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STUDY ON THE REACTION STABILITY OF FLY ASH-BASED GEOPOLYMERS

Fly ash-based geopolymers' quality varies based on their constituent materials' quantity and reactivity. Determination of the ratio of fly ash as a base material reacted with the ratio and quantity of the alkaline activator as a reagent is a challenge in producing a stable geopolymer reaction. This study aimed to provide insight into the stability of the mixture of fly ash-based geopolymers. Variations in the ratio and amount of alkaline activator to fly ash in a wide range of quantities could provide an overview of the stability of the geopolymer reaction. The fundamental indicators of the stability characteristics of geopolymers are their physical stability and changes in strength. Evaluation of the stability of the geopolymer mortar was observed from the development of compressive strength, visual inspection of efflorescence during partial immersion, and the strength changes after a heating treatment of 150°C for 4 hours. The results showed that the more alkaline activator content in the mortar, the stability of the resulting geopolymer is reduced, as seen from the appearance of efflorescence on the specimen surface, expansion cracks, and a decrease in compressive strength. The ratio of alkaline activator also affected the compressive strength resulting in a range of optimum ratios. Meanwhile, depending on the calcium content in the fly ash, a secondary pozzolanic reaction could also occur in the geopolymer concrete at a later age.

Keywords: Geopolymer; reaction; stability; fly ash; efflorescence

1. Introduction

Fly ash-based geopolymer can substitute for Portland Cement to reduce the carbon dioxide emission for the construction industry. An alkaline activator is needed to react with alumina and silica content in fly ash to create a polymer bond as the geopolymer concrete's base structure without using Portland Cement [1,2]. Fly ash-based geopolymer is made by mixing it with liquid alkaline activators in sodium hydroxide and sodium silicate solution [3,4]. These alkaline activators then activate and dissolve the fly ash to create a geopolymerization reaction making a geopolymer binder [5].

Fly ash-based geopolymers may vary in quality. The variation is due to varying fly ash properties, fly ash compositions, and alkaline activator compositions [6,7]. Variations in fly ash reactivities are the main factors affecting geopolymer quality variations [6-11]. Many researchers have used a selection ratio of alkaline activators and fly ash with varying properties to evaluate produced geopolymer's properties [8-10]. However, their fly ash is one of a kind and cannot be directly comparable with the other references. Their finding resulted in the variation of the recommended alkaline activator ratio value that can be applied as the optimum value only for their specific fly ash. The variation of fly ash source and quality predominantly impacts the resulting geopolymer concrete rather than its optimum ratio of alkaline activator [9]. Fly ash acts as a reactant and requires a reactor to proceed with the geopolymerization reaction [12]. An alkaline activator acts as the reactor to make geopolymer mortar. Besides the correct ratio of the alkaline activator, the proper ratio between the fly ash and the alkaline activator provides a balance and complete reaction. When choosing between higher reactant or reactor amounts, it is advisable to choose the first. Thus the amount of alkaline activator in the geopolymer concrete needs to be reduced as much as possible.

The appearance of the pozzolanic reaction depending on the calcium content in the fly ash could cause further complexity in the geopolymer binder. Low-calcium fly ash undergoes a geopolymerization reaction, while high-calcium fly ash could have a geopolymerization reaction accompanied by a pozzolanic reaction [8,13]. The increased compression strength at a later age shows the appearance of a pozzolanic reaction. The difference in the increase in compressive strength was illustrated in Fig. 1, where the geopolymerization reaction results without and with a pozzolanic reaction mainly depend on the calcium content in

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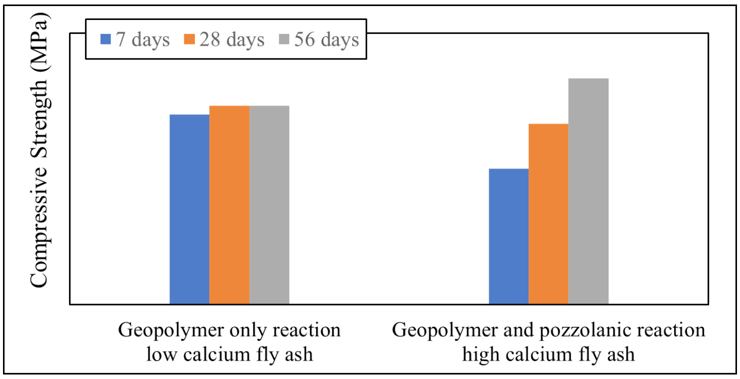

Fig. 1. Illustration of reaction in the fly ash-based geopolymers (a) geopolymerization only reaction and (b) geopolymerization and pozzolanic reaction

the fly ash precursor. The appearance of the pozzolanic reaction caused uncertainty if the mixture's geopolymerization reaction was complete. An incomplete geopolymerization reaction may indicate an unstable composition of the reaction products and cause further uncertainty about the durability of the concrete produced.

The uncertainty of the geopolymerization reaction accompanied by a pozzolanic reaction might result in a reaction with unstable characteristics. A reaction product in a geopolymer mortar is called stable if the product can maintain its characteristics continuously [14]. The characteristics of stable reaction products have become a concern in geopolymer research. Fly ash could have varying reactivity even though it was taken from the same source. Most studies varied fly ash source or sampling period with an alkaline activator ratio to evaluate the characteristics of the resulting geopolymers and proposed an optimum alkaline ratio [8-10]. The alkaline activators ratio, molar concentration, and quantity in the mixture influence the resulting reaction that was also shown with the decrease of compressive strength at a later age of 28 days with a water-fly ash ratio or a ratio between specific alkali activators [15-18]. A decrease in the compressive strength of geopolymers due to the appearance of efflorescence is shown by some authors [19-24]. The efflorescence on the concrete surface indicates that the reaction results in the mortar are not yet stable. In addition, a high-temperature exposure can also be an indicator of geopolymer reaction stability. High-temperature treatment was often carried out to evaluate the geopolymer's resistance to fire and repeated high temperatures with a temperature range of 150-550°C. A stable geopolymer typically shows excellent resistance to high-temperature exposure indicating a proper selection of the mixture composition and manufacturing process [25-28].

This paper aims to show the stability evaluation of the geopolymer mortar made with excessive alkaline activator ratio and content and its effect on the hardened properties. One sampling of fly ash was collected to isolate the influence of fly ash variation. In this study, fly ash with an intermediate calcium oxide content was obtained to study the effect of calcium oxide on the resulting geopolymer. The alkaline activator ratio, concentration, and quantity in the mixture were varied to demonstrate that the unbalanced or unstable geopolymer reactions were mainly determined by the improper alkaline activator composition and caused the instability of the geopolymer mortar. The properties evaluated were compressive strength, efflorescence occurrence, and strength change after exposure to a high-temperature condition.

2. Experimental research

2.1. Material

The geopolymer was evaluated in mortar specimens with binder and fine aggregate only. Materials used to make the mortars are fly ash, alkaline activators, water, and natural silica sand. Fly ash used in this research is class F fly ash from a pulverized coal combustion power plant in Sudimoro, Pacitan, East Java, Indonesia. The fly ash sample was taken directly from the powerplant and kept in an air-tight container.

Alkaline activators used in this research are sodium hydroxide (NaOH) and sodium silicate (Na_2SiO_3). Based on our previous study [8,9], a solution of sodium hydroxide with a molarity of 8M is used. The sodium silicate used in this research is a liquid with 49.76% water content. The fine aggregates used in this research are natural silica sand. Based on ASTM C778, the fineness modulus of the sand must be between 1.9-2.19 [29]. The fineness modulus used in this research is 2.053.

Normal consistency, specific gravity, and pH of Sudimoro fly ash are shown in TABLE 1. The normal consistency of the fly ash was measured at 0.18, showing a low water requirement of the fly ash in the mixture. The normal consistency value was used as a target reference for the water content needed to react optimally. The pH value was measured by dissolving 20 g of fly ash in 80 g distilled water. The fly ash had a specific gravity of 2.61. The pH of 10.3 of the fly ash indicated a low possibility of a flash setting. The result of the XRF analysis of fly ash is shown in TABLE 2. The fly ash can be classified as class F with an intermediate calcium oxide content.

TABLE 1

Normal consistency, specific gravity, and pH of the fly ash sample

Fly Ash	Normal Consistency	Specific Gravity	pH
Sudimoro	0.18	2.61	10.3

TABLE 2

Chemical composition of fly ash from XRF Analysis (% by mass)

Fly Ash	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	TiO_2	MnO	P_2O_5	BaO	Other
Sudimoro	40.8	13.25	25.25	13.9	0.5	1.5	1.84	1.55	0.31	0.83	0.25	0.02

2.2. Mixture Composition of Mortar

This research divides the mix-design into two phases. The first phase of this research used a constant water-to-fly ash ratio of 0.35. The ratios of the alkaline activators, which is the ratio of the sodium silicate solution to 8M sodium hydroxide solution (Na_2SiO_3: NaOH), varied at 0.15, 0.3, 0.5, 1.0, 2.0, 3.0, 4.0, and 5.0. The silica sand to fly ash ratio (s/fa) was fixed at 2 by mass for all mortar. The first phase mix design is shown in TABLE 3.

The second phase of this research used a constant sodium silicate solution to 8M sodium hydroxide solution ratio of 1.0 and varied its water to fly ash ratio. The selected water-to-fly ash ratios (w/fa) were 0.15, 0.25, 0.35, 0.45, 0.55, and 0.65. The second phase mix design is shown in TABLE 4.

2.3. Specimen Preparation and Testing Method

This research was divided into two phases, with the first consisting of 8 mixtures and the second phase comprising 6 mixtures. Each mixture produced 12 specimens of 5×5×5 cm cubes and two specimens of Ø5×10 cm cylinders. Each mixture's compressive strength and density were tested at ages 7, 28, and 56 days. Cylindrical specimens made with plastic molds were used to visually observe efflorescence every day until the specimens reached 28 days. The one-time clear plastic mold was used to avoid using a demolding agent on its surface when making the geopolymer specimens.

All mixtures used the same method of heat-curing the sealed fresh specimens in an oven at 60°C for 24 hours. After curing, they were removed from their mold and kept at room temperature inside plastic seal bags. Mortar cube specimens were tested for compressive strength at 7, 28, and 56 days with three samples tested for each testing time.

High-temperature treatment on three cube specimens was done in the oven at 150°C for 4 hours [28]. This treatment was done 24 hours after the heat curing. The high-temperature treated (HT) specimens were tested for compressive strength after cooling to room temperature for an hour at 2 days of age.

Two cylindrical mortar specimens were made for visual observation, divided into heat-curing specimens and specimens with high-temperature treatment. After the treatment, the cylinder specimens were placed inside a basin filled with 1 cm depth water and left in the laboratory condition. The observation was done every day until the specimens reached 56 days.

3. Results and discussions

3.1. Compressive strength

The geopolymer mortars were tested for compressive strengths at 7, 28, and 56 days. In the first phase, the mixture used a water-to-fly ash ratio (w/fa) of 0.35, a concentration of 8M NaOH solution, and a sand-to-fly ash ratio of 2 by mass. Fig. 2 shows the mortars' compressive strengths with various alkaline activator ratios. In each ratio, the mortar showed a compressive strength increase along with its age which is a good indicator of fly ash reactivity. The alkaline activator's sodium silicate to sodium hydroxide ratio greatly influenced the compressive strength obtained. The highest compressive strength was obtained with the sodium silicate to sodium hydroxide ratio of

TABLE 3

Mix design of geopolymer mortars with variations in the alkaline activator ratios for 3 mortar cubes

Materials	**The ratio between alkaline activators (Na_2SiO_3: NaOH)**							
	0.15	**0.3**	**0.5**	**1**	**2**	**3**	**4**	**5**
Silica sand (g)	600	600	600	600	600	600	600	600
Fly ash (g)	300	300	300	300	300	300	300	300
Sodium silicate (*l*) (g)	18.57	33.55	49.53	77.08	106.76	122.49	132.23	138.85
Sodium hydroxide [8M] (g)	123.78	111.82	99.06	77.08	53.38	40.83	33.06	27.77

TABLE 4

Mix design of geopolymer mortars with variations in the water to fly ash ratios for 3 mortar cubes

Materials	**Water to fly ash ratio (w/fa)**					
	0.15	**0.25**	**0.35**	**0.45**	**0.55**	**0.65**
Silica sand (g)	600	600	600	600	600	600
Fly ash (g)	300	300	300	300	300	300
Sodium Silicate (*l*) (g)	33.03	55.05	77.08	99.1	121.12	143.14
Sodium hydroxide [8M] (g)	33.03	55.05	77.08	99.1	121.12	143.14

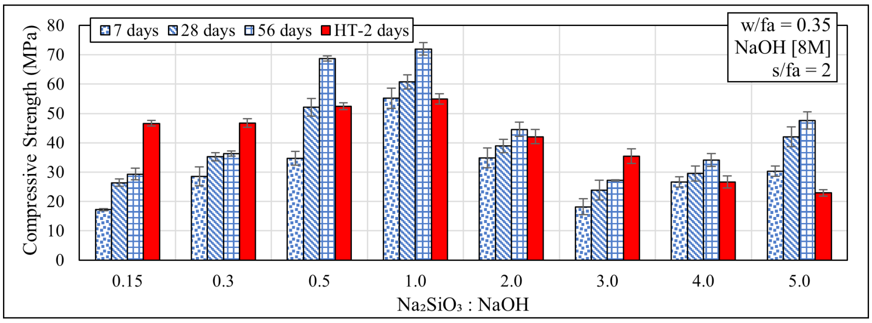

Fig. 2. Compressive strengths of mortars with alkaline activator ratios

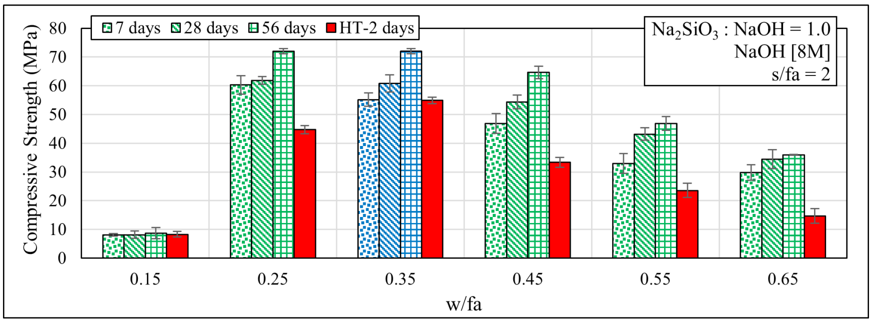

Fig. 3. Compressive strengths of mortars with water to fly ash ratios

1.0 in alkaline activators ratio and decreases when the ratio is either increased or decreased. It was observed that compressive strength started to rise again at the ratio of 4.0 and continued to rise at 5.0. However, the excessive sodium silicate would increase the cost of making geopolymer, and hence lowest sodium silicate content is preferred.

High-temperature treatment was done to check its compressive strength stability. Mortars were tested after they were taken out of the oven and cooled down to room temperature. Fig. 2 shows the mortar's compressive strength stability against high-temperature exposure, labeled HT. The compressive strength obtained was higher than mortars at the age of 7 days within most of the ratios. Mortars with ratios of 0.5 and 2.0 produce compressive strengths higher than mortars at 28 days. Mortars with ratios of 0.15, 0.3, and 3.0 produce compressive strengths higher than mortars at 56 days. The increase showed that mortars have stable compressive strengths against high temperatures in all ratios except 5.0. The results show that the optimum alkali activator ratio and concentration can be predicted early by exposing the geopolymer mortar to a high-temperature condition.

The second phase uses the same sodium silicate to sodium hydroxide ratio of 1 and sand to fly ash ratio of 2 by mass. The water-to-fly ash ratios varied from 0.15 to 0.65 with 0.1 increments. The second phase of mortar compressive strength is shown in Fig. 3. In each ratio, mortar showed an increase in compressive strength with age. Compressive strength test results showed that the optimum water-to-fly ash ratio was 0.35. The compressive strength was reduced when the ratio either increased to 0.65 or decreased to 0.15. The compressive strength of the mortar with the ratio of 0.15 was minimal due to the lack of water and alkaline activator in the mortar, which resulted in the fly ash being unable to react and lack of lubrication for a cohesive mixture.

The results were contrary compared to the high-temperature treated mortars (HT). All ratios except 0.35 resulted in the mortars having weaker compressive strengths than mortars at 7 days. The optimum water-to-fly ash ratio showed a stable range of compressive strength against temperature, possibly due to the expansive vapor gases or drying of the specimens. A significant result is not seen in the ratio of 0.15 due to the fly ash's inability to react well.

Fig. 2 and Fig. 3 also showed differences in compressive strengths with an increase in time. Two alkaline activator ratios with prominent differences were the ratios 0.5 and 1.0. There was still a significant increase in the compressive strength of the mortar between ages. The result contradicted the compressive strength test results of the alkaline activator ratios of 0.3 and 2.0, where compressive strength was shown not to increase with age. The difference can happen because the reaction combined pozzolanic and geopolymerization for the prior mixture [8,13]. Higher later-age strength than the high-temperature treated specimen could be used as an indicator of the occurrence of secondary pozzolanic reaction in the geopolymer mortar. The secondary pozzolanic reaction can be observed for the alkaline activator ratio of 0.5, 1.0, and 5.0 in Fig. 2 and the water-to-fly ash ratio of all but 0.15 in Fig. 3.

3.2. Partial Immersion Stability Test

The test was done on a cylinder sample to check their stability by observing the occurrence of efflorescence. Samples were put into a basin filled with 1 cm depth of water, then left for

56 days and documented periodically to identify efflorescence and observe the occurrence of expansion cracks. TABLES 5 and 6 show the resulting visual observation of phase one and phase two of the partial immersion stability test.

First-phase samples at the age of 56 days with the ratios (Na_2SiO_3: NaOH) starting from 0.15 to 5.0 was found to have efflorescence on their surface. The occurrence of efflorescence appears gradually with the increase in time. The samples with alkaline activator ratios of 0.3, 3.0, and 4.0 were also found to have a high amount of self-cracks due to expansion and underwent a large scale of efflorescence at the middle part of the cylindrical sample. Samples with slight efflorescence and cracks had alkaline activator ratios of 1.0 and 5.0. Meanwhile, samples with the alkaline activator ratio of 0.15 and 2.0 only underwent efflorescence with no crack. However, only mortar samples with the sodium silicate to sodium hydroxide ratio of 1.0 exposed to 150°C temperature underwent minor efflorescence. This result could show that the curing regime of 60°C for 24 hours could still be insufficient to ensure all alkaline activators reacted with the fly ash or that the high-temperature treatment significantly dried the alkaline activator in the specimen and reduced its solubility. Further study is needed to investigate this phenomenon.

Second-phase samples at the age of 56 days with water to fly ash ratio of 0.15 to 0.65 also underwent efflorescence. The sample with a ratio of 0.15 also had its top surface cracked outwards. Expansion cracks were also found in the water-to-fly ash ratio of 0.35, and larger expansion cracks were also found in the 0.55 and 0.65 ratios. Meanwhile, the sample with a w/fa ratio of

TABLE 5

Visual observation of the mortar for efflorescence and self-induced crack for phase one

Ratio of Na_2SiO_3 : NaOH							
0.15	**0.3**	**0.5**	**1.0**	**2.0**	**3.0**	**4.0**	**5.0**
56 days							
							
56 days – After 150°C – 4 h exposure (HT)							
							

TABLE 6

Visual observation of the mortar for efflorescence and self-induced crack for phase two

w/fa ratio					
0.15	**0.25**	**0.35**	**0.45**	**0.55**	**0.65**
56 days					
					
56 days – After 150°C – 4 h exposure (HT)					
					

0.45 only had a slight efflorescence. Only slight efflorescence was found on mortars exposed to high-temperature treatment. A sample with w/fa of 0.45 had cracks on its top, and large cracks also appeared in samples with w/fa ratios of 0.55 and 0.65 exposed to high-temperature treatment. The self-cracks could be due to the excessive amount of the liquid in the higher w/fa mixture being dehydrated during high-temperature treatment.

4. Conclusions

Based on the results and observations obtained from the experimental study, several conclusions can be obtained:

- The alkaline activator content in the mortar mixture significantly affects the stability of the geopolymer concrete produced. Although there was enough geopolymerization reaction to produce sufficient compressive strength, the unreacted alkaline activator still could be available in the matrix and cause an unwanted reaction when exposed to water or humid condition. This effect was prominent when a high w/fa ratio was used to make geopolymer.
- The ratio of sodium silicate to sodium hydroxide on the alkaline activator in the geopolymer mixture also influences the mixture's stability, especially when the ratio is not ideal. A higher ratio of sodium silicate to sodium hydroxide would cause a significant expansion in the specimen when exposed to the partial immersion test.
- An increase of later age strength in the geopolymer concrete could show that the heat curing was not enough to complete the geopolymer reaction. However, the increase in strength could also be due to the pozzolanic reaction due to the calcium oxide content initially available in the fly ash. The pozzolanic reaction was shown to proceed, especially from the later age strength increase of the mortar.
- Evaluation of the optimum mix design for the geopolymer concrete should also observe the stability of the resulting specimen in long-term tests such as partial immersion test, besides only checking its maximum strength for a given alkaline activator ratio.
- The high-temperature treatment could indicate the stability of the geopolymer produced. A stable geopolymer should have a good performance when exposed to high temperatures and have only a slight strength reduction or even an increase in strength. The high-temperature treatment could also act as an indicator for the pozzolanic reaction shown by the heat-cured mortar that has higher later age strength than the high-temperature treated specimens.

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