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

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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: A*cid 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 CO_2 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 ^{o}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 H$_2$SO$_4$ ionization could destroy the alumino-silicate network

2

68 in geopolymer and yielded silicic acid (Si (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 m^2/kg, 370 m^2/kg and 450 m^2/kg respectively.

91   The activating chemicals were sodium silicate with a chemical composition of (wt.

92 %): Na_2O = 11.5, 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 $50 \times 50 \times 50$

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 ($20\pm2°C$) at a relative humidity of $70\pm10\%$. 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 2h-range of 5–80Θ. 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

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

3. Results and discussion

3.1. Flow behaviour of fresh geopolymer mortar

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

3.2. Compressive strength

The compressive strength developments of the fly ash geopolymer mortars with 0%, 1%, 2% and 3% nano-silica are shown in Fig. 2. Each value is an average of the results obtained from 3 identical specimens. The coefficients of variation of the results were mostly within 5%. For example, the coefficients of variation of the 28 day-compressive strengths all the geopolymer 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 3.575×10^{-3} mm/s$^{1/2}$ to 3.980×10^{-3} mm/s$^{1/2}$ and that of the mixes with 2% nano-silica

219   was in the range of 1.247×10^{-3} mm/s$^{1/2}$ to 2.157×10^{-3} 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 3.575×10^{-3} mm/s$^{1/2}$ to

222   1.247×10^{-3} 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.

3.4 Resistance to attack by sulfuric acid

236

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 $Ca(OH)_2$ 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.

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 GGFBS 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

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

4. Conclusions

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

- Inclusion of nano-silica improved the early-age strength of geopolymer mortars based on fly ash alone or that blended with OPC or GGBFS. Flow of the freshly mixed mortars gradually decreased with the increase of nano-silica because of its high specific surface. The compressive strength of the ambient-cured geopolymer mortars varied from 17 to 19 MPa at 7 days and from 29 to 60 MPa at 28 days. Strength development in ambient condition continued to the age of 90 days, however at slower rates after 56 days. The optimum dosage of nano-silica for maximum compressive strength was found to be 2% of the binder.

- Sorptivity of the specimens with 2% nano-silica was less than that of the control specimen. All the specimens remained intact after 90 days of immersion in 3% sulfuric acid solutions with some erosion on the surface of the specimens containing OPC. The average mass loss of the specimens of three series decreased from 2.6% to 1.8% after 90 days of immersion. The strength loss of the specimens without nano-silica ranged from 30% to 41% while that of the specimens with 2% nano-silica ranged from 9% to 11% after 90 days of immersion. Therefore, the acid resistance of geopolymer mortars significantly improved with the inclusion of 2% nano-silica.

- After 90 days of immersion in acid solutions, the microstructures of the specimens with nano-silica were found to be more compact as compared to the specimens without nano-silica. The combined effects of the nano-silica as a filler and enhanced reactivity of the aluminosilicate source materials refined the pore structure to develop a more compact microstructure. This reduced the porosity and sorptivity of the binder

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

Acknowledgments

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Table 1. Chemical compositions of fly ash, OPC and GGBFS (% mass)

Material	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	MnO	K_2O	Na_2O	P_2O_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	-	-	-	-	-	-	-	-	-

[a] Loss on ignition

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

[a]Sodium hydroxide, [b]Sodium silicate

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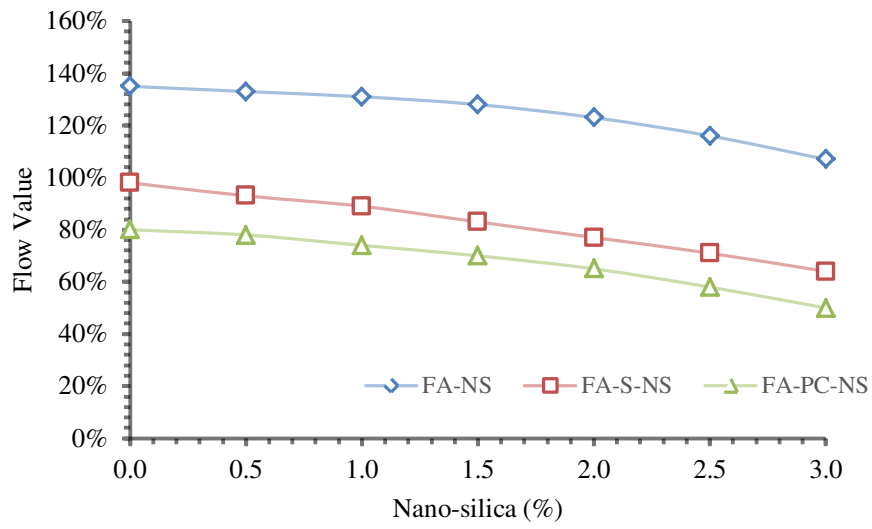
Fig. 1. Change in flow of geopolymer mortars with nano-silica.
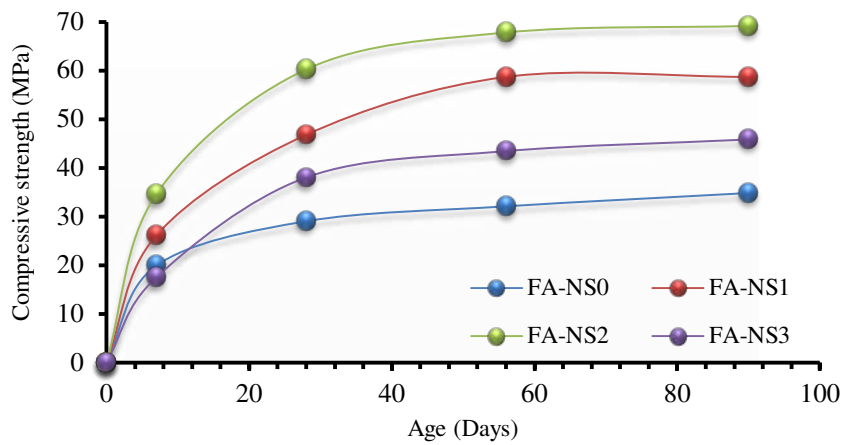
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529   **Fig. 2.** Strength development of fly ash based geopolymer mortars with nano-silica
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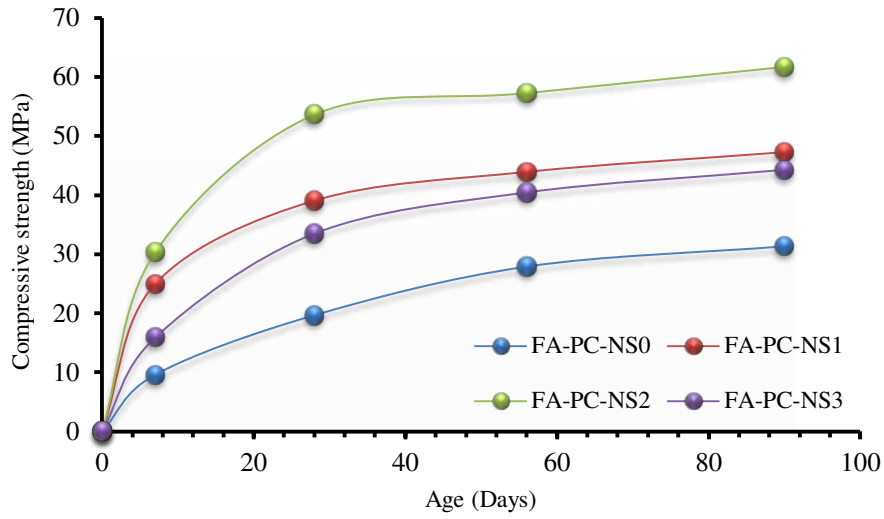
Fig. 3. Strength development of OPC blended fly ash based geopolymer mortar with nano-silica

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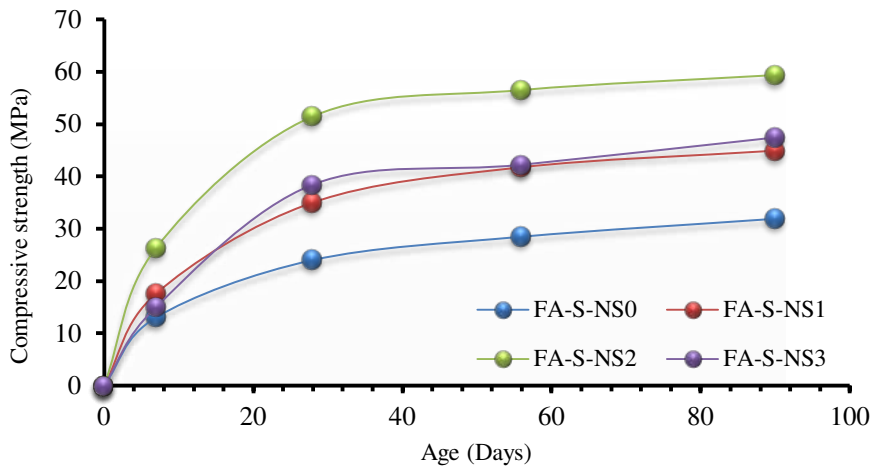
Fig. 4. Strength development of GGBFS blended fly ash based geopolymer mortar with nano-silica
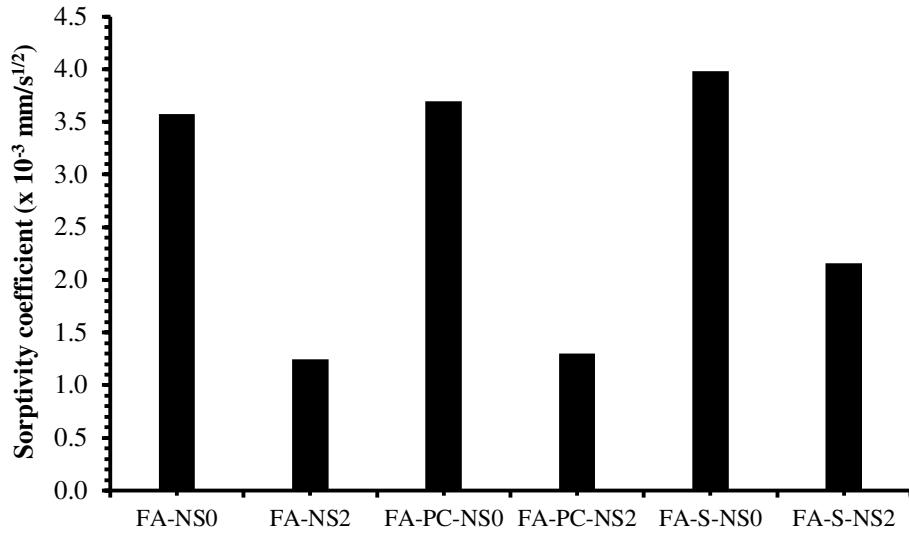
**Fig. 5.** Sorptivity coefficient of geopolymer mortars with nano-silica.
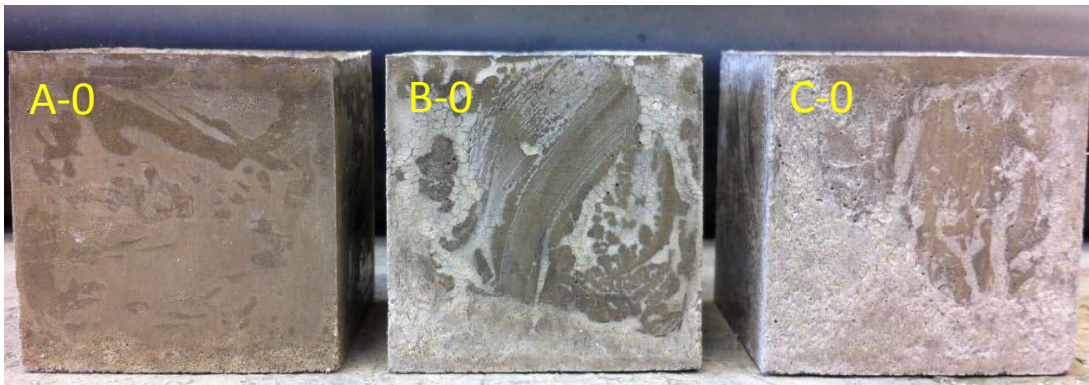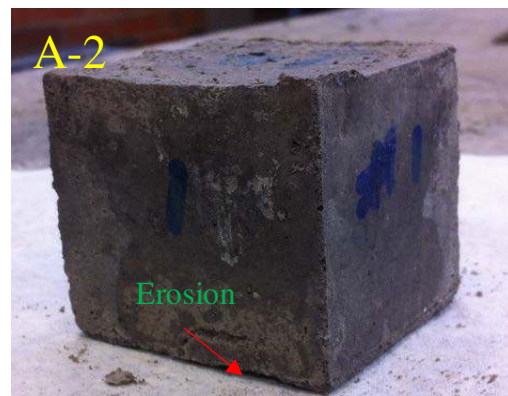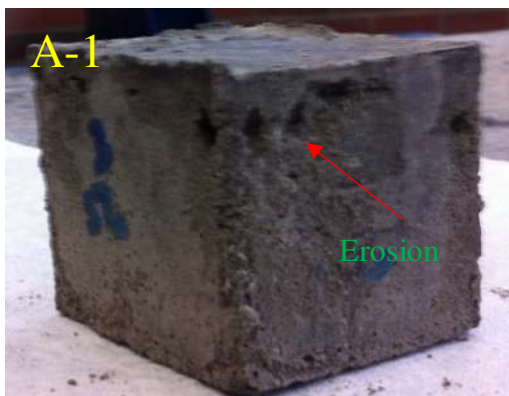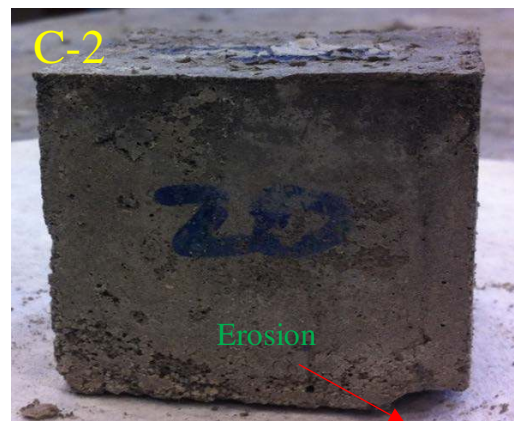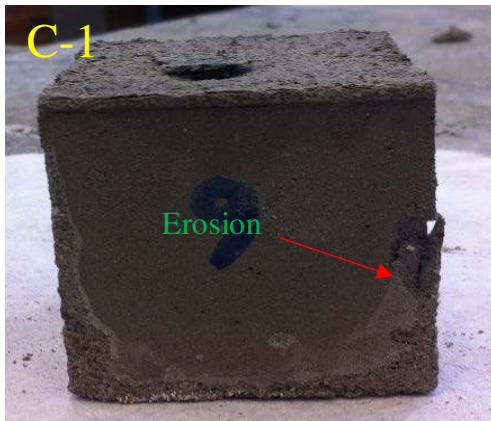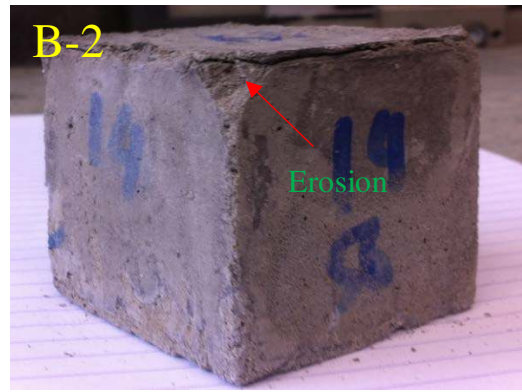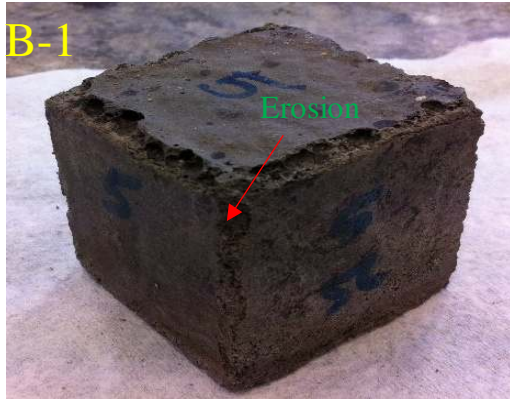
Fig. 6. Visual appearance of geopolymer specimens before acid submerged (A-0: FA-NS0, B-0: FA-PC-NS0, C-0: FA-S-NS0) and after 90 days acid exposure (A) A-1: FA-NS0, A-2: FA-NS2 (B) B-1: FA-PC-NS0, B-2: FA-PC-NS2, (C) C-1: FA-S-NS0, C-2: FA-SNS2.
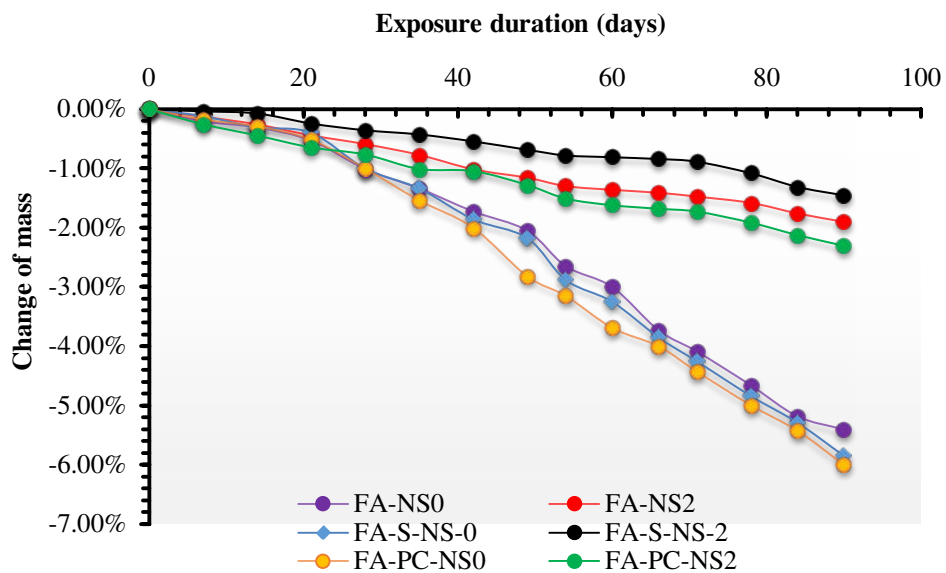
Fig. 7. Change in mass of mortar specimens after immersion in 3% sulfuric acid solution.
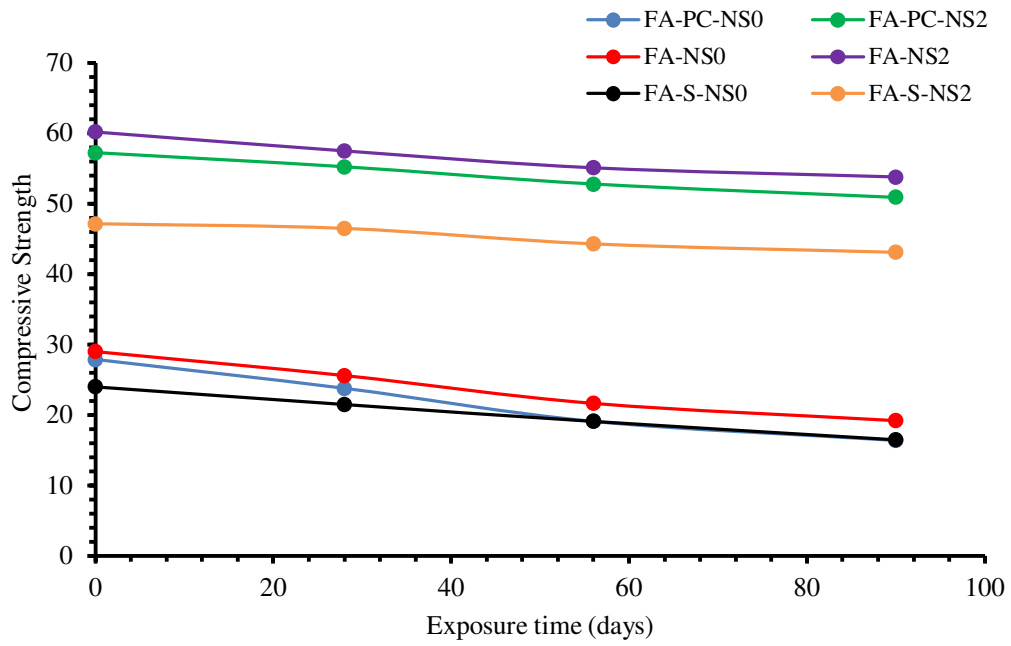
Fig. 8. Change in compressive strength of geopolymer mortars in sulfuric acid exposure.
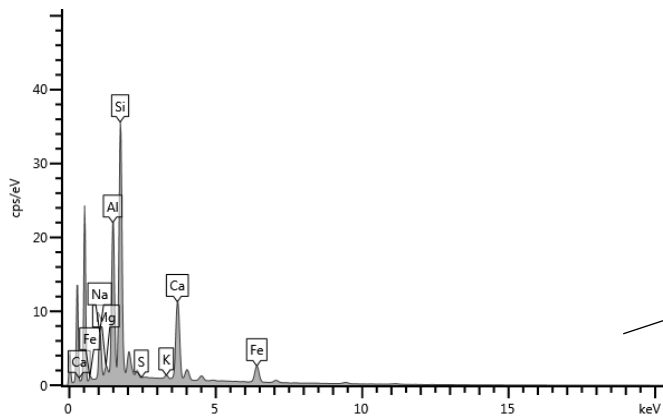
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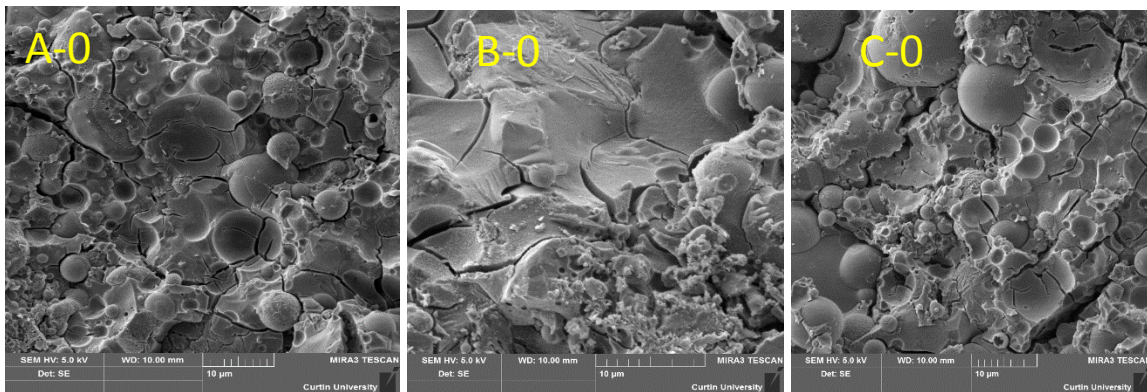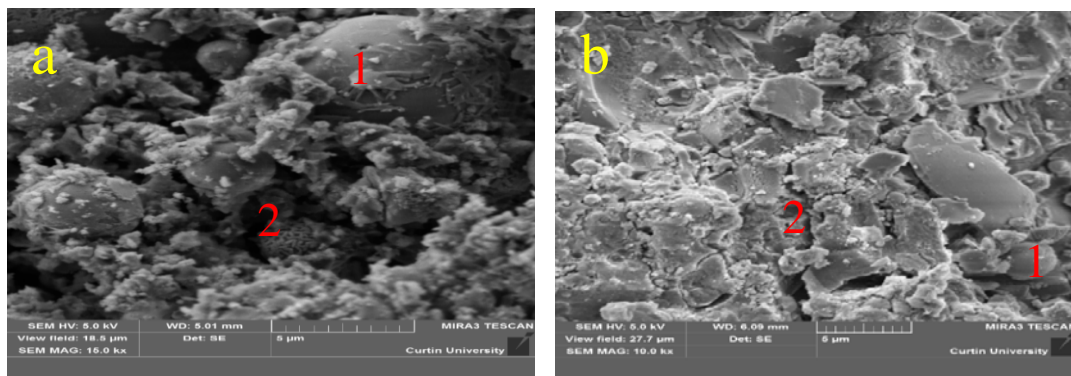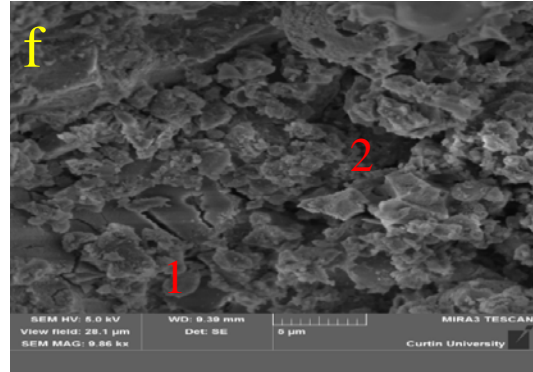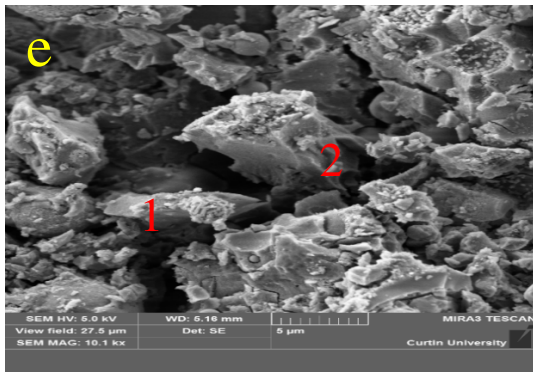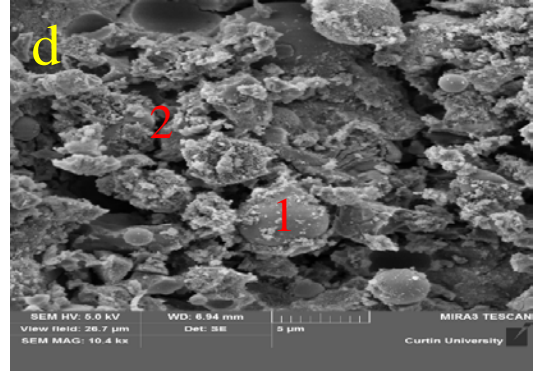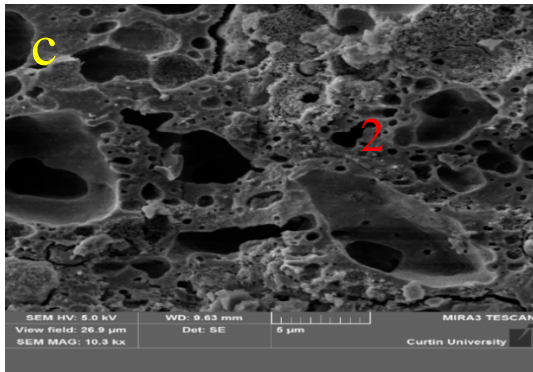
567 **Fig. 9.** SEM images of geopolymer mortars before acid submerged (A-0: FA-NS2, B-0: FA-
568 PC-NS2, C-0: FA-S-NS2) and after 90 days acid exposure (a) FA-NS0, (b) FA-NS2, (c) FA-
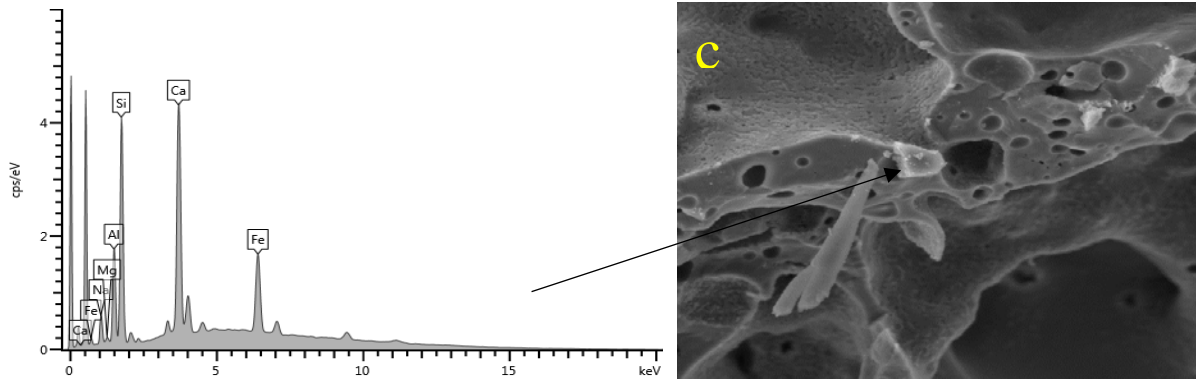569 PC-NS0, (d) FA-PC-NS2, (e) FA-S-NS0 and (f) FA-S-NS2

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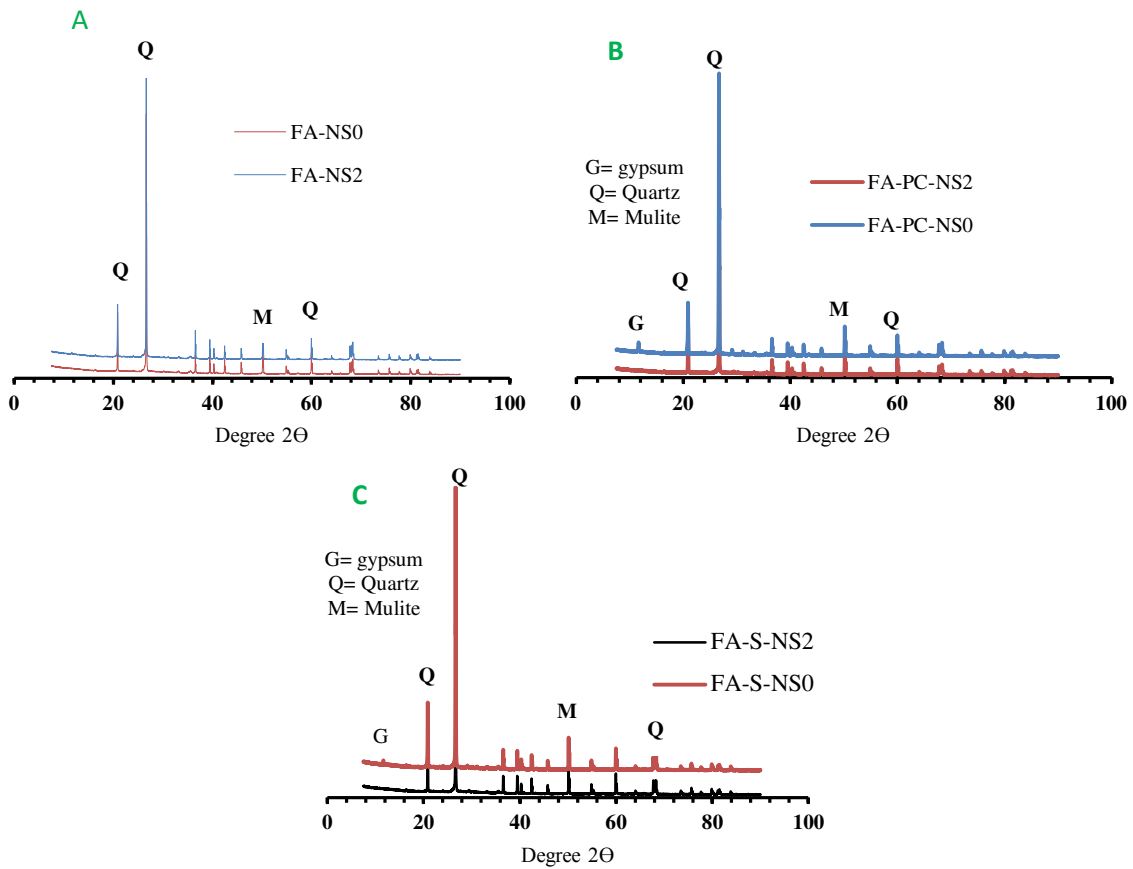
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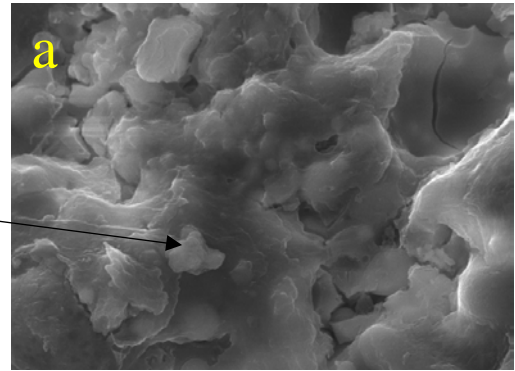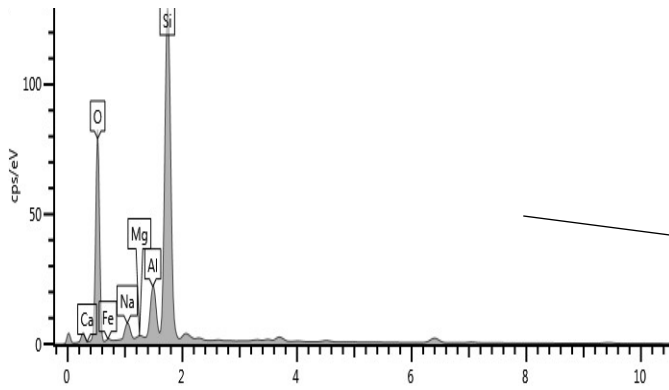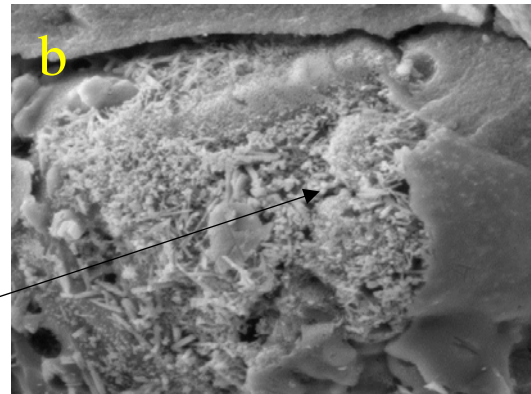
Fig.10. EDX spectra of geopolymers mortar without nano-silica under acid exposure (a) Fly-ash only, (b) OPC blended fly-ash and (c) GGBFS blended fly-ash

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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.

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