1   *In-situ* dynamic WetSEM imaging and electrical impedance

2   measurements on Portland cement during early hydration

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28 **Highlights**

29 • Dual testing methodology for *in-situ* monitoring of early hydration presented

30 • Automated image collection applied to the WetSEM technology for the first time

31 • WetSEM images correlate with data from electrical impedance measurements

32 • Portlandite precipitation alters both conduction and polarization processes

33 • Double-layer and interfacial processes give rise to the bulk polarization

34

35

36 **Abstract**

37 Wet scanning electron microscopy (WetSEM) and electrical impedance measurements have been

38 employed to study the physico-chemical processes during the early hydration of Portland cement. The

39 WetSEM study employed the Quantomix WetSEM capsule, allowing examination of the morphology

40 of hydrating cement directly *in situ* via 36 semi-electron-transparent windows under SEM vacuum

41 conditions over the initial 24-h after gauging whilst maintaining the test sample under atmospheric

42 conditions. This qualitative assessment was used to aid interpretation of the stages of early hydration

43 identified from impedance measurements, which were taken on a replicate specimen over the

44 frequency range 1kHz–1MHz. It is shown that detailed frequency- and time- domain impedance

45 measurements allowed identification of key processes during setting and early hardening which were

46 correlated with data from the WetSEM study. Attention is directed to the sequence of hydration

47 obtained from the two techniques and how they provide both supporting and complementary

48 information.

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50 **Keywords:** early hydration; electrical properties; cement; WetSEM; electrical impedance.

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1. INTRODUCTION

Cement hydration is a dynamic process involving a series of complex and interrelated physico-chemical processes taking place immediately from gauging throughout setting and early hardening. Given that the early hydration of cement is exothermic by nature, these processes have been traditionally studied using isothermal conduction calorimetry and adiabatic temperature rise testing [1-6]. These methods do not, however, provide direct information on microstructural changes which are more relevant to long-term durability and performance of concrete. More advanced techniques have been employed in this respect, including environmental scanning electron microscopy (ESEM), transmission electron microscopy, nuclear magnetic resonance, ultrasonic pulse velocity, X-ray diffraction and X-ray tomography [see, for example, 7-15].

In terms of microstructural changes during early hydration, the present work employs the WetSEM technology [16] whereby a hydrating cement paste is continuously imaged under atmospheric conditions within an *environmental* capsule inside a scanning electron microscope (SEM) over a 24-h period after gauging. In traditional SEM operation, examination of cement hydration is generally made by stopping the hydration process at various stages, typically by plunging in liquid nitrogen or by high-pressure freezing before examination by cryo-SEM [17, 18]. Such studies are important as they address information on the physical changes of cement hydration over time. However, the action of freezing the hydration process, particularly plunge freezing, may introduce artefacts and not provide a true reflection of hydration processes in its natural state. To address this issue, the environmental SEM (ESEM) was developed to provide a high-resolution method of studying cement in its wet state [19-21]. However, artefacts can still be introduced during chamber pump-down and maintaining samples hydrated during hydration and curing, with associated exothermic reactions, has been proven to be difficult. This has led to the development of the WetSEM technology through the use of a WetSEM capsule (viz, the Quantomix [16, 22]). In essence, a WetSEM capsule offers a sealed micro-environment, impervious to vacuum, with access to the hydrating test sample through a series of semi-electron-transparent windows. As such, it is possible to minimize artefacts introduced

82   as a consequence of vacuum as in normal SEM operation. Such capsules are particularly useful for a

83   range of materials, including biological specimens, pharmaceutical and hydraulic materials [16, 23-

84   24].

85

86   *In-situ* dynamic imaging of cement hydration using WetSEM technology has now been demonstrated

87   by several researchers. Katz et al. [16] was the first to employ this technology to follow the dynamic

88   nature of the hydration process of gypsum and cement paste at varying water-to-binder ratios, with

89   observations undertaken at magnifications up to 20k×. Whilst the study was carried out over a 24-h

90   period, only interpretations at 6-h and 24-h of hydration were presented, with a highlight being made

91   on the presence of Portlandite at 6-h and the development of calcium-silicate-hydrate (C-S-H) around

92   cement grains, when observed at the end of the test period (24-h after gauging). The use of WetSEM

93   at a prolonged exposure and higher magnifications than 10k× was not recommended as it can generate

94   extra heat which may accelerate the hydration process. Gallucci and Scrivener [25] further discussed

95   the strengths and limitations of the technology and highlighted the importance of sample preparation

96   for successful imaging. In their study, repeated low-magnification observations were made to

97   highlight the sequence of hydration during the early age and the precipitation of C-S-H was found not

98   only around cement grains but also in the pore space between the grains. Hexagonal Portlandite was

99   found to precipitate at less than 3 hours, which then eventually blocked the observation window at

100 ~13-h, possibly due to prolonged beam heating. To minimize extra heat from the electron beam,

101 Venkiteela and Sun [26] employed the blank beam function in a SEM to facilitate repeated

102 observations on a 15-min cycle during the initial eight hours after gauging. In their study, cement

103 pastes with varying water-to-cement ratios were contained within WetSEM capsules and the images

104 obtained from the repeated observations were then processed using image analysis. It was found that

105 the water volume decreases with increasing hydration time while the total solid volume shows an

106 opposite trend, which was interpreted as particle growth.

107

108 The primary aim of the present work is to employ two different, yet complimentary, experimental

109 techniques:

110   (i)   WetSEM, with the aim of providing qualitative information on the morphology of the

111   hydration products during the initial stages of hydration; and,

112   (ii)   Electrical property and internal temperature measurements [27], with the aim of providing

113   quantitative information on the physico-chemical processes occurring during early hydration.

114

115   Regarding (i), an automated technique employing the WetSEM capsule is introduced for the first time

116   to obtain time-lapse images of the physical and morphological changes within the paste throughout

117   setting and early hardening. Regarding (ii), monitoring the electrical properties of cementitious

118   systems represents a relatively simple testing technology to study setting and hardening under non

119   iso-thermal conditions; samples are not necessarily restricted to cement pastes and mortars, concretes

120   can also be studied [27, 28], thereby offering the potential for deployment in real-world concreting

121   operations [29]. These two techniques differ in the information they provide and this paper attempts,

122   for the first time, to correlate measurements obtained from WetSEM imaging with electrical

123   impedance measurements.

124

125   **2. EXPERIMENTAL PROGRAMME**

126   **2.1 Materials and sample preparation**

127   The cement paste was prepared using CEM I 52.5N to EN197-1 [30] (see the typical oxide

128   composition in Table 1) and mains tap-water with a resistivity of ~160 Ωm. These two materials were

129   mixed at a relatively high water-to-cement ratio (w/c=0.55) to ensure sufficient consistency for the

130   WetSEM study, detailed below. All test samples were produced from the same bag of cement to

131   minimize the influence of variability of materials on test results. The cement bag and the mixing water

132   were pre-conditioned in a temperature controlled laboratory (22±1°C) for more than 24-h prior to the

133   start of testing.

134

135   During the production of the sample for the WetSEM study detailed below, 0.5-litres of cement paste

136   was hand mixed for 2-min and an aliquot was then pipetted into a Quantomix QX-102 capsule (see

137   Fig. 1(a)). The capsule comprised two main parts: an upper cell into which the paste was injected and

138   a sealing stub which formed the base of the capsule. These two parts were connected by a flexible

139   rubber packing to ensure air and water tightness, as well as relieving excessive pressure during cell

140   closure. The upper cell had a semi-electron-transparent thin membrane, reinforced with metal grid to

141   provide the required strength to withstand the pressure difference while under vacuum in the SEM.

142   The metal grid divided the top membrane into 36 equally-sized semi-electron-transparent windows,

143   resulting into an arrangement displayed in Fig. 1(b). In this figure, the white grid corresponds to the

144   metal supporting frame whereas the black rounded squares represent the observation windows. It is

145   through these windows that continuous imaging of the physical changes in the paste, which was in

146   contact with, or in close proximity to, the inner surface of the membrane was possible, as it hydrated

147   under atmospheric conditions.

148

149   Together with the sample for the WetSEM study, a paste specimen with the same w/c ratio was

150   prepared for electrical measurements using a 2-litre Hobart planetary motion rotary mixer. The paste

151   was mixed for 2-min before being compacted into a Plexiglas cuboidal cell with internal dimensions

152    $50\times50\times50$ mm^3 (see Figure 1(c)). Following a previous study [27], a pair of stainless steel pins (grade

153   316L), each 2.4 mm in diameter, were embedded centrally inside the cell to a depth of 25 mm with a

154   centre-to-centre spacing of 25 mm. Immediately after compaction, the top surface of the cell was

155   covered with a plastic film to minimize evaporation and the cell was then contained within a benchtop

156   climatic chamber at a temperature of 22°C and relative humidity of 95%.

157

158   **2.2 Measurements and data processing**

159   *Scanning electron microscope*. A Quanta 650 field-emission gun scanning electron microscope (FEI,

160   Hillsboro, US) fitted with an Oxford Instruments X-max^N 150 mm Energy Dispersive X-ray (EDX)

161   detector was used for the study. Before starting the imaging sequence, one WetSEM capsule

162   containing a freshly prepared paste was positioned onto the stage of the SEM, with the cell membrane

163   facing the electron beam. Imaging was then taken using a backscattered electron (BSE) detector in

164   high vacuum mode, with the SEM operating at 20 kV using a spot size of 5.2 and a working distance

165   of 10mm [31].

166   Automated image acquisition was performed 10 minutes after gauging, using the FEI MAPS software

167   (Version 2.1, 64-bit, FEI). The mapping process involved the acquisition of a series of BSE images

168   across a regular tile pattern, following the sequence described in the schematic shown in Figure 1(d).

169   From each individual tile, high resolution 4096×4096 (16M) pixels low magnification (600×) BSE

170   image was acquired, starting from Tile 1 (top left) and then moving systematically from left-to-right

171   and top-to-bottom toward Tile 36 (bottom right). At this resolution, it took approximately 35-min to

172   obtain the image of the entire area (36 tiles). The same mapping process was then repeated until 24-h

173   after gauging (or 42 times), producing a total of 1,512 images. The advantages of acquiring images in

174   this manner are threefold:

175   (i)   a reduction in the electron beam exposure which minimizes local heating and hence the

176   risk of membrane failure due to electron beam heating;

177   (ii)   minimize the additional heat generated by the electron beam thereby reducing its

178   influence on the physico-chemical processes during the early hydration; and

179   (iii)   generate 36 notionally identical samples from a single experiment run, allowing the

180   evaluation of the inherent variability among the samples whilst maintaining the quality of

181   individual images.

182   On completion of experiment, the individually acquired images were manually aligned using the

183   GIMP software (Version 2.8.10) to form a time-lapse complete montage of the paste (see, for

184   example, Fig. 2). The images were further processed to create GIF animations which are provided as a

185   video component to the electronic version of this article.

186

187   *Electrical measurements*. An E4980AL high-precision LCR meter (Keysight, Santa Rosa, US) was

188   used to perform a logarithmic impedance sweep at 61 spot frequencies within the range 1kHz-1MHz,

189   under a signal amplitude of 350 mV. The LCR meter was controlled by a desktop PC using a custom-

190   designed virtual instrument in LabVIEW (Version 2015, National Instruments, Austin, US).

191   Communication with the LCR meter was established across a USB interface using Keysight IO

192   Library Suite software (Version 2017.1). Electrical measurements were undertaken by connecting the

193   electrodes to the voltage high/low and current output/input terminals in the LCR meter via

194   individually screened coaxial cables, with connection at the electrodes by means of alligator clips.

195   Measurements were undertaken in voltage-drive mode on a four-minute cycle throughout the initial

196   24-h after gauging. One measurement cycle over the full frequency range took approximately 15-s.

197   The LCR meter was placed in standby mode between measurement cycles until the next measurement

198   was triggered.

199

200   Lead inductive effects were *nulled* from the measured impedance response using a measurement

201   correction protocol implemented in Microsoft Excel; full details of the protocol are provided

202   elsewhere [32]. Two sets of calibration data were acquired prior to the start of experiment, comprising

203   (i)   An open-circuit correction, with sweep measurement taken with the coaxial cables connected to

204   the pin electrodes positioned within an empty cell; and

205   (ii)   A short-circuit correction, with sweep measurement taken on the same setup, but with the

206   electrodes being short-circuited.

207   In addition to impedance measurements, the internal temperature of the test specimen and the climatic

208   chamber were monitored every 2 minutes using a 5K thermistor via an auto-ranging data logger.

209

210   **2.3 Preliminaries for electrical measurements**

211   The electrical properties of a porous, saturated cementitious material rely on the ease with which

212   charges can contribute to conduction and polarization processes within the system and depend,

213   primarily, on the frequency of the applied electrical field and the time-variant nature of both the

214   evolving pore structure and pore-fluid chemistry [33, 34]. To provide a detailed insight into chemical

215   reactions, microstructural changes and pore structure development within a cement paste, these

216   measurements are taken over three orders of magnitude of frequency (viz, 1kHz–1MHz).

217

218   From an electrical standpoint, the impedance, $Z(\omega)$, of a material at any angular frequency, ω, can be

219   written as,

220$$Z(\omega) = Z'(\omega) - iZ''(\omega) \qquad (1)$$

221 where $Z'(\omega)$ is the resistive (real) component (in Ohm), $Z''(\omega)$ is the reactive (imaginary) component

222 (in Ohm), $i = \sqrt{-1}$ and $\omega = 2\pi f$ with f being the frequency of the applied field (Hz). At any

223 frequency, the electrical response of such a system will result from the superposed phenomena of

224 conduction and polarization which can be quantified, respectively, by the bulk conductivity, $\sigma(\omega)$

225 (S/m), and the relative permittivity, $\varepsilon_r(\omega)$. These parameters can be de-embedded from the resistive

226 and reactive components by [35],

227
$$\sigma(\omega) = \left(\frac{Z'(\omega)}{Z'(\omega)^2+Z''(\omega)^2}\right)\frac{L}{A} \qquad (2)$$

228
$$\varepsilon_r(\omega) = \frac{1}{\varepsilon_o\omega}\left(\frac{Z''(\omega)}{Z'(\omega)^2+Z''(\omega)^2}\right)\frac{L}{A} \qquad (3)$$

229 where ε_o is the permittivity of a vacuum (8.854×10^{-12} Farads/m) and L/A (/m) is a factor which is

230 related to the electrode geometry and sample configuration. As the electrical field between the

231 electrodes is non-uniform, the geometrical constant L/A in above equations cannot be readily

232 calculated. This was thus determined by impedance measurements on a liquid of known conductivity

233 placed within the same test cell. For the electrode arrangements and test cell used in the current work,

234 the geometrical factor L/A was evaluated as 34.92 m^{-1}. Given that the relative permittivity calculated

235 using Eq. 3 can extend over several orders of magnitude, the term normalised permittivity, denoted

236 $\varepsilon_N(\omega)$, is introduced to aid comparative analysis. This is defined as $\varepsilon_{r,t}(\omega)/\varepsilon_{r,o}(\omega)$, with $\varepsilon_{r,o}(\omega)$

237 representing the measured permittivity at the start of the test and $\varepsilon_{r,t}(\omega)$ representing the corresponding

238 value measured at time, t, after the start of the test.

239

240 **3. TEST RESULTS AND DISCUSSION**

241 **3.1 *In-situ* dynamic imaging**

242 To provide a qualitative assessment of early hydration process, Figs. 2(a)–(d) present a complete

243 montage of the 36 individually acquired BSE images at four selected points in time during the 24-h

244 period. In the initial state displayed in Fig. 2(a), the bright dots correspond to the upper part of the

245 cement grains which was in close proximity or in contact with the inner surface of the semi-electron-

246 transparent membrane. The dots are surrounded by darker regions which occupy a larger fraction of

247   the observation windows and represent the interstitial aqueous phase between the cement grains. In

248   some windows, the appearance of one to two large dark regions is evident, corresponding to the

249   presence of occluded micro air voids which have adhered to the inner side of the membrane. Thin

250   horizontal and vertical lines extending across the entire image are evident which indicate the grid/tile

251   boundaries (see the gridlines in Fig. 1(d)). It is apparent from Figs. 2(a)–(d) that the vertical gridlines

252   become progressively displaced to the right due to slight inherent drift in the electron beam. This does

253   not, however, impair the usability of the proposed technique as the individually collected BSE images

254   can be stitched together to construct the montage. Given the large area to scan and the considerable

255   time required to follow the dynamic nature of the hydration process, it is essential to ensure that the

256   electron beam source is stable, with regard to BSE intensity. This is required to remove inadvertent

257   variance in BSE intensity which would render interpretation of the results difficult. The results

258   presented in Figs. 2(a)–(d) reveal that this is not an issue as all windows within each figure display

259   comparable brightness with no notable variations in BSE intensity levels.

260

261   With reference to Figs. 2(a)–(d), it is evident that as hydration reactions progress, the water level

262   within the capsule subsides with time revealing a porous surface comprising partially hydrated cement

263   grains which are bright and pore space which is dark (see Figs. 2(c) and (d)). At the same time, the

264   interstitial pore space is also progressively filled by hydration products although most of this space is

265   covered by water which is not electron transparent and hence most of this infilling process remains

266   undetectable. Another prominent feature from Figs. 2(c) and (d) relates to the presence of large,

267   elongated, bright crystals of Portlandite which are scattered over the top surface of the paste. The

268   amount and geometry of this crystal formation varies from one window to another and would be

269   indicative of inherent variability in the available pore space between the cement grains and in the

270   concentration of Ca^{2+} in the interstitial aqueous phase.

271

272   To provide a better insight into the process of cement hydration, the complete time-lapse BSE images

273   for Window 14 (3-6 in Fig. 1(b)) are displayed in Fig. 3. This is also provided as a video component

274   to the electronic version of this article; to access this video component, simply click on the image

275   visible below (see Video 1 in the electronic version of this article). As before, the upper part of the

276   cement particles which was in close proximity or in contact with the membrane was observed as

277   bright dots, whereas the liquid covering the remainder of the particles is shown as dark areas. No

278   obvious differences in morphology are evident during the initial state i.e. the first three images,

279   indicating that there have been no significant physical changes to the cement grains when observed at

280   this low magnification. The first prominent feature can be seen from ~1-h 45-min after gauging, or

281   image 4 on Fig. 3 where the precipitation of elongated, calcium-rich crystals (i.e. Portlandite) are

282   evident in the water-filled capillary space between the grains, as indicated by the circle in image 4

283   (Fig. 3). The nucleation of Portlandite at this early age agrees with the findings of Gallucci and

284   Scrivener [25] although in their study this was observed at a later stage (~3-h after gauging). Marked

285   crystal growth is evident from the successive images displayed in Fig. 3, transforming into a *massive*

286   crystal which is angular in shape with smooth sides and some perforations. To highlight the growth

287   process, enlarged images of the area indicated by the rectangles in images 8, 14, 21 and 32 in Fig. 3

288   are presented in Figs. 4(a)–(d); for clarity, the lime-lapse images of this crystal growth are also

289   included as Video 2 in the electronic version of this article. The nucleation of similar crystals but

290   varying in size and shape is evident in Fig. 3 throughout the 24-h test period. Apart from Portlandite,

291   the precipitation of much smaller hydration products is also apparent on the grain surface (see, for

292   instance, Fig. 4(d)) and is discussed below. It is also evident from Fig. 3 that the exposed surface of

293   the cement grains (the bright dots) becomes brighter and the free water-content of the paste reduces

294   with time, which is indicative of water consumption resulting from the hydration reactions and could

295   give a false impression of particle growth viz. the gradual decrease in water-level is interpreted

296   exclusively as particle growth.

297

298   Another notable feature from Fig. 3 (and Video 1) is related to the increasing rate of reduction in free

299   water-content resulting from the hydration reactions from ~8-h (image 14), thereby exposing the

300   underlying structures comprising partially hydrated cement particles and capillary pores (dark

301   regions). This is highlighted on the image by the two circled areas, with the enlarged version

302   displayed in Figs. 4(e) and (f). As hydration progresses, the free water-content continues to reduce,

303   most notably from ~10-h after gauging (see image 18 onwards on Fig. 3), signifying a period of

304   chemical activity. The result is a porous surface which has been depleted of water, giving a *coral reef*

305   appearance.

306

307   Fig. 5 displays BSE images of Window 2 (1-4 on Fig. 1(b)) at six selected times over the 24-h test

308   period, with four enlarged images at 24-hours presented in Figs. 6(a)–(d) and the corresponding video

309   component included as Video 3 in the electronic version of this article. It is evident from Fig. 5 that

310   the sequence of events is comparable to those presented earlier in Fig. 3, although the time that

311   corresponds to a particular event varies to some extent from one window to another indicating the

312   temporal and spatial variations in hydration response. This includes: (i) the time at which the

313   Portlandite starts to crystalize; and (ii) the time when the interstitial aqueous phase starts decrease.

314   Fig. 8, for clarity, presents the respective times for each window at which Portlandite appears and the

315   decreasing free water-content process starts; the mean values were found to be, respectively, 2-h 15-

316   min with a coefficient of variation (CoV) of 33% and 8-h 25-min with a CoV of 20%.

317

318   With reference to the enlarged images taken at 24-h, it is evident from Figs. 6(a)–(d) that the large

319   Portlandite crystals are surrounded by cement grains covered by fibrillar outgrowths comprising C-S-

320   H and some longer, needle-like (ettringite) crystals [15, 17, 21, 36, 37]. To highlight the growth

321   process of these crystals, Figs. 7(a)–(f) present the time-lapse of Fig. 6(d) at 2.5-h, 4-h, 6.5-h, 8-h, 10-

322   h and 12.5-h after gauging, with the complete time-lapse provided as Video 4 in the electronic version

323   of this article. No notable outgrowth from the grain surface are apparent at 2-h (Fig. 7(a)), although

324   local precipitation may have occurred on the grain surface (see, for instance, [17]). However, this

325   remains undetected as it is beyond the resolution of the acquired BSE image. Notable outgrowths are

326   evident from ~4-h after gauging (Fig. 7(b)), with a more rapid outgrowth detected from ~6.5-h after

327   gauging (Fig. 7(c)), which continued over the remainder of the test period (viz, Figs. 6(d) and 7(d)–

328   (f)). To obtain more detailed insights into the hydration processes on the grain surface, further

329   research involving the freezing of cement paste sample at various stages of hydration and further

330   examination by cryo-SEM is required.

331 Figs. 9(a) and (b) present, respectively, the BSE images and elemental EDX maps of Windows 11, 12,

332 17, 18, 24 and 25 (see Fig. 1(d)) at 24-h after gauging. Figs. 9(c) and (d) present an enlargement of the

333 selected area shown in Window 18 (on Fig. 9(a)) and the respective elemental EDX map whose

334 spectra are presented in Fig. 9(e). The map indicates that the large bright crystal displayed in the BSE

335 image in Fig. 9(c) is calcium rich which agrees with the strong peak of calcium in Spectrum 1 (Fig.

336 9(e)), indicating Portlandite. Spectrum 2, representing the darker area in Fig. 9(c), displays strong

337 peaks due to calcium and silicon from calcium-silicate-hydrate (C-S-H) [38] (similar to the

338 precipitates covering the cement grains presented earlier in Figs. 6(c)), and weak peaks due to

339 aluminium and sulphur from monosulphoaluminate (AFm) and ettringite (AFt) [38]. While hydrogen

340 is a key component in C-S-H, it does not appear in the elemental analysis as it has only one electron-

341 shell, and hence is not X-ray reflective. Spectrum 3 displays strong peaks due to silicon from the

342 silicate phase in the cement and other peaks due to calcium, aluminium, potassium and sulphur.

343 Spectra 4, 5 and 6 display strong peaks due to calcium, aluminium and silicon and weak peaks due to

344 magnesium, sulphur, potassium and iron, suggesting the presence of partially hydrated aluminate and

345 ferrite crystals covered by hydrates comprising C-S-H and ettringite (AFt) [38, 39].

346

347 **3.2 Electrical property measurement**

348 *3.2.1 Preliminaries*

349 Immediately on gauging, cement and water takes the form of a heterogeneous colloidal suspension

350 which gradually turns into a solid matrix through a series of complex physico-chemical processes.

351 Under the action of an alternating electrical field, some charges (ions in solution) are free to drift

352 through the continuous aqueous phase and discharge at the electrodes, producing an ionic conduction

353 effect. Other charges, which are electrostatically held onto grain or gel surfaces, oscillate about their

354 zero-field equilibrium position in sympathy with the alternations of the electric field. This can induce

355 large dipole moments which increases the overall polarizability of the system (see Fig. 10(a)). This is

356 a low-frequency polarization mechanism and generally referred to as the double-layer polarization

357 [40, 41]. In addition to this mechanism, albeit operating over an intermediate frequency (high kHz–

358 MHz), is an interfacial polarization process [42] which is schematically shown in Fig. 10(b). As

359   hydration progresses, free charges in the aqueous phase may accumulate at internal interfaces within

360   the material; whilst such charges do not contribute to the overall ionic conduction process, it increases

361   the polarizability of the paste. The polarizability of the system can be quantified by the relative

362   permittivity (Eq. 3) whereas the conductive effect can be quantified by the bulk conductivity (viz, Eq.

363   2). Given that both parameters are influenced by free and bound charges, the measurement of both

364   parameters throughout setting and hardening processes could offer detailed insights into the dynamic,

365   time-variant nature of early hydration.

366

367   *3.2.2 Interpretation of test results*

368   To provide a quantitative assessment of the physical changes and chemical processes during the early

369   hydration process, the electrical response of the cement paste is discussed below. For clarity, only

370   every 10th data marker is highlighted on Figs. 11(a)–(c).

371

372   Fig. 11(a) presents the change in the conductivity, $\sigma(\omega)$, over the 24-hour test period together with its

373   derivative, $d\sigma/dt$, with the conductivity presented at a frequency of 100kHz. This frequency was

374   found high enough to ensure that the influence of electrode polarization was negligible (discussed

375   below), thereby allowing accurate evaluation of the bulk response. The change in normalised relative

376   permittivity, $\varepsilon_N(\omega)$, during the same test period is presented in Fig. 11(b). While data were measured

377   at 20 frequencies per decade over the frequency range 1kHz–1MHz, $\varepsilon_N(\omega)$ is only presented at five

378   spot frequencies viz. 1kHz, 100kHz, 250kHz, 500kHz and 1MHz, with $\varepsilon_{r,o}(\omega)$ presented in Table 2. In

379   general terms, the conductivity increases up to ~1-h 40-min and then decreases over the remainder of

380   the test period, with a weakly developed *shoulder* detected between 8-h and 12-h. $\varepsilon_N(\omega)$ measured at

381   1kHz, 100kHz and 250kHz (Fig. 11(b)) displays a similar trend to the conductivity, with the shoulder

382   becoming more prominent with increasing frequency of applied field. The shoulder is, however,

383   absent at higher frequencies (viz, 500 kHz and 1 MHz) and $\varepsilon_N(\omega)$ displays a monotonic increase from

384   ~8-h.

385

386 On closer examination, the conductivity response and its derivative, $d\sigma/dt$, can be further subdivided

387 into six distinct regions indicated I–VI in Figs. 11(a)-(c) to highlight several stages of the hydration

388 process. This was possible due to the short time interval between sweep measurements, allowing more

389 detailed information than was previously available over the frequency range under consideration.

390 Note that reference to the WetSEM images below mainly relates to Fig. 3 (and Video 1 in the

391 electronic version of this article).

392

393 *Region I: 0 – 20-min (WetSEM Images 1 and 2)*

394 This region is characterised by a rapid increase in conductivity and a positive rate of change of

395 conductivity (i.e. $d\sigma/dt$), with $d\sigma/dt$ decreasing with time. The increase in conductivity is attributed to

396 the rapid dissolution of alkalis and sulphate (Na^+, K^+, Ca^{2+}, SO_4^{2-} and OH^-) into the aqueous phase and

397 is accompanied by an increase in internal temperature as shown in Fig. 11(c). The reduction in $d\sigma/dt$

398 over this period would indicate that the surfaces of the cement grains are gradually covered by early

399 hydration products thereby hindering the dissolution process, and hence an overall reduction in

400 reaction rate. These physical changes were, however, not detectable in WetSEM study as such

401 changes occur locally on the grain surface which was masked by the gauging water which is not

402 electron transparent.

403

404 The rapid increase in $\varepsilon_N(\omega)$ (Fig. 11(b)) occurring concurrently at all selected frequencies mimics the

405 rise in conductivity and would imply an increasing amount of charges developing on the grain

406 surface, forming an electrical double layer (see Fig. 10(a)). Polarization of the double-layer can

407 induce high permittivity values [40-42]; however, superimposed upon this polarization mechanism

408 will be electrode polarization effects [43-45]. Electrode polarization is a low-frequency process which

409 reduces with increasing frequency of applied field. At 1kHz, electrode effects will make a substantial

410 contribution to the permittivity and it is only at higher frequencies ($\geq$100kHz) that the true bulk

411 response will be revealed over this Region. Confirmation of this comes from the fact that $\varepsilon_{r,o}(\omega)$ (see

412 Table 2) decreases by more than three orders of magnitude as the frequency increases by two decades

413   from 1kHz ($\varepsilon_{r,o} = 7.49 \times 10^6$) to 100kHz ($\varepsilon_{r,o} = 2.11 \times 10^3$) whereas $\varepsilon_{r,o}(\omega)$ changes by approximately one

414   order of magnitude as the frequency increases by two decades from 100kHz to 1MHz ($\varepsilon_{r,o} = 1.42 \times 10^2$

415   at 1MHz). As the test frequency increases from 100kHz to 1MHz, it becomes more difficult for ions

416   in the diffuse double-layer to follow the alternations of the electrical field which results in a reduction

417   in permittivity with increasing frequency as presented in Table 2.

418

419   *Region II: 20-min – 1-h 40-min (WetSEM Images 2 thru 4)*

420   This region is characterised by a slower increase in conductivity and a reducing value of dσ/dt (Fig.

421   11(a)). This implies that the dissolution process continues albeit at a reduced rate, possibly due to

422   early hydrate formation around the cement grains such as ettringite and C-S-H [17, 36, 37]. Over this

423   period, the internal temperature of the cement paste reduces, approaching the ambient temperature

424   (Fig. 11(c)). Despite the initial growth on the cement grains, the ε_N response presented in Fig. 11(b)

425   displays a similar trend to that of the conductivity implying that, at this w/c ratio, double-layer

426   processes dominate over any reduction in charge mobility due to initial hydrate formation.

427   Unfortunately, these physical changes are not evident under the WetSEM as they were masked by the

428   gauging water. The conductivity and relative permittivity at all selected test frequencies reach their

429   maximum values at the end of this Region.

430

431   *Region III: 1-h 40-min – 2-h 10-min (WetSEM Images 4 and 5)*

432   This is a short-lived region and marks a sudden reduction in conductivity, indicated by the change

433   from a period of increasing conductivity to a period of decreasing conductivity over the remainder of

434   the 24-h period. The decrease in conductivity within this region is very rapid as dσ/dt reaches its

435   global minimum (see Fig. 11(a)). It is now proposed that the sudden reduction in conductivity is

436   associated with the crystallization of Portlandite infilling the water-filled capillary space between the

437   grains as the time of occurrence of this Region coincides with the time of occurrence of Portlandite

438   formation observed in the WetSEM study at 2-h 15-min (see Fig. 8). The slight difference in time is

439   attributed to the fact that whilst the precipitation of Portlandite occurs within the entire volume of the

440   paste, only precipitates which are in contact with, or in close proximity to, the inner surface of the

441   semi-electron-transparent membrane are detectable in the WetSEM and hence the apparent delay of

442   its occurrence. Portlandite formation between the cement grains will limit the concentration of Ca^{2+} in

443   the aqueous phase (or even result in a concentration reduction when the gypsum is depleted [46-47])

444   and in more discontinuous and tortuous electrolytic conduction pathways, both of which would have

445   the effect of decreasing the overall conductivity. Video 2 in the electronic version of this article

446   displays the time-lapse of Portlandite growth observed in Window 14 throughout the test period.

447

448   Occurring in parallel with the decrease in conductivity in Fig. 11(a) is a corresponding reduction in ε_N

449   (see Fig. 11(b)). The reduction in polarizability of the paste (hence ε_r) is now attributed to the

450   formation of Portlandite crystals within the microstructure which will reduce charge concentration

451   and mobility. Despite the formation of Portlandite, the internal temperature of the paste over this

452   Region continues to decrease, as shown in Fig. 11(c).

453

454   *Region IV: 2-h 10-min – 8-h (WetSEM Images 5 thru 14)*

455   From Fig. 11(a), the conductivity over this period continues to decrease whereas dσ/dt remains

456   relatively constant up to ~4-h, thereafter decreasing over the remainder of this Region. The decrease

457   in dσ/dt at ~4-h coincides with the increase in internal temperature at this time (Fig. 11(c)) which

458   would indicate the start of a period of chemical activity. It is proposed that this feature is due to

459   secondary reactions on the C_3S phase and the gradual formation of a more crystalline microstructure.

460   The continual decrease in conductivity could be attributed to the continuous growth of Portlandite

461   (see Figs. 3, 4(a) and (b), and Video 2) and C-S-H crystals (see Figs. 6(d), 7(a)-(f) and Video 4),

462   causing an increase in rigidity of the paste.

463

464   In a similar fashion, Fig. 11(b) shows that the permittivity of the paste continues to decrease over this

465   Region, although this decrease becomes less pronounced with increasing frequency. Indeed, over the

466   period 4-h to 8-h, the permittivity at 500kHz and 1MHz starts to display a slight increase. At these

467 higher frequencies, it is expected that the increase in permittivity must involve a short-range

468 movement of charges occurring locally on grain surfaces or at crystal boundary interfaces (see, for

469 instance, Figs. 7(a)-(d) or Video 4). Regarding the latter, the increasing surface area of the cement

470 grains due to the formation and outgrowth of ettringite and C-S-H crystals would increase the

471 polarizability of the paste through enhanced double-layer and interfacial processes.

472

473 ***Region V: 8-h – 12.5-h (WetSEM Images 14 thru 22)***

474 The conductivity continues to decrease although a *shoulder* occurs in the response which results in a

475 local maximum on the $d\sigma/dt$ curve over the central portion of this Region and a local minimum at the

476 end. Interestingly, at 100kHz and 250kHz, the permittivity also displays a local maximum, whereas at

477 500kHz and 1MHz the permittivity shows a continual increase over this Region. The conduction and

478 polarization processes within the paste can result from several synergistic effects:

479 (i) the continuous growth of Portlandite and a more rapid outgrowth of fibrillar C-S-H crystals

480   from the grain (see Figs. 7(e) and (f) or Video 4), resulting in an increase in surface area hence

481   enhanced double-layer polarization on crystal surfaces. Conduction, on the other hand, would

482   be reduced due to the development of more tortuous continuous pathways;

483 (ii) a release of ions into the capillary pore network through renewed chemical activity such as the

484   transformation of AFt to AFm, with the subsequent release of Ca^{2+} and SO_4^{2-}, and reaction on

485   the C_3A phases releasing alkalis bound up in them. This would increase conductive processes

486   and enhance the polarizability of the paste through both interfacial and double-layer effects;

487 (iii) the accretion and infilling of the pore space by the products of hydration thereby forming a

488   rigid structure which would serve to decrease both the conduction and polarizability of the

489   paste due to space restriction and reduced charge mobility; and,

490 (iv) as the paste is hydrating under non-isothermal conditions, the increase in temperature would

491   result in an increase in charge mobility, thereby increasing both polarization and conductive

492   processes [48]. However, as the temperature rise within the paste is <1°C over this Region, this

493   effect is considered negligible in comparison to the influence of (i)-(iii) above.

494

From the WetSEM study presented in Fig. 3 (images 14–22) and Video 1, it is evident that the intense chemical activity also has the effect of increasing water consumption thereby causing a reduction in the free water-content. This is estimated as occurring at ~8-h 25-min (see Fig. 8) and coincides with the beginning of Region V. It is interesting to note from images 14–22 in Fig. 3 and Figs. 4(b) and (c) that the growth of Portlandite over this Region did not displace the surrounding cement particles which were much smaller in size, indicating that the hydration products at this stage were sufficiently strong to hold the particulate material within the aqueous paste together. At the end of this region, the products of hydration (Portlandite and gel) have resulted in a percolated pore network thereby forming a rigid matrix.

Region VI: 12.5-h – end of test (WetSEM Images 22 thru 42)

This final region identified within the 24-h test period is characterized by a continual decrease in conductivity due to continued crystal growth and microstructural densification, resulting in a more tortuous, constricted and disconnected capillary pore network (see Videos 1–4). The ε_N response at 100kHz and 250kHz is similar to the conductivity as it displays a decreasing trend; however, at 500kHz and 1MHz, the permittivity increases with time. Regarding the increase in polarizability of the paste at 500kHz and 1MHz, this could result from increased interfacial processes at crystal boundary interfaces within the pore structure (see Fig. 10(b)), resulting from an increase in ionic concentrations in the pore fluid i.e. the continued release of ions from the AFt to AFm transformation. Interfacial polarization is a high frequency process and is only revealed – i.e. becomes more dominant over double-layer effects – as the frequency increases. As there is no detectable increase in conductivity caused by release of ions into the pore network, it would indicate that changes in the pore structure due to hydration are having a dominant influence on the conductivity of the paste than changes in pore-fluid chemistry.

4. Conclusions and Concluding Comments

Dual testing methodology utilizing electrical impedance measurements and WetSEM observations have been presented to provide information of the stages in the early hydration and complementary information on hydrate formation and crystal morphology. With regard to the impedance measurements, these were presented as conductivity (σ) and permittivity (ε_r), with the permittivity presented over the frequency range 1kHz–1MHz. The WetSEM observations were undertaken on a sealed vacuum-tight miniature capsule via 36, 300-μm square semi-electron-transparent windows and a novel, fully automated image collection technique was used to allow *in-situ* dynamic imaging under atmospheric conditions. The following conclusions can be drawn from this study:

1. The conductivity (σ), its rate of change $d\sigma/dt$ and the relative permittivity (ε_r) could be divided into six distinct regions which were used to identify key stages in the early hydration of cement paste. Over the frequency range 1kHz-1MHz, unlike the conductivity, the permittivity response changed markedly with electrode polarization processes dominant at low frequencies; however, at frequencies >100kHz the bulk response was revealed and related to double-layer and interfacial polarization processes occurring within the paste.

2. The WetSEM study revealed the nucleation of large, angular Portlandite crystals between the cement grains from ~2-h 15-min after gauging. This feature was coincident with the significant decrease in both conductivity and relative permittivity which took place at this time (viz, Region III).

3. The first half of Region IV is characterised by a reduction in conductivity and an almost constant $d\sigma/dt$ value. The decrease in conductivity could be associated with the continuous growth of Portlandite, as observed in the WetSEM study over the same period. This was then followed by a reduction in $d\sigma/dt$ (viz, become more negative) and an increase in internal temperature, indicating the start of a period of renewed chemical activity. During this period, a slight increase in permittivity at high frequencies (viz, 500kHz and 1MHz) was observed, occurring concurrently with the outgrowth of ettringite and C-S-H crystals from the WetSEM study. The increase in permittivity was as a result of the increase in the surface area of the

548   cement grains which increased the polarizability of the paste through enhanced double-layer

549   and interfacial polarization processes.

550   4. The WetSEM study detected a reduction in the water-content of the paste at ~8-h 25-min after

551   gauging which was coincident with the beginning of Region V identified from conductivity

552   and relative permittivity measurements. The electrical measurements also underwent

553   significant changes over Region V and explained in terms of dissolution processes and

554   hydrate formation on grain surfaces.

555   5. Region VI is characterized by a continual decrease in internal temperature, conductivity and

556        $d\sigma/dt$ due to continued crystal growth and microstructural densification, as observed in the

557   WetSEM study.

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685   **Figure captions**

686

687   **Fig. 1.** (a) Schematic of the Quantomix capsule; (b) close-up of the top windows numbered according

688   to their position, with the prefix representing the row number and the suffix representing the column

689   number; (c) test cell for electrical measurements; and (d) layout of tile numbered according to the

690   sequence of image collection, overlain on the windows shown in (b).

691

692   **Fig. 2.** Stitched BSE images showing the progress of cement hydration on all windows: (a) 30-min;

693   (b) 4.5-h; (c) 12-h and (d) 18-h after gauging.

694

695   **Fig. 3.** Time-lapse imaging of Window 14 (3-6 on Fig. 1(b)) with images taken every ~35-min over

696   the initial 24-h after gauging. Images are arranged from left-to-right and top-to-bottom in the order of

697   measurement sequence, with each row displaying successive changes over a ~3-hour period. Each
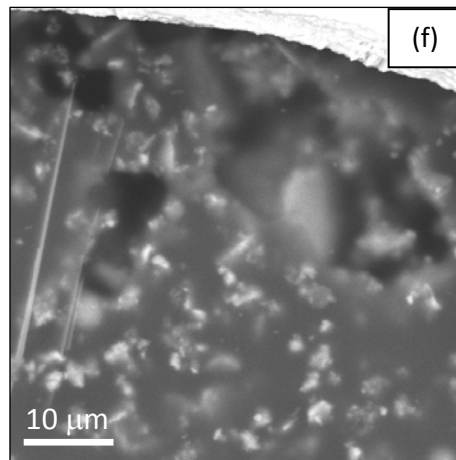
698   window is 300□m square.

699

700   **Fig. 4.** Enlarged BSE images of the progressive formation of Portlandite crystals indicated by the

701   rectangles in Fig. 3 at (a) ~4-h (image 8), (b) ~8-h (image 14), (c) ~12-h (image 21) and (d) ~18-h

702   (image 32). (e) and (f) are enlarged images of areas indicated by the circles on image 14 in Fig. 3

703   where the first indication of a reduction in water-content is evident.

704

705   **Fig. 5.** Selected time-lapse images of Window 2 (1-4 on Fig. 1(b)) at (a) the initial state, (b) 6-h, (c) 8-

706   h, (d) 10-h, (e) 12-h and (f) 24-h after gauging. The bright dots at the initial state are the upper part of

707   the cement particles while the dark areas represent the interstitial aqueous phase. A porous surface is

708   evident as the water-level has reduced, revealing partially hydrated cement grains which are bright

709   and capillary pores which are much darker.

710   **Fig. 6.** Enlarged images of selected areas of Window 2 (indicated on Fig. 5(f)) taken at 24 hours after

711   gauging showing the presence of: (a) and (b) large Portlandite crystal surrounded by cement grains

712   covered by fibrillar outgrowths comprising C-S-H and some longer needle-like (ettringite) crystals;

713   (c) and (d) smaller hydration products where the Portlandite crystal is absent.

714

715   **Fig. 7.** Time-lapse images of Fig. 6(d) at (a) 2.5-h; (b) 4-h; (c) 6.5-h; (d) 8-h; (e) 10-h; and (f) 12.5-h

716   after gauging.

717

718   **Fig. 8.** Observed time of the first appearance of Portlandite crystals and the first indication of a

719   reduction in water-content resulting from hydration reactions. The mean values are indicated in the

720   Figure by the dashed lines.

721

722   **Fig. 9.** (a) BSE images of Windows 11, 12, 17, 18, 24 and 25 (see Fig. 1(d)) after 24-h hydration; (b)

723   respective EDX maps of Windows after 24-h hydration where red represents potassium, green is

724   sulphur, yellow is calcium, pink is silicon and cyan represents areas rich in aluminum; (c) is enlarged

725   image of rectangle indicated on Window 18 in (a) with the respective EDX map shown in (d); green

726   represents areas rich in aluminum, yellow is calcium and cyan is silicon; and (e) is typical elemental

727   composition of selected areas in (d). These figures appear in colour in the electronic version.

728

729   **Fig. 10.** Schematic showing (a) double layer polarization and (b) interfacial polarization.

730

731   **Fig. 11.** (a) Conductivity, $\square$, and its derivative, d$\square$/dt, during initial 24-hours, with Regions I–VI

732   indicated; (b) normalized relative permittivity, $\square_N$, at five selected spot frequencies; and (c) variation

733   in internal temperature of cement paste.

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740   **Video Captions**

741   **Video 1.** Animation of Window 14 (3-6 on Fig. 1(b)) displaying Portlandite formation and general

742   microstructural densification over the 24-h test period.

743

744   **Video 2.** Animation of Portlandite growth in Window 14 over the 24-h test period.

745

746   **Video 3.** Animation of Window 2 (1-4 on Fig. 1(b)) where fewer numbers of Portlandite precipitates

747   are evident over the 24-h test period.

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749   **Video 4.** Animation of precipitates on grain surfaces within the area indicated by the rectangle in Fig.

750   5(f) over the 24-h test period.

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768 (a)   (b)

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771 (c)   (d)
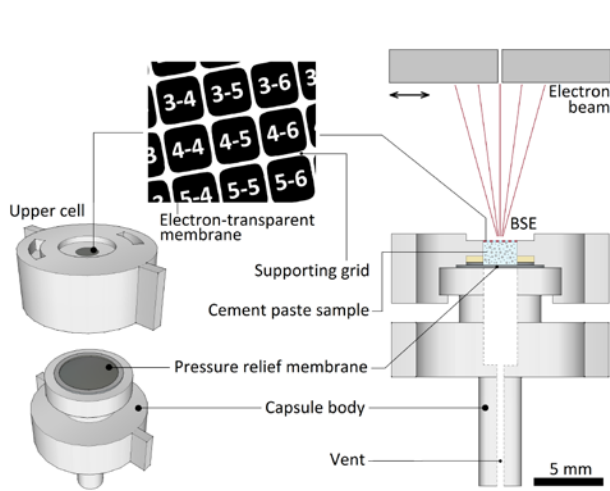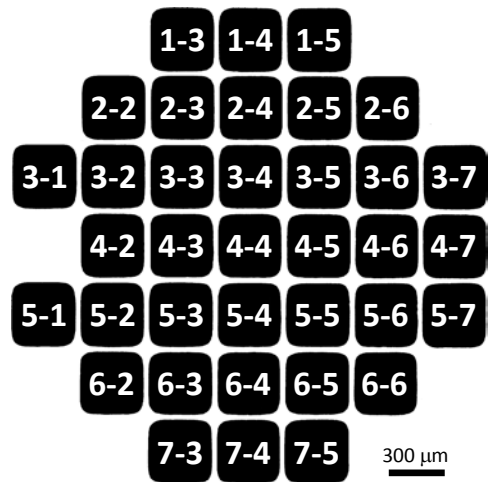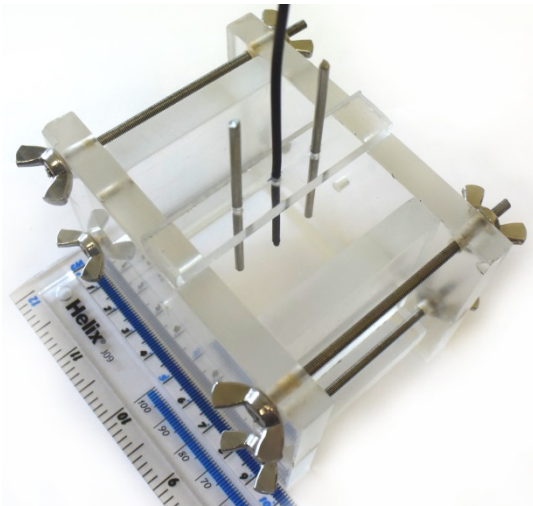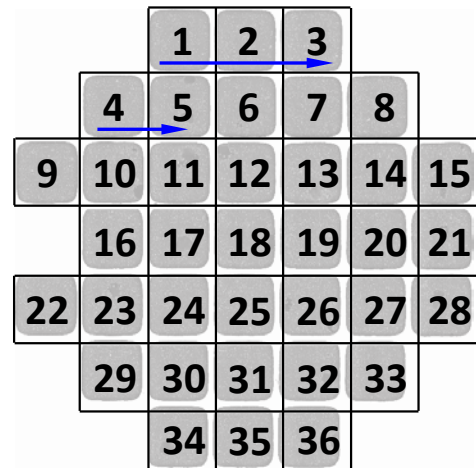
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773 **Fig. 1.** (a) Schematic of the Quantomix capsule; (b) close-up of the top windows numbered according

774 to their position, with the prefix representing the row number and the suffix representing the

775 column number; (c) test cell for electrical measurements; and (d) layout of tile numbered according

776 to the sequence of image collection, overlain on the windows shown in (b).

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(a) 30-min

(b) 4-h 30-min

(c) 12-h

(d) 18-h

300 μm
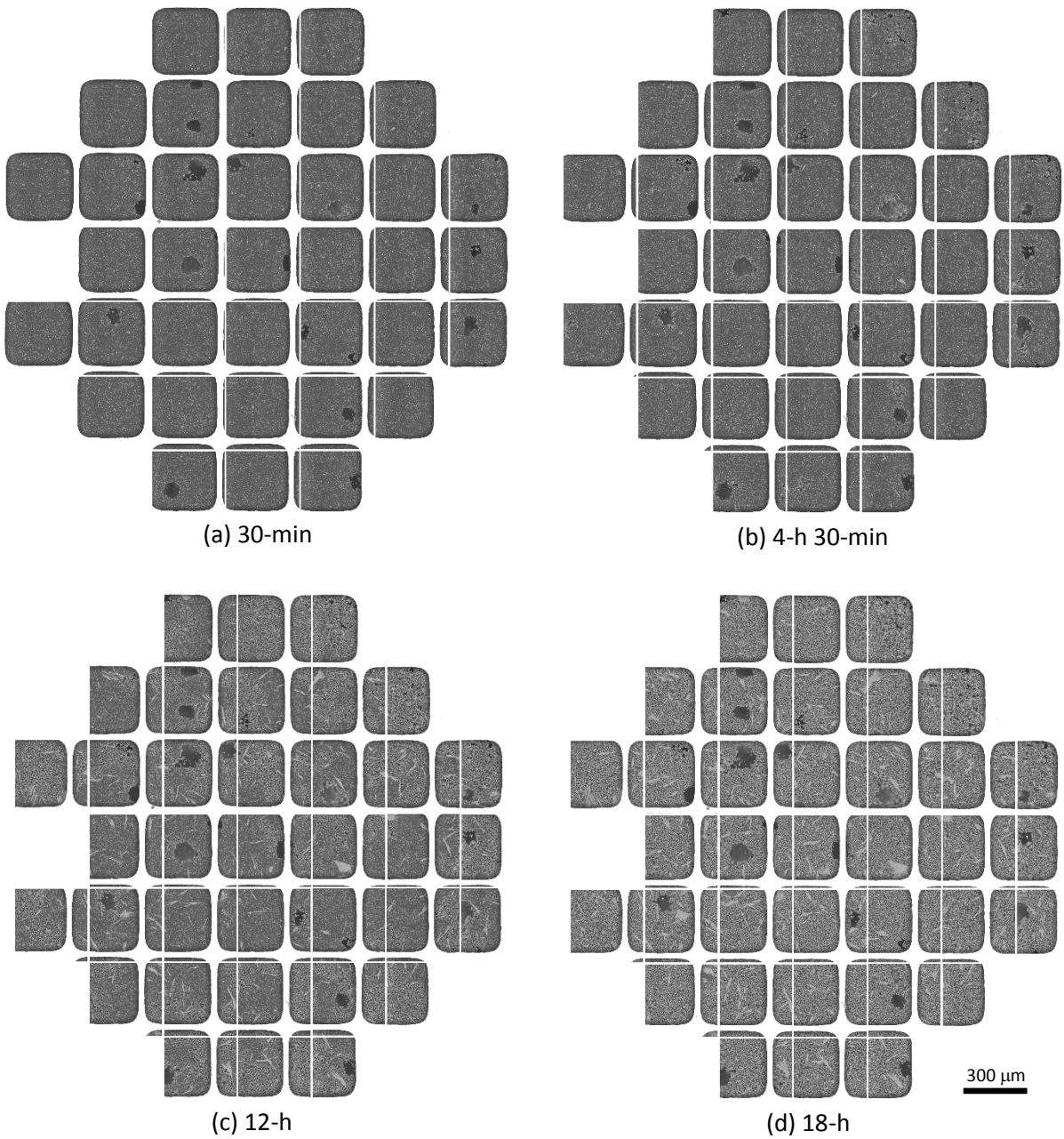
Fig. 2. Stitched BSE images showing the progress of cement hydration on all windows: (a) 30-min; (b) 4.5-h; (c) 12-h and (d) 18-h after gauging.
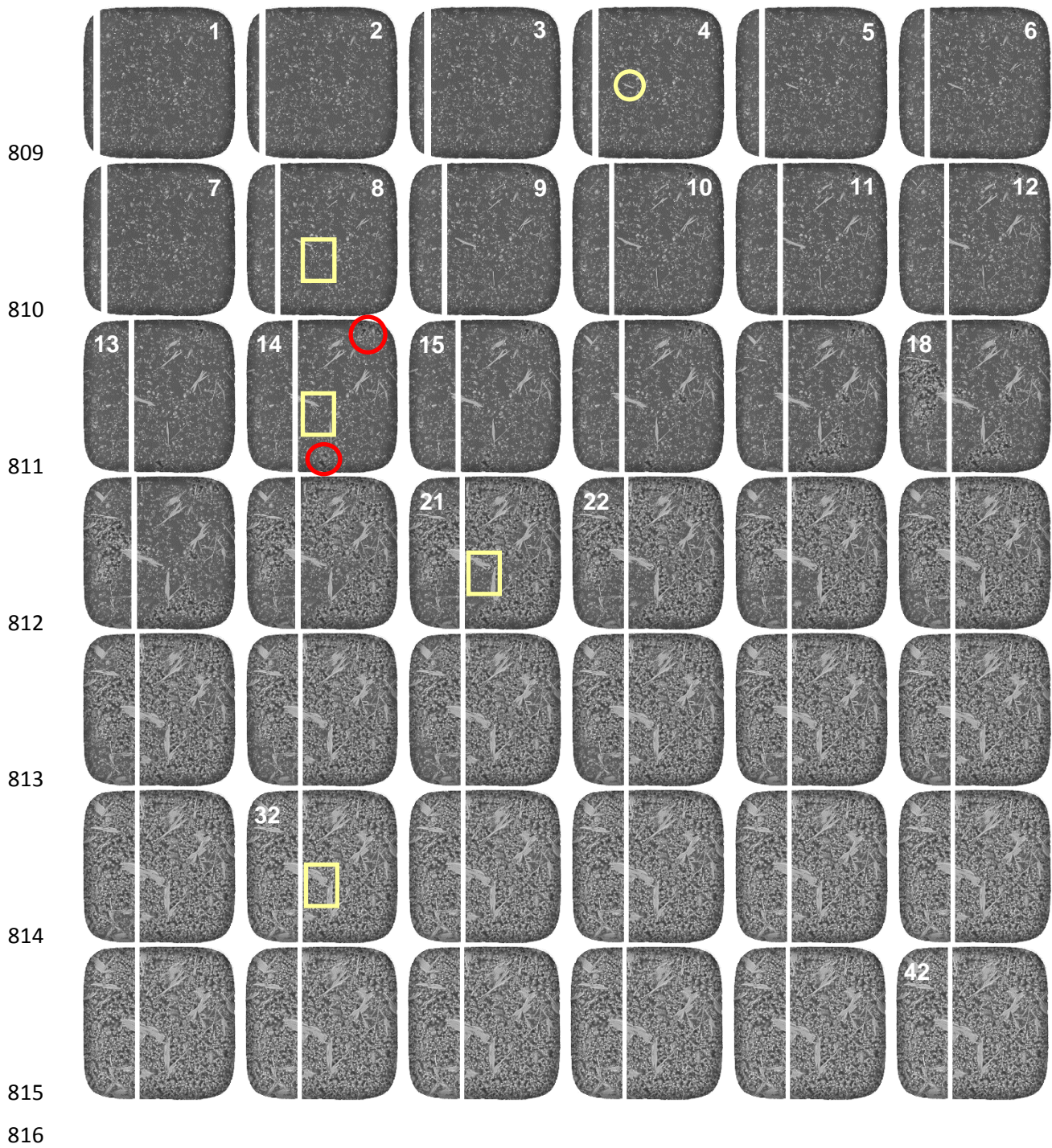
Fig. 3. Time-lapse imaging of Window 14 (3-6 on Fig. 1(b)) with images taken every ~35-min over the initial 24-h after gauging. Images are arranged from left-to-right and top-to-bottom in the order of measurement sequence, with each row displaying successive changes over a ~3-hour period. Each window is 300μm square.

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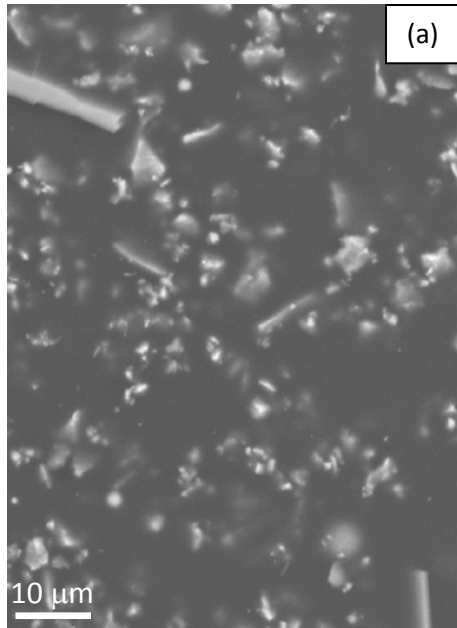
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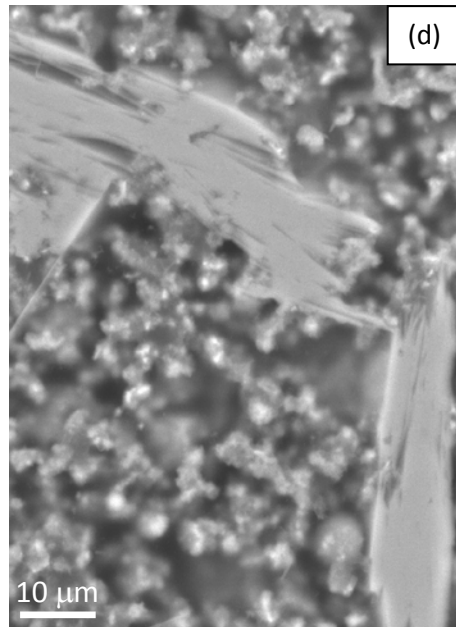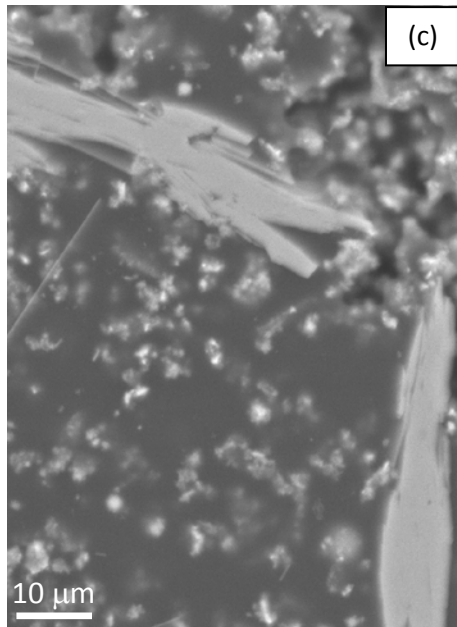
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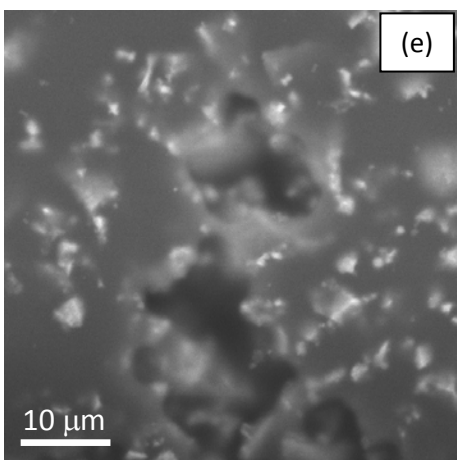
826   **Fig. 4.** Enlarged BSE images of the progressive formation of Portlandite crystals indicated by the

827   rectangles in Fig. 3 at (a) ~4-h (image 8), (b) ~8-h (image 14), (c) ~12-h (image 21) and (d) ~18-h

828   (image 32). (e) and (f) are enlarged images of areas indicated by the circles on image 14 in Fig. 3

829   where the first indication of a reduction in water-content is evident.

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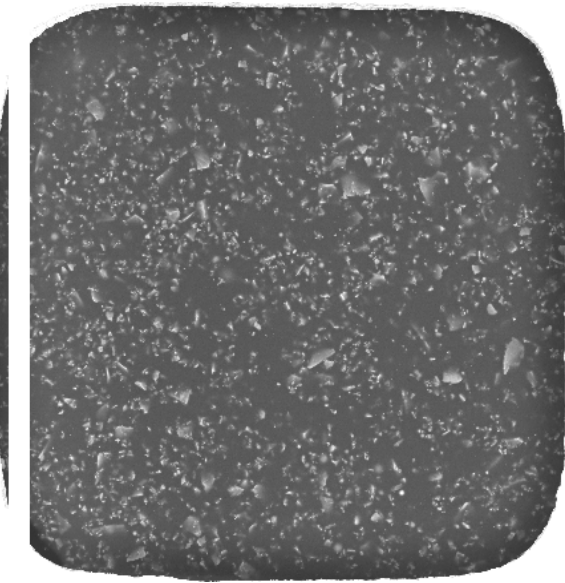
(a) Initial
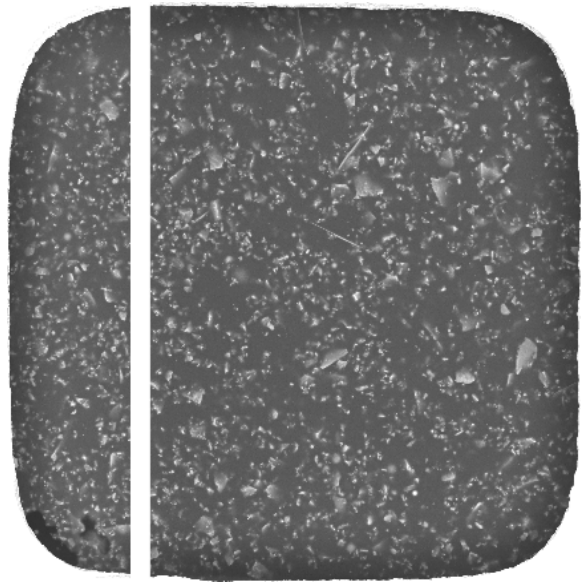
(b) 6-h

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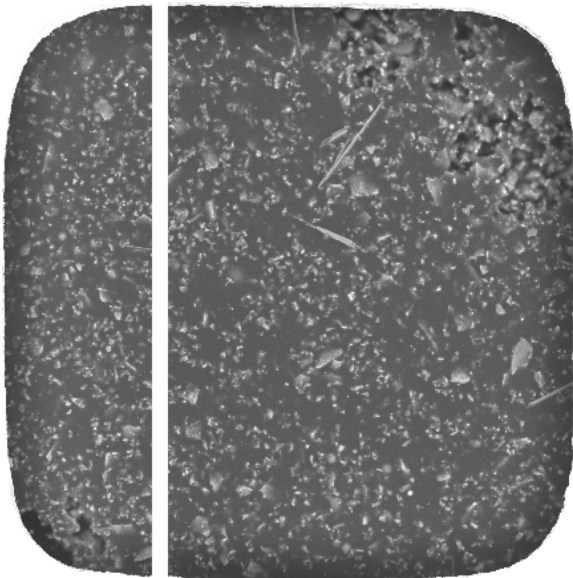
(c) 8-h

(d) 10-h

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(e) 12-h

(f) 24-h

6(d) and 7

6(b)

6(c)

6(a)
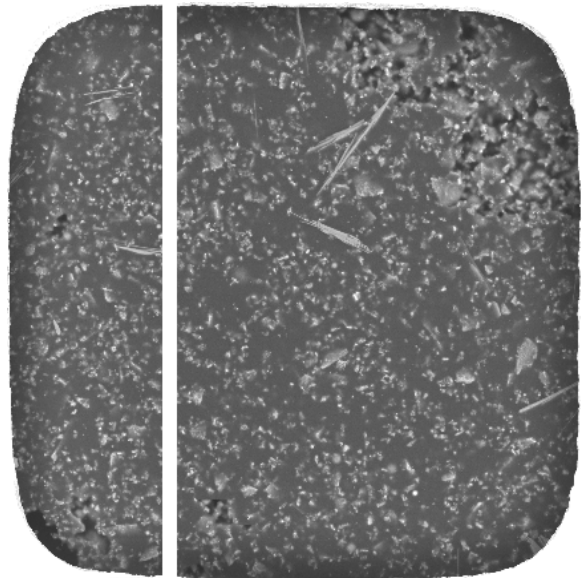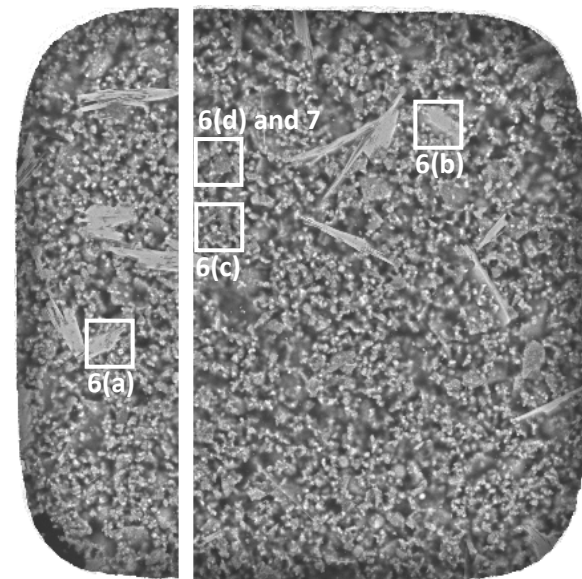
50 µm

852 **Fig. 5.** Selected time-lapse images of Window 2 (1-4 on Fig. 1(b)) at (a) the initial state, (b) 6-h, (c) 8-

853 h, (d) 10-h, (e) 12-h and (f) 24-h after gauging. The bright dots at the initial state are the upper part

854 of the cement particles while the dark areas represent the interstitial aqueous phase. A porous

855 surface is evident as the water-level has reduced, revealing partially hydrated cement grains which

856 are bright and capillary pores which are much darker.

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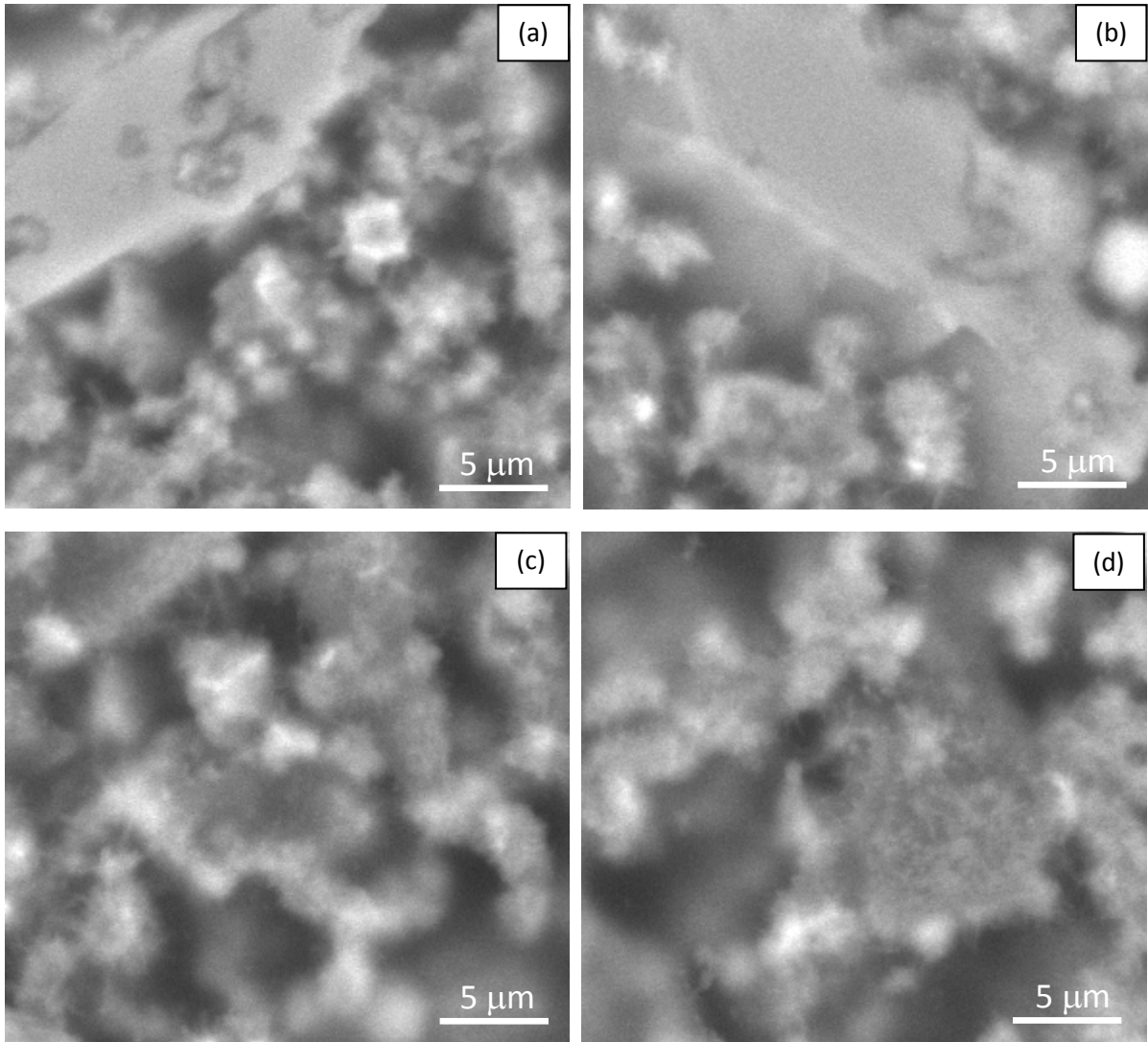
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881 **Fig. 6.** Enlarged images of selected areas of Window 2 (indicated on Fig. 5(f)) taken at 24 hours after

882 gauging showing the presence of: (a) and (b) large Portlandite crystal surrounded by cement grains

883 covered by fibrillar outgrowths comprising C-S-H and some longer needle-like (ettringite) crystals; (c)

884 and (d) smaller hydration products where the Portlandite crystal is absent.

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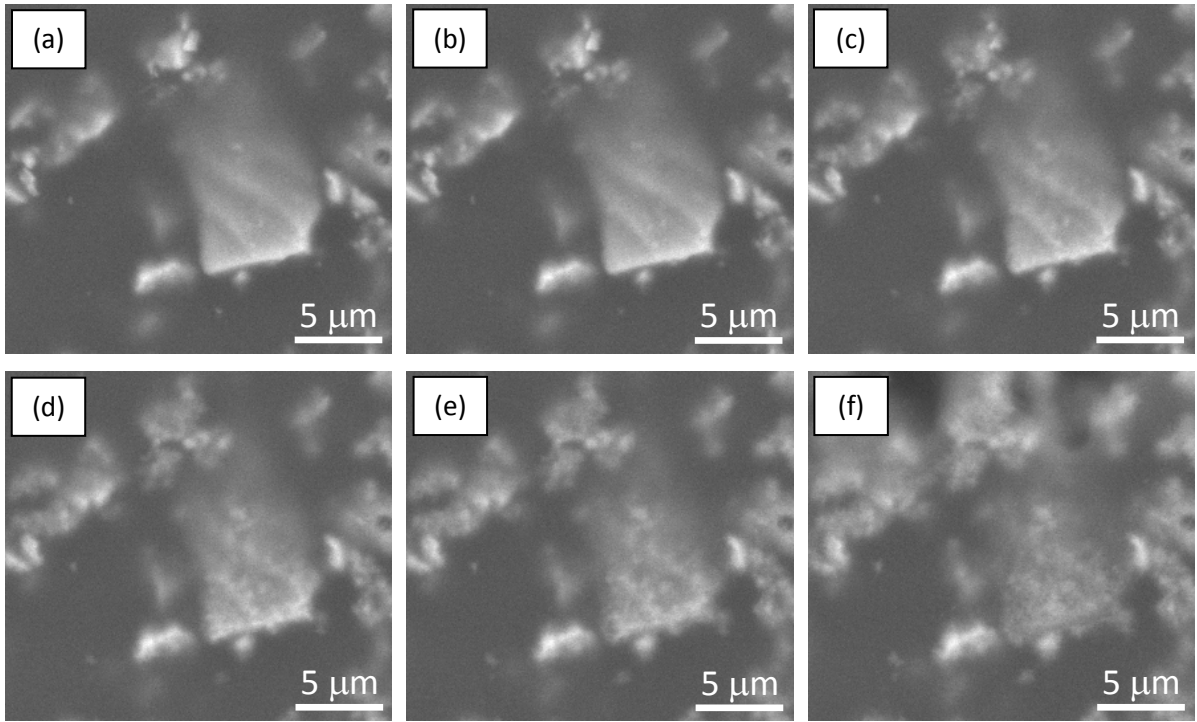
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Fig. 7. Time-lapse images of Fig. 6(d) at (a) 2.5-h; (b) 4-h; (c) 6.5-h; (d) 8-h; (e) 10-h; and (f) 12.5-h

after gauging.

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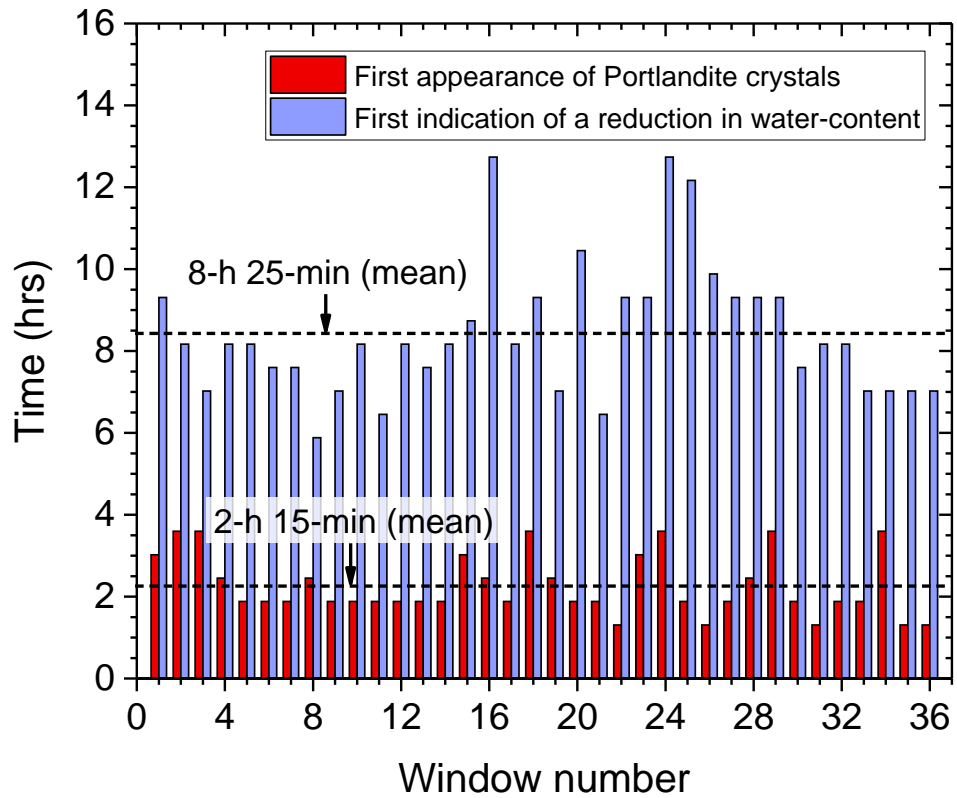
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Fig. 8. Observed time of the first appearance of Portlandite crystals and the first indication of a

reduction in water-content resulting from hydration reactions. The mean values are indicated in the

Figure by the dashed lines.

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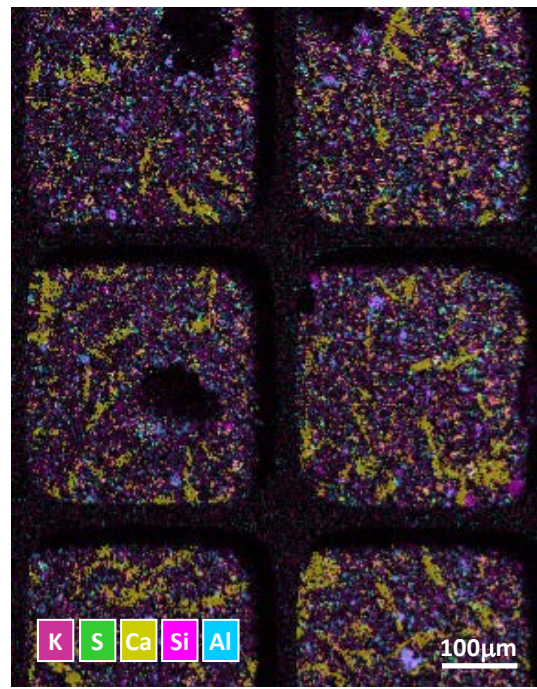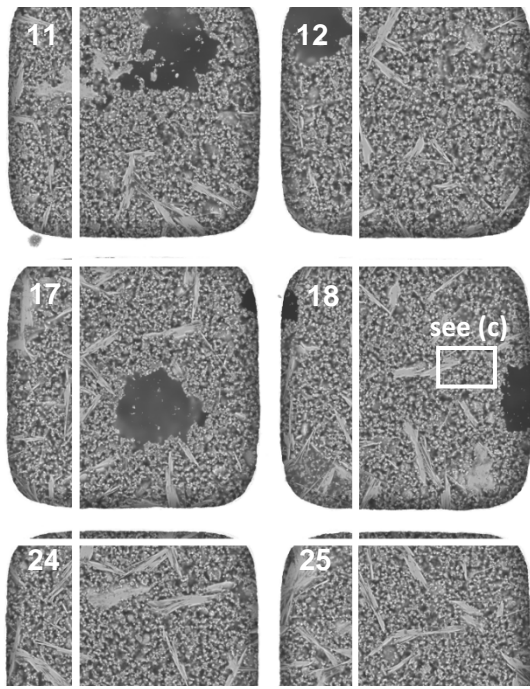
(a)

(b)
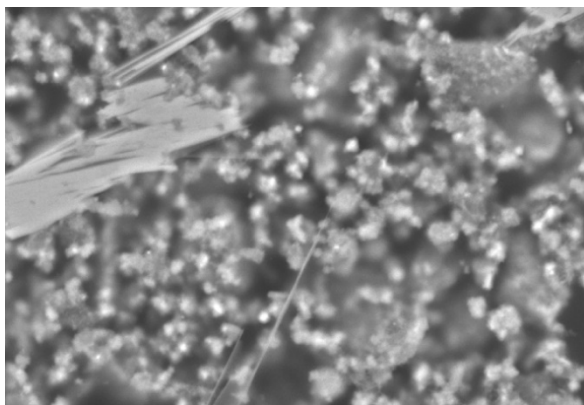
(c)
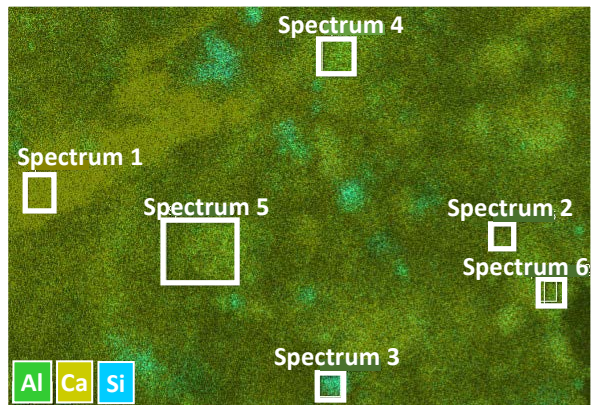
(d)
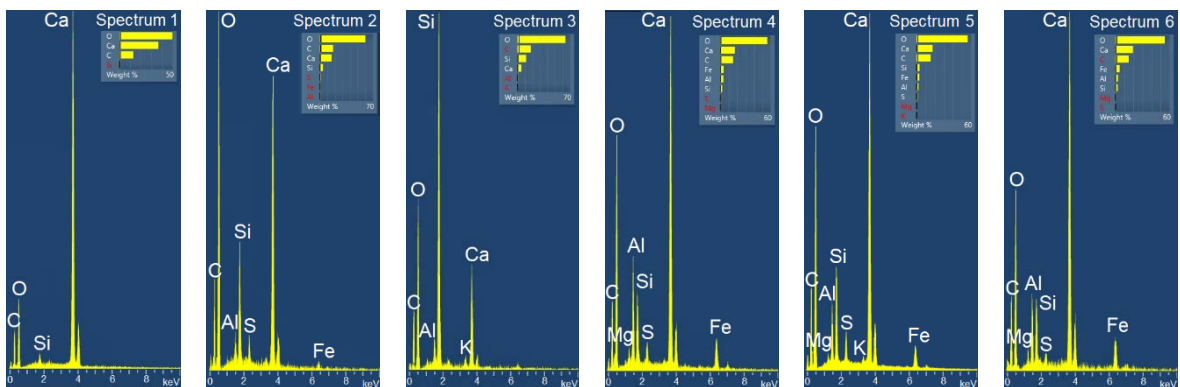
(e)

Fig. 9. (a) BSE images of Windows 11, 12, 17, 18, 24 and 25 (see Fig. 1(d)) after 24-h hydration; (b) respective EDX maps of Windows after 24-h hydration where red represents potassium, green is

sulphur, yellow is calcium, pink is silicon and cyan represents areas rich in aluminum; (c) is enlarged

image of rectangle indicated on Window 18 in (a) with the respective EDX map shown in (d); green

represents areas rich in aluminum, yellow is calcium and cyan is silicon; and (e) is typical elemental

composition of selected areas in (d). These figures appear in colour in the electronic version.

Fig. 10. Schematic showing (a) double layer polarization and (b) interfacial polarization.

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Fig. 11. (a) Conductivity, σ, and its derivative, dσ/dt, during initial 24-hours, with Regions I–VI

indicated; (b) normalized relative permittivity, ε_N, at five selected spot frequencies; and (c) variation

in internal temperature of cement paste.
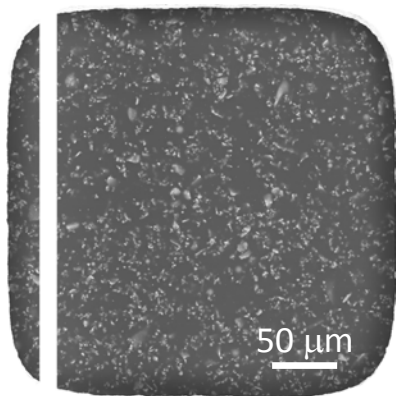
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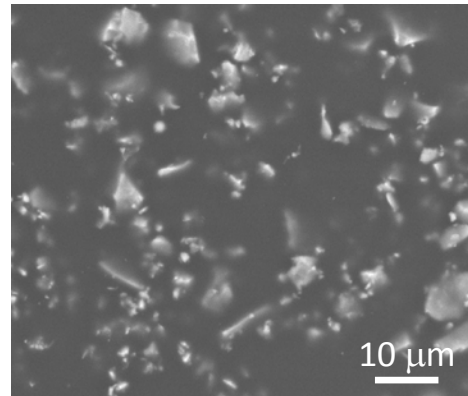979

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984   **<u>Video thumbnails</u>**

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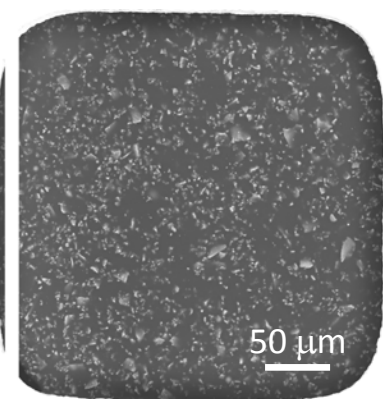987   Thumbnail image for **Video 1**   Thumbnail image for **Video 2**

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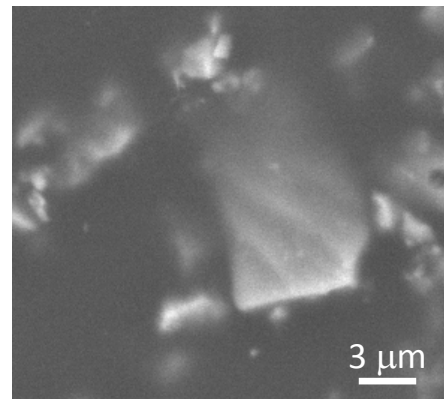989

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991   Thumbnail image for **Video 3**   Thumbnail image for **Video 4**

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999 **Table captions**

1000 **Table 1**. Typical oxide analysis of the cement.

1001 **Table 2**. Initial values of relative permittivity, $\varepsilon_{r,o}(\omega)$, at selected five spot frequencies.

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Table 1. Typical oxide analysis of the cement.

Content	By weight (%)
SiO_2	20.95
Al_2O_3	5.20
Fe_2O_3	3.42
CaO	59.86
MgO	2.25
K_2O	0.56
Na_2O	0.21

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1021   **Table 2**. Initial values of relative permittivity, $\varepsilon_{r,o}(\omega)$, at selected five spot frequencies.

Frequency (kHz)	$\varepsilon_{r,o}(\omega)$
1	7.49×10^6
100	2.11×10^3
250	5.45×10^2
500	2.50×10^2
1,000 (1 MHz)	1.42×10^2

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