Effect of Air-Cooled Slag and Granulated Blast Furnace Slag Addition as Substitutor on Fly Ash based Geopolymer

Abstract

Air Cooled Slag and Granulated Blast Furnace Slag is a waste material from steelmaking process that not utilized, even though it rich in silica and CaO that can increase mechanical properties of building materials. Therefore, this material is potential as substitutor for geopolymer. Geopolymer is an alkali activated material consists of aluminosilicate precursor activated by NaOH and waterglass as activator. One of the common aluminosilicate binder used is fly ash. Geopolymer was made by mixing fly ash and air cooled slag or granulated blast furnace slag in certain ratio with alkali activator solution. The aim for this study is to obtain the best ratio of slag to fly ash binder that produces the highest compressive strength. The best compressive strength was 29.80 MPa achieved in fly ash:air cooled slag 40:60 ratio and 31.33 MPa achieved in fly ash:granulated blast furnace slag 40:60 ratio. X-Ray Diffraction test showed the appearance of anorthite (Ca, Na (Al, Si)4 O8). FTIR characterization showed the appearance of siloxo and sialate bonding which commonly found in geopolymerization.

INTRODUCTION

Air-cooled slag (ACS) is a waste material from steelmaking industry made from blast furnace cooled by aircooling method while granulated blast furnace slag (GBFS) is a waste material from steelmaking industry made from blast furnace cooled by water spraying method. Crushed product was used for road base, coarse aggregate, and clinker raw material. One ton of steelmaking produces around 20% slag waste, which is quite high. ACS waste is a non-metalic material consisting of silica, calcium oxide and alumina as main components, together with other compounds of iron oxide and magnesia. ACS waste production PT Krakatau POSCO is 25.000 ton/year, while GBFS waste production in PT Krakatau POSCO is 800.000 ton/year. Most of them are stored as waste stockpile rather than used as source materials for example in conctructions. There are economic, environmental and social needs to increase the value of air-cooled slag waste to result in reduced quantities of disposal materials [1] as Portland cement replacement materials due to its ability to enhance mechanical properties of materials [2]. In this work, ACS or GBFS combined with fly ash, which is also by product material containing high silica and alumina, then activated by alkali solution consists of sodium hydroxide (NaOH) and waterglass (Na2SiO3) was used in production of geopolymers. The activation of fly ash with alkali activator forms an inorganic binder through geopolymerization [3]. Silica and alumina were reacted with alkali activator to generate aluminosilicate materials with CaO from air-cooled slag and granulated blast furnace slag facilitated the setting of the materials. The aim for this study is to determine the chemical composition by X-Ray Diffraction (XRD), molecular bond by Fourier Transform Infrared (FTIR) spectroscopy, and mechanical properties of resulting geopolymer.

MATERIALS AND METHODS

Materials

Class-F fly ash was obtained from Suralaya Coal Fired Power Plant Banten, air-cooled slag and ground granulated blast furnace slag was obtained from PT Krakatau POSCO Cilegon, Banten (Figure 1). The oxides composition of these materials is shown in Table 1 by using X-Ray Fluorescence (XRF) method. Technical grade of sodium hydroxide and water glass were purchased from Bratachem Bandung.

FIGURE 1. Air-Cooled Slag (a) and Granulated Blast Furnace Slag (b) in PT Krakatau POSCO

TABLE 1. The oxides composition of Class-F fly ash and air-cooled slag (ACS) and granulated blast furnace slag (GBFS) which shows that both ACS and GBFS contains high CaO content

Material	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO
Fly Ash	52.30	26.57	6.00	7.28	2.13
ACS	35.92	7.11	44.17	0.44	2.01
GBFS	34.20	11.70	41.20	1.43	8.81

Methods

Precursor consists of class-F fly ash used were varied from 20-60 wt% and air-cooled slag and granulated blast furnace slag used for aggregate was varied from 40-80 wt%. Detailed mix design can be seen at Table 2. Air cooled slag was put in ball mill for 6 hours until it reach 25 mesh size, while Granulated blast furnace slag used as is. Both can be seen in Figure 2. Alkali activator consists was prepared by mixing sodium hydroxide solution 12M and sodium silicate 10M with 2:1 ratio [4]. Geopolymer was made by mixing class-F fly ash, air-cooled slag or granulated blast furnace slag, and alkali activator to result in slurry, it was then poured into 50 x 50 x 50 mm mold.

TABLE 2. Mix Design of ACS and GBFS based Geopolymer

Name	Fly Ash (%)	ACS (%)	GBFS (%)
ACS40	60	40	0
ACS50	50	50	0
ACS60	40	60	0
ACS70	30	70	0
ACS80	20	80	0
GBFS40	60	0	40
GBFS50	50	0	50
GBFS60	40	0	60
GBFS70	30	0	70
GBFS80	20	0	80

The mold was cured under ambient condition for 28 days. The compressive strength of resulting geopolymer was measured using Universal Testing Machine (UTM) conformed to ASTM C-39. Debris from compression strength was collected for characterization purposes. The X-Ray Diffraction (XRD) measurement was performed on Philips Diffractometer PW1710 with Cu as anode. Resulting diffraction pattern was compared to Joint Committee on Powder Diffraction Standards (JCPDS).

FIGURE 2. Geopolymer samples, prepared from fly ash, alkali activator, and (a) ACS or (b) GBFS

RESULT AND DISCUSSIONS

Compressive Strength

Figure 2a shows samples of geopolymer samples, containing 60% fly ash and 40% air-cooled slag, while Figure 2b shows samples of geopolymer samples, containing 60% fly ash and 40% granulated blast furnace slag. It shown that fly ash and both slags was properly mixed. The mortar took ±6 hours to be fully cured. The higher percentage slags resulted in the decrease of the compressive strength of geopolymers (Figure 3). The air-cooled slag comprises 44.17% CaO, and granulated blast furnace slag comprises 41.20% CaO that both is much higher than fly ash (6%) (Table 1). The CaO content in air-cooled slag and granulated blast furnace slag facilitates the sample to harden faster, but too high concentration of CaO is not desirable as it leading to cause crack in the surfaces [5]. Sample was tested its compressive strength after 28 days, The ratio of air-cooled slag to fly ash 40:60 and after 28 days curing resulted in 29.80 MPa compressive strength. The ratio of granulated blast furnace slag to fly ash 40:60 and after 28 days curing resulted in highest compressive strength, 31.33 MPa (Figure 1), which makes this material can be used for construction application such as low traffic roads [6].

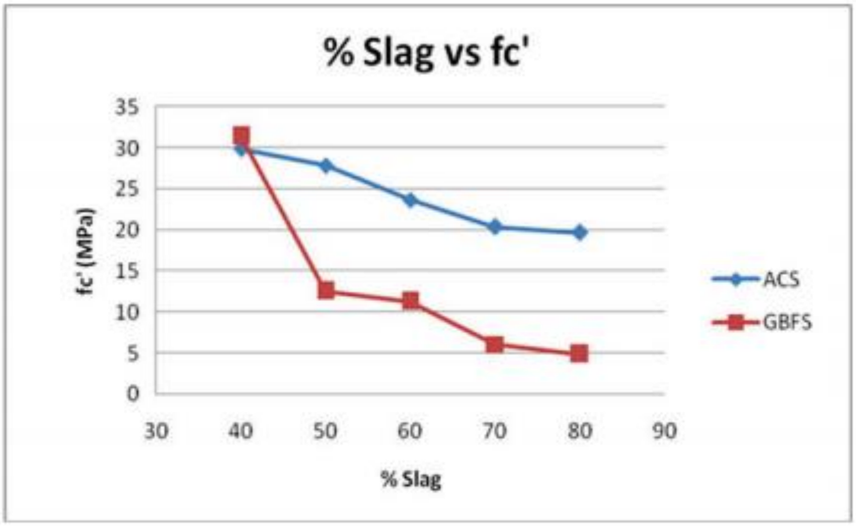

FIGURE 3. Compression strength results of geopolymers, prepared from various ratio air-cooled slag or granulated blast furnace slag to fly ash and alkali activator (NaOH 12M and water glass 10 M).

X-Ray Diffraction (XRD) Results

XRD difractograms (Figure 4) demonstrated the presence of quartz (SiO2) (Peak Q, JCPDS No. 461045) in Class-F fly ash and geopolymer samples, whereas gehlenite (Ca2Al2SiO7) (Peak G, JCPDS No. 350755) and anorthite (Ca, Na (Al, Si)4 O8) (Peak A, JCPDS No. 411481) only found in geopolymer. The formation of new compound anorthite indicates the reaction between precursors (air-cooled slag or granulated blast furnace slag and fly ash) and alkali activator (sodium hydroxide and water glass) has successfully occurred [7]. Silica and alumina contents in air-cooled slag or granulated blast furnace slag and fly ash dissolved in alkali activator and then reacted with water glass as source of Na+ ion and silica. The reaction is similar with geopolymerization, it resulted in aluminosilicate compounds as shown by the presence of anorthite which has similar formula with geopolymer (Mn [- (SiO2)z-AlO2]n. wH2O) and base peak line hump XRD pattern has shifted. It was show in 25^0, $27{,}5^0$, and $29^0 2\theta$

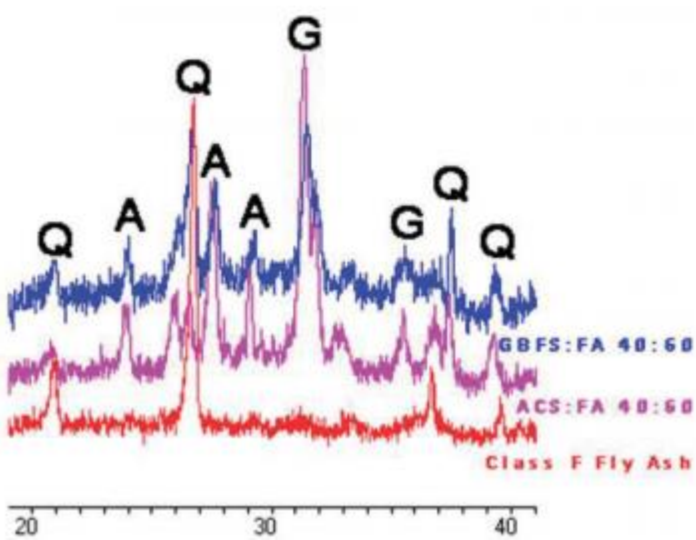

FIGURE 4. XRD difractograms of class-F fly ash and Geopolymer. XRD peaks represent: A= Anorthite, G= Gehlenite, Q= Quartz. ACS:FA denotes ratio of air-cooled slag and fly ash in the samples, while GBFS:FA denotes ratio of granulated blast furnace slag and fly ash in the samples

Fourier Transform Infrared Spectroscopy (FTIR) Results

Figure 5 show FTIR spectra of Air-Cooled Slag based and Granulated Blast Furnace Slag Geopolymer samples. The summary was shown in Table 3. Peak at 460 cm-1 originates from bending vibration Si-O-Si bonding. The highest peak of Si-O-Al and Si-O-Si are shown by absorption at 560-760 cm-1 and 1010-1020 cm-1 that indicate formation of albite, a typical compound of alkali-activated material in these variants as the result of silica and alumina dissolution that found in fly ash. Fernandez-Jimenez [8] reported the similar spectra and claimed that the formation of solidification product as geopolymerization marked with wavelength number reduction in similar bonding that lie in fly ash based alkali-activated material. Broad peak at 3400 cm-1 indicates the presence of O-H bending vibration. FTIR spectra support the XRD results, showing that geopolymerization has been occurred as demonstrated by the presence of anorthite functional groups.

TABLE 3. FTIR results summary of (a) ACS based and (b) GBFS based geopolymer

Code	Stretching –OH (cm-1)	Bending H-O-H (cm-1)	Stretching Si-O-Si (cm-1)	Symmetric Vibration Si-O-Al (cm-1)		Bending Vibration Si-O-Si (cm-1)
ACS Based GP	3448.72	1641.42	1012.63	775.38	578.64	472.56
GBFS Based GP	3450.65	1641.42	1010.70	775.38	578.64	449.41

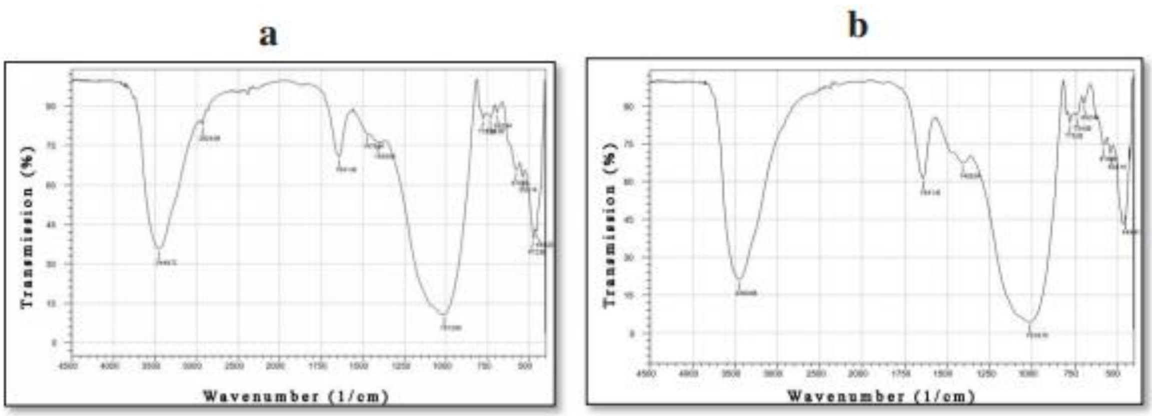

FIGURE 5. FTIR Spectra of (a) ACS based Geopolymer (b) GBFS based Geopolymer

Geopolymer samples were successfully prepared by mixing class-F fly ash and air-cooled slag or granulated blast furnace slag with alkali activator solution followed by ambient curing. The best compressive strength was achieved by granulated blast furnace slag : fly ash 40:60% ratio results in 31.33 MPa. XRD shows some of significant mineral that commonly found as geopolymerization process such as anorthite due to high silica content in air-cooled slag and granulated blast furnace slag.

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REFERENCES

1. M. Criado, A. Palomo, and Fernandez-Jimenez, A: Alkali Activation of Fly Ash. Part I : Effect of curing condition on The Carbonation of The reaction Products, Fuel, 84, 2048-2054., (2005). DOI = http://dx.doi.org/10.1016/j.fuel.2005.03.030

2. D.W. Law, A.A. Adam, T.K. Molyneaux, and I. Patnaikuni, Mater. Struct. 45, 1425 (2012).

3. V.F.F. Barbosa, K.J.D. MacKenzie, and C. Thaumaturgo, Int. J. Inorg. Mater. 2, 309 (2000).

4. D. Hardjito, and S.S. Fung,: Fly Ash-Based Geopolymer Mortar Incorporating Bottom Ash, Modern Applied Science, 4(1) , (2010). DOI = http://dx.doi.org/10.5539/mas.v4n1p44

5. R. Pouhet, and M. Cyr,: Alkali±silica reaction in metakaolin-based geopolymer mortar, Materials and Structures pp 571-583, (2015). DOI = http://dx.doi.org/10.1617/s11527-014-0445-x

6. J. Brozovsky, O. Matejka, and P. Martinec,: Concrete Interlocking Paving Blocks Compression Strength Determination using Non-Destructive Methods, The 8th International Conference of the Slovenian Society for Non-Destructive Testing, pp.91-97, (2005). DOI = http://dx.doi.org/10.1016/j.proeng.2013.09.039

7. P.H. Simatupang, R. Hanafi, B. Sunendar, I. Imran, and I. Pane,: The Study of Red Mud Addition Influences in Metakaolinite-Based Geopolymer Characteristics, Journal of Advanced Materials Research, 450-451, pp.281- 285., (2012). DOI = http://dx.doi.org/10.4028/www.scientific.net/AMR.450-451.281

8. M. Criado, A. Palomo, and Fernandez-Jimenez, A., and Banfill, P.F.G.: Alkali Activated Fly Ash : Effect of Admixtures on Paste Rheology, Rheol Acta, pp. 447-455, (2009). DOI = http://dx.doi.org/10.1007/s00397-008- 0345-5