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# Heat Evolution of Class C Fly Ash Geopolymers with Different Molarity of Sodium Hydroxide: Nucleation Growth and Morphology Properties towards Early Strength Evaluation

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**Abstract.** The heat evolved during setting of class C fly ash geopolymers with different molarity of sodium hydroxide are discussed. The reaction kinetics and microstructure properties of geopolymers are studied towards the early strength development. Differential Scanning Calorimeter was applied to determine the heat evolved and Johnson-Mehl-Avrami-Kolmogorov Model was used to analyse the reaction kinetics during setting of the geopolymers. Morphology and strength development were monitored. The results revealed that the heat evolved increased proportionally with increasing molarity of sodium hydroxide. This indicated rapid reaction of geopolymerization due to the increasing of hydroxide ion content thus mainly affect dissolution process. It was also found that the geopolymerization during setting was governed by one-dimensional growth with instantaneous heterogeneous nucleation and this was supported by the morphology of the geopolymers observed. Among the activator molarities, the molarity of 12 (12M) was observed to be most influential based on its highest compressive strength (up to 46MPa at 7-days) and supported by the morphology properties results.

## 1. Introduction

Production of Ordinary Portland Cement (OPC) has been known as harmful due to emission of high amount of carbon dioxide leading to greenhouse effect. Geopolymers has been introduced as one of future alternative for Ordinary Portland Cement (OPC) due to its better performance of cement-like properties. Geopolymers can easily be produced by reacting raw materials with high aluminosilicate content with an alkali activator (usually sodium hydroxide (NaOH) or combination of sodium hydroxide and sodium silicate) [1,2]. Geopolymers also has been reported as having a ceramic-like that is similar to the zeolite in terms of its chemical structure, however has an amorphous to semi-crystalline structure. Lots of researches have been carried out on exploring the properties of geopolymers including



compressive strength, durability and setting as to make it suitable to be applied in construction field [3-6].

Generally, geopolymers are created by mixing raw materials with high aluminosilicate content with alkali solution. Alkali solution used for synthesis of geopolymerization must be high alkalinity and solution that are commonly used is sodium hydroxide(NaOH) or Potassium Hydroxide (KOH) or can be mixture of NaOH/KOH and sodium silicate( $\text{Na}_2\text{SiO}_3$ ) [7-9]. Geopolymerization process is simply described as consists of dissolution of silica (Si) and Alumina (Al) species from raw materials forming monomers, polymerization of monomers forming bonds of geopolymers and followed by polycondensation of poly(sialate) frame network thus hardened the geopolymers. However, an overall reaction is difficult to analyse since the reactions mostly overlapped within each other. In order to understand the reaction occurred within geopolymerization, many approaches have been introduced to characterize the geopolymerization process including calorimetric technique by monitoring heat evolution [10-14] and in-situ technique by monitoring structural evolution during geopolymerization.

Calorimetric technique has been introduced to monitor the heat of hydration in OPC as excessive amount of heat leads to thermal cracking of the cement. Therefore, calorimetric technique has been applied in geopolymer researches for the same purpose. This technique is considered as reliable technique since it provides real-time information by monitoring the heat evolution during the reaction. The calorimetric data obtained can be further used to analyse the reaction kinetics of the process. However, most of the studies focussed on optimizing the curing temperature of the geopolymerization process and few studies were available on correlating the reaction kinetics to the properties of the geopolymers. In addition, only few studies available on determining the reaction kinetics using Johnson-Mehl-Avrami-Kolmogorov Model (JMAK Model). This model generally can be used for any system which transforms by the process of nucleation and growth therefore make it reliable to be applied in evaluating the growth of geopolymers during setting [15]. The model can be expressed as in equation 1.

$$\ln[-\ln(1 - \alpha)] = n \ln t + \ln k \quad (1)$$

Where  $\alpha$  is the degree of reaction. By plotting the linear graph of  $Y=mX+C$  using equation 1, the value of  $n$  and  $k$  can be obtained and can be used to describe the reaction kinetics of geopolymerization.  $n$  describes the crystallization mechanism of the nucleation meanwhile  $k$  represents the crystallization rate of the growth. According to Siyal et al. [15], the value of  $n$  is usually within 1-4, or fractions ( $n < 1$ ), the latter meaning that the reaction could undergo a second crystallization and nuclei linear growth.

In this study, the heat evolution of class C fly ash geopolymerization was monitored using differential scanning calorimeter with different molarity of Sodium Hydroxide(NaOH) applied. The purpose of varying molarity of NaOH as it is one of parameters that affect the properties of the geopolymers. The calorimetric data obtained was further used to evaluate the reaction kinetics using Johnson-Mehl-Avrami-Kolmogorov Model (JMAK Model). The reaction kinetics was then correlated to the microstructure properties of the geopolymers at early age as well as compressive strength.

## 2. Methodology

### 2.1. Materials

Fly ash was used as precursor of geopolymers in this study. From the chemical composition determined by X-Ray Fluorescence (XRF), the fly ash was classified as class C fly ash based standard specification of American Society for Testing and Materials (ASTM) C618. The chemical composition was determined using X-Ray Fluorescence (XRF) and tabulated as in Table 1.

**Table 1.** Chemical Composition of Raw Class C Fly Ash

Chemical Compound	Quantity (%)
Silicon dioxide (SiO <sub>2</sub> )	30.8
Calcium oxide (CaO)	22.3
Iron oxide (Fe <sub>2</sub> O <sub>3</sub> )	22.99
Aluminium oxide (Al <sub>2</sub> O <sub>3</sub> )	13.1
MgO	4.0
K <sub>2</sub> O	1.6
TiO <sub>2</sub>	0.89
SO <sub>3</sub>	2.67
MnO	0.21

Alkali activator used for geopolymerization is mixture of sodium hydroxide, NaOH and sodium silicate, Na<sub>2</sub>SiO<sub>3</sub>. NaOH was required to be dissolved for required molarity by dissolving the pellets in distilled water and must be prepared at least 24 hours' prior usage. Sodium silicate used was in form of solution with properties of Grade A53 with SiO<sub>2</sub> = 29.43 %, Na<sub>2</sub>O = 14.26 % and water = 56.31 % were used. Combination of both NaOH and Na<sub>2</sub>SiO<sub>3</sub> was fixed in ratio of 2.5 and this is known as alkali activator.

The material used for the epoxidation are fatty acid palm oils as main solvent, acetic acid and hydrogen peroxide (30%) for peracetic formation, sulphuric acid as catalyst, and hydrogen bromide and crystal violet droplet as indicator for titration. For hydrolysis reaction to produce DHPA, distilled water and alumina as catalyst is used.

### 2.2. Mixing design

In this study, solid-liquid ratio of and the alkali activator ratio (NaOH: Na<sub>2</sub>SiO<sub>3</sub>) used were fixed at 2.5:1 following previous work [16-19]. Meanwhile, molarity of sodium hydroxide, NaOH were varied from 6M, 8M, 10M, 12M to 14M. The same mix designs were used to prepare fresh paste (for heat evolution determination) and hardened paste (for compressive strength and morphology determination).

## 3. Testing procedure

### 3.1. Heat evolved testing using differential scanning calorimeter, DSC

Heat evolved during setting of fly ash geopolymerization was determined by using DSC, Perkin Elmer DSC and following standard specification of ASTM D3417. The geopolymer paste required was in small quantity (less than 20 miligram) to be placed in a sample pan of DSC. The weight difference between sample pan and weight of sample pan with geopolymer paste was calculated. The geopolymer paste was kept in isothermal condition at temperature of 30°C (minimum temperature of DSC) in the period of setting (65 minutes) as this study focused on geopolymerization at ambient temperature. The changes of heat flow were considered as heat changes occurred within geopolymerization process.

### 3.2. Degree of Reaction and Reaction Kinetics

The calorimetric data obtained was further used to calculate the degree of reaction,  $\alpha$  which is a requirement in order to evaluate the reaction kinetics of geopolymerization using JMAK Model. The degree of reaction ( $\alpha$ ) can be determined using equation 2 where  $Q(t)$  represents by the heat at a specific time and  $Q_{max}$  represents the total heat of a reaction. By plotting a linear graph of  $y = mX + C$ , where  $y = \ln[\ln(1-\alpha)]$ ,  $x = \ln t$ , the Avrami kinetic parameters were obtained, as both  $n$  and  $k$  represent the slope and  $y$ -intercepts of the graph.

$$\alpha = \frac{Q(t)}{Q_{\max}} \quad (2)$$

### 3.3. Compressive strength testing

Geopolymer pastes with different molarity were casted in a 50mmx50mmx50mm molds and cured in an ambient temperature. Compressive strength of the geopolymer cubes were tested at early age of 1-day, 3-days and 7-days. Compressive strength testing was carried out by following the standard test procedure, ASTM C109 using Universal Testing Machine (UTM), Shimadzu Japan, UH-1000 kNI at the rate of load speed 0.6 N/mm2/s.

### 3.4. Morphology properties

The morphology of geopolymers after setting with different molarity of NaOH was observed using Scanning Electron Microscope (SEM) with magnification of 5000x.

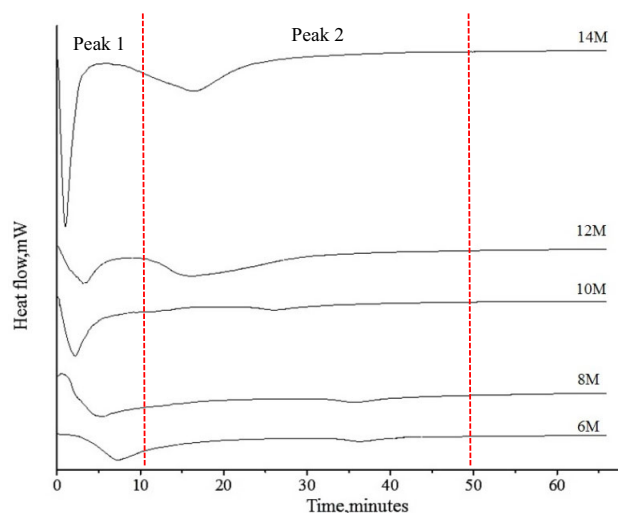
## 4. Results and discussions

### 4.1 Heat evolution of class C fly ash geopolymerization

Figure 1 represents the calorimetric data of DSC of class C fly ash geopolymerization with different molarity of sodium hydroxide, NaOH applied. The amount of heat evolved throughout

geopolymerization was calculated by integration of equation 3 where  $\frac{dH}{dt}$  is the enthalpy change or can be represent as  $\Delta H$ . t1 and t2 represent the time limit between the curve. The calculated result was presented as in table 2.

$$\Delta H = \int_{t_1}^{t_2} \frac{dH}{dt} dt \quad (3)$$



**Figure 1.** Heat flow of class C fly ash geopolymerization with different molarities

From Figure 1, two exothermic peaks were observed and these indicated that the geopolymerization process involved in releasing heat. Peak 1 was directly formed after mixing of fly ash and alkali activator and this is known as dissolution peak. As increasing in molarity of sodium hydroxide, NaOH used, Peak

1 became narrower and appeared much faster (within 10 minutes) in which indicated increment in the amount of heat evolved. This indicated the rapid dissolution occurred due to increasing high amount of OH<sup>-</sup> ions available to attack the surface particles of fly ash forming monomers[16]. As monomers of alumina (AlO<sup>4+</sup>) and silica (SiO<sup>2-</sup>) formed, the monomers directly polymerize forming geopolymers backbone thus leads to hardening of geopolymers and this was depicted by Peak 2. The formation of Peak 2 is dependent on the dissolution process of Peak 1. Increment in reaction rate of Peak 1 leads to faster formation of Peak 2 therefore making it less broad as increasing in molarity of NaOH. The formation of both peaks were in agreement with previous researches [19,21].

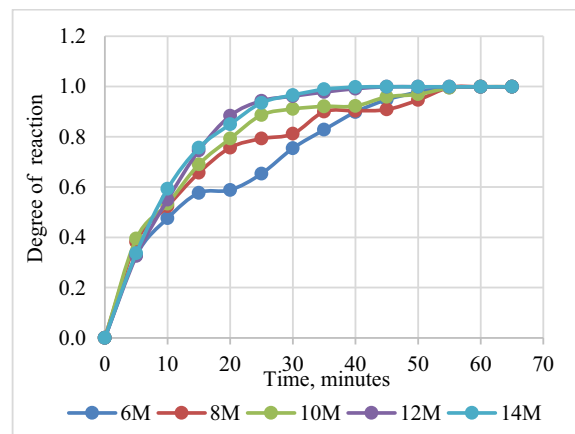
According to Table 2, the amount of heat evolved increased as increased in molarity of NaOH. This shown that most of the heat evolved occurred due to rapid reaction occurred with high content of OH<sup>-</sup> ions. OH<sup>-</sup> ions has a significant role as initiator of the geopolymerization process. Increasing amount of OH<sup>-</sup> ions leads to increasing more breakage of bonds of fly ash particles forming monomers. However, too high amount of heat evolved during reaction is undesirable as it leads to micro cracking and thermal cracking of the geopolymers as this often occurred in hydration of cement[20-22].

**Table 2.** Overall Heat Evolved during geopolymerization of class C fly ash

Molarity	Overall heat evolved
6M	-113.677
8M	-140.310
10M	-201.821
12M	-212.214
14M	-276.097

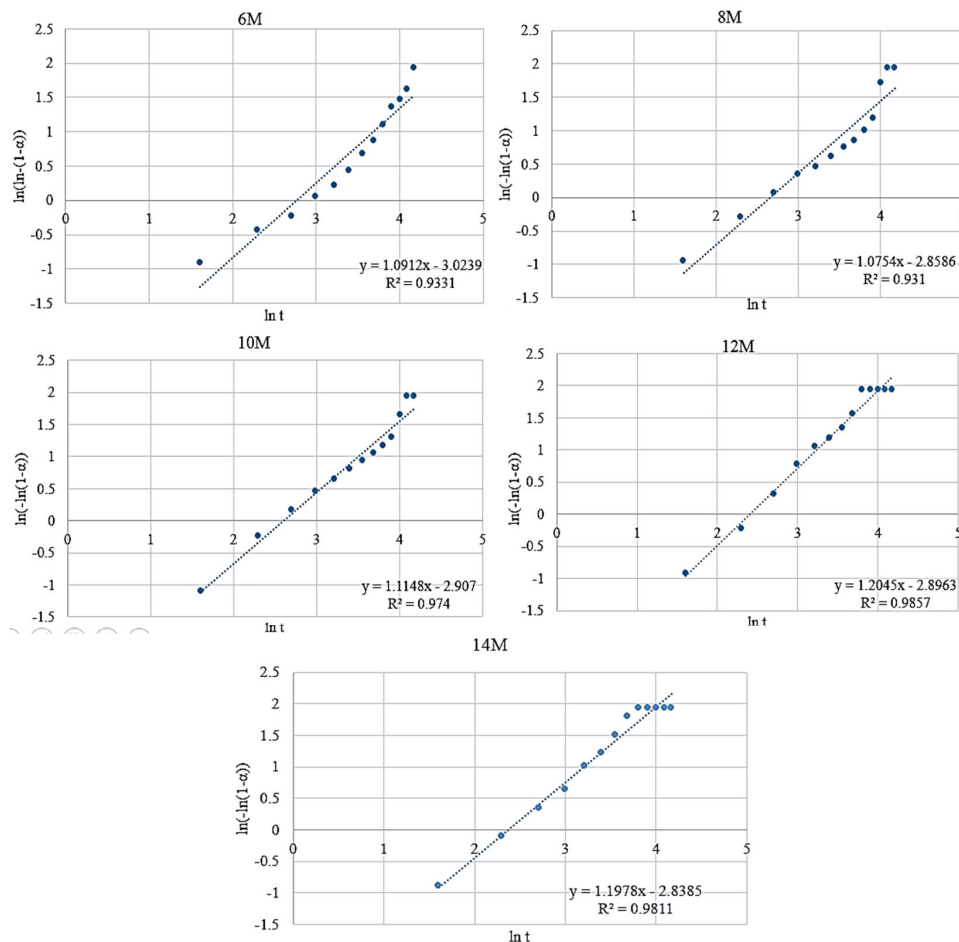
#### 4.2 Degree of reaction and reaction kinetics

For each molarity used, the degree of reaction was calculated using the heat evolution data obtained during setting of the geopolymers. It must be noted that the degree of reaction was calculated up until the geopolymers fully set only. The result was illustrated in Figure 2 by plotting degree of reaction,  $\alpha$  vs time. From 0 to 30 minutes, it can be seen that the degree of reaction increased rapidly due to increasing molarity of sodium hydroxide, NaOH. This has been explained by the presence of more OH<sup>-</sup> ions content leading to rapid dissolution process.



**Figure 2.** Degree of reaction

Johnson-Mehl-Avrami-Kolmogorov Model (JMAK Model) was used to elucidate the reaction kinetics during geopolymerization of class C fly ash geopolymers. By using degree of reaction,  $\alpha$ , a plot of  $\ln[-\ln(1-\alpha)]$  vs  $\ln t$  was illustrated for each molarity and represented as in Figure 3.



**Figure 3.** Avrami's plot of class C fly ash geopolymerization

From Figure 3, values of  $n$  and  $k$  were extracted from the equation of the straight line and the values were tabulated as in Table 3. The value of  $n$  enables us to quantify the crystallization behaviour of the geopolymers during the setting process meanwhile  $k$  values represents the growth rate of crystallization of the geopolymers.

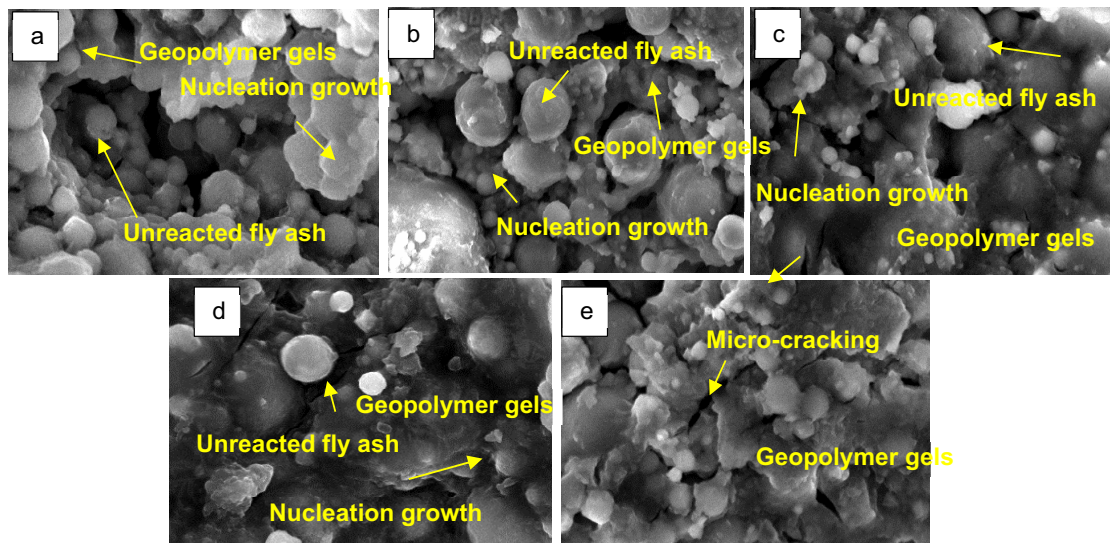
**Table 3.** Avrami's parameter of class C fly ash Geopolymerization

Molarity of Sodium Hydroxide, NaOH	Avrami exponent ( $n$ )	Avrami growth rate ( $k$ )
6M	1.091	0.0486
8M	1.0754	0.0573
10M	1.195	0.0536
12M	1.2045	0.0552
14M	1.1978	0.0585

Generally, increasing in molarity increases the  $n$  values. This could be due to increasing in rate of geopolymerization. From the  $n$  values obtained, it was concluded that the geopolymerization of class C fly ash was having instantaneous one dimensional growth with heterogeneous nuclei formation. Meanwhile, the fluctuation of growth rate ( $k$ ) can be explained by the compactness of the geopolymer system.

#### 4.3 Morphology of class c fly ash geopolymers after setting

The morphology of geopolymers with different molarities applied were observed with magnification of 5000x and were presented as in Figure 4.



**Figure 4.** Morphology of class C fly ash geopolymers after setting; a)6M, b) 8M, c) 10M, d) 12M and e)14M

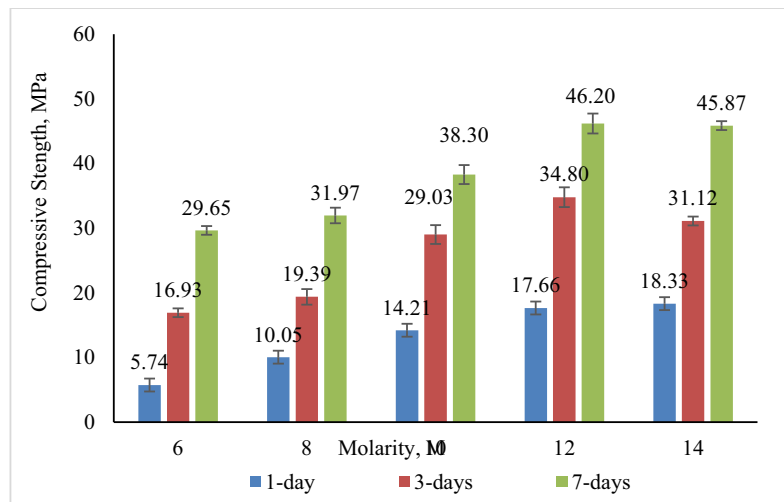
From figure 4, generally it was concluded that geopolymerization was not directly completed at setting as there were still some pores visible for all molarities applied. Increasing molarities decreased the pores visibility as the geopolymer system became compact and filled. However, as been said by previous section, too much heat evolved is undesirable as it leads to micro cracking in which was observed at morphology of 14M. Micro cracks were usually formed by the uneven distribution of internal stresses/shrinkages due to the non-uniform water evaporation during curing and internal heat liberation in which leads to low strength development[22].

#### 4.4 Compressive strength of class c fly ash geopolymers at early ages

The development of compressive strength was observed at early ages of the geopolymers (1, 3 and 7 days) as the development of geopolymers is significant during these ages. The results of compressive strength in this study was presented as in figure 5.

Generally, compressive strength throughout aging days indicates the development of geopolymeric networks occurring after the hardening of the geopolymers [23]. In this study, increasing in molarities of sodium hydroxide (NaOH), generally causing an increment in compressive strength. Throughout the aging days (from 1-day to 7-days), the strength development of the geopolymers keep increasing (> 40 MPa), which could be indicative of the potential of class C fly ash as a geopolymer precursor [24]. In detailed, at 1-day age or also known as after setting, small development of strength was observed and the highest strength achieved was 14M. This was comparable to the compactness observed on the morphology after setting. The strength started to develop as twice of 1-day at 3-days for each molarity. This proved that the geopolymerization process still occurred after setting of the geopolymers. However, the strength of 14M was lower compared to 12M. This could be due to the microcracks occurred when

using 14M. As the same observation observed at 7-days age, 12M was considered as the optimum molarity to achieve the best strength performance compared to other molarities.



**Figure 5.** Compressive Strength of class C fly ash Geopolymers at Early Age

## 5. Conclusions

In conclusion, heat evolution during geopolymerization of class C fly ash geopolymers was significant as one of indicators to elucidate the reaction occurred throughout the process. Increment in heat evolved could be concluded as dependent on OH-ions from sodium hydroxide (NaOH) as OH- ions act as initiator of the geopolymerization process. From analysis of reaction kinetics using Johnson-Mehl-Avrami-Kolmogorov Model (JMAK Model), 12M was considered as optimum molarity due to its highest  $n$  values. 12M was concluded as the best molarity to be used geopolymerization of class C fly ash geopolymers due to its strength performance of early ages and supported by the optimum compactness observed from its morphology.

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