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Original Research Paper

Geopolymerisation behaviour of size fractioned fly ash

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ABSTRACT

Fly ash is a fine powder residue resulted from combustion of pulverized coal in thermal power plants. Different size fractions of fly ash have different properties. Four size fractions (with characteristic particle diameter D_{50} of 40.37, 23.64, 10.33 and 2.98 μm respectively) collected from different fields of an electrostatic precipitator and representing the entire particle spectrum of fly ash has been selected for the study. These fractions have been characterized for their granulometry, chemistry, glass content and mineralogical phases. Geopolymerisation of size fractioned fly ash has been carried out at ambient (27 °C) and elevated (60 °C) temperature using isothermal conduction calorimetry (ICC) and the microstructure has been studied using X-ray diffractometry (XRD), scanning electron microscopy with X-ray microanalysis probe (SEM-EDS) and Fourier transform infrared spectroscopy (FTIR). Calorimetric studies showed that the heat flow curve during geopolymerisation has linear correlation with the glass content of fly ash. The compressive strength development at both ambient and elevated temperature was due to the combined effect of SiO_2/Al_2O_3 ratio, particle size and glass content. SEM-EDS studies have shown more reaction product in finer fractions and unreacted particles in coarser fractions. Formation of more thermonatrite phase was due to poor reactivity of coarse size fraction resulting into free alkali which in presence of atmospheric carbon formed $Na_2CO_3{\cdot}H_2O$.

1. Introduction

Fly ash is a by-product of thermal power plants resulted from the combustion of pulverized coal. It is a granular material with particle size typically varying from submicron size to 250 μm [1]. Interestingly the different size fractions of fly ash vary considerably in terms of chemistry, mineralogy and reactivity [2]. Due to its pozzolanic property, small particle size, flow characteristic and combination of crystalline and amorphous phase, fly ash is preferred material for many applications such as production of cement, concrete and brick [3]. Due to its unique combination of properties, uses of fly ash not merely as filler material, but as reactive component are continuously being explored. One such potential application where fly ash actively participates in reaction is its use for geopolymer synthesis.

Geopolymers are new class of inorganic polymer materials synthesized by reaction between alumino-silicate and alkali compounds at ambient or near ambient temperature [4]. Due to easy process of synthesis, low environmental impact and versatility in properties, they are fast emerging materials of choice for a range of building materials, fire resistant ceramics, composites, matrix for immobilization of toxic wastes, and many others. Traditionally metakaolin has been used as raw material for geopolymer synthesis [5,6]. Recently, there has been a change in trend where emphasis on raw material has been shifted from pure and naturally occurring materials to waste and by-products, more specifically fly ash. The reason for increased attention on fly ash is associated with easy availability, technical superiority, environmental and economic benefits [7–10]. The mechanism of geopolymerisation of fly ash is considered similar to metakaolin based geopolymer, but the degree of reaction varies due to the reactive and non-reactive fractions of fly ash [11]. The property of resulting geopolymer is influenced by the chemistry and reactivity of fly ash. The effect on role of chemistry on the properties of fly ash based geopolymer is well documented [12–15]. The reactivity of the fly ash in geopolymer system is mainly governed by two factors, (a) presence of reactive amorphous phase, and (b) fine particle size. Geopolymerisation of different size fractions of fly ash and its influence on the properties has been studied by many researchers [16–19]. However, in the majority of the studies, the different sizes have

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been obtained either by air classification or by milling of fly ash [16–19]. In the present work, the different size fractions of fly ash have been collected from the different hoppers of an electrostatic precipitator (ESP). The rationale for collecting from hoppers is based on ESP structure and existing practice of fly ash collection. Typically ESP has many hoppers in the direction of gas flow for the collection of fly ash. The fly ash collected in different hoppers has different properties. For example, the particle size decreases and specific surface area increases as the collection hopper gets distance from the boiler [20–22]. In practice, the fly ash collected from different hoppers is blended together before storage or disposal. Thus the distinct advantage of the properties of different size fractions is lost. Again for getting those properties, either fly ash is classified or milled. Also the chemistry and particle size distribution of fly ash collected in hoppers of ESP is not similar to those of air classifiers as they operate on different principles. In ESP, the separation efficiency depends on particle size, conductivity and gas viscosity, whereas in air classifiers, it depends on air flow rate and density [23]. Thus the resulting fly ash is different in chemistry and reactivity, even if they are close in particle size distribution. We have carried out studies on suitability of air classified and mechanically activated fly ash for synthesis of geopolymers [16]. The objective of the present work was to develop geopolymers from size classified fly ash directly collected from hoppers of ESP. The focus of the study is to elucidate the effect of different size fractions on geopolymerisation reaction using isothermal conduction calorimeter. The microstructure obtained after reactions were studied using XRD, FTIR and SEM-EDS. Attempt has been made to correlate the size, reaction, structure and properties.

2. Experimental

The different size fractions of fly ash were collected from different fields of ESP at Tata Power, Jamshedpur, India. Out of samples of various size fractions, four representative samples were selected with characteristic particle diameter D_{50} of 40.37, 23.64, 10.33 and 2.98 μm and labeled as FA1, FA2, FA3 and FA4 respectively. The chemical analysis of the fly ash was carried out using combination of X-ray fluorescence, atomic absorption spectrophotometer and classical analysis. The glass content of the fly ash was determined by counting the grains in a polarizing microscope. The particle size analysis of fly ash was carried out using a laser particle size analyzer (MASTERSIZER S, Malvern, U.K.).

The rate of heat evolution during the reaction ($\mathrm{d}q/\mathrm{d}t$) was measured using an eight channel isothermal conduction calorimeter (TAM AIR, Thermometric AB, Jarafalla, Sweden). The process involved the preparation of the alkaline activator solution at least 24 h before use, mixing of an alkaline activator with the powder sample, and loading of the mix in the calorimeter. Analytical grade sodium hydroxide in flake form (98% purity) was used to prepare the alkaline activator solution. An alkaline activator of 6 M concentration was prepared in distilled water. The choice of 6 M concentration was based on our previous works [7,9] where it was found that higher concentration often leads to free alkalies which are more susceptible to carbonation. 7 g Solid sample and 3.5 ml of activator solution were used throughout the study. The samples were mixed and then loaded into the calorimeter. Calorimetric studies were carried out at 60 °C. The results obtained were presented in offset mode. Fourier Transform Infrared Spectroscopy (FT-IR-410 JASCO, U.S.A) was used for structural characterization of geopolymers. The samples were prepared by mixing the powder with KBr.

XRD patterns were recorded on a SIEMENS X-ray diffractometer (Model D500), using Co Kα radiation with a Fe-filter. The scanning speed of 1 deg/min was used and the samples were scanned from 10° to 60° 2θ angle. Morphological characterization of the fractured samples was done by a scanning electron microscope (JEOL SEM 840A) fitted with a Kevex Energy Dispersive Spectrometer (EDS) for X-ray micro-analysis after carbon coating on the fractured surface. The X-ray micro-analysis of areas of interest was determined from the average of minimum six analyses and used to calculate elemental ratios.

For all the physical testing, liquid (alkali solution) to solid ratio was kept at 0.35. The samples were prepared at 27 ± 2 °C and under relative humidity of 65%. For compressive strength $70 \times 70 \times 70$ mm cubic samples were prepared by vibro-casting of geopolymer paste. Compressive strength was tested on an Automatic Compression Testing Machine (AIMIL COMPTEST 2000, India) at age of 3, 7, 14 and 28 days after casting the samples at 27 °C followed by curing at 60 °C for 24 h. Averages of six samples were tested for each result.

3. Results and discussion

3.1. Characterization of size fractioned fly ash

Fig. 1 shows the schematic diagram of a typical electrostatic precipitator. The coarser fraction of fly ash is collected close to entry side whereas the finer fraction is collected close to exit side of ESP. The fly ash used in the present study was collected from different fields of the hoppers. Table 1 shows chemical analysis of size fractioned fly ash. The glass content of fly ash has also been included in the table. It is interesting to note that SiO_2 content decreased with the fineness whereas the Al_2O_3 content remained more or less constant. Fe_2O_3 concentration was also found to be higher towards coarser size fractions. The increase in LOI in coarser particles was mainly due to the presence of free unburned carbon. The composition of glass fraction was mainly silicate with little amount of alumino-silicates. No clear trend of glass content with size fraction has been observed. However, the finer fractions have shown higher and coarser fractions have shown lower glass content. Fig. 2 shows the particle size distribution of FA1, FA2, FA3 and FA4 samples. The characteristic particle diameters D_{10}, D_{50} and D_{90} have been tabulated in Table 2. A wide variation in particle size was observed in the fly ash. In FA4, 90% particles were <20 μm size whereas in the FA2, the coarser size just exceeded 100 μm. The mineralogical composition of fly ash is given in Fig. 3. FA4 sample, which has the finest particle side distribution, has shown the low intensity of quartz peak. The featureless hump between 15° and 40° 2θ was more prominent in FA3 and FA4, which was due to the presence of amorphous and poorly crystalline phase. In all the size fractions, similar crystalline phases but with different peak intensity were detected. The most common phases were quartz (PDF 46-1045), hematite (PDF 88-2359) and Mullite (PDF 85-1460).

3.2. Geopolymerisation reaction

To study the effect of size fractions on geopolymerisation reaction, isothermal conduction calorimeter was used under the following two conditions: (a) at ambient temperature (27 °C), and

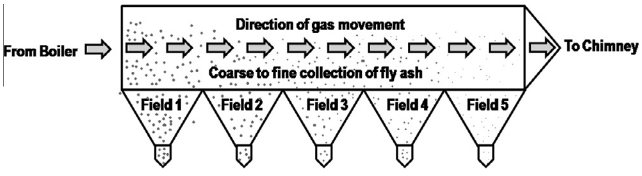

Fig. 1. Schematic diagram of a typical electrostatic precipitator.