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The Effect of Sodium Hydroxide Molarity on Strength Development of Non-Cement Class C Fly Ash Geopolymer Mortar

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Abstract. The use of fly ash as cement replacement material can overcome the environmental issues, especially the global warming problem caused by the greenhouse effect. This is attributed to the CO2 gas produced during the cement manufacturing process, which 1 ton of cement is equivalent to 1 ton CO2. However, the major problem of fly ash is the requirement of activators to activate the polymer reactions. The most common activator used in non-cement or geopolymer material is the combination of sodium hydroxide (NaOH) and sodium silicate. This study aims to identify the effect of NaOH molarity as activator on strength development of non-cement class C fly ash geopolymer mortar. The molarity variations of NaOH were 6 Molar (M), 8M, 10M, 12M, 14M and 15M. The compressive strength test was performed at the age of 3, 7 and 28 days in accordance with ASTM standard, and the specimens were cured at room temperature. The results show that the highest compressive strength was achieved by geopolymer mortar with a molarity of 12M. It exhibits a higher strength to that normal mortar at 28 days. However, the use of NaOH molarity more than 12M tends to decrease the strength of non-cement geopolymer mortar specimens.

1. Introduction

Cement-based concrete is the most commonly used construction material. Concrete is conventionally manufactured by using Ordinary Portland Cement (OPC) as the primary binder, sand and gravel materials. The ratio of OPC in conventional concrete is approximately 10% to 15% by the total mass of concrete [1,2]. However, the use of OPC in concrete has an adverse problem for the environment. According to Davidovits [3], the production of 1 ton of OPC also released about 0.7-1 ton CO_2. The contribution of cement production alone is approximately 6% anthropogenic CO_2 gas emissions which cause the greenhouse effect and leads to the occurrence of global warming problems. Furthermore, this condition corroborated with the impact on the environment due to the depletion of quarries resources of limestone as OPC raw materials has led to the search for more environmentally friendly cement replacement materials.

Fly ash, a waste product from burning coal power plant, has been commonly used as an additive or cement replacement material due to the pozzolanic characteristic to improve mechanical and durability properties of concretes [4-6]. Recent researches also show that fly ash can be used as fully cement replacement materials with the addition of alkaline activator. This non-cement fly ash based concrete material is known as geopolymer [3, 4, 8, 9]. According to Davidovits [7], the mechanism of geopolymer reaction involves the polycondensation reaction of alumino-silicate-oxide with alkali polysialates resulting polymeric Si-O-Al bonds and forms a geopolymer matrix. This hydration product is more polymer than C-S-H gel on conventional concrete [3].

The strength properties of geopolymer are influenced by the molarity of alkaline activator, particularly in the molarity of sodium hydroxide (NaOH). Increasing the NaOH molarity will significantly increase the strength development of geopolymer specimen [10, 11]. According to Ryu et al. [11], it attributes to the activation of the reaction of the internal silicate (Si) and aluminate (Al) components caused by the increased breakage of the glassy chain of fly ash precursor, in which it is provoked by the high alkalinity resulting from the increase of the molarity of NaOH.

This study presents the effect of sodium hydroxide molarity on strength development of non-cement class C fly geopolymer mortar. The strength properties were identified by the compressive strength test at the age of 3, 7 and 28 days in accordance with ASTM standard [12].

2. Method

2.1. Materials

Class C fly ash from Paiton Power Plant Indonesia was used as primary material to develop class C fly ash geopolymer mortar specimens. It has a high ferrite (Fe) and a low silicate (Si) contents. The chemical breakdown for class C fly ash material was identified by the X-Ray Fluorescence (XRF) test using PANalytical type Minipal 4 equipment. The chemical content of class C fly ash are shown in Table 1.

Table 1. Chemical composition of class C fly ash (mass %).

Materials	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	TiO_2	Mn_2O_3	SO_3
Fly ash class C	13.47	4.92	53.48	18.36	0.00	1.54	1.35	0.51	0.32

Fly ash in this study was class C fly ash. It had CaO of 18.36% (> 10%), the total SiO_2+Al_2O_3+ Fe_2O_3 of 71.87% (> 50%), and SO_3 of 0.32% (< 5%) in accordance with ASTM C618 [13]. A mix of sodium silicate with SiO_2/Na_2O ratio of 3.30 and sodium hydroxide (NaOH) were used as alkaline activators.

2.2. Mix design and proportion

The details of class C fly ash geopolymer (FACG) mortars mix proportion are shown in Table 2.

Table 2. Mix proportions of class C fly ash geopolymer mortars (FACG)

Mixture	Portland Cement	Class C fly ash	Fine sand	Sodium silicate	NaOH	Water	Molarity (M)
OPC	1	-	2.75	-	-	0.40	-
F`ACG-1	-	1	2.75	0.32	0.21	-	6
FACG-2	-	1	2.75	0.32	0.21	-	8
FACG-3	-	1	2.75	0.32	0.21	-	10
FACG-4	-	1	2.75	0.32	0.21	-	12
FACG-5	-	1	2.75	0.32	0.21	-	14
FACG-6	-	1	2.75	0.32	0.21	-	15

Mix proportions of FACG mortars were developed from previous research [14, 15], while OPC mortar specimen as control was developed in accordance with ASTM C109 [12] with a sand to binder ratio of 2.75. A sodium silicate to NaOH (SS/SH) ratio of 1.5 was applied in accordance with previous research [14]. A water to solid ratio of 0.35 was used for FACG mortars rather than a water binder ratio due to a solid content in NaOH and sodium silicate. The quantity of water in FACG mortars was calculated as the total sum of water in sodium silicate and NaOH solutions, while the quantity of solid was determined from the mass of the solid content in activator solution and class C fly ash raw material [15]. A normal curing temperature at room temperature used for OPC mortar was applied for FACG mortars. This is attributed to the high calcium (Ca) content in the raw class C fly ash material.

2.3. Testing mortar specimens

The strength characteristics of class C fly ash geopolymer mortars in 5 x 5 x 5 cm^3 cube specimens were carried out by compressive strength test using Universal Testing Machine (UTM) in accordance with ASTM C109 [12]. Three mortar geopolymer cubes were tested at the age of 3, 7 and 28 days after casting.

3. Results and Discussions

3.1. Strength development of FACG mortars

Table 3 and Figure 1 give the strength development reported for the FACG mortar specimens for all mixes curing at room temperature.

Table 3. Compressive strength of FACG mortars curing at room temperature

Mixture	Compressive strength (MPa)		
	3 days	7 days	28 days
OPC	10.28 ± 0.17	12.93 ± 0.17	18.31 ± 0.22
FACG-1	4.92 ± 0.41	7.46 ± 0.31	12.95 ± 1.36
FACG-2	5.22 ± 0.54	8.26 ± 0.15	15.85 ± 0.69
FACG-3	5.69 ± 0.11	8.91 ± 0.16	18.58 ± 1.31
FACG-4	6.21 ± 0.32	9.16 ± 0.18	22.47 ± 0.46
FACG-5	5.36 ± 0.17	8.01 ± 0.15	15.56 ± 0.12
FACG-6	3.92 ± 0.25	6.51 ± 0.23	15.05 ± 0.41

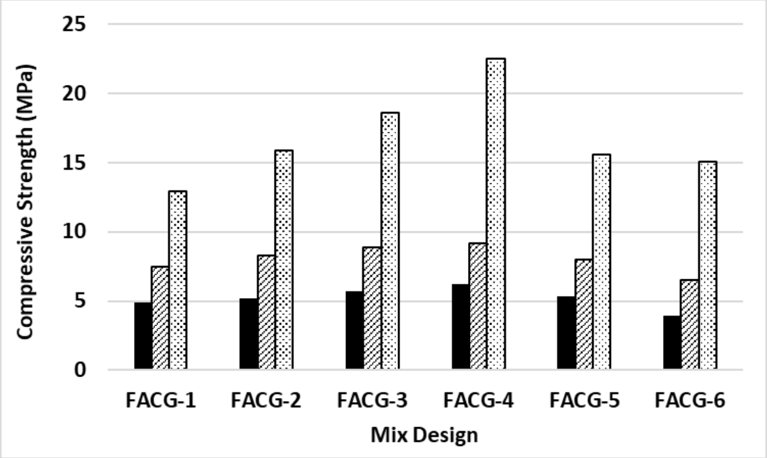

Figure 1. Strength development of FACG mortars throughout 28 days age

The result shows that FACG mortars exhibited a lower strength at early age compared to that OPC mortar. The highest early strength of FACG mortar specimens had merely achieved a compressive strength of 9.16 MPa (FACG-4), lower than OPC mortar with the strength of 12.93 MPa. However, all mixes demonstrated a significant increase in strength with time.

The highest compressive strength at early age was achieved by FACG-4 with 6.21 MPa (27.64% of final strength at 28 days) and 9.16 MPa (40.77%) at 3 days and 7 days, respectively, followed by FACG-3 with the strength of 5.69 MPa (30.62% at 3 days) and 8.91 MPa (47.95% at 7days). FACG-4 mortar was also demonstrated the highest final strength to all FACG mortars at 28 days with the strength of 22.47 MPa. The final strength of FACG-4 even exceeded the compressive strength of OPC mortar with 18.31 MPa at 28 days.

Table 4. Strength development ratio of FACG mortars from 3 to 28 days age

Mixture	Compressive strength ratio		
	3 to 28 days	7 to 28 days	28 days (Final)
OPC	0.56	0.70	1
FACG-1	0.38	0.58	1
FACG-2	0.33	0.52	1
FACG-3	0.31	0.48	1
FACG-4	0.27	0.41	1
FACG-5	0.34	0.51	1
FACG-6	0.27	0.43	1

Table 4 shows the strength development ratio of FACG mortar specimens throughout 28 days age. Ratio of strength development was determined based on the final strength at 28 days. The standard ratio of strength development of OPC (normal) mortar is 0.56 and 0.70 at 3 and 7 days, respectively as shown in Table 3. This finding was in accordance with ASTM Standard. According to ASTM C1074 [16], the maturity ratio of concrete strength development to the final strength at 28 days is 0.54 and 0.72 at the 3 days and 7 days, respectively. In contrary, all FAGC mortars demonstrates a lower strength development ratio at early age compared to OPC concrete. The highest ratio of FACG mortar was achieved by FACG-1 with the ratio of 0.38 and 0.58 at 3 days and 7 days, respectively. This ratio was significantly lower than the standard ratio of OPC mortar and ASTM C1074 standard. This indicated that the reaction rate of geopolymeric reaction are slower compared to that C-S-H reaction rate at OPC concrete. According to Silva et al. [17], the amount of aluminate (Al) available for the geopolymer reaction during synthesis process appears to have a significant effect of setting time, with an increase in molarity leading to a longer setting time. This was considered to be due to the alteration of the properties of the geopolymer during condensation. Despite the FAGC mortars exhibits the low value on strength development ratio, these mortars, i.e. FACG-4, show a better strength performance at later age.

3.2. *Effect of molarity on strength development*

Figure 2 displays the effect of molarity on strength development of non-cement class C fly ash geopolymer mortar specimens (a) at 3 days and 7 days age, and (b) at 28 days age.

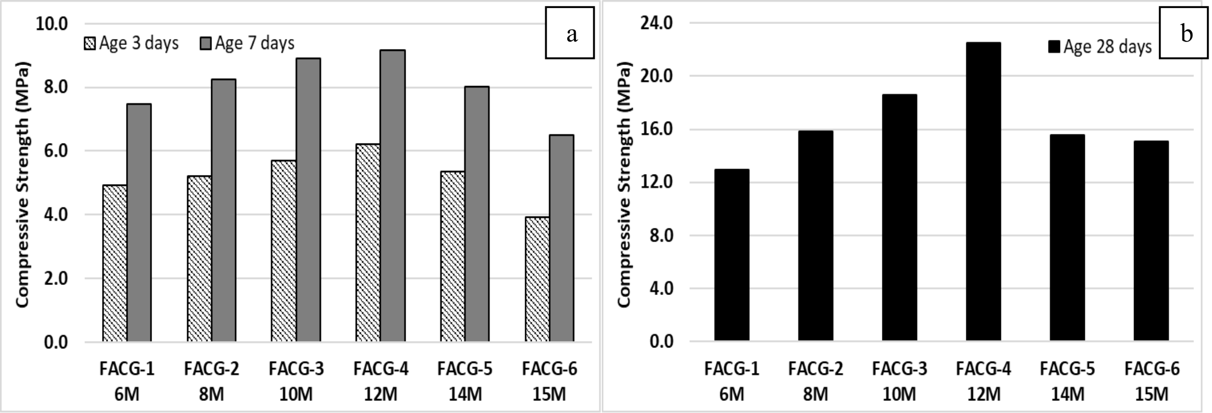

Figure 2. The effect of molarity on strength development of FACG mortar specimens at (a) 3 and 7 days, (b) 28 days

Figure 2 shows that sodium hydroxide (NaOH) molarity significantly affects the strength development of non-cement class C fly ash geopolymer (FACG) mortar specimens. The increase in molarity significantly increase the strength performance of FACG mortars. An increase of 7.55% strength showed in FACG-1 (strength of 4.92 MPa) to FACG-2 (strength of 5.22 MPa) with molarity of

6 Molar to 8 Molar at 3 days age. A further increase with an average strength increase of 9.07% has also identified in FACG-2 (8 Molar, 5.22 MPa) to FACG-3 (10 Molar, 5.69 MPa) and FACG-3 to FACG-4 (12 Molar, 6.21 MPa); with the highest strength performance was achieved by FACG-4 with 12 Molar at the age of 3 days. Similar strength performance was also identified on FACG mortars at the age of 7 days with the total increase of 22.79% from FACG-1 (6 Molar) to FACG-4 (12 Molar) with the strength increase from 7.14 MPa and 9.16 MPa. The highest increase of strength was demonstrated at the final ages (28 days) with the total strength increase of 73.51%. The final strength of FACG mortars increased from 12.95 MPa to 22.47 MPa along with the increase of molarity from 6 Molar (FACG-1) to 12 Molar (FACG-4). This finding was in accordance with previous researcher. According to Hardjito [18], the molarity of the NaOH as activator solution has a significant effect on the strength performance of the fly ash-based geopolymer specimens. In the geopolymer reaction, increasing the molarity will promote an acceleration in the reaction rate due to an increase in the soluble silicate and the higher concentration of reactants [18].

Figure 2 displays that an increase of molarity above 12 Molar did not significantly affect the strength performance of FACG mortar specimens. It tended to reduce the compressive strength at higher molarity. The increase of molarity from 12 Molar (FACG-4) to 14 Molar showed a strength reduction throughout 28 days. A decrease of 13.69% and 12.55% were shown in 3 days and 7 days with a strength reduction from 6.21 MPa to 5.36 MPa and from 9.16 MPa to 8.01 MPa, respectively. Further strength reduction was also observed at high molarity (15 Molar) with total reduction of 26.87% (at 3 days) and 18.73% (at 7 days) from 5.36 MPa to 3.92 MPa and from 8.01 MPa to 6.51 MPa, respectively. Similar behavior was also observed at 28 days age. A total strength reduction of 33.02% from 22.47 MPa to 15.05 MPa has identified at the increase of molarity from 12 Molar (FACG-4) to 15 Molar (FACG-6). Similar finding was found by previous researcher. According to Fernandez-Jimenez et al. [19], higher alkali modulus did not affect the strength development of geopolymer specimens. Increasing the alkali modulus causes a NaOH content reduction which is used to dissolve the Al_2O_3 and the SiO_2 monomer from the fly ash grain precursor material. Reducing the NaOH content will cause a reduction on the Na cations and affects the electric neutrality of Si-O-Al-O monomer in the geopolymeric matrix. This leads to a lower strength at higher molarity [19].

4. Conclusions

The effect of NaOH molarity on strength development of class C fly ash geopolymer mortars were studied experimentally from 3 to 28 days age. The primary conclusions may be drawn based on this study are: (1) Molarity of NaOH significantly affected the compressive strength development of class C fly ash geopolymer mortar specimens. (2) The optimum compressive strength was achieved by FACG-4 mortar with the molarity of 12 Molar throughout 28 days age. (3) Increasing molarity above 12 Molar did not significantly affect the strength development of class C fly ash geopolymer mortar but tend to decrease the mortar strength at higher value. (4) Despite the class C fly ash geopolymer mortar demonstrated a lower strength at early age, however, the 12 Molar geopolymer mortar showed a better strength performance compared to OPC mortar at later age.

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