Advanced Powder Technology xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Advanced Powder Technology

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

Mechanical activation of fly ash and its influence on micro and nano-structural behaviour of resulting geopolymers

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ARTICLE INFO

Article history:
Received 14 March 2016
Received in revised form 7 October 2016
Accepted 30 November 2016
Available online xxxx

Keywords:
Fly ash
Mechanical activation
Reactivity
Geopolymerisation
Reaction
Microstructure
Nanostructure
Gel porosity

ABSTRACT

Fly ash, mechanically activated for 0–120 min, has been used to synthesize geopolymers at ambient temperature. Fourier transform infrared spectroscopy (FTIR), quantitative X-ray powder diffractometry (XRD) and transmission electron microscopy (TEM-EDS) have been used for the structural characterization. The decrease in characteristic particle diameter up to 60 min and then increase is related to particle breakage and aggregation/agglomeration respectively. The manifestation of mechanical activation (MA) during geopolymerisation resulted in enhanced dissolution and precipitation of Si and Al. The appearance of a new FTIR band in 1080–1096 cm^{-1} region in MA geopolymers is attributed to SiQ^n (n = 3–4) structural units of quartz. The increment in amorphization in MA fly ash resulted in an increase in crystallinity of geopolymers. The shift in characteristic XRD amorphous hump towards lower d(A) value in geopolymers is associated with incorporation of OH^- and Na resulting in structural changes in amorphous phase. TEM-EDS revealed that geopolymers from as received fly ash exhibited predominance of primary structures such as nano-crystalline mullite, microcrystalline quartz and alumino-silicate glass. Whereas geopolymers from MA fly ash has shown secondary features mainly N-A-S-H gel, whose nano-porosity increased due to changes in gel characteristic. Finally, a conceptual mechanism of reaction is presented.

1. Introduction

Geopolymers are synthetic alumino-silicate binders formed by the reaction between oxides and silicates of Si and Al [1]. They are amorphous in nature and exhibit characteristic three-dimensional frameworks of SiO_4 and AlO_4 tetrahedra similar to that of zeolite structure [2]. In the recent times, the emphasis of geopolymer research has been shifted from the use of pure and natural raw material to waste and by-product [3–6]. Among these, fly ash is the most investigated material due to its alumino-silicate composition, good flowability and easy availability [7,8]. Similar to the geopolymerisation mechanism of metakaolin, fly ash also undergoes various reactions such as dissolution, precipitation, gel formation, restructuring and polycondensation [9]. However, the extent of reaction and the path may vary significantly due to chemical and mineralogical heterogeneity of fly ash. Fly ash consists of crystalline phases such as mullite and quartz, which are stable and un-reactive, and amorphous phases, which are reactive. Here, the reactivity can be defined as the ability of fly ash to react with alkali solution and form secondary reaction product, and is the combined effect of particle size, glass content and glass composition [10,11]. During the reaction, the reactive fraction undergoes geopolymerisation whereas the un-reactive portion behaves like aggregate. Thus, the development of mechanical properties in geopolymers is influenced by the reactivity of fly ash. The low reactive fly ash results in delayed setting and low strength development. In many cases, the dissolution of fly ash phases is not complete before the final hardened structure is formed [12].

The importance of MA for improving bulk and surface reactivity of materials is well known [13,14]. Due to MA, the collective effects of increased surface area and physicochemical changes induced in particle through high energy milling results into improved reactivity [15]. Use of MA fly ash in cement or geopolymers is getting increased attention as it provides an opportunity to improve and tailor the mechanical properties [16–18]. Due to MA of fly ash, multiple increases in the compressive strength of resulting geopolymers have been reported [19]. Geopolymers with as high as 120 MPa strength has been prepared by optimizing milling and synthesis parameters [20,21]. MA was also found effective for low reactivity deposited brown coal ash and lignite fly ash, resulting in the development of good quality geopolymers [22].

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http://dx.doi.org/10.1016/j.apt.2016.11.027
0921-8831/

In a recent study, it has been demonstrated that geopolymers synthesized from MA fly ash has given the comparable strength to the geopolymers prepared from a mixture of fly ash and granulated blast furnace slag [23].

The role of processing parameters on microstructure development and consequently mechanical properties of as received fly ash has been extensively studied [24–27]. Although positive effects of MA in the resulting geopolymers have been reported, very little information is available about the reason for the improvement. In some reports, it has been correlated with compact microstructure, at other places with the reaction product [19,20]. It is obvious from all these observations that microstructure plays an important role in the improvement of the properties of geopolymers from MA fly ash. This is the genesis of the present work, which has been carried out with an objective to understand the micro and nano-structure of the finally reacted geopolymers. The geopolymers samples were synthesized at 27 ± 2 °C temperature using fly ash mechanically activated for different periods in an eccentric vibratory mill (EVM). The effect of MA on the geopolymerisation reaction has been studied using an isothermal conduction calorimeter. The focus of the research is on the structural characterization using QXRD, FTIR and TEM-EDS. Finally, an attempt is made to correlate the processing parameters, reaction pathways and created material structure.

2. Experimental

The fly ash used in the study was a class F type supplied by Tata Power Co Ltd, Jojobera, India. The chemical composition of the fly ash is given in Table 1. Milling and mechanical activation of fly ash has been carried out in a laboratory size Eccentric Vibratory Mill (EVM) (SIEBTECHNIK, ESM 234, Germany). The mechanism of grinding in EVM is discussed elsewhere [28]. The batch size used was 2 kg. The material to media ratio was kept at 1:30, using monodisperse 12.5 mm size steel balls. As received fly ash has been used as reference and labelled as FA0. The fly ash was milled for 30, 60, 90 and 120 min and labelled as FA1, FA2, FA3 and FA4 respectively. Particle size distribution of all the samples was measured using a laser particle size analyzer (MASTERSIZER S, Malvern, U.K) after dispersing the samples in distilled water using ultrasonic vibration. The geopolymerisation behaviour of fly ash samples was studied in an 8 channel isothermal conduction calorimeter (ICC) (TAM Air, Thermometric AB, Sweden). The samples were mixed with an 8 M NaOH solution using liquid/solid ratio 0.5. The samples were mixed outside and then loaded into ICC with a time difference of 1 min between mixing and loading. For microstructural studies, the samples used for ICC were allowed to continue reaction at 27 °C for 28 days and then the reaction was stopped by repeatedly washing by ethanol. The loss of structural water with temperature in geopolymers was measured using differential thermo gravimetric analyzer (DTG) (Model: STA 7300, Hitachi, Japan) in air atmosphere using platinum crucible. Fourier transform infrared spectroscopy (Nicolet 5700 FTIR, Thermo Electron Corporation) in transmittance mode was used to measure the absorption spectra of the bonds in the range of 400 –4000 cm^{-1}. The samples were prepared by mixing with KBr. The phase composition of samples was investigated using Bruker D8 Advance diffractometer using Cu Kα, 40 kV and 40 mA in parallel-beam geometry by Göbel-mirror [29]. Amorphous content was determined by the "amorphous hump" method with the broad peak included in the Rietveld-refinement. To check the accuracy of the method, first it has been tested on a synthetic mixture comprising of glass (90%) + quartz + zinc oxide + calcite and results were found to be ±0.5% accurate. Transmission electron microscopy has been used to study the micro and nano structure of geopolymers samples. The samples were mechanically polished and then prepared using ion beam milling. An FEI Tecnai G2 device equipped with EDS (Energy Dispersive Spectroscopy) microprobe was used for TEM investigations.

3. Results and discussion

3.1. Characterization of raw and MA fly ash

Typically fly ash is hard and abrasive and difficult to grind. The fly ash mechanically activated in the eccentric vibratory mill has shown a visible change in the physical properties. The specific surface area of the particles has been increased. The milled fly ash has shown the lower flowability than the unmilled fly ash, which is due to breaking of large size spherical cenospheres and plerospheres [20]. However, there was no negative influence of MA fly ash on the workability of geopolymer paste Fig. 1 shows the cumulative particle size distribution of raw fly ash and fly ash milled for different time in EVM. Interestingly, the FA4 sample has shown coarser particle size distribution than FA2 and FA3, mainly in the size range above 3 m. For a better understanding of particle granulometry after MA, the characteristic particle diameter X_{10}, X_{50}, and X_{90} were plotted as a function of milling time (Fig. 2). The X_{10} values, which were <1 m diameter, have shown a continuous decrease in size from 0.92 m down to 0.32 m with milling time but the change was insignificant. The decrease in particle diameter X_{50} and X_{90} continued up to 90 and 60 min milling time respectively and then increased. This behaviour of particle size can be compared with different mechanism of MA [30–32]. The coarse grinding in the beginning can be correlated to 'Rittinger' stage. The second stage is attributed to 'Aggregation', where fine grinding leads to decrease in size. Here particles start to interact with each other through weak and reversible Van der Waals type adhesion forces. In the final 'Agglomeration stage', the size reduction stops and even increases because of intense particle interaction. This stage involves very strong irreversible interaction of particles in which chemical bonding plays an important role. The energy input to the particles during this stage takes place through plastic deformation as per the following equation:

$$\Delta E = \Delta E_u - \Delta(e_\gamma a_s) = \eta_z W_z \quad (1)$$

(where ΔE is change in bonding energy due to grinding, ΔE_u is change of bonding energy due to the grinding of the non-dispersed system, e is specific surface energy, a_s is specific surface area, W_z is the work expended during grinding, and n_z is the efficiency of grinding). Mechanical activation and change in crystal structure usually occurs during this stage.

The XRD analysis of fly ash samples FA0 (Unmilled) to FA4 (Milled for 120 min) has revealed that the main crystalline phases are quartz (JCPDS 85-0796) and mullite (JCPDS 74-4143). Minor peaks of hematite (JCPDS 86-0550) was also observed. A broad hump was observed between 20 and 40° 2θ, which is due to presence of amorphous and semi-amorphous phases [20]. With milling

Table 1
Chemical analysis of fly ash.

Constituents	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	SO_3	P_2O_5	LOI
Wt.%	56.3	26.0	5.1	4.1	1.0	0.8	1.1	1.3	0.6	0.1	2.2

Please cite this article in press as: S. Kumar et al., Mechanical activation of fly ash and its influence on micro and nano-structural behaviour of resulting geopolymers, Advanced Powder Technology (2016), http://dx.doi.org/10.1016/j.apt.2016.11.027