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Microstructural and morphological evolution of fly ash based geopolymers

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HIGHLIGHTS

- Geopolymer microstructure and morphology changed with alkali concentration and curing temperature.
- Geopolymers formed at 8M shown more reaction product and low carbonation.
- The reaction product contains amorphous N-A-S-H gel and crystalline hydroxisodalite and zeolite ZK.
- EDX confirmed enhanced dissolution of Si with alkali concentration and Al with curing temperature.

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ABSTRACT

The microstructural and morphological evolution of fly ash geopolymer have been studied in relation to synthesis condition. The variable parameters for synthesis were NaOH concentration (6, 8 and 10M) and curing temperature (27, 45 and 60 °C). The effect of these parameters on the early geopolymerization was elucidated using Isothermal conduction calorimeter (ICC) whereas on the final reaction product through Thermo gravimetric analysis (TGA). ICC results revealed that the main reaction peak corresponding to geopolymerization increases linearly with alkali concentration. The maximum weight loss in samples cured at 45 °C as shown by TGA was due to formation of N-A-S-H (N=Na_2O, A=Al_2O_3, S=SiO_2, H=H_2O) gel with more OH^- molecules. Scanning electron microscopy, X-ray diffractometer and Fourier transform infrared spectroscopy have been used for structural characterization and indexing of morphological features. The dependency of structural re-organization on alkali concentration and curing temperature was evidenced by the change in Si/Al ratio in the reaction products, shifting of spectrum corresponding to Si—O—Si and Al—O—Si, and formation of new phases. The increase in Si/Al ratio with the higher molarity and decrease with elevating temperature shows that dissolution of silica was more influenced by alkali concentration whereas dissolution of alumina was more influenced by curing temperature.

1. Introduction

Geopolymers are one of the widely discussed topics of material science in recent times due to its vast potential as alternate binder material to cement. It has been reported that fly ash geopolymer concrete is more durable in sulfate and acid environment and possesses high compressive strength than OPC concrete [1]. Due to higher bond and tensile strength, high energy is required to initiate crack though its fracture energy is similar with cement concrete [2,3]. It also exhibits superior environmental performance in terms of energy consumption and green house gas emission. Geopolymer cement produces 80% less CO_2 and 30–40% lower embodied energy than Portland cement [4–6]. The term geopolymer was first used by Davidovits for inorganic polymers with 3 dimensional framework structure similar to zeolite [7]. These are synthesized by chemical reactions between various alumino-silicate oxides and silicates under highly alkaline conditions, yielding polymeric Si—O—Al—O bonds [7,8], as described by the formula:

$$Mn[-(Si-O_2)z-Al-O]n.wH_2O \quad (1)$$

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(where, M is an alkaline element, the symbol '—' indicates presence of a bond, z is 1, 2 or 3, and n is degree of polymerization). The alumino-silicate mineral polymers formed may have amorphous to semi crystalline structure.

As SiO_2 and Al_2O_3 are the essential constituent, usually alumino-silicate mineral such as metakaolin which is a dehydroxylated form of the clay mineral kaolin is used for geopolymer synthesis. In recent time, there has been a shift in the trend from use of naturally occurring and pure material to waste and by-products [9]. A number of industrial by-products have been investigated such as fly ash, granulated blast furnace slag, silico-manganese slag, copper and zinc slag, red mud, construction and demolition waste, etc [1–3,10–23]. Among these, fly ash is the most studied material due to its chemical and mineralogical suitability, easy and cheap availability worldwide and good mechanical properties of the resulting product.

Majority of research on fly ash geopolymer is directed towards product development, role of alkali and their concentration on the mechanical properties, durability studies, etc [21–26]. Microstructure of geopolymer has also been discussed in the literatures but in majority of the cases it has been used to explain the strength development [13,27,28]. X-ray diffraction (XRD), Scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR) are some of the extensively used characterization tools for studying of the microstructures [23,27–29]. It has been reported that the microstructure in fly ash geopolymer develops from the solution formed due to partial dissolution of fly ash in alkali solution [30]. The microstructure as well as the Si/Al and Na/Al ratios of the aluminosilicate gel undergoes changes as a function of the activator type [31]. It is reported that the main reaction product in alkali activated fly ash is N-A-S-H (N=Na_2O, A=Al_2O_3, S=SiO_2, H=H_2O) gel regardless of the thermal treatment and curing time [32]. However, the microstructure varies to a large extent depending on the characteristic of fly ash and synthesis parameters. Even in N-A-S-H gel, there can be wide variation in Si/Al ratio and Na/Al ratio [12].

The development of geopolymer microstructure depends on the characteristics of raw material and process parameters especially alkali concentration and curing temperature. The objective of the present work was to carry out a systematic study of evolution of morphology and microstructure of geopolymer derived from fly ash in relation to alkali concentration and curing temperature, as the raw material was kept constant. The early reaction corresponding to dissolution and precipitation was monitored through Isothermal conduction calorimetry (ICC) whereas, Thermo gravimetric analysis (TGA) has been used to study the loss of structural water in final reaction product. The morphological features especially the reaction products obtained by Field emission gun-scanning electron microscope (FEG-SEM) have been indexed along with their elemental ratios. An attempt has been made to correlate the reaction parameters with microstructural features. The properties of geopolymer product depend largely on the microstructure. The present work will provide the scientific background to predict properties on the basis of microstructures.

2. Materials and methods

Class F fly ash used in the study was obtained from Tata Power Co Ltd, Jamshedpur, India. Combination of analytical techniques such as Inductive coupled plasma optical emission spectrometer (ICP-OES) (Vista MPX, Varian), Atomic absorption spectroscopy (AAS) (iCE 3000 series, Thermo Scientific) and conventional wet chemical method has been used for chemical analysis of fly ash. Laser particle size analyzer (MASTERSIZER, Malvern, UK) has been used for particle size analysis of as received fly ash. Mineralogical phases of the fly ash and reaction products were identified using X-ray diffractometer (XRD) (D8, Discover, Bruker, US). For raw fly ash, scan rate was kept at 0.2 s per step with step size of 0.02° and for the geopolymer samples, 0.03 steps per 8 s with step size of 0.03°. The CuKα radiation (=1.5418 Å) was generated at 40 kV and 40 mA. The microstructure of raw fly ash and geopolymer samples were observed under FEG-SEM (Nova NanoSEM, FEI 430) fitted with energy dispersive X-ray spectrometer (SEM-EDX) operated at 15.0 kV. Fractured surface of the geopolymer samples were used after gold or carbon coating.

Alkali solutions of 6, 8 and 10M concentration were used for geopolymer sample preparation. The choice of these concentrations is based on our previous work and other literatures [13,33–36]. The solutions were prepared by dissolving NaOH pellets (analytical grade, >99% purity, make: Merck, Germany) with required amount of water. As the dissolution of NaOH pallet in water is exothermic reaction, the initial solution gets heated and becomes unstable. Thus the solution was prepared at least 24 h before use and cured at room temperature of ~27 °C to get the stable solution without further loss in volume due to evaporation. Samples of geopolymers were prepared by mixing the dry fly ash and alkali solution in 2:1 ratios inside the plastic bottles. These bottles were then sealed and cured at different temperatures (27, 45 and 60 °C) for next 48 hours. After curing, the samples were kept at ambient temperature i.e. 27 ± 2 °C as specified in Indian cement standard IS: 4031, 1988 upto 28 days of casting [37]. Thereafter the fully set solid samples were taken out from plastic bottle and dipped into acetone to stop further reaction. The different batch composition and their nomenclatures are given in Table 1. The nomenclatures are based on their synthesis parameters such as alkali concentration and curing temperature. FA stands for fly ash. 6M, 8M and 10M stands respective alkali concentration and 27, 45 and 60 represents their corresponding curing temperature.

The geopolymerization behavior of different batches was studied in an 8 channel Isothermal conduction calorimeter (ICC) (TAM Air, Thermometric AB, Sweden). Following steps were involved for sample preparation: (a) preparation of alkaline solutions of 6, 8 and 10M as described earlier, (b) mixing outside of dry fly ash with alkali solution in 2:1 ratio into calorimeter bottle, (c) loading of the bottle containing fly ash alkali mix into calorimeter channel. Calorimetric test temperatures were selected according to curing temperatures (27, 45 and 60 °C).

For characterizations, geopolymer samples were taken out from acetone and washed repeatedly with fresh acetone. The samples were then dried at 80 °C in air oven to free acetone from inside. Dried cakes were crushed into powder for TGA, XRD and FTIR analysis, and broken small pieces were used for microstructural study. Differential thermo gravimetric analyzer (DTG) (Model: STA 7300, Hitachi, Japan) was used to measure the weight loss of the geopolymer samples with temperature using platinum crucible in air atmosphere. Fourier transform infrared spectroscopy (Nicolet 5700 FTIR, Thermo Electron Corporation) in reflectance mode was used to record the absorption spectra of the bonds in the range of 400–4000 cm^{-1}. FTIR analysis samples were prepared by mixing with KBr powder.

3. Results and discussions

3.1. Characterization of fly ash

The result of chemical analysis of fly ash shows that the ratio of silica to alumina is ~2.0, which is considered suitable for geopolymerization (Table 2). Fig. 1 shows the particle size distribution along with the characteristic particle diameter. The fly ash is of good fineness with 90% particles below 17 μm size. As particle size also influences reactivity, it may be considered a reactive fly ash [36]. Fig. 2 shows the XRD pattern of the phases of fly ash sample. The major crystalline peaks were identified as quartz and mullite. The characteristic hump between 15 and 35° 2θ indicates the presence of amorphous phases. SEM-EDX of fly ash shows that the main morphological feature is alumino-silicate spherical grain ranging in size between 1 and 15 μm (Fig. 3).

Table 1
Batch composition of geopolymer paste samples.

Material	NaOH concentration	Solid/Alkali solution ratio	Curing temp. (°C)	Sample code
Class F fly ash	6M	2	27	FA6M27
		2	45	FA6M45
		2	60	FA6M60
	8M	2	27	FA8M27
		2	45	FA8M45
		2	60	FA8M60
	10M	2	27	FA10M27
		2	45	FA10M45
		2	60	FA10M60

[#]FA: denotes fly ash; 6M/8M/10M: respective alkali concentration; 27/45/60: respective 48 hours curing temperature.