Effects of Thermal Resistance to Fly Ash-Based Lightweight Geopolymer

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Abstract. Geopolymers are inorganic polymeric materials and cementations materials that replace the Ordinary Portland Cement. This study aimed to determine the effect of thermal resistance of fly ash based lightweight geopolymer and to investigate the physical, mechanical and microstructure properties of lightweight geopolymer at different thermal resistance. Considering the fire endurance assessment of geopolymers, the evolution of geopolymer during thermal exposure is of interest. This paper presents a comparative study of the characteristic of unfoamed (control sample) and lightweight geopolymers after exposure to elevated temperatures which is 200 °C, 400 °C, 600 °C and 800 °C. Lightweight geopolymers were prepared by adding foaming agent which is polyoxyethylene alkyether sulphate with geopolymer paste. Fly ash, alkaline activator and foam were mixed to produce a homogeneous mixture, which was placed into a cube 50 mm x 50 mm x 50 mm mould and cured at 80 °C for 24 hours. The compressive strength, density, chemical composition, microstructure and functional group analyses were studied. Unfoamed geopolymer exhibit higher compressive strength at 47.04 MPa compared to the highest strength of lightweight geopolymer which is 33.26 MPa at 200 ºC. However, the lightweight geopolymer produced low density in range 1200 kg/m³ to 1500 kg/m³ compared to the density of unfoamed is 1813.79 kg/m³.

1. Introduction
Geopolymers are inorganic polymeric materials, firstly developed by Joseph Davidovits in 1970s. Recently discovered geopolymers are the cementations materials to replace cement produced by adding pozzolanic compound or mineral rich alumino silicate (Si-Al) catalysts, including sodium silicate solution (Na2SiO3) and sodium composition hydroxide ceramic materials that are which are transformed into reaction product by polymerisation in a high pH environment. This geopolymerization reaction is exothermic and takes place under atmospheric pressure at relatively low temperatures which is up to 100 °C [1]. The attraction closer to the implementation of latest technology for the manufacture of extremely good prospects lightweight geopolymer based totally products has gradually grown [2]. Low strength of geopolymer are the requirements of manufacturing
from common raw materials and their inflammability at high temperatures, these compounds are attracting increasing interest as ecologically friendly fireproof building materials, sound and warmth insulators and substances for encapsulating dangerous wastes for storage or disposal [3].

Lightweight geopolymers have good mechanical properties like excessive compressive electricity, low permeability, tremendous mechanical houses, consisting of low density and thermal stability [4]. The density of lightweight concrete normally tiers from 300 kg/m$^3$ to 1800 kg/m$^3$ whereas the density of ordinary concrete is about 2400 kg/m$^3$ [5]. Fire endurance of geopolymers will present as the most effective insulating lightweight geopolymer when fly ash are added compared with conventional concrete that have good thermal resistance behaviour and mechanical performance. Based on study from El-Gamal & Hashem [6], the residual compressive strength value for OPC when exposed to elevated temperature is decreases by 98 %, 62 %, 46 % and 12 % after firing at 200 ºC, 400 ºC, 600 ºC and 800 ºC, respectively.

In this study, lightweight geopolymer materials were subjected to thermal resistance which is exposed to elevated temperatures from 200 ºC to 800 ºC. Geopolymer concretes experienced a lesser reduces in weight but greater energy loss with increasing exposing temperatures than geopolymer mortar. On the basis, geopolymers undergo phase changes like mechanical strength when exposed to fires. The responses of geopolymers towards the elevated temperature hereafter lead to microstructural stresses [7]. Previous studies claimed that geopolymers have the better thermal endurance to normal concrete or maybe some excessive overall performance concretes [8]. The concern on the thermal performance and fire resistance of building materials has become one of the research interests because the thermal stability is important to ensure that they are safe for usage at certain temperature range and improved environmental sustainability.

2. Methodology

2.1. Raw Materials
In this study, low calcium Class F [9] was collected from a coal combustion plant in Manjung, Perak, Malaysia. Class F Fly ash was used as the aluminosilicate source as the base material. Class F Fly ash was analysed by X-Ray Fluorescence (XRF).

A mixture of sodium hydroxide (NaOH) solution and liquid sodium silicate (Na$_2$SiO$_3$) was used as the alkaline activator solution to activate the fly ash. The NaOH was in pellet form with 99 % purity and it solution was prepared by dissolving NaOH pellets in distilled water to obtain 12 M of NaOH concentration based on previous study [10]. Sodium silicate solution (Vitrosol D - A53) was used. The chemical composition of sodium silicate solution contains Na$_2$O = 14.7 %, SiO$_2$ = 29.4 %, Water = 55.9 %, Specific gravity of 1.53 g/cm³ and Viscosity at 20 ºC =400 cP.

The foaming agent used in this study is Polyoxy Ethylene Alkyether Sulfate. This type of foaming agent is known as surfactant which are utilized by entraining air during blending while the chemical products was mixed into the geopolymer paste to generate bubbles which produces a lightweight material.

2.2. Mix Design and Mixing Procedure
Lightweight geopolymer bricks were produced by mixing the foaming agent, Fly ash, and alkaline activator solution. The alkaline activator solution was prepared first by mixing a Na$_2$SiO$_3$ solution with NaOH solution and stir for at least 5 minutes. Then, the fly ash was added and continue mixing for 5 minutes until the mixture homogeneous to produce geopolymer paste. The foaming agent was added to the geopolymer paste mixture with ratio of foaming agent/water of 1/10 and foam/geopolymer paste of 1.0, by volume [11]. Afterwards, the pastes were poured into cube moulds (50 x 50 x 50 mm) and cured in the oven for 24 hours at 80ºC. After 24 hours of curing, the samples were left at room temperature for testing at 7 days of ageing. Table 1 shows the mix design for this study.
Table 1. Vickers hardness properties of un-aged and aged Al-Cu with different TiB₂ contents

| Mix Design                                      | Range Value          |
|------------------------------------------------|----------------------|
| Ratio of Na₂SiO₃/NaOH                          | 2.5 (by mass)        |
| Ratio of fly ash/alkaline solution             | 2.0 (by mass)        |
| Ratio of foaming agent/water                   | 1/10 (by volume)     |
| Ratio of foam/geopolymer paste                 | 1/1 (by volume)      |
| Thermal resistance                             | 200, 400, 600, 800°C |

2.3. Thermal Resistance to the Fly Ash Lightweight Geopolymer

For exposure to elevated temperature, the 7 days cured lightweight geopolymers were heated in a furnace at 200 °C, 400 °C, 600 °C, and 800 °C to determine the effect of different thermal resistance of fly ash based lightweight geopolymer with a heating rate of 10 °C/min and soaking time of 2 hours. Then, the specimens were left to cool inside the furnace to room temperature. For comparison, one set of the samples was kept at ambient temperature which is 29 °C. In general, all geopolymers samples exposed to heating retained in cubic shape up to 800 °C without showing any destruction or dimensional change.

3. Results and Discussion

3.1. Chemical Composition Analysis of Fly Ash and Foaming Agent

In this study, the chemical composition of fly ash and foaming agent were analyses using X-Ray Fluorescence (XRF) analysis. Each composition of Class F fly ash and foaming agent used are summarized in Table 2 and Table 3 respectively.

| Compound          | Mass (wt%) |
|-------------------|------------|
| SiO₂              | 55.9       |
| Al₂O₃             | 27.8       |
| Fe₂O₃             | 7.093      |
| TiO₂              | 2.25       |
| CaO               | 3.95       |
| V₂O₅              | 0.096      |
| SO₃               | 0.33       |
| K₂O               | 1.55       |

Table 2 shows that the main constituents of fly ash are SiO₂ and Al₂O₃ which is about 83.7 % of the total composition and this indicated that this fly ash was classified as class F fly ash according to the ASTM C 618 [9] standard specifications. Percentage of Fe₂O₃ also is higher than the other compound for Class F fly ash. Material with high silica and alumina content are good for binding action [10] . The result also shows that these material rich in silica and alumina which could be have a potential to produce geopolymer materials with good mechanical and thermal properties.

| Compound          | Percentage (%) |
|-------------------|----------------|
| SiO₂              | 1.80           |
| SO₃               | 78.60          |
Table 3 shows the major constituents of Polyoxyethylene Alkyether Sulfate are SO$_3$ and PdO with 78.60 % and 11.0 %, respectively. This type of foaming agent are called as synthetic foaming agent which are an amphiprotic substance that are strongly hydrophilic and easily dissolve in water yielding air bubbles [11].

3.2. Effect of ageing

The compressive strengths of geopolymer samples when exposing at different temperatures are summarized in Figure 1. The strength of unfoamed and unexposed fly ash geopolymer is 47.04 MPa. For the lightweight geopolymer specimens that exposed at 200 °C reached the highest compressive strength 33.26 MPa. The results obtained depicted that the compressive strength kept decreased to 27.72 MPa and 19.40 MPa when exposed to 400 °C and 600 °C respectively until it reach the lowest strength at 800 °C which is 18.62 MPa. This result represent the relationship between compressive strength and density of geopolymer. With decreases in density of geopolymer, compressive strength was also decreases. As stated above, the loss of water with increasing temperature led to producing of more pores in structure and consequently reduce the strength. However, in addition of foam, the merging of bubbles is seemed to produce larger voids that result in a wide distribution of void size and also lower the strength [11]. Besides, the microstructure shows in Figure 4 also can relate in decreasing of compressive strength as a more open microstructure like pores and cracks which is consistent with its lower strength [12].

![Figure 1. Compressive strength of the geopolymer when exposed and unexposed to elevated temperature.](image-url)
3.3. Density Analysis

Figure 2 presents the test result on the density of lightweight geopolymer after exposure to the thermal resistance. The density data shown in Figure 2 is average value of three samples and the results reported the density values of the lightweight geopolymer are in the range between 1200 kg/m³ to 1500 kg/m³. As can be seen from Figure 2, the density of the unfoamed and unexposed geopolymer is 1813.79 kg/m³ and the highest from the exposed fly ash lightweight geopolymer is at 200 °C that presented 1493.65 kg/m³ density. The density keep decrease in the exposure to elevated temperatures to 1418.56 kg/m³ at 400 °C and 1314.35 kg/m³ at 600 °C. The lowest which is 1294 kg/m³ density value appeared at the sample with 800 °C. It was clearly shows that an addition of foaming agent and the increasing of the thermal resistance exposure decreased the density of lightweight geopolymer. There was a slight decrease in the density of lightweight geopolymer that affected from the presence of pore and crack to the surface of the sample [13]. In addition, the foaming agent caused the amount of voids inside the material with air contained could be generated, thus resulting in the reduction of density. This is due to the creation of tiny air bubbles in the geopolymer samples, which resulted in higher porosity and also reduced compressive strength of lightweight geopolymer [14].

![Figure 2. The density of lightweight geopolymer exposed and unexposed to elevated temperatures](image)

3.4. Functional Group Analysis

Functional group analysis of high-temperature exposure can be analysed through Fourier transform infrared (FTIR) represented in Figure 3. Shifting of functional groups from fly ash toward fly ash geopolymers were identified using spectrum spectrometer. The specimen was powdered samples scanned from 4000 cm⁻¹ – 600 cm⁻¹ at the resolution of 4 cm⁻¹. Figure 3 shows the FTIR spectra of selected geopolymer samples. At 600 °C, 800 °C and unexposed fly ash geopolymer. The IR spectrum of fly ash geopolymer shows main absorption bands at 689 cm⁻¹, 981 cm⁻¹, 1453 cm⁻¹, 2348 cm⁻¹ and 3350 cm⁻¹. The O-H stretching bands also showed a well-defined trend at ~3300 cm⁻¹ -3610 cm⁻¹ for each of the sample. Deformation vibration of H-O-H for this lightweight geopolymer is at ~2348 cm⁻¹. It is noted also a small peak stretching of the C-O appears at ~1520 cm⁻¹. The bands become sharper and shift towards the lower frequencies ~689 cm⁻¹ which show the symmetric stretching of Al-O in Si-O-Al linkages. The entire sample at elevated temperature including the unexposed showed main broad absorption band at ~980 cm⁻¹ which corresponding to the asymmetrical stretching vibration of Si-O-Si and Si-O-Al. Table 4 shows the assignment of main FTIR bands.

With the concentration of network depolymerisation cations increasing, the vibrations attributed to stretching of Si–O and Al–O systematically shifts towards lower frequencies. The broadened peak
around 3300 cm\(^{-1}\) - 3610 cm\(^{-1}\) is attributed to molecular water absorbed into the surface of the geopolymer [13]. At 2348 cm\(^{-1}\), Ahmad et al., [15] stated deformation vibration of H-O-H groups from the weakly-bound water molecules that were trapped in the large cavities between the rings of the geopolymeric products. However, Zhang et al., [16] also defined 1420 cm\(^{-1}\) - 1660 cm\(^{-1}\) as the vibrational stretching frequency of the O-C-O in the carbonate, and caused by the unreacted alkali cations and the dissolved CO\(_2\). The peak of band around 980 cm\(^{-1}\) exists in all mechanical activated materials prior to their geopolymerisation which formation of a new product called the amorphous aluminosilicate gel phase due to dissolution of fly in alkaline activator. This assigned to the Si (Al)–O–Si asymmetric stretch. This band is typical of the spectra of silicate glasses, and its frequency depends slightly on the state of hydration and Al content [17].

![Figure 3. FTIR spectra of the geopolymer after exposure to elevated temperatures.](image)

Table 4. Shows the assignment of main FTIR bands.

| Bands     | Assignments                      |
|-----------|----------------------------------|
| 3350 cm\(^{-1}\)  | Strong OH stretching vibration    |
| 2348 cm\(^{-1}\)  | Bending vibration of H-O-H groups|
| 1453 cm\(^{-1}\)  | Stretching vibration of the O-C-O |
| 980 cm\(^{-1}\)  | Asymmetrical stretching vibration of Si-O-Si and Si-O-Al |
| 689 cm\(^{-1}\)  | Symmetric stretching of Al-O in Si-O-Al |

3.5. Microstructure Analysis

Microstructure of fly ash based lightweight geopolymer with different exposed thermal resistance were examined by using Scanning Electron Microscope (SEM). For the exposure to elevated temperature of the lightweight geopolymer, it is clearly seen in Figure 4 that the number of pores distributed throughout the matrix increases due to addition of foaming agent. There is fine pores and no crack at exposure to 200 °C and 400 °C. Comparatively, the micrographs of the sample heated at 600 °C and 800 °C shows large cracks and pores. However, micrograph exposure at 800 °C shows the lightweight geopolymer matrix intervened with each other forming continuous matrix and also shows hollow cavities due to spaces left behind by dissolved fly ash particles. The results show that
the increases of exposure to thermal resistance, the average pores size and cracks presence also increases. This change has occurred in the microstructure because of sintering and further geopolymerization with the increase in temperature [18]. Porosity is caused by different developments of microstructure skeletons in the porous geopolymer. The foam to geopolymer paste give large affects to the volume of voids and porosity in the lightweight geopolymer which directly influences the strength of geopolymer [19].

![Figure 4. Micrographs of exposed to thermal resistance (a) 200 ºC, (b) 400 ºC, (c) 600 ºC and (d) 800 ºC](image)

4. Conclusions
In this research presented the effect of fly ash unfoamed and lightweight geopolymer exposed to elevated temperatures. No disintegration and spalling of geopolymer samples occurred when subjected to high temperature. Unexposed unfoamed geopolymer exhibited excellent compressive strength which is 47.04 MPa with very high density 1813.79 kg/m³. With the addition of Polyoxyethylene Alkyether Sulphate as foaming agent, lightweight geopolymer was obtained. However, the strength was reduced from that of unfoamed geopolymer in range (18 MPa – 33 MPa) with lower density (1290 kg/m³-1500 kg/m³). When the geopolymers were heated at elevated temperature, the density and compressive strength decreased. It was deemed that the fast evaporation of water from the geopolymer structure induces internal damage to the structure within resulting in high water absorption. Foaming of geopolymers helped to minimize the disruption effect caused by thermal treatment as the pores provides room to counteract the damage by heat. It can be concluded that thermal resistance 400 ºC to the fly ash lightweight geopolymer gives better properties in terms of density, compressive strength and water absorption compared to the others thermal resistance. However, it can be simplified that lightweight geopolymer have very excellent properties at exposing to the thermal resistance compared to the conventional concrete.
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