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Research Article

MECHANICAL STRENGTH DEGRADATION OF SLAG AND FLY ASH BASED GEOPOLYMER SPECIMENS EXPOSED TO SULFURIC ACID ATTACK

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ABSTRACT

In this study, mechanical properties and durability performances of fly ash based geopolymer concrete (FAGPC) and slag based geopolymer concrete (SGPC) were investigated against 5% sulfuric acid attack. The low calcium (F-type) fly ash (FA) and ground granulated blast furnace slag (GGBS) were utilized as binder materials with an amount of 360 kg/m^3, and a combination of sodium silicate and 14 M sodium hydroxide with a silicate to hydroxide ratio of 2.5 were used as an alkaline activator in order to produce geopolymer concretes. The binder amounts were selected in accordance with the XA3 chemical environmental condition given in TS EN 206 standard. An ordinary Portland cement concrete (OPC) was also produced and exposed to sulfuric acid attacks for comparison. The effect of sulfuric acid on 150x150x150 mm cube and 100x200 mm cylinder specimens was evaluated by visual inspection, weight change, compressive and splitting tensile strength tests. Results indicated that similar surface deterioration was observed on the cube and cylinder specimens due to acid exposure. However, cube specimens showed more weight loss than the cylinder specimens, which can be attributed to the higher acid influenced area due to the size effect. In addition, the SGPC specimens exhibited superior mechanical performance, while FAGPC specimens showed the poorest mechanical performance when low binder amounts (360 kg/m^3) were utilized under sulfuric acid attack. The results also pointed out that slag based geopolymer concrete can be utilized in structural applications instead of ordinary Portland cement concrete.
Keywords: Fly ash based geopolymer concrete (FAGPC), slag based geopolymer concrete (SGPC), sulfuric acid attack, durability, mechanical performance.

1. INTRODUCTION

Deterioration of the structural elements under sulfuric acid attack is one of the important durability problems that increases the maintenance costs and decreases the life span of the substructures. The sulfuric acid can be detrimental to reinforced concrete (RC) elements of foundations (groundwater, resulting from the oxidization of pyrite in backfill) and RC slab, beam, column elements at chemical plants due to chemical wastes and acid rains [1]. In addition, the degradation of the sewer system due to the sulfuric acid attack may cause significant

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infrastructure problems such as contamination of groundwater, loss of ability to transport sewerage, and ground settlements [2].

Supplementary cementitious materials (fly ash, ground granulated blast furnace slag) have been partially used in order to improve the durability of concrete against chemical environment [3]. Recently, a novel cement-free material, geopolymer concrete (GPC) becomes an alternative to ordinary Portland cement (OPC) concrete. GPC requires less energy during production [4] and releases approximately 6 times less CO_2 amount than the OPC [5, 6]. In addition, the disposal of the waste materials (fly ash, slag) reduces air pollution and their utilization in the GPC production provides a favourable impact on the global economy and environment. Due to the less energy requirement and environmental friendliness nature, GPC may become an alternative construction material to OPC concrete. Researches regarding the mechanical and durability performance of the GPC has been carried out in order to use GPC instead of OPC in recent years. The researches pointed out that GPC showed high mechanical strength and good chemical resistance [7, 8]. However, there is a limited number of study about the chemical resistance of GPC specimens and further durability studies are required in order to use GPC specimens instead of OPC specimens under chemical environments.

There are different assessment methods in order to evaluate the chemical resistance of the concrete specimens, such as visual inspection [8, 9], weight change [10, 11] and compressive strength change [12, 13]. In the scope of the research, the chemical resistance of the slag based GPC (SGPC) and FA based GPC (FAGPC) samples were studied by visual inspection, weight loss, compressive strength and splitting tensile strength tests after the sulfuric acid attack at the ages of 28., 56., and 90. days. In addition, the effect of the sulfuric acid on cube and cylinder specimens were also evaluated via visual inspection and weight loss. The obtained results can be significant for the structural elements in order to improve the service life of the structures under the sulfuric acid attack.

2. EXPERIMENTAL PROGRAM

2.1. Materials and Mix Design

In this study, low calcium (F-type) fly ash (FA) and ground granulated blast furnace slag (GGBS) were used in order to obtain fly ash based geopolymer concrete (FGPC) and slag based geopolymer concrete (SGPC). For the comparison, an ordinary Portland cement concrete (OPC) produced with Type 1 cement was produced. As an alkali activator of the GPC, the sodium hydroxide (NaOH) and silicate (Na_2SiO_3) solutions and with a hydroxide to silicate ratio of 1/2.5 was used by weight. The sodium silicate liquid with an alkaline modulus of 2 and sodium hydroxide pellets were taken from a local supplier. The sodium hydroxide powder was dissolved in tap water to obtain 14 M NaOH, which was the weakest concentration against chemical attacks [14]. The alkaline solution was prepared about 30 min before mixing. A polycarboxylates based superplasticizer (SP) was utilized to obtain S4 slump class concrete. No I (5-12 mm) and No II (12-22 mm) with specific gravities of 2.71 g/cm^3 and 2.72 g/cm^3 were utilized as coarse aggregates. As fine aggregates, natural sand and crushed sand with specific gravities of 2.65 g/cm^3 and 2.70 g/cm^3 were used. The aggregates were used as saturated surface dry moisture condition. Table 1 illustrates the chemical composition and physical properties of the ground granulated blast furnace slag, Type I OPC cement, and F-Type fly ash materials.

The sulfuric acid environment can be classified as XA3 environment – a very aggressive chemical environment in accordance with TS EN 206-1 standard. In TS EN 206-1 standard, a minimum cement content of 360 kg/m^3 and maximum water to cement ratio of 0.45 were proposed under the XA3 chemical environment condition. Therefore, an ordinary concrete was designed according to the criteria of the standard. For the chemical resistances of slag based GPC (SGPC) and fly ash based GPC (FAGPC) against sulfuric acid attack, a minimum binder content of 360 kg/m^3 and a maximum alkaline activator (sum of sodium silicate and hydroxide) to binder content of 0.45 were also used to investigate the probability of utilization of the geopolymer concretes under XA3 chemical environment. Table 2 illustrates the mix ingredients of the slag based geopolymer concrete (SGPC), and ordinary Portland Cement Concrete (OPC) and fly ash based geopolymer concrete (FAGPC).

Table 1. Chemical composition and physical properties of the binder materials

Chemical Composition	Slag	Cement	Fly Ash
CaO (%)	37.92	64.28	1.79
Al_2O_3 (%)	13.27	4.91	26.37
SiO_2 (%)	37.97	20.17	56.15
Fe_2O_3 (%)	1.16	3.41	6.44
MgO (%)	5.64	1.18	2.35
SO_3 (%)	0.23	2.84	0.056
Na_2O (%)	0.84	0.13	1.1
K_2O (%)	0.56	0.96	3.8
Cl (%)	0.015	0.042	0.09
Loss on ignition (%)	0.01	1.61	2.2
Specific Gravity (g/cm^3)	2.95	3.14	2.05
Specific Surface (cm^2/g)	5131	3910	3870

Table 2. Mix proportions of the SAGPC, OPC, and FAGPC specimens

Ingredients	SAGPC	OPC	FAGPC
Fly Ash	0	0	360
Slag	360	0	0
Cement	0	360	0
No I (5-12mm)	560	560	560
No II (12-22mm)	560	560	560
Crushed sand	373	373	373
Sand	373	373	373
Sodium silicate (Na_2SiO_3)	115.7	0	115.7
Sodium hydroxide (14M NaOH)	46.3	0	46.3
Superplasticizer	6	6	6
Water	37.5*	162	25*

* Water amount in order to obtain similar workability as OPC

During mixing, dry materials; coarse and fine aggregates, slag, cement and fly ash (for SGPC, OPC, and FAGPC) were included and mixed 2 min in a mixer. The liquid solutions (sodium silicate + sodium hydroxide) and half of the SP included, then the mixture mixed for 2 min. Then water and half of the SP were mixed together and added in 1 min and mixed additional 1 min for homogeneity. For the enhancement in workability and further geopolymerization, water incorporation into the mixes was also reported in the earlier investigations [15, 16].

The produced mixes were cast into the moulds for mechanical strength and durability tests. 150x150x150 mm cube specimens were produced for the compressive strength tests and 100x200 mm cylinder specimens were cast for the splitting tensile strength tests. After the compaction process, the top surfaces of the specimens were covered with plastic sheets in order to prevent alkaline solution evaporation. The specimens were demoulded after 3 days later from the concrete production in order to have required strength gain before demoulding, especially important for FAGPC specimens. The oven-curing was applied to the geopolymer specimens at 70°C for 48 hours since compressive strength improvement became negligible after 48 hours [17]. After the heating procedure, geopolymer samples were located in the laboratory environment for 28 days. Meanwhile, water-curing is applied to the OPC samples for 28 days.

2.2. Test Method

The chemical immersion method was used to investigate the sulfuric acid resistance of the specimens. For this purpose, both cube and cylinder specimens were immersed in the 5% sulfuric acid solutions and compressive strength tests were applied according to ASTM C39 standard and splitting tensile strength tests were executed in accordance with ASTM C496 after the chemical exposure time of 28 days (28+28 days) and 62 days (28+62 days). All specimens were removed from acid solutions at the end of the test days and left to the laboratory environment for drying at 24h before mechanical tests and weight measurements. The eroded surface photos of the specimens were taken for visual observation and weights of the specimens were measured to evaluate the variations in weights after chemical exposure. Then, mechanical strength tests were conducted to evaluate the deterioration of the specimens due to 5% sulfuric acid attack.

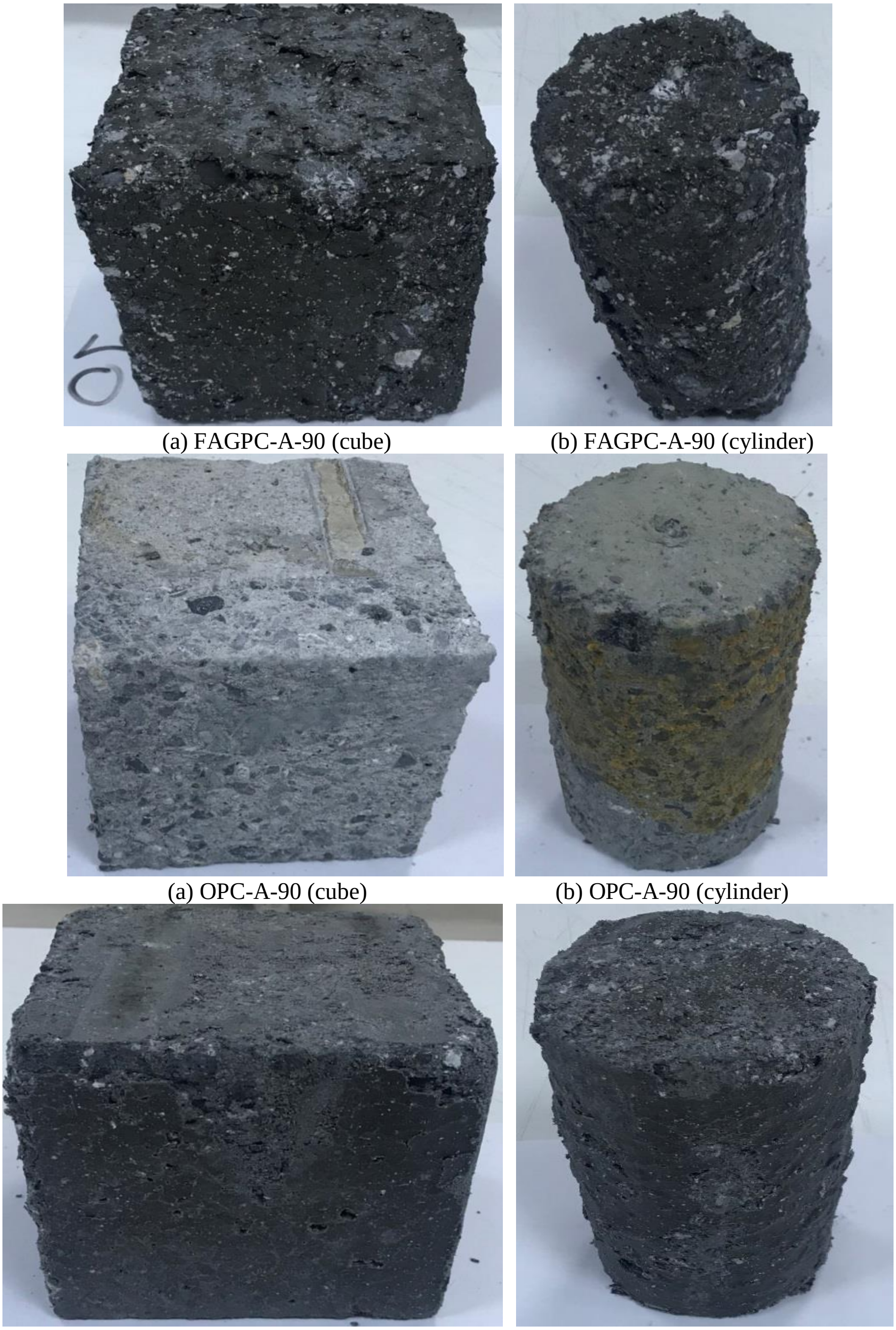
3. RESULTS AND DISCUSSIONS

3.1. Visual Observation

Fig. 1 illustrates the visual inspection of the FAGPC, OPC, and SGPC (cube and cylinder) specimens after two months of exposure against acid solution. Results indicated that severe surface deterioration was observed on the FAGPC and OPC specimens and the moderate surface erosion was observed on SGPC specimens. For the FAGPC specimens, macrocracks and the expansion of geopolymer mortar on the cube and cylinder specimen surfaces were easily observed. In addition, severe white deposits were observed on the specimen surface. The severe degradation of the FAGPC specimen surfaces may be attributed to the increased permeability due to the macrocracks. For the OPC specimens, the cement mortar on the surface was almost lost and the severe surface erosion was observed after the sulfuric acid attack. The high amount of degradation can be attributed to the reaction between sulfate ions in the sulfuric acid solution and CaO in the cement phase. For the SGPC specimens, little amount of white deposits and negligible surface deterioration were observed on the specimen surfaces. When the deterioration amount on the surfaces of the cube and cylinder specimens were considered, there is no clear difference was observed between cube and cylinder specimens. However, the acid-influenced surface area becomes higher for the cube specimens than the cylinder specimens due to its bigger sizes.

3.2. Weight Change

Figs. 2 and 3 present the weight change of the 150x150x150 mm cube specimens and 100x200 mm cylinder specimens at the ages of 56 and 90 days, respectively. After the two months of exposure, weight loss was observed on all specimens. It may be attributed to the loss of the binder phase from the surfaces of the specimens as can be seen in visual observation. When the 150x150x150 mm cube specimens were under consideration, the highest weight loss was observed on FAGPC specimens (0.88%) and the lowest weight loss was observed on SGPC specimens (0.4%). However, when the weight change of the 100x200 mm cylinder specimens was evaluated, the highest weight loss was observed on OPC specimens and the lowest weight loss was observed again on SGPC specimens (0.11%). The results indicated that the deterioration on the cube specimens was found to be more than the cylinder specimens after two months of sulfuric acid exposure, only except for the OPC specimens. The more deterioration in cube specimens can be attributed to the higher acid influenced surface area of the cube specimens.



(a) FAGPC-A-90 (cube)   (b) FAGPC-A-90 (cylinder)

(a) OPC-A-90 (cube)   (b) OPC-A-90 (cylinder)

(c) SGPC-A-90 (cube)   (d) SGPC-A-90 (cylinder)

Figure 1. Visual inspection of the specimens under sulfuric acid attack

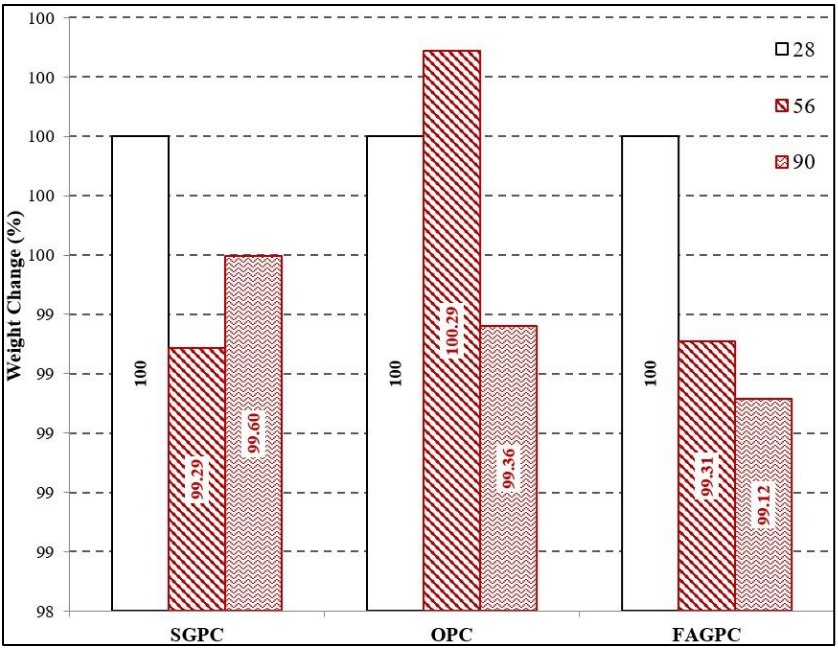


Figure 2. Variation in weights of the cube (150 mm) samples against 5% sulfuric acid attack

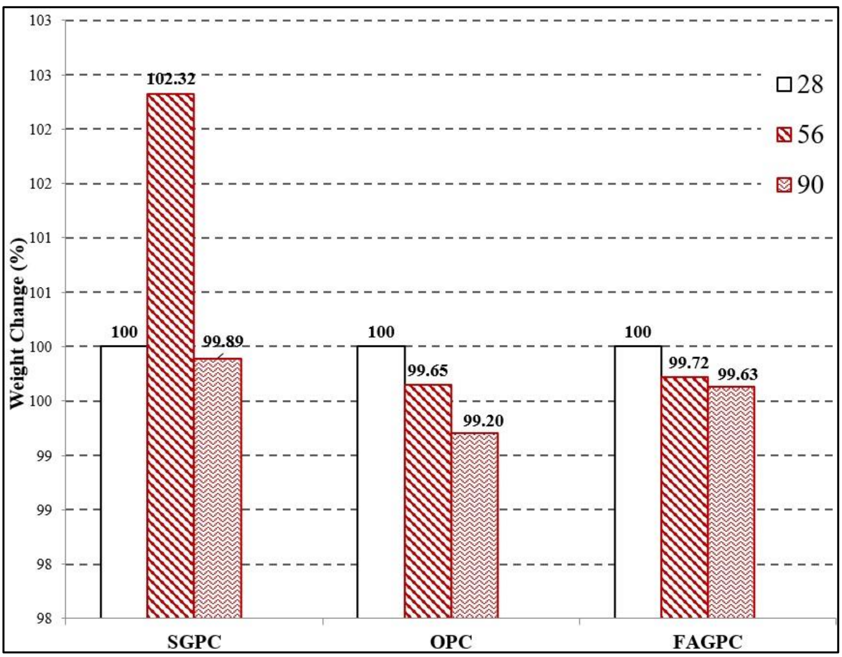


Figure 3. Variation in weights of the cylinder (100x200 mm) samples against 5% sulfuric acid attack

3.3. Change in the Compressive Strength

Fig. 4 shows compressive strengths of the sulfuric acid exposed samples at the ages of 28 days (control), 56 days (28 days of acid exposure) and 90 days (62 days of acid exposure). Results indicated that the compressive strengths of the specimens reduced as chemical exposure time increased. It can be attributed to the further chemical reactions between sulfate ions and cement/binder phases, resulting in more deterioration of the specimens. The compressive strength of the specimens at the ages of 28 days indicated that the highest compressive strength was obtained in SGPC (~78 MPa) specimens, while the least compressive strength was obtained on FA based GPC samples (~22 MPa) and the moderate strength was obtained in OPC samples (~50 MPa). The lowest compressive strength of the FA based GPC samples may be due to the low activity of FA particles [18], and less CaO amount [8, 19]. In addition, low fly ash amount (360 kg/m^3) may be another parameter for the poor compressive strength. After the 5% sulfuric acid exposure, compressive strength of the specimens reduced to 63 MPa (20% loss) and 45 MPa (42% loss) for SGPC specimens, 35 MPa (29% loss) and 29 MPa (41% loss) for OPC specimens, and 13 MPa (43% loss) and 11 MPa (49% loss) for FAGPC specimens at the ages of 56 and 90 days, respectively. The highest deterioration was found on FAGPC specimens, which may be attributed to the unreacted fly ash particles-less dense microstructure, low fly ash content, alkali activator type and amounts, and increased permeability. Meanwhile, a similar deterioration amount was observed on SGPC and OPC specimens, which can be attributed to the high CaO content.

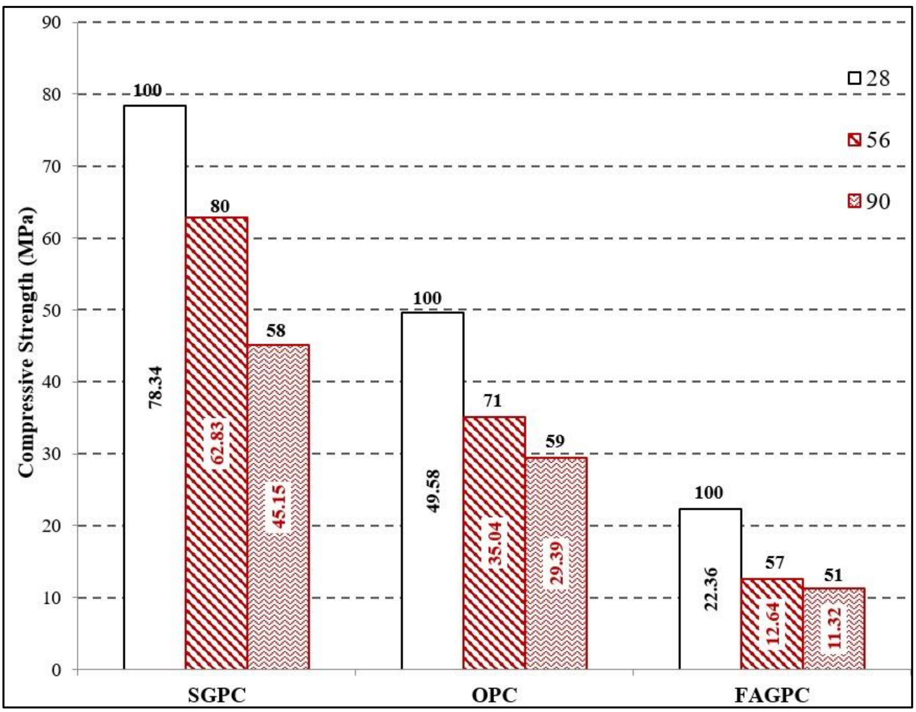


Figure 4. Variations in the compressive strengths of the cube samples (150x150x150 mm) under sulfuric acid attack

3.4. Change in the Splitting Tensile Strength

Fig. 5 shows splitting tensile strengths of the specimens under 5% sulfuric acid attack. The splitting tensile strengths of the SGPC specimens were found to be 2.80 MPa, 3.44 MPa (23% increase), and 3.60 MPa (28% increase) at the ages of 28 days, 56 days, and 90 days, respectively. The increase in the splitting tensile strength of SGPC specimens may be attributed to the ongoing hydration reactions so that strength gain can be obtained over time. Another reason may be attributed to the fact that chemical reactions occur only the surface regions and the top and bottom surfaces experience compressive stresses instead of tensile stresses during splitting tensile strength tests; therefore, core regions may not be influenced from acid solutions, resulting in higher tensile strength capacities for SGPC specimens. Wallah and Rangan [20] investigated the sulfuric acid attack on cylinder specimens and observed that only 20 mm surface region was affected under acid attack and the core regions remained sound. A similar observation was also investigated in the previous study [9]. For the OPC specimens, splitting tensile strengths were 2.78 MPa, 3.38 MPa (22% increase), and 2.63MPa (5% loss) for 28, 56 and 90 days, respectively. The results indicated that an increase in the splitting tensile strength was observed after 28 days of acid exposure; however, further acid exposure yielded more deterioration, which resulted in a decrease in the splitting tensile strength of the specimens. The lowest splitting tensile strength was achieved in the FA based GPC samples. The tensile strengths of the fly ash based GPC samples were 0.97 MPa, 0.88 MPa (9% loss), and 0.84 MPa (13% loss), respectively at the ages of 28 days, 56 days, and 90 days, respectively. The splitting tensile strength deterioration started before the 28 days of acid exposure for FAGPC specimens, and tensile strength reduction was obtained after the 28 days of acid exposure for the OPC specimens, while for the SGPC specimens splitting tensile strength was not decreased after the 56 days of sulfuric acid exposure. The tensile strength test results pointed out that slag based GPC specimens were less affected by the sulfuric acid solution, while FA based GPC specimens were highly deteriorated.

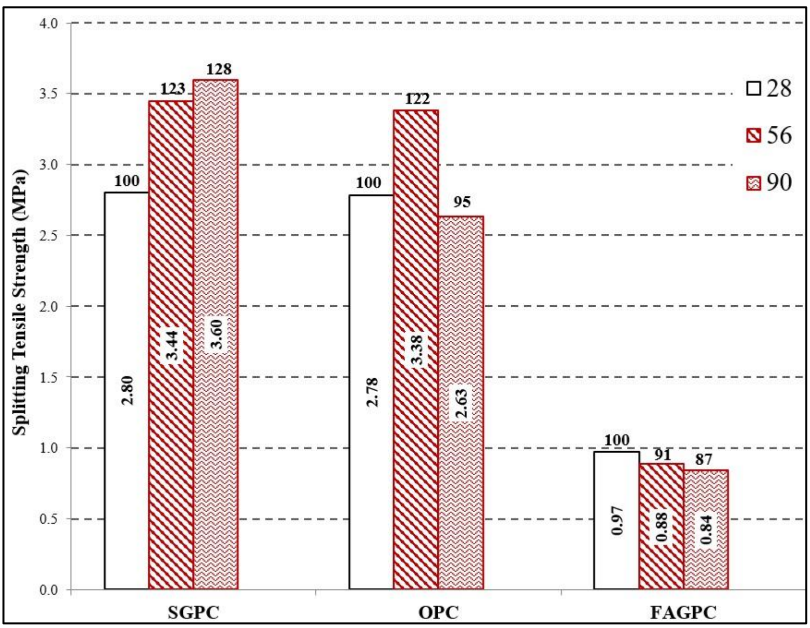


Figure 5. Variation in the splitting tensile strengths of the cylinder (100x200 mm) samples under acid attack

4. CONCLUSIONS

In this study, the durability performance of the oven-cured fly ash and slag based geopolymer concrete specimens (SGPC and FAGPC) were investigated against 5% sulfuric acid attack according to XA3 environment condition given in TS EN 206 standard. For comparison, an ordinary Portland cement concrete was also produced and tested under 5% sulfuric acid solution. The following results were obtained:

- Visual inspection results showed that severe surface deterioration was observed on FAGPC and OPC specimens, while moderate surface erosion was observed on SGPC specimens. In addition, there is no clear difference was found on the surface deterioration of the cube and cylinder specimens.
- The weight change results showed that the degradation on the 150x150x150 mm cube specimens was found higher than the 100x200 mm cylinder specimens after two months of sulfuric acid exposure, which can be attributed to the more sulfuric acid influenced surface area of the cube specimens due to the size effect.
- Compressive strength test results indicated that the compressive strengths of the specimens were increased in the order of: FAGPC (22 MPa) < OPC (50 MPa) < SGPC (78 MPa). The lowest compressive strength of the FAGPC specimens can result from the low activity of fly ash particles, low fly ash amount in the mix, and low CaO content. After the sulfuric acid attack, the highest deterioration (49% loss) was also observed on FAGPC specimens and similar compressive strength reduction (~42%) was obtained for the OPC and SGPC specimens. The high amount of degradation in FAGPC specimens can be also attributed to higher permeability and porosity due to the less dense microstructure. The deterioration of the SGPC and OPC specimens in the sulfuric acid solution can result from the high CaO content.
- Splitting tensile strength results pointed out that an increase in the splitting tensile strength of the SGPC specimens was observed due to the continuous hydration reactions under sulfuric acid attack at the ages of 56 and 90 days. For the OPC specimens, an increase in the splitting tensile strength was obtained at the ages of 56 days; however, reduced splitting tensile strength was observed with further acid exposure (90 days), indicating that sulfuric acid became hazardous after 28 days of acid exposure. For the FAGPC specimens, a continuous reduction in splitting tensile strength was observed at the ages of 56 and 90 days, respectively. It may be attributed to less dense microstructure, and higher porosity and permeability of the FAGPC specimens.
- The findings indicated that SGPC samples can be utilized in structural applications since SGPC specimens performed better mechanical and durability performance than OPC specimens even under low slag content (360 kg/m3). However, FAGPC specimens with low fly ash content (360 kg/m3) and high Na2SiO3/NaOH ratio (2.5) showed poor performance than the OPC samples against 5% sulfuric acid attack. For better mechanical performance and durability properties of FAGPC specimens, more FA content (>400 kg/m3) and/or different alkaline activator ratios (Na2SiO3/NaOH) should be utilized for the structural applications under sulfuric acid attack.

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