Advanced Powder Technology 25 (2014) 1087–1093

Contents lists available at ScienceDirect

Advanced Powder Technology

journal homepage: www.elsevier.com/locate/apt

Original Research Paper

Strength and resistance to sulfate and sulfuric acid of ground fluidized bed combustion fly ash–silica fume alkali-activated composite

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ARTICLE INFO

Article history:
Received 13 November 2013
Received in revised form 20 January 2014
Accepted 11 February 2014
Available online 22 February 2014

Keywords:
Alkali-activated composite
Geopolymer
Fluidized bed coal combustion
Silica fume

ABSTRACT

Fluidized bed combustion (FBC) is an environmentally friendly process for burning of coal and is used in many small factories located in urban area. The FBC fly ash is an environmental problem and needs good disposal or utilization. This research studied the strength and resistance to sulfate and acid of alkali-activated FBC fly ash–silica fume composite. The FBC fly ash was interground with silica fume (at the dosage levels of 1.5%, 3.75% and 5.0%) to make the source material homogenous with increased reactivity. Addition of silica fume enabled the adjustment of SiO_2/Al_2O_3 ratios (6.55-7.54) of composite and improved the strength and resistance to sulfate and acid of composite. The composite with 3.75% silica fume showed the optimum strength with 28-day compressive strength of 17.0 MPa. The compressive strengths of composite with 3.75% silica fume immersed in 5% magnesium sulfate solution and 3% sulfuric acid solutions were substantially higher than the control. The strength loss was from the high calcium content of FBC fly ash and incorporation of silica fume thus increased the durability of the composite.

1. Introduction

Fluidized bed combustion (FBC) is a promising environmentally-friendly coal combustion process with operating temperature of 800–900 °C comparing with pulverized coal combustion. The low temperature prohibits the nitrogen oxides (NOx) emission [1]. The amount of FBC fly ash has, therefore, increased significantly over the past few years owing to the rapid growth of FBC technology [1]. The fly ash has low glassy phase material and possesses very low pozzolanic property. Improvement on its reactivity can be obtained from an intense grinding to reduce the particle size [2]. In addition, it contains high amount of calcium compounds (CaO and $CaSO_4$) from the use of lime powder to capture SO_2. The use of FBC fly ash as a pozzolan to partially replace Portland cement is therefore not recommended [3].

Researches have focused on the utilization of fly ash as a source material in alkali-activated composite or “geopolymer” [4,5]. This composite is alumino-silicate compound and can be produced from the alumino-silicate source materials (e.g. fly ash or metakaolin) in alkaline solutions e.g. sodium hydroxide and sodium silicate solutions [6–8]. Heat curing (60–90 °C) is usually applied to accelerate the reaction. The aluminosilicate product with high early strength and stability up to temperature of 1400 °C could be obtained [9].

In addition, fly ash geopolymer is resistant to acid and sulfate solutions compared with OPC materials. Immersion of geopolymer in these solutions has small impact on the strength of material because of the nature of aluminosilicate gel in geopolymer [7,8]. The stability of materials depends on the type of activator and type of cation in the sulfate media [8]. For magnesium sulfate immersion, gypsum, $Mg(OH)_2$, SiO_2, and magnesium silicate hydrate can be formed. This caused the deterioration of materials and reflected in compressive strength loss [7].

Researchers have investigated the use of FBC fly ash as an alternative source material for preparation of alkali-activated composite [2,10,11]. However, as-received FBC fly ash provided both low strength and acid resistance owing to high calcium content in composite [2,10].

Due to high content of calcium compounds in FBC fly ash, additional pozzolanic reaction is possible in geopolymer which will lead to the formation of calcium silicate hydrate (C–S–H). Silica fume is a micro sphere of non-crystalline silica with very high surface area. It contains more than 78% SiO_2 in glassy form and is suitable for use as cement additive [12] with a large filler effect in concrete. In concrete application, the use of silica fume improves the strength and other physical properties of concrete [13,14]. It

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http://dx.doi.org/10.1016/j.apt.2014.02.007
0921-8831/

has also been shown that silica fume can also be used to prepare sodium silicate for geopolymer synthesis using sol–gel condensation reaction [15].

The use of silica fume as a silica source to enhance the properties of alkali-activated FBC fly ash composite is, therefore, promising. High calcium fly ash reacts and forms C–S–H and other calcium compounds e.g. $Ca(OH)_2$ in the presence of alkali solution [2,9]. This research has proposed that active silica fume should react with these calcium compounds (from FBC fly ash and products) forming the C–S–H in composite and contributing to the strength gain and good physical properties of alkali-activated composite. Owing to low reactivity and high pore volume of FBC fly ash, grinding of FBC fly ash was recommended to remove the void, refine the pore structure and increase surface area before using as source material for geopolymer preparation [2]. Therefore, grinding of the source materials was performed in this research.

2. Experimental procedure

2.1. Materials

The FBC-fly ash and silica fume were used as source materials for the synthesis of alkali-activated composite. This FBC fly ash mainly consisted of silica (SiO_2), alumina (Al_2O_3), lime (CaO) and sulfur trioxide (SO_3) determined by X-ray fluorescence (XRF) as tabulated in Table 1. High CaO content of 38.7 wt% was found in FBC fly ash owing to the addition of lime for sulfur absorption. SEM image of FBC fly ash showed that the particle shapes were irregular (Fig. 1) with the median particle size (D_{50}) of 24 μm. FBC fly ash contains low glassy material due to the low burning temperature. Three dosages of silica fume addition of 1.5%, 3.75% and 5% by weight were selected to intergrind with FBC fly ash. Intergrinding of materials helped to obtain the homogeneous blended powder. The blend was ground in a laboratory ball mill for 2 h as a longer milling time only marginally increased the fineness of the blend. The homogeneous blends with a median particle size (D_{50}) of 5–7 μm measured by particle size analyzer (Malvern Mastersizer S), which retention on sieve No. 325 (45 μm opening) of 3.5–4.0 wt% were obtained. XRD patterns of raw materials are presented in Fig. 2. Quantitative XRD analysis of source materials was performed to obtain the amorphous content by using α-Al_2O_3 (corundum) as an internal standard. It was found that the amorphous contents of FBC fly ash and silica fume were 37% and 97% respectively. Therefore, incorporation of silica fume into FBC fly ash resulted in more glassy phases of the blend as the broad peak was detected in the XRD curve.

In addition to the source materials, 15 M sodium hydroxide (15 M NaOH) and commercial grade sodium silicate solution (Na_2SiO_3) with 9 wt% Na_2O and 30 wt% SiO_2 were used as an alkaline activator. For mortar preparation, the river sand with specific gravity of 2.65 and fineness modulus of 2.8 was employed. The compressive strength of mortars was tested in accordance with ASTM C109 at the ages of 7, 28 and 90 days. The results were reported as the average of five samples.

Table 1
Chemical composition and FBC fly ash and silica fume.

Chemical composition	FBC fly ash (wt%)	Silica fume (wt%)
SiO_2	21.2	98.2
Al_2O_3	10.7	–
CaO	38.7	–
Fe_2O_3	7.0	–
SO_3	14.9	–
Na_2O	2.5	0.5
K_2O	0.9	0.6
TiO_2	1.1	–
MgO	1.9	0.7
P_2O_5	0.1	–
Loss on ignition (LOI)	1.0	–

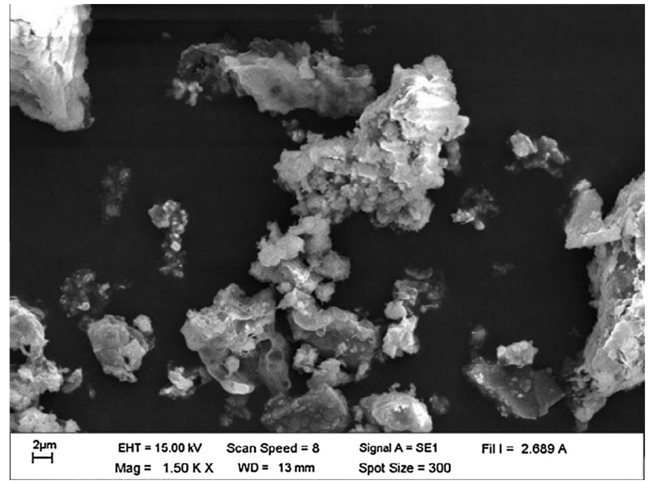

Fig. 1. Microstructure of FBC fly ash.

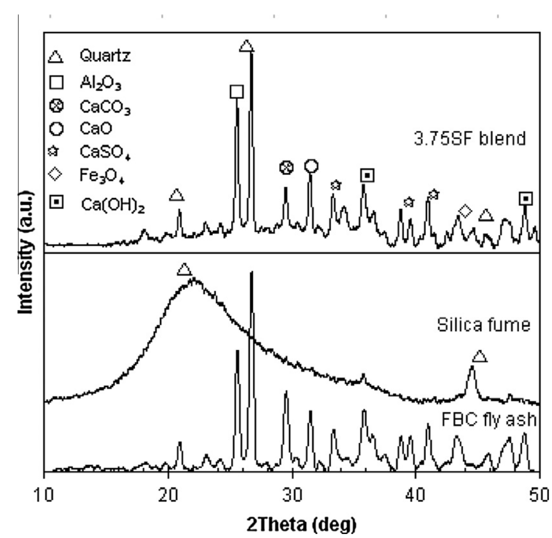

Fig. 2. XRD patterns of source materials.

2.2. Composite preparation

From a preliminary study, there was no ettringite formation in FBC geopolymer with NaOH concentration higher than 15 M [16]. The high NaOH concentration converted gypsum in the FBC fly ash system to calcium hydroxide ($Ca(OH)_2$) and aqueous sodium salt as shown in Eq. (1) and hindered the ettringite formation [17]. $Ca(OH)_2$, then, reacted with SiO_2 and resulted in C–S–H in the composite matrix.

$$CaSO_4 \cdot 2H_2O\ (s) + NaOH\ (aq) \rightarrow 4Ca(OH)_2\ (s) + Na_2SO_4\ (aq) \quad (1)$$

The Na_2SiO_3-to-NaOH mass ratio of 2 was used for the study as the higher ratio resulted in low strength composite as a result of excess silica gel and zeolite formation [18]. The blended powder-to-liquid mass ratio of 1.0 was employed. 15 M NaOH was thoroughly mixed with blended source material and Na_2SiO_3 was subsequently added to the mixture. The mix proportion is