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Chemical characteristic of fly ash and bottom ash as potential source for synthesis of aluminosilicate-based materials

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ABSTRACT: The world's population has reached 7 billion or doubled from the previous half-century and continues to increase every year. This increase in population is directly proportional to the increase in electrical energy consumption. Electricity needs in Indonesia are mostly met by Steam Power Plants. Unfortunately, the use of coal as an energy source in Steam Power Plants can cause environmental pollution, namely the waste generated by fly ash and bottom ash. However, even though it is classified as hazardous materials, silica (SiO₂) and alumina (Al₂O₃) content in the waste are high enough so that it can be used for the synthesis of aluminosilicate-based materials. The ash waste in this study was obtained from the Steam Power Plant in Kapuas Regency, Central Kalimantan Province which was tested according to the ASTM D93-10 standard. The composition of SiO₂, Al₂O₃, Fe₂O₃ and CaO in fly ash was 56.44; 31.31; 0.51; 0.78%. The compositions of SiO₂, Al₂O₃, Fe₂O₃ and CaO in the bottom ash were 66.66; 17.09; 0.31; 5.40%. Based on its composition, fly ash and bottom ash are classified as type F ash. In addition, fly ash and bottom ash have SiO₂/Al₂O₃ ratios of 3.90 and 1.80, respectively. It can be concluded that fly ash and bottom ash has the potential to be used as basic materials for the manufacture of aluminosilicate-based materials such as geopolymers, zeolites, and others.

INTRODUCTION

The world's population continues to increase every year until it has more than doubled from the previous half-century, as many as 7 billion people [1,2]. Indonesia is the fourth most populous country after China, India, and the United States. The population in Indonesia reaches 250 million people with a population density of 135 people per km² [3]. The high population of the world's population is related to the increasing demand for electrical energy. In Indonesia, the need for electrical energy reached 186,457.23 GWh in 2019 [4]. Most of this electrical energy need is met by Steam Power Plants that use coal as fuel [5]. However, the use of coal actually produces waste that can pollute the environment, namely fly ash and bottom ash. Heavy metals contained in fly ash will reduce soil fertility, pollute the waters, and harm human health if exposed to it. Exposure of fly ash can cause health problems such as irritation of the eyes, nose, throat, skin, respiratory system and nervous system disorders such as decreased brainpower, kidney disease and inhibition of bone growth.

However, behind the toxicity of fly ash and bottom ash, this material has the potential to be used as a base material for aluminosilicate-based materials. This is due to the high content of SiO_2 and Al_2O_3 in fly ash and bottom ash [6,7]. Two of the aluminosilicate-based materials that can be synthesized from waste ash are geopolymers and zeolites [8–12]. Both have a basic framework composed of alumina and silica compounds. The synthesis of geopolymers from coal ash was carried out in a previous study and it gave better results

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than geopolymers made from Portland cement-based on compressive strength, resistance to high temperatures, and economic aspects [6].

Therefore, this study aims to examine the chemical characteristics of fly ash and bottom ash waste obtained from one of the Steam Power Plants in Central Kalimantan in order to obtain data on its chemical composition, Si/Al ratio, and classification.

RESULT AND DISCUSSION

Coal ash that has been studied divided into two categories, namely fly ash and bottom ash. Fly ash is typically composed of 90-99% inorganic material, 1-9% organic material, and <0.5% fluid components. Meanwhile, bottom ash is composed of the residual coal ash that settles on the bottom of the boiler after the combustion process [7]. The main difference between coal fly ash and coal bottom ash involves geometry and particle size. Coal fly ash particles are generally spherical. However, the particles of coal bottom ash are irregular and range from fine gravel to natural sand [8].

The chemical contents in fly ash and bottom ash studied is shown in Table 1 and 2. The contents of SiO₂, Al₂O₃, Fe₂O₃ and CaO in fly ash is 54.44; 31.31; 0.58 and 0.78% respectively. Meanwhile the bottom ash has SiO₂, Al₂O₃, Fe₂O₃ and CaO contents 66.66; 17.09; 0.31, and 5.40% in a row.

Oxides	Percentation (%)
SiO ₂	56.44
Al ₂ O ₃	31.31
Fe ₂ O ₃	0.51
CaO	0.78
MgO	0.39
SO ₃	0.68
Na ₂ O	0.79
K ₂ O	0.47
Loss of Ignition	1.92

Table 1.	Chemical	composition	of fly ash.
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Oxides	Percentation (%)
SiO ₂	66.66
Al_2O_3	17.09
Fe_2O_3	0.31
CaO	5.40
MgO	0.28
SO ₃	3.39
Na ₂ O	0.86
K ₂ O	0.47
Loss of Ignition	1.92



According to the American Society for Testing Materials (ASTM C618-12a) (ASTM C618-12a, 2012) (ASTM C618), type F fly and bottom ash is consisting of higher than 70% of SiO₂, Al₂O₃ and Fe₂O₃ [9]. Another indication of type F ash, the calcium content (CaO) is less than 5% [8] [14]. In contrast, type C fly and bottom ash has less than 70% of SiO₂, Al₂O₃ and Fe₂O₃. This type is also contain CaO greater than 5% [10]. Based on its chemical composition, fly ash and bottom ash can be classified in type F ash as shown in Table 3.

According to previous study, coal ash type plays a major role in synthesis of aluminosilicate-based materials. Geopolymer as one of aluminosilicate-based material, shows better compressive strength with type C fly ash as material source. As can be seen in Table 4., type C fly ash-based geopolymer (FA3) has better compressive strength than type F fly ash-based geopolymer reaches 36.62 MPa with 28 days curing time. The compressive strength in geopolymer can be improved by geopolymerization and hydration process where the immobilization of heavy metals in ash affect. 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 [10].

Ash	Туре	References
Fly Ash	F	[7]
Bottom Ash	F	[9]

Table 3. Type of ash

Table 4. Compressive strength	(MPa) of geopolymer concrete	under seawater condition [10]
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Different Concerts Min	Curing Time (Day)			
Different Concrete Mix	28	56	90	180
Without Bottom Ash	35.7	42.8	49.8	48.3
With Bottom Ash	43.0	55.6	54.9	52.4

Utilization of type F bottom ash have ever been studied in geopolymer concrete synthesis exposed to sea water in previous study [9]. As can be seen in Table 5., bottom ash addition in geopolymer concrete synthesis can reduce the seawater effects on the concrete. When the geopolymer concrete is exposed to the seawater, pozzolanic reaction could be stimulated. Because seawater comprises chloride, sulphate and sodium, once they entered in the concrete, it could activate the pozzolanic reaction and results the reduction of pore sizes in the concrete and ultimately gives better strength performances. However, it was agreed earlier that the pozzolanic reaction spent calcium hydroxide and makes denser concrete, though seawater is rich in sulphate which cause the development of ettringite. But, the bottom ash contains lower portion of calcium oxide, so it could reduce the production of ettringite.

Table 5. Compressive strength (MPa) of geopolymer concrete under seawater condition [11	
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The opposite occurs in the synthesis of zeolite. Fly-ash based zeolite had good crystallinity if it used type F fly ash as raw material under hydrothermal condition. The high content of Ca could hinder zeolitisation process due to the formation of hydroxysodalite and increased intensity of calcite reflections [11].

Another factor that affects the quality of the aluminosilicate-based material from coal ash is the ratio of Si/Al. The SiO₂/Al₂O₃ ratio is one of the main factors for determining the quality of aluminosilicate-based materials such as geopolymers and zeolites. The SiO₂/Al₂O₃ ratio value is obtained by comparing the mol percentage of SiO₂ and Al₂O₃ in fly ash or bottom ash. Based on its SiO₂ and Al₂O₃ content, the SiO₂/Al₂O₃ ratio owned by fly ash and bottom ash is 1.80 and 3.90. It can be seen in Figure 1. that bottom ash has greater Si content than fly ash.

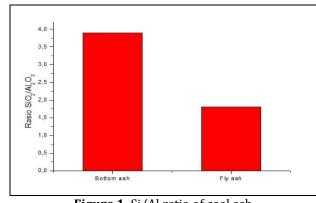


Figure 1. Si/Al ratio of coal ash

The effect of coal ash SiO_2/Al_2O_3 ratio to the value of aluminosilicate-based material have been studied before. In geopolymerization process, the SiO_2/Al_2O_3 ratio play a major role. The high ratio of SiO_2/Al_2O_3 means the high content of Si. Vice versa, the low SiO_2/Al_2O_3 ratio indicates the low Si content with high Al percentage. The high silica content facilitates the formation of a stronger Si-O-Si bond than Si-O-Al bond, so that the compressive strength of geopolymer will increases, as can be seen in Table 6 [12].

Si/Al Ratio	Compressive Strength (MPa)		
1.5	10		
2.0	8		
2.5	10.5		
3.0	9.5		
3.5	12.5		

Table 6. Compressive strength of geopolymer [12]

The effect of SiO_2/Al_2O_3 ratio on zeolite material was reported. The SiO_2/A_2O_3 ratio affects the proton selectivity in zeolites. Zeolites with a high SiO_2/A_2O_3 ratio have many Si-O-Si bonds and less of Si-O-Al bonds which play a big role in influencing the degree of proton adsorption selectivity in zeolites. This factor affects the electrostatic potential and the strength of the proton bond interactions on the negative side of the charge which leading to increased or decreased proton selectivity. The higher Al content, the easier Si-O-Al bonds are formed than Si-O-Si. Based on the Lewis acid-base reaction, hydrogen bonds are formed through the oxygen bridge in the Si-O-Al bonds in the zeolite structure to form Si-OH-Al

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with connected by covalent bonds. The formation of Si-OH-Al covalent bonds is very strong compared to the electrostatic force between Na⁺ and the negative charge. Thus, increasing the SiO_2/A_2O_3 ratio in zeolites causes a decrease in proton selectivity [13].

CONCLUSION

Based on the result, it can be concluded that the characteristics of coal ash affect on the quality of the aluminosilicate-based material. As the raw material for synthesis of aluminosilicate-based materials, the SiO_2/Al_2O_3 ratio and the type of coal ash are important factors in determining the quality of material. Fly ash and bottom ash are classified as type F ash. Utilization of type F ash in geopolymerization will decreases its compressive strength, while in zeolite will hinder the zeolitisation process. The highest SiO_2/Al_2O_3 ratio is owned by bottom ash (3.90), while the lowest SiO_2/Al_2O_3 ratio is owned by fly ash (1.80). Increasing the SiO_2/Al_2O_3 ratio results in an increase in the compressive strength of the geopolymer material. The increase in SiO_2/Al_2O_3 ratio in zeolites causes a decrease in proton selectivity. Hence, the coal ash from Kapuas Regency's steam power plant is possible to be applied as raw material for synthesis of aluminosilicate-based material.

MATERIAL AND METHOD

In this study, the coal ash studied was obtained from steam power plant in Kapuas Regency, Central Kalimantan Province, Indonesia. The SiO_2 , Al_2O_3 , Fe_2O_3 and CaO content in fly ash and bottom ash were analyzed by ASTM D93-10 standard method. ASTM D93-10 can be used to find out the chemical composition content of coal ash based on its flash point. A sample of coal ash is heated at a certain speed in a closed container. Then the ignition test is carried out at a certain temperature by bringing the igniter closer to the surface of the sample until the flash point is detected.

DECLARATION

There is no conflict of interest from authors for this research.

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