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Waste glass as partial mineral precursor in alkali-activated slag/fly ash system

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15 **Abstract**

16 The feasibility of a waste glass powder residue (GP) from glass recycling as partial mineral
17 precursor to produce alkali-activated materials is investigated. GP served as powder coal fly
18 ash (PCFA) replacement within a reference system composed of 50% PCFA and 50% ground
19 granulated blast furnace slag (GGBS). Compared with PCFA, GP was better involved in the
20 alkali activation process by having a higher silica and Ca dissolution. Furthermore, increasing
21 GP replacement up to 30% prolonged the induction period, facilitated the gel formation and
22 yielded a 35% higher 28-day compressive strength. These observations are similar to the effect
23 of using both sodium hydroxide and sodium silicate as alkali activator in alkali-activated
24 slag/fly ash systems. A higher polymerization of the gel network was also observed.
25 Microstructure analysis indicated that the main reaction product is a calcium silicate hydrate
26 type gel substituted with Al and Na (C-(N)-A-S-H type gel).

27 This work largely contributes to the understanding of the reactivity and potential of GP and
28 promotes its practical utilization as a mineral precursor in the production of alkaline cements.

29 **Keywords:** Waste glass; Alkali activated material; Microstructure; Fly ash; Slag

30

31 1 Introduction

32 Fast growing world population and its related industrialization have raised concerns about the
33 environmental consequences of waste handling. Nowadays, many industries have started
34 investing in optimization of waste disposal management systems to fulfill the national and
35 international legislations. The development of a circular economy of mineral waste materials
36 within the Netherlands and the European Union (EU) has been found to be highly potential
37 and economical profitable. The potential waste materials are promoted to be recycled and re-
38 used as primary or secondary raw materials in other industrial processes to lower their
39 negative environmental impacts and preserve natural resources.

40 Within glass industry, the glass recycling has reached a relatively high average rate (>70% in
41 the EU and >90% in the Netherlands) [1]. However, there are still some challenges related to
42 non-recyclable glass fraction which does not meet the criteria for reuse in the production
43 process of new glass. About 20,000 tons/year of such glass residue (glass powder and glass
44 granular) are produced in the Netherlands [2] and most of this waste is sent to landfills. One
45 possible solution for managing this waste glass fraction is to use it as a solid precursor in
46 building materials. Previous studies [3-5] have already shown attempts to incorporate glass
47 fractions into Ordinary Portland cement (OPC) concrete, with general focus on replacement
48 of fine aggregate. However, their use as supplementary cementitious materials (SCMs) in OPC
49 concrete is still scarce.

50 In recent decades, alkaline activation technology has emerged as an effective tool able to use
51 different wastes and industrial by-products as solid precursors to produce cementitious
52 materials. Compared with OPC, alkali activated materials (AAMs) offer a large reduction in CO₂

53 emissions (up to 80%) [6] and have comparable or better performance (such as high
54 mechanical strength at early ages, high stability in aggressive environments and resistance to
55 elevated temperatures). Fly ash and blast furnace slag are currently the most intensively used
56 solid precursors to produce alkali activated cement/concrete [7-10]. Many researchers have
57 found that the binary system of alkali-activated slag/fly ash has an improved mechanical
58 properties and durability [11-13]. The enhanced mechanical performance and durability of
59 alkali-activated slag/fly ash have attracted great attention by both scientific community and
60 construction industry. The previous studies on alkali-activated slag/fly ash are mostly on the
61 microstructure and mechanical properties, as well as some efforts on understanding the
62 chemical makeup and formation mechanism of the reaction products [10, 14, 15].

63 To our best knowledge, studies on using waste glass in alkali-activated slag/fly ash systems
64 are still rare. Only few studies dealing with waste glass as precursor in AAMs can be found in
65 the literature. For instance, Tashima et al. [16] investigated the properties and microstructure
66 of glass fiber waste activated by alkaline metal sodium (Na) and potassium (K) solutions. A
67 compressive strength of 77 MPa was found for mortars activated by 10M NaOH solution and
68 cured for 3 day at 65°C. Pascual et al. [17] used metakaolin (MK) to replace a part of the GP to
69 introduce Al and also to stabilize alkali ions in the system and observed increment of the
70 compressive strength with MK content of up to 8%. In contrast, the compressive strength
71 decreased when the content of the MK was lower than 3%. Redden et al. [18] reported that
72 NaOH activated GP provides higher compressive strength than NaOH activated fly ash.
73 Through microstructural analysis, they observed that the main reaction product was a sodium
74 silicate gel in alkali activated GP, while a combination of sodium silicate and sodium

75 aluminosilicate (N-A-S-H) gels was identified in GP-fly ash blends. Torres-Carrasco et al. [19,
76 20] investigated the possible use of waste glass as an activator in alkali activated slag mortar
77 and found that using $\text{NaOH}/\text{Na}_2\text{CO}_3$ and glass mixture solution as activator increases the
78 compressive strength.

79 This work presents an investigation on the utilization of waste glass as partial mineral
80 precursor in alkali-activated slag/fly ash systems for production of alkaline cements. The main
81 aim is to valorize this kind of waste to enlarge its utilization in other industrial processes and
82 to promote a sustainable construction.

83

84 **2 Materials and methods**

85 **2.1 Materials**

86 The mineral precursors used in this study are a granulated blast furnace slag (GGBS), a class F
87 powder coal fly ash (PCFA) according to ASTM C 618 and a waste glass powder (GP) residue
88 fraction supplied by Van Gansewinkel Maltha, the Netherlands. Unlike ordinary GP which is
89 manufactured by crushing and grinding, this fine GP residue fraction is collected during the
90 bottle glass recycling process. Material density for GGBS, PCFA and GP are 2890 kg/m³, 2440
91 kg/m³ and 2174 kg/m³, respectively. Their particle size distribution curves are shown in Figure
92 1, with d₅₀ particle size to be 17.88 µm for GGBS, 33.19 µm for PCFA and 5.07 µm for GP.
93 Chemical compositions of all precursors were determined by X-ray fluorescence (XRF)
94 considering the loss on ignition (LOI) at 950 °C and is shown in Table 1.

95 The alkaline activator solution was prepared by dissolving NaOH pellets (analytical grade,
96 purity≥98%) in distilled water. The selected NaOH concentration is 4M, which is defined to be
97 optimal taking into account the fresh and hardened performance of alkali activated
98 GGBS/PCFA system [21-24] as well as the final costs.

99 **2.2 Methods**

100 **2.2.1 Mix design**

101 The starting point was a reference mixture of 50% PCFA and 50% GGBS (named R). Through a
102 partial replacement of PCFA by GP, 3 paste mixtures with 10%, 20%, and 30% of GP (named
103 respectively G10, G20 and G30) were prepared. The mix design of 4 mixtures is shown in Table
104 2. To study different levels of GP to PCFA replacement as main variables, the liquid to solid
105 (L/S) ratio was kept at 0.42 to maintain a suitable workability for all the investigated mixtures.

106 The solid precursors were firstly mixed for 5 min using a HOBART® mixer at a low speed.
107 Alkaline activator solution was then added gradually and the batches were mixed for
108 additional 5 min at a medium speed. The fresh pastes mixtures were cast in polystyrene prism
109 molds (40 mm x 40 mm x 160 mm) and then compacted with a vibration table for four times
110 (each time for 30 seconds) before finally sealed with a plastic foil. The samples were cured in
111 a climate room (20 °C and ≥98% RH) until testing.

112 **2.2.2 Testing Methods**

113 The reactivity of both GP and PCFA were measured by chemical dissolution treatment as
114 described elsewhere [25-27]. The solid minerals were dissolved in the concentrated acid
115 solution and were afterwards treated with boiling potassium hydroxide solution. The obtained
116 residue was rinsed, heated up to 950 °C and then was cooled to room temperature in a
117 desiccator. The dissolved fraction corresponding to the mass loss after chemical dissolution
118 treatment is determined as the amorphous phase content. The amount of reactive SiO₂ and
119 Al₂O₃ was also calculated.

120 Element dissolution tests of PCFA and GP in alkali activator solution were performed following
121 the modified NEN 7341 standard [25]. In total 5 g of mineral powder was added into 50 ml of
122 NaOH solution and stirred at 300 rpm using a magnetic stirrer. For each precursor, different
123 dissolution times were set as 5 min, 0.5 h, 1 h, 2 h, 6 h and 12 h. After these times, the solutions
124 were separated from the remaining solids through vacuum filtration using a 45 µm glass
125 micro-filter paper. The eluate was acidified with 5 vol.% nitric acid and diluted 100 times
126 before the Si, Al, Ca concentrations were measured using an Optima 5300 DV inductively
127 coupled plasma optical emission spectrometry (ICP-OES).

128 Mechanical properties and microstructural characterization tests were performed on paste
129 samples cured for 1, 7, and 28 days as follows:

130 • Compressive strength was measured in accordance with NEN-196-1 [28] at 1, 7, and 28
131 days.

132 • X-ray diffraction (XRD) was conducted using a Philips PW 1830 powder X-ray
133 diffractometer, with Cu Ka (1.5406 Å) radiation, tube setting to be 40 kV and 40 mA, a
134 step size of 0.030 °, and a 2θ range of 5-70 °.

135 • Fourier transform infrared spectroscopy (FTIR) was performed using a Spectrum TM 100
136 Optical ATR-FTIR spectrometer over the wavelength range of 600 to 4000 cm⁻¹ with a
137 resolution of 1 cm⁻¹.

138 • Isothermal calorimetry was conducted using a TAM-Air-314 isothermal conduction
139 calorimeter. Calibration was done at 20 °C before measurements, which lasted for a
140 period of 120 h. The data were recorded every 1 min and two replicates for each mixture
141 were measured.

142 • Differential thermogravimetry (DTG) was performed in a TG-449-F3-Jupiter instrument.
143 The powder of samples was put in a small aluminum oxide crucible and heated from 40 °C
144 to 1100 °C at 10 °C/min in an argon protection atmosphere at a flow speed of 50 µL/min.

145 • Environmental scanning electron microscopy (ESEM), with energy dispersive X-ray (EDX)
146 analysis, was performed using a Philips-XL30-ESEM. Samples were impregnated using an
147 epoxy and were polished prior to ESEM analysis. The EDX was performed at an
148 accelerating voltage of 20 kV. For 1, 7, and 28-day samples, 20 to 30 EDX measurements
149 were conducted on R and G30 at each curing age.

150 **3 Results and discussions**

151 **3.1 Precursor reactivity**

152 **3.1.1 Crystalline phases**

153 The X-ray diffraction (XRD) patterns of GP, PCFA and GGBS are shown in Figure 2. The main
154 crystalline phases in GP are quartz (SiO_2) and calcite (CaCO_3) while the minor phases are
155 chamosite ($\text{Fe}_3\text{Si}_2\text{O}_5(\text{OH})_4$), tobermorite ($\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2$), and tremolite ($\text{CaMg}_3(\text{SiO}_4)_3$). These
156 crystalline phases can be related to the initial ceramic particle contaminates within the input
157 glass fraction. The PCFA crystalline phases are mainly quartz (SiO_2), mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$) and
158 hematite (Fe_2O_3). In agreement with XRF results in Table 1, crystalline phases in GP and PCFA
159 also show high SiO_2 contents. GGBS contains mainly amorphous phases. All precursors contain
160 considerable amount of amorphous phases as can be reflected from the wide hump in the
161 XRD patterns (from 17° to 35° for GP or PCFA and from 25° to 35° for GGBS). As the existence
162 of abundant amorphous phases in GP is an indicator of reactivity, GP has the potential to be
163 used as precursor to produce cementitious materials.

164 **3.1.2 Reactive phases composition**

165 It is commonly recognized that the reactivity of aluminosilicate precursors is proportional to
166 the content of reactive SiO_2 and Al_2O_3 . The presence of these elements is the key for
167 developing the geopolymersization process and gel formation [29, 30]. The reactivity in this
168 study is also represented by the amount of reactive SiO_2 and Al_2O_3 in the precursor.
169 The amorphous phase content and related reactive SiO_2 and Al_2O_3 content in GP and PCFA
170 were obtained by analyzing their insoluble residue (I.R.) and soluble fractions derived from
171 the chemical dissolution treatment. The reactive SiO_2 , Al_2O_3 in GP and PCFA were calculated

172 using the corresponding chemical composition of original precursors (Table 1) and I.R. (Table
173 3) together with its related I.R. fraction. The reactive amount of each element was calculated
174 using eq. (1):

$$175 \quad \omega_{reactive}^{M-O} = \frac{m_{total} \times \omega_{total}^{M-O} - m_{residual} \times \omega_{residual}^{M-O}}{m_{total}} = \omega_{total}^{M-O} - \omega_{residual} \times \omega_{residual}^{M-O} \quad (1)$$

176 where M-O is SiO_2 or Al_2O_3 , ω is the percentage (%) and m is the mass (g).

177 The obtained results on reactivity of GP and PCFA are presented in Table 4. The analysis shows
178 that the amorphous content in GP is slightly higher (82%) than that in PCFA (77%). In addition,
179 about 80% of the total SiO_2 was found to be reactive. However, a significant difference in the
180 chemical composition was observed concerning Al_2O_3 and CaO. The reactive Al_2O_3 content in
181 GP (0.92%) is extremely low compared to that in PCFA (27%). On the contrary, the total CaO
182 content in GP (22%) is much higher, while PCFA only has very limited CaO content. These
183 results clearly imply that GP serves as silica and calcium precursor that has low aluminum
184 content. On the other hand, PCFA serves as silica and alumina precursor which is low in
185 calcium. These inherent differences in reactivity may eventually influence the microstructure
186 development of alkali-activated slag/fly ash with GP incorporation.

187 **3.1.3 Solubility/dissolution rate**

188 The element dissolution from mineral precursors is strongly related to their physical state and
189 chemical composition. The results of reactivity experiments have already indicated clear
190 differences between PCFA and GP and their reactive element composition. Dissolution
191 experiments of both precursors over time were performed to provide further details on
192 specific element release, which helps understanding the reaction kinetics and the early age

193 microstructure development. A quantitative analysis was carried out on dissolution kinetics
194 of element Si, Al, and Ca in 4M NaOH solutions, which is shown in Figure 3. It is worth noting
195 that the NaOH concentration is equal to that of the alkali-activator used in paste mixture
196 preparation.

197 The Si release rate of GP and PCFA shown in Figure 3(a) are relatively stable and roughly linear
198 within the first 12 h. GP tends to have a slightly higher dissolution rate as its reactive SiO_2
199 content is about 10% higher than PCFA, which results in a higher Si dissolution capacity. The
200 high rate Si solubility of GP could be also attributed to its smaller particle size [31].

201 The Al dissolution rate and concentration of PCFA shown in Figure 3(b) are much higher than
202 those of GP. This result is consistent with the reactivity of both precursors, since PCFA has
203 much higher reactive Al_2O_3 content than GP. Figure 3(c) indicates a higher rate and
204 concentration of Ca release in GP than PCFA, which is in agreement with its higher Ca content.

205 Both curves reach a plateau after 2 h, indicating a high dissolution kinetics of Ca from
206 precursors in high alkaline medium. Since the energy required for detachment of Ca from the
207 system is much lower than Al-O or Si-O bond energy, Ca as network modifier in the

208 aluminosilicate glass as well as Ca in the more depolymerized slag structures is known to
209 dissolve quickly via metal-proton exchange reactions in alkaline environment [32, 33]. This is

210 also the reason behind the fast early-age reaction kinetics of high Ca AAMs. It is observed that
211 the final dissolved Ca concentration is not proportional to the original Ca composition, which

212 is due to the reason that a part of the Ca from dissolution has been already consumed in
213 precipitation reactions forming 'hydrated' cementitious gel [34] or reincorporated in the
214 reacting surface of precursor [35].

215 **3.1.4 Reaction heat of precursors**

216 Isothermal calorimetry is conducted to evaluate the potential of NaOH activated precursors
217 and their reaction kinetics, which can also reflect their reactivity. Figure 4(a) plots the heat
218 flow of GGBS, PCFA and GP activated by 4M NaOH solution with an L/S ratio of 0.6 over the
219 first 80 hours. Two sub-calorimetric peaks are observed in each curve: The first peak correlates
220 with wetting and dissolution of the material. The second peak represents the reactions among
221 dissolved species like Si, Al and Ca. From the heat flow rate in Figure 4(a), GGBS shows the
222 highest reactivity while GP and PCFA only exhibit lower reactivity, although GP is slightly more
223 reactive than PCFA. Additionally, their cumulative heat evolution in Figure 4(b) displays the
224 same trend, where GGBS generates significantly the highest cumulative heat followed by GP
225 and then PCFA. This trend is in line with previous studies indicating higher reactivity of GGBS
226 compared with PCFA [36].

227 **3.1.5 FTIR analysis**

228 The reactivity of GP and PCFA have been analyzed by FTIR, which allows for monitoring the
229 chemical bond changes induced by the precursor reaction. The spectra collected before
230 chemical dissolution treatment is noted as 'original', while the spectra after treatment are
231 noted as 'residue'. The FTIR spectrum of dissolved amorphous phases were obtained by the
232 subtraction of spectrum 'residue' from spectrum 'original' using OMNIC software [14]. The
233 spectrum obtained from subtraction is referred as 'dissolved'.

234 The FTIR spectra of original, residue and dissolved phases in GP are presented in Figure 5(a).
235 Spectrum original of GP indicates a peak for quartz at 777 cm^{-1} [37]. Both the peak at 874 cm^{-1}
236 and the relative broad hump at 1420 cm^{-1} are associated with the presence of carbonate (CO_3^{2-})

237 with different vibration modes: $\nu_2[\text{CO}_3]^{2-}$ for 874 cm^{-1} and $\nu_3[\text{CO}_3]^{2-}$ for 1420 cm^{-1} [38]. The
238 broad peak centered at approximately 1005 cm^{-1} is associated with asymmetric stretching of
239 Si-O-Si bonds. The stretching of Si-O-M (M being an alkali metal or alkali-earth metal) is found
240 at wavenumber 919 cm^{-1} [39]. Considering GP is rich in Ca, the wavenumber could be
241 associated with Si-O-Ca bonds. For the spectrum residue of GP, the peak at 965 cm^{-1} may be
242 associated with $\nu_3(\text{Si-O})$ stretching vibrations in SiO_4 tetrahedral. The existence peak may be
243 related to other crystalline Si phases like tremolite. For spectrum dissolved of GP, it is evident
244 that peaks at 1005 cm^{-1} and 919 cm^{-1} are mainly attributed to its reactive silica content.

245 The spectra of original, residue and dissolved phases in PCFA are plotted in Figure 5(b). The
246 peaks at 777 cm^{-1} and 796 cm^{-1} correspond to quartz. The main band at 1039 cm^{-1} represents
247 the Si/Al amorphous phases, which could be composed of high Al content [39]. For the
248 spectrum dissolved of PCFA, a huge drop of the broad hump at 1039 cm^{-1} is found after the
249 chemical dissolution treatment which is related to dissolution of high amounts of Si and Al
250 from the solid precursor. The two peaks near 800 cm^{-1} may be attributed to Si (Al)-O bonds or
251 Si-O-Al stretching bonds. The PCFA bonds at 1088 cm^{-1} and 1162 cm^{-1} are associated with
252 asymmetric stretching of (Si, Al)-O-Si of mullite phase.

253 The FTIR analysis of GP and PCFA shows that the reactive chemical bonds generally fall in the
254 range $1085\text{-}1092 \text{ cm}^{-1}$, $997\text{-}1001 \text{ cm}^{-1}$ and $900\text{-}915 \text{ cm}^{-1}$, which mostly correspond to silicon
255 dominant structures (Si, Al^{IV})-O-Si bonds or (Si, Al^{IV})-O-M (M=Na or Ca) [40]. These bonds are
256 found to be highly reactive and largely determine the reactivity of aluminosilicate precursors
257 [40, 41].

258 **3.2 Compressive strength**

259 The compressive strength development of paste mixtures with increasing GP as PCFA
260 replacement (from 0 to 30%) is shown in Figure 6. The 1-day strength is similar within all
261 mixtures whereas compressive strength increases significantly at 7 and 28 days with higher
262 amount of GP replacement. Compared with R (0% replacement), up to 35% strength gain is
263 observed in G30 (30% GP as PCFA replacement). This increase could be attributed to the
264 higher GP reactivity and availability of soluble silica provided by reaction between GP and
265 NaOH, which facilitates the geopolymersation process and leads to higher amount of gel
266 formation (Sections 3.3.3 and 3.3.4). In fact, the global activation process is comparable to the
267 conjugational effect of using sodium silicate and sodium hydroxide as alkali activator (Section
268 3.3.3). Previous studies also confirmed that this conjugational effect results in additional
269 available silica in the system and accelerates the gel polycondensation [42], which contributes
270 to better mechanical properties.

271 Additionally, fly ash is known to contain 'hollow' cenospheres and plerospheres, which are
272 prone to surface opening within dissolution process. Accordingly, the reaction products
273 formation is assumed to be stimulated on the inner PCFA surface [43, 44]. This phenomenon
274 has been also confirmed in PCFA cement paste blends, where reacted hollow PCFA particles
275 provide extra space for the reaction products [45]. The opening of the 'closed' voids in PCFA
276 was studied by alkaline solution treatment to substantiate that the PCFA in this study may
277 also accommodate reaction products. A comparison of the pore structure between original
278 and treated PCFA with 4M NaOH solutions for 2 h reveals obvious differences. As shown in
279 Figure 7(a), the total porosity of the original ash was 5.69% and increased to 17.42% after

280 treatment. Additionally, Figure 7(b) indicates that the range of pore size broadens from 3-6
281 μm towards 2-10 μm after alkaline solution treatment. All these evidences suggest that the
282 surface opening of hollow PCFA may increase the accessibility of the finer pores and hence
283 promote the reaction products formation inside PCFA particles. However, these reaction
284 products formed inside the PCFA ineffectively contribute to the bonding of particles, which
285 leads to a decrease in compressive strength. This effect tends to be weakened with increasing
286 the GP content because of the reduced potential for the PCFA to accommodate reaction
287 products. Therefore, increasing the GP content eventually leads to increment of the
288 compressive strength.

289 However, a considerable strength decrement is found in G10 compared to R at 7 and 28 days,
290 which implies that different mechanisms are involved at low replacement levels. This
291 unexpected tendency may be induced by finer particle size distribution of GP compared with
292 PCFA. Smaller particle size of GP as well as its angular shape may have a negative influence on
293 the packing density of mixture [46], which could lead to a compressive strength decrease.
294 Meanwhile, the lower density of mixture with GP replacement may also contribute to the
295 strength decrement. It is worth noting that these effects are only dominant on the
296 compressive strength development at low GP replacement levels ($\leq 10\%$). With higher GP
297 replacement levels ($\geq 20\%$), the dominating factor may gradually change from the physical
298 effect to a chemical one. Compared with R mixture, only a minor increase of gel formation is
299 found in G10 while a significant increase is observed in G20 and G30 mixtures (will be
300 discussed in Section 3.3.4). Consequently, only the G10 reveals the strength decrease
301 compared to R at 7 and 28 days.

302 **3.3 Microstructure Characterization**

303 **3.3.1 XRD analysis**

304 The XRD patterns of samples after 1 day and 28 days curing are illustrated in Figure 8(a) and
305 (b) respectively. At each curing age, the XRD spectra are stacked to investigate the effect of
306 GP as PCFA replacement.

307 In all XRD patterns calcium silicate hydrate (C-S-H) phases ($1.5\text{CaO}\cdot\text{SiO}_2\cdot x\text{H}_2\text{O}$, PDF# 00-033-
308 0306) are found near 29.4° which is in agreement with previous studies where C-S-H type gel
309 was the main reaction product in slag dominated AAMs [8, 10, 12, 47, 48]. Considering the Al
310 content in raw materials, this C-S-H type gel could have moderate Al incorporation into its
311 structure. The abundance of C-S-H phases is found to increase with higher GP contents. As
312 shown in Figure 8(b), the increase of GP replacement leads to a higher peak intensity of C-S-H
313 phase. This may imply that the reaction kinetics and microstructure development are affected
314 by GP replacement, which is in agreement with the observed difference in the reactivity and
315 the element dissolution of both precursors (Section 3.1). It is believed that a higher amount
316 of gel formation is achieved by increasing the GP content. To further validate such assumption,
317 isothermal calorimetry and differential thermogravimetric analyses were carried out and the
318 obtained results are further discussed in Sections 3.3.3. and 3.3.4.

319 Hydrotalcite ($\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16}\cdot 4\text{H}_2\text{O}$, PDF# 00-041-0191) is found at around 10.2° as the
320 second main reaction product in all mixtures at 1 and 28 days, which has been reported in
321 GGBS containing alkali activated systems [8, 47]. Hydrotalcite is found in all samples with
322 different levels of GP replacement, indicating that its formation within this alkali activated
323 system is dominated by GGBS with sufficient composition of Mg and Al. Quartz, mullite and

324 hematite peaks are identified as the remnant crystalline phases of incompletely reacted PCFA
325 and their intensities change with different levels of GP replacement.

326 **3.3.2 FTIR analysis**

327 The FTIR spectra of paste mixture R, G10, G20 and G30 are shown in Figure 9. The overall
328 broad band of interest is located between 800 and 1200 cm⁻¹ as a result of phase overlapping
329 from both precursors and reaction products. This band is widely accepted in the literature as
330 the main T-O asymmetric stretching band and is used to study the changes of the amorphous
331 gel structure (Ca/Si or Al/Si ratio) in AAMs [49, 50]. The main band in all spectra is centred at
332 approximately 950 cm⁻¹, which is assigned to Si-O and/or Si-O-M bonds (M being alkali metal
333 or alkali earth metal) [51]. More specifically, it could be associated with the Si-O-Si bonds of
334 SiO_n units (n=2) [52], which is the representative structure of aluminosilicate chains containing
335 C-A-S-H type gel formed in alkali activated GGBS.

336 From the analysis of the main T-O bands near 950 cm⁻¹, it can be observed that when the GP
337 content increases, this band first shifts towards lower wavenumber from 1 day to 7 days but
338 then it shifts to a higher wavenumber from 7 days to 28 days. This behavior can be associated
339 with the type of vibrations: (i) the inner bond vibration inside T-O tetrahedral (T=Si or Al) and
340 (ii) the vibration between T-O tetrahedral [53]. The lower force constant of Al compared with
341 Si in the harmonious vibration model leads to lower vibration frequencies of Al-O bonds than
342 Si-O bonds. Consequently, the observed main band shifts towards lower wavenumbers is due
343 to the formation of the reaction products with an increased substitution of Si by Al [54, 55]. It
344 is believed that Al dissolves more easily from the solid precursor structure due to the lower
345 binding energy of Al-O compared with Si-O bonds. Therefore, the reaction products at 1 and

346 7 days curing have the tendency to form Al-rich structures [54, 56]. These findings are also in
347 line with previous studies on alkali activated fly ash [27]. At 28 days, the main band eventually
348 shifts to higher wavenumbers, indicating that more Si is incorporated into the gel network,
349 forming a more complete Si-rich structure. The phenomenon of main band movement to
350 higher wavenumber is also reported in cementitious systems as hydration proceeds and
351 indicates a higher polymerization degree and/or higher cross-linking of silica network in C-S-
352 H gel [57].

353 Furthermore, a more distinctive effect of the main band shifts can be observed in Figure 10.
354 A decline of the main band wavenumber at 1 and 7 days is found with higher GP replacements.
355 This effect can be associated with polymerization degree of the reaction products. Previous
356 studies on alkali activated GP observed sodium silicate gel formation within the system [18].
357 Higher GP replacement increases the amount of available silica at early ages, which have
358 major influence on the polymerization process. With higher silica concentration, soluble silica
359 in the pore solution at early ages is more likely to exist as monomer rather than highly
360 polymerized species [58]. Therefore, the initial average polymerization degree of the reaction
361 product is considerably lower. Accordingly, the main band is at lower wavenumber with higher
362 GP replacement at 1 and 7 days. On the other hand, the main band at 28 days with a higher
363 GP replacement shifts to higher wavenumber, which is in agreement with previous works
364 forming more Si rich and stable gel [54, 57, 59]. This also indicates a higher polymerization of
365 reaction products within the structure.

366 **3.3.3 Paste heat evolution**

367 Isothermal calorimetry is conducted on alkali activated pastes to evaluate their reaction
368 kinetics and reaction degree. Heat flow curves of paste sample R, G10-G30 are shown in Figure
369 11(a). Two sub-calorimetric peaks are observed in all mixtures: The first peak is due to the
370 wetting and dissolution of precursors particles and the second broader peak corresponds to
371 the formation of reaction products. These results are in good agreement with those reported
372 for silicate activated GGBS or GGBS/PCFA blends [15, 36, 60]. A decrease in the intensity of
373 the second peak and a delay in its appearance is found with increasing GP. This longer
374 induction period corresponds to a slow initial reaction kinetics because of dissolution of GP,
375 after which the reactions finally accelerates when the ionic concentration reaches a critical
376 threshold concentration [61]. The fast formation of initial reaction products around the
377 unreacted GGBS or PCFA particles may account for this longer induction period. [62]. It is
378 believed that the layer of reaction products thickens with increasing GP amount and prolongs
379 the time required for available alkali and other useful species to penetrate through. Another
380 reason is the higher amount of available silica species dissolved at initial stage, which increases
381 the local activator modulus and eventually changes the local content of alkali activator.
382 Previous studies by ^{29}Si NMR proved that higher amount of silica species with low
383 polymerization degree (monomers) is achieved by lowering the activator modulus [63], which
384 can speed up the gel formation. On the contrary, increased local activator modulus by GP
385 replacement retards the reaction process and prolongs the induction period. Similar results
386 have also been found in previous studies in activated GGBS/PCFA mixtures [15, 64].

387 The cumulative heat evolution of the paste mixtures is shown in Figure 11(b). A higher
388 cumulative heat is found with increasing GP content. It is well known that the total heat
389 release reflects the extent of reaction which may be correlated with enhanced compressive
390 strength development. The higher cumulative heat of activated GP compared to activated
391 PCFA (discussed in Section 3.1.4) can therefore be partly accounted for the observed higher
392 compressive strength (Figure 6) in these samples.

393 However, on the other hand, NaOH activated GP can produce soluble silica monomers that
394 are quite similar to the silica provided by water glass [19]. In fact, the calorimetric curves of
395 mixtures with increasing GP replacement share similar characteristics with those of alkali
396 activated GGBS/PCFA mixtures using NaOH and solid sodium silicate increasing silicate
397 modulus as activator [60]. Therefore, the higher cumulative heat release and the higher
398 compressive strength with increasing GP levels can also be partly due to the enhanced
399 reaction of GGBS by the more abundant released soluble silica.

400 **3.3.4 Thermogravimetric analysis**

401 Differential thermogravimetric (DTG) curves of the paste mixtures (R and G10-G30) of 28 days
402 are presented in Figure 12(a). The major DTG peaks for all samples are between 105 to 300 °C,
403 while the curves stabilize gradually after 500 °C. The observed loss from 105 to 300 °C in DTG
404 curves represents decomposition of major reaction products. Such results are in good
405 agreement with previous literature reporting that the C-S-H type gel dehydration is found in
406 the temperature range of 180 to 300 °C in OPC systems [65] and of 105 to 300 °C in alkali
407 activated GGBS [15]. Additionally, the C-A-S-H type gel was reported to decompose between
408 105 and 300 °C [66]. Accordingly, these results may imply that C-A-S-H type gel is the dominant

409 reaction products in all investigated mixtures, which is responsible for the major mass loss.

410 The minor DTG peaks present at 300 to 400 °C in Figure 12(a) is attributed to the dehydration

411 and decarbonation of the present hydrotalcite [47], in line with existence of hydrotalcite

412 detected by XRD. Furthermore, very weak peaks are observed between 500 to 800 °C and

413 after 800 °C, mainly due to carbonated phases, decomposition and formation of new

414 crystalline phases.

415 It is assumed that the amount of main reaction products can be reflected by the percentage

416 of mass loss from 105 to 300 °C on the thermogravimetric (TG) curves in Figure 12(b). The

417 calculation is made with the assumption that the dominant reason for the mass loss within

418 105 to 300 °C is dehydration of C-A-S-H type gel. The sequence of mass loss is shown as

419 G30(6.36%)>G20(5.50%)>G10(4.33%)>R(4.16%), indicating that GP has significant effect on

420 the reaction process and largely facilitates the gel formation especially at higher replacement

421 levels. This result is in line with the data obtained from the calorimetry study which also

422 confirmed that the GP replacement enhances the total reaction degree of precursors and

423 leads to a higher cumulative heat production.

424 **3.3.5 ESEM/EDX analysis**

425 Back Scattered electron (BSE) imaging was performed on all paste mixtures (R and G10-G30)

426 after 1, 7, and 28 days curing. Representative images of R and G30 mixtures are shown in

427 Figure 13. PCFA particles are light gray colored and generally have regular spherical shapes.

428 GP and GGBS particles are irregular polygonal shaped and are brighter due to the greater

429 amount of Ca. The gel phase generally shows a darker grey color with grey level lower than

430 PCFA, whereas pores filled with epoxy are black.

431 Comparison of the images of R and G30 pastes at the same curing time shows that G30 yields
432 a denser and more homogenous microstructure at all ages, with more areas for gel phases
433 and less pores. While paste R shows heterogeneously distributed pores, indicating a more
434 porous matrix. These results are in good agreement with those deduced from the
435 thermogravimetry and isothermal calorimetry, which again qualitatively prove that increasing
436 GP enhances the gel formation.

437 In order to get additional information about the reaction products, EDX analysis of multiple
438 randomly-selected points within the binder region (excluding unreacted particles) was carried
439 out on R and G30 at 1, 7, and 28 days. Calcium, aluminum and silicon are normalized to 100%
440 on an oxide basis and plotted in the CaO-SiO₂-Al₂O₃ ternary diagram in Figure 14, which can
441 reflect the nature of the reaction products in R and G30. It can be observed that for both R
442 and G30 the experimental data fall in the region of alkali activated slag [42, 47, 67] as well as
443 GGBS/PCFA systems [8, 10, 12, 15, 68-70]. Considering the poorly crystalline C-S-H phase
444 presence detected by the XRD and typical chemical bonds identified by FTIR analysis, the main
445 reaction products are assumed to be C-S-H gel dominant. In addition, Al incorporation into
446 the structure is identified by EDX indicating formation of a C-A-S-H type gel. Presences of Na
447 in the reaction products are also confirmed by EDX analysis on R and G30 mixture at 28 days,
448 which suggests the existence other analogous gel types. For instance, N-A-S-H type gel
449 intermixing with C-A-S-H type gel or C-(N)-A-S-H type gel (sodium incorporated C-A-S-H gel),
450 in which Na cations serve as negative charge balance in the structure. N-A-S-H type gel is
451 widely accepted as a 3-dimensional aluminosilicate network existing in activated PCFA [9, 27,
452 71] or activated GGBS/PCFA binders with a dominant fly ash content [10, 15]. Its gel structure

453 is commonly accepted to be “zeolite” related and is strongly correlated with the formation of
454 crystalline zeolite within the system [22, 72]. In this study, the XRD patterns of all the paste
455 mixtures up to 28 days did not give any evidence of zeolite phases. Furthermore, FTIR revealed
456 no absorption band inside the main T-O band for N-A-S-H type gel. All these evidences imply
457 that N-A-S-H gel was not formed in the structure and the main reaction product in all alkali-
458 activated binders is a C-(N)-A-S-H type gel.

459

460 **4 Conclusions**

461 This paper investigated the reactivity and potential of waste glass as partial replacement for
462 PCFA in alkali activated GGBS/PCFA systems. The precursors were systematically
463 characterized followed by a detailed microstructural analysis of the paste mixtures as well as
464 the reaction kinetics. The following conclusions can be drawn from this research:

465 • Waste glass powder exhibits high reactivity for alkaline activation under room
466 temperature compared with PCFA, which is due to its finer particle size, higher specific
467 area, high amorphous phases contents and high reactive phases content (Si, Ca).

468 • The compressive strength increased by 35% with increasing GP (as a PCFA replacement)
469 up to 30% in the GGBS-PCFA-GP system. These results along with thermogravimetry and
470 calorimetry analysis confirm that the GP is actively involved in the reaction process.

471 • GP as PCFA replacement contributes to more available silica and Ca dissolution and
472 largely facilitates the gel formation. A higher polymerization of the gel network is also
473 observed.

474 • The compressive strength increment, the enhanced gel formation and the prolonged
475 induction period are similar with the conjugational effect of using both sodium hydroxide
476 and sodium silicate alkali activator in alkali-activated slag/fly ash system.

477 • The microstructural analysis shows that the dominant reaction product is a C-(N)-A-S-H
478 type gel. No N-A-S-H type gel is formed in the system.

479 • The feasibility of potential use of waste glass as binder precursor for production of AAMs
480 was confirmed. This can offer a solution for both alkaline cement industry to provide a
481 new precursor and glass industry to solve the storage issue and their related economic

482 cost and environmental impact.

483

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716 **Tables**

717

718 Table 1: Chemical composition of solid precursors by XRF.

Oxide (wt. %)	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	LOI ₉₅₀
GP	65.60	2.37	2.40	22.06	2.17	0.39	1.99	0.86	2.00
PCFA	52.90	26.96	6.60	4.36	1.50	0.73	0.17	-	3.37
GGBS	32.91	11.84	0.46	40.96	9.23	1.60	-	0.33	1.15

719

720

721 Table 2: Paste mixture designs

Sample	L/S ratio	Activator	GGBS (wt. %)	PCFA (wt. %)	GP (wt. %)
R	0.42	4M NaOH Solution	50	50	0
G10				40	10
G20				30	20
G30				20	30

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723

724 Table 3: Insoluble residue (I.R.) chemical composition of GP and PCFA by XRF

Oxide (wt. %)	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	TiO ₂
GP	62.24	7.96	0.77	18.01	3.86	0.16	0.59	3.29	1.82
PCFA	43.59	50.59	3.18	0.189	-	0.12	-	0.69	1.46

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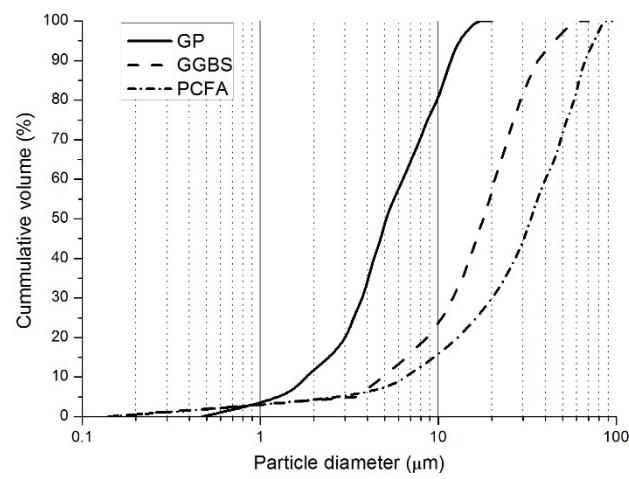
726

727 Table 4: Amorphous phase and reactive element content (wt.%) in GP and PCFA

Precursor	I.R.	Amorphous content		Total SiO ₂	Reactive SiO ₂	Total Al ₂ O ₃	Reactive Al ₂ O ₃	Total CaO
		18.14	81.86	65.60	54.31	2.37	0.92	22.06
GP	22.63	77.37		52.90	43.04	26.96	15.51	0.19

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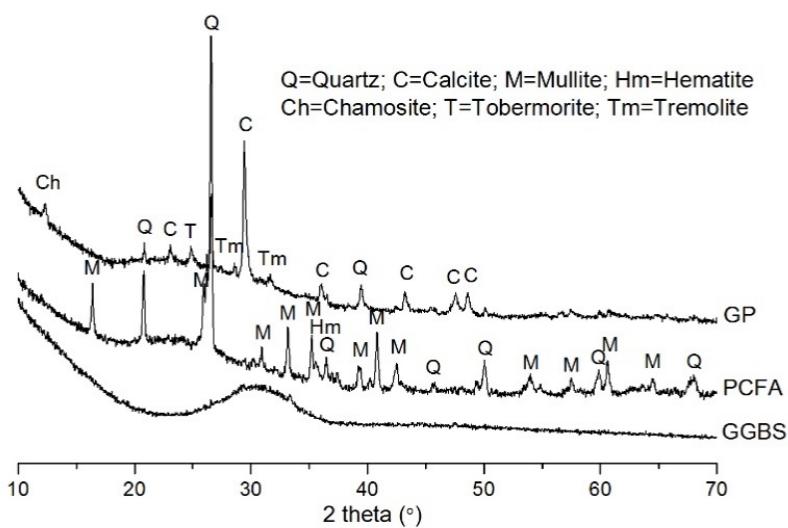
729 **Figures**



730

731 **Figure 1: Particle size distribution of GP, PCFA and GGBS.**

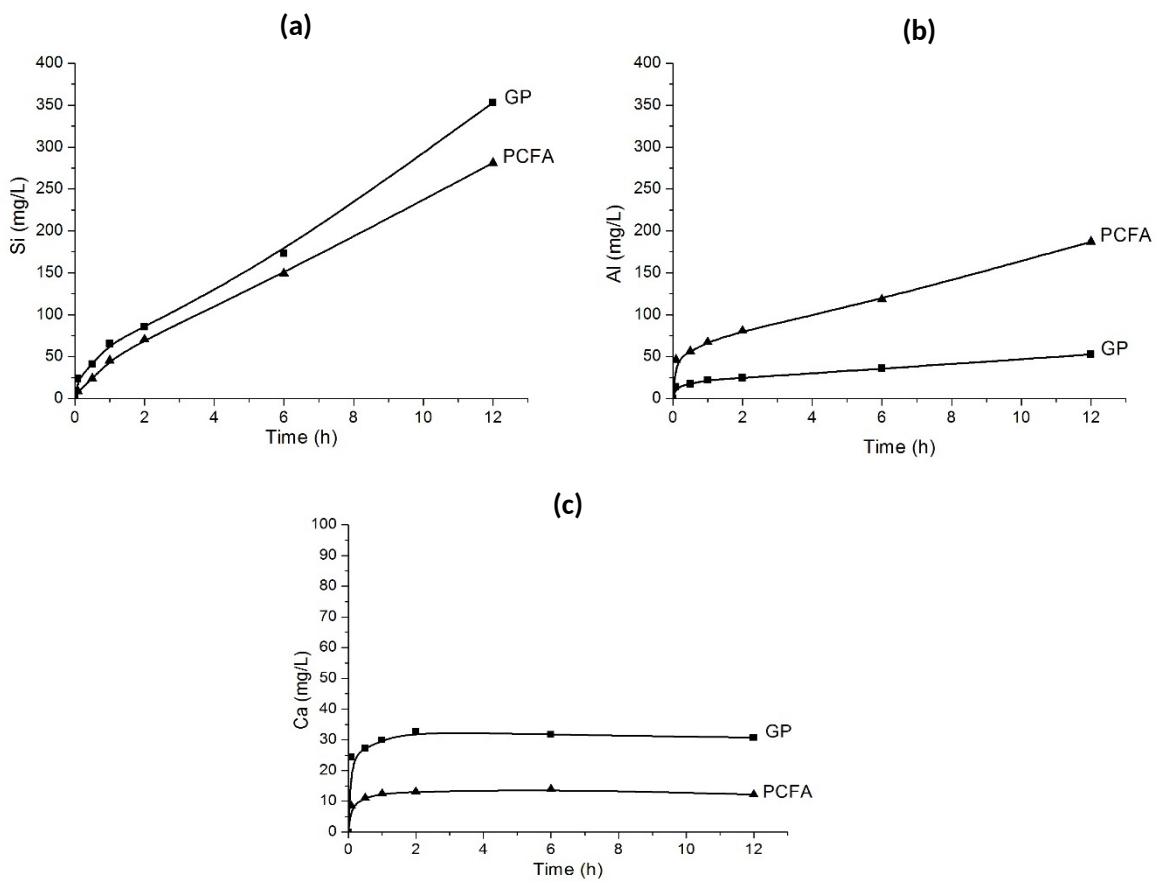
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733

734 **Figure 2: XRD patterns of unreacted solid precursors**

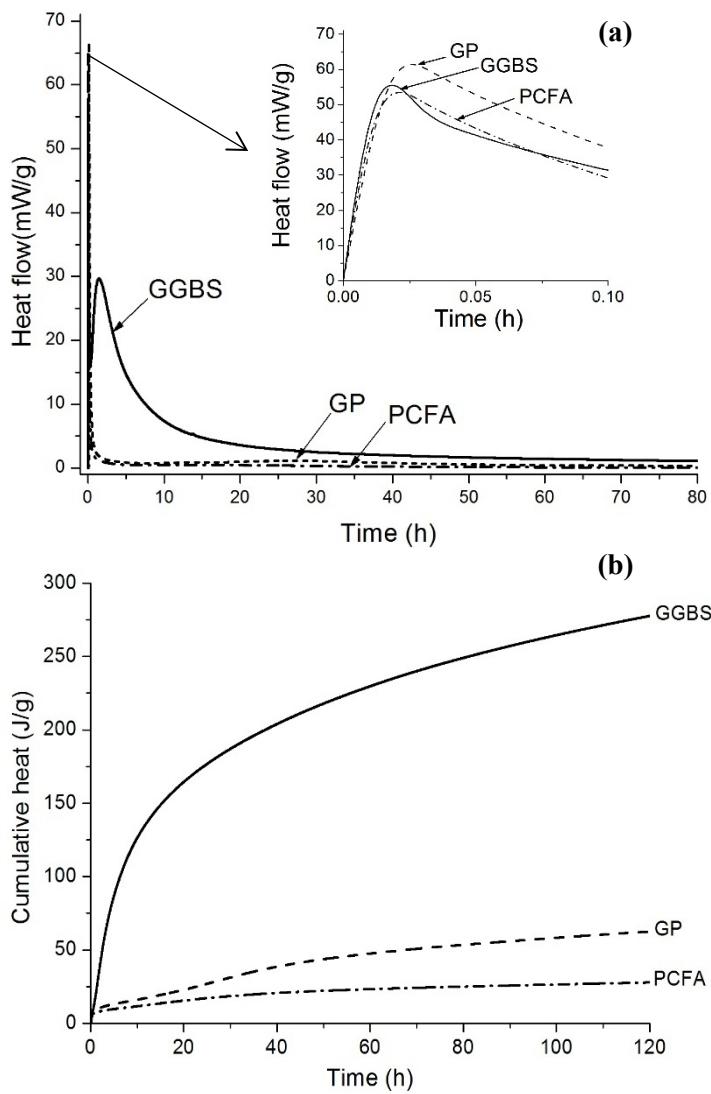
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736

737 **Figure 3: Element dissolution in time of Si (a), Al (b) and Ca (c) for PCFA and GP.**

738

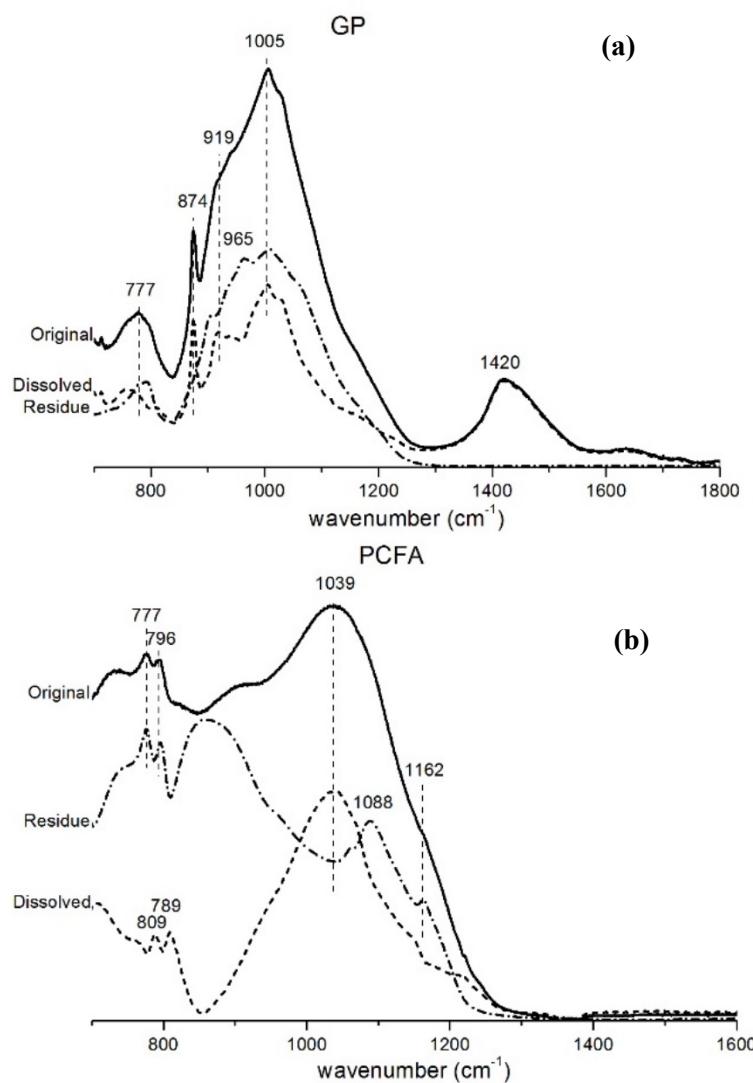


739

740 **Figure 4: (a) heat flow and (b) cumulative heat evolution of alkali activated precursor**

741 **(L/S=0.6).**

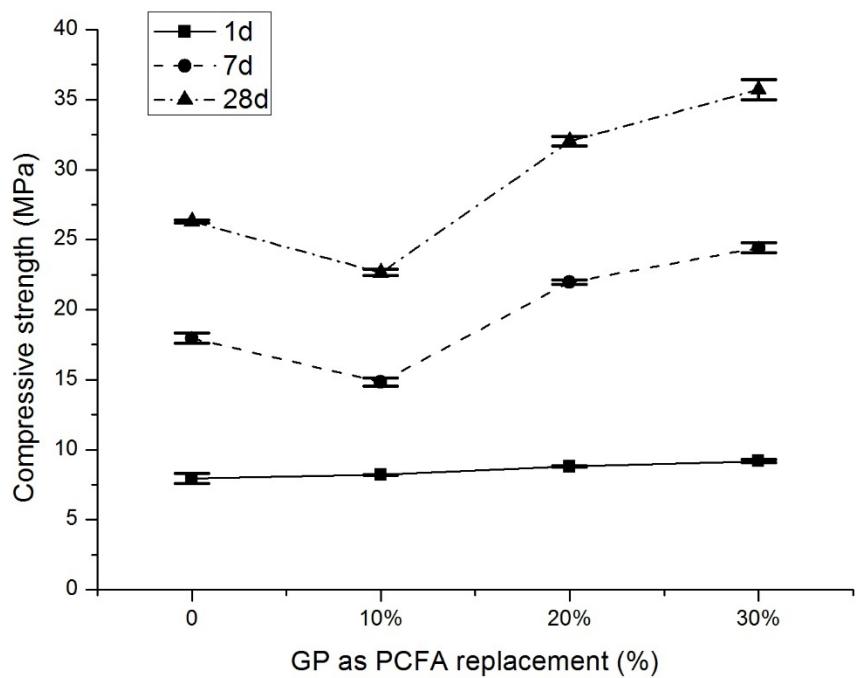
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743

744 **Figure 5: FTIR spectra of original, residue and dissolved phases in (a) GP and (b) PCFA.**

745

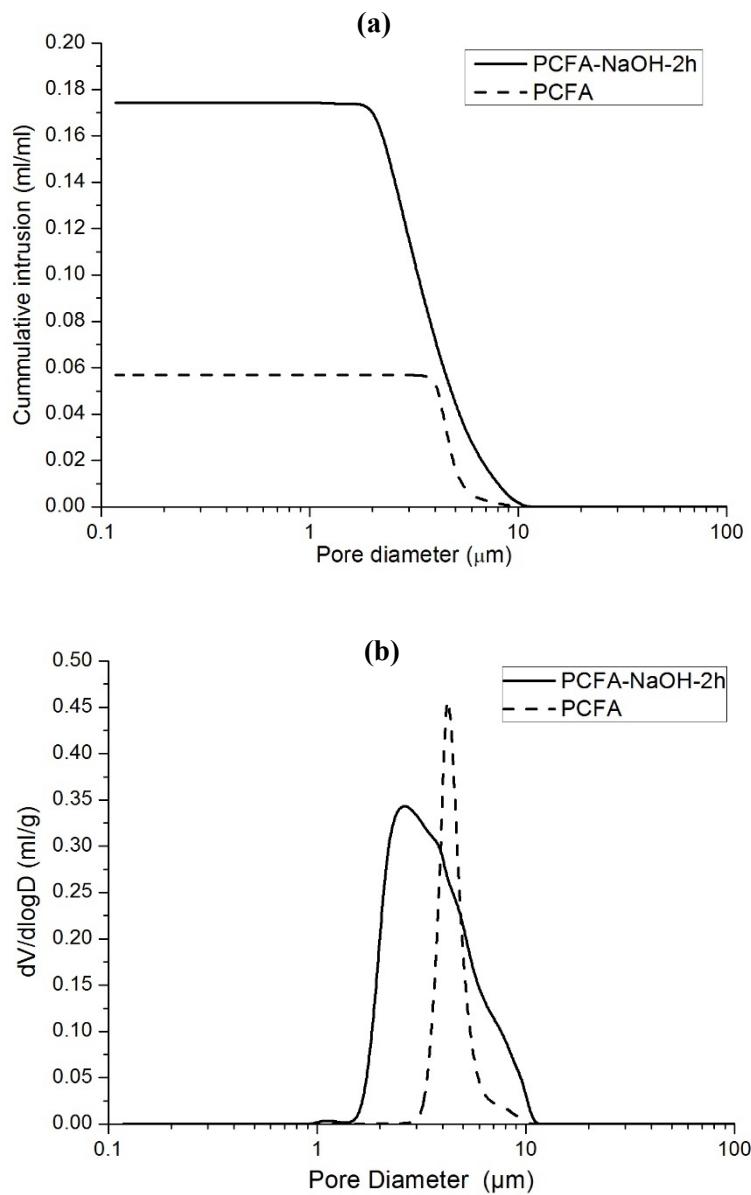


746

747 **Figure 6: Compressive strength development of paste mixtures with increasing GP as PCFA**

748 **replacement.**

749

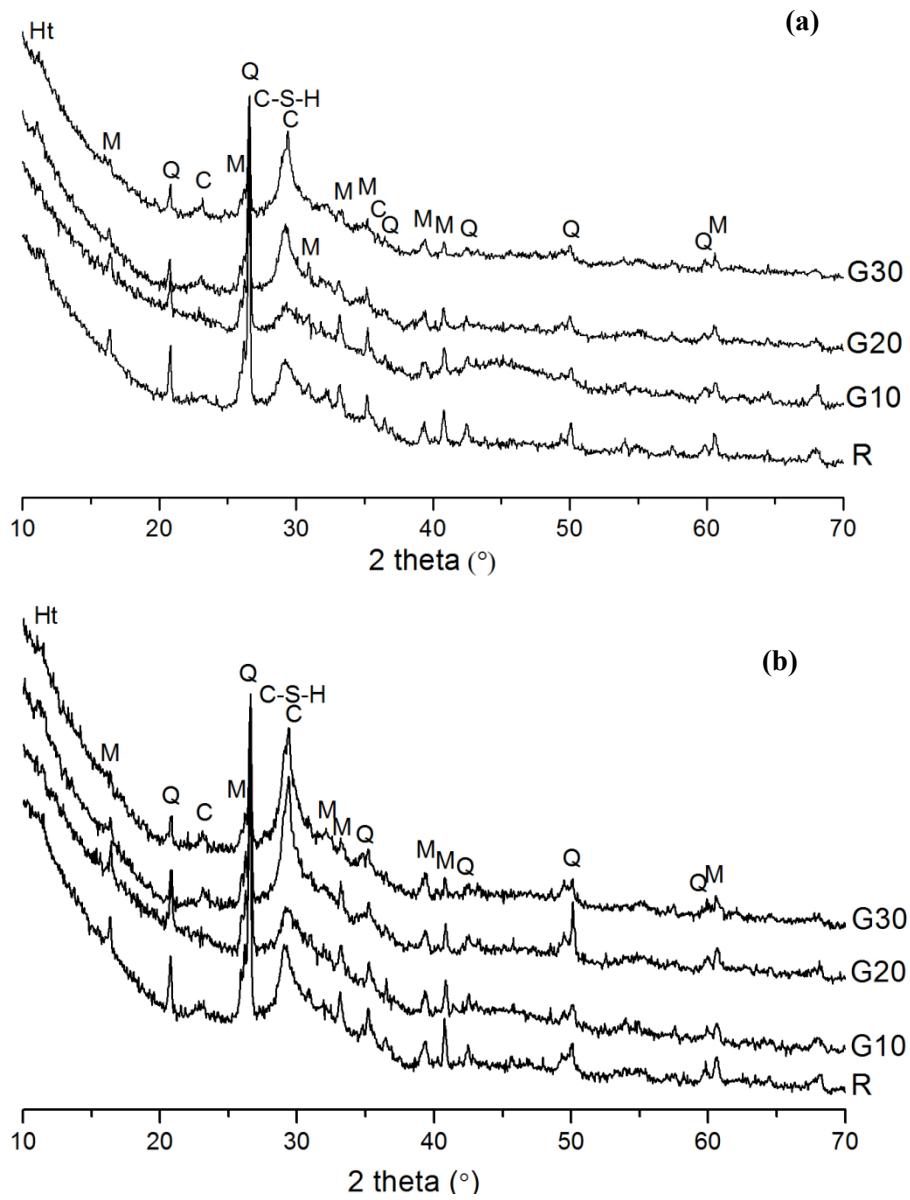


750

751 **Figure 7: Pore structure of original PCFA and 4M NaOH-treated PCFA: (a) cumulative pore**

752 **size distribution and (b) differential pore size distribution.**

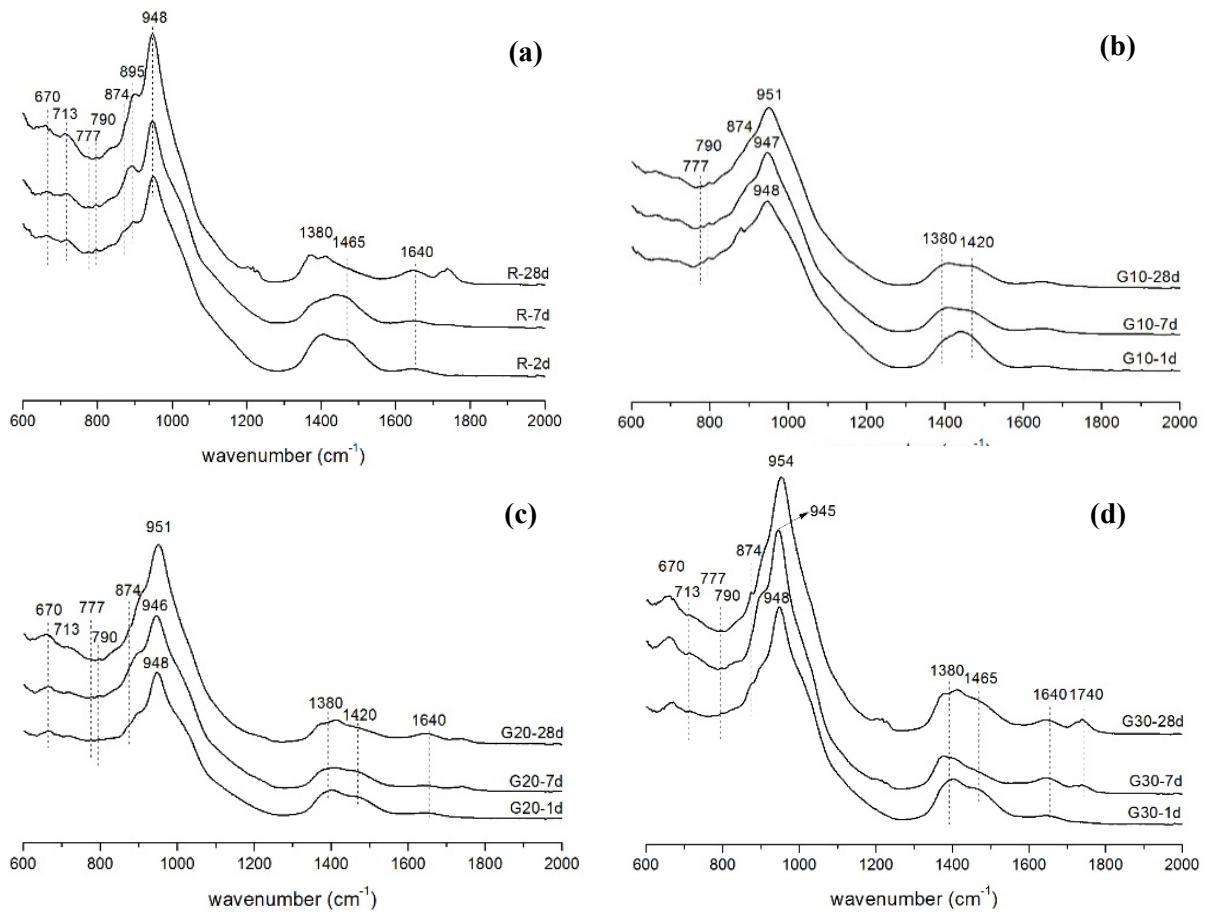
753



754

755 **Figure 8: XRD pattern of GGBS/PCFA pastes with various amounts of GP as PCFA**
 756 **replacement at (a) 1 day and (b) 28 days, (C-S-H=Calcium Silicate Hydrate; Q=Quartz;**
 757 **M=Mullite; C=Calcite; Ht=Hydrotalcite).**

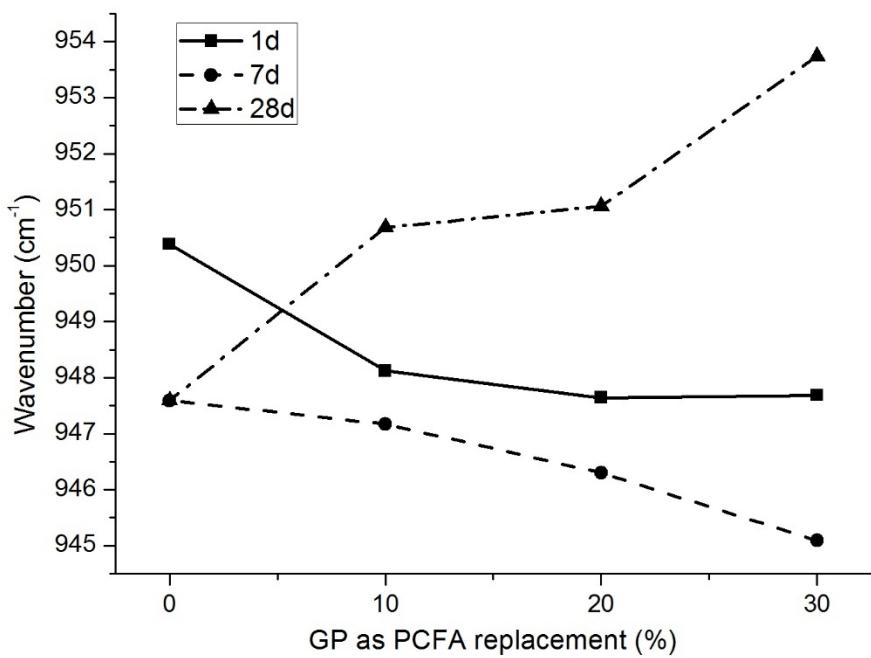
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759
760 **Figure 9: FTIR spectra of pastes mixtures (a) R, (b) G10, (c) G20 and (d) G30 at 1, 7, and 28**

761 **days.**

762

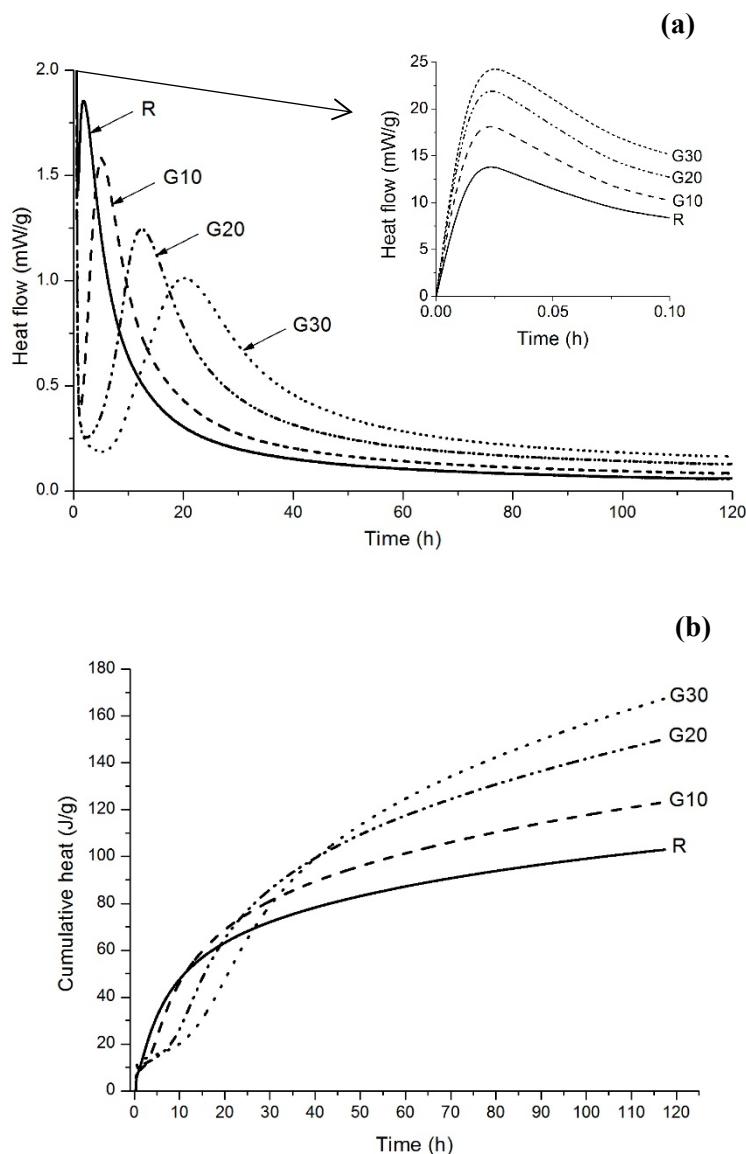


763

764 **Figure 10: Changes in wavenumber of the main T-O band for paste mixtures as a function of**

765 **curing time and GP as PCFA replacement.**

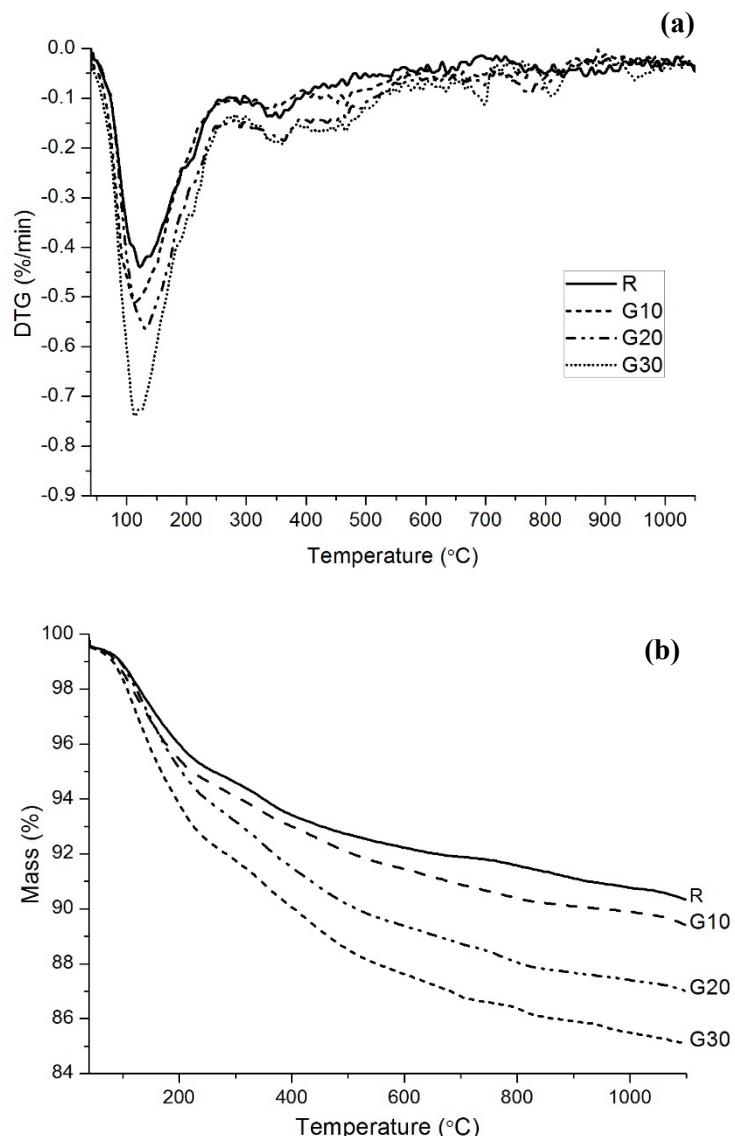
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767

768 **Figure 11: (a) Heat flow rate and (b) cumulative heat evolution of alkali activated paste
769 mixtures (L/S ratio 0.42).**

770

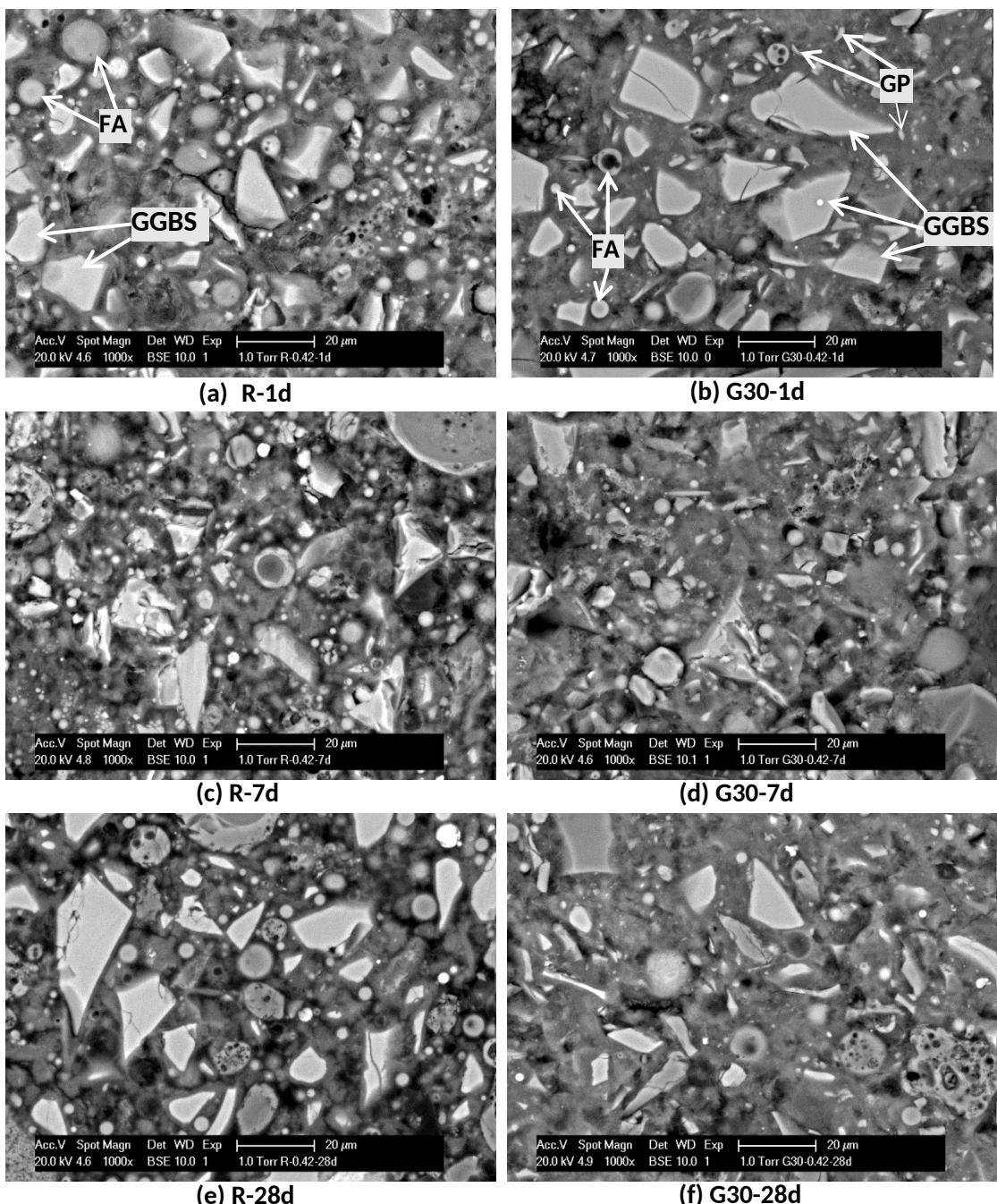


771

772 **Figure 12: (a) Differential thermogravimetry (DTG) and (b) thermogravimetry (TG) curves of**

773 **alkali activated paste mixtures.**

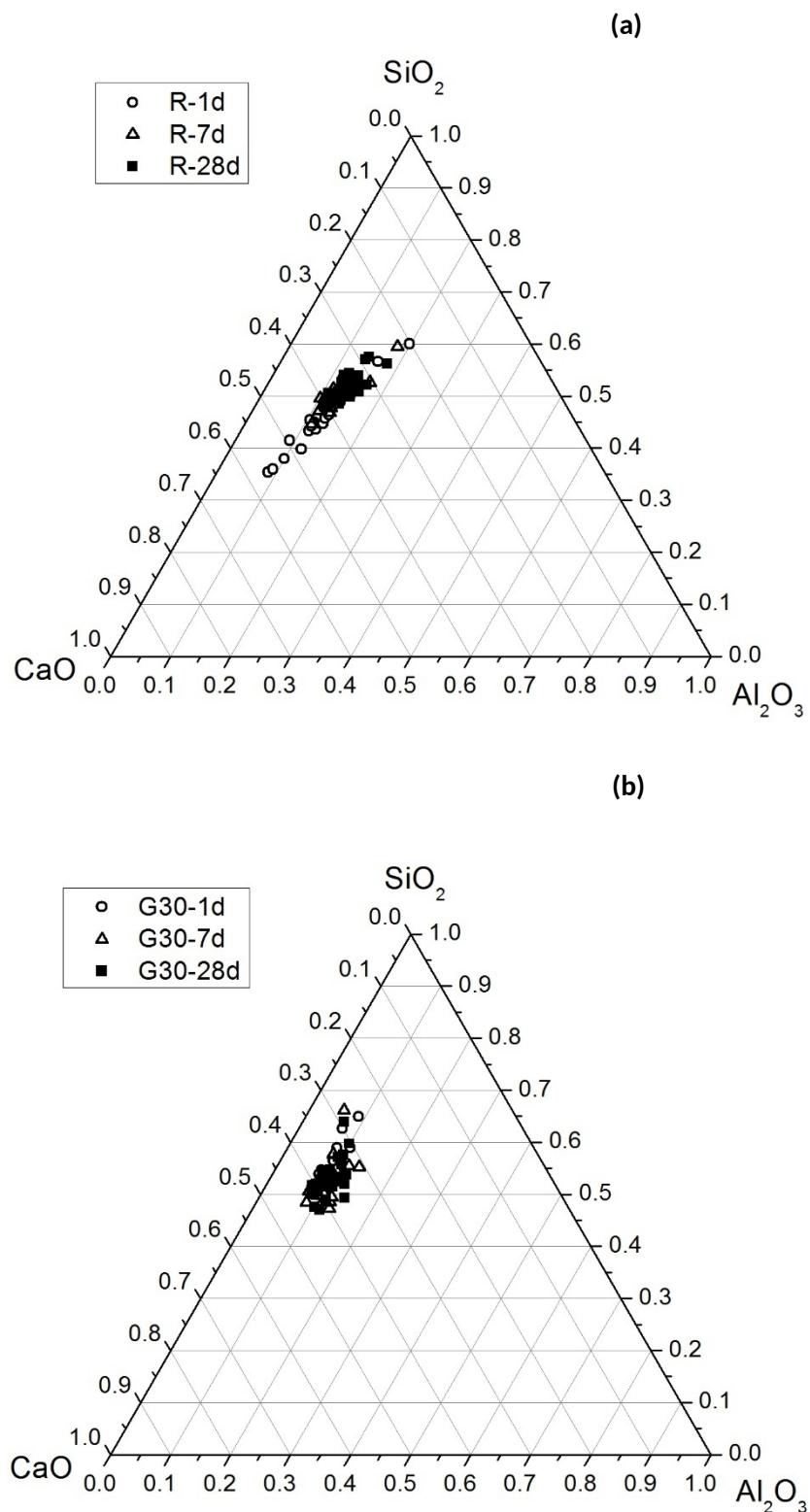
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775

776 **Figure 13: Representative BSE images of paste mixture R and G30 cured for 1, 7 and 28 days.**

777



778

779 **Figure 14: Ternary diagram of EDX spot analysis of (a) R and (b) G30 mixtures cured for 1, 7,**

780 **and 28 days.**