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1 **Synchrotron X-ray micro-tomography investigation of the early hydration of blended cements: a**  
2 **case study on CaCl<sub>2</sub>-accelerated slag-based blended cements**

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14  
15 **Abstract**

16 *In situ* X-ray Micro-Tomography (XMT) analyses with a pixel size of 0.325 μm were conducted on  
17 slag-based blended cements containing 75% of Ground-Granulated Blast-Furnace Slags (GGBS) and  
18 25% of Ordinary Portland Cement (OPC), with or without CaCl<sub>2</sub> acceleration. Results show the  
19 identification of the main cementitious phases and the need to perform data repeatability tests in order  
20 to allow their quantification. Investigation of the early hydration during the first 31 h of hydration by  
21 image subtraction showed (i) the dissolution of OPC/GGBS, (ii) the precipitation of hydrates including  
22 C-S-H, (iii) the accelerating effect of CaCl<sub>2</sub>, and (iv) phase-identification based on their specific grey  
23 level.

24  
25 **Keywords:** *In situ* X-ray Computed Micro-Tomography, low-carbon cement, early hydration,  
26 microstructure, repeatability, image subtraction.

27  
28  
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## 31 I. Introduction

32 Blended cements with high substitution rates of Ordinary Portland Cement (OPC) by  
33 Supplementary Cementitious Materials (SCMs) have the potential to significantly lower CO<sub>2</sub> emissions  
34 in the construction industry. Typical SCMs include blast-furnace slag, fly ash, silica fume, natural  
35 pozzolans, metakaolin and limestone [1–4]. At high substitution rates (>20-30%), the early strength  
36 development of blended cements is, however, reduced compared to plain OPC, because most SCMs  
37 have slower hydration rates than clinker phases [5,6]. Accelerating admixtures such as calcium chloride  
38 (CaCl<sub>2</sub>) improve the early age reactivity and microstructure development of blended cements [7–10].

39 Cement hydration is a coupled dissolution/precipitation reaction, where clinker (C<sub>3</sub>S, C<sub>2</sub>S, C<sub>3</sub>A,  
40 C<sub>4</sub>AF) and SCM phases dissolve in a basic medium to precipitate hydrate minerals such as C-S-H,  
41 portlandite (CH), ettringite and AFm in the pore space. Traditional tools to investigate the hydration  
42 reaction include Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD), solid-state Nuclear  
43 Magnetic Resonance spectroscopy (NMR), Thermogravimetric analyses (TGA), isothermal calorimetry  
44 and mercury intrusion porosimetry (MIP) [11]. These techniques are suitable for observing, identifying  
45 and/or quantifying the evolution of the unreacted phases, hydrates and porosity during hydration.  
46 However, at early ages of hydration (i.e., during the first 48 h), the use of conventional tools is limited  
47 by sample preparation as (i) early age blended cement pastes have not hardened enough to be cut,  
48 polished and resined for SEM observation [12], (ii) the physicochemical reactions progress quickly,  
49 which requires a hydration stoppage (usually leading to microstructure alterations) [13], and (iii)  
50 carbonation, i.e., reaction between hydrated phases and CO<sub>2</sub>, is a supplementary source of degradation  
51 of the original matrix [11]. In addition, SCM hydration is sometimes difficult to monitor and to  
52 discriminate from that of OPC, as dissolution of both SCM and OPC leads to similar hydration products  
53 (e.g., C-S-H), and because most SCMs are amorphous alumino-silicates hardly detectable by common  
54 lab devices [3]. In theory, an ideal tool to investigate the early hydration of blended cements would  
55 involve (i) an *in situ* analysis, and thus no hydration stoppage, (ii) short acquisition times, and (iii) the  
56 possibility of differentiating between the SCM and OPC reactions.

57 Synchrotron X-ray Micro-Tomography (XMT) allows 3D visualization of a given sample using  
58 a pixel size of about 1 μm under *in situ* conditions. This technique has been used to study the  
59 microstructure, degree of hydration, permeability, fracturing, and damage of various cements at later  
60 stages of hydration [12,14–17]. A 3D volume of a sample is reconstructed from thousands of 2D images  
61 recorded at various angles [18–21]. The 2D projections, also called radiographs, record the variations in  
62 the X-ray linear attenuation coefficients  $\mu$ , which are dependent on the incident X-ray beam energy, and  
63 elemental composition and density of the sample components. In cements, Gastaldi et al., 2012 have  
64 reported a  $\mu$  value of 1.8 cm<sup>-1</sup> for water, 17.5 cm<sup>-1</sup> for ettringite, 32.0 cm<sup>-1</sup> for C-S-H, 44.8 cm<sup>-1</sup> for  
65 portlandite, 55.8 cm<sup>-1</sup> for C<sub>3</sub>A, 63.1 cm<sup>-1</sup> for C<sub>2</sub>S, 65.4 cm<sup>-1</sup> for C<sub>3</sub>S, and 102.6 cm<sup>-1</sup> for C<sub>4</sub>AF, for an

66 incident beam energy of 14 keV [22]. The relatively close  $\mu$  values imply that most of the phases have  
67 low grey level contrasts on the XMT images and corresponding histograms. Nevertheless, the porosity,  
68 hydration products, and anhydrous phases can be differentiated.

69 Lately, XMT has been used to study the early hydration of various highly reactive cements  
70 [12,22–24]. In most studies, the same samples are scanned at fixed time intervals during the first day(s)  
71 of hydration, and the resulting XMT images and corresponding grey level histograms are compared to  
72 evidence (i) the progressive dissolution of clinker phases, (ii) the precipitation of hydrates, and (iii) the  
73 reduction of porosity. For example, Chotard et al., 2003 studied the microstructure development of a  
74 calcium aluminate cement between 1 and 24 h of hydration, and showed that the X-ray linear attenuation  
75 coefficient varied with the hydration time. Helfen et al., 2005 investigated the formation and  
76 development of microcracks and pores in an OPC paste between 8.4 and 16.5 h of hydration. Gastaldi  
77 et al., 2012 monitored the precipitation and dissolution of cementitious phases from 1 to 12 h on three  
78 cement pastes (OPC, calcium sulfoaluminate cement (CSA) and an OPC/CSA mix), and proposed a new  
79 method to determine the specific grey levels of various cementitious products in the histograms. Finally,  
80 Parisatto et al., 2015 evaluated the influence of the water/cement ratio on two OPC pastes, from 1.75 to  
81 71 h of hydration. Most of the time, the microstructural changes were evidenced on histograms because  
82 of the complexity and heterogeneity of the materials in the XMT images. Image segmentation was  
83 performed in order to quantify the amount of cementitious phases on a Representative Elementary  
84 Volume (REV), which *a priori* represents the structural and macroscopic properties of the material  
85 [12,14,25–28].

86 From the above-cited literature, XMT appeared ready for common use to monitor early  
87 hydration. Therefore, in the present study, XMT was used to investigate more complex and slower  
88 reacting materials, i.e. blended cements containing 75% of Ground-Granulated Blast-furnace Slags  
89 (GGBS) as SCM and 25% of OPC, with or without  $\text{CaCl}_2$  addition as an accelerator. The samples were  
90 cast into 300  $\mu\text{m}$  capillaries and scanned during the first 31 h of hydration, resulting in XMT images  
91 with a pixel size of 0.325  $\mu\text{m}$ . The images were first qualitatively analyzed by morphological and  
92 histogram analyses in order to identify the cementitious phases. Then, the REV size was determined in  
93 view of phase quantification. Data repeatability tests were carried out in order to evaluate the method  
94 error. Early hydration was further investigated by based on histograms and image comparisons of  
95 samples scanned at different hydration times. Finally, image subtraction was used to evidence the  
96 hydration reactions, such as the dissolution of the anhydrous phases, precipitation of hydrates, as well  
97 as their specificities (spatial distributions, specific grey levels in the histograms).

98

## II. Materials & Methods

### 2.1. Sample preparation

GGBS (produced by ArcelorMittal, and ground/commercialized by Ecocem Materials) and OPC (CEM I 52.5R, Lafarge) were used as raw materials to prepare slag-blended cement pastes composed of 75% GGBS and 25% OPC with a water/binder ratio of 0.4 by mass. Powders were mixed and hand-stirred for 2 min after addition of water. The mixing water was distilled water for the non-accelerated samples, and a 1 wt.%  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  solution (Sigma-Aldrich) for the accelerated samples [29]. After homogenization, the pastes were cast in 300  $\mu\text{m}$  borosilicate capillaries by applying slight underpressure (WJM-Glas, Müller GmbH) 6 hours or 24 hours prior to the measurements. The capillaries were then sealed and stuck into sample holders.

Six samples were prepared to represent the desired compositions and hydration times (Table 1). Two of them were hydrated for 6 h or 24 h without  $\text{CaCl}_2$  activation (S75\_6h and S75\_24h) and two replicates (R) were prepared in order to estimate the method error (S75\_6h\_R and S75\_24h\_R). Two samples were accelerated with 1 wt.% of  $\text{CaCl}_2$  and hydrated for 6 h or 24 h (S75\_ $\text{CaCl}_2$ \_6h and S75\_ $\text{CaCl}_2$ \_24h). The 6 capillaries were rescanned about six hours after the initial scan in order to monitor the early hydration. The suffix “rescan+xh” was added to their name, where xh refers to time elapsed after the initial scan.

115

**Table 1:** List of samples

Name of samples	Hydration time of initial scan	$\text{CaCl}_2$ activation	Name of rescans	Hydration time of rescan
S75_6h	6h	No	S75_6h_rescan+5h30	11h30
S75_24h	24h	No	S75_24h_rescan+7h15	31h15
S75_6h_R	6h	No	S75_6h_R_rescan+5h05	11h05
S75_24h_R	24h	No	S75_24h_R_rescan+7h15	31h15
S75_ $\text{CaCl}_2$ _6h	6h	Yes	S75_ $\text{CaCl}_2$ _6h_rescan+5h20	11h20
S75_ $\text{CaCl}_2$ _24h	24h	Yes	S75_ $\text{CaCl}_2$ _24h_rescan+6h50	30h50

116

### 2.2. X-ray micro-tomography imaging

XMT analyses were carried out at the Swiss Light Source (SLS) of the Paul Scherrer Institut, Switzerland, on the TOMCAT beamline. A beam energy of 21 keV was chosen for imaging all samples, providing a high photon flux that permits fast scans. Transmitted X-ray photons were converted into visible light using a 20  $\mu\text{m}$  LuAG:Ce Scintillator, and 1501 projections were taken over an angular range of 180° with an exposure time of 180 ms each. This setting led to a scanning time of about 15 min per sample, and enabled quick mapping of the hydration reaction. Diffraction-limited microscope optics and

123

124 a PCO.Edge 5.5 camera were used to magnify ( $\times 20$ ) and capture the radiographs. Images were corrected  
125 for the noise of the camera (dark field subtraction) and for inhomogeneities of the beam (divided by flat  
126 field). Phase retrieval [30] was also applied prior to the tomography reconstruction [31] using a Paganin  
127 algorithm. A distance of 5 mm and a delta/beta ratio of 100 were chosen for the reconstruction. Each  
128 reconstruction was of  $2560 \times 2560 \times 2160$  voxels with isotropic size of  $0.325 \mu\text{m}$ . This image resolution  
129 is about 5 and 1.5 times higher than that reported in other XMT studies on slag-blended cements [16,32–  
130 36] and OPC pastes [12,14,25,28], respectively.

### 131 *2.3. XMT data processing*

132 The reconstructed volumes were processed using the Avizo<sup>®</sup> software on a Dell Precision T3600  
133 workstation (64 GB RAM, 6 GB Nvidia graphics card). The 16-bit data sets were first normalized and  
134 reduced to 8-bit data sets in order to reduce the amount of data to be processed. During normalization,  
135 the grey level ranges were calibrated between initial scans and rescanned images using a linear  
136 interpolation procedure, assigning fixed values to the exterior air signal and the GGBS signal maximum  
137 peaks. After 8-bit conversion, the calibrated greyscale of the images ranged from 0 to 255. To allow for  
138 further image comparison, each image pair was then registered in the same (x,y,z) coordinate system  
139 using a rigid-body transformation based on mutual information optimizer. Finally, image subtraction  
140 was performed twofold, either by subtracting the initial scan to the rescan image or vice-versa, thus  
141 offering the possibility to distinguish the solid phases that disappeared from the ones that formed during  
142 the hydration process.

143 Visualization and quantification of the OPC/GGBS dissolution, removal of transitional dense phase in  
144 the pore space, and precipitation of portlandite and hydrates\* was performed on subvolumes of  $200 \times$   
145  $200 \times 600 \mu\text{m}$  after image subtraction and a simple thresholding method (see section 3.3.1 for details).  
146 Note that hydrates\* refers to all hydrate phases except portlandite, e.g. C-S-H, AFm and ettringite for  
147 slag based blended cements. The upper and lower thresholding values were chosen manually in order to  
148 extract the phase(s) of interest identified based on their morphology, and minimize the contribution of  
149 the other phases due to overlapping grey levels.

## 150 **III. Results and Discussion**

### 151 **3.1. Preliminary study of XMT images**

#### 152 *3.1.1. Identification of phases*

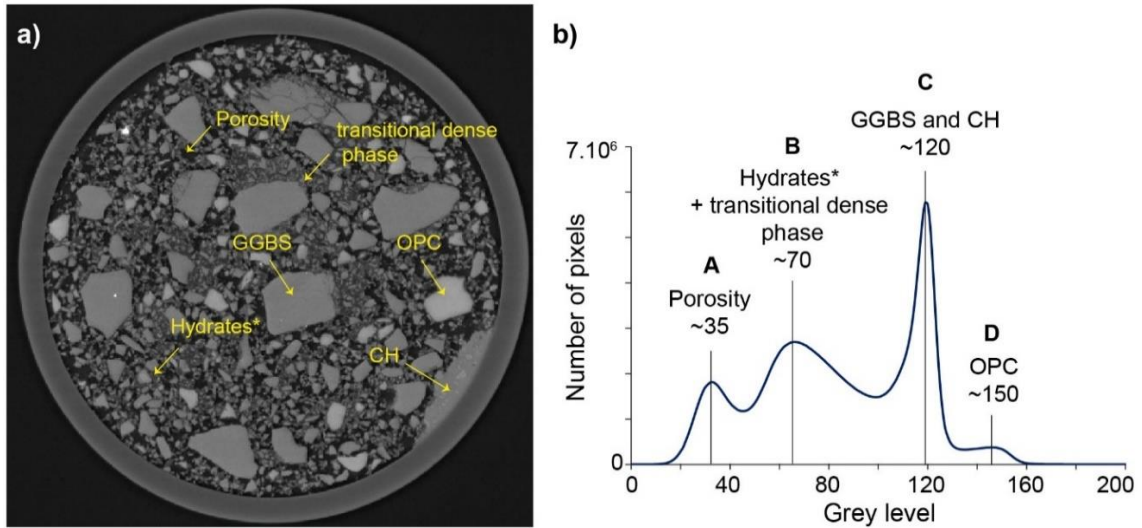
153 Figure 1 shows a slice of slag-blended cement with the corresponding histogram extracted from the  
154 subvolume of  $200 \times 200 \times 600 \mu\text{m}$ . The cementitious phases were identified by morphological analysis  
155 and comparison of histograms with the literature [14,22,37]. Seven main phases were identified:

- 156 • porosity in dark grey level (air bubbles, water filled pore network),

- 157 • hydrates\* in fairly dark grey level (small interconnected particles in the pore network),
- 158 • portlandite in intermediate grey level (zones of irregular shape with a grey level in the GGBS
- 159 range),
- 160 • GGBS in light grey (angular grains of various particle sizes),
- 161 • OPC in very light grey level (rounded grains),
- 162 • and metallic iron particles in white (local bright spots).

163 In addition, a transitional dense phase was systematically observed in the pore space, except for  
164 S75\_24h (see further, the blue arrows in Figure 3.a). This phase exhibited an irregular shape and was  
165 distributed very heterogeneously in the samples. It had an intensity in the darker range of the grey levels  
166 of hydrates\*, and appeared as a grey background in the pore network. Only a high magnification allowed  
167 it to be distinguished from hydrates\*. Analysis of the later samples (Figure 3.b) showed that the phase  
168 disappeared in all samples after the first few hours of hydration, while the hydrates remained in place.  
169 After 31 h of hydration, the transitional dense phase was no longer present in the rescanned samples.  
170 Therefore, it is unlikely that this phase consisted of solid hydrates. According to its morphology,  
171 behavior, and relatively high absorption coefficient, the transitional dense phase was attributed to a  
172 mobile pore water enriched in ions or nuclei. As far as we know, no previous study conducted on OPC  
173 or slag-based cements has reported this transitional dense phase. It may form according to the following  
174 processes: first of all, the high proportion of GGBS (75 wt.%) and its slow dissolution rates compared  
175 to clinker phases allows Ca and Si ions to diffuse into the pore space, so they do not necessarily  
176 precipitate around slag grains [38]. This makes stronger oversaturation and nucleation in solution  
177 possible. Secondly, the resolution here was 5 times higher than that reported in other slag-based cement  
178 studies [16,32–36,39]. Therefore, other authors may not have observed it, or may have confused it with  
179 hydrates\*.

180 The histograms derived from image analysis of the subvolumes were composed of four major peaks  
181 centered around grey levels of 35 for porosity (peak A), 70 for hydrates and transitional dense phase  
182 (peak B), 120 for GGBS and portlandite (peak C), and 150 for OPC (peak D). The respective phases  
183 overlap strongly in the histograms. For example, GGBS and CH are strongly convoluted and no  
184 thresholding method could differentiate between the two phases. The peak areas in the histogram are  
185 proportional to the amounts of corresponding phases in the samples.



186

187 **Figure 1:** Identification of the cementitious phases in the XMT image of S75\_CaCl<sub>2</sub>\_6h and in the  
 188 corresponding histogram.

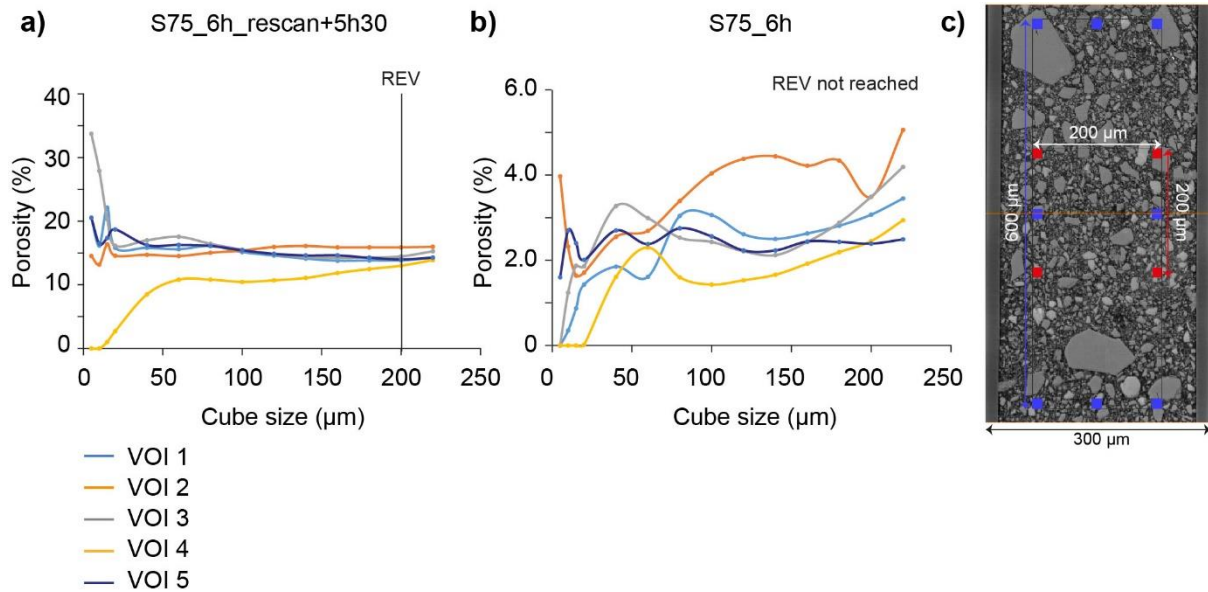
189 *3.1.2. Determination of the Representative Elementary Volume (REV)*

190 XMT often produces large datasets. In order to reduce the amount of data to be processed and  
 191 to avoid edge effects, a smaller volume, called Representative Elementary Volume (REV) can be  
 192 extracted. This volume corresponds to the smallest volume representing the structural and macroscopic  
 193 properties of a given material. In practice, several techniques allow the REV size to be determined  
 194 [40,41]. In this study, the methodology of Wan et al., 2014 was applied. This method measures the  
 195 porosity in cubic volumes of increasing size, starting from a random point in the capillary. The  
 196 measurement is performed multiple times in order to evaluate the smallest volume at which porosity  
 197 converges to a constant value. This volume defines the REV.

198 Figure 2.a. shows an example of the REV determination on S75\_6h\_rescan+5h30. The porosity  
 199 was measured by thresholding the fluid (porosity) from the solid phase in the histogram (grey level  
 200 = 50). The cube edge size was increased progressively from 5  $\mu\text{m}$  to 220  $\mu\text{m}$  from a random point. The  
 201 procedure was repeated 5 times in different areas of the sample. The porosity converged from an edge  
 202 size of 100  $\mu\text{m}$  onwards, and stabilized around 200  $\mu\text{m}$ . This value corresponds to the REV size, which  
 203 is equal to a cubic volume of about  $8.10^6 \mu\text{m}^3$  and a mean porosity of 14% (Figure 2.c, red volume).  
 204 Note that the REV size is similar to that calculated in previous studies [14,36]. However, it is worth  
 205 mentioning that REV could not be determined in the initial scans of this sample (Figure 2.b) due to the  
 206 presence of the transitional dense phase in the pore space, which led to an underestimation of the porosity  
 207 since its grey level fell into the range of hydrates\* (while it should account for porosity). In the initial  
 208 scan, no convergence was found for volumes with up to 220  $\mu\text{m}$  edge length; the calculated mean  
 209 porosities were 3 to 6 times lower (2.5 to 5.0 %) than in the rescan (14%). Even by further increasing  
 210 the subvolume size to  $200 \times 200 \times 600 \mu\text{m}$  a porosity of 3.3 % was calculated, taking almost the whole



211 capillary into account but still avoiding edge effects (Figure 2.c, blue volume). We decided to extract  
 212 the histograms on subvolumes of  $200 \times 200 \times 600 \mu\text{m}$  to compare the initial scan and the rescanned  
 213 samples in order to avoid artifacts due to the heterogeneous distribution of the transitional dense phase.



214

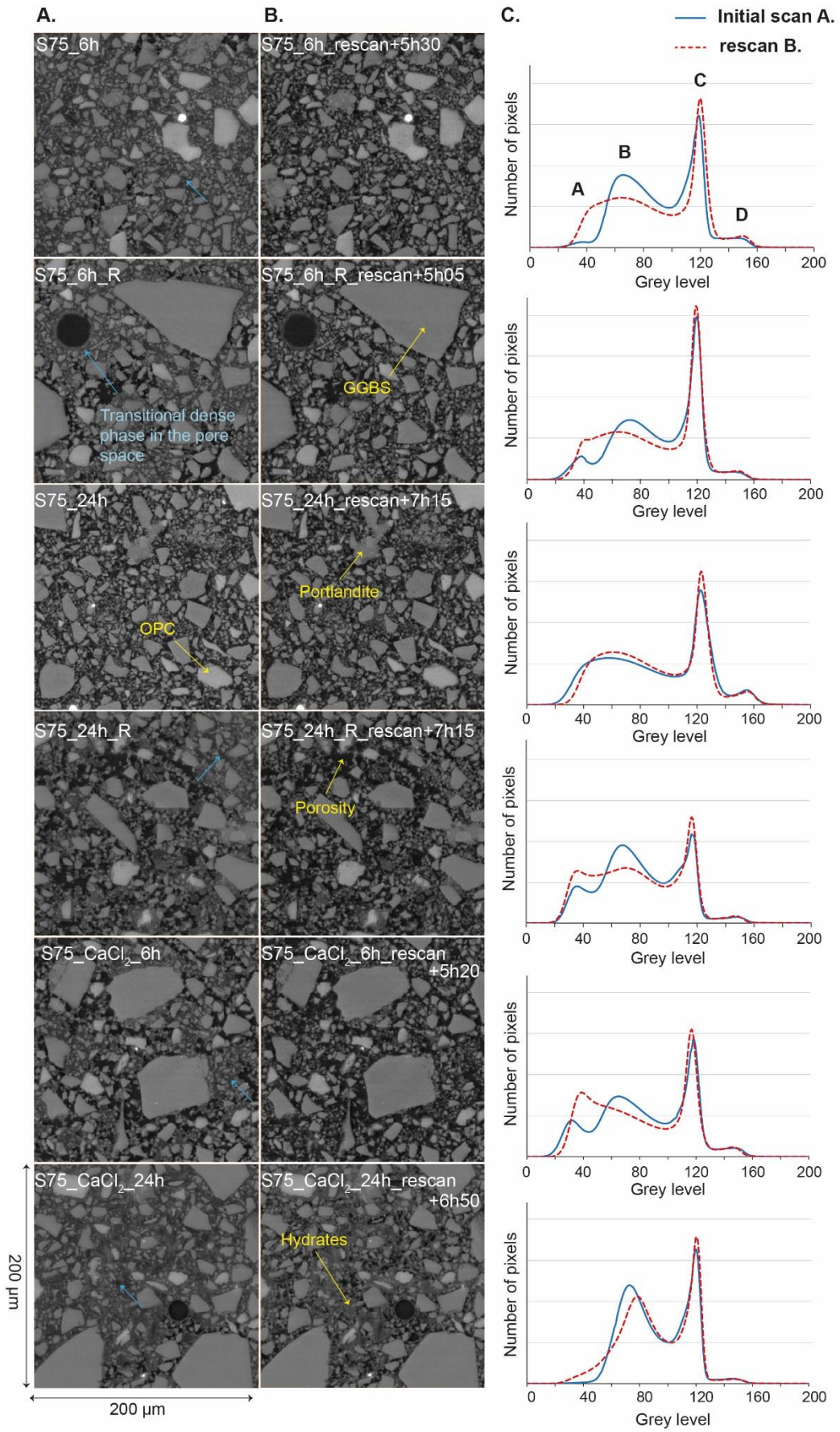
215 **Figure 2:** a) Determination of the REV size on S75\_6h\_rescan+5h30, according to the methodology  
 216 of Wan et al., 2014 (VOI: Volume Of Interest). b) Attempt at REV determination on S75\_6h, which  
 217 contained a large amount of transitional dense phase in the pore space. c) Representation of the two  
 218 subvolumes of  $200 \times 200 \times 600 \mu\text{m}$  (blue) and  $200 \times 200 \times 200 \mu\text{m}$  (red: REV).

### 219 3.1.3. Evaluation of experiment repeatability

220 Repeatability refers to the closeness of the agreement between several tests carried out under similar  
 221 conditions [42]. In this study, two samples (S75\_6h and S75\_24h) were replicated (S75\_6h\_R and  
 222 S75\_24h\_R) in order to check the repeatability of the experiment, and because data repeatability is rarely  
 223 reported in the literature. Figure 3, lines 1 to 4, shows the initial scan and rescanned slices of these  
 224 samples, and their corresponding histograms. Differences in peak height of about 20% for peaks B, C,  
 225 and D, and of about 80% for peak A were observed between S75\_6h and S75\_6h\_R. In S75\_24h, the  
 226 peaks A and B were not distinguishable, while there were two distinct peaks in S75\_24h\_R. In addition,  
 227 peak C was around 15% higher in S75\_24h than in S75\_24h\_R, but thinner. Surprisingly, this means  
 228 that two samples prepared in two different capillaries showed substantial differences in the fluid and  
 229 mineral phase distribution despite the fact that REV was reached. This implies that comparison of  
 230 histograms and absolute quantifications were limited to variations greater than the measurement error.

231 Two reasons may explain the lack of data repeatability. First of all, the heterogeneous distribution and  
 232 variable amount of the transitional dense phase in the pore space may have induced variations in the  
 233 intensity of peak B. However, this explanation cannot account for the variations of peaks C and D, as

234 these peaks are not correlated to the presence of the transitional dense phase. The second reason may  
235 arise from the small size of the capillaries (300  $\mu\text{m}$ ), which may have lowered the paste homogenization  
236 and prevented the sample preparation to be repeatable. However, glass capillaries of few hundred  
237 micrometers are regularly used in the literature, resulting in the use of regions of interest smaller or  
238 similar to the subvolume size (200  $\times$  200  $\times$  600  $\mu\text{m}$ ) used in this study for phase quantifications  
239 [12,14,22,25]. Therefore, our experimental methodology can be considered in line with that reported in  
240 the literature. Our results should encourage future studies to control their data repeatability in order to  
241 allow for quantitative comparisons. In our case, only qualitative analyses were performed.



243 **Figure 3:** Influence of the hydration time on the XMT images and histograms: a) Initial scan  
244 images, b) rescan images, and c) corresponding histograms taken from subvolumes of  $200 \times 200 \times 600$   
245  $\mu\text{m}$ . Note that the replicates S75\_6h\_R and S75\_24h\_R do not show the same histogram shapes than  
246 the original samples S75\_6h and S75\_24h, respectively.

### 247 **3.2 Investigation of the early hydration of blended cements from histograms and image** 248 **comparison**

249 Early hydration of blended cements was investigated by histogram and image comparison of  
250 samples scanned at different hydration ages during the first 31 h of hydration. Since no data repeatability  
251 was obtained, no phase quantification was attempted.

252 Rescans in time and space are useful to monitor the evolution of a single sample during hydration.  
253 Indeed, under this configuration, changes in the histogram peak area and shape result from the evolution  
254 of sample mineralogy/chemistry, and not from variations induced by inter-sample variability. Figure 3  
255 compares the XMT images of the initial samples (column a), rescanned samples (column b), and  
256 corresponding histograms (column c). The first two lines compare the non-accelerated replicates after 6  
257 h and 11 h of hydration, the two following lines compare the non-accelerated replicates after 24 h and  
258 31 h of hydration, and the last two lines the  $\text{CaCl}_2$ -accelerated samples after 6 h and 11 h, and 24 h and  
259 31 h of hydration. The initial scans and rescanned images of each sample show little evolution in the  
260 grey level distribution and therefore give little information on the hydration reactions. Only the  
261 disappearance of the transitional dense phase in the pore space can be identified (blue arrows). Since the  
262 transitional dense phase has a grey level in the range of hydrates\* (but, theoretically, should account for  
263 porosity), its removal decreases the intensity of peak B, and increases the intensity of peak A in the  
264 histograms, leading to the apparent contradiction that older samples contain less hydrates. Information  
265 about the precipitation of hydrates\* was therefore lost.

266 Following the dissolution of GGBS/OPC was also difficult, as the XMT images did not show any  
267 major changes in particle size during hydration, and no evidence of GGBS/OPC dissolution was  
268 observable on the histograms: the intensity of peak C increased during hydration but sharpened, leading  
269 to similar peak area, and the intensity of peak D did not show significant variations on either the  
270 accelerated or non-accelerated samples. Therefore, image and histogram comparison of rescanned  
271 samples did not allow the early hydration to be monitored due to the complex phase assemblage and  
272 slow hydration rates of the materials.

### 273 **3.3. Image subtraction: an alternative method to reveal (blended) cement hydration**

#### 274 *3.3.1. Principle of image subtraction*

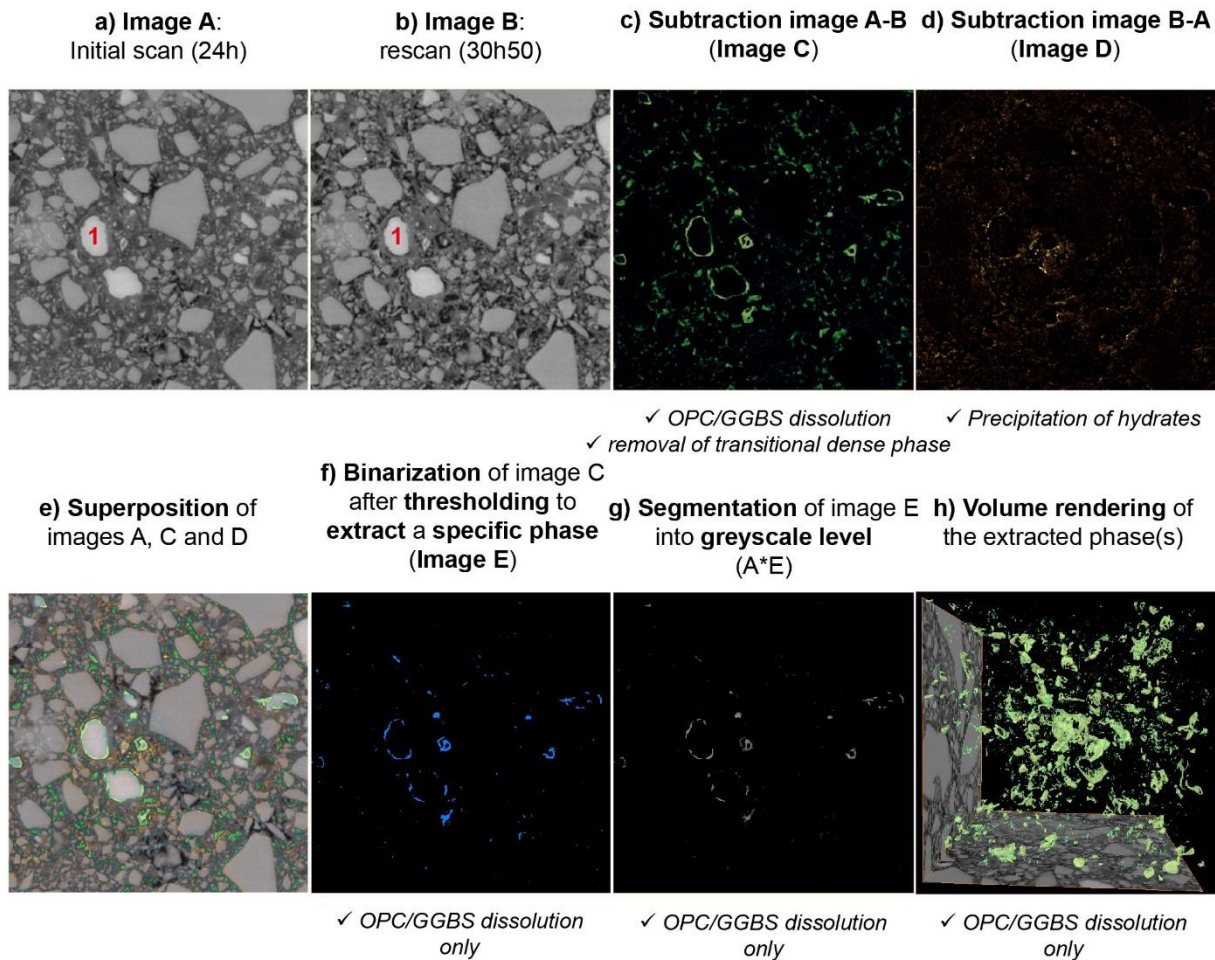
275 XMT image subtraction reveals small differences in pairs of nearly identical images [43–46]. In  
276 this study, the method was applied to early hydration of un-accelerated and  $\text{CaCl}_2$ -accelerated blended

277 cements. In image subtraction, the initial image of a rescanned sample is subtracted from the final image,  
278 or vice-versa. The pixel grey level of the subtraction image “A-B” or “B-A” corresponds to the absolute  
279 difference of pixel grey levels between the two images. Negative values are set to 0. In theory, the  
280 subtraction image of two strictly identical images should be black, but in the case of cements, the  
281 hydration reactions lead to some differences. The A-B images show the dissolution of initially present  
282 phases whereas B-A show the newly precipitated phases.

283 Figure 4 shows an example of subtraction performed on S75\_24h\_CaCl<sub>2</sub> and on its rescan 6 h  
284 50 later (image B). The image of the subtraction “A-B” (Figure 4.c) reveals the dissolution zones of  
285 OPC and GGBS, as the difference of pixel grey levels between OPC/GGBS between the initial scans  
286 (~150 and 120 respectively), and the resulting porosity (~35) or hydrates (~70) after dissolution or re-  
287 precipitation was positive. Note that a green color scale was used to enhance the visibility of the changes  
288 in the images. The removal of the transitional dense phase in the pore space was also made visible by  
289 this operation, as the difference of pixel grey levels between the transitional dense phase (~70) in the  
290 initial scans, and porosity (~35) after its removal was positive. All other chemical transformations  
291 leading to null or negative values were set to 0, and appear in black. On the other hand, the B-A  
292 subtraction (Figure 4.d.) highlights the precipitation zones of hydrates, as the difference of pixel grey  
293 levels between portlandite/hydrates\* in the rescans (~120 and ~70 respectively), and the initial pore  
294 space (~35) remained positive. A gold color scale was set in the present case. At the end, the  
295 superposition of the two subtraction images with the original XMT image reveals a dissolution rim  
296 around the OPC grain “1”, as well as the precipitation of hydrates\* in its vicinity (Figure 4.e). Further  
297 information will be extracted in sections 3.3.2 and 3.3.3 by comparing the subtraction images of the un-  
298 accelerated and CaCl<sub>2</sub>-accelerated systems, at various hydration ages.

299 Segmentation based on simple thresholding was then employed to extract one or more phases  
300 from the subtraction images. The thresholding range was set by fitting only the pixel areas of the phase(s)  
301 of interest, based on the morphological attribution of section 3.1.1. Either the transitional dense phase  
302 in the pore space, GGBS/OPC, or portlandite, and/or other hydrates\* could be separated from the other  
303 phases in the subtraction image, depending on the thresholding range used. The quality of the extraction  
304 depends on the separation of grey levels, since a large overlap would prevent the appropriate  
305 thresholding of the phase of interest: if the thresholding range is too large, the phase of interest will be  
306 polluted by other phases and, if it is too small, a part of the phase of interest will not be represented.  
307 Therefore, a compromise had to be found. In Figure 4.f., only the dissolution of OPC and GGBS was  
308 extracted, and the signal of the transitional dense phase was removed. Since the grey levels of OPC  
309 edges (~130) and GGBS (~120) overlapped strongly in the histograms, the two phases could not be  
310 separated from each other.

311 After thresholding, a binary image was obtained, and its multiplication with the initial XMT  
 312 image allowed to represent the selected phase(s) in its original grey scale levels (Figure 4.g).  
 313 Subsequently, the grey scale histogram of the selected phase(s) was extracted. Finally, the extracted  
 314 phases were represented in 3D (Figure 4.h). In this study, no quantification was performed due to the  
 315 non-repeatability of the experiments and the poor quality of the phase extraction (the signal was  
 316 systematically polluted by other contributions regardless of the phase extracted). However, this step is  
 317 theoretically possible, and the amount of extracted phase(s) would correspond to the integral of the peak  
 318 of interest in the histogram of Figure 4.g.



320 **Figure 4:** Principle of image subtraction performed on S75\_24h\_CaCl<sub>2</sub> and on its rescan 6 h 50 later.

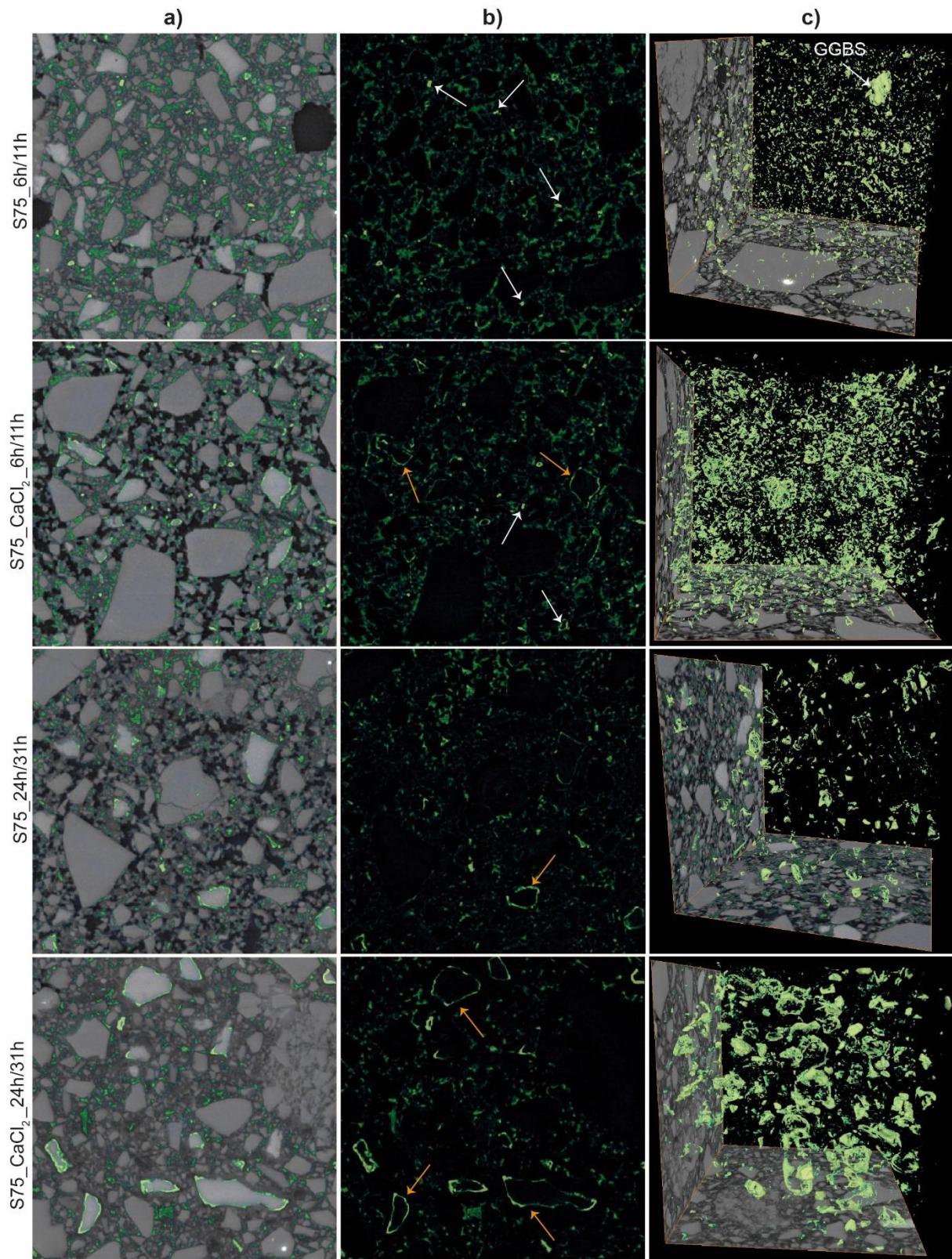
321 3.3.2. "A-B" Image subtraction: GGBS/OPC dissolution, removal of transitional dense phase  
 322 in the pore space

323 Figure 5 represents the A-B subtraction images of the non-accelerated and CaCl<sub>2</sub>-accelerated  
 324 samples, in the hydration ranges of about 6h/11h and 24h/31h. Column 1 shows the extracted phases  
 325 overlaid on the original XMT images, column 2 the image subtraction only, and column 3 the volume

326 rendering of the extracted phases (OPC and/or GGBS dissolution, without transitional dense phase in  
327 the pore space).

328         Between 6 h and 11 h of hydration, the subtraction images show mainly removal of the  
329 transitional dense phase in the pore space. In the non-accelerated sample (S75\_6h/11h), some small  
330 GGBS grains also dissolved. Their dissolution appears as a multitude of small bright spots with a size  
331 of about 1 – 4  $\mu\text{m}$  in the subtraction image (white arrows in Figure 5). Some bigger GGBS grains (~10  
332  $\mu\text{m}$ ) dissolved more locally, as can be seen in the 3D volume. In presence of  $\text{CaCl}_2$  (S75\_6h/11h),  
333 less GGBS dissolution was observed, but dissolution rims around the OPC grains were visible (orange  
334 arrows in Figure 5). This appears to be in contradiction with a former report on an accelerated slag  
335 reaction in presence of  $\text{CaCl}_2$  [29]. In that study, the contribution of slag to heat release in isothermal  
336 calorimetry appeared after 10 hours of hydration in presence of  $\text{CaCl}_2$ , i.e. earlier than the 15 hours of  
337 hydration in absence of  $\text{CaCl}_2$ . This corresponds to the appearance of AFm phases in XRD. In our study,  
338 it is thus possible that, in the accelerated sample, the initial dissolution of GGBS had already taken place  
339 during the first 6 hours of hydration (i.e., before the initial scan), so that this initial dissolution was only  
340 visible on the non-accelerated sample.

341         Between 24 h and 31 h of hydration, no GGBS dissolution was observed in either the non-  
342 accelerated or the  $\text{CaCl}_2$ -accelerated samples. This supports the idea that the initial GGBS dissolution  
343 had already taken place in the accelerated sample, as no dissolution was observed afterwards (until 31  
344 h of hydration). In absence of  $\text{CaCl}_2$ , only little OPC dissolution was observed in the subtraction images  
345 and volume rendering. In presence of  $\text{CaCl}_2$ , the OPC dissolution was stronger and affected almost all  
346 OPC grains. The comparison of the two volume renderings showed a clear accelerating effect of  $\text{CaCl}_2$   
347 on the dissolution of OPC. This is consistent with the fact that  $\text{CaCl}_2$  accelerates the dissolution of OPC  
348 at early ages [29,47–49].



349

350 **Figure 5:** “A-B” image subtractions: a) extracted phases superposed on the original XMT images, b)  
 351 subtraction images only (OPC/GGBS dissolution, with transitional dense phase in the pore space), and  
 352 c) volume rendering of the extracted phases (OPC/GGBS dissolution, without transitional dense phase



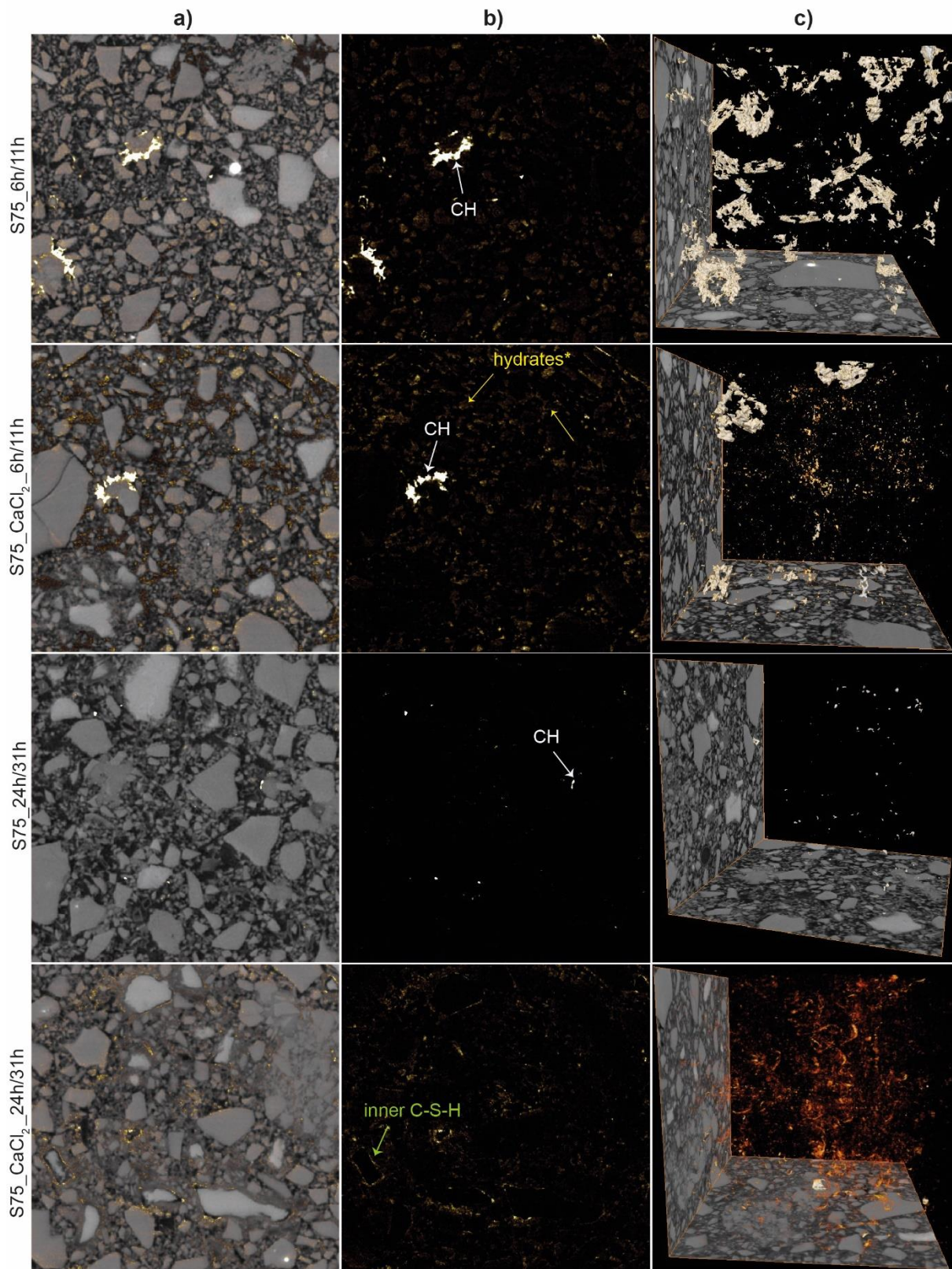
353 in the pore space). The arrows were added to highlight dissolution of GGBS (white) and OPC (orange)  
354 grains.

### 355 3.3.3. “B-A” Image subtraction: precipitation of hydrates

356 Figure 6 shows the B-A image subtractions of the non-accelerated and CaCl<sub>2</sub>-accelerated  
357 samples. This operation enables visualization of the precipitation of portlandite and/or other hydrates in  
358 blended cements.

359 Between 6 h and 11 h, only the formation of portlandite is visible in the non-accelerated sample.  
360 Numerous CH rims appear in both the subtraction image and the volume rendering of Figure 6 (white  
361 arrows). The light orange areas may correspond to the precipitation of other hydrates in the pore  
362 network, or slight variations in X-ray beam intensity during image acquisition, as some areas fall into  
363 the zone of GGBS grains (no precipitation is expected inside GGBS grains). In presence of CaCl<sub>2</sub>  
364 (S75\_CaCl<sub>2</sub>\_6h/11h), less portlandite formation was observed but more other hydrates\* precipitated into  
365 the pore space (Figure 6, yellow arrows). This is especially visible in the zoom presented in Figure 7.  
366 The light orange areas fall almost exclusively within the pore space, which is consistent with faster pore  
367 space filling by hydrates\* in presence of CaCl<sub>2</sub> as previously reported [47–49]. The higher presence of  
368 portlandite in S75\_6h/11h also agrees with the works of Steger, 2019 [50], who showed more portlandite  
369 precipitation at early ages in the non-accelerated slag cements at a similar time scale, by *in-situ* XRD.

370 Between 24 h and 31 h, precipitation of portlandite almost stopped in both the accelerated and  
371 non-accelerated samples. However, in the CaCl<sub>2</sub>-accelerated paste, an increased formation of other  
372 hydrates\* was observed around the OPC grains. According to the morphology and localization of the  
373 phases, they probably correspond to inner product C-S-H, as they fill the volume of dissolved OPC  
374 grains (Figure 6, green arrows and volume rendering). In the non-accelerated sample, no hydrate  
375 development was observed, except for very small amounts of portlandite.



376

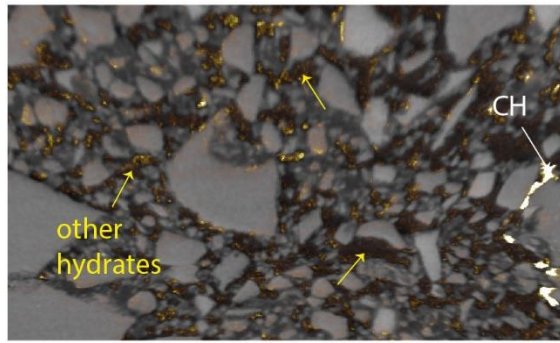
377

378

379

**Figure 6:** "B-A" image subtractions: a) extracted phases superposed on the original XMT images, b) subtraction images only (CH and/or hydrates\* and/or noise), and c) volume rendering of the extracted phases (CH and/or C-S-H).

380



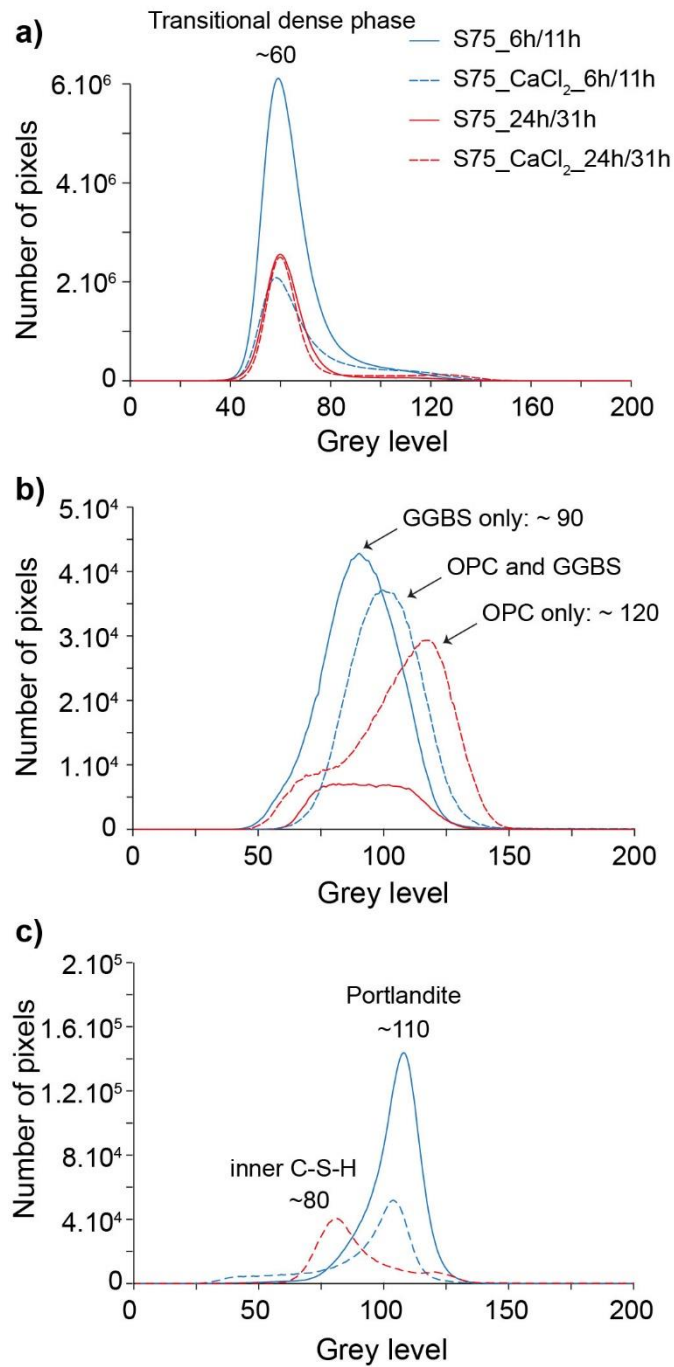
381

382 **Figure 7:** Zoom on the precipitation of hydrates\* in the porosity of S75\_CaCl<sub>2</sub>\_6h/11h.

383 *3.3.4. Determination of the specific grey levels of the extracted phases by image subtraction*

384 Extraction of the grey level distribution from the histograms after phase segmentation (i.e.  
385 Figure 4.g) gave the specific grey levels of the transitional dense phases, i.e., OPC, GGBS, portlandite,  
386 and inner C-S-H (Figure 8). The extraction was performed by selecting a specific grey level range of  
387 the original images in the subtraction images, which fitted the phase of interest identified base on  
388 morphology and comparison with the same spot on the initial scans (see section 3.1.1 and 3.3.1 for  
389 details).

390 The results showed a mean grey level of about ~60 for the transitional dense phase, ~80 for the  
391 inner product C-S-H, ~90 for GGBS, ~110 for portlandite and ~120 for OPC. The grey levels overlapped  
392 strongly, spanning  $\pm 20$  to  $\pm 40$  grey level units. Note that the dissolved OPC showed slightly lower grey  
393 level (~120) than the average value observed in Figure 1 (~150), probably because of the preferential  
394 dissolution of grain edges (Figure 8.b). Edge effects probably associated to partial volume effects / phase  
395 contrast decreased the mean grey level of the dissolved OPC compared to the center of the grains.  
396 Similarly, in samples where only GGBS was dissolved, the mean grey level of dissolved GGBS is  
397 slightly lower (~90) than the average value (~120) determined in section 3.1.1. In systems where OPC  
398 and GGBS dissolve, the grey level of the dissolved phases is in between the values for dissolved GGBS  
399 (~90) and OPC (~120). Note that in S75\_24h/31h, the signal of OPC is very low due to the difficulty of  
400 extracting the OPC phase.



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**Figure 8:** Extraction of the specific grey levels of a) the transitional dense phase in the pore space, b) GGBS and/or OPC, and c) portlandite/inner C-S-H, by combining simple thresholding in the subtraction images with the original image, from (cf. Figures 6 and 7). The number of pixels is not correlated with the amount of a given phase in the samples here, due to the non-repeatability and grey level overlapping.

## 407 **V. Conclusions**

408 In this study, XMT was used to highlight the early hydration of both CaCl<sub>2</sub>-accelerated and non-  
409 accelerated slag-based blended cements with a pixel size of 0.325 μm. Seven cementitious phases were  
410 identified in the XMT images and histograms: porosity, OPC, GGBS, portlandite, other hydrates,  
411 metallic iron particles and a transitional dense phase in the pore space with a grey level similar to that  
412 of the hydrates. For the first time, data repeatability tests were reported for cement pastes cast into glass  
413 capillaries of 300 μm. Surprisingly, different capillaries filled with the same paste do not give repeatable  
414 results, despite the fact that the REV size was reached, and that sample preparation was similar to what  
415 is frequently presented in the literature. This result should encourage future studies to control the data  
416 repeatability before conducting quantitative analyses. The early hydration of samples scanned at  
417 different hydration times was then qualitatively investigated during the first 31 h of hydration by  
418 histogram and image comparisons. These methods gave only limited information on the hydration  
419 reaction, due to the complex phase assemblages and slow hydration rates of the materials. Therefore,  
420 image subtraction of the same samples was used as an alternative method in order to evidence small  
421 differences in the fluid and solid phases. This method allowed to show (i) the dissolution of OPC and  
422 GGBS, (ii) the precipitation of portlandite and inner C-S-H, (iii) the accelerating effect of CaCl<sub>2</sub>, (iv)  
423 the distribution of dissolved/precipitated phases in 3D, and (v) the specific grey levels of the different  
424 phases. More specifically, CaCl<sub>2</sub> was shown to accelerate the dissolution of OPC and increase the  
425 precipitation of hydrates between 6 h and 11 h of hydration. The effect was even stronger between 24-  
426 31 h of hydration, with numerous dissolution rims around OPC grains and C-S-H clusters in the pore  
427 space. In absence of CaCl<sub>2</sub>, the dissolution/precipitation reactions were slower and were visible only  
428 after 24 h of hydration. However, GGBS dissolution was observed between 6-11h of hydration (and  
429 suspected before 6 h in the CaCl<sub>2</sub>-accelerated sample), and showed to contribute to the microstructure  
430 development of slag-based blended cements at early ages.

## 431 **Author contributions**

432 S.B., L.S. and C.P. prepared the samples and performed the XMT analyses under the supervision of  
433 A.B. and M.O. A.B. developed the experimental setup. M.O. performed the beamline calibration and  
434 data pre-processing. M.P. post-processed the whole dataset and wrote the first draft of the article. C.N.  
435 provided the computational equipment, managed data post-processing, and initiated the image  
436 subtraction method. M.P., S.B., M.C. and C.P. participated in numerous meetings to discuss the results  
437 and all co-authors participated in reviewing and editing the article. M.C. and J.K. led the overall project  
438 and acquired funding.

## 439 **Declaration of interests**

440 The authors declare that they have no known competing financial interests or personal relationships that  
441 could have influenced the work reported in this paper.

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