A COMPARATIVE STUDY OF GEOPOLYMERS SYNTHESIZED FROM OXY-COMBUSTION AND CHEMICAL LOOPING COMBUSTION BOTTOM ASHES

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Abstract

The generation of geopolymers from OXY-FBC and CLC bottom ashes has not yet been reported. In this study, geopolymers from OXY-FBC and CLC bottom ash were synthesised and compared with geopolymers from FBC bottom ash. The bottom ashes used in this study were generated from the combustion of high ash South African coal. FBC and OXY-FBC bottom ashes were divided into two, viz: the first half was coarse, while the second half was grinded into fine particles. The bottom ashes were mixed with sodium silicate (Na_2SiO_2) and sodium hydroxide solutions (5M, 10M and 15M) and the pastes were cured at 60^oC for 10 days. The properties of the geopolymers were characterized using: TGA, FTIR and SEM-EDX techniques. TGA analysis showed that FBC geopolymer with 5M NaOH had the least amount of % weight loss, which indicates that it had a better thermal stability than synthesizing geopolymers with higher NaOH concentrations. Coarse FBC geopolymer (C-A1) had a higher thermal stability than fine FBC geopolymer (F-B1), therefore indicating that there is no need to grind the ash. OXY-FBC showed the opposite, therefore indicating the need to grind the ash in order to attain a better thermal stability of the geopolymer. The EDS analysis showed that the geopolymers produced an N-A-S-H gel and an incomplete N-A-S-H gel, instead of the C-(A)-S-H gel. Geopolymers synthesized from 5M NaOH (C-A1, F-B1 and C-C1), 10M NaOH (F-D2) and 15M NaOH (F-E3) had the most degree of geopolymerisation as seen on the FTIR spectrum. Geopolymers (F-D2) synthesized from 10M NaOH and fine OXY-FBC bottom ash had greater degree of geopolymerisation.

Keywords: Oxy-FBC, chemical looping combustion, bottom ash, geopolymers

1. Introduction

The depletion of high quality coals has resulted in the growth of the combustion of low grade coals for power. Fluidized bed combustors (FBC) are better suited for low grade coals because of its low operating temperature (800-950^{o}C) [1]. However, there is still the production of greenhouse gases, such as carbon dioxide (CO_2). The CO_2 emission can be reduced by using fluidized bed combustor (Oxy-FBC), which recycles the CO_2 back into the boiler for better capture [2]. Oxy-FBC also produce lower NO_x and SO_x emissions when compared to Air-FBC process. The absence of nitrogen in the oxidant leads to a lower NO_x emissions[2]. Sulphur capture is higher in OXY-FBC than in Air-FBC because the high partial pressure of CO_2, in OXY-FBC prevents the calcination of limestone and there increasing the sorption capacity of the limestone. In Air-FBC the rate of calcination of the limestone is high and this reduces its sorption capacity [2].

Another CO_2 capture technology that is carried out under fluidised bed conditions, is Chemical looping combustion (CLC). CLC is a process where metal oxides are used to transport the oxygen between the two reactors, fuel reactor and air reactor [3-5]. In the fuel reactor the metal oxide reacts with the fuel to produce CO_2 and H_2O as fuel gases [$(C_nH_n)_m + (2n+m)Me_xO_y \rightarrow nCO_2 + mH_2O + (2n+m)Me_xO_{y-1}$].The reduced metal oxide is transported into the air reactor in order to be oxidized by air [$O_2 + 2Me_xO_{y-1} \rightarrow 2Me_xO_y$], then oxidized metal oxide is cycled back into the fuel reactor where it will be reduced to (cyclization process) oxides fuels while capturing CO_2. There is a lower energy penalty for CO_2 capture in CLC than in OXY-FBC .

The bottom ashes generated from these CO_2 capture process (OXY-FBC and CLC) cannot be disposed to the environment (ground water and surface water) because of the enrichment of toxic trace elements in the ash samples. Font et al [6] reported that there was enrichment of Ca, Zr, Sb, Cr and V in coal ash generated from OXY-FBC process. Mendiara et al [7] reported that of Ni and Zn in coal ash generated from CLC process.

The production of gepolymers from the bottom ash can reduce or solve the waste disposal problem[8]. Coal bottom ashes have high content of silica and alumina are the key ingredients for the production of geopolymers[9].

Geopolymer is a synthetic inorganic alkali-activated aluminosilicates that is able to produce a Si-O-Al framework, which reacts and set rapidly at low temperatures resulting in a hard and stable product at high temperatures up to 1250ºC [10] Geopolymers have a variety of applications, such as new ceramics and cements, matrices for hazardous waste stabilization, tooling and molding, fire-resistant materials and high-tech materials [11]. Geopolymerization reaction involved four steps and they involve the following [12]

i. dissolution of Al and Si oxides from the ash aluminosilicate due to the strong alkaline liquid attack caused by sodium hydroxide and sodium silicate,
ii. formation of oligomer bonds such as Si–O–Si and Si–O–Al by polymerization
iii. formation of three dimensional aluminosilicate structures by the polycondensation of the oligomers and
iv. bonding of the remaining unreactive solid filler particles to the aluminosilicate network, to further enhance its strength and thermal stability

The reaction mechanism is illustrated in Figure 1 below[13].

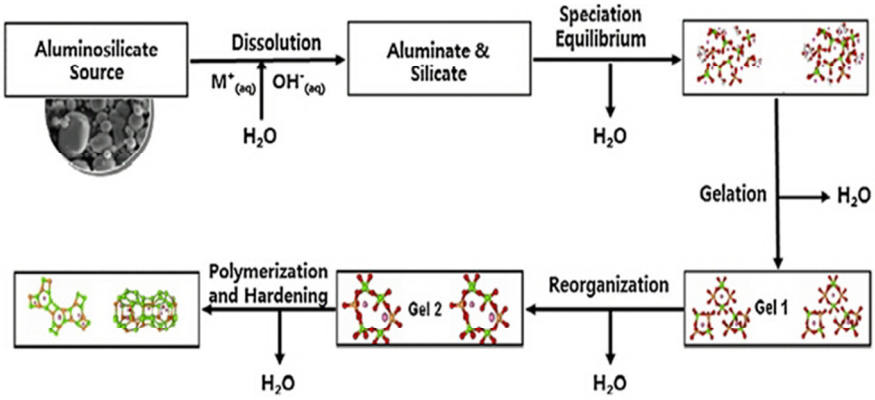

Figure 1: The reaction mechanism of geopolymerisation.[10-11]

The generation of gepolymers from Oxy-FBC and CLC bottom ashes has not been reported. The main objective of this study is to compare the properties of the geopolymer precursors produced from OXY-FBC, CLC and FBC bottom ashes. The degree of geopolymerisation was determined by FTIR, TGA and SEM-EDS analyses.

2. Experimental

2.1 Materials

The bottom ash was generated from the combustion of a high ash South African coal from FBC, OXY-FBC and CLC processes using a bubbling fluidised bed reactor. Full details of this reactor and the experimental conditions for bottom ash generation can be found in Mathekga et al. [12] FBC and OXY-FBC bottom ashes were divided into two halves, one half was grinded into fine particles (75 microns) and the other half was kept as coarse particles (600 microns). CLC bottom ash was grinded into fine particles (75 microns). An analytical grade of sodium hydroxide was prepared by mixing the NaOH pellets with distilled water in order to make 5M, 10M and 15M NaOH solutions, which were used as alkali fusion pre-treatment for the bottom ash. An industrial grade 3379 of sodium silicate (29.80% SiO_2, 9.16% Na_2O and 61.04% H_2O) was used for the preparation of the activating solution together with the prepared NaOH solutions [13-14]. The specific gravity of sodium silicate was 1.39g/cm^3.

2.2 Sample preparation

Fifteen geopolymer precursors (6 FBC, 6 OXY-FBC and 3 CLC) were prepared from mixing the activating solution (NaOH:Na_2SiO_3) with the ash for 7 minutes until a homogeneous mixture was obtained. [13] The activating solution was kept at a ratio of 1. Tables 1 and 2 indicate the proportions (ratios) in which the activating solution was mixed with the ash in order to obtain the geopolymer precursors. The C-A's and C-C's are coarse bottom ash from FBC bottom ash and OXY-FBC bottom ash, respectively, while the F-B's, F-D's and F-E's are the fine bottom ash from FBC bottom ash, OXY-FBC bottom ash and CLC bottom ash, respectively. The geopolymer precursors produced were poured into cubic polypropylene trays and the trapped air bubbles were removed by vibrating the polyethylene tray. The mold trays were then sealed with polyethylene film (to prevent moisture loss) and set in the oven at 60^{o}C for 48 hours, which was the initial curing [15]. After the initial curing, the sample were demoulded and then returned into the oven for the second curing for 192 hours at 60^{o}C, making a total curing time in the oven at 60^{o}C of 10 days.[15] The geopolymer precursors were then cured at room temperature for 10 days after the 10 days curing in the oven was completed.

Table 1: The mixing ratios for the geopolymer precursors synthesized from coarse bottom ashes

Precursors	C-C1	C-A2	C-A3	C-C1	C-C2	C-C3
[NaOH]	5M	10M	15M	5M	10M	15M
Bottom ash	FBC	FBC	FBC	OXY	OXY	OXY
Ash:Activation solution	1	1	1	1	1	1

Table 2: The mixing ratios for the geopolymer precursors synthesized from fine bottom ashes

Precursors	F-B1	F-B2	F-B3	F-D1	F-D2	F-D3	F-E1	F-E2	F-E3
[NaOH]	5M	10M	15M	5M	10M	15M	5M	10M	15M
Bottom ash	FBC	FBC	FBC	OXY	OXY	OXY	CLC	CLC	CLC
Ash: Activation solution	1	1	1	1	1	1	1	1	1

2.3 Analysis

Geopolymer precursors were analyzed with: FTIR, TGA and SEM coupled with EDS. Fourier transformation infrared spectroscopy (FTIR) was performed with a Perkin Elmer spectrum RX FT-IR system, the samples were analyzed using the KBr pellet technique (3mg powder sample mixed with 100mg of KBr) [16]. Thermo-gravimetric analysis (TGA) was conducted with Perkin Elmer TGA 7, with ~10mg per sample analyzed between the temperature range of 30-1000^{o}C in a nitrogen gas atmosphere, at a heating rate of 20^{o}C per minute [16-17] Scanning electron microscopy (SEM), coupled with energy dispersive X-ray spectrometer (EDS) was used for the study of the sample morphology, with the sample coated with gold particles in order to improve conductivity [16-18].

142

143 ## 3. Results

144 ### 3.1. FTIR spectrums for the raw bottom ashes and the synthesised geopolymers

145 Table 3 indicates the type of vibrational modes which are present on the spectra of observed
146 of the geopolymers and the range at which each mode vibrates (wavenumbers). The FTIR
147 spectrum shows the effectiveness of geopolymerisation by revealing the peaks that are not
148 present in the bottom ash, but are very prominent in the geopolymer. Figure 2 shows the
149 comparison between the bottom ashes spectra and it can be seen from the figure that there is
150 not a lot of difference in the spectra when they are superimposed on each other. FBC bottom
151 shows a broad peak of Si-O-Si at 1091cm^{-1}, while CLC shows a more prominent peak at
152 461cm^{-1} of the Si-O-Si group than the other ashes (seen in Table 3), following rearrangement
153 to form Si-O-Al during geopolymerisation. All the three ashes have no prominent peaks of
154 CO_2 and H_2O, which signifies the formation of geopolymers.

155 Table 3: The chemical composition of the geopolymer precursor and the bottom ash obtained
156 from a FTIR spectrum

Wavenumber (cm^{-1})	**Modes**
450-460	Si-O-Si and O-Si-O vibrational bending
675-685	Si-O-Si and Aℓ-O-Si symmetric stretching
770-780	Si-O-Si symmetric stretching
880	Si-O stretching
980-1100	T-O-Si (T=Si or Aℓ) Asymmetric stretching
1400-1460	CO_2 vibrational stretching (atmospheric carbonation)
1500-1600	H-O-H vibrational bending
2300-3500	(-OH) vibrational stretching

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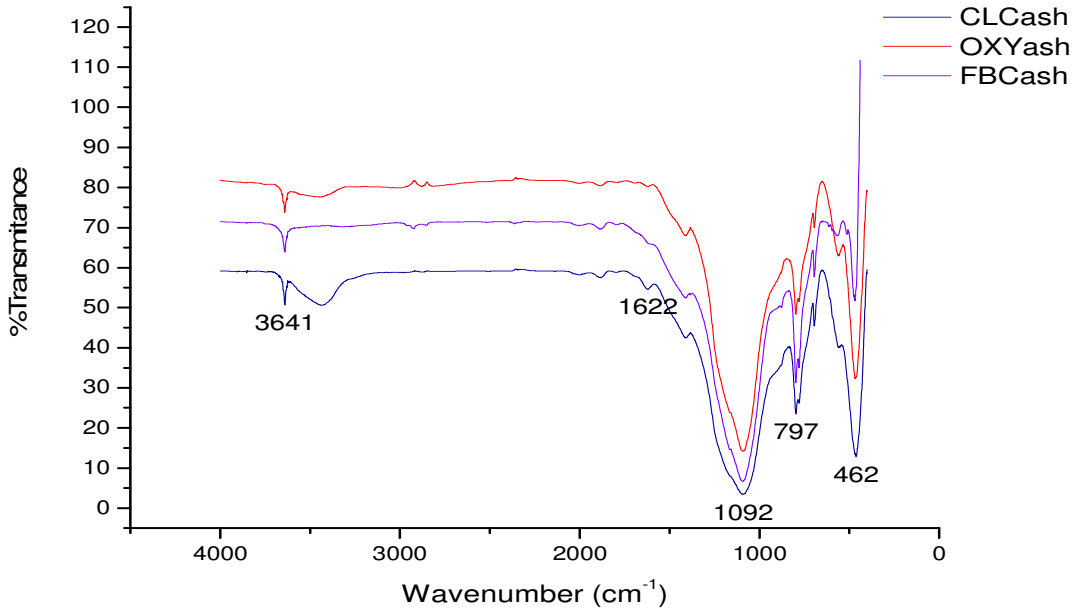
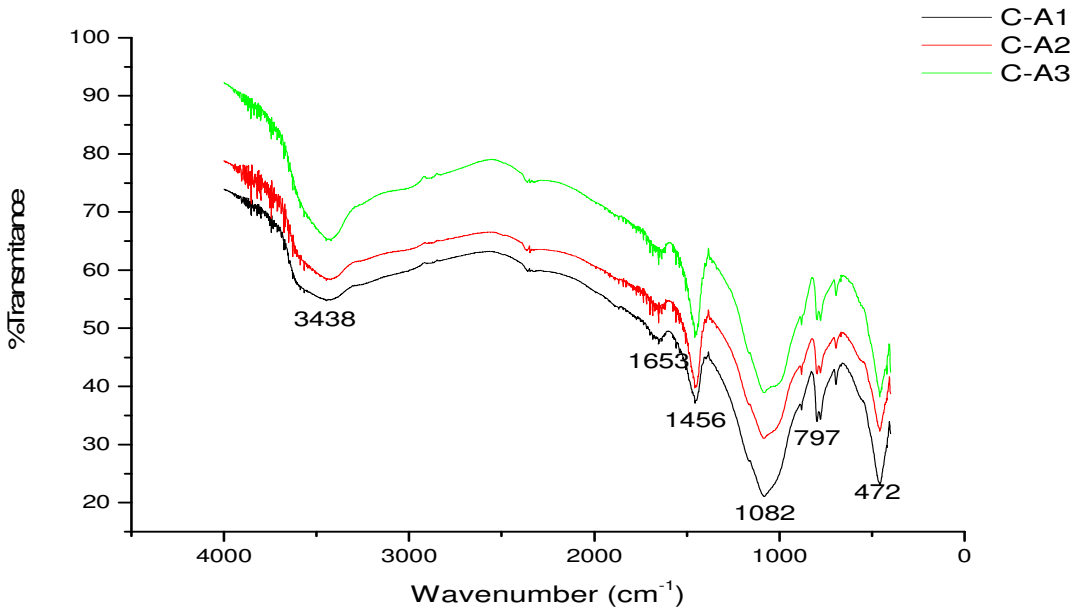


158

159 *Figure 2: The infrared spectrum for the bottom ashes*

160 The infrared spectra for geopolymers synthesied from the coarse FBC bottom ash, using
161 different NaOH cocentratiions are presented in Figure 3. The result shows that there is
162 evidence of geopolymerisation as seen from the presence of prominent peaks at 1460cm^{-1} for
163 O=C=O, 1645cm^{-1} which indicates the presence of water absorbed (H-O-H bending
164 vibration) and the broad band of T-O-Si (T=Si or Aℓ) asymmetric stretching as a
165 consequence of polycondensation with alternating Si-O or Al-O (T=Si or Aℓ), which are not
166 prominent in the Figure 2 for the FBC bottom ash C-A1 with 5M NaOH had the most
167 prominent/broad peaks at the indicated wavenumbers, which signifies geopolymerisation and
168 indicating the fact that more geopolymerisation took place with 5M NaOH than the other
169 NaOH concentrations.

170 The infrared spectra of the geopolymers synthesied from fine FBC bottom ash using
171 different NaOH cocentratiions are presented in Figure 4. F-B1 with 5M NaOH has the most
172 prominent/sharp peak at 1074cm^{-1}, and the highest degree of geopolymersiation. Similar
173 result was reported in the literature for a blend of fly ash and bottom ash from a circulating
174 fluidised bed reactor [15]. They obtained an increase in the broadness of bands 1095 cm^{-1} and
175 1089 cm^{-1} in the FTIR spectra using a 5M NaOH solution.



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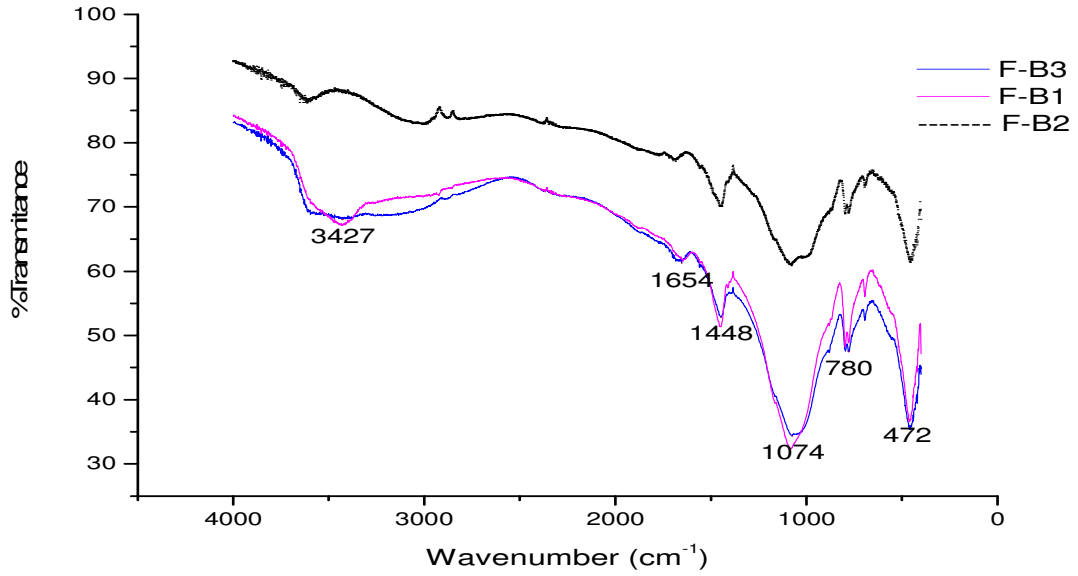
177 *Figure 3: Infrared spectrum for geopolymers synthesized from coarse FBC bottom ash*

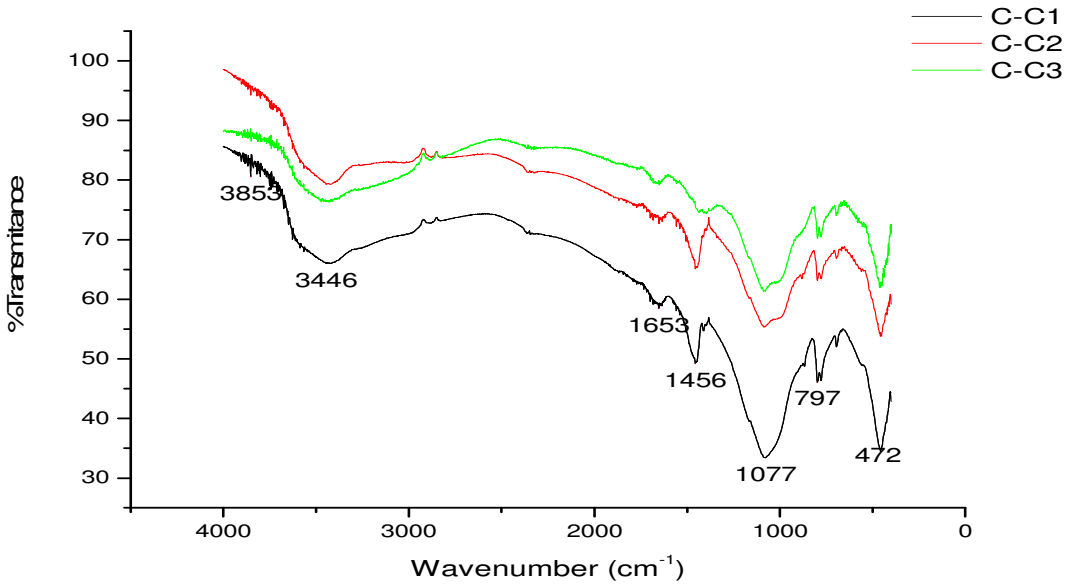


178

179 *Figure 4: Infrared spectrum for geopolymer synthesized from coarse FBC bottom ash*

180 The FTIR sprectra of the geopymers synthesized from coarse and fine OXY-FBC bottom
181 ashes are shown in Figures 5 and 6, respectively. It can be clearly seen that there is a degree
182 of geopolymerisation, since there are prominent peaks of CO_2 vibrational stretching, H-O-H
183 vibrational bending and –OH vibrational stretching, which are not prominent in the OXY-

184 FBC ash[7-8]. The geopolymers sythensised from coarse bottom ash C-C1 with 5M NaOH
185 had the most prominent/sharp peak at 1077cm^{-1}, therefore indicating a higher degree of
186 geopolymerisation than in C-C2 and C-C3 ashes. The geopolymers sythensised from fine
187 bottom ash F-D2 with 10 M NaOH had the most prominent peak at wavenumber 1082cm^{-1}
188 than the other geopolymer precursors (F-D1 and F-D3), therefore indicating that F-D2 had
189 the most 3D network structure being formed.



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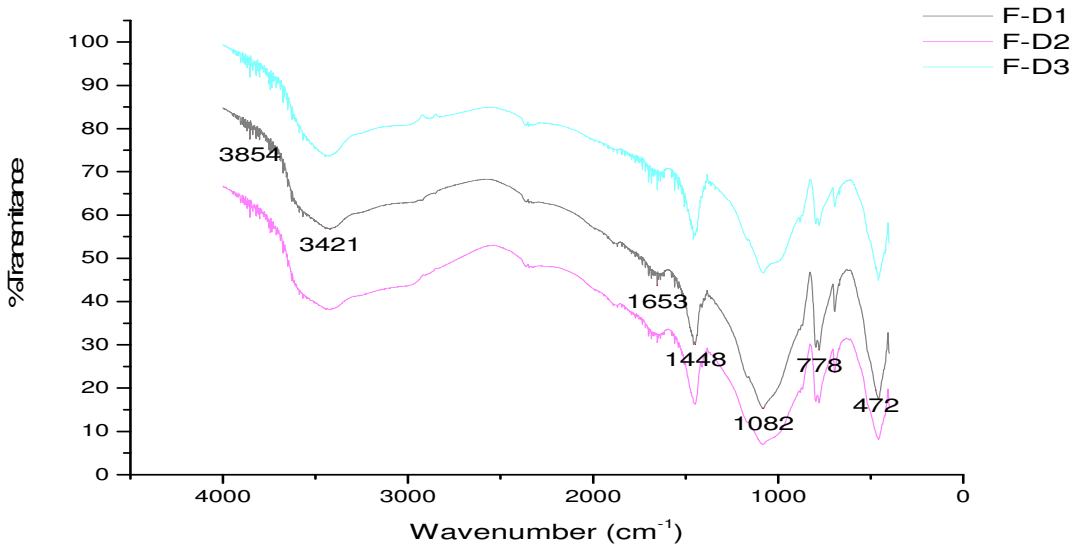
191 *Figure 5: Infrared spectrum for geopolymers synthesized from coarse OXY-FBC bottom ash*



192

193 *Figure 6: Infrared spectrum for geopolymers synthesized from fine OXY-FBC bottom ash*

The spectra in Figure 7 show that the peaks for CO_2 and H-O-H were more prominent for the geopolymer than for the CLC bottom ash shown in Figure 2. Between the three geopolymers, F-E3 had the most prominent peaks, indicating the fact that geopolymers synthesized from 15M NaOH resulted in greater degree of geopolymerisation than those synthesized with low NaOH concentration.

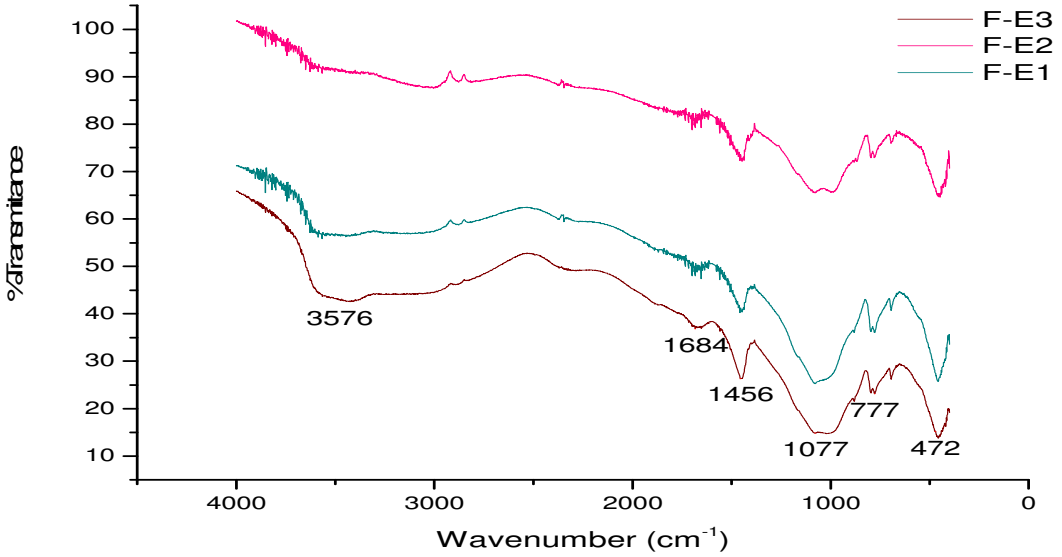
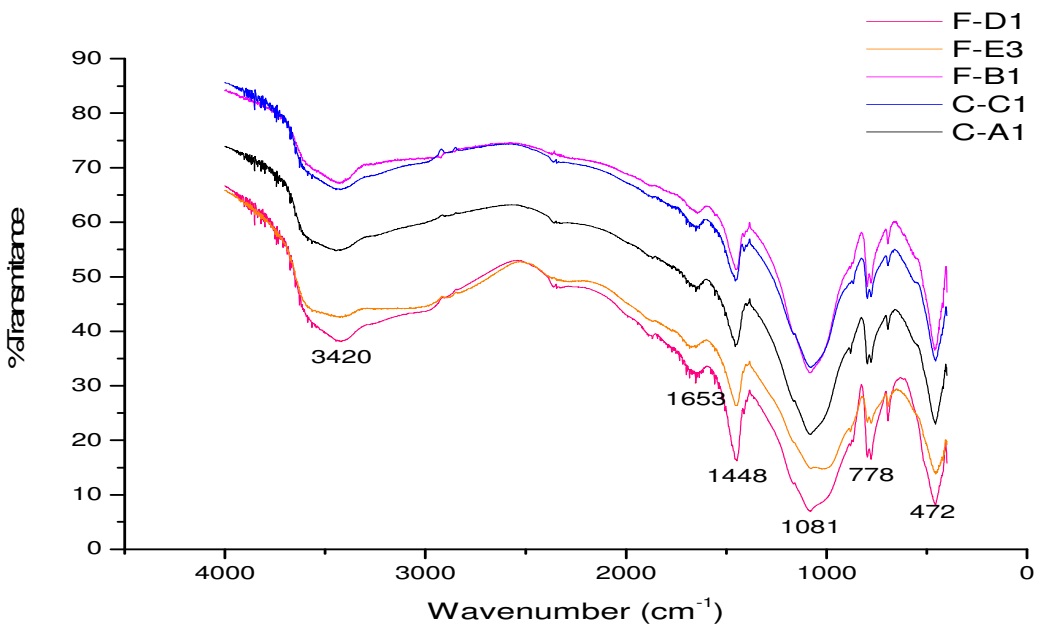


Figure 7: The infrared spectrum for geopolymers synthesized from CLC bottom ash

A comparasion of the best conditions for the various gepolymers sythensised from coarse and fine bottom ashes of FBC, OXY-FBC and fine bottom ash from CLC is presented in Figure 8. From the spectra, it can be seen that F-D2 had the most prominent peaks at 1081cm^{-1} and 1446cm^{-1}, which indicate a good degree of geopolymerisation and therefore confirming the fact that fine OXY-FBC bottom ash with 10M NaOH produced the best geopolymer than the other geopolymer precursors.



209

210 *Figure 8: Comparison of infrared spectrum for geopolymers with the most degree of*
211 *polymerisation*

212

213 3.2 The TGA analysis for geopolymers synthesized from bottom ashes

214 The thermal stability of the geopolymers were evaluated by a TGA. The reduction in weight
215 loss was due to the loss of water during the curing of the geopolymer precursors at 60°C. At
216 temperature below 250°C, a certain degree of weight loss is attained, while the remaining
217 water was either tightly bounded or less able diffuse to the surface of the geopolymer,
218 therefore continues to evolve at higher temperature, above 250°C in a dehydration reaction,
219 where it is lost as gas [$2(SiO_3^{2-} \cdot 2M+) \rightarrow (SiO_3^{2-} \cdot 2M+)_2 + \uparrow H_2O$ (g)] [16, 20-21]. The three
220 bottom ashes had a similar % weight loss trend, except for the FBC bottom ash that has a 2%
221 weight loss, while CLC and OXY-FBC bottom ashes had 1% and 1.1%, respectively, as seen
222 in Figure 9.

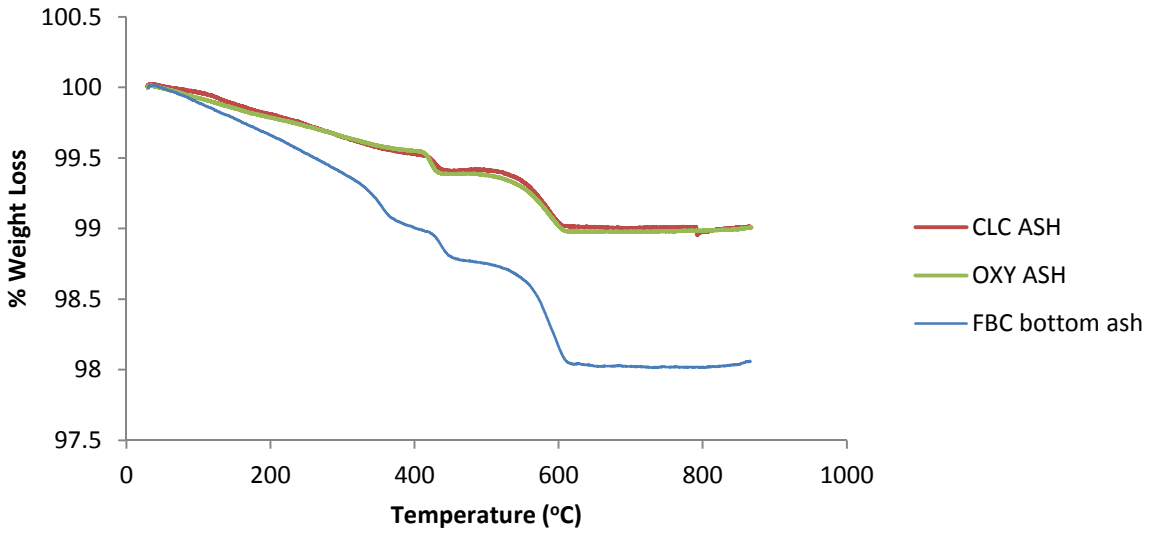
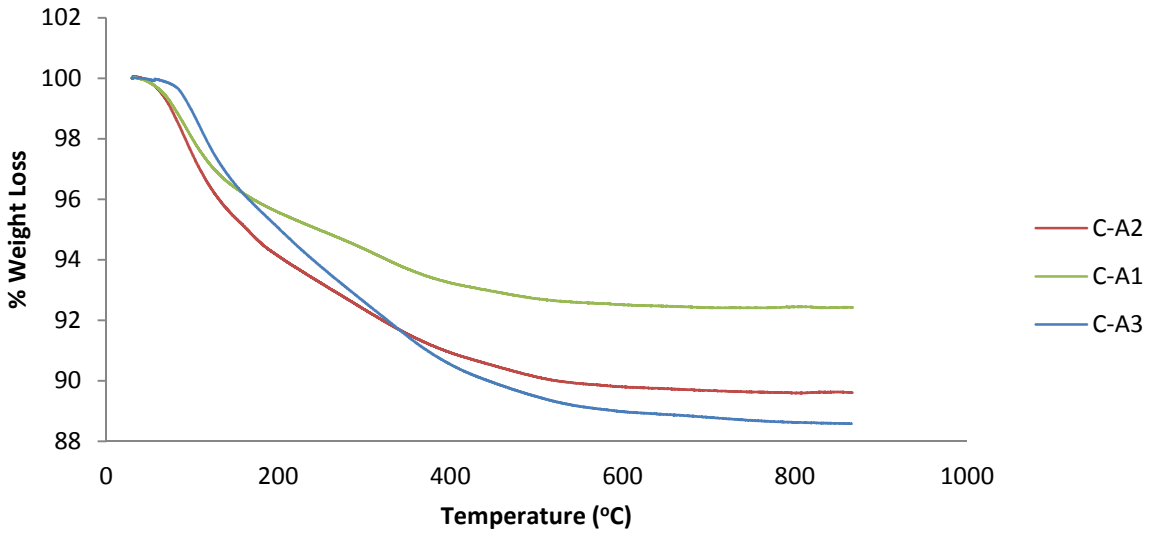


Figure 9: Comparison of the % weight loss of the three bottom ashes

Figures 10 and 11 show the weight losses for the coarse and fine geopolymer precursors, respectively. The results were similar. The coarse FBC geopolymers, C-A1 (5M NaOH) had the least amount of weight loss of 5% at <250^{o}C and a 3% weight loss, as gas at higher (>250^{o}C) temperature. C-A2 (10M NaOH) and C-A3 (15M NaOH) had lost ~11% and 11.6%, respectively with 6% loss at <250^{o}C, while the rest of the water lost as gas at higher (>250^{o}C) temperature. The fine FBC geopolymers, F-B1 (5M NaOH) had the least amount of weight loss with a total of 9.2%. F-B2 and F-B3 had 11.8% and 14.2% weight losses, respectively, where 6.5% of water was lost <250^{o}C, while the rest of the water evolved as gas at higher (>250^{o}C) temperature. As a group, geopolymers synthesized from coarse FBC bottom ash had a lower weight loss when compared with geopolymers synthesized from fine FBC bottom ash and therefore, indicating the fact that coarse FBC geopolymers had a better thermal stability and hence, it is unnecessary to grind the FBC bottom ash before its synthesis into geopolymers.



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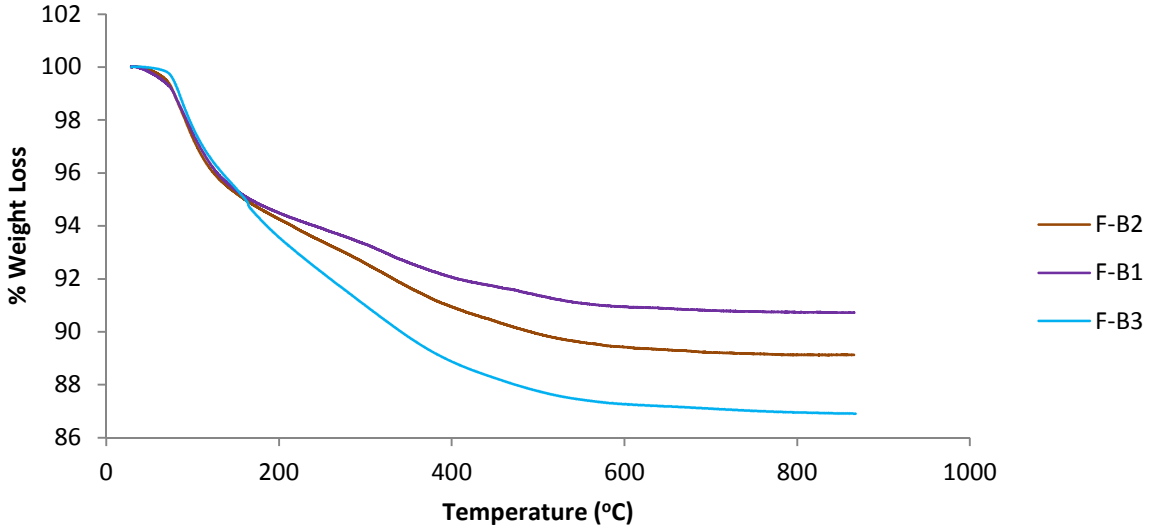
240 *Figure 10: Comparison of % weight loss of geopolymers precursors synthesized from coarse*
241 *FBC bottom ash*



242

243 *Figure 11: Comparison of % weight loss of geopolymers precursors synthesized from fine*
244 *FBC bottom ash*

245 The % weight loss for geopolymers synthesized from the coarse and fine OXY-FBC ashes
246 (Figure 12 and 13) had similar thermal stability as the FBC geopolymers (Figures 9 and 10).
247 Geopolymers synthesized with 5M NaOH from the coarse (C-C1) and fine (F-D1) OXY-FBC
248 ashes, had the least amount of weight loss during curing at 60^{o}C, as seen in Figures 12 and
249 13. F-D1 had the least amount of weight loss when compared with C-C1 (8.4% and 8.8%,
250 respectively), therefore F-D1 exhibited a better thermal stability than C-C1, which shows that

there is a need to grind the OXY-FBC bottom ash before geopolymers synthesis. Geopolymers synthesized with 10M NaOH from the coarse(C-C2) and fine (F-D2) OXY-FBC bottom ashes, had the same amount of weight loss of ~10.4%, indicating the fact that their thermal stability is the same. Geopolymers synthesized with 15M NaOH from the coarse (C-C3) and fine (F-D3) OXY-FBC bottom ashes, showed that fine OXY-FBC geopolymer (C-C3) had better thermal stability than F-D3, since the weight losses were 11% and 12.4%, respectively.

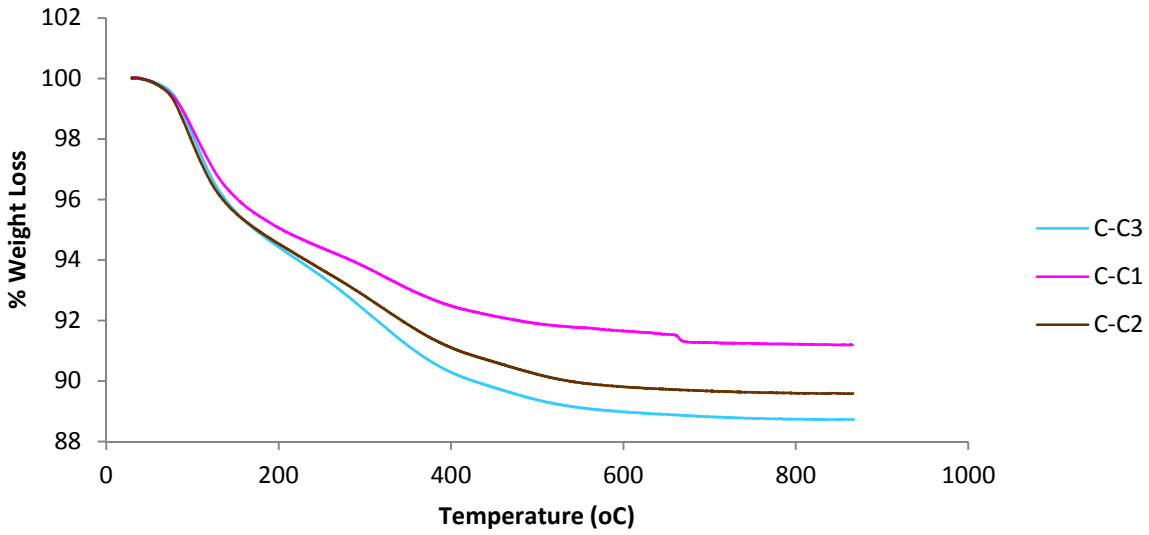


Figure 12: Comparison of % weight loss of geopolymer precursors synthesized from coarse OXY-FBC bottom ash

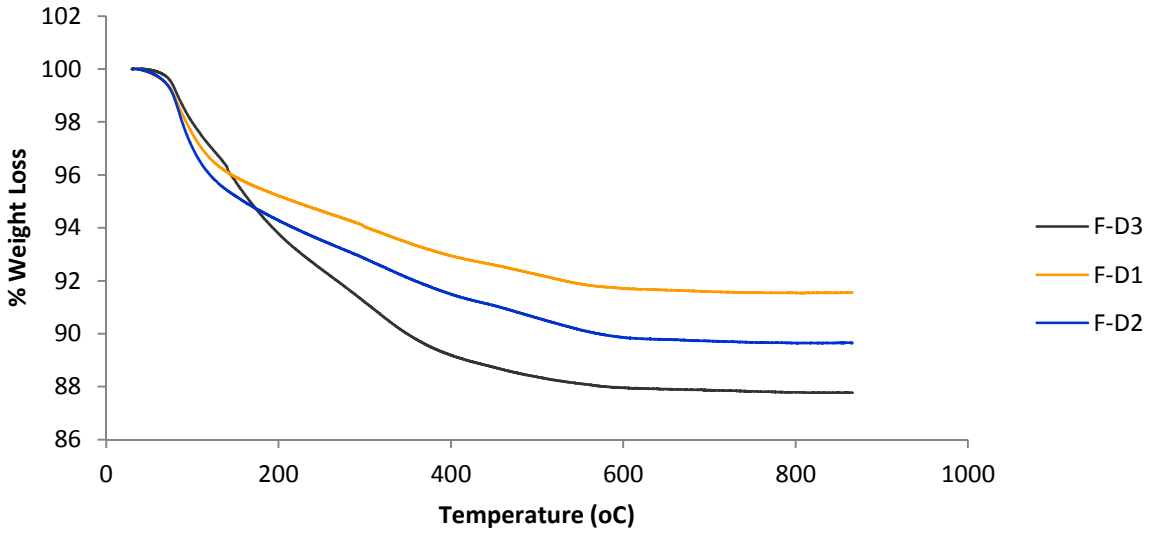


Figure 13: Comparison of % weight loss of geopolymer precursors synthesized from fine OXY-FBC bottom ash

Figure 14 shows the weight losses of fine CLC geopolymer precursors and F-E1 (5M NaOH) had the a least amount of weight loss than CLC geopolymer precursors synthesized at higher temperatures. F-E1 had about 9.2% weight loss which is the same as F-B1 weight loss, while F-E2 had about 10.8% and F-E3 had about 13.2%. F-E1 had a better thermal stability, indicating the fact that CLC bottom ash requires low NaOH concentration in order to produce geopolymer with good thermal stability.

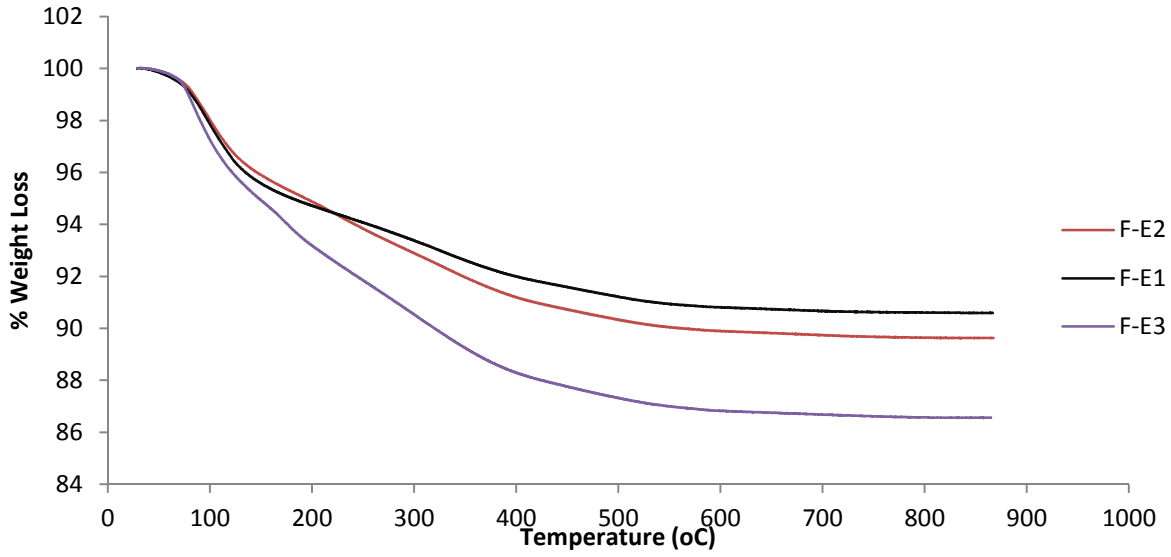


Figure 14: comparison of % weight loss of geopolymer precursors synthesized CLC bottom ash

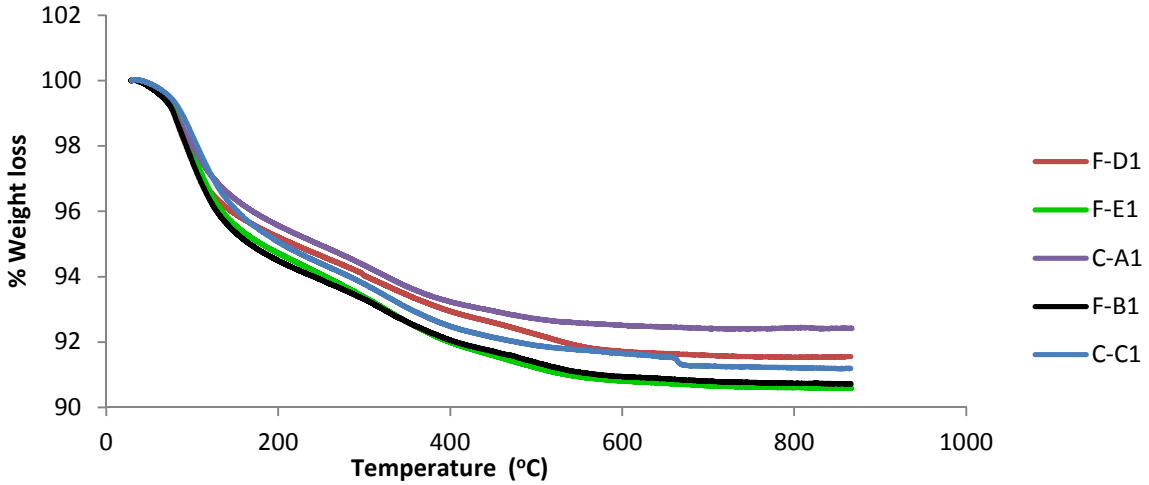


Figure 15: comparison of geopolymer precursors with the least % weight loss

Figure 15 shows the comparison between the geopolymer precursors with the least weight loss, which will help in the identification of the geopolymer with the highest thermal stability. Geopolymers synthesized with 5M NaOH had greatest thermal stability than those synthesized with higher NaOH concentrations. F-E1 and F-B1 had the same weight loss, hence they are superimposed on each other, as seen in Figure 15. C-A1 had the least weight loss, indicating a better thermal stability than the rest of the geopolymers and therefore, it can be inferred that coarse FBC bottom ash produces a better geopolymer.

3.3 SEM and EDS results for geopolymers synthesized from bottom ash

SEM-EDS analysis is one of the tools used in evaluating the microstructural properties of geopolymers. The morphology of geopolymers is evaluated using the SEM analysis and the elemental composition of the geopolymer is evaluated by doing the EDS analysis. The EDS analysis for geopolymers synthesized from air-FBC bottom ash is presented in Table 3 and based on the composition of the geopolymer, it has an N-A-S-H gel[22-23] The Si/Na ratio of geopolymers (C-C1-3) synthesized from coarse FBC bottom ash is greater than 2, therefore, indicating a moderate degree of reaction in the system due to the high content of unreacted Si[22-23]. C-A1 had a higher Si/Aℓ ratio, indicating that it should result in a high compressive strength[22-23]. Fine FBC geopolymer precursors resulted in an incomplete N-A-S-H gel since the Si/Na ratio was greater than 1, therefore there was a moderate degree of geopolymerisation reaction.

Table 3: EDS data for geopolymers synthesized from FBC bottom ash

	O	**Na**	**Aℓ**	**Si**	**P**	**K**	**Ca**	**Mg**	**Si/Aℓ**	**Si/Na**	**Na/Si**
C-A1	53.75	5.65	5.75	23.71	1.78	0.26	0.37	-	4.12	4.19	0.24
C-A2	60.21	3.07	8.67	23.48	1.29	0.28	-	-	2.71	7.65	0.13
C-A3	49.62	7.74	15.37	21.03	0.96	0.84	-	0.28	1.37	2.72	0.37
F-B1	59.08	5.21	1.99	28.45	0.77	0.29	2.15	-	14.30	5.46	0.18
F-B2	45.85	9.28	11.80	14.13	0.91	1.42	2.84	-	1.20	1.50	0.66
F-B3	45.75	10.25	5.86	29.31	0.50	-	2.48	-	5	2.86	0.35

Based on Figure 16, it is clearly seen that an incomplete N-A-S-H gel was formed for geopolymers synthesized from coarse FBC bottom ash, since there are unreacted particles on the geopolymer surface [24-25]. C-C3 had cracks on the surface due to the extra water retained during curing [24-25]. From Figure 16-f, it can be seen that the surface of F-B3 geopolymer is similar to the incomplete N-A-S-H gel in F-B1 and F-B2 with large unreacted Si or Aℓ particles.

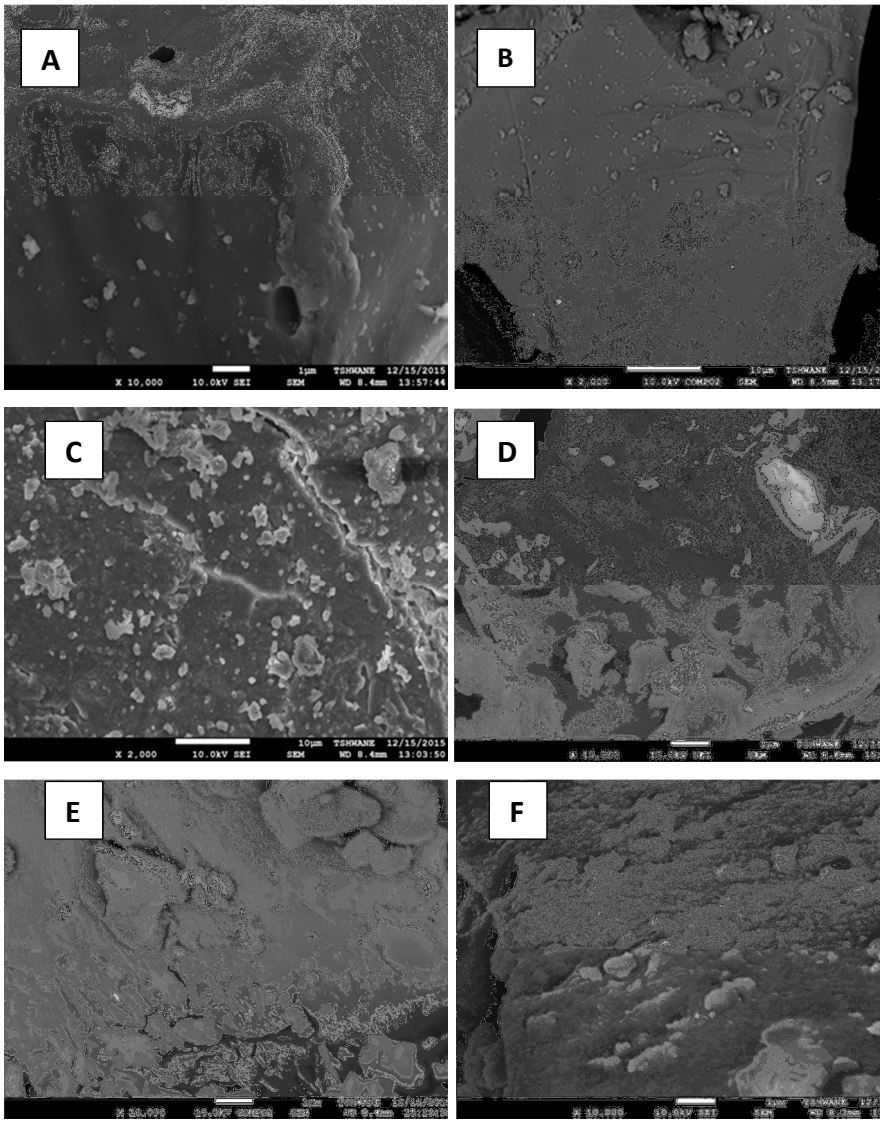


Figure 16: SEM morphology of FBC coarse and fine geopolymer precursors; (a) C-A1 with 5M NaOH, (b) C-A2 with 10M NaOH, (c) C-A3 with 15M NaOH, (d) F-B1 with 5M NaOH, (e) F-B2 with 10M NaOH and (f) F-B3 with 15MNaOH

Table 4: EDS data for geopolymers synthesized from OXY-FBC bottom ash

	O	Na	Aℓ	Si	P	K	Ca	Br	Si/Aℓ	Si/Na	Na/Si
C-C1	51	4.75	11	15.99	-	-	-	-	1.45	3.37	0.30
C-C2	50.88	12.86	3.24	24.24	-	0.27	0.40	-	7.08	1.88	0.53
C-C3	52.55	13.30	10.36	11.48	-	0.31	-	-	1.11	0.89	1.12
F-D1	28.43	3.45	51.81	-	2.75	-	-	3.93	-	-	-
F-D2	43.04	7.36	1.13	34.79	0.96	-	-	-	30.79	4.73	0.21
F-D3	53.83	18.38	1.36	16.33	0.96	-	3.72	-	12	0.89	1.13

Table 4 shows that geopolymers synthesized from OXY-FBC bottom ash had three incomplete N-A-S-H gels formed, viz: C-S-H gel and two compact amorphous N-A-S-H structures. C-C1, C-C2 and F-D2 had an incomplete N-A-S-H gel formed since their Si/Na ratio was greater than 2, while C-C3 had Si/Na ratio which was approximately 1, therefore indicating a compact amorphous N-A-S-H structure had formed [22-23]. C-C2 is expected to have higher compressive strength since the Si/Aℓ ratio is huge. F-D1 had resulted in a C-S-H gel structure, since there was zero content of Si, therefore forming aluminates structures. F-D2 had an incomplete N-A-S-H gel formed, while F-D3 had a compact amorphous N-A-S-H structure since the ratio of Si/Na was approximately 1 [22-24]. Oxy-FBC bottom ash had a diversity of ash particle sizes, with some being large while others were small as seen from Figure 17-a. Coarse OXY-FBC geopolymer (C-C1) had more cracks with particles of ash on the surface, which indicates an incomplete geopolymerisation [22-25]. C-C2 had few large ash particles on the surface. C-C3 had large particles of compared structure with few tiny ash particles on the surface. Fine OXY-FBC geopolymer prepared with 5M NaOH had crystal particles and large unreacted particles on the surface, which can be Aℓ atoms, since zero content of Si was not detected by the EDS, as seen in Figure 17-e [22-23]. F-D2 had irregular surface, which indicates incomplete reaction of the geopolymerisation [22-25]. F-D3 had a large crack which resulted from the retention of more water during the curing of the material.[22-26]

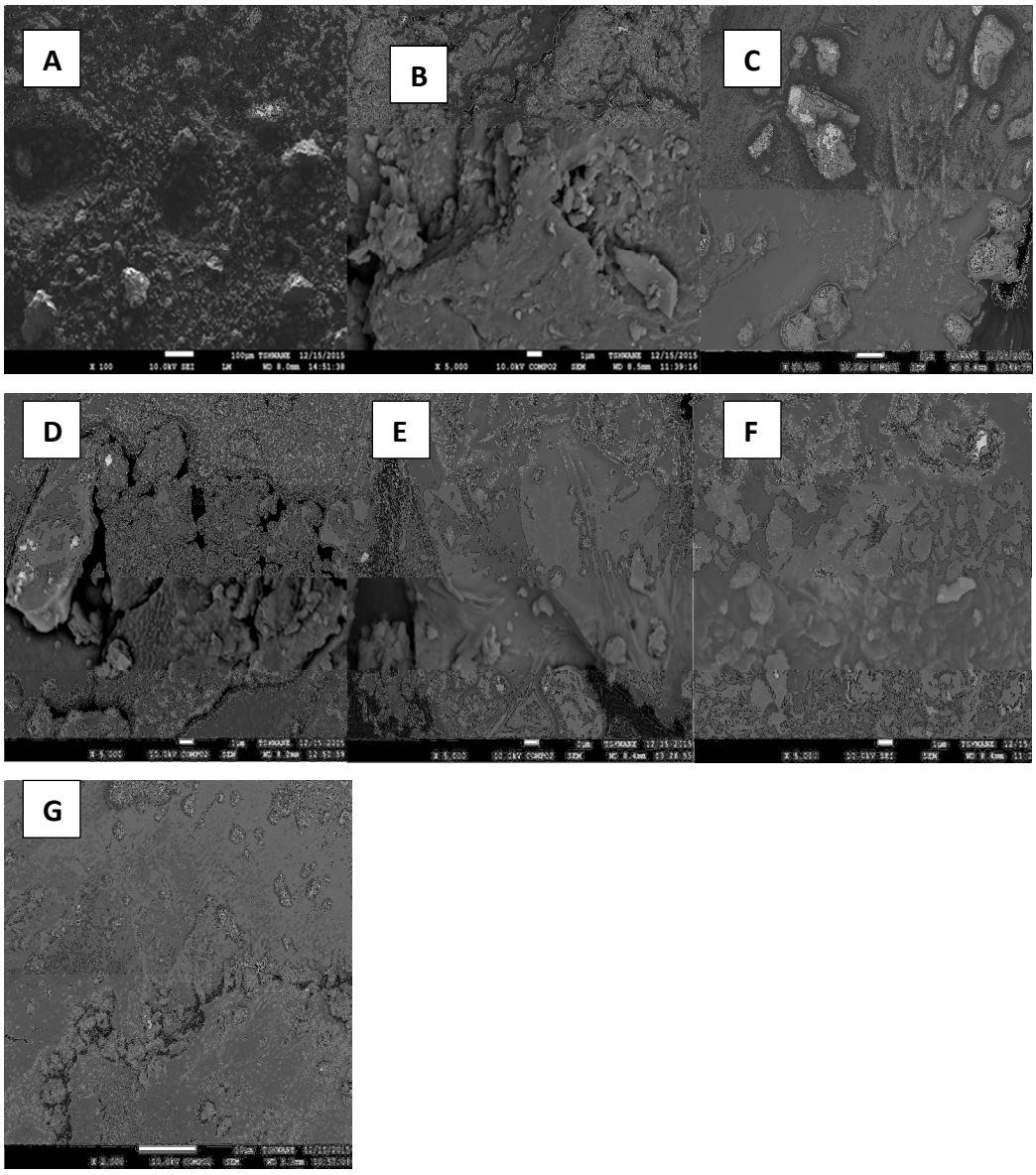


Figure 17: SEM morphology of OXY-FBC ash and geopolymers; (a) Oxy-bottom ash, (b) F-D1 with 5M NaOH, (c) F-D2 with 10 M NaOH, (d) F-D3 with 15M NaOH, (e) C-C1 with 5M NaOH, (f) C-C2 with 10M NaOH and (g) C-C3 with 15M NaOH

Table 5: EDS data for geopolymers synthesized from CLC bottom ash

	O	Na	Aℓ	Si	K	P	Ca	Cu	Si/Aℓ	Si/Na	Na/Si
F-E1	51.52	11.11	10.25	18.52	1.67	-	0.97	-	1.81	1.67	0.61
F-E2	50.79	2.54	4.98	33.25	1.53	-	-	2.39	6.68	13.09	0.08
F-E3	47.65	4.30	18.10	22.80	2.09	5.09	-	-	1.26	5.30	0.19

The CLC geopolymers had incomplete N-A-S-H gel being formed, since the Si/Na ratio for all three CLC geopolymers were greater than 1, as seen in Table 5. F-E2 had the most drastic incomplete N-A-S-H gel formed with Si/Na ratio of ~13.90, indicating the fact that the precursor paste solidified faster before the geopolymerisation could come to completion, which is seen by the high content of silica that forced the reaction not to come to completion [22-24]. F-E1 had a better N-A-S-H gel structure since its Si/Na ratio was not far from 1 when compared with the other two CLC geopolymers [22-24]. F-E2 is expected to have a high compressive strength due to the high Si/Aℓ ratio[22-24]. CLC bottom ash morphology showed large irregular particles with varied sizes and tiny pores on their surfaces, as seen in Figure 18-a [25-26]. F-E1 had many large cracks on the surface and many irregular particles, which are similar to the CLC ash in Figure 18-a. F-E2 had the most compact structure with large particles on the surface, while F-E3 had tiny particles (in size) on the surface with a large crack, as seen in Figure 18-c,d [25-26].

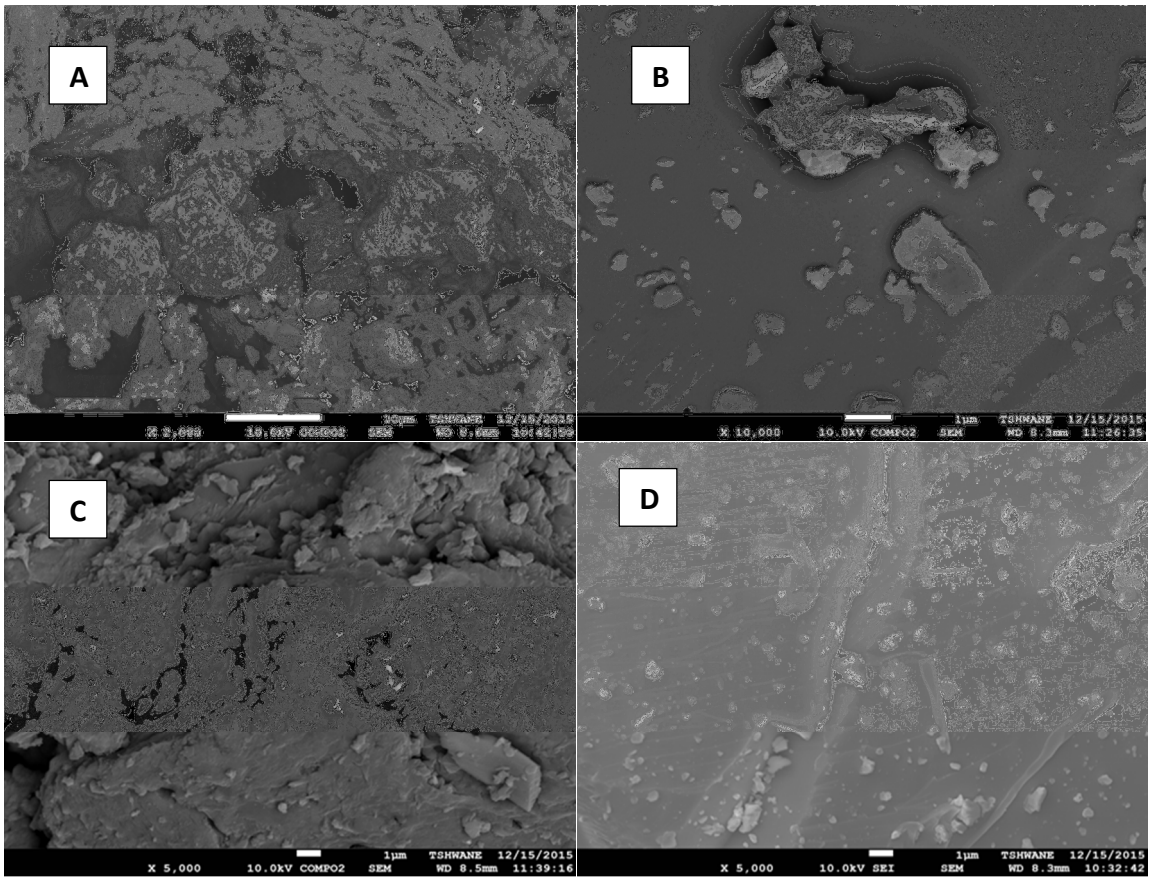


Figure 17: SEM morphology of CLC ash and geopolymers; (a) CLC bottom ash, (b) F-E1 with 5M NaOH, (c) F-E2 with 10M NaOH and (d) F-E3 with 15M NaOH

4. Application of geopolymer binders from FBC, OXY-FBC and CLC bottom ashes for the construction industry

There might be a need for the blending of a more reactivity material such as metakaolin with FBC, OXY-FBC and CLC bottom ashes in the production of geopolymer for binders in the construction industry. This is due to an incomplete formation of a dense N-A-S-H gel, hence a low moderate degree of geopolymerisation. This was more prominent in the geopolymer synthesized from CLC bottom ash.

Conclusions

This study has proved that geopolymers can be synthesized from FBC, OXY-FBC and CLC bottom ashes. Geopolymers synthesized from bottom ash has resulted in similar qualities as geopolymers synthesized from fly ash. The use of different NaOH concentrations, has resulted in a diversity of the degree of geopolymerisation. Geopolymers synthesized with 5M NaOH (C-A1, F-B1 and C-C1), 10M NaOH (F-D2) and 15M NaOH (F-E3) had the most degree of geopolymerisation, as seen in their FTIR spectra. Geopolymers (F-D2) synthesized with 10M NaOH and fine OXY-FBC bottom ash had greater degree of geopolymerisation. The EDS has shown that a N-A-S-H and an incomplete N-A-S-H gels had formed during the geopolymerisation of the ashes at different NaOH concentrations. Only two geopolymers synthesized from OXY-FBC bottom ash had resulted in amorphous compact N-A-S-H gels, one synthesized from coarse OXY-FBC bottom at 15M NaOH and the other from fine OXY-FBC bottom ash at 15M NaOH. The SEM images displayed a variety of complex structures with most of them having particles on their surfaces and, some having large cracks which had resulted in structural integrity being lost.

The thermal stability of the geopolymer precursors was analysed using TGA, where most of the water was lost below 250^{o}C, while the remaining water evolved as gas at hightemperature. Geopolymers synthesized with 5M NaOH using FBC, OXY-FBC and CLC bottom ashes (C-A1, F-B1, C-C1, F-D1 and F-E1) had the most thermal stability. C-A1 proved to have highest thermal stability, since it had lost the least amount of water, therefore indicating the fact that FBC bottom ash does not need to be grinded before synthesis into geopolymers. In the case of OXY-FBC geopolymers, the ash needs to be grinded since the coarse OXY-FBC geopolymer (C-C1) retained more water than the fine OXY-FBC geopolymer F-D1).

5. References

1. Basu P and Fraser SA. Circulating fluidized bed boilers: Design and operations. USA. Butterwort-Heinemann. 1991. Pg 95-112 & 256-257
2. Wu Y, Wang C, Tan Y, Jai L and Anthony EJ.. Characterization of ashes from a 100kWth pilot scale circulating fluidized bed with oxy fuel combustion. Applied Energy 2011. (88): 2940-2948
3. Lyngfelt A. Oxygen carriers for chemical looping combustion-4000h of operational experience. Oil & Gas Science and Technology – Rev. IFP Energies nouvelles 2011 (66): 161-172
4. Cormos CC, Cormos AM and Petrescu L. Assessment of chemical looping-based conceptual designs for high efficient hydrogen and power co-generation applied to gasification processes. Chemical Engineering Research and Design 2014. (92): 741-751
5. Hallberg P, Jing D and Rydén, M. Chemical Looping Combustion and Chemical Looping with Oxygen Uncoupling Experiments in a Batch Reactor Using Spray-Dried $CaMn1–xMxO_3$ (M=Ti, Fe, Mg) Particles as Oxygen Carriers. Energy and Fuels. 2013. 27(3): 1473-1481
6. Font O, Cordoba P, Lieva C, Romeo LM, Bolea I, Gueada I, Moreno N, Querol X, Fernandez, Diez LI. Fate and abatement of mercury and other trace elements in a coal fluidised bed oxy combustion pilot plant. Fuel 2012; 95:272-81.
7. Mendiara T, Gayan P, Abad A, Garcia-Labiano F, de Diego LF, Adanez J. Characterisation for disposal of Fe-based oxygen carriers from a CLC unit burning coal. Fuel Processing Technology 2015;138:750-757.
8. Sathonsaowaphak A, Chindaprasit P and Pimraka K.. Workability and strength of lignite bottom ash geopolymer mortar. Journal of Hazardous Material 2009. (168): 45-50
9. Li Q, Xu H, Li P, Li F, Shen L and Zhai J. Synthesis of geopolymer composites from blends of CFBC fly ash and bottom ashes. Fuel 2012 (97): 366-372.
10. Bakharev T. Geopolymeric material prepared using class F fly ash and elevated temperature curing. *Cement and Concrete Research,* 2005. (35): 1224-1232
11. Davidovits, J. 2002. 30 years of successes and failures in geopolymer applications. Market trends and potential breakthroughs. *Keynote Conference on Geopolymer Conference.*

12. Mathekga HI Oboirien BO, Engelbrecht A, North BC and K Premlall. Performance evaluation of South African coals under Oxy-fuel combustion in a Fluidised Bed Reactor. Energy and Fuels, 2016 (30):6756-6763
13. Swanepol JC and Strydom CA... Utilisation of fly ash in a geopolymeric material. Applied Geochemistry 2002. (17). 1143-1148
14. Christopoulos K, Mousios E, Anastasiadou K and Gidarakos E. solidification/stabilization of fly and bottom ash from medical waste incineration facility. Journal of Hazardous Materials 2012. (207-208): 165-170
15. Xu H, Li Q, Shen L, Wang W and Zhai J. synthesis of thermostable geopolymers from circulating fluidized bed combustion (CFBC) bottom ashes. Journal of Hazardous Materials 2010 (175):198-204
16. Van Deventer JSJ, Provis JL, Duxson P and Lukey GC. Reaction mechanisms in the geopolymeric conversion of inorganic waste to useful products. Journal of Hazardous Materials 2007. (139): 506–513
17. Rosas-CAsarez CA, Arrendondo-Rea SP, Gómez-Soberón JM, Alamaral-Sanchez JL, Corral-Higuer R, Chinchillas-Chinchillas MJ and etc. Experimental study of XRD, FTIR and TGA techniques in geopolymeric materials. International Journal of Advances in Computer Science and Its Applications,.2014. 4(4). 221-226
18. Zhang Z, Provis JL, Reid A and Wang H. Fly ash-based geopolymers. The relationship between composition, pore structure and efflorescence. 23rd Australasian Conference on the Mechanics of Structures and Materials (ACMSM23) Byron Bay, Australia, 9-12 December 2014, S.T. Smith (Ed.)
19. Santa RAAB, Bernardin AM, Humbetro GR and Kuhen NC. Geopolymer synthesized from bottom ash coal ash and calcined paper sludge. Journal of Cleaner Production 2013. (57): 302-307
20. Lancelloti I, Cannio M, Ballino F, Catauro M, Barbieri L and Leonelli C. Geopolymers: An option for the valorization of incinerator bottom ash derived "end waste" Ceramics International 2015. (41): 2116-2123
21. Haqn E, Padmanabhan SK and Licciulli A. Synthesis and characteristics of fly ash and bottom ash based geopolymers–A comparative study. Ceramics International 2014. (40): 2965–2971
22. Zhu P, Kai G, Kenan F, Sanjayan JG, Wenhui D and Collins F. Damping capacity of fly ash-based geopolymer. 18th International Conference on Composite Materials 2014

469 23. Topçu IB and Toprak MU. Properties of geopolymers from circulating fluidized
470 bed combustion coal bottom ash Materials Science and Engineering: A, 2011.
471 (528). 1472-1477
472 24. Gou X, Yu QL and Brouwers HJH. Reaction kinetics, gel character and strength of
473 ambient temperature cured alkali activated slag-fly ash blends. Construction and
474 Building Materials 2015. (80). 105-115
475 25. Arioz E, Arioz O and Mete Kockar O. leaching of F-type fly ash based
476 geopolymers. Procedia Engineering 2012 (42). 114-1120
477 26. Marjanovic N, Komljenovic M, Bascarevic Z and Nikolic V. improving reactivity
478 of fly ash properties of ensuing geopolymers through mechanical activation.
479 Construction and Building Materials 2014 (57). 152-162