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Microstructural evolution of fly ash geopolymer: effect of alkali concentration

S. K. Nath[1], S. Maitra[2], S. Mukherjee[3], and Sanjay Kumar[1]

[1]CSIR-National Metallurgical Laboratory, Jamshedpur - 831007, India
[2]Govt. College of Engineering & Ceramic Technology, Kolkata - 700010, India
[3]Jadavpur University, Kolkata-700032, India

Abstract

Geopolymer is formed when a source of alumino-silicate is activated with highly concentrated alkaline hydroxide or silicate solution. Fly ash is a by-product of coal fired power plant and considered as suitable material for geopolymer due to its chemistry, spherical shape, and abundance availability. Microstructure of any synthetic material depends of nature of starting material and processing conditions. Similarly microstructure of fly ash based geopolymeric material also depends on fly ash characteristics, nature of activator, curing conditions and age of curing. Any change in the above parameters reflected in microstructure and developed properties accordingly.

In this paper the effect of alkali activator concentration on microstructural evolution of fly ash geopolymer was studied. The reactivity of fly ash alkali mix was measured using isothermal conduction calorimeter with different alkali concentration from 4M to 10M NaOH solution. Micro-structural characterization such as X-ray diffraction, Fourier transforms infrared spectroscopy, FEG-SEM with EDAX analysis and TEM of selected samples were carried out. It was observed reactivity increased with alkali concentration and developed more reaction phases as gel. EDAX analysis of gel phase confirmed the presence of ASH geopolymer gel.

Keywords: Fly ash, Geopolymer, Activator, Microstructure, geopolymer gel

1.0. Introduction

Geopolymer first coined by J. Davidovits, is a synthetic material consisting of alumino-silicate networking structure[1]. When a source of alumino-silicate based precursor is activated with highly concentrated alkaline and/or alkali silicate solution a binder with three dimensional network of -Si-O-Al-O- bond is formed [2-3]. This binder is emerged as a good alternative of Portland cement as it reduces 80% CO_2 emission, requires low energy and water and produces more durable products. Fly ash, a byproduct of coal fired thermal power plant generated during combustion of coal is considered as one of the potential precursor for geopolymer reaction due to its alumino-silicate chemistry, presence of glassy phases, free flowing nature and easy availability etc [4-8]. Using of fly ash into geopolymer also addresses the issues of waste utilization, natural resource conservation and cost reduction. The microstructure of any synthetic materials is influenced by parameters like raw material characteristics, synthesis conditions etc. The microstructure of fly ash geopolymer is controlled by geopolymer reaction and geopolymer reaction is depends on several factors such as fly ash characteristics, nature and amount of alkali activator, curing conditions etc. Here the role of alkali concentration on microstructural development of fly ash geopolymer is discussed. The reactivity of fly ash and alkali combination is monitored by isothermal conduction calorimetry (ICC). XRD analysis was carried out to determine the developed phases. FEG-SEM and TEM was performed to observe the morphological features of geopolymer samples. FTIR analysis was done to know the functional group and band position into geopolymer. An attempt has been made to compare the change in reactivity with alkali concentration with their microstructural development.

2.0. Materials & Methods:

Fly ash was supplied by Tata Power Ltd., Jojobera Plant, Jamshedpur, India. Analytical grade sodium hydroxide pellets were used to prepare alkali solution. Alkali concentration was varied from 4M to 10M range and the ratio of fly ash powder to alkali

solution was fixed at 2:1. 7 g fly ash and 3.5 ml alkali solution of different molarity was taken and mixed intimately into calorimeter bottle. These bottles were placed into calorimeter channel for testing. Calorimeter recorded the heat evolution of reaction with time.

Geopolymer samples inside calorimeter bottles were taken out after 28 days of testing and crushed into powder form. Microstructural analysis such as XRD, TEM, FTIR and SEM with EDAX analysis was done on fracture surface of geopolymer samples.

3.0. Result & Discussions

Chemical analysis and physical properties of fly ash is given in Table 1. It was observed that fly ash is a alumino-silicate material bearing Fe_2O_3, CaO as minor constituents.

Table 1: Chemical analysis & physical properties of fly ash

Chemical analysis		Physical properties
Constituents	Wt (%)	Sp. Gravity – 2.34 Glass content – 63% Major crystalline phases - Quartz, Mullite Particle size D_{10} : 0.36 µm D_{50} : 4.72 µm D_{90} : 16.55 µm
SiO_2	52.60	
Al_2O_3	26.55	
Fe_2O_3	05.29	
CaO	05.10	
MgO	01.76	
Na_2O	00.61	
K_2O	01.12	
LOI	03.10	

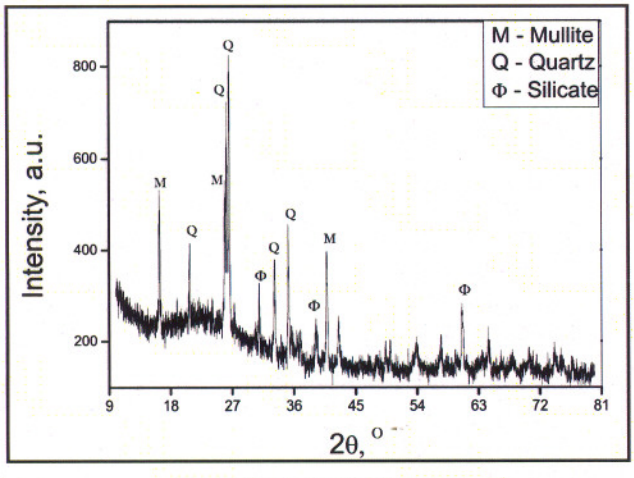

Fig. 1: XRD graph of fly ash

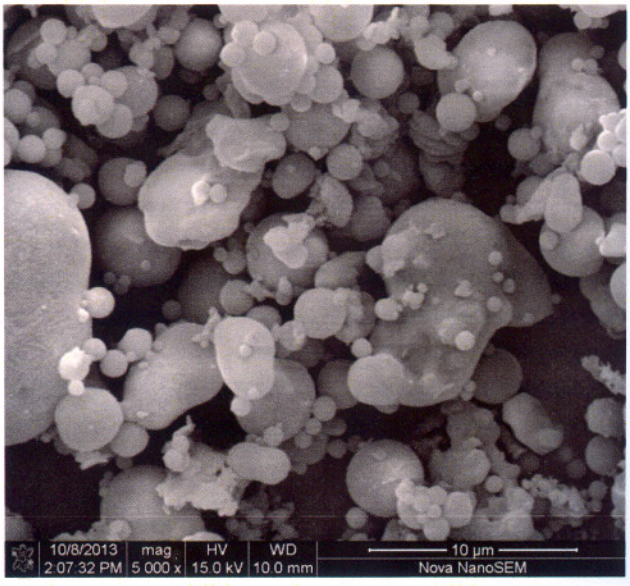

Fig. 2: SEM micrograph of fly ash

Particle size distribution (PSD) was measured by laser particle size analyzer and average particle diameter was observed under 5 µm. Phases like quartz and mullite were present as major and some silicates and iron bearing phases were present as minor. Mainly spherical shape grains with some irregular shape observed under SEM.

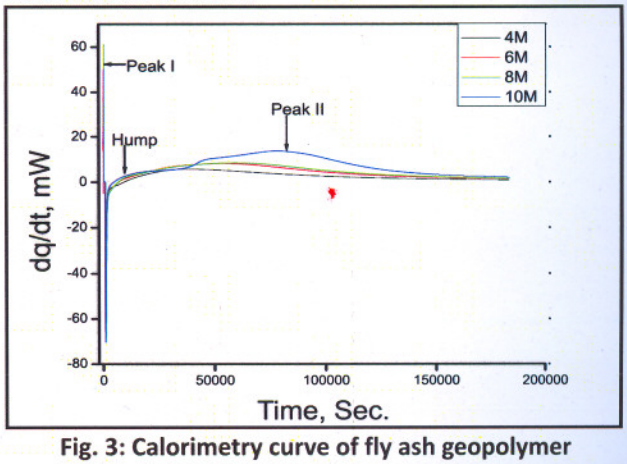

Fig. 3: Calorimetry curve of fly ash geopolymer

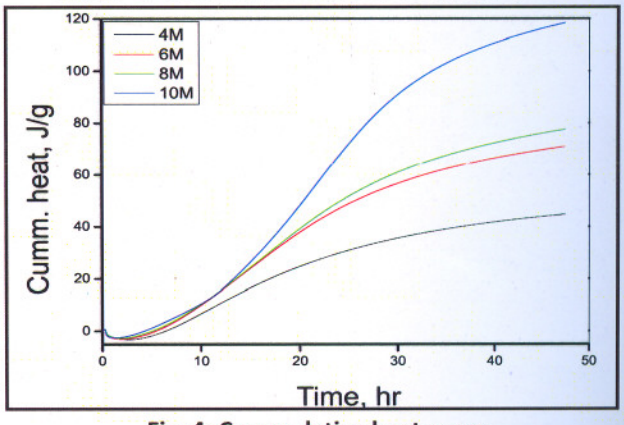

Fig. 4: Cummulative heat curve

Fly ash geopolymerization is defined by various stages such as dissolution, precipitation, oligomer formation, polymerization/poly-condensation[9-10]. These steps may overlap with each other. The sharp peak, peak I of Fig. 3, at the beginning is due to dissolution of alumina and silica into alkali solution. After this a short dormant period was observed. One hump was appeared (Fig. 3) which indicated the initiation of peak due to precipitation and oligomer formation. After that peak II was appeared because of polymerization. It was found that peak intensity was increased with alkali concentration. From peak intensity as well as cumulative heat evolution in Fig. 4, it is confirmed that with alkali concentration fly ash reactivity for geopolymer reaction is increasing. For better understanding heat curve analysis is given in Table 2.

Table 2: Heat curve analysis

NaOH Conc. (M)	Solid/ Liquid	Na_2O (g)	Hump/Peak Value (mW/g)			Cumulative heat released after 48 hrs (J/g)
			Peak I	Hump	Peak II	
4	2.42	0.434	38.1	~0.4	5.32	44.7
6	2.68	0.651	43.1	1.3	8.10	70.8
8	2.98	0.868	61.0	2.67	8.39	77.4
10	3.34	1.085	50.2	3.21	13.57	118.4

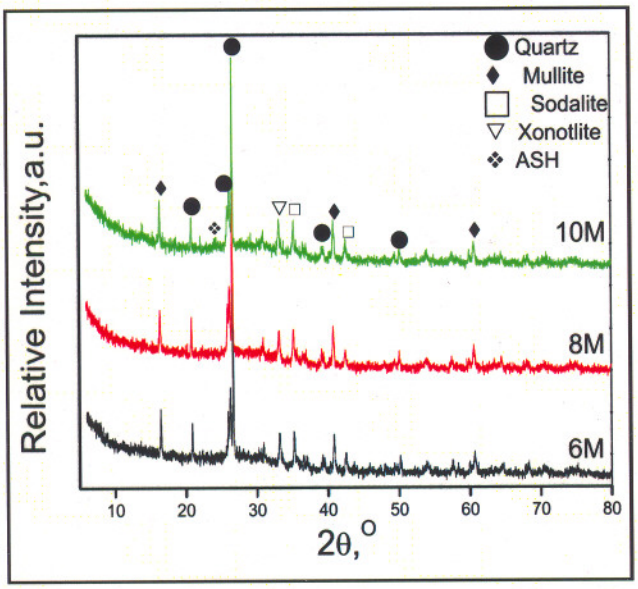

Fig. 5: XRD analysis of fly ash geopolymer

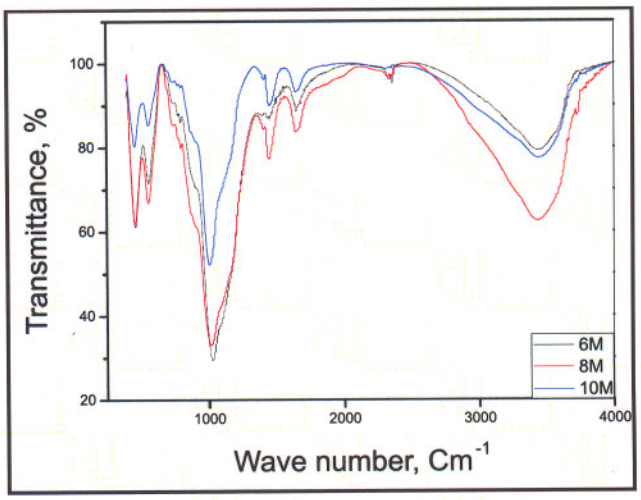

Fig. 6: FTIR analysis of fly ash geopolymer

During geopolymerization one X-ray phase is converting into another amorphous phase. X-ray diffraction pattern of geopolymer samples prepared using different molar alkali solution is presented in Fig. 5. As fly ash is a mixture of amorphous and crystalline components and only the amorphous part of fly ash is reacted with alkali. Both amorphous hump and sharp crystalline peaks were detected in XRD. Hump between 25 to 35° of 2θ values was reflected due to geopolymer gel. Other identified phases were quartz, mullite, sodalite, xonotlite, ASH etc. Phases such as sodalite, xonotlite and ASH were formed due to interaction of fly ash with alkali solution. Quartz and mullite phases were present as the remnant crystalline phases of fly ash. The peak intensity of main crystalline quartz peak was increased with alkali concentration because of higher dissolution of other phases in 10M concentrated alkali solution.

FTIR analysis of fly ash geopolymer is shown in Fig. 6. Peak position and characteristics of all geopolymer samples are similar. Though, peak shape of T-O-T (T can be Si or Al) asymmetric stretching band at around 1000 cm^{-1} of 10M alkali activator based geopolymer was different from other two. This indicated more gel formation in early stage of geopolymerization when higher concentration was used. Other recorded peaks were Al-O/Si-O band in plane and bending vibration at around 460 cm^{-1} and 560 cm^{-1} respectively. At around 1650 cm^{-1} and 3450 cm^{-1} wave numbers O-H vibration and stretching bands were detected.

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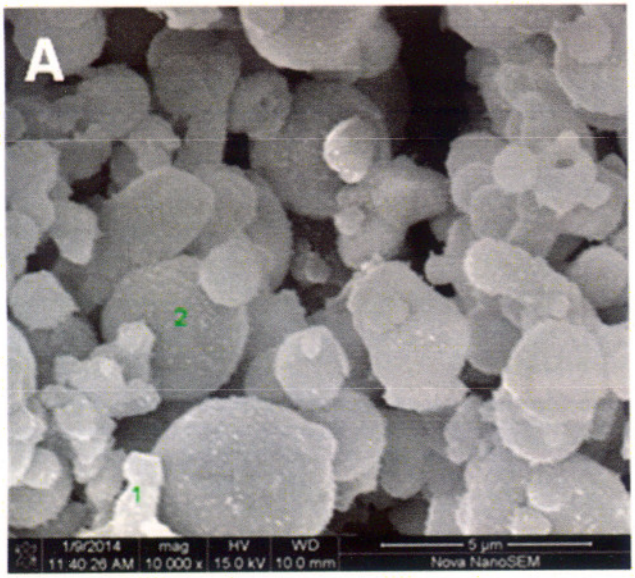

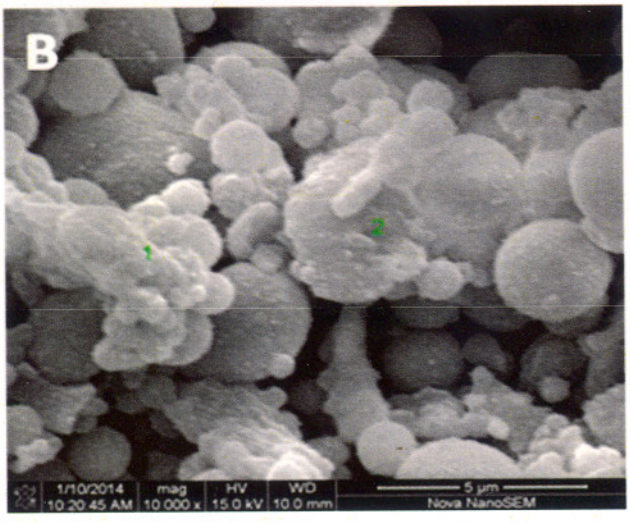

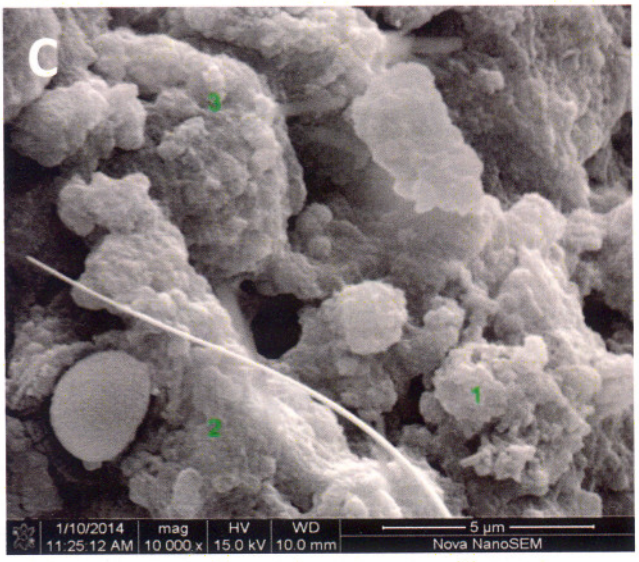

Fig. 7 (A–C): SEM micrographs of fly ash geopolymer, A: 6M, B: 8M, C:10M

Table 3: EDAX analysis

Sample	Point	Si/Al	Si/Na
A	1	1.45	3.98
	2	1.42	18.07
B	1	1.09	3.62
	2	0.93	4.4
C	1	1.58	4.64
	3	0.92	5.88

FEG-SEM micrographs of fracture surface of geopolymer samples are presented in Fig. 7 (A-C). Compact microstructures with gel were observed. Gel formation was increased with alkali concentration attributed more reactivity with high alkali concentration. EDAX analysis of different points of micrographs is shown in Table 3. TEM analysis of geopolymer samples are presented in Fig. 8 (A-B). In Fig. 8A The fly ash grains were observed in a geometrical shape. Whereas, fly ash started reaction on surface and grains were diffused as shown in Fig. 8B when 8M solution was used.

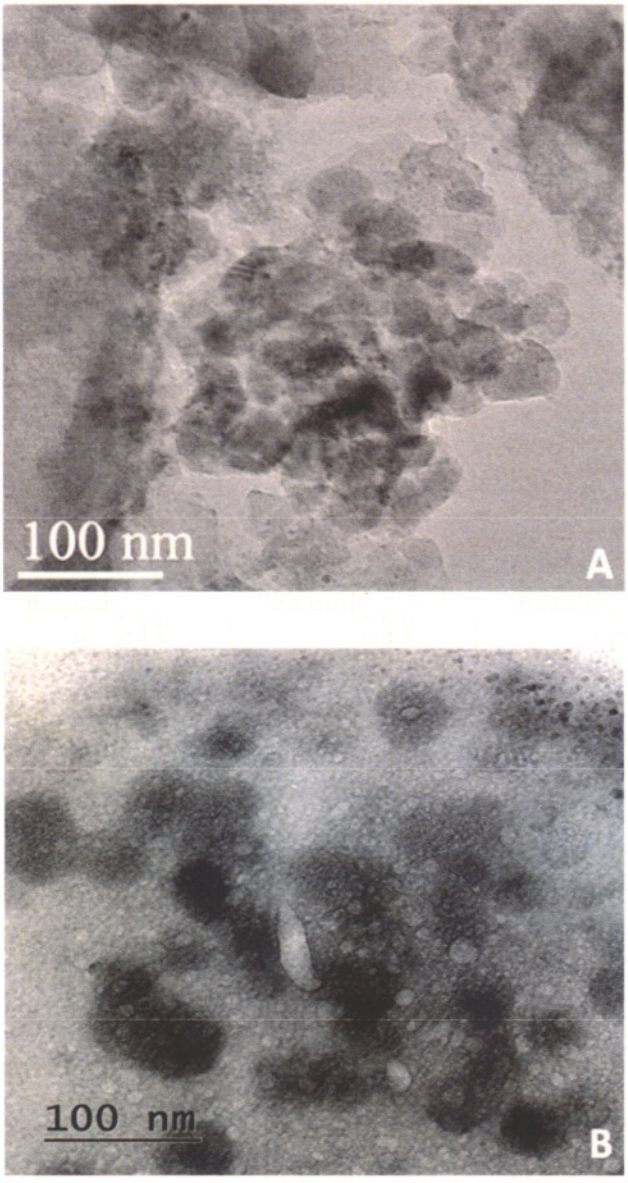

Fig. 8 (A-B): TEM micrographs of fly ash geopolymer, A: 6M, B: 8M

4.0. Conclusions

The following conclusions were drawn from the above study-

1. Reactivity of fly ash for geopolymer reaction was monitored by ICC and it was increased with alkali concentration.
2. Higher reactivity in terms of higher heat evolution and higher peak intensity was recorded when higher concentrated alkali solution is used as activator.
3. The behavior of FTIR peak of 10M geopolymer sample was different from other two lower concentrated samples which indicated higher amount of geopolymer gel formation at early stage of reaction due to higher reactivity with higher alkali concentration.
4. With alkali concentration the intensity of prominent crystalline phases was increased which indicated dissolution of other phases was more in higher concentrated sample.
5. Phases like sodalite, xonotlite, ASH etc were identified by XRD which are known phases of geopolymer/zeolite.
6. More reactive product i.e. gel was observed when increased the alkali concentration. Compact microstructures were observed in all samples.
7. Diffused fly ash particles due to geopolymer reaction were observed under TEM study when 8M solution was used. Whereas sample with 6M solution particles were present in a particular geometrical shapes.

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