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1 **Effect of polycarboxylate superplasticizer on hydration**
2 **and properties of belite ye'elimit ferrite cement paste**

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8 **Abstract**

9 Belite-Ye'elimit-Ferrite (BYF) cements have received increasing attention in view of
10 their lower CO₂ footprint and their interesting performances. This work deals with the
11 effect of polycarboxylate superplasticizer (SP) on BYF cement paste. It was found that
12 SP dosage must be low in order to avoid destabilization, and thus improve the resistance
13 to bleeding and segregation. Also, the good affinity of polycarboxylate based
14 superplasticizer with cement surface improves the cement particles dispersion and
15 causes a significant diminution of the yield stress during the low activity period.
16 Furthermore, it is shown that SP causes a delay in the early age hydration, inducing a
17 decrease in the compressive strength at early age while it increases them after 90 days.

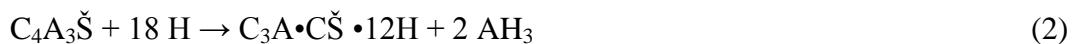
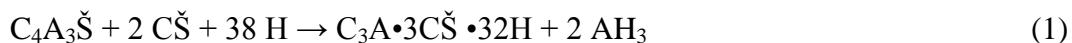
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19 **Keywords:** Belite ye'elimit ferrite cement, admixture , hydration , rheology , cement paste

20 **1 Introduction**

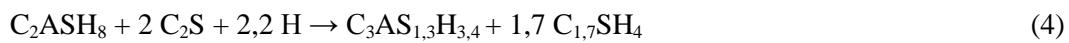
21 Cement industry is responsible for 8% of global anthropogenic CO₂ emissions [1],
22 mainly due to ordinary Portland cement (OPC) production. In order to reduce them, new
23 binders are developed such as Belite-Ye'elimitite-Ferrite (BYF) cements, which
24 production releases up to 30 % less CO₂ [2,3]. They were recently proposed as
25 alternative to OPC considering that their performances tend to be similar [4]. The main
26 raw materials used for making BYF are bauxite, limestone, clay, and gypsum and this
27 leads to a mineralogical composition very different than Portland cement. The three
28 main phases present in BYF clinkers are, in the order of content (cement notation will
29 hereafter be used: C = CaO, S = SiO₂, A = Al₂O₃, F = Fe₂O₃, Š = SO₃, H = H₂O): belite
30 (C₂S), ye'elimitite (C₄A₃Š) and ferrite (C₄AF). Calcium Sulfo-Aluminate (CSA) clinkers
31 are usually co-grinded with 15 to 25 wt% of calcium sulfate to optimize strength
32 development and volume changes [5].

33 Previous studies concerning hydration of this cement have shown different hydration
34 steps. First, only ye'elimitite and calcium sulfate react [6] during the first day, to form
35 ettringite and aluminum hydroxide [7] (usually poorly crystallized [8–10]) according to
36 the following chemical reaction (1). Then, local concentration of sulfate decreases [11];
37 they react to form calcium monosulfoaluminate (AFm) according to the second
38 chemical reaction (2). Due to its high reactivity, the conversion rate of ye'elimitite can
39 reach 85 % in 6 hours [9].



40 Afterwards, belite begins to hydrate. First, it reacts with aluminum hydroxide originated
41 from ye'elimitite hydration to form strätlingite (C₂ASH₈) according to reaction (3). Its

42 hydration can lead to pH increase [12] which destabilizes strätlingite, usually around
43 28 days of hydration [9,13,14]; strätlingite reacts with belite to form siliceous
44 hydrogarnet ($C_3AS_{1.3}H_{3.4}$) and C-S-H gel according to reaction (4). Some portlandite can
45 also be formed by the hydration of belite according to reaction (5), but this reaction is
46 more likely to occur in Portland cement or in BYF cements with a particularly high
47 belite content [15].



48 The hydration of ferrite in these cements have not yet well been elucidated, it is
49 suspected to react in the same time as belite, as iron can replace aluminum in strätlingite
50 [11,16]. Iron has also been found in ettringite and aluminum/iron hydroxide [17–20],
51 which suggests its hydration takes place at the same time as ye'elimitite.

52 The hydration of BYF cements remains complex; different experiments and
53 thermodynamic modelling were performed for ye'elimitite-containing cements to
54 understand their hydration. Their early hydration – that mainly depends on ye'elimitite
55 reactivity – can be tailored by varying the nature [21–23] and amount
56 [5,11,12,21,24,25] of calcium sulfate, or the water-to-binder ratio [12,14,16]. The effect
57 of some retarders on BYF cement hydration was also studied: tartrate, gluconate, borax
58 [26,27] as well as citric acid [28]. Also, the compatibility with polycarboxylate
59 superplasticizer was proved [29,30]; and some studies on the effect of polycarboxylates
60 on CSA cements shown that their dispersion effect was limited in time due to the
61 ettringite precipitation [31,32]. However, the number of studies on the effect of
62 admixtures on this kind of cement remains limited. Therefore, this work deals with the

63 effect of a polycarboxylate superplasticizer on hydration and rheological properties of
64 BYF cement paste.

65 Polycarboxylate superplasticizers (PCEs) are widely used in concrete industry since
66 they enable a better workability for concrete, hereby decreasing the placing costs and
67 allowing diminution of water-to-cement ratio. PCEs act by adsorption at the cement
68 particles surface and induce electrostatic repulsion and steric hindrance which enhance
69 the dispersion of cement particles and thus improve the rheology the paste.

70 Besides their dispersion effect, superplasticizers have an influence on the cement
71 hydration. They strongly interact with ettringite [33] and are known to delay its
72 precipitation [34–36].

73 The aim of this paper is to investigate the effect of polycarboxylate superplasticizer on
74 microstructure and properties of fresh and hardened BYF cement pastes. Hydration was
75 studied using isothermal calorimetry; phase composition was determined by Rietveld
76 quantitative XRD coupled with TGA. Moreover, consumption of superplasticizer was
77 assessed by TOC measurements and the effect of the SP on rheological and mechanical
78 behavior was also investigated.

79 **2 Experimental section**

80 **2.1 Materials**

81 The cement used was obtained by mixing BYF clinker with 10 wt% of natural
82 anhydrite. Its granular properties are given in Table 1, as well as its elemental and
83 mineral composition. The oxide content was determined by XRF, and the mineral
84 content was determined by Rietveld quantitative X-ray powder diffraction. The

85 amorphous and crystalline non-quantified content (ACn) were determined using an
86 external standard ZnO as detailed in the method section (2.2.3).

87 **Table 1: Granular and chemical properties of the BYF cement used**

Granular data		Oxide content (wt%)		Mineral content (wt %)	
Density (g/cm ³)	3.10	CaO	49.2	β-belite	32.8
Blaine surface area (m ² /g)	0.40	Al ₂ O ₃	19.3	ye'elite	24.5
BET surface area (m ² /g)	0.77	SiO ₂	12.2	ferrite	21.0
Mean grain size (μm)	16.9	SO ₃	10.0	gehlenite	1.6
Median grain size (μm)	11.2	Fe ₂ O ₃	7.5	perovskite	1.8
Minimal grain size (μm)	0.04	TiO ₂	0.44	anhydrite	9.3
Maximal grain size (μm)	110	MgO	0.29	gypsum	0.4
		K ₂ O	0.24	calcite	0.3
		MnO	0.1	ACn	7.3
		Na ₂ O	0.1		
		P ₂ O ₅	0.1		

88

89 A commercial polycarboxylate based superplasticizer (Master-Glenium 201, BASF,
90 France) was used. The dry extract was determined in accordance with the European
91 standard EN 480-8. The measured dry extract (19.5 wt%) is the same as that provided
92 by BASF. The characteristics of this superplasticizer are provided in the appendix. The
93 dosage of superplasticizer will hereafter be expressed as mass of dry extract per mass of
94 cement. According to BASF, the recommended range of use of this superplasticizer
95 corresponds to 0.3 – 3 % by total mass of cement, which corresponds to 0.06-0.6% of
96 dry extract. In this study, when SP is used in higher amounts than 0.06 % (i.e. 0.1 % and

97 0.4 %), the cement paste is strongly destabilized, which means that an excessive
98 bleeding is observed.

99 Cement pastes were prepared with water to cement weight ratio (w/c) of 0.4 by pouring
100 cement into an aqueous solution containing the appropriate amount of SP
101 (corresponding to time zero of the hydration), while stirring at 500 rpm for 1 min, and
102 then for a further minute at 1000 rpm using a planetary agitator Stuart SS30.

103 Samples were cured at ambient temperature ($23^{\circ}\text{C} \pm 2^{\circ}\text{C}$) and $86 \pm 3\%$ relative
104 humidity on the first day of hydration, and then in tap water. For rheological
105 measurements and interstitial liquid extraction, 5 min before the experiments, the paste
106 was stirred at 1000 rpm for 20 s then at 2000 rpm during 10 s.

107 **2.2 Methods**

108 **2.2.1 Isothermal calorimetry**

109 A conduction calorimeter (TAM Air, Thermometric AB, Sweden) operating at 25°C
110 was used to determine the hydration heat flow. About 5 g of paste were weighed into
111 sealed glass flasks and transferred into the calorimeter within 3 min. Results are
112 presented after a normalization by the weight of anhydrous cement.

113 **2.2.2 Thermal analysis**

114 Hydration was stopped by immersing fine powder of the crushed paste for 5 minutes in
115 isopropanol and rinsing twice with diethyl ether. TGA (NETZSCH STA 449F5) was
116 performed using about 80-100 mg of powder at a heating rate of $10^{\circ}\text{C}.\text{min}^{-1}$ under argon
117 between 30 and 950°C , after 10 min of stabilization at 30°C .

118 **2.2.3 X-ray diffraction**

119 Three types of samples were analyzed by X-ray diffraction: anhydrous cement
120 (powder), fresh cement paste (suspension), hardened cement paste (slice). The latter
121 were not analyses quantitatively, as explained in the result part. Patterns were recorded
122 on a Bruker AXS D8 Advanced diffractometer in a θ - θ configuration. X-ray diffraction
123 was performed on anhydrous cement, fresh cement paste and hardened cement paste.
124 Data were collected from 5° to 70° (2θ) during approximatively 1 h ($\text{Cu K}\alpha$, $\lambda=1.54 \text{ \AA}$)
125 during which the sample is rotating to improve the crystallites orientation statistics, for
126 all samples except for fresh cement paste.

127 Clinker composition was determined thanks to powder X-ray diffraction. An external
128 standard ZnO (G- factor approach) was used to quantify X-ray amorphous and
129 crystalline non-quantified part according to the method presented by Jansen et al. [37],
130 and applied to BYF clinker using X'pert PANalytical software. The structure model
131 used for the Rietveld refinement of the CSA are given in [38]. The mass attenuation
132 coefficients of the samples were calculated using data from X-ray fluorescence analysis
133 (Table 1). The hydrated paste samples were analysed qualitatively

134 The composition of fresh cement pastes was determined thanks to *in situ* measurements.
135 To this end, the freshly prepared paste was cast into a sample holder, and covered with a
136 Kapton film to avoid evaporation. Data were collected from 5° to 50° (2θ) during
137 17.5 min for the first 4 hours of hydration. Rietveld refinements were performed on
138 these patterns.

139 Hardened cement pastes were analysed without crushing them nor stopping their
140 hydration in order to avoid dissolution of ettringite in solvent. Slices (diameter 2 cm)

141 were sawn under isopropanol with a diamond-coated blade and immediately placed in
142 the diffractometer for XRD pattern acquisition.

143 **2.2.4 Microscopic observations**

144 The fractured cement pastes were observed using Scanning Electron Microscopy (SEM)
145 Quanta 200 FEG (FEI)using Back-Scattered Electron mode (BSE).

146 **2.2.5 Superplasticizer consumption**

147 The amount of consumed SP was determined by the depletion method [39]. The
148 interstitial liquid was extracted from the paste by centrifugation (10 min at 10000 rpm),
149 filtered (PTFE 0.45 µm), diluted with milli-Q water and analyzed using a vario TOC
150 cube (Elementar) in total carbon mode, using superplasticizer calibration. To avoid
151 precipitation of hydrates, the measurements were made during the same day as the
152 extraction of interstitial liquid. The result for the reference in which no SP was added
153 was considered to correspond to the amount of inorganic carbon in all samples.

154 **2.2.6 Rheological behavior**

155 Rheological measurements were carried out using an experimental AR 2000ex
156 rheometer from TA Instruments, equipped with parallel-plate geometry covered with
157 sand paper. The measurement procedure consists of a pre-shear phase (during 80 s at
158 100 s^{-1}) followed by shear rate sweep (from 100 s^{-1} to 0.1 s^{-1}). Due to the complexity of
159 obtaining the steady state flow, for each shear rate, the shear stress was measured at a
160 similar equilibrium time of 20 s for all cement pastes. The dynamic yield stress was
161 determined by extrapolating the Herschel-Bulkley model. All measurements were
162 performed on cement pastes hydrated for 40 min, which corresponds to a low heat
163 activity period.

164 **2.2.7 Compressive strength**

165 Compressive strengths were measured on 20 x 20 x 20 mm cubes of cement pastes
166 prepared in plastic 3D-printed molds. The compressive strength tests were performed
167 mechanical using testing machine (3R-RP40) with force control. The load was applied
168 at a uniform rate of 0.1 MPa/s. The specimens were tested at 1, 7, 90 and 180 days of
169 hydration.

170 Table 2 summarizes all the performed tests and the used mixtures.

171 **Table 2 : The performed tests and the used mixtures**

%SP	time of hydration	isothermal calorimetry	In-situ XRD	SEM	TOC	rheology	TGA	XRD	compressive strength
0 %, 0.05 %	0 - 300 min	x	x						
	40 min				x	x			
	5 h			x					
	1, 7, 28, 90 days						x	x	x
0.025 %	1, 7, 28, 90 days								x
0.015 % 0.025 % 0.04 % 0.06 %	40 min	x			x	x			

172

173 **3 Results and discussion**

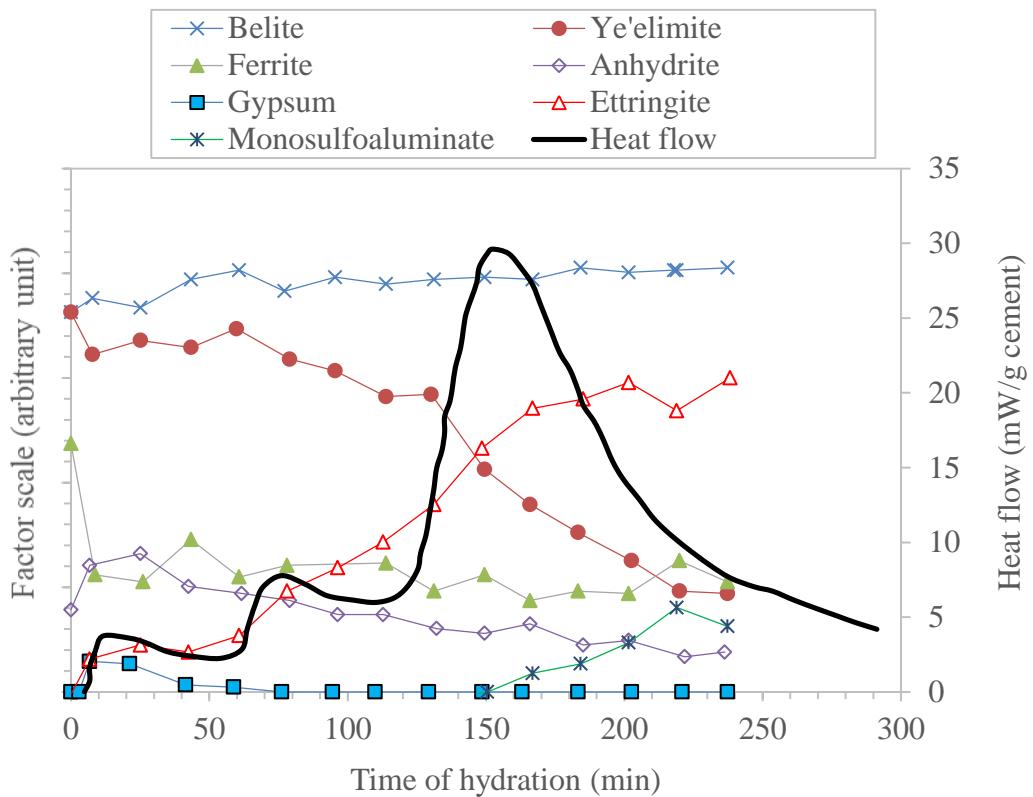
174 **3.1 Effect of SP during the early age**

175 **3.1.1 Early age hydration of the BYF cement without admixture**

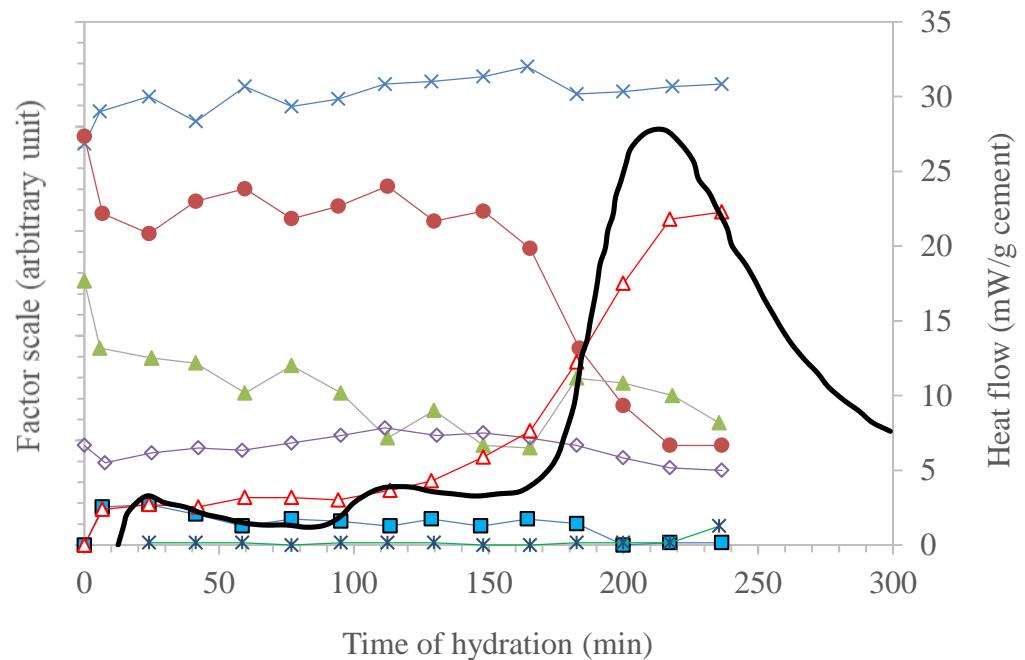
176 Fig 1 (top) shows the variation of the phase composition and the heat flow with
177 hydration time during the first four hours of hydration.

178 Due to the introduction of the sample into the calorimeter, the heat flow signal is
179 disturbed at the beginning of the measurement. The wetting of the cement grains and
180 first dissolution of the first anhydrous species is usually exothermic, leading to a first
181 hydration peak that could not be measured. Yet, its existence is confirmed by the signal
182 rapidly increasing and then decreasing before the first hour of hydration, thereby
183 showing the end of the first phase of hydration and beginning of a low heat activity
184 period. This first period corresponds to the first dissolution of ye'elimit and anhydrite,
185 the latter immediately forming some gypsum, probably due to a local small quantity of
186 other ions than Ca^{2+} and SO_4^{2-} in the interstitial solution. Also, precipitation of ettringite
187 according to (1) seems to start immediately. The gypsum hereby formed has a higher
188 kinetics of dissolution than anhydrite, and, once formed, it quickly dissolves to become
189 the sulfate source consumed by ettringite formation.

190 After a quick period where the heat flow decreases, at 1 hour of hydration, a slight
191 acceleration in the dissolution of anhydrite and ye'elimit takes place, in accordance
192 with stronger precipitation of ettringite. After 2 hours of hydration, the most intense
193 heat flow peak is observed. It corresponds to even stronger dissolution of ye'elimit,
194 leading not only to the formation of ettringite but also to the first precipitation of
195 calcium monosulfoaluminate (AFm) according to (2). The width of the XRD peaks of
196 the latter (not shown) suggests it is poorly crystallized. At the end of this third peak, the
197 dissolution of anhydrous phases seems to decelerate.



198



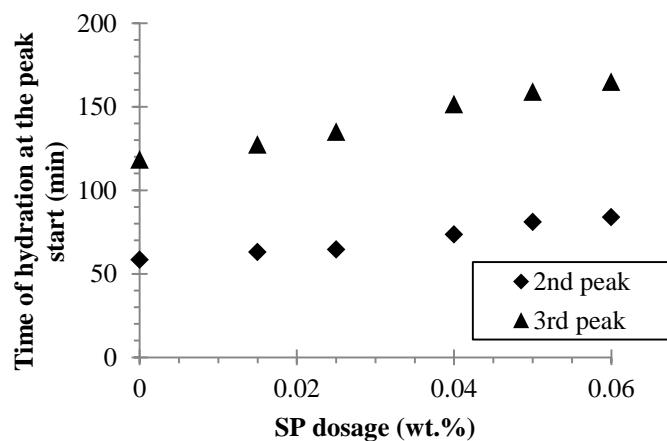
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200 Fig 1: Phase composition and heat flow of the cement paste containing (top) no SP and
201 (bottom) 0.05 % SP, measured by in-situ RQXRD coupled with isothermal calorimetry.

202 **3.1.2 Effect of polycarboxylate superplasticizer**

203 The results of isothermal calorimetry of the cement paste without SP and with a dosage
204 of 0.05 % are shown respectively in Fig 1 (bottom) and Fig 2. This SP dosage does not
205 destabilize the cement paste. By comparing these results, it appears that the hydration is
206 delayed when SP is added. Also, with 0.05 % SP, the main peak seems to be a bit larger,
207 which can be due to a slower AFm precipitation, that is observed in Fig 1 and can be
208 hypothesized for longer hydration times.

209 The delay in the hydration was quantified by measuring the time of hydration at which
210 the calorimetry heat flow increased, corresponding to the beginning of the two
211 detectable peaks (second and third, the first being difficult to measure as previously
212 mentioned). This was measured for increasing amounts of SP and is presented in Fig 2.
213 As shown in this figure, increasing superplasticizer dosage leads to more retarding
214 effect. Especially, the addition of increasing amounts of SP seems to retard the second
215 peak of hydration, when ettringite precipitates massively. The same trends were
216 observed by Su et al. [30] with four superplasticizers on belite rich calcium
217 sulfoaluminate cements. Moreover, after approximately one day of hydration, the
218 cumulated heat is equivalent for all systems.



221 Fig 2: Time of hydration of the cement paste at the beginning of the two main calorimetric
222 peaks for different SP dosages

223 Fig 1 (bottom) shows the phase composition and the evolution of heat flow of the
224 cement paste containing 0.05 % of SP. At the beginning of hydration, ye'elimit is
225 consumed as well as anhydrite, allowing ettringite and gypsum to immediately
226 precipitate. With 0.05 % SP, gypsum is still detected until more than 3 hours of
227 hydration even if it is quickly (less than half an hour) consumed in the reference. Also,
228 anhydrite seems not to dissolve until there is no gypsum left in the cement; which is
229 consistent with its slower dissolution.

230 Furthermore, ettringite precipitation is slower when SP is added, but the hydration
231 scheme is similar: its precipitation is accelerated, which causes the second calorimetry
232 peak. Then, its further acceleration in accordance with a faster ye'elimit dissolution
233 causes the third stronger calorimetry peak. At 4 hours of hydration, the amounts of
234 ettringite, ye'elimit and ferrite are in the same order of magnitude whatever the SP
235 content.

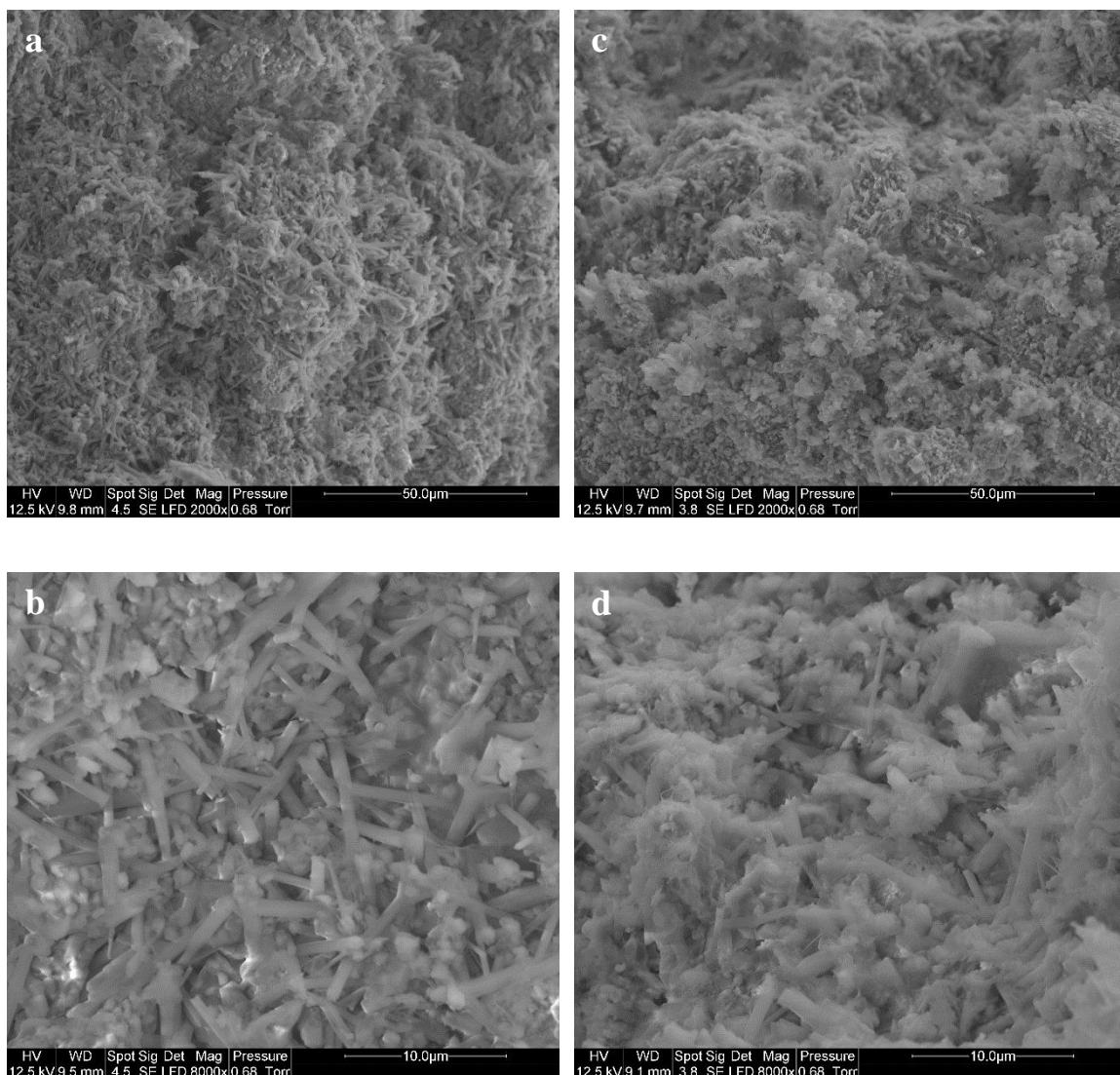
236 As for AFm, it is detected earlier in presence of SP (from 1.5 h of hydration instead of
237 2.5 h), but in very low amount, suggesting local low concentrations of sulfate. Also,
238 there is no significant evolution of AFm quantity until 4 hours of hydration, whereas it
239 precipitates continuously at the beginning of the third peak of hydration in the cement
240 without SP.

241 Concomitant dissolution of gypsum and ye'elimit, as well as ettringite precipitation
242 acceleration are clearly linked. Therefore, SP must act either to a retardation of
243 dissolution of the anhydrous species or to a prohibition of the hydrates nucleation and/or
244 growth [40]; and when its effect is stopped, all hydration reactions directly continue.

245 **3.1.3 Ettringite morphology**

246 SEM micrographs of ettringite crystals formed in the cement paste with and without SP
247 are presented on the Fig. 3 after 5 hours of hydration.

248



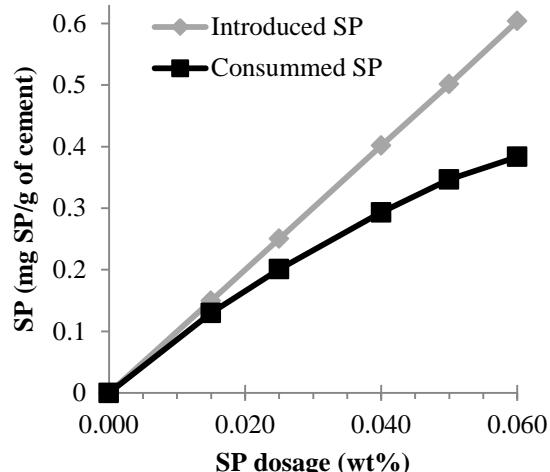
249 **Fig. 3: SEM micrographs of fractured surfaces of BYF cement paste hydrated for 5 hours**
250 **(a, b) without SP and (c, d) with 0.05 %SP**

251 In cement paste with superplasticizer, heterogeneous sizes of ettringite crystals can be
252 observed with the higher magnification (Fig. 3d); all of them seeming at first sight
253 shorter or equivalent to the reference sample, even though one of the two ends of the

254 crystals is usually difficult to determine. Moreover, their diameters seem very
255 heterogeneous, from less than 0.1 μm to 1 μm . With the smaller magnification (Fig. 3c),
256 ettringite crystals are more difficult to recognize. Generally, it shows that ettringite
257 crystals are globally smaller when SP is added, suggesting a strong effect of SP on
258 ettringite precipitation. Previous studies on model systems [36,41] showed that
259 superplasticizers can inhibit crystal growth and therefore favor its nucleation; leading to
260 smaller crystals in a higher amount.

261 **3.1.4 Adsorption of the SP**

262 The amount of consumed SP was determined by subtracting the amount of remaining
263 superplasticizer in solution after centrifugation from the total amount of SP added to the
264 sample (depletion method [39]). The consumption isotherm of the SP at 40 min of
265 hydration is presented in Fig 4. The isotherm shows a high surface interaction between
266 SP and cement particles, which increases with the amount of SP added to cement. For
267 example, nearly 90 % of the SP added is consumed by the particles for cement paste
268 with 0.015 % SP. The isotherm starts to flatten out but does not reach a plateau with the
269 studied dosages. As shown in Fig 4, a continuous consumption of SP with increasing its
270 dosage is observed. This might be due to co-precipitation with the hydrates [42,43]
271 and/or the increase of available surface due to formation of small ettringite particles. It
272 is generally admitted that the presence of SP around the particles leads to electrosteric
273 repulsion, therefore the high adsorption of SP suggests a high potential of dispersion;
274 this will be discussed below, in the part 3.1.5 Rheological measurements.



275

276 **Fig 4: Consumption isotherm of the SP at 40 min of hydration**

277 On the other hand, since the consumption rate concomitantly with the delay of
 278 hydration increase with the amount of SP added to the cement paste, it is expected that
 279 these two behaviors are linked.

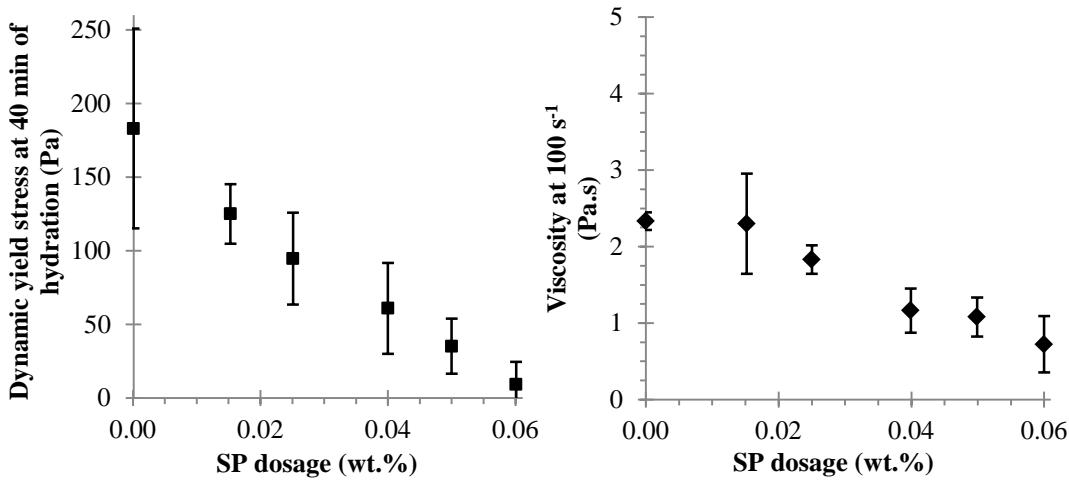
280 Indeed, Plank and Hirsch showed that polycarboxylate superplasticizers have a
 281 preferential adsorption onto ettringite [33]. The effect of SP on ettringite morphology
 282 earlier described suggests the affinity between SP and ettringite. It can be speculated
 283 that when the solution is oversaturated with ettringite, nuclei form but don't grow
 284 because of SP adsorption onto them; the solution stays oversaturated so no further
 285 dissolution in ye'elinite, anhydrite nor gypsum can continue, which would explain the
 286 retardation of the hydration.

287 **3.1.5 Rheological measurements**

288 Yield stress corresponds to the minimum stress required to initiate flow. Depending on
 289 the measurement method, different types of yield stress can be defined. The yield stress
 290 determined by extrapolating the equilibrium flow curve to very low shear rates using
 291 rheological models is commonly termed dynamic yield stress. As reported by Roussel
 292 [44], yield stress is a relevant parameter able to describe the effect of superplasticizer on

293 the fluidity of cement pastes. Yield stress and viscosity at 100 s^{-1} of the cement paste
294 with different additions of SP are presented in Fig 5. All measurements were made after
295 40 min of cement hydration, during the period of low activity. Indeed, it was pointed
296 out by several authors that the fluidity of CSA pastes mostly depends on the amount of
297 ettringite formed [30–32,45]. At the early stage of the hydration, it was previously
298 shown that ettringite immediately precipitates, so the measurements were done during
299 the low activity period, at a hydration time when the ettringite content was shown
300 constant by *in situ* XRD. When increasing the amount of SP, the viscosity and shear
301 stress decreases almost linearly. The shear stress almost reaches a zero-value when
302 0.06 % SP is added, while still showing a shear-thinning behavior. This shows that SP
303 has a good dispersive action. Moreover, Su et al. [30] showed that fluidity is conserved
304 as long as the ettringite amount is stable. The results of *in situ* XRD (Fig 1) showed that
305 the precipitation of ettringite is delayed by the presence of SP; the fluidity can therefore
306 be maintained longer with the use of SP.

307 The dispersive effect and rheological behavior of cementitious materials are closely
308 related to the adsorption amount of SP onto the surface of cement particles. The
309 optimum dispersion is reached when the total surface of cement particles is covered by
310 superplasticizer (at the plateau) or sometimes before the plateau in the adsorption
311 isotherm [46]. In fact, the electro-steric effect which controls the dispersive action
312 depends on the surface coverage and the conformation of polymer [47]. At the
313 saturation dosage (plateau), this effect only depends on the conformation of the polymer
314 [47,48]. The minimum yield stress is generally reached after the plateau [49]. The
315 adsorption isotherm presented in Fig 4 shows a beginning of a plateau at a dosage of
316 0.06%. At this dosage, cement paste displays a very low yield stress, which means that
317 the saturation dosage could be close to 0.06%.



318

319 Fig 5: Effect of different amounts of the SP on rheological properties of cement paste at
320 40 minutes of hydration: a) shear stress and b) viscosity

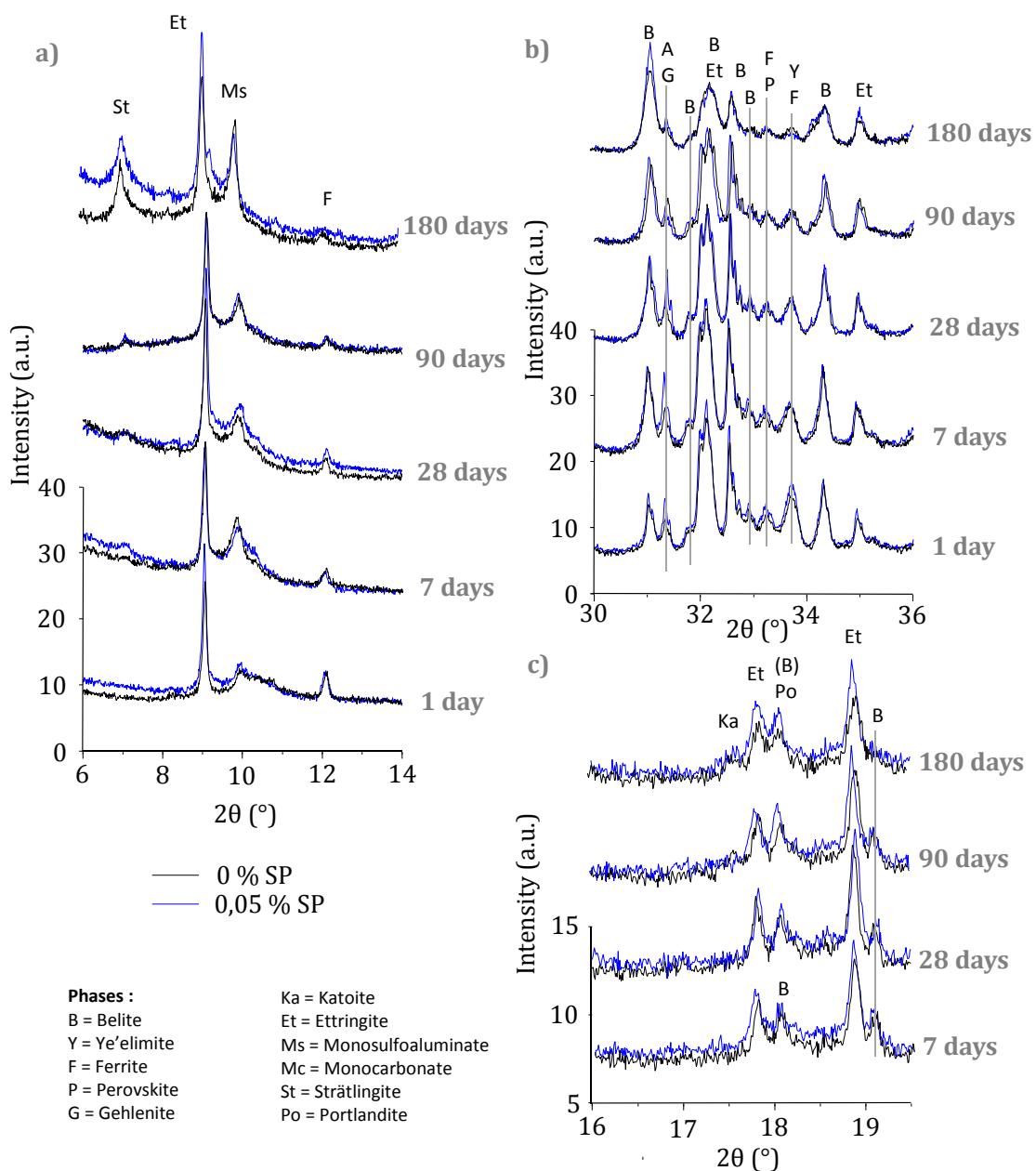
321 **3.2 SP effect at later ages**

322 **3.2.1 Phase composition**

323 XRD results are shown in Fig 6. Due to the diversity of the AFm phases and the width
324 of the resulting peak, the authors were not able to obtain a satisfying Rietveld
325 refinement; consequently, the results were treated qualitatively.

326 In accordance with the previous results on hydration during the first hours and reactions
327 (1) and (2), it shows that at 1 day of hydration, whatever the SP content, ye'elimité and
328 anhydrite have reacted to form ettringite, monosulfoaluminate and aluminum hydroxide.
329 Indeed, aluminum hydroxide is amorphous to X rays, but its presence is detected by
330 TGA (not shown) with the weight losses after 230 °C [5,17,50,51]. Without SP (Fig 6),
331 monosulfoaluminate continues to form while the amount of anhydrite decreases until 28
332 days of hydration. The first hydration product of belite is strätlingite (reaction (3)), it is
333 first detected at 28 days of hydration. At this time, some ferrite has dissolved, this phase
334 is suspected to be a source of iron and aluminum resulting in both formations of AFm
335 and strätlingite [11]. At 90 days, katoite starts to precipitate, showing a partial

destabilization of strätlingite according to (4). At 6 months of hydration, the belite and ferrite contents are lower, showing a stronger reactivity of the two phases. XRD peak at 18° and weight losses at 450°C indicate the presence of portlandite, which forms in the same time as C-S-H gel according to (5). The presence of amorphous hydration products is consistent with the relatively low amounts of strätlingite and katoite and high reactivity rates of belite and ferrite.



342

Fig 6: XRD patterns of cement without and with SP during its long-term hydration

344 With the addition of 0.05 % SP, during the first day of hydration fewer amounts of
345 ettringite and calcium monosulfoaluminate have precipitated, according to both TGA
346 and XRD results. This is linked with the retarding effect of SP. Monosulfoaluminate
347 content increases until 7 days. At this time, some strätlingite precipitation is observed,
348 way earlier than in the cement without SP. At 28 days of hydration the amount of
349 strätlingite seems the same whatever the SP content, but the sample with SP has
350 dissolved more belite and ferrite than the reference. A few portlandite precipitated,
351 earlier than in the reference. Until 6 months of hydration, the amount of portlandite,
352 strätlingite and katoite increases, in accordance with the decrease of belite, ferrite and
353 aluminum hydroxide content. At 6 months, XRD pattern are almost stackable, showing
354 a similar state of hydration.

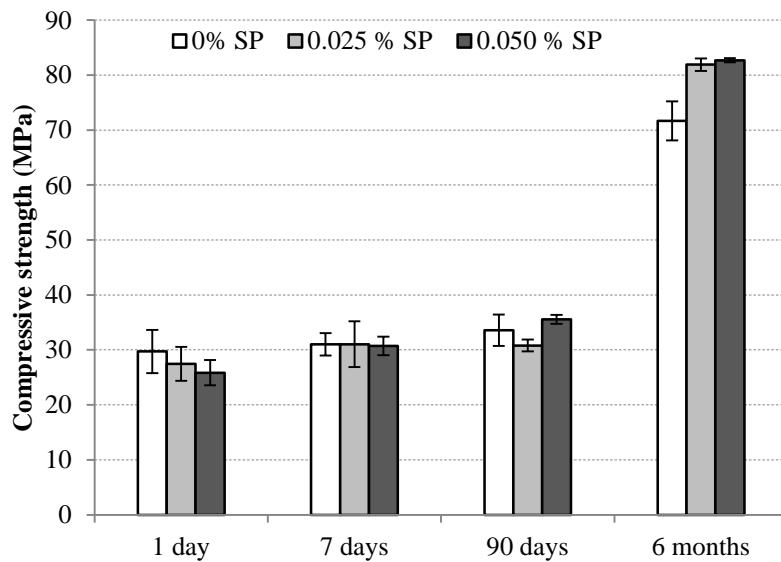
355 As a conclusion on the effect of SP on the late age hydration, it can be pointed out that
356 it diminishes the hydration rate of ye'elimit and anhydrite, but belite and ferrite react
357 faster. Indeed, both strätlingite and portlandite were detected at earlier times when SP is
358 added to the BYF cement paste; also, the hydration rate of belite and ferrite seems
359 greater with SP from 7 to 90 days. However, at 6 months of hydration, both samples
360 show the same phase assemblage.

361

362 **3.2.2 Compressive strength**

363 The compressive strength of the cement pastes at 1 day, 7 days, 90 days and 6 months
364 are shown in the Fig 7. At one day of hydration, the compressive strength of the cement
365 without SP is a bit higher than with increasing its amount. This is consistent with the
366 calorimetry results, which show that at very short term, the SP has a retarding effect on
367 the cement paste; and that this delay in the formation of the hydrates affects the

368 properties of the paste at least on the first day of hydration. For the next 90 days of
369 hydration, no significant evolution in the compressive strength is observed, suggesting a
370 very slow rate of hydration of the cement. Moreover, during this period, no significant
371 effect of the SP on the compressive strength was neither observed; this consistent with a
372 previous study [52]. Garcia Maté et al. [51] also tested the effect of a superplasticizer on
373 the compressive strength of a CSA cement at young age (3, 7 days of hydration), and
374 showed that it causes a slight increase or decrease, depending on the amount of calcium
375 sulfate, which confirms that the effect of the superplasticizer on the compressive
376 strength depends on the early age reactivity. It has to be noted that even if the hydration
377 rate is slightly better in the presence of SP, the resulting compressive strengths are
378 almost equivalent.



379

380 **Fig 7: Compressive strength of cement paste containing different dosage of SP at different**
381 **times of hydration**

382 Nevertheless, between 90 days and 6 months of hydration, the compressive strength
383 strongly increases; the increase is higher than the double of the 90 days value,
384 suggesting a high reaction rate. The XRD data showed a strong activity in belite

385 hydration between those two hydration dates, suggesting the importance of the
386 formation of a C-S-H in the strength of the paste. Moreover, at 6 months, the two
387 samples containing SP show a compressive strength slightly higher than the ones
388 without SP.

389 **4 Conclusions**

390 A polycarboxylate superplasticizer was shown to be compatible with the BYF cement
391 paste for low dosages (below 0.06 %). Its effect on the hydration of a BYF cement paste
392 was investigated both during the early and the later age. At short term, it was shown that
393 SP has a retarding effect on the hydration, which increases with the SP dosage. The
394 retard in hydration was related to the high adsorption capacity of the superplasticizer on
395 the cement particles, and particularly, its interaction with ettringite results in its
396 precipitation delay and a considerable change of morphology. Moreover, SP improves
397 the rheological properties of the paste by decreasing both yield stress and viscosity;
398 therefore a better workability is expected. In addition, the compressive strength is
399 decreased during the first week due to the hydration delay. However, the delay is caught
400 up at 7 days of hydration, and the strength is equivalent whatever the SP dosage until
401 90 days. During this period the cement hydration activity is very low. Nevertheless,
402 after belite begins to react (between 3 and 6 months), the compressive strength strongly
403 increases.

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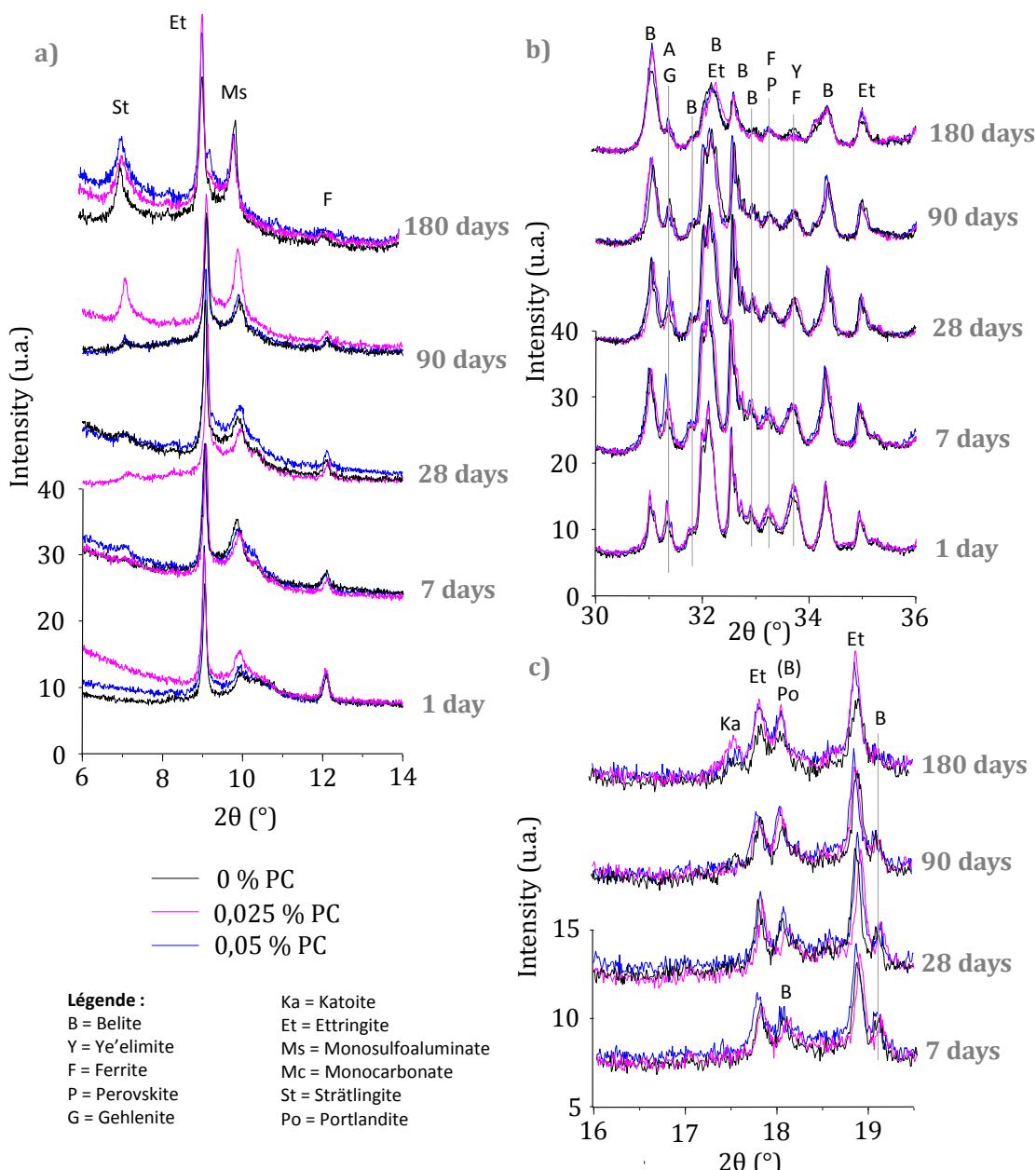
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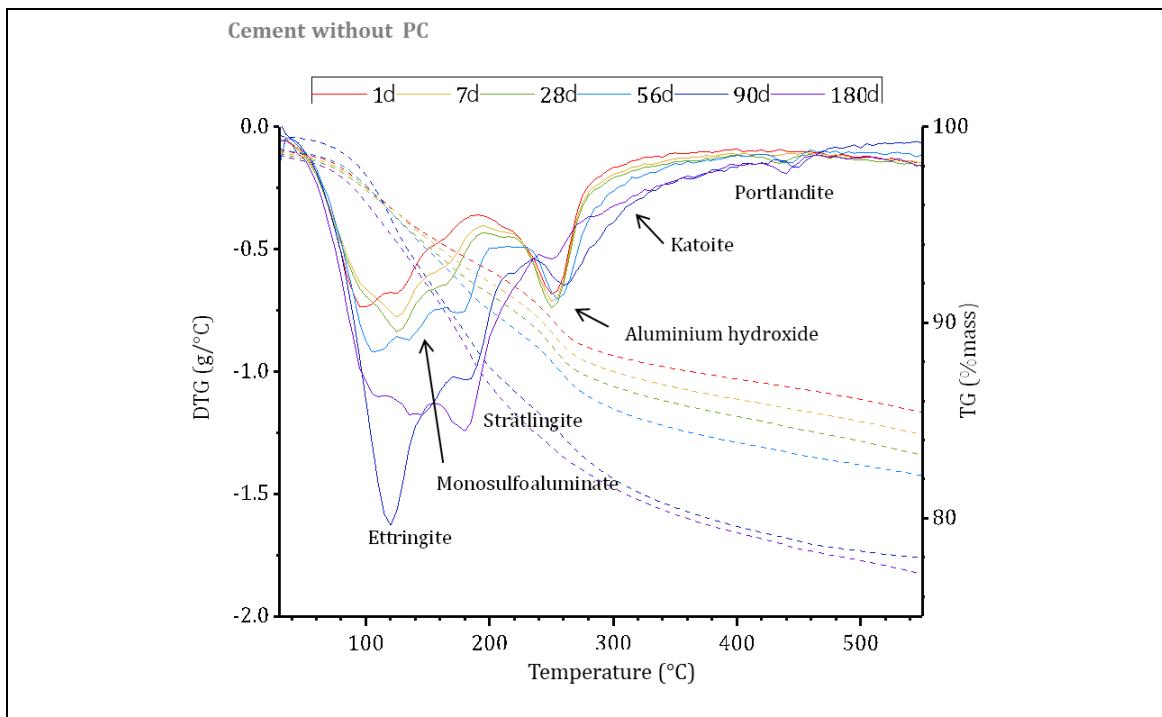
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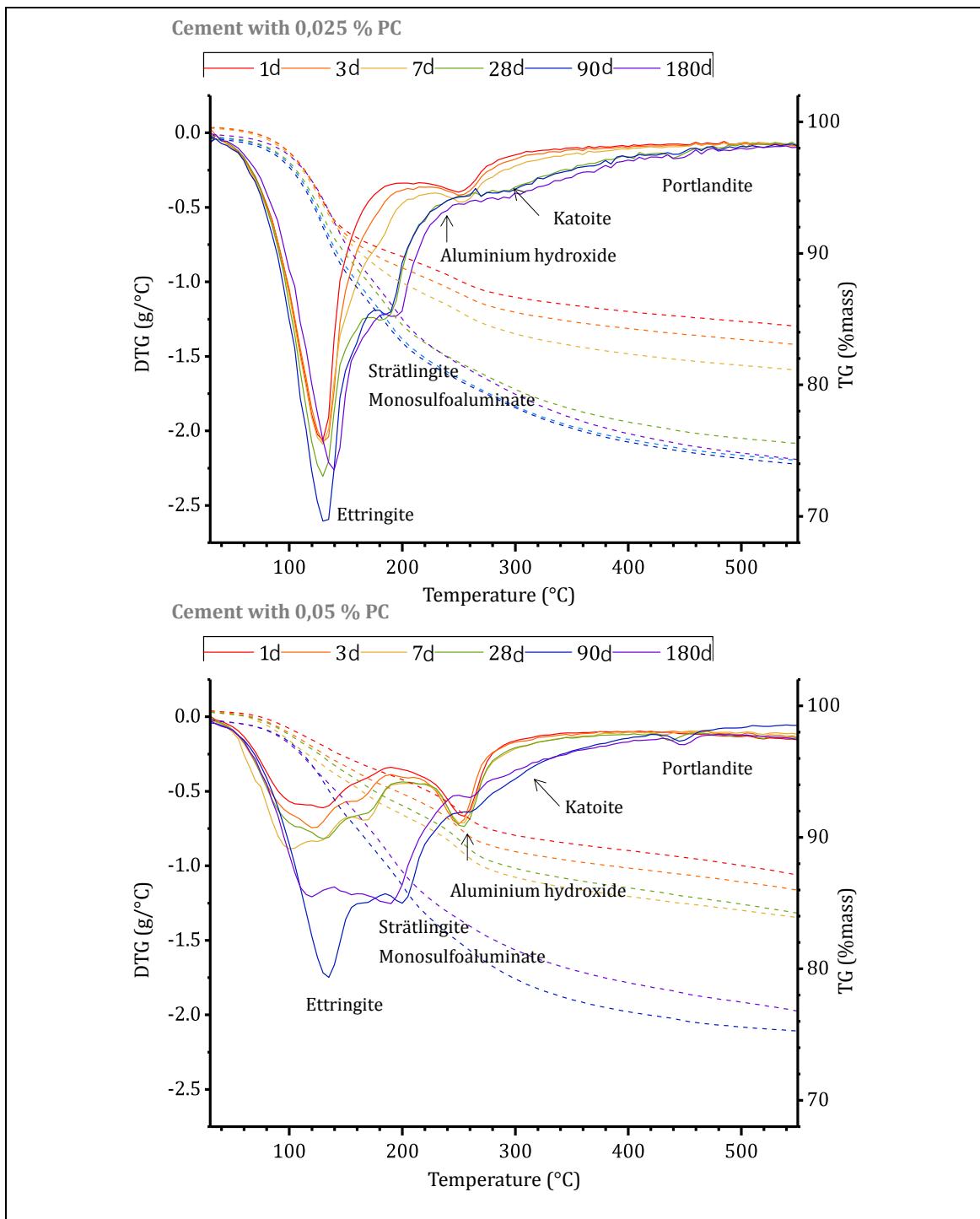
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Appendix



577 Fig. 1.A. XRD patterns of the hydrated cement pastes in the presence of polycarboxylate-
578 based superplasticizer





579

Fig. 2.A. TGA analysis of BYF cement pastes

580