

DOI: <https://doi.org/10.24425/amm.2022.137791>ROSNITA MOHAMED^{1,3}, RAFIZA ABD RAZAK^{1,2*}, MOHD MUSTAFA AL BAKRI ABDULLAH^{1,3}, LIYANA AHMAD SOFRI^{1,2}, IKMAL HAKEMAZIZ¹, NOOR FIFINATASHA SHAHEDAN¹

SETTING TIME AND AFTER SETTING PROPERTIES OF HIGH CALCIUM FLY ASH GEOPOLYMERS WITH DIFFERENT CONCENTRATION OF SODIUM HYDROXIDE

Setting time in geopolymers is known as the time taken for the transition phase of liquid to solid of the geopolymer system in which is represented in the initial setting and final setting. Setting time is significant specifically for application in the construction field. This study intends to determine the setting time of high calcium fly ash geopolymers and the properties of the geopolymers after setting (1-day age). This includes the determination of heat evolved throughout geopolymerization using Differential Scanning Calorimeter. After setting properties determination includes compressive strength and morphology analysis at 1-day age. High calcium fly ash was used as geopolymer precursor. Meanwhile, for mixing design, the alkali activator was a mixture of sodium silicate and sodium hydroxide (concentration varied from 6M-14M) with a ratio of 2.5 and a solid-to-liquid ratio of 2.5. From this study, it was found that high calcium fly ash geopolymer with 12M of NaOH has a reasonable setting time which is suitable for on-site application as well as an optimal heat evolved (-212 J/g) which leads to the highest compressive strength at 1-day age and no formation of microcracks observed on the morphology. Beyond 12M, too much heat evolved in the geopolymer system can cause micro-cracks formation thus lowering the compressive strength at 1-day age.

Keywords: high calcium fly ash geopolymers; setting time; heat evolved; early age properties; concentration of sodium hydroxide

1. Introduction

Inorganic polymeric materials with empirical formula of $Mn\{-(SiO_2)_z-AlO_2\} \cdot wH_2O$ where M is a cation (K^+ , Na^+ , or Ca^{2+}) and n is a degree of polycondensation is introduced as geopolymers by Davidovits in 1970s. Geopolymers have been exposed in construction field as alternatives of Ordinary Portland Cement, OPC due to its excellent properties as reported by previous studies including high compressive strength, good acid resistance and good fire resistance [1-10,12,13]. Geopolymers is also believed to help in reducing the emission of carbon dioxide (CO_2) greenhouse gases. Therefore geopolymers are commonly referred as 'green' material [8]. Geopolymers can be made by mixing any aluminosilicate materials and alkali activator and this process is called geopolymerization process. Aluminosilicate materials that are commonly used as geopolymer precursors include fly ash, kaolin, and slag. Meanwhile, alkali activator usually has high alkalinity and consists of a combination of

sodium hydroxide/potassium hydroxide (NaOH/KOH) with sodium/potassium silicate (Na/KSi_2O_3).

Geopolymerization is commonly described as having three essential steps; 1) dissolution of aluminosilicate precursor into monomers, 2) nucleation growth and polymerization and 3) polycondensation and reorientation of geopolymeric network [9]. To elucidate these reactions, a calorimetric technique has been used by monitoring the heat evolved throughout geopolymerization. This determination of heat evolved is known as a calorimetric method in which has been applied in measuring the heat of hydration in OPC by following ASTM C1702 [1]. Calorimetric method provides real-time information in terms of heat evolved during the process and have been widely reported by previous researchers in monitoring heat evolved [9,13]. Therefore, the overall heat evolved obtained can be correlated to the increment in geopolymerization rate since the heat is monitored throughout the geopolymerization process. Isothermal Conduction Calorimetry and Differential Scanning Calorimeter are commonly used

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to monitor the heat evolution of a reaction in isothermal mode. According to previous studies, this method managed to prove that geopolymerization is an exothermic reaction as well as the formation of peaks of the reactions that occurred including dissolution peaks, gelation peaks, and polycondensation and reorganization peaks of geopolymerization [12]. However, excessive heat released during geopolymerization is harmful to the geopolymers produced as it leads to micro-cracks which occur due to uneven internal stress in the geopolymer system. Therefore, an optimal heat evolved should be determined throughout geopolymerization to ensure the geopolymers produced has excellent properties especially on strength properties.

In this study, high calcium fly ash geopolymers were investigated in the duration of early age (1-day age) to determine the early properties including heat evolved, compressive strength, and morphology. High calcium fly ash geopolymers have been investigated for use as a repair material due to their reasonable setting time and hardening which can be applied in on-site application such as repair materials and coating [13]. Therefore, this study intends to provide further information on high calcium fly ash geopolymers in terms of the setting as well as early age properties (1-day age). In this work, the concentration of sodium hydroxide was chosen as a manipulative variable as it controls the hydroxide ions (OH^-) which is significant specifically during the dissolution of aluminosilicate materials.

2. Methodology

2.1. Materials and mixing design

In this study, fly ash with high calcium content is used as aluminosilicate sources and according to the chemical composition obtained from X-Ray Fluorescence, XRF, the fly ash used met the requirement of class C fly ash based on standard specification of American Society for Testing and Materials (ASTM) C618. The main chemical composition of the fly ash used includes Silicon dioxides (SiO_2) = 30.80%, Aluminium Oxide (Al_2O_3) = 13.10%, Calcium Oxide (CaO) = 22.30% and Iron Oxide (Fe_2O_3) = 22.90%. As fly ash used is a waste product of thermal plant, this fly ash also consisted of other heavy metals including magnesium oxide (MgO) = 4.00%, sulphur trioxide (SO_3) = 2.67%, potassium oxide (K_2O) = 1.60%, titanium dioxide (TiO_2) = 0.89% and manganese oxide (MnO) = 0.21%.

A mixture of sodium hydroxide (NaOH) and sodium silicate (Na_2SiO_3) was used as alkali activator in this study. NaOH was required to be dissolved with distilled water to obtain desired concentration 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 SiO_2 = 29.43%, Na_2O = 14.26% and water = 56.31%. Sodium hydroxide, NaOH and sodium silicate, Na_2SiO_3 were used as alkali activator in this study. Combination of both NaOH and Na_2SiO_3 was fixed in ratio of 2.5 and this is known as alkali activator ratio

or also called as ratio of NaOH to Na_2SiO_3 . The mix design used in this study was listed as in Table 1. The same mix design was applied throughout the experiment.

TABLE 1

Mixing Design for setting time and heat evolved testing

Molarity of Sodium Hydroxide, NaOH (M)	Solid-to-liquid ratios (S/L ratio)	Alkali activator ratio
6	2.5	2.5
8	2.5	2.5
10	2.5	2.5
12	2.5	2.5
14	2.5	2.5

3. Testing procedure

3.1. Setting time and heat evolved testing using Differential Scanning Calorimeter, DSC

A fresh high calcium fly ash geopolymers paste was prepared with different concentration of sodium hydroxide (NaOH) for setting time testing using Vicat apparatus as followed from American Society for Testing and Materials (ASTM) C191. The same paste with minimal amount (less than 20 miligram in order to avoid excessive weight of geopolymer paste which will cause destruction to the DSC if sample is heavier than the specified weight) also being determined for its heat evolved throughout setting of the geopolymers using Differential Scanning Calorimeter (DSC) at isothermal mode (30°C). The amount of heat evolved throughout geopolymerization was calculated using Eq. (1) where dH/dt is the enthalpy change, or ΔH . t_1 and t_2 are the time limits between the curve.

$$\Delta H = \int_{t_1}^{t_2} \frac{dH}{dt} dt \quad (1)$$

3.2. After setting properties determination : density and compressive strength

Geopolymer paste with respective mix design as in Table 1 were moulded in a 50 mm×50 mm×50 mm molds and cured at an ambient temperature. Density of 1-day age of the geopolymers were measured using calculation of Eq. (2). Compressive strength testing was carried out at 1-day age 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. Surface morphology of the hardened geopolymer pastes at lowest, optimum and highest concentration of NaOH were observed using Scanning Electron Microscope (SEM) with magnification of 5000×.

$$\text{Density, } \rho = \frac{m}{v} \quad (2)$$

Where m is mass of the 50 mm cubic mass of the geopolymers (in gram) and v is volume of the 50 mm cubic geopolymers at 1-day age.

4. Results and discussions

4.1. Setting time of high calcium fly ash geopolymers

The setting time was recorded in term of its initial and final setting. The initial and final setting time of the geopolymers paste was recorded and presented as in Figure 1.

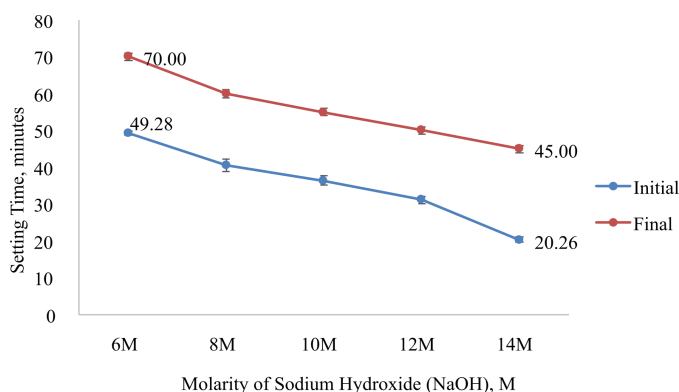


Fig. 1. Setting time of high calcium fly ash geopolymers

According to Figure 1, the setting time of geopolymer paste generally decreased with the increasing concentration of sodium hydroxide (NaOH) used. The initial setting of class C fly ash geopolymers decreased from 6M (49.28 minutes) to 14M (20.26 minutes) which is associated with the contribution of hydroxide ions (OH^-). OH^- ions act as an initiator for geopolymerization as the OH^- ions attack on the surface of fly ash particles with high alumina (Al) and silica (Si) species thus leads to the formation of monomers. It is believed that increment in degree of dissolution leads to more monomers formed thus reducing the time taken for polymerization to occur [14]. A similar observation was found with the final setting time of the geopolymers. Final setting time of the geopolymers shown that class C fly ash geopolymers required less than an hour to harden (except for 6M). 6M took the longest setting time (70 minutes) for geopolymerization as fewer OH^- ions available for polymerization. Meanwhile, rapid hardening was observed at 14M (final setting: 45 minutes) due to the high content of OH^- ions available for polymerization. This fast setting of the geopolymers is advantageous for certain applications such as coatings application and this was supported by the previous finding of Cornelis et al. [15].

4.2. Heat evolved during setting of high calcium fly ash geopolymers

The heat evolved during the geopolymerization process of high calcium fly ash geopolymers was monitored throughout the

setting and the enthalpy of heat obtained was calculated from the DSC curve obtained using Eq. (1). Increasing in molarities of NaOH generally increases the amount of heat evolved from 6M (-113.677 J/g), 8M (-140.310 J/g), 10M (-201.821 J/g), 12M (-212.214 J/g) to 14M (-256.097 J/g). The lowest heat evolved was found at a concentration of 6M (-113.677 J/g) in which can be explained due to its insufficient hydroxide ions (OH^- ions) for dissolution process in which was proven from its delayed setting time compared to other molarities [16]. Increasing in OH^- ions increases the breakage of bonds for monomer formation therefore more heat was released as by-products of dissolution. This occurrence was confirmed by the highest heat evolved during geopolymerization at 14M (-256 J/g). Excess heat was also produced from the nucleation and polymerization of the monomers produced. The heat also can be contributed by calcium (Ca) content in the geopolymer precursor. Hydration of Ca might occur thus contributing to the heat evolution. During dissolution, along with the heat, water is released as a by-product as the hydrogen reacts with the oxygen from the alkali activator. It is believed that the water formed directly reacts with the excessive calcium content (CaO) in the geopolymer system, thus causing a certain amount of heat released [13]. In this study, heat evolution was found to be completed as beyond the setting of the geopolymers, no more observable heat was found as the DSC curve became stagnant. The heat evolved determination is believed to be beneficial specifically in determining the reaction kinetics of the geopolymerization process.

4.3. Density of high calcium fly ash geopolymers

The density of high calcium fly ash with different concentration of NaOH applied was presented as in Figure 2. The densities were in the range of 2.00-2.241 g/cm^3 . The density of Class C fly ash geopolymers was generally increased with increasing molarities of sodium hydroxide (NaOH) used. The highest density of geopolymers was observed when using 12M (2.241 g/cm^3) meanwhile the lowest density was found at 6M (2.044 g/cm^3). Increasing concentration causing rapid dissolution thus led to an increase in geopolymers networks. This has caused an increase in compactness of the geopolymer system thus filling the voids in the geopolymer system. However, the density was slightly dropped at a concentration of 14M (2.224 g/cm^3). It is believed that the geopolymerization occurred improperly. This can be inferred with the presence of its OH^- ions contents. It is believed that too high OH^- ions on the geopolymer system can cause a distraction to the geopolymeric network formation by hindering the polymerization process.

The decrement in density at 14M also can be explained due to the microcracks observed from morphology analysis which can be inferred based on the high heat evolved obtained. High heat evolved indicates the rapid reaction of the geopolymerization process. However, excessive heat liberation can cause uneven internal stress of the geopolymer system thus leading to micro cracks. Microcracks are usually formed by the uneven

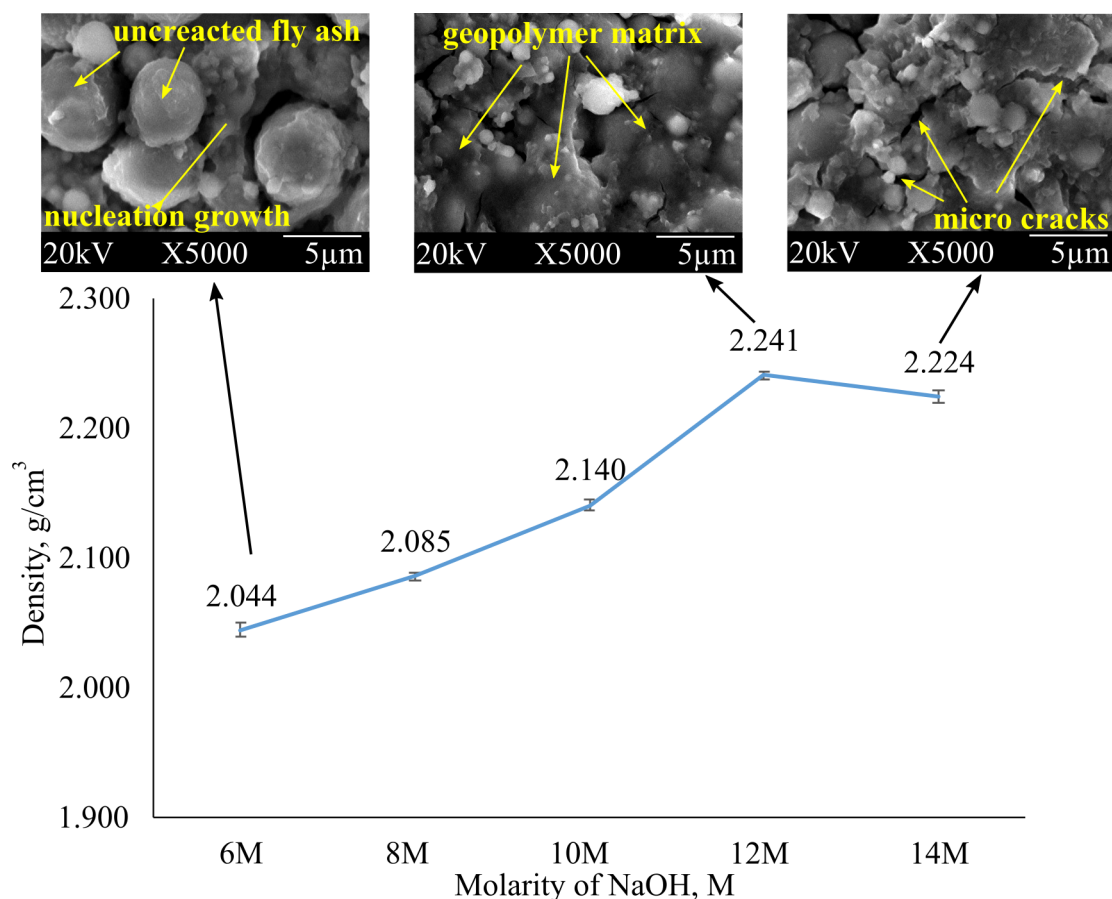


Fig. 2. Density of high calcium fly ash geopolymers

distribution of internal stresses/shrinkages due to internal heat liberation, resulting in low strength achieved. Meanwhile, unreacted fly ash particles were observed at the lowest concentration (6M) which can be inferred due to low OH^- ions for the dissolution process to form monomers of geopolymers. The observation from morphology obtained explained the lowest density achieved by this concentration. In addition, the highest density at 12M found was in parallel with the compactness of the geopolymer matrix observed from the morphology. There were no observable microcracks found at concentration 12M, therefore, suggesting the high density obtained than the 14M.

4.4. Compressive strength of early age of high calcium fly ash geopolymers

Generally, the compressive strength throughout the aging days indicates the development of geopolymeric networks occurring after the hardening of the geopolymers. The compressive strength of high calcium fly ash geopolymers was presented as in Figure 3. From the figure, it can be seen that increasing the concentration of the NaOH generally increases the strength of the geopolymers due to the increment in the geopolymerization rate. Compressive strength of 1-day age of high calcium fly ash geopolymers represented the initial strength of the geopolymers after setting as well as after heat evolution was completed. At this

age, a small increment was observed from 6M to 12M as increasing in molarities increased the geopolymerization rate, which was further confirmed by the heat evolved. The highest compressive strength obtained at this age was at 12M (17.66 MPa). It is believed that the compactness of the geopolymer system leads to the high compressive strength of the geopolymers [17-19]. However, a notable decrement (1.24 MPa) was observed at the compressive strength of high calcium fly ash geopolymers between 12M and 14M. It is believed that the geopolymers system at 14M started to compact with too much OH^- ions thus hindering the nucleation growth to occur with a minimal amount of fly ash articles available leading to a reduction in the compressive strength of

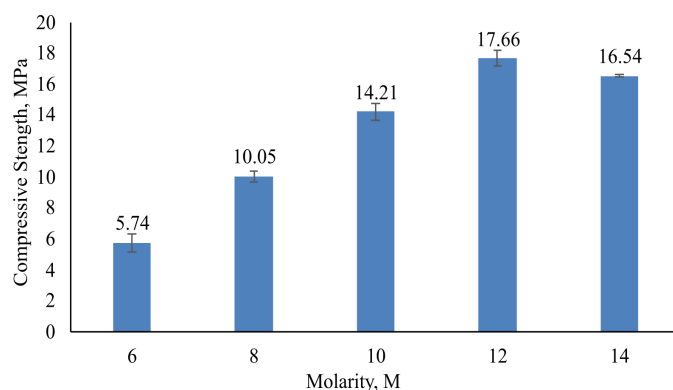


Fig. 3. Compressive strength at 1-day age

the geopolymers at early ages. This was supported by Azzahran et al. [20] suggesting that too high OH^- ions on a geopolymer system can increase the geopolymerization growth rate but also can hinder the polymerization process.

5. Conclusions

As a conclusion, the concentration of sodium hydroxide at 12M was concluded as optimum concentration obtained in this study due to its reasonable setting time (initial setting: 31.12 minutes, final setting: 50 minutes) which is suitable to be applied as repair materials application as well as for the on-site application. The heat evolved obtained (-212 J/g) was considered as optimal heat evolved produced due to the production of the geopolymers with the highest compressive strength (17.66 MPa) and highest density observed (2.241 g/cm^3) with no micro cracks observed in morphology analysis. In addition, since the heat evolved during setting is noted as by-product of geopolymerization process, therefore the heat evolved obtained can be directly correlated to the properties of the geopolymers after setting.

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