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Effect of nano-silica on the chemical durability and mechanical performance of fly ash based geopolymer concrete

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A R T I C L E   I N F O

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A B S T R A C T

In this study, the effect of nano silica on the short term severe durability performance of fly ash based geopolymer concrete (GPC) specimens was investigated. Four types of GPC were produced with two types of low calcium fly ashes (FAI and FAII) with and without nano silica, and ordinary Portland cement concrete (OPC) concrete was also cast for reference. For the geopolymerization process, the alkaline activator has selected a mixture of sodium silicate solution (Na_2SiO_3) and sodium hydroxide solution (NaOH) with a ratio (Na_2SiO_3/NaOH) of 2.5. Main objectives of the study were to investigate the effect of usability or replaceability of nano silica-based low calcium fly ash based geopolymer concretes instead of OPC concrete in structural applications and make a contribution to standardization process of the fly ash based geopolymer concrete. To achieve the goals, four types of geopolymer and OPC concretes were subjected to sulfuric acid (H_2SO_4), magnesium sulfate ($MgSO_4$) and seawater (NaCl) solutions with concentrations of 5%, 5%, and 3.5%, respectively. Visual appearances and weight changes of the concretes under chemical environments were utilized for durability aspects. Compressive, splitting tensile and flexural strength tests were also performed on specimens to evaluate the mechanical performance under chemical environments. Results indicated that FAGPC concretes showed superior performance than OPC concrete under chemical attacks due to low calcium content. Amongst the chemical environments, sulfuric acid (H_2SO_4) was found to be the most dangerous environment for all concrete types. In addition, nano silica (NS) addition to FAGPC specimens improved both durability and residual mechanical strength due to the lower porosity and more dense structure. The FAIIGPC specimens including nano silica showed the superior mechanical performance under chemical environment.

1. Introduction

Global warming becomes a critical issue nowadays and the released CO_2 due to cement production is considered to be responsible for approximately 7% of all greenhouse gases released worldwide [1]. The released CO_2 amount increases with an increase in population. Therefore, the adverse effect of CO_2 releases or cement production to the environment is a significant trouble for both cement producers and human being. Novel structural materials are required to be used instead of OPC concrete to overcome this environmental issue. To date, researchers focused on the partial use of alternative cementitious materials (fly ash, silica fume, slag etc.) to improve the durability and mechanical performance of concrete [2]. Recently, a new type of environmentally-friendly geopolymer concrete becomes popular and it gives a chance to replace cement by appropriate aluminosilicate source such as fly ash [3]. Research showed that geopolymer concrete (GPC) showed superior performances to chemical attacks, shrinkage, and creep [4,5] compared to OPC concrete.

The fundamental materials of GPC are the alkali-activated solution and the alumina-silicate based materials [6,7]. The selection of alumina-silicate based materials to produce GPC depends on the cost and availability of the material, and type of application [8,9]. The mechanism of GPC represented by strong alumina-silicate ($Al\text{-}SiO_2$) polymeric structures results from the generation of alumina and silica by sodium hydroxides (NaOH) or potassium hydroxides (KOH) and sodium silicates (Na_2SiO_3) as an alkaline solution [10]. In addition, the existence of calcium (Ca) compound plays an important role since the calcium ions are able to act as a charge balancing cation in the geopolymer binder [11–13]. As an alkaline activator, together with the use of sodium silicate and sodium hydroxide or potassium hydroxide is the most common alkali-activated solution in geopolymerization [14]. The increased NaOH concentration in fly ash based GPC specimens

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enhances the compressive strength when heat curing is applied at 60 °C for 48 h [15,16]. OPC concrete more susceptible to chemical attacks due to its alkaline nature [17], while GPC specimens showed superior resistance to sulfuric acid attack [18] and acetic acid and sulfate attacks [19,20] due to its more stable and strong cross-linked alumina-silicate polymer structure. Daviodovits et al. studied the weight losses under chemical attacks and they found that OPC specimens showed 78% and 95% weight losses, while GPC specimens showed only 6% and 7% under the exposure of 28 days to the sulfuric acid and hydrochloric acid, respectively [21]. A high resistance to chemical attack resulted from both the high alkaline concentration and the presence of Ca in the geopolymer binder, which contributed the high strength development of the alkali binders [22,23].

Low calcium fly ash based geopolymer concrete can be an alternative to OPC concrete due to its higher durability resistance. Researchers focused on the molar concentrations, curing temperatures generally ranges from 45 °C to 80 °C and mix proportions of the fly ash based GPC specimens [24]. FAGPC specimens require heat curing for strength development, which limited the use of FAGPC in situ applications. Such limitation can overcome by the addition of a suitable amount of nano-silica in the mixture [25]. GPC specimens with nano silica increase the dissolution degree of Si and Si–Al phases and these phases strongly improve the polymerization process [26]. The mechanical strength of FAGPC concrete enhanced with the addition of nano silica up to the particular dosage and mechanical strength started to decrease with the further nano silica addition [27].

The use of nano-silica in OPC concrete was widely investigated and nano silica takes the greatest attention due to its improved effect on the durability and mechanical performance of OPC concrete. However, the effect of nano silica on durability and mechanical performance of low calcium fly ash based geopolymer concrete is limited in the literature. Limited studies were not found adequate for the use of fly ash based concrete in structural design codes or application. Required research is needed for further knowledge about the mechanical behavior of geopolymer concretes under long term and short term severe chemical environments. Therefore, the objective of the study was to investigate the effect of nano silica on mechanical and short-term severe durability performance of low calcium fly ash based geopolymer concrete.

2. Experimental program

2.1. Materials

Four types of geopolymer concrete, FAI, FAII, FAI with nano-silica, FAII with nano-silica and reference concrete (OPC) were produced to evaluate the performance of the geopolymer concretes under chemical environments. Two types of F type fly ash (FAI and FAII), conforming to ASTM C 618, were used in the research and they were obtained from different sources. The crushed limestone was used as a coarse aggregate with a maximum grain size of 10 mm (D_{max}: 10 mm), crushed limestone (≤ 4 mm) and natural sand were used as fine aggregates. The aggregate grading curves were found similar to previous studies [28,29]. The alkaline solution was prepared with a mixture of sodium silicate solution (Na_2SiO_3) and sodium hydroxide solution (NaOH). The sodium silicate solution (Na_2O:13.7%, SiO_2: 29.4, water: 55.9% by mass) was obtained from a local supplier. The sodium hydroxide (NaOH) solution was obtained in pellets with 97–98% purity. The NaOH solids were dissolved in water with 14 M concentration, which was considered to be the weakest concentration amount of GPC under chemical attack [6]. The alkaline solution was prepared in the laboratory at least one day prior to its use. A polycarboxylates based high range water reducing admixture was used as a superplasticizer for workability. Table 1 illustrates the chemical composition and physical properties of FAI, FAII, OPC, and NS (nano silica). The FAII had higher SiO_2 and lower CaO amounts than FAI and the nano-silica material composed of 99.8% SiO_2.

2.2. Mix design, casting, and curing of specimens

Several geopolymer trial batches were cast and tested, and the mixes which achieved the best cohesive and workable concrete were chosen as shown in Table 2 for detailed analyses. Aggregate amount, alkaline solution to fly ash ratios, sodium silicate to sodium hydroxide ratio and curing methods affect the strength and durability of the geopolymer concrete. Sodium silicate to sodium hydroxide ratio becomes in the range of 1.5–2.5for economic reasons [30] and it was used as 2.5 in the study. Activator liquids/ fly ash ratio was selected as 0.45.

Mixing procedure was as follows; dry ingredients; coarse aggregates (SSD condition) and fine aggregates, FAI, FAII, NS, cement (for related mixes) were added into the mixer and mixed for 2.5 min. The prepared alkaline solution and superplasticizer added in 1-min duration together and then further mixed for 2.5 min for homogeneity.

FAIGPC, FAINSGPC, FAIIGPC, FAIINSGPC and OPC specimens were produced to see the effect of fly ash and nano silica materials on the durability and mechanical aspects. Cube specimens with dimensions of 100 × 100 × 100 mm, cylinder specimens with a diameter of 100 mm and height of 200 mm, and prismatic specimens with dimensions of 100 × 100 × 500 mm were cast and tested. Required compaction was applied to specimens to eliminate the air void. After the completion of casting procedure, specimens were covered with plastic bags to minimize evaporation of the alkaline solution. Then, specimens together with the molds were cured in an oven at 70 °C for 48 h to activate geopolymerization since strength enhancement was found insignificant beyond 48 h [31]. After the oven curing period, GPC specimens were put into room temperature at 23 ± 2 °C in the laboratory for 28 days, while OPC specimens were cured in a water tank for 28 days.

2.3. Specimens preparation

There is no standard test method available to determine the durability of concretes under chemical environment. ASTM C 267 test method [32] recommends that specimens should be waited in the water for 24 h to obtain water saturated specimens prior to chemical exposure. Therefore, specimens were soaked in water for 24 h and the initial saturated weights of the concretes were measured. Then, specimens were kept in 5% sulfuric acid, 5% magnesium sulfate and 3.5% sea water solutions for one month. At the same time, control specimens for each concrete were also kept in an ambient condition at a room temperature of 23 ± 2 °C in the laboratory for one month for comparison. The chemical resistance of the concretes was assessed via visual inspection, change in mass, and the variations in the compressive, splitting tensile and flexural strengths.

2.4. Testing procedures

Compressive strength tests on 100 × 100 × 100 cube specimens were executed according to ASTM C39 [33]. Splitting tensile strength tests were done on 100 × 200 mm cylinder specimens in accordance with ASTM C496 [34]. Three-point bending tests were conducted on notched 100 × 100 × 500 mm prismatic specimens according to RILEM 50-FMC/198 Committee [35] using Instron 5500 R closed-loop displacement controlled test machine. A linear variable displacement transducer (LVDT) was utilized to measure vertical displacement at mid-span of the notched prismatic specimens. Notches were realized at the bottom mid-point of the specimens with a 3 mm width and 40 mm height (notch/depth:0.4). Specimens were loaded at a rate of 0.02 mm/min under displacement control. Flexural strength of specimens was calculated using 1st equation [36].

$$f_{flex} = \frac{3P_{\max}L}{2b(d-a)^2} \tag{1}$$

Where P_{max}, L, b, d and a are the peak load (N), span length (mm), the width of the specimen (mm), depth of specimen (mm) and depth of the

Table 1
Chemical composition and physical properties of FAI, FAII, OPC and NS.

Component		CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	K_2O	Na_2O	Loss on ignition	Specific gravity	Blaine Fineness (m^2/kg)
FAI	(%)	2.235	59.197	24.363	7.074	1.404	0.285	3.366	0.378	1.517	2.040	379
FAII	(%)	1.568	62.352	21.137	7.347	2.350	0.103	0.726	2.445	2.071	2.300	387
OPC	(%)	62.115	19.087	5.155	2.876	1.168	2.627	3.881	0.168	2.985	3.150	326
NS	(%)	–	99.796	–	–	–	–	–	–	< 1.000	2.200	–

Table 2
Geopolymer concretes mix ingredients (w/b:0.45).

Materials	Quantity (kg/m^3)				
	FAIGPC	FAINSGPC	FAIIGPC	FAIINSGPC	OPC
Cement	–	–	–	–	500
FAI	500	500	–	–	–
FAII	–	–	500	500	–
Nano silica	–	15	–	15	–
Na_2SO_3 + NaOH	225	225	225	225	–
Water	–	–	–	–	225
Coarse aggregate	1150	1150	1150	1150	1150
Fine aggregate	575	575	575	575	575
Superplasticizer	6	6	6	6	6

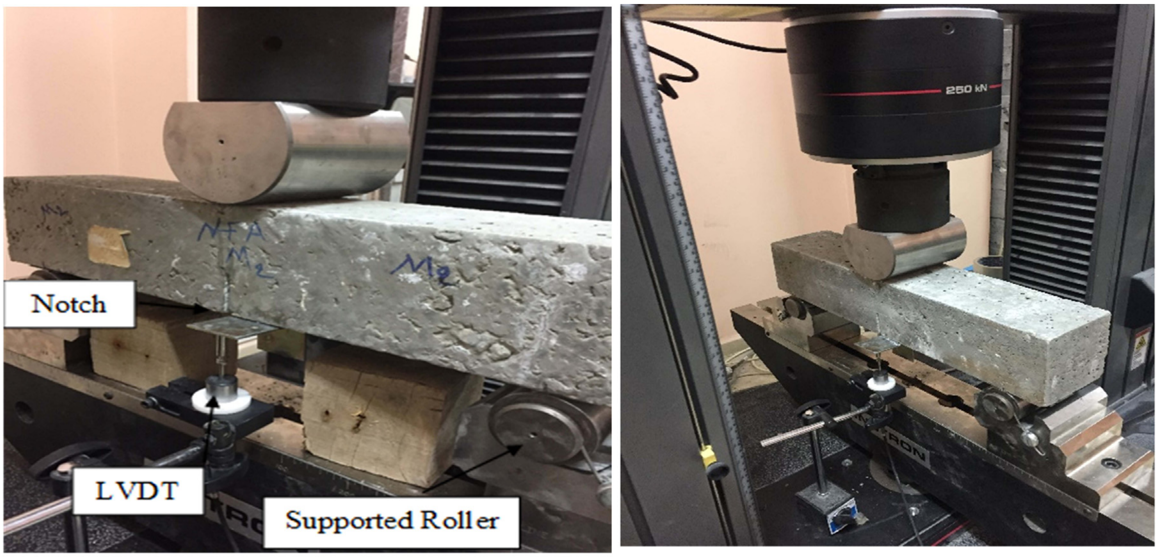
notch (mm), respectively. Three-point bending test set-up details and tested specimens were shown in Fig. 1.

Fracture energy (G_F) of prismatic beam specimens was obtained under three-point bending loading using RILEM [35] formula as following:

$$G_f = \frac{(w_o + mg\delta_s)}{A_{lig}} \tag{2}$$

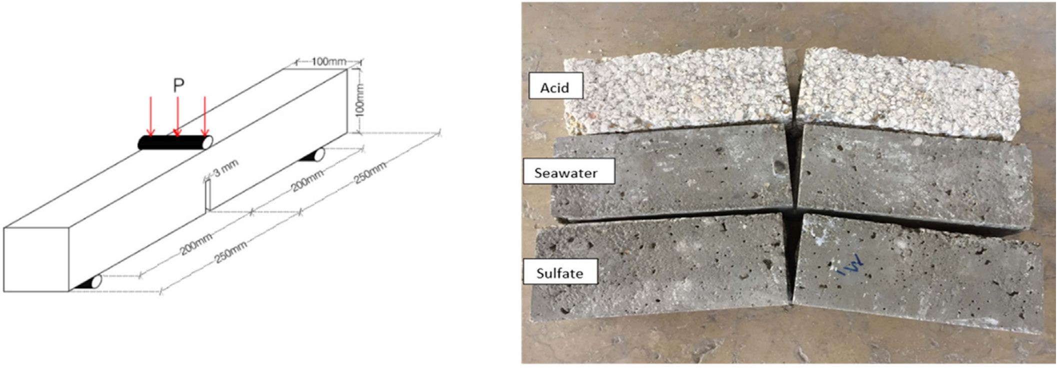
Where w_o, m, g, δ_s, and A_{lig} are the area under the load-displacement curve (N-m), the mass of the beam (kg), acceleration caused by gravity (9.81 m/s^2), specific displacement (m) and area of the ligament (m^2), respectively.

The critical stress intensity factor (K_{IC}) was also calculated using 3rd following equation [37]:



(a) Three-point bending test scheme

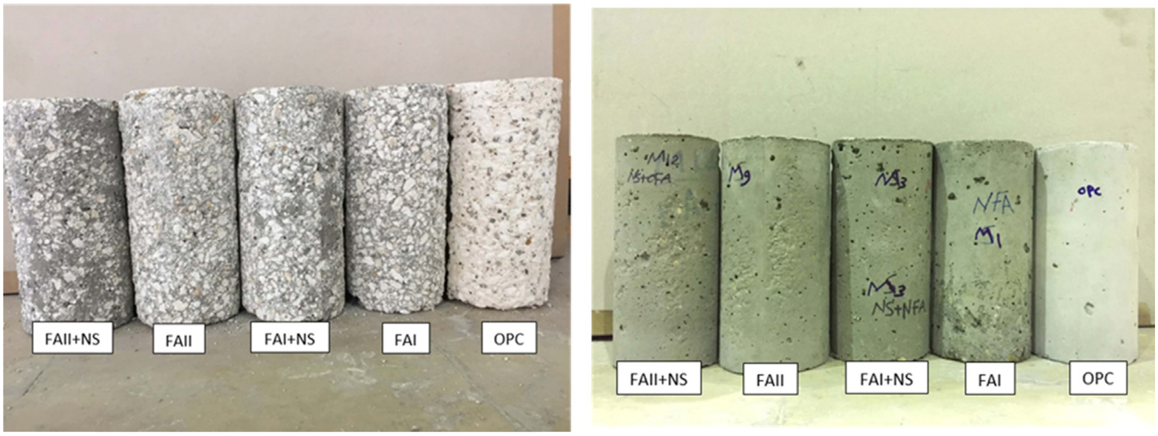
(b) GPC under fracture test



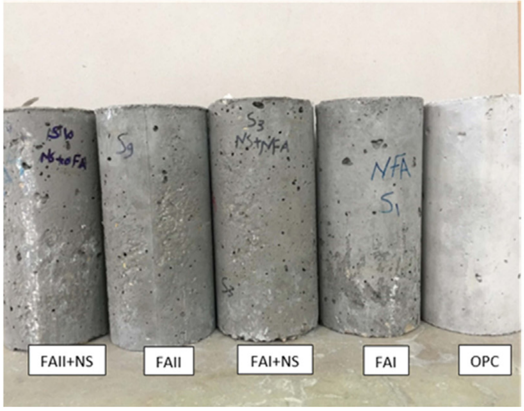
(c) Specimen test geometry

(d) Failure of the specimens under chemical solutions

Fig. 1. Test set-up and specimens under three-point bending loading.



(a) Specimens exposed to sulfuric acid (b) Specimens exposed to magnesium sulfate



(c) Specimen exposed to sea water

Fig. 2. Visual appearance of test specimens exposed to chemical attack for period of 30 days.

$$K_{IC} = \frac{3P_{\max} l}{2bd^2}\sqrt{a_0}\,(1.93 - 3.07A + 14.53A^2 - 25.11A^3 + 25A^4) \tag{3}$$

Where P_{max}, l, b, d, a_0, and A are the peak load, span length, width of specimens, depth of specimens, depth of the notch, and notch depth to specimen depth, respectively.

3. Results and discussion

3.1. Visual appearance

3.1.1. Specimens exposed to the sulfuric acid solution

Fig. 2.a presents the visual appearances of GPC and OPC specimens under 5% sulfuric acid solutions for one month. GPC specimens exposed to sulfuric acid (H_2SO_4) solution showed moderate surface erosion at their surfaces. The erosion amount increased with an increase in the exposure time and OPC specimens showed severe surface erosion due to its higher CaO content. FAIINSGPC specimens, which have lowest CaO amount and highest SiO_2 content showed the lowest surface erosion among specimens due to lower CaO amount and porosity resulted from nano-silica. Fly ash-based GPC specimens without nano silica showed slightly more surface deterioration than the specimens including nano-silica. Therefore, the favorable effect of nano silica on the durability performance of GPC can be clearly observed even in the short-term period. However, the softening of the surfaces was realized on all specimens when compared to unexposed specimens.

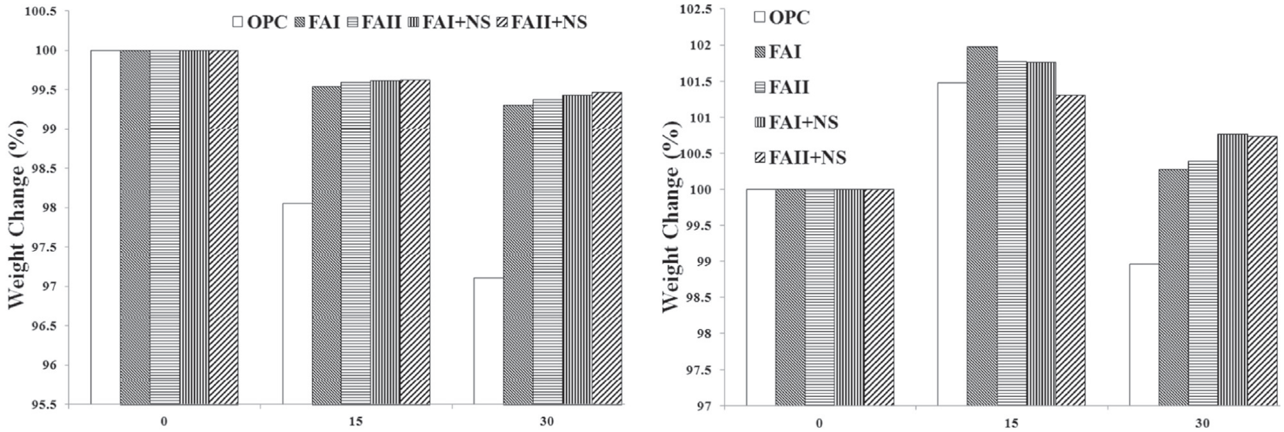
3.1.2. Specimens exposed to magnesium sulfate and seawater (NaCl) solutions

Fig. 2.b and c illustrate the specimens exposed to magnesium sulfate and seawater solutions. Fly ash-based GPC samples maintained their initial conditions and hence no gypsum formation, color change, spalling and cracking was observed on the sample surfaces. On the contrary, the surface color of OPC concrete changed from gray to white. All specimens were observed to be structurally intact. Similar findings were also found by other researchers [38,39]. It can be concluded that sulfuric acid attack seems more hazardous than magnesium sulfate and sea water solutions for both fly ashes based geopolymer and OPC concretes.

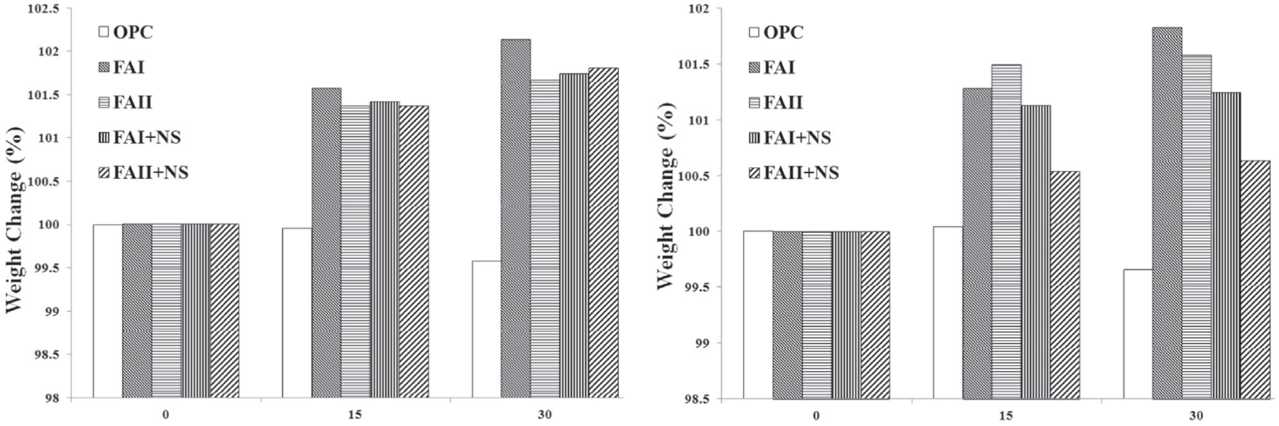
3.2. Weight change

Weight change of the GPC and OPC specimens were observed after two weeks and one month later from different chemical environments. Dummy or control specimens were left in an ambient environment for comparison. Fig. 3.a illustrates the weight change of the control specimens. The reduction in weight was observed in all control specimens at ambient environment due to continuous hydration reaction [40,41]. The weight loss of the OPC specimens was more than 3-times the weight loss of the GPC specimens. It may be attributed to oven curing condition (70 °C for 48 h) of the GPC specimens since most of the hydration reactions took place on the first days. When fly ash based GPC specimens were evaluated, similar weight losses (∼ 0.5%) were obtained during hydration process after one-month exposure to the ambient condition. Results also indicated that small amount of nano-silica addition (3% by binder weight) had no or negligible effect on weight change of the specimens at ambient environment.

Fig. 3.b shows the weight change of specimens under the 5% sulfuric acid environment. The weight gain was observed for the specimens after two weeks of chemical exposure. The weight gains of the



(a) Specimens exposed to ambient environment (b) Specimens exposed to sulfuric acid



(c) Specimens exposed to magnesium sulfate (d) Specimens exposed to seawater

Fig. 3. Weight change of the specimens under different environment.

specimens were 1.48%, 1.98%, 1.77%, 1.76%, and 1.30% for OPC, FAI, FAII, FAI + NS, and FAII + NS based GPC specimens, respectively. Weight gain resulted from sulfuric acid exposure were also reported in the earlier research [42,43]. After two weeks of exposure, however, specimens started to lose their increased weights, which attributed to alkali and some material dissolution from concretes into the acidic environment [43]. For OPC concrete, sulfuric acid attack neutralized the hydration products and disrupted the interfacial transition zone, so disintegration of the aggregate particles from OPC concrete took place [44]. After one month exposure to the 5% sulfuric acid attack, the weight loss for OPC specimens was around 1%, while the weight gains for GPC specimens were 0.28%, 0.39%, 0.77% and 0.74% for FAI, FAII, FAI + NS, and FAII + NS based GPC specimens, respectively. In addition, the nano-silica including mixes showed less weight reduction for both fly ash mixes due to the more dense structure, and decreased porosity and permeability [45]. OPC specimens showed higher weight losses than fly ash based GPC specimens due to the reaction between CaO in the OPC and the harmful ions from sulfuric acid solution [17].

Fig. 3.c and .d present the fly ash based GPC with/out nano silica specimens exposed to 5% magnesium sulfate and 3.5% seawater solutions, respectively. The weight gains due to magnesium sulfate solutions were 1.57%, 1.37%, 1.42%, and 1.36% for two weeks and 2.13%, 1.67%, 1.74%, and 1.80% for one-month exposure of FAI, FAII, FAI + NS, and FAII + NS based GPC specimens, respectively. In addition, the increased weights under seawater environment were 1.28%, 1.49%, 1.13%, and 0.54% for two weeks and 1.83%, 1.58%, 1.25%, and 0.64% for one-month exposure of FAI, FAII, FAI + NS, and FAII + NS based GPC specimens, respectively. The reduced amount of chemical absorption was observed for FAI and FAII based GPC specimens with nano silica, indicating decreased porosity and permeability of the specimens and increased dense structure resulted from nano-silica. In addition, the nano silica-based GPC specimens showed very less amount weight change with an increasing exposure time and hence nano-silica can be more significant for long-term durability of GPC specimens. The weight gain due to absorption of the chemical solution was also reported by Thokchom et al. [46] and Wallah and Rangan [5]. In the case of OPC specimens, the weight losses under 5% magnesium sulfate and 3.5% seawater environment were 0.43% and 0.35%, respectively. The similar weight loss was also reported in the previous study [44].

3.3. Compressive strength

Fig. 4 illustrates the compressive strength test results of the GPC and OPC specimens under control, 3.5% seawater, 5% magnesium sulfate and 5% sulfuric acid environments. Numbers in the top of each related graphics data indicated the residual compressive strengths (%) of the specimens after the related chemical exposure. Three identical samples were used to obtain an average compressive strength value for each concrete. Compressive strength test results of control OPC specimens showed slightly higher compressive strength than fly ash based GPC specimens. The lowest compressive strength in FAGPC specimens was attributed to the low activity of fly ash [47] and low calcium content [48,49]. Chi et al. studied the effect of slag, fly ash and slag/fly ash combinations on compressive strength in geopolymer and OPC

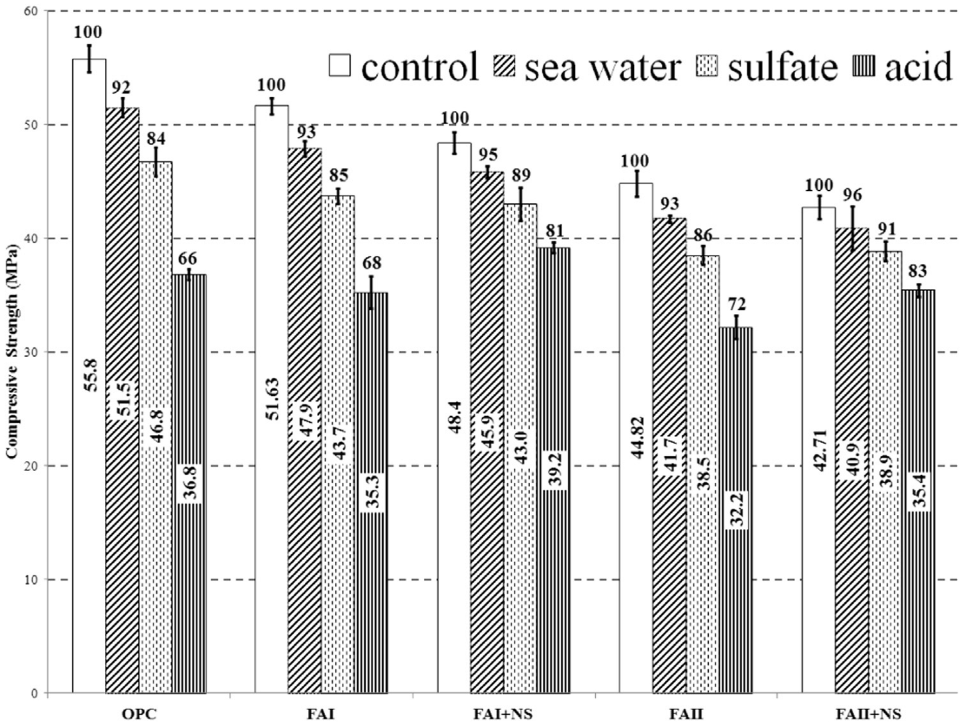


Fig. 4. Compressive strength change of the specimens exposed to various chemical environment.

concretes and they found that compressive strength of the concretes were increased in the order of fly ash based GPC < OPC < fly ash/slag combination GPC < slag based GPC. After XRD results on the FAGPC (100% fly ash) specimens, less content of reactive calcium resulted in the reduced amount of calcium silicate hydrate (C-S-H). Therefore, low mechanical strength was obtained for FAGPC specimens since the less amount of calcium in the fly ash did not participate in the calcium silicate hydrate formation (the main product that responsible for strength) [47]. In this study, FAGPC specimens including nano silica showed lower compressive strength values than the FAGPC specimens without nano-silica. It may be attributed to the unreacted nano-silica particles since they cause an excessive self-dehydration and cracks in the matrix that eventually reduces the compressive strengths of the specimens [49].

The decrease in the compressive strengths of OPC specimens were 8%, 16% and 34% under seawater, magnesium sulfate, and sulfuric acid, respectively. The reduction in the compressive strengths of FAI and FAI + NS specimens (GPC produced with the first type of fly ash) were 7%, 15%, and 32% and 5%, 11%, and 19% exposed to seawater, magnesium sulfate, and sulfuric acid, respectively. The decline in the compressive strength for FAII and FAII + NS specimens (GPC produced with the second type of fly ash) were 7%, 14%, and 28%, and 4%, 9% and 17% exposed to seawater, magnesium sulfate and sulfuric acid environments, respectively. The reduction in the strength of fly ash based GPC specimens exposed to acid attack may be attributed to destroy of the oxy-aluminum bridge (-Al-Si-O) of geopolymeric gel [50]. In addition, the nano-silica addition to fly ash based GPC specimens increased the residual concrete strength due to the lower porosity and the denser structure. The lowest compressive strength reduction was observed in FAII + NS specimens than FAI + NS specimens as FAII materials included the lowest amount of calcium. It was concluded that low amount of calcium is adequate for the chemical reactions and therefore, CaO can be responsible for the deterioration of concrete under chemical attacks. Similar results were also found in the previous study [51].

The fly ash based GPC specimens performed a slight better compressive strength than OPC under chemical environment and the strength difference was found highest especially in the sulfuric acid environment. This strength difference may increase further with an increase in the exposure time especially for the FAII + NS specimens. In addition, sulfuric acid (5%) and seawater (3.5%) environments were found as the most and the least dangerous environments for both OPC specimens and fly ash based GPC specimens. The deterioration mechanism exposed to sulfuric acid for OPC can be identified that as sulfuric acid spreads the C-S-H and N-A-S-H decalcifies and hence Ca/Si ratio diminishes. Due to the high calcium content in OPC, Ca/Si ratio increases and the free calcium is responsible for the deterioration of the cement paste by the formation of gypsum and ettringite which can cause expansion, dimensional instability, cracking, spalling and loss of mechanical performance [17,52]. Bacharev also studied the resistance of geopolymer concrete under acid attack and stated that the loss of mechanical performance due to acid attack was attributed to zeolites and the grains that have low intercrystalline bond strength [19].

Degradation mechanism for sulfate attacks by ions in the soil, groundwater, and seawater can be explained that sulfate ions diffuse into the hydrated cement paste and react with C_3A in the presence of Ca$(OH)_2$ to form ettringite and gypsum, causing expansion and deterioration of concrete [19]. Brucite ($Mg(OH)_2$) is also formed due to magnesium sulfate attack and the brucite retards the adverse outcomes of sulfate attack at a preliminary phase. However, in the following stages, decomposition of CSH gel to MSH gel occurs, which results in softening of the binder and decreased mechanical strength [53]. For GPC, alkalis from geopolymer concrete diffuse into the magnesium sulfate solution, and magnesium and calcium ions diffuse into the subsurface areas to react with the sodium silicate or sodium hydroxide and potassium hydroxides in alkaline solution, resulting in ettringite generation and the poor mechanical performance [39]. Therefore, FAGPC specimens showed lower mechanical strength and durability characteristics. However, similar compressive strength results were obtained even in this case; therefore, OPC specimens can be replaced by FAGPC specimens in structural applications.

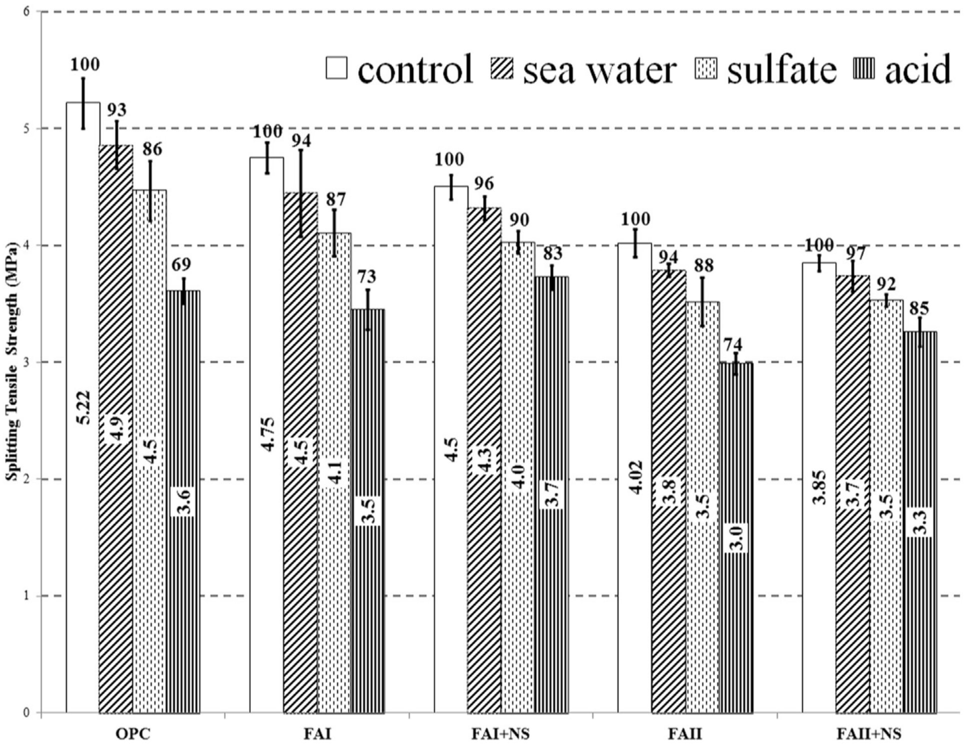


Fig. 5. Splitting tensile strength change of the specimens exposed to various chemical environment.

3.4. Splitting tensile strength

Fig. 5 illustrates the splitting tensile strength test results. Numbers in the top of each related graphics data indicated the residual compressive strengths (%) of the specimens after the related chemical exposure. The decline in the splitting tensile strengths of OPC specimens were 7%, 14%, and 31% under seawater, magnesium sulfate, and sulfuric acid, respectively. The reduction in the splitting tensile strength for FAI and FAI with nano silica specimens were 6%, 13%, 27%, and 4%, 10%, 17% exposed to seawater, magnesium sulfate, and sulfuric acid environment, respectively. The decrease in the splitting tensile strength for FAII and FAII with nano silica specimens were 6%, 12%, 26%, and 3%, 8%, 15% under seawater, magnesium sulfate, and sulfuric acid, respectively.

The addition of nano-silica led to reducing the splitting tensile strength due to the unreacted nano-silica, which was responsible both for the extreme self-desiccation in the matrix and lower splitting tensile strength [49]. However, the favorable effect of nano-silica on the residual tensile strength was observed clearly under chemical environment, especially under sulfuric acid environment. It may be resulted from the increased density of specimens due to nano-silica, since nano-silica make the mixture less permeable, thereby increasing the chemical resistance. In addition, the incorporation of NS in GPC specimens increase the magnitude of soluble silica, reducing the extent of damage caused by sulfuric acid in the alumina silicate structure [54].

FAII based GPC specimens showed less strength loss than FAI based specimens with and without nano silica under chemical environment. This may be attributed to low calcium amount in the second type of fly ash particles (FAII), causing less amount of ettringite and gypsum formation. The strength reduction was due to the presence of harmful ions from exposure solution. The harmful ions destroy the alumina-silicate-bonds (-Al-Si-O) inside fly ash based GPC specimens and result in the reduction in strength, weight and physical damage at the surface of the specimens. Splitting tensile strength test results also proved that sulfuric acid (5%) was the most hazardous and the seawater (3.5%) was the least hazardous environment.

For structural design codes and specifications of fly ash based geopolymer concrete, one of the aims of the study was to check whether or not the existing formulas that proposed for OPC can be applied for the geopolymer concrete. For this purpose, the ACI 363-R92 [55] and CEB-FIP [56] proposed formulas according to OPC (4th and 5th) between compressive strength versus splitting tensile strength were investigated.

$$fsp = 0.59*(fc')^{0.5} \tag{4}$$

$$fsp = 0.301*(fc')^{0.67} \tag{5}$$

The proposed formulas complied with the experimental results with an average error of 3.7% for ACI 363-R92 and 6.83% for CEB-FIP model as shown in (Fig. 6). In addition, the experimental results and proposed formulas matched with well prior to 50 MPa. Therefore, these formulas can be applied for the structural design of normal strength fly ash based geopolymer concrete. After 50 MPa, for the high strength concretes, these formulas deviated from the experimental results and therefore, novel formulas should be proposed for the high strength geopolymer concrete with further investigations.

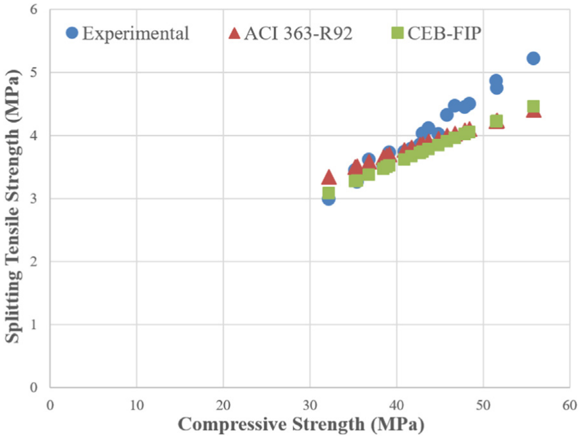
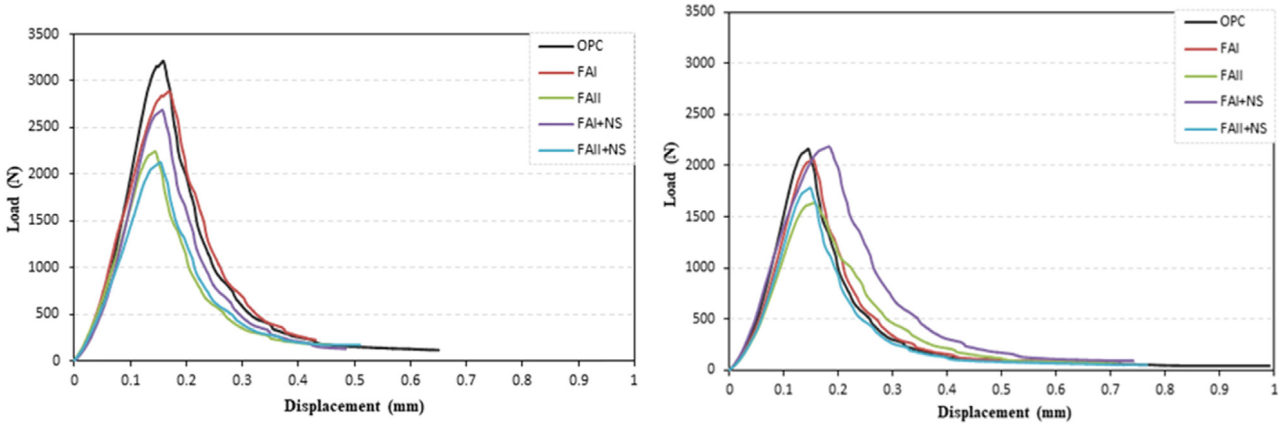
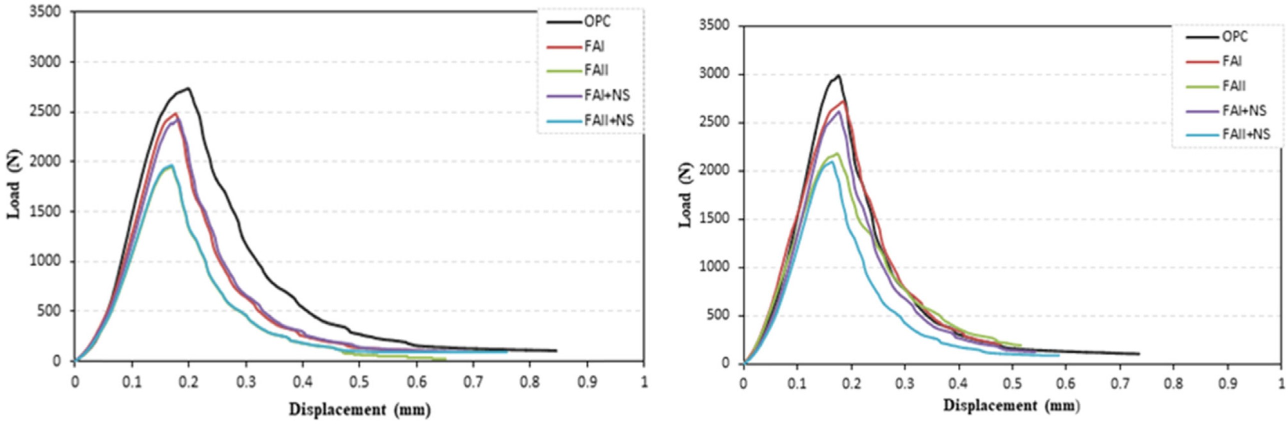


Fig. 6. Compressive strength versus splitting tensile strength relationship.



(a) Specimens under ambient environment

(b) Specimens under sulfuric acid environment



(c) Specimens under magnesium sulfate environment

(d) Specimens under sea water environment

Fig. 7. Typical load versus displacement curves of the specimens exposed to different chemical environment.

3.5. Flexural strength

Fig. 7 presents the load-displacement curves of fly ash based geopolymer and OPC concretes under 5% sulfuric acid, 5% magnesium sulfate and 3.5% seawater environment for one-month exposure.

In general, all GPC and OPC curves showed a linear upward slope until first cracking and strain softening behavior was observed for all specimens. The load-displacement curves of geopolymer specimens showed slightly lower flexural behavior than OPC specimens. In addition, the higher displacement capacities were observed for the unexposed specimens than the exposed specimens due to the poor adherence resulted from the deleterious chemical products/reactions between chemical solutions and concrete specimens. Fig. 8 illustrates the flexural strength changes of the specimens under different chemical environments. The highest flexural strength was obtained for OPC specimens than fly ash based GPC specimens. However, the difference in the residual flexural strengths became smaller in the chemical environments, and the smallest difference was obtained under sulfuric acid environment. In other words, the reduction in the flexural strength was highest for OPC concrete and the lowest for FAII + NS specimens under chemical environments. The favorable effect of nano silica on the residual flexural strength was found obvious. The nano-silica including fly ash based GPC specimens showed superior performance than specimens without nano silica under all various chemical environments. In addition, the best performance was obtained for the specimens including the second type of fly ash (FAII) than the first type of fly ash (FAI) due to the lower Ca content. Sulfuric acid was found the most dangerous environment among the tested chemical environments.

Fig. 9 presents the mechanical strength relationships of the specimens under different chemical environments. A good relationship between compressive strength and flexural strength was observed (R^2: 0.91) for fly ash based specimens and a high relationship was also found (R^2: 0.98) between splitting tensile strength and flexural strength. Flexural and splitting tensile strength test results of geopolymer concrete were similar to OPC, indicating fly ash based geopolymer concretes can also be used instead of OPC concrete in structural design. Nazari et al. [57] also investigated the flexural strengths of ordinary concrete and boroaluminosilicate geopolymer concrete with different steel fiber fractions (2–5 wt%) and found that the improved flexural strengths (up to 50% increase with a steel fiber of 5 wt%) were obtained with an increased amount of steel fibers for geopolymer concretes. The steel fiber effect on flexural strength was also obvious for geopolymer concrete. They concluded that geopolymer concretes can be used instead of OPC concrete in flexural load-bearing structural elements.

3.6. Fracture performance

Figs. 10 and 11 illustrate the fracture energy (G_f) and stress intensity factor (K_{IC}) of the specimens under different chemical environments. The area under the load-displacement curve for each prismatic specimen was calculated using 2nd and 3rd equations to achieve the fracture energy (G_f) and stress intensity factor (K_{IC}) of the specimens. Results showed that OPC concrete specimens showed slightly higher fracture performance than the FAGPC specimens. However, fracture energy and stress intensity factor losses due to chemical environments were lower in the case of FAGPC specimens, especially for the specimens including nano-silica and the second type of fly ash (FAII + NS) due to the low calcium content.

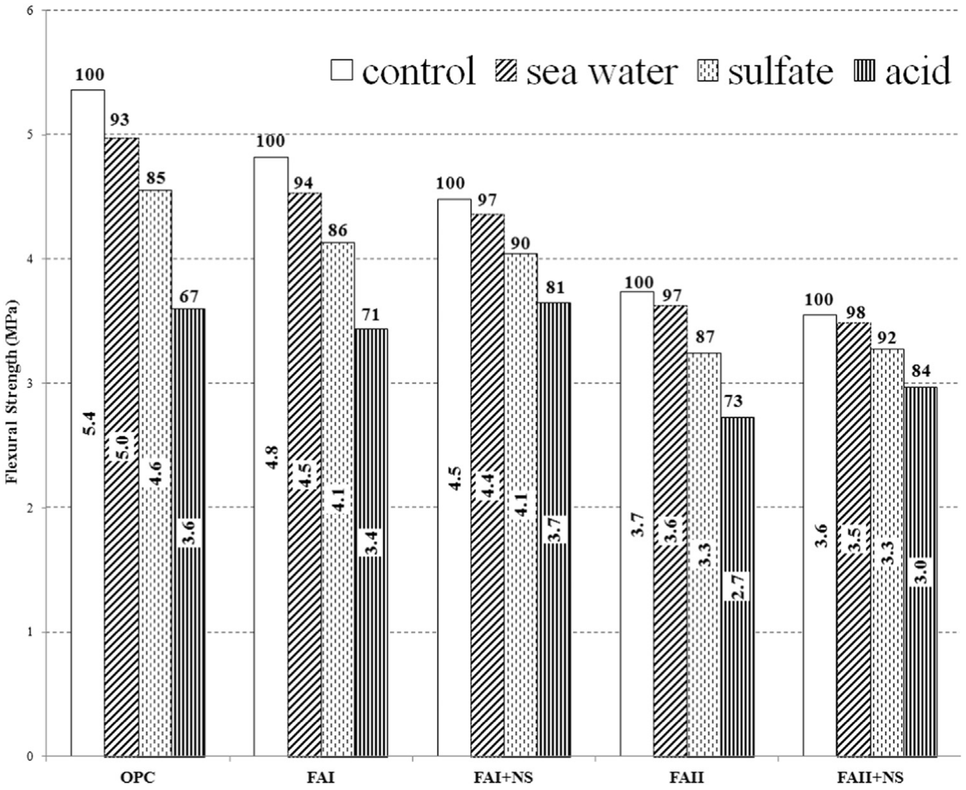
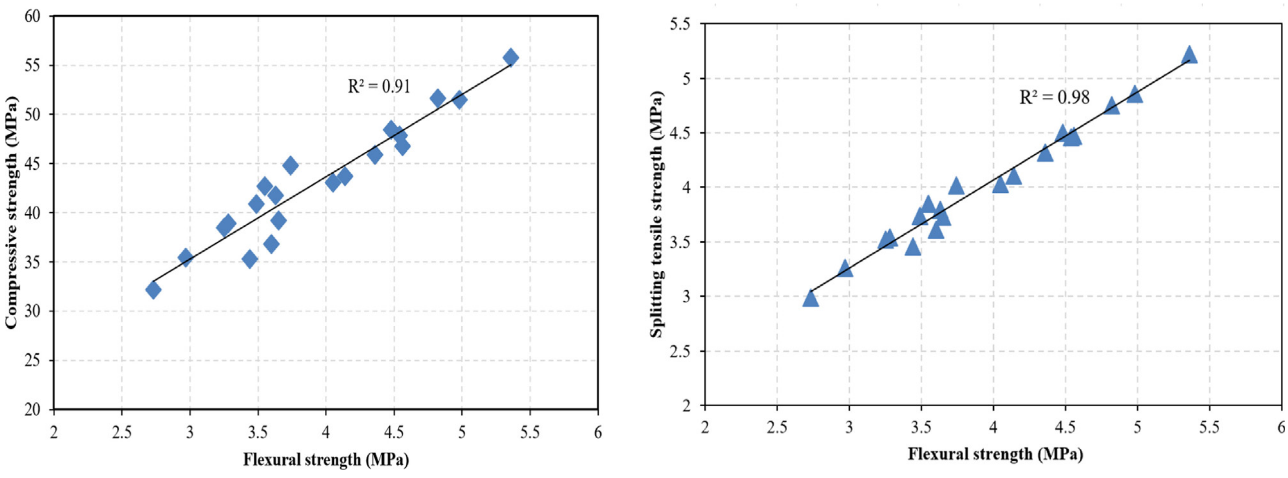


Fig. 8. Flexural strength changes of the specimens under chemical attacks.

Fracture performance of the specimens was investigated to see the effect of mechanical strength on the fracture properties of geopolymer and OPC specimens using fracture energy and critical stress intensity factor versus compressive and splitting tensile strength relationships. The fracture energy and critical stress intensity factor of the specimens increased with an increase in both compressive and splitting tensile strengths as shown in Fig. 12. Good relationships were found between fracture energy and compressive strength (R^2: 0.92), fracture energy and splitting tensile strength (R^2:0.92), critical stress intensity factor (K_{IC}) and compressive strength (R^2: 0.91), and critical stress intensity factor (K_{IC}) and splitting tensile strength (R^2: 0.98) as shown in (Fig. 12.a, .b, .c and .d), respectively. A similar observation was also reported by Sarker et al. [58] that fracture energy of the heat cured fly ash based GPC specimens increased with an increase in the compressive strength. They concluded that fracture energy depends on the both compressive and splitting tensile strength of concrete; however, the effect of splitting tensile strength on critical stress intensity factor (K_{IC}) was found more significant than the effect of compressive strength. In addition to this, Nazari and Danjayan [59] studied fracture energy and the stress intensity factor in functionally graded geopolymer specimens and they found that fracture properties more depend on the notch tip position than the mixture ingredients. Therefore, notch tip position can be another important factor in fracture calculations as well as compressive and splitting tensile strengths of the geopolymer concretes.

4. Conclusion

In this article, the mechanical properties and durability performance of



(a) Compressive vs flexural strength relationship (b) Splitting tensile vs flexural strength relationship

Fig. 9. Mechanical strength relationships of the specimens under different environments.

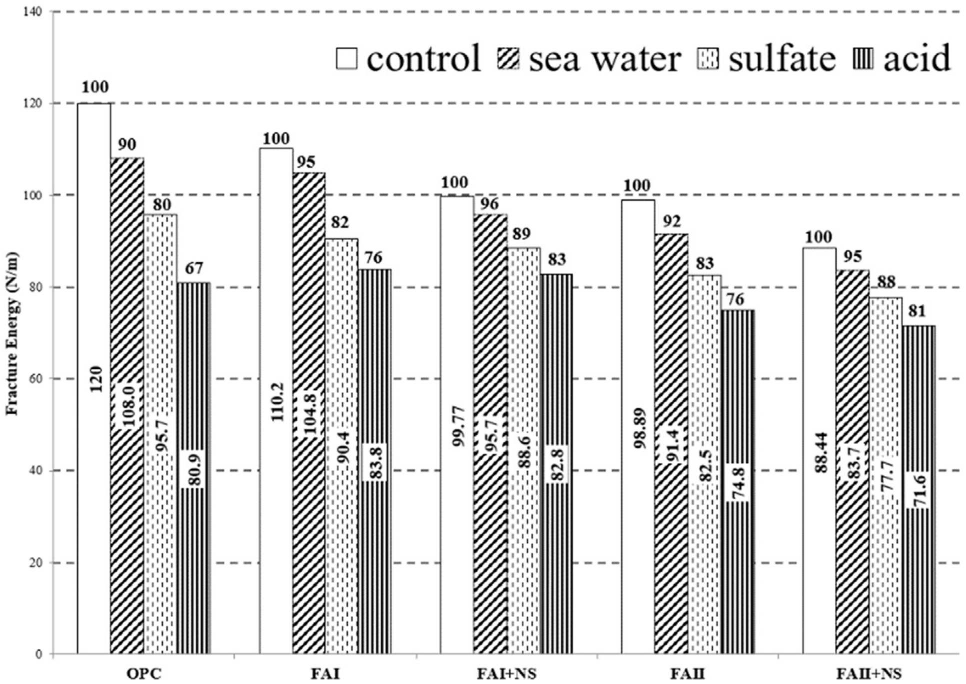


Fig. 10. Fracture energy of specimens under different chemical environments.

fly ash based geopolymer concretes with and without nano silica were investigated under chemical environments (5% sulfuric acid, 5% magnesium sulfate and 3.5% seawater) and the obtained results were compared to OPC concretes. In addition, the use of geopolymer concretes instead of OPC concrete was also investigated. The following findings were summarized below;

- Visual inspection results indicated that GPC specimens showed moderate surface erosions at their surfaces, while OPC concrete specimens showed severe surface erosions due to higher CaO content under sulfuric acid environment. In addition, GPC specimens maintained their initial conditions under magnesium sulfate and seawater environment, while the color of the OPC concrete specimens changed from gray to white. The favorable effect of nano silica on the durability performance of GPC can be clearly observed even in the short term period of chemical exposure.
- The weight loss of OPC concrete specimens due to hydration reactions in an ambient condition (control specimens) was more than 3-times than the weight loss of heat cured FAGPC specimens. Results also indicated that the nano-silica addition (3% by binder weight) had no or negligible effect on the weight change of the specimens.
- The weight enhancement was found for almost all specimens under all chemical environments during the first 15 days of exposure due to the solution absorption and the expansion occurred by gypsum

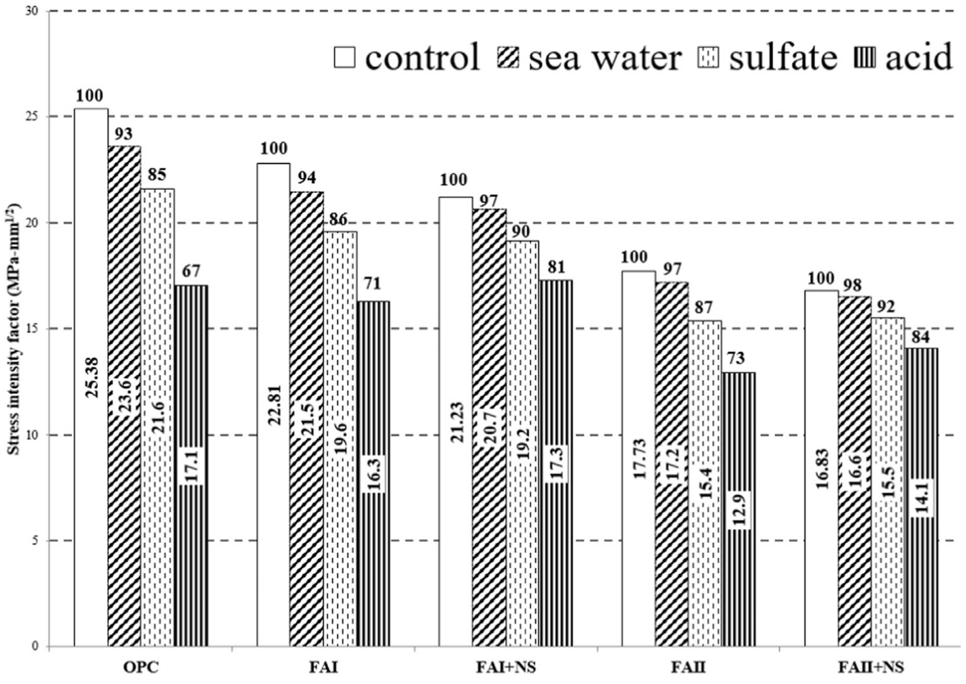
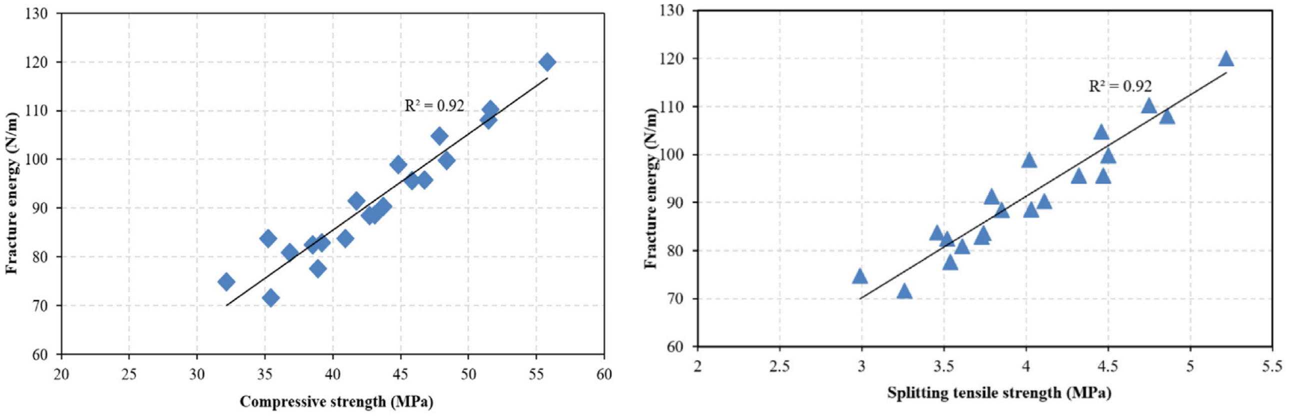
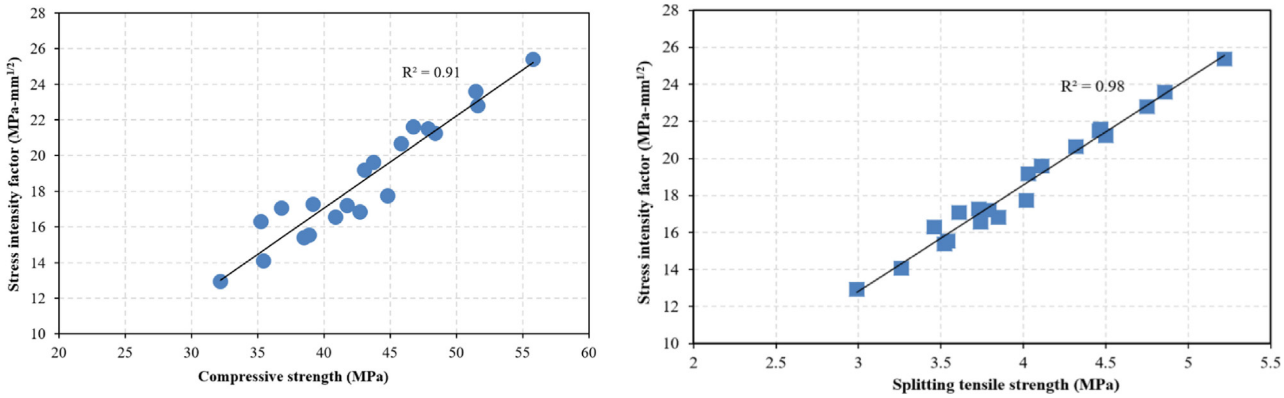


Fig. 11. Stress intensity factor of specimens under different chemical environments.



(a) Fracture energy vs compressive strength

(b) Fracture energy vs splitting tensile strength



(c) Critical stress intensity factor vs compressive strength

(d) Critical stress intensity factor vs splitting tensile strength

Fig. 12. Fracture relationships of the specimens under different chemical environments.

formation. The highest weight gain was obtained under sulfuric acid solution.

- After one month of exposure, the weight gain was observed for all specimens as compared to the initial weights. The weight gain continued up to 30 days of exposure to chemical environments, except for the sulfuric acid environment. The weight decrease was observed in specimens exposed to the sulfuric acid environment since sulfuric acid attack became hazardous to concrete from the earlier exposure times. Specimens including nano silica showed less weight reduction under sulfuric acid and less weight gain under seawater and magnesium sulfate environments due to its denser structure, thereby decreasing the porosity and permeability of concretes.
- Compressive strengths, splitting tensile strength, flexural strength, fracture energy, and stress intensity factor results decreased with the chemical environments in the order of sulfuric acid > magnesium sulfate > seawater > control (ambient) environments for all concrete types. Sulfuric acid and seawater attacks were observed to be the most and least dangerous environments, respectively.
- Mechanical strength (compressive, splitting, flexural, i.e) results indicated that OPC specimens performed slightly better performance than the fly ash based GPC specimens at the same water to cement or alkaline solution to binder ratio. However, mechanical strength deterioration was observed to be highest for OPC specimens under chemical attacks, especially under sulfuric acid environment due to high CaO content.
- The lowest mechanical strength reduction under chemical attack was observed in FAII + NS specimens than FAI + NS specimens since FAII (second types of fly ash) specimens included the lowest amount of calcium. It can be concluded that CaO can be responsible for the deterioration of concrete under chemical attacks even in the short-term of chemical exposure. FAII + NS type of GPC concrete was found to be appropriate for the structures exposed to harsh environments.
- Splitting tensile strength results of FAGPC specimens were predicted by using ACI 363-R92 and CEB-FIP models of OPC, and excellent relationships were obtained between mechanical and fracture properties of FAGPC specimens. In addition, mechanical strength relationships of FAGPC specimens showed similar behavior with OPC, indicating fly ash based geopolymer concretes can be used in structural applications.
- Nano silica addition into the both FAI and FAII GPC specimens improved the residual mechanical strengths and its contribution was observed to be highest under the more severe chemical environment (sulfuric acid) due to the lower porosity and permeability resulted from the dense structure. Therefore, the use of nano-silica should be widespread to extend the lifespan of the structures under severe chemical environments.

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