

# EFFECT OF GGBS ADDITION ON PROPERTIES OF FLY ASH-BASED GEOPOLYMER AT HIGH TEMPERATURES

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## ABSTRACT

This study presents the microstructure and mechanical properties of geopolymer paste made from low-calcium fly ash and ground granulated blast-furnace slag (GGBS) after exposure at elevated temperature. Five series of specimens were prepared with different ratios of GGBS to fly ash with an aim to investigate the effect of GGBS on the high temperature resistance of the geopolymer specimens. At the age of 28 days, the specimens were exposed at elevated temperatures (500°C, 750°C, and 950°C). The microstructural investigation and compressive strength test were carried out for specimens before and after heating. The results showed that for unheated specimens, the addition of GGBS significantly improved the compressive strength due to the formation of calcium silicate hydrate gel that helps to form denser structure. However, exposure at high temperature caused excessive dehydration of water and decomposition of C-S-H gel inside the specimen, resulting in strength loss and re-crystallizations.

**Keywords:** fly ash, GGBS, geopolymer, microstructure, compressive strength

## 1. INTRODUCTION

Cement is one of the most widely used materials in the world as binder for concrete productions. However, its manufacture has been identified with negative impact on environment because of the large consumption of energy and high CO<sub>2</sub> emission [1-3]. The production of Portland cement contributes around 5-7% of the global CO<sub>2</sub> emissions [4]. Therefore, the demand for environmentally friendly construction materials increased continuously to reduce the environmental degradation caused by CO<sub>2</sub> emissions.

Geopolymer technology has been studied in the past years and it is considered as an environmentally friendly material with high compressive strength, good acid and fire resistance [5-7] and can be synthesized from low cost materials such as fly ash and blast furnace slag, or from natural alumina silicate sources such as clay and metakaolin [3, 5-8]. It has been reported that geopolymers concrete can replace the conventional concrete [9]. However, geopolymer still has to be proven to be more cost-effective and has better performance and durability than Portland cement binder to ensure its feasibility in practical construction application.

Geopolymer was first coined by Joseph Davidovits and was classified as an inorganic material synthesized by the reaction of alumina silicate source with alkaline solution through a polycondensation process. Geopolymers have three-dimensional amorphous structure with tetrahedrally coordinated aluminum (Al) and silicon (Si) [8].

There are many factors affecting the mechanical properties and microstructures of geopolymer-based materials, such as the type of alumina silicate sources,

the alkaline activator solutions, and curing conditions [8,10-12]. A previous study has been carried out to investigate the effect of ground granulated blast-furnace slag (GGBS) addition on the microstructure and mechanical properties of fly ash-based geopolymer. The results indicated that the addition of GGBS significantly improved the compressive strength due to the formation of calcium silicate hydrate (C-S-H) gel that helps to form denser structure [13]. Another study has also revealed that the addition of GGBS in fly ash geopolymer can improve the setting time [14]. This is beneficial since geopolymers which are made only from fly ash exhibited very long setting time.

On the other hand, the issue of making concrete more resistant to high temperature has become a vital need due to the experiences of catastrophic fire. However, it is difficult to balance both the mechanical strength and the fire resistance properties of a material. A study by Rickard et al. revealed that the high-strength geopolymer is more vulnerable to dehydration damage than low-strength geopolymer when exposed to high temperature [15]. Since the addition of GGBS gives significant improvement on compressive strength of the fly ash-based geopolymer, further study on durability such as effect of high temperature is needed to look at the potential application of this material. Although resistance of geopolymer to elevated temperatures has been often investigated, there is limitation in the understanding of the effect of high temperatures in microstructural level. Therefore, in this study we focused on the microstructural and strength evolution after high temperature exposure. In the present study, the response of geopolymer pastes to high temperature was evaluated by considering the amount of GGBS present in the mixes.

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## 2. EXPERIMENTAL PROGRAMS

### 2.1 Materials

Low-calcium fly ash (Blaine fineness = 3,550 cm<sup>2</sup>/g, density = 2.24 g/cm<sup>3</sup>) which conforms to JIS A 6201 and GGBS (Blaine fineness = 4,170 cm<sup>2</sup>/g, density = 2.91 g/cm<sup>3</sup>) which conforms to JIS A 6206 were prepared as precursors. The detailed chemical compositions of both precursors are shown in Table 1.

Sodium silicate solution consisting of 17.5% Na<sub>2</sub>O, 35.6% SiO<sub>2</sub> and 46.9% water by mass and sodium hydroxide (NaOH) solution of 14 M were used as alkaline solutions. Both solutions were prepared one day prior to mixing. The ratio of alkaline solution to binder (fly ash + GGBS) and the ratio of sodium silicate to sodium hydroxide were kept constant as 0.45 and 2.0 by mass, respectively. These ratios were adopted from the preliminary study in which better workability and compressive strength were obtained with NaOH solution of 14 M.

Table 1 Chemical compositions of raw materials

Composition	Fly ash (mass%)	GGBS (mass%)
SiO <sub>2</sub>	64.44	35.45
Al <sub>2</sub> O <sub>3</sub>	20.65	14.06
Fe <sub>2</sub> O <sub>3</sub>	4.18	0.27
CaO	2.25	43.78
K <sub>2</sub> O	1.53	0.23
TiO <sub>2</sub>	1.19	0.56
MgO	0.58	5.84
Na <sub>2</sub> O	-	0.24
S	-	0.62
LOI	2.9	0.05

### 2.2 Synthesis procedures

In this experimental study, five series of geopolymer paste, namely FAS0, FAS15, FAS30, FAS45, and FAS60, were prepared by partially replacing fly ash with GGBS by mass, with replacement levels 0%, 15%, 30%, 45%, and 60%, respectively. The reference sample comprised no GGBS.

The geopolymer paste specimens were synthesized as follows: fly ash and GGBS were first dry-mixed together in a pan mixer for 2 minutes. The sodium silicate solution and NaOH solution of 14 M were added and mixed together with the solid materials rapidly and continuously for 4 minutes to form geopolymer paste. Subsequently, the fresh geopolymer paste was casted in cylindrical plastic molds (50mm x 100mm). After casting, the specimens were cured in a chamber at 70°C and 70% of relative humidity (RH) for 24 hours and were kept at room temperature for the further 24 hours before demolded. After demolded, the specimens were stored and cured at 20°C and 60% RH until the age of 28 days.

### 2.3 Test procedures

The prepared geopolymer paste specimens were weighed before firing. Subsequently, the specimens were exposed into a furnace at temperatures of 500, 750, and 950°C at the age of 28 days at a heating rate of 20°C/min.

When the target temperature was reached, it was maintained for an additional 1 hour. The furnace was then cooled down to room temperature.

### 2.4 Characterization and measurements

Microstructure analysis of specimens was conducted by scanning electron microscopy (SEM) of JEOL JSM-6010PLUS, in which energy dispersive spectroscopy (EDS) was used to investigate the distribution of elements in the specimen. The samples for analysis were collected from the failure surfaces of the specimens after loading test. SEM images were acquired from each specimen, and then the elemental analysis was conducted for an image area of about 375 x 625 μm at 15 kV of accelerated voltage.

The X-ray diffraction (XRD) test was conducted to investigate the phase composition of the specimens before and after exposure at high temperature. The test was performed using a Bruker AXS D2 Phaser X-ray diffractometer in 2-theta range of 5-65 deg using a Cu Kα X-ray source. The sample was prepared into powder form using a ball mill grinding machine.

A compressive strength test on cylindrical geopolymer paste specimens was performed using a universal testing machine with a compression capacity of 250 kN. The loading rate was 0.2 mm/min. The test was repeated for 3 samples and an average was taken.

The thermogravimetric analysis was performed to study the thermal stability of geopolymers from mass loss with increase in temperature. It was carried out using Simultaneous DTA-TG apparatus DTG-60H with a heating rate of 20°C/min from room temperature to 1000°C. Additionally, the mass of the specimen after heating was measured and was compared to the initial mass, and was determined as percentage of mass loss by the following equation:

$$\text{Loss in mass} = \frac{m_i - m_f}{m_i} \times 100\% \quad \dots (i)$$

Where  $m_i$  is the mass measured before heating and  $m_f$  is the mass measured after heating.

## 3. RESULTS AND DISCUSSION

### 3.1 Elemental analysis

Table 2 shows the elements identified in the geopolymer paste specimens made from different ratio of GGBS. High concentration of silicon, aluminum, and oxygen were contained in all specimens, which indicated the formation of alumina-silicate gels [16]. The high concentration of calcium was also found when GGBS was presented in the mixes; this indicated the formation of additional calcium silicate hydrates [16]. Moreover, the concentration of calcium was found to increase with the addition of GGBS, which indicates the formation of calcium silicate hydrate gel may also increase.

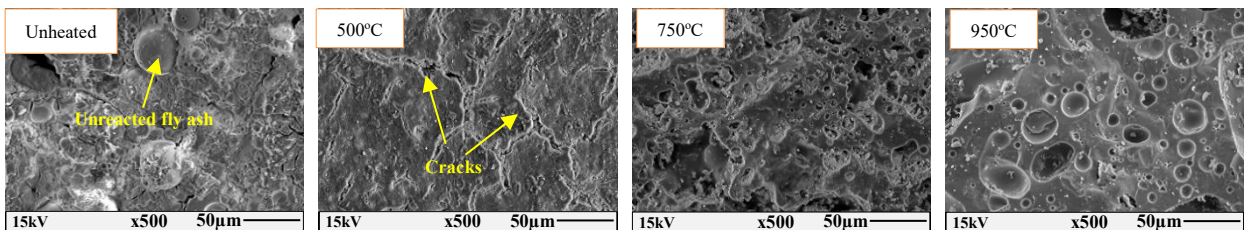
### 3.2 Microstructure analysis

The SEM micrographs of heated and unheated geopolymer pastes are shown in Fig. 1. Some unreacted fly ash particles were found in unheated specimens. It was also observed that the addition of GGBS was found to produce the denser structure due to the formation of

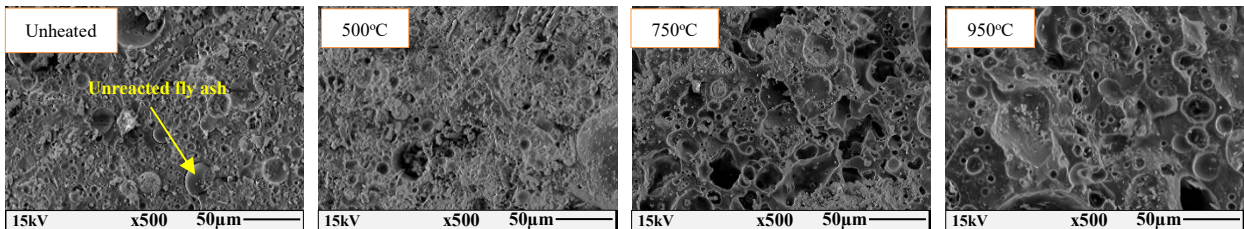
Table 2. Elemental analysis of geopolymer paste specimens with various amount of GGBS.

Element	Mass (%)				
	FAS0	FAS15	FAS30	FAS45	FAS60
Carbon	10.89	11.49	7.90	11.47	7.81
Oxygen	45.49	46.38	45.51	42.39	42.79
Sodium	5.86	6.08	5.95	5.73	6.70
Magnesium	0.40	0.90	1.46	1.94	2.54
Aluminum	9.01	8.57	9.83	8.92	8.17
Silicon	22.72	19.63	19.66	16.91	16.61
Sulphur	-	0.16	0.18	0.28	0.30
Potassium	0.63	0.50	0.52	-	-
Calcium	0.71	3.07	5.34	6.98	9.64
Titanium	0.48	0.40	0.33	0.27	0.33

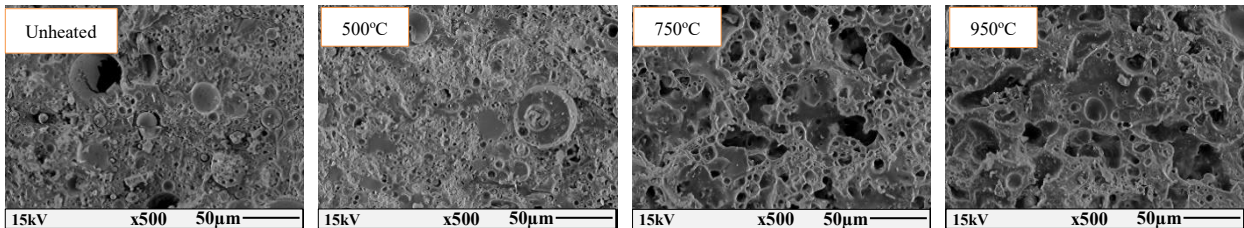
**FAS0**



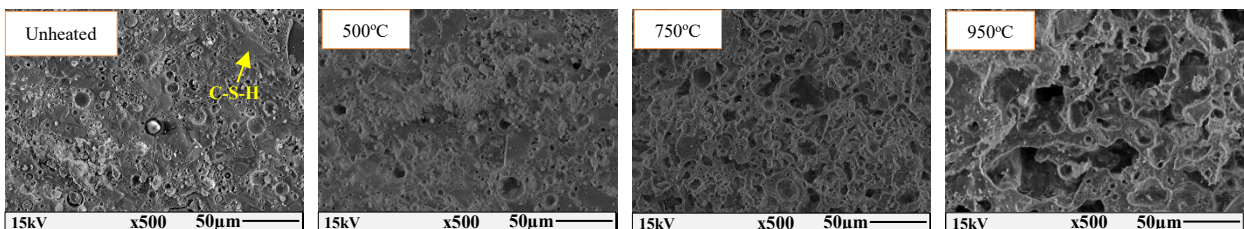
**FAS15**



**FAS30**



**FAS45**



**FAS60**

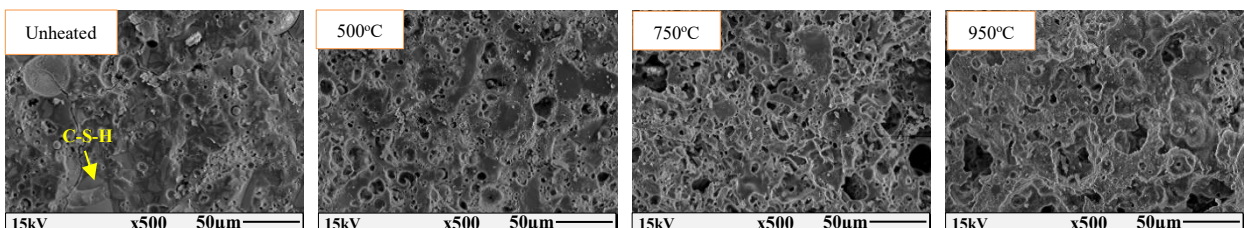


Fig. 1 SEM micrographs of unheated and heated specimens

calcium silicate hydrate gel. As the GGBS dosage in specimens increased, the calcium content resulting from the dissolution of GGBS also increased, and thus increased the formation of C-S-H gel and contributed to the development of denser microstructure.

When exposed at high temperatures, the specimens containing GGBS showed more significant microstructure degradation due to the decomposition of C-S-H gel, when compared to the specimen without GGBS. This is understandable since the C-S-H gel which is found to be present in specimens containing GGBS, is not stable by high temperature, and its decomposition caused the development of highly-porous structures. Since the C-S-H gel plays an important role to the strength development, its decomposition can reduce the strength to some extent. This indicated that the addition of GGBS reduces the high temperature resistance properties of geopolymer paste. However, this is still comparable with the cement paste specimens which

totally lost its strength when heated at temperature up to 800°C [7]. Apart from this, in the specimen containing no GGBS, there was evidence of sintering in the microstructure when heated at 750°C and it becomes more prominent when heated at 950°C. This results in more homogenous and denser microstructure than that before high temperature exposure and leads to crack healing.

### 3.3 XRD analysis

XRD analysis was performed to investigate the phase composition of the reaction products of geopolymers. Fig. 2 shows the XRD patterns of both heated and unheated specimens. The XRD patterns of all unheated specimens showed the broad hump at 15-40° 2-theta which indicates the amorphous characteristic of geopolymers.

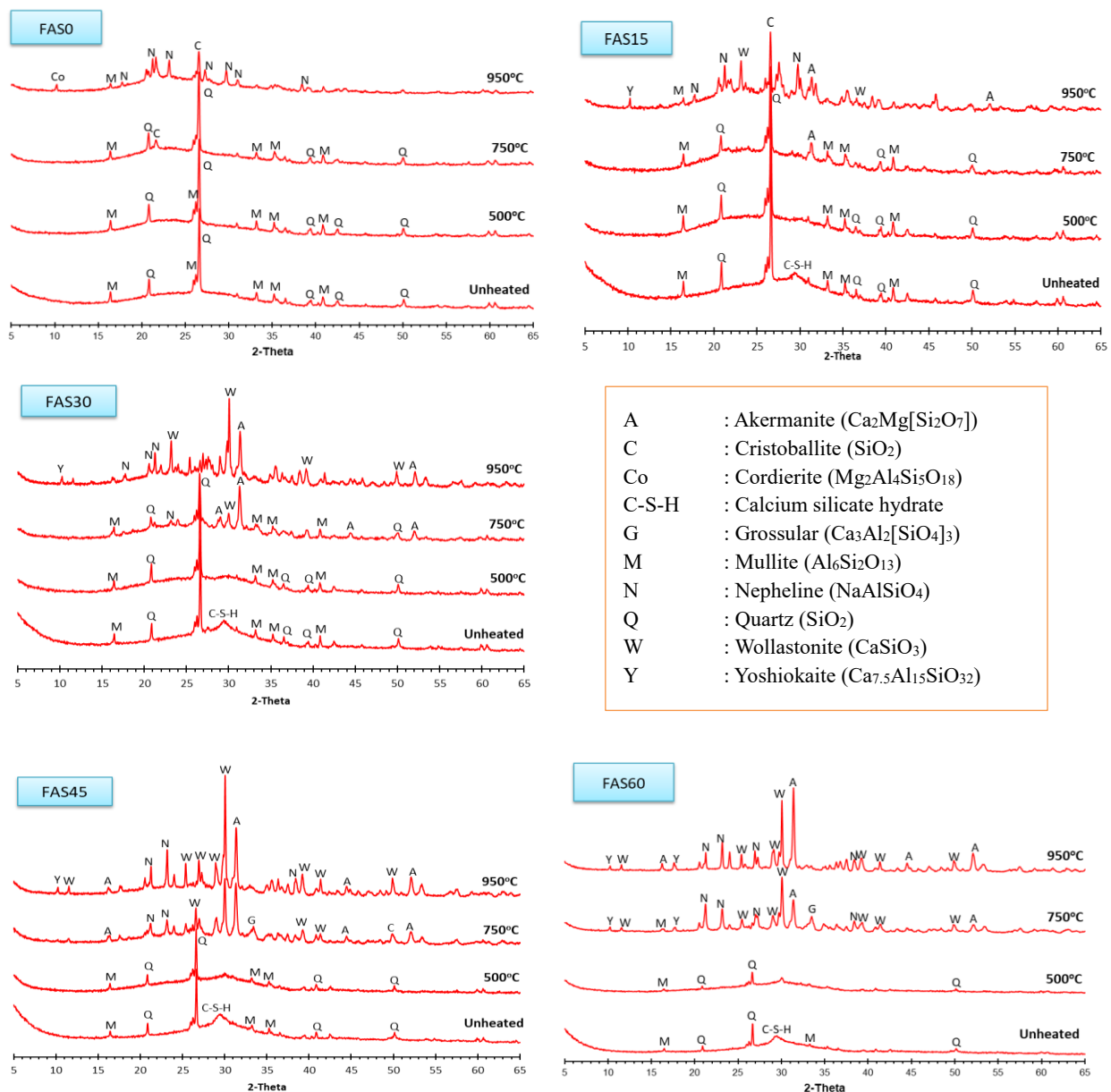


Fig. 2 XRD patterns of geopolymers before and after heating at 500, 750, and 950°C.

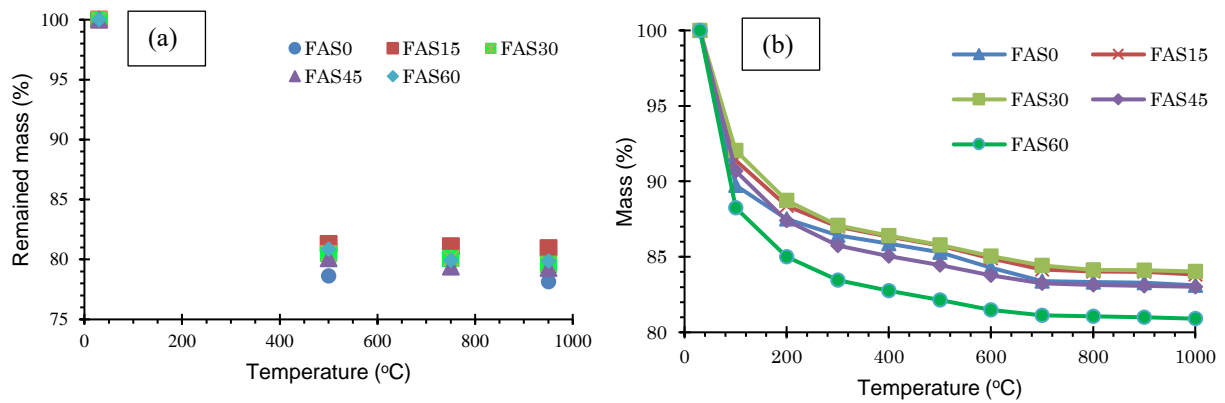


Fig. 3 Thermal stability of geopolymers under different ratio of GGBS: (a) Mass loss measured after heating in furnace, (b) Mass loss by thermogravimetric analysis

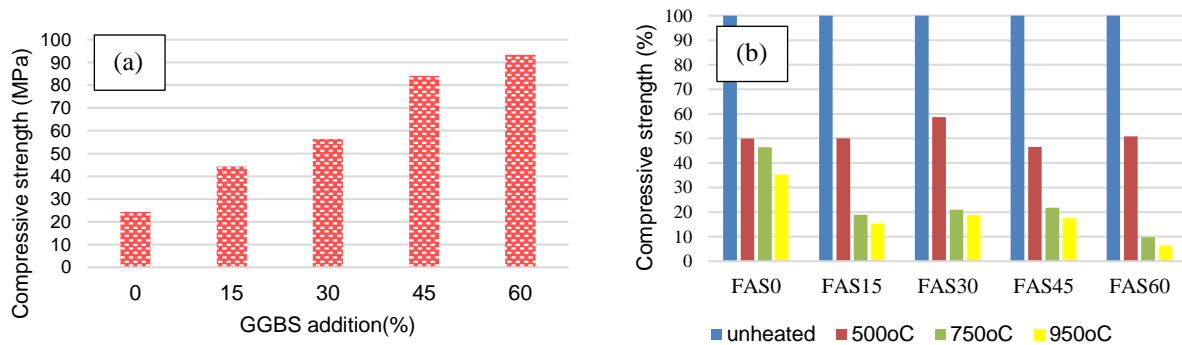


Fig. 4 Compressive strength of specimens: (a) before heating and (b) after heating.

When GGBS was present in the mixes, the new poorly-crystalline diffraction peak was found to be generated around  $30^\circ$  2-theta and it was noticed as the formation of C-S-H gel. When exposed to elevated temperature up to  $500^\circ\text{C}$ , the C-S-H peak in those specimens containing GGBS disappeared, while other peaks still remain and no new peak is generated. The increase in temperature to  $750^\circ\text{C}$  and  $950^\circ\text{C}$  promotes their re-crystallization into secondary mineral phases which are the dominant minerals of the earth's crust, such as akermanite, wollastonite, nepheline, yoshiokaite, and grossular.

In specimens containing 0% and 15% of GGBS, the formation of cristoballite was found after heating up to  $750^\circ\text{C}$  and  $950^\circ\text{C}$ . Other new crystalline peaks such as nepheline and cordierite were generated at  $950^\circ\text{C}$ . Moreover, compared to specimens containing GGBS, it can be seen that specimens without GGBS and with 15% of GGBS did not exhibit significant change in structure due to the high temperature exposure, and still maintained their amorphous structures even after heated up to  $950^\circ\text{C}$ .

The re-crystallization of geopolymer which led to the formation of the analogies to natural minerals after heating at elevated temperatures is in contrast with the phase composition of ordinary Portland cement. The ordinary Portland cement is represented by the compounds not having analogies to natural minerals, thus results in some problems related to the durability of OPC concrete [17]. A well-hydrated OPC paste mainly consists of C-S-H and calcium hydroxide which are

associated with poor durability and poor fire resistivity.

### 3.4 Mass loss

The mass of all specimens was measured before and after heating at high temperatures and the percentage of the mass loss was calculated using the Eq.(i). The results (Fig. 3a) showed that all specimens lost about 20% of their initial mass. This behaviour can be explained by the result of thermogravimetric analysis which is shown in Fig. 3b. A sharp decrease in mass before  $200^\circ\text{C}$  was attributed to the evaporation of free water. From  $200^\circ\text{C}$  to  $950^\circ\text{C}$ , the further increase in mass loss under slow rate was due to the removal of chemically bound water and hydroxyl groups, which can subsequently cause the deterioration of the overall structure of geopolymers. In addition, the surface spalling was found to occur only in FAS60 due to its high density which also contributed to the mass loss measured after heating. The result of thermogravimetric analysis also showed that FAS60 exhibited the lowest thermal stability.

### 3.5 Compressive strength

Fig. 4 shows the compressive strength of geopolymer paste specimens before and after exposure at elevated temperature. It was found that the addition of GGBS to fly ash geopolymers increased the initial compressive strength. The improvement is due to the formation of calcium silicate hydrate gel that produced the denser structure.

When exposed to high temperature up to  $500^\circ\text{C}$ ,

all specimens lost about 50% of their initial strengths. This behavior was attributed to the formation of macrocracks, dehydration and the decomposition of calcium silicate hydrate in the specimens containing GGBS. However, when heated at temperature up to 950°C, the specimen containing no GGBS exhibited better performance, when compared to specimens containing GGBS. The compressive strength of the specimen containing no GGBS is slowly decreased when heated at temperatures above 500°C due to the sintering of unreacted fly ash particles. Fly ash geopolymer specimen has large numbers of interconnected pores which facilitate the escape of moisture when heated, resulting in minimal damage to the matrix.

The significant loss on compressive strength of the specimens after heating up to 750°C and 950°C was observed in the specimens containing GGBS. This was attributed to structural degradation caused by the further decomposition of C-S-H, resulting in development of highly-porous microstructure, as can be observed from the SEM micrographs.

#### 4. CONCLUSIONS

In this study, the effect of GGBS addition on the microstructure and mechanical properties of fly ash-based geopolymer after exposure at 500, 750, and 950°C has been investigated. From the experimental results, the following conclusions can be drawn :

1. The addition of GGBS produced denser structure and significantly increased the initial compressive strength of geopolymer specimens due to the formation of calcium silicate hydrate gel.
2. When exposed to high temperatures, the specimens containing GGBS were not structurally stable and significantly lost their strength when compared to the specimen without GGBS. This behavior was attributed to the decomposition of C-S-H by high temperature, resulting in the development of porous structures.
3. Despite losing strength, high temperature exposure promoted the recrystallization of geopolymers into secondary mineral phases which allowed the specimens to perform residual compressive strength with a slight decrease between 750°C and 950°C. It is considered that 45% is the optimum replacement level of fly ash by GGBS, because over this value, the specimen (with 60% GGBS) possessed very high strength loss and surface spalling.

Geopolymers made from fly ash and GGBS have been proven to provide a potential use as a base material for construction due to their high compressive strength and good fire resistance both in terms of strength loss in elevated temperature and spalling resistance.

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