

Sulfate and Acid Resistance of Fly Ash-Based Geopolymer Concrete

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1. Introduction

Geopolymer concrete is emerging as a new material that offers the benefit of an environmentally friendly construction material for sustainable development. It utilises waste materials such as fly ash and has a low rate of greenhouse gas emission compared to Ordinary Portland Cement (OPC) concrete.

The term 'geopolymer' was first introduced by Davidovits (1987) to describe a family of mineral binders based on aluminosilicates. This inorganic polymer has a wide range of applications in civil engineering [1, 2]. In geopolymer concrete, the silica and the alumina present in the source materials are induced by alkaline activators to form a gel. This geopolymer gel binds the loose aggregates and other unreacted materials in the mixture to form the geopolymer concrete. The chemical process involved in the formation of geopolymer binders is very different to that of OPC concrete.

This paper presents the study of the resistance of fly ash-based geopolymer concrete to sulfate and acid attack. Test specimens were soaked in sodium sulfate solution and sulfuric acid solution for certain periods of time, and the resistance of geopolymer concrete was studied by evaluating the amount of expansion, the change in mass, and the residual compressive strength of test specimens after exposure. Test variables included exposure period and the concentration of the acid solution.

2. Previous research

Several laboratory studies have been reported to identify the parameters that influence the properties of geopolymers. Davidovits [1, 2] found that after a 4-hour curing period at 20°C, geopolymer mortar attains a compressive strength of 20 MPa and the final 28-day compressive strength is in the range of 70 to 100 MPa. Curing period and type of activators were found to be significant factors affecting the mechanical strength of geopolymers [3, 4, 5]. Longer curing time and higher curing temperature usually resulted in higher compressive strength.

In the previous studies, the authors [6] reported the results of the research into engineering properties of geopolymer concrete. The concrete mixtures were made using low-calcium class F fly ash, sodium hydroxide (NaOH) and sodium silicate (Na_2SiO_3) solutions as alkaline activators, and locally available aggregates. It was found that for curing temperatures up to 60°C, there was a significant increase in the compressive strength, while the increase in strength was not significant when the samples were cured above 60°C. Also, curing for 24 hours increased the compressive strength substantially compared to a 4-hour curing. In addition, it was also shown that as the Na_2SiO_3 -to-NaOH ratio increased the compressive strength increased. Test results obtained from specimens cured at 60°C for 24 hours revealed that the compressive strength of geopolymer concrete did not vary with the age of concrete because of the fast polymerisation process of the geopolymer gel [7]. Other tests by the authors also identified the significant effect of water content in the mixture, expressed as water to geopolymer solids ratio, on the compressive strength of geopolymer concrete [8]. The fresh concrete could be handled up to 120 minutes without any sign of setting and without any effect on the compressive strength [9]. Studies on the behaviour and the strength of geopolymer concrete columns were also reported [10]. Earlier, the authors reported some preliminary results on the resistance of geopolymer concrete to sulfate attack [11]. It was also found that the material undergoes very little drying

shrinkage and low creep [12, 13]. From the study of geopolymer paste, Bakharev [14, 15] found that the specimens prepared using sodium hydroxide performed the best under sulfate and acid attack.

3. Experimental program

3.1 Materials and specimen preparation

Geopolymer concrete in this study utilised the low calcium (class F) fly ash from Collie Power Station, Western Australia as the source material. Table 1 shows the chemical composition of the fly ash as determined by X-Ray Fluorescence (XRF) analysis. It can be seen from Table 1, the silicon and aluminium oxides constitute about 80% of the fly ash and the Si-to-Al ratio is about 2. From particle size analysis, as presented in Fig. 1, it was found that the specific surface area of the fly ash was $1.94 \text{ m}^2/\text{cc}$. Graph A shows the percentage of the volume passing and Graph B shows the percentage volume for certain sizes. Local aggregates, comprising 20 mm, 14 mm and 7 mm granite-type coarse aggregates and fine sand, in saturated surface dry conditions, were used in the experimental work. The fineness modulus of the combined aggregates was 5.0. The alkaline activator was a combination of sodium hydroxide (NaOH) solution and sodium silicate (with $\text{Na}_2\text{O} = 14.7\%$, $\text{SiO}_2=29.4\%$ and water= 55.9% , by mass) solution. The sodium hydroxide flakes with 98% purity were dissolved in water to make a solution with a concentration of 8M ($8 \times 40=320$ grams of NaOH flakes per litre of solution). In order to improve the workability, a high range water reducer superplasticiser of 1.5% by mass of the fly ash was added to the mixture.

TABLE 1 Chemical composition of fly ash (% by mass)

SiO_2	47.80
Al_2O_3	24.40
Fe_2O_3	17.40
CaO	2.42
Na_2O	0.31
K_2O	0.55
TiO_2	1.328
MgO	1.19
P_2O_5	2.00
SO_3	0.29
Cr	0.01
MnO	0.12
LOI*	1.10

The fly ash and the aggregates were first mixed together in a pan mixer for about three minutes. The sodium hydroxide and the sodium silicate solutions were mixed together with the superplasticiser and then added to the dry materials and mixed for another four minutes. Immediately after mixing, the fresh concrete was cast into 100mmx200mm cylindrical molds in

three layers and 75mmx75mmx285 mm prismatic molds in two layers. Each layer was given 60 manual strokes using a rodding bar and vibrated on a vibrating table for 10 seconds. About 30 minutes after casting, the specimens were placed in the oven for curing at 60°C for 24 hours. After curing, the specimens were left to air-dry in the laboratory.

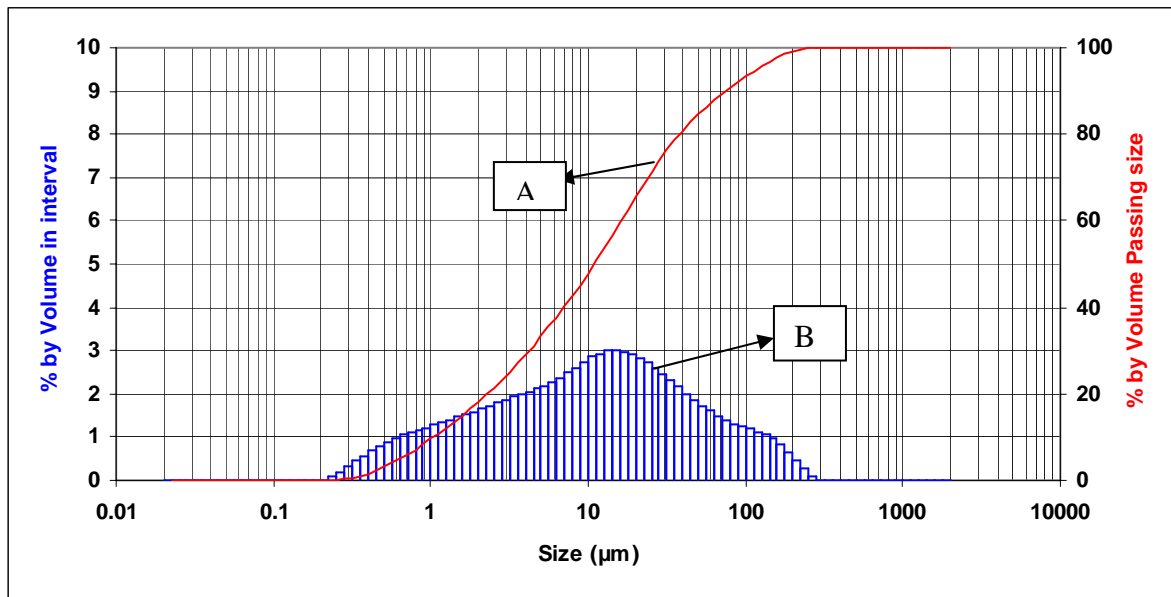


Figure 1 Particle size distribution of fly ash

The mixture proportion of geopolymer concrete selected for this study was one of the mixtures used in authors' previous research [6, 7, 9]. The details are given in Table 2.

TABLE 2 Mixture proportions for geopolymer concrete

Materials	Mass (kg/m ³)
Coarse aggregates	1294
Fine aggregates	554
Fly ash	408
Sodium hydroxide solution (8M)	41
Sodium silicate solution	103
Super plasticizer	6

3.1 Test variables and test procedures

In order to study the sulfate and acid resistance of geopolymer concrete, the specimens were soaked in sodium sulfate solution and sulfuric acid solution for various periods of time. The specimens were soaked in 5% sodium sulfate solution [16, 17, 18] to simulate the sulfate exposure and the changes in mass, length and compressive strength after exposure were

measured. For acid exposure, the specimens were soaked in various concentrations of sulfuric acid solution [16, 17, 18] and the changes in mass and compressive strength were measured. In order to maintain the required concentration, the solutions were replaced every month. The test specimens were immersed in the solutions one week after casting, and the solutions were made one day before the test specimens were soaked.

After soaking for various periods of time, the change in length, mass and compressive strength of the specimens were measured immediately after removing the specimens from the solution. For the length change tests, three 75mmx75mmx285 mm specimens were used, and the changes in length were measured using a horizontal length comparator. For change of mass tests, four 100mmx200 mm cylinder specimens were used, and the mass was measured using a laboratory scale. Four 100mmx200 mm cylinder specimens were used for compressive strength tests, and the tests were performed in accordance with the relevant Australian Standard for testing concrete. For comparison, two sets of four 100mmx200mm cylinders were also made. One of these sets was left in ambient conditions in the laboratory, and the other set was soaked in tap water.

The results plotted in various Figures are the average of the values of the specimens in each category.

4. Test results

4.1. Visual appearance

Figure 2 shows the visual appearance of the specimens after 1-year of exposure in ambient conditions, water, sodium sulfate solution, and sulfuric acid solution. There was no significant change in the external appearance of the surface of specimens soaked in sodium sulfate. The same was true for the specimens soaked in tap water. However, the surface of specimens soaked in sulfuric acid solution pitted and eroded after exposure.

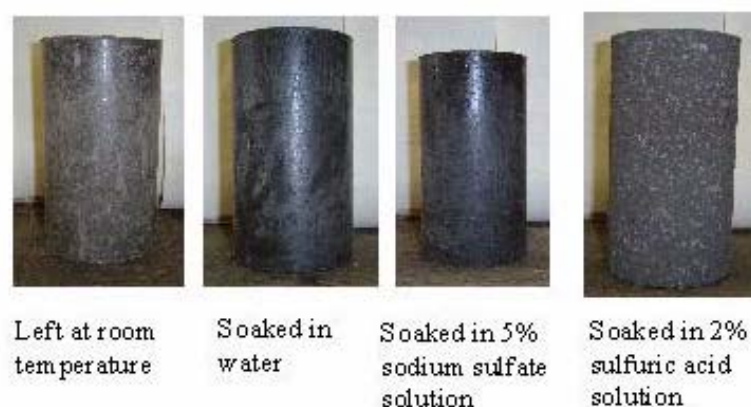


Figure 2 Visual appearance after 1 year of exposure

4.2. Change in length

Figure 3 shows that the change in length of specimens soaked in sodium sulfate solution for various periods of exposure is very small indeed and less than 0.015%.

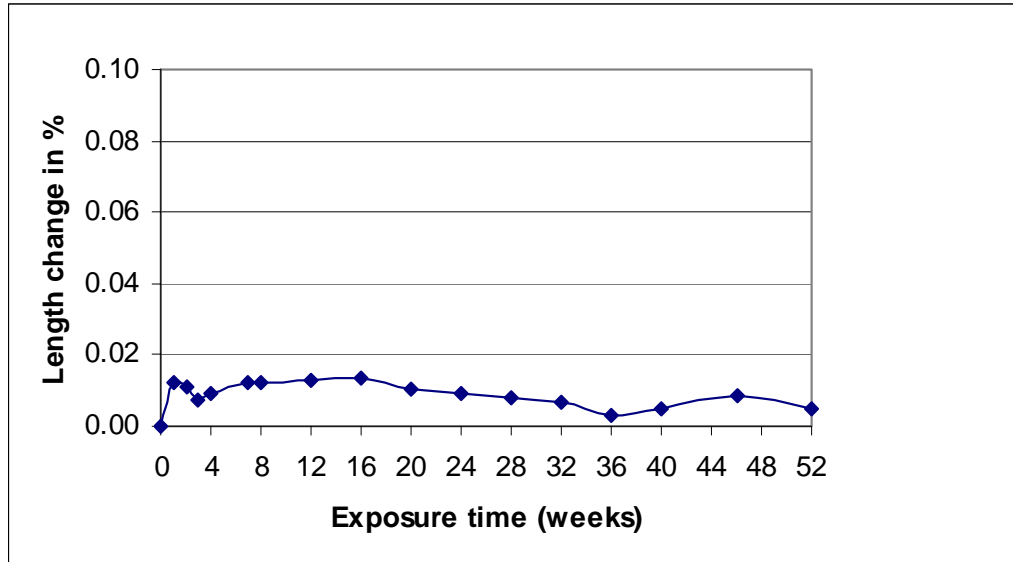


Figure 3 Length change after sodium sulfate exposure

4.3. Change in mass

The average unit weight of concrete in ambient conditions was 2356 kg/m^3 . There was very little change in this value for specimens soaked in tap water and in sodium sulfate solution. In the case of specimens soaked in 2% sulfuric acid solution, the mass decreased by about three percent after one year of exposure.

4.4. Change in Compressive strength

Figures 4 to 9 show the variation in the compressive strength of specimens after various periods of exposure to 5% sodium sulfate solution, 2% sulfuric acid solution and water as compared to the value of compressive strength of specimens left in the laboratory ambient conditions and tested one week after casting. It can be seen from these data that exposure to sodium sulfate solution or water up to one year has very little effect on the compressive strength (see dashed line in Figure 9).

However, a significant change in the compressive strength is observed in the case of specimens exposed to 2% sulfuric acid solution. In the first 24 weeks of exposure, the compressive strength of these specimens decreased substantially as the period of soaking increased. Between 24 weeks and 1 year, the decrease in compressive strength is relatively small (see Figure 9). Visual examination of the broken pieces of test cylinders revealed that the acid solution penetrated about 20 mm from the exposed surface (Figure 10). The significant loss of strength in the case of specimens soaked in 2% sulfuric acid solution may be due to the degradation of the geopolymer matrix in these outer rings of the test cylinders.

The 2% concentration of sulfuric acid solution may be considered to represent an extreme situation [18]. Therefore, the tests are currently being carried out for sulfuric acid solutions with concentrations of 1% and 0.5%. The results of these tests are given in Table 3. It can be seen that the degradations in the compressive strength for these concentrations of sulfuric acid are significantly less.

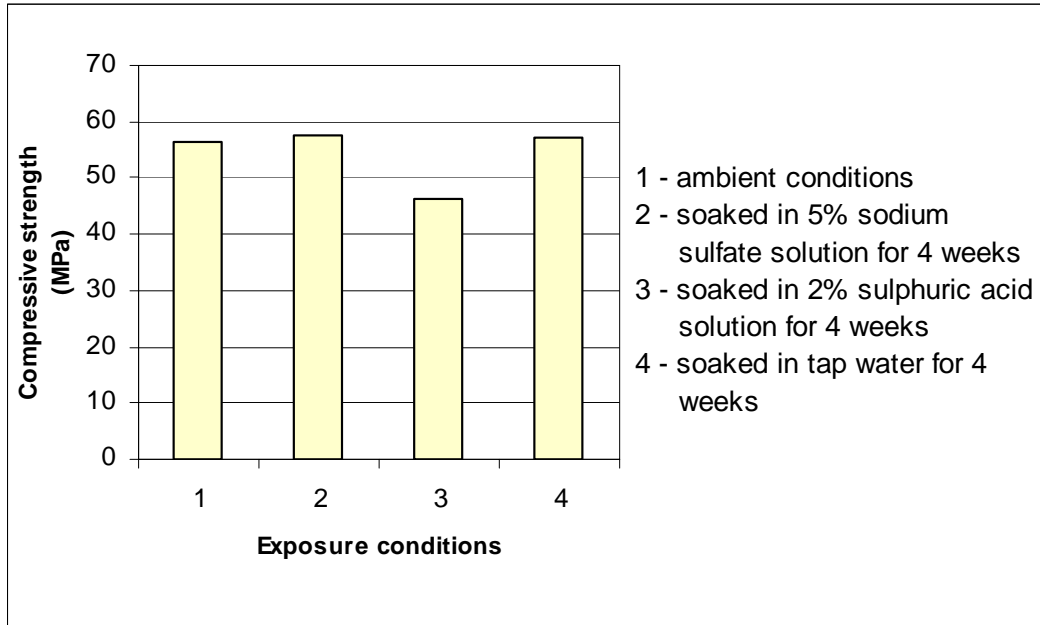


Figure 4 Compressive strength after 4-week of exposure

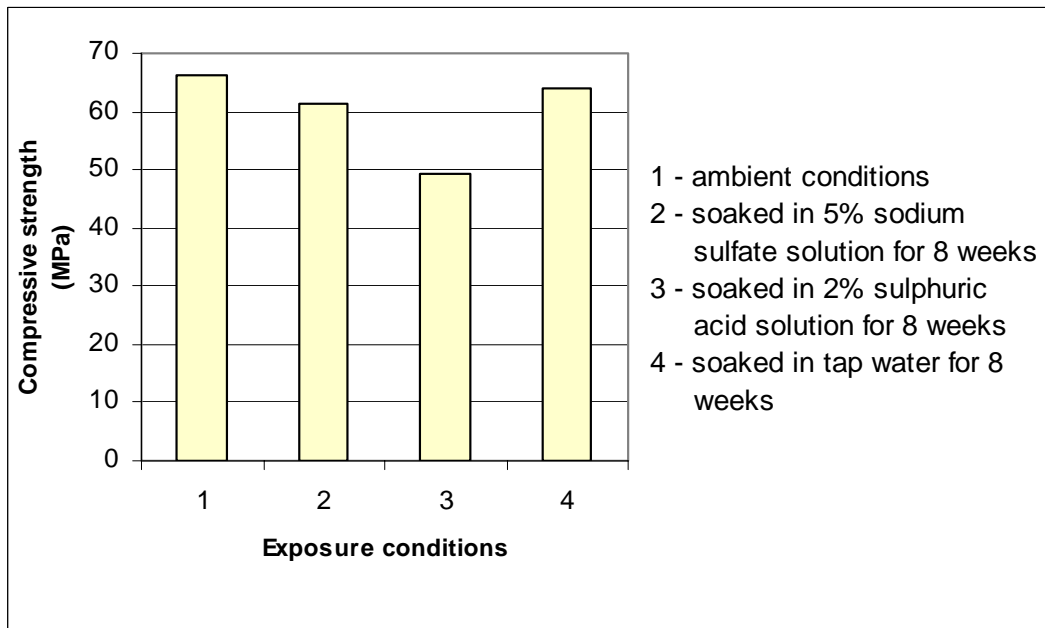


Figure 5 Compressive strength after 8-week of exposure

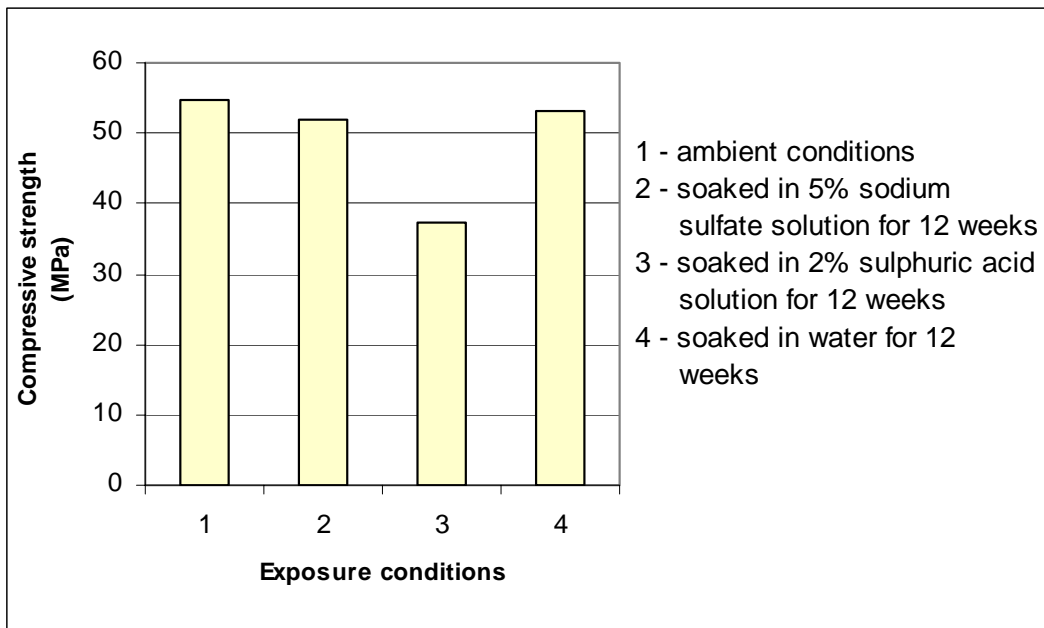


Figure 6 Compressive strength after 12-week of exposure

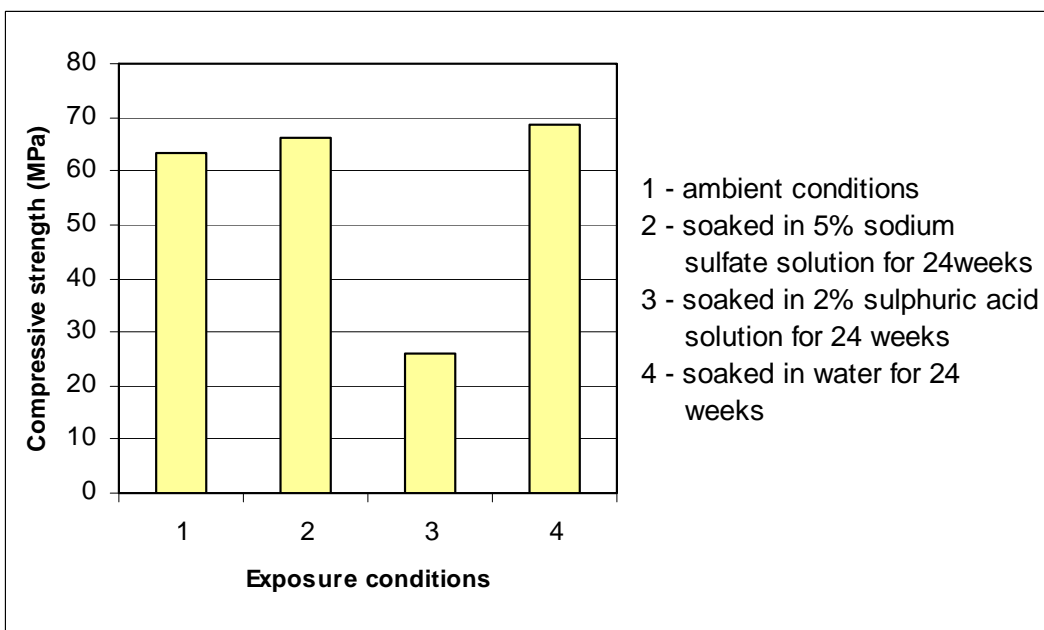


Figure 7 Compressive strength after 24-week of exposure

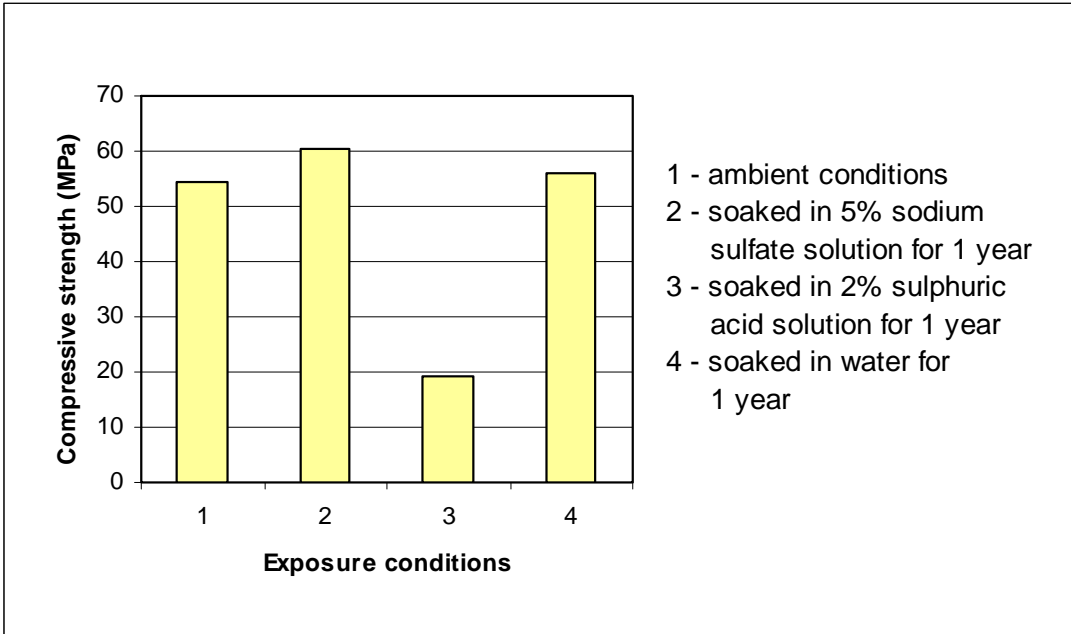


Figure 8 Compressive strength after 1-year of exposure

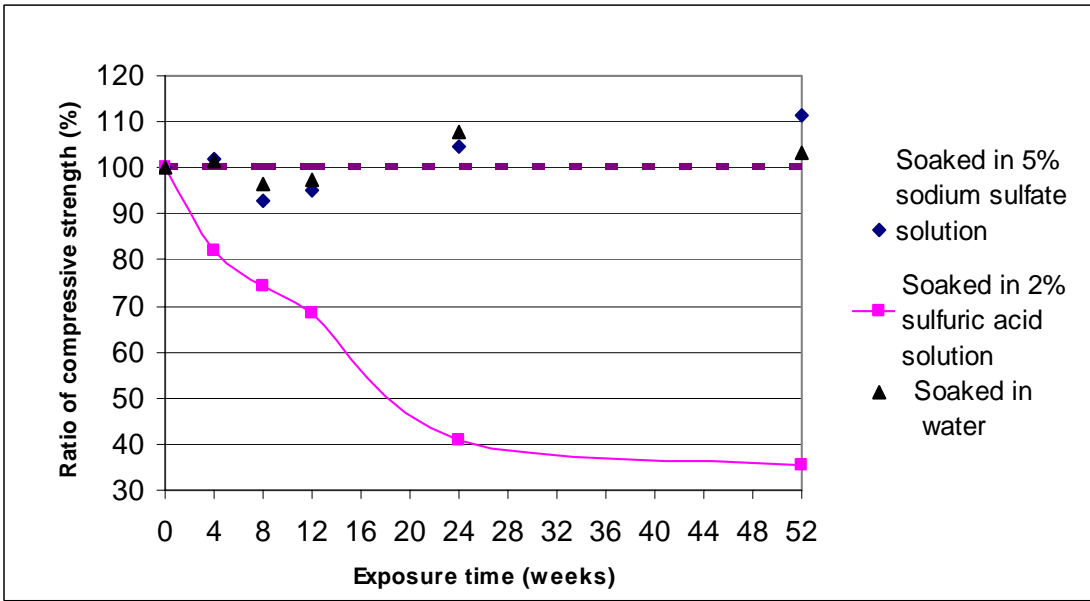


Figure 9 Degradation in compressive strength after various exposures

Table 3 Residual compressive strength after sulfuric acid exposure
(Percentage of the value at ambient conditions tested one week after casting)

Exposure time (Weeks)	Concentration of sulfuric acid solution		
	2%	1%	0.5%
4 weeks	82	87	102
12 weeks	68	78	100



Figure 10 Penetration of sulfuric acid after 1 year of exposure

5. Concluding remarks

The resistance of fly ash-based geopolymer concrete to sulfate and acid attack has been studied by soaking test specimens in 5% sodium sulfate solution, and in 2%, 1%, and 0.5% concentrations of sulfuric acid solution. The changes in compressive strength, mass, and length of the specimens were measured for various exposure periods up to one year. The test results showed that the fly ash-based geopolymer concrete has an excellent resistance in sulfate environment. On the other hand, the acid attack damaged the surface of the specimens and significantly reduced the compressive strength of geopolymer concrete when the concentration of the sulfuric acid solution was 2%. The reduction in the compressive strength was significantly smaller in the case of 1% and 0.5% concentrations.

6. References

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