

Effect of NaOH content on hydration, mineralogy, porosity and strength in alkali/sulfate-activated binders from ground granulated blast furnace slag and phosphogypsum

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1 **EFFECT OF NaOH CONTENT ON HYDRATION, MINERALOGY,**
2 **POROSITY AND STRENGTH IN ALKALI/SULFATE-ACTIVATED**
3 **BINDERS FROM GROUND GRANULATED BLAST FURNACE SLAG**
4 **AND PHOSPHOGYPSUM**

5

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21 **Declarations of interest:** none

22 **Abstract**

23 This study investigates the effect of NaOH content on alkali/sulfate-activated binders from 90
24 wt.% ground granulated blast furnace slag (GGBFS) and 10 wt.% phosphogypsum (PG).
25 Alkali activators were prepared with a NaOH molarity ranging from 0 M to 4 M. The hydration
26 was monitored using in-situ X-ray diffraction (XRD) and isothermal calorimetry. The hydration
27 product assemblage was investigated using XRD, thermogravimetric analysis (TGA),
28 Fourier-transformed infrared (FTIR) spectroscopy, nitrogen adsorption/desorption and
29 compressive strength tests. A molarity of 0 M NaOH gave rise to the highest porosity and
30 highest strength, although setting occurred only after 7 days. From a molarity of 2 M NaOH
31 and higher, ettringite disappeared and got replaced by a monosulfate phase (i.e.,
32 $\text{NaCa}_4\text{Al}_2\text{O}_6(\text{SO}_4)_{1.5} \cdot 15\text{H}_2\text{O}$) and amorphous aluminum-hydroxide. This study shows the
33 potential of using GGBFS and PG for the development of novel by-product based
34 cementitious binders.

35

36 **Keywords**

37 Ground granulated blast furnace slag, phosphogypsum, supersulfated cement, alkali-
38 activated binder

39

40 **1. Introduction**

41 Compared to other conventional construction products, such as steel or aluminum, the
42 average CO₂ emission of ordinary Portland cement (OPC) production is relatively low (0.83
43 tonnes/tonne OPC, 3 tonnes/tonne steel and 15 tonnes/tonne aluminum) [1–3]. Due to the
44 enormous global production volumes, however, it makes a significant contribution to overall
45 global CO₂ emissions [1,2,4], together with the fact it is difficult to recycle. For this reason,
46 the construction industry is highly interested in the development of novel cementitious

47 binders, preferably based on secondary industrial by-products, with equivalent performance
48 to OPC but with a lower CO₂ footprint [5–7]. One such alternative is supersulfated cement
49 (SSC), which comprises typically a mixture of 70-90 wt.% ground granulated blast furnace
50 slag (GGBFS), 10-20 wt.% calcium sulfate and an alkaline activator (mostly < 5 wt.%),
51 usually OPC or clinker [8]. If the slag has an Al₂O₃ content exceeding 13 wt.%, the hydration
52 could, in **fact**, occur without the addition of an alkaline activator. **However**, most GGBFS is
53 characterized by Al₂O₃ contents lower than 13 wt.% [5], which results in a very slow reaction
54 rate. Therefore, the addition of an alkaline activator (**potentially in combination with adapted**
55 curing conditions) is necessary to accelerate the hydration reaction [8–12]. The use of
56 phosphogypsum (PG) [13–15], a by-product generated in the phosphate industry, as calcium
57 sulfate source further decreases the environmental footprint of SSC. Because PG contains
58 remnants of phosphoric acid (among other impurities such as fluorine), however, its use
59 might result in a higher alkaline-demand for such matrices [16]. PG **might also contain**
60 **elevated** concentrations of naturally occurring radionuclides [17], which can be problematic
61 when considering its use for building purposes. A previous in-depth investigation into this
62 aspect [18] concluded that a maximum of 10 wt.% PG could be incorporated from a
63 radiological perspective. It should be kept in mind that the radionuclide content of PG
64 streams [19,20], and industrial by-products in general [21,22], can **vary** significantly. **Also,**
65 **sand and aggregates can either increase or dilute the total radionuclide content of a building**
66 **material**. Each individual case therefore needs careful evaluation.

67 The proposed system in this investigation differs from SSCs because it includes 10 wt.% PG
68 as calcium sulfate source, and **completely** excludes the use of OPC by choosing NaOH as
69 alkali activator. Nevertheless, this system might behave in a similar way. Typical hydration
70 products of SSCs are ettringite (AFt, 3CaO·Al₂O₃·3CaSO₄·32H₂O) and monosulfates (AFm,
71 3CaO·Al₂O₃·CaSO₄·nH₂O where n = 8-14) [23], along with other crystalline or amorphous
72 phases such as e.g. portlandite, aluminum-hydroxide, **calcium-aluminosilicate- hydrate**

73 (CASH) or calcium-silicate-hydrate (CSH) [24,25]. The NaOH content, **however**, might
74 significantly influence the hydration product formation and final assemblage.

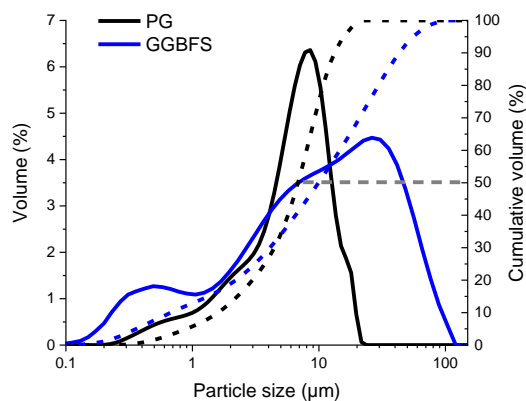
75 This study therefore investigates the influence of the NaOH content on the hydration,
76 mineralogy, porosity and compressive strength using in-situ and ex-situ X-ray diffraction
77 (XRD), isothermal calorimetry, thermogravimetric analysis (TGA), Fourier-transformed
78 infrared (FTIR) spectroscopy, nitrogen adsorption/desorption and compressive strength tests.
79 **In contrast to previous studies on alkali-activated binders from 90 wt.% GGBFS and 10 wt.%**
80 **PG [18,26,27], this study aims to decrease the alkali content in view of increased production**
81 **safety, and lower production costs and environmental footprint imposed by the production of**
82 **alkalis [28] (while simultaneously obtaining adequate properties).**

83

84 **2. Materials and methods**

85 **2.1 Materials**

86 GGBFS was supplied by a Belgian iron and steel production company. PG was collected
87 from a PG processing plant in Gdansk (Poland), and subsequently milled and homogenized
88 by the International Atomic Energy Agency (IAEA) (reference material IAEA 434) [29].
89 GGBFS was dried in a laboratory oven at 110 °C, and thereafter milled to a Blaine fineness
90 of 4050 ± 200 cm²/g, measured according to EN 196-6 [30]. The density of GGBFS was 2.9
91 g/cm³, determined according to ASTM C204 [31] with a Quantachrome Multipycnometer
92 MVP-6DC. The particle size distribution of GGBFS and PG was investigated by laser
93 scattering (Mastersizer Micro Plus, Malvern, Worcestershire, UK) using isopropanol to avoid
94 hydration during the measurement, and is presented in Fig. 1. GGBFS showed a bimodal
95 particle size distribution from 0.1 µm to 103.6 µm and a d₅₀ of 10 µm. PG (used as received)
96 presents an unimodal particle size distribution from 0.2 µm to 24 µm and a d₅₀ of 7 µm.



97

98

Figure 1: Particle size distribution of GGBFS and PG

99 The chemical composition of GGBFS was investigated by X-ray fluorescence (XRF) analysis
 100 (Philips PW 1830), while the chemical composition of PG was provided by the IAEA. The
 101 results are summarized in Table 1.

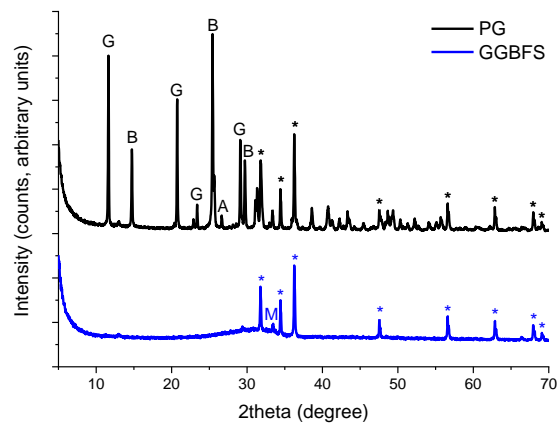
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Table 1: Chemical composition (in wt.%) of GGBFS and PG

Chemical compound	GGBFS	PG
CaO	44.1	35.2
SiO ₂	32.5	0.9
Al ₂ O ₃	10.5	0.2
MgO	8.6	-
SO ₃	1.8	50.3
TiO ₂	0.8	-
K ₂ O	0.5	-
Na ₂ O	0.4	-
Fe ₂ O ₃	0.3	-
P ₂ O ₅	-	1.3
F ⁻	-	1.1
LOI at 950 °C	0.1	11.0

103

104 XRD analysis was carried out to investigate the mineralogy of GGBFS and PG. As an
 105 internal standard, 10 wt.% ZnO (purity 99.9%, Merck) was added [32,33]. The measurements
 106 were performed using a D2 PHASER (Bruker) automated diffractometer with Cu-K α -radiation
 107 equipped with a Lynx-eye super speed position sensitive detector, operated at 30 kV and 10
 108 mA in continuous PSD (position sensitive detector) fast mode. The scan range was from 5°
 109 to 70° 2 θ , the step width was 0.02° 2 θ , and the counting time was 0.3 s per step. A beam
 110 knife slit was positioned 3 mm above the sample, which was prepared using the back loading
 111 technique. During acquisition, the sample was rotated at 15 rpm. The diffractograms
 112 obtained are shown in Fig. 2 and the peaks from ZnO are indicated with an asterisk.



113

114 **Figure 2:** Diffractograms obtained from XRD of GGBFS and PG (merwinite: M, gypsum: G,
 115 bassanite: B, anhydrite: A)

116 Qualitative analysis of the diffractograms was performed with EVA V.3.1 (Bruker AXS)
 117 software. For quantitative analysis, MAUD (Material Analysis Using Diffraction) [34] was used
 118 based on the Rietveld method [35–37] and the background was fitted by a 15 coefficient
 119 polynomial function [38]. From the known initial ZnO content, the crystalline and amorphous
 120 contents were recalculated, and the results are summarized in Table 2.

121

Table 2: Mineralogy (in wt.%) of GGBFS and PG

Phase	GGBFS	PG

Merwinite ($\text{Ca}_3\text{MgSi}_2\text{O}_8$)	5.3 ± 0.8	-
Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, $\text{C}\bar{\text{S}}\text{H}_2$)	-	33.2 ± 0.9
Bassanite ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$, $\text{C}\bar{\text{S}}\text{H}_{0.5}$)	-	27.1 ± 0.9
Anhydrite (CaSO_4 , $\text{C}\bar{\text{S}}$)	-	32.1 ± 1.0
Amorphous	94.7 ± 0.8	7.6 ± 2.8

122

123 2.2 Sample mixtures

124 Based on a previous radiological investigation [18], a maximum of 10 wt.% PG can be
 125 incorporated in order to comply with the **European Union Basic Safety Standards (EU-BSS)**
 126 for building materials [39]. **Therefore, a mixture of 90 wt.% GGBFS and 10 wt.% PG was**
 127 **chosen**. The GGBFS and PG were mixed for 2 h in a Turbula T2C mixer for homogenization
 128 (referred to as 'binder'). Chemical grade NaOH (purity 99%, Chem-Lab) and distilled water
 129 (ASTM type II) were used for the synthesis of the alkali activators, which was done 1 day
 130 prior to sample preparation. **The $\text{H}_2\text{O}/\text{Na}_2\text{O}$ molar ratios of the alkali activators (taking into**
 131 **account the density of the solutions at 20 °C) were 55.56/0.00 (0 M NaOH), 55.56/0.25 (0.5**
 132 **M NaOH), 55.56/0.50 (1 M NaOH), 55.56/1.00 (2 M NaOH), 55.00/1.50 (3 M NaOH) and**
 133 **55.00/2.00 (4 M NaOH).** A total of 6 pastes (P1-P6) and 6 mortars (M1-M6) were prepared.
 134 **The** details of the mixtures are summarized in Table 3. Based on previous experimental work
 135 [18,26,27], the **alkali activator/binder weight ratio (AA/B)** was established at 3/5 and was
 136 retained for all pastes and mortars for the sake of comparison. For the preparation of the
 137 pastes, the alkali activator was manually mixed with the binder for 3 min. Due to the small
 138 volumes involved, manual mixing was chosen instead of using a Hobart mixer in order to
 139 obtain good homogeneity. For the preparation of the mortars, CEN standard sand (DIN EN
 140 196-1) was used with a **sand/binder weight** ratio (S/B) of 3/1 according to EN 196-1 [40]. The
 141 mixing of the mortars was performed in accordance with EN 196-6 [30]. All pastes and
 142 mortars were prepared under laboratory conditions (room temperature 20 ± 2 °C, relative

143 humidity about 50%). The SO₃ content of the binder amounts to 6 wt.%, which is consistent
 144 with the requirements of the European standard for SSCs (5 wt.% ≤ SO₃ ≤ 12 wt.%) [41].

145 **Table 3:** Sample mixtures

Sample*	Binder		Alkali activator	AA/B	S/B
	wt.% GGBFS	wt.% PG	H ₂ O/Na ₂ O (NaOH molarity)		
P1, M1	90	10	55.56/0.00 (0 M)	3/5	0/1, 3/1
P2, M2	90	10	55.56/0.25 (0.5 M)	3/5	0/1, 3/1
P3, M3	90	10	55.56/0.50 (1 M)	3/5	0/1, 3/1
P4, M4	90	10	55.56/1.00 (2 M)	3/5	0/1, 3/1
P5, M5	90	10	55.00/1.50 (3 M)	3/5	0/1, 3/1
P6, M6	90	10	55.00/2.00 (4 M)	3/5	0/1, 3/1

146 *P1-P6 and M1-M6 refer to pastes and mortars, respectively.

147 2.3 Sample dimensions and curing regimes

148 For in-situ XRD and isothermal calorimetry on fresh pastes, the measurements were
 149 executed immediately after the mixing procedure. For XRD, TGA, FTIR and nitrogen
 150 adsorption/desorption, fresh pastes were cast in polystyrene cubic molds with dimensions 25
 151 mm × 25 mm × 25 mm and covered with plastic film to avoid water evaporation and
 152 carbonation. After 24 h, the pastes were demolded and further cured in plastic bags under
 153 laboratory conditions (temperature 20 ± 2 °C, relative humidity about 50%). For XRD, the
 154 curing times were 3, 7, 14 and 28 days. For TGA, FTIR and nitrogen adsorption/desorption,
 155 the curing time amounted to 28 days. There was no need to stop the hydration (with e.g.
 156 isopropanol) as all measurements were scheduled exactly in time. For compressive strength
 157 testing, fresh mortars were cast in polymer coated steel molds with dimensions 40 mm × 40
 158 mm × 160 mm and vibrated for 60 s at a frequency of 1 Hz [30]. A plastic film was placed
 159 over the opening surface of the molds to prevent water evaporation and carbonation. After 24
 160 h, the mortars were demolded and further cured in plastic vessels for 28 days under

161 laboratory conditions (temperature 20 ± 2 °C, relative humidity about 50%). M1 was
162 demolded after 14 days because it did not gain enough strength during the first 24 h,
163 whereafter the same curing regime was applied as for the other mortars.

164

165 **2.4 In-situ XRD and isothermal calorimetry**

166 For in-situ XRD measurements, the same D2 PHASER (Bruker) diffractometer was used as
167 for the XRD analysis of the materials. After the mixing procedure, the fresh pastes were
168 poured into the sample holder (25 mm diameter and 1 mm depth), and the surface was
169 smoothed. No internal standard was added because of the potential influence on the
170 hydration product formation. The sample holder was sealed with Kapton film to prevent water
171 evaporation and carbonation. A total of 110 diffractograms were recorded in continuous PSD
172 fast mode between 6° and 55° 2θ at time intervals of 13 min, with a step width of 0.02° 2θ
173 and a counting time of 0.3 s per step. The X-ray tube was operated at 30 kV and 10 mA. A
174 beam knife slit was positioned 1 mm above the sample and the temperature inside the
175 diffractometer case was kept constant at 20 °C during acquisition. The diffractograms were
176 qualitatively evaluated with EVA V.3.1 (Bruker AXS) software.

177 A TAM-Air Isothermal Calorimeter (TA Instruments) was used for heat flow calorimetry under
178 isothermal conditions (20.0 ± 0.1 °C) during the first 6 days of hydration. After the mixing
179 procedure, the fresh pastes were poured into glass ampoules, which were inserted in the
180 calorimeter. P1 was additionally monitored for 28 days.

181

182 **2.5 XRD**

183 After their curing period (i.e., 3, 7, 14 and 28 days), the hardened pastes were manually
184 milled in a porcelain mortar. P1 could not be measured after 3 and 7 days because it did not
185 gain enough strength. As an internal standard, 10 wt.% ZnO (purity 99.9%, Merck) was

186 added [32,33]. The measurements were performed using the same diffractometer, settings
187 and procedure as for the XRD analysis of the materials. A beam knife slit was positioned 1
188 mm above the sample. Qualitative and quantitative analysis were performed in the same way
189 as for the materials.

190

191 **2.6 TGA, FTIR and nitrogen adsorption/desorption**

192 After their curing period (i.e., 28 days), the hardened pastes were investigated. Prior to TGA
193 and FTIR, the pastes were manually milled in a porcelain mortar. TGA (Q55, TA Instruments)
194 was carried out on a sample weight of 20 mg under nitrogen atmosphere from room
195 temperature to 995 °C at a heating rate of 10 °C/min. For FTIR, a Vertex 70 spectrometer
196 (Bruker) with an ATR diamond crystal (Pike) was used. Spectra were acquired in
197 wavenumber ranges from 4000 cm⁻¹ to 600 cm⁻¹ at a resolution of 4 cm⁻¹ and with 32 scans
198 per measurement, using a DTGS detector. Nitrogen adsorption/desorption tests were carried
199 out using a TRISTAR 3000 Micromeritics device at -196.2 °C. Prior to degassing, the pastes
200 were dried in a laboratory oven at 40 °C for 2-3 days until a constant weight was achieved.
201 Thereafter, they were degassed using the vacuum degas method with a Schlenk line at 20
202 °C for 72 h at a pressure/vacuum of 100 Pa. The specific surface area was obtained from the
203 adsorption data by the BET (Brunauer, Emmett and Teller) method [42] over the P/P_0 range
204 of 0.05-0.30 (where P is the partial vapor pressure of the adsorbate gas in equilibrium and P_0
205 is the saturated pressure of the adsorbate gas at -196.2 °C). From the desorption data, the
206 mesopore size distribution and the cumulative mesopore volume were found using the BJH
207 (Barrett, Joyner and Halenda) method [43]. The micropore volume and micropore surface
208 area were obtained from the adsorption data using the T-plot analysis method [44].

209

210 **2.7 Compressive strength testing**

211 After their curing period (i.e., 28 days), the hardened mortars were tested for their
212 compressive strength. An Instron 5985 machine equipped with a 250 kN load cell was
213 employed for testing 5 specimens of each formulation.

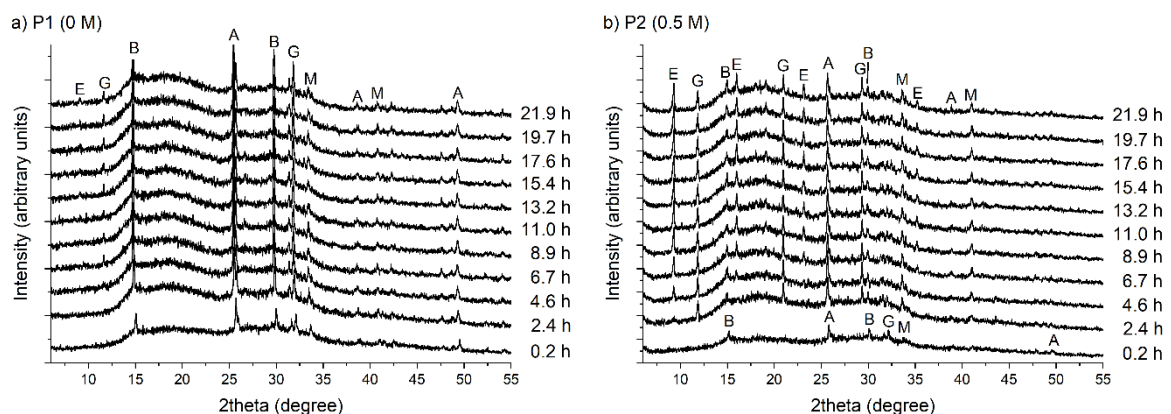
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215 **3. Results and discussion**

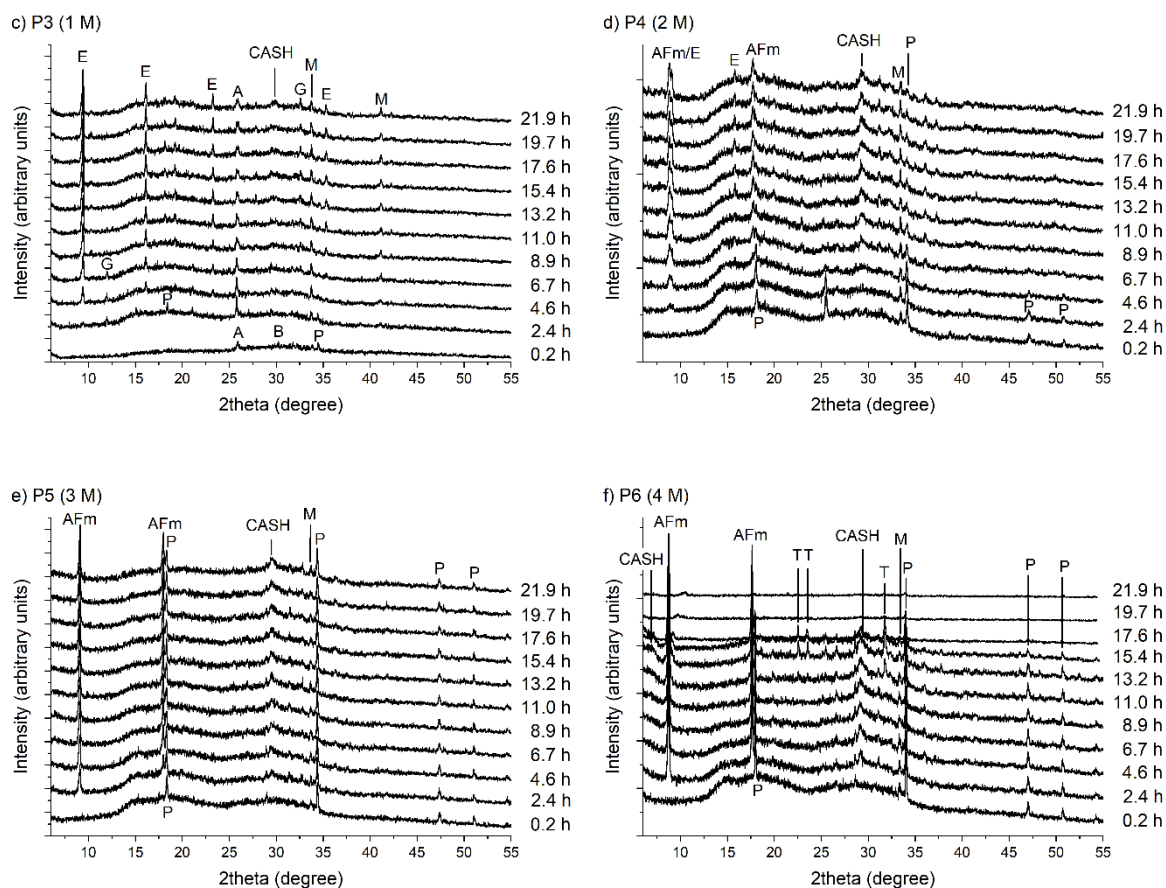
216 **3.1 In-situ XRD and isothermal calorimetry**

217 In Fig. 3, a selection of the recorded in-situ XRD diffractograms are plotted (at regular time
218 steps of 130 min) for P1-P6. Quantitative analysis of those data is not feasible as no internal
219 standard was added. The following phases were recognized: merwinite, gypsum, bassanite,
220 anhydrite, ettringite, CASH [45–47], portlandite, a monosulfate phase, and thenardite. The
221 monosulfate phase constitutes $\text{NaCa}_4\text{Al}_2\text{O}_6(\text{SO}_4)_{1.5} \cdot 15\text{H}_2\text{O}$ (PDF 44-0272 in the PDF1999-
222 database). The hump in the diffractograms from approximately 12° to 25° 2θ is mainly
223 caused by the presence of Kapton film, while the remaining water in the sample contributes
224 to a lesser extent to the broader hump from approximately 12° to 45° 2θ . From Fig. 3a, it is
225 clear that the mineralogy of the paste remains quite similar during the first 24 h upon mixing
226 the binder with a 0 M NaOH solution. The peaks in the diffractograms mainly originate from
227 merwinite, gypsum, bassanite and anhydrite from the binder. When increasing the molarity of
228 the NaOH solution from 0.5 M to 4 M (Fig. 3b to Fig. 3f), the dissolution of the binder and the
229 formation of hydration products, simultaneously or in sequence, is recognizable in the
230 diffractograms. For example, the formation of ettringite at around 9° 2θ is clearly
231 distinguishable in Fig. 3b and Fig. 3c and the intensity of this peak grew slightly over time.
232 The higher the molarity, the faster the peaks from the binder disappear and peaks from the
233 hydration products appear, suggesting a faster setting time. However, even at the highest
234 molarities of 3 M and 4 M, merwinite is still present at 21.9 h, which may be due to an initial
235 fast coverage of the binder by the hydration products, hindering proper dissolution of the
236 binder. Gypsum and bassanite appear to dissolve more easily compared to anhydrite, which
237 is still present in P3 after 21.9 h. A similar effect is described in [48–50]. From a molarity of 1

238 M and higher, the formation of CASH is deduced from the hump at around $29^\circ 2\theta$ [46,47].
 239 Another peak typical for the CASH phase appears gradually for P6 at around $7^\circ 2\theta$ [51]. At a
 240 molarity of 1 M, portlandite is initially formed and remains present in the paste until
 241 approximately 3-4 h after mixing. At a molarity of 2 M, initially formed portlandite remains
 242 present in the paste until approximately 4-6 h after mixing. At a molarity of 3 M and 4 M,
 243 portlandite is recognized in all diffractograms. The formation of portlandite increases the pH
 244 and promotes further slag dissolution [25]. Therefore, from a molarity of 1 M and higher, the
 245 system behaves as a hybrid one consisting of a cascade of amplifying reactions. As further
 246 discussed in section 3.3, P3-P6 showed the lowest porosity. Ettringite is formed in P1-P4. At
 247 a molarity of 2 M, ettringite and a rather crystalline monosulfate phase coexist, while at
 248 molarities of 3 M and 4 M only the monosulfate phase is present in the sample, and ettringite
 249 is absent. Thenardite (Na_2SO_4) appears in P6 approximately 10-11 h after mixing. The
 250 formation of thenardite, which is a soluble salt, is undesirable from the leaching point of view.
 251 For P6, all intensities drop away after 16 h, which is likely to be the consequence of sample
 252 swelling or shrinkage, obscuring proper diffraction at the sample surface. Volume expansion
 253 due to the (partial) dissolution of the monosulfate phase might be a possible explanation [52],
 254 which then induces thenardite formation.



255



256

257

258 **Figure 3:** Diffractograms obtained from in-situ XRD for a) P1, b) P2, c) P3, d) P4, e) P5 and

259 f) P6 (merwinite: M, gypsum: G, bassanite: B, anhydrite: A, ettringite: E, calcium-

260 aluminosilicate-hydrate: CASH, portlandite: P, a monosulfate phase: AFm, and thenardite: T)

261 The heat release and cumulative heat during the first 6 days of hardening are shown in Fig.

262 4a (and during the first 24 h in Fig. 4b and Fig. 4c). For all samples, an initial wetting and

263 dissolution peak is observed after inserting the paste into the calorimeter. For P1, which was

264 prepared with a 0 M NaOH solution, no exothermic reactions took place during the first 6

265 days. The initial exothermic peak between 0 h and 2 h for P2, P3 and P4 (the combination of

266 wetting and dissolution) is followed by an induction period of approximately 3 h, whereafter a

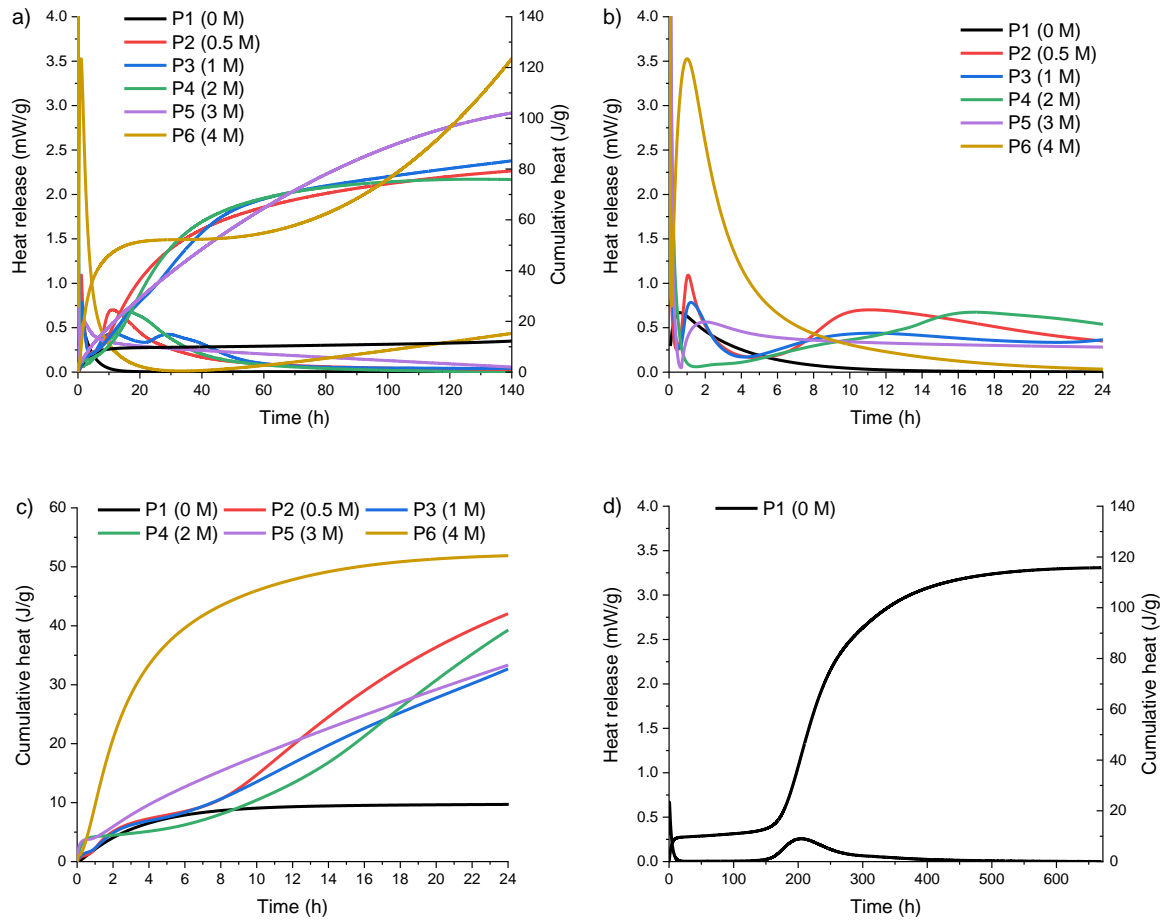
267 second exothermic peak from 5 h to 60 h is presumably caused by the formation of hydration

268 products (which is consistent with in-situ XRD where the ettringite peak became clearly

269 visible after 4.6 h). For P5 and P6, no induction period is observed between the first and

270 second exothermic peak, indicating that immediately after dissolution a critical concentration

271 was reached to initiate the hydration product formation (consistent with in-situ XRD, where
272 e.g. portlandite was already recognized in the first diffractogram). The heat release curve of
273 P6 is significantly different from the other curves because of its major heat release during the
274 first 10 h, followed later by a sharp increase in heat release after 40 h. A potential cause
275 might be the initial coverage of a portion of the binder due to a fast initial hydration product
276 formation (e.g. the fast initial formation of the monosulfate phase during the first 10 h), which
277 gets further hydrated after 40 h. The same phenomenon has been reported in [25,53,54].
278 The cumulative heat of P2, P3 and P4 is comparable, reaching around 80 J/g after 6 days.
279 Comparable values are reported in the literature [55]. The cumulative heat for P5 and P6 is
280 25% (100 J/g) and 50% (124 J/g) higher at that time, respectively. Fig. 4a shows that
281 hydration is an ongoing process that continues even after 6 days. The calorimetric monitoring
282 of P1 was prolonged to 28 days and the curves are presented in Fig. 4d. After the initial
283 wetting and dissolution peak, a very long induction period is observed until approximately
284 160 h, followed by a second exothermic peak that reaches a maximum at 200 h. From these
285 data, it is assumed that the setting of P1 starts only after 7 days. After 28 days, the
286 cumulative heat of P1 reached 116 J/g. To be in accordance with the European standard for
287 SSCs, the cumulative heat at 7 days should not exceed 220 J/g [41]. SSCs have the
288 advantage of generating a much lower heat during hydration compared to OPC [56]. The
289 combined effect of OPC's low thermal conductivity and its high heat during hydration might
290 induce cracking [57].



291

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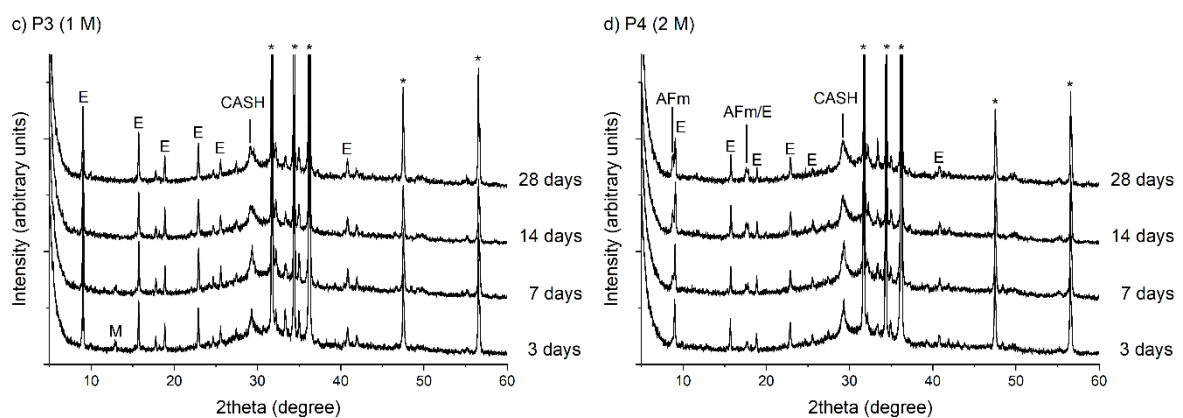
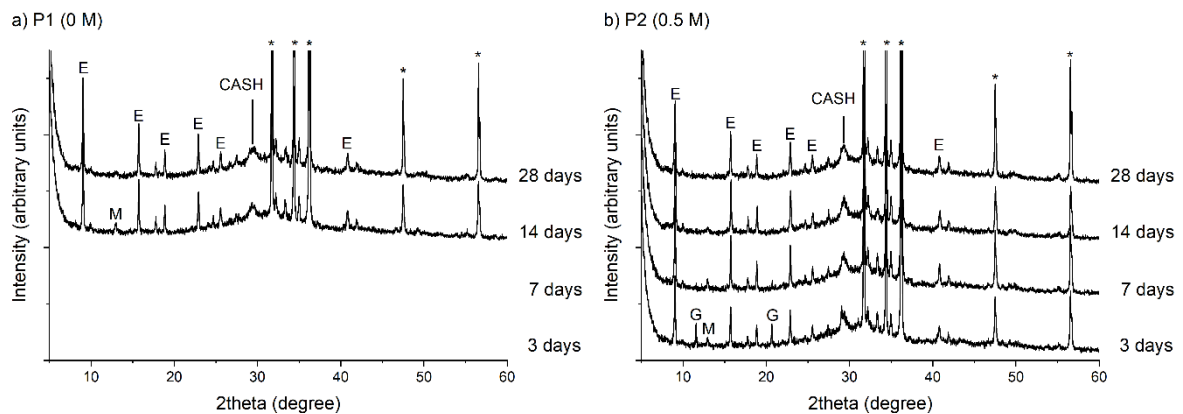
293 **Figure 4:** a) Heat release and cumulative heat during 6 days for P1-P6, b) heat release
 294 during 24 h for P1-P6, c) cumulative heat during 24 h for P1-P6, and d) heat release and
 295 cumulative heat during 28 days for P1

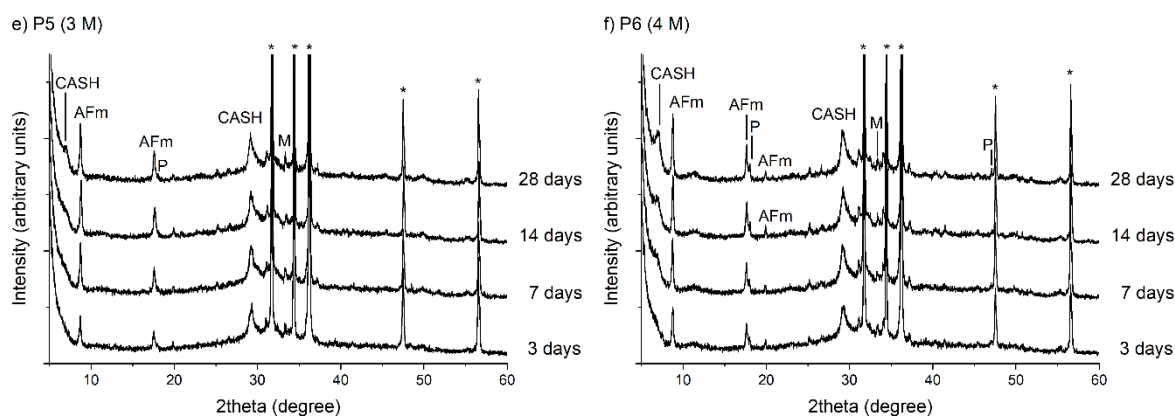
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297 3.2 XRD

298 XRD analysis was performed after curing periods of 3, 7, 14 and 28 days. The diffractograms
 299 are plotted from 5° to 60° 2θ and are presented in Fig. 5. P1 did not gain enough strength
 300 after 3 and 7 days and could therefore only be measured after 14 and 28 days of curing. The
 301 peaks of ZnO are indicated with an asterisk. Merwinite and gypsum originate from the
 302 undissolved GGBFS and PG particles, respectively. It has to be noted here that thenardite
 303 and calcite (not indicated in Fig. 5) are considered to be side-products. The main hydration
 304 products identified were ettringite, CASH [45–47], a monosulfate phase [47,58], and

305 portlandite. As with in-situ XRD (section 3.1), the monosulfate phase constitutes
 306 $\text{NaCa}_4\text{Al}_2\text{O}_6(\text{SO}_4)_{1.5} \cdot 15\text{H}_2\text{O}$. Other minor hydration products (not indicated in Fig. 5) found
 307 were cuspidine and $\text{Mg}_2\text{P}_2\text{O}_7$. An amorphous aluminum-hydroxide phase is also expected to
 308 be present (further confirmed by TGA in section 3.3 for P4-P6), yet not recognizable by XRD
 309 [48]. The presence of a CSH phase could not be identified due to its highly amorphous
 310 nature, yet it is visible for P1-P4 in TGA (section 3.3). Anhydrite and bassanite were not
 311 recognized, while merwinite and gypsum peaks gradually disappear upon extended curing
 312 times. From a molarity of 2 M and higher, neither merwinite nor gypsum peaks were
 313 observed. The peaks originating from the hydration products grew slightly over time. Upon
 314 increasing the molarity of the alkali activator, CASH development is promoted, as well as the
 315 monosulfate phase. As with in-situ XRD, ettringite and monosulfate coexist in P4, while
 316 ettringite is absent in P5 and P6.

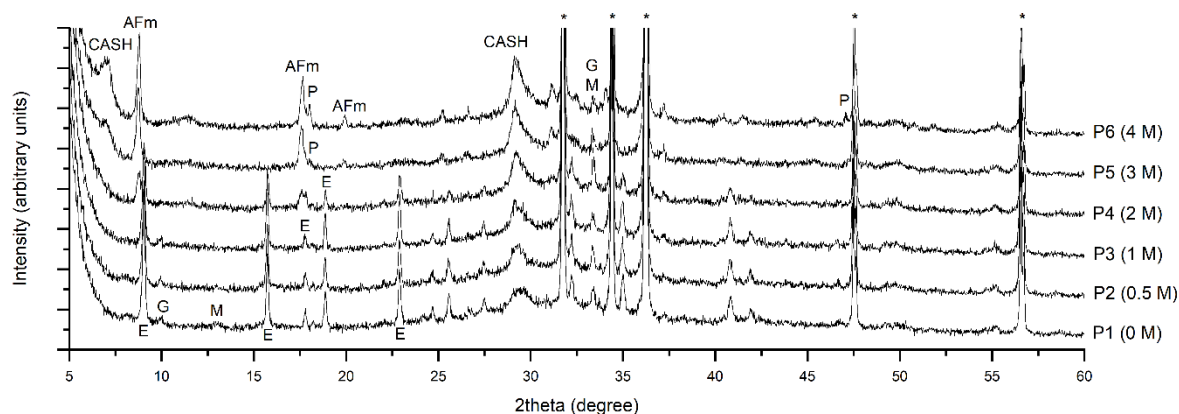




319

320 **Figure 5:** Diffractograms obtained from XRD after 3, 7, 14 and 28 days of curing for a) P1, b)
 321 P2, c) P3, d) P4, e) P5 and d) P6 (merwinite: M, gypsum: G, ettringite: E, calcium-
 322 aluminosilicate-hydrate: CASH, portlandite: P, and a monosulfate phase: AFm)

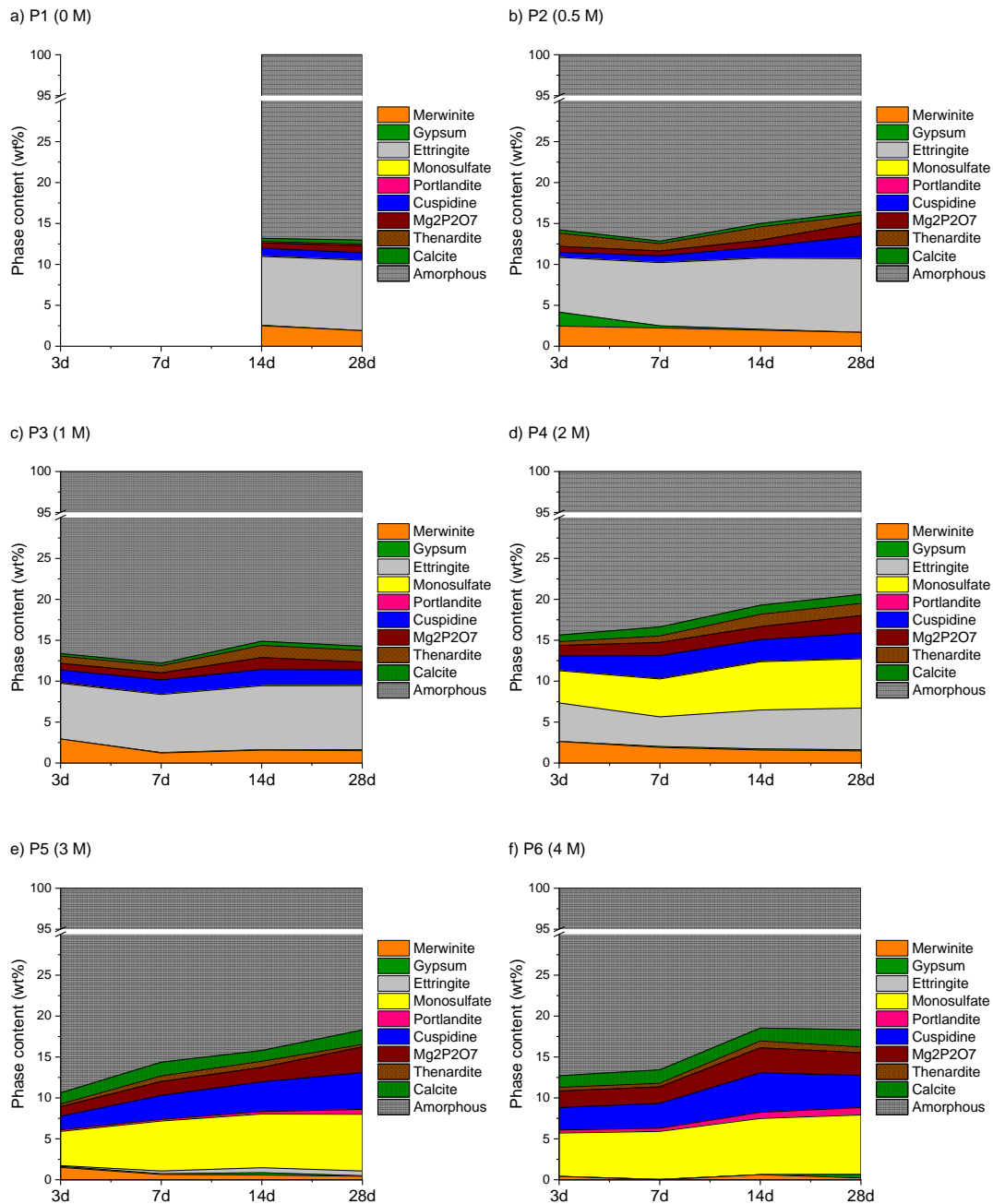
323 Fig. 6 compares the diffractograms obtained after 28 days of curing for the different samples.
 324 From Fig. 6, the shift from ettringite (P1, P2, P3, P4) to the monosulfate phase (i.e.,
 325 $\text{NaCa}_4\text{Al}_2\text{O}_6(\text{SO}_4)_{1.5} \cdot 15\text{H}_2\text{O}$) (P4, P5, P6) is clearly distinguishable at around 8 to 9° 2θ and at
 326 around 17° to 18° 2θ [58]. In most cases monosulfate phases are amorphous and difficult to
 327 quantify using XRD [59–61], although in this system this phase appears to be rather
 328 crystalline. Portlandite (near 18° and 47° 2θ) is observed for P5 and P6. For all samples, the
 329 intensity of the CASH peak at around 29° 2θ [46,47] (and at around 7° 2θ [51] for P5 and P6)
 330 gradually increases when the molarity of the alkali activator is increased, while the full width
 331 at half maximum (FWHM) gradually decreases. This suggests that the presence and
 332 crystallinity of the CASH phase is increasing, when the molarity of the alkali activator is
 333 increased.



334

335 **Figure 6:** Diffractograms obtained from XRD after 28 days of curing (merwinite: M, gypsum:
 336 G, ettringite: E, calcium-aluminosilicate-hydrate: CASH, portlandite: P, and a monosulfate
 337 phase: AFm)

338 Fig. 7 gives the quantitative XRD (QXRD) analysis. As mentioned, due to insufficient strength
 339 development, P1 was only measured after 14 and 28 days of curing. It should be noted that
 340 CASH, CSH and aluminum-hydroxide are ascribed to the amorphous part. Overall, the phase
 341 assemblage continues to develop after 3 days of curing. Anhydrite and bassanite are not
 342 present, while gypsum and merwinite from the binder gradually disappear with extended
 343 curing times, and their dissolution is enhanced by an increased molarity of the alkali
 344 activator. Approximately 8 wt.% of ettringite was present for P1-P3, while from a molarity of 2
 345 M and above ettringite gradually disappeared and the monosulfate phase showed up.
 346 Cuspidine and $Mg_2P_2O_7$ are more favored at higher molarities, their content gradually
 347 increased upon increasing the curing time for all samples. **Portlandite peaks were clearly
 348 distinguishable in the in-situ XRD diffractograms for P3-P6 (section 3.1). For P3 and P4, this
 349 phase gradually disappears upon extended curing periods and performs as an intermediate
 350 (hydration) product. For P5 and P6, portlandite was recognized during the first 22 h of
 351 hydration, whereafter its content slightly increased from 3 days up to 28 days of curing.**
 352 Thenardite and calcite are, as already mentioned, considered to be side-products.
 353 Thenardite was found for all samples, while the calcite content was highest at molarities of 3
 354 M and 4 M.



355

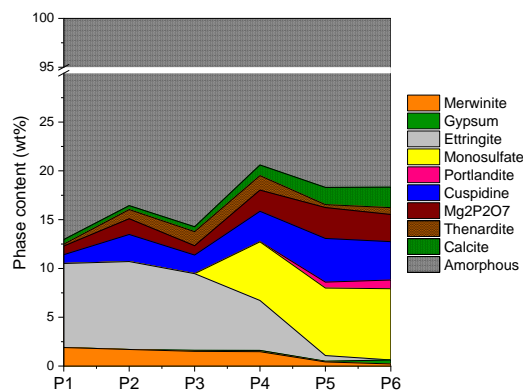
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357

358 **Figure 7:** XQRD after 3, 7, 14 and 28 days of curing for a) P1, b) P2, c) P3, d) P4, e) P5 and
 359 **d) P6**

360 Fig. 8 provides the quantitative analysis of the diffractograms after 28 days of curing in
 361 function of the NaOH molarities of the alkali activators. Ettringite converts to the monosulfate
 362 phase from a molarity of 2 M and above. The stability of this monosulfate phase should be
 363 investigated further. The cuspidine and Mg₂P₂O₅ content gradually increases when the
 364 molarity is increased, which is likely to be related to the enhanced GGBFS dissolution

365 (inversely proportional to the decreasing merwinite content upon increasing the molarity).
 366 Gypsum in P5 and P6 might be secondary gypsum [25], which can exert adverse effects on
 367 the strength if it is formed after final setting. The potential occurrence of delayed ettringite
 368 formation (DEF) [62] at later ages for P4-P6 will be dependent on the Ca^{2+} , Al^{3+} and SO_4^{2-}
 369 balance in the pore solution and its pH, and should be elucidated.



370

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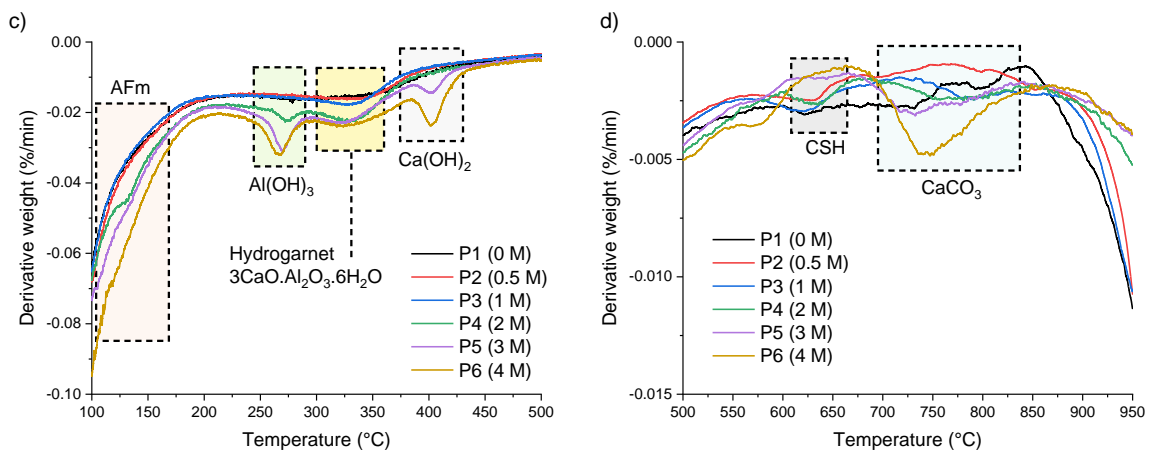
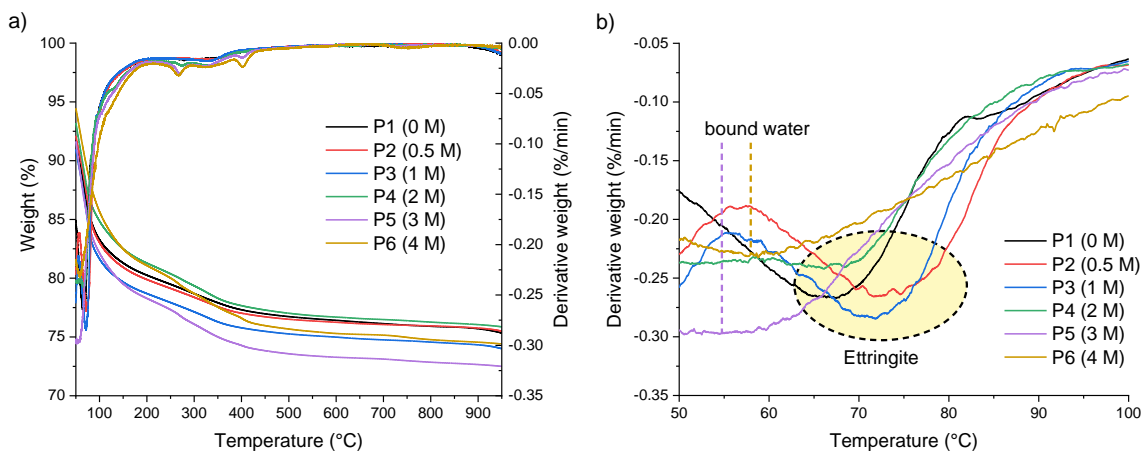
Figure 8: QXRD after 28 days of curing

372

373 3.3 TGA, FTIR and nitrogen adsorption/desorption

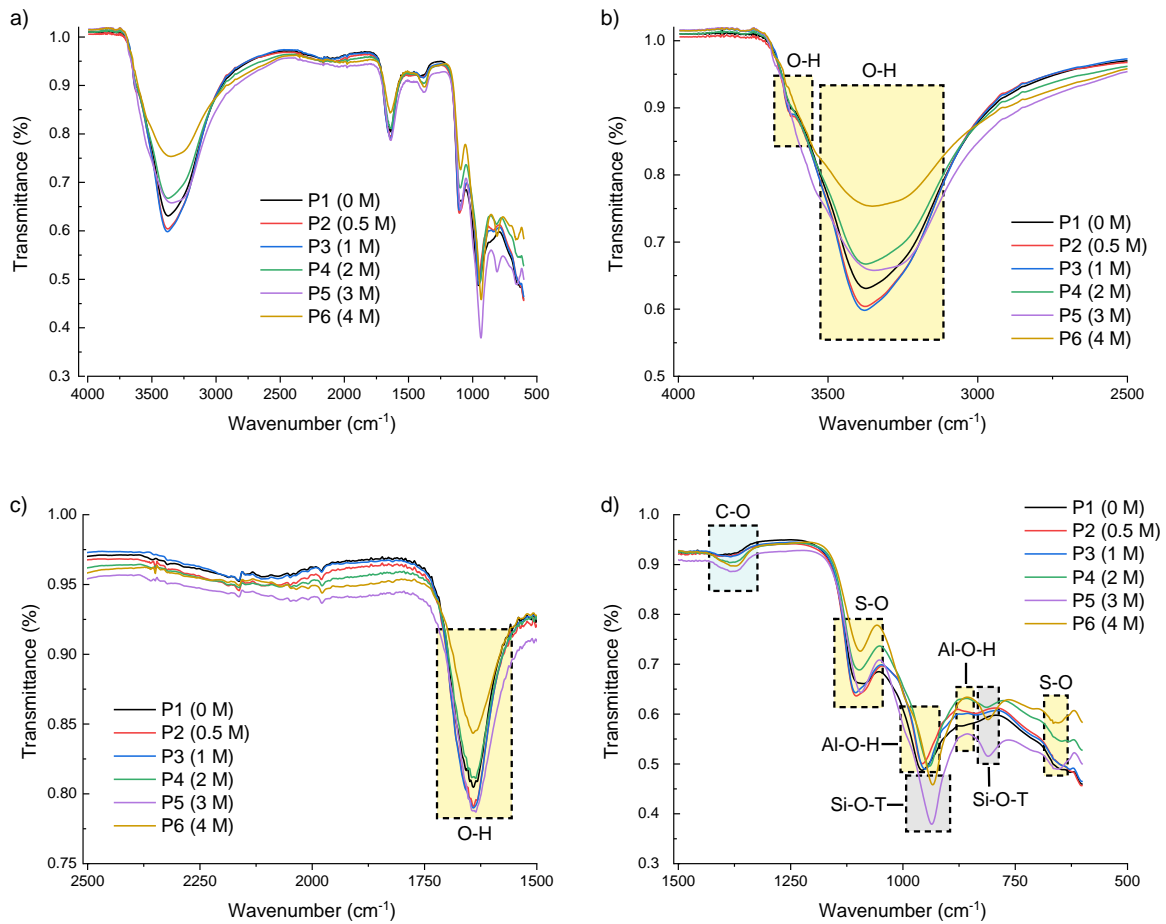
374 The thermogravimetric (TG) and derivative thermogravimetric (DTG) curves are shown in
 375 Fig. 9. The mass loss under 90 °C is caused by the loss of bound water (P5-P6) and the
 376 decomposition of ettringite [63] (P1-P4) (see Fig. 9b). Monosulfate is recognized for P4-P6
 377 (consistent with XRD and QXRD) from 110-170 °C [48]. Contrary to XRD analysis,
 378 amorphous aluminum-hydroxide is detectable due to its water loss at around 270 °C [64],
 379 and was only present from a molarity of 2 M and higher. The TG/DTG results revealed the
 380 presence of hydrogarnet ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$) for P4-P6, which decomposes at around 325 °C
 381 [65]. This phase might be formed due to the higher heat release during curing for those
 382 samples, which is in agreement with [60,66–69] where it was observed that hydrogarnet
 383 formed under hydrothermal curing conditions (e.g. in [67] hydrogarnet was formed at 90 °C,
 384 in [68] formation of hydrogarnet is predicted at temperatures above 50 °C). Hydrogarnet is

385 thermodynamically stable in the temperature range from 20 to 250 °C [70,71]. Remnants of
 386 portlandite were highest for P6, which agrees with QXRD. The condensation of structural
 387 hydroxyl groups from the CSH phase is recognized at 610-630 °C [72] for P1-P4. As this
 388 phase was not found in the XRD diffractograms of P1-P4, this CSH phase is expected to be
 389 highly amorphous. The CSH phase is not observed for P5-P6 in the TG/DTG curves, which
 390 is also consistent with XRD in section 3.2 where it was found that a semi-amorphous CASH
 391 showed up when the molarity of the alkali activator was increased, which also caused its
 392 crystallinity to increase. A similar observation is presented in [25], where a low alkaline
 393 content increased CSH formation and higher alkalinities increased its crystallinity. The weight
 394 loss at 750 °C corresponds to the decomposition of CaCO_3 to CaO and CO_2 [73]. Calcite was
 395 also confirmed by QXRD after 28 days of curing, where the highest content was found for
 396 P6.



399 **Figure 9:** a) TG and DTG curves after 28 days of curing, b) DTG curves from 50 to 100 °C,
400 c) DTG curves from 100 to 500 °C and d) DTG curves from 500 to 950 °C

401 The FTIR spectra are shown in Fig. 10. The bands located between 3750 cm⁻¹ and 3000 cm⁻¹
402 and near 1600 cm⁻¹ are assigned to O-H vibrations [74,75]. The bands at around 960 cm⁻¹
403 and 850 cm⁻¹ are related to the Al-O-H bond [76], while the S-O bond stretching occurs at
404 1100 cm⁻¹ (asymmetrical ν_3 vibrations) and at 660 cm⁻¹ (asymmetrical ν_4 vibrations) [77,78].
405 The FTIR spectra provide evidence of the gradual disappearance of ettringite when the
406 molarity of the alkali activator is increased, which is in agreement with XRD and TGA. It
407 should be kept in mind, however, that other phases such as the monosulfate phase,
408 aluminum-hydroxide or gypsum may contribute to those bands as well, which is difficult to
409 distinguish in FTIR spectra. The C-O bonding is evident in the band near 1400 cm⁻¹ [79,80]
410 and molarities of 2 M and higher gave rise to an increased carbonation compared to lower
411 molarities, which is also seen in the QXRD and TGA data. The stretching vibrations of the Si-
412 O-T units (where T stands for Al or Si) are clearly distinguishable for P5 and P6 at 940 cm⁻¹
413 (typical for Q² units) [81–84] and at 800 cm⁻¹ (typical for Q¹ units) [84,85], while both bands
414 are absent for P1-P4. None of the samples contained Q³ Si-O-T units, which are normally
415 recognized from a band around 1200 cm⁻¹ [84]. The intensity of the Si-O-T bands was
416 highest for P5, while the intensity for P6 was lower. As confirmed by XRD, those bands
417 originate from a CASH phase (as these bands are not observed for P1-P4). The location and
418 breadth of the Si-O-T bands for P5 and P6 is comparable, indicating similar amorphousness
419 and Ca/Si and Al/Si ratios [86].



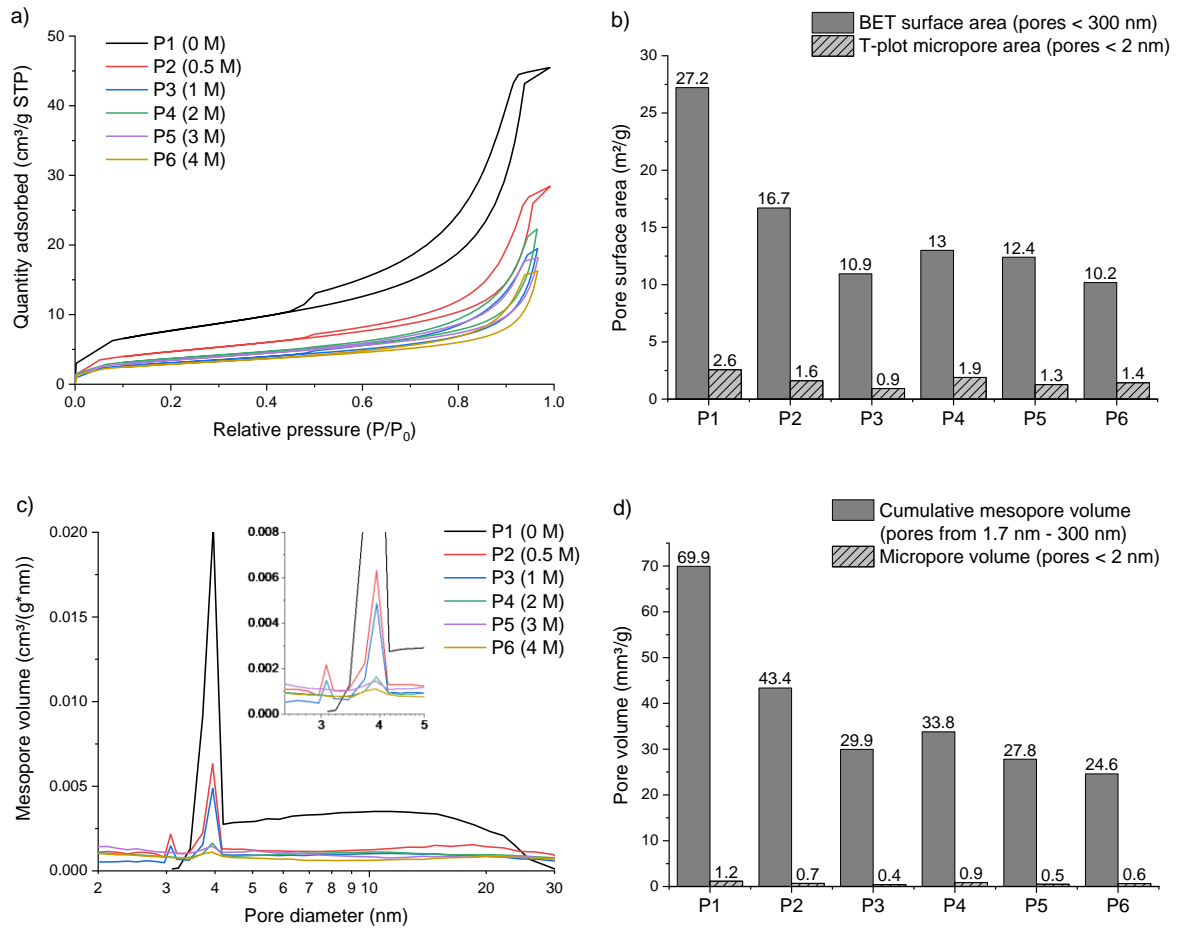
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421

422 **Figure 10:** a) FTIR curves after 28 days of curing, b) FTIR curves from 4000 to 2500 cm⁻¹, c)
 423 FTIR curves from 2500 to 1500 cm⁻¹ and d) FTIR curves from 1500 to 500 cm⁻¹

424 The results from nitrogen adsorption/desorption tests are presented in Fig. 11. The isotherms
 425 in Fig. 11a are characterized by a type IIb shape [87] with an H5 (P1, P2 and P3) or an H3
 426 (P4, P5 and P6) hysteresis loop [88], indicating that the meso- and macropores in those
 427 samples are predominant in addition to fewer slit-shaped micropores. The H5 hysteresis loop
 428 is typical for structures containing both open and partially blocked mesopores, while an H3
 429 hysteresis loop indicates plate-like particles (as in certain clays) [88]. The plateau at high
 430 relative pressure suggests that all pores were filled [89]. An increase in the molarity of the
 431 alkali activator resulted generally in a decreased maximum amount of nitrogen adsorbed at
 432 the maximum relative pressure (a non-linear relation is observed) and a decreased
 433 hysteresis loop surface. Fig. 11b presents the pore surface area obtained using the BET and
 434 T-plot methods. The surface area of the pores generally decreases when the molarity of the

435 alkali activator is increased, although a small increase is noted when moving from a 1 M to a
436 2 M solution. The decrease in pore surface area is expected to be caused by a higher
437 dissolution rate of the precursors and consequently a denser hydration product matrix. OPC
438 typically has a pore surface area (obtained with nitrogen adsorption/desorption and the BET
439 method) of around 50 m²/g [90], which is 2-5 times higher than the pore surface area of the
440 pastes in this investigation. The mesopore size distribution, obtained using the BJH method
441 (cylindrical pores are hypothesized for the calculation), is plotted in Fig. 11c. As the pore
442 shape remains unknown, however, those results are indicative (nevertheless comparative for
443 this series of samples) [89]. It should also be noted that the valid pore size range is from 2-30
444 nm, due to the upper P/P_0 limit of around 0.97 [91,92]. P1 shows a bimodal profile, with a
445 sharp peak from 3-4 nm and a much broader one from 4-25 nm. P2 and P3 are also
446 characterized by a bimodal distribution although the peaks occur at lower pore diameters
447 with a maximum at 3 nm and 4 nm. P4, P5 and P6 show a unimodal distribution with a
448 maximum at 4 nm. The pore volume is presented in Fig. 11d, where generally a decrease is
449 observed when the molarity of the alkali activator is increased, which is likely to be due to an
450 increasing precursor dissolution grade when moving from P1 to P6 and the effect of
451 carbonation.



452

453

454

Figure 11: Nitrogen adsorption/desorption data after 28 days of curing: a)

455

adsorption/desorption isotherms, b) pore surface area, c) mesopore size distribution and d)

456

pore volume

457

458

3.4 Compressive strength

459

The compressive strength (1σ error) of the mortars after 28 days of curing is shown in Fig.

460

12. Although P1 was characterized by a very long setting time of over 7 days, M1 reaches

461

the highest compressive strength (41.8 ± 1.2 MPa) after 28 days of curing. The strength of

462

M2-M5 is in the same order of magnitude (16.5 ± 1.2 MPa, 14.0 ± 0.7 MPa, 16.2 ± 0.1 MPa

463

and 12.6 ± 0.7 MPa, respectively), while the strength of M6 is slightly higher (23.4 ± 1.5

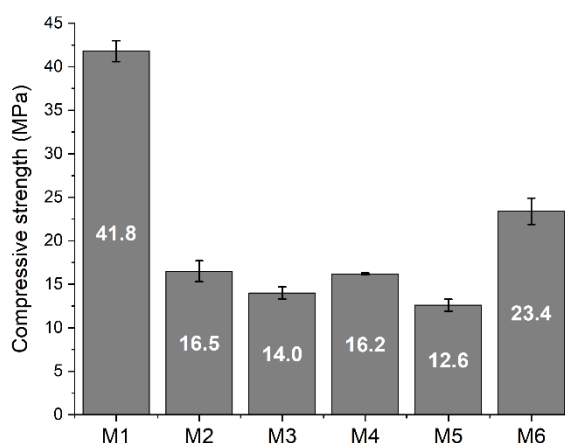
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MPa). A high heat release might confirm the hydration of a significant amount of reaction

465

products. The cumulative heat of P1 was, however, not significantly higher compared to P5

466 and P6. After 28 days, the cumulative heat of P1 was 116 J/g. The cumulative heat of P5 and
467 P6 reached 100 J/g and 124 J/g, respectively, after 6 days. A denser matrix often leads to a
468 higher strength, but P1 was characterized by the highest porosity. A high ettringite content
469 can result in an increased strength. However, the ettringite content of P1 and P2 was
470 comparable (8.6 wt.% and 9.0 wt.%, respectively), while the compressive strength of M2 was
471 less than half of M1. The high compressive strength of M1 might be due to its highest
472 amorphous content (87.0 wt.%) and/or lowest cuspidine and $Mg_2P_2O_7$ content (0.9 wt.% and
473 0.9 wt.%, respectively). Also, the amorphous CSH content was highest for P1 in TGA. The
474 European standard for SSCs [41] includes minimum characteristic values for cement but not
475 for mortars. The minimum compressive strength at 28 days should be 32.5 MPa for pastes
476 [41], though it should be kept in mind that mortar strength is often actually lower than pure
477 paste strength [93].



478
479 **Figure 12: Compressive strength of mortars after 28 days of curing**

481 4. Conclusions

482 This study investigated the effect of the NaOH content on alkali/sulfate-activated binders
483 from 90 wt.% GGBFS and 10 wt.% PG. Alkali activators were prepared with a NaOH molarity
484 ranging from 0 M to 4 M. The hydration, mineralogy, porosity and compressive strength of
485 the produced pastes and mortars were investigated. **These are the main conclusions:**

- 486 • A molarity of 0 M gave rise to the highest porosity and highest strength, although the
487 setting occurred only after 7 days.
- 488 • At molarities of 1 M and higher, portlandite appeared during the first few hours of
489 hardening and acted as a catalyst that promoted further slag dissolution.
- 490 • The molarity of the alkali activator significantly influenced the phase assemblage, which
491 developed continuously during the first 28 days. At lower molarities (from 0 M to 1 M), an
492 amorphous CSH phase was present, while molarities of 2 M and higher favored CASH
493 development, together with cuspidine and $Mg_2P_2O_7$.
- 494 • From a molarity of 2 M and higher, ettringite disappeared and was replaced by a
495 monosulfate phase (i.e., $NaCa_4Al_2O_6(SO_4)_{1.5} \cdot 15H_2O$) and amorphous aluminum-
496 hydroxide. Their content gradually increased as the curing time was increased for all
497 samples.
- 498 • The formation of thenardite, which is a salt, is undesirable from the leaching point of view.
- 499 • Carbonation was enhanced when the molarity of the alkali activator was increased. From
500 the environmental point of view, however, carbonation should not necessarily be viewed
501 as unwanted, as long as it has no negative influence on the properties and durability of
502 the material, due to its ability to capture atmospheric CO_2 .

503 Further investigation of the mineralogy, porosity and strength over extended curing times
504 (e.g. over 1-3 years) is advised in order to define appropriate applications.

505

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507

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514

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