Influence of Alkali activator Dosage on Strength of CFBC Fly Ash Based Geopolymer

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CONFERENCE: 2017 World of Coal Ash – (www.worldofcoalash.org)

KEYWORDS: CFBC fly ash, geopolymer, alkali activator, sodium hydroxide

ABSTRACT

Geopolymer, which is environmentally friendly and needs moderate energy to produce, has been a developing and cost-effective solution to use solid waste and by-products. But for circulating fluidized bed combustion (CFBC) fly ash, a kind of by-products of power plants, the geopolymerization procedure of which is still indistinct. In this report, geopolymer was synthesized with CFBC fly ash as the main raw material, sodium hydroxide and water glass solution as alkali activator. With the analysis results of XRD and FTIR, potential mechanism and effect of alkali activator dosage on structure and strength of CFBC fly ash was investigated and discussed.

1. INTRODUCTION

Circulating fluidized bed combustion (CFBC) is an advanced, clean and reliable coal combustion technology for power generation, which has met the environmental requirements for reduction in NO_x and SO_2 emissions from coal-fired power plants.[1-3] Currently, CFBC has been growing steadily all over the world ever since its commercialization in the 1970s and more than 1000 CFBC boilers are in operation in China.[4, 5]

However, the CFBC fly ash, captured from the duster, has long posed more severe challenges than pulverized coal combustion (PC) fly ash to utilization in construction applications, whereas most PC fly ash can be recycled used in the cement and concrete industry.[6] The low combustion temperature of 850-950^{o}C makes CFBC fly ash differ greatly in physical and chemical properties from PC fly ash, the typical firing temperatures of which are 1200-1400^{o}C. Actually, the low firing temperature may lead to low pozzolanic activity, which plays an important role for fly ash used in construction industry.[7, 8] Besides, the use of CFBC fly ash in concrete may result in structure damage and strength decrease due to the high presence of f-CaO, SO_3 and water requirement.

In spite of the utilization limitation in cement and concrete industry, CFBC fly ash contains a substantial amount of SiO_2 and Al_2O_3 which can be used as a source material for preparing geopolymer.

Geopolymer, named by Joseph Davidovits in 1970s, is a type of cross-linked long chain inorganic polymer materials formed under high alkali condition from aluminosilicate solid and alkali silicate solution.[9] The three dimensional structures are built in geopolymer with tetrahedral AlO_4 and SiO_4 units.[10] Some investigations have shown that geopolymer could be synthesized with CFBC fly ash, but the geopolymerization mechanism on the alkali-activated CFBC fly ash hasn't been clear yet, for example, the influence of Na_2O/SiO_2 ratios on structure of CFBC fly ash based geopolymer.[11-13]

In this study, therefore, synthesis and characterization of CFBC fly ash based geopolymer investigated with sodium hydroxide and sodium silicate solution as alkali activator. With the analysis results of compressive strength, XRD, and FT-IR, potential mechanism and effect of alkali activator dosage on structure and strength of CFBC fly ash was investigated and discussed.

2. MATERIALS AND EXPERIMENTAL PROCEDURES

2.1 Materials

Anthracite CFBC fly ash from Yong'an power plant in China was used for this study. Chemical compositions were determined by a RIX-2100 X-ray fluorescence spectrometer (XRF) (Rigaku, Japan) and the results are shown in Table1. Sodium silicate (analytical grade) with 25.5% SiO_2, 10.6% Na_2O and 63.9% H_2O by weight and NaOH solutions were used as alkali activators.

Table1. Chemical composition of raw CFBC fly ash（/wt.%）

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	TiO_2	Na_2O	SO_3	LOI
38.1	18.0	8.36	11.36	1.49	1.82	0.971	0.362	3.53	7.39

2.2 Geopolymer synthesis

Geopolymer paste samples were synthesized by mixing of alkali activator solution and CFBC fly ash at mass ratio of 0.4, and activator solution contains 34 wt% of sodium silicate. It should be noted that various sodium solution of 2.2, 4.1, 4.8, 6.0 and 7.1 molar were used in samples with the Na_2O/SiO_2 (Na/Si) ratios of 0.15, 0.23, 0.27, 0.32, and 0.38.

2.3 Sample preparation and testing

The geopolymer pastes were cast in 2 cm×2 cm×2 cm cubic moulds for strength test. The cast samples were covered with clingfilm to avoid loss of water and cured in an electric oven at 70ºC, 95%RH for 1 day. Then, they were unmolded and left standing in the curing room (20 ºC, 60%RH) until the age of 6 days. The compressive strength test was performed at the age of 7 days. The reported results are the average of three specimens.

The microstructures of geopolymer paste were investigated by X-ray diffraction (XRD) (Rigaku, Japan) and the Fourier Transform Infrared Spectroscopy (FTIR) (PerkinElmer, Japan). The broken portion of the compressive strength specimens were used for these analyses.

3. RESULTS AND DISCUSSION

3.1 Compressive strength of CFBC fly ash based geopolymer

Just as the ordinary Portland cement, the compressive strength of geopolymer increased with the curing age development, which is shown in Figure 1. Besides, the compressive strength of CFBC fly ash based geopolymer varied with different dosage of alkali activator, for geopolymerization is effected by alkali activator concentration, as well as ratio of Na_2O/SiO_2 (Na/Si). With the increasing of Na/Si from 0.15 to 0.27, compressive strength of CFBC fly ash improved. It may be resulted from that alkali activator acts as the accelerator for Si and Al dissolution in CFBC fly ash.[14] However, compressive strength decreased when Na/Si was above 0.27. Some investigations have shown that the high concentration of alkali activator, on one hand, could promote the dissolution of Si and Al in CFBC fly ash, but for another hand, it may hinder the polycondensation of Si and Al group. Besides, the exorbitant concentration of OH^- made the Si and Al gel precipitate in the early of geopolymerization, which may resulted in the low compressive strength.[15-17]

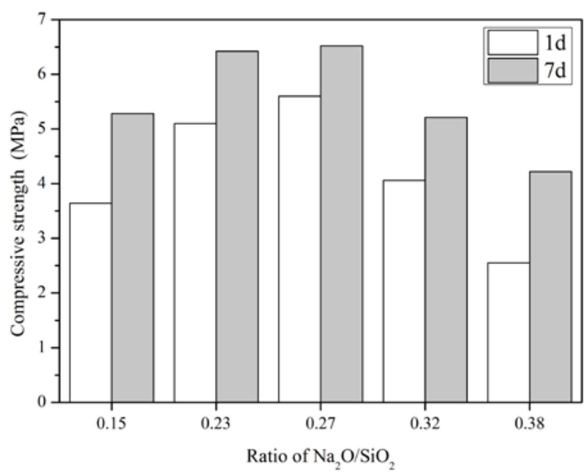

Figure 1. Compressive strength of CFBC fly ash based geopolymer

3.2 XRD analysis of CFBC fly ash based geopolymer paste

As show in Figure 2, the major minerals in raw CFBC fly ash include anhydrite ($CaSO_4$), quartz (SiO_2), limestone ($CaCO_3$) and free lime (CaO) with little amount of calcium hydroxide ($Ca(OH)_2$) and hematite (Fe_2O_3). But for CFBC fly ash based geopolymer, only few minerals were tested, such as quartz (SiO_2), limestone ($CaCO_3$) and hematite

(Fe_2O_3). As for the high crystallinity of quartz in CFBC fly ash with low reactivity, there was still much quartz existing in geopolymer paste for 7days geopolymerization.
As shown previously, addition of alkali activator was helpful to promote the dissolution of Si and Al in CFBC fly ash, as well as the geopolymerization. Figure 2 has shown that a hill existed in 2θ between 20° and 35°, which belonged to Si and Al gel, a kind of glass phase. The result of Feng W. had shown the similar phenomenon in investigation of alkali-activated slag based geopolymer.[18]

With the existence of alkali activator, a series of chemical reactions occurred among different minerals in CFBC fly ash. For one thing, large amount of tetrahedral AlO_4 and SiO_4 units built the three dimensional structures in geopolymer.[19] For another, anhydrite reacted with sodium hydroxide to product Na_2SO_4 and $Ca(OH)_2$, then $CaCO_3$ generated with $Ca(OH)_2$ and CO_2.

$$CaSO_4+2NaOH=Ca(OH)_2+Na_2SO_4 \quad \cdots\cdots \quad (1)$$

$$Ca(OH)_2+CO_2=CaCO_3+H_2O \quad \cdots\cdots \quad (2)$$

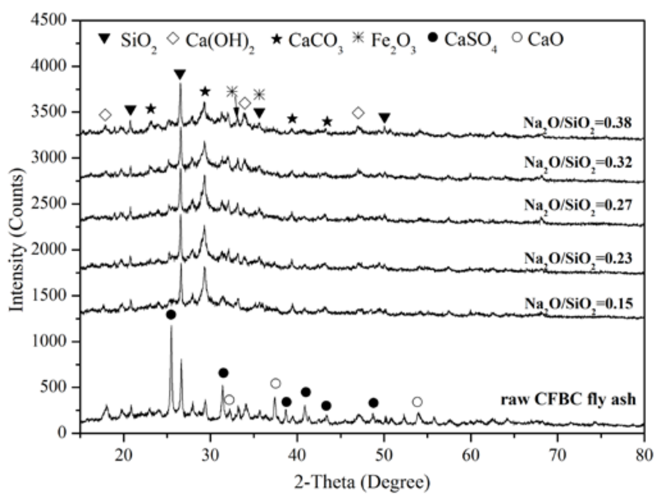

Figure 2. XRD analysis of CFBC fly ash based geopolymer (7 days)

3.3 FT-IR analysis of CFBC fly ash based geopolymer paste

FTIR spectra of raw CFBC fly ash and selected geopolymers are shown in Figure 3. The central prominent peaks of 1102cm^{-1} are attributed to the Si-O-Al and Si-O-Si asymmetric stretching, which shown that there are much tetrahedral SiO_4 and AlO_4 in CFBC fly ash.[20] Compared with the raw CFBC fly ash, the selected geopolymer with Na/Si=0.23 undergoes a very small shift of its Si-O-Si position of 1052 cm^{-1} to lower wavenumbers as a consequence of polycondensation with alternating Si-O and Al-O bonds.[21] With the ratio of Na/Si increasing, a shift of the main Si-O-Al and Si-O-Si asymmetric stretching band to lower frequency indicates a lengthening of the Si-O-Al and Si-O-Si bond, a reduction in the bond angle, and a decrease of the molecular vibrational force constant.[22] The results of FTIR also indicated that alkali activator promoted the dissolution of tetrahedral SiO_4 and AlO_4 in CFBC fly ash.

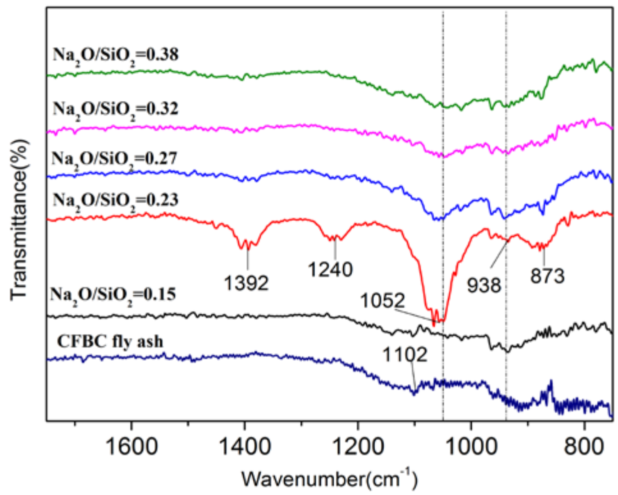

Figure 3. FTIR analysis of CFBC fly ash based geopolymer (7 days)

4. CONCLUSIONS

(1) With the existence of alkali activator, crystal and amorphous phase was destroyed to generate tetrahedral SiO_4 and AlO_4 for geopolymerization.

(2) When Na/Si was between 0.23 and 0.27, the compressive strength reached the highest value, as well as the main peaks of Si-O-Si and Si-O-Al.

(3) Compressive strength decreased and the main Si-O-Al and Si-O-Si asymmetric stretching band shifted to lower frequency as Na/Si was above 0.27.

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