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Sigvardsen, Nina M.; Geiker, Mette R.; Ottosen, Lisbeth M.

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1 Phase development and mechanical response of 2 low-level cement replacements with wood ash and 3 washed wood ash

4 Nina M. Sigvardsen^{a,*}, Mette R. Geiker^b, Lisbeth M. Ottosen^a

5 ^a Department of Civil Engineering, Technical University of Denmark, Kgs. Lyngby, Denmark

6 ^b Department of Structural Engineering, Norwegian University of Science and Technology, Trondheim, Norway

7

8 **Abstract**

9 A significant increase is seen worldwide in the amounts of wood ashes (WAs) produced by the
10 heating and power industry. This study investigates the potential utilisation of two different
11 WAs as low-level cement replacements, in an untreated and a washed version. Phase
12 development and mechanical response were investigated. Results indicated ettringite formation
13 mainly to contribute to the strength development until excessive formation. Indications of an
14 optimum SO_3/C_3A ratio for mixtures with a low-level cement replacement with WA was
15 between 0.4 and 0.5. Washed WA originating from grate combustion appeared to be most
16 promising of the tested WAs in cement-based materials.

17 *Keywords:* Wood ash, low-level cement replacement, phase development, mechanical
18 response, cement-based material.

19

20 **1. Introduction**

21 Cement production accounts for 8-9% of the total anthropogenic CO₂ emissions [1], and the
22 percentage is increasing due to a growing need for cement in developing countries [2]. One

* Corresponding author.

E-mail address: nimasi@byg.dtu.dk (N.M. Sigvardsen).

Abbreviations (not standard): WA1: untreated wood ash no. 1, WA2: untreated wood ash no. 2, WA1-W: wood ash no. 1 exposed to a preliminary washing treatment, WA2-W: wood ash no. 2 exposed to a preliminary washing treatment.

23 way to decrease the associated CO₂ emissions from cement production is the use of blended
24 cement where a part of the cement is substituted with other materials. The production of ash
25 deriving from biomass, organic materials such as wood, is increasing due to a withdrawal of
26 the traditional coal-fired power plants in Europe [3], substituting coal with biomass in the
27 heating and power production [4]. Currently, approximately 10 million tonnes of biomass ash
28 are produced annually worldwide alone from the electricity production, thus for heat-only
29 production, additional quantities of biomass ash can be added to the quantities [4]. This leads
30 to a series of potentially new types of materials which can be used as a partial cement
31 substitution in blended cement. Such a potential new material could be wood ash (WA),
32 originating from combustion of wood and wood products [5].

33 The performance of wood ash in mortar and concrete, studied in the literature [5–11], vary
34 significantly depending on the physicochemical characteristics of the WA utilised, again
35 depending on, e.g. the type of wood fuel and combustion process used for the energy
36 production [12,13]. This is clearly seen, e.g. from compressive strength measurements of
37 mortar samples with a partial cement replacement of cement with different WAs; Udoeyo et
38 al. [11], Berra et al. [6], and Elinwa and Mahmood [10] all saw a decrease in the compressive
39 strength with increasing replacement rates, while Rajamma et al. [14] and Ramos et al. [7]
40 observed a maintained compressive strength for samples with 10 and 20% cement replacements
41 compared to a reference sample. Further, the properties of a WA can be improved by different
42 types of pre-treatments; Berra et al. [6] included a washing step, Doudart de la Grée et al. [15]
43 included both a sieving and washing step, and Rosales et al. [16] included grinding, heating
44 and removal of remnants of charred wood, all pre-treatments improving the compressive
45 strength measurements of cement-based materials with WA as a partial cement replacement.
46 Washing of the WA reduces the content of soluble salts (such as chlorides and sulfates) [15].
47 These promising results encourage further studies, including pre-treatments and following both
48 the strength and the phase development over time, as the latter has not been included in any of
49 the previous studies, in order to increase the knowledge on how pre-treatment of WA influences
50 the two. Based on previous studies, only low-level replacements (10wt%) of cement with WA,
51 have seen to be feasible based on the compressive strength. This study continues these
52 investigations on low-level replacements in order to determine the effects on the compressive
53 strength and phase development at low-level cement replacements with WA.

54 The objectives of this study are: (1) to determine the impact of sieving and washing treatment
55 of the WAs on the physicochemical characteristics; (2) to investigate the impact of a low-level

56 cement replacement with WA on the mechanical response and phase development as a function
57 of time; and (3) to determine the influence of sieving and washing treatments before utilisation
58 of WA as a low-level cement replacement according to the strength and phase development.

59 In the presented study, two types of WA originating from different types of combustion but
60 using the same type of biofuel were investigated. The two investigated WAs originate from
61 combustion of wood chips. One originates from grate combustion, and the other from
62 circulating fluidised bed combustion. Wood chips for the energy production are one of the most
63 commonly used biomasses, and the use has increased in consumption over the last 20 years
64 (841% increase in the consumption of wood chips for the energy production since 2000 [17]).
65 According to a recently published report by representatives from Austria, Canada, Denmark,
66 Germany, Italy and the Netherlands [4] grate combustion is predominately used for combustion
67 of biomass, but circulating fluidised bed combustion is gaining ground in many of the
68 countries. These types of plants, grate or circulating fluidised bed combustion, have the highest
69 efficiency when solely biomass is used [18], and are the most common type of plants regarding
70 combustion of biomass. This means that the two chosen WAs represent common types of WAs.

71

72 **2. Materials and methods**

73 *2.1. Materials*

74 The materials used for this study were Portland cement, Rapid Aalborg Cement from Aalborg
75 Portland, Denmark (CEM I), inert quartz (Qz) [19], and two types of wood fly ash, sampled at
76 Skærbækværket Biomass Power Plant, Denmark (WA1) and Värtaverket Combined Heat and
77 Power Plant, Sweden (WA2). WA1 is a residue from grate combustion (600-1,000°C). WA2
78 is a residue from circulating fluidised bed combustion (760-930°C). The fuel used at both plants
79 was a similar type of wood chips originating from whole trees, primary pine trees, including
80 bark and needles [20]. After sampling, the WAs were stored in closed plastic buckets protected
81 from moist, heat and light sources. The buckets were rotated by hand in order to increase the
82 uniformity of the WA before smaller portions of WA for further treatment were sampled. The
83 WA samples were divided into two portions. The WAs were dried at 50°C and sieved. The
84 sieving removed the particles $\geq 250\mu\text{m}$, which consisted only of larger remnants from charred
85 wood. The larger remnants of charred wood accounted for approximately 25% of WA1 and <
86 2% of WA2 when received from the power plants. Smaller particles of charred wood, which

87 can be found in the fraction $\leq 250\mu\text{m}$ [15], are not removed. One portion of each WA was
88 subjected to drying at 50°C and sieving to a particle size of $\leq 250\mu\text{m}$ (termed WA1 and WA2).
89 The other portion was washed after drying and sieving (termed WA1-W and WA2-W). The
90 washing procedure was as follows: 100 g ash was mixed with distilled water to a liquid-to-
91 solid ratio (L/S) of 5 and shaken manually for 1 min [21]. After settling (app. 5 min.), the water
92 was decanted. This procedure was repeated three times, the suspension was filtered (retention
93 $12\text{-}15\mu\text{m}$), and the ash was subsequently dried at 50°C .

94 2.2 Methods

95 2.2.1 WA characterisation

96 Selected characteristics of the WAs, CEM I and Qz, are given in Tab. 2. Loss on ignition (LoI)
97 was measured at 950°C , according to EN 196-2 [22]. The element content was determined by
98 X-ray fluorescence (XRF) spectrometry measured by the use of a SPECTRO GmbH X-LAB
99 2000 with a Pd-tube on samples ground to a particle size of less than $200\mu\text{m}$. The software
100 used was TQ-3945r, and the equivalent content of oxides was calculated based on the element
101 content. Cl^- and SO_4^{2-} were measured with Ion Chromatography (IC) on a 1:2.5 solid-to-liquid
102 ratio suspension in distilled water after 1 hour of agitation. The free calcium oxide contents in
103 the WAs were measured according to EN 451-1 [23].

104 The particle size distribution was found by laser diffraction by the use of Mastersizer 2000.
105 The pH was measured for all materials in 1:2.5 solid-to-liquid ratio suspensions in distilled
106 water with a pH electrode after 1-hour agitation. The electric conductivity was determined on
107 the same suspension with an electrical conductivity meter. The particle density was measured
108 by the use of a helium gas pycnometer Micrometecs AccuPyc 1340 in accordance with EN 196-
109 6 [24].

110 The crystalline phases in the materials were identified by XRD. The WA was loaded into the
111 sample holder using backloading. A PanAnalytical X-ray diffractometer, sat at the PW3064
112 Spinner stage for standard powder samples have been used for the measurements. Cu-K α
113 radiation with a wavelength of 1.54 \AA was used as the x-ray source. The samples were
114 measured between $4^\circ 2\theta$ and $100^\circ 2\theta$ with a step size of $0.002^\circ 2\theta$ and a sampling time per
115 step of 24.8 s. The XRD plots were qualitatively evaluated using X'Pert HighScore Plus
116 software, with data from the International Centre for Diffraction Data (ICDD). A
117 semiquantitative analysis has been performed in X'Pert HighScore Plus software, determining

118 approximate amounts (in %) of the crystalline phases. The detection limited of the XRD
119 analysis is 2 wt%. Grain morphology was analysed by the use of Scanning Electron Microscope
120 (SEM)-images performed on a FEI Quanta 200. The pictures were magnified X1500, and the
121 accelerating voltage of the beam was 20 keV with a large field detector under low vacuum
122 conditions.

123 The thermogravimetric analysis (TGA) was performed on both WAs and WA-Ws.
124 Approximate 40 mg of the sample was poured into 85 μ l aluminium oxide crucibles (diameter
125 6.8mm), and the weight loss was measured from room temperature to 900 °C in a NETZSCH
126 STA 449 F3 Jupiter. First, the temperature was raised to 40 °C and held for 10 min.; then the
127 temperature was increased to 900 °C with a heating rate of 10 °C/min. During the
128 measurements, the cell was purged with 50 ml/min of nitrogen gas. The data were processed
129 using the analysis software Proteus Analyzer. The unburned carbon content was determined
130 from LoI and TGA measurements.

131 2.2.2. *Paste preparation and double solvent exchange*

132 Six paste mixes were prepared, one reference and with 10% replacements of cement either with
133 one of the four WAs or Qz with a constant w/b = 0.5. The pastes were mixed using a high
134 shear mixer (Whip Mix Power Mixer Model B). The mixing procedure was adapted from EN
135 196-1 [25]: mixing for 90 s, resting for 90 s, and mixing for 60 s. The pastes were cast in 5 ml
136 polythene tubes (diameter 12 mm) and stored for one day in a temperature-controlled room
137 (20°C, <80% RH). The pastes were demoulded and transferred into larger 25 ml vials (diameter
138 25 mm), subsequently filled with lime water (3 g calcium hydroxide/L distilled water [26]) and
139 stored in a temperature-controlled room (20°C). The pastes were tested after 1, 3, 7, 14, 28, 90,
140 182 and 365 days of hydration.

141 Double solvent exchange was used for hydration stoppage [27]. Four 2 mm thick slices
142 (diameter 12 mm) were cut from the middle of the cured paste samples. The slices were crushed
143 in a porcelain mortar until the whole paste sample could pass through a 1 mm sieve.
144 Approximately 3g of the crushed sample was immersed in 50 mL isopropanol. The suspension
145 was shaken for 30 sec, left to rest for 5 min, and subsequently decanted. This isopropanol
146 treatment was performed twice, and then the suspension was vacuum-filtered. The crushed
147 sample was then immersed in 10 mL diethyl ether, shaken for 30 sec, left to rest for 5 min., and
148 vacuum-filtered [27]. The crushed cement paste (< 1mm) sample was shortly subjected to an

149 oven drying process (8 min. at 40°C) in order to remove the easily volatile diethyl ether. This
 150 method does not alter the hydrate products significantly [27]. For the TGA and XRD analysis,
 151 the paste samples were further crushed in a porcelain mortar, right before test execution, until
 152 the whole paste sample could pass through a 63µm sieve [27].

153 2.2.3. Thermogravimetric analysis (TGA)

154 Thermogravimetric analysis (TGA) was performed on pastes subsequently to the double
 155 solvent exchange treatment, drying and crushing. The TGA was performed as described in
 156 section 2.2.1. From the TGA measurements, the loss of bound water and decomposition of
 157 ettringite and calcite were determined by the use of a horizontal step and decomposition of
 158 portlandite was determined by the use of a tangential step. The step for bound water was 50°C
 159 and 550°C [27], for ettringite 50°C and 120°C [28], for portlandite 400°C and 550°C [27], and
 160 for calcite 550-800°C [27], respectively. It should be noted that the temperature interval for
 161 ettringite also includes carbonate AFm phases and C-S-H [28]. However, the included mass
 162 loss due to carbonate AFm phases was expected to be very small as the main peak of the
 163 carbonate AFm phases was determined to be above 120°C (approximately 160°C) as displayed
 164 in Fig. 5. The mass loss due to decomposition of C-S-H cannot be separated from the mass loss
 165 corresponding to ettringite as the TGA peaks overlap. This might lead to an overestimation of
 166 the amount of ettringite formed. However, this is acceptable as the WAs are not expected to
 167 contribute significantly to the formation of C-S-H compared to the formation of ettringite [29]
 168 due to a low content of silica in the WA, and the increase due to C-S-H can therefore mainly
 169 be attributed to the cement hydration. The equations for the quantification of the bound water
 170 (H), portlandite (CH), ettringite (C₆A₃S₃H₃₂) and calcite (C \bar{C}) relative to the dry mass or clinker
 171 content (c.f. [27]) are given in Eqs. (1)-(12).

$$H_{measured} = WL_{50-550} \quad (1)$$

$$172 \quad H_{anhydrous} = \frac{H_{measured}}{weight \text{ at } 550^{\circ}C} \quad (2)$$

$$H_{clinker} = \frac{H_{measured}}{weight \text{ at } 550^{\circ}C} \times \frac{100}{\%clinker} \quad (3)$$

$$CH_{measured} = WL_{400-550} \cdot (74/18) \quad (4)$$

$$173 \quad CH_{anhydrous} = \frac{CH_{measured}}{weight \text{ at } 550^{\circ}C} \quad (5)$$

$$CH_{clinker} = \frac{CH_{measured}}{weight \text{ at } 550^{\circ}C} \times \frac{100}{\%clinker} \quad (6)$$

$$C_6As_3H_{32}_{measured} = WL_{50-120} \cdot (1255/(32 \cdot 18)) \quad (7)$$

$$C_6As_3H_{32}_{anhydrous} = \frac{C_6As_3H_{32}_{measured}}{weight\ at\ 550^\circ C} \quad (8)$$

$$C_6As_3H_{32}_{clinker} = \frac{C_6As_3H_{32}_{measured}}{weight\ at\ 550^\circ C} \times \frac{100}{\%clinker} \quad (9)$$

$$\bar{C}\bar{C}_{measured} = WL_{550-800} \cdot (100/44) \quad (10)$$

$$\bar{C}\bar{C}_{anhydrous} = \frac{\bar{C}\bar{C}_{measured}}{weight\ at\ 550^\circ C} \quad (11)$$

$$\bar{C}\bar{C}_{clinker} = \frac{CaCO_{3_{measured}}}{weight\ at\ 550^\circ C} \times \frac{100}{\%clinker} \quad (12)$$

176 The standard deviations of these quantifications were based on three independent
177 measurements and quantifications of the bound water (H), portlandite (CH), ettringite
178 ($C_6As_3H_{32}$) and calcite ($\bar{C}\bar{C}$) of a control sample at 28 days of hydration.

179 2.2.4. X-ray diffraction (XRD)

180 X-ray diffraction (XRD) analysis was performed on the same pastes used for the TGA
181 subsequently to the double solvent exchange treatment, drying and crushing. The XRD analysis
182 was performed, as described in section 2.2.1. Semiquantitative analysis was performed in
183 X'Pert HighScore Plus software, determining approximate amounts (in %) of the crystalline
184 phases.

185 2.2.5. Preparation of mortar samples and compressive strength testing

186 Mortar mixes were prepared according to the mixing procedure prescribed in EN 196-1 [25]
187 with a constant w/b = 0.5. One control mix without WA (REF), five mixes with 10%, and five
188 mixes with 20% replacements of cement (in accordance with ASTM C311/C311M-13 [30]),
189 either with one of the four WAs or Qz. WA or Qz was added to the unhydrated cement before
190 mixing. Super plasticiser (Dynamon XTend from Mapei) was added to the mixing water and
191 in order to achieve standard consistency, thus keeping a constant w/b ratio. The consistency
192 was determined by flow table according to EN 1015-3 [31] for mixes containing WA or Qz,
193 see Tab. 1. Mortar prisms (40 x 40 x 160 mm) were cast in accordance with EN 196-1 [25].
194 Three mortar prisms were prepared for each of the mixes for each of the hydration ages. After
195 1 day in a temperature-controlled room (20°C, <80% RH) the three prisms from each mix were
196 demoulded and stored in separate boxes submerged in lime water (3 g calcium hydroxide/L

197 distilled water [26]) in a temperature-controlled room (20°C). The mortar specimens with 10%
198 replacements were tested after 1, 3, 7, 14, 28, 90, 182 and 365 days of hydration and the mortar
199 specimens with 20% replacements were tested after 7 and 28 days of hydration [32].

200 After hydration, the compressive strength of the mortar specimens was determined according
201 to EN 196-1 [25]. The mortars were split in two with an electro-mechanic test machine (Instron
202 6022) by increasing the load by 0.05 kN/s [25], and the compressive strength was measured
203 for all the subsequent six pieces of mortar with a servohydraulic test machine (Toni Technik
204 300Ton) by increasing the load by 2.4 kN/s [25]. The air content of mortars was determined in
205 accordance with Osbæck [33] by the use of the weight at demoulding and the theoretical air
206 void free mortar. The compressive strength was then normalised to an air content of 2 vol% by
207 the use of Bolomeys equation [34]. SAI was calculated according to ASTM C311/C311M-13
208 [30].

209

210 **3. Results**

211 *3.1 Characteristics of WAs and Qz*

212 DTG curves for all materials are displayed in Fig. 1. Some prehydration of CaO resulting in
213 portlandite formation were seen for the washes ashes as a result of the washing treatment. The
214 chemical composition of the materials is presented in Tab. 2 and the physical properties are
215 presented in Tab. 3. A total below detection limit of Cl^- and SO_4^{2-} and a reduction in the content
216 of alkali metals K_2O and Na_2O are results from the washing of WAs. Tab. 4 displays the
217 crystalline phases for the materials and hydration of CaO to $\text{Ca}(\text{OH})_2$ is seen for washed WAs.
218 The grain morphology is shown by SEM images (Fig. 3). This reveals large, angular particles
219 for both WAs. A layer of soluble compounds covers the untreated WAs, Fig. 3 (a) and (c), seen
220 as minor particles covering larger particles. When the WAs were washed, Fig. 3. (b) and (d),
221 this layer was removed. More spherical particles were found in WA1-W compared to WA2-
222 W. The washing did not improve LoI of the WAs, which are high ($\geq 15\%$) for all WAs. The
223 unburned carbon content was $\leq 1\%$ for both WA1 and WA1-W and 6 and 7% for WA2 and
224 WA2-W respectively.

225 *3.2. Strength activity index*

226 For pozzolanic activity, the ASTM C618 [32] requires an SAI above 0.75 compared to the
227 reference after 7 and 28 days of hydration for a mortar sample containing 20% possible
228 pozzolan and 80% CEM I as binder. The SAI are presented in Tab. 5 and only WA1 mortar
229 does not comply with the limit. The washing treatment leads to an increase in the SAI for both
230 types of WAs. Qz also complies with the limit, even though it being completely inert.

231 *3.3. Compressive strength development*

232 At 1 day of hydration, the compressive strength of the WA1 mortar is comparable to REF, see
233 Fig. 4 and Tab. 6. The rest of the WA mortars obtains a slightly lower compressive strength,
234 and a tendency is seen, where the washed WA mortars are more comparable with the Qz mortar.
235 At 3 days the compressive strength for all WA mortars is comparable to REF and higher than
236 the Qz mortar. From 7 days of hydration, the compressive strength of REF exceeds all WA and
237 Qz mortars. At $90 \leq$ days of hydration, all WA mortars have a slightly higher compressive
238 strength compared to the Qz mortar. The WA1-W mortar exceeds the compressive strength of
239 all other WA mortars, followed by, in decreasing order, the WA2, WA1 and WA2-W mortar.

240 *3.4. Phase development*

241 The phase development was analysed by XRD and TGA. Tab. 7 is an overview of the detected
242 phases in the pastes determined by XRD. Depletion of alite was seen after 3 days of hydration
243 for all pastes. Depletion of belite and ferrite are seen after 14 days of hydration for WA1-W
244 and Qz paste, and for the remaining pastes after 28 days of hydration. Portlandite and ettringite
245 were detected in all pastes from 1 days of hydration and monocarbonate was detected in all
246 pastes from $14 \leq$ days of hydration. Quartz is detected in WA, and Qz pastes, at all hydration
247 ages. Calcite is detected at 1 day of hydration for all WA pastes. However, dissolution of the
248 calcite is seen for WA2 and WA2-W pastes since no calcite is detected again before 90 days
249 of hydration.

250 Differential thermogravimetric (DTG) curves, determined with TGA for all pastes at 28 days
251 of hydration, are presented in Fig. 5. The DTG curves show peaks of weight changes related to
252 the decomposition of ettringite (Et) and C-S-H, monocarbonate (Mc) and portlandite (CH).
253 Above 550°C , calcite decomposes by emitting CO_2 [27], substantiating the change from
254 hydration to carbonation to be at 550°C as used in the formulas (1) – (12).

255 Quantification of bound water, portlandite, ettringite/C-S-H and calcite in all pastes are
256 presented in Fig. 6, 7, 8 and 9, (a) calculated as wt%/anhydrous binder weight and (b) calculated
257 as wt%/clinker content. The standard deviation was 0.67%wt for the quantification of bound
258 water, 0.56%wt for the quantification of portlandite, 0.27%wt for the quantification of
259 ettringite and 0.33%wt for the quantification of calcite. This is illustrated as error bars in the
260 figures 6-9.

261 *3.4.1. Bound water*

262 At 1-3 days of hydration, a slightly larger amount of water was bound in the WA pastes
263 compared to REF, see Fig. 6 (a)). After 7 days of hydration, the amount of bound water in REF
264 and WA pastes were comparable. At 14 and 28 days of hydration, the amount of water bound
265 in REF slightly exceeds the amount bound in the WA pastes. At 365 days the amount of bound
266 water in REF and WA pastes are in the same range, but with a slightly higher amount of bound
267 water in WA2 and WA2-W pastes compared to WA1 and WA1-W pastes. Qz had the lowest
268 content of bound water of all pastes.

269 *3.4.2. Portlandite*

270 At 1-3 days of hydration, the portlandite content in WA and Qz pastes is similar or slightly
271 higher than REF (Fig. 7 (a)). At 7 days, the portlandite content for REF paste increases
272 compared to WA and Qz pastes, which remains comparable for the rest of the hydration period.

273 *3.4.3. Ettringite*

274 Ettringite has been determined for both REF and WA pastes at all ages (Tab. 7). A comparable
275 ettringite content (Fig. 8 (a)) is seen for WA pastes from 1 to 7 days of hydration. From $14 \leq$
276 days of hydration, the ettringite content in the WA pastes exceeds REF. This is especially
277 notable for WA2 paste from 90 days of hydration and, at later ages ($182 \leq$ days of hydration),
278 the same is seen for WA1 paste. Qz had the lowest content of ettringite at all ages.

279 *3.4.4. Calcite*

280 A clear difference is seen in the calcite content between WA1 and WA1-W pastes, and WA2
281 and WA2-W pastes at all ages (Fig. 9 (a)), with WA1 and WA1-W pastes having the highest
282 content of calcite. The calcite content decreased from 1-90 days of hydration for all pastes
283 followed by an increase after 90 days.

284 3.4.5. Dilution effect

285 In the pastes, the most reactive part (the cement) is replaced with a less or non-reactive material
286 (WA or Qz). In order to take this dilution effect into account when analysing the results, the
287 amount of bound water, portlandite, ettringite and calcite are calculated as wt%/clinker content,
288 see Fig. 6, 7, 8 and 9 (b). The WA pastes have a higher amount of bound water than REF, and
289 Qz pastes at all ages, see Fig. 6 (b). From 28 days of hydration, a slight increase in the
290 portlandite content is seen for REF compared to WA and Qz pastes (Fig. 7 (b)). For the
291 ettringite (Fig. 8 (b)) and calcite content (Fig. 9 (b)), Qz exceeds the contents calculated for
292 REF.

293

294 4. Discussion

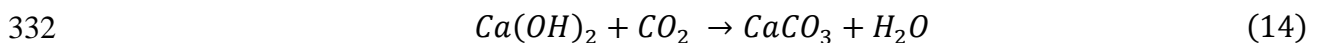
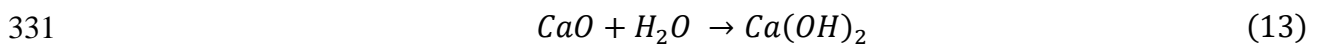
295 In the following section, the objectives 1-3 outlined in section 1 will be discussed based on the
296 results presented in section 3.

297 4.1. Impact of the washing on the physicochemical characteristics of the WAs

298 Washing of the WAs resulted in a slight increase of the particle size distribution (Fig. 2) by
299 removing the soluble fraction consisting of compounds with smaller particle sizes. This is
300 supported by the SEM images (Fig. 3). Fig. 3 (a) and (c) reveals a layer of smaller compounds
301 covering the particles of the raw WAs. These compounds are removed by washing, see Fig. 3.
302 (b) and (d), and are thus assumed soluble, probably salts with Cl^- and SO_4^{2-} and the alkali
303 metals, K and Na such as KCl , K_2SO_4 (Tab. 4) and NaCl , Na_2SO_4 , as these chemical elements
304 are removed to below detection limit or significantly reduced (Tab. 2). No decrease of neither
305 LoI nor the unburned carbon content is seen as a result of the washing. The sieving effectively
306 removed unburned carbon from WA1 and WA1-W, however, smaller particles ($\geq 250\mu\text{m}$) of
307 unburned carbon are found in WA2 and WA2-W, containing 6 and 7% unburned carbon,
308 respectively. The unburned carbon can lead to an increase in the water requirement [12,35,36].
309 However, this was not seen for the WAs investigated in this study. The high LoI measured for
310 all WAs are primarily due to the content of hydrate phases and especially carbonate phases and
311 not a high content of unburned carbon. The content of free CaO is decreased by the washing,
312 however, it could still present an issue regarding soundness of the blended cement.

313 Several other issues are possible when utilising these WAs as a partial cement replacement,
314 e.g. P_2O_5 can cause delayed set, alkalis can cause alkali silica reactions and SO_3 can cause
315 sulfate attack. In relation to the durability, washing improves the possible use of WAs as a
316 partial cement replacement, but further treatments will possibly be required before utilisation
317 in cement-based materials is possible. However, as these issues are not investigated in this
318 study, this needs to be addressed further in a subsequent study.

319 The washing further caused a difference in the phase composition of the WAs. From the DTG
320 curves (Fig. 1) of the unhydrated materials, C-S-H (as no ettringite was determined by XRD)
321 and an increase in the calcite content can be found in the washed WAs. The increase in calcite
322 is substantiated by the XRD (Tab. 4.) and is due to removal of other water-soluble compounds
323 and carbonation. Portlandite has been determined for all WAs by the XRD (Tab. 4.), but the
324 DTG curves (Fig. 1) reveals a difference in the impact of the washing on the Portlandite content
325 between the two types of WAs. The content of portlandite increases after the washing of WA1,
326 but decreases for WA2. For both washed WAs, a chemical prehydration process between CaO
327 and the content of water forming portlandite following reaction (13) is expected [29], as no
328 CaO are found in the washed WAs (Tab. 4.) and a significant reduction is seen in the content
329 of free CaO (Tab. 2) are seen. Subsequently, carbonation occurs in WA2-W, decreasing the
330 content of portlandite and leading to calcite formation, following reaction (14) [37–39].



333 The initial content of portlandite and calcite in the untreated ashes are a consequence of water
334 and CO_2 in the air during ash storage at the power plants, following reactions (13) and (14).

335 Arcanite (K_2SO_4) was determined in WA1 by XRD WA1, see Tab. 4. Formation of arcanite in
336 the ash is due to a higher release of alkali metals by volatilisation facilitated by the high
337 temperatures in grate combustion, compared to a fluidised bed system [40]. Arcanite is water-
338 soluble and is removed during the washing, and thus it is not present in WA1-W (Tab. 4).

339 Sylvite (KCl) and anhydrite ($Ca(SO_4)$) were identified in WA2 by XRD, see Tab. 4. Thus, in
340 WA2 potassium is primarily bound with chloride rather than sulfate, and sulfate is bound
341 primarily to calcium. Anhydrite is a result of a sulphation process at the power plant were
342 limestone are added to capture SO_2 , an important process in a fluidised bed system,

343 precipitating anhydrite [40]. Neither sylvite nor anhydrite is present in WA2-W (Tab. 4)
344 because these compounds are water-soluble, and the lime present in WA2 is hydrated to
345 portlandite following reaction (13).

346 The initial presence of calcite has a beneficial impact on the properties of a cementitious
347 material due to the potential formation of hemi- and monocarbonate. These AFm phases are
348 more stable than monosulfate in the presence of carbonates [41], and as a consequence,
349 ettringite does not transform into monosulfate, but is stabilised. Stabilisation of ettringite leads
350 to an increase in compressive strength, as ettringite has a larger content of hydrate water and is
351 more voluminous, leading to a reduction in the porosity [29,42–44]. Reactions (13) and (14)
352 can occur during hydration of cement paste with partial cement replacement with WA due to
353 hydration of CaO and subsequently carbonation [39], as CaO is present in both WA1 and WA2
354 and Ca(OH)₂ is present in all WAs (Tab. 4.).

355

356 *4.2. Impact of the partial cement replacement of cement with WA on SAI, mechanical response* 357 *and phase development*

358 *4.2.1. Strength activity index*

359 From the results from the SAI test (Tab. 5), WA1-W, WA2 and WA2-W are seen to possess
360 pozzolanic properties, meeting the requirements set by ASTM C618 [32] at both 7 and 28 days
361 of hydration. A decrease of 20% and 15% decrease in the strength compared to REF are seen
362 for Qz at 7 and 28 days of hydration, respectively, thus Qz complies with the requirements set
363 by ASTM C618 [32]. However, Qz is completely inert and does not contribute through either
364 nucleation processes or particle packing, due to the large particle size of Qz compared to CEM
365 I (Fig. 2) [45].

366 The SAI test an indirect method measuring a physical property indicating the extent of
367 pozzolanic activity of a material [46]. According to the literature [47–49], there are several
368 drawbacks of this method. An unreactive material can be misread as having pozzolanic
369 properties, e.g. due to nucleation processes and particle packing effects [50,51] and other
370 hydrate phases contributing to the compressive strength cannot be distinguished from the
371 hydrate phases resulting from pozzolanic activity. Further ASTM C618 [32] requires
372 measurements only at 7 and 28 days of hydration, which for some types of pozzolans is

373 inadequate, e.g. coal fly ash shows very little pozzolanic reactivity 28 days of hydration [38].
374 Amorphous silica and aluminosilicate leads to pozzolanic activity [52]. Due to the WAs
375 consisting of large and fibrous particles (Fig. 3) and not the typical glassy aluminosilicate
376 spherical particles found in commercial coal fly ash [53], the amount of amorphous glass are
377 considered to be limited in the WAs. Further, the content of silica in WA1 and WA1-W are
378 low ($< 13\%$), see Tab. 2. The silica content in WA2 and WA-2-W is higher (23.8 and 26.5%,
379 respectively), but this can be attributed to inert sand particles, which make the suspension bed
380 and are carried with the flue gas during combustion with the circulating fluidised bed
381 technology ending up in the fly ash fraction [40]. Thus a very limited pozzolanic reaction with
382 silica [43] can be expected and the increase in strength can mainly be due to the WAs
383 contributing through hydration of other hydrate phases, like ettringite, contributing to an
384 increase in compressive strength [42]. No contribution through heterogeneous nucleation
385 processes from WAs are expected either due to their particle size distribution being equivalent
386 or larger than CEM I, see Fig. 2 [45].

387

388 *4.2.2. Mechanical response*

389 The development of compressive strength, when WAs are used as a partial cement replacement,
390 is seen in Fig. 4. At 1 day of hydration WA1 and WA2 mortars have compressive strength
391 comparable to the compressive strength of REF, and higher compressive strength compared to
392 the mortars with WA1-W, WA2-W and Qz. The compressive strength of the mortar with WA1
393 is comparable to REF at both 1 and 3 days of hydration. All mortars containing WA, has a
394 slightly higher compressive strength than the mortar with Qz at 1-7 days of hydration.

395 No contribution through heterogeneous nucleation processes from the WAs are expected, as
396 described in section 4.2.1, thus the increase in the compressive strength of WA mortars being
397 comparable to REF and not Qz at yearly age indicates an influence from chemical reactions
398 due to dissolution of easily soluble salts leading to strength improving hydration products
399 [29,42–44].

400 At late age, $90 \leq$ days of hydration, all WA mortars have a higher compressive strength than
401 the Qz mortar. The low compressive strength of Qz is due to the inert nature of the Qz and a
402 low density (2650kg/m^3 compared to 3180kg/m^3 for CEM I), resulting in a larger volume based

403 addition of Qz, leading to relatively less space available for the hydrate formation further
404 decreasing the strength.

405 At 365 days of hydration the average compressive strength for mortar with WA1 arrives at
406 86%, WA2 at 87%, WA1-W at 91%, WA2-W at 84% and Qz at 82% compared to the
407 compressive strength of REF. The lower compressive strength of WA mortars reflects the
408 dilution effect, decreasing the amount of hydrated cement and the larger volume based addition
409 of the WA compared to CEM I. However, the increase in compressive strength compared to
410 Qz indicates that the WA mortars facilitates the development of phases contributing to an
411 increase in the compressive strength.

412 *4.2.3. Phase development*

413 *4.2.3.1. Bound water*

414 An increase in the amount bound water is seen for WA pastes at 1-3 days of hydration (Fig. 6
415 (a)) compared to REF. Such increase can be explained by the dissolution of easily soluble salts
416 enhancing the initial growth of hydrated phases. From 14 to 90 days of hydration, the bound
417 water in REF exceeds all WA pastes, but at 365 days of hydration, all WA pastes have
418 approximately the same amount of bound water as the REF, indicating a continuous hydration
419 of phases in the WA pastes compared to REF. WA2 and WA2-W pastes contain a slightly
420 higher amount of bound water compared to WA1 and WA1-W pastes. This is explained by
421 WA2 and WA2-W binding more water in phases such as ettringite (see Fig. 8).

422 The amount of bound water for WA pastes exceeds Qz at all ages (Fig. 6 (a)). These
423 observations correspond to the WAs contributing through a quick initial dissolution of the
424 particles at early age and development of phases contributing to the compressive strength at
425 later ages.

426 *4.2.3.2. Portlandite*

427 Initially (1-7 days), the content of portlandite for all pastes with WAs exceeds the content of
428 portlandite for pastes with Qz (Fig. 7 (a)). The increase in portlandite, compared to Qz, can be
429 explained by an additional formation of portlandite due to a reaction between CaO in the WAs
430 and H₂O (Eq. 13).

431 After 28 days of hydration, the portlandite content in WA pastes is slightly exceeded by the
432 portlandite content of Qz when the dilution effect is considered (Fig. 7 (b)). This is explained
433 by consumption of portlandite in the WAs either as a result of, to a minor extent, the pozzolanic
434 reaction or formation of ettringite occurring at the expense of portlandite, aluminium and
435 sulfate [41].

436 4.2.3.3. *Ettringite/C-S-H*

437 As discussed previously (section 2.2.3.) the formation of C-S-H cannot be separated from the
438 mass loss corresponding to ettringite as the TGA peaks overlap, thus ettringite discussed in this
439 section can include C-S-H. Some initial C-S-H is determined for washed WAs, however, based
440 on the discussions presented in section 4.2.1. and 4.2.2. the WAs are not expected to contribute
441 significantly to the formation of C-S-H compared to the formation of ettringite, substantiated
442 by the literature [29]. Further, ettringite has been determined for both REF and WA pastes by
443 XRD at all ages (Tab. 7).

444 A difference is seen at 1 day of hydration for the ettringite content between pastes with
445 untreated and washed WAs (Fig. 8), corresponding to the initial C-S-H content and not
446 ettringite found in WA1-W and WA2-W (Fig. 1.) A rapid increase in the ettringite content is
447 seen for WA1 and WA2 from 1 to 3 days of hydration, corresponding to the dissolution of
448 SO_4^{2-} in the untreated ashes (Fig. 8.).

449 All WA pastes have a higher content of ettringite than Qz at all ages and REF from 28 days of
450 hydration, see Fig. 8 (a). The increase mainly contributed to the ettringite formation in WA
451 pastes is attributed to an increase in the $\text{SO}_3/\text{C}_3\text{A}$ ratio [38] and not formation of C-S-H. The
452 content of ettringite was highest in the paste with WA2, corresponding well to WA2 having
453 the largest initial content of SO_3 (Tab. 2). WA1 has the second-largest initial content of SO_3
454 and the second-largest content of ettringite at $182 \leq$ days of hydration. These tendencies are
455 consistent with the increased amount of bound water (Fig. 6 (b)) in WA pastes. Due to the
456 amount of hydrate water, ettringite is voluminous, which leads to a reduction in the porosity
457 and consequently to an increase in compressive strength [29,42–44]. At $182 \leq$ days of
458 hydration, the washed WA pastes have a lower ettringite content, compared to the untreated
459 WAs, due to a lower SO_3 content (Tab. 2).

460 There was no decrease in the ettringite content due to stabilisation as a result of the presence
461 of calcite and formation of monocarbonate (determined by the TGA, Fig. 5, and XRD Tab. 7.).

462 4.2.3.4. Calcite

463 A significant difference in the content of calcite at 1 day of hydration is seen between pastes
464 with WA1 and WA1-W, WA2 and WA2-W, and Qz and REF, see Fig. 9 (a). This is due to a
465 difference in the initial content of the materials: calcite contribution from WA and 5 %
466 limestone filler in CEM I. WA1 and WA1-W pastes have approximately 2 wt% higher content
467 of calcite than WA2 and WA2-W pastes (Fig. 9 (a)), attributed to a higher initial content of
468 calcite in WA1 and WA1-W (Fig. 1).

469 A decrease in calcite content is seen for all pastes from 1-90 days of hydration, especially
470 profound for WA pastes, due to formation of mono- and hemicarbonates at the expense of calcite
471 (determined by the TGA, Fig. 5, and XRD Tab. 7.). An increase in the calcite content is seen
472 from $90 \leq$ days of hydration (Fig. 9 (a) and (b)), due to carbonation at later ages for WA pastes.

473

474 4.3. Impact of washing on phase and compressive strength development

475 Several differences were seen between the two types of WAs, before and after washing when
476 utilised in as low cement-replacements in cement-based materials. More ettringite is found in
477 pastes with untreated WA, compared to pastes containing washed WA, due to a larger SO_3
478 content in untreated WAs. The washing leads to a higher content of calcite due to removal of
479 soluble and carbonation occurring during washing. In general, the contribution to the
480 compressive strength from the WAs is mainly due to the formation of ettringite as a result of
481 an increased $\text{SO}_3/\text{C}_3\text{A}$ ratio and stabilisation by calcite forming monocarbonate [41]. However,
482 excessive formation of ettringite can lead to micro-cracking and a decrease in strength if the
483 stress exceeds the tensile strength of the binder [38]. This can explain the different results
484 obtained for WA mortars, where WA1-W obtains a compressive strength above 90% the
485 reference strength and the compressive strength of WA1, WA2 and WA2-W all arrive at
486 between 84-87%.

487 A sufficient amount of ettringite is precipitated in WA1-W in order to increase the strength,
488 but low enough not to facilitate micro-cracks. The content of C_3A in the clinker can be
489 calculated by the use of Bogue calculations based on the content of Al_2O_3 and Fe_2O_3 [41], and
490 the $\text{SO}_3/\text{C}_3\text{A}$ ratios are calculated for the WAs: WA1 = 0.5, WA1-W = 0.4, WA2 = 0.5, and
491 WA2-W = 0.5. This indicates the optimum $\text{SO}_3/\text{C}_3\text{A}$ ratio of a mixture with a partial cement

492 replacement with WA to be: $0.4 \leq \text{optimum} < 0.5$. This provides an indication of a sufficient
493 removal of the SO_3 from a WA by a washing treatment order to obtain a sufficient, but not
494 excessive amount of ettringite contributing positively to the strength development. The
495 washing removed 76% of the SO_3 from WA1 and only 39% of SO_3 from WA2, thus further
496 treatment should be conducted for WA2-W indicating WA1-W to be more promising as a low-
497 level partial cement replacement.

498 Again, it should be noted that washing improves the possible use of WAs as a partial cement
499 replacement, but further treatments will possibly be required before utilisation in cement-based
500 materials is possible, especially considering several possible durability issues.

501

502 **5. Conclusion**

503 Two wood ashes (WAs), originating from two different power plants using circulating fluidised
504 bed combustion and grate combustion, respectively, were investigated in an untreated as well
505 as washed version for the purpose of low cement replacements (10%) in cement-based
506 materials. The time-dependent development of bound water, portlandite, ettringite(/C-S-H) and
507 calcite were measured in cement pastes with 10% replacement with the WAs. In general,
508 increased content of bound water, ettringite and calcite, and decreased content of portlandite
509 were seen for all pastes with WA compared to the Portland cement reference.

510 If only the mechanical response is considered, the results indicate that the WAs contributes to
511 a minor extent to the compressive strength through pozzolanic reactions and the main
512 contribution to the compressive strength are determined to be the ettringite content. However,
513 excessive formation of ettringite leads to micro-cracking and a decrease in strength. Thus, the
514 optimal ettringite content, contributing to the strength and not to micro-cracking, are found
515 based on the $\text{SO}_3/\text{C}_3\text{A}$ ratio for mixtures with low-level cement replacement with WA between
516 0.4 and 0.5.

517 For the two WAs investigated in this study, washed WA originating from grate combustion
518 appears to be more promising as a low-level cement replacement a cement-based material
519 compared to both untreated and washed WA originating from circulating fluidised bed
520 combustion based on the compressive strength development.

521

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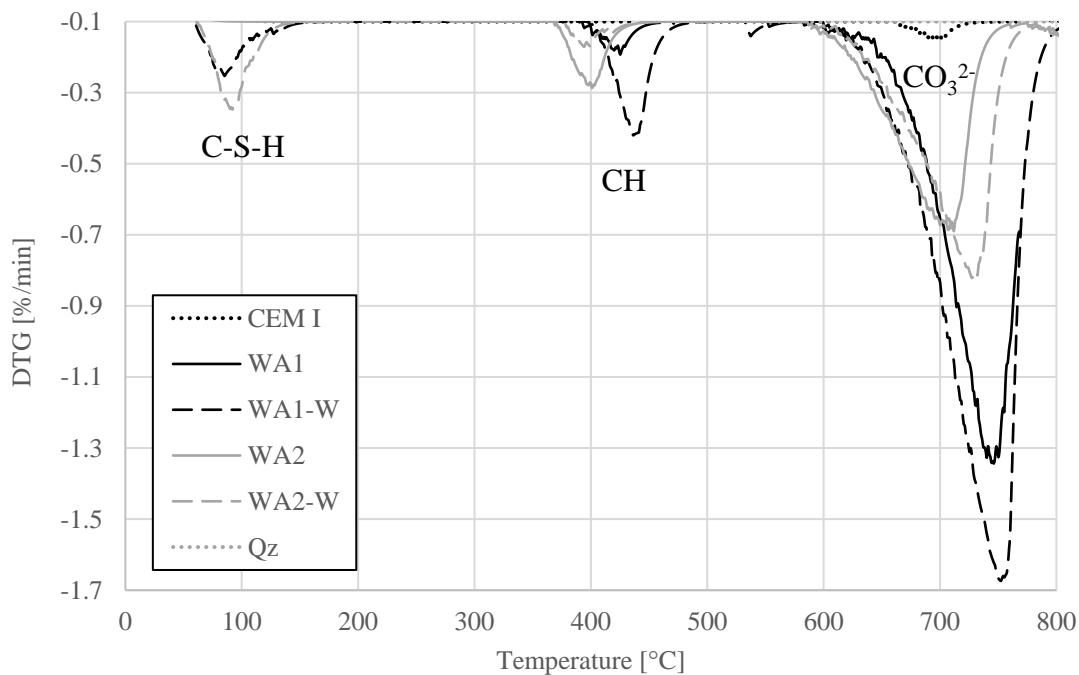
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651

652 **Table 1.** Consistency measured by flow table. The value SP to obtain REF are calculated via linear interpolation
653 of the measured flow values in order to obtain a flow value equal to the average flow value of REF.

	SP	Measure 1	Measure 2	Measure 3	Measure 4	Average	SP to obtain REF
	[g]	[mm]	[mm]	[mm]	[mm]	[mm]	[g]
REF no. 1	0	173.0	176.0	176.2	175.0	174.3	-
REF no. 2	0	167.0	175.6	175.5	176.2	174.3	-
WA1 no. 1	0.5	148.8	146.2	146.9	144.8	146.7	
WA1 no. 2	1.0	183.8	184.6	177.1	178.7	181.0	1.2
WA1 no. 3	2.4	206.7	201.9	206.5	207.0	205.1	
WA1-W no. 1	0.6	148.8	148.1	143.0	152.3	147.8	
WA1-W no. 2	1.0	169.1	173.7	166.8	159.1	167.2	1.2
WA1-W no. 3	1.5	182.8	194.2	181.6	191.1	187.4	
WA2 no. 1	0.5	172.2	178.9	171.6	166.5	172.3	
WA2 no. 2	0.8	183.6	182.5	179.8	185.1	182.7	0.6
WA2 no. 3	1.0	184.9	189.0	177.4	181.0	183.1	
WA2-W no. 1	0.5	174.0	172.4	164.4	164.0	166.9	
WA2-W no. 2	0.8	175.4	164.2	159.8	173.5	168.2	0.8
WA2-W no. 3	1.0	185.2	181.9	184.6	182.4	183.5	

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656 **Figure 1.** Differential thermogravimetric (DTG) curves for unhydrated materials. C-S-H: Calium silicate
657 hydrate, CH: Portlandite.

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660 **Table 2.** Chemical composition (%) of CEM I, WA1, WA1-W, WA2, WA2-W, and Qz. \pm defines the standard
 661 deviation. ND: not determined.

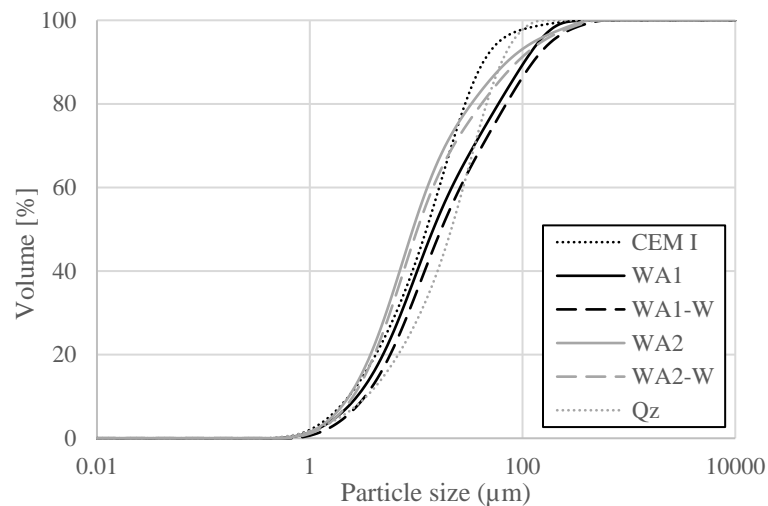
	CEM I	WA1	WA1-W	WA2	WA2-W	Qz
SiO ₂	19.7	11.0	12.7	23.8	26.5	99.4
Al ₂ O ₃	5.4	2.4	3.0	5.6	6.3	0.10
Fe ₂ O ₃	3.8	2.9	3.2	3.1	3.3	0.03
CaO	64.1	53.6	65.0	44.7	45.0	0
MgO	1.0	4.2	5.8	4.1	4.4	0
K ₂ O	0.4	14.6	4.4	7.6	5.7	0
Na ₂ O	0.3	1.0	1.0	0.8	0.9	0
P ₂ O ₅	0.3	2.9	3.8	3.8	4.2	0
SO ₃	3.2	5.4	1.3	6.1	3.7	0
CaO, free	ND	12.3	5.9	6.4	1.6	0
Cl ⁻	0.0 \pm 0.0	0.8 \pm 0.0	0.0 \pm 0.0	0.4 \pm 0.0	0.0 \pm 0.0	0.0 \pm 0.0
SO ₄ ²⁻	0.0 \pm 0.0	3.8 \pm 0.0	0.0 \pm 0.0	1.8 \pm 0.0	0.0 \pm 0.0	0.0 \pm 0.0
LoI, 950°C	1.9 \pm 0.0	15.0 \pm 0.1	19.6 \pm 0.1	16.2 \pm 0.3	19.7 \pm 0.1	0.0 \pm 0.0
Unburned carbon	-	\geq 1.0	\geq 1.0	5.7	6.7	-

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663 **Table 3.** Physical characteristics of CEM I, WA1, WA1-W, WA2, WA2-W, and Qz. \pm defines the standard
 664 deviation.

	CEM I	WA1	WA1-W	WA2	WA2-W	Qz
pH	12.8 \pm 0.0	13.0 \pm 0.1	12.5 \pm 0.0	12.7 \pm 0.1	12.5 \pm 0.2	7.7 \pm 0.1
Conductivity (mS m ⁻¹)	18.1 \pm 0.2	76.6 \pm 0.4	11.1 \pm 0.1	29.0 \pm 1.3	11.9 \pm 0.2	40.0 \pm 2.5
Particle density (kg/m ³)	3180	2740	2640	2710	2650	2650

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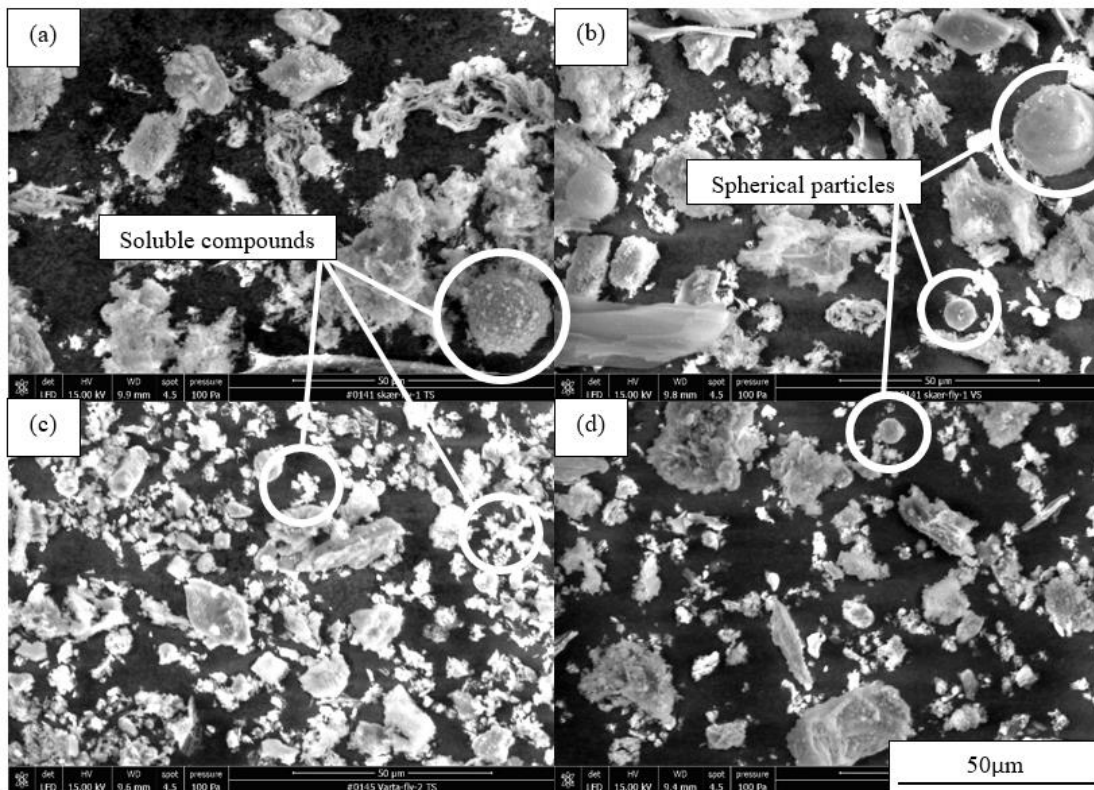
667 **Figure 2.** Particle size distribution of CEM I, WA1, WA1-W, WA2, WA2-W, and Qz, determined by laser
 668 diffraction.

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670 **Table 4.** Crystalline phases for unhydrated materials determined qualitatively by XRD diffraction. x: < 15%, xx:
 671 ~ 25%, xxx: ~ 50% and xxxx: ~ 100% of crystalline phases identified according to semiquantitative analysis.

	Alite	Belite-β	C ₃ A	Ferrite	Portlandite	Lime	Quartz	Calcite	Sylvite	Arcanite	Anhydrite
CEM I	xxx	x	x	x							x
WA1					x	x	xx	xxx		x	
WA1-W					x		xx	xxx			
WA2					x	x	xxx	xx	x		x
WA2-W					x		xxx	xxx			
Qz							xxxx				

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 677 **Figure 3.** Grain morphology of (a) WA1, (b) WA1-W, (c) WA2 and (d) WA2-W.
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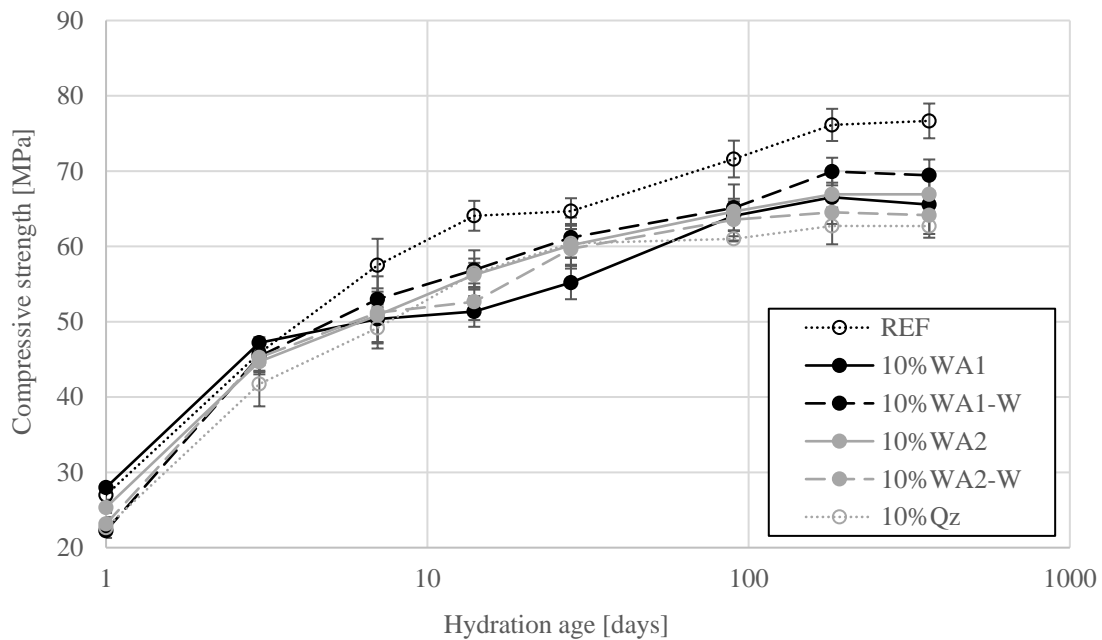
679 **Table 5.** Measured compressive strength, air content, compressive strength normalised to an air content of 2 vol%
 680 by the use of Bolomeys equation [34] and SAI calculated according to ASTM C311/C311M-13 [30].

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	Compressive strength (MPa)	SD	Air content (% vol)	Normalised compressive strength (MPa)	SAI
M7-REF	59.5	3.6	1.1	57.5	-
M7-20%WA1	44.1	0.7	1.0	42.6	0.74
M7-20%WA1-W	50.4	1.1	1.1	46.7	0.81
M7-20%WA2	50.3	0.7	1.0	48.7	0.85
M7-20%WA2-W	49.3	0.4	1.1	46.04	0.80
M7-20%Qz	45.9	0.9	1.0	44.1	0.77
M28-REF	69.9	1.8	1.1	64.7	-
M28-20%WA1	51.1	1.3	1.0	49.4	0.76
M28-20%WA1-W	59.3	2.7	1.1	55.0	0.85
M28-20%WA2	59.4	1.4	1.0	57.4	0.89
M28-20%WA2-W	57.0	0.7	1.1	53.24	0.82
M28-20%Qz	57.2	1.4	1.0	54.9	0.85

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685 **Figure 4.** Development of compressive strength of REF and mortars with 10% replacements of cement with WA1,
 686 WA1-W, WA2, WA2-W, and Qz after 1, 3, 7, 14, 28, 90, 182 and 365 days of hydration at 20°C. The compressive
 687 strength normalised to an air content of 2 vol% by the use of Bolomeys equation [34]. The error bars defines the
 688 standard deviation.

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691 **Table 6.** Measured compressive strength, air content and compressive strength normalised to an air content of 2
 692 vol% by the use of Bolomeys equation [34].

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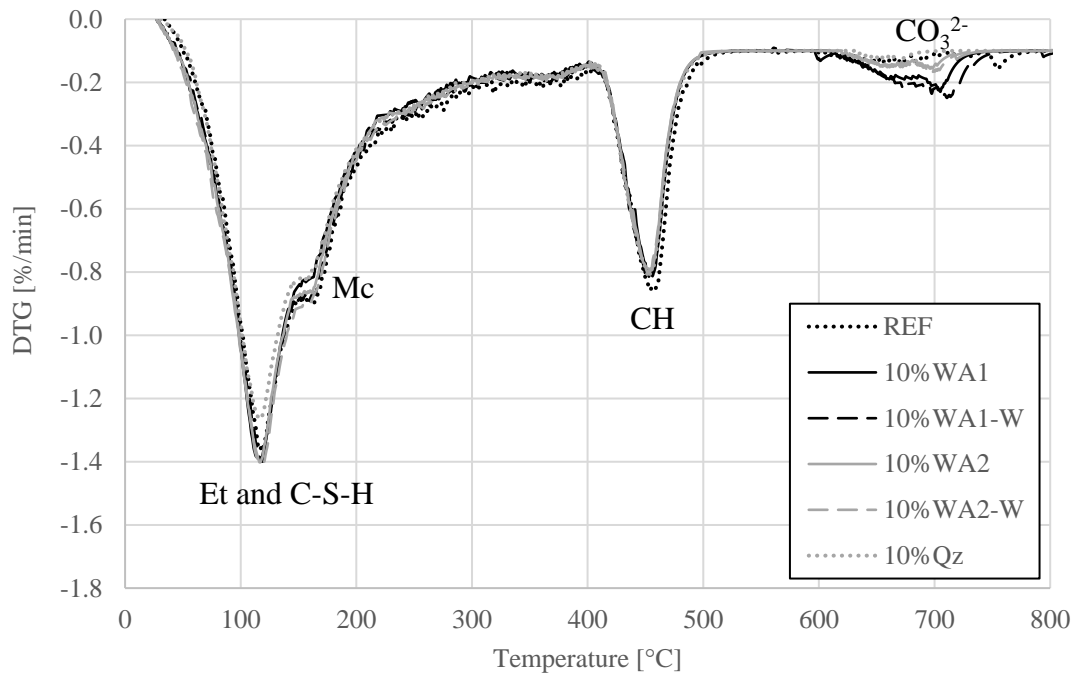
	Compressive strength (MPa)	SD	Air content (%vol)	Normalised compressive strength (MPa)
M1-REF	27.9	0.6	1.1	27.0
M1-10%WA1	30.1	0.7	0.1	28.0
M1-10%WA1-W	23.2	1.0	0.9	22.3
M1-10%WA2	26.1	0.7	1.2	25.3
M1-10%WA2-W	24.8	0.9	0.2	23.2
M1-10%Qz	23.8	0.9	0.8	22.7
M3-REF	47.4	1.6	1.1	45.8
M3-10%WA1	50.8	0.8	0.1	47.2
M3-10%WA1-W	47.4	2.2	0.9	45.4
M3-10%WA2	46.1	1.7	1.2	44.7
M3-10%WA2-W	48.4	1.9	0.2	45.3
M3-10%Qz	43.8	3.1	0.8	41.7
M7-REF	59.5	3.6	1.1	57.5
M7-10%WA1	54.2	3.5	0.1	50.4
M7-10%WA1-W	55.3	3.2	0.9	53.0
M7-10%WA2	52.5	3.7	1.2	50.9
M7-10%WA2-W	54.8	1.2	0.2	51.2
M7-10%Qz	51.6	2.9	0.8	49.2
M14-REF	67.1	2.1	1.1	64.1
M14-10%WA1	55.3	2.2	0.1	51.4
M14-10%WA1-W	59.4	2.7	0.9	56.9
M14-10%WA2	58.0	1.6	1.2	56.2
M14-10%WA2-W	56.4	2.6	0.2	52.7
M14-10%Qz	59.2	2.0	0.8	56.4
M28-REF	69.9	1.8	1.1	64.7
M28-10%WA1	59.4	2.4	0.1	55.2
M28-10%WA1-W	63.9	2.8	0.9	61.2
M28-10%WA2	62.1	2.7	1.2	60.2
M28-10%WA2-W	63.9	2.8	0.2	59.7
M28-10%Qz	63.6	1.8	0.8	60.4
M90-REF	74.1	2.5	1.1	71.6
M90-10%WA1	68.9	2.1	0.1	64.1
M90-10%WA1-W	68.0	3.2	0.9	65.1
M90-10%WA2	66.7	1.1	1.2	64.6
M90-10%WA2-W	68.0	3.0	0.2	63.6
M90-10%Qz	64.0	0.4	0.8	61.0
M182-REF	78.8	2.2	1.1	76.1
M182-10%WA1	71.6	2.1	0.1	66.5
M182-10%WA1-W	73.0	1.9	0.9	69.9
M182-10%WA2	69.1	2.8	1.2	66.9
M182-10%WA2-W	69.1	1.7	0.2	64.5
M182-10%Qz	65.8	0.4	0.8	62.7
M365-REF	77.0	2.5	1.1	76.7
M365-10%WA1	70.5	1.4	0.1	65.6
M365-10%WA1-W	71.5	2.2	0.9	69.4
M365-10%WA2	69.1	2.4	1.2	66.9
M365-10%WA2-W	68.6	2.7	0.2	64.1
M365-10%Qz	67.9	1.6	0.8	62.7

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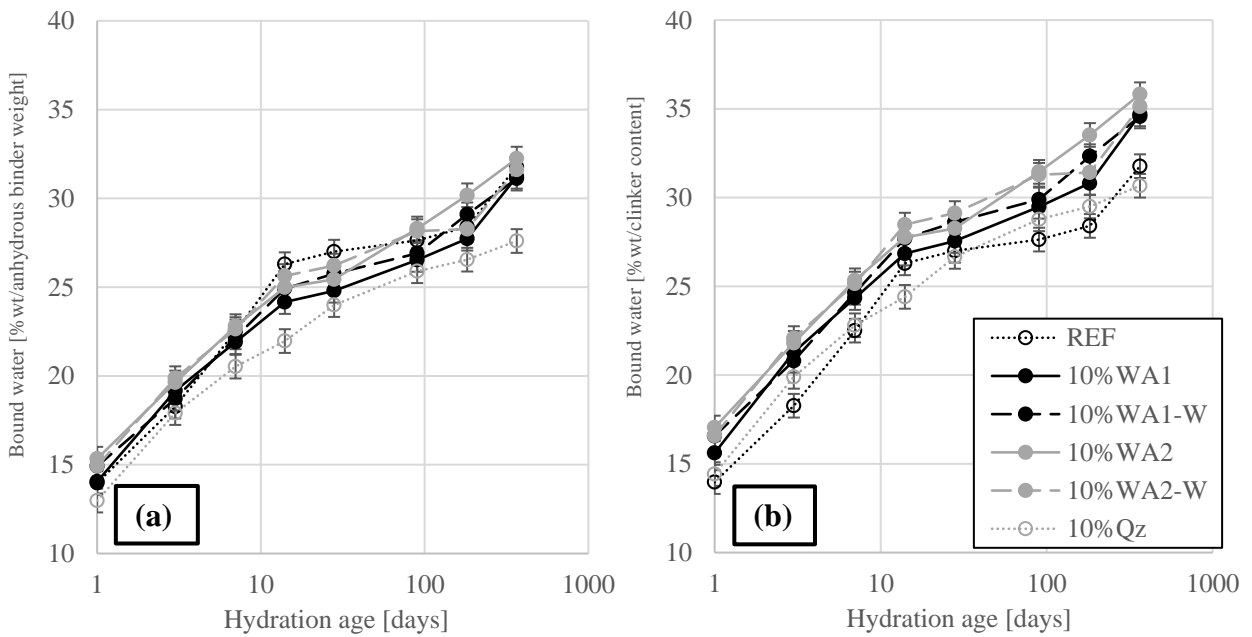
Table 7. Crystalline phases for paste samples investigated after 1, 3, 7, 14, 28, 90, 182 and 365 days of hydration at 20°C determined qualitatively by XRD diffraction. x: < 15%, xx: ~ 25% and xxx: ~ 50% of crystalline phases identified according to semiquantitative analysis.

	Lime	Alite	Belite-β	Ferrite	Portlandite	Ettringite	Quartz	Calcite	Monocarbonate
P1-REF		XX	XX	X	XX	X			
P1-10%WA1	X	XX	XX	X	XX	X	X	X	
P1-10%WA1-W		XX	XX	X	XX	X	X	X	
P1-10%WA2	X	XX	XX	X	XX	X	X	X	
P1-10%WA2-W		XX	XX	X	XX	X	X	X	
P1-10%Qz		XX	X	X	X	X	XX		
P3-REF		XX	XX	X	XX	X			
P3-10%WA1		X	XX	X	XX	XX	X	X	
P3-10%WA1-W		XX	XX	X	XX	XX	X	X	
P3-10%WA2		X	XX	X	XXX	XX	X		
P3-10%WA2-W		X	XX	X	XX	XX	X		
P3-10%Qz		X	X	X	XX	XX	XX		
P7-REF			XX	X	XX	XX			
P7-10%WA1			XX	X	XX	XX	X	X	
P7-10%WA1-W			XX	X	XX	XX	X	X	
P7-10%WA2			X	X	XXX	XX	X		
P7-10%WA2-W			X	X	XX	XX	X		
P7-10%Qz			X	X	XX	XX	XX		
P14-REF			XX	X	XXX	XX			X
P14-10%WA1			X	X	XXX	XX	X	X	X
P14-10%WA1-W			X	X	XXX	XX	X	X	X
P14-10%WA2			X	X	XXX	XX	X		X
P14-10%WA2-W			X	X	XXX	XX	X		X
P14-10%Qz			X	X	XXX	XX	XX		X
P28-REF			X	X	XXX	XX			X
P28-10%WA1					XX	XX	X	X	X
P28-10%WA1-W			X	X	XX	XX	X	X	X
P28-10%WA2			X	X	XX	XX	X		X
P28-10%WA2-W			X	X	XX	XX	X		X
P28-10%Qz					XXX	XX	XX		X
P90-REF					XXX	XX			X
P90-10%WA1					XXX	XXX	X	X	X
P90-10%WA1-W					XXX	XX	X	X	X
P90-10%WA2					XXX	XX	X	X	X
P90-10%WA2-W					XXX	XX	X	X	X
P90-10%Qz					XXX	XX	XX		X
P182-REF					XXX	XX			X
P182-10%WA1					XXX	XXX	X	X	X
P182-10%WA1-W					XXX	XX	X	X	X
P182-10%WA2					XXX	XX	X	X	X
P182-10%WA2-W					XXX	XX	X	X	X
P182-10%Qz					XXX	XX	XX		X
P365-REF					XXX	XX			X
P365-10%WA1					XXX	XXX	X	X	X
P365-10%WA1-W					XXX	XX	X	X	X
P365-10%WA2					XXX	XXX	X	X	X
P365-10%WA2-W					XXX	XX	X	X	X
P365-10%Qz					XXX	XX	XX		X

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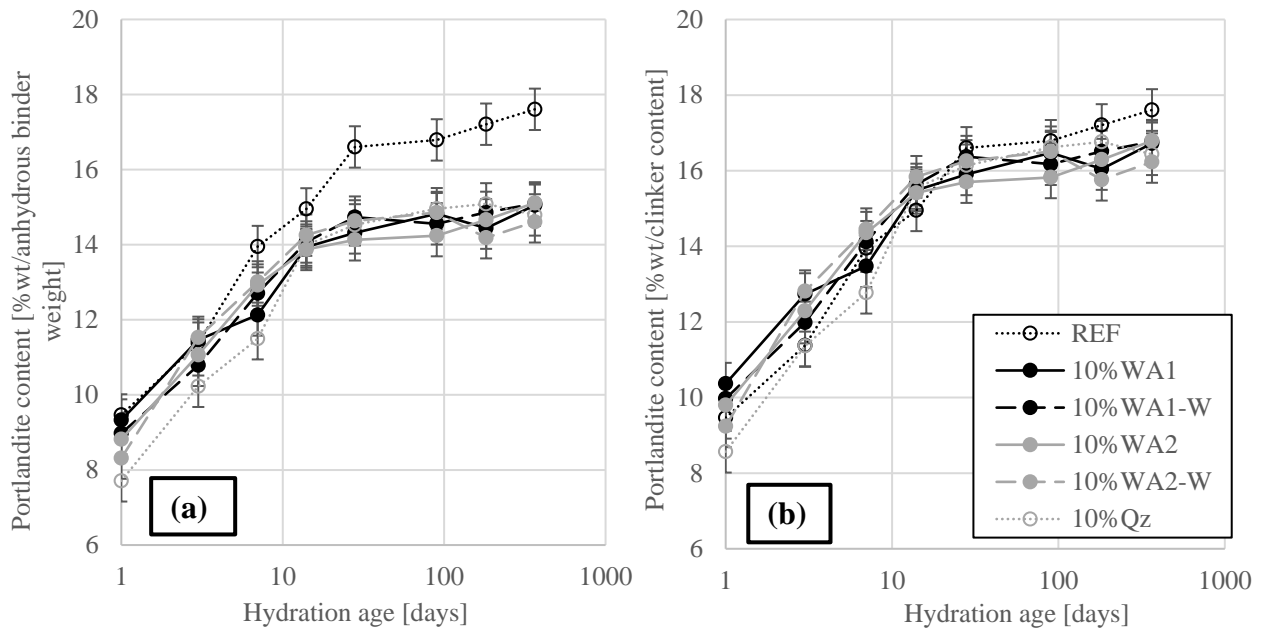
704 **Figure 5.** Differential thermogravimetric (DTG) curves for paste samples investigated at 20°C after 28 days of
 705 hydration. Et: Ettringite, C-S-H: Calcium silicate hydrate, Mc: Monocarbonate, CH: Portlandite.
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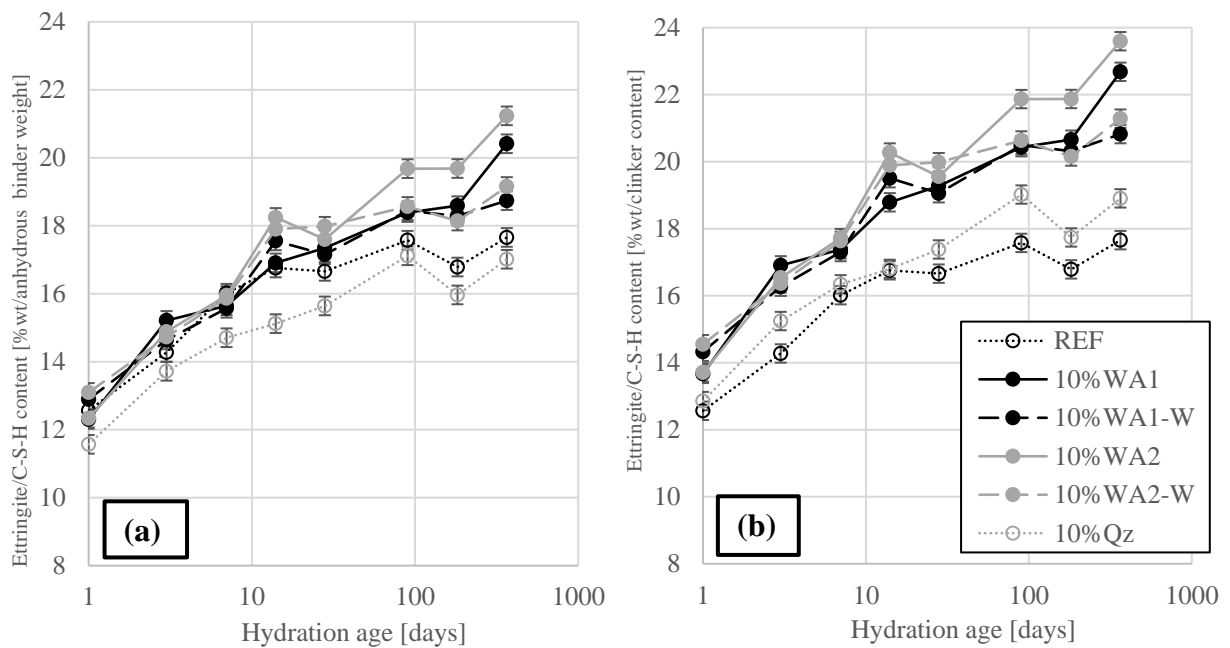
708 **Figure 6.** Quantification of bound water in paste samples investigated after 1, 3, 7, 14, 28, 90, 182 and 365 days
 709 of hydration at 20°C. The results are normalised to the anhydrous binder (a) and clinker content (b). Standard
 710 deviations are based on three independent measurements and quantifications of the bound water of a control
 711 sample at 28 days of hydration.
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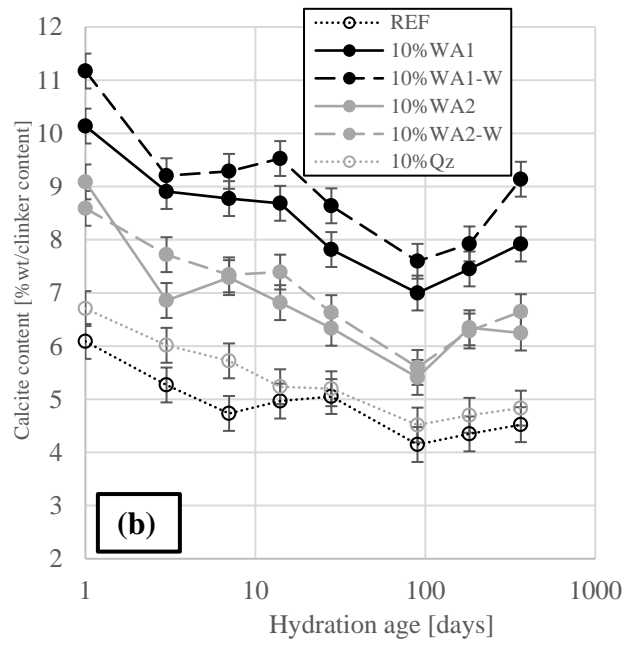
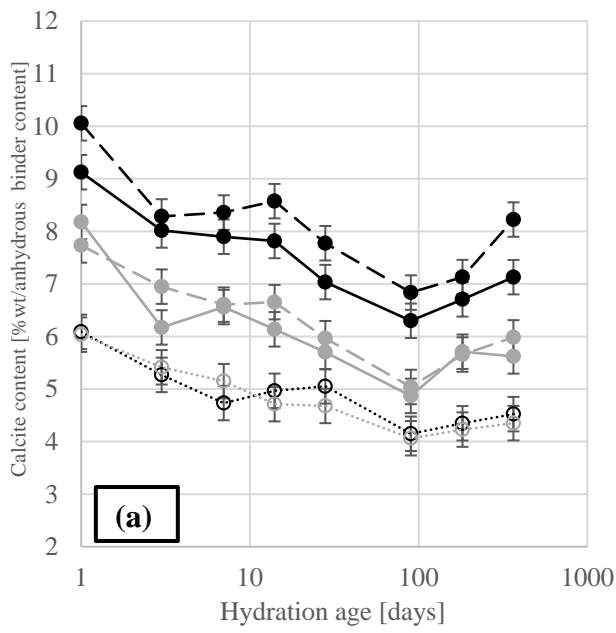
Figure 7. Quantification of portlandite in paste samples investigated after 1, 3, 7, 14, 28, 90, 182 and 365 days of hydration at 20°C. The results are normalised to the anhydrous binder (a) and clinker content (b). Standard deviations are based on three independent measurements and quantifications of the portlandite of a control sample at 28 days of hydration.



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Figure 8. Quantification of ettringite/C-S-H in paste samples investigated after 1, 3, 7, 14, 28, 90, 182 and 365 days of hydration at 20°C. The results are normalised to the anhydrous binder (a) and clinker content (b). Standard deviations are based on three independent measurements and quantifications of the ettringite of a control sample at 28 days of hydration.

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Figure 9. Quantification of calcite in paste samples investigated after 1, 3, 7, 14, 28, 90, 182 and 365 days of hydration at 20°C. The results are normalised to the anhydrous binder (a) and clinker content (b). Standard deviations are based on three independent measurements and quantifications of the calcite of a control sample at 28 days of hydration.