

## Effect of Fluidized Bed Coal Combustion Fly Ash on Geopolymer's Properties

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**Abstract:** This study reveals the effect of the particle size of fluidized bed coal combustion (FBC) fly ash on geopolymer's properties. Original FBC fly ash was ground into small sizes, with 20,000 rph for 5 and 10 h, resulting in mean particle sizes of 10 and 8  $\mu\text{m}$ , respectively. Geopolymer paste was prepared by mixing the different mixtures of fly ash with  $\text{Na}_2\text{SiO}_3$  solution-to-15M NaOH ratio (G/N) of 2. The geopolymer with smaller particle size of FBC fly ash shows the dense and homogeneous matrix. G/N ratio can take the effect on geopolymer's properties. The reaction in the FBC fly ash geopolymer increases when the fly ash particles were smaller. The compressive strength of 8FBC-geopolymer is highest of 27 MPa at 90-days. Longer curing age caused more the completed geopolymerization reaction.

**Keywords:** Geopolymer, Fluidized bed coal combustion, Particle size

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### I. Introduction

The global demand of cement for construction of infrastructures has been continuously increasing, due to the ongoing growth and accommodation of increasing population. Ordinary Portland cement (OPC) is commonly used as a binder in concrete. It is estimated that about 1 tonne of carbon dioxide ( $\text{CO}_2$ ) is emitted into the atmosphere in the manufacturing process of 1 tonne of cement. This makes a significant contribution to the global greenhouse gas emission [1]. Therefore, in order to aid in the reduction of global  $\text{CO}_2$  emission, there is a need for more environmentally friendly building materials. One material that is the focus of much research for use in this capacity is a geopolymer, which can be used as a replacement for OPC. A geopolymer is a synthetic amorphous aluminosilicate, generated from materials with a large content of  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$ , which are generally referred to as the base material. The based material is combined with an activating solution which allows it to be broken down and reformed into a monolith, containing three-dimensional aluminosilicate networks. Industrial waste products with high in  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$ , such as fly ash, are commonly used as base materials for geopolymers. Metakaolin [2] and blast furnace slag [3], as well as fly ash blended with blast furnace slag [4] and rice husk ash [5], can also be used to make geopolymers. It has been reported that geopolymers emit less  $\text{CO}_2$  than that of portland cement [6]. This can make a significant contribution to the reduction in global greenhouse gas emission [1].

The reaction of a solid aluminosilicate, with a highly concentrated aqueous alkali hydroxide or silicate solution, produces a synthetic alkali aluminosilicate material which is commonly called 'geopolymer' [7]. This material shows comparable performance to traditional cementitious binders in numerous applications, but with the added advantages of significantly reduced greenhouse emissions [8]. Geopolymer is synthesized by mixing aluminosilicate-reactive material with strong alkali solutions, such as sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium silicate or potassium silicate. The mixture can be cured at room temperature. Under a strong alkali solution, aluminosilicate-reactive materials dissolve and form free  $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedral units [9]. Fly ash is the most common source material for making geopolymers. Normally, good high-strength geopolymers can be made from class F fly ash. However, it has been shown that high-calcium fly ash from lignite can also be used to produce geopolymer mortar with a compressive strength up to 65.0 MPa [10]. Moreover, geopolymers have a potential to be used in high temperature applications, such as fire proof coatings, structural concrete in fire prone areas and thermal insulation for refractory type applications, due to their intrinsic thermal stability [11].

Fly ash is traditionally obtained from pulverized coal combustion (PCC) which is the combustion in electricity production. PCC is operated at temperature of 1300-1700°C, and the process releases  $\text{NO}_x$  and  $\text{SO}_2$  emission [12]. Due to the high temperature of PCC, the fly ash is formed in spherical shape with high amorphous properties [12]. Generally, this PCC fly ash is used as pozzolanic material in concrete process [1]. Another combustion process is fluidized bed combustion (FBC) which is considered as clean technology, using calcium carbonate injection to absorb sulfur. This process is operated at 800-900°C and can reduce  $\text{NO}_x$  emission, owing to low combustion temperature, Fly ashes from FBC and PCC are different in chemical components, particle shape and amorphous properties. Typically, FBC fly ash has particle size of 1-300  $\mu\text{m}$  and

contains high crystalline phases, whereas particle size of PCC fly ash is 1-200  $\mu\text{m}$  and filled with more amorphous properties. FBC fly ash also has more CaO and  $\text{CaSO}_4$ , so it is limited in the application as pozzolanic material [12].

To increase utilization of FBC fly ash, the present study has developed properties of geopolymer, produced from FBC fly ash, and extended the use of FBC fly ash, by grinding the FBC fly ash into smaller sizes and increasing specific surface area. It could activate more reaction and further increase its potential in commercial utilization.

## II. Experimental procedure

### 2.1 Materials

The FBC fly ash was used as a source material for geopolymer production. The chemical components of FBC fly ash were analyzed using X-ray fluorescence (XRF) method and its result is shown in Table 1. It is shown that the FBC fly ash composes of silica ( $\text{SiO}_2$ ), calcium oxide (CaO), and sulfate compounds. Due to lime injection, in order to absorb sulfur dioxide ( $\text{SO}_x$ ) in the FBC, the fly ash, that contains high CaO content, is commonly used as main component. The morphological property of FBC fly ash was analyzed using X-ray diffraction (XRD) technique. It is clear that several peaks of crystalline were detected, showing low reactive of FBC fly ash, as shown in Fig 1. The FBC fly ash was ground into a small size, with 20,000 rph for 5 and 10 h, resulting in mean particle sizes of 10 and 8  $\mu\text{m}$ , respectively. The particles size of original FBC fly ash was 24.6  $\mu\text{m}$ . The chemical solutions, used in geopolymer preparation, were  $\text{Na}_2\text{SiO}_3$  (with 31%  $\text{SiO}_2$  and 9%  $\text{Na}_2\text{O}$  by weight) and 15 M concentration NaOH [13]. River sand, with sieve no.8 particle size (3.8 cm opening), is used as filler for geopolymer mortar.

**Table 1 Chemical components and approximate particle size of fly ashes**

Samples	Symbol	Quantity (wt.%)								LOI	Mean particle size( $\mu\text{m}$ )
		$\text{Na}_2\text{O}$	MgO	$\text{Al}_2\text{O}_3$	$\text{SiO}_2$	$\text{SO}_3$	CaO	$\text{TiO}_2$	$\text{Fe}_2\text{O}_3$		
Original fly ash	OFBC	0.8	1.8	16.2	37.8	4.9	22.3	1.1	14.4	0.8	24.6
Ground fly ash at 20,000 rph for 5 h	10FBC	0.8	1.7	15.3	40.4	4.8	21.7	1.1	13.9	0.5	10.1
Ground fly ash at 20,000 rph for 10 h	8FBC	0.8	1.7	15.1	40.9	4.6	21.6	1.0	14.1	0.3	8.7

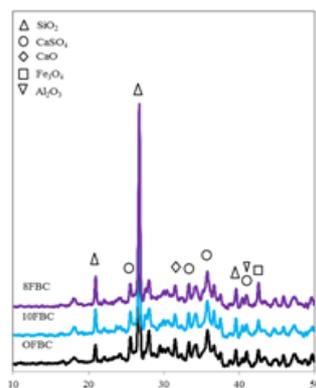


Fig. 1 XRD of FBC fly ashes

### 2.2 Geopolymer preparation

Geopolymer paste was made by mixing each fly ash (OFBC, 10FBC and 8FBC) with  $\text{Na}_2\text{SiO}_3$  solution and 15M NaOH which  $\text{Na}_2\text{SiO}_3$  solution-to-15M NaOH ratio (G/N) was 2 and 2.5, and fly ash-to-total substances (S/T) was 0.55. Sample were cast in plastic mould and covered with plastic to avoid rapid vaporization on the surface. The samples were cured in an oven at  $65^\circ\text{C}$  for 24 h. After that, samples were demolded and kept in a controlled temperature of  $25\pm 3^\circ\text{C}$ . Mix proportion of samples was tabulated in Table 2. Geopolymer paste was tested for chemical properties and morphology. For geopolymer mortar preparation, sand was added to the fresh paste, with sand-to-fly ash mass ratio of 2, and mixed for 1 min, before casting in the mold as same as paste preparation. Geopolymer mortar was prepared for strength test.

**Table 2 Geopolymer mixtures**

Samples	Ratio		Fly ash(g)	$\text{Na}_2\text{SiO}_3$ (g)	15 M NaOH (g)
	S/T	G/N			
S55G20	0.55	2.0	55	30	15
S55G25	0.55	2.5	55	32	11

when S/T = fly ash (solid)-to- all substances (fly ash, Na<sub>2</sub>SiO<sub>3</sub> and 15M NaOH) mass ratio  
 G/N = Na<sub>2</sub>SiO<sub>3</sub>-to-15 M NaOH mass ratio  
 Samples 'SxxGyy' = 'xx' represented S/T ratio and 'yy' represented G/N ratio

## 2.3 Geopolymer analysis

### 2.3.1. Morphological study

Geopolymer pastes were ground and analyzed using XRD, in order to identify phases presented in products, obtained from geopolymerization. In addition, microstructure of geopolymer pastes were investigated using SEM technique. Geopolymer pastes were broken into small pieces and coated with gold to obtain clear images.

### 2.3.2. Compressive strength

Compressive strength of geopolymer mortars, with the size 5×5×5 cm, were tested at the curing age of 7, 30 and 90 days, according to ASTM C-109 standard.

## III. Results and discussion

### 3.1 Morphology of geopolymer paste

Morphology of geopolymer pastes of OFBC, 10FBC, and 8FBC fly ashes were analyzed and shown in Fig. 2. The G/N ratio content was varied from 2.0 to 2.5.

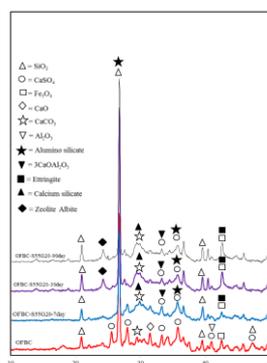


Fig. 2 XRD patterns of OFBC fly ash and OFBC geopolymer pastes at 7, 30 and 90 days.

The XRD results of OFBC fly ash and OFBC geopolymer are presented in Fig. 2. The XRD pattern of OFBC fly ash shows numerous sharp peaks of crystalline phases. Calcium and silica are the main compounds detected in all ashes. The low active FBC fly ash can be converted to a material with high amorphous content by the geopolymerization process. This corresponds to the detection of aluminosilicate in the geopolymer matrix. New compounds of aluminosilicate, calcium-silicate, calcium-aluminate, ettringite, and zeolite albite (NaAlSi<sub>3</sub>O<sub>8</sub>) are also formed. The peaks of ettringite and zeolite albite are at 43° 2θ and 24° 2θ, respectively. The peak of ettringite is obvious when it was cured at 30 days, the peak of zeolite albite (NaAlSi<sub>3</sub>O<sub>8</sub>) is at 24° 2θ for 90 days curing.

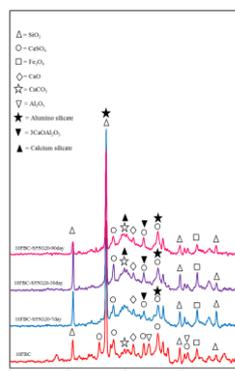


Fig. 3 XRD patterns of 10FBC fly ash and 10FBC geopolymer paste that were cured at 7, 30 and 90 days

Fig. 3 shows the XRD patterns of 10FBC fly ash and 10FBC geopolymer paste. The XRD pattern of 10FBC fly ash is similar to that of OFBC. The XRD pattern of 10FBC geopolymer shows the peak of aluminosilicate, calcium-aluminate, and calcium-silicate, as a result of geopolymerization reaction. The peak of

ettringite is found at  $45^\circ 2\theta$ . However, zeolite ( $\text{NaAlSi}_3\text{O}_8$ ) of 10FBC geopolymer paste is not detected at  $24^\circ 2\theta$ , at which smaller particles of fly ash, silica and alumina were active in reaction and aluminosilicate was formed. As a consequence, there is less aluminium that can form the zeolite.

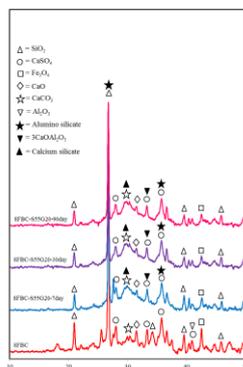


Fig. 4 XRD pattern of 8FBC fly ash and 8FBC geopolymer paste that were cured at 7, 30 and 90 days

The XRD patterns of 8FBC fly ash and 8FBC geopolymer paste are presented in Fig. 4. The XRD pattern of 8FBC fly ash is also similar to that of OFBC. However, the width of the peak in geopolymer is wider than that of fly ash. The XRD pattern of OFBC fly ash shows the peak of  $\text{NaAlSi}_3\text{O}_8$  at  $24^\circ 2\theta$ . The peak of ettringite at  $45^\circ 2\theta$  is not detected, similar to that of 10FBC geopolymer. The results show that OFBC fly ash, 10FBC and 8FBC, produced as geopolymer, have several peaks of aluminosilicate, calcium-silicate, and ettringite that are products of geopolymerization reaction. Ettringite and zeolite are detected in OFBC geopolymer, but not detected in both 10FBC and 8FBC. It is also found that curing age can affect the peak of ettringite. The longer the curing age, the clearer the ettringite peak. The peak of zeolite is clearer when curing age is longer, due to aluminium and silica reaction. Moreover, when the ratio of  $\text{Na}_2\text{SiO}_3$ -NaOH (G/N) is higher, the water requirement of geopolymer is also higher. This results in higher concentration and faster formation.

### 3.2 Microstructural study

Fig. 5 presents microstructural images of FBC fly ash and geopolymers. The composite consists of unreacted fly ash particles, crushed FBC fly ash, 10FBC and 8FBC, geopolymer matrix and other compounds.

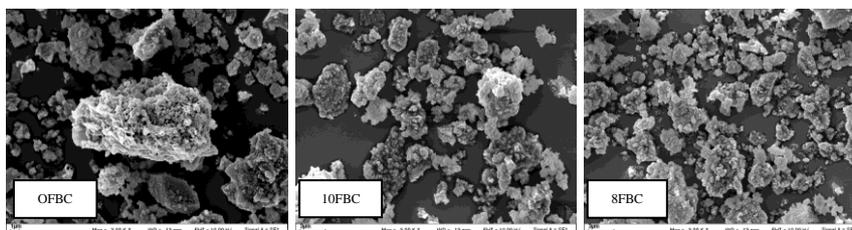


Fig. 5 Microstructural images of FBC

Fig. 6 shows microstructure of geopolymer pastes from FBC fly ash with different particle sizes. The unreacted particles of OFBC fly ash are also found. It can be seen that the geopolymer has dense and homogeneous matrix. The content of unreacted 8FBC geopolymer is less than the 10FBC fly ash. Fig. 7 shows the EDX of geopolymer that was cured at 30 days. It is found that Si, Al, and Ca are rich in the geopolymer.

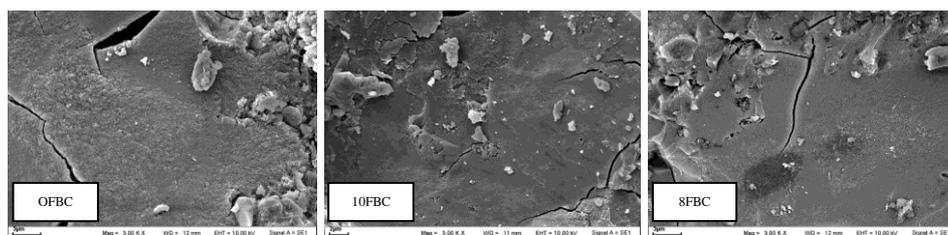


Fig. 6 Microstructural images of FBC geopolymer S55G20 that were cured at 30 days

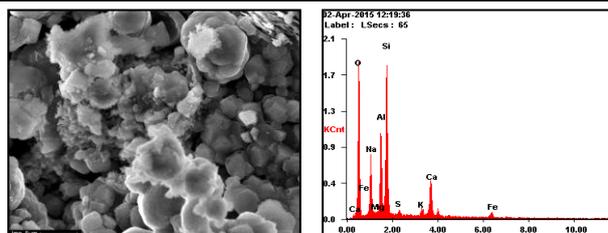


Fig. 7 the results of EDX analysis of OFBC that was cured at 30 days

### 3.3 Compressive strength of FBC geopolymer

The compressive strength of FBC fly ash geopolymer mortar, cured at 7, 30 and 90 days, are presented in Fig. 8. At 7-day, the compressive strength of 8FBC, 10FBC and OFBC are 20, 19 and 12 MPa, respectively. This is due to low reactive amorphous phase and high crystallinity of the as-received starting material. The compressive strength increased with the curing age, owing to high calcium content of FBC fly ash and the formation of calcium silicate hydrate (C–S–H) in the composite. In addition, aluminosilicate compound, Al–S–H is also another significant factor, enhancing the strength of FBC fly ash geopolymer. The leaching of minerals, such as silicon and aluminum ions, occurred when fly ash came into contact with NaOH and sodium silicate solutions [13].

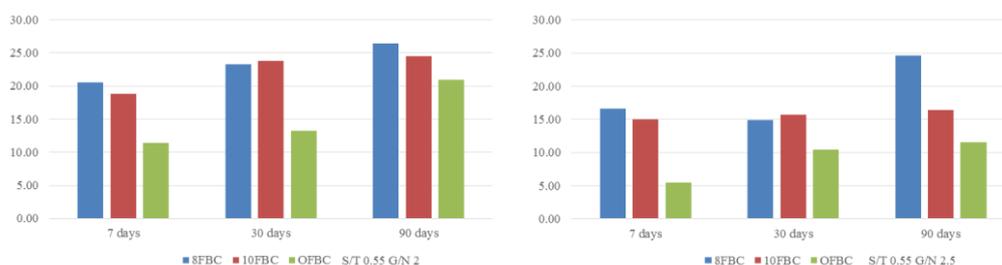


Fig. 8 Compressive strength of 10FBC geopolymer that were cured at 7, 30 and 90 days

The particle sizes of geopolymer affect the reaction of geopolymerization, which lead to the effect of compressive strength. It is found that the ground FBC fly ash is better in the reaction of geopolymerization, resulting in smaller pore size and decreasing porosity. As a result, the crushed FBC has higher compressive strength. For OFBC and 10FBC, compressive strengths are less than that of 8FBC. This results in pozzolanic reaction and leads to strength gain of the geopolymer.

## IV. Conclusion

The present study reveals that the particle size of FBC fly ash take effects on geopolymer properties. The geopolymer with smaller particle size of FBC fly ash shows the dense and homogeneous matrix. The S/T and G/N ratios can take effects on geopolymer properties. The compressive strength of 8FBC geopolymer is highest at S/T of 0.55 and G/N of 2.0. Higher G/N value results in higher water requirement of geopolymer, resulting in less formation at short curing age and higher compressive strength, due to the length of curing age. Longer curing age causes more completed geopolymerization reaction.

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