GEOPOLYMERS, FLY ASH REACTIVITY AND MECHANICAL ACTIVATION

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Abstract

The foucs this paper is on the reactivity of fly ash in relation to its geopolymerisation, that is structure and properies of geopolymer. A comparision of the mechanically induced reactivity by vibration and attrition milling and glass content induced reactivity obtained through size classification in a high speed air classifier has been made. It has been shown that for the fly ash of nearly same size (~ 5 μm), mechanical activation results in higher reactivity or geopoymerisation rate as compared to the air classified samples. Reactvity can also be altered by mixing raw fly ash with processed fly ash. Much wider variation in the reactivity is possible by mixing raw fly ash with mechanically activated fly ash than with classified fly ash. Higher reactivity of the mechanically activated fly ash results higher strength vis-à-vis raw and air classified fly ash.

Introduction

Fly ash, a silico-aluminate by-product material from coal fired thermal power plants, consist of SiO_2, Al_2O_3, Fe_2O_3 as the major constituents and varying amount of CaO, MgO, SO_3^{2-}. The environmental impact of fly ash in terms of its massive generation, large usage of land for disposal and, short and long term impact on surrounding areas is well known [1,2].

Geopolymers have emerged as a potential application of fly ash which can lead to bulk utilisation of fly ash with value addition [2]. Geopolymers, represented by the general formula (M_n [– (Si – O_2)$_z$ – Al – O]$_n$. wH_2O) (where M is an alkaline element, z is 1, 2 or 3, and n is degree of polymerization) are amorphous to semi-crystalline synthetic three-dimensional alumino-silicate mineral polymers having possibilities for a wide range of structures and novel materials for diverse applications [3]. The presence of silico-aluminate phases in fly ash makes it a suitable raw material for geopolymer synthesis and research, especially over the last 5-10 years have been recently reviewed [2-5].

Reactivity of fly ash is a major concern in the development of novel geopolymer materials. The importance of fly ash processing is increasingly being realised [6-9] to enhance reactivity. Ash beneficiation and classification technologies, and specialised milling techniques for fly ash, e.g. those used in the production of energetically modified cement, fly ash micronisation etc, are becoming increasingly important [1,2,5,10,11].

The effect of mechanical activation and classification on fly ash reactivity is not well understood and this paper describes results of the study that was taken up to bridge this gap. Classification was carried out to separate fine fraction of fly ash. Since, fine particles cool faster due to higher specific surface area, these are expected to have higher glass content. 'Mechanical Activation' refers to enhanced reactivity of fly ash from combined effects of increased surface area and physicochemical changes induced in the bulk as well as on the surface through high energy milling by vibratory mill, attrition mill etc [1,2,12,13]. In essence, the research focus was on a physico-chemical characterisation of raw, mechanically activated and classified fly ash, comparison between mechanical activation and glass content induced reactivity of fly ash, and effect of enhancement in reactivity on the strength development in geopolymer cements.

Materials and Methods

Materials

The fly ash used in the study was collected from a captive thermal power plant located in the state of Chattisgarh, India. The chemical composition of the fly ash (in weight %) was as follows : SiO_2 – 60.5, Fe_2O_3 – 4.52, Al_2O_3 – 28.15, CaO – 1.71, MgO – 0.47, SO_3 – traces, Na_2O – 0.14, K_2O – 1.41, and loss on ignition (LOI) – 1.59. Based on the total SiO_2, Fe_2O_3 and Al_2O_3 content, ~ 85%, the fly ash belonged to Class F as per ASTM standards. SiO_2/Al_2O_3 ratio of fly ash was 2.15 and suited for geopolymer application. The glass content of the fly ash, which had a density of 1.89 m^2/g, was 43%. The crystalline phases present in the fly ash included quartz (α-SiO_2) and mullite ($3Al_2O_3$ $2SiO_2$).

Methods

Laboratory classifier (HOSOKAWA ALPINE, 50 ATP Germany) was used for the classification of fly ash. Raw fly ash was used as feed material and classified using the classifier speed in the range of 3000-21000 rpm at ambient temperature. Mechanical activation of fly ash was carried out in attrition and vibratory mills. Attrition milling was carried out using a batch type attrition mill (Model PE-075, NETZSCH Feinmahltechnik GmbH, Selb, Germany) at 1000 rpm using 2 mm diameter steel balls. The material was milled for 10 minutes in deionised water and then dried. Vibration milling was carried out in eccentric vibratory mill (SIEBTECHNIK, ESM 234, Germany) for 30 min. The 10 min and 30 min milling time in attrition and vibration mill were used to obtain particle size distribution with a median size (X_{50}) value close to 5 μm. The raw, classified, attrition-milled and vibratory milled fly ash used in the study was labeled as RFA, CFA, AMFA and VMFA respectively. The particle size analysis of fly ash was carried out using laser particle size analyser (MASTERSIZER S, Malvern, U.K).

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Analytical grade sodium hydroxide in flake form (98% purity) was used to prepare alkaline activator solution. Sodium hydroxide was dissolved in water atleast 24 hours before use. The sodium hydroxide to fly ash ratio was kept 0.05 for all the experiments. Samples were prepared by mixing alkaline activator solution with fly ash keeping solid to liquid ratio of 0.5. Samples were kept in sealed condition for 24 hours at 27°C followed by heat curing for geopolymerisation at 60°C for 24 hours. The heat evolution during geopolymerisation reactions was monitored by Isothermal conduction calorimeter (TAM AIR, Thermometric AB, Jarafalla, Sweden). Immediately after calorimetry, the samples were subjected to microstructural analysis.

For compressive strength determination, 50x50x50 mm^3 size briquette samples were made varying the sodium hydroxide to fly ash ratio (w/w) in the range of 0.05 to 0.25 and keeping solid to liquid ratio fixed at 0.5. The samples were subjected to same curing cycle as used for the preparation of calorimetric samples, i.e. 24 hours at 27°C followed by 24 hour at 60°C. AIMIL Compression Testing Machine was used to test the strength of samples.

XRD patterns were recorded on a Siemens diffractometer (Model D500) using CoKα radiation. The morphology of the samples was analysed using JEOL 840 Scanning Electron Microscope after gold coating. FT-IR spectra of the different fly ash materials after milling were recorded on a NECOLET-570 Fourier transform infrared spectrometer using KBr pallets in the range of 400 to 4000 cm^{-1} at a resolution of 4 cm^{-1}.

Results and Discussions

Characterization of Raw, Classified and Mechanically Activated Fly ash

Figure 1 shows typical particle size distribution of RFA, CFA, AMFA and VMFA. Based on the particle size, the fly ash samples can be arranged in following order: RFA (34 μm) >VMFA (5 μm) ≈ AMFA (4.3 μm) > CFA (2.2 μm).
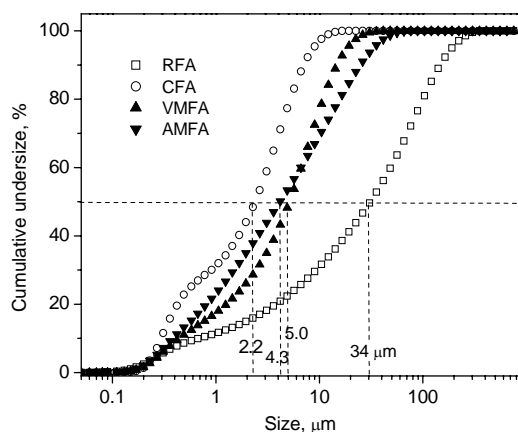

Figure 1. Typical particle size distribution of RFA, CFA, AMFA and VMFA

The morphology of the RFA, CFA, AMFA and VMFA is given in Fig. 2. The RFA contains spherical to irregular particles (Fig. 2(a)). Typically, the size of cenospheres is in the range of 2 to 15 μm. In contrast to RFA, CFA is characterised by cenospheres having size in the range of 1 to 3 μm (Fig. 2(b)). Different particle morphology was obtained in milled samples. VMFA mostly consisted of spherical to semi-angular particles and also showed particle aggregation (Fig. 2(c)). AMFA showed mostly small size spherical particles without any aggregation (Fig. 2(d)).
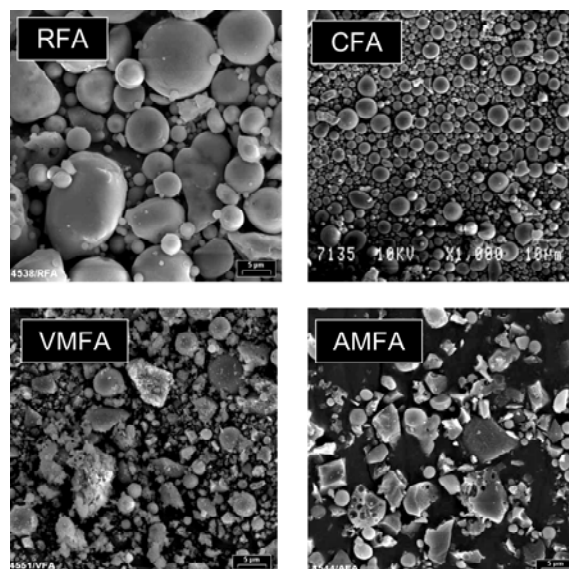

Figure 2. SEM micrograph showing morphological features of fly ash samples: (a) RFA, (b) CFA, (c) VMFA, and (d) AMFA

Figure 3 shows the comparison between the X-ray powder diffraction pattern of CFA (3000 and 11000 rpm), AMFA and VMFA vis-à-vis RFA. The diffraction pattern of RFA comprises of X-ray background which is typical of glass phase. After classification, the fly ash samples show an increase in X-ray background indicating an increase in glass content in CFA samples; the increase at higher classification speed of 11000 rpm (CFA11000) is being higher than at 3000 rpm (CFA3000) indicating higher amount of glass content in the sample classified at higher speed. In sharp contrast, both the mechanically activated samples (VMFA, AMFA) shows lower X-ray background than RFA which points towards lowering of glass content. Mullite and Quartz are the two crystalline phases present in RFA. There is a sharp increase in the mullite peaks in CFA samples. Mullite phase remains more or less unaltered after mechanical activation in AMFA and VMFA. The intensity of peak at 2θ ~ 31° (d = 3.33-3.35 Å), which is assigned to quartz decreases after classification (this is more clearly revealed when only this peak is plotted and magnified). Interestingly, an increase in the intensity of quartz peak was observed in both AMFA and VMFA. The VMFA showed a higher increase and a possible shift in the peak towards higher angle. The reduction in glass content on hand and change in the peak at ~ 3.34 Å in the AMFA and VMFA suggested possibility of structural change in these samples due to mechanical activation.

Figure 4 shows the IR spectra of CFA, VMFA, and AMFA along with RFA. Peak assignment in the spectra was done based on the published literature [14] as summarised in Table 1.
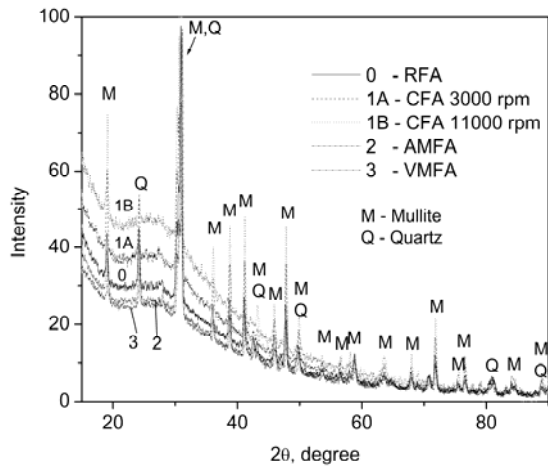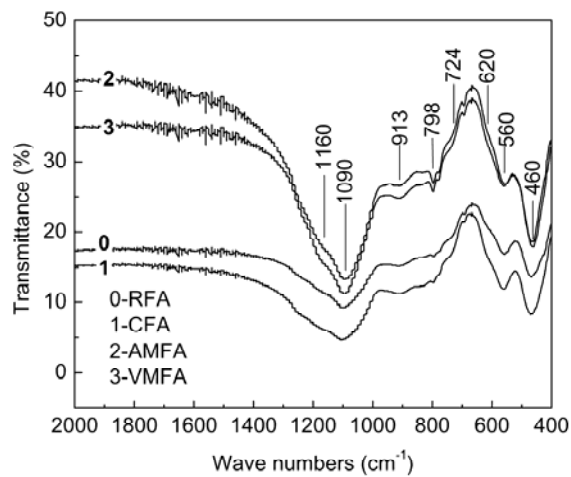

Figure 3. XRD patterns of RFA, CFA, AMFA and VMFA

Figure 4. IR spectra of RFA, CFA, AMFA and VMFA

Table 1. Peak assignment in the IR spectra of fly ash [14]

IR band (cm^{-1})	Peak assignment
1165 (sh)	Asymmetric stretching (Si–O–Si)
1138 (sh)	Asymmetric stretching (Si–O–Si and Al–O–Si)
1080 (sh)	Asymmetric stretching (Si–O–Si and Al–O–Si)
1074 (s)	Asymmetric stretching (Si–O–Si and Al–O–Si)
882 (s)	Si–O stretching, OH bending (Si–OH)
798 (s)	Symmetric stretching (Si–O–Si)
727 (sh)	Symmetric stretching (Si–O–Si and Al–O–Si)
620 (s)	Symmetric stretching (Si–O–Si and Al–O–Si)
561 (s)	Symmetric stretching (Al–O–Si)
466 (s)	Bending (Si–O–Si and O–Si–O)

IR spectra of RFA and CFA are quite similar in nature. FTIR spectra of VMFA and AMFA show changes in the intensity of IR peaks corresponding to Si-O-Si bending (460 cm^{-1}), and T-O-Si (T=Si, Al) asymmetric stretching (913, 1090 & 1160, 798 cm^{-1}). In addition, a new peak at 798 cm^{-1} corresponding to Si-O-Si symmetric stretching is observed in both the mechanically activated samples. This peak corresponds to Si-O-Si symmetric stretching. The peak at 798 cm^{-1} becomes increasingly more prominent with an increase in mechanical activation time in attrition as well as vibratory mill [15]. The IR results for mechanically activated samples further points towards structural arrangement during mechanical activation. Recrystallisation/ ordering in glass phase during mechanical activation have been reported in literature. Both XRD and IR studies have indicated structural rearrangement during mechanical activation of fly ash. Due to mechanical activation, possible recrystallisation/ ordering of glass phase present in fly ash require further studies for corroboration.

Fly Ash Reactivity

Fly ash mixed with alkali solution in equal proportion was geopolymerised at 60 °C for 24 h. The progress of geopolymerisation was monitored by using a multi-channel isothermal conduction calorimeter (TAMAIR, ThermometricAB, Sweden). The results of conduction calorimetry are given in Fig 5, which shows the rate of heat evolved (dq/dt) versus time. The highest rate [(dq/dt)$_{max}$] was taken as a measure of reactivity. Based on the rate of heat evolved, the fly ash samples in terms of increasing reactivity can be arranged as follows : VMFA > AMFA > CFA > RFA. Both mechanical activation and classification results in enhancement of reactivity. It is interesting to note that in spite of a higher size ($d_{50} \sim 5$ μm), the mechanically activated samples show higher reactivity as compared to classified fly ash ($d_{50} = 2.3$ μm). Higher reactivity of VMFA over AMFA highlights the importance of mechanical activation device.
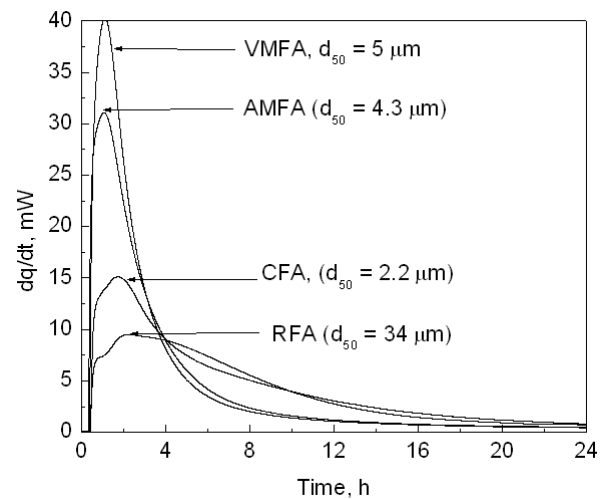

Fig. 7 Calorimetric response during geopolymerisation of RFA, CFA, VMFA and AMFA at 60 °C.

The reactivity of fly ash was further assessed in the mixture of RFA along with one of the pre-processed fly ash sample (CFA, VMFA, AMFA) and these results are summarized in Fig. 8. (100-

RFA) in Fig. 8 indicates percentage of preprocessed fly ash. To obtain the same reactivity as that of CFA, only 20% of VMFA and 27% of AMFA are required. These results may have important technological significance since entire fly ash needs not be activated if mechanical activation is used as a pre-processing step to enhance reactivity. Classification is based on separation of more reactive finer constituent and an alternate use of less reactive coarse component needs to be found out. The entire volume of fly ash can be used with mechanical activation. In addition, depending upon the proportion of activated fly ash, the reactivity can be controlled over a much wider range (Fig. 8).
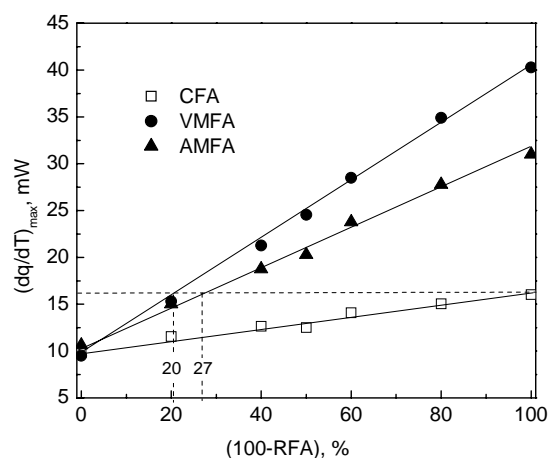

Figure 8. Reactivity [measured as $(dq/dt)_{max}$ from calorimetric data] of mixtures of RFA with CFA, VMFA and AMFA during geopolymerisation at 60 ^{o}C

Compressive Strength of Geopolymer Cements

Table 2 shows the compressive strength of geopolymer cements prepared using RFA, CFA, AMFA and VMFA for different amount of alkali addition. A broad correlation between fly ash reactivity and strength obtained is evident from the results. RFA which has the least reactivity shows lowest strength. The highest strength is obtained for VMFA followed by AMFA and CFA. It is interesting to note, mechanical activation provides flexibility to tailor compressive strength over a wide range upto 120 MPa [31].

Table 2. Compressive strength of geopolymer cements prepared using Raw Fly Ash (RFA), Classified Fly Ash (CFA) and mechanically activated fly ash using Attrition Mill (AMFA) and Vibratory Mill (VMFA)

Fly ash	Compressive strength (MPa) for different NaOH addition (wt. % of fly ash)		
	5	15	25
RFA	15	55	64
CFA	16	51	67
AMFA	18	55	77
VMFA	36	101	122

Summary and Conclusions

1. Characterisation of raw, classified and mechanically fly ash indicates that
   (a) Classification results in an increase in glass and mullite contents and a decrease in quartz content
   (b) Mechanical activation results in a decrease in glass content and no perceptible change in mullite.
   (c) Possibility of structural changes due to mechanical activation is indicated by both XRD and IR.
2. Study of geopolymerisation by isothermal conduction calorimetry indicates that both mechanical activation and classification results in enhancement of reactivity. AMFA and VMFA show higher reactivity in spite of their coarser size. In terms of increasing reactivity, the samples can be arranged as follows: VMFA (5 μm) > AMFA (4.2 μm) > CFA > RFA. Higher reactivity of VMFA over AMFA highlights the importance of mechanical activation device.
3. Much wider variation in the reactivity of fly ash can be achieved by mixing RFA with mechanically activated fly ash (VMFA and AMFA) than with CFA. The reactivity similar to CFA can be achieved by mixing 20-30% VMFA
4. A broad correlation between fly ash reactivity and strength obtained is observed. RFA which has the least reactivity shows lowest strength. The highest strength is obtained for VMFA followed by AMFA and CFA. Mechanical activation provides flexibility to tailor compressive strength over a wide range upto 120 MPa.

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