

DOI: <https://doi.org/10.24425/amm.2022.137775>OOI WAN-EN^{1,2}, LIEW YUN-MING^{1,2*}, HEAH CHENG YONG^{2,3}, HO LI-NGEE^{2,4},
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EFFECT OF SODIUM ALUMINATE ON THE FRESH AND HARDENED PROPERTIES OF FLY ASH-BASED ONE-PART GEOPOLYMER

The one-part geopolymer binder was synthesis from the mixing of aluminosilicate material with solid alkali activators. The properties of one-part geopolymers vary according to the type and amount of solid alkali activators used. This paper presents the effect of various sodium metasilicate-to-sodium aluminate ($\text{NaAlO}_2/\text{Na}_2\text{SiO}_3$) ratios on fly ash-based one-part geopolymer. The $\text{NaAlO}_2/\text{Na}_2\text{SiO}_3$ ratios were set at 1.0 to 3.0. Setting time of fresh one-part geopolymer was examined through Vicat needle apparatus. Mechanical and microstructural properties of developed specimens were analysed after 28 days of curing in ambient condition. The study concluded that an increase in NaAlO_2 content delayed the setting time of one-part geopolymer paste. The highest compressive strength was achieved at the $\text{NaAlO}_2/\text{Na}_2\text{SiO}_3$ ratio of 2.5, which was 33.65 MPa. The microstructural analysis revealed a homogeneous structure at the optimum ratio. While the sodium aluminium silicate hydrate (N-A-S-H) and anorthite phases were detected from the XRD analysis.

Keywords: Geopolymer; One-part geopolymer; Fly ash; Sodium Aluminate; Sodium Metasilicate

1. Introduction

Geopolymer is an inorganic polymer that can be synthesized from aluminosilicate precursor in a highly alkalisied condition [1,2]. The resulting product is an amorphous to semi-crystalline cementitious material [3]. Geopolymer possesses comparable properties than Ordinary Portland Cement (OPC) [4-6]. Geopolymer is also an environmentally friendly product, as the source materials can be extracted from industrial waste, such as fly ash, blast furnace slag and rice husk ash. The carbon dioxide equivalent emission ($\text{CO}_2\text{-e}$) footprint generated from the production of geopolymer concrete is 9% lower than concrete produced from OPC [7]. Therefore, geopolymer technology gains popularity and has been developing rapidly since the 1970s with the aim to substitute OPC in construction applications.

One-part geopolymer synthesis is in accordance with the production method of OPC. Solid alkali metals are mix with aluminosilicate materials first, followed by the addition of water into the dry binder to initiate the geopolymerization reaction. The one-part geopolymer production method eliminates the

storage and transport of corrosive alkaline solutions that are required for the synthesis of traditional geopolymer. Despite the processing differences, the geopolymerization reaction and resulting properties are similar. Although the workability of one-part geopolymer paste was lower in comparison to the traditional geopolymer [8], their mechanical properties are comparable. The resulting properties of the one-part geopolymer can be altered through different types and amounts of activators applied. Hence it is important to understand the influence of the alkali activators on the characteristics of products.

Anhydrous sodium metasilicate (Na_2SiO_3) has been a commonly used solid activator for slag and/or fly ash-based one-part geopolymer. Meanwhile, solid sodium aluminate (NaAlO_2) has usually been applied for silicate-rich starting materials such as rice husk ash [9,10], geothermal silica [11] and micro-silica [12,13]. In this study, NaAlO_2 was used as one of the activators to develop a fly ash-based one-part geopolymer. The objective of this study was to examine the effects of partial replacement of Na_2SiO_3 by NaAlO_2 solid activator on the fly ash-based one-part geopolymer. The research was conducted through the

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manipulation of the $\text{NaAlO}_2/\text{Na}_2\text{SiO}_3$ ratio. Developed paste and hardened specimens were tested for the fresh and hardened properties. Laboratory tests such as Vicat setting time, mechanical test, microstructural analysis and phase identification were conducted to evaluate the effects of the $\text{NaAlO}_2/\text{Na}_2\text{SiO}_3$ ratio on the one-part geopolymer.

2. Experimental method

2.1. Materials

The materials used in this research were fly ash, anhydrous Na_2SiO_3 and NaAlO_2 . Class C fly ash in accordance with the American Society for Testing Materials (ASTM C618-19) was employed as the aluminosilicate precursor. The material was obtained from Manjung Coal-fired power plant based in Perak, Malaysia. The chemical compositions of fly ash were determined through X-ray fluorescence (XRF) spectrometer and are presented in TABLE 1. The solid Na_2SiO_3 and NaAlO_2 were used as an activator for the fly ash. Anhydrous Na_2SiO_3 of brand Alfa Aesar was supplied by Fisher Scientific (M) Sdn. Bhd. Lastly, anhydrous NaAlO_2 of brand Sigma-Aldrich was supplied by Merck Sdn. Bhd.

TABLE 1

Chemical composition of fly ash

Chemical oxides	Wt.%
SiO_2	36.7
CaO	19.1
Al_2O_3	18.7
Fe_2O_3	17.2
SO_3	3.04
K_2O	1.78
TiO_2	1.68
Others	1.85

2.2. Sample preparation

The mix proportions of five fly ash-based one-part geopolymers activated from anhydrous Na_2SiO_3 and NaAlO_2 are illustrated in TABLE 2. Mixes A1 to A5 were formulated with the alkali activator-to-fly ash (AA/FA) ratio of 0.20, water-to-binder (W/B) ratio of 0.40. The variable in this research was the NaAlO_2 -to- Na_2SiO_3 ratio which ranged from 1.0 to 3.0. Fly ash was dry-mixed with NaAlO_2 and Na_2SiO_3 until homogeneous. Subsequently, water was added into the dry binder and mixed for three minutes. A viscous slurry was obtained. The fresh one-part geopolymer paste was poured into 50 mm × 50 mm × 50 mm plastic moulds. The slurry was compacted in accordance with ASTM C109. The moulded samples were wrapped in cling wrap to prevent water evaporation. Specimens were demoulded after 1 day and cured in ambient condition (30°C) for 28 days.

TABLE 2

Mix proportion of samples

Sample name	$\text{NaAlO}_2/\text{Na}_2\text{SiO}_3$ ratio	Binder proportion (wt%)		
		Fly ash	Na_2SiO_3	NaAlO_2
A1	1.0	80	10.0	10.0
A2	1.5	80	8.0	12.0
A3	2.0	80	6.7	13.3
A4	2.5	80	5.7	14.3
A5	3.0	80	5.0	15.0

2.3. Testing and analysis

Setting time analysis was conducted to investigate the hardening behavior of one-part geopolymer paste. Vicat setting time apparatus was used in accordance with ASTM C191. The first drop of the Vicat needle was dropped from the top of the specimen after 30 minutes of mixing. The penetration depth of the needle was recorded and the procedure was repeated at a 15-minutes interval. The initial setting time was determined as the duration for which the specimen marked less than 25 mm depth of the Vicat needle penetration. While final setting time was recorded when the Vicat final setting needle does not leave an obvious circular impression on the surface of the specimen.

The 28-days compressive strength of specimens was determined in accordance with ASTM C109. A universal testing machine (UTM) modeled Shimadzu UH-1000 kN was employed for this test. Samples were tested with loading placement at 5 mm/min constant rate. Three specimens from each mix proportion were tested. The average test results were then calculated and reported.

The microstructural analysis of specimens was observed through Scanning Electron Microscope (SEM). The microscope of the model JEOL JSM-6460LA was employed with 15 kV accelerating voltage. The test was conducted on two chosen specimens after 28 days of ageing.

The phases present in the fly ash and the one-part geopolymer were analysed through the Shimadzu X-ray Diffractometer (XRD) of model XRD-6000. The analysis was conducted with the scan rate of 2° per minute and scan degree ranged from 10° to 50°. The diffractograms obtained were analysed with the HighScore Plus software.

3. Result and discussion

3.1. Setting time

Fig. 1 illustrates the initial and final setting time of one-part geopolymer paste with an increasing $\text{NaAlO}_2/\text{Na}_2\text{SiO}_3$ ratio from 1.0 to 3.0. The variances of initial setting time among the mixes were not significant. The initial setting time of fresh one-part geopolymers ranged from 20 to 30 minutes. The final setting time increased gradually from 330 to 690 minutes as $\text{NaAlO}_2/\text{Na}_2\text{SiO}_3$ ratio changed from 1.0 to 3.0. The initial setting times

were considerably fast as the system was high in aluminate content, promoted Al-rich gel formation at the early stage of geopolymerization. Geopolymerization reaction initiated with the dissolution of aluminate and silicate species from the fly ash. As the concentration of Al in the system was high, the driving force for Al removal from fly ash was reduced, thereafter inhibited the dissolution of silicate [11]. The overall rate of dissolution of fly ash became low, which prolonged the geopolymerization reaction. Therefore, the increasing $\text{NaAlO}_2/\text{Na}_2\text{SiO}_3$ ratio did not result in a significant difference in initial setting time but driven a longer final setting time.

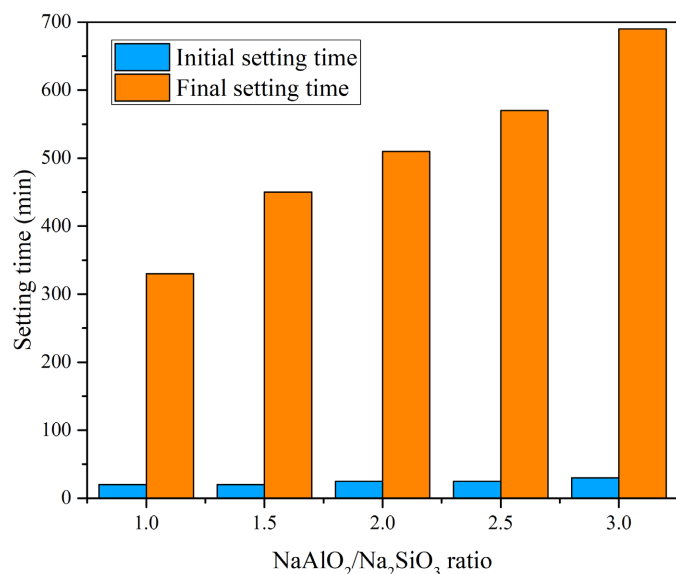


Fig. 1. Initial and final setting time of one-part geopolymer paste

3.2. Mechanical property

Fig. 2 displays the compressive strength of fly ash-based one-part geopolymer activated by NaAlO_2 and Na_2SiO_3 . The 28-day compressive strength of specimens was raised when $\text{NaAlO}_2/\text{Na}_2\text{SiO}_3$ ratio increased from 1.0 to 2.5, followed by a marginal drop when the ratio extended to 3.0. The strength increased

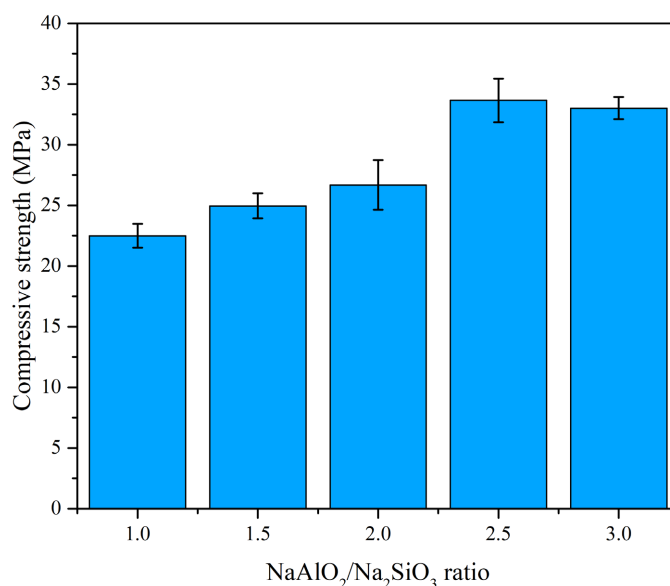


Fig. 2. Compressive strength of fly ash-based one-part geopolymer varying $\text{NaAlO}_2/\text{Na}_2\text{SiO}_3$ ratio

from 22.49 MPa to 33.65 MPa, then drop to 33.01 MPa. The result corresponded to the fresh property discussed previously. When $\text{NaAlO}_2/\text{Na}_2\text{SiO}_3$ ratio was increased, the setting time was prolonged. In return, the additional setting time allowed more geopolymer network or gel development which enhanced the mechanical property of the end product [14]. However, when excessive NaAlO_2 was supplied, the dissolution of fly ash was impeded, leading to a lower degree of reaction, thus impacted negatively towards the mechanical strength. In short, the compressive strength of the synthesized geopolymer was optimum at the $\text{NaAlO}_2/\text{Na}_2\text{SiO}_3$ ratio of 2.5.

3.3. Microstructural analysis

Fig. 3 reveals the SEM micrographs of selected specimens after 28 days of ambient curing. Both images show one-part

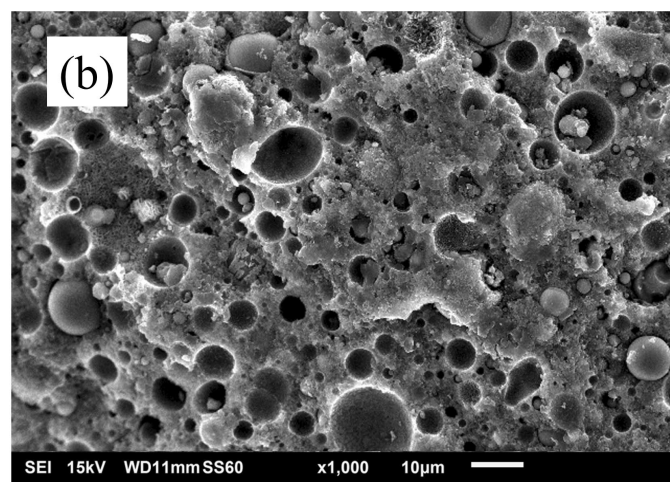
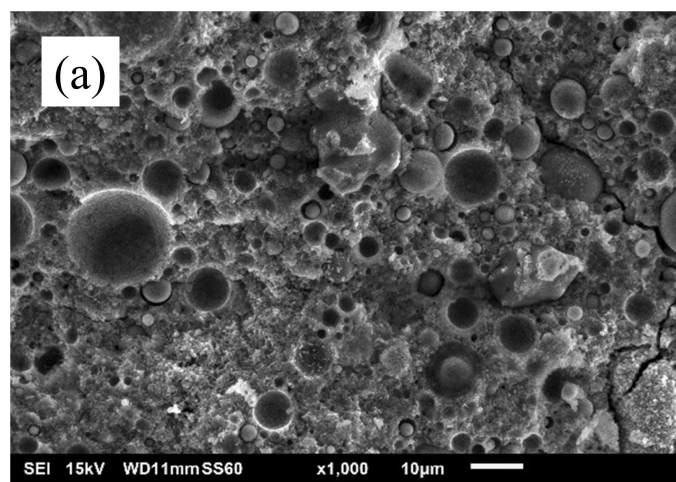


Fig. 3. SEM images of fly ash-based one-part geopolymer with magnification of 1000 \times for mixes A2 ($\text{NaAlO}_2/\text{Na}_2\text{SiO}_3$ ratio = 1.5) and A4 ($\text{NaAlO}_2/\text{Na}_2\text{SiO}_3$ ratio = 2.5)

geopolymer samples with high pores content. Water was responsible for the transport of ions and the dissolution of fly ash. Water molecules were physically bonded to the geopolymer matrix. During the ageing process, water was evaporated, subsequently caused pores and voids formation within the matrix [15]. With a high W/B ratio (W/B ratio = 4.0), one-part geopolymer incorporated with substantial pores was anticipated. The air voids also corresponded to the moderate compressive strength measured. Besides that, unreacted fly ash particles were found embedded within the hardened matrix in both images. This indicated that the source material was not fully reacted. An obvious difference can be observed from Fig. 3(a) and (b). Fig. 3(a) shows a friable structure when compared to Fig. 3(b). The less-dense microstructure comprised of more air voids, gave rise to one-part geopolymer with lower compressive strength (24.96 MPa). On the other hand, Fig. 3(b) displays a smoother and more homogeneous base which represents the presence of higher geopolymeric gel development. This showed that the $\text{NaAlO}_2/\text{Na}_2\text{SiO}_3$ ratio of 2.5 drove a higher extend of geopolymerization and favored a more interconnected geopolymer network formation. The finding was in line with the higher mechanical strength attained (33.65 MPa).

3.4. Phase identification

Fig. 4 shows the XRD pattern of the fly ash and the A4 one-part geopolymer. Fly ash showed diffuse halo at 10° to $40^\circ 2\theta$. Peaks contributed by hematite, quartz, mullite and small amount of anhydrite were observed from the XRD spectrum of fly ash. These minerals were formed from the major elements of the fly ash, as presented in TABLE 1. The broad humps shifted to 20° to $40^\circ 2\theta$ that were observed from the XRD spectra signified

the amorphous character of geopolymers [11-13]. The one-part geopolymer consisted of a similar phase as the fly ash, which was the hematite, indicating that the fly ash in the A4 mixture was not completely reacted. The finding corresponded to the microstructure of the one-part geopolymers (Fig. 3), where spherical fly ash particles remained in the structure after 28 days of ageing. Other than hematite, the A4 mixture consisted of sodium aluminium silicate hydrate (N-A-S-H), as well as anorthite phases. The N-A-S-H phase was the main reaction product of geopolymers [16], while anorthite phase contributes to the mechanical strength development [17], yielded one-part geopolymer with applicable compressive strength.

4. Conclusion

This paper presented a comprehensive study on the influence of NaAlO_2 on the fresh and hardened properties of fly ash-based one-part geopolymer. First and foremost, the development of one-part geopolymer from fly ash, anhydrous Na_2SiO_3 and anhydrous NaAlO_2 are viable without the need for an alkaline activating solution. The effect of the $\text{NaAlO}_2/\text{Na}_2\text{SiO}_3$ ratio on fly ash-based one-part geopolymer was significant. The increase of $\text{NaAlO}_2/\text{Na}_2\text{SiO}_3$ ratio from 1.0 to 3.0 had delayed the final setting time of the one-part geopolymer system, but that does not significantly influence the initial setting time. The optimum one-part geopolymer achieved 28-day compressive strength of 33.65MPa at $\text{NaAlO}_2/\text{Na}_2\text{SiO}_3$ ratio of 2.5. The microstructure showed a built-up matrix into a more compact structure that complied with the trend of mechanical strength. The mechanical strength was attributed to the presence of N-A-S-H and anorthite phases in the one-part geopolymer.

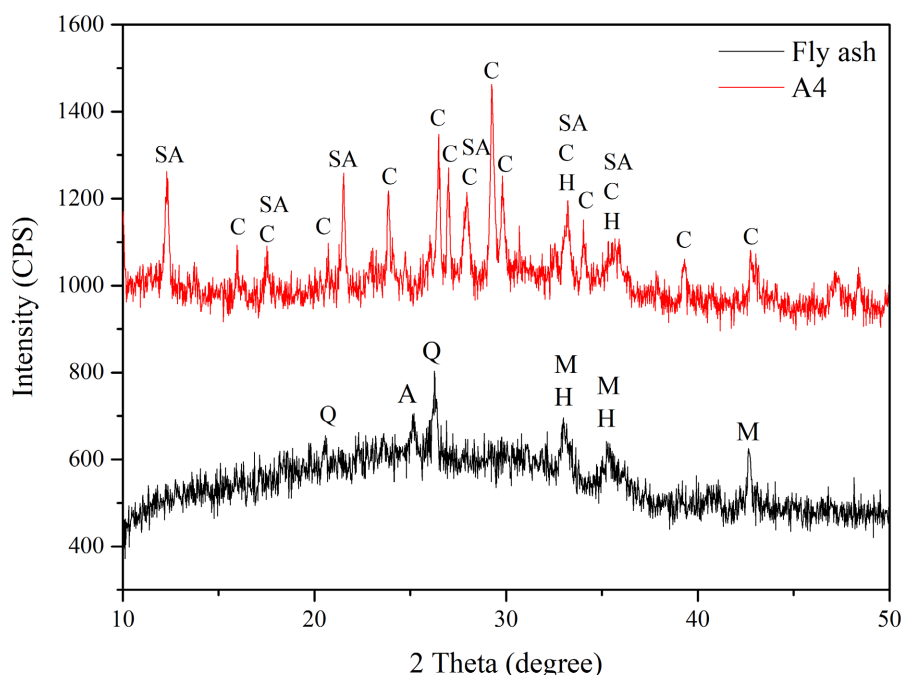


Fig. 4. XRD diffractograms of fly ash and A4 mixture (Q = quartz, A = anhydrite, M = mullite, H = hematite, SA = sodium aluminium silicate hydrate, C = anorthite)

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