

Parametric Study of Geopolymer Paste with the Different Combination of Activators

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Abstract – The research evolves the parametric study of geopolymer paste resulting from various combination of alkali activation. In this experimental study 4 series of geopolymer paste differing in the combination of alkali activation were prepared by activating low calcium fly ash. For every case activators were subjected to a controlled temperature (35°C) for duration of 24 hours. The geopolymer specimens were allowed for a hot curing under 85°C temperature for 48 hours. The parameters like workability, strength and micro-structure were analyzed. Scanning electron microscopy along with EDAX was conducted in a manner to evaluate microstructural and mineralogical aspects of geopolymer specimens.

Keywords – Geopolymer, Activator, Fly Ash, Microstructure, Workability.

I. INTRODUCTION

We know that, Geopolymerization is a geosynthesis (i.e. reaction that chemically integrates minerals) that involves naturally happening silico-aluminates [1]. Any pozzolanic compound or source of silica and alumina, which is readily dissolved in the alkaline solution, is a well known source of geopolymer acting as geopolymer precursor species and contributes itself in geopolymerization [3]. A geopolymer is a kind of alkali aluminosilicate cementitious material which has superior mechanical, chemical and thermal properties as compared to Portland-based cements, and with significantly lower CO₂ production [2]. Mechanism of geopolymers involves the polycondensation reaction of geopolymeric precursors i.e. alumino-silicate oxide with alkali polysilicates yielding polymeric Si–O–Al bond [4, 5, 6, 7]. $Mn[-(Si - O)_z - Al - O]_n$ can be expressed as the basic polymeric formula . wH_2O where M is the alkaline element, z is 1, 2, or 3 and n is the degree of polycondensation [6]. The mechanism involved in leaching and geopolymerization is revealed by the cation anion pair theory. Mainly because of dissimilar size Na⁺ and K⁺ effects differently though having the same electric charges. The cation with the smaller size favours the ion-pair reaction with the smaller silicate oligomers, such as silicate monomers, dimers and trimers [8, 9, 10]. From Hua Xu's observation the smaller silicate oligomer like monomer, dimer which subsist during the dissolution of Al-Si minerals are better stabilized by Na⁺ (Sodium ion) having smaller size, resulting higher extent of dissolution. But (due to addition of more silicate solution) larger silicate oligomers increase significantly which can be better coordinated by K⁺ cation having larger size, which evidently leads to a higher extent of geopolymerization [11].

In spite of these findings, the exact impact of the different activators on the geopolymer is still not fully understood, which can be an effective factor in wide-scale commercial utilization of this technology.

From this incident a comparative study may be established in connection with different activator which is proper against situation depending on the concentration of sodium silicate in activator solution. Strength and workability along with microstructure of four series of geopolymer paste has been evaluated in this program.

II. EXPERIMENTAL

A. Materials

Low calcium Class F fly ash was used in this research work and collected from Kolaghat Thermal Power Plant near Kolkata, India and the chemical composition of it is given in Fig. 1.1. About 75% of particles were finer than 45 micron and Blaine's specific surface was 380m²/kg. In this present research work laboratory grade Potassium Hydroxide (84% purity) and Sodium Hydroxide in pellet form (98% purity) were used. Sodium silicate solution (SiO₂ =26.5%, Na₂O= 8% and 65.5% water) with silicate modulus ~ 3.3 and a bulk density of 1410 kg/m³ was supplied by Loba Chemie Ltd, India. The alkaline activating solutions were prepared by dissolving required quantity of Alkali Hydroxide pellets directly into water. The solution (Alkali Hydroxide and water) was left for 24 hours at 35°C temperature and after that predetermined quantity of sodium silicate solution was added 3 hours before being used to manufacture geopolymer specimens. SiO₂/X₂O ratio (Here X₂O indicates the summation of K₂O and Na₂O in the activator solution) was maintain as 0.5 and 1.5 respectively. Again it had X₂O content equal to 8.0% of fly ash for every case. Water to Fly ash ratio was of 0.33.

B. Preparation of specimens and testing

In Hobart mixer fly ash was mixed with predetermined quantity of activator solution for 5 minutes. The mix was then transferred into 50mm x 50mm x 50mm cubes. To eject any entrapped air table vibration was provided for 2 minutes. After 1 hour, the cubes were cured in an oven at 85°C for a period of 48 hours and then inside the oven, allowed to cool [12]. Before testing, specimens were removed and stored at room temperature at a dry place. Mix data of the present study are given in the Table 1. After 3 days from casting, the geopolymer specimens were tested for its compressive strength and micro structural properties including scanning electron microscopy, electron diffraction spectrum.

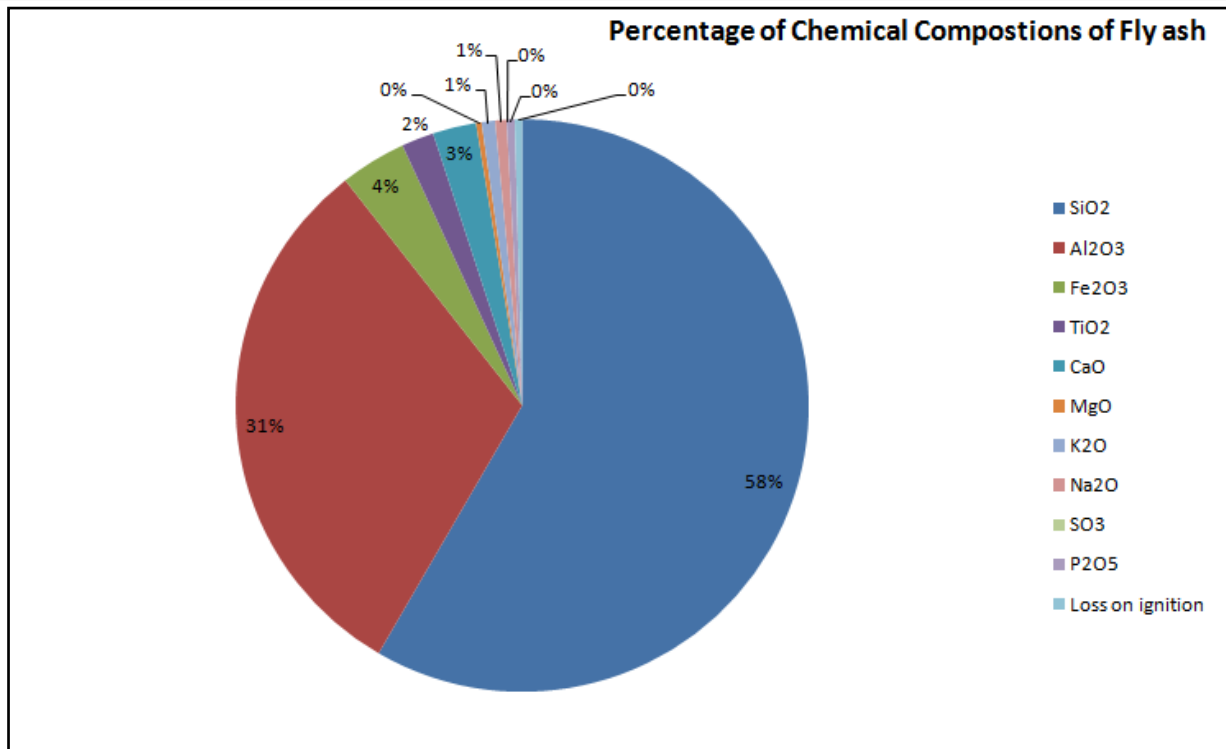


Fig.1.1. Chemical composition of Fly ash

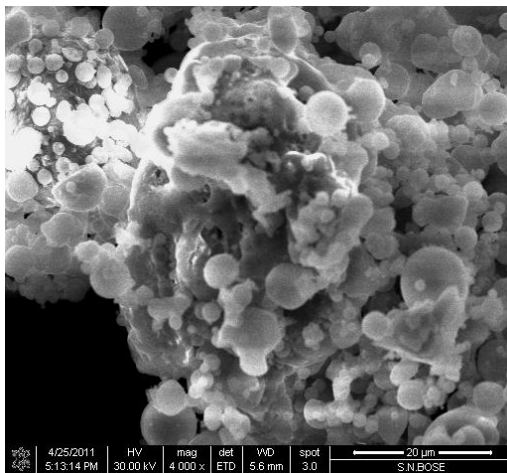


Fig.1.2. SEM Image of Fly ash

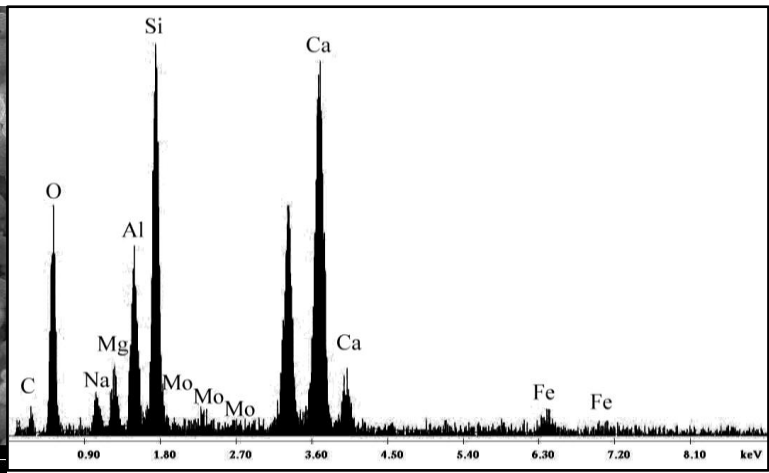


Fig.1.3. EDAX of Fly ash

Table 1: Details of Geopolymer Specimens

Sample ID	X ₂ O* content in Activator (%) of fly ash	Equivalent Silicate modulus (SiO ₂ /X ₂ O)	Type of specimen	Water / fly ash ratio	Curing temp. and duration
GPS1	8	0.5	Paste	0.33	85°C and 48 hrs
GPS2	8	1.0	Paste	0.33	85°C and 48 hrs
GPSK1	8	0.5	Paste	0.33	85°C and 48 hrs
GPSK2	8	1.0	Paste	0.33	85°C and 48 hrs

*Here X refers to alkali Cation. In case of GPS1 & GPS2, X₂O represents Na₂O where as for GPSK1 & GPSK2 X₂O indicates combination of Na₂O & K₂O. Here the term activator solution indicates combination of Sodium Silicate & Alkali Hydroxide. In case of GPS1 and GPS2 the source of Na₂O in activator are both the Sodium Hydroxide and Sodium silicate. For GPSK1 and GPSK2 source of K₂O and Na₂O are Potassium Hydroxide and Sodium Silicate respectively. Here a details proportion has been elaborated in Table 2.

Table 2: Combination of Different Alkali Oxide

Sample Id	X ₂ O %	Na ₂ O %	K ₂ O %	K ₂ O/Na ₂ O
GPS1	8	8	0	0
GPS2	8	8	0	0
GPSK1	8	1.12	6.78	5.6
GPSK2	8	2.42	5.58	2.3

2.3 Workability Setup

A polar graph has been used to measure the flow characteristics of the geopolymer paste, in which there 50 concentric circles and 40 spokes are dividing the area into smaller parts to measure the areal change of the slump of the geopolymer paste. Generally a polar graph is defined as graph in polar co-ordinate. In this system of coordinates the location of a point is resolute by its distance from a permanent point at the center of the coordinate space (called the pole) and by the measurement of the angle created by a permanent line (the polar axis, corresponding to the *x*-axis in Cartesian coordinates) and a line from the pole through the specified point. As shown in the Fig. 2.1, a circular glass slab and cylindrical container have been used. The flow behavior of the geopolymer paste indicates the change in polycondensation which effect on strength and workability.

The workability of a particular geopolymer sample paste has been determined by careful observation and study of the extent of spread of that particular geopolymer paste. A 7 mm thick circular glass slab of 50cm diameter was used in the experimental set-up. To study the extent of the spread, a polar graph was used. The polar graph consists of 50 concentric circles, equally spaced, with the outermost circle having a diameter of 50 cm. Each circle was again divided into a number of sectors by 40 number of spokes (i.e., radial lines). This polar graph was placed below the glass slab. It is evident that it can be easily determined the area of a small division between two consecutive spokes. As the space between two consecutive circles is 0.5 cm, the diameter of a particular circle is indicated by its number measured from center. Such as the

diameter of 50th concentric circle is 50 cm when the diameter for the 1st circle is 1 cm. We have just counted the small divisions to measure the flow area for the sake of simplicity and the rapidness of the experiment. The brass cylinder has been manufactured in such a way that the diameter of the cylinder matches with a particular circle of the polar graph which represents the initial diameter. The glass slab is cut according to the outermost diameter of the polar graph. So the centre of the polar graph denotes the centre of the glass slab and the cylinder is placed in such a way over the glass slab so that it becomes also concentric to the polar graph.

Again in these experiments a simple cylinder was used instead of a mini slump cone or a Marsh cone because geopolymer concrete is very much flow able so initial gradient for flow was not needed by using a cone. Besides to make the experiment simple is also a motive to use a simple cylinder. A mould of bronze cylinder of 8cm in height and 6cm in diameter, was used to hold the geopolymer paste. The mould was placed exactly at the center of the setup, ensuring that its center coincides with the center of the glass slab and that of the polar graph. After filling the mould with geopolymer paste, it was raised vertically and slowly, ensuring that allowing the paste to flow. The flow area was not measured after a certain time rather measured the flow area when the geopolymer paste had stopped flowing, i.e. became steady. After stopping of the flow, the readings corresponding to the outermost periphery of the flow was taken. It was very easy as nth the radii of all the concentric circles, the area of spread was calculated. To get an idea of the workability of the different geopolymer sample pastes, the same procedure was carried out for all the samples and the calculations were made.

It is here defined by the ratio of the final area of the slump to the area of the cylinder. The more the area factor increases indicates that the workability increases. Thus the workability changes were assessed corresponding to activators by the factor.

III. RESULTS AND DISCUSSION

A. Area Factor

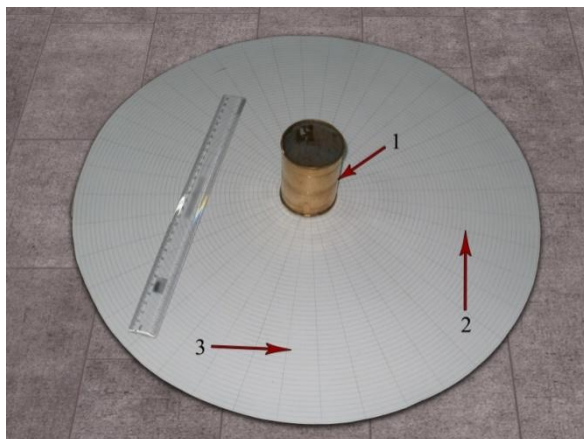


Fig.2.1. The Experimental Setup



Fig.2.2. Geopolymer Paste

1. Cylindrical Brass Container
2. Polar Graph
3. Circular Glass Slab

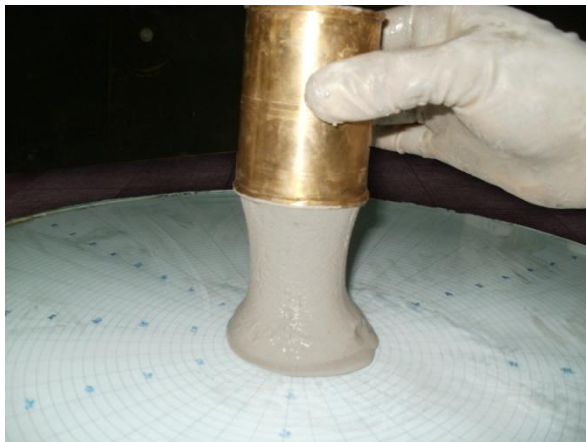


Fig.2.3. Flow Pattern of Geopolymer Paste

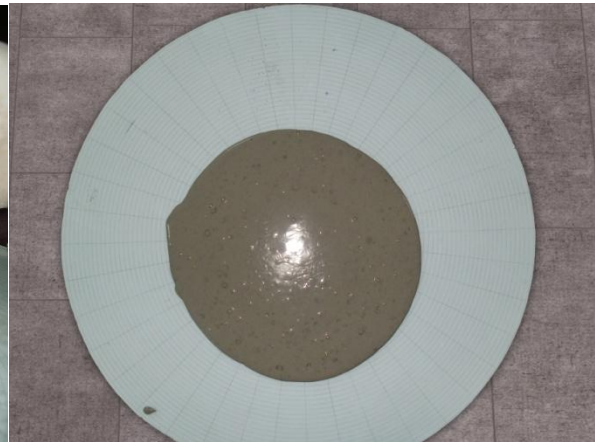


Fig.2.4. Measurement of Workability

Table 3: Results of workability test of the geopolymer paste activated by different activators

Sample ID	Initial Diameter (D1) (cm)	Final Equivalent Diameter (D2) (cm)	Initial Area (A1) (cm ²)	Final Area After Flow (A2) (cm ²)	Area Factor =A2/A1
GPS1	6	19	28.26	283.45	10.03
GPS2	6	22	28.26	379.94	13.44
GPSK1	6	17	28.26	226.86	8.03
GPSK2	6	25	28.26	490.62	17.36

The GPS1, GPSK2 gives better consistency and adhesiveness in compare to GPSK1 and GPS2 respectively. The polymerization is initiated with Sodium Silicate at the infancy stage. It means at the very earlier stage polymerization is started with the SiO₂ presence in Sodium Silicate rather than the same in fly ash. But after the formation of monomer, dimer, trimer, smaller oligomer, oligomer, polymer successively the chemistry

includes SiO₂ presence in fly ash. So, at the initial level presence of smaller oligomers or larger oligomers is extensively depends on the quantity of sodium silicate at the mix. It is noticeable that due to small size of cation Na⁺ effectively stabilized the monomers and smaller oligomers where as in the presence of excess Sodium Silicate higher concentration of larger oligomers are better stabilized by K⁺ which is quite larger.

B. Microstructural investigations

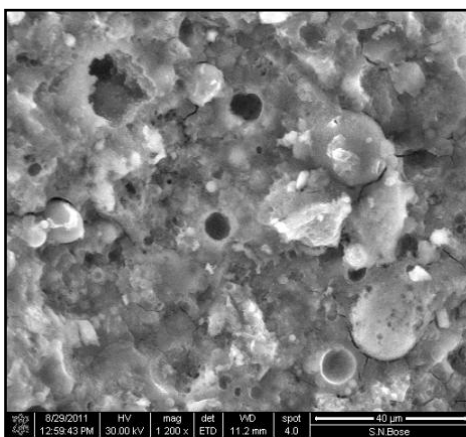


Fig.3.1. GPS1

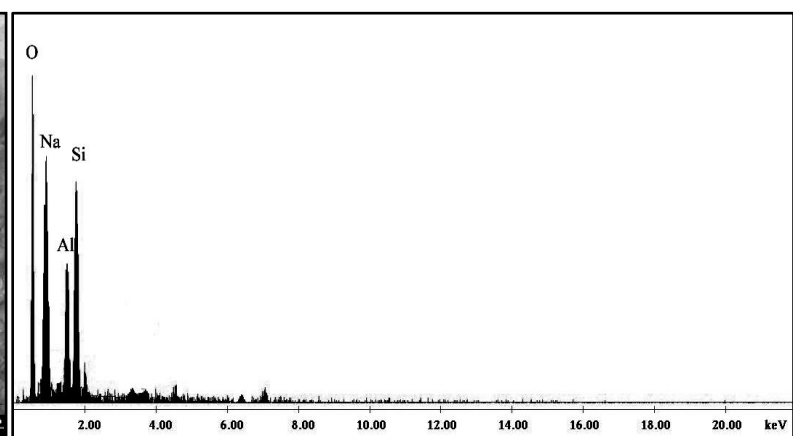


Fig.3.2. EDAX of GPS1

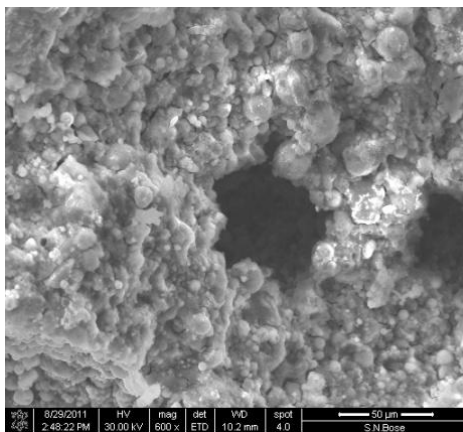


Fig.3.3. GPS2

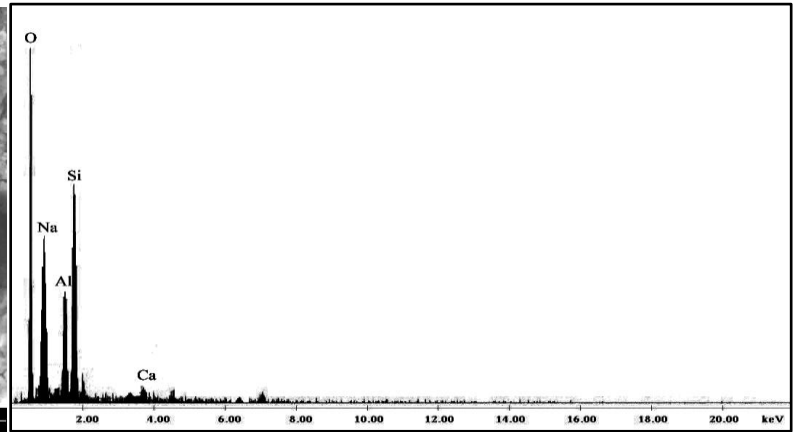


Fig.3.4. EDAX of GPS2

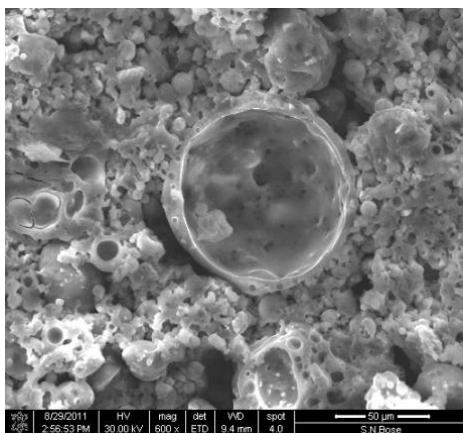


Fig.3.5. GPSK1

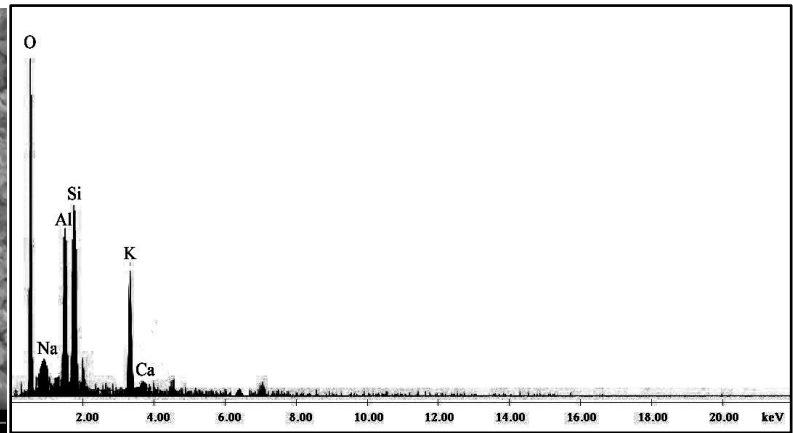


Fig.3.6. EDAX of GPSK1

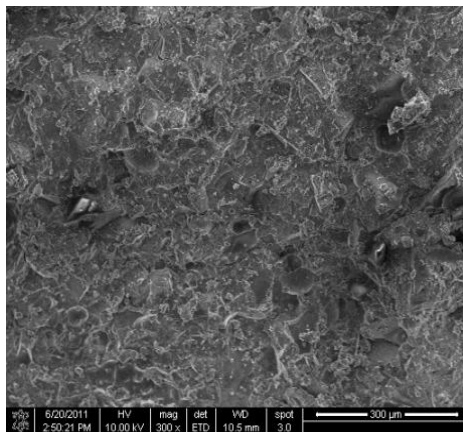


Fig.3.7. GPSK2

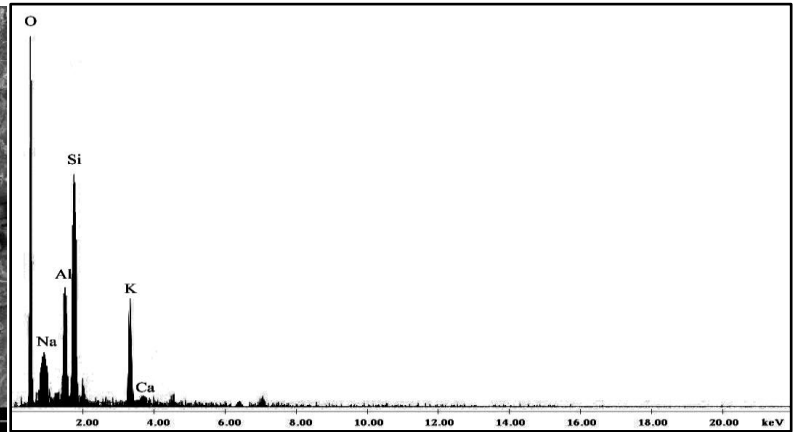


Fig.3.8. EDAX of GPSK2

Scanning electron microscopy (SEM) was performed to study pore morphology and to view the reacted and unreacted regions of the samples. The SEM is used to generate high-resolution images of geopolymers sample and to show variations in chemical compositions. An electrically conductive coating was applied to the samples for study in this mode of SEM. At least 25 mm² of sampling area is needed to obtain a reliable result [13]. SEM- EDAX test was done in the BOSE INSTITUTE in QUANTA 2000 made in Germany. The size of the samples was kept about 5-8 mm in size. Dimension of the

sample should not exceed 8 mm. While the thickness was maintained as small as can be handled easily without damaging the sample or region of interest on the sample. If the sample size is large the region of interest on the sample should be sketched on a paper ahead of SEM/EDAX analysis. The sample was collected in a form of cheap at the time of crushing. The parameter like age for each sample was kept fixed so as to remove the consideration regarding influence of time on surface texture.

The above figures present the ESEM micrographs for geopolymer paste specimens GPS1, GPS2, GPSK1 and

GPSK2 along with their EDAX traces. It depicts a microstructure having more unreacted and partly reacted particles embedded in the geopolymer gel in case of GPS2 and GPSK1. Mostly an amorphous phase with fewer pores of various sizes was observed for GPSK2 and GPS1. EDAX spectra of specimens shows major elements such as oxygen (O), aluminum (Al), silicone (Si), potassium (K), Calcium (Ca) and sodium (Na). The weight percentages of some important elements according to EDAX quantification of GPS1 were O (21.89%), Si (13.39%), Al (7.79%), Na (15.39%), K(0%), Ca(0%). However, the weight percentages of important elements for GPS2 are different which shows O (31.34%), Si (18.15%), Al (9.14%), Na (14.38%) and K(0%), Ca(0.08%). For GPSK1 specimen EDAX analysis yielded the following O (22.09%), Si (12.78%), Al (11.12%), K (8.91%), Na (3.36%) and Ca (0.11%). For GPSK2 specimen EDAX analysis yielded the following O (33.39%), Si (20.13%), Al (10.09%), K (9.07%), Na (4.78%) and Ca (0.12%). As the geopolymer specimen is heterogeneous in nature EDAX at any tentative point is not enough to conclude the quantitative analysis. It is only

right enough to proof the existence of constitute element. Higher Sodium Silicate concentration emphasis KOH (potassium hydroxide) while concentration of Sodium Silicate is low Sodium Hydroxide exhibits better performance.

The ESEM images for geopolymer specimen GPS1, GPS2, GPSK1, GPSK2 are shown in Fig. 3.1, 3.3, 3.5, 3.7 along with their EDAX spectrum as shown in Fig. 3.2, 3.4, 3.6, 3.8 respectively. Fig. 3.1 & Fig. 3.7 exhibits better microstructure in compare to Fig. 3.3 & Fig. 3.5. EDAX spectra of specimens shows major elements such as Oxygen, Aluminium, Silicon, Potassium & Sodium. The percentage of few important elements by weight as per EDAX quantification are tabulated below.

Though geopolymer is heterogeneous compound in nature EDAX at any tentative point is not enough to draw a conclusion. Perhaps EDAX partially demonstrate the typical constitute elements in a manner to support the actual chemistry. Higher concentration of sodium silicate is appreciable for KOH in corporation as an activator. Whether in lower concentration of sodium silicate sodium hydroxide plays better role.

Table 4: EDAX report

Sample ID	Oxygen by weight	Silicon by weight	Aluminium by weight	Potassium by weight	Sodium by weight	Calcium by weight
GPS1	21.89	13.39	7.79	0	15.39	0
GPS2	31.34	18.15	9.14	0	14.38	0.08
GPSK1	22.09	12.78	11.12	8.91	3.36	0.11
GPSK2	33.39	20.13	10.09	9.07	4.78	0.12

C. Compressive Strength

As fracture behavior of the samples was often unpredictable as few areas were chip of prior to ultimate failure, successful samples were defined only when there was a single break of the materials [14]. Around 50 samples of each series were tested for compressive strength. The compressive strength of geopolymer paste

was determined after 3 days. Compressive strength obtained for the geo polymer specimens are presented in Fig. 4. The result supports that higher concentration of Sodium Silicate is better stabilized by Potassium Hydroxide while lower concentration of Sodium Silicate is compatible with Sodium Hydroxide.

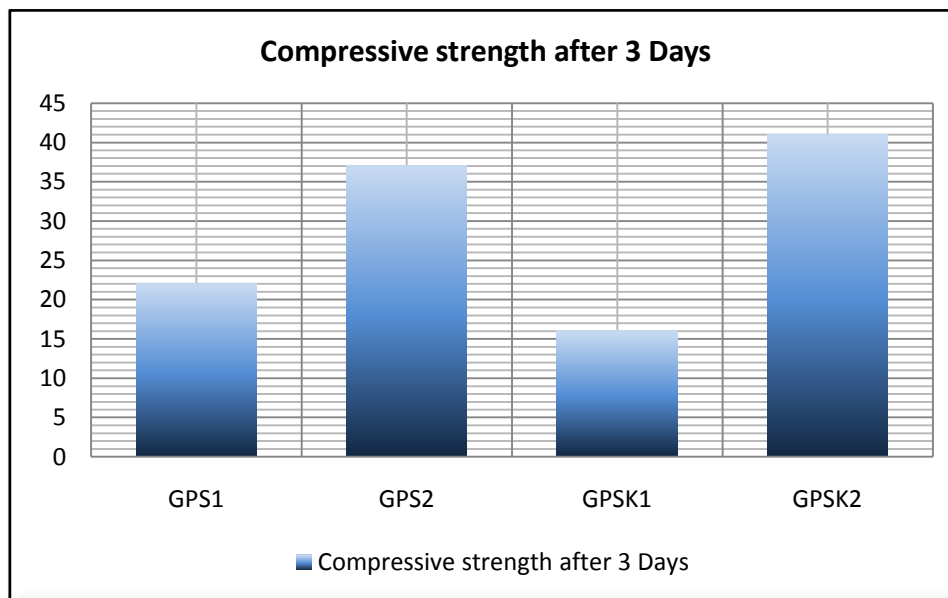


Fig.4. Data of Compressive strength

IV. CONCLUSION

Based on the present investigation the following conclusions were drawn:

- Combination of Potassium Hydroxide and Sodium Silicate as an activator better activates fly ash in higher value of Sodium silicate.
- Sodium Hydroxide plus Sodium Silicate better stabilize the fly ash based geopolymer under lower value of Silicate Modulus.
- For Silicate Modulus equal to one, fly ash based geopolymer paste exhibits better consistency and strength with the choice of Potassium Hydroxide as an alkali hydroxide used for activation.
- Sodium Hydroxide as an activator with Na_2SiO_3 shows better performance in connection with strength and consistency when the silicate modulus of the activator is 0.5.
- Microstructure study supports the result of hardened property for every cases. Sample GPS1 and GPSK2 shows smooth and compact structure in compare to GPS2 and GPSK1 under Scanning electron Microscopy.
- Elemental changes of different molecules for every case have been suitably found out by EDAX spectrum.

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AUTHOR'S PROFILE



Dr. Somnath Ghosh

is presently serving as Professor of Civil Engineering, Jadavpur University, Kolkata- 7000 32. (India). Dr. Ghosh has over 30 yrs of Teaching, Research and Industrial experience He is also a consultant to a number of prestigious projects at national level. He has authored 6 books through an

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Dr. Ghosh has contributed significantly in the area of High performance concrete, Geopolymer composites and FEM analysis of concrete structures. His contribution on 'Fly ash based Geopolymer composite' has added a new dimension in the area of nonconventional green binder material using waste and is acclaimed internationally.

Dr. Ghosh has demonstrated his skill by providing technical advice on a number of occasions and the same has been implemented very successfully in practice. Repair and restoration techniques adopted for the earthquake damaged structures of the Kandla special economic zone (SEZ) through his expertise deserve a special mention. Another noteworthy contribution is the restoration of Assembly building at Sikkim. His skill in computer aided analysis of structure has been demonstrated through the design of a Buddha statue of 52m tall, on the top of a hill at Namchi, Sikkim and a cricket stadium in Guwahati. His selection as the Country Head of a division in a multinational company in Nigeria speaks about his skill and expertise. During this period, Dr. Ghosh has successfully guided a good number of students for their Ph.D and Master's degree. He has acted as expert member on several occasions for CSIR, AICTE, UGC, IIT, NIT & other Universities. Dr. Ghosh has contributed immensely both in academics as well as in practice through his activities.



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MBA (Construction Management). He is pursuing Doctor in Philosophy from Jadavpur University, Kolkata under the guidance of Dr. Somnath Ghosh. At the very outset of his professional career; he gathered experience regarding Metro- Railway Project. He has an experience as a trainee in Variable Energy Cyclotron Centre; Kolkata. He has about 30 international publications in the field of Civil and Mechanical Engineering. He is a life time member of CET (India), formerly known as IET (India). His areas of expertise include Polymer Concrete, Characterization and Performance Evaluation of Blended Concrete, Replacement of Conventional Cement Concrete, Performance and Emission Parameters Analysis of Engine etc. Again his fields of interests include other aspects like Air Pollution Modeling, Prediction Regression Model of Typical Traffic Volume etc. Presently he is working on the betterment of Geopolyme in connection with production and application.