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The Effect of Pulp Industrial Waste as Chemical Admixture to Compressive Strength of Fly Ash Based Alkali Activated Materials

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Abstract. Black liquor is a toxic by-product from industrial pulp manufacture. It contains sodium hydroxide that can be used as precursor activator for alkali activated material, which is an aluminosilicate material that can be prepared from thermal activation of solid material containing alumina and silica as precursor and alkali activator solution. In this work, alkali activated mortar was prepared by mixing fly ash as main precursors, aggregate, followed by addition of activator solution containing sodium hydroxide solution and waterglass, and chemical admixture which is lignin or black liquor. The best compressive strength was 34.40 MPa achieved in addition of 10 wt% of black liquor to alkali activated mortar. X-ray diffraction demonstrated the formation of albite in mortars, indicating that geopolymerization have been successfully formed. FTIR spectra showed the presence of siloxo and sialate peaks which commonly found in geopolymerization.

1 Introduction

Industrial paper manufacture involves a procedure known as the Kraft process, where wood is converted into wood pulp and then into paper. However, this process produces a toxic byproduct referred as black liquor. This primarily liquid mixture of pulping residues (like lignin and hemicellulose) and inorganic chemicals from the Kraft process (sodium hydroxide and sodium sulfide, for example) is toxic and until the invention of recovery boilers in the early 20th century was often simply released into. Recovery boilers allowed paper manufacturers to reuse and recover inorganic chemicals and extract energy from the pulping residues. Where recovery boiler capacity is limited and a bottleneck in the pulp mill the lignin in the black liquor may be extracted. Lignin used by plants for structure, water transport, and defense, and it is the second most abundant biopolymer on Earth after cellulose [1]. Due to presence of sodium hydroxide in black liquor and lignin, this material can be used as chemical admixture for alkali activated materials.

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In this work, chemical admixture combined with fly ash, which is also by product material containing high silica and alumina, was used in production of alkali activated materials. The activation of fly ash with alkali activator forms an inorganic binder through geopolymerization. Silica and alumina were reacted with alkali activator to generate aluminosilicate materials with CaO facilitated the setting of the materials. In this work, fly ash was utilized as precursor in geopolymerization to make alkali activated material (AAM). Fly ash that has reacted after geopolymerization will not leach out to the surrounded environment. Alumina and silica consisted in fly ash were first reacted with alkali activator solution and then it was combined with aggregate to make alkali activated mortars. In order to enhance the mechanical properties of fly ash-based AAM, chemical admixture in form of lignin, and black liquor were added to geopolymeric body up to 10% (wt/wt). The effect of various chemical admixtures toward macroscopic and microscopic properties of resulting AAM was also evaluated.

2 Materials

Most of the materials used in this experiment were originally come from industrial waste. Fly ash was obtained from Suralaya Coal Fired Power Plant in Banten. The oxides composition of fly ash was determined using X-Ray Fluorescence. The fly ash contains SiO_2 (52.30 %), Al_2O_3 (26.57 %), CaO (6.00 %), Fe_2O_3 (7.28 %), and some metal oxides. Cimalaka sand in saturated surface-dry (SSD) was used as fine aggregate for making mortar phase. NaOH 12M solution was made by mixing 480g of solid NaOH with 1 litre of aquadest. Alkali activator solution was made by mixing water glass solution and sodium hydroxide (NaOH) 12M. The alkali activator was stored at least 4 hours before used in geopolymerization [2]. Lignin and black liquor were kindly provided by Center of Pulp and Paper, West Java, Indonesia

3 Experimental procedure

Alkali activated mortar was made by mixing fly ash, aggregate, alkali activator solution and lignin or black liquor as chemical admixture. All components were mixed using Hobart™ mixer to form slurry. Once the slurry has been mixed thoroughly and reached proper consistency, it was then tested using Flow Test Table conformed to ASTM C192 to study its workability. The slurry was filled into cubical mould 5cm x 5cm x 5cm. The mortars were cured under ambient (Room Temperature). After few hours, through hydration the mortars hardened and were put out from the mould. The samples were stored at room temperature until it perfectly set. Ratio of alkali activator to binder used was kept constant at 0.5.

The composition of various mortars is shown in Table 1. All composition ratios indicated in that table are in weight unit. The ratio of activator: binder: filler was kept 1 : 2 : 3 [3]. After 28 days, the samples were tested by using Universal Testing Machine (UTM) conformed to ASTM C-39 to obtain the maximum compressive strength data. Chemical composition analysis was performed by using X-Ray diffraction (XRD) and Fourier Transform infrared spectroscopy (FTIR). XRD provided the information of phase identification of a crystalline material of resulting mortars using Philips Diffractometer PW1710. FTIR used to obtain an infrared spectrum of the absorption or emission of a solid, liquid or gas from the broken mortars using (FTIR) Prestige 21 Shimadzu.

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Table 1. Mix design of alkali activated materials.

Code	Act:Prec: Aggregate	Curing Method	Admixture
Control	1:2:3	Ambient	-
FAL	1:2:3	Ambient	Lignin
FABL	1:2:3	Ambient	Black Liquor

4 Results and discussion

4.1 Compressive strength test result

The values of compressive strength are shown in Figure 1. Control samples demonstrated average compressive strength of 26.40 MPa, while FAL and FABL showed the increased values of compressive strength which is 30.33 MPa and 34.40 MPa, respectively. It shows that the addition of lignin and black liquor increase the compressive strength from sample without admixture. This is due to high concentration of NaOH used in making black liquor (14M), which means there are addition of Na^+ in the solution is sufficient to bind silicate in fly ash. Samples containing black liquor showed denser mortars than others.

Table 2. AAM mix design, workability and compression strength results.

Code	Workability Result (cm)	Compressive Strength (MPa)
Control	15	26.40
FAL	19	30.33
FABL	20	34.40

4.2 Workability test result.

Workability of FAL (19 cm) and FABL (20 cm) was higher than Control (15 cm), thus makes the slurry of FAL and FABL easier to pour into mould because of extra liquid presents in chemical admixture. It makes lignin and black liquor might be sufficient as water reducer chemical admixture also.

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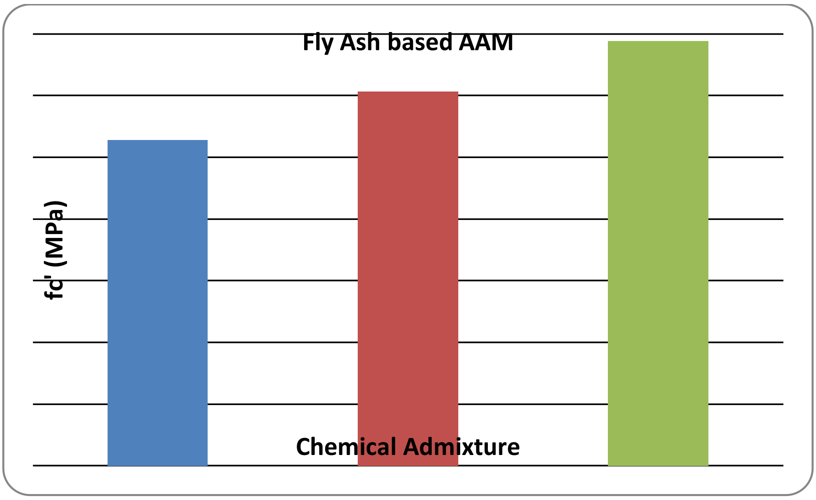

Fig. 1. The effect of various chemical admixture of fly ash based AAM towards compresive strength (fc').

4.3 XRD test result

XRD diffractograms which according to Joint Committee on Powder Diffraction Standards (JCPDS) are presented in Figure 2. demonstrated the presence of quartz (SiO_2) (Peak Q, JCPDS No. 46-1045), Hematite (Fe_2O_3) (Peak H, JCPDS No. 33-0664), both presents in fly ash precursor and alkali activated mortars. Alkali activated mortars has albite ($NaAlSi_3O_8$) (Peak A, JCPDS No. 20-0572), which is only found in alkali activated materials. The formation of albite indicates the reaction between fly ash precursors and alkali activator (sodium hydroxide and water glass) has successfully occurred. Silica and alumina contents in 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, resulted in aluminosilicate compounds as shown by the presence of albite that has similar formula with alkali activated material (Mn [-(SiO_2)z-AlO_2]n. wH_2O) and base peak line hump XRD pattern has shifted as shown in Figure 3. It means that resulting mortars have more semi crystalline area than fly ash or in the other words fly ash is less amorphous than product which is in agreement with the work of Skavara [4].

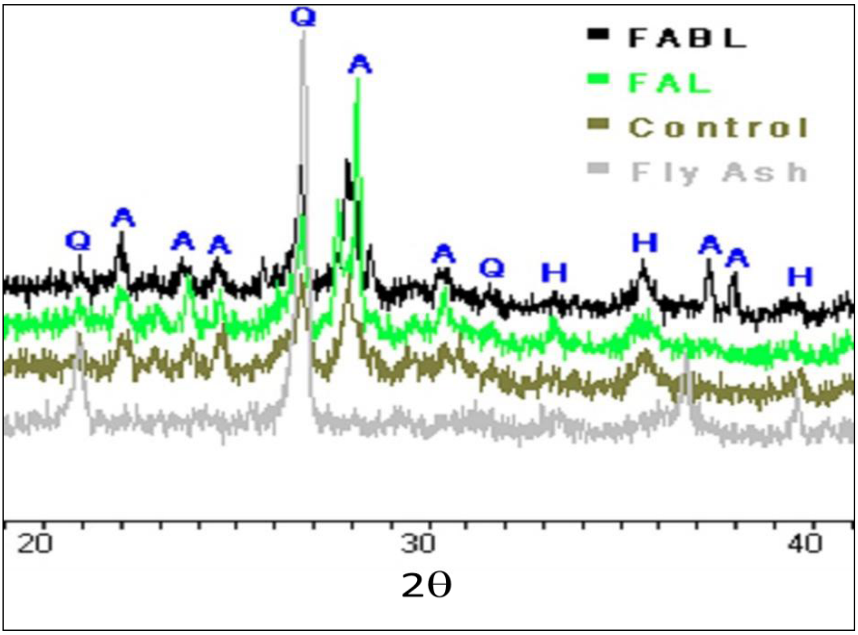

Fig. 2. XRD patterns of various fly ash-based AAM.Peaks A=albite, Q=quartz and H=hematite.

4.4 FTIR result

FTIR results of various alkali activated mortars are shown in Table 3, while Figure 3 shows FTIR spectra of Control, FAL and FABL samples. Peak around 470 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 570-780 cm^{-1} and 1010-1030 cm^{-1} indicating formation of albite, a typical compound of alkali-activated material in these variants as the result of alumina and silica dissolution in fly ash.

Table 3. FTIR results summary of various alkali activated mortars.

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)
Control	3448.72	1641.42	1012.63	775.38	578.64	472.56
FAL	3450.65	1641.42	1010.70	775.38	578.64	449.41
FABL	3448.72	1641.42	1020.34	775.38	578.64	472.56

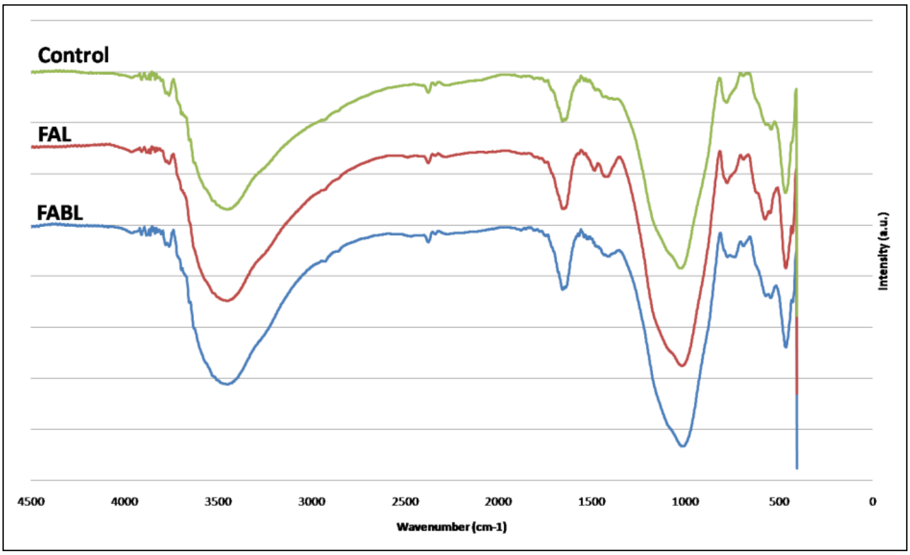

Fig. 3. FTIR spectra of various AAM samples.

The similar spectra in Criado works and stated that the formation of solidification product marked with wavelength number reduction in similar bonding in fly ash based alkali-activated material [5]. Broad peak around 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 functional groups.

5 Conclusions

Alkali activated mortars have been successfully prepared from fly ash, aggregate, alkali activator solution, and chemical admixture followed by curing. The compressive strength of resulting mortars can be varied by changing the chemical admixture, where the addition of black liquor in AAM resulting in highest compressive strength (34.40 MPa). Thus, lignin and black liquor was a potential chemical admixture to be developed for alkali activated materials.

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