

Investigating Alumina silicate Source in Geopolymer Compressive Strength: Surface Morphology and Crystal Phase Study

Anggarini Ufafa^{1*} and Sukmana Ndaru Candra²

1. Department of Chemical Engineering, Universitas Internasional Semen Indonesia, Jln. Veteran Kompleks PT Semen Indonesia, Gresik-East Java, INDONESIA

2. Department of Engineering Management, Universitas Internasional Semen Indonesia, Jln. Veteran Kompleks PT Semen Indonesia, Gresik-East Java, INDONESIA

*ufafa.anggarini@uisi.ac.id

Abstract

In this present study, geopolymer, which is a cementitious specimen was synthesized with Fly and Bottom Ash to form aluminosilicate source. The geopolymer was synthesized by sol gel method at SiO_2/Al_2O_3 ratio of 4. The percentage of SiO_2 weight in fly ash was higher than bottom ash which was about 31.96 wt% and 21.07 wt% for each material. The Al_2O_3 content in fly ash also has a higher value than bottom ash at 22.62 wt% and 5.92 wt%, respectively. In order to study the surface morphology and X-ray Diffraction (XRD) for crystal phase analysis, the characteristics of Geopolymer from fly ash and bottom ash were compared using the Scanning Electron Microscope (SEM).

The diffractogram result showed that geopolymer that synthesized from fly ash has a higher amorphous phase than bottom ash geopolymer, which indicated that fly ash geopolymer is not only more reactive than bottom ash geopolymer, it also has an impact on good polymerization processes. This result is parallel with the SEM result that shows fly ash geopolymer has less unreacted particle than bottom ash geopolymer. It was found that reactive SiO_2 and Al_2O_3 in fly ash produced geopolymer with a high compressive strength of 68 Mpa while bottom ash produced geopolymer with the compressive strength of 51 Mpa.

Keywords: Geopolymer, Fly ash, Bottom ash, SEM, XRD.

Introduction

In recent years, coal combustion has become the biggest source to produce electricity energy. According to the Indonesian Directorate General of Minerales and Coal¹, the production of coal for the year 2016 is 434 million ton compared to the initial target of 419 million ton. Contrarily, based on the Directorate's report, Indonesia's coal resource was about 32,263 million ton in 2015 and decreased to 28,457 million ton in 2016. Based on this value, it was deduced that the consumption of coal increased until 2016 but its resource was limited. As the consumption of coal increases, its burning process produces a high content of carbon dioxide and ash.

The combustion of coal in power plants produces two kinds of by-product of ash that are known as fly ash and bottom ash. The particles of fly ash typically have diameters ranging from 1-150 μm considered as fine particles and they are removed by dust collection before being discharged to the atmosphere² whereas the bottom ash consists of bigger particle sizes³ and it can be found in the bottom of the power plant combustion. The utilization of both materials is only limited for landfills and could lead to severe environmental problems⁴.

Another utilization of fly ash and bottom ash is to form geopolymer as cementitious material that is environmentally safe. Previously, geopolymer manufacturing has been done from several researches in an optimal room temperature so it can minimize energy consumption. Geopolymer is synthesized from aluminosilicate binder material and alkaline activator solution that has amorphous structure⁵. Rattanasak et al⁴ stated that geopolymer is prepared by mixing alkaline solution, sodium silicate and aluminosilicate source and then activating the said mixture via temperature curing. The process of geopolymer synthesis has seen several years of effort to develop and perfect it so as to produce environmentally safe cement materials⁶ and to reduce the amount of CO_2 production⁸.

In this research, the investigation of aluminosilicate source has been done using fly ash and bottom ash to synthesize geopolymer that has high compressive strength. Geopolymer surface morphology and crystalline phase was determined using Scanning Electron Microscope (SEM) and X-ray Diffraction (XRD) respectively. The phase and microstructure of resulting geopolymer influenced by raw materials were determined in this experiment. The results that were obtained in this experiment can be used to further determine the correlation between the reactivity of raw materials with the compressive strength of geopolymer.

Material and Methods

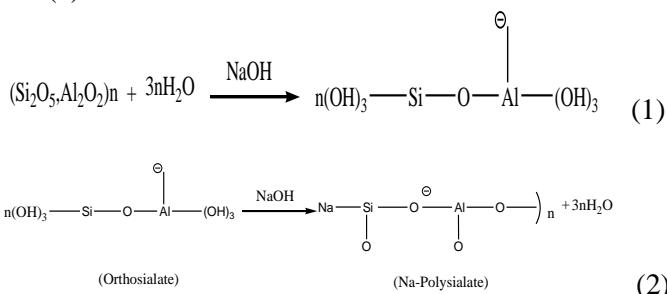
Materials: Fly ash and bottom ash PT Petrokimia Gresik were used as aluminosilicate sources to synthesize geopolymer. Both materials were prepared by sieving and drying the particle at 105°C for 24 hours. Sodium Silicate technical grade and sodium hydroxide were used as alkaline activator solutions. The concentration of sodium hidroxide solution was capped at 7 M. This solution was prepared by dissolving sodium hidroxide technical pellet in distilled water.

Synthesis of Geopolymer Specimen: Geopolymer specimen was manufactured by adding amount of alkaline activator solution into aluminosilicate source of fly ash and bottom ash, and mixed for 5 minutes. In this experiment, fly ash geopolymer and bottom ash geopolymer synthesis were carried with Si/Al ratio of 4. Geopolymer paste was then cast in cube mold with dimension of $5 \times 5 \times 5$ cm³ for 24 hours at a temperature of 25°C. After that, the mold was removed and the geopolymer specimen was cured up to 28 days. The compressive strength of geopolymer was finally measured after 7, 14 and 28 days in Physical Laboratorium of PT Semen Indonesia (Persero) Tbk.

Characterization: The oxide composition percentages of fly ash and bottom ash were determined by X-Ray Fluorescence (XRF) as given in table 1. These data could be used to specify the composition of geopolymers specimen. The crystallinity of geopolymers was determined using Powder X-Ray Diffraction (XRD) with Cu κ radiation to identify the crystal phase of the specimens. The characterization of crystal phase used 2θ from 10-50°. The surface morphology images were then collected using Scanning Electron Microscope (SEM). The compressive strength of geopolymers specimens was investigated using compressive strength test machine, and the results were compared between fly ash geopolymers and bottom ash geopolymers.

Results and Discussion

The Effects of Oxide Composition on Geopolymer: The composition of aluminosilicate as starting material for geopolymer synthesis plays a significant role in the mix design and geopolymersynthesis process. Davidovits⁶ developed polymer material with cross-linked chain that contains alumina and silicate, named Geopolymer. The reactions that are involved in geopolymersynthesis were hydroxylation and polycondensation. The mechanism of geopolymersynthesis is as can be seen in equations (1) and (2)⁷:



Alumina and silika were interconnected by sharing all the oxygen atoms, thus building the polymeric structure of a geopolymers. Sodium hydroxide acts as a catalyst and for the dissolution of alumina and silica while sodium cation maintains the neutrality of geopolymers structure⁷. Polymer structure that resulted from this process becomes a material that has a high compressive strength. The main requirement of the materials that can be used for geopolymers synthesis is such that they are rich in Si and Al contents⁸. This

characteristic is reflected by ash that resulted from coal burning.

The combustion of pulverized coal in thermal power plant produces two kinds of fine particulate residues that are in the form of fly ash and bottom ash whereby their composition as used in this experiment is presented by XRF instrumentation in table 1.

Fly ash that was used in this experiment was classified as class C with a high content of CaO (more than 8% weight), that means it is a product from lignite and subbituminous coal⁹. In support of this, Ramezanianpor² also stated that the combustion of subbituminous coal produces fly ash with a high content of calcium and less iron. Bottom ash in this experiment has a low content of CaO, so it can be classified into F class of ash. Fly ash from subbituminous coal contains less unburned carbon whereas bottom ash consists of high unburned carbon. These facts are appropriate with the physical properties of fly ash in our experiment. Fly ash is grey in colour while bottom ash is black. It means that bottom ash has higher unburnt carbon than fly ash.

Both materials have high contents of SiO₂ and Al₂O₃, but the percentage of oxide value of fly ash is higher than bottom ash. Bottom ash particles are more adsorbent to air humidity than fly ash, thus affecting the amount of water that is involved in the polymerization process to form geopolymer. Based on the oxide composition of fly ash and bottom ash, the mixing design of geopolymer is as determined in table 2.

Effects of Aluminosilicate Source against the Surface Morphology of Geopolymer: The surface morphology of geopolymer was collected by Scanning Electron Microscope (SEM), to identify the polymerization process. Figure 1 shows surface morphology of geopolymer specimen from fly ash and bottom ash as raw materials.

Fly ash geopolymers surface shows a little unreacted fly ash grain. This result can be seen as rough particle above the geopolymers surface. Besides that, some cracks can be observed with a fine fractional line. The surface morphology of bottom ash geopolymers showed high unreacted bottom ash particle with perforated surface area. The bottom ash geopolymers surface was covered with granules that cannot be fused. Several unreacted aluminosilicate sources indicated the reactivity of SiO_2 and Al_2O_3 from ash source resulting in geopolymers reaction under alkaline condition.

The dissolution of SiO_2 and Al_2O_3 from both ash coal started by breaking the Si-O-Si bond and Al-O-Al bond followed by the rearrangement polimeric model of geopolymers⁵. High contents of unreacted aluminosilicate produce geopolymers with low compressive strength due to incomplete polymerization.

Effects of Aluminosilicate Content against the Crystallinity of Geopolymer: The crystal phases of fly ash

geopolymer and bottom ash geopolymer were characterized using X-ray Diffraction as seen in figure 2. Both types of geopolymer microstructure are more amorphous phase than crystalline. It can be observed from the XRD pattern that shows a lot of hump peak. The diffractogram pattern of fly ash geopolymer consists of quartz, mullite, hematite and magnetite phase whereas the bottom ash diffractogram pattern shows two types of phase that were mullite and quartz. The diffractogram of fly ash geopolymer has hump peak at 20 of 26-30°.

Haq et al¹⁴ stated that a hump under quartz peak in fly ash indicated the presence of more amorphous phase compared to bottom ash. The highest crystalline peak of bottom ash geopolymer at 20 of 26.55° confirmed a high crystalline of quartz phase. The presence a lot of quartz phase decreased the reactivity of material to result in geopolymers process. Another phase in bottom ash geopolymer was mullite that can be observed at 20 of 25-30°.

The peak intensity of bottom ash geopolymer was higher than fly ash geopolymer, suggesting that fly ash geopolymer still has a high reactivity and resulting in good polycondensation reaction. Bakri et al⁸ declared that the composition of geopolymer specimen is similar with

zeolite, but the crystalline phase is different. Geopolymer microstructure was amorphous. Chindaprasit et al¹⁵ in their experiment results show that fly ash is more reactive than bottom ash; hence, aluminosilicate source could produce a higher degree of polymerization process in geopolymer synthesis.

Effects of Aluminosilicate Source against the Compressive Strength of Geopolymer: Figure 3 shows the compressive strength of fly ash geopolymer and bottom ash geopolymer. The compressive strength of geopolymer was carried out in 7, 14 and 28 days. The measurement of compressive strength has been done in an ambient temperature.

All geopolymer specimens have increased in their compressive strength pattern from day 7 to day 28. The high compressive strength obtained in the fly ash geopolymer specimen is 68 Mpa at 28 days and the compressive strength for bottom ash geopolymer is 51 Mpa at 28 days. This result indicated that bottom ash has lower compressive strength than fly ash. The reactivity of fly ash as aluminosilicate source was higher than bottom ash; hence, fly ash geopolymer produces a higher compressive strength than bottom ash geopolymer.

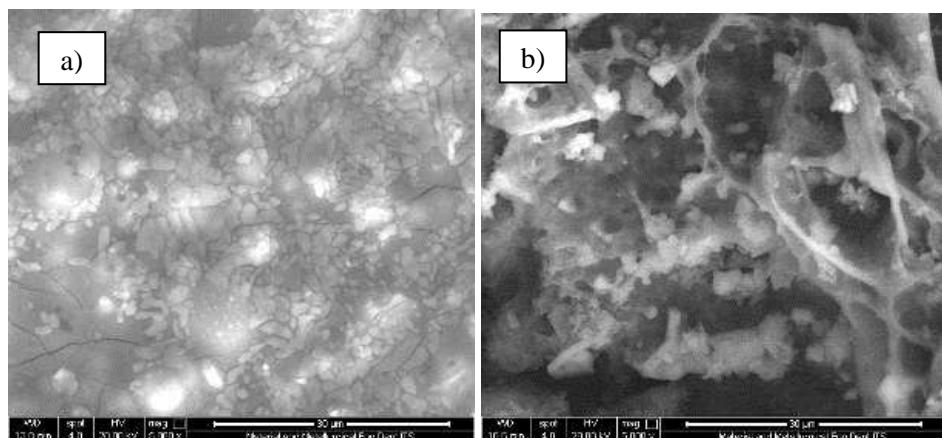


Figure 1: Surface morphology of a) Fly ash geopolymer and b) Bottom ash geopolymer

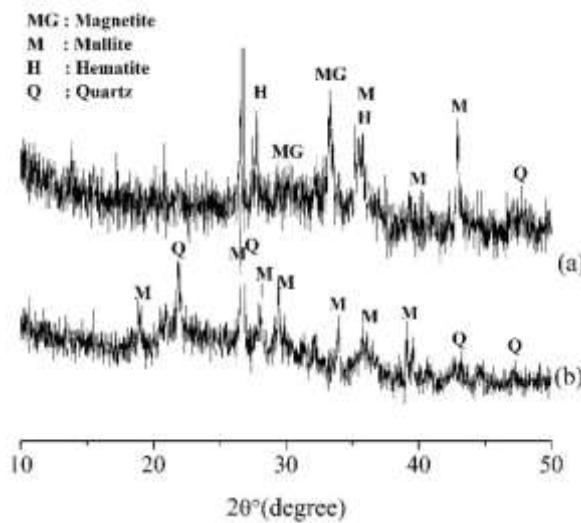


Figure 2: The X-ray Diffraction pattern of a) fly ash geopolymer and b) bottom ash geopolymer

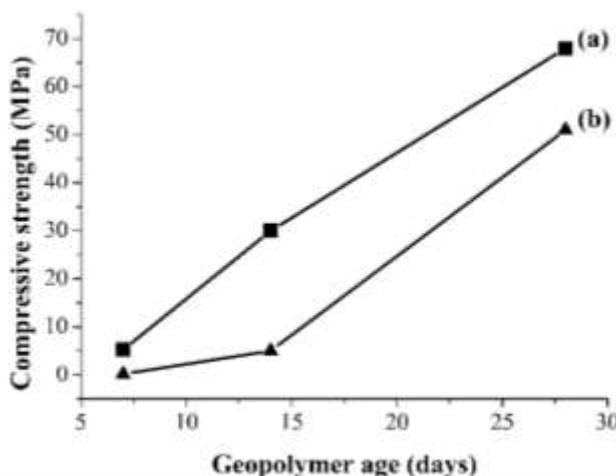


Figure 3: The Compressive strength of a) fly ash geopolymer and b) bottom ash geopolymer

Table 1

Oxide composition percentage (% mass) of fly ash and bottom ash as aluminosilicate source

| Oxide Composition (wt %) | Fly Ash | Bottom Ash |
|--------------------------------|---------|------------|
| Al ₂ O ₃ | 22.62 | 5.92 |
| SiO ₂ | 31.96 | 21.07 |
| CaO | 18.94 | 5.42 |
| Fe ₂ O ₃ | 15.20 | 10.25 |
| K ₂ O | 1.20 | 2.19 |
| MgO | 11.22 | 2.28 |

Table 2
Composition mixing design of geopolymers

| | Fly ash | Bottom ash |
|--|---------|------------|
| Aluminosilicate source(gr) | 600 | 600 |
| Sodium silicate (gr) | 327.41 | 188.84 |
| Sodium hydroxide (gr) | 32.58 | 171.16 |
| SiO ₂ /Al ₂ O ₃ | 4 | 4 |
| H ₂ O/Na ₂ O ratio | 19.18 | 31.46 |
| Na ₂ O/SiO ₂ ratio | 0.18 | 0.14 |

Conclusion

In this study, geopolymers were synthesized using fly ash and bottom ash. The XRD pattern shows a lot of amorphous phase in fly ash while bottom ash is more crystalline. Additionally, the SEM images show that the fly ash geopolymers have less unreacted particle than bottom ash and both materials have fractural line on the surface. The highest compressive strength was recorded at 68 MPa from fly ash geopolymers. This result shows that the reactivity of fly ash geopolymers is higher than bottom ash resulting to a geopolymers with a high degree of geopolymersization.

Acknowledgement

The authors gratefully acknowledge LPPM UISI for providing Hibah Riset Terapan, contract number 02/KP.03/11-01/05.17 dated March 1st, 2017 and Physical Laboratory at PT Semen Indonesia (Persero) Tbk.

References

1. www.minerba.esdm.go.id/library/publish/LAKIN%20MI_NERBA%202016.pdf (2016)
2. Ramezani A., Cement Replacement Materials, Springer-Verlag, Berlin (2014)
3. Jaturapitakkul C. and Cheerarot R., Development of bottom ash as pozzolanic material, *Journal of Materials in Civil Engineering*, **15**, 48–53 (2003)
4. Rattanasak U. and Chindaprasirt P., Influence of NaOH solution on the synthesis of fly ash geopolymers, *Minerals Engineering*, **22**(12), 1073-1078 (2009)
5. Davidovits J., Geopolymer: Inorganic Polymeric New Materials, *Journal of Thermal Analysis and Calorimetry*, **37**(8), 1633-1656 (1991)

6. Davidovits J. and Sawyer J.L., US Patent No. 4509985 (**1985**)
7. Khale D. and Chaudhary R., Mechanism of geopolymmerization and factors influencing its development: a review, *Journal of Materials Science*, **42(3)**, 729-746 (**2007**)
8. Al Bakri A.M., Kamarudin H., Bnhussain M., Nizar I.K. and Mastura W.I.W., Mechanism and chemical reaction of fly ash geopolymers-A review, *Journal of Asian Scientific Research*, **1(5)**, 247-253 (**2011**)
9. Jayaranjan M.L.D., Van Hullebusch E.D. and Annachhatre A.P., Reuse option for coal fired power plant bottom ash and fly ash, *Reviews in Environmental Science and Bio/Technology*, **13(4)**, 467-486 (**2014**)
10. Abdullah M.M.A., Hussin K., Bnhussain M., Ismail K.N. and Ibrahim W.M.W., Mechanism and chemical reaction of fly ash geopolymers cement-a review, *International Journal of Pure and Applied Science and Technology*, **6(1)**, 35-44 (**2011**)
11. Xu H. and van Deventer S.J., Effect of source materials on geopolymmerization, *Industrial & Engineering Chemistry Research*, **42(8)**, 1698-1706 (**2003**)
12. Saker P.K., Bond strength of reinforcing steel embeded in fly ash-based geopolymers concrete, *Journal of Materials and Structure*, **44(5)**, 1021-1030 (**2011**)
13. Lampis C., Lupo R. and Cheeseman C.R., Geopolymerisation of slit generated from construction and demolition waste washing plants, *Waste Management*, **29(1)**, 368-373 (**2009**)
14. Haq E., Padmanabhan S.K. and Licciulli A., Synthesis and characterization of fly ash and bottom ash based geopolymers-A comparative study, *Ceramics International*, **40(2)**, 2965-2971 (**2014**)
15. Chindaprasirt P., Jaturapitakkul C., Chalee W. and Rattanasak U., Comparative study on the characteristics of fly ash and bottom ash geopolymers, *Waste Management*, **29(2)**, 539-543 (**2009**).