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1 Long-term performance of novel high-calcium one-part alkali-activated
2 cement developed from thermally activated lime kiln dust

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9
10 **Highlights**

- 11 • One-part earth alkaline activated dry cementitious mixture was produced
12 using thermally activated lime kiln dust (LKD) waste material as a source of
13 CaO activator and metakaolin and natural pozzolan as a source of alumina-
14 silicate
- 15 • The proportion of LKD and metakaolin in the ternary blend and thermal
16 activation of LKD not only increased the reactivity but also induced higher
17 degree of alkali-activation.
- 18 • Significant increase in the rate of strength development after 28 days of curing
19 and continued until 180 days that reached 51 MPa for increased proportion of
20 950°C calcined LKD and metakaolin in the blend was revealed.
- 21 • Considerable changes in mineralogy and amorphicity were evidently
22 accredited to thermal treatment.
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30 Abstract

31 The traditional activation approach for alkali-activated cement AAC has several problems
32 resulting mainly from the hazardous and corrosiveness of the alkaline chemicals, such as (NaOH,
33 Na₂SiO₃), which in turn impede the utilisation of AAC in the construction fields. In this study, A
34 second generation of alkali activated binder was developed using Metakaolin (MK) and natural
35 pozzolan material (NP) (as a source of alumina-silicate), these materials were activated using high-
36 calcium lime kiln dust as solid activator to transform the alumina-silicate crystalline phases to
37 cementitious hydrated products. This was achieved with the aid of heat treatment of materials at
38 different temperatures. Raw materials and final AAC samples were characterised using analytical
39 methods, such **X-Ray powder diffraction (XRD)**, Thermogravimetric Analysis (**TG-DTA**), Fourier
40 Transform Infrared Spectroscopy (**FTIR**) and Scanning Electron Microscope (**SEM**). Additionally,
41 long-term compressive strength, chemical and microstructural performance were investigated. The
42 transformation of raw materials from crystalline to amorphous phases happened due to the effect
43 of the heat treatment and the formation of stratlingite products in the final AAC paste, which were
44 evidenced using the mentioned characterisation methods. The findings of the present study proved
45 that the compressive strength of the new binder reached 27 MPa and 51 MPa after 28 and 180 days
46 of curing, respectively, **ensuring a progressive as well as a higher degree of alkali-activation and**
47 **disappearance of unreacted alkaline substances in the final AAC products.**

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52 Keywords

53 Alkali activated cement, heat treatment, Lime waste, XRD, TG-DTA, FTIR.

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63 1. Introduction

64 The world production of the Ordinary Portland Cement OPC is significantly growing, where the
65 estimated global production in 2018 was 4.1 billion metric tonnes [1]. The use of OPC in concrete
66 construction is under serious evaluation because of the substantial challenges that are facing the
67 method of production of conventional cement. Firstly, the high energy consumption through the
68 whole process [2]. Secondly, a high quantity of carbon dioxide gas (CO₂) is released to the
69 atmosphere during the production of cement [3]. To overcome these challenges, several
70 investigations were commenced to develop other types of cements that are entirely free of OPC
71 and based principally on supplementary materials. Mineral Products Association (MPA), in the
72 UK, listed a number of novel low carbon (non-Portland) cements with low energy of production
73 in their fact sheet [4]. One of these novel cements is Alkali Activated Cement AAC, which is a
74 cementitious material formed as a result of an alkaline activation of amorphous or vitreous
75 alumina-silicates. When mixed with alkaline activators (solid or liquids), in a chemical reaction
76 called alkali-activation or alkanination, these materials set and harden, yielding a material with
77 good binding properties [5,6]. There is a conventional two-part alkali activation, wherein a solid
78 raw material is activated with alkaline chemical solution. This solution is categorised as extremely
79 corrosive materials. From an operational viewpoint, they are difficult and expensive to handle,
80 with significant occupational health and safety concerns. On the other hand, the activator solution
81 provide the highest single contribution to the embodied carbon dioxide of AAC [7–9]. Until now,
82 it cannot be said that AAC is based on user friendly and low carbon process, as the production of
83 the chemical solutions releases large amounts of CO₂ to the environment [10].

84 Several efforts have been made to develop a second generation of geopolymers with one-part AAC
85 that can be found under different terminologies in the literature, such as one-part alkali activated
86 cement, self-activating cement or one-part alkali alumina-silicate hydraulic cement [11–13]. In
87 one-part AAC, only a dry mixture is needed in addition to water. The dry mixture is prepared by
88 mixing a solid alkali-activator with a solid alumina-silicate precursor, with or without an assisted
89 activation approach [8,12].

90 Provis [14] defined the activators as any substance that represents an alkaline source that raises
91 the pH of the reaction mixture and simplifies dissolution. This includes alkali cations (Na⁺, K⁺) or
92 earth alkaline cations (Ca⁺², Mg⁺²). A significant body of literature explored the synthesis of one-
93 part AAC using alkaline commercial solid chemical activators, including sodium silicates
94 (Na₂SiO₃) and sodium carbonates (Na₂CO₃). Realistic reports revealed that these chemicals are
95 expensive and primarily contribute to the total cost of production of AAC [9,15–17]. Therefore,
96 many synthetic chemicals do not represent a realistic commercial or environmental optimised
97 solution for use as an activator [8].

98 Previous studies focused on the use of (CaO) and Ca(OH)₂ as potential alternative activators, as
99 these activators are cheaper than (Na₂SiO₃) and (Na₂CO₃) [17,18]. These activators provide
100 alkaline earth cations in place of alkali cations, which ease the creation of different binding phases,

101 when compared to blends of low calcium content [8,19]. **Cabrera and Rojas [20]** investigated the
102 reaction kinetics of metakaolin-lime in water at 60°C, using thermal analysis. The study confirmed
103 the appearance of reaction products, mainly strätlingite (C_2ASH_8) and (C_4AH_{13}), as the reason for
104 binder strength development. Kim et al. [17] used synthetic commercial CaO solid powder and
105 ground granulated blast furnace slag (GGBS) (as the Si/Al source material) to produce non-cement
106 binder . When compared to Ca (OH)₂, CaO activator was found to yield a higher mechanical
107 strength, 53 MPa after 56 days, due to the production of more calcium silicate hydrate (C-S-H)
108 than Ca (OH)₂. Nevertheless, when investigating the energy and ecological analysis of
109 synthesising high purity chemical CaO powder, it was discovered that the synthesis process is
110 complex, consuming high energy and it requires a high level of accuracy [21-22]. Different
111 activation assisted methods were used in the production of a one-part AAC. For example, thermal
112 activation (calcination) has been recently used as an assisted approach to improve the reactivity
113 and the amorphicity of supplementary cementitious materials, such as natural pozzolans [11,23].
114 During the thermal treatment of undisturbed material, crystalline bonds are broken down and
115 transformed to a glassy or amorphous phase, which results in a more reactive binder. When
116 reviewing recent attempts directed to develop the one-part AAC, limited research projects have
117 been devoted to investigate the long-term performance and properties of these materials, especially
118 in the presence of unreactive alkaline substances. In fact, the latter must be precisely investigated
119 as the excessive unreacted alkaline solution can be diffused to a concrete surface, and reacts with
120 CO₂ in the air, forming efflorescence on the surface and degrading the appearance and strength of
121 concrete [24].

122 Recently, Abdel-Gawwad et al.[25] carried out a study about one-part AAC comprised of GGBS
123 and concrete waste treated by dry NaOH, with the addition of lead bearing sludge. The study
124 assessed the compressive strength of hardened one-part AACs after 120 days, which was 44 MPa
125 for a blend containing 65.9 wt. % GGBS, 15 wt. % lead bearing sludge, 34.10 wt. % concrete
126 waste, 3.10 wt. % NaOH, 2 wt. % Na₂O, and water/powder ratio of 0.29. On the other hand, there
127 is no study until now for evaluating the long-term strength of one-part AAC, activated by earth
128 alkaline cations, such as CaO or MgO, embodied in the material.

129 The principal aim of this work is to develop of novel approach to produce a second-generation
130 alkali-activated cement, that is completely free of commercial chemical activators. This was
131 achieved by providing the earth alkaline source from lime kiln dust (LKD), which is primarily
132 composed of reactive CaO. LKD is a by-product material of quick lime production process, which
133 is usually disposed of in landfills worldwide. For instance, in the USA, it is estimated that about
134 2.5 million metric tonnes of high-calcium LKD is produced annually [26]. Thus, LKD must be
135 reused to minimise its environmental impacts, and to meet the sustainability requirements. LKD
136 is mainly composed of a CaO compound and high alkaline materials (high pH). Metakaolin, which
137 is the crystallo-graphically disordered layered product of dehydroxylation of kaolinite (an alumina-
138 silicate clay) [27], was combined with volcanic tuff or natural pozzolan(as an alumina silicate
139 (Al/Si) source) to formulate the one-part dry AAC powder that just needs water to induce the
140 alkali-activation process. Volcanic tuffs provide an extensive variety of reactivity, depending on

141 their degree of crystallinity and mineralogy. The proposed alumina-silicate precursors, undertake
142 dissolution and precipitation processes when mixed with lime or CaO, yielding calcium alumina-
143 silicate hydrate (C-A-S-H) [28]. Furthermore, the current research examines the long-term (after
144 180 days) mechanical and physico-chemical properties of the novel AAC cement, which helps to
145 assess the sustained progression of alkali-activation in the absence of unreacted alkaline.

146

147 **2. Materials and methods**

148 2.1 Materials

149 The alumina-silicate source was produced by combining metakaolin (MK) and natural pozzolan
150 (NP) from volcanic tuff material. LKD has been used as a source of alkaline material in the
151 proposed blend. The elemental composition of raw materials was determined as they were received
152 condition by using a Shimadzu EDX 720 and energy dispersive X-ray fluorescence (EDXRF)
153 spectrometer. The key oxide elements and the physical properties of raw materials are listed in
154 Table 1. Both MK and NP are composed of similar compositions of minerals, which could be
155 considered as an ideal source of siliceous and aluminate materials, with minor quantities of CaO,
156 Na₂O, K₂O and MgO in NP. LKD was mostly rich in CaO (about 80.1wt.%) with slight amounts
157 of SiO₂ and Na₂O, and therefore it was considered as calcareous source. The specific surface area
158 was determined by air permeability test (Blaine method) that is described in BS EN 196-6 [29]. It
159 was found that MK and NP have surface area of 19.6 and 17.2 m²/g, respectively, while LKD has
160 10.1 m²/g, LKD has high alkalinity with pH of 12.3, which confirms its suitability to be alkaline
161 activator. MK and NP have nearly the same density; 2.69 and 2.57 g/cm³, respectively, while LKD
162 has a density of 2.7 g/cm³ as measured by Quantachrome gas expansion multi-pycnometer purged
163 with helium gas.

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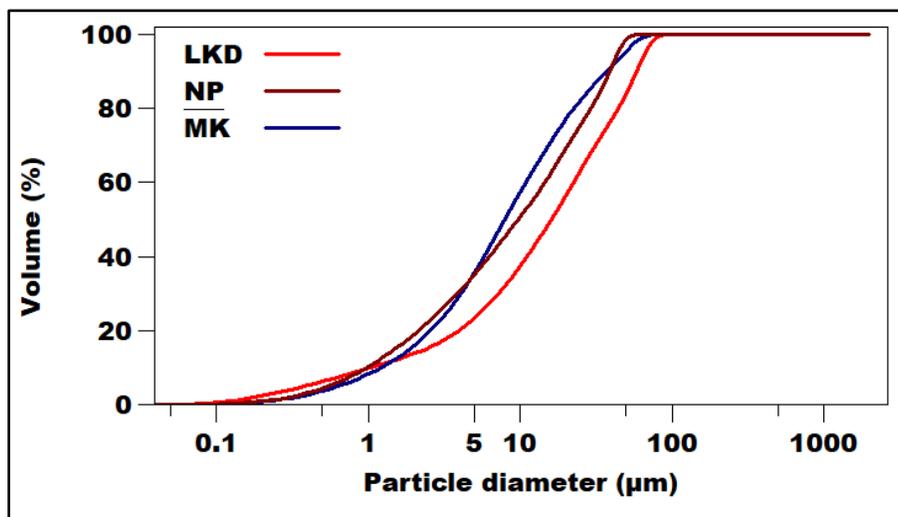
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Table 1. Chemical and physical properties of as received materials.

Chemical composition (Wt.%)	Raw materials		
	MK	NP	LKD
SiO ₂	55	46.6	14.6
Al ₂ O ₃	40	30.4	0.2
Fe ₂ O ₃	1.4	3.8	0.1
CaO	0.15	4.5	80.1
Na ₂ O	0.4	3.9	1.8
K ₂ O	0.4	6	0.5
MgO	0.95	4.2	0.6
TiO ₂	1.7	0.6	0.1
Physical Properties			
Specific surface area (Blaine) (m ² /g)	19.6	17.2	10.1
Density (g/cm ³)	2.69	2.57	2.7
pH	6	6	12.3

176

177 Particle size distribution (PSD), was determined using Beckman Coulter laser diffraction particle
 178 size analyser, as displayed in Fig. 1. It has been found that MK and NP have similar size
 179 distributions with D₅₀ of 9.22 and 7.87μm, respectively. Conversely, LKD was found to be coarser,
 180 with a D₅₀ of 15.94μm. This particle size range of raw materials has a high positive effect on alkali
 181 activation. Rashad et al. [30], reported that MK with grain size less than 32 μm yields a workable
 182 mix with higher compressive strength.



183

184

Figure 1. Particle size distribution (PSD) of starting materials.

185 2.2 Testing methods

186 The set of experimental tests that have been conducted in this study comprises of fresh properties
187 indexed by the setting time, mechanical properties indexed by the compressive strength, thermal
188 analysis presented by thermogravimetric analysis (TGA) and microstructural analysis introduced
189 by x-ray diffraction (XRD), Scanning Electron Microscope (SEM) and Fourier transform infrared
190 spectroscopy (FT-IR).

191 2.2.1 Setting time

192 The standard consistency and setting time of the developed one-part AAC binder were investigated
193 according to British standard 196-3 [31].

194 2.2.2 Compressive strength

195 The compressive strength of mortar prisms, was used as a function for evaluating the mechanical
196 properties of specimens and was measured according to the British standard 196-1 [32]. The test
197 was carried out using a Control Automax 5 compression tester, with a load rate of 0.4 MPa/sec.

198 2.2.3 Thermal analysis (TGA)

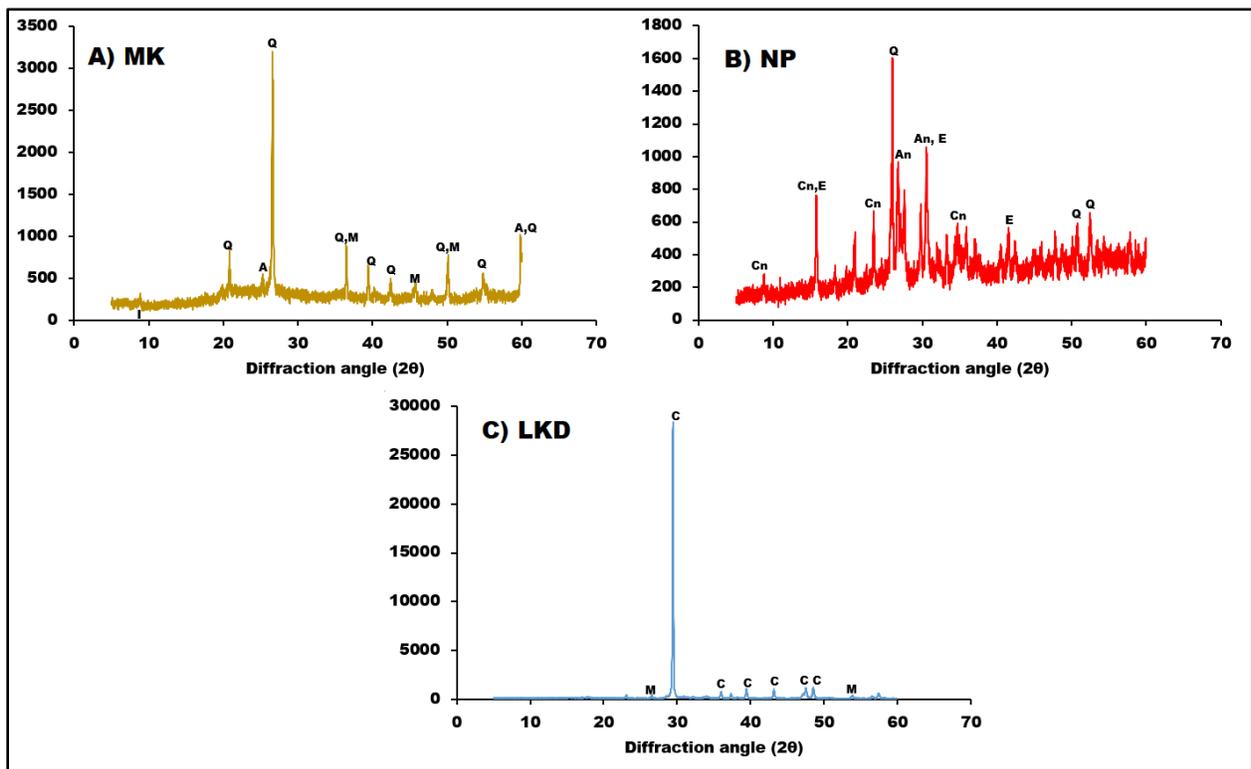
199 Thermal analysis used in this investigation, consisted of Thermogravimetric analysis (TG), which
200 is usually used to determine weight loss of the samples that subjected to thermal events. However,
201 this technique does not detect phase change, such as “melting”; thus, differential thermal analysis
202 (DTA) is employed, which is the first derivative of the weight loss curve. DTA indicates phase
203 changes as endothermic and exothermic peaks [33]. Therefore, it is denoted as TG-DTA technique.
204 The tests were completed using the Perkin Elmer TGA Q50 V20.13 Build 39. The thermal
205 performance of materials was investigated by TG-DTA, with a heating range 20-900 °C and a
206 heating rate of 10 °C/min. In this study, TG-DTA investigations were performed on raw materials
207 to assess their thermal behaviours during individual calcination.

208 2.2.4 Microstructural analysis

209 The microstructural and morphological analyses were carried out on the raw materials before and
210 after thermal treatment. Additionally, the selected pastes of AAC, with the highest strength after
211 they have been hydrated and hardened, were finely ground, dried, and have gone through XRD,
212 SEM and FT-IR analysis after 28, 90 and 180 days of curing. The XRD test was carried out using
213 a Rigaku mini-flex diffractometer (mini-flex goniometer), with CuK X-ray radiation (30 kV
214 voltage and 15mA current at scanning speed of 2.0 deg./min in continuous scan mode) and
215 scanning range (2θ) of 5–60°. Scanning Electron Microscope (SEM) morphological analysis and
216 observations were conducted using an Oxford Inca x-act detector (45nA prob current and 100 sec
217 counting time) and a FEI Company SEM model Inspect S (20kV accelerating voltage). Fourier
218 transform infrared spectroscopy (FT-IR) analysis was carried out using a Perkin-Elmer Spectrum
219 BX series Fourier transform infrared spectrometer (FT-IR), equipped with a Miracle ATR
220 accessory (Specac, UK). The spectrum of the sample was recorded using accumulating 16 scans
221 at 4 cm⁻¹ resolution and wavelength between (550 cm⁻¹ and 2000 cm⁻¹).

222 2.3 Characterisation of raw materials

223 The powder (XRD), (SEM) and (FT-IR) analyses of undisturbed materials are illustrated in Figs.
224 2 to 4. From the X-Ray diffractions of MK, Fig. 2, it is observable that MK comprises many
225 crystalline phases and is primarily composed of quartz (SiO_2) and Mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$), in major
226 crystalline peaks. Illite ($\text{K}, \text{H}_3\text{O}$) ($\text{Al}, \text{Mg}, \text{Fe}$) $_2(\text{Si}, \text{Al})_4\text{O}_{10}[(\text{OH})_2, (\text{H}_2\text{O})]$ and anatas (TiO_2)
227 compounds in minor peaks. The highest quartz peak occurred at (2θ) 26.73° . Diffractogram
228 patterns of NP, which have closely crystalline peaks of quartz peak and feldspars, such as anorthite
229 ($\text{CaAl}_2\text{Si}_2\text{O}_8$) and clinoptilolite ($\text{KNa}_2\text{Ca}_2(\text{SiO}_{29}\text{Al}_7)\text{O}_{72} \cdot 24\text{H}_2\text{O}$). Additionally, edenite
230 ($\text{Ca}_2\text{NaMg}_5(\text{AlSi}_7)\text{O}_{22}(\text{OH})_2$) was present in NP diffractions with high quantities. Diffractions
231 of LKD, showed one recognised crystalline peak of calcite (CaCO_3) with a higher intensity.
232 Smaller peaks exist in the forms of mullite. The presence of such compounds increases alkalinity
233 activity in LKD; these compounds are similar to the content of commercial activator water glass
234 (Na_2SiO_3).



235

236

Figure 2. Powder XRD-patterns of initial materials

237

Q: Quartz, M: Mullite, A: Anatas, I: Illite, Cn: Clinoptilolite, An: Anorthite, E: Edenite, C: Calcite.

238

239 SEM images illustrate the particles of original materials, as shown in Fig.3. MK seems to have
240 fine and lamellar particles with random non-uniform shapes. Particles of LKD look coarser and
241 have less surface area with flaky shapes. The raw NP particles, as shown in the SEM image, are
242 irregular in shape and size.

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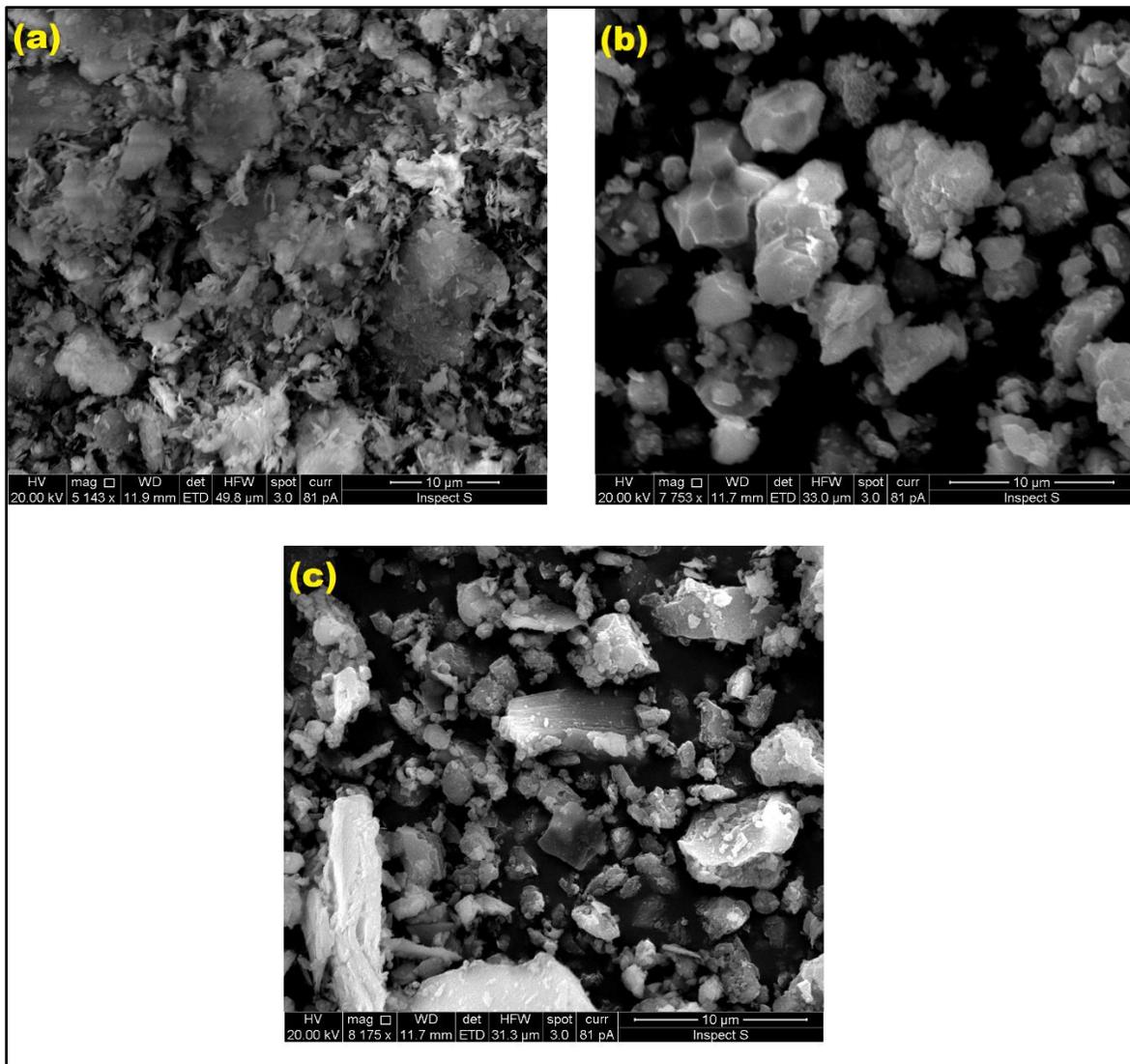


Figure 3. SEM micrographs of undisturbed materials a) MK, b) LKD and c) NP.

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246 Fig. 4 shows the results of the FT-IR measurements of raw MK and NP, which indicate that the
 247 highest absorption band of these raw materials are 1046 and 996cm^{-1} , respectively These values
 248 are attributed to the strong bands of Si–O–Al and tetrahedral Si–O–Si of bridging oxygen (BO)
 249 atoms of the original alumina-silicate framework [34]. The characteristic peaks appearing at
 250 794cm^{-1} and 724cm^{-1} , are ascribed to the stretching vibration Si–O and stretching Al 6-coordinated
 251 geometry (AL, Mg)–O–OH [35]. Both absorptions Si–O–Si and Si–O, are supporting the presence
 252 of quartz, while Si–O–Al is supporting the presence of kaolinite [35,36]. These peaks are related
 253 to the alumina-silicate prevalence phases in both MK and NP. The strong presence of calcite
 254 (CaCO_3), presented by the C–O bond, was evidently presented by the bands at 1402 , 872 and
 255 712cm^{-1} [37]. The presence of these bands is accredited to the tendency of CaO to react naturally
 256 with CO_2 in the atmosphere.

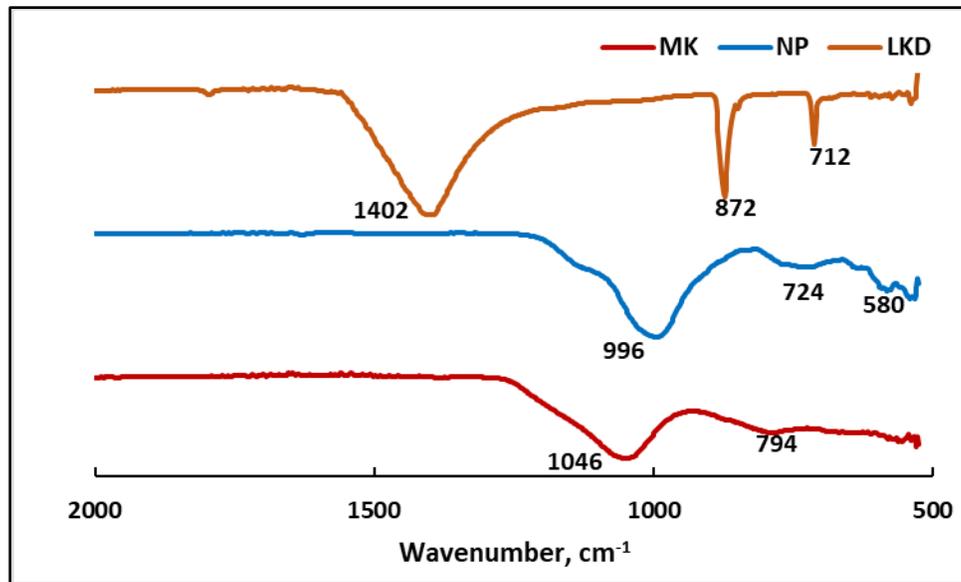


Figure 4. FTIR-spectra of *as received* materials

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259 2.4 One-part AAC cement preparation

260 2.4.1 Heat treatment mechanism

261 Thermal treatment or calcination, means heating the substance to high temperature (500-2000 °C)
 262 within a controlled atmosphere, in order to increase their reactivity by changing their mineralogy
 263 [23]. Thermal treatment is used as one of the assisting activation methods to produce one-part
 264 AAC cement. Most of the materials, which are clayey in origin, require calcination in order to be
 265 reactive. For instance, metakaolin ($\text{Al}_2\text{Si}_2\text{O}_7$) is originally synthesised from the calcination of
 266 kaolin clay ($\text{Al}_2\text{SiO}_5(\text{OH})_4$) [38] at a temperature of 750 °C that used in current study. During the
 267 calcination process, dehydroxylation is carried out, leading to the loss of the long-range order of
 268 alumina and silica layers and conversion of the powder to an amorphous form so that when they
 269 react with calcium hydroxide and water, they undergo a pozzolanic reaction to form hydration
 270 products responsible of improving the strength and durability [39]. Another change is that the
 271 alumina transforms from the octahedral coordination to tetrahedral coordination, due to calcination
 272 [40]. On the other hand, recent studies demonstrated that the transformation of metakaolin into
 273 spinel structure of Si-containing $\gamma\text{-Al}_2\text{O}_3$ and amorphous silica does not occur in temperatures less
 274 than 920 °C [41,42]. Therefore, in order to enhance the reactivity of calcined kaolins so that it can
 275 be used as a pozzolanic cement products, a proper thermal treatment for metakaolin (for structure
 276 disorder) is essential [41,43].

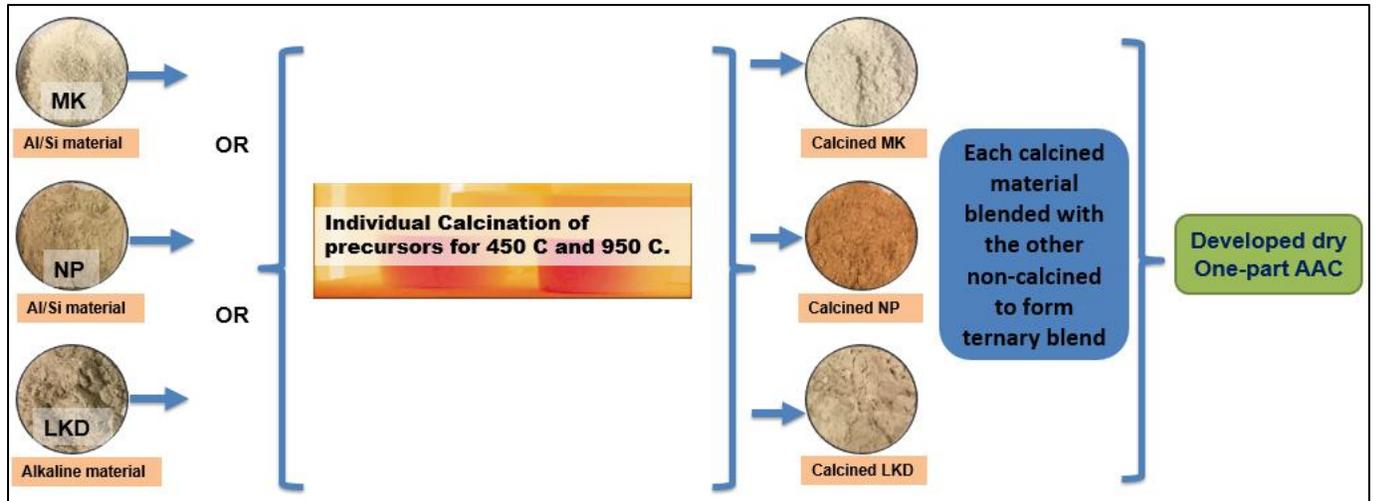
277 On another aspect, significant amounts of lime kiln dust (LKD) are produced, during the
 278 calcination process of limestone, and collected from dust control systems. LKD usually contains
 279 variable amounts of free/available CaO/and un-calcined calcium carbonates, and less amounts of
 280 impurities, such as MgO, derived from the limestone [44] and dumped in waste landfills due to its
 281 high amounts of impurities which is environmentally not favourable alternative. Earlier

282 investigation by Strydom et al.[45] to determine the reactivity and phase changes of precipitator
283 dust from lime kilns upon heating to 500 °C and 1000 °C, has observed slight reduction in the
284 intensity of the recognised calcite at temperature 500 °C and complete disappearance of calcite
285 and transformation to CaO at 1000 °C, which makes LKD as hydraulic materials to participate in
286 hydration reaction. Furthermore, NP, which is a natural pozzolan material, is considered as a good
287 source of silicate and aluminate, but in a poor reactivity state it must be treated by various methods,
288 such as chemically or thermally, to enhance its reactivity which was repeatedly confirmed
289 previously by many literature [46–48].

290 Thermal activation was performed, in this study, for the candidate materials individually to
291 increase their reactivity. Subsequently, mixing each calcined material with the other two non-
292 calcined precursors, according to the blending concept (Si/Al+alkaline), was carried out to
293 synthesise a dry hydraulic cement, as illustrated in Fig. 5. Thermal treatment was conducted in a
294 muffle furnace with a ramping temperature of 20 °C/min for 2 hours. Two foundry cylindrical
295 silicon carbide graphite crucibles (500ml) and two alumina cylindrical crucibles (175ml), were
296 used during calcination process. The relevant literature demonstrated that crystallinity and
297 reactivity of most materials rich in alumina-silicate content can increase with temperatures up to
298 950-1000°C, but after this temperature range, their reactivity can be decreased [49,50]. In this
299 study, activation at temperatures of 450°C and 950°C have been investigated to evaluate and
300 compare the phase transitions. Activation at 450°C temperature at mid-range between 0 and 950°C
301 to evaluate and compare the phase's transitions aimed for saving energy. It is noteworthy to
302 mention that the choice of activation temperatures was based on TGA and XRD analysis
303 (discussed later), which revealed that most phase transitions occur at these levels.

304 Additionally, it is noteworthy that during thermal activation process; some of the material colours
305 have been changed in both stages of temperatures, as displayed in Fig 5. The colour of MK was
306 becoming whiter, with the increase of temperature, while, the colour of NP has shown considerable
307 change from greyish to brown, as the temperature rose. The colour transformation of NP attributed
308 to the increment of anorthite mineral that has been observed clearly in XRD patterns, which turns
309 to be brown in nature [51]. LKD originally white but turned into light grey at 950°C.

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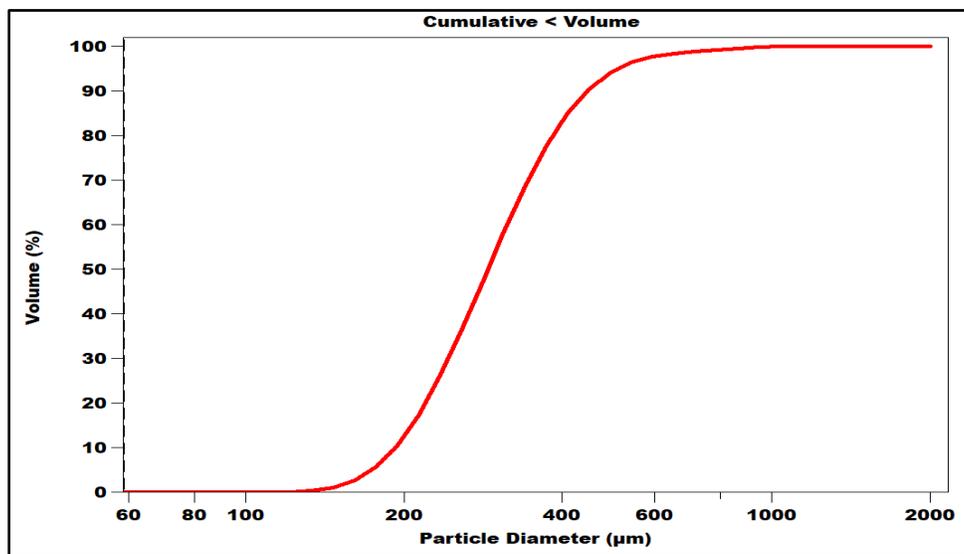
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Figure 5. Preparation steps of one-part alkali activated cement.

313 2.4.2 Preparation of one-part AAC mortars

314 Mortars were mixed with kiln dried sand, with a specific gravity of 2.62, with sand to binder ratio
 315 of 1:2. The particle size distribution of the used sand is shown in Fig. 6. The mixing process was
 316 conducted according to the requirements of British standard 196-1 [32]. Initially, 0.55 water/binder
 317 ratio was chosen, but it was found that the mortars were extremely flowable, therefore; it was
 318 reduced to 0.45 for all the mortars, where appropriate consistency was achieved at this stage.



319

320

Figure 6 Particle Size Distribution of the sand used for mortar.

321 Mortars were mixed, using a Hobart 5L countertop Mixer N50, and poured in steel prism moulds
 322 (40mm x 40mm x 160mm). Mortars were prepared using ternary blended binder with proportions,
 323 as shown in Table 2. These mix proportions, in the ternary blends, were achieved after several
 324 initial trials, as the ternary blended with only non-calcined constituent, showed no cementing
 325 property after 28 days of curing.

Table 2 Mixing proportions of ternary blends used for preparing mortar specimen.

Mix ID	Binder contents	Calcination temperature (°C)	Calcined constituent
AAC1	40%MK 40%LKD 20%NP	950	NP
AAC2	40%MK 40%LKD 20%NP	950	MK
AAC3	40%MK 40%LKD 20%NP	950	LKD
AAC4	40%MK 40%LKD 20%NP	950	NP, MK, LKD
AAC5	35%MK 35%LKD 30%NP	950	NP
AAC6	35%MK 35%LKD 30%NP	950	MK
AAC7	35%MK 35%LKD 30%NP	950	LKD
AAC8	35%MK 35%LKD 30%NP	950	NP, MK, LKD
AAC9	35%MK 35%LKD 30%NP	450	NP
AAC10	35%MK 35%LKD 30%NP	450	MK
AAC11	35%MK 35%LKD 30%NP	450	LKD
AAC12	35%MK 35%LKD 30%NP	450	NP, MK, LKD

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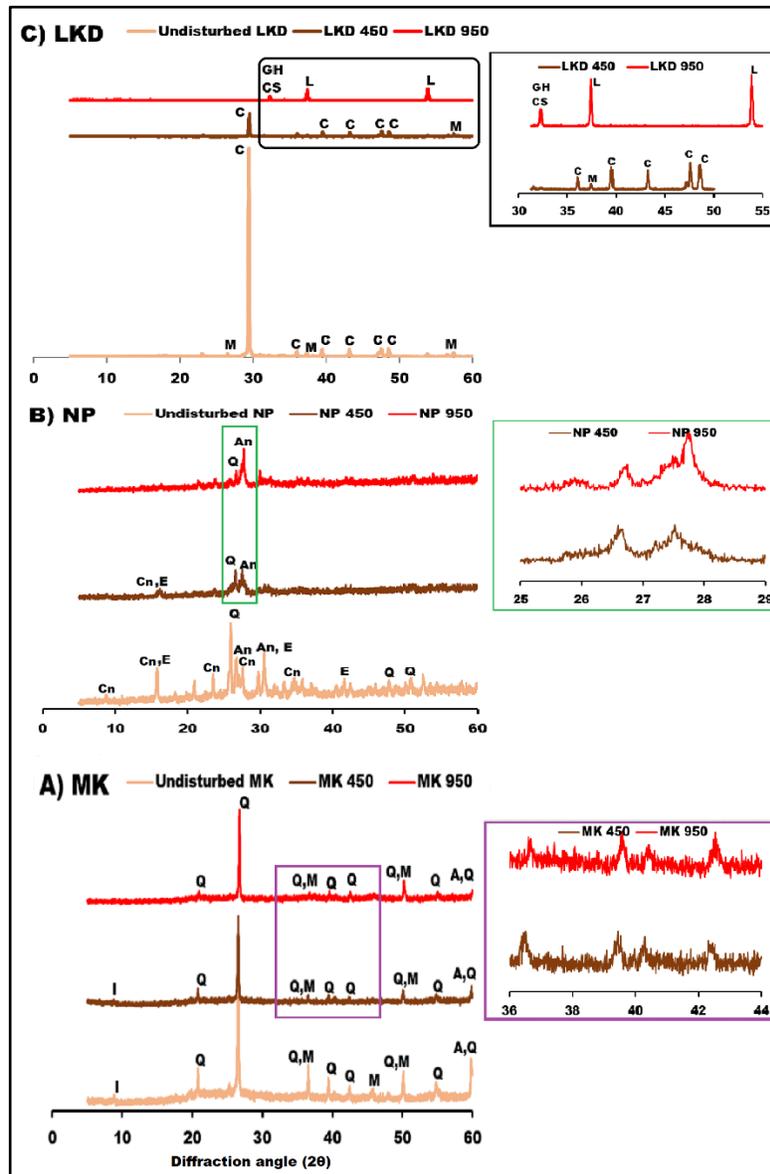
328 The mortars were cured in a hot water curing regime, to enhance the reactivity and the alkali-
 329 activation rate of the mortars and to avoid potential problems, such as efflorescence and micro
 330 cracking, which can lead to a reduction in the compressive strength [52]. Curing temperature was
 331 fixed to 50 °C for the first 7 days, and then cured in normal water (20 °C) for the desired period,
 332 as suggested by Perera et al. [53] and Singh et al. [54].

333 3. Results and discussion

334 3.1 XRD analysis after heat treatment

335 The powder diffraction of calcined materials has been presented in Fig. 7. Diffractograms of MK
 336 revealed a significant reduction and disappearance of peaks, such as mullite and illite, after both
 337 levels of calcination indicating semi-transformation of material to an amorphous phase. While
 338 peak of quartz has shown no change on both calcination level, XRD spectrums of calcined NP at
 339 both levels, indicated a huge transformation of crystalline phases to amorphous phases through the
 340 loss of quartz and clinoptilolite, in a range of 2θ from 30° to 60° . It can be noticed, that crystalline
 341 quartz, which peaked at $2\theta = 26^\circ$, has disappeared entirely when NP calcined to 450°C and 950°C ,
 342 introducing strong evidence of the increment of amorphicity. This was confirmed by the
 343 formulation of a broad amorphous hump of anorthite existed at $2\theta = 26.7^\circ$ and $2\theta = 27.8^\circ$ at 950°C
 344 patterns. Remarkably, this intense calcite peak in LKD was reduced markedly when calcined to
 345 450°C and **completely disappeared in calcination at 950°C** which could indicate the total
 346 decomposition of calcite CaCO_3 to lime CaO and introduced as new peaks at $2\theta = 37^\circ$ and 54° .

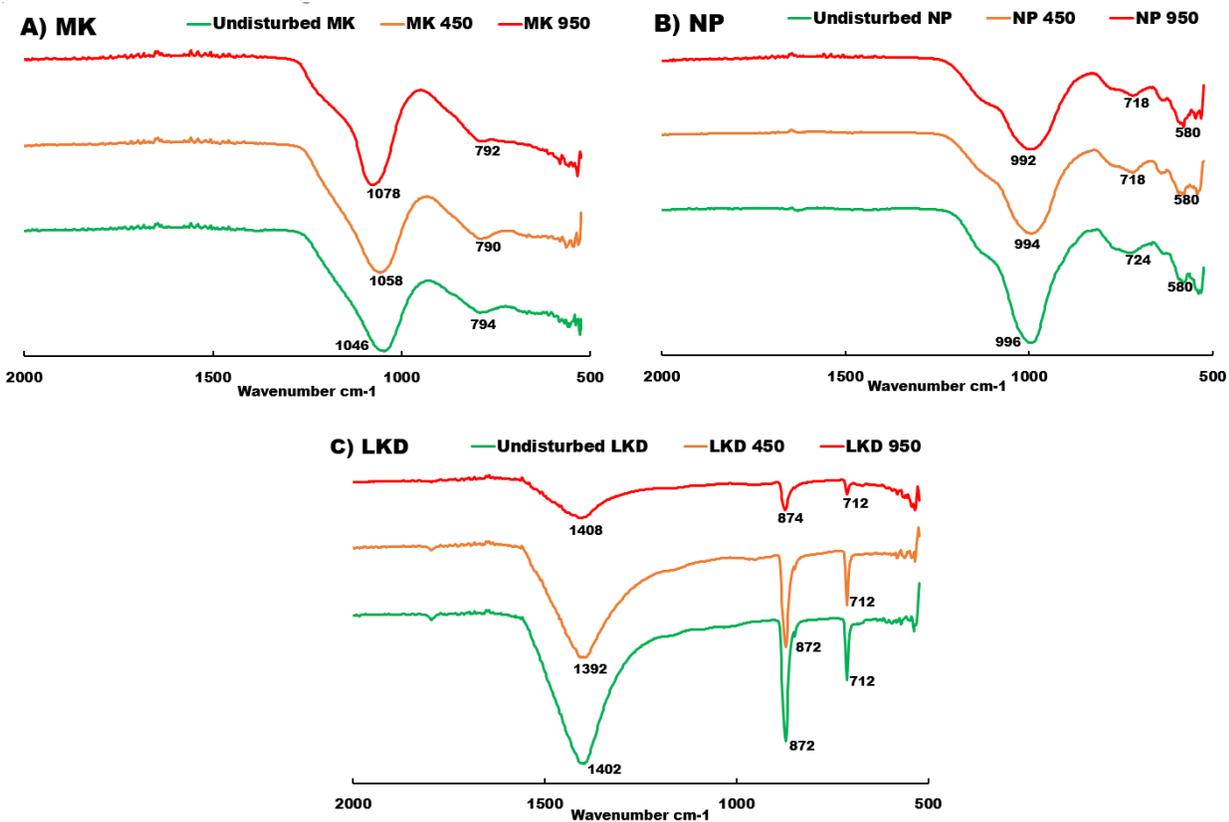
347 The appearance of new diffraction patterns of calcined LKD at 950°C, indicated the formulation
 348 of new compounds, but it was composed of the same elements as untreated LKD (CaO, SiO₂ and
 349 Al₂O₃), in the form of periclase cementitious minerals, di-calcium silicate C₂S (2CaO.SiO₂) and
 350 gehlenite (Ca₂Al(Al Si)O₇) [45]. This would suggest that mullite (3Al₂O₃.2SiO₂) exist in raw LKD
 351 has decomposed and reacted with CaO to formulate these new phases [45]. The complete
 352 disappearance of the intense crystalline CaO after 950°C calcination, which indicated that
 353 calcination had caused a large combination of lime CaO with the compounds of SiO₂ and Al₂O₃,
 354 to form the above hydraulic minerals.



355
 356 *Figure 7. Powder XRD patterns of materials after thermal activation, A) MK, B) NP, and C) LKD.*
 357 *Q: Quartz, M: Mullite, A: Anatas, I: Illite, Cn: Clinoptilolite, An: Anorthite, E: Edenite, L: Lime, C:*
 358 *Calcite, CS: dicalcium-silicate, GH: gehlenite*

359 3.2 FT-IR analysis after heat treatment

360 The FT-IR spectrums of thermally treated materials are illustrated in Fig. 8. The alumina-silicate
361 bands Si-O-Si and Si-O-Al have become higher from 1046 cm^{-1} , in untreated MK, to 1058 cm^{-1} at
362 450 °C and 1078 cm^{-1} at 950 °C. This is while the opposite to this tendency took place with the
363 spectra of NP. This kind of shifting and enhancement of broadness of these bands, leads to the
364 transformation of crystalline phases to an amorphous structure and high deformation in the lengths
365 and angles of Si-O-Al and Si-O-Si bonds [25]. This transformation is satisfied by the increment
366 of non-bridging oxygen atoms due to thermal treatment [55]. A considerable reduction and width
367 increment of the intensity of C-O bond during the treatment at 950°C, indicates the transformation
368 of the crystalline phase into the glassy phase and interprets the increment of CaO amounts released
369 from CaCO_3 [56,57].



370

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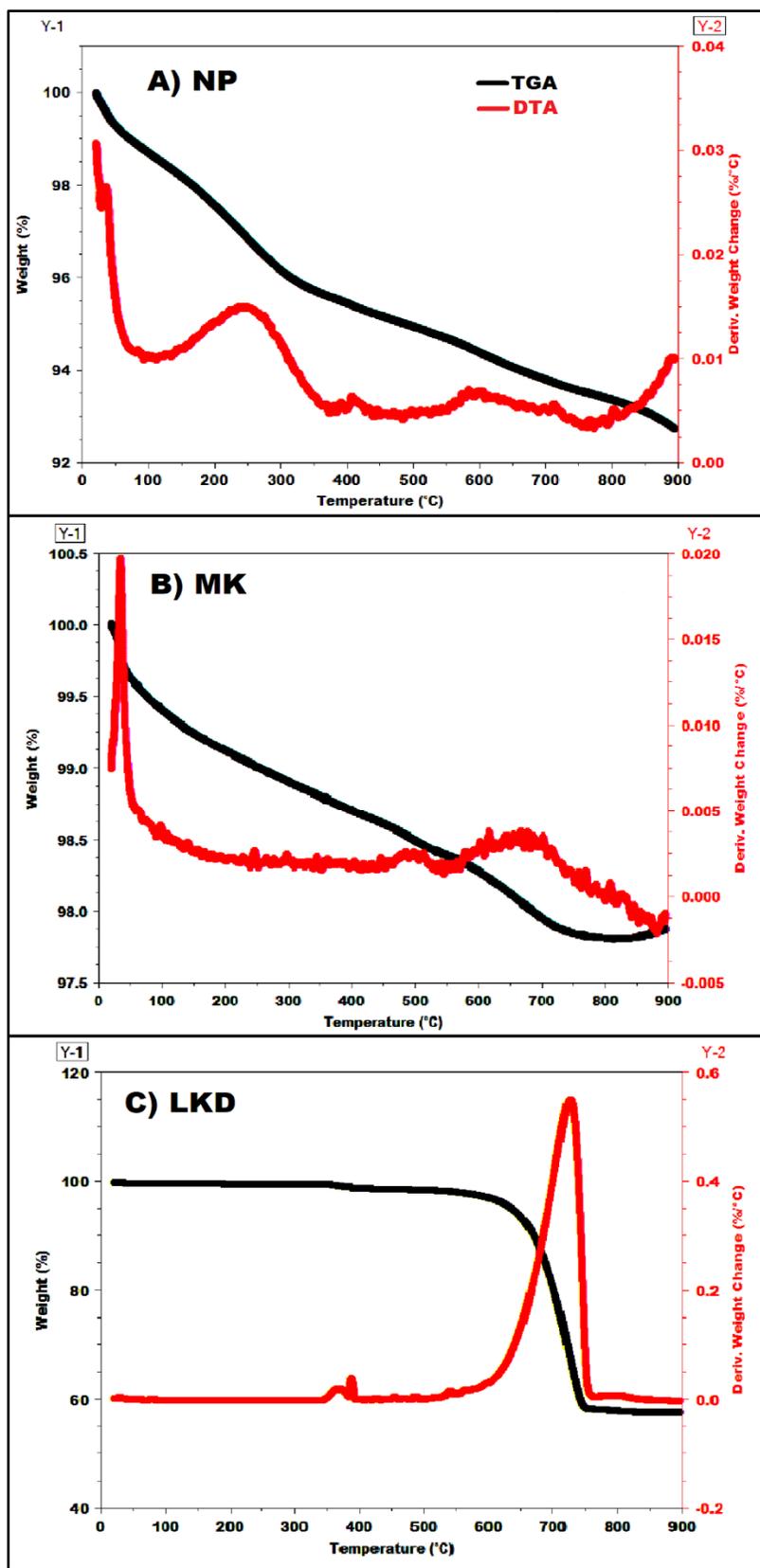
Figure 8. FTIR spectra of materials after thermal activation.

372

373 3.3 Thermogravimetric Analysis (TG-DTA) after heat treatment

374 Fig. 9 (A) exhibits the thermal performance of NP investigated by TG-DTA, when calcined to
375 900°C. As can be seen, some mass-loss phases are present in its patterns caused by endothermic
376 and exothermic reactions. The Thermogravimetric (TG) patterns of NP mass-loss from room
377 temperature to 900°C is approximately 7% of total weight, which might be attributed to the loss of

378 chemically and physically adsorbed water and breakdown of crystal phases, which was evidenced
379 by XRD analysis. The loss of weight can be divided into three stages. The loss in temperature
380 range of 20-320°C is due to the evaporation of adsorbed water. The loss in the range of 320 –
381 620°C, is because of calcining amounts of impurities and contaminants. While loss in the range
382 620 - 900°C is due to decomposition of unburnt carbons [58,59]. As for the DTA curve, there was
383 endothermic convexity at 119°C, which relates to the evaporation of water followed by exothermic
384 concavity at 250°C. The TG curve of MK has shown a very small weight change within 2% of the
385 total weight, with a reasonably straight DTA curve, as shown in Fig. 9B. The TG patterns of LKD,
386 revealed that it has not lost any weight until 350°C; when there was only a slight weight loss until
387 620°C, when the weight changed dramatically with a 35 % loss of original weight and an
388 exothermic sharp peak of the DTA curve, which is shown clearly in Fig. 9C. This loss is markedly
389 attributed to the transformation and loss of the CaO crystalline intense peak, which was further
390 evidenced by the XRD analysis of 950°C calcination, when this peak disappeared from the
391 diffraction pattern.



392

393

Figure 9. TG-DTA analysis of initial materials, A) NP, B) MK, and C) LKD

394 3.4 Influence on compressive strength after heat treatment and blending.

395 One-part mortar samples were prepared and cured using the mix proportion, with two levels of
396 thermally activated materials as stated in table 2, and their resulting compressive strengths are
397 displayed in Figs. 10 and 11. The blend containing 950°C calcined LKD (AAC3), has shown a
398 compressive strength of 24.54 MPa after 28 days. The regular growth in strength of up-to 28 days
399 for this blend, indicates the progressive alkali-activation that attributes to the calcination of LKD
400 with the presence of sufficient amounts of reactive silicate and calcium oxide from the NP. A
401 considerable amount of strength was developed within the blends, containing calcined materials
402 individually and collectively, which showed no cementitious properties prior to thermal treatment.
403 Calcination at 950°C, clearly contributed to a huge variation in LKD mineralogy and substantial
404 reduction in its crystallinity, which was observed in the XRD patterns. In order to optimise the
405 strength, these mortar mixes were repeated with same procedures, but with increased proportion
406 of NP (35% MK, 35% LKD, and 30% NP). The increment of the NP was due to the suitable
407 composition of NP, which contains a various range of alkaline elements including CaO, Na₂O and
408 K₂O, as shown in XRF results. Noticeably, the highest compressive strength was achieved at this
409 stage with 27.3 MPa in 28 days for the blend that contains 950°C calcined LKD (AAC7), as shown
410 in Fig. 10. The increment of NP content by 10% within the blends, resulted more growth of C-A-
411 S-H products. The addition of more NP contributed to extra dissolution of quartz silicate, caused
412 by CaO and Na₂O that exists in the calcined LKD and NP, yielding high binding properties.
413 Therefore, a higher transformation to vitreous mineralogy led to a higher strength of AAC7.
414 Moreover, the reduced strength for AAC4 and AAC8, when all three components were calcined,
415 indicated less dissolution of Si/Al compounds from MK and NP (at both composition), which
416 means that less activation was caused by the LKD.

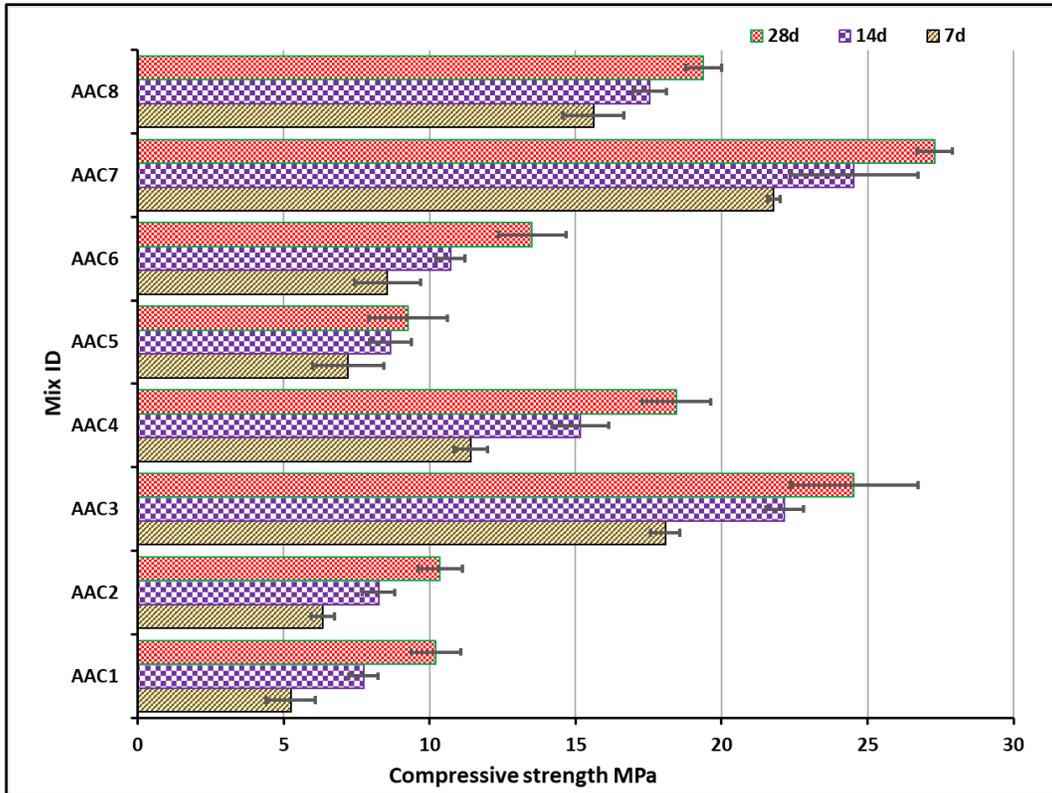


Figure 10. Compressive strength of blends with 950 °C calcined materials.

417

418

419 The TG-DTA curves have shown that the weight loss of the individual constituent of the ternary
 420 blend, starts at the temperatures in the range 350-500°C. This was evidenced by XRD patterns,
 421 where raw materials after 450 °C treatment have displayed a considerable change in their
 422 diffraction. Therefore, the ternary blends of 35% MK, 35% LKD and 30% NP were formulated
 423 after calcination of 450°C. The resulting compressive strength offered by the ternary blends after
 424 450°C thermal activation, has been shown in Fig. 11. A similar trend of higher strength in the case
 425 of calcining LKD individually at 450 °C, was evident in AAC11 with 23.4 MPa at 28 days.
 426 Although both early and longer-term strengths were higher in the case of 950°C treatment, no
 427 remarkable strength generation was observed compared to a lower temperature (450°C). This
 428 similar development of strength is ascribed to mineralogical and chemical changes that were
 429 noticed in both XRD and TG-DTA results, which indicated that most of diffraction patterns were
 430 starting to transform around and after 450°C.

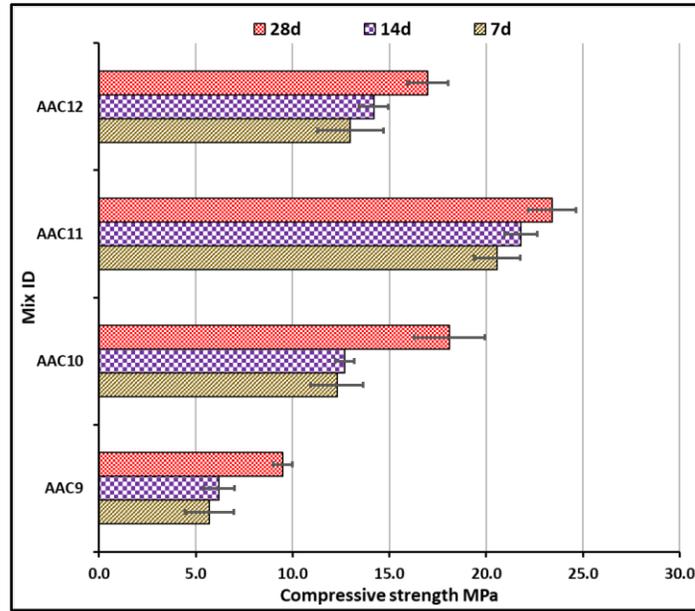


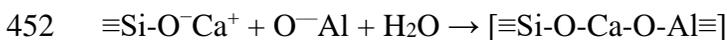
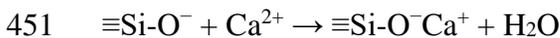
Figure 11. Compressive strength of blends with 450 °C calcined materials.

431

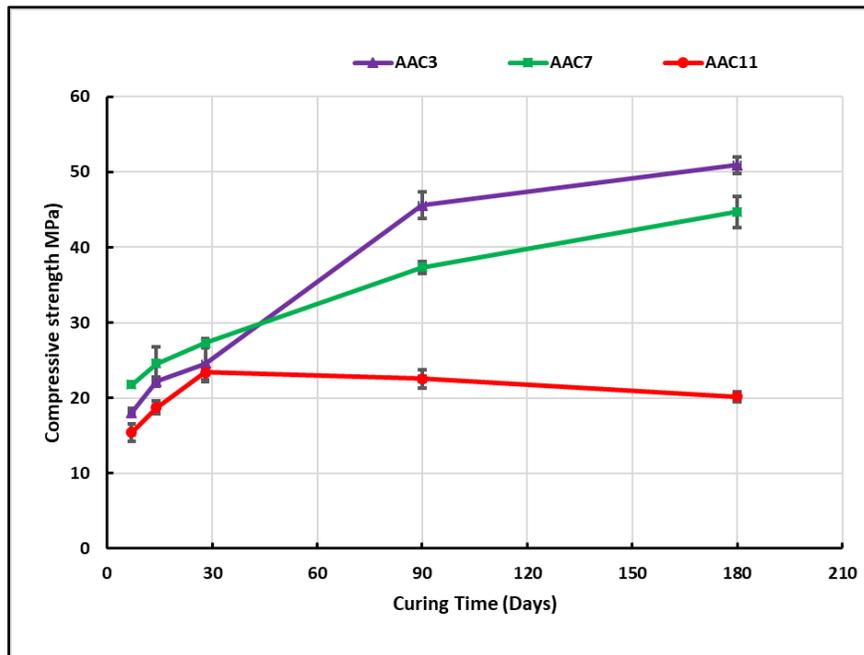
432

433 3.4.1 Long-term compressive strength for optimal blends

434 The compressive strength after 90 and 180 days of curing was investigated for the blends, which
 435 showed a higher alkali-activation rate in the case of calcined LKD at both level of calcination and
 436 mix proportion (AAC3, AAC7 and AAC11), as presented in Fig. 12. Although AAC3 has a lower
 437 compressive strength than AAC7 until 28 days of curing, it showed significant increase in rate of
 438 strength development just after 28 days and continued till 180 days. The higher rate of strength
 439 growth has been witnessed at the later age of 180 days which has shown increment of strength to
 440 reach 51 MPa for blend AAC3 and 45 MPa for AAC7 with increment of about 11% and 18% at
 441 age of 90 days of both mixes respectively; indicating that there was a high degree of alkali-
 442 activation within the system until 180 days, without showing any marks of efflorescence. The
 443 higher degree of polymerisation within AAC3 compared to AAC7 was due to the formulation of
 444 balanced alumina silicate and alkaline materials, which was achieved through reducing 10% of NP
 445 and adjusting the others accordingly. This is was due to the higher CaO contained in AAC3 that
 446 promoted formulation of further amounts of geopolymeric products and more stable
 447 microstructure. This can be justified that calcium cations (Ca^{+2}) might be bonded in the
 448 geopolymeric gel that results in charge balance by replacing cations within the geopolymer [60].
 449 The chemical mechanism of combining calcium cations in geopolymeric gel is illustrated by the
 450 following reactions [61,62]:



454 Contrariwise, sample containing calcined LKD at 450°C (AAC11), has promoted a slight
 455 deterioration in strength immediately after 28 days and continued until 180 days. This signifies the
 456 inhibition of the alkali-activation reaction after 28 days in this blend. While the combined
 457 procedures of impurities disappearance that were contained in the chemical composition of LKD
 458 as a by-product material and the mineralogical changes after thermal treatment have strongly
 459 introduced the fact that reactivity of LKD has increased just after thermal treatment. To confirm
 460 this fact, this was investigated by preparing a mortar sample similar to AAC7 but without the
 461 application of thermal treatment to LKD, as this sample has the optimal strength at the age of 28
 462 days, 51% lower compressive strength (18 MPa) after 28 days was achieved from that blend, that
 463 comprised un-calcined LKD, and decreased to 16 MPa at age of 180 days.



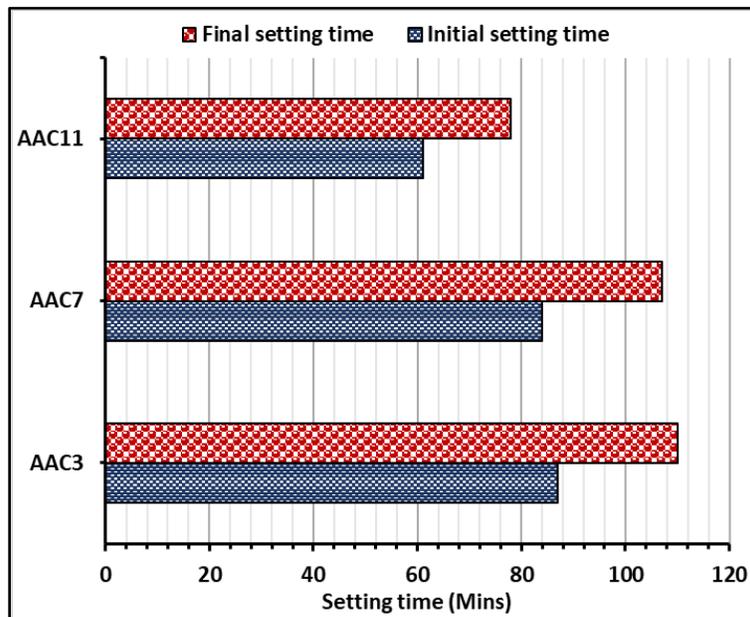
464
 465 *Figure 12 : Long-term strengths of one-part blends containing activated LKD at 450 °C and 950 °C.*

466 **3.5 Setting time**

467 Fig. 13 shows the initial IS and final FS setting time of the optimum blends AAC3, AAC7 and
 468 AAC11. It can be observed that the setting times for blends are fluctuating between 61-87 min for
 469 the initial setting time and between 78-110 minutes for final setting time. It can also be noticed in
 470 Fig.13 that nearly parallel IS and FS for blends AAC3 and AAC7, indicating that slower alkali
 471 activation is due to the higher content of calcined LKD (40 Wt.% and 35 Wt.%), which acts here
 472 as a key activation agent. Higher amounts of alkaline cations of Ca⁺² from LKD in the system is
 473 leading to the formation of extra Ca(OH)₂ that causes more breaking and dissolving of Si and Al
 474 chains that accelerates the alkali-activation reaction, and consequently increases the setting time
 475 [63]. However, lower IS and FS were observed in AAC11, as shorter levels of reactions occurred
 476 due to the low reactive LKD and, therefore, lower alkali activation. The effect of the alkaline
 477 cations, from the activator (LKD), was clearly seen on the setting time. The result was evident, as

478 the alkaline part became more reactive, as there was more dissolution, leading to longer setting
479 time.

480 In terms of application and use of AAC, a higher setting time is a significant parameter for
481 transporting far distances, storage and a shorter setting time, which is important for quick repairs
482 of damaged surfaces [63]. The current results of IS and FS are in a good agreement with the results
483 of past studies. For example, Luukkonen et al. [8] revealed in their review that IS and FS of
484 developed one-part AAC in past attempts were from 23-150 and 69-230 minutes, respectively.
485 Additionally, the obtained results of initial setting time in this study are in agreement with initial
486 setting times for cement types in British standards 197-1 [64]. Furthermore, setting times can be
487 easily increased if needed in some applications with the aid of setting retardant agents such as
488 lignosulfonate which was proven as a suitable retarder for one-part AAC in past studies [65].



489

490

Figure 13 Initial and Final setting times of optimum one-part AAC blends.

491 3.6 XRD analysis of hydration products

492 XRD analysis was performed on pastes of samples with the highest strength (AAC3, AAC7 and
493 AAC11) at 28 days and for longer ages (at 90 and 180 days), as presented in Fig. 14. Major
494 hydration products can be identified and are composed chiefly from CaO-Al₂O₃-MgO-SiO₂
495 compounds. The utilisation of a dry alkaline (CaO) activator, in the mix, transforms the
496 crystallinity diffraction patterns into amorphicity status and leads to the presence of prevailing
497 vitreous phases. The major products phases were specifically tetra calcium aluminate hydrate,
498 CAH (C₄AH₁₃), calcium alumina silicate hydrates, St (stratlingite – C₂ASH₈), and Akermanite,
499 (Ak) (Ca₂MgSi₂O₇) [17][66][67][56]. Moreover, Gameiro [67] stated that calcium silicate hydrate
500 (CSH) overlaps with the lime (calcite) peak in these blends, with higher MK (≥ 33% MK). XRD
501 patterns of AAC3 as presented in Fig. 14a. This figure reveals that at the age of 28 days, a slight
502 reduction of the dominant Quartz (SiO₂) crystalline phase that existed in the raw MK at 2θ = 26°.

503 This slight reduction indicates the remaining large amounts of this crystalline quartz are in a non-
504 reactant status. On the other hand, this reduction was sharp at age of 90 days and even more at age
505 of 180 days, presenting more dissolution of crystalline SiO₂ and transforming into alkaline-
506 silicates strains. This dissolution was induced by the formation of extra Ak products at the longer
507 ages. The fact of reducing crystalline quartz phases and the formation of vitreous Ak, led to the
508 development of significant strength after 90 and 180 days of (AAC3)[63]. Additionally, a glassy
509 phase of alumina-silicate gel (C-A-S-H) can be indicated in the 2θ range of 25°-30° at age of 28
510 days, however, due to the semi- amorphous nature, this product disappeared at age of 180 days
511 [69,70]. At the same time, the strong presence of St, is noticed as a permanent phase in the matrix.
512 The formulation of St as dominant substance in the three blends, indicating that this product is
513 stable and is verified as the product responsible for the enhancement of mechanical strength
514 [67,71]. Regardless of the slight increment of the Ak mineral peak at 90 and 180 days of AAC7
515 (in Fig. 14b), crystalline quartz can be noticed in an increment trend from 28 to 180 days. The
516 growth of St peaks can be noticed clearly, through the entire range of diffraction with increment
517 of LKD, causing a higher strength for AAC7. This indicates that the lime (CaO) generated from
518 LKD is causing a significant dissolution of aluminate and silicate species [72], and consumes all
519 alkaline substances resulting no mark of any efflorescence. The high amounts of MgO from NP
520 have strongly contributed to presence of amorphous phases, such as Ak together with the reactive
521 CaO from LKD. This reaction introduced new bonds such as Ca-Mg-Si, which have a high
522 contribution to the strength. C₄AH₁₃ (CAH) was present in minor quantities due to the instability
523 of this phase through the curing aging [67]. Additionally, portlandite (Ca(OH)₂) peaks were not
524 found extensively due to the modified LKD and MK in the blends, as this peak may appear in low
525 MK blends [67]. A range of reaction products can be noticed similarly in AAC11 as in Fig. 14c,
526 with LKD calcined at 450°C. The amounts of Ak can be observed with less quantities in the all
527 ages of AAC11 with higher amounts calcite (C) than AAC3 and AAC7 that formulated through
528 the ages. This was observed in the strength development for both levels of thermal treatment.
529 However, the diffraction patterns of this blend are presenting growth of crystalline quartz in two
530 major peaks at 2θ =26° and 47°. This caused a dip in the equivalent of 90- and 180-days strength,
531 for AAC11.

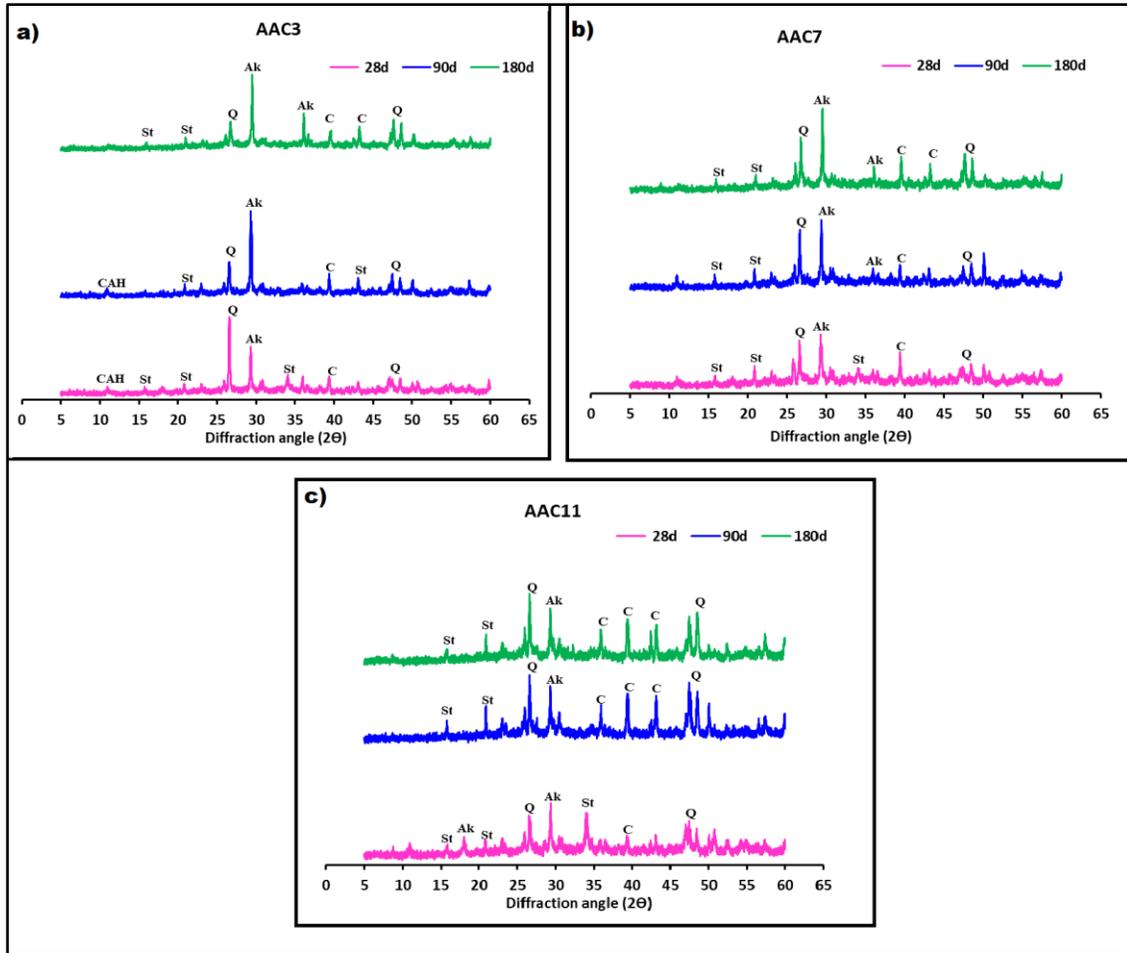


Figure 14. XRD patterns of a) AAC3, b) AAC7, c) AAC11 at 28, 90 and 180 days.

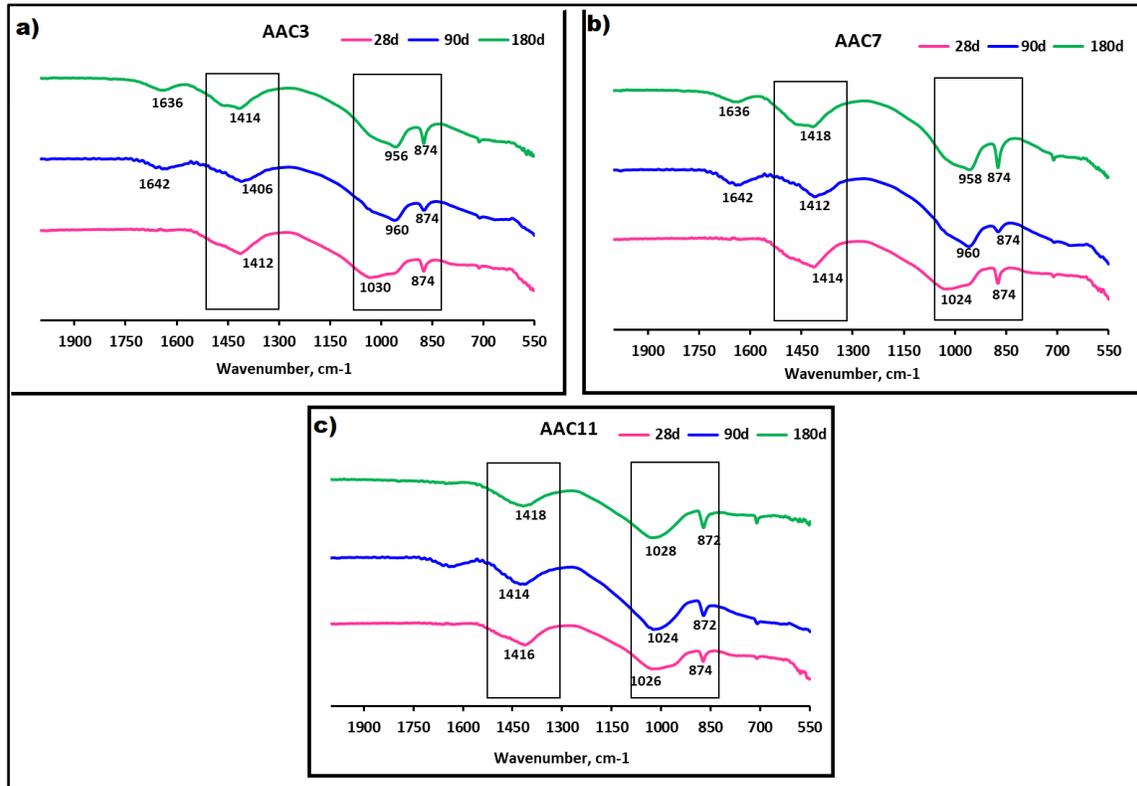
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534 3.7 FTIR analysis of hydration products

535 The FTIR (Fourier-transform infrared) spectra was reproduced for pastes of AAC3, AAC7 and
 536 AAC11 blends, and were investigated after 28,90 and 180 days of curing, as shown in Fig. 15a
 537 new absorption bands were recorded at 1642 and 1636 cm^{-1} , for the vibration bending H–O–H in
 538 all blends at 90 and 180 days. The appearance of water absorption bands are a clue for the
 539 crystalline H_2O of the hydrated products such as C-S-H or C-A-H [73]. In all spectra, the typical
 540 carbonate phases C-O band, appeared in the following bands 1406-1418 and 874 cm^{-1} was
 541 observed. This is similar to infrared in the raw LKD in Fig. 4. However, the intensity of this band
 542 was reduced with the right shifting of its location and has become wider at 90 and 180 days for the
 543 blends, except for the AAC11 blend, as shown in Fig. 15a-c. This attributed to the calcined LKD
 544 at 950 $^\circ\text{C}$, has purer and more reactive CaO than 450 $^\circ\text{C}$ calcination in the case of AAC11, which
 545 has more groups of CaCO_3 . The asymmetric stretching band starting from 1200-900 cm^{-1} region
 546 of Si-O and Al-O were noticed in all spectra of the blends. These bands reveal the strong evidence
 547 of Aft/AFm phases such as stratlingite (C_2ASH_8) and mono-carboaluminate $\text{Ca}_4\text{Al}_2(\text{CO}_3)(\text{OH})_{12} /$
 548 $5\text{H}_2\text{O}$ [74]. It can be noticed that this band was very wide at 28 days and transformed to be sharp

549 and narrow at 90 and 180 days with shifting to lower wavenumber in both blends AAC3 and
 550 AAC7. It was revealed that such this phenomenon is correlated to the breakdown of covalent bonds
 551 of silicate networks, which become less strong and lead to the formation of more non-bridging
 552 oxygen (Si–O bonds) that was simply undergone to more condensation and polymerisation [75].
 553 Contrarily, these bands remained unchanged in blend AAC11 for ages of 28, 90 and 180 days.
 554 This has led to the development of phases with a non-ordered structure, with a variation of bond
 555 length and angles [76], which was in accordance with the reduced strength of AAC11.

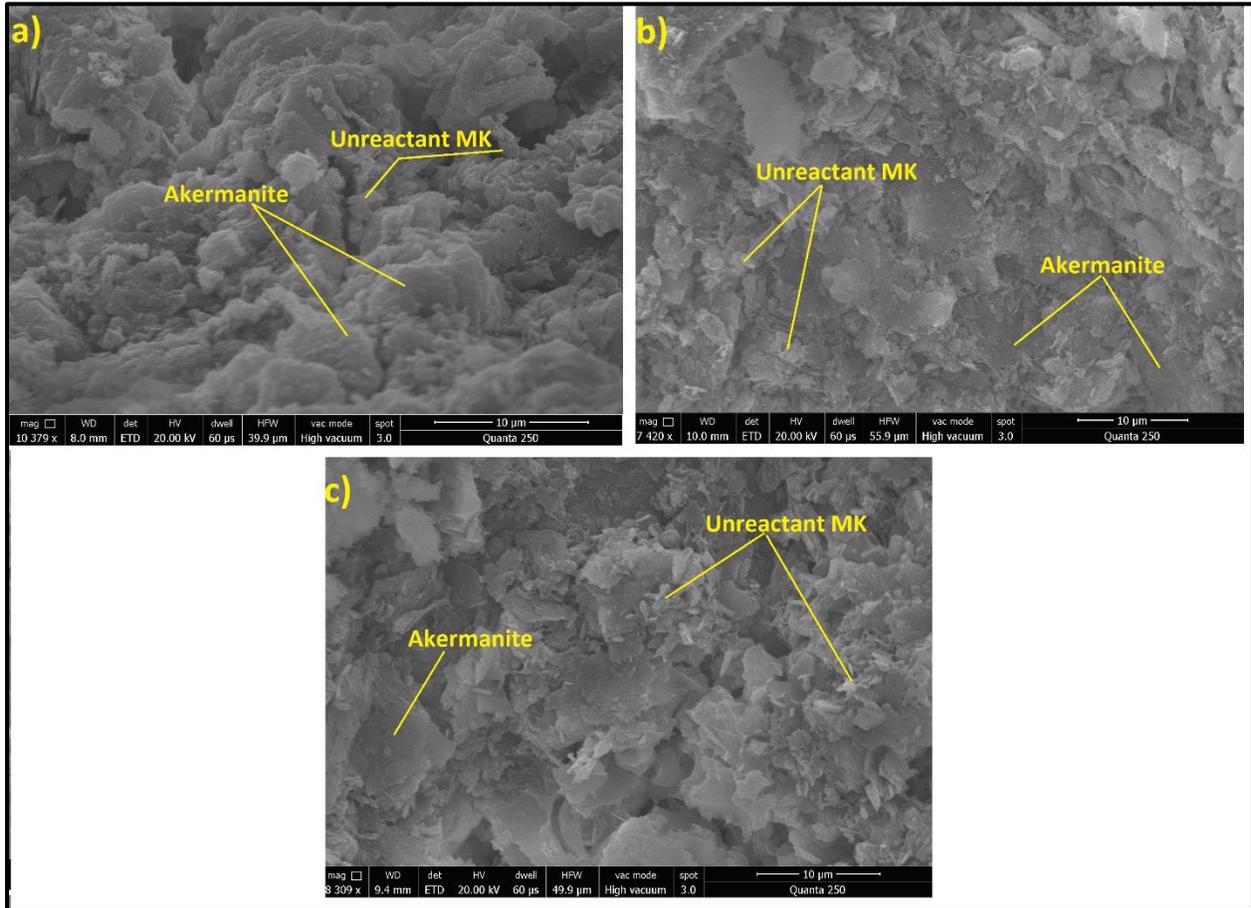


556
 557 *Figure 15. FTIR-spectra of hardened pastes of a) AAC3, b) AAC7, c) AAC11 after 28, 90 and 180days*
 558 *curing.*

559 3.8 SEM analysis of hydrates

560 The SEM micrographs for AAC3,7 and 11 at 28 days of curing are shown in Fig. 16. The
 561 microstructure of hardened pastes shows the significant existence of the un-reactant MK in all
 562 blends at 28 days, which can be identified by fine and lamellar particles with random non uniform
 563 shapes and similar to particles of raw MK appeared previously in Fig. 3c. However, the un-reactant
 564 MK has very limited quantities in blend AAC3, as shown in Fig. 16a, and highest quantities in
 565 AAC11, as seen in Fig. 16c. This illustrates the pozzolanic reaction of Si and Al with Ca⁺² cations,
 566 which encourages further dissolution and breaking the Si–O and Al–O bonds in both MK and NP
 567 [77]. Ak products can be distinguished clearly as a predominant phase of flat continuous gels in
 568 all blends, but its lowest appearance can be seen in AAC11, which agrees with the XRD patterns.
 569 The trend of reaction mechanism during the hydration process is with the increment of reactive

570 calcined LKD at 950 °C, where there is an increment in the operation of extra dissolution of Al/Si
571 constituents.

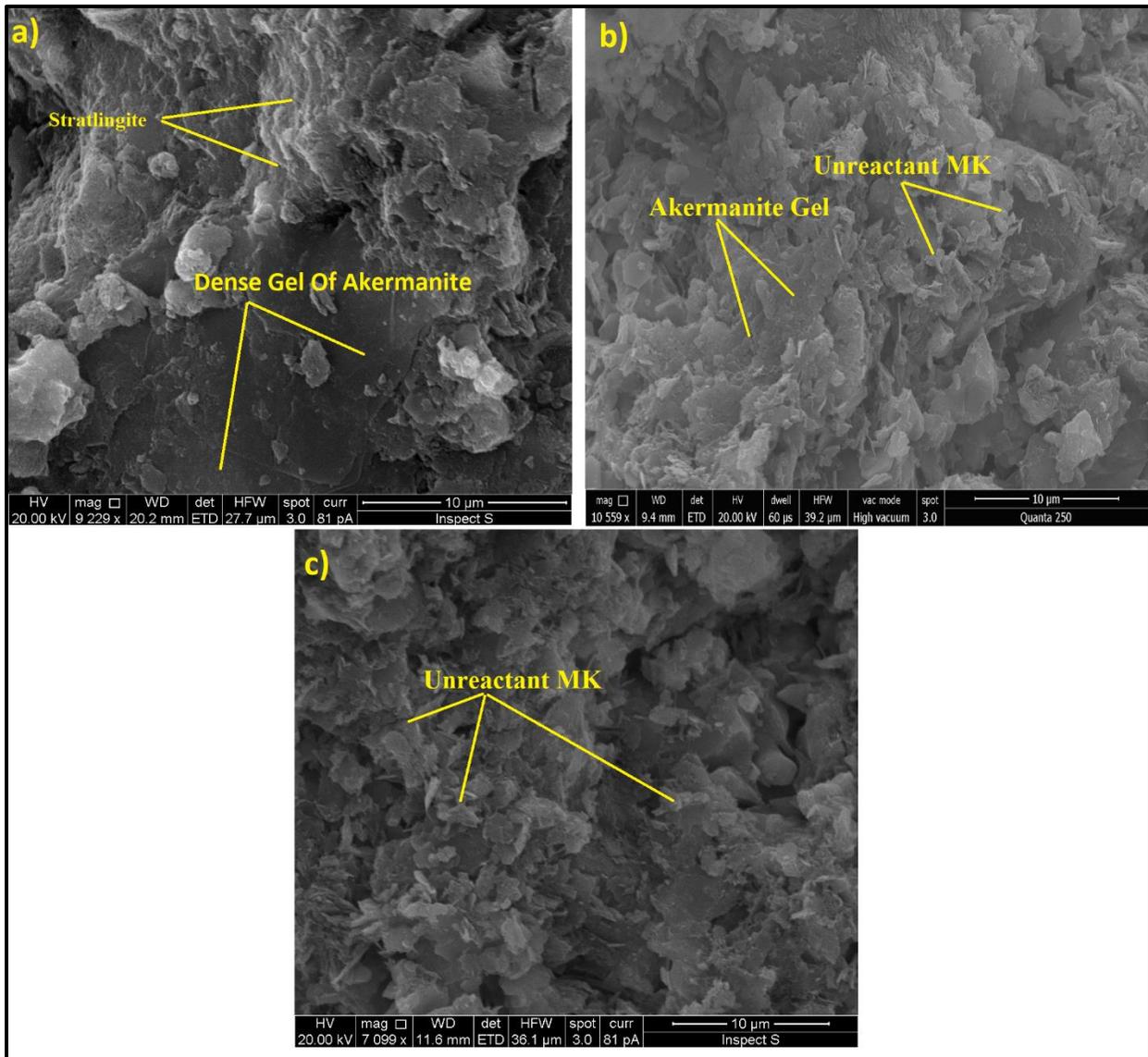


572

573

Figure 16. SEM micrographs for a) AAC3, b) AAC7 and c) AAC11 at 28 days

574 Fig. 17 presents the SEM micrographs of hardened pastes of optimum blends AAC3, 7, 11 at
575 curing age of 90 days. While the matrix of blend AAC7 and AAC11, presented in Fig. 17b and c,
576 is exhibiting un-reactant particles of MK. The amounts of these particles, decreased in blend AAC7
577 at the age of 90 days compared to 28 days, with the development of more hydrates, such as Ak and
578 St of darker grey tone. On the other hand, it can be significantly recognised from the microstructure
579 of AAC3, as shown in Fig. 17a, that this blend is mostly free any un-reactant particles and showed
580 higher microstructure density. This indicates a large transformation of MK and NP particles into
581 dense gels of hydration products (Ak and St) through long term curing, which in turn resulted in a
582 significant development of strength for the AAC3 blend.



583
 584 *Figure 17. SEM micrographs for a) AAC3, b) AAC7 and c) AAC11 at 90 days*
 585

586 While it could be clearly noticed that the internal matrix of AAC3 as in Fig. 18a at the age of 180
 587 day, has significant increment of the formulation of a dense phase characteristic of cementitious
 588 Ak compared to 90 day which strongly reveals the progression of alkali-activation till the age of
 589 180 day and the total disappearance of any un-reactant grains. However as shown in Fig. 18b, this
 590 dense gel was less presence in AAC7. On the other hand, the microstructure of AAC11 has shown
 591 prevalence of un-reactant particles such as MK and very low gels of Ak as shown in Fig. 18c.
 592

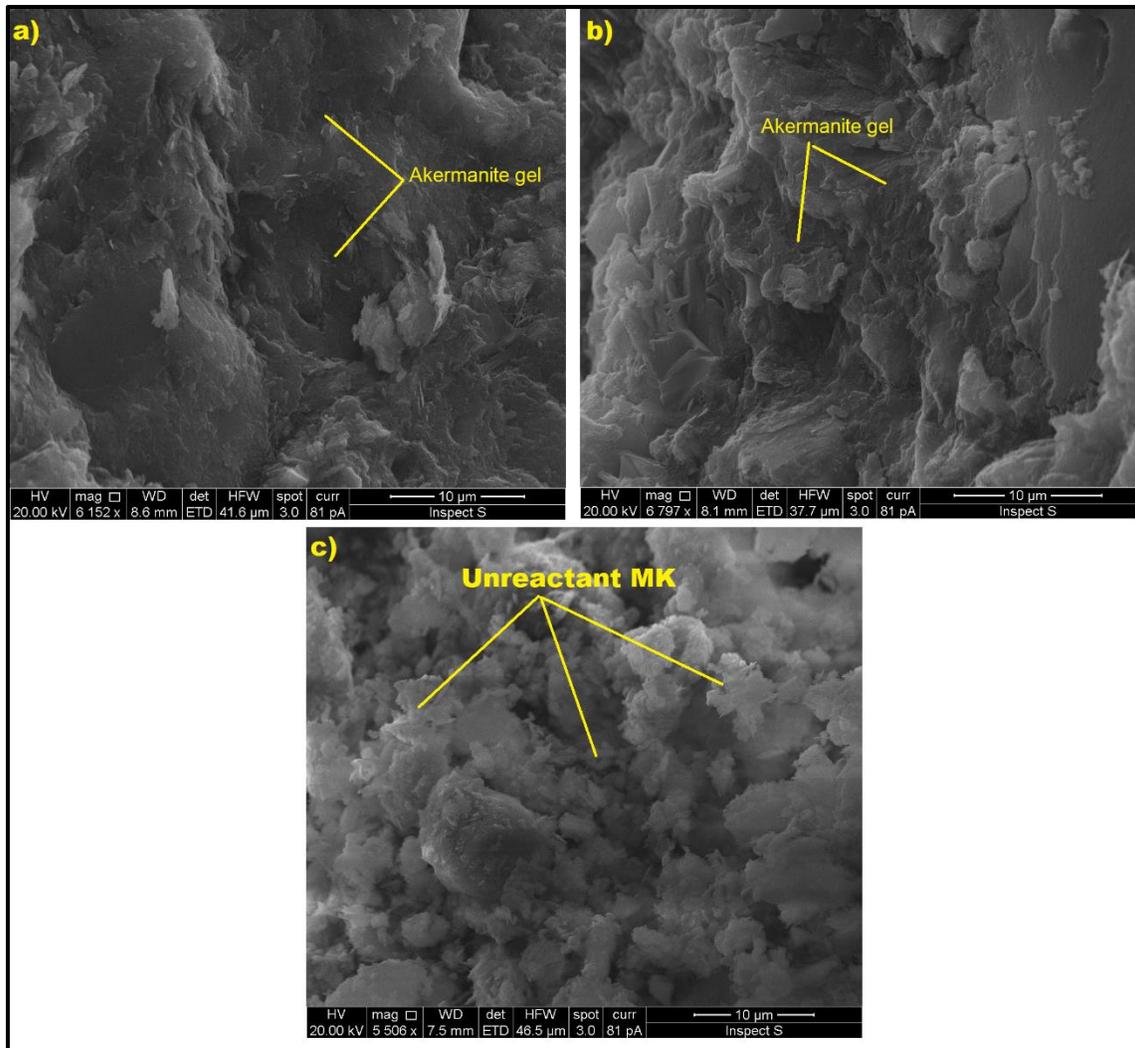


Figure 18 SEM micrographs for a) AAC3, b) AAC7 and c) AAC11 at 180 days

593

594

595

596 4. Conclusions

597 Based on the experimental outcomes of using thermally activated Lime Kiln Dust (LKD) that was
 598 proposed as solid waste material rich in calcium oxide in the formulation of a second generation
 599 one-part AAC cement, the following points can be summarised:

- 600 • More than 51% increase in strength after 28 days of curing just for highly reactive calcined
 601 LKD at temperature of 950°C was achieved in the blend containing metakaolin (35 wt.%) and
 602 natural pozzolan (30 wt.%).
- 603 • Significant increase of rate of strength development after 28 days of curing and continued until
 604 180 days that reached 51 MPa for increased proportion of 950°C calcined LKD and metakaolin
 605 was revealed.

- 606 • A high degree of alkali-activation was developing within the synthetic system until 180 days,
607 without showing any marks of efflorescence or presence of unreacted alkaline substances were
608 reported.
- 609 • The setting times of the optimised blends were in the acceptable range of setting times in the
610 past studies of one-part AAC and cement types in British standards.
- 611 • According to the results of XRD, TG-DTA and FTIR, the thermal treatment at 950°C were
612 evidently participating in breaking the crystalline phases of the original materials and showed
613 strong evidence of transforming to amorphous phases.
- 614 • The characterisation findings by XRD, FTIR and SEM, have confirmed that the development
615 of hydration products is responsible for the strength at 28, 90 and 180 days. These products
616 include stratlingite, St (C_2ASH_8) and Akermanite, (Ak) ($Ca_2MgSi_2O_7$).
- 617 • The developed one-part AAC has introduced a comparable performance, in regard of the
618 strength, setting times and morphology compositions, to the traditional AAC synthesised from
619 commercial hazardous chemicals. However, there are some limitations, i.e. the durability
620 investigations such as chloride and alkaline attacks which are recommended as a future work.
621

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626

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