2021 年臺灣國際科學展覽會
優勝作品專輯

作品編號 030030

參展科別 化學

作品名稱 Sustainable G-Polymer From Industrial Waste

國　　家 Malaysia

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關鍵詞 Geopolymer、paper sludge ash、compression test

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Abstract

This study focuses on the pre-treatment of paper sludge ash (PSA) as a by-product of paper milling industry that contains high amount of calcium, yet low in silica. The presence of high calcium content in geopolymer system will accelerate the setting time of fresh geopolymer and may disrupt the development of its mechanical strength. Therefore, in this study, the refinement of PSA properties was conducted by treating raw PSA in hydrochloric acid solution with different molarities of 0.5 M, 1.0 M and 2.0 M. The pre-treatment process was mainly purposed to decrease the amount of calcium and other impurities through leaching mechanism.

Based on the experimental results, 2.0 M hydrochloric acid solution (HCl) was determined as the optimum concentration due to its ability in removing higher amount of calcium from the ash, yet still able to increase the amount of silica. Compression test on the hardened properties of geopolymer specimen also showed the deceleration of fresh fly ash based geopolymer and produced a more workable fresh geopolymer.

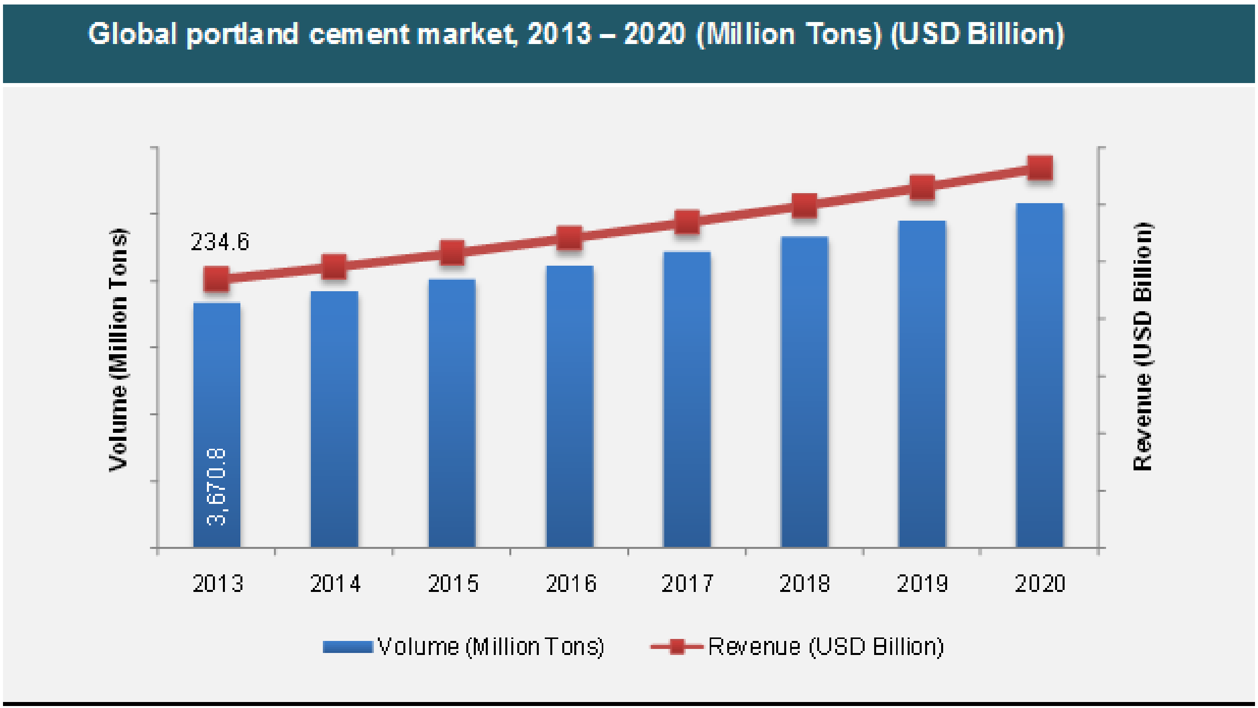
1.0 Introduction

The contribution of ordinary portland cement (OPC) production worldwide to greenhouse gas emissions is estimated to be approximately 1.35 billion tons annually or approximately 7% of the total greenhouse gas emissions to the earth's atmosphere[1] Also, it has been reported that many concrete structures, especially those built in corrosive environments, start to deteriorate after 20 to 30 years, even though they have been designed for more than 50 years of service life[2].The concrete industry has recognized these issues. For example, the U.S. Concrete Industry has developed plans to address these issues in "Vision 2030: A Vision for the U.S.

Concrete Industry." In this document, strategies to retain concrete as a construction material of choice for infrastructure development, and at the same time to make it an environmentally friendly material for the future, have been outlined[3]

To produce environmentally friendly concrete, Mehta [4] suggested the use of fewer natural resources, less energy, and to minimize carbon dioxide emissions. He categorized these short-term efforts as industrial ecology. The long-term goal of reducing the impact of unwanted by-products of industry can be attained by lowering the rate of material consumption. In line with the above view, one of the efforts to produce more environmentally friendly concrete is to partially replace the amount of OPC in concrete with by-product materials such as fly ash. An important achievement in this regard is the development of high-volume fly ash (HVFA) concrete that uses only approximately 40% of OPC, and yet possesses excellent mechanical properties with enhanced durability performance. The test results show that HVFA concrete is more durable than OPC concrete[5]

Another effort in this regard is the development of inorganic alumino-silicate polymer, called geopolymer, synthesized from materials of geological origin or by-product materials such as fly ash that are rich in silicon and aluminium[6]. The geopolymer paste can be used as a binder to produce concrete, instead of the cement paste.



Source: ICIS, PCA, CMA, CEMBUREAU, WBCSD, USGS Primary Interviews, Transparency Market Research

Diagram 1 : Global Portland cement market

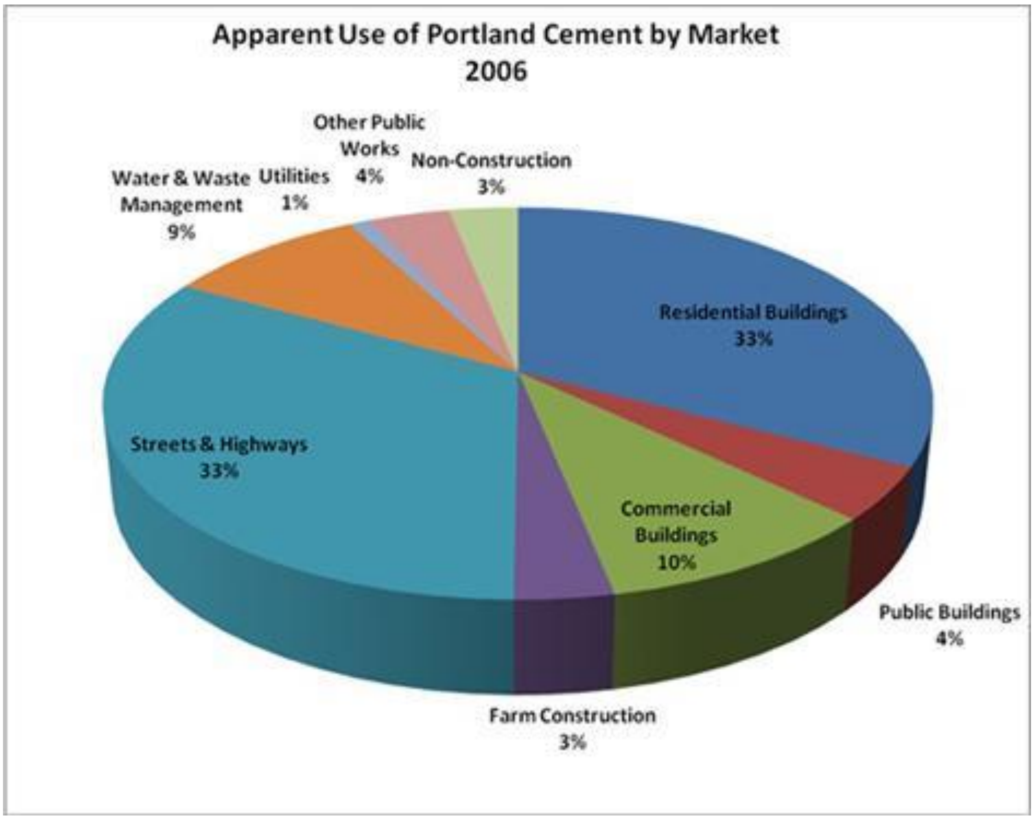


Diagram 2 : Apparent use of Portland Cement market

1.1 Geopolymer

The term ‘geopolymer’ was first introduced by Davidovits in 1978 to describe a family of mineral binders with chemical composition similar to zeolites but with an amorphous microstructure. He also suggested the use of the term ‘poly(sialate)’ for the chemical designation of geopolymers based on silico-aluminate (Davidovits, 1988a, 1988b, 1991; van Jaarsveld et. al., 2002a); Sialate is an abbreviation for silicon-oxo-aluminate.

From a terminological point of view, geopolymer cement [1] is a binding system that hardens at room temperature, like regular Portland cement. If a geopolymer compound requires heat setting it may not be called geopolymer cement but rather geopolymer binder.

Geopolymer cement is an innovative material and a real alternative to conventional Portland cement for use in transportation infrastructure, construction and offshore applications. It relies on minimally processed natural materials or industrial by products to significantly reduce its carbon footprint, while also being very resistant to many of the durability issues that can plague conventional concretes.

Creating geopolymer cement requires an alumina silicate material, a user-friendly alkaline reagent [2] (sodium or potassium soluble silicates with a molar ratio MR $SiO_2:M_2O>1,65$, M being Na or K) and water (See the definition for "user-friendly" reagent below). Room temperature hardening relies on the addition of calcium cations, essentially iron blast furnace slag. Geopolymer cements cure more rapidly than Portland-based cements. They gain most of their strength within 24 hours.

However, they set slowly enough that they can be mixed at a batch plant and delivered in a concrete mixer. Geopolymer cement also has the ability to form a strong chemical bond with all kind of rock-based aggregates.

Why Geopolymer ...

Simple process

Wide range of applications

80% less CO_2 generation than OPC

Low energy & water consumption

Better durability & longevity

Qualifies as GREEN

Fly ash, one of the source materials for geopolymer binders, is available abundantly worldwide, and yet its use to date is limited. From the 1998 estimation, the global coal ash production was more than 390 million tonnes annually, but its use was less than 15%.7 In the future, fly ash production will increase, especially in countries such as China and India. From these two countries alone, it is estimated that by the year 2010 the amount of the fly ash produced will be 780 million tonnes annually.5 Accordingly, efforts to use this by product material in concrete manufacture are important to make concrete more environmentally friendly.

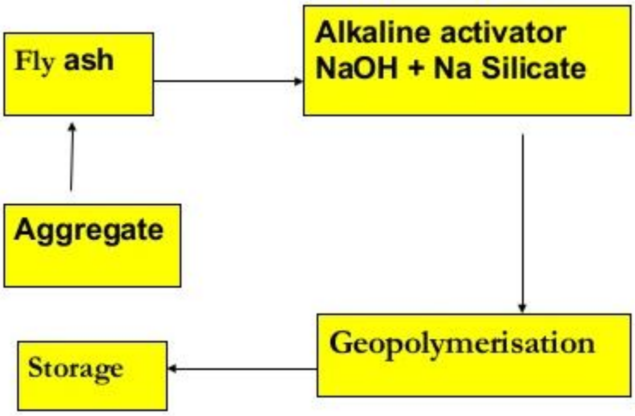


Diagram 3 : Preparation of geopolymer concrete

Ordinary Portland Cement VS Geopolymer

- ✓ Geopolymer using fly ash
- ✓ Greater corrosion resistance
- ✓ Substantially higher fire resistance
- ✓ High compressive and tensile strength
- ✓ Rapid strength gain and lower shrinkage
- ✓ Greenhouse gas reduction potential as much as 90 precentage when compared with OPC

1.2 Fly ash

Fly ash is the finely divided residue that results from the combustion of pulverized coal and is transported from the combustion chamber by exhaust gases. Fly ash is produced by coal-fired electric and steam generating plants. Typically, coal is pulverized and blown with air into the boiler's combustion chamber where it immediately ignites, generating heat and producing a molten mineral residue. Boiler tubes extract heat from the boiler, cooling the flue gas and causing the molten mineral residue to harden and form ash. Coarse ash particles, referred to as bottom ash or slag, fall to the bottom of the combustion chamber, while the lighter fine ash particles, termed fly ash, remain suspended in the flue gas.

Currently, over 20 million metric tons (22 million tons) of fly ash are used annually in a variety of engineering applications. Typical highway engineering applications include: portland cement concrete (PCC), soil and road base stabilization, flowable fills, grouts, structural fill and asphalt filler.

Fly ash utilization, especially in concrete, has significant environmental benefits including: (1) increasing the life of concrete roads and structures by improving concrete durability, (2) net reduction in energy use and greenhouse gas and other adverse air emissions when fly ash is used to replace or displace manufactured cement, (3) reduction in amount of coal combustion products that must be disposed in landfills, and (4) conservation of other natural resources and materials.

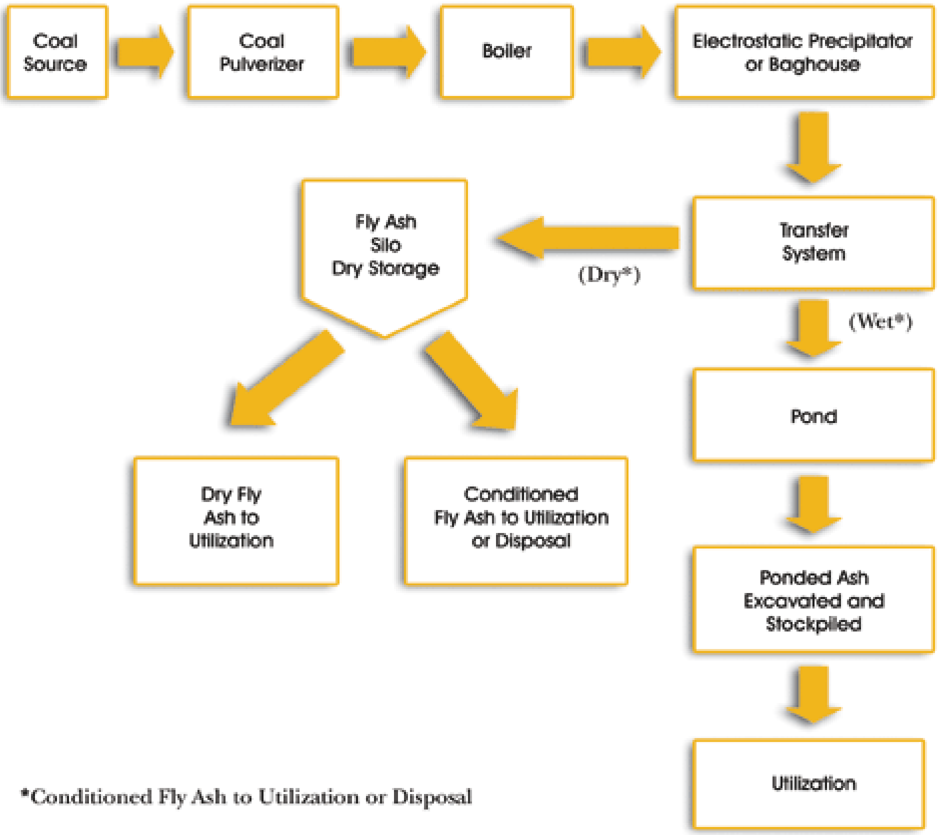


Diagram 4 : method of fly ash transfer can be dry, wet or both

The 62 million metric tons (68 million tons) of fly ash produced in 2001, only 20 million metric tons (22 million tons), or 32 percent of total production, was used. The following is a breakdown of fly ash uses, much of which is used in the transportation industry.

Diagram 5 : Fly ash from industrial waste

Table 1: Fly ash uses.

	Million Metric Tons	**Million Short Tons**	**Percent**
Cement/Concrete	12.16	13.40	60.9
Flowable Fill	0.73	0.80	3.7
Structural Fills	2.91	3.21	14.6
Road Base/Sub-base	0.93	1.02	4.7
Soil Modification	0.67	0.74	3.4
Mineral Filler	0.10	0.11	0.5
Mining Applications	0.74	0.82	3.7
Waste Stabilization /Solidification	1.31	1.44	6.3
Agriculture	0.02	0.02	0.1
Miscellaneous/Other	0.41	0.45	2.1
Totals	**19.98**	**22.00**	**1**

Fly ash can be tan to dark gray, depending on its chemical and mineral constituents. Tan and light colors are typically associated with high lime content. A brownish color is typically associated with the iron content. A dark gray to black color is typically attributed to an elevated unburned carbon content. Fly ash color is usually very consistent for each power plant and coal source.

Fly ash consists primarily of oxides of silicon, aluminum iron and calcium. Magnesium, potassium, sodium, titanium, and sulfur are also present to a lesser degree. When used as a mineral admixture in concrete, fly ash is classified as either Class C or Class F ash based on its chemical composition. American Association of State Highway Transportation Officials (AASHTO) M 295 [American Society for Testing and Materials (ASTM) Specification C 618] defines the chemical composition of Class C and Class F fly ash.

Class C ashes are generally derived from sub-bituminous coals and consist primarily of calcium alumino-sulfate glass, as well as quartz, tricalcium aluminate, and free lime (CaO). Class C ash is also referred to as high calcium fly ash because it typically contains more than 20 percent CaO.

Class F ashes are typically derived from bituminous and anthracite coals and consist primarily of an alumino-silicate glass, with quartz, mullite, and magnetite also present. Class F, or low calcium fly ash has less than 10 percent CaO.

Table 2: Sample oxide analyses of fly ash and portland cement

Compounds	Fly Ash Class F	Fly Ash Class C	Portland Cement
SiO_2	55	40	23
Al_20_3	26	17	4
Fe_2O_3	7	6	2
CaO (Lime)	9	24	64
MgO	2	5	2
SO_3	1	3	2

1.3 Paper sludge ash

The pulp and paper industry in Europe produces 11 million tonnes of paper sludge waste per annum [16]. During processing paper sludge is often dewatered and combusted to recover energy and reduce the volume of waste requiring disposal to landfill. This produces paper sludge ash (PSA), with 10–15 kg generated for every tonne of paper manufactured [16].

Although the composition of PSA varies, it typically contains lime (CaO), silica (SiO_2) and alumina (Al_2O_3) and for this reason has been used as a supplementary cementitious material (SCM) [8,17]. Paper sludge contains a high proportion of organic matter, in the form of cellulose, as well as inorganic compounds, such as clays and calcium carbonate.
The mineralogical composition of PSA depends on the combustion temperature.

Paper mill sludge is often incinerated for heat recovery and volume reduction. In Italy, about 600,000 t of paper mill sludge is produced yearly. About 6 kg of sludge is produced per ton of paper produced. The paper mill sludge is recovered from a primary mechanical separation process. When it is combusted as a single fuel source, it produces paper mill sludge ash (PSA)

1.4 Problem Statement

How to change paper sludge ash an alternative material for geopolymer ?

1.5 Hypothesis

It is able to change paper sludge ash an alternative material for geopolymer ?

1.6 Objective

The specific objectives of this research were to :

- ✓ To utilize treatment paper sludge ash as an alternative sources material for geopolymer.
- ✓ To determine the compressive strength of fly ash based geopolymer contain paper sludge ash.

1.7 Scope of research

- ✓ Fly ash was used as the primary aluminosilicate source and activated with a combination of sodium hydroxide (NaOH) and sodium silicate (Na_2SiO_3) solution.
- ✓ Fly ash was substituted with PSA with the replacement percentage of 5%, 10%, 15% (by weight of fly ash).
- ✓ To overcome the rapid stiffening, PSA is treated with hydrochloric acid solution with the concentration of 0.5M, 1.0M and 2.0M.
- ✓ After casting process, geopolymer specimens were cured in oven with the temperature of 30 °C and 80 °C for 24 hours.
- ✓ The properties of hardened geopolymer mortar is determined by compressive strength.

2.0 Methodology

2.1 Prepare a material

In this research, fly ash was used as the primary source material and partially replaced with pre-treated PSA at certain proportions to be mixed with alkali solutions. Fly ash was collected from Manjung coal fired power plant and paper mill sludge ash was obtained from Malaysia Newsprint Industries Mentakab. Sodium silicate solution with the composition of Na_2O = 14.73 %; SiO_2 = 29.75 % and H_2O = 55.52 % was used as the alkali solution. Table 1 shows the detail of mixture proportion used in this study.

Table 1: Detail of mixture proportions.

No	Fly ash (g/m^3)	Sand (g/m^3)	Sodium silicate (g/m^3)	Sodium hydroxide (g/m^3)	Water (g/m^3)	PSA (g/m^3)	Pre-treated PSA (g/m^3)			Temperature (^oC)
							0.5M	1.0M	2.0 M	
1	300	800	180	45	30	0	-	-	-	30/80
2	285	800	180	45	30	15	-	-	-	30/80
3	270	800	180	45	30	30	-	-	-	30/80
4	255	800	180	45	30	45	-	-	-	30/80
5	285	800	180	45	30	-	15	-	-	30/80
6	270	800	180	45	30	-	30	-	-	30/80
7	255	800	180	45	30	-	45	-	-	30/80
8	285	800	180	45	30	-	-	15	-	30/80
9	270	800	180	45	30	-	-	30	-	30/80
10	255	800	180	45	30	-	-	45	-	30/80
11	285	800	180	45	30	-	-	-	15	30/80
12	270	800	180	45	30	-	-	-	30	30/80
13	255	800	180	45	30	-	-	-	45	30/80

Diagram 6 : Fly ash collected from Manjung coal fired power plant

2.2 Pretreatment of Paper Sludge Ash (PSA)

Pre-treatment process to minimize the presence of calcium from paper mill sludge ash was conducted by using different molarities of hydrochloric acid solution i.e. 0.5 M, 1.0 M and 2.0 M. The inclusion of paper mill sludge ash in geopolymer system was done by partially replaced fly ash amount at 5%, 10%, and 15% (by weight of fly ash).

i. 10g of PSA washed with 100ml 0f HCl 2.0M
ii. Mixture a shacked in a incubator for 2 hours

iii. The solution filtered through whatman

iv. PSA residue washed with 100ml distilled water

v. Dried in oven for 24 hours at 60°C

	
Untreated paper sludge ash	Treated paper sludge ash

Diagram 7 : Paper sludge ash collected from Malaysia Newsprint Industries Mentakab

Diagram 8 : Measure the volume of HCl used form treatment

2.3 Preparation Geopolymer mortar

Geopolymer mortar was prepared with conventional mixing method. Fly ash, fine aggregate and paper mill sludge ash (if any) were mixed in a bowl mixer for a minute to obtain a well dispersed dry mixture. Sodium silicate was poured into the dry mixture and continued with wet mixing process for 2 minutes to get the homogeneous mixture.

Diagram 9 : Weight a substance based on mixture proportions.

Diagram 10 : Fly ash, fine aggregate and paper mill sludge ash (if any) were mixed in a bowl mixer for mixing process .

Fresh geopolymer mortar was then cast into 50 mm cube mould and cured in electronic oven for 24 h at 30 and 80 °C. After 24 h, the hardened specimens were de-moulded and taken out from electric oven to be kept at room temperature until the testing day.

Diagram 11: Cube mould

Diagram 12: Cast a geopolymer

Diagram 13: Geopolymer cube

2.4 Testing

For each batch of geopolymer concrete made in this study, 100x200 mm cylinders specimens were prepared. At least three of these cylinders were tested for compressive strength at an age of seven days after casting. The unit weight of specimens was also determined at the same time. For these numerous specimens made from Mixture-1 and Mixture-2 and cured at 60oC for 24 hours, the average results are presented in Table 4.1.

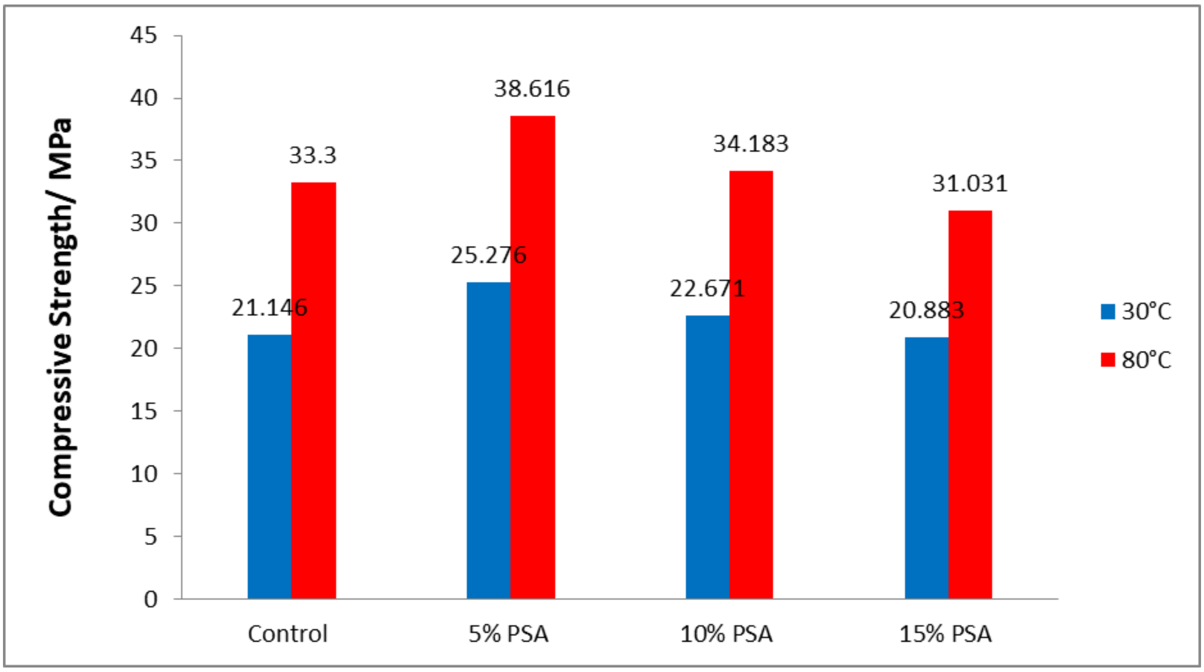
For the evaluation of compressive strength, all cylinder specimens were subjected to test using a 2000 kN-capacity compressive testing machine under ASTM C873M standard. Moreover, snap shots of the specimen under testing were obtained to document its failure mode. Diagram shows the compressive testing machine and the test set-up of the study.

Diagram 14 : Compressive testing machine Diagram 15 compressive test

3.0 Result and Discussion

Chemical oxides in aluminosilicate source play an important role in the geopolymerization process and significantly affect the final geopolymer product. Geopolymerization process involves the chemical reaction between the dissolved silicates and aluminates (Al^{3+} in four-fold coordination) in the presence of alkali activator solution and form –Si-O-Al-O poly(sialate), -Si-O-Al-O-Si-O poly(sialate-siloxo) and –Si-O-Al-O-Si-O-Si-O poly(sialate) [6].

Based on the reaction, SiO_2 and Al_2O_3 function as the backbone formation for geopolymer framework, while Ca, Na and K cations have a role in balancing the framework.



Graph 1 : Effect temperature and percentage of PSA on Compressive strength

In graph 1, the effect of high temperature curing to the outcome of geopolymerization is properly displayed, where the specimens rapidly gained their strength start from early age. Elevated curing temperature is known to enhance the extension period of dissolution of precursors from the amorphous phases in fly ash and other source material particles, and accelerate the development of hard structure particularly in the early-phase of geopolymerization **[**11,12].

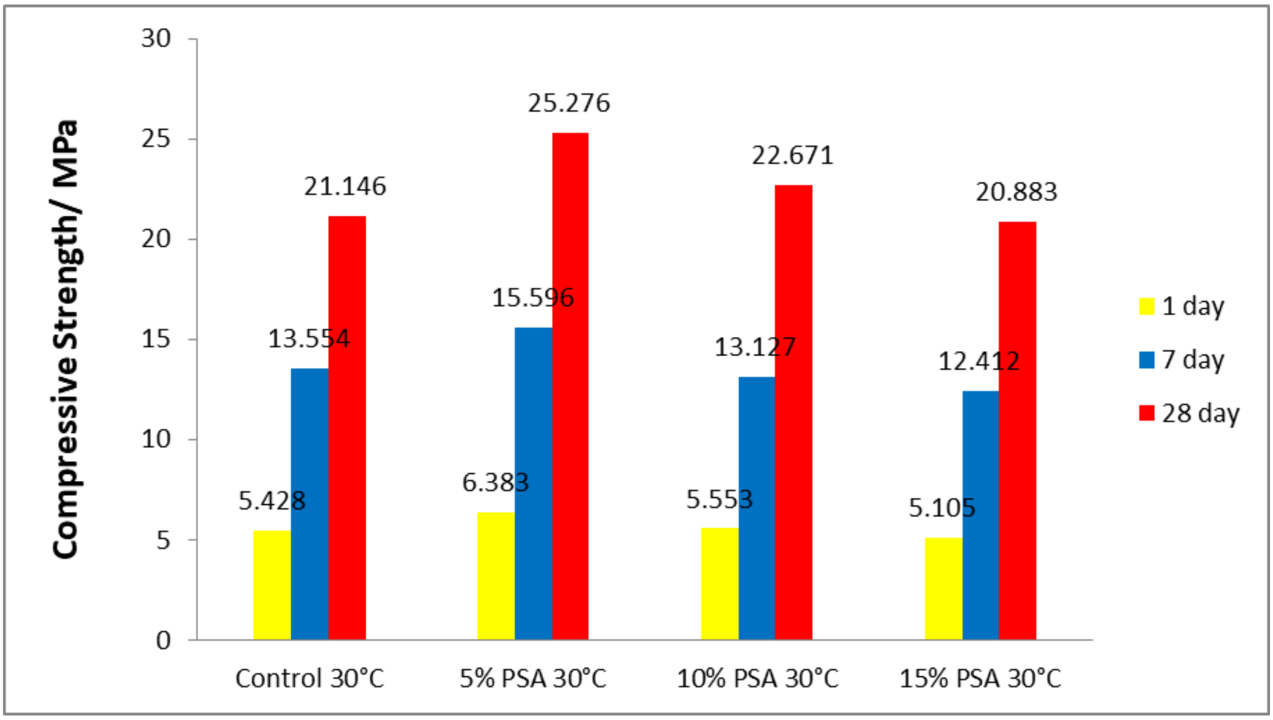
At 80°C curing temperature is better (elevated curing temperature) is known to enhance the extension period of dissolution process of precursors from the amorphous phases in fly ash and other sources material particles and accelerate the development of hard structure particularly in the early-phase of geopolymerization.

Besides a gel formation of main product of geopolymer, at a high temperature it will produces a zeolite. Zeolite ni secondary product of geopolymer.

Zeolite will enter the pore of geopolymer and void. To reduce void, zeolite and CSH gel will function to cover it. This will enhance the geopolymerization process dan increase the compressive strength

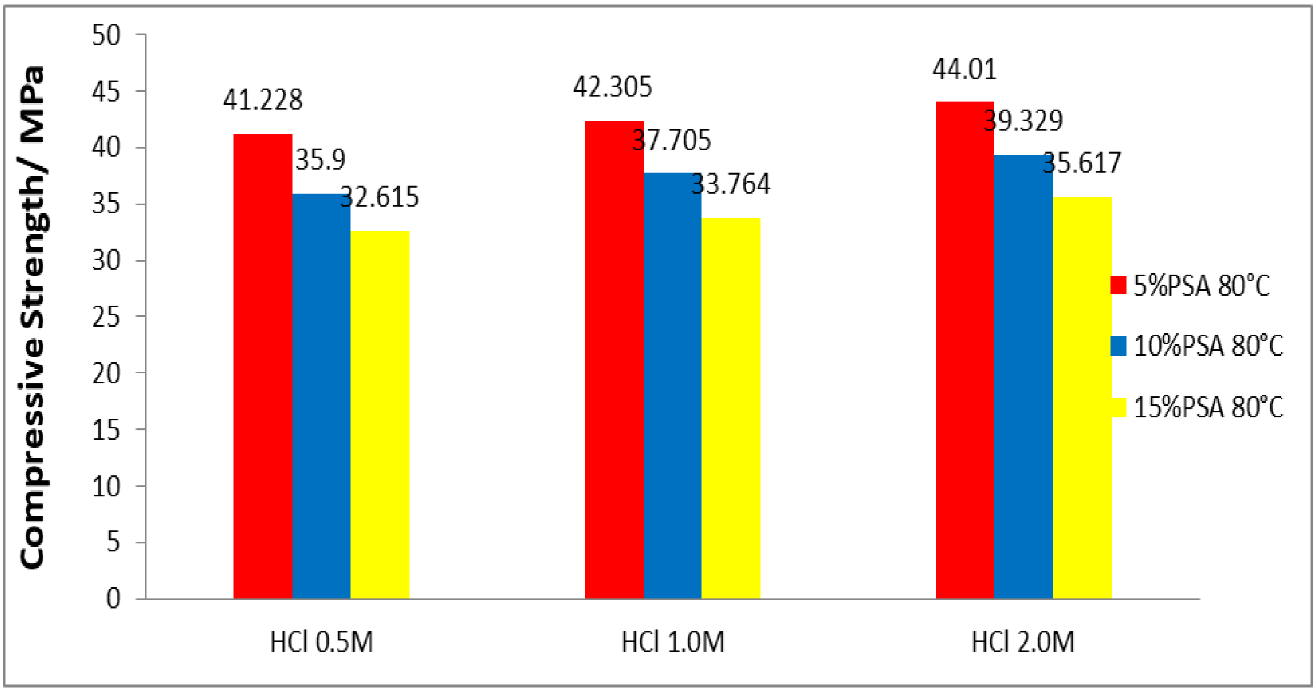
Additional availability of silica from PSA has benefited the framework via the formation of poly(sialate-siloxo), which supported the strength development of hardened geopolymer mortar. Nevertheless, reduction of Al based precursors due to lower fly ash content, has resulted in the strength reduction for 10% and 15% PSA specimens.

Reduction of compressive strength when the amount of PSA is increased to10% and 15% was attributed to the changes of CaO, SiO_2, and Al_2O_3 composition in the blended source material. Lack of alumina due to higher replacement of fly ash was aggravated by the increasing amount of CaO from higher content of PSA. CaO could interfere the polymerization process and alter the microstructure of geopolymer. In addition, rapid stiffening process would initiate the early formation of hardened geopolymer gel.



Graph 2 : Effect curing time on Compressive strength

From graph 2 show as the increase of curing days, the geopolymerization is properly displayed. At this age, geopolymer mortar had reached the equilibrium state and produced stronger three dimensional aluminosilicate networks.



Graph 3 : Effect concentration of HCl on compressive strength

Graph3 shows when concentration of HCl increase, the compressive strength increase. The highest compressive strength when 2.0M treated PSA

Ca content plays an important part in the initiation of geopolymerisation process and it is believed that the effect of calcium on the yield stress of geopolymer system may also be affected by the presence of soluble calcium in fly ash.

Dissolution process occur when remove silica and alumina faster. In 0.5M treated PSA have highest content of alumina. Dissolution process occur at a slow rate causes geopolymer mortar will harden at a slow rate.
But when high Ca content it will accelerate of geopolymer mortar will harden. As we know, one of geopolymer product is gel formation. More gel formation will produces when high content of alumina and silica. So alumina and silica will decelerate the hardening process of geopolymer mortar

4. 0 Conclusion

1. Pre treatment process using hydrochloric acid solution was able to reduce CaO content in PSA. The highest CaO reduction obtained in this study was achieved at 2.0 M HCl solution.

2. The use of pre-treated PSA as an alternative replacement material to fly ash has presented a positive effect where higher compressive strength.

3. The highest compressive strength achieved at 80°C curing temperature (28 days) with the inclusion of 2M 5% treated PSA.

4. Based on this study, pre-treated PSA has a prospective feature to be used as the partial replacement to fly ash in geopolymer mixture.

5.0 Reference

1. Davidovits, J., (1991), Geopolymers: Inorganic Polymeric New Materials, *J. Thermal Analysis*, **37**, 1633–1656. See also Chapter 24 in *Geopolymer Chemistry and Applications*, Joseph Davidovits, Institut Géopolymère, Saint- Quentin, France, 2008, ISBN 9782951482050 (3rd ed., 2011).

2. See the examples at the Geopolymer Institute page http://www.geopolymer.org/applications/geopolymer-cement

3. Williams R. Determination of the reactive component of fly ashes for geopolymer production. Annual geopolymer meeting geopolymer – 2009, Centre for Sustainable Resource Processing, 15–16 July, 2009, Perth, Australia.

4. http://www.geopolymers.com.au/science/geopolymerization

5. Rangan RV. Low-calcium fly-ash based geopolymer concrete. In: Nawy EG, editor. Concrete construction engineering handbook. New York: CRC Press;2007.

6. Hardjito H, Rangan RV. Development and properties of low-calcium fly ash based geopolymer concrete. Research report GC1. Perth, Australia: Faculty of Engineering, Curtin University of Technology; 2005.

7 Temuujin J, van Riessen A, Williams R. Influence of calcium compounds on the mechanical properties of fly ash geopolymer pastes. J Hazard Mater 2009;167:82–8.

8. Lee WKW, van Deventer JSJ. The interface between natural siliceous aggregates and geopolymers. Cement Concrete Res 2004;34:195–206.

9. Subaer. Influence of aggregate on the microstructure of geopolymer. PhD thesis. Department of Applied Physics, Curtin University of Technology; 2004.

10.Garcia-Lodeiro I, Palomo A, Fernandez-Jimenez A. Alkali-aggregate reaction in activated fly ash systems. Cement Concrete Res 2007;37:175–83.

11.Corinaldesi V, Gnappi G, Moriconi G, Montenero A. Reuse of ground waste glass as aggregate for mortars. Waste Manage 2005;25(2):197–201

12. Garcia R, Vigil de la Villa R, Vegas I, Frias M, Sanchez de Rojas MI. The pozzolanic properties of paper sludge waste. Constr Build Mater 2008;22(7):1484–90.

13. Monte MC, Fuente E, Blanco A, Negro C. Waste management from pulp and paper production in the European Union. Waste manage 2009;29(1):293–308.

14. Pera J, Amrouz A. Development of highly reactive metakaolin from paper sludge. Adv Cem Based Mater 1998;7(2):49–56.

【評語】030030

The students tried to apply G-polymers from industrial waste for high-strength materials. The idea is simple but fit with the society needs. However, the material did not undergo too-much chemical transformations. The research work is mostly engineering. The enthusiasm toward scientific research should be encouraged.