

Sulfate and Sulfuric Acid Resistance of Geopolymer Mortars Using Waste Blended Ash

M. Aamer Rafique Bhutta^{a*}, Nur Farhayu Ariffin^b, Mohd Warid Hussin^a, Nor Hasanah Abdul Shukor Lim^b

^aConstruction Research Centre (UTM CRC), Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia

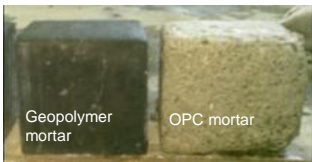
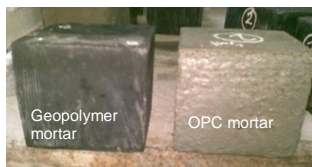
^bDept. of Structures & Materials, Faculty of Civil Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia

*Corresponding author: marafique@utm.my

Article history

Received :1 November 2012
Received in revised form :15 January 2013
Accepted :15 March 2013

Graphical abstract



2% Sulfuric acid exposure for 360-d

Abstract

This paper presents the chemical resistance of geopolymer mortars prepared from the combination of palm oil fuel ash (POFA) and pulverized fuel ash (PFA) from agro-industrial waste as cement replacement and activated by alkaline solution. Alkaline solution was prepared by combining sodium silicate and sodium hydroxide. The concentration of alkaline solution used was 14 Molar. The optimum mix proportions of geopolymer mortars with PFA: POFA mass ratio of 70:30 was used together with alkaline solution. The ratio of sodium silicate solution-to-sodium hydroxide solution by mass was 2.5:1. The mass ratio of sand to blended ashes was 3:1. Test specimens 70×70×70 mm cube were prepared and cured at room temperature (28°C) for 28-d and heat-cured at 90°C for 24 h, respectively. Then specimens were exposed to 5% sodium sulfate solution and 2% sulfuric acid solution for 28-d, 56-d, 90-d, 180-d and 365-d. The evaluation was done by visual observation, mass change, and loss of compressive strength. The test results revealed that geopolymer mortars showed higher resistance to acids as compared to ordinary Portland cement mortar due to the elimination of cement in the mixture.

Keywords: Sulfate resistance; sulfuric acid resistance; geopolymer mortar; mass change; residual compressive strength

Abstrak

Kertas kerja ini membentangkan ketahanan mortar geopolymer disediakan daripada gabungan bahan api abu sawit (POFA) dan bahan api terhancur (PFA) daripada sisa perindustrian pertanian sebagai pengganti simen dan diaktifkan oleh larutan alkali. Larutan alkali telah disediakan dengan menggabungkan natrium silikat dan natrium hidroksida dengan kepekatan larutan adalah 14 Molar. Nisbah jisim campuran optimum abu PFA: POFA adalah 70:30 telah digunakan bersama-sama dengan larutan alkali. Nisbah larutan natrium silikat kepada larutan natrium hidroksida mengikut jisim adalah 2.5:1. Nisbah jisim pasir kepada abu dicampur adalah 3:1. 70×70×70 mm kiub telah disediakan dan diletakkan pada suhu bilik (28°C) selama 28 hari dan pada suhu 90°C untuk 24 jam. Selapas itu, mortar dibiarkan di dalam larutan 5% larutan sodium sulfat dan 2% larutan asid sulfuric untuk 28, 56, 90, 180 dan 360 hari. Penilaian telah dilakukan berdasarkan perubahan permukaan, perubahan jisim dan penurunan jumlah kekuatan mortar. Keputusan ujian menunjukkan bahawa mortar geopolymer menunjukkan rintangan yang lebih tinggi untuk sulfat dan asid berbanding dengan mortar simen Portland biasa kerana penghapusan simen di dalam campuran mortar geopolymer.

Kata kunci: Rintangan; mortar geopolymer; perubahan jisim; kekuatan

© 2013 Penerbit UTM Press. All rights reserved.

1.0 INTRODUCTION

The ordinary Portland cement (OPC) continues to be the most commonly used material in construction industry. Many studies show that OPC gives poor performance in resistance to chemical attacks such as acids and sulphate and hence render it unsuitable in adverse conditions. Moreover, a large amount of Green House Gas (CO₂) is released into the atmosphere during its manufacturing process. In the past few decades, geopolymer

has emerged as one of the possible alternative to OPC due to its high early strength, excellent durability, performance and environment friendliness. Geopolymer is a new material which is being used for construction all over the world. Davidovits (1990; 1994; 1991; 1994) proposed that an alkaline liquid could be used to react with the silicon (Si) and the aluminum (Al) in a source material of geological origin or in by-product materials such as fly ash and rice husk ash to produce binders. As the

chemical reaction involved is polymerisation process, he coined, the term 'Geopolymer' to represent these binders.

Most of the previous researches in geopolymer used only fly ash as a replacement (Hardjito, 2005; Rangan, 2008; Thokchom, 2009) but this study employed POFA which is an abundant waste material in Malaysia being the largest producer of palm oil and palm products in the world. As a new material for construction, not much information is available on the durability of geopolymer concrete or mortar (Bhutta, 2011). The durability of concrete or mortar is an important requirement for performance in aggressive environments throughout its design life period. This study investigates the resistance of geopolymer mortars incorporating PFA and POFA blended ash to sulfate and sulfuric acid resistance.

2.0 EXPERIMENTAL

2.1 Materials

2.1.1 Blended Ash and Fine Aggregate

Lignite PFA from Kapar power station, Selangor, Malaysia was used. POFA was obtained from burning of palm oil shell and husk (in equal volume) at 940°C from a Kahang mill, Kluang, Johor. The PFA and POFA have a mean particle size of 45 µm with percentages retained 92.9% and 90% on the sieve. The obtained ashes were greyish and the losses on ignitions (LOI) were 0.112% for PFA and 20.9% for POFA. The chemical compositions of PFA and POFA are given in Table 1. Local crushed granite sand with a specific gravity of 2.62 was used for making mortar.

Table 1 Chemical compositions of PFA and POFA

Material	PFA	POFA
SiO ₂	46.7	53.5
Al ₂ O ₃	35.9	1.9
Fe ₂ O ₃	5.0	1.1
CaO	3.9	8.3
MgO	0.8	4.1
Na ₂ O	0.6	1.3
K ₂ O	0.5	6.5
P ₂ O ₃	0.4	2.4

2.1.2 Alkaline Solutions

To activate the blended ash, commercial grade sodium hydroxide (NaOH) and sodium silicate (Na₂SiO₃) solutions were used as alkaline activator. Distilled water was used to dissolve sodium hydroxide pellets to prevent any effect of unknown contaminants. The mass of NaOH solids in a solution varies depending on the concentration of the solution. The range of NaOH concentration used in this research was 14 molar. In order to improve the workability, a super plasticizer and extra water were added to the mixture.

2.2 Experimental Procedures

2.2.1 Preparation of Geopolymer Mortar Specimens

The optimum mix proportion was used to prepare geopolymer mortars as shown in Table 2. All geopolymer mortar specimens were prepared with sand to blended ash ratio of 3:1, whereby the sand was prepared to saturated surface dry condition. The concentration of alkaline solution used was 14 molar. The ratio (by mass) of sodium silicate (Na₂SiO₃) to sodium hydroxide (NaOH) was 2.5:1. The optimum PFA to POFA ratio of 70:30 in the mix proportions was used. First, the blended ash, super plasticizer and sand were dry mixed in pan mixer for about three minutes. Then alkaline liquid was added along with extra water to maintain the workability of geopolymer mortars. The liquid component of the mixture was mixed for another five minutes. The mixing was carried out at room temperature of approximately 28°C. The flow of geopolymer mortars was determined and fixed in the range of 130±5 according to ASTM C 1437. The test specimens 70×70×70 mm cubes were prepared. The specimens were casted and well compacted in two layers. Additional vibration of about 2 minutes was applied using vibrating table. The specimens were wrapped with plastic sheets to prevent from moisture loss.

For cement mortar, the ratio of cement to sand was 1:3 with water-cement ratio of 0.45%. The mortar was mixed and the flow was determined in accordance with the procedures given in ASTM C 1437 and fixed to 130±5.

Table 2 Optimum mix proportion of geopolymer mortar

Mix proportion, kg/m ³	
Blended Ash	527
Alkaline Solution	237
Sand	1586
SP	5.2
Liquid / Blended Ash	0.45

2.2.2 Curing

Two curing conditions were considered for geopolymer mortars: room temperature and heat curing. For room temperature curing, specimens were subjected to room temperature of approximately 28°C for 28 days. For heat curing, test specimens were placed in an oven at 90°C for 24 hours and then placed at room temperature until the day of testing.

2.2.3 Sulfate and Sulfuric Acid Resistance Tests

In order to determine the durability of geopolymer mortars, the cubic specimens were immersed in sulfate and sulfuric acid solutions up to a years. OPC mortar specimens as control were also immersed in the same solutions and results were compared.

Sulphate resistance: To study the durability of geopolymer mortar, specimens were immersed in 5% sodium sulphate solution, the duration of exposure were 28-d, 56-d, 90-d, 180-d and 365- d. The effects of sodium sulphate on the geopolymer mortar specimen were constantly monitored through visual inspection, measurement of mass change and by determining the

residual compressive strength. The compressive strength was determined according to ASTM C 109.

Sulfuric acid resistance test: The test specimens were immersed in 2% sulphuric acid solution after initial curing. The duration of exposure was 28-d, 56-d, 90-d, 180-d and 365-d and specimens were kept fully immersed in the acid solution. The effects of sulfuric acid on the geopolymer mortar specimen were constantly monitored through visual inspection, measurement of mass changes and by determining residual compressive strength test in accordance with ASTM C 109.

Residual compressive strength was calculated based on the following equation:

$$\text{Residual compressive strength (\%)} = [B/A] \times 100 \quad (1)$$

where $A = \text{Initial compressive strength}$
 $B = \text{Compressive strength after exposure}$

3.0 RESULTS AND DISCUSSION

3.1 Sulphate Resistance

Tests were conducted to evaluate the sulphate resistance of heat-cured and room temperature-cured blended ash geopolymer mortars. The sulphate resistance was evaluated based on change in visual appearance, mass and change in compressive strength of the specimens after exposure in 5% sodium sulphate solution.

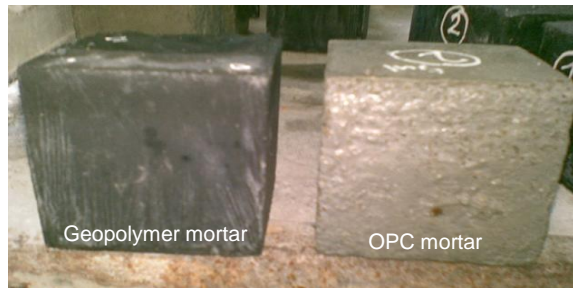


Figure 1 Physical appearance of mortar specimens after 365-d immersion in 5% sodium sulphate solution

Figure 1 shows the specimens condition after 365-d of immersion in 5% sodium sulphate solution. Specimens did not show any change in dimension and remained structurally intact without visible cracks. As seen in Figure 1, there were no changes observed on surface of geopolymer mortar while OPC mortar showed significant surface deterioration after one year exposure in 5% sodium sulphate solution.

Figure 2 represents the mass change of mortar specimens after 365-d immersion in 5% sodium sulphate solution. The change in mass was observed within the immersion period of up to one year. The mass of all specimens was gradually increased over the immersion periods. Compared to OPC mortar, the mass change of all geopolymer mortars was much lower. At 28-d, both geopolymer mortar specimens slowly gained some mass of 0.4% and 0.6% for heat cured and room temperature cured specimens, respectively.

This increase in mass continued for another 365-d of immersion and reached to about 2%. On the other hand, OPC mortars gained a mass of 1.3% at 28-d and gradually increased to 3.5% over a period of 365-d. This increase in mass can be attributed to relatively higher water absorption by OPC mortar.

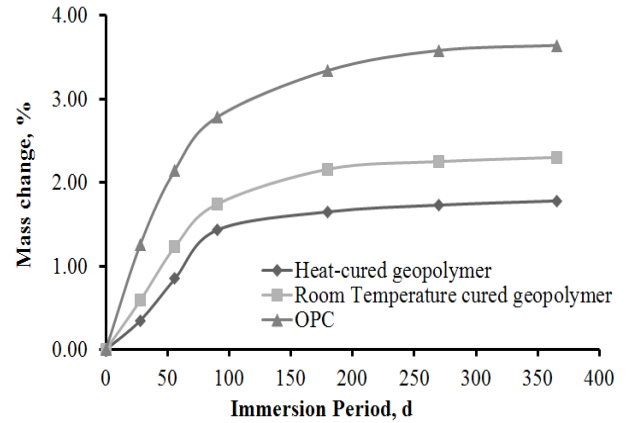


Figure 2 Mass changes of mortar specimens after 365-d immersion in 5% sodium sulphate solution

Figure 2 represents the mass change of mortar specimens after 365-d immersion in 5% sodium sulphate solution. The change in mass was observed within the immersion period of up to one year. The mass of all specimens was gradually increased over the immersion periods. Compared to OPC mortar, the mass change of all geopolymer mortars was much lower. At 28-d, both geopolymer mortar specimens slowly gained some mass of 0.4% and 0.6% for heat cured and room temperature cured specimens, respectively.

Figure 3 represents the result for compressive strength of mortar specimens. In general, the compressive strength of all specimens decreased gradually as exposure period increased. For heat-cured and room temperature-cured geopolymer mortars, the relative compressive strength decreased to 15% and 18% respectively, after 90-d sulphate solution immersion. At the age of 365-d, the relative compressive strength was recorded to decrease to 32% and 35% of strength for heat-cured and room temperature-cured geopolymer mortars respectively.

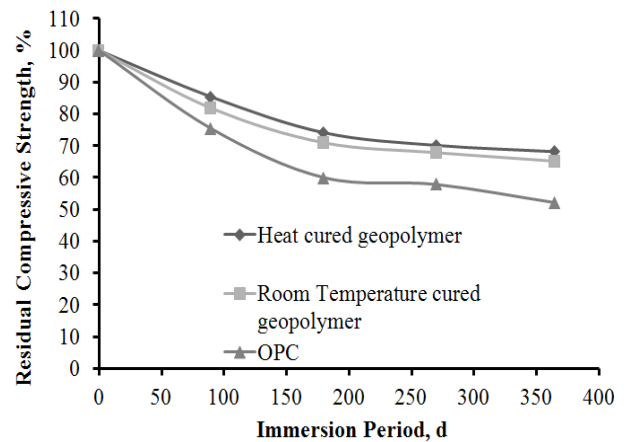


Figure 3 Residual compressive strength of specimens after 365-d immersion in sodium sulphate solution

On the other hand, the relative compressive strength of OPC mortars decreased to 25% at 90-d and continued to decrease to more than 50% at prolonged 365-d in 5% sodium sulphate solution. The deterioration of OPC mortar was

significant due to the reaction of sulphate with calcium hydroxide and calcium monosulfoaluminate to form gypsum and ettringite which led to strength loss, expansion, cracking and scaling of the surface of mortar specimens. The geopolymer mortars, however, showed a different mechanism. The main geopolymerization products were different from OPC hydration products and were less susceptible to sulphate attack compared to OPC hydration products (Bakharev, 2005).

3.2 Sulfuric Acid Resistance

Figure 4 shows the visual observation of geopolymer mortar and OPC mortar. It can be seen that geopolymer mortars did not exhibit any noticeable color change and showed no visible signs of deterioration. The specimens were seen to remain structurally intact. In contrast, the surfaces of OPC mortar specimens became deteriorated and rough.



Figure 4 Geopolymer and OPC mortar specimens after 365-d immersed in 2% of sulphuric acid solution

Figure 5 exhibits the mass change of specimens immersed in 2% sulphuric acid solution for 28, 56, 90, 180, 270 and 365 days. Figure 5 represents the relationship between the mass change due to 2% sulphuric acid attack on heat-cured, room-temperature cured and OPC mortars and the period of immersion. A sudden gain in mass of all mortars was noticed at 28-d due to absorption property of mortars. After 56-d of sulphuric acid solution immersion, the mass of all specimens started to decrease and this trend was observed up to one year immersion. As for OPC mortar, mass loss was determined to be more than 3.0% which is more than twice that of geopolymer mortars.

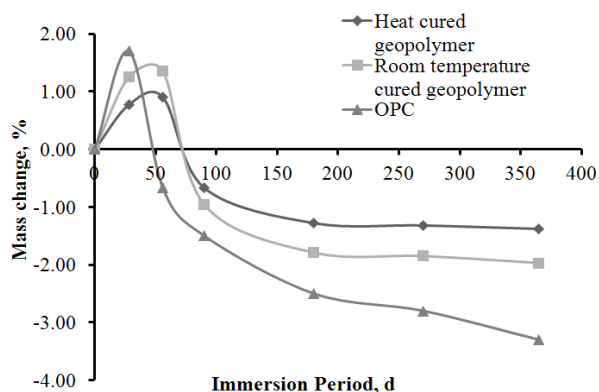


Figure 5 Mass changes of specimens in 2% sulphuric acid solution

This can be attributed primarily to the reaction between calcium hydroxide presented in the cement mortar specimens and the acid, which can induce tensile stress, resulting in cracking and scaling of mortar. The mass loss of geopolymer mortars after 365-d immersed in solution was observed to be more than 1.0% for heat-cured and 1.5% for room temperature-cured. The geopolymer mortars had low mass loss under acid attack due to the low water absorption of geopolymer binder and also to their low calcium content compared to that of OPC mortar.

Figure 6 shows the residual compressive strength of geopolymer mortars and OPC mortars immersed in 2% sulphuric acid solution. The residual compressive strength was gradually decreased with sulphuric acid attack for up to one year immersion period and the residual compressive strengths for heat-cured and room-temperature geopolymer mortars were 40% and 44%, respectively. On the other hand, the residual compressive strength of OPC was decreased to about 70% for one year immersion period.

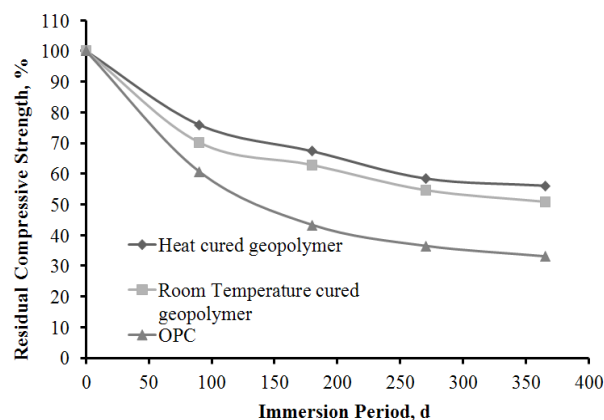


Figure 6 Residual compressive strength of specimens after 365-d immersion in sulphuric acid solution

The mortars immersed in sulphuric acid showed loss in compressive strength due to breakage of aluminium silicate bonding caused by acid attack (Bakharev, 2005). Alumino silicate bonding is important as it gives strength to geopolymer mortar. The strength loss in heat-cured geopolymer mortar is lower than that of room temperature-cured geopolymer mortar. This is attributed to complete polymerization due to heat curing that gives strong alumino silicate bonding than room temperature curing. The geopolymer mortars showed better resistance than OPC mortars when exposed to acid due to chemical and phase compositions.

4.0 CONCLUSIONS

This study investigates the durability of geopolymer mortars incorporating PFA and POFA blended ash to 5% sodium sulfate and sulfuric acid solutions. Based on the results, the following conclusions can be drawn:

(1) Heat-cured blended ash geopolymer mortar has an excellent resistance to sulfate attack. There was no significant damage to the surface of test specimens after exposure to 5% sodium sulfate solution up to one year. The geopolymer mortars were less susceptible to the attack by 5% sodium sulfate solution

compared to OPC in terms of mass change and decrease in compressive strength.

(2) The visual appearance of specimens after 2% sulfuric immersion showed that acid attack slightly damaged the surface of specimens. The maximum mass loss of geopolymer mortar specimens of about 1.5% and 1.0% in sulfuric and hydrochloric acid solutions after one year was relatively small compared to that of OPC mortar.

(3) Exposure to acid caused degradation in the compressive strength, the extent of degradation was related to the type of acid, concentration and period of exposure.

(4) The residual compressive strengths for heat-cured and room temperature-cured geopolymer mortars exposed to 2% sulfuric acid up to one year were 40% and 44%, respectively. The deterioration of OPC mortar immersed in 2% sulfuric acid solution for one year was significant and the residual compressive strength of OPC was about 70% up to one year immersion period.

Acknowledgements

The authors are grateful to the Ministry of Higher Education, Malaysia (MoHE) and Research Management Centre (RMC), Universiti Teknologi Malaysia (UTM) for financial support under grant: Q.J.130000.7122.01J76. The authors are also thankful to the staff of Materials & Structures Laboratory, Faculty of Civil Engineering for the facilities and support for experimental work.

References

- [1] Bhutta, M. A. R., Hussin, M. W., Azreen, M. A., Nor Hasanah and Nur Farhayual. 2011. Mix Design and Compressive Strength of FA-POFA-Based Geopolymer Mortar. Proceedings of 9th International Symposium on High Performance Concrete, Rotorua, New Zealand. 14.
- [2] Bakharev, T. 2005. Durability of Geopolymer Materials in Sodium and Magnesium Sulfate Solutions. *Cement and Concrete Research*. 35: 1233–46.
- [3] Bakharev, T. 2005. Resistance of Geopolymer Materials to Acid Attack. *Cement and Concrete Research*. 35: 658–70.
- [4] Davidovits, J. 1991. Geopolymer: Inorganic Polymeric New Materials. *Them Anal*. 37:1633–56.
- [5] Davidovits, J., Comrie, D. C., Paterson, J. H., and Ritcey, D. J. 1990. Geopolmeric Concretes for Environmental Protection. *ACI Concrete International*. 12: 30–40.
- [6] Davidovits, J. 1994. Geopolymer Man-Made Rock Geosynthesis and The Resulting Development of Very Early High Strength Cement. *J. Mater. Educ*. 16: 91.
- [7] Davidovits, J. 1994. Properties Of Geopolymer Cements. Proceedings of the First International Conference on Alkaline Cements and Concretes, vol.1, SRIBM, Kiev, Ukrain. 131–149.
- [8] Thokchom, S., Dr. Partha Ghosh, P. and Ghosh, S. 2009. Acid Resistance of Fly Ash Based Geopolymer Mortars. *International Journal of Recent Trends in Engineering*. 1(6): 39.
- [9] Rangan, B. V. 2008. Studies on Fly Ash Based Geopolymer Concrete. *Malaysia Construction Research Journal*. 3: 124.
- [10] Hardjito, D. and Rangan, B. V. 2005. Development and Properties of Low Calcium Fly Ash-based Geopolymer Concrete. Research Report GC1. Curtin University of Technology, Perth, Australia.
- [11] Rangan, B. V. 2008. Low-Calcium Fly Ash-Based Geopolymer Concrete. Chapter 26 in *Concrete Construction Engineering Handbook*. Second Edition. New York: CRC Press,
- [12] Rangan, B. V. 2009. Engineering Properties of Geopolymer Concrete. Chapter 13 in *Geopolymer: Structures, Processing, Properties, and Applications*. Editors: J.Provis and J. van Deventer. London: Woodhead Publishing Limited,