



UNIVERSITY OF LEEDS

This is a repository copy of *Sorptivity and acid resistance of ambient-cured geopolymer mortars containing nano-silica*.

White Rose Research Online URL for this paper:
<http://eprints.whiterose.ac.uk/142834/>

Version: Accepted Version

Article:

Deb, PS, Sarker, PK and Barbhuiya, S (2016) Sorptivity and acid resistance of ambient-cured geopolymer mortars containing nano-silica. *Cement and Concrete Composites*, 72. pp. 235-245. ISSN 0958-9465

<https://doi.org/10.1016/j.cemconcomp.2016.06.017>

Reuse

This article is distributed under the terms of the Creative Commons Attribution-NonCommercial-NoDerivs (CC BY-NC-ND) licence. This licence only allows you to download this work and share it with others as long as you credit the authors, but you can't change the article in any way or use it commercially. More information and the full terms of the licence here: <https://creativecommons.org/licenses/>

Takedown

If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing eprints@whiterose.ac.uk including the URL of the record and the reason for the withdrawal request.



eprints@whiterose.ac.uk
<https://eprints.whiterose.ac.uk/>

Sorptivity and acid resistance of ambient-cured geopolymer mortars containing nano-silica

Partha Sarathi Deb^{a*}, Prabir Kumar Sarker^b, Salim Barbhuiya^c

^a PhD student, Department of Civil Engineering, Curtin University, GPO Box U1987, Perth, WA 6845, Australia

^b Senior Lecturer, Department of Civil Engineering, Curtin University, GPO Box U1987, Perth, WA 6845, Australia

^c Lecturer, Department of Civil Engineering, Curtin University, GPO Box U1987, Perth, WA 6845, Australia

*Tel | +61 8 9266 7568; Fax | +61 8 9266 2681 email: partha.deb@postgrad.curtin.edu.au

Abstract

This study investigated the effects of nano-silica on flowability, strength development, sorptivity and acid resistance properties of fly ash geopolymer mortars cured at 20°C. The changes in mass, compressive strength and microstructure of the specimens after immersion in acid solutions for different durations were determined. The microstructures were studied by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD) analysis. It was found that addition of nano-silica in geopolymer mortars based on fly ash alone or fly ash blended with 15% GGBFS or 10% OPC improved the compactness of microstructure by reducing porosity. Thus, the nano-silica reduced sorptivity and increased compressive strength of the mixes. The average mass loss after 90 days of immersion in acid solutions reduced from 6.0% to 1.9% by addition of 2% nano-silica. Similarly, significant reduction in strength loss after immersion in acid solution was observed in the specimens by using nano-silica.

Keywords: *Acid resistance; ambient curing; fly ash; geopolymer; nano-silica; sorptivity*

1. Introduction

Works on the development of geopolymer binder as an alternative to traditional cement has been considerably increased in the recent years. This is because of the numerous benefits of geopolymers over traditional cement binder such as lower CO₂ emission [1], requirement for less processing of the raw materials [2] and development of desired strength and structural

34 properties [3, 4, 5]. Geopolymerization is a process where the glassy constituents of the
35 aluminosilicate source materials are transformed into a compact binder [6]. Several factors
36 such as reactivity of the source materials [7], curing temperature, alkaline activator to source
37 material ratio [3, 8, 9] and the type of alkaline activator play important roles in the
38 geopolymerization process. Selection of the binder compositions is an important factor
39 affecting the properties of fresh and hardened geopolymers [8, 9]. Geopolymers based on
40 low-calcium fly ash cured at ambient temperature takes very long time to set and it develops
41 relatively low strength as compared to those cured at elevated temperature such as at 60 °C.
42 Previous studies [3, 9] showed that the setting and strength development of low-calcium fly
43 ash geopolymers can be improved by a small percentage of ground granulated blast furnace
44 slag (GGBFS) or ordinary Portland cement (OPC) in the binder.

45 Improvements in the mechanical properties of a cementitious matrix by the addition
46 of nano materials were reported by numerous studies [10-13]. It was observed that a small
47 percentage of nano-silica in the cementitious system can result in a considerable strength
48 improvement with a denser microstructure. However, the performance of nano-silica in
49 cementitious materials is dependent on its morphology, method of preparation and its
50 uniform dispersion in the mixture [14, 15]. It was reported by Adak et al. [16] that addition of
51 6% nano-silica increased compressive strength of fly ash geopolymers. Gao et al. [17]
52 showed that nano-silica increased the strength of alkali activated slags. These studies focused
53 on the improvements of strength properties of alkali activated binders by using nano-silica.
54 Studies on the durability of fly ash geopolymers in aggressive chemical environment are
55 scarce in literature. Especially, it is necessary to study if the durability properties of
56 geopolymers can be improved by using nano-silica. Concrete structures are often exposed to
57 acidic environment such as in ground water, industrial effluents and acid rains. Therefore,
58 acid resistance of concrete is an important property for its performance in aggressive
59 environment.

60 Mehta [18] observed that acid attack on a cementitious binder caused decalcification
61 and formation of soluble products. Chindaprasirt et al. [19] noted that the high strength loss
62 by the acid exposure of alkali activated fly ash-silica fume composites was due to the low
63 initial strength of the mortar and the favourable dissolution of excess silica in the acid
64 solution. However, Bakharev [20] observed better resistance of geopolymers than OPC
65 binders in exposure to aggressive environment. Breck [21] noted that polymer structures with
66 a Si/Al ratio of 1 are more easily attacked by the acid than more siliceous polymers. Ismail et
67 al. [22] found that the H⁺ from H₂SO₄ ionization could destroy the alumino-silicate network

68 in geopolymer and yielded silicic acid ($\text{Si}(\text{OH})_4$) and aluminium ions (Al^{3+}) from the gel
69 polymer.

70 It was shown that addition of nano-silica in OPC or other cementitious binders
71 significantly enhanced the compressive strength along with its durability properties. Addition
72 of a small percentage of nano-silica could be a potential way to improve the strength and
73 durability properties of low-calcium fly ash geopolymers cured at ambient temperature. Thus
74 a comprehensive study is required to understand the possible beneficial effects of nano-silica
75 in fly ash geopolymers cured at room temperature. This study investigated the effects of the
76 addition of 0-3% nano-silica on the flowability, strength and porosity of geopolymer mortars
77 based on fly ash only and fly ash blended with GGBFS or OPC. The durability properties
78 such as sorptivity and resistance to acid were studied by determining the changes in mass and
79 strength after immersion in an acid solution. The microstructural changes were studied by
80 using SEM, EDS and XRD analysis to obtain an insight into the observed strength and
81 durability properties.

82 **2. Experimental work**

83 **2.1. Materials**

84 Low-calcium fly ash was used as the main aluminosilicate source for all geopolymer mortars.
85 Commercially available GGBFS and OPC were blended with fly ash to accelerate the setting
86 of geopolymers for curing at room temperature. Commercially available nano-silica (NS)
87 with average particle diameter of 15 nm was used as an additive to improve the properties of
88 fresh and hardened properties of geopolymer mortars. The chemical compositions of these
89 materials are given in Table 1. The blaine's fineness of the regular fly ash, OPC and GGBFS
90 were $340 \text{ m}^2/\text{kg}$, $370 \text{ m}^2/\text{kg}$ and $450 \text{ m}^2/\text{kg}$ respectively.

91 The activating chemicals were sodium silicate with a chemical composition of (wt.
92 %): $\text{Na}_2\text{O} = 11.5$, $\text{SiO}_2 = 30.0$ and water = 58.5, and 8M sodium hydroxide solution prepared
93 from analytical grade sodium hydroxide pellets. The fine aggregate was natural sand with a
94 nominal maximum size of 1.18 mm.

95 **2.2. Geopolymer mixtures**

96 The mix proportions of geopolymer mortars were designed taking the final unit weight as
97 2200 kg/m^3 . The composition of the geopolymer mortar mixtures were calculated based on
98 the authors' previous works [3, 4, 15] on geopolymers cured at room temperature. The mix
99 proportions are given in Table 2. The mixtures are classified into three groups named as fly
100 ash only, GGBFS blended fly ash and OPC blended fly ash series. Mixture FA-NS0, without

101 nano-silica, was the control mixture designed with fly ash alone as the binder for the fly ash-
102 only geopolymer series. Similar control mixtures were prepared for GGBFS (FA-S-NS0) and
103 OPC (FA-PC-NS0) blended fly ash geopolymer mortars. The mixtures are designated based
104 on the constituents of the binder. For example, the designation FA-S-NS3 represents a
105 geopolymer mixture having 3% nano-silica (NS) in the GGBFS (S) blended fly ash (FA)
106 geopolymer mortar. The percentages of GGBFS and OPC were fixed at 15% and 10% of the
107 binder respectively. The binder to alkaline liquid ratio and the molarity of NaOH were fixed
108 at 0.4 and 8M respectively. These proportions were used based on authors' previous studies
109 [3, 8, 9].

110 **2.3. Mixing of geopolymer mortars and the test methods**

111 The alkaline activator was a combination of sodium silicate and sodium hydroxide solutions
112 with a mass ratio of 2.0. The nano-silica particles were dispersed in the silicate solution by
113 using ultra-sonication prior to mixing of the mortar [15]. The fly ash and the fine aggregates
114 were first mixed together in a Hobart mixer. This was followed by addition of the activator
115 solution to the dry materials. The mixing was then continued further for about 3-5 minutes to
116 produce fresh geopolymer mortar. Flow test of fresh geopolymer mortar was conducted in
117 accordance with ASTM C1437-13 standard [23]. Cube mortar specimens of size 50 × 50 × 50
118 mm were cast for compressive strength tests and 100 × 50 mm cylinder specimens were cast
119 for sorptivity tests. The specimens were demolded at 24hrs after casting and then cured at
120 room temperature (20±2°C) at a relative humidity of 70±10%. Compressive strength tests of
121 the specimens were performed at 7, 28, 56 and 90 days in accordance with the ASTM C109
122 [24] Standard.

123 The morphology of the hardened samples was examined by a MIRA3 TESCAN using
124 a scanning electron microscope (SEM). X-ray diffraction (XRD) experiments were conducted
125 on a Siemens D500 Bragg–Brentano diffractometer in a 2θ-range of 5–80°. Operating
126 conditions for the XRD were set a 40 kV and 30 mA using a Cu ka X-ray source. Crystalline
127 phases of the geopolymers were identified by comparison with a Powder Diffraction File
128 (PDF).

129 Resistance to sulfuric acid was determined by the modified test method B of the
130 ASTM C 267 Standard [25]. The geopolymer cube mortar specimens were fully immersed in
131 3% sulfuric acid solution at the age of 28 days for 12 consecutive weeks. The acid solution
132 was replaced weekly and the pH level was monitored regularly to maintain the designated pH
133 of 3.0. The specimens were removed from the acid solution after the exposure period and
134 brushed carefully to remove the loose particles from its surface. They were then left for

135 drying under room temperature for 1hr before recording the mass changes. Strength and
136 microstructure of the geopolymer specimens were also investigated after different exposure
137 periods. Sorptivity tests were conducted with 100 mm diameter and 50 mm height specimens
138 in accordance with ASTM C1585-13 [26]. The sides of the specimens were coated with
139 epoxy to allow free water movement only through the bottom face.

140 **3. Results and discussion**

141

142 **3.1. Flow behaviour of fresh geopolymer mortar**

143 The effects of the percentage of nano-silica on the flow of fresh geopolymer mortars are
144 shown in Fig. 1. It can be seen that the flow values of the mixes containing GGBFS and OPC
145 were less than those of the fly ash only mixes. The decrease in flow is because of the early
146 reaction of the calcium contained in GGBFS and OPC. The trend is similar to the
147 observations in previous works [3, 4, 8, 9]. Nath and Sarker [9] and Provis et al. [27] reported
148 that the flow of fly ash geopolymer mortars decreased with the increase of calcium bearing
149 components in the binder. Gao et al. [17] noted that lower slag content provided a better
150 flowability due to their morphological differences. It can be seen from Fig.1 that the flow of
151 geopolymer mortars gradually decreased with the increase of nano-silica. The flow of fly ash
152 only geopolymer mortars decreased from 135% (FA-NS0) to 115% (FA-NS3) with the
153 addition of 3% nano-silica. The flow decreased from 98% to 64% by the addition of 3%
154 nano-silica in the GGBFS blended fly ash geopolymer mortar. Similarly, flow decreased from
155 80% to 50% by 3% nano-silica in the OPC blended fly ash geopolymer mortar. The decrease
156 of flow in the mixes of all three series by the inclusion of nano-silica is attributed to the
157 increased liquid demand and accelerated reaction because of its high specific surface. The
158 geopolymer mortars based on GGBFS and OPC blended fly ash containing 3% nano-silica
159 were relatively stiff in nature and showed low workability.

160 **3.2. Compressive strength**

161 The compressive strength developments of the fly ash geopolymer mortars with 0%, 1%, 2%
162 and 3% nano-silica are shown in Fig. 2. Each value is an average of the results obtained from
163 3 identical specimens. The coefficients of variation of the results were mostly within 5%. For
164 example, the coefficients of variation of the 28 day-compressive strengths all the geopolymer
165 mixtures were in the range of 0.38% to 5.1%.

166 It can be seen from the figure that the rate of strength development slowed down significantly
167 after 28 days and it was negligible after the age of 56 days. Noticeable increase of strength
168 can be seen in the fly ash geopolymer mixtures containing nano-silica. The extent of the
169 increase in strength is dependent on the percentage of nano-silica. The highest strengths at all
170 ages up to 90 days were found in the mixes with 2% nano-silica. While the strength of the
171 mix with 3% nano-silica was higher than that of the control mix (FA-NS0), it was less than
172 that of the mix with 2% nano-silica. Fernandez and Palomo [28] reported that the fineness of
173 the source material played an important role in the strength development of geopolymer
174 binders. Temuujin et al. [29] also showed that the reduction of particle size and change in
175 morphology increase the dissolution rate which eventually increased the compressive strength
176 of geopolymer binder.

177 It was shown in previous works [3, 8, 9] that curing temperature, molarity of sodium
178 hydroxide and the reactivity of the source materials played crucial roles on the strength
179 development of fly ash geopolymers. Generally, geopolymers based on fly ash only and
180 cured at room temperature showed low compressive strength because of the slow
181 geopolymerization process. The strength development in the specimens of the mixes without
182 nano-silica showed similar trend in Fig.2. The nano-silica takes part in the reaction process
183 from an early age because of its high specific surface. A greater degree of reaction of the
184 aluminosilicate source materials is expected to give higher strength [30]. However, the results
185 of this study suggest that there is a limiting value on the percentage of nano-silica beyond
186 which no further strength increase is obtained. Thus, the optimum dosage of nano-silica for
187 this mix series is found to be 2%. Belkowitz et al. [31] noted that the unreacted nano-silica
188 caused an excessive self-desiccation and cracking in the matrix that eventually reduced the
189 strength. Therefore, the less strength of the mix with 3% nano-silica than that of the mix with
190 2% nano-silica is attributed to the presence of unreacted particles acting as defect sites.

191 The strength developments of OPC and GGBFS blended series with the different
192 amounts of nano-silica are shown in Figs. 3 and 4. As mentioned earlier, low-calcium fly ash
193 was blended with either 10% OPC or 15% GGBFS in order to accelerate the setting of these
194 mixes. As other ingredients remained constant, Figs. 3 and 4 show the influence of nano-
195 silica addition on the strength development.

196 It is noteworthy that inclusion of nano-silica from 0 to 3% in the OPC and GGBFS
197 blended series increased compressive strength by 40 to 64% as compared to the
198 corresponding control mixes. Chindaprasirt et al. [32] and Somna et al. [33] reported that
199 larger surface area of the source materials increased the geopolymerization process and

200 eventually increased the strength. It is noted from Fig.4 that mixes with 1%, 2% and 3%
201 nano-silica, in the OPC blended series exhibited 41%, 63% and 50% higher strength
202 respectively than the mix without nano-silica. Similar trend was also observed for GGBFS
203 blended geopolymer mortars. The pore refinement process of nano-silica has resulted in
204 higher strength of the geopolymer mixes. The addition of nano-silica increases the supply of
205 the Si required for the geopolymerization process. It is noteworthy that due to its very large
206 specific surface, nano-silica is highly reactive as compared to that of other cementitious
207 materials such as fly ash, OPC and GGBFS. The main effect of the nano-silica addition in
208 OPC and GGBFS blended series was the acceleration of the interconnected structure growth
209 due to higher geopolymerization process that eventually resulted in higher compressive
210 strength. The effect of nano-silica on strength development was similar in all the three series
211 of mixes and the optimum percentage of nano-silica was found as 2%.

212 **3.3. Sorptivity**

213 Sorptivity tests were conducted for the mortar mixes without nano-silica and with 2% nano-
214 silica. Nano-silica dosage of 2% was selected for the sorptivity and acid resistance tests since
215 this percentage was found to maximise the compressive strength. The sorptivity coefficients
216 of the fly ash only, OPC and GGBFS blended fly ash geopolymer mortars are given in Fig.5.
217 As shown by the results, sorptivity coefficient of the mixes without nano-silica was in the
218 range of $3.575 \times 10^{-3} \text{ mm/s}^{1/2}$ to $3.980 \times 10^{-3} \text{ mm/s}^{1/2}$ and that of the mixes with 2% nano-silica
219 was in the range of $1.247 \times 10^{-3} \text{ mm/s}^{1/2}$ to $2.157 \times 10^{-3} \text{ mm/s}^{1/2}$. Thus, it is apparent from the
220 results that the sorptivity coefficient decreased with 2% nano-silica in the mortar mixes of all
221 the three series. For example, sorptivity coefficient decreased from $3.575 \times 10^{-3} \text{ mm/s}^{1/2}$ to
222 $1.247 \times 10^{-3} \text{ mm/s}^{1/2}$ by 2% nano-silica in the fly ash only geopolymer mortar. Sorptivity
223 reduced by nano-silica in the GGBFS and OPC blended fly ash geopolymer mortars in a
224 similar way. The decrease in sorptivity of the specimens indicates a reduction in the porosity
225 by inclusion of nano-silica. The effect of nano-silica on the improvement of porosity is
226 attributed to two reasons. Firstly, the particle packing of nano-silica in the wide distribution
227 of binder particle sizes resulted in a denser matrix. Secondly, the reaction of nano-silica in
228 geopolymerization process produced further amount of aluminosilicate gel along with the
229 reaction products from the main source materials. It is likely that additional reaction product
230 precipitated in the available pore structures. As described by Law et al. [34], an increase in
231 SiO_2 increases the density of the matrix. Therefore, the combined filling effect of nano-silica
232 by the improved particle packing and the additional reaction product produced a denser

233 binding matrix that reduced the porosity and increased compressive strength as seen in Figs.
234 2 to 4.

235 **3.4 Resistance to attack by sulfuric acid**

236

237 **3.4.1. Change in mass**

238 The geopolymer mortar specimens were immersed in 3% sulfuric acid solution for 90 days
239 and the changes in mass were determined on a weekly basis. The change in mass of a
240 specimen was calculated by comparing mass measured after exposure to acid solution to the
241 initial mass before the exposure. The specimens were visually inspected for any deterioration
242 by the exposure to acid solution. Photographs of the specimens without and with 2% nano-
243 silica after 90 days immersion in the acid solution are shown in Fig.6. Photographs of the
244 specimens before acid exposure are also shown in this figure for comparison. Generally,
245 some minor erosion could be observed in all the specimens by the acid attack. Also, there
246 were relatively more damages, especially at the corners of specimens without nano-silica and
247 those containing OPC and GGBFS.

248 Changes in mass for specimens of all the geopolymer mixes are presented in Fig 7. The
249 results show that mass of the geopolymer specimens gradually decreased with exposure time.
250 It can be seen that the mass loss after 90 days of acid exposure for fly ash only geopolymer
251 mix without nano-silica was 5.41% as compared to 1.9% for the mix with 2% nano-silica.
252 After the same exposure period, the mass loss of the OPC blended fly ash geopolymer mixes
253 without nano-silica (FA-PC-NS0) and with 2% nano-silica (FA-PC-NS2) were 6.0% and
254 2.3% respectively. Similarly, the 90-day mass losses for the GGBFS blended fly ash
255 geopolymer mortars were 5.8 % without nano-silica (FA-S-NS0) and 1.5% with 2% nano-
256 silica (FA-S-NS2). Overall, the mass loss varied from 1.9% to 6.00% for all the geopolymer
257 mixes. These mass losses of the nano-silica incorporated fly ash geopolymer mortars are very
258 small as compared to the mass losses usually shown by OPC based cementations materials
259 [35, 36]. Previous studies [36, 37] on OPC based binders showed that sulfuric acid has a
260 highly deleterious effect on mass loss. This is because sulfuric acid causes decomposition of
261 the $\text{Ca}(\text{OH})_2$ and forms gypsum that deteriorates the matrix by scaling and softening. Though
262 the penetration of sulfuric acid can be reduced, the formation of gypsum in the regions close
263 to the surface causes progressive disintegration of the matrix [37]. Therefore, the mass losses
264 observed in the geopolymer specimens without nano-silica were much smaller than that can
265 be expected in OPC based binders under the same exposure condition. However, addition of

266 2% nano-silica has further reduced the mass loss of geopolymer specimens. The effect of
267 nano-silica on the changes in strength and microstructures by the exposure to sulfuric acid are
268 studied in the following sections.

269 **3.4.2. Change in compressive strength**

270 The 28-day compressive strength of each geopolymer mix before exposure to acid solution is
271 used as a benchmark to calculate the strength loss after each exposure period of 28, 56 and 90
272 days. The compressive strengths of the mortar specimens from 6 mixes are presented in Fig.
273 8. It can be seen from the figure that loss of strength occurred in all the geopolymer mixes
274 and it increased with the increase of exposure period. It is noteworthy from Fig.8 that fly ash
275 only, OPC and GGBFS blended fly ash geopolymer specimens without nano-silica exhibited
276 higher strength loss as compared to those with nano-silica. The strength loss in the specimens
277 without nano-silica ranged from 30% to 41% while that in the specimens with nano-silica
278 ranged from 9% to 11%. For example, the strength value of mix FA-NS2 (2% nano-silica)
279 after 90 days of sulfuric acid exposure was 54.0 MPa, as compared to 60.0 MPa prior to acid
280 exposure. Whereas, the compressive strength of mix FA-NS0 (0% nano-silica) reduced from
281 29.0 MPa to 19.1 MPa after 90 days of immersion in sulfuric acid. Bakharev [20] showed
282 that depolymerisation of the aluminosilicate polymers in acidic media resulted in a significant
283 strength loss of alkali activated binders. Chindaprasirt [38] noted that the oxy-aluminium
284 bridge ($-Al-Si-O$) of geopolymeric gel probably gets destroyed in acidic environment and
285 leads to strength reduction of alkali activated binders. Reduction of permeability helps reduce
286 the ingress of acid in to geopolymer matrix and thus improves the resistance to acid attack
287 [35]. It is apparent from Fig.8 that incorporation of 2% nano-silica in fly ash based
288 geopolymer can effectively reduce the rate of acid attack expressed in terms of strength loss.
289 Belkowitz et al. [31] noted that the pore refinement process by nano-silica usually prevents
290 the passage of aggressive elements into the deeper layers of hydrated gel structure. It means
291 that the optimum amount of nano-silica present in the geopolymer mixes produces a denser
292 structure that reduces the degradation by an acid. The results of the present study are also
293 supported by the findings of Fattuhi and Hughes [36], and Israel et al. [37] that the lower
294 porosity improved the acid resistance of hydrated gel.

295 Also, as expected, the strength loss in OPC blended fly ash based geopolymer mortar
296 without nano-silica is greater than that of with 2% nano-silica incorporated samples (FA-PC-
297 NS2). The strength loss reduced from 11.5 MPa (FA-PC-NS0) to 6.5 MPa (FA-PC-NS2) by
298 2% nano-silica in the OPC blended geopolymer mix (Fig.8). This highlights the poor

299 resistance of mix FA-PC-NS0 (without nano-silica) against a highly corroding and aggressive
300 environment as compared to mix FA-PC-NS2 (with nano-silica). Incorporation of 2% nano-
301 silica leads to a denser and less permeable pore structure prolonging the negative effects of
302 acid attack. This observations correlates well with the findings of Hartman and Fogler [39]
303 which showed that the increased amount of soluble silica produces a denser layer and helps to
304 reduce the extent of damage in the aluminosilicate structure with the removal of each of the
305 aluminium atoms under acid attack.

306 Similarly, In the GGBFS blended mix, the strength loss after 90 days of immersion
307 reduced from 7.5 MPa (FA-S-NS0) to 4.0 MPa (FA-S-NS2) by 2% nano-silica. The results of
308 this study show that inclusion of 2% nano-silica in all geopolymer series made a significant
309 improvement in the strength loss as compared to that of the mix without nano-silica.

310 **3.4.3. Change in microstructure**

311 The SEM images of the fly ash only, OPC and GGBS blended fly ash based geopolymer
312 mortars with and without nano-silica after 90 days exposure to sulfuric acid are presented in
313 Figs. 9(a) to 9(f). Images of the specimens before acid exposure are also shown in the figure.
314 Significant differences in microstructure were observed in all the specimens after 90 days of
315 sulfuric acid exposure. It can be seen that the relatively compact microstructure of
316 geopolymers before the acid exposure became more porous after the exposure to sulphuric
317 acid. However, geopolymer mortar with nano-silica showed less deterioration than the fly ash
318 geopolymer mortar without nano-silica. It is noted from Fig 9(a) that fly ash only geopolymer
319 mortar without nano-silica (FA-NS0) immersed in sulfuric acid for 90 days exhibited porous
320 and disintegrated gel clusters (point 2) around the unreacted particles (point 1). Similar
321 observations can also be noted in the microstructures of the OPC and GGBFS blended fly ash
322 geopolymer mortars. More compact and less porous structures can be observed in the mixes
323 with nano-silica when comparisons are made between the microstructure of Fig. 9(d) to that
324 in Fig. 9(c) and the microstructure of Fig. 9(e) to that in Fig. 9(f). Bakharev [20] pointed out
325 that disintegration of microstructure along with significant loss of strength in geopolymer
326 materials is due to low inter crystalline bond strength. In a similar study, Ismail et al. [22]
327 also noted that the presence of H^+ could destroy the alumino-silicate network of geopolymer
328 materials and eventually lead to disintegration of the polymer gel. The findings of Lloyd et al.
329 [35] concluded that H_3O^+ and HSO_4^- ions from the sulfuric acid could diffuse into the gel
330 phase, where H_3O^+ attacks the gel and severely damage the gel network. However, Fig 9(b)
331 indicates that inclusion of 2% nano-silica in the fly ash only geopolymer reduced acid

332 aggravation due to its additional reaction products. The mechanisms involved in the process
333 are related to mechanical percolation along with pore filling effects of nano-silica. It appears
334 that the aluminosilicate gel of the mix with 2% nano-silica (FA-NS2, Fig. 9(b)) was more
335 compact than that of the control mix (FA-NS0, Fig. 9(a)). Similar differences are also
336 observed in the mixes of the other two series. This observation on the differences in
337 microstructures is consistent with the less strength loss of the mixes with 2% nano-silica, as
338 shown in Fig. 8. It suggests that the introduction of 2% nano-silica reduced the porosity and
339 increased the acid resistance in terms of strength loss and disintegration of the microstructure.
340 The dense microstructure formed by nano-silica provides resistance to the penetration of
341 acidic ions reducing the extent of disintegration in the microstructure and eventual less
342 strength loss.

343 The energy dispersive X-ray patterns for fly ash only, OPC and GGBFS blended fly
344 ash based geopolymers without nano-silica are shown in Figs. 10(a) to 10(c). Notable traces
345 of silicon, sodium, aluminium and calcium elements were observed in the EDX patterns of
346 the OPC and GGBFS blended fly ash geopolymers. Presence of the first three elements is
347 from the sodium aluminosilicate gel, whereas the calcium is from gypsum formed in OPC
348 and GGBFS blended geopolymers. Strong peaks of calcium were observed in the OPC and
349 GGBFS blended geopolymers without nano-silica (Figs. 10(b) and 10(c)). These phenomena
350 agreed well with the studies reported by other researchers [35, 41] that the exchanged
351 calcium ions diffusing toward the acid solution react with the counter-diffusing sulfate anions
352 resulting in the formation and deposition of gypsum crystals inside the corroding layer. The
353 XRD patterns (Figs. 11(b) and 11(c)) also suggest a possible alteration and restructuring of
354 the polymer network in the OPC and GGBFS blended geopolymers without nano-silica.

355 The XRD spectra of the samples after 90 days exposure to acid solution are shown in
356 Figs. 11(a) to 11(c). It is confirmed from the XRD spectrum that the formation of gypsum
357 takes place in both OPC and GGBFS blended fly ash geopolymers without nano-silica. The
358 traces of gypsum are likely due to the reaction between available depleted calcium from the
359 OPC and GGBFS with sulphur ions from the sulfuric acid. However, it is noted from Figs.
360 11(b) and 11(c) that the traces of gypsum entirely disappeared for both OPC and GGBFS
361 blended geopolymers with 2% nano-silica. It seems Ca^{2+} that was released from the
362 dissolution of OPC and GGBFS interacted with silicate ions and formed calcium silicate
363 oligomers. However, no peaks of gypsum traces were observed for fly ash only geopolymers
364 with and without nano-silica. Bakharev [20] and Lloyd et al. [32] noted that the acid
365 resistance kinetics of polymer modified mortars depends on its material composition. In the

366 previous study [15] formation of aluminosilicate and CSH gel as final hydrated products were
367 observed in GGBFS and OPC blended fly ash geopolymers. The presence of calcium silicate
368 hydrate (CSH) in mixes FA-PC-NS0 and FA-S-NS0 might have reacted with H_2SO_4 and
369 disintegrated in the form of calcium sulfate or as an amorphous silica gel at the end [39, 40].
370 Puertas et al. [41] and Wallah and Rangan [42] also concluded that the higher calcium
371 content in the alkali activated binder generates greater amounts of gypsum during acidic
372 exposure and might precipitate into and cover the pores of the mortar.

373 **4. Conclusions**

374 The effects of nano-silica on the flowability, compressive strength and acid resistance of
375 ambient-cured geopolymer mortars were investigated. The geopolymer binders were based
376 on fly ash alone or that blended with small proportions of GGBFS (15%) or OPC (10%). The
377 following conclusions are drawn from the results obtained in this study:

- 378 • Inclusion of nano-silica improved the early-age strength of geopolymer mortars based
379 on fly ash alone or that blended with OPC or GGBFS. Flow of the freshly mixed
380 mortars gradually decreased with the increase of nano-silica because of its high
381 specific surface. The compressive strength of the ambient-cured geopolymer mortars
382 varied from 17 to 19 MPa at 7 days and from 29 to 60 MPa at 28 days. Strength
383 development in ambient condition continued to the age of 90 days, however at slower
384 rates after 56 days. The optimum dosage of nano-silica for maximum compressive
385 strength was found to be 2% of the binder.
- 386 • Sorptivity of the specimens with 2% nano-silica was less than that of the control
387 specimen. All the specimens remained intact after 90 days of immersion in 3%
388 sulfuric acid solutions with some erosion on the surface of the specimens containing
389 OPC. The average mass loss of the specimens of three series decreased from 2.6% to
390 1.8% after 90 days of immersion. The strength loss of the specimens without nano-
391 silica ranged from 30% to 41% while that of the specimens with 2% nano-silica
392 ranged from 9% to 11% after 90 days of immersion. Therefore, the acid resistance of
393 geopolymer mortars significantly improved with the inclusion of 2% nano-silica.
- 394 • After 90 days of immersion in acid solutions, the microstructures of the specimens
395 with nano-silica were found to be more compact as compared to the specimens
396 without nano-silica. The combined effects of the nano-silica as a filler and enhanced
397 reactivity of the aluminosilicate source materials refined the pore structure to develop
398 a more compact microstructure. This reduced the porosity and sorptivity of the binder

399 matrix. As a result there was less damage in the matrix after immersion in acid
400 solution and hence reduced loss of mass and strength in the specimen's containing
401 nano-silica.

402 **Acknowledgments**

403 The authors wish to gratefully acknowledge the support of Coogee Chemicals for supplying
404 the chemicals used in this study. The use of equipment, scientific and technical assistance of
405 the Curtin University Electron Microscope facility, which has been partially funded by the
406 university, State and Commonwealth Governments is also gratefully acknowledged.

407 **Reference**

- 408 1. Duxson P, Fernandez JA, Provis JL, Lukey GC, Palomo A, Deventer JSJ. Geopolymer
409 technology: the current state of the art. *J Mater Sci* 2007; 42 (9): 2917–2933.
- 410 2. Khale D, Chaudhary R. Mechanism of Geopolymerization and Factors Influencing Its
411 Development: A Review. *J Mater Sci* 2007; 42:729-746.
- 412 3. Deb P, Nath P, Sarker PK. The effects of ground granulated blast-furnace slag
413 blending with fly ash and activator content on the workability and strength properties
414 of geopolymer concrete cured at ambient temperature. *Mater Design* 2014; 62: 32-39.
- 415 4. Deb PS, Nath P, Sarker PK. Strength and Permeation Properties of Slag Blended Fly
416 Ash Based Geopolymer Concrete. *Adv Mater Res* 2013; 651:168-173.
- 417 5. Rahman MM, Sarker PK. Geopolymer concrete columns under combined axial load
418 and biaxial bending. *Concrete* 2011: 25th Biennial Conference of the Concrete Institute
419 of Australia: Western Australia, 2011.
- 420 6. Fernandez JA, Torre AG, Palomo A, Olmo GL, Alonso MM, Aranda MAG. Alkali
421 Activated Materials. *Fuel* 2006; 85:625–634.
- 422 7. Diaz EI, Allouche EN, Eklund S. Factors affecting the suitability of fly ash as source
423 material for geopolymers. *Fuel* 2010; 89: 992–996.
- 424 8. Nath P, Sarker PK. Effect of GGBFS on setting, workability and early strength
425 properties of fly ash geopolymer concrete cured in ambient condition. *Constr Build*
426 *Mater* 2014; 66:163–171.
- 427 9. Nath P, Sarker PK. Use of OPC to improve setting and early strength properties of low
428 calcium fly ash geopolymer concrete cured at room temperature. *Cement Concrete*
429 *Comp* 2015; 55: 205–214.
- 430 10. Quercia G, Spiesz P, Hüsken G, Brouwers HJH. SCC modification by use of
431 amorphous nano-silica. *Cement Concrete Comp* 2014; 45: 69–81.

- 432 11. Senff L, Hotza D, Repette WL, Ferreira VM, Labrincha JA. Mortars with nano-SiO₂
433 and micro-SiO₂ investigated by experimental design. *Constr Build Mater* 2010;
434 24(8):1432-1437.
- 435 12. Jalal M, Mansouri E, Sharifi M, Pouladkhan AR. Mechanical, rheological, durability
436 and microstructural properties of high performance self-compacting concrete
437 containing SiO₂ micro and nanoparticles. *Mater Design* 2012; 34:389–400.
- 438 13. Parida SK, Dash S, Patel S, Mishra BK. Adsorption of organic molecules on silica
439 surface. *Advan in Colloid and Interf Scie* 2006; 121:77–110.
- 440 14. Sobolev K, Flores I, Torres MLM, Valdez PL, Zarazua E, Cuellar EL. Engineering of
441 SiO₂ nanoparticles for optimal performance in nano cement based materials. *Nanotech*
442 *Constr* 3. Spring 2009; 139–48.
- 443 15. Deb PS, Sarker PK, Barbhuiya S. Effects of nano-silica on the strength development
444 of geopolymer cured at room temperature. *Constr Build Mater* 2015; 10(1): 675–683.
- 445 16. Adak D, Sarkar M, Mandal S. Effect of nano-silica on strength and durability of fly
446 ash based geopolymer mortar. *Constr Build Mater* 2014;70: 453–459
- 447 17. Gao X, Yu QL, Brouwers HJH. Characterization of alkali activated slag–fly ash blends
448 containing nano-silica. *Constr Build Mater* 2015;98: 397–406
- 449 18. Mehta PK. Studies on chemical resistance of low water/cement ratio concrete.
450 *Cement Concrete Res* 1985; 15: 969.
- 451 19. Chindaprasirt P, Paisitsrisawat P, Rattanasak U. Strength and resistance to sulfate and
452 sulfuric acid of ground fluidized bed combustion fly ash–silica fume alkali-activated
453 composite. *Adv Powder Technol* 2014; 25:1087–1093.
- 454 20. Bakharev T. Resistance of geopolymer materials to acid attack. *Cement Concrete Res*
455 2005; 35: 658–670.
- 456 21. Breck DW. *Zeolite Molecular Sieves: Structure, Chemistry and Use*. New York:
457 Wiley-Inter science, 1974. p. 415–418.
- 458 22. Ismail I, Bernal SA, Provis JL, Hamdan S, Deventer JSJ. Microstructural changes in
459 alkali activated fly ash/slag geopolymers with sulfate exposure. *Mater Struct* 2013; 46:
460 361–373.
- 461 23. American Society of testing materials. Standard Test Method for Flow of Hydraulic
462 Cement Mortar. ASTM C1437-13
- 463 24. American Society of testing materials. Standard Test Method for Compressive
464 Strength of Hydraulic Cement Mortars (Using 2-in. or [50-mm] Cube Specimens),
465 ASTM C109/C109M; 2002.

- 466 25. American Society of testing materials. Standard Test Methods for Chemical Resistance
467 of Mortars, Grouts, and Monolithic Surfacing and Polymer Concretes. ASTM C 267
468 26. American Society of testing materials. Standard test method for measurement of rate
469 of absorption of water by hydraulic-cement concretes. ASTM C1585-13.
470 27. Provis JL, Duxson P, Deventer JSJ. The role of particle technology in developing
471 sustainable construction materials. *Adv Powder Technol* 2010; 21:2–7.
472 28. Fernandez JA, Palomo A. Characterisation of fly ashes. Potential reactivity as alkaline
473 cements. *Fuel* 2003; 82: 2259–2265.
474 29. Temuujin J, Williams RP, Riessen A. Effect of mechanical activation of fly ash on the
475 properties of geopolymer cured at ambient temperature. *J Mater Proces Tech* 2009;
476 209: 5276–5280.
477 30. Fernandez JA, Monzo M, Vicent M , Barba A, Palomo A. Alkaline activation of
478 metakaolin–fly ash mixtures: Obtain of Zeoceramics and Zeocements. *Micropor*
479 *Mesopor Mat* 2008; 108:41–49.
480 31. Belkowitz JS, Belkowitz WB, Nawrocki K, Fisher FT. the impact of nano silica size
481 and surface area on concrete properties. *Mater J* 2015; 112:419-428.
482 32. Chindaprasirt P, Jaturapitakkul C, Sinsiri T. Effect of fly ash fineness on
483 microstructure of blended cement paste. *Constr Build Mater* 2007; 21:1534–41.
484 33. Somna K, Jaturapitakkul C, Kajitvichyanukul P, Chindaprasirt P. NaOH- activated
485 ground fly ash geopolymer cured at ambient temperature. *Fuel* 2011; 90(6):2118–24
486 34. Law DW, Adam AA, Patnaikuni I, Molyneaux TK, Wardhono A. Long term durability
487 properties of class F fly ash geopolymer concrete. *Mater Struct* 2015; 48:721–731.
488 35. Lloyd RR, Provis JL, Deventer JSJ. Acid resistance of inorganic polymer binders. 1.
489 Corrosion rate. *Mater Struct* 2012; 45:1–14.
490 36. Fattuhi N, Hughes B, The performance of cement paste and concrete subjected to
491 sulphuric acid attack. *Cement Concrete Res* 1988; 18 (4):545–553.
492 37. Israel D, Macphee DE, Lachowsk EE. Acid attack on pore-reduced cements. *J Mater*
493 *Sci* 1997; 32:4109-4116.
494 38. Chindaprasirt P, Taebuanhuad S, Rattanasak U. Resistance to acid and sulfate
495 solutions of microwave-assisted high calcium fly ash geopolymer. *Mater Struct* 2013;
496 46:375–381.
497 39. Hartman RL, Fogler HS. Understanding the dissolution of zeolites. *Langmuir* 2007;
498 23(10):5477–5484

499 40. Allahverdi A, Skavara F. Sulfuric acid attack on hardened paste of geopolymer
500 cements. Part 1. Mechanism of corrosion at relatively high Concentrations. Ceram-
501 Silikaty 2001; 45(3): 81-88

502 41. Puertas F, Mejía GR, Fernández JA, Delvasto S, Maldonado J. Alkaline cement
503 mortars. Chemical resistance to sulfate and seawater attack. Mater Construcc 2002;
504 52:55–71.

505 42. Wallah SE, Rangan BV. Low Calcium Fly Ash Based Geopolymer Concrete: Long
506 Term Properties”. Research Report GC2, Faculty of Engineering, Curtin University of
507 Technology, Perth, Australia.2006: 01-97.

508
509
510
511
512
513
514
515
516
517 **Table 1.** Chemical compositions of fly ash, OPC and GGBFS (% mass)
518

Material	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	MnO	K ₂ O	Na ₂ O	P ₂ O ₅	TiO ₂	SO ₃	LOI ^a
Fly ash	46.69	29.14	13.81	3.29	1.4	0.16	0.72	0.86	1.63	1.34	0.43	-
OPC	21.1	4.7	2.7	63.6	2.6	-	-	-	-	-	2.5	2
GGBFS	29.96	12.25	0.52	45.45	-	-	0.38	0.31	0.04	0.46	3.62	2.39
Nano-silica	99.5	0.001	0.001	-	-	-	-	-	-	-	-	-

519 ^aLoss on ignition
520

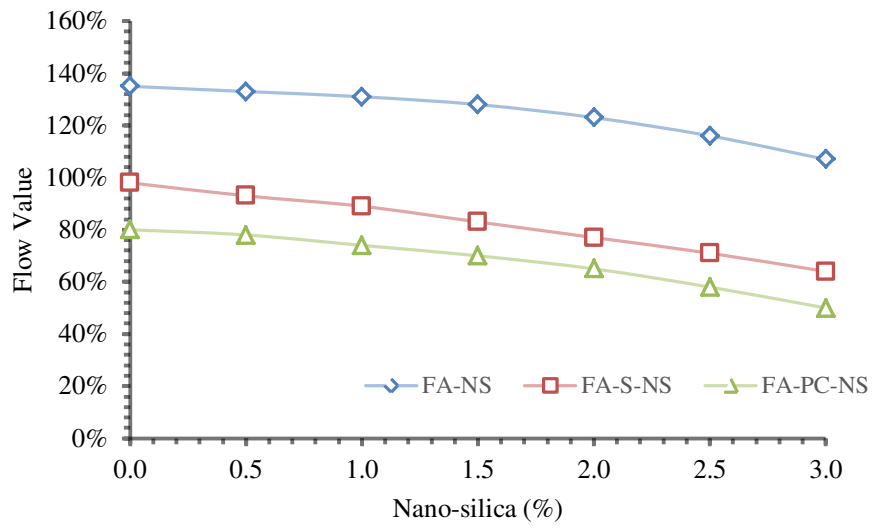
521 **Table 2.** Mix proportions of geopolymer mortars (Kg/m³)

Mix	Fly ash only				OPC blended Fly ash				GGBFS blended Fly ash			
ID	FA-NS0	FA-NS1	FA-NS2	FA-NS3	FA-PC-NS0	FA-PC-NS1	FA-PC-NS2	FA-PC-NS3	FA-S-NS0	FA-S-NS1	FA-S-NS2	FA-S-NS3
Sand	1173	1173	1173	1173	1173	1173	1173	1173	1173	1173	1173	1173
Fly ash	734	726	718	711	660	652.67	645.33	638.00	623.33	616.00	608.67	601.33
GGBFS	-	-	-	-	-	-	-	-	110.00	110.00	110.00	110.00
OPC	-	-	-	-	73.33	73.33	73.33	73.33	-	-	-	-
SH ^a	97.78	97.78	97.78	97.78	97.78	97.78	97.78	97.78	97.78	97.78	97.78	97.78
SS ^b	195.56	195.56	195.56	195.56	195.56	195.56	195.56	195.56	195.56	195.56	195.56	195.56
Nano silica	-	7.33	14.67	22.00	-	7.33	14.67	22.00	-	7.33	14.67	22.00

522 ^aSodium hydroxide, ^bSodium silicate
523

524

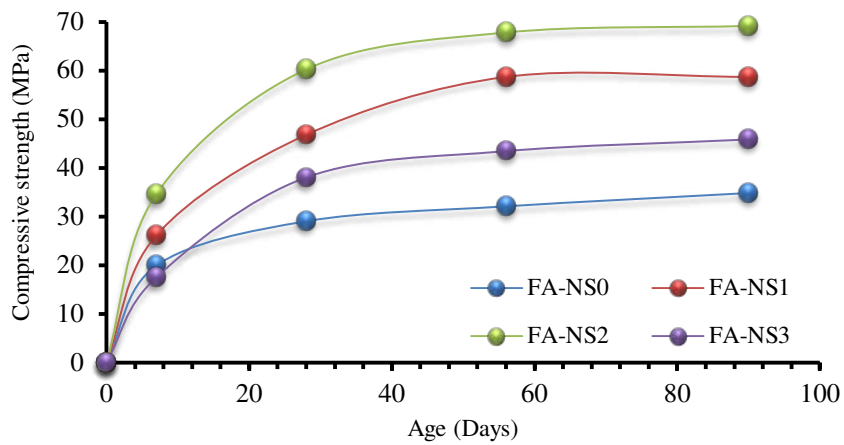
525



526

527

Fig. 1. Change in flow of geopolymer mortars with nano-silica.

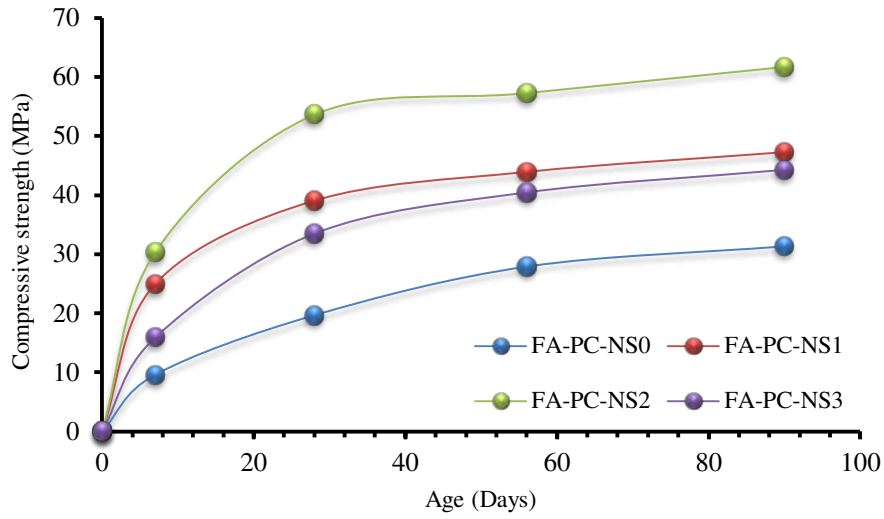


528

529

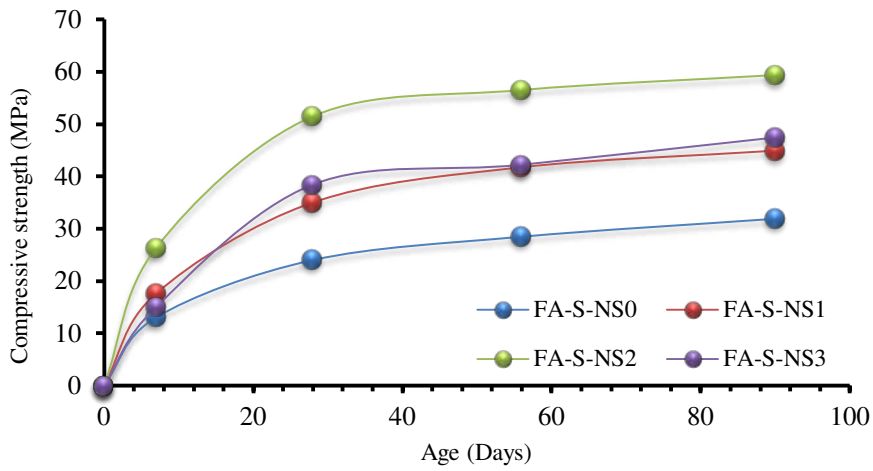
530

Fig. 2. Strength development of fly ash based geopolymer mortars with nano-silica



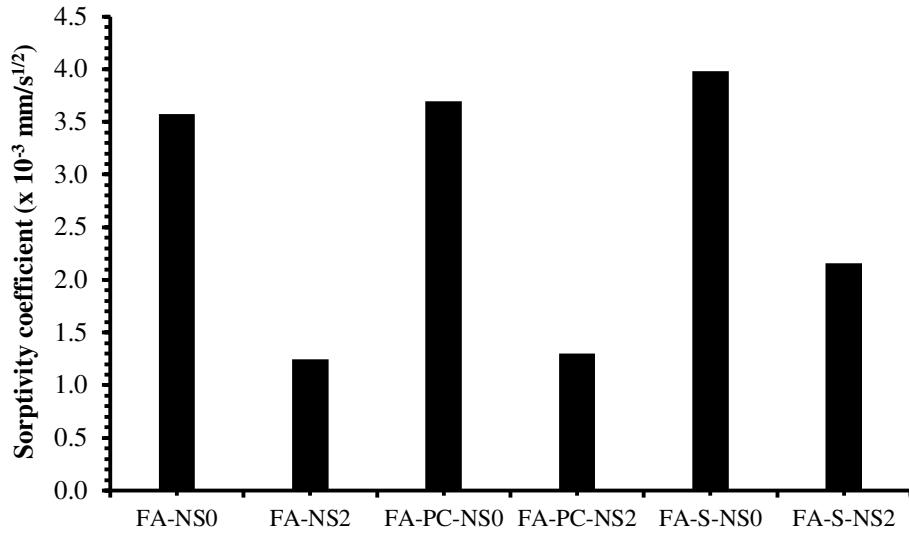
531

532 **Fig. 3.** Strength development of OPC blended fly ash based geopolymer mortar with nano-
533 silica



534

535 **Fig. 4.** Strength development of GGBFS blended fly ash based geopolymer mortar with
536 nano-silica
537
538



539

Fig. 5. Sorptivity coefficient of geopolymer mortars with nano-silica.

540

541

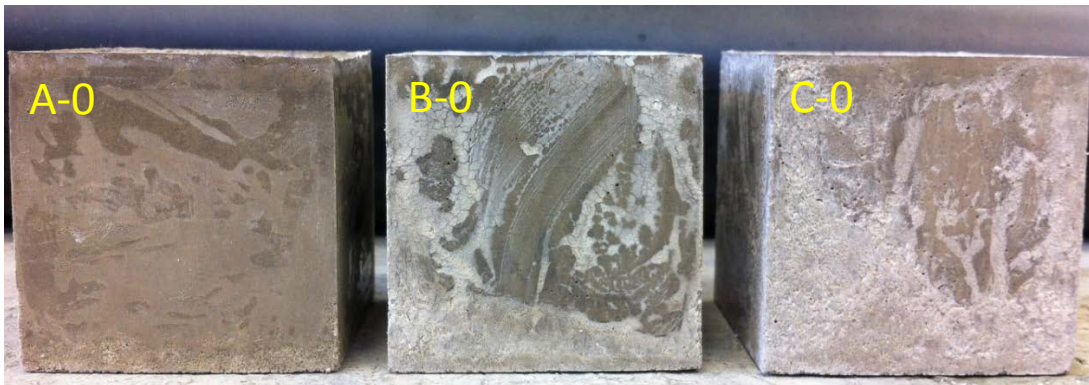
542

543

544

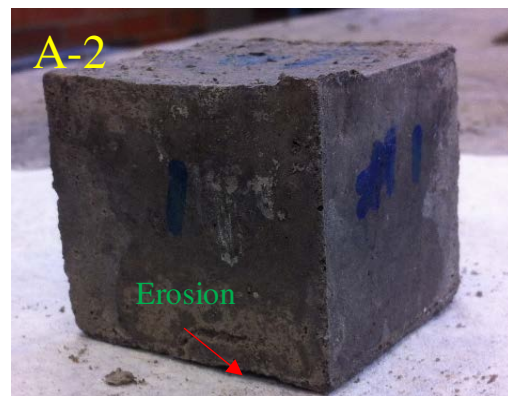
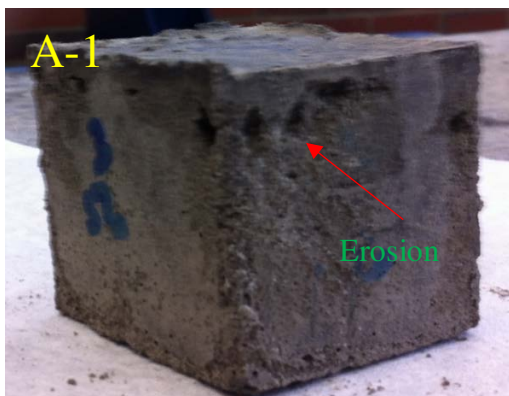
545

546



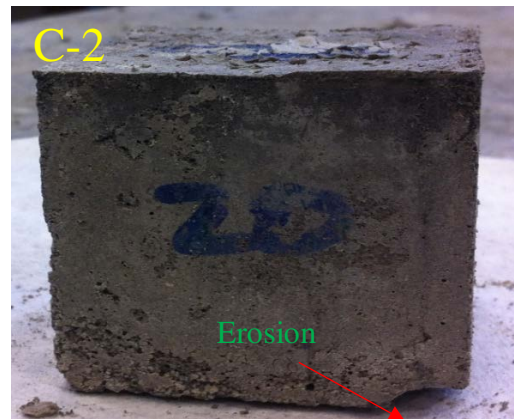
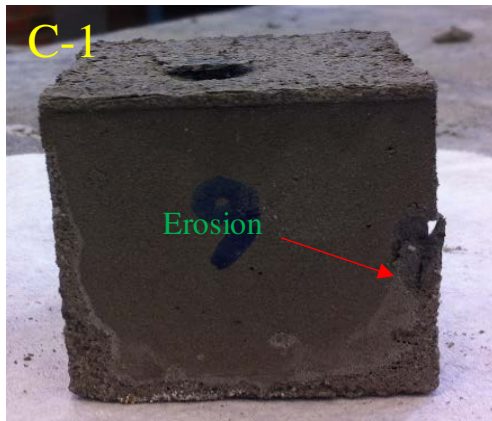
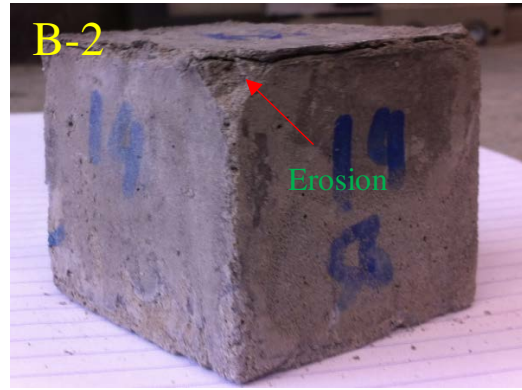
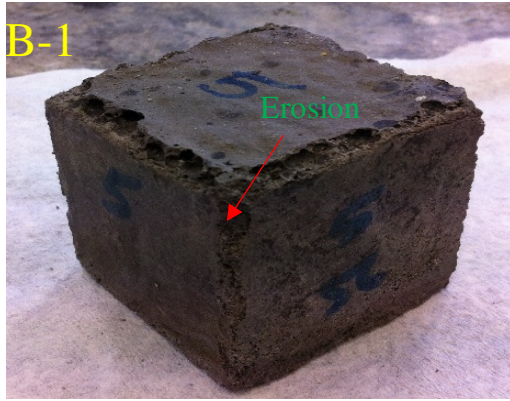
547

548



549

550

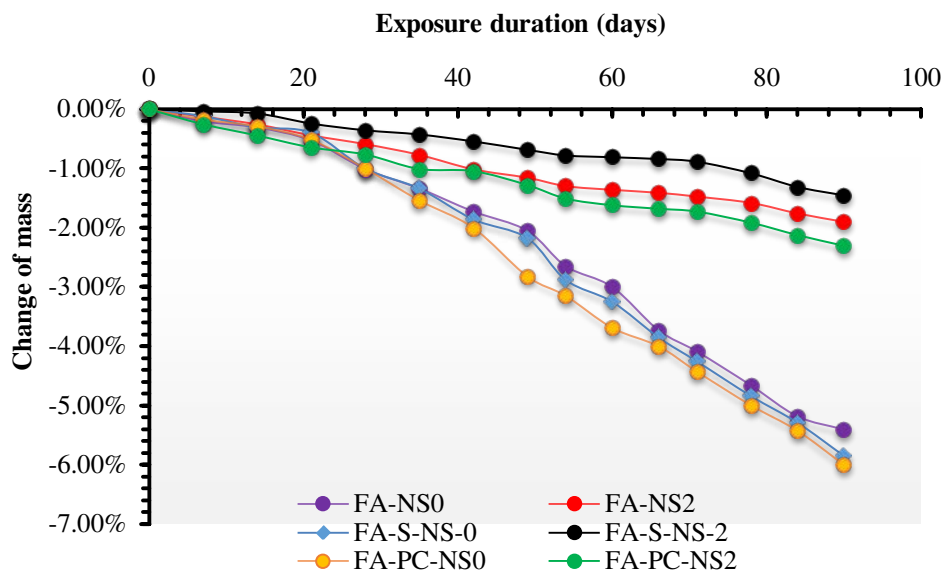


551
552

553
554

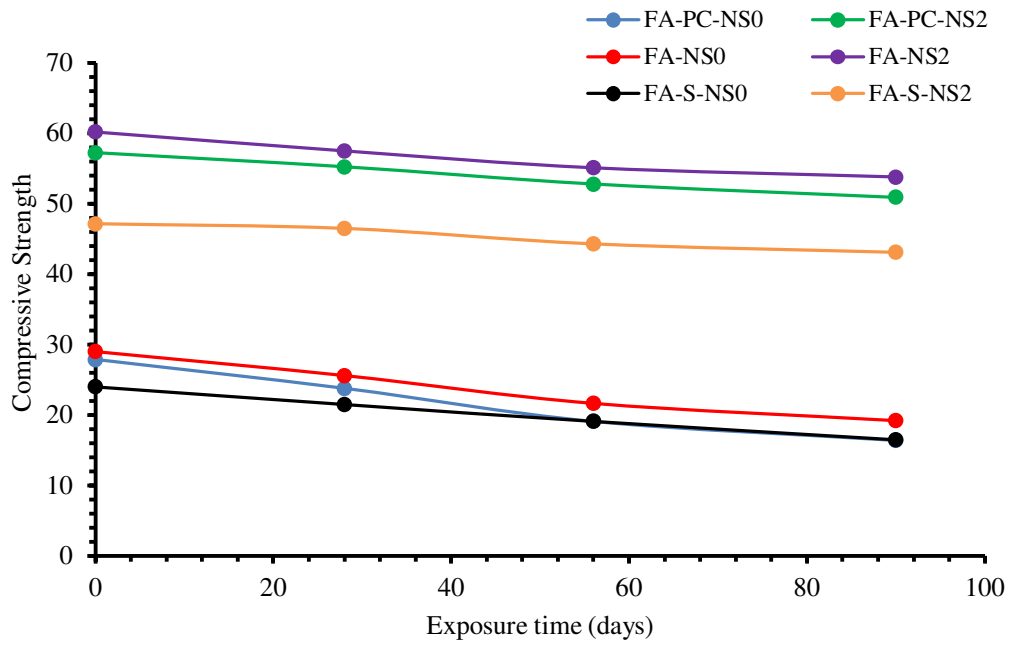
555 **Fig. 6.** Visual appearance of geopolymer specimens before acid submerged (A-0: FA-NS0,
556 B-0: FA-PC-NS0, C-0: FA-S-NS0) and after 90 days acid exposure (A) A-1: FA-NS0, A-2:
557 FA-NS2 (B) B-1: FA-PC-NS0, B-2: FA-PC-NS2, (C) C-1: FA-S-NS0, C-2: FA-SNS2.

558



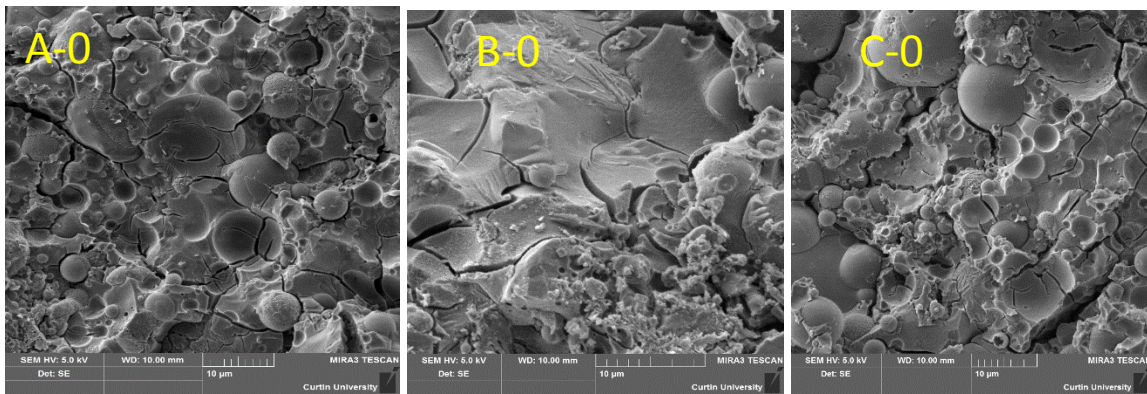
559
560

Fig. 7. Change in mass of mortar specimens after immersion in 3% sulfuric acid solution.

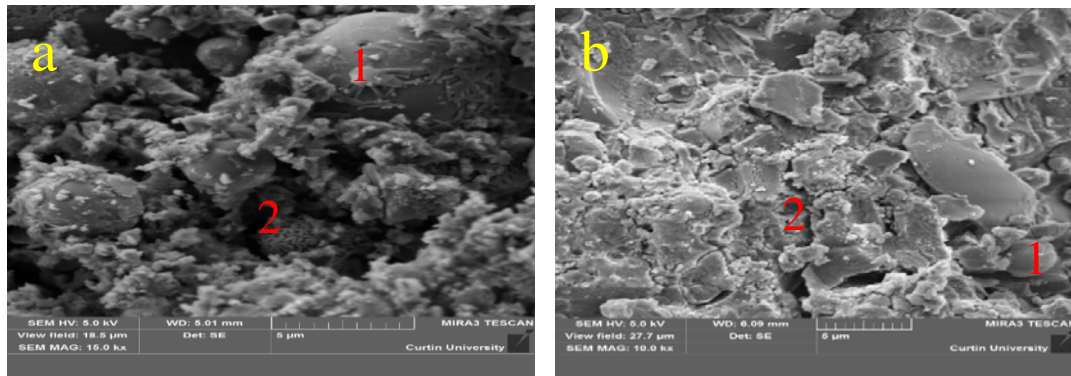


561
562

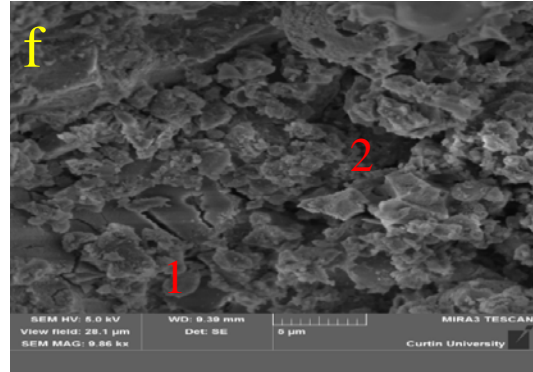
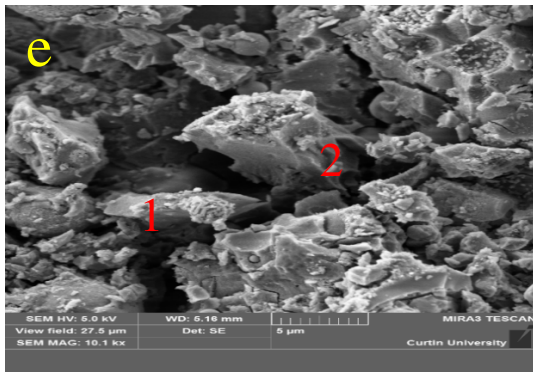
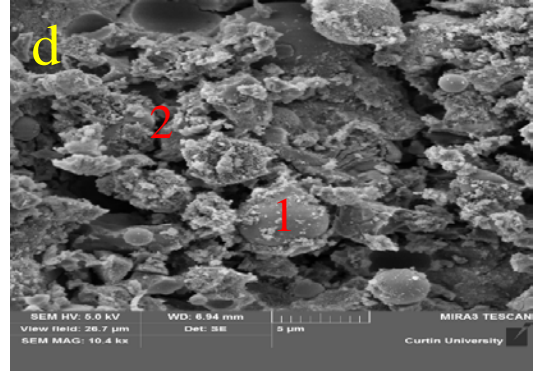
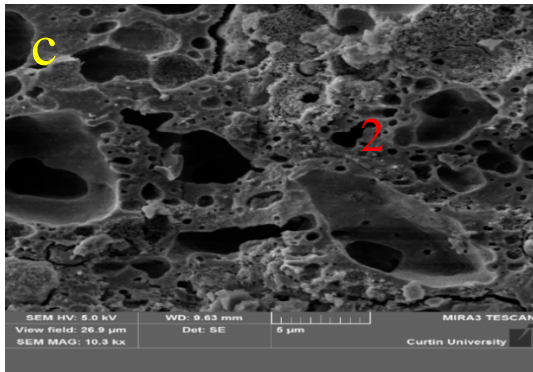
Fig. 8. Change in compressive strength of geopolymer mortars in sulfuric acid exposure.



563



564

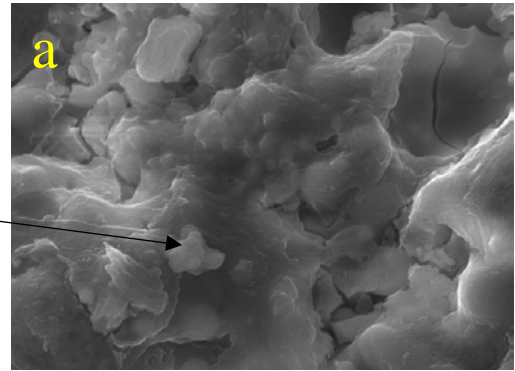
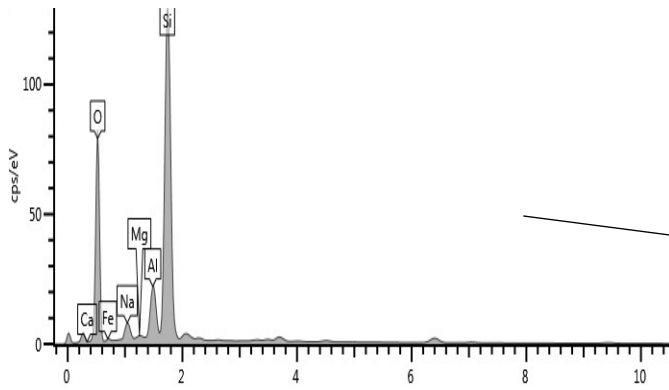


565

566

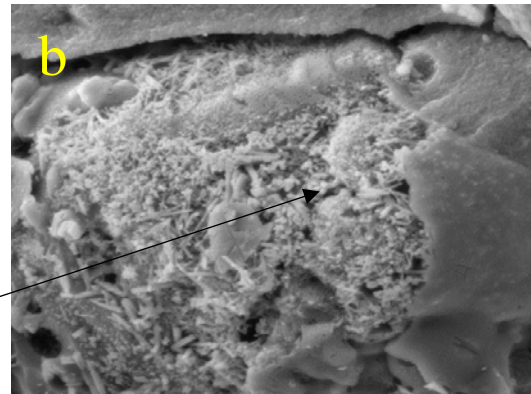
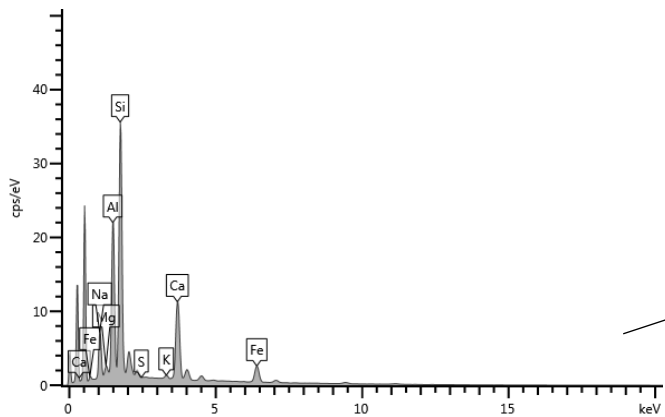
567 **Fig. 9.** SEM images of geopolymer mortars before acid submerged (A-0: FA-NS2, B-0: FA-
 568 PC-NS2, C-0: FA-S-NS2) and after 90 days acid exposure (a) FA-NS0, (b) FA-NS2, (c) FA-
 569 PC-NS0, (d) FA-PC-NS2, (e) FA-S-NS0 and (f) FA-S-NS2

570

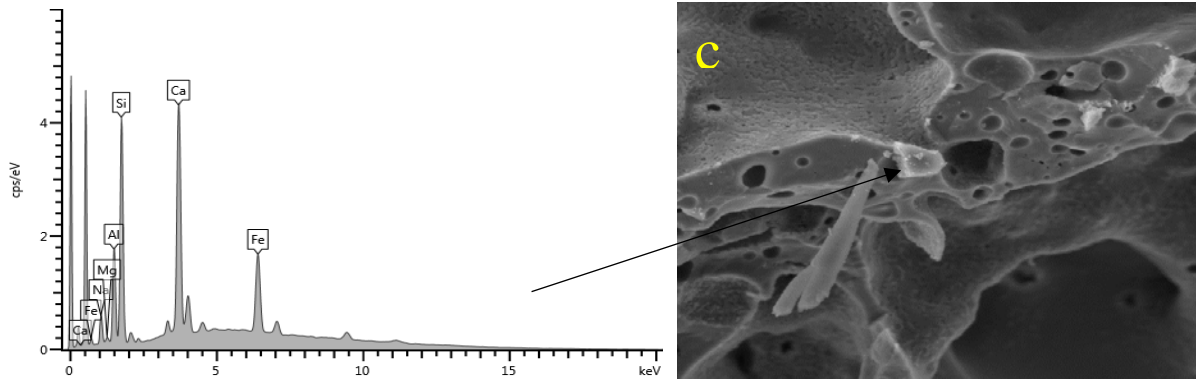


571

572



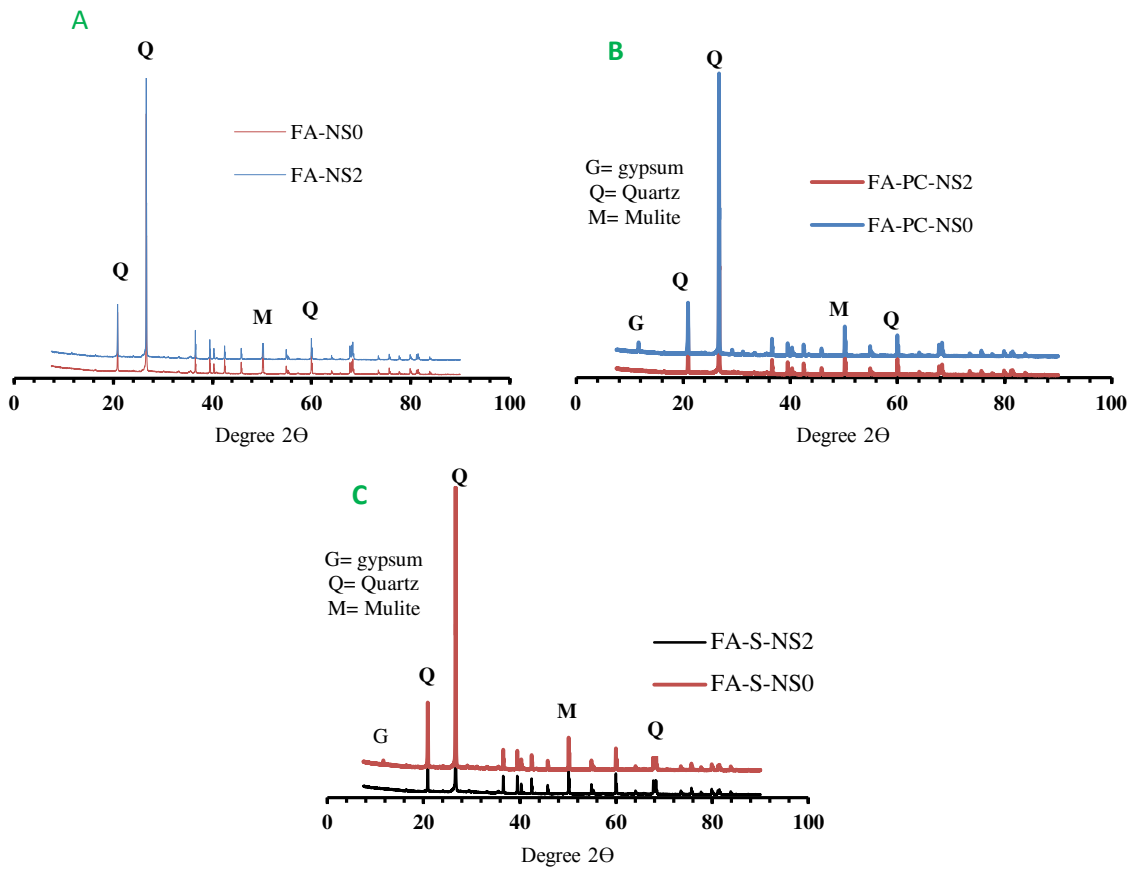
573



574

575
576

Fig.10. EDX spectra of geopolymers mortar without nano-silica under acid exposure (a) Fly-ash only, (b) OPC blended fly-ash and (c) GGBFS blended fly-ash



577

578

579

580

581

582

583

584

585

586

587

588

589

Fig. 11. X-ray diffraction patterns of geopolymers mortar under sulfuric acid exposure: (A) fly ash only with 0% and 2% nano-silica. (B) OPC blended fly ash with 0% and 2% nano-silica (C) GGBFS blended fly ash with 0% and 2% nano-silica.