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Performance of Geopolymer Concrete Under Sulfate Exposure

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Synopsis: As a relatively 'new' material, geopolymer concrete offers the benefits as a construction material for sustainable development. It utilises waste materials such as fly ash and has a very low rate of green house gas emission. This paper presents the study of the performance of fly ash based geopolymer concrete to sulfate attack. Test specimens were soaked in sodium sulfate solution and sulfuric acid solution for various periods of time, and the performance of geopolymer concrete is studied by evaluating the effect on the compressive strength, change in length and change in mass. Test results show that exposure to sodium sulfate has no significant effect on geopolymer concrete, whereas exposure to sulfuric acid affects the compressive strength.

Keywords: fly ash, geopolymer concrete, sodium sulfate, sulfuric acid

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INTRODUCTION

The development of environmentally friendly concrete for sustainable development is crucial for continued use of this material. In this respect, geopolymer concrete is emerging as an alternative to Ordinary Portland Cement (OPC) concrete as a construction material for sustainable development. Geopolymer concrete that utilises waste material containing silica (*Si*) and alumina (*Al*) such as fly ash is a good alternative because it has a very low rate of greenhouse gas emissions compared to OPC concrete. The term 'geopolymer' was first introduced by Davidovits (1987) to describe a family of mineral binders based on silico-aluminates. 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 first 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.

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 fly ash based geopolymers [3, 4, 5]. Longer curing time and higher curing temperatures 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 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 significantly. 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]. The recent 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 for about 120 minutes without any sign of setting and without any effect on the compressive strength [9]. The test results also show that geopolymer concrete undergoes low creep [10]. This paper presents the study of the sulfate resistance of geopolymer concrete.

EXPERIMENTAL PROGRAM

Materials and Mixture Proportions

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, 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 $1.29 \text{ m}^2/\text{cc}$. 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 coarse aggregates and fine sand, in saturated surface dry conditions, were used in the experimental work. The fineness modulus of combined aggregates was 5.0. The alkaline activators were analytical grade sodium hydroxide (NaOH) in flake form with 98% purity and sodium silicate (with $\text{SiO}_2/\text{Na}_2\text{O}$ ratio of 2.00 and $\text{SiO}_2=29.4\%$ by mass). In order to improve the workability, high range water reducer superplasticiser of 1.5% by mass of the fly ash was added to the mixture.

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.

Specimen Preparation

The sodium hydroxide flakes were dissolved in distilled water to make a solution with a concentration of 8 M at least one day prior to use. The fly ash and the aggregates were first mixed together in a pan mixer for about 3 minutes. The sodium hydroxide and the sodium silicate solutions were mixed together with superplasticiser and then added to the dry materials and mixed for about 4 minutes. Immediately after mixing, the fresh concrete was cast into 100 x 200 mm cylindrical molds in three layers and 75x75x285 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 chosen periods. After curing, the specimens were left to air-dry in the laboratory.

Test Variables and Test Procedures

The specimens were soaked in sodium sulfate solution and sulfuric acid solution for intended periods of time and the changes in compressive strength, length and mass were measured.

The concentration of the sodium sulfate (Na_2SO_4) in the solution was 5 percent by mass and that of the sulfuric acid (H_2SO_4) was 2 percent by mass [11, 12, 13]. The pH value of the sodium sulfate solution was between 6 and 8 and that of sulfuric acid solution was about 2. In order to maintain these concentrations 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.

Test variables selected for this study are grouped into two series. In the first series, the changes in compressive strength and length of the specimens soaked in sodium sulfate solution were observed. Specimens were cured in the oven at 60°C for the periods of 24 hours and 48 hours. For the length change tests, three specimens were made for each variable and the changes in length were measured using a horizontal length comparator one hour after removing the specimens from the immersion tank. Four specimens were made for each variable for compressive strength tests. The tests were performed one week after

removing the test specimens from sodium sulfate solution and tested in compression in accordance with the relevant Australian Standard for testing concrete.

In the second series, the changes in compressive strength and mass of the specimens soaked in sodium sulfate solution and sulfuric acid solution were observed. After each exposure period, the specimens were tested immediately after removing them from the solution. For change of mass tests, four specimens were made for each test variable and the mass was measured using a laboratory scale. Four specimens were made for each variable for compressive strength tests and the tests were performed in accordance with the relevant Australian Standard for testing concrete. For comparison, an additional set of specimens were soaked in tap water.

The test variables are summarized in Table 3. The results plotted in various Figures are the average of the values of the specimens in each category.

TEST RESULTS

Visual Appearance

There was no significant change in the external appearance of the surface of specimens soaked in sodium sulfate up to 12 weeks. The same was true for the specimens soaked in tap water. However, the surfaces of specimens soaked in sulfuric acid solution started to erode even after one week of exposure.

Compressive Strength

Figures 2 and 3 show the variation in the compressive strength of specimens tested one week after removing the specimens from sodium sulfate solution after various weeks of exposure. For both curing periods (24 hours and 48 hours), the variation in compressive strength is not significant compared to the result obtained for the companion specimens left in the laboratory ambient conditions and tested one week after casting. Figures 4, 5 and 6 show the compressive strengths of specimens soaked in sodium sulfate solution, sulfuric acid solution and tap water for exposure periods of 4, 8 and 12 weeks respectively as compared to the compressive strengths of companion specimens left in the laboratory ambient conditions and tested one week after casting the specimens. It can be seen from these data that exposure to sodium sulfate

solution or tap water up to 12 weeks has very little effect on the compressive strength. However, a significant change in compressive strength is observed in the case of specimens exposed to sulfuric acid solution. The compressive strength of these specimens decreased substantially as the period of soaking increased. For the 12 weeks soaking period, the reduction of compressive strength was about 30 %. It appears that the penetration of sulfuric acid may have affected the microstructure and decreased the bond between geopolymer paste and the aggregates, thus resulting in a decrease in compressive strength.

Change in Length

Figure 7 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 0.01%.

Change in Mass

The average unit weight of concrete in ambient conditions was 2356 kg/m³. This value did not change for specimens soaked in sodium sulfate solution. In the case of specimens soaked in sulfuric acid, the mass decreased less than one percent after 12 weeks.

CONCLUDING REMARKS

The performance of geopolymer concrete under sulfate exposure has been studied by soaking the specimens in sodium sulfate solution and sulfuric acid solution. After 12 weeks of exposure, by observing the change in compressive strength, change in mass and change in length of the specimens, the results showed that in form of sodium sulfate, sulfate attack did not have significant effect on geopolymer concrete. On the other hand, the sulfate attack in the form of sulfuric acid damaged the surface of the specimens and reduced the compressive strength of geopolymer concrete. Tests are continuing for at least one year in order to substantiate the trends observed so far.

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REFERENCES

1. Davidovits, J., Geopolymers: Inorganic Polymeric New Materials. *Journal of Thermal Analysis*, 1991. 37: p. 1633-1656.
2. Davidovits, J. Properties of Geopolymer Cements. Presented at the First International Conference on Alkaline Cements and Concretes. 1994. Kiev, Ukraine.
3. Davidovits, J. High-Alkali Cements for 21st Century Concretes. Presented at the V. Mohan Malhotra Symposium on Concrete Technology: Past, Present And Future. 1994. University of California, Berkeley: ACI.
4. van Jaarsveld, J.G.S., van Deventer, J.S.J., and Lukey, G.C., The effect of composition and temperature on the properties of fly ash- and kaolinite-based geopolymers. *Chemical Engineering Journal*, 2002. Article in press: p. 1-11.
5. Palomo, A., M.W.Grutzeck, and M.T.Blanco, Alkali-activated fly ashes A cement for the future. *Cement And Concrete Research*, 1999. 29(8): p. 1323-1329.
6. Hardjito, D., Wallah, S.E., and Rangan, B.V. Research Into Engineering Properties of Geopolymer Concrete. Presented at the Geopolymer 2002 International Conference. 2002. Melbourne, Australia.
7. Hardjito, D., Wallah, S.E., and Rangan, B.V., Study on Engineering Properties of Fly Ash-Based Geopolymer Concrete. *Journal of the Australasian Ceramic Society*, 2002. 38(1): p. 44-47.
8. Hardjito, D., Wallah, S.E., Sumajouw, D.M.J., and Rangan, B.V. Properties of Geopolymer Concrete with Fly Ash as Source Material: Effect of Mixture Composition. Presented at the Seventh CANMET/ACI International Conference on Recent Advances in Concrete Technology. 2004. Las Vegas, USA.
9. Hardjito, D., Wallah, S.E., Sumajouw, D.M.J., and Rangan, B.V. Properties of Geopolymer Concrete With Fly Ash as Its Source Material. Presented at the 21st Biennial Conference Of The Concrete Institute of Australia. 2003. Brisbane, Australia: Concrete Institute of Australia.
10. Wallah, S.E., Hardjito, D., Sumajouw, D.M.J., and Rangan, B.V. Creep Behavior of Fly Ash-Based Geopolymer Concrete. Presented at the Seventh CANMET/ACI International Conference on Recent Advances in Concrete Technology. 2004. Las Vegas, USA.
11. Standards-ASTM, Standard Test Method for Length Change of Hydraulic-Cement Mortars Exposed to a Sulfate Solution. 1995. C 1012 - 95a.
12. Hime, W.G., Comments on Geopolymer Concrete, Private Communication. 2003.

13. Li, G. and Zhao, X., Properties of concrete incorporating fly ash and ground granulated blast-furnace slag. *Cement & Concrete Composites*, 2003. 25(3): p. 293-299.

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

SiO ₂	53.36
Al ₂ O ₃	26.49
Fe ₂ O ₃	10.86
CaO	1.34
Na ₂ O	0.37
K ₂ O	0.8
TiO ₂	1.47
MgO	0.77
P ₂ O ₅	1.43
SO ₃	1.70
LOI*	1.39

* loss on ignition

TABLE 2 Mixture proportions for geopolymer concrete

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

TABLE 3 Test variables and other details

Parameters	Specimens	Curing period	Exposure conditions
Series-1			
Compressive strength	Cylinders 100/200 mm	24 and 48 hours	Sodium sulfate solution
Change in length	Prisms 75/75/285 mm	24 and 48 hours	
Series-2			
Compressive strength, and change in mass	Cylinders 100/200 mm	24 hours	Sodium sulfate solution, sulfuric acid solution, and tap water

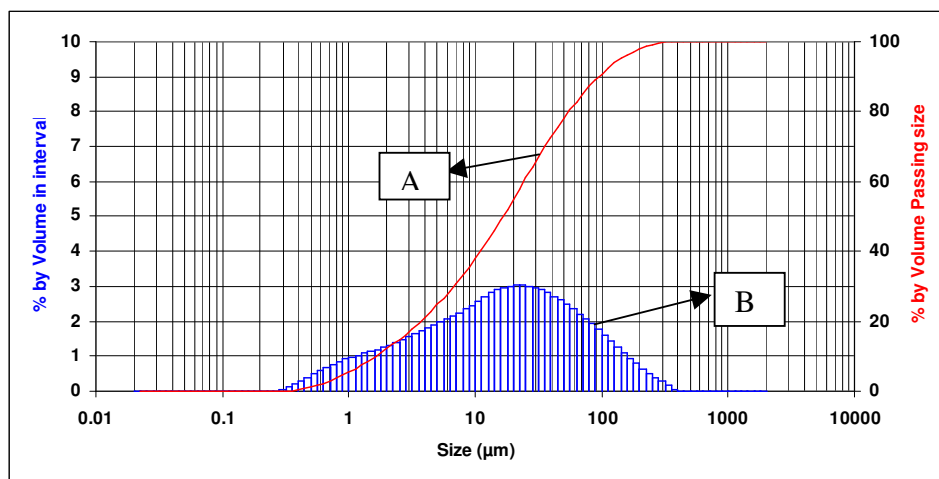


Fig. 1 Particle size distribution of fly ash

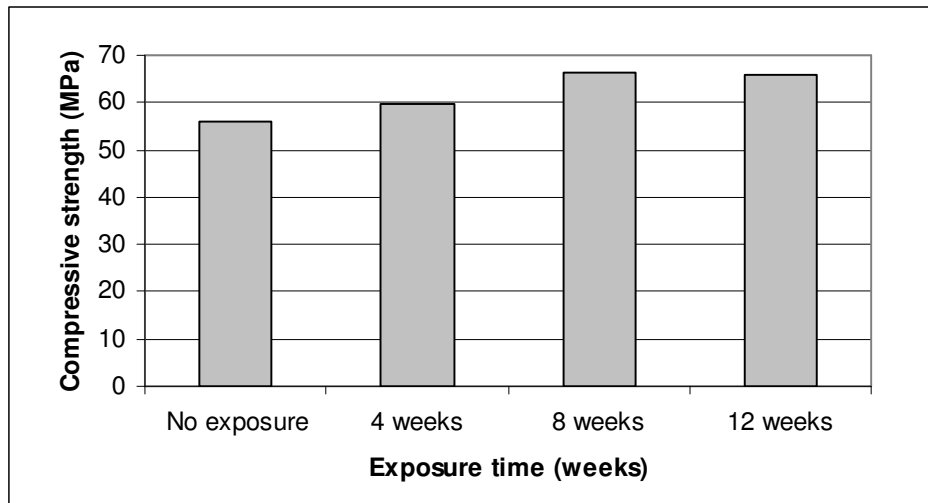


Fig. 2 Compressive strength after sodium sulfate exposure for specimens cured for 24 hours

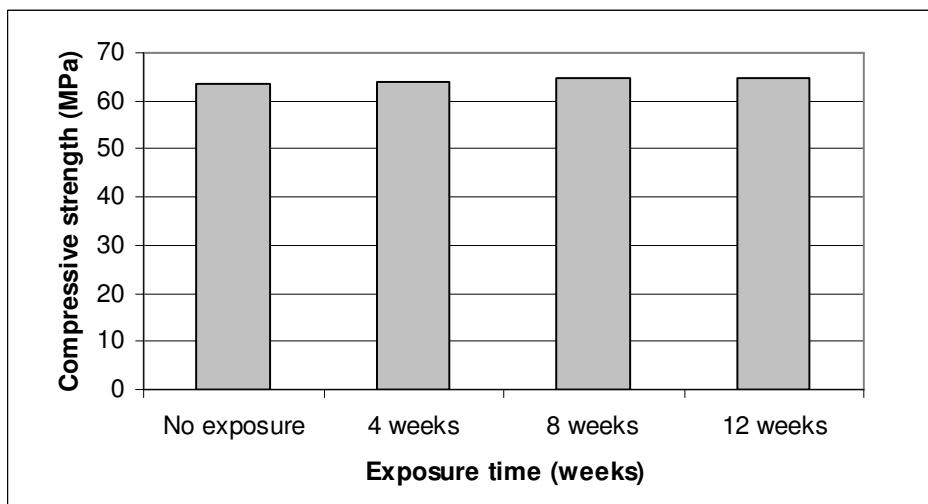


Fig. 3 Compressive strength after sodium sulfate exposure for specimens cured for 48 hours

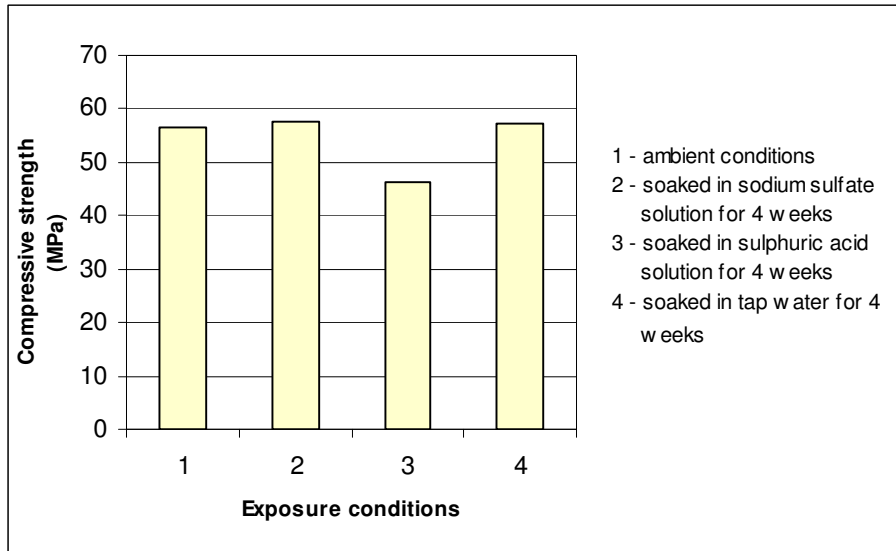


Fig. 4 Compressive strength after 4-week of exposure

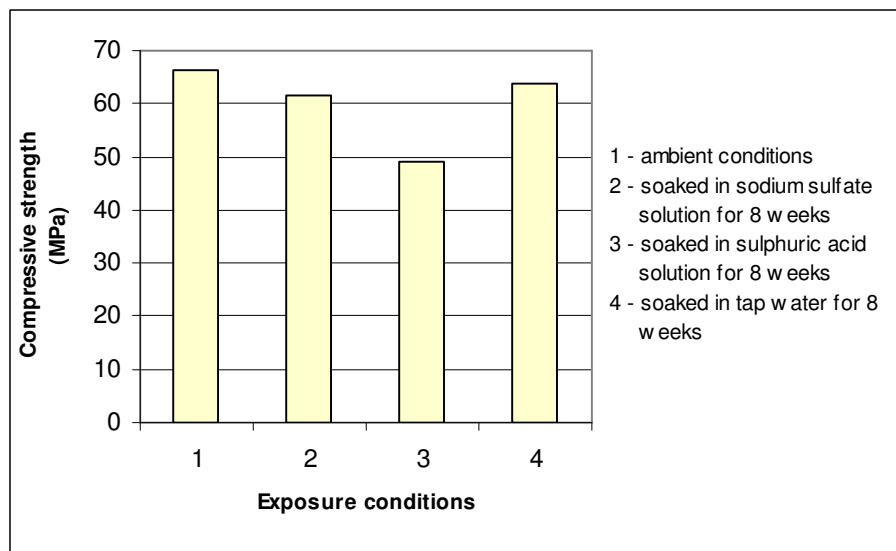


Fig. 5 Compressive strength after 8-week of exposure

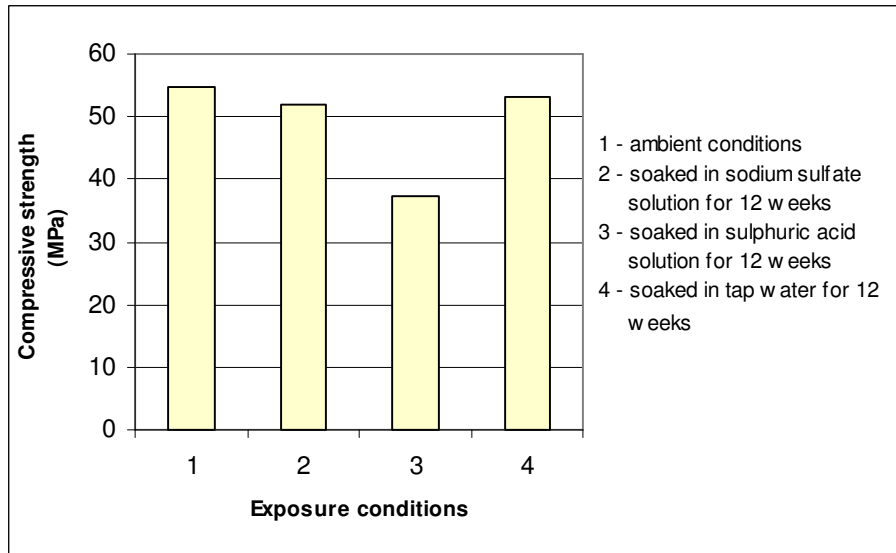


Fig. 6 Compressive strength after 12-week of exposure

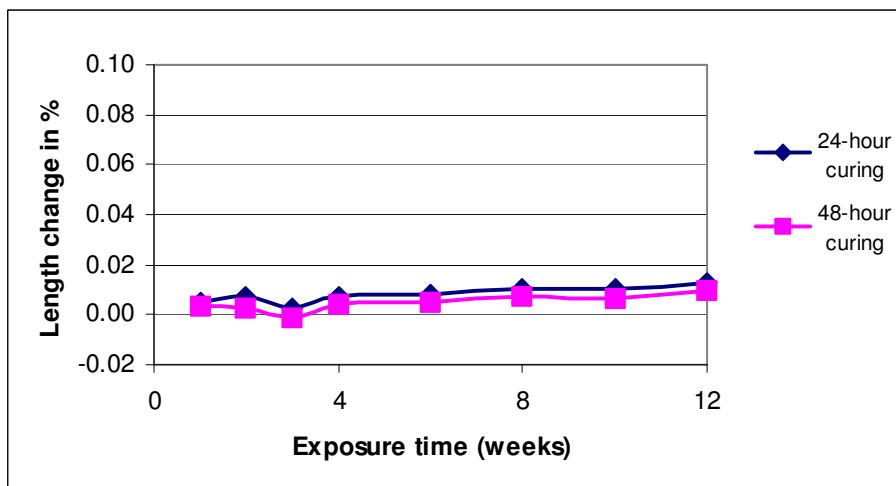


Fig. 7 Length change after sodium sulfate exposure