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EFFECT OF SYNTHESIZING PARAMETERS ON COMPRESSIVE STRENGTH OF FLYASH BASED GEOPOLYMER PASTE

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Abstract. The objectives of the present research is to appreciate the effect of synthesizing parameters on engineering properties of Geopolymer composites manufactured using locally available low calcium fly ash . Fly ash used are lignite coal based and falls under class F category. The current research utilizes low calcium fly ash obtained from a thermal power plant located near Kolkata, India. The broad areas of present research include: Manufacturing of Geopolymer and a comprehensive study on the effect of synthesizing parameters on compressive strength of Geopolymer paste. The effect of synthesizing parameters such as Alkali content (Na_2O/Al_2O_3), Silica content (SiO_2/Al_2O_3) and Water to Geopolymer binder ratio have been studied and arrived at certain level of understanding regarding manufacturing and compressive strength, which will be useful to the researchers and manufacturers.

Keywords – Compressive strength, Geopolymer, Porosity, Microstructure, Flyash

1 Introduction

Geopolymers is an inorganic polymeric materials formed by activating silica-aluminum rich minerals with alkaline or alkaline-silicate solution at ambient or higher temperature level. Potential applications includes: fire resistant materials, thermal insulating material, low energy tiles , waste containment, paver blocks etc.

Geopolymerisation is a very complex multiphase exothermic process, involving a series of dissolution-reorientation-solidification reaction analogous to zeolite synthesis. High alkaline solutions are used to induce the silicon and aluminium atoms in the source material to dissolve, forming three dimensional polymeric structure consisting of -Si-O-Al-O- bonds, represented as follows

$$M_n [-(SiO_2)_z–AlO_2]_n . wH_2O$$

Where: M = the alkaline element or cation such as potassium, sodium or calcium; the symbol – indicates the presence of a bond, n is the degree of polycondensation or

polymerisation; z is 1, 2, 3, or higher. The exact reaction mechanism which explains the setting and hardening of geopolymers is not yet quite understood, although it is thought to be dependent on the aluminosilicate base material as well as on the composition of alkaline activator. (Ref. to Fig.1).

Optimization of such a complex system requires systematic study of a number of synthesizing parameters as well as of their interactions. Secondly, fly ash from different sources show different level of reactivity under specific geopolymer synthesis conditions and consequently affects the final properties. Hence for manufacturing high performance geopolymer binder from fly ash, it is necessary to understand the effects of a various synthesis parameters and their relationship with mechanical properties and microstructure. The Geopolymer mix composition is normally controlled by adjusting alkali and silicate content of activating solution. The SiO_2/Al_2O_3 molar ratio is an extremely important parameter which has major influence on physical and mechanical properties as well as on its microstructure.

The properties of fly ash based geopolymer in fresh and hardened state depends on chemical composition and quantity of fly ash as well as activator solution. Curing condition is also another important aspect. It may be noted here that, percentage of Na_2O (by weight of fly ash) and SiO_2/Na_2O ratio of the mix significantly affect workability, setting time and physico-mechanical properties of geopolymer. The workability of the mix depends on viscosity of mix. The viscosity of gel increases with time due to geopolymerisation process. A study on loss of flow with time is necessary to determine handling time of geopolymer mix. The percentage of Na_2O and SiO_2/Na_2O ratio of mix also affect development of internal pore structure of geopolymers and subsequently the strength and durability. The characterisation of internal pore structure can be made by using simple methods like measuring water absorption, apparent porosity and water sorptivity. Therefore, the effect of synthesizing parameters on engineering properties of geopolymer composites has been considered for systematic research . Moreover, these studies are important for locally available fly ash for wide applications in the industry.

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2. EXPERIMENTAL INVESTIGATION

The experimental investigation has been conducted mainly at Jadavpur University, Kolkata, India. Some studies have been made at University Science and Instrument

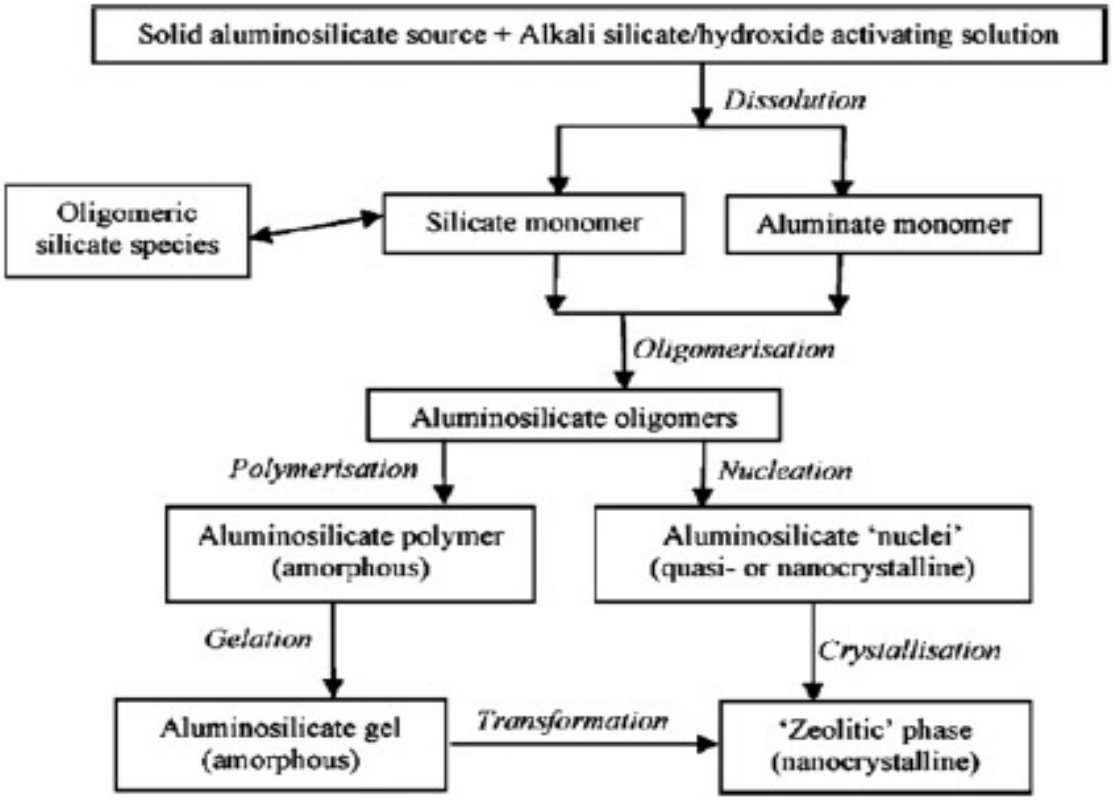

Figure- 1.1 : Schematic outline of the reaction processes in geopolymerisation

Center (USIC), Jadavpur University and Central Glass and Ceramic Research Institute (CGCRI), Kolkata, India. The humidity and ambient temperature in the laboratory are ranging from 75% to 90% and 25°C to 40°C respectively. The experimental methodology was divided in to two main parts: (1) preparation of geopolymer mix and test specimen and (2) testing and characterization of geopolymer. The laboratory tests were conducted as per relevant Indian standard /ASTM codes. The characterisation of geopolymers was carried out using XRD to elucidate

mineralogical changes leading to microstructure changes. 50x50x50 cube specimens were tested.

2.1 Raw Materials

Typical locally available low calcium Class F fly ash from a thermal power station near Kolkata was used throughout the research. The alkaline activator solutions were prepared by mixing sodium hydroxide in pellets form in sodium silicate solution and distilled water.

2.1.1 FLYASH

In the present research work, typical low calcium, Class F dry fly ash obtained from a local thermal power plant, located near Kolkata, India, was used as the basic aluminosilicate material to manufacture geopolymers. The chemical compositions of the fly ash, as determined by X-Ray Fluorescence (XRF) analysis, are given in Table 2.1.

Oxide	Mass (%)
SiO_2	55.15
Al_2O_3	30.85
Fe_2O_3	3.15
TiO_2	1.85
CaO	2.45
MgO	0.35
K_2O	0.8
Na_2O	0.65
SO_3	Nil
P_2O_5	0.5
LOI*	0.45

Table 2.1: Chemical composition of the fly ash (mass %)

The total percentage of (SiO_2+ Al_2O_3+ Fe_2O_3) is greater than 70%. The calcium oxide content is less than 10%. Hence, as per ASTM C 6128-03, it can be classified as

class F fly ash (or siliceous pulverised fuel ash conforming to IS 3812(Part-I)-2003 specifications). The colour of the fly ash was dark gray. About 90% of the particles were smaller than 45μm, and the Blain specific surface area of fly ash was 395m^2/kg. The Scanning Electron Microscopy (SEM) image of fly ash show that the fly ash particle are generally spherical in shape of varying size.

The mineral composition of fly ash was obtained by XRD analysis and it was found that the major crystalline constituents of fly ash included quartz (SiO_2), mullite (Al_2O_3), and magnetite (Fe_3O_4). The fly ash is also constituted of an X-ray amorphous phases indicated by the broad hump registered between 2θ =20° and 30°

2.1.2 ACTIVATOR SOLUTION

The alkaline activator was combination of sodium silicate and sodium hydroxide solutions. The sodium hydroxide solids were laboratory grade in pellets form, with a specific gravity of 2.15, 97% purity. To avoid effects of unknown contaminants, distilled water was used for preparing the activator solutions.

The sodium hydroxide (NaOH) solution was prepared by dissolving NaOH pellets in water. The mass of NaOH solids in a solution was varied depending on the required concentration of the solution. The chemical composition of the sodium silicate solution was Na_2O=14.7%, SiO_2=29.4%, and water 55.9% by mass. The other characteristics of the sodium silicate solution were specific gravity=1.48 g/cc. The activator solution was prepared at least one day prior to its use .

2.2 MANUFACTURING PROCESS

Following steps were followed during manufacturing of Geopolymer

- Mixing of sodium silicate solution, sodium hydroxide pellets and water according to predefined proportion to make alkaline activator, at least one day prior to its use .
- Hobart mixer with rotating blades, was used for preparing geopolymer mix
- Mixing of fly ash and alkaline activator in the Hobart mixer for about five to six minutes to get a homogeneous paste.
- Casting of cubes (50x50x50) with geopolymer mix using steel molds and placed on vibration table for 2-3minutes to remove entrapped air in the mix.
- After two hours fresh specimens are placed in the oven for thermal curing The rate of heating in oven is 0.5°C per minute . Heat curing was made at 85°C for 48 hours[25]
- Release the specimens from molds at room temperature and were left to at room temperature until tested.

2.3 SYTHESIZING PARAMETERS

The objective of the experimental investigation was to study the effect of synthesizing parameters on compressive strength of low calcium fly ash-based

geopolymer paste. The proportion of geopolymer mix was varied by changing quantity and proportion of sodium silicate and sodium hydroxide in activating solution. The effect of alkali content (Na_2O/Al_2O_3), silicate content (SiO_2/Al_2O_3) and water to geopolymer binder ratio on direct compressive strength of geopolymer paste specimens was studied. The direct compressive strength of geopolymer paste specimens was obtained at the age of 3 and 7 days. For explaining variation in compressive strength X-Ray Diffraction (XRD) was carried out.

2.4 MIX COMPOSITION AND COMPRESSIVE STRENGTH

At the beginning, the effect of alkali content (Na_2O/Al_2O_3) of the mix was studied. The alkali content was changed from 0.4 to 0.65 by varying quantity of sodium hydroxide solids in activator solution. Later on, the effect of silica content (SiO_2/Al_2O_3) was studied. The silica content of the mix was varied between 3.5 and 4.5 by changing quantity of silica powder (SiO_2). Other parameters of mix i.e. quantity of silicate solution and sodium hydroxide was kept constant for all specimen. The effect of water content expressed as water to geopolymer binder (geopolymer binder is sum total of mass of fly ash + mass of solids in activating solution). Water to Geopolymer binder ratio (W/B ratio) was varied from 0.225 to 0.35 by changing quantity of water. The alkali content and silica content was kept constant to 0.5 and 4.0 respectively. The mix proportions are presented in tabular form below.

Composition of Geopolymer Mix (Molar ratio)				Compressive Strength (MPa)	
Mix No.	Na_2O/Al_2O_3	SiO_2/Al_2O_3	H_2O/Al_2O_3	3day	7day
S1	0.45	4.0	6	15.42	19.23
S 2	0.50	4.0	6	22.78	27.37
S 3	0.55	4.0	6	27.77	34.50
S 4	0.60	4.0	6	33.36	38.67
S 5	0.65	4.0	6	36.37	42.36
S 6	0.50	3.75	6.	19.19	22.63
S 7	0.50	3.875	6	24.54	29.37
S8	0.50	4.00	6	27.57	33.50
S9	0.50	4.125	6	28.06	32.67
S10	0.50	4.25	6	23.26	28.36

Composition of Geopolymer Mix (Molar ratio)				Compressive Strength (MPa)	
Mix No.	Na_2O/Al_2O_3	SiO_2/Al_2O_3	W/B ratio	3day	7day
S 11	0.50	4.00	0.225	34.43	38.85
S 12	0.50	4.00	0.25	36.36	41.83
S 13	0.50	4.00	0.3	37.72	44.36
S 14	0.50	4.00	0.325	35.34	40.30
S 15	0.50	4.00	0.35	32.69	39.20

3. DISCUSSION ON TEST RESULTS

It is generally accepted that the dissolution rate of aluminosilicate oxides in fly ash is directly related to the surface concentration of hydroxyl ions. Increasing alkali concentration in geopolymeric system, the concentration of hydroxyl ions also increased which resulted in higher dissolution rate of Si and Si–Al phases of fly ash and improved the overall geopolymerisation process. The compressive strength of geopolymer paste depends on the quantity of aluminosilicate gel formed during process of geopolymerisation. In general, higher the degree of geopolymerisation, higher will be the compressive strength. Further, polycondensation of oligomeric precursors took place in presence of soluble silica, which is the most important process of strength development in geopolymeric materials. It can be said that the geopolymer matrix comprises of gel phase and unreacted/partially unreacted fly ash particles. It can be also observed that increasing alkali content from 0.45 to 0.65 , the formation of more aluminosilicate gel. The quantity of gel and interface between

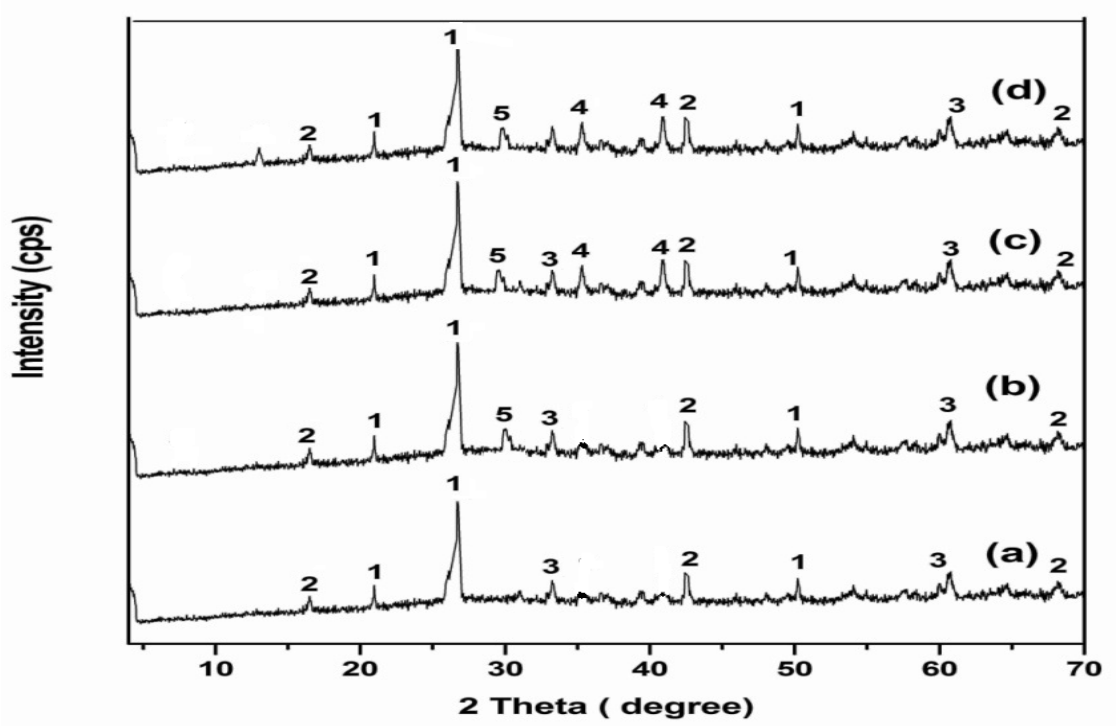

Figure-3.1: X-ray diffractogram of (a) Fly ash (b) S3 (c) S4 (d) S5 (1) Quartz, (2) Mulite, (3) Magnetite, (4) Hydroxysodalite, (5) Herschelite

aggregate and gel is expected to have significant bearing on compressive strength of geopolymer paste. X-Ray diffractogram of fly ash and Geopolymer specimen S3, S4 and S5 is shown in above. It can be observed from the X-Ray diffractograms that the crystalline phases originally existing in the fly ash (i.e. quartz, mullite, magnetite etc.) have not been apparently altered by the activation reactions. However, the XRD pattern of sample S4 and S5, shows formation of new crystalline phases (zeolites) like hydroxysodalite ($Na_4Al_3Si_3O_{12}H$) and herschelite ($NaAlSi_2O_6.3H_2O$). These newly formed crystalline phases contributed in improvement of compressive strength of Geopolymer specimens.

It can be observed that the compressive strength increased almost linearly with silica content up to 4.0. Further increasing silica content, decreased the compressive strength of the Geopolymer specimens. It was found that at higher silica content beyond the threshold value of 4.0, leads to inhibition of Geopolymerisation reaction, indicated by decreased compressive strength. It was found that at high silica content, the polymerization of aluminosilicate gel was not favored. Instead, the dissolved precursors tend to form zeolites.

In the present test , silica content of the Geopolymer system was increased by adding silica powder. Reactive silica is essential for initiation of oligomers formation and accordingly for the polycondensation of oligomers in Geopolymerisation process. The reactive silica controls the rate of polycondensation of Si and Al in aluminosilicate gel. It was observed that the increasing silica content from 3.75 to 4.0 leads to an improvement in the compressive strength suggesting a higher degree of reaction has taken place.

Under almost constant alkali content, the continuous addition of silica causes positive effects on the mechanical properties in initial stage. However, the beneficial effect of the increased silica content on the compressive strength of the geopolymeric materials is not endless and has an upper limit. In the case of the fly ash based geopolymer studied in the present research, the geopolymer mix composed under the highest examined silica content of 4.25 could be hardly molded to make cubic specimens. These specimens resulted in low compressive strength. The geopolymerisation is a complex process having as a first stage the dissolution of the easily dissolved phases of fly ash, is often performed under high alkali concentrations. It is also necessary to add initially increased some amounts of silica to keep high values of silica content in the mix to promote polycondensation process. Otherwise, higher alkali concentrations will cause negative effect on the geopolymerisation process causing decrease in the compressive strength.

Compressive strength of geopolymers more or less increased linearly as the W/B ratio was increased from 0.225 to 0.3. However, further increasing W/B ratio, reduction in compressive strength was observed. As the water content in the synthesis decreases, the alkali concentration in the geopolymer system increases

substantially. Taking into account that the dissolution rates of aluminosilicate oxides and the extent of surface hydroxylation depends on alkali concentration, it may be concluded that the increase of alkali concentration due to reduction in water content causes a substantial acceleration of the dissolution of base material promoting geopolymerisation process. However, there are practical limitations to reduce water content of mix for obtaining desire workability. When W/B ratio was below 0.3 , proper mixing and compaction could not be achieved. Moreover, reducing W/B ratio below 0.225, the water was insufficient for wetting of fly ash particles which negatively affects ion transport mechanism in geopolymerisation and reduction in compressive strength was observed.

Increasing water to binder ratio above 0.3, the alkali concentration in the geopolymeric system reduced making the mix more fluid. The dissolution process was affected due to addition of water and lesser compressive strength was observed.

Therefore, it may be said that water content is a crucial parameter of geopolymer synthesis affecting immediately the mechanical strength. The water content in the synthesis of geopolymer mix ought to be minimized to get better results at all stages of geopolymerisation process, at the same time the geopolymeric mix must retain its reasonable workability.

4. CONCLUSION

The study on effect of geopolymer synthesizing parameters revealed that the development of compressive strength as well as microstructure depended basically on alkali content (Na_2O/Al_2O_3), silica content (SiO_2/ Al_2O_3), water to binder ratio . Strong alkali solutions are needed to dissolve fly ash during the process of geopolymerisation. The improvement in compressive strength was observed with increasing alkali content (Na_2O/Al_2O_3) of the geopolymer mix. Addition of reactive silica affected polycondensation process positively indicated by improvement in compressive strength with silica content. However, increasing silica content beyond 4.0 resulted in reduction of compressive strength. Higher silica content beyond 4.0, inhibited geopolymerisation process indicated by reduction in compressive strength. Water plays important role during dissolution, polycondensation and hardening stages of geopolymerisation. The water content should be adjusted to the minimum level considering desired workability of the geopolymer mix.

REFERENCES

1. ASTM C 109/C 109M-02: Standard Test Method for Compressive Strength of Hydraulic Cement Mortars using 50 mm Cube specimens.
2. Bai, J, Wild, S and Sabir, B.B, Sorptivity and strength of air cured and water cured PC-PFA-MK concrete and the influence of binder composition, *Cement and Concrete Research,* 32, 2002, pp.1813-1821.

3. Collins, F, Sanjayan**, J. G,** Early Age Strength and Workability of Slag Pastes Activated by NaOH and Na_2CO_3, *Cement and Concrete Research,* 28, 1998, pp. 655-664.
4. Criado, M., Palomo, A, Fernandez-Jimenez, A, Alkali activation of fly ashes. Part 1: Effect of curing condition on the carbonation of the reaction products, *Fuel,* 84, 2005, pp. 2048-2054.
5. Criado, M, Palomo, A, Fernandez-Jimenez, An XRD study of the effect of the SiO_2/Na_2O ratio on the alkali activation of fly ash, *Cement and Concrete Research,* 37, 2007, pp. 671-679.
6. Criado, M, Palomo, A, Fernandez-Jimenez, A, Palomo, A, Sobrados, I and Sanz, J, Effect of the SiO_2/Na_2O ratio on the alkali activation of fly ash. Part II: 29Si MAS-NMR Survey", *Journal of Microporous and Mesoporous Materials,* 109, 2008, pp. 525-534.
7. Davidovits, J, Geopolymer chemistry and properties, Proceedings of 1st International Conference on Geopolymer'88, France, 1-3 June 1988, Vol.1, pp. 25-48.
8. Deventer, J.S.J, Provis, J.L, Duxson, P, Lukey, G.C, Reaction mechanisms in the geopolymeric conversion of inorganic waste of useful products, *Journal of Hazard Materials,* 139, 2007, pp. 506-513.
9. De Silva, P, Sagoe-Crenstil K, Sirivivatnanon, V, Kinetics of geopolymerisation: Role of Al_2O_3 and SiO_2, *Cement and Concrete Research,* 37, 2007, pp. 512-518.
10. Fernández-Jiménez A, Palomo, A, and Cecilio López-Hombrados, Engineering properties of Alkali-Activated Fly Ash Concrete, *ACI Materials Journal,* 103, 2006, pp. 106-112.
11. García-Lodeiro I, Palomo, A, Fernández-Jiménez A, Alkali-aggregate reaction in activated fly ash systems, *Cement and Concrete Research,* 37, 2007, pp.175-183.
12. Hardjito, D, Wallah, S.E, Sumajouw, D.M.J and Rangan, B.V**,** On Development of Fly ash Based Geopolymer Concrete, *ACI Materials Journal,* 2004, pp. 467-472.
13. Hardjito, D and Rangan, B.V, Development and properties of low calcium fly ash based geopolymer concrete, *Research Report GC-1,* Faculty of Engineering, Curtin University of Technology, Pert, Australia.
14. IS 3812 (Part-1), Pulverized Fuel ash Specifications, Part-1, For Use as Pozzolans in Cement, Cement Mortar and Concrete, Bureau of Indian Standard, New Delhi, India, 2003.
15. IS 3812 (Part-2), Pulverized Fuel ash Specifications, Part-2, For Use as Admixtures in Cement, Cement Mortar and Concrete, Bureau of Indian Standard, New Delhi, India, 2003.
16. IS 383: Specification for coarse and fine aggregates from natural sources for concrete, Bureau of Indian Standard, New Delhi, India, 1970.
17. Keyte, L.M, Lukey, G.C, van Deventer, J.S.J, The effect of Coal Ash Chemistry on the tailored design of waste-based geopolymeric products, Department of

Biomolecular Engineering, The University of Melbourne, Victoria 3010 Australia, 2005.

18. Kong Daniel L.Y, Sanjayan J.G, Sagoe-Crentsil Kwesi, Comparative performance of geopolymers made with metakaolin and fly ash after exposure to elevated temperatures " *Cement and Concrete Research,* 37, 2007, 2007, pp.1583-1589.
19. Kong Daniel L. Y, Sanjayan J.G and Sagoe-Crentsil Kwesi, Factors Affecting the performance of metakaolin geopolymers exposed to elevated temperatures, *Journal of Material Science,* 43, 2008, pp.824-831.
20. Kong Daniel L.Y, Sanjayan J. G, Damage behavior of geopolymer composites exposed to elevated temperature" *Cement & Concrete Composites,* 30, 2008, pp. 986-991.
21. Kovalchuk, G, Fernandez-Jimenez, A, Palomo, A, Alkali-activated fly ash: Effect of thermal curing condition on mechanical and Microstructural development – Part II, *Fuel,* 86, 2007, pp.315-322.]
22. Panias D, Ioanna P. Giannopoulou and Theodora Perraki, Effect of synthesis parameters on the mechanical properties of fly ash-based geopolymers, *Colloids and Surfaces A: Physicochem. Engineering Aspects,* 301, 2007, pp.246-254.
23. Puertas, F and Fernandez-Jimenez, A, Mineralogical and microstructural characterisation of alkali-activated fly ash/ slag pastes, *Cement and Concrete Composites,* 25, 2003, pp. 287-292.
24. Rangan, B.V, Fly Ash-Based Geopolymer Concrete, *Research Report GC4,* 2008, Faculty of Engineering, Curtin University of Technology, Perth, Australia.
25. Thakur, Ravindra N., Ghosh, Somnath., Book on Fly ash based Geopolymer composites :- Manufacturing and Engineering properties – Published by Lap Lambert Publishing House – Germany
26. van Jaarsveld, J.G.S, van Deventer, J.S.J, Effect of the alkali metal activator on the properties of fly ash based geopolymers, 2006, *Industrial and Engineering Chemistry Research,* 38, 2006, pp. 3932 – 3941.
27. Xu, H and van Deventer, J.S.J, The Geopolymerisation of alumino –silicate minerals, *International Journal of Mineral Processing,* 59, 2000, pp.247-266.