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Tailoring Geopolymer Properties Through Mechanical Activation of Fly Ash

Sanjay Kumar and Rakesh Kumar

National Metallurgical Laboratory, Council of Scientific & Industrial Research, Jamshedpur – 831 007, India,
Email :<sanjay_kumar_nml@yahoo.com>, <rakesh_kumar_nml@yahoo.com>

ABSTRACT

The influence of mechanical activation of fly ash on the tailoring of properties of geopolymer has been investigated. Fly ash was mechanically activated by vibrating samples for 5-90 minutes in an eccentric vibratory mill. Mechanical activation resulted into an increase in the reactivity of the fly ash and enhanced the geopolymerisation reactions. In an effort to understand the scientific basis of tailoring the properties, an attempt has been made to correlate the reactivity of fly ash with rate of geopolymerisation and development of structure and properties. The improvements in physical properties were found to be associated with microstructural changes that resulted from the enhanced geopolymerisation in mechanically activated samples.

INTRODUCTION

Geopolymers are aluminosilicate polymers formed through chemical reaction that approximate natural rock forming processes. The general formula to describe the geopolymers is:

$$M_n [-(SiO_2)_z - AlO_2]_n \cdot wH_2O$$

where z is 1, 2 or 3, M is an alkali cation (such as potassium or sodium), and n is the degree of polymerization [Davidovits, 1989]. These new class of materials 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. Using geopolymers as an alternative to the use of portland cement seems to be the most significant possibility. Theoretically any aluminosilicate material can be used for geopolymer synthesis. The three most widely used materials for geopolymer as supplementary cementitious materials are calcined clay, blast furnace slag and fly ash [Duxson et al., 2007].

Fly ash is the residue of power plants generated during combustion of coal. They consist mostly of SiO_2, Al_2O_3 and Fe_2O_3. Due to alumino-silicate composition, low water demand and high workability, fly ash has become a material of interest for geopolymer synthesis [Swanepoel et al, 2002, Rangan et al, 2005]. It is reported that fly ash based geopolymers show enhanced durability [Granizo et al, 2002]. The limiting factor which has hindered the development of fly ash based geopolymers is its low reactivity. The reactivity of fly ash largely depends on its amorphous content which undergoes faster dissolution in alkali

solution, whereas the crystalline fraction takes a longer time. In many cases the dissolution of fly ash is not completed before the final hardened structure is formed [Van Jaarsveld, 2002]. This often leads to slow setting and strength development. Studies have been carried out to tailor the properties of fly ash geopolymer for specific application such as cement and concrete [Palomo et al, 1999, Duxton et al 2007a]. Most of the research effort on tailoring is directed towards addition of calcium bearing substance such as $Ca(OH)_2$, limestone and blast furnace slag [Yip, 2004, Buchwald et al, 2007]. The modification of precursor chemistry often leads to additional reaction paths which are not desirable.

The present approach of tailoring geopolymer properties is based on improving the reactivity of fly ash by mechanical activation. The merit of mechanical activation (MA) for improving the surface and bulk reactivity of solids has been widely accepted. MA of solids offers the possibility to alter the reactivity of solids through physicochemical changes in bulk and surface but without altering the overall chemistry of the material [Boldyrev, 2006, Balaz, 2008]. Some very interesting results on the MA of blast furnace slag and fly ash has been obtained very recently. It was reported that hydration of slag can be controlled through MA and without any chemical addition [Kumar et al, 2005a, Kumar et al, 2008]. The reactivity of fly ash can be altered through MA, and, consequently, it was shown that the strength of geopolymer binder can be tailored without change in other geopolymerisation condition [Kumar et al, 2005b, Kumar et al, 2007a, Kumar et al, 2007b].

Fly ash was mechanically activated in an Eccentric Vibratory Mill (EVM). The rationale for using EVM is our previous experience where geopolymer developed from vibratory milled fly ash has displayed better mechanical properties than those developed from fly ash of similar particle size milled in other mechanical activation devices [Kumar et al, 2005b, Kumar et al, 2007a, Kumar et al, 2007b]. Fly ash mechanically activated in vibratory mills for different times was used as a starting material for geopolymers. The effect of milling time of fly ash on geopolymerisation reaction, structure and properties were studied. To develop the scientific understanding of tailoring of properties, processing – reaction – structure – properties relationship has been studied.

MATERIALS & METHODS

The fly ash used in the study was collected from a thermal power plant located in the state of Chhattisgarh, India. The chemical analysis and physical properties of the fly ash is given in Table 1. The fly ash is classified as a class F (ASTM C 618).

Table.1. Physicochemical Properties of Fly Ash

Chemical Composition (wt. %)							
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	LOI*
60.48	28.15	4.52	1.71	0.47	0.14	1.41	1.59
Physical Properties							
Glass content, %				43			
Mineral phases				Quartz, Mullite			

* Loss on ignition

Eccentric Vibratory Mill (EVM) (SIEBTECHNIK, ESM 234, Germany) was used for mechanical activation of fly ash. A 2 kg batch of fly ash was milled keeping material to media (stainless steel ball of 12.5 mm dia) ratio at 1:35 size was used for milling. The particle size analysis of raw and milled fly ash was carried out using laser particle size analyser (MASTERSIZER S, Malvern, U.K). MICROMERITICS ASAP2020 specific surface area analyser was used to measure specific surface area of milled samples. Isothermal conduction calorimetry (TAM AIR, Thermometric AB, Jarafalla, Sweden) was used to monitor the rate of heat evolution (dq/dt) during the geopolymerization. Analytical grade sodium hydroxide flakes (98% purity) was used to prepare alkaline activator solution of 6 M concentration. Seven g solid sample and 3.5 ml alkaline activator were used throughout the study.

The reaction products after geopolymerisation were characterized by powder X-ray diffraction (XRD) technique and Scanning electron microscopy (SEM) with X-ray energy-dispersive microanalysis (EDS). Powder XRD patterns were recorded on a SIEMENS X-ray diffractometer (Model D500), using CoKα radiation with a Fe-filter. A scanning speed of 1 deg/min was used and the samples were scanned from 10-60 °2θ. Morphological characterization of the fractured samples was done by a scanning electron microscope (SEM 840A, JEOL with an EDS attachment) after carbon coating on the fractured surface.

For all the physical testing such as setting time, compressive strength, bulk density, Young's modulus and macrohardness, alkali to solid ratio was fixed at 0.06. All the samples were prepared at 27±2 °C and relative humidity 65%. For setting time, a consistent paste of each batch with alkali solution was made by thoroughly mixing it. Setting time was determined by using Vicat Apparatus (AIMIL, India). For compressive strength samples of 7 cm^3 was prepared by mixing the each batch with alkali solution. The paste was then casted into moulds and covered with lids to minimize the water loss during reaction. Compressive strength was tested on the samples cured at 27 °C after 28 days and samples cured at 27 °C for 24 hours followed by geopolymerisation at 60 °C for 4 hours. Compression Testing Machine (AIMIL COMPTEST 2000, India) was used to test the compressive strength of the samples using the pace rate of 2. Bulk density was measured by water displacement method. Young's modulus was measured using acoustic resonance method using Modulo Elastic Equipment, India. Vickers microhardness (Hv) was measured by the indentation technique at different load using a macrohardness tester.

RESULTS & DISCUSSIONS

Geopolymerisation of mechanically activated fly ash

Figure 1 (a) shows typical particle size distribution of fly ash milled for different time in EVM. The rate of particle size reduction was greatest during the initial 10 min of milling during which the characteristic particle diameter X_{50} reduced from 37.7 μm to 5.88 μm. The particle size gradually decreased with milling time and reached to 2.27 μm in 90 min. The specific surface area which was 0.969 m^2/g in raw fly ash increased to 2.57 m^2/g after 90 min milling. The fly ash mechanically activated for different duration was also subjected to X-ray analysis but no significant changes were observed so results are not presented here.

Isothermal conduction calorimetry has been used to study the effect of mechanical activation on reaction kinetics during geopolymerisation. Fig. 2(a) shows the heat flow curve of samples geopolymerised at 60 °C after curing at 27 °C for 24 hours. The peak corresponding to RFA

was broad and spread over entire duration of calorimetry i.e. 48 hours. With duration of MA, the peak started sharpening and shifting towards Y axis. This is due to fast and intense geopolymerisation. For better understanding, the time at which peak maxima occurred and the heat evolution were plotted as function of milling time and displayed in Figure 2 (b). The time of reaction decreased from ~16 hours to ~5 hours in 90 min milled samples. The peak intensity increased from 28 mV to 55 mV with milling time. Both these changes are quite significant and indicate a faster reaction mechanism.

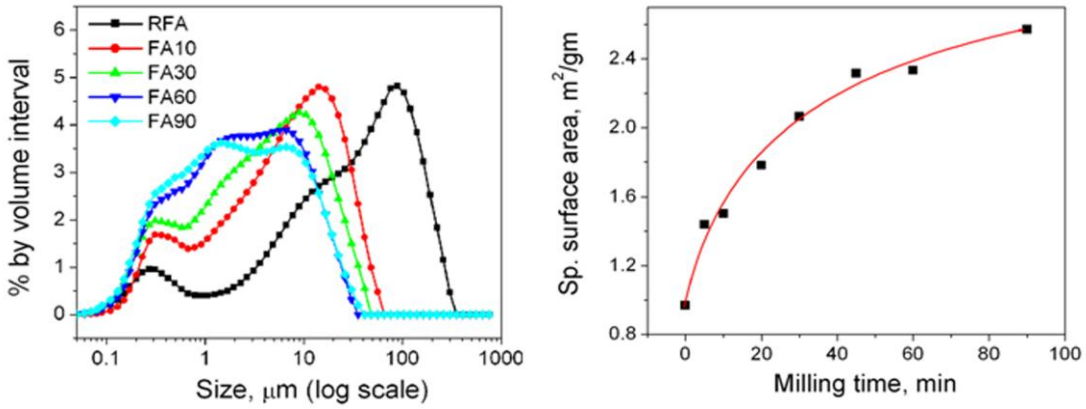

Figure 1: Effect of Milling Time on (a) Particle Size Distribution, and (b) Specific Surface Area of Fly Ash

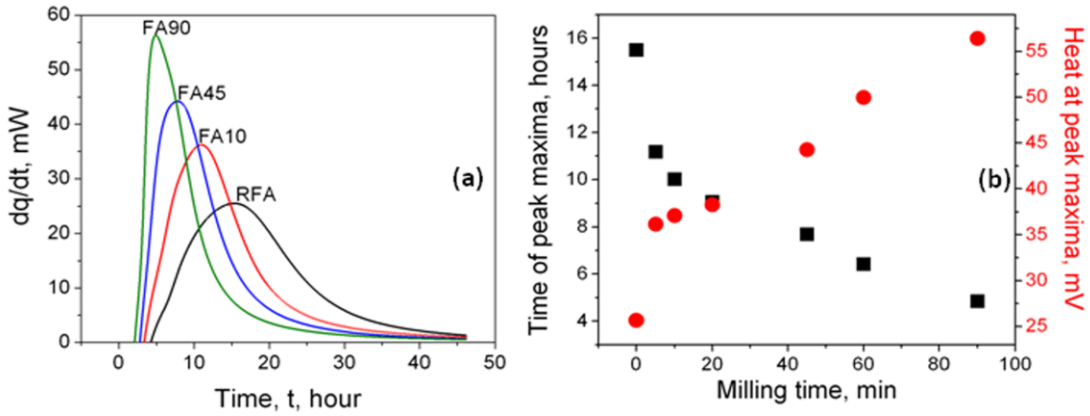

Figure 2: (a) Isothermal Conduction Calorimetric Curves showing Heat Flow during Geopolymerisation of Fly Ash Mechanically Activated for Different Duration, (b) Variation in Time and Heat of Peak Maxima in Relation to Milling Time

Microstructural studies

Figure 3 shows the XRD patterns of geopolymers derived from raw and mechanically activated fly ash. For all the studied samples, the intensity of quartz and mullite peak was progressively decreased with milling time. This decrease is related to the higher reactivity of fly ash which resulted into formation of A-S-H gel (10-20° regions). Reflections of phases such as sodalite which are product of geopolymerisation were also present [8].

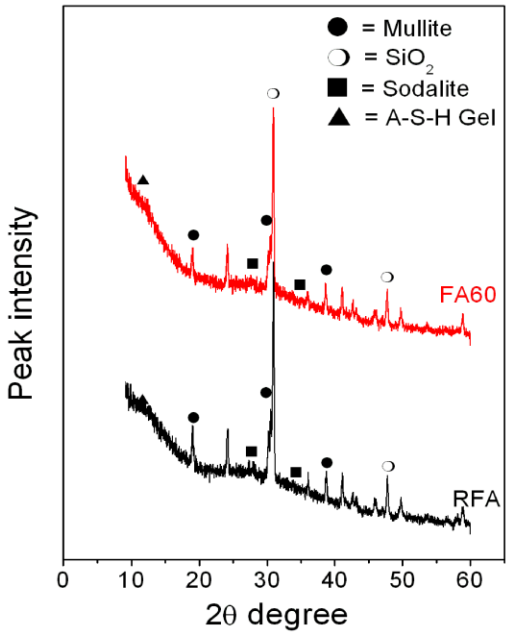

Figure 3: X-ray Diffractogram of Geopolymer Synthesised from Raw Fly Ash (RFA) and Fly Ash Mechanically Activated for 60 min (FA60).

The development of the microstructure in geopolymers resulted from the reaction between fly ash and NaOH solution at elevated temperature (Figure 4a-b). In general, the compactness of microstructure improved with duration of mechanical activation which may be explained by the formation of aluminosilicate gel. In RFA samples, partially reacted cenosphere with presence of gel were main feature (Figure 7a). With mechanical activation, the change in microstructure in terms of new morphological features, reaction products and compactness was distinctly evident. To identify the new reaction products, EDS studies were carried out. EDS analysis showed the gel corresponds to alumino-silicate hydrate with Na in structure. In RFA samples, the gel phase showed the ratio of Si/Al was ~2.2-2.9 and Si/Na was ~0.9-1.2. With the mechanical activation, this ratio increased and in FA30 sample the ratio to Si/Al was ~2.9-3.2 and Si/Na was ~3.5-4.2.

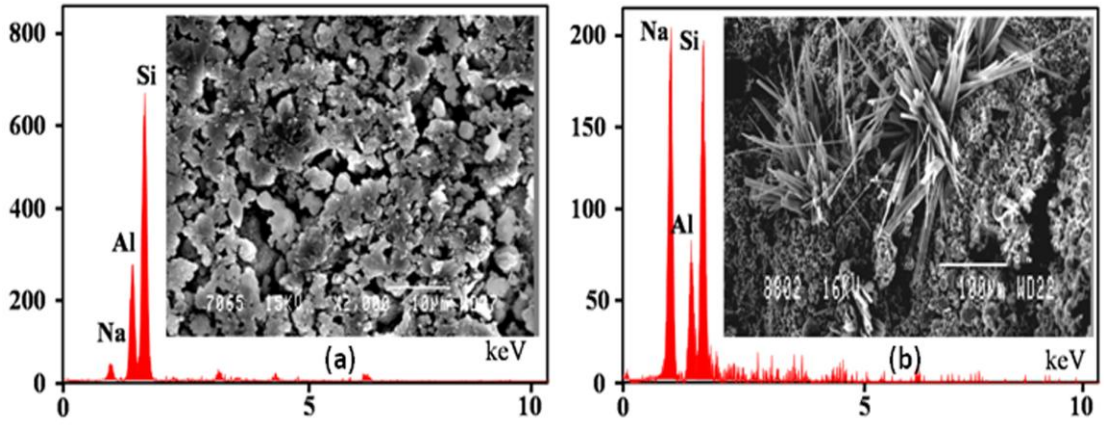

Figure 4: SEM-EDS of Geopolymer Synthesised from Raw Fly Ash (RFA) and Fly Ash Mechanically Activated for 30 min (FA30).

Physical properties of geopolymer

The physical properties of the geopolymers were tested as function of milling time and presented in Figure 5 (a)-(d). The RFA samples took long time, 285 min to set (Figure 5a). A gradual decrease in setting time with milling duration was obtained. Figure 5b shows the compressive strength of the samples. The compressive strength increased with milling time and samples which are milled for ≥20 min have shown 34 MPa and higher strength. This is reasonable good strength values as comparable to the compressive strength of raw fly ash based geopolymers heat treated at 60 °C or higher temperature [8]. Figure 5c shows the effect of milling time on bulk density and Young's modulus. The bulk density increased and Young's modulus decreased with milling time. The bulk density curve was inversely proportional to the Young's modulus. The effect of milling time was prominent on the macro hardness.

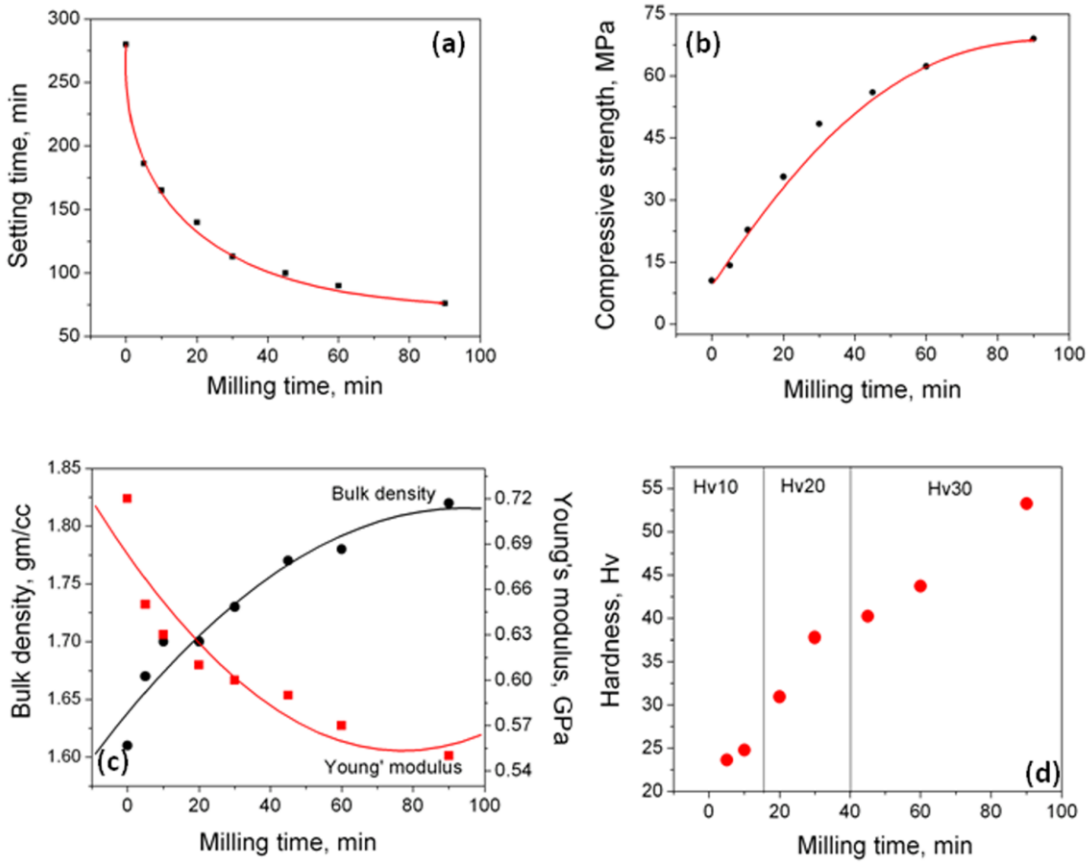

Figure 5: Effect of Milling Time on (a) Setting Time, (b) Compressive Strength, (c) Bulk Density and Young's Modulus, and (d) Macrohardness

Processing – Reaction – Structure – Properties Relationship

The geopolymerisation reaction was enhanced by altering the reactivity of fly ash by mechanical activation. The intensity of reaction increased and time of reaction decreased with the duration of mechanical activation (Figure 2 (a) –(b)). Enhanced geopolymerisation

resulted into more consumption of quartz and mullite phases and formation of new reaction products (Figure 3). Microstructural features such as increase in compactness, formation of more reaction product and changes in nature of gel are also associated with duration of mechanical activation (Figure 4). There appears to be a direct qualitative correlation between the mechanical activation of fly ash, as revealed by SEM, and physical properties such as setting time, compressive strength, bulk density, Young's modulus and hardness of the samples. The development of physical properties was linked with the reactivity of the constituents and evolution of dense and compact microstructure in different samples. Higher reactivity of mechanically activated samples may be ascribed to a combined effect of lower particle size, angular shape, structural defects as well as bulk and surface changes during milling.

Based on the above discussions, the following order of relationship was found: *Mechanical activation → Enhanced reactivity → Accelerated geopolymerisation → Change in microstructure → Improvement in properties.* Thus there is possibility to tailor the properties of geopolymer by controlling the mechanical activation.

CONCLUSIONS

The major conclusions of this study are:

1. The rate of heat flow during geopolymerisation of fly ash at 60°C is associated with duration of mechanical activation. The alteration in reaction kinetics of geopolymerisation is due to combined effect of particle size, increase in surface area and change in bulk and surface reactivity due to MA.
2. Microstructural changes such as decrease of peak intensity of quartz and mullite and new morphological features are associated with milling time. The change in intrinsic structure and increase in compactness of microstructure improved the physical properties such as setting time, compressive strength, bulk density, Young's modulus and hardness.
3. Mechanical activation of fly ash offers possibility to tailor the properties of geopolymer without changing its chemistry.

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