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Investigation of Heat Released during Geopolymerization with Fly Ash based Geopolymer

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Abstract. Geopolymerization consists of several chemical reactions that has been reported widely as an exothermic reaction. Previous studies on heat released during geopolymerization used metakaolin and fly ash of F class as a precursor for geopolymer. Meanwhile, in this study, fly ash of C class is used and a preliminary study has been conducted on determining the exothermic reaction of the geopolymerization with various ratios of solid-to-liquid ranging from 1.5 to 2.5. The amount of heat released was determined by using Differential Scanning Calorimeter. It was proven that different solid-to-liquid ratio affected the amount of heat released during geopolymerization as the highest amount of the heat released were recorded at the optimum solid-to-liquid ratio of 2.0.

1. Introduction

Production of OPC consumes energy during and emits high amount of carbon dioxide during its production. Alternatives researches have been reported widely on evaluating suitable methods and materials as a future replacement for OPC. Geopolymer was introduced by Davidovits around 1970s to describe the product that formed when any aluminosilicate materials react with alkaline solution. Geopolymer have been studied extensively particularly in terms of mechanical properties, microstructure and thermal properties.

Geopolymer have been accepted widely by researchers as one of alternative for Portland Cement, OPC. Any material with high aluminosilicate content has a great potential to be used as raw materials for geopolymers in which including waste or by-products such as slag, fly ash and rice husk [1]. The variability of chemical composition of fly ash, blast furnace slag or volcanic ash usually leads to geopolymers whose physical and mechanical properties vary from one aluminosilicate raw material to another [2]. Geopolymer has empirical formula of $Mn\{-(SiO^2)_z-AlO^2\}\cdot nH_2O$ where M is a cation (K^+ , Na^+ , or Ca^{2+}), n is a degree of polycondensation, and z is 1, 2, and 3[3].

Geopolymerization is a process in which involves multiple reaction to produce a geopolymer. Generally, geopolymerization involve three steps which are dissolution of Si and Al atoms from materials, transportation or orientation of precursor's ions into monomers and polycondensation of



monomers into polymeric structures. Geopolymerization had been reported widely as an exothermic reaction. Heat is evolved during the reaction and this heat released have been evaluated by previous studies. Zhang et al., reported that metakaolin geopolymerization consists of three exothermic reactions and the amount of heat released was affected by curing temperature [4].

In OPC, too much heat evolved will lead to temperature rise thus causing thermal cracking. As geopolymer have been studied widely as an alternative for OPC, therefore this study will be crucial in determining the amount of heat released during geopolymerization. Besides, the heat release profile during the setting and hardening reaction is also used as a highly sensitive measure of the kinetics of reaction of cement, including the balance between the reaction rates of different components present in the cement in which making it crucial to be evaluated for geopolymers too.

One of common method used for evaluating heat released during geopolymerization is calorimetric study. Isothermal conduction calorimeter (ICC) and Differential Scanning Calorimeter (DSC) are commonly used to monitor the peak formation and enthalpy of geopolymerization process isothermally. This study will focus on using Differential Scanning Calorimeter, DSC to monitor the reaction that occurs in class C fly ash geopolymerization. Various solid-to-liquid ratio will be applied in this study to identify its effect to the amount of heat released during the reaction. Class C fly ash was chosen as precursor since determination of heat released leading to kinetic study of class F fly ash have been reported briefly by [5].

2. Methodology

2.1. Materials

Class C fly ash was used in this study as a raw material for geopolymer and was obtained from Manjung Coal-Fired Power Station, Lumut, Perak Malaysia. The chemical composition of class C fly ash was determined by using X-Ray Fluorescence, XRF and listed in table 1. This fly ash should be achieved the standard specification of American Society for Testing and Materials (ASTM) C 618 in which stated that the sum of silicon dioxide (SiO_2), aluminum oxide (Al_2O_3) and iron oxide (Fe_2O_3) is equal to or greater than 50% by mass in order to be classified as class C fly ash. Morphology of the fly ash was also observed by using Scanning electron microscopy (SEM), SEM JSM-6460 LA Jeol Japan in School of Material Engineering, Universiti Malaysia Perlis (UniMAP) and the result is presented as in figure 1.

Table 1. Chemical Composition of Raw Class C Fly Ash

Chemical Compound	Quantity (%)
Silicon dioxide (SiO_2)	30.8
Calcium oxide (CaO)	22.3
Iron oxide (Fe_2O_3)	22.99
Aluminium oxide (Al_2O_3)	13.1
MgO	4.0
TiO ₂	0.89
SO ₃	2.67

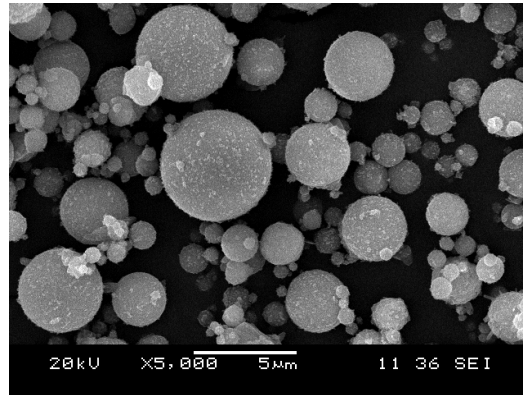


Figure 1. Morphology of Raw Class C Fly Ash

Alkaline activator used in this study was a mixture of sodium hydroxide, NaOH and sodium silicate, Na_2SiO_3 . NaOH was required to be dissolved with distilled water to obtain desired molarity as it is in pellet form with 97% purity and must be prepared at least 24 hours' prior usage. Sodium silicate used was in form of solution with properties of Grade A53 with $\text{SiO}_2 = 29.43\%$, $\text{Na}_2\text{O} = 14.26\%$ and water = 56.31% were used.

2.2. Mix Design And Mixing Procedure

Solid-to-liquid ratio was the main parameter to be varied in this study meanwhile optimum molarity of NaOH and ratio of $\text{Na}_2\text{SiO}_3/\text{NaOH}$ used were followed from previous work by Mustafa et al[6]., 12M and 2.5 respectively. The mix design was listed as in table 2 and was used for heat released testing and setting time.

Table 2. Mixing Design Procedure for Setting Time and Heat Released Testing

Mix Design	Solid-to-liquid ratio, (S/L ratio)	Raw material	Ratio of alkaline activator, $\text{Na}_2\text{SiO}_3 : \text{NaOH}$	Molarity of NaOH, M
1	1.5	Fly Ash	2.5	12M
2	2.0			
3	2.5			

2.3. Testing and Procedure Test

2.3.1. Setting Time Testing

By following the mix design, a freshly prepared geopolymer paste was tested for its setting time using Vicat apparatus as followed from American Society for Testing and Materials (ASTM) C191. This testing was conducted in room temperature to avoid any humidity disturbance to the paste.

2.3.2. Heat Released Testing using Differential Scanning Calorimeter, DSC

Differential scanning calorimeter, DSC was used to determine the amount of heat released during geopolymerization of fly ash based geopolymer. DSC used was Perkin Elmer DSC. Only small amount of geopolymer paste (less than 20 milligram) was required and it was directly inserted into a small aluminium crucible with lid in which also referred as sample pan. The weight of empty sample pan and the weight of sample pan with geopolymer paste was weighed to ensure no excessive weight of geopolymer paste contained in the pan as this will cause destruction to the DSC. The geopolymer paste was kept in DSC for duration of setting time period testing isothermally at 30°C as this study focuses on self-curing condition.

3. Results and Discussion

3.1. Effect of Different Solid-to-Liquid ratio on Setting Time of Geopolymer

Setting time can be defined as the transition of fresh concrete from liquid phase to solid phase[7]. Setting time is also can be indicated as a time required or available for transport, placing and compaction of paste. Class C fly ash based geopolymer has faster setting time compared to class F fly ash based geopolymer due to the calcium content[8]. Setting time also could be affected by different parameters including solid-to-liquid-ratio. As presented in figure 2, higher solid-to-liquid ratio gave faster setting time as increasing the ratio cause faster hardening or also called as gelation process and more rapid bonding to occur. In this study, the highest ratio of solid-to-liquid which is the fastest setting time. However, fast setting time did not always have a good benefit as too fast setting time may result geopolymer to improper geopolymer bonding and the networking is low thus lead to the low compressive strength[9] and also setting time has to be suits with requirement for the application in construction .

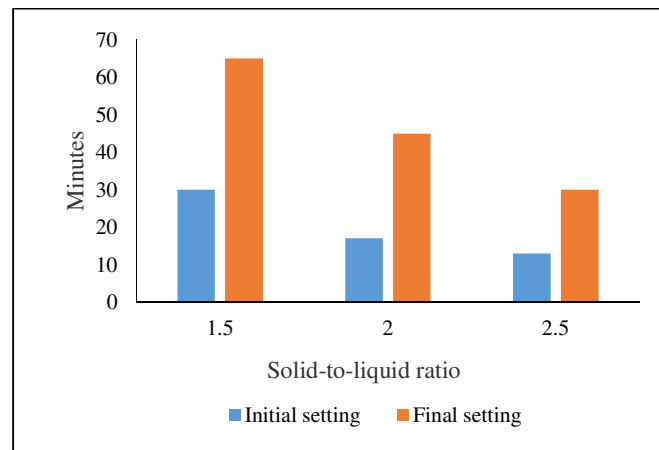


Figure 2. Setting time of Class C Fly Ash based Geopolymer

Table 3. Initial and Final Setting Time of Class C Fly Ash based Geopolymer

Solid-to-liquid ratio	Initial setting, min	Final setting, min
1.5	30	65
2.0	17.07	45
2.5	13.02	30

3.2. Enthalpy of class C Fly Ash based Geopolymer Determined by using Differential Scanning Calorimeter,DSC.

Geopolymerization is a chemical reaction in which heat is dissipated during the reaction. In this study, the heat released during geopolymerization was recorded by using Differential Scanning Calorimeter, DSC. The enthalpy of process that occurred was calculated by using equation (1) and (2).

$$\left(\frac{dQ}{dt}\right)_p = \left(\frac{dH}{dt}\right) \tag{1}$$

$$\Delta H = \int_{t_1}^{t_2} \frac{dH}{dt} dt \quad (2)$$

Where $\frac{dQ}{dt}$ is the amount of heat evolved and $\frac{dH}{dt}$ is the enthalpy change or can be represent as ΔH . t_1 and t_2 represent the time limit between the curve.

As in figure 3, there were two distinctive peaks appeared on the heat flow graph of the DSC in this study. The first narrow and sharp exothermic peak appeared immediately less than five minutes represented a dissolution peak in which is similar to the first peak formed when geopolymerization was investigated using isothermal conduction calorimeter, ICC[5][4][10]. This peak also indicates on the absorption of alkaline activator onto the fly ash particles in which leading to dissolution.

According to Table 4, peak 1 was highly exothermic and this increased as the solid-to-liquid ratio increased. The OH⁻ anions attacks became more rapid as increasing in solid-to-liquid ratio due to the more surface available for it to attacks thus causing rapid gel formation in which leading to faster setting time. However, when the highest solid-to-liquid ratio was applied (2.5), the peak became less narrower and a bit broader in which having lowest enthalpy (-43.5067J/g) of peak 1 compared to solid-to-liquid ratio of 1.5 (-50.0302 J/g) and 2.0 (-52.3927 J/g). Besides, the first noting of the peak was endothermic or also known as an endothermic start-up hook and this was a normal behaviour in heat flow graph of DSC due to the differences in heat capacities of the pans (sample pan and reference pan) was not noted as part of the reaction in geopolymerization. Another endothermic peak formed after the first peak could be an induction period. Induction period is period of inactivity that separates the rapid initial dissolution that occurs when fly ash and alkaline activator first come into contact from the polymerization or gelation that leads to set. This period became narrower and shorter as the solid-to-liquid ratio increased.

Second exothermic peak (Peak 2) was observed and it is broader compared to the first peak (Peak 1). The amount of heat released was also lower compared to the first peak as some of the reaction could be occurred directly after dissolution thus causing the first exothermic peak had higher heat released. This peak represented the polymerization and gelation process that occurred during geopolymerization. Formation of alumina/silica-hydroxyl species and oligomers such as OSi(OH)³⁻, Al(OH)⁴⁻, (OH)³⁻-Si-O-Al-(OH)³ occurred rapidly during this process in which leading to set of the geopolymers[10].

By correlating the setting time and the DSC curve obtained, it could be seen that increased in solid-to-liquid ratio making the setting time became faster but the peak 2 appeared later when using the highest solid-to-liquid ratio (2.5) compared to solid-to-liquid ratio 1,5 and 2.0. Although the second peak was included in setting time of the geopolymer when using solid-to-liquid ratio of 2.5, the late appearance of the peak could be due to the rapid dissolution in which leading to gelation and polymerization occurred faster making it less detectable in the peak 2 of DSC curve.

Other than that, since this study used DSC, the third peak observed in previous studies using isothermal conduction calorimeter could not be determined. This could be due to the low sensitivity of DSC or the peak merged together with the second peak as class C fly ash geopolymer hardened faster comparing to the geopolymer that using other materials as precursor. Therefore, the amount of heat released was assumed by total sum of the two peaks formed in the DSC curve.

In this study, solid-to-liquid ratio had been applied in order to observed the heat released during geopolymerization. Increased in solid-to-liquid ratio thus not only causing faster setting time but also higher in amount of heat released. However, same as mechanical properties researches reported by previous studies, an optimum ratio of solid-to-liquid was selected. This study obtained an optimum ratio of solid-to-liquid ratio at 2.0 since it has the highest amount of heat released. At 2.5, the amount of heat released became decreased. This could be occurred due to the heat released quicker during dissolution comparing to during polymerization. Solid-to-liquid ratio of 2.0 also was proven in this study to have an optimum setting time when comparing to ratio of 1.5 and 2.5.

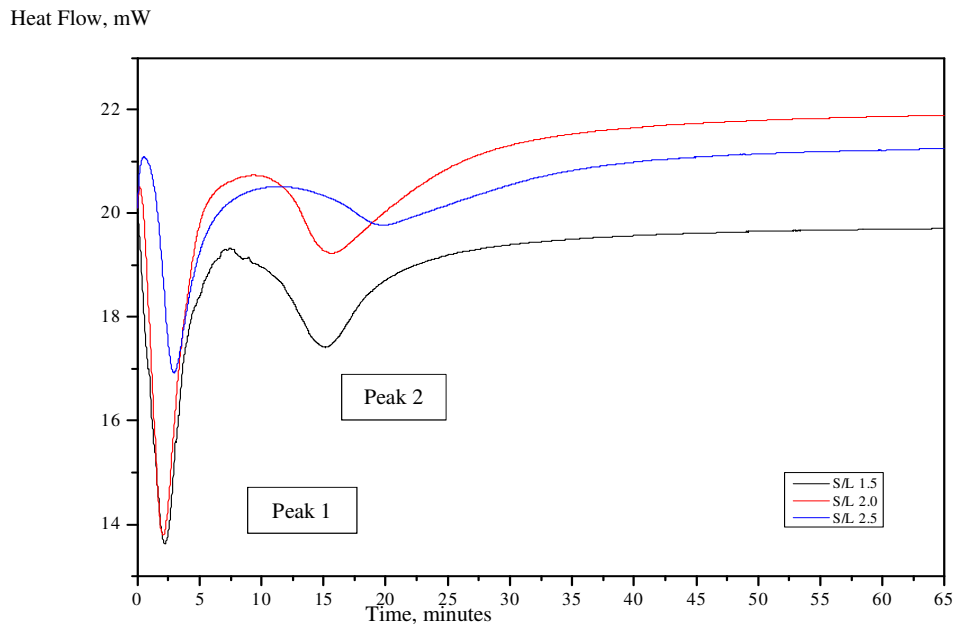


Figure 3. DSC Curve of Class C Fly Ash based Geopolymer with Various Solid-to-Liquid Ratio (S/L ratio)

Table 4. Enthalpy of Fly Ash Geopolymer with Different Solid-to-Liquid ratio

Solid-to-Liquid Ratio	Enthalpy of Peak 1(ΔH),J/g	Enthalpy of Peak 2(ΔH),J/g
1.5	-50.0302	-31.0944
2.0	-52.3927	-43.8944
2.5	-43.5067	-26.5124

4. Conclusions

In this study, class C fly ash was used as a starting materials for geopolymer. The raw fly ash was characterized and the chemical composition determined by XRF is equivalent to the standard specification of ASTM C 618. Sample was prepared with different solid-to-liquid ratio at room temperature as to evaluate the self-curing of the geopolymerization. Based on the setting time and enthalpy of the geopolymerization, it could be concluded that the optimum ratio of solid-to-liquid ratio applied in this study was 2.0 in which has the maximum amount of heat released, -96.2871 J/g. When ratio of 2.5 was applied, the enthalpy became decreased which was 70.0191 J/g. The influence of solid to liquid ratio were also evaluated based on the time taken for the formation of the exothermic peaks observed as well as the setting time of the geopolymerization higher ratio used lead to faster formation of exothermic peaks (exceptional when solid-to-liquid ratio of 2.5 was applied).

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