

Sulphate Resistance of Geopolymer Concrete Based on High Calcium Fly Ash

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Abstract—The inclusion of fly ash class C, which is widely available locally, can influence the progress of strength and durability qualities of geopolymer concrete when exposed to significant environmental conditions. Alternative geopolymer combinations appropriate for curing at ambient temperatures were employed to investigate the impacts of high calcium (class C) fly ash -based geopolymer concrete. A combination of sodium hydroxide and sodium silicate alkaline activator was used to react with fly ash class C. Fly ash class C was added as 20% of the total binder without using ordinary Portland cement. The durability of fly ash class C-based geopolymer concrete in sulphate environments was tested. The changes in weight, length, and compressive strength due to exposure in magnesium sulphate solution for different periods of time were determined. The test results demonstrate that fly ash class C-based geopolymer concrete cured at normal temperatures has good resistance to sulphate attack. In general, inclusion of high calcium fly ash in geopolymer concrete improved strength and performed satisfactorily in sulphate environments when cured in ambient temperature.

Keywords—Ambient curing, Durability, Geopolymer, High calcium fly ash, Sulphate attack

I. INTRODUCTION

Portland cement is the primary material for the production of concrete globally, with an annual demand of more than 1.5 billion tons [1], [2]. However, Portland cement manufacture is energy-intensive and emits a substantial amount of carbon dioxide (CO₂) into the atmosphere [3]. Thus, the development of geopolymer concrete can play an important role in terms of sustainability and environmental concerns [4], [5]. Geopolymer binders can give an equivalent performance to standard cementitious binders in various applications while simultaneously reducing greenhouse gas emissions [6], [7].

The choice of raw materials for geopolymers is influenced by availability, affordability, application, and end-user demand [8], [9]. Even though the microscopic characteristics of alumina-silicate-based geopolymers may appear identical, the microstructure and properties of geopolymers depend heavily on the nature of the initial raw materials [10].

Due to the creation of a compact microstructure in the geopolymer matrix, fly ash-based geopolymers cured by heat displayed a high compressive strength [11]. Permeability is the primary determinant of the durability of concrete. Lower permeability provides more excellent resistance to the admission of hostile ions into concrete, hence reducing the degree of concrete deterioration. Sulphate resistance is a crucial characteristic of concrete. This is due to the fact that sulphate can occur naturally in soil and groundwater, as well as in industrial and mining effluents. When exposed to a sulphate environment, the mass and compressive strength of the concrete may diminish. It was discovered that heat-cured geopolymer concrete had excellent sulphate resistance [2], [12].

External sulphate attacks are a chemical breakdown mechanism in which sulphate ions from an external source attack cement paste components (calcium hydroxide,

calcium silicate hydrate, and aluminate components). According to previous research, sulphate attack on OPC concrete results in cracking, softening, and disintegration. Due to the presence of aluminosilicate gel in geopolymer materials, the interaction of geopolymer materials with sulphate solution differs dramatically from that of OPC. Moreover, the geopolymer concrete's stability depends on the kind and concentration of activator and the type of cation in the sulphate medium [7], [13].

The majority of prior studies were conducted on geopolymer concrete that was heat-cured. The production of heat-cured concrete that is excellent for precast goods requires a heating source. In addition to precast applications, the production of geopolymer concrete by curing at room temperature would enable its usage in cast-in-situ applications. Early age strength growth of fly ash-based geopolymer concrete cured at room temperature was less than that of heat-cured specimens [14], [15]. At ambient temperature, the main disadvantages of fly ash-based geopolymer concrete are its slow setting and strength growth. Consequently, this work aimed to develop geopolymer concrete appropriate for ambient curing conditions. The use of high calcium fly ash or called fly ash class C, considering the availability of waste materials from industrial sectors, which over 60% are classified as this type of fly ash. In addition, the use of this type of fly ash also accelerates the curing of ambient temperatures due to its mechanical compound that is easy to harden. It is also considered to have high compressive strength compared to low calcium fly ash or fly ash class F which is challenging to attain. Further, the resistance against the sulphate attack of geopolymer concrete was studied.

II. METHOD

A. Materials

High calcium 'Class C' fly ash locally available in East Java, Indonesia, was used for this study. Then, to know its effect, micromechanically investigation under X-ray

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Diffraction and X-ray Fluorescence was included in the investigation. Table 1 shows the chemical composition of the fly ash class C. This type of fly ash normally used as Portland cement replacement ranging from 20 to 35% of the mass of cementitious material.

Other ingredients used in this study included local coarse and fine aggregates, alkaline solutions, and water. The coarse aggregate consisted of crushed granite with nominal maximum sizes of 7, 10, and 20 mm, as specified by Indonesian Standard [16]. The final combined aggregate volume comprised 41% of 20 mm aggregate, 9% of 10 mm aggregate, 15% of 7 mm aggregate, and 35% of sand. All three types of coarse aggregates were mixed with sand to produce a properly graded aggregate mixture. In total fineness modulus of the combined coarse aggregate was 6.12. Fine aggregates having a specific gravity of 2.82, unit weight of 1600 kg/m³, and fineness modulus of 2.25 was used. Then, coarse aggregate has slightly different values for specific gravity, 2.73, unit weight of 1300 kg/m³, and fineness modulus of 3.59. Both materials have water absorption, 0.69 % and 2.19%, where moisture is 0.57 % and 0.52%, respectively. The alkaline activator was a combination of sodium hydroxide and sodium silicate solution. A sodium hydroxide solution of 14M concentration was prepared by mixing 97-98% pure pallets with tap water. Sodium silicate solution with SiO₂ to Na₂O ratio by mass of 2.61 (SiO₂=29.11%, Na₂O=29%, and water 1%) was used.

TABLE 1.

CHEMICAL COMPOUNDS OF HIGH CALCIUM FLY ASH

Sample	Fly ash (%)	Class C fly ash ^a (%)	Class F fly ash ^a (%)
SiO ₂	9.45	-	-
Al ₂ O ₃	24.85	-	-
Fe ₂ O ₃	30.7	-	-
SiO ₂ + Al ₂ O ₃ +	65	50.0 min	70.0 min
Fe ₂ O ₃			
CaO	27.2	-	10.0 max
Na ₂ O	0.36	-	-
K ₂ O	1.26	-	-
SO ₃	0.35	5.0 max	5.0 max
P ₂ O ₅	0.45	-	-
TiO ₂	1.3	-	-
MnO	0.315	-	-
MoO ₃	3.4	-	-
LOI ^b	0.68	6.0 max	6.0 max

^a ASTM C618 [17], ^b Loss on ignition

TABLE 2.

MIXTURE PROPORTIONS (KG/M³) UNDER DRY AND WET CONDITIONS

Content	Dry (kg/m ³)	Portion(%)	Wet (kg/m ³)	Portion (%)
CA ^a	1242.61	49.7	1242.61	49.7
Sand	548.83	21.9	548.83	21.9
Fly Ash	467.36	18.7	467.36	18.7
Cement	-	-	-	-
SH ^b	119.18	4.8	48.6	1.9
SS ^c	119.18	4.8	55.45	2.2
Water	-	0.0	134.3	5.4
SP ^d	4.67	0.2	4.67	0.2

^a Coarse aggregate, ^b Sodium hydroxide, ^c Sodium silicate,

^d Superplasticizer

B. Manufacture of Geopolymer Concrete

The proportions of the concrete mixtures were based on earlier research on geopolymer concrete cured at ambient temperature [10], [11], [14], [15], [18], [19]. During the investigation, the following characteristics were considered: aggregate content, alkaline activator solution, sodium silicate to NaOH ratio, the molarity of NaOH solution, and curing process. The geopolymer mixes were designated according to their varied ingredients using wet and dry methods to categorize weight. These two methods can be seen in Table 2.

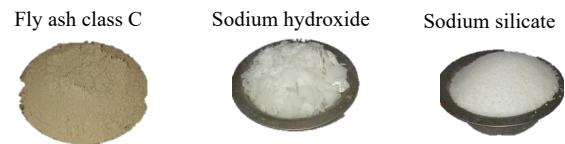


Figure 1. Main ingredient of fly ash based geopolymer



Figure 2. Semi-automated grinding machine



Figure 3. Specimen under ambient temperature



Figure 4. The specimen under sulphate solution

For example, in this mixture, cement was replaced by fly ash for geopolymer mixtures. This replacement also considers several aspects as cited in prior research [20], [21]. SP was added to increase the workability of the mixture. The mixtures were designed with variable silicate to sodium hydroxide ratio (SS/SH), containing fly ash as 20% of the total binder. Illustrated materials can be seen in Figure 1, whereas the grinding process is shown in Figure 2. Figure 3–4 shows cured cylinder specimens under two different case studies, i.e., ambient temperature and sulphate solutions.

The alkaline activator consisted of a fluid mixture of sodium silicate and sodium hydroxide. Approximately

thirty minutes prior to the actual mixing of the concrete, the alkaline activator was made in the laboratory by combining sodium silicate and sodium hydroxide solutions in the needed proportion. Initially, the fly ash and aggregates were combined in a pan mixer. The activator solutions were then added to the dry components, mixing proceeded for 3 to 5 minutes to make fresh geopolymer concrete.

C. Testing of Geopolymer Concrete Specimens

The workability of fresh concrete was determined by slump test using the ASTM C 143 method (13). 100 mm in diameter and 200 mm in height geopolymer concrete specimens were cast and cured in ambient conditions at 15-20°C and 70±10% relative humidity. 100 mm in diameter and 200 mm in height cylinder specimens were cast for compressive strength (14) and change in mass testing. 7-day-old prism samples were submerged in a 5% magnesium sulphate solution for length change testing. At the age of 28 days, the cylinder samples were immersed in a sulphate solution to determine the changes in compressive strength and mass.

III. RESULTS AND DISCUSSION

A. Workability of fresh concrete

The workability of freshly mixed geopolymer concrete was evaluated using the slump test per ASTM C 143 and SNI 1970-2008 [17] immediately after the concrete was mixed. Slump values are presented in Figure 5. The spherical shape of fly ash class C particles and the lubricating effect of magnesium silicate solution enhances the fresh geopolymer concrete's flowability and slump values. Sodium silicate and sodium hydroxide solutions, which are more viscous than water, are typically used to increase the cohesiveness of geopolymer concrete. Incorporating water and superplasticizer into the fly ash-blended mixtures enhanced their workability. The slump values of the mixtures ranged from 155 to 180 millimeters, satisfying the code in the range of 150 to 230. During the casting process, it was observed that the mixtures had adequate workability. In contrast, when it compared to the OPC mixture, geopolymer concrete mixtures exhibited greater cohesiveness.

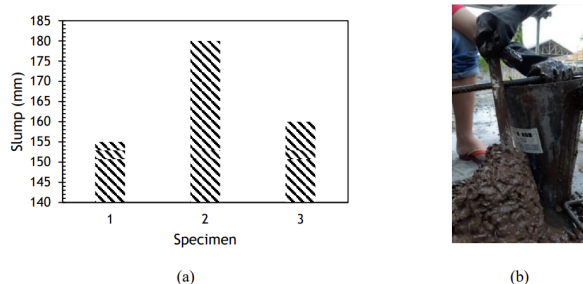


Figure 5. Slump test under different specimens; (a) slump value varied by specimens, (b) illustrated taken sample of slump test in accordance with ASTM C 143 [22]

B. Compressive Strength

The compressive strength of the geopolymer concrete mixtures using fly ash class C for up to 90 days is given in Table 3. The strength development of geopolymer concrete mixtures under ambient temperature relatively slowed after 7 days and continued at slower rates until 90

days of age. Regarding the sulphate resistance specimen, similar conditions were applied to inform relatively high compressive strength value with high intensity of decreasing. It continued lower after 28 days until 90 days.

Geopolymer concrete with fly ash class C, developed strength at a slow rate when cured in ambient conditions. When geopolymer concrete was incorporated in the sulphate (added MgSO₄ solution), the strength increased significantly. At 28 days, geopolymer under sulphate increased by over 20% whereas concrete at normal condition was limited to increase by under 2%. The change in compressive strength was determined by testing the specimen after 28 days to 90 days of immersion in 5% magnesium sulphate solution. As a comparison of the change in compressive strength in sulphate solutions, a set of concrete specimens from the same batch cured at ambient conditions was also prepared and tested in the same manner.

TABLE 3. COMPRESSIVE STRENGTH UNDER TWO DIFFERENT CONDITIONS – NORMAL VS SULPHATE [23]

Sample	Geopolymer concrete with fly ash class C (MPa)	
Label	Normal condition / ambient temperature	Sulphate resistance
7 days	42.78	42.78
28 days	42.44	50.89
56 days	43.54	48.04
90 days	42.44	39.98

C. Mass Change

For various durations of immersion in sulphate solution, the change in mass of the concrete cylinders was measured by ASTM C267-01 [24]. Table 4 displays the mass changes of all geopolymer concrete specimens in magnesium sulphate solution. During the first week of immersion, the concrete specimens gained a small amount of mass due to the solution absorption. The geopolymer concrete specimens did not lose mass when exposed to the sulphate solution, as shown in Table 4. This indicates that, in contrast to geopolymer concrete under ambient temperature, geopolymer concrete was not eroded when exposed to the sulphate solution. The results demonstrate that the geopolymer concrete mass is stable in sulphate solution.

The visual appearance of samples after immersion in magnesium sulphate for 90 days showed a change in appearance which appeared the formation of several layers of softening on the surface of the concrete. The long immersion forms a thick white layer on the concrete surface.

The sulphate will bind to the hydration products of the binder, which calcium silicate hydrate (CSH), calcium hydroxide (CH), and calcium aluminate hydrate (C3A). This reaction produces the following products: gypsum, ettringite, thomasite, and brucite. Gypsum is a CH or CSH reaction product, SO₄²⁻ and water. The formation of gypsum will result in a reduction in stiffness and strength, expansion and cracking, and ultimately the transformation of the material into a mushy and incohesive mass.

Ettringite is produced from the reaction between sulphate, Ca^{2+} , and mono-sulphate ($\text{C}_4\text{ASH}_{12}$). This reaction expands enormously, resulting in microstructure densification. Then, it is followed by internal stresses that cause cracking and crushing of the concrete. Thomasite is formed from sulphate or ettringite, which reacts with CSH, CO_3^{2-} , Ca^{2+} , and excess water. It is generally assumed that Thomasite is formed at temperatures below 15°C . The formation of thomasite causes loss of strength and decomposition (change) of the microstructure.

The interaction between the hydrated cement paste and the MgSO_4 solution is the reaction between the salt and CH of the paste, producing gypsum and brucite, $\text{Mg}(\text{OH})_2$. Brucite is practically insoluble, and its formation destabilizes CSH. In the end, this phase changes to amorphous silica hydrate (SiO_2 – silica gel) or magnesium silicate hydrate (MSH). In addition, CH is released in the solution. CH reacts again with MgSO_4 , and the process continues. Mg^{2+} can also displace Ca^{2+} from CSH and form MSH. MSH causes loss of strength and expansion, while brucite forms a protective layer, which slows down the degradation process

TABLE 4.

MASS CHANGE UNDER TWO DIFFERENT CONDITIONS – NORMAL VS SULPHATE

Sample	Geopolymer concrete				
Exposed period (days)	0	7	28	56	90
Average sample cured at ambient	3894	3891	3888	3882	3880
Average sample at sulphate solution	3900	3898	3893	3892	3890
Change in mass (%)	+ 6	+ 7	+ 5	+ 10	+ 10
Change in strength (%)	+ 0	+ 16	+ 8.45	+ 4.5	-2.46

D. Environment control-change in pH Solution

The pH test was carried out to determine the change in the degree of acidity or pH contained in the magnesium sulphate solution. This change in pH needs to be conducted to ensure the environmental condition that relates to the changing behavior of specimen. The results obtained after taking measurements using a pH meter are presented in Figure 6. There was no significant effect after cycle times 14 days. In the first two weeks of investigation, pH relatively changes due to the difference of solution within the condition of the concrete. The same behavior was also reported by previous studies [25], [25], when pH intent to stabilize after a certain amount of time.

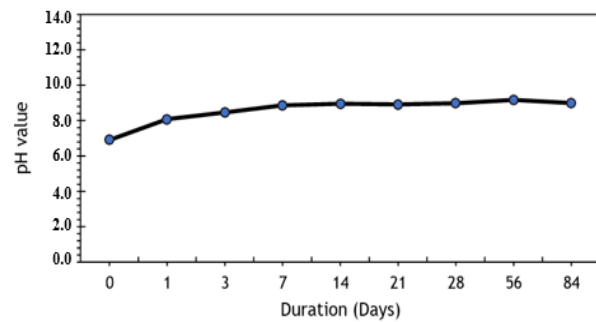


Figure 6. Environment pH control under magnesium sulphate solution

IV. CONCLUSION

A development of geopolymer concrete were designed with fly ash class C as the binder sources materials. Compressive strength and sulphate resistance of the ambient cured geopolymer concrete specimens were compared to coo borate findings. The results of the study are summarized as follows. Inclusion of fly ash class C up to 20% of the total binder improved early-age strength. The ambient cured geopolymer concrete's compressive strength is nearly the same at 42 MPa compared to that of the sulphate solution, which varied from 42 MPa to 51 MPa. The resistance to sulphate attack improved with the mixtures' fly ash class C content. There was no significant change in mass of specimen in the duration of 90 days of investigation of sulphate exposure. Moreover, the geopolymer concrete showed high compressive strength under sulphate solution.

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