Geopolymerization of Fly Ashes From 6 Indonesian Power Plants Using A Standardized Recipes

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Abstract. Geopolymers were synthesized using fly ash as raw material from six steam power plants, Adipala (FA1), Indramayu (FA2), Paiton 9 (FA3), Asam-asam (FA4), Pulau Pisang (FA5), and Sanggau (FA6). Fly ash was tested for several characteristics using XRF, XRD, and SEM. XRF analysis showed FA1, FA4, and FA5 included in class C fly ash while FA2, FA3, and FA5 included in class F. The XRD analysis results showed that there were typical peaks of quartz, mullite, calcite, magnetite, and hematite in the fly ash samples. SEM analysis shows the morphology of the fly ash FA1, FA2, FA3, and FA4 spherical with different particle sizes, but in the fly ash FA5 and FA6, the morphological shape is irregular. The highest compressive strength test results obtained by geopolymers made from FA3 after 28 days with compressive strength values of 36.62 MPa. The intensity of the crystalline geopolymer phase decreases when compared to its fly ash. Geopolymer morphology shows the presence of unreacted fly ash particles.

1. Introduction

Fly ash is a hazardous materials from burning coal in the steam power plant [1, 2]. Fly ash consists of inorganic materials that unburnt in coal which are fused during combustion into amorphous glass structures. Combustion of coal in the power plant produces solid waste in the form of fly ash and bottom ash [3,4]. Ash particles carried by the flue gas are called fly ash, while ash left behind and removed from the furnace is called bottom ash [5]. Fly ash production in Indonesia continues to increase every year. Fly ash production is increasingly abundant in line with the implementation of the Minister of Energy and Mineral Resources (ESDM) Decree 2018 concerning procurement (Independent Power Producer/IPP) with a target of 35,000 MW. This high electricity capacity target is directly proportional to the consumption of coal used as the main energy source. This is also seen by coal production which has increased every year, namely 456 million tons in 2016 and increased to 538 million tons in 2018 [6,7]. Fly ash is generally piled up on landfills or simply piled inside industrial areas. The buildup of fly ash causes problems for the environment and health because it is dangerous.

Another way to solve this problem is to convert fly ash into other materials useful and valuable material, such as geopolymers [8,9]. The name geopolymer was first popularized by Davidovits, who began looking for non-flammable construction materials [10-12]. Geopolymers are the result of alkaline activation by materials containing alumina and silica [13]. Fly ash is one of the ingredients containing alumina and silica.
In 2016 the Ministry of Energy Resources reported that Indonesia has 136 power plants distributed throughout the islands in Indonesia. Power plants in Java differ in power capacity from power plants in Kalimantan, so the character of the fly ash produced also varies. The properties of geopolymers were dependent on the characteristics of the fly ash used (chemical composition, levels of morphants, number of silicate ions and soluble aluminates, and particle size distribution) [14-17]. The properties of the fly ash depend on the type of raw coal and the coal combustion process. Each fly ash has different chemical and physical properties and this affects the geopolymerization process of fly ash [18-20]. Therefore, in this study, an investigation was conducted on the influence of the chemical-physical properties of fly ash produced from various sources on the synthesis of geopolymers and the properties of the resulting geopolymers.

2. Methodology

2.1 Materials
In this study, fly ashes (FA) were collected from coal fired-power plants in Java namely Adipala (FA1), Indramayu (FA2), Paiton 9 (FA3), and in Kalimantan namely Asam-Asam (FA4), Pulau Pisang (FA5), and Sanggau (FA6). Analytical grade Al(OH)₃ (Sigma-Aldrich) and NaOH (Merck) were used to make an alkali activator with a technical grade sodium Sodium silicate or Na₂SiO₃ solution (water glass that composed of 28.69% SiO₂, 19.25% Na₂O and 52.06% H₂O), supplied by PT. Bratacem.

The alkaline activator solutions were prepared by mixing NaOH 14 M solution with Na₂SiO₃ solution (water glass). The alkaline activators were cured at room temperature for 24 h to eliminate the effect of heat that was released during mixing.

2.2 Characterization

The chemical composition of fly ash was determined by X-ray Fluorescent (XRF) spectrometer (S8 Tiger WD XRF, Bruker) while the mineral composition was characterized by X-ray diffraction (XRD) method using Cu Kα1 radiation (λ= 1.5406 Å). The diffraction patterns were recorded in the range of 5 to 95° 2θ, at a speed of 2° per minutes and 0.02° step size. The XRD was operated at 40 kV and 30 mA. The shape and surface morphology of fly ash particles were characterized by Zeiss Evo MA 10 Scanning Electron Microscope (SEM). The compressive strength of the resulting geopolymers were measured at the age of 7, 14, and 28 days.

2.3 Synthesis of geopolymers
All geopolymers were synthesized based on a method that was reported earlier [21] with a small modification where the fly ash was initially mixed with Al(OH)₃ suspension in water with the mass ratio of fly ash: Al(OH)₃ = 76.5. The mixtures were then dried at 105°C for 24 h. An alkaline activator which was comprised of 2.86 mass ratio of Na₂SiO₃ solution to NaOH pellets, was added to the dried mixture and mixed for 240 s to forms a thick but workable paste. Mass ratio between the dried mixture to the alkaline activator was 3.6. The pastes were poured into cylinder molds with the hight to diameter ratio was 2 and cured for 24 h at room temperature. The cylindrical dry pastes were demolded, put into a plastic bag and cured at 55°C in an oven for 24 h. Finally, the resulting geopolymers were taken out of the plastic bag and kept at room temperature and ambient atmosphere for 7, 14, or 28 days before being subjected to compressive strenght tests.

3. Results and Discussion

3.1 Characteristic of fly ash

3.1.1 Chemical composition of fly ash
X-ray fluorescent (XRF) analysis was carried out to determine the elements present in the fly ashes as shown in table 1. The most abundant oxides in the fly ashes were Al₂O₃, SiO₂, and Fe₂O₃. The combined
amount of them called pozzolanic compound is calculated following ASTM C 618-12 standard if the percentage were higher than 70% and CaO was less than 10% are classified as class F [1]. Nevertheless, if the pozzolanic compound percentage less than 70% and CaO more than 10% are categorized in class C. FA2, FA, and FA6 were classified as class F because it has the pozzolanic compound 83.89, 78.78, and 76.36%, respectively. The content of the pozzolanic compound was the lowest in FA3 (61.02%), followed by FA6 (63.06%).

| Sample Code | Composition (%) | LOI (%) | SiO2/Al2O3 Type |
|-------------|-----------------|---------|----------------|
| FA1         | 41.90           | 17.41   | 11.55          |
| FA2         | 50.55           | 13.12   | 7.44           |
| FA3         | 31.03           | 41.33   | 14.84          |
| FA4         | 53.35           | 15.96   | 9.50           |
| FA5         | 36.66           | 15.8    | 16.02          |
| FA6         | 38.09           | 23.10   | 15.17          |

The ratio of SiO2 and Al2O3 in the fly ash is a dominant factor for geopolymer formation and one of the important parameters to govern the mechanical strength of geopolymer [22,23]. It was ranging from 1.65 to 5.36. Also, the unburned particles measured by loss on ignition for all fly ashes were less than 10%, representing that the fly ashes were suitable to be a raw material for geopolymer.

3.1.2 Mineral and crystallinity phase compositions of fly ash

XRD patterns of the the six fly ashes are shown in figure 1 which shows that quartz, mullite and calcite are found in all fly ashes. Hematite was also found in FA2, FA3, FA5, and FA6 while maghnetite was not found in FA6. Amorphous phase was found in all fly ash as indicated by humps in figure 1 at 20 between 20 and 30° [24]. The amorphous phase is believed as the main ingredient in fly ash as an aluminosilicate source who will easily geopolimerized [25-27] while the crystalline phase will behave as micro-aggregates in the resulting geopolymers.

![Figure 1. X-ray diffractogram of fly ashes. C, G, H, M and Q indicates Calcite, Magnetite, Hematite, Mullite and Quartz, respectively.](image-url)
3.1.3 Microstructural analysis

SEM characterization was carried out to determine the morphology of fly ashes. SEM characterization was also carried out to determine the particle size distribution from fly ash. The results of the SEM characterization of fly ash are shown in figure 2. Generally, fly ashes have spherical morphological forms. However, the morphological form of the FA5 and FA6 fly ash is different from other fly ashes.

![SEM analysis of fly ash.](image)

**Figure 2.** SEM analysis of fly ash.

3.2 Geopolymer

3.2.1 Compressive Strength

Compressive strength was measured on geopolymers that had been cured for 7, 14 and 28 days. Measurements were stopped until cured for 28 days. Measurement of compressive strength after 28 days did not show a significant difference [28,29].

Cured of geopolymer affects the compressive strength, the longer cured of the geopolymer, the higher the compressive strength due to the formation of C-A-S-H (Calcium-aluminosilicate-hydrate) chains in geopolymers is longer. The results of geopolymer compressive strength are shown in figure 3. The compressive strength of geopolymers from FA5 and FA6 fly ash does not exist because geopolymers cannot form. One of the causes of FA5 and FA6-based geopolymers is not successfully synthesized is the irregular shape of FA5 and FA6 particles and relatively larger size than other fly ash.

The results of compressive strength measurements show that the lowest strength obtained was 7.17 MPa which occurred in geopolymers from FA1 at 7 days while the highest compressive strength was 36.62 MPa on geopolymers from FA3 at 28 days. Several factors affect the size of the compressive
strength of geopolymers were the composition of fly ash, the solubility value of Si and Al in fly ash, morphology of fly ash, the type of fly ash used and the unburnt carbon content in fly ash.

![Figure 3. Compressive strength of geopolymer.](image)

3.2.2 Mineral phase composition of geopolymer

Figure 4 depicts XRD pattern of fly ashes-based geopolymer. The remnant phases of quartz and mullite is the major identified crystalline peaks. However, compared to fly ash the peaks intensity has been reduced after geopolymerization due to the formation of amorphous gels. A small halo in the 2h range of 20-35 is because of the formation of amorphous gel as a reaction product.

![Figure 4. XRD pattern of fly ashes-based geopolymer.](image)

3.2.3 Microstructural changes

SEM micrography is discussed in figure 5. All samples show some unreacted fly ash particles. GP2 and GP3 show the growth of new needle-shaped crystals. This crystal growth can be considered to have a positive effect on the compressive strength of geopolymers, similar to the case of ettringite formation in Portland cement-based materials. However, the effect of the crystallinity of geopolymerization reactants on strength development has not been revealed quantitatively.
These morphological changes observed in the geopolymer are caused by the dissolution of SiO$_2$ and Al$_2$O$_3$ in alkaline solution leading to the formation of aluminosilicate gel and acts as a precursor to geopolymer formation [30,31]. The morphology and the composition of the resulting geopolymer matrix depend on the chemical composition of natural pozzolan, curing temperature and type of alkali activating solution and its SiO$_2$/Na$_2$O molar ratio. The different features generally observed in the microstructure includes unreacted particles and reacted phases. The latter may be constituted of a geopolymer phase, hydrated gel and new crystalline phases.

![Figure 5. SEM image of fly ash-based geopolymer.](image)

### 4. Conclusions

Geopolymers that have been successfully synthesized are geopolymers made from fly ash FA1, FA2, FA3, and FA4. The compressive strength of geopolymers from FA1 fly ash is 7.17; 7.96, and 10.35 MPa for ages 7, 14, and 28 days, respectively. The results of the compressive strength of geopolymers from FA2 are 9.55; 15.13, and 28.66 MPa for ages 7, 14, and 28 days, respectively. The compressive strength of geopolymers from FA3 fly ash is 12.74; 20.70 and 36.62 MPa for ages 7, 14, and 28 days, respectively. The compressive strength of geopolymers from FA4 is 7.96; 8.76, and 10.35 MPa for ages 7, 14, and 28 days, respectively.

The properties of fly ash which greatly affect the geopolymer properties include the morphology of fly ash, the composition of the fly ash element and LOI value. The morphological shape of fly ash that produces geopolymers with good properties is spherical and has a particle size of ≤ 10 μm. The ratio of SiO$_2$/Al$_2$O$_3$ in fly ash to produce geopolymers with good properties is in the range of 2.50 to 5.63. LOI values of fly ash to produce geopolymers are good, in the range of 0.38-8.47.

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