Optimization of SiO$_2$/Al$_2$O$_3$ Ratio in the Preparation of Geopolymer from High Calcium Fly Ash

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Abstract. High-calcium fly ash-based geopolymers have been successfully synthesized. The source of fly ash used in this study is fly ash from PT. IPMOMI, PT. Holcim and Paiton PLTU 9. The variation in the mole ratio of SiO$_2$/Al$_2$O$_3$ carried out in this study was 3,0; 3,3; 3,6; 3,9 and 4,2. Compressive strength tests were carried out on geopolymers aged 7, 14, and 28 days. A geopolymer with a ratio of 3,6 has the best compressive strength. The compressive strength test results for IPMOMI, Holcim, and Paiton 9 geopolymers were 75,37; 50,95; and 39,25 MPa. The highest geopolymers with compressive strength were characterized using XRD and SEM. The results of the XRD showed that geopolymers had an amorphous phase and gibbsite mineral in the three geopolymers which indicated that there was still Al(OH)$_3$ which had not reacted. Microstructure analysis using SEM shows the all of three solid structure of geopolymers. There is efflorescence on Holcim and Paiton 9 geopolymers which causes lower compressive strength than IPMOMI geopolymers.

1. Introduction
The increasing number of power plants (PLTU) will increase the used of coal which also affects the production of ash especially in the form of fly ash by 80-90% and bottom ash 10-20% [1]. Fly ash waste treatment process is difficult to do because it is dense, insoluble, and nonvolatile, so it makes fly ash categorized as hazardous and toxic wasted (B3). Fly ash is a material with the main content of silica and alumina. Silica and alumina from fly ash are very important in the formation of Si-O-Al chains in geopolymers. According to ASTM C 618 (1994). Fly ash can be classified into two class based on their content, namely C and F. Class C fly ash is produced from the combustion of lignite and subbituminous coal type which have silica and alumina content of less than 50% and calcium oxide content (CaO) more than 10% (ASTM C 618, 1994). Whereas Class F fly ash produced from burning anthracite and bituminous coal contains silica and alumina content more than 50% and CaO less than 10% [2]. The different types of fly ash used will affect the synthesized geopolymer. Class C fly ash (High Ca content)
is composed of glassy phases that rich in calcium-alumino-silicate and various crystalline phases that not found in class F fly ash. This indicated that C class fly ash has higher reactivity than grade fly ash F and this can be seen from the shorter setting time when synthesized into geopolymer [3].

The factors that affect the geopolymerization of the dissolved reactants are well understood, some of which relate to the ratio of dissolved metal reactants such as SiO$_2$/M$_2$O, SiO$_2$/Al$_2$O$_3$, M$_2$O/H$_2$O dan M$_2$O/Al$_2$O$_3$, where M is sodium or potassium [4]. Based on previous study, the Si/Al molar ratio is very influential in the microstructure and mechanical properties of geopolymers that are formed at room temperature [5]. [6] report that the SiO$_2$/Al$_2$O$_3$ ratio plays an important role in the increase of geopolymer strength. At low Si/Al molar ratios, the initial strength is very dependent on the amount of the Al$_2$O$_3$ so geopolymer will harden more quickly. Whereas in geopolymers having higher SiO$_2$/Al$_2$O$_3$ ratios, they will harden longer. This happens because the Al species control the hardening time of the geopolymer. Also, the SiO$_2$/Al$_2$O$_3$ ratios affect the compressive strength of geopolymers. Geopolymers with high SiO$_2$/Al$_2$O$_3$ have greater strength than the lower ratio of SiO$_2$/Al$_2$O$_3$. This is because the solubility of Al$_2$O$_3$ is greater than SiO$_2$. So, the optimum SiO$_2$/Al$_2$O$_3$ ratio needs to be investigated to get the best geopolymer. [6] added that, geopolymers with the best strength at the SiO$_2$/Al$_2$O$_3$ mole ratios of 3.4-3.8. Therefore this research was carried out by geopolymer synthesis of 3 types C basic ash (high calcium contents) namely the basic ash from PT. IPMOMI, PT. Holcim and PT. Paiton unit 9 with various SiO$_2$/Al$_2$O$_3$ ratios to find the best characteristic of geopolymer.

2. Experimental

2.1. Material

The material used for the epoxidation are Fly ash (FA) from Java, Indonesia. Fly ash was collected from three different Power Plant in Indonesia (IPMOMI, Holcim, and Paiton 9 Power Plant). Alkaline activator used is a combination of Sodium Hydroxide (Merck, 14M) and 80 gram of commercial Sodium Silicate (PT. Brataco, 28,79% SiO$_2$, 19,35% Na$_2$O, dan 28, 94% H$_2$O), Al(OH)$_3$ (Sigma-Aldrich, 99%) was added to provide the Al species on geopolymer and SiO$_2$/Al$_2$O$_3$ ratio on geopolymer also distilled water.

2.2. Geopolymer synthesis

Alkaline activator is prepared by combining sodium hydroxide and sodium silicate. NaOH pellets are dissolved in distilled water until homogeneous. Sodium silicate (Na$_2$SiO$_3$) was added to the NaOH solution to form an alkaline activator with the regenerate heat from the reaction. Solid of Al(OH)$_3$ was dissolved in distilled water to form Al(OH)$_3$ suspension. Fly ash is mixed with Al(OH)$_3$ suspension and stirred for a few minutes. Then the alkaline activator (NaOH and Na$_2$SiO$_3$) was added with the fly ash mixture and mixed for 4 minutes. The homogeneous paste is then formed and poured into a cylindrical PVC mold with a height: diameter of 2:1. Geopolymer paste is vibrated to remove the gas bubbles that formed and placed at room temperature until it hardens (24 h). After that, a geopolymer can be taken out from the mold and then cured with temperatures carried out in the oven at 55 °C for 24 h. Furthermore, geopolymer is placed at room temperature for 7, 14 and 28 days and then its compressive strength will be tested.

2.3. Characterization

X-Ray Diffraction Xpert PANalytical characterization result with Cu Kα radiation (λ=1,5406 Å), 40kV and 30mA of voltage and current, 2°/minute angular speed with 0,02° stepsize (2θ = 5-90°). The chemical bond analysis was carried out by FTIR in the ITS Chemistry Instrument Laboratory. The spectra were detected at 400 to 4000 cm$^{-1}$. Geopolymer sample powder was mixed with KBr at a ratio of 1:9. Morphological analysis of geopolymer particles was done by SEM at the Energy and Environmental Laboratory, Institute of Research and Community Service (LPPM) ITS using SEM brand Zeiss EVO MA-10. The compressive strength of Synthesized geopolymer with 7, 14 and 28 day aged will be tested.
with the Universal Testing Machine in the Infrastructure engineering of ITS laboratory. The compressive strength will be reported in MPa units with Indonesian Brick Standard Number (SNI 03-0349-1989) with a minimum of 9.8 MPa.

3. Results and Discussions

3.1. Analysis chemical content of fly ash
Fly ash from different sources is likely to have different characteristics. This because of its characteristics that influenced by the method of combustion, coal sources, and combustion temperature used in each power plant (PLTU) [7]. The chemical composition analysis was carried out using X-ray Fluorescence (XRF). The results of XRF analysis present in the form of a percentage of elements in the form of oxides such as SiO$_2$, Al$_2$O$_3$, Na$_2$O, and CaO. IPMOMI fly ash is 50.67%, 13.76%, 0.19%, and 12.70%. Holcim fly ash is 42.19%, 20.33%, 2.25%, and 13.04%. Paiton 9 fly ash is 31.03%, 8.66%, 1.65%, and 14.84%. The results of the analysis using XRF can be used to determine the type of fly ash used included in type C or F. Fly Ash from IPMOMI, Holcim, and Paiton 9 power plants show a Ca content above 10%, so that is classified as a type C (ASTM, C618). The high content of Ca in geopolymers can speed up the setting time of geopolymers [8]. So, the results of the synthesized geopolymer will harden faster than geopolymers from type F.

This hardening occurs because calcium ions (Ca$^{2+}$) help the formation of geopolymer networks and accelerate the geopolymerization process by forming more N-A-S-H (Sodium-Alumnum-Silicate Hydrated) gel, so the compressive strength becomes higher. However, more Ca$^{2+}$ content also increase the hydration in addition to the geopolymerization process. The formed gel product changes from N-A-S-H gel to C-S-H (Calcium Silicate Hydrated) and can affect the polymerization of Si-O-Al and Si-O-Si bonds. Ca$^{2+}$ ions are more reactive than Na$^+$ and K$^+$ ions, so Ca$^{2+}$ ions can react faster with SiO$_4^{4-}$ or Si-O-Si bonds to form C-S-H gel. The C-S-H gel weaker than an N-A-S-H gel at ripening room temperature, but has a faster setting time [9].

3.2. Determination the Optimum SiO$_2$/Al$_2$O$_3$ Molar Ratio on Geopolymer Synthesis
The molar ratio of SiO$_2$/Al$_2$O$_3$ is one of the important factors in geopolymer synthesis. The ratio of Si and Al in geopolymer can affect the microstructure and physical character of the geopolymer which will be synthesized [10]. The SiO$_2$/Al$_2$O$_3$ ratio can be determined by calculating the silicate and aluminate molar ratios dissolved in the geopolymer mixture. In this study, the varying Si/Al molar ratios were done by varying the molar of Al$_2$O$_3$ with constant SiO$_2$ molar. This because varying the Si/Al molar ratio with constant SiO$_2$ only needs to adjust the amount of Al(OH)$_3$ without changing other compositions, so the other variables such as the solid/liquid ratio can be constant. In this study, SiO$_2$/Al$_2$O$_3$ molar ratio variations start from 3; 3.3; 3.6; 3.9; 4.2 with the addition of Al(OH)$_3$. According to the [11], the best geopolymer can be obtained with a Si/Al molar ratio between 3.3-4.5. In addition, the previous study by [12] obtained the maximum compressive strength of geopolymers at the SiO$_2$/Al$_2$O$_3$ molar ratio of 3-3.8.

3.3. Compressive Strength
Geopolymers were subjected to compressive strength tests at 7, 14, and 28 days. This test was conducted to determine the optimum SiO$_2$/Al$_2$O$_3$ geopolymer molar ratio so that it has the highest compressive strength. The last test was carried out at 28 days because after 28 days the geopolymer did not show significant strength changes. The results of the compressive strength test can be seen in table 1. Increasing the SiO$_2$/Al$_2$O$_3$ mole ratio to 3.6 causes the compressive strength increase. However, the mol ratio of 3.9 and 4.2 the compressive strength has decreased. The high compressive strength in geopolymers can be caused by two factors. First, because the higher SiO$_2$/Al$_2$O$_3$ ratio can produce more Si-O-Si bonds. The Si-O-Si bond is a stronger bond than the Si-O-Al bond, so the more Si-O-Si bonds are formed, the higher the compressive strength of the geopolymer. The second factor is that the
remaining silica can act as a reinforcement. This is because silica has a strong interface bond between the binding phase and silica [10].

### Table 1. Compressive strength of geopolymer.

| Geopolymer   | 7 days (MPa) | 14 days (MPa) | 28 days (MPa) |
|--------------|--------------|---------------|---------------|
| IPMOMI-4,2   | 10.62        | 47.77         | 75.37         |
| IPMOMI-3,9   | 26.54        | 47.8          | 48.83         |
| IPMOMI-3,6   | 26.53        | 26.53         | 75.37         |
| IPMOMI-3,3   | 12.74        | 23.35         | 46.71         |
| IPMOMI-3,0   | 13.80        | 14.86         | 44.58         |
| Holcim-4,2   | 12.74        | 35.03         | 38.22         |
| Holcim-3,9   | 18.04        | 37.16         | 46.71         |
| Holcim-3,6   | 28.66        | 42.46         | 50.95         |
| Holcim-3,3   | 12.80        | 22.29         | 47.77         |
| Holcim-3,0   | 16.98        | 25.48         | 49.89         |
| Paiton 9-4,2 | 9.56         | 10.61         | 31.85         |
| Paiton 9-3,9 | 16.98        | 16.98         | 25.48         |
| Paiton 9-3,6 | 11.67        | 22.29         | 39.28         |
| Paiton 9-3,3 | 8.49         | 6.36          | 15.93         |
| Paiton 9-3,0 | 7.43         | 7.43          | 11.67         |

### 3.4. Characterization Geopolymer

#### 3.4.1. Geopolymer Phase Analysis using X-Ray Diffraction.

The sample tested was a geopolymer with a SiO$_2$/Al$_2$O$_3$ molar ratio of 3.6 for all types of fly ash. The amorphous phase was indicated by the appearance of humps, while the crystalline phase is indicated by the appearance of the sharp peaks. From figure 1 can be seen humps at $2\theta = 15$-40° which is an amorphous phase in all three geopolymers. This indicated that the geopolymer matrix has formed as a result of the dissolution of the amorphous phase of fly ash in a strongly alkaline solution. However, only the reactive Si and Al which have an amorphous phase and are easily dissolved in a base that will form a geopolymer matrix. In addition to the amorphous phase, the three geopolymers also contain quartz and mullite minerals as the main minerals. Quartz mineral has shown at the highest peak of $2\theta = 26.96^\circ$. Other quartz mineral peaks are shown at $2\theta = 21.16^\circ, 31.14^\circ, 50.44^\circ$ dan $50.5^\circ$. Whereas the mineral mullite is shown at $2\theta = 33.4^\circ, 35.58^\circ, 35.74^\circ$; dan $60.2^\circ$. Beside quartz and mullite, there are other minerals in the form of gibbsite at $2\theta = 18.36^\circ, 36.86^\circ$ dan $41.16^\circ$. The presence of gibbsite minerals indicated that there is Al(OH)$_3$ in the crystalline phase which is not reactive or dissolved in the alkaline activator. Al(OH)$_3$ which is not reactive will become a space filler in the geopolymer structure [13].

Based on the diffractogram results, there are differences in geopolymer diffractograms, Holcim geopolymers does not have several quartz and gibbsite peaks, such as IPMOMI and Paiton 9 at $2\theta =$
18,36°, 41,16°, 50,44° dan 50,5°. However, Holcim geopolymers does have mullite peaks appear at 2θ = 60.2°, which in IPMOMI and Paiton 9 geopolymers does not appear. This can be caused by the reactive silica and alumina content in Holcim more than IPMOMI and Paiton 9 so that the ability to form Si-O-Al bonds is more as well and geopolymerization is faster to form mullite. This reasoning is in accordance with the compressive strength results of 7, 14, and 28 days. That at the age of 7 and 14 days geopolymers, Holcim geopolymers have higher compressive strength compared to IPMOMI and Paiton 9 geopolymers.

![Difractogram geopolymer](image)

Figure 1. Difractogram geopolymer.

3.4.2. Morphological Analysis of Geopolymer using Scanning Electron Microscope. Geopolymer analyzed with a SiO$_2$/Al$_2$O$_3$ mole ratio of 3.6 at the age of 28 days which has the highest compressive strength. This analysis is done to find out the effect of the SiO$_2$/Al$_2$O$_3$ mole ratio to the geopolymer microstructure. Figure 2 (a-c) shows the three geopolymers have a solid structure and are bound to one another indicates reactants undergo a geopolymerization process. IPMOMI geopolymers have fewer pores than other geopolymers. Fewer pores causing geopolymer structure to be denser and stronger high press. Many pores are caused by bubbles air trapped during the synthesis process. However on IPMOMI geopolymers (figure 2a) still look fly ash who have not reacted. This can be seen in the microstructure IPMOMI geopolymers still have small particles. In Holcim and Paiton geopolymers, there are white fibers can be seen in figure 2c. These fibers were the result of efflorescence. Efflorescence is the formation of white salt around the surface geopolymer. The emergence of efflorescence due to excess alkaline solution involving the reaction of Ca(OH)$_2$ with water and CO$_2$ [14]. Efflorescence has a negative impact on geopolymer strength. This is because efflorescence appears in geopolymer pores and growing bigger can damage the structure in geopolymers. Also, efflorescence too consumes alkaline bases, thus disturbing the system geopolymerization [15].
4. Conclusions
Fly ash-based geopolymers with high calcium content can be synthesized using \( \text{SiO}_2/\text{Al}_2\text{O}_3 \) mole variations with the addition of \( \text{Al(OH)}_3 \) as a source of \( \text{Al}_2\text{O}_3 \). The highest compressive strength obtained at the \( \text{SiO}_2/\text{Al}_2\text{O}_3 \) molar ratio of 3.6 for geopolymer Paiton 9, Holcim, and IPMOMI sequentially namely 67.94; 50.95; and 39.25 MPa. The XRD analysis results showed that the Paiton 9, Holcim and IPMOMI geopolymers have an amorphous phase with quartz and mullite minerals. There are gibbsite minerals in the three geopolymers which indicate that there is still \( \text{Al(OH)}_3 \) that has not yet reacted. Microstructure analysis using SEM shows the three solid structure geopolymers. IPMOMI geopolymers have fewer pores than others, but there are still unreacted fly ash particles. There is efflorescence on Holcim and Paiton 9 geopolymers which causes lower compressive strength than IPMOMI geopolymers.

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