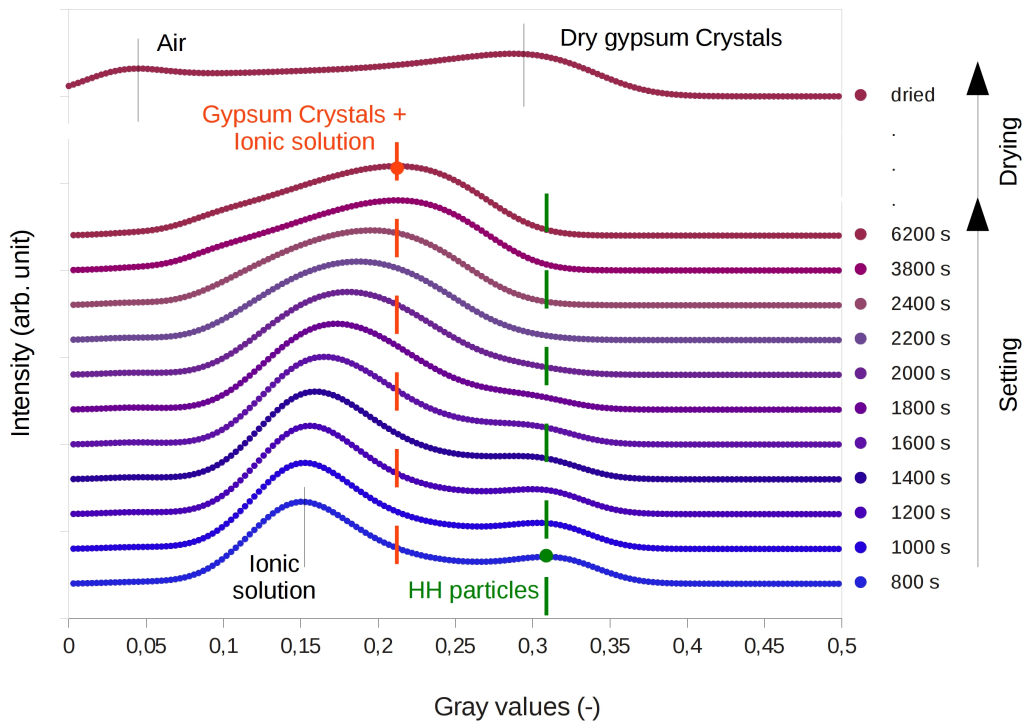
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333 Fig. 3. Histograms of the gray values measured in the volumes for different times during setting and  
 334 then subsequent drying at 45°C.

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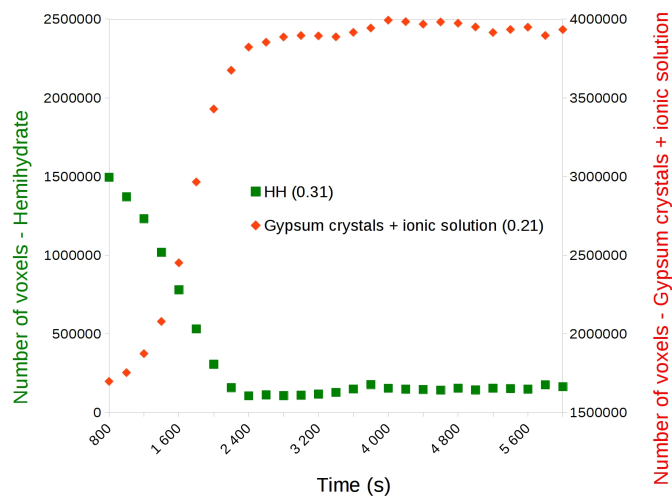
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344 Fig. 4. Evolution of the intensity of the HH peak (dashed line in Figure 3, gray level value = 0.31)  
 345 and of the gypsum peak (dashed line in Figure 3, gray level value = 0.21).

346 3.2.2. Local analysis - Influence of the HH particle size

347

348 As shown in Figure 1, the particle size of initial HH particles influenced their dissolution kinetics.

349 To quantify this further, two single HH particles of different sizes were chosen and their dissolution  
350 was studied, by monitoring the evolution of the gray level profiles across the thickness of the  
351 particles with hydration time.

352 Figure 5 presents the evolution of the gray profile for a small HH particle, 20  $\mu\text{m}$  thick, together  
353 with the corresponding micro-tomographies. At 800 s, the gray profile highlights the presence of a  
354 HH particle located between 11 and 38  $\mu\text{m}$  (gray value above 0.3 typical of the HH phase, as shown  
355 previously), surrounded by the ionic solution, of characteristic gray values comprised between 0.15  
356 and 0.18. For short times, nearly no evolution of this profile could be detected. Then the particle  
357 completely dissolved within a few minutes, between 1600 and 3200 s, leading to a mesoporosity  
358 filled with ionic solution (gray value around or below 0.1) surrounded by a shell made of gypsum  
359 crystals and microporosity, again filled with ionic solution. The profiles clearly showed, as already  
360 seen in Figure 1, that solid matter was progressively transported from the HH particle to the  
361 surrounding ionic solution where gypsum crystalline needles nucleated and grew, as confirmed by  
362 the increase of the gray level in the immediate vicinity of the initial HH particle.

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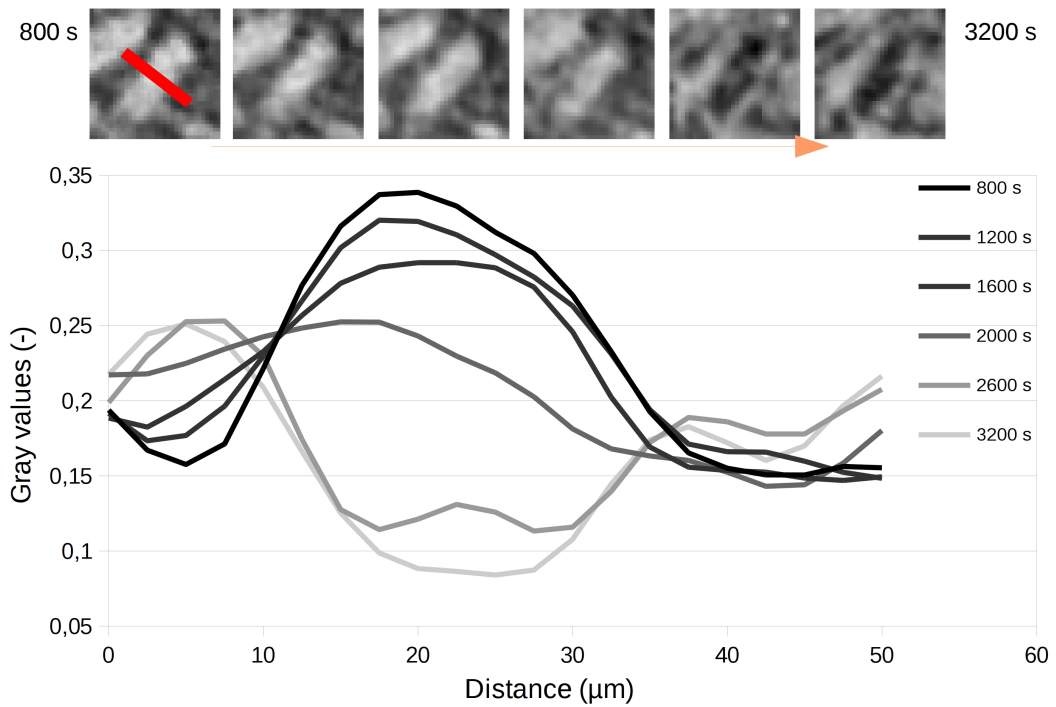
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384 Fig. 5. Gray values profile along the red line taken at different setting times. The measurement was  
385 focused on a small HH particle (20 µm thick).

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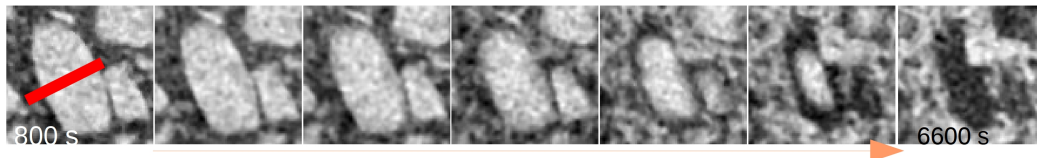
388 An example of the same analysis carried out on a large HH particle (approximately 70 µm thick), is  
389 illustrated in Figure 6. No evolution in the size of the particle was noted before the starting of  
390 dissolution at 1600 s. The dissolution suddenly started, occurring first at the surface of the particle.  
391 Again, the gray value of the area surrounding the HH particle increased during the dissolution of the  
392 particle: HH dissolved and matter was transported from the initial particle into the surrounding  
393 matrix where entangled needles of gypsum nucleated and grew. One can however note the existence  
394 of a shell of around 5 to 7 µm around the HH particle, where the gray value remained at 0.13 all  
395 along the dissolution, indicating that the HH particle was surrounded by a shell of ionic solution  
396 through which the matter had to diffuse towards the outside growing crystals. After complete  
397 dissolution, a remaining mesopore filled with ionic solution was left where the initial HH particle

398 was present. An outer shell made of a network of gypsum crystals and microporosity filled with  
399 ionic solution was observed. Figures 5 and 6 show that the behaviors of both small and large HH  
400 particles were very similar, excepted for the notable influence of the particle size on the dissolution  
401 kinetics. For the smallest HH particles present in the paste (below 20  $\mu\text{m}$  in thickness), this  
402 phenomenon was probably too quick to be observed at our temporal resolution.

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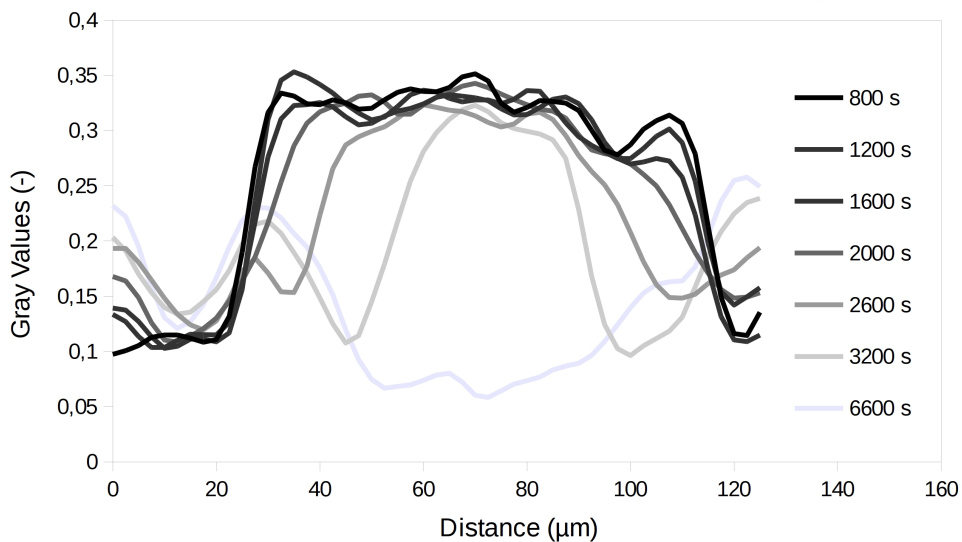
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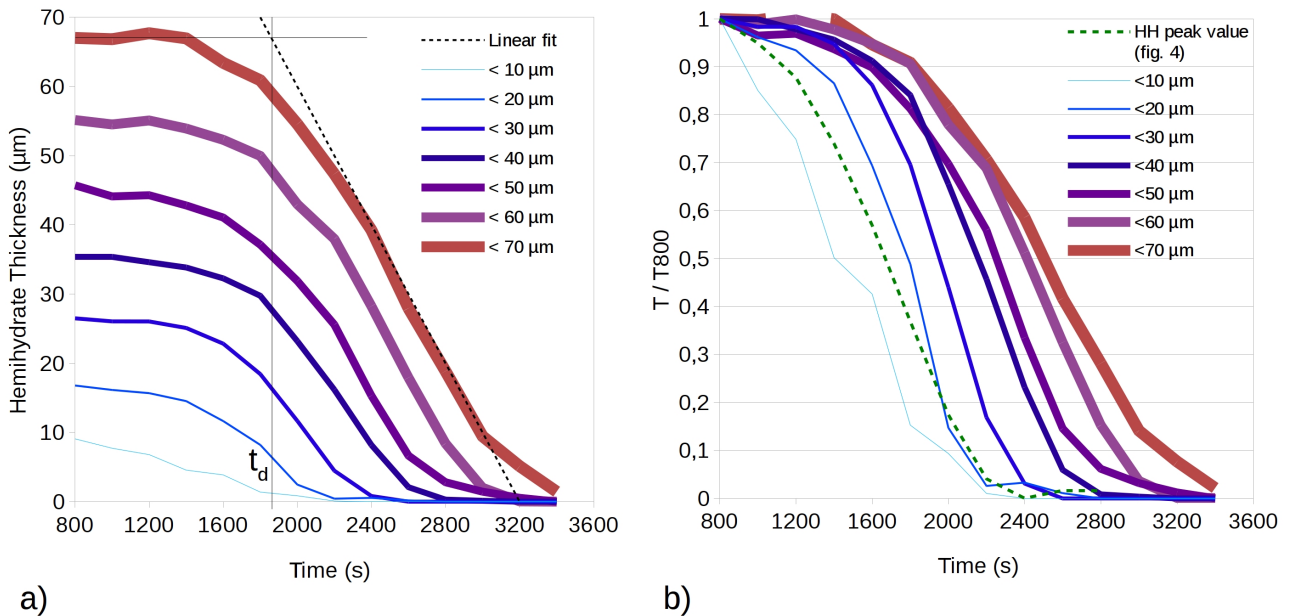
415 Fig. 6. Gray values profile along the red line taken at different setting times. The measurement was  
416 focused on a large HH particle (70  $\mu\text{m}$  thick).

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418 The evolution within time of the mean thickness of 70 different HH particles is presented in Figure  
419 7a and confirms statistically the two individual cases discussed above. Even if, at 800 s, the  
420 dissolution had apparently already started for HH particles of size 20  $\mu\text{m}$  and below, for most of the  
421 largest particles, dissolution had not yet started. Except for the smallest particles, an incubation time  
422  $t_d$  could indeed be defined (intersection of the two tangent lines, see Figure 7a), during which the  
423 particle thickness remained rather constant. This time was computed for each size class of HH

424 particles and it was shown that  $t_d$  slightly increased with size, except for the largest HH particles, for  
 425 which it was equal to 1820 s (Table 2). After  $t_d$ , the dissolution speed started to increase, slowly  
 426 first, then reached a constant rate (steady state of dissolution) and finally decreased again just before  
 427 the particles were fully dissolved. The linear part of the curve shown in Figure 7a could be used to  
 428 compute the dissolution speed expressed as the change of the half-thickness versus time ( $dT/2dt$ ).  
 429 The calculated dissolution rates are collected in Table 2. For all particles above 50  $\mu\text{m}$ , rates were  
 430 all around  $1.5 \mu\text{m}\cdot\text{min}^{-1}$ . For HH particles of thicknesses below 40  $\mu\text{m}$ , the dissolution speed  
 431 decreased slightly with size. Note that this parameter was not calculated for the smallest particles  
 432 (below 10  $\mu\text{m}$ ) because their dissolution had obviously started earlier than 800 s.

433



435 Fig. 7. a) HH thickness evolution during setting for different classes of initial particle sizes b)  
 436 Normalized thickness evolution of HH particles (solid lines). The dashed line corresponds to the  
 437 average HH dissolution throughout the whole volume as measured from data of Figure 4 (evolution  
 438 of normalized intensity of HH gray value peak).

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Initial HH particles thickness ( $\mu\text{m}$ )	< 20	< 30	< 40	< 50	< 60	< 70
$dT/2dt$ in the steady state ( $\mu\text{m}\cdot\text{min}^{-1}$ )	0.84	1.08	1.14	1.44	1.5	1.5
Incubation time $t_d$ (seconds)	1500	1600	1690	1780	1820	1820

442

443 Table 2. Dissolution speed of the HH particles in the steady state regime (linear fit from Figure 7a)  
 444 and incubation time  $t_d$  for the different granulometric classes.

445

446

447 To be able to compare the dissolution kinetics of HH particles of different initial thicknesses, the  
 448 dissolution curves plotted in Figure 7 were normalized: Figure 7b illustrates the evolution of  $T/T_{800}$   
 449 – thickness of the HH particle at a given time (denoted  $T$ ) to its value at 800 s (denoted  $T_{800}$ ) – for  
 450 the different HH particle sizes. Also, the global HH dissolution curve shown in Figure 4 is reported  
 451 in dashed line for comparison. It is close to the evolution of HH particles below 20  $\mu\text{m}$ .

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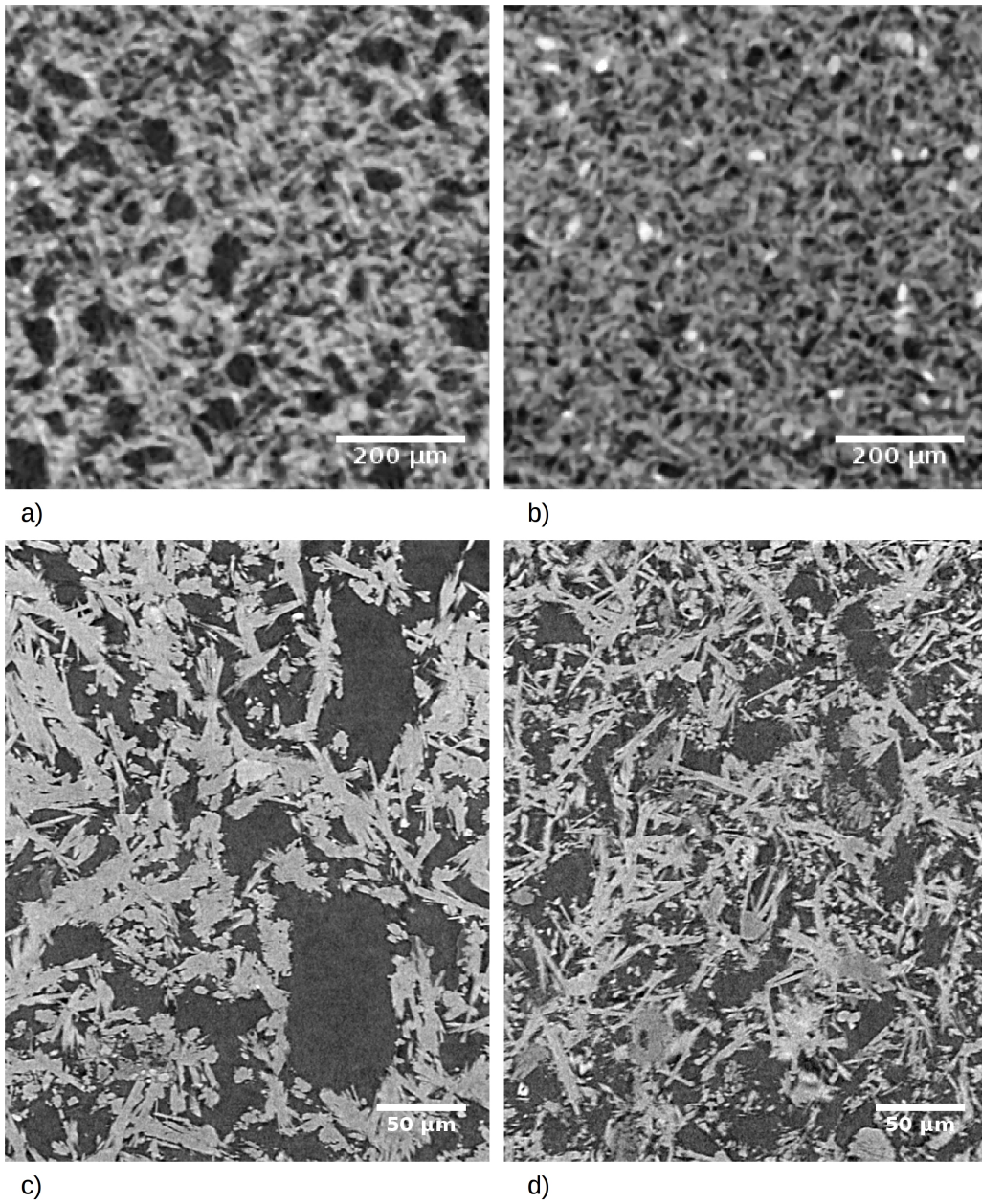
### 454 3.3. Quantitative observation of final microstructure - influence of HH particles 455 granulometry

456

457 Set plasters obtained from the unsieved reference powder, and from HH powder sieved through two  
 458 different mesh sizes ( $40 \mu\text{m} < \text{HH particles} < 63 \mu\text{m}$  and  $\text{HH particles} < 40 \mu\text{m}$ ), were characterized  
 459 after complete setting and drying. Slices of two reconstructed volumes with a voxel size of  $2.5 \mu\text{m}^3$   
 460 are presented in Figure 8a and b. Mesopores observed in the set plaster obtained after sieving of the  
 461 HH powder below  $40 \mu\text{m}$  (Figure 8b) were significantly smaller than mesopores of the reference  
 462 material (Figure 8a). Besides, the global observation of the set material seems to reveal that the  
 463 plaster obtained from the sieved HH powder was more homogeneous as compared to the reference  
 464 plaster. We also noted the presence of a larger volume fraction of impurities (in white) in the sieved  
 465 powder, the volume fraction of which was possibly increased during sieving.



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484 Fig. 8. Reconstructed 2D slices extracted from 3D volumes of set plaster samples obtained with a)  
485 the as-received HH powder and b) HH powder sieved below 40 μm – voxel size of 2.5 μm<sup>3</sup> and set  
486 plasters samples prepared with c) as-received powder and d) powder sieved below 40 μm – voxel  
487 size of 0.4 μm<sup>3</sup>.

488  
489 To better observe the influence of sieving the initial powder at a smaller scale, the microstructures  
490 of both set plasters shown in Figure 8a and b were also observed at a resolution of 0.4 μm<sup>3</sup> per  
491 voxel (Figure 8c and d). This confirmed the critical role of the large HH particles on the formation

492 of mesopores in the final material. For the sieved particles, the resulting gypsum network was more  
493 homogeneous, with numerous individual crystals and thinner bundles of crystals than in the  
494 reference plaster.

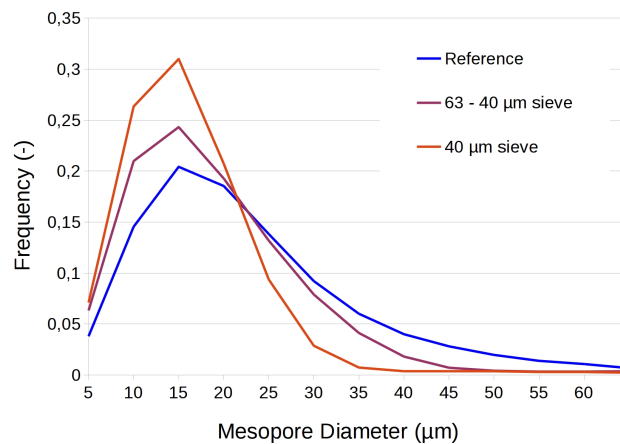
495 For quantification purposes, Figure 9 shows the mesopore size measured using the aforementioned  
496 granulometry technique from the tomographic scans of set plasters acquired with a voxel size of  
497  $2.5 \mu\text{m}^3$  on volumes of  $(1.25 \text{ mm})^3$ . Note that trapped air bubbles were easily excluded from the  
498 porosity analysis thanks to their much larger size (diameter  $> 80 \mu\text{m}$ ) and spherical shape.

499 The results obtained confirmed the influence of the initial HH particle size on the mesoporosity  
500 size: the smaller the initial HH particles, the smaller the resulting mesopores. When HH particles  
501 below  $63 \mu\text{m}$  were used, no mesopores larger than  $50 \mu\text{m}$  were found and when HH particles below  
502  $40 \mu\text{m}$  were used, no mesopores larger than  $40 \mu\text{m}$  were detected.

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512 Fig. 9. Size distribution of mesopores in set plaster for different HH granulometry. « Reference » for  
513 sample prepared with as-received HH powder, «  $< 40 \mu\text{m}$  » for HH sieved below  $40 \mu\text{m}$ .

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515

516 Quantitative analysis of the granulometry of both solid and porous phases (including microporosity  
517 and mesoporosity) was also carried out on the tomographic scans of set plasters acquired at high

518 resolution (voxel size of  $0.4 \mu\text{m}^3$ ). Results are displayed in Figure 10. Data confirmed the finest  
519 microstructure generated by the sieved powder: interestingly, when the HH particles were sieved,  
520 not only the pore size was smaller but the gypsum crystals were also thinner and/or more  
521 individualized (as already shown in Figure 8).

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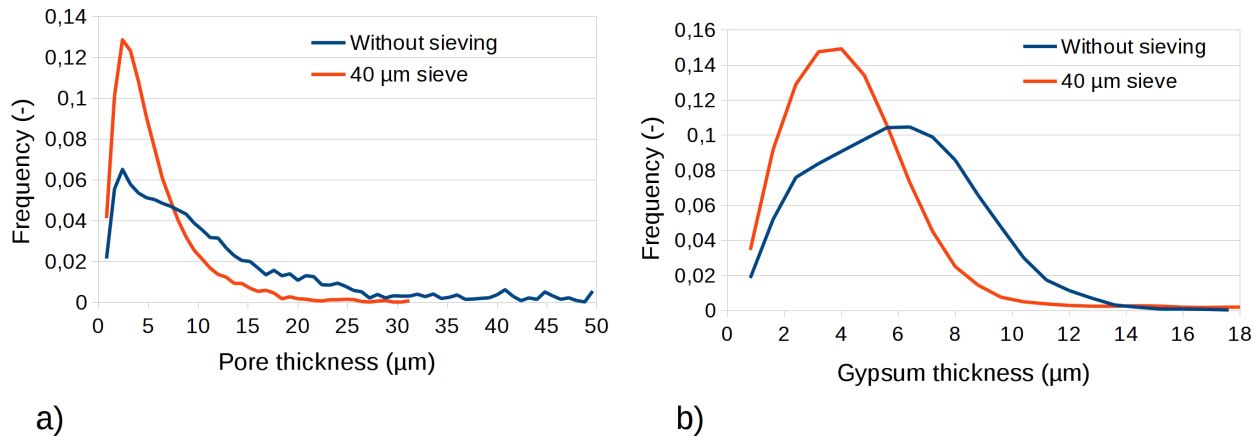


Fig. 10. Granulometry of the porous « phase » (a) and of the gypsum phase (b) measured from high resolution acquisitions ( $0.4 \mu\text{m}^3$  voxel size).

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526 The relative density of both set materials could be estimated by a simple count of the white pixels  
527 after image thresholding of the high resolution images. The relative density for the reference  
528 material was found to be 0.46 compared to 0.51 for the one obtained from the powder sieved below  
529  $40 \mu\text{m}$ , with an analyzed volume of  $300 \times 300 \times 300 \mu\text{m}^3$ . As the W/P ratio was the same for the two  
530 materials, the final density should be exactly the same. The small difference noted could be due to  
531 an increase of impurities after sieving or by a more difficult control of the preparation of the sieved  
532 material, due to the limited amount of powder and to the higher surface to volume ratio of the  
533 sample, favoring water evaporation.

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535

## 536 4. Discussion

537

538 The *in-situ* X-Ray tomographic observations during plaster setting and the quantitative analysis  
539 performed on the reconstructed volumes produced substantial information on the hydration process  
540 and on the resulting microstructure.

541 Figure 11 shows a schematic representation of the microstructural changes observed in Video 1  
542 during plaster setting, starting from 800 s after the contact of HH powder with water (Figure 11a).  
543 No gypsum nuclei could be observed at this stage due to the limitation in spatial resolution.  
544 However, based on the results presented here, it can be assumed that some gypsum crystals were  
545 already formed. The dissolution of HH, beginning with the dissolution of the smallest HH particles,  
546 and the growth of dihydrate inside the surrounding ionic solution occurred simultaneously (Figure  
547 11b). The formation of a network of gypsum needles was gradually observed (Figure 11c) while  
548 locally some large HH undissolved particles were still present confirming the observation by [9]  
549 and [10]. Although the limited resolution of the scanned volumes during hydration does not allow a  
550 direct observation of nucleation and growth of the gypsum crystals, it was clearly observed that  
551 gypsum crystals did not form at the surface of the initially large HH particles, and that an ionic shell  
552 permitting the transport of matter from the dissolving HH particles towards the growing crystals  
553 existed (Figure 11c). The observations showed that the dissolution process was not yet completed  
554 after 3000 s and that part of initially large HH particles still remained (Figure 11c). After setting,  
555 gypsum crystals were not observed where large HH particles were originally located (Figure 11d).  
556 The resulting mesopores had nevertheless a smallest size compared to the HH particles at 800 s  
557 (52% of the initial volume), due to gypsum precipitation in the outlying areas. This is clearly shown  
558 by the evolution of the gray values around HH particles between initial and final times in Figures 5  
559 and 6.

560 It has also been noted that some mesopores located close to entrapped air bubbles began to be filled  
561 with air rather than ionic solution at the last step of hydration (starting from 2200 s in Figure 1).

562 This phenomenon probably arose from the consumption of water during the hydration equation of  
563 HH particles (Eq. 1) inducing a desaturation of large pores. It is commonly encountered in Portland  
564 cement pastes and associated to an important shrinkage due to the very small pore size of this  
565 materials (few nanometers). In our study, the global volume variation of the plaster during setting,  
566 measured via the distance between air bubbles, was negligible. The hydration reaction of gypsum is  
567 accompanied with a 10 % volumetric shrinkage (usually referred to as Le Chatelier contraction),  
568 often counterbalanced by an expansion during gypsum crystal growth [18] as it seems to be the case  
569 in our study.

570 A decrease by 8% of the total volume of entrapped air was observed between the first and the last  
571 volume acquired. Since the inter-bubble distance did not change during hydration, this could be  
572 linked to the formation of gypsum crystals on the edges of trapped air bubble (Figure 11d).

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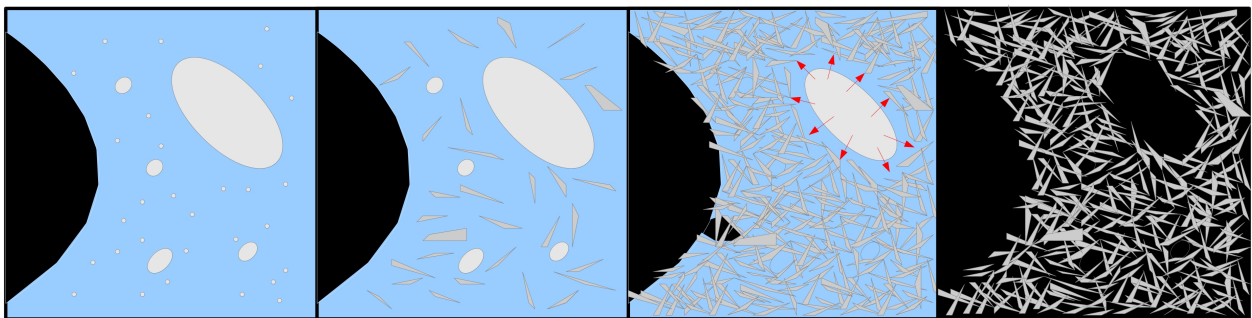


Fig. 11. Schematic representation of the hydration process as monitored by X-Ray tomographic observation (blue : water ; black : entrapped air ; white : HH particles of typical size between a few  $\mu\text{m}$  and tens of  $\mu\text{m}$  ; gray : DH crystals).

575

576

577 Quantitative analysis on the whole volume permitted to compute histograms of the gray values  
578 measured at different times (Figure 3). A logical decrease of peaks associated to HH particles and  
579 ionic solution was observed throughout the setting process (Eq. 1). A concomitant increase of the  
580 peak associated to DH crystals was noted. During setting, this peak shifted towards higher gray

581 values due to gypsum precipitation and densification of the solid matrix. After drying, it showed an  
582 even stronger shift towards high values. The precipitation of gypsum during evaporation of the  
583 remaining water cannot explain such a strong shift. Indeed, a rapid calculation shows that, for the  
584 W/P ratio used here, the precipitation of crystals from the remaining ions would lead to a maximum  
585 1 wt. % increase of gypsum. Nevertheless, this last scan has been acquired in different conditions  
586 than the previous ones. In particular, the presence of water inside the paste during *in-situ*  
587 observations is known to have a potential detrimental effect on the images contrast (because of X-  
588 Ray beam scattering).

589 The microstructural degree of reaction highlighted two distinct regimes (Figure 4). Starting from  
590 800 s, there was an acceleration followed by a slowing down of HH dissolution and DH  
591 precipitation until no more significant changes could be monitored. The times at maximum rates  
592 were slightly different for the two phenomena: DH precipitation was logically delayed compared to  
593 HH dissolution.

594 Regarding the influence of HH particle size, at 800 s, the smallest particles had already begun to  
595 dissolve whereas large particles seemed unaffected (Figure 7). It seems logical that the incubation  
596 time  $t_d$  increased with the HH particle thickness (Table 2), as smaller particles are more unstable due  
597 to their higher surface to volume ratio. Interestingly, the particle size had also an effect on the  
598 dissolution rate, which increased with HH initial thickness (Table 2).

599 Comparing the HH dissolution curve derived from gray value measurements throughout the volume  
600 (Figure 4) with the curves obtained for different ranges of particle sizes showed that the kinetics  
601 measured globally was close to that observed for small particles (Figure 7 b). This can be explained  
602 by the large amount of small particles found in the initial powder, which could not be imaged due to  
603 the spatial resolution of the tomograph used in this study. It seemed indeed that very few particles  
604 of diameter below 20  $\mu\text{m}$  had begun to dissolve at 1200 s (Figure 7), as confirmed by the incubation  
605 times (Table 2). However, the knife setting time of this plaster was equal to 1200 s. This time is  
606 known to correspond to the percolation of the gypsum phase in the microstructure, meaning that the

607 small HH particles (below 20  $\mu\text{m}$ ) controlled the initial strengthening of the paste. This first stage  
608 could unfortunately not thoroughly be studied in these experimental conditions. Nevertheless, this  
609 study shows that the microstructuration of plaster is far from being completed when the knife  
610 setting time is reached and that bigger HH particles also play a key role in this evolution.

611 The granulometry of HH powder had indeed a direct influence on the kinetics of dissolution and  
612 precipitation but also on the pore size observed after setting. The comparison of set gypsum  
613 prepared from as-received HH powder and HH powder sieved either between 63 and 40  $\mu\text{m}$  or  
614 below 40  $\mu\text{m}$  clearly confirmed the strong correlation between HH particles size distribution and  
615 mesopore size distribution (Figure 9). This could lead to a possible control of mesopore sizes in the  
616 set material. Although the relative density measured for the reference material and for the one  
617 obtained after powder sieving was approximately the same, the microstructure of dried plaster  
618 obtained with sieved powder was more homogeneous (Figure 8), due to both the decrease of the  
619 mesopores size and to the crystallization of thinner or/and better individualized gypsum crystals.  
620 Indeed, the gypsum crystals size distribution was wider when as-received HH particles were used  
621 (Figure 10b). Such a behavior may be explained by the difference in dissolution times depending on  
622 the size of HH powder as emphasized in this work. For a narrow size distribution of small HH  
623 particle, the dissolution and subsequent precipitation of gypsum crystals probably occurred over a  
624 limited time range, leading to a network of random individualized crystals. For a wide HH size  
625 distribution, the dissolution of the smallest particles led to the formation of an initial network of  
626 gypsum (controlling the knife setting time). Then, the dissolution of the largest particles released  
627 more calcium and sulfate ions leading to additional precipitation of gypsum crystals upon the  
628 existing network, as monitored by the *in-situ* observation of the setting. To the best of our  
629 knowledge, it is the first time that a study reports and quantifies that the control of the reactant  
630 powder size distribution could permit to regulate the thickness and the agglomeration state of the  
631 growing gypsum crystals. This appears therefore to be an interesting way of tuning the final  
632 mechanical properties of the set plaster [19].

633 It cannot not be completely ensured that the X-Ray beam had no influence on the setting kinetics of  
634 plaster. Nevertheless, the impact on the setting process is likely to be negligible. Thermal effects for  
635 example, are probably very small compared to the exothermicity of the setting reaction.

636 Also, additional work is required to know if, to get an homogeneous microstructure, the  
637 determining characteristics of the HH reactive powder is the mean particle size, the width of the  
638 particle size distribution, or both.

639 The results presented in this paper could feed analytical or numerical models of plaster hydration  
640 [10,20,21], even if single gypsum crystals could not be individualized due to the resolution used  
641 here.

642 X-Ray computed tomography is becoming a very powerful technique to monitor the  
643 microstructuration of setting materials but this type of measurements requires high resolution and  
644 low noise images. Both a higher spatial resolution and a quicker acquisition would permit to get  
645 more insights into the setting process and especially into the first stages of the process. Fast X-Ray  
646 computed tomography experiments could be done using synchrotron, which, owing to the high flux  
647 of high-energy X-Ray available, would enable a complete high resolution (1  $\mu\text{m}$ ) tomography  
648 acquisition to be performed within a few seconds, instead of several minutes.

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650

## 651 5. Conclusions

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653 The real time imaging of the plaster setting was carried out for the first time, with a paste rheology  
654 close to an industrial one.

655 The observation of both the dissolution of HH and the formation of a network of gypsum crystals  
656 was possible. A critical role played by HH particle size was evidenced: small HH particles were  
657 rapidly dissolved, whereas large particles were still not completely dissolved long after the material  
658 had started to set. It was also shown that the final dissolution of the largest particles led to the



659 formation of mesopores in the hydrated material. To our knowledge, this is the first time that the  
660 origin of the presence of such mesopores in set plaster is provided, thanks to *in-situ* experiments.  
661 3D image analysis was performed to obtain quantitative information both on a local scale (selected  
662 particles) and on a global scale (whole volume). A local dissolution front speed ranging from  
663 1.5  $\mu\text{m}/\text{min}$  for large particles to 0.8  $\mu\text{m}/\text{min}$  for small ones and a degree of setting reaction based  
664 on microstructural evolution were computed. These data could be used in a future study for  
665 comparison with the chemical degree of reaction and the development of strength during setting.  
666 Another clear outcome of this study is the evidence of the possibility to play on the morphology of  
667 the set material by the granulometry of the starting powder, in order to target better mechanical  
668 properties at a similar porosity.

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## 736 Figure Captions

737

738 1. Microstructural changes during the setting of plaster. Reconstructed 2D slices extracted from the  
739 3D volumes acquired during the *in-situ* tomography experiments, between 800 and 3000 seconds.  
740 The last slice (24h) was obtained after drying at 45°C.

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742 2. 3D rendering of a) HH particle (800 s), length = 123  $\mu\text{m}$  b) Resulting mesopore after setting and  
743 drying (24 h), length = 113  $\mu\text{m}$ .

744

745 3. Histograms of the gray values measured in the volumes for different times during setting and  
746 then subsequent drying at 45°C.

747

748 4. Evolution of the intensity of the HH peak (dashed line in Figure 3, gray level value = 0.31) and of  
749 the gypsum peak (dashed line in Figure 3, gray level value = 0.21).

750

751 5. Gray values profile along the red line taken at different setting times. The measurement was  
752 focused on a small HH particle (20  $\mu\text{m}$  thick).

753

754 6. Gray values profile along the red line taken at different setting times. The measurement was  
755 focused on a large HH particle (70  $\mu\text{m}$  thick).

756

757 7. a) HH thickness evolution during setting for different classes of initial particle sizes b)  
758 Normalized thickness evolution of HH particles (solid lines). The dashed line corresponds to the  
759 average HH dissolution throughout the whole volume as measured from data of Figure 4 (evolution  
760 of normalized intensity of HH gray value peak).

761

762 8. Reconstructed 2D slices extracted from 3D volumes of set plaster samples obtained with a) the  
763 as-received HH powder and b) HH powder sieved below 40  $\mu\text{m}$  – voxel size of 2.5  $\mu\text{m}^3$  and set  
764 plasters samples prepared with c) as-received powder and d) powder sieved below 40  $\mu\text{m}$  – voxel  
765 size of 0.4  $\mu\text{m}^3$ .

766

767 9. Size distribution of mesopores in set plaster for different HH granulometry. « Reference » for  
768 sample prepared with as-received HH powder, « < 40  $\mu\text{m}$  » for HH sieved below 40  $\mu\text{m}$ .

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770 10. Granulometry of the porous « phase » (a) and of the gypsum phase (b) measured from high  
771 resolution acquisitions (0.4  $\mu\text{m}^3$  voxel size).

772

773 11. Schematic representation of the hydration process as monitored by X-Ray tomographic  
774 observation (blue : water ; black : entrapped air ; white : HH particles of typical size between a  
775 few  $\mu\text{m}$  and tens of  $\mu\text{m}$  ; gray : DH crystals).

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## 778 Supplementary Online Materials

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780 Video 1: time lapse movie of plaster setting