

## Impact of initial silica modulus of sodium silicate on the compressive strength of alkaline activated fly ash based mortar

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### ABSTRACT

This study investigates the impact of silica modulus ( $M_s = \text{SiO}_2/\text{Na}_2\text{O}$ ) on the compressive strength of (AAMFA) fly ash based mortar. Three mixtures of alkaline activated mortar C1, C2 and C3. The alkali activator solution (AAS) was comprised of sodium hydroxide (10 Mole) and sodium silicate. The sodium silicate with various initial silica modulus were characterized by their  $\text{SiO}_2/\text{Na}_2\text{O}$  molar ratio of 2.0, 2.2, and 3.3, respectively. The sample from each mixture was characterized based on the CS and microstructure changes using useful tools of XRD and FTIR analysis. The results obtained indicated that the highest CS achieved among the three mixtures were 48.23 MPa of mixture C2 prepared with  $\text{SiO}_2/\text{Na}_2\text{O}$  molar ratio of 2.2. This was mainly due to higher binder formation (N-A-S-H gel type) and a higher rate of reaction of the main source material. This result is in line with XRD and FTIR analysis results finding.

**Keywords:** fly ash, alkaline activated,  $\text{Na}_2\text{SiO}_3$

### Introduction

A new type of cement is being constantly developed in order to meet the increasing demand for ordinary Portland cement (OPC) as an essential construction material and to reduce the environmental impact on air quality and the ozone layer associated with the clinker production [1, 2]. The clinker production to produce cement emits to the atmosphere nearly 1.5 billion tons of  $\text{CO}_2$  annually and this gives a share in about 6% of the total synthetic  $\text{CO}_2$  emission in 2015 [3, 4]. Therefore, due to these problems the research initiatives and efforts for the continuation of mitigating measures to lessen the unfriendly outcomes resulting from the continual emission. The substitution of cement via supplementary cementation materials have been highly recommended for its contribution towards

decreasing the global carbon warming. Despite all these efforts, the production of OPC still to be unavoidable. The recycle of pozzolans as supplementary cementation masteries which is essentially industrial or agriculture by-products such as fly ash (FA), silica fume (SF), granulated blast furnace slag (GGBFS), and palm oil fuel ash (POFA), helps to reduce the overall pollution from dumping these wastes in landfill and store this material in the earth [5, 6]. The synthesis of new type of binder known as geopolymer in construction materials formed as the result of the alkaline activation of pozzolanic materials that are rich in  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and/or  $\text{CaO}$  gives credit for this achievement to the work of German cement chemist and engineer Kuhl in 1930, to obtain an ordinary Portland cement (OPC) alternative material [7]. The synthesis of geopolymer via FA as main source materials rich in  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  based alkaline activated mortar have been widely investigated through various research [6, 8-13]. The ratio between the main oxide's chemical composition of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  demonstrated the effects of setting time and final strength of hardening geopolymer products [14, 15]. The alkaline activator has been used in geopolymer production were prepared from various type combination and concentrations [8, 16-18]. The alkaline activator of  $\text{NaOH}$  and  $\text{Na}_2\text{SiO}_3$  have mostly been used [5, 19]. Despite a few papers have been published to investigate the influence of different  $\text{SiO}_2/\text{Na}_2$  molar ratio derived from various sodium silicate with initial silica modulus on the reaction formation of final products [20-24]. The influence of total oxides concentrations of  $\text{SiO}_2$  and  $\text{Na}_2\text{O}$  derived from the different grade of  $\text{Na}_2\text{SiO}_3$  solution remains unclear [24, 25]. This going research aimed to investigate the influence of various sodium silicate with initial silica modulus on the reaction formation of gel binder based alkaline activated fly ash. It will also promote the utilization of locally available waste materials towards the development of alternative and sustainable construction material for general construction applications.

## Materials and Methods

### 2.1. Materials

#### 2.1.1. Fly Ash

The main source material utilized in this research fly ash was collected from by Lafarge Malaysia Berhad (Rawang Plant). According to ASTM:C618-12a, fly ash is specified into low-calcium fly ash (Class F,  $\text{CaO} < 10\%$ ). The chemical composition and physical properties are shown in Tables (1) and (2), respectively.

**Table (1) Chemical compositions of FA analysed by XRF**

Oxides (%)	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{CaO}$	$\text{MgO}$	$\text{P}_2\text{O}_5$	$\text{K}_2\text{O}$	$\text{SO}_3$	$\text{TiO}_2$	$\text{Na}_2\text{O}$	LOI
FA	49.053	23.516	6.422	5.080	0.698	1.018	1.309	0.475	1.121	0.2102	2.130

**Table (2) Physical properties of FA**

Materials	Specific gravity	Median particle size, $d_{50}$ $\mu\text{m}$	Surface area $\text{m}^2/\text{kg}$	Colour
FA	2.42	9.8	320	grey

### 2.1.2. Alkaline Activators

The combination of alkaline activator consists of sodium hydroxide and sodium silicate solutions and an additional amount of water. The analytical grade of NaOH was used in pellet form having CAS No: 1310-73-2 provided by Qrec Sdn. Bhd, Malaysia. Furthermore, the sodium silicate with initial silica modulus was characterized based on  $\text{SiO}_2/\text{Na}_2\text{O}$  molar ratio to three different types 2.0, 2.2, and 3.3, respectively.

### 2.1.3. Fine Aggregates

Local natural river sand located in area of Nibong Tebal, Penang was used. The collected aggregate was sieved passed through a 1.18 mm and was retained on a 150  $\mu\text{m}$  sieve as described in ASTM C778 (ASTM, 2000), having fineness modulus of 2.8, and a specific gravity of 2.65.

## 2.2. Design of Mixtures

In this study, three mixtures of AAFM consist from the source material, alkaline activator and fine aggregate, which were designed per cubic meter using the absolute volume method are represented in Table 3. A homogenization mixes proportion from fine sand to the source material of 1.5 was used. The alkaline activator combination and concentration was exactly as described in a previous study [19]. The added water was used as 5 wt.% from the total binder content [19].

## 2.3. Preparation geopolymer fly ash mortar and testing

The mixtures were prepared using source material of fly ash and alkaline activator solution in required quantities. The mixture was prepared by keeping the fly ash constant but changing the sodium silicate with initial silica modulus with keeping the NaOH (10 Molre) and water content constant as shown in Table 3. The three various sodium silicate with initial silica modulus was used which characterized by their  $\text{SiO}_2/\text{Na}_2\text{O}$  (S/N) molar ratio of 2.0, 2.2, and 3.0 depending on designed mixture of C1, C2, and C3, respectively. Period before the mixing process, a dry homogenization of source material and sand were performed. The dry solid material and activator solution was added to L5 automatic Hobart N50 mixer as illustrated in ASTM C305 [26] and the mixing process followed was exactly the same as a previous research [27]. The prepared mixture was casted in to cubic molds and compacted in 2 layer according to ASTM C109 [28]. And vibrated for 2 min to eliminate entrapped air bubbles during the mixing process. After 24 h the demolded samples were covered in plastic sheets to diminish water evaporation and left for 24 h at room temperature, followed by curing for 24 h in an oven set at 75° [27]. Samples were then cured in laboratory conditions until testing.

Table (خطأ! لا يوجد نص من النمط المعين في المستند.) The mixture proportions of the Fly ash based alkalin activated mortars (kg/M<sup>3</sup>)

Mix	Solid material (kg)	Sand (kg)	Alkaline Activator			
			Na <sub>2</sub> SiO <sub>3</sub> (kg)	NaOH 10 M (kg)	Water (kg)	Added Water 10 M NaOH (kg)
C1 Ms (2.0)	Fly ash 847	1270	303	40	80	60
C2 Ms (2.2)	Fly ash 847	1270	303	40	80	60
C3 Ms (3.3)	Fly ash 847	1270	303	40	80	60

### 3. Results and Discussion

#### 3.1. Effect of initial silica modulus of Na<sub>2</sub>SiO<sub>3</sub>

Fig. 1 shows the variation of CS with sodium silicate. This effect was studied by varying of Na<sub>2</sub>SiO<sub>3</sub> with initial silica modulus which characterized by their SiO<sub>2</sub>/Na<sub>2</sub>O (S/N) molar ratio of 2.0, 2.2, and 3.0 depending on a designed mixture of C1, C2, and C3, respectively. The CS increased with S/N molar ratio up to a certain limit but decrease when the S/N molar ratio increased. The strength obtained was 46.73 MPa and increased to 48.72 MPa when the S/N molar ratio increased to 2.2. By increasing the S/N molar ratio from 2.2 to 3.3, the maximum CS decreased by 29.64%. It was revealed that the CS increased as S/N molar ratio increased up to 2.2 but beyond that, it reduces linearly. The current outcome results are in line with other research findings [29]. The observation also could be attributed to the higher dissolution rate of the complex aluminosilicate minerals in the Fly ash as the prime or source material at different grades of Na<sub>2</sub>SiO<sub>3</sub> solution[29].

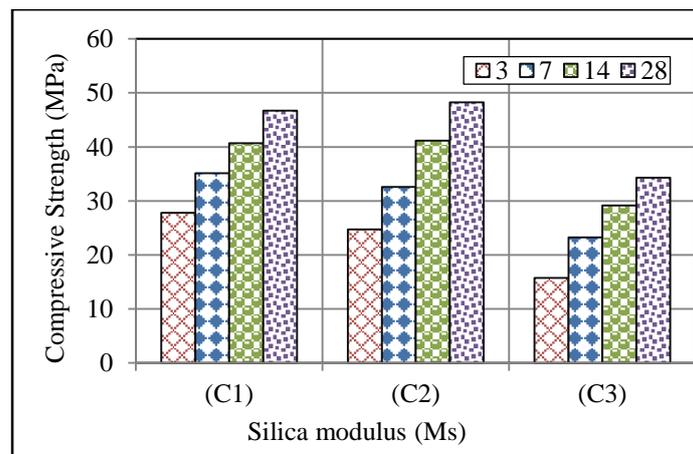


Figure (1) Compressive strength of alkali activated AAMFA mortar at 3, 7, 14, and 28 days

### 3.2 Mineralogical analysis result

The X-ray diffraction was performed to identify the phase compositions in the alkaline activated fly ash (AAMFA). The phase changes were investigated within curing time of 28 day. The results of mixtures (C1-C3) indicated the presence of mullite with chemical composition of  $(Al_6Si_2O_{13})$  (ICSD no. 98-006-4581) and quartz (ICSD no. 98-004-6928). The peak at  $29.7^\circ 2\theta$  was attributed to the formation of N-A-S-H type gel with a structure close to mullite. The peak intensity increased with the increase in S/N molar ratio but beyond that, it decreased. The CS increased with the peak intensity to a certain extent but reversed in the presence of excess S/N molar ratio. The molar ratio of S/N in the mixture determines the rate of dissolution and activation of fly ash as source material. Furthermore, the presence of high  $SiO_2(OH)_2^{2-}$  or  $SiO(OH)_3^{-1}$  species, derived from alkaline activator solution that would react with dissolved  $Al(OH)_4^-$  species to form the gel binder which results in a high rate of reaction. Besides, the high concentration of  $Na_2O$  that leads to higher pH values which plays a crucial role in degree of condensation process of main gel binder [30].

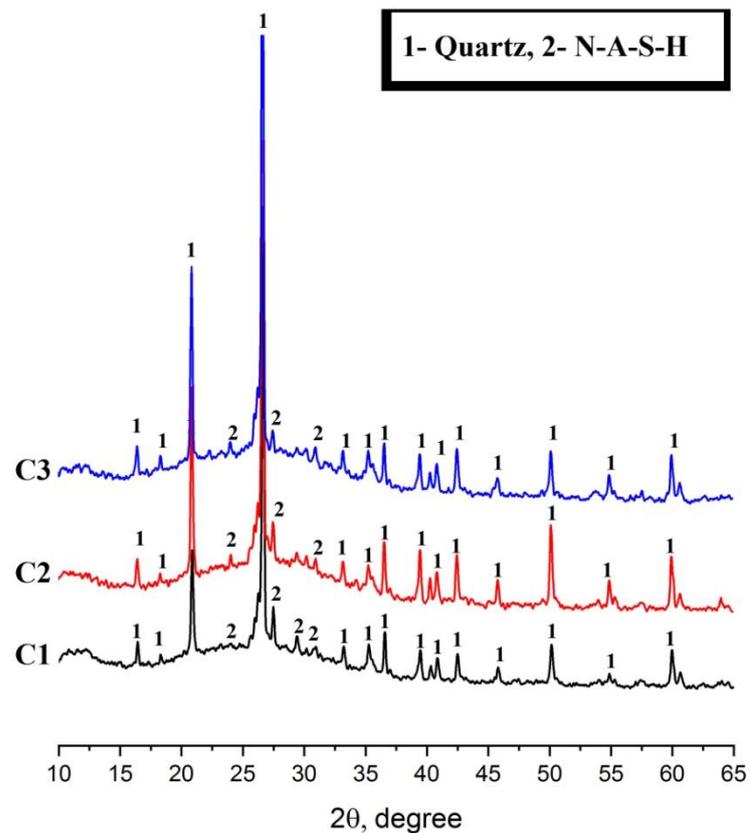


Fig.2 XRD diffractograms of AAMFA ash mortar mixture # C1, C2, and C3

### 3.3 Fourier Transform Infrared Spectroscopy (FTIR)

Fig. 3 presents the FTIR spectra of different mixtures (C1, C2, and C3) synthesized from different concentration S/N ratio after 28 days. The results are tabulated in table (6), which depict the FTIR data associated with band positions and assignments of AAFA. The results indicated through the change in band vibration of AAFA backbone in the region 900-1200  $\text{cm}^{-1}$ . This region of vibration frequency is the main feature in AAMFA [18]. The change in the ratio of S/N ratio from 2.0 to 3.3 was found to influence the gel binder formation by providing a reasonable quantity of dissolved  $\text{SiO}_2$  to the system since the early stage of the reaction. The main vibration modes at 1024.72  $\text{Cm}^{-1}$  observed at C1 related to bending vibration mode of the Al-O-Si bonds. The formation of this band stated to increase at C<sub>2</sub> rather than C<sub>1</sub> and C<sub>3</sub>, which vibration moved close to 1000  $\text{Cm}^{-1}$  then stated to increase in C<sub>3</sub>. This was attributed to a highly crosslinked of N-A-S-H gel binder framework as it's also confirmed by XRD analysis.

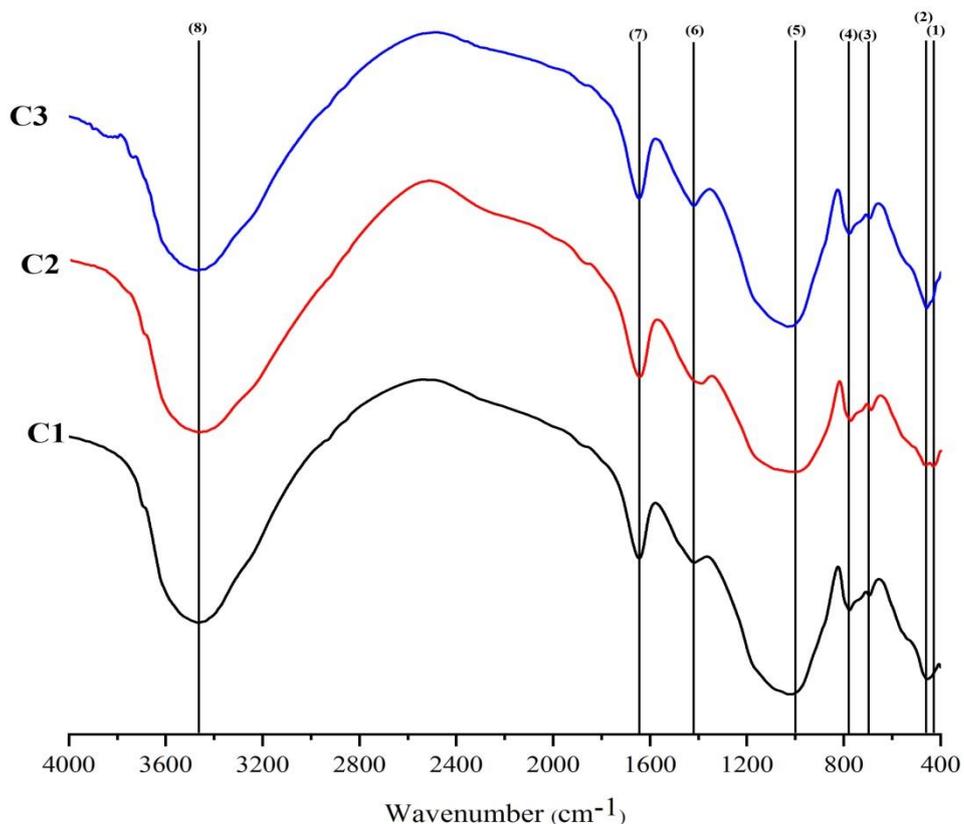


Figure (3) FTIR spectra AAMFA ash mortar mixture C1, C2, and C3 at 28 days

**Table 6: FTIR vibration bands of AAMFA mixtures at 28 days.**

Vibration bands #	Mixture			Assignment
	C1	C2	C3	
1	455.43	438.52	459.34	$\delta$ Si–O (SiO <sub>4</sub> Td)
2	-	471.83	-	$\delta$ Si–O–Si
3	695.22	692.54	692.54	$\delta$ Si–O–Si
4	776.15	775.82	777.9	Quartz double band
5	1024.72	1007.20	1032.90	Alkaline aluminosilicate (N–A–S–H) gel band (T–O, T=Si or Al)
6	1415.2	1398.4	1423.4	$\sqrt{3}$ C–O (CO <sub>3</sub> <sup>2-</sup> )
7	1644.76	1647.67	1645.97	$\delta$ O–H (H <sub>2</sub> O)
8	3466.68	3467.56	3468.70	$\sqrt{O}$ –H (H <sub>2</sub> O)

### Conclusion

The impact of initial silica modulus of sodium silicate on the compressive strength of alkali-activated mortar (AAMFA) has been investigated in this research. The compressive strength of 48.72 MPa was achieved with SiO<sub>2</sub>/Na<sub>2</sub>O ratio of 2.2 and reduction or increase in this ratio caused a reduction in compressive strength. This was mainly due to that the high concentration of Na<sub>2</sub>SiO<sub>3</sub> activating solution lowers pH and raises solution viscosity, inducing a weakening in the degree of reaction of fly ash with low gel binder formation of N-A-S-H. This was also consistent with XRD and FTIR analysis.

### Acknowledgements

The authors gratefully acknowledge the Ministry of Higher Education, Malaysia and Universiti Sains Malaysia for providing financial support through the Fundamental Research Grant Scheme (203/PAWAM/6071365) for the undertaking of the research work. Special thanks are due to Lafarge Malaysia Berhad, (Associated Pan Malaysia Cement Sdn Bhd) for providing the fly ash.

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