GREENER JOURNALS

Greener Journal of Science, Engineering and Technology Research

ISSN: 2276-7835 ICV 2012: 5.62

Microstructure of Geopolymerized Building Brick Under Atmospheric Curing

By

S.D. Muduli
B.D. Nayak
B.K. Mishra

Research Article

Microstructure of Geopolymerized Building Brick Under Atmospheric Curing

[1]S.D. Muduli, [2]B.D. Nayak* and [3]B.K. Mishra

[1]Women Scientist, CSIR-Institute of Minerals and Materials Technology, Bhubaneswar.
[2]Chief Scientist, CSIR-Institute of Minerals and Materials Technology, Bhubaneswar.
[3]Director, CSIR-Institute of Minerals and Materials Technology, Bhubaneswar.

*Corresponding Author's Email: surabhidipali@gmail.com

ABSTRACT

This research work has been carried out to tailor the development of different type of microstructure in geopolymerized fly ash building brick. During the experimental, work alkaline activator containing both soluble sodium silicates (1:1 solution) and sodium hydroxide (1:1 solution) in presence of anions has been used to improve the reactivity of fly ash. Fly ash and alkaline activator in different weight % are mixed on 100 kg scale followed by water for preparation of the wet mix. Then the wet mixture has been used in casting of brick (230X75X11mm size) by hydraulic press applying 15-20 ton of compaction pressure and then shifted for atmospheric curing at 35°C. Compressive strength, and microstructure of the bricks have been investigated. The raw mix consisting of 87% of fly ash and alkaline activator has been used by maintaining $Na_2O/(Al_2O_3+SiO_2)$ ratio of 0.025 to 0.038 to manufacture building materials ranging in crushing strength of 6 to 12 MPa. The structural changes, i.e. crystalline structure of geopolymerized building brick under the scanning electron micrograph have been observed.

Keywords: Microstructure, geopolymerized building brick and atmospheric curing.

INTRODUCTION

Geopolymerization is an exothermic process that is carried out through oligomers (dimer, trimer) which provide the actual unit structures for the three dimensional macromolecular edifice (Davidovits, 1988b). It involves a heterogeneous chemical reaction between solid aluminosilicate and alkali metal silicate solutions at high alkaline conditions and mild temperatures yielding amorphous to semicrystalline polymeric structures, which consist of Si–O–Al and Si–O–Si bonds (Dimas et al., 2009). Geopolymerization is a geosynthesis (reaction that chemically integrates minerals) that depend on the ability of the aluminium ion (6-fold or 4-fold coordination) to induce crystallographical and chemical changes in a silica backbone (Davidovits, 2005). Fernandez-Jimenez & Palomo studied the composition and microstructure of alkali activated fly ash binder and found that the main reaction product of fly ash based geopolymer is an alkaline silico-aluminate gel (Fernandez-Jimenez et al., 2005). The OH^- ion acts as a reaction catalyst during the activation process; and the alkaline metal (Na^+) acts as a structure-forming element. The structure of prezeolite gel contains Si and Al tetrahedral randomly distributed with the polymeric chains that are cross linked so as to provide cavities of sufficient size to accommodate the charge balancing hydrated sodium ions. The amorpohous to semi-crystalline three dimensional silico-aluminate structures of geopolymers based on silico-aluminate and also categorised the geopolymers structure based on the ratio of Si/Al (Davidovits, 2005).

From the SEM study of fly ash based geopolymer mortar, Fernandez-Jimenes and Palomo observed that the microstructure of geopolymer mortar mainly contain amorpohous aluminosilicate gel and the unreacted spheres of fly ash (Fernandez-Jimenez et al., 2005). However, they also detected some crystalline of the aluminosilicate gel and a little group of bright particles which they believe were zeolite crystals. Duxson, et al. found that the microstructure of geopolymers varied depend on the Si/Al ratio (Duxson et al., 2005). Specimens with Si/Al ratio >1.40 exhibit a microstructure comprising clustered dense particulates with large interconnected pores. Specimens with Si/Al ≥1.65 appear homogeneous with porosity distributed in small pores. Closer inspection of the microstructure of geopolymers with 1.40≤Si/Al≤1.65 revealed that the evolution of the microstructure with increasing silicon content is rapid yet continuous within the small compositional region. Petermann et.al has also studied the advantages and disadvantages of using geopolymer concrete for industrial applications, the benefits and risks associated with binder variables (alkaline concentration, pozzolan ratios, curing methodologies), mechanical variance resulting from differences in microstructural evolution and performance in harsh environments. The dissolution of solid Al_2O_3

regions by the activating solution controls the rate, stoichiometry, and extent of solution phase reactions and is dependent on several variables including pH level, binder temperature, the Si/Al ratio and alkali concentration (Petermann et al., 2010). For this reason, the composition and mineralogy of raw pozzolans is critical in the formulation of alkali-activated geopolymer materials. The increase in performance relative to the Si/Al ratio can be summarized by illustrating increasing densities with increasing Si/Al ratios (Vijaya Rangan, 2008). However, the heat-curing temperatures can be as low as 30 °C, which would be attainable in tropical climate conditions (Fernandez-Jimenez et al., 2008). The final reaction product of alkali-activated fly ash is an amorphous to semi-crystalline structure similar to a zeolite precursor. The activation process and degree of reaction within the geopolymer paste is directly related to the glassy content of the ash material (Vara, 2007).

Therefore it is a challenge in synthesizing fly ash based geopolymers at ambient temperatures, while it may be feasible to expose test specimens to elevated temperatures in a laboratory, a full scale pavement project would be difficult to efficiently heat during cure. The objective of the current research work is to investigate geopolymer designs with the potential to successfully harden under atmospheric temperature and observe the changes in the microstructure of the geopolymer building brick.

Materials and method

Table - 1 Chemical analysis of fly ash

Constituent %	**Na_2O**	**MgO**	**PO_2O_5**	**SO_3**	**CaO**	**Al_2O_3**	**SiO_2**	**TiO_2**	**Cr_2O_3**	**Fe_2O_3**
Fly ash	0.09	0.285	0.51	0.14	0.47	35.5	59.5	0.94	0.01	2.01

Table- 2 Raw material mix design

Raw material (wt. %)	**Mix-1 (K1)**	**Mix-2 (K2)**	**Mix-3 (K3)**	**Mix – 4 (K4)**	**Mix – 5 (K5)**
Fly ash	87	87	87	87	87
Activator solution	4	5	6	7	8
Water	9	8	7	6	5
$Na_2O/(Al_2O_3+SiO_2)$	0.025	0.038	0.052	0.065	0.078

Table- 3 Quantitative elemental analysis of different spectrum of the crystalline phases of EDX image of Na-crosslinked fully reacted geopolymer

Element	**At different spectrum in %**								
Na_2O	13.82	7.4	6.58	14.9	15.1	6.53	2.77	8.93	3.64
MgO	0.47	1.39	0.49	0.42	ND	1.14	ND	1.11	0.58
Al_2O_3	31.1	30.58	33.78	30.4	37.1	30.7	3.98	28.5	32.7
SiO_2	45	50.56	52.01	44.9	41.6	51.4	91.9	47.9	54.1
P_2O_5	0.54	1.21	ND	0.57	ND	1.16	ND	0.65	0.56
SO_3	1.6	ND	0.85	1.4	0.72	0.77	0.11	1.22	0.4
K_2O	0.89	0.79	1.18	0.94	1.04	0.88	0.22	0.91	1.22
CaO	2.35	3.16	0.69	2.45	1.07	2.31	ND	0.6	1.44
TiO_2	1.46	1.08	1.33	1.46	0.9	1.66	0.22	0.91	1.52
FeO	2.79	3.82	3.05	2.5	2.19	3.47	0.41	9.23	3.84
Total	100	99.99	99.96	99.9	99.7	100	99.7	99.9	100

In the present research work, low calcium, Class F dry fly ash obtained from one of the Thermal Power station of Odisha, was used as base material to make the geopolymer fly ash building brick. Chemical analysis of the raw material is given in Table-1. The fly ash used in this research is classified as class F fly ash according to the requirement of American Society for Testing and Materials (ASTM- C618-08, 2008) as given in Table – 2. The percentage of carbon in the used fly ash is low as indicated by the low loss on ignition (LOI) therefore it has a higher pozzolanic activity and lower water demand. The SO_3 is less than 1% which will ensure high volume stability and also good for durability. The alkaline activator used in this study is a sodium silicate based solution which means that the alkaline activator contained sodium silicate and sodium hydroxide in presence of some Cl and SO_4 based anions (Nayak et al., 2009). The sodium hydroxide solution was prepared by dissolving sodium hydroxide pellets in water at least 1 day prior to mixing. Subsequently sodium silicate solution (1:1) was added to prepare a suitable alkaline activator solution, which was used for manufacture of building brick. Fly ash and alkaline activator in different weight % are mixed on 100 kg per batch to the pan mixer. The ratio of $Na_2O/(Al_2O_3+SiO_2)$ of different mix design for alkaline activator and fly ash has given in Table-3. Fly ash and alkaline activator as per the desired quantity was added to the pan mixer and allowed to mix for 15 minutes followed by water for preparation of the suitable mixture. Then the resulted wet mixture is discharged from the pan-mixer for feeding to the brick press machine for casting of brick of 230x110x75mm in size. After that the green bricks are kept exposed in the atmospheric air for hardening and development of strength shown in Figure – 1a. The bricks are cured up to 25 days to observe the durability and mechanical strength. The crushing strength of the brick has been calculated as per the procedure IS. 3495 (IS 3495, (Parts 1 to 4): 1992.) and given in figure – 1b.

Figure-1: a. atmospheric curing of geopolymer fly ash building brick (at 35^{o}C)

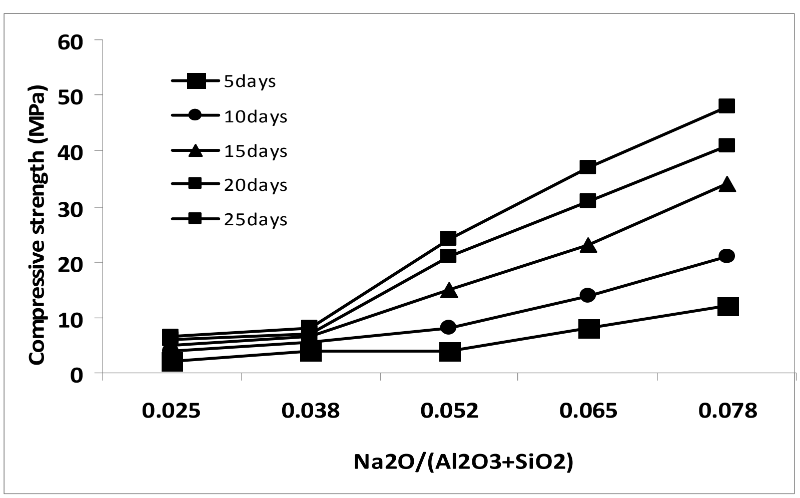
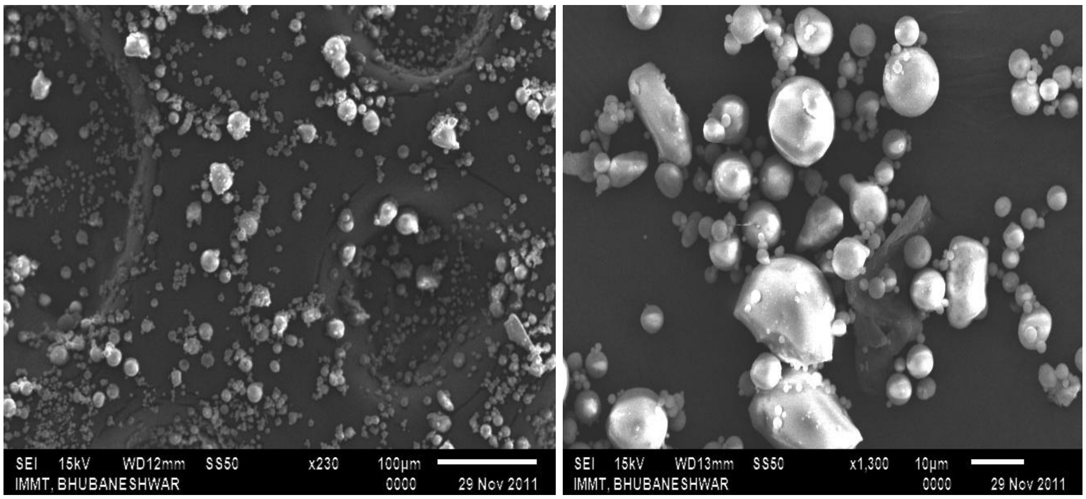
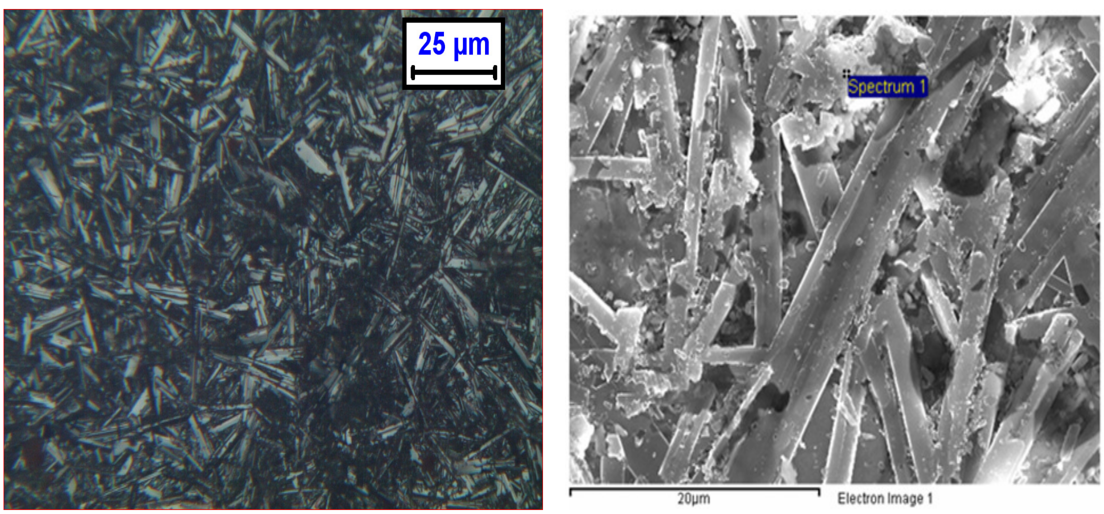


Figure-1: b: Crushing Strength of atmospheric cured geopolymer fly ash building brick

After getting a suitable crushing strength, the microstructure of geopolymer building brick has been observed under Scanning Electron microscopy. The electron micrograph of the fly ash and fully reacted solidified fly ash product obtained has been shown in the Figure- 2. To observe the elemental distribution of fly ash and geopolymerized solidified fly ash product both the samples are under gone for SEM mapping study given in Figure-3 a and Figure-3 b respectively. By observing the distribution of major elements like Al, Si, Na etc. EDX analysis of some spectrum of crystalline phases of fully reacted regions of Na-crosslinked geopolymer has been carried out (shown inTable-4).



Fly ash



Geopolymerised solidified fly ash product

Figure- 2: Scanning Electron Micrography of fly ash and geopolymerised flyash

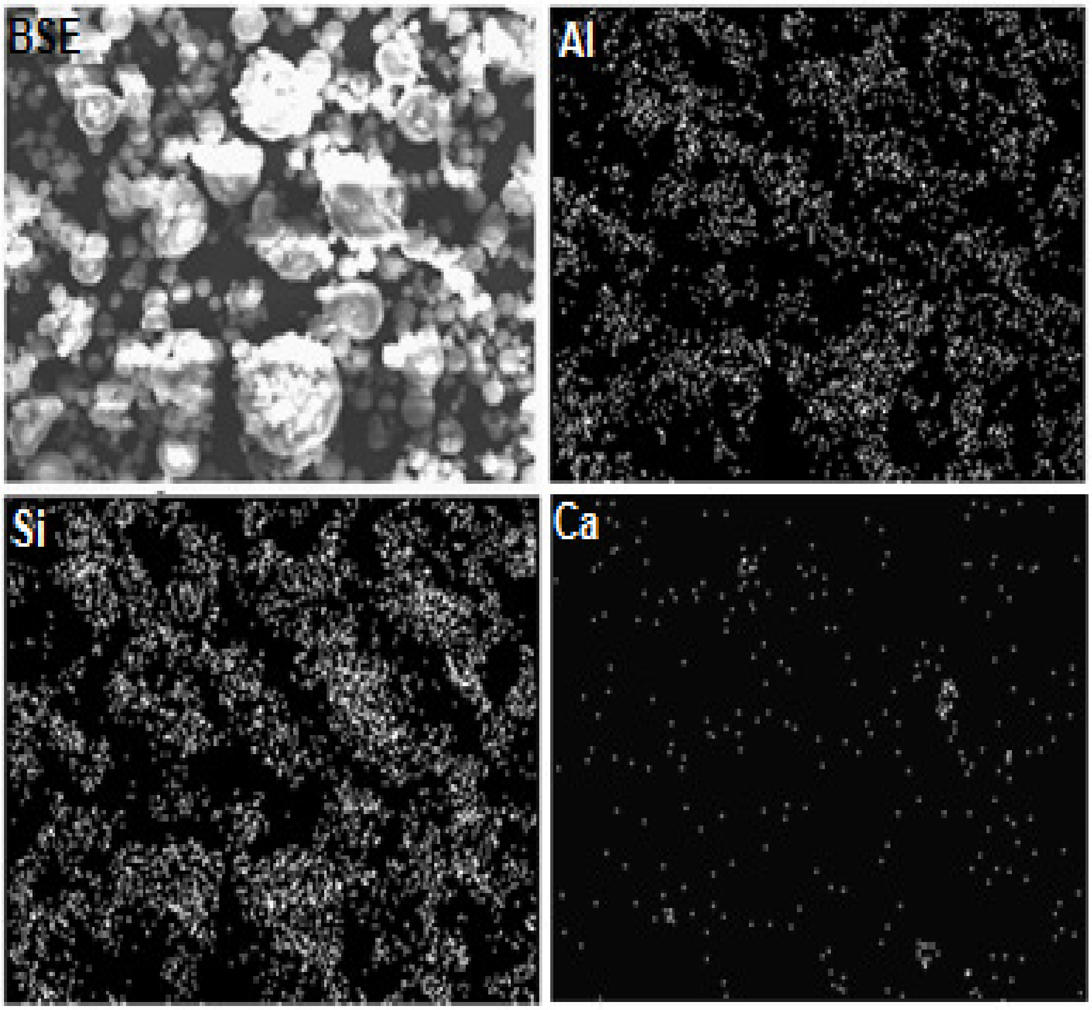


Figure-3.a: Mapping of fly ash sample for Al, Si and Ca

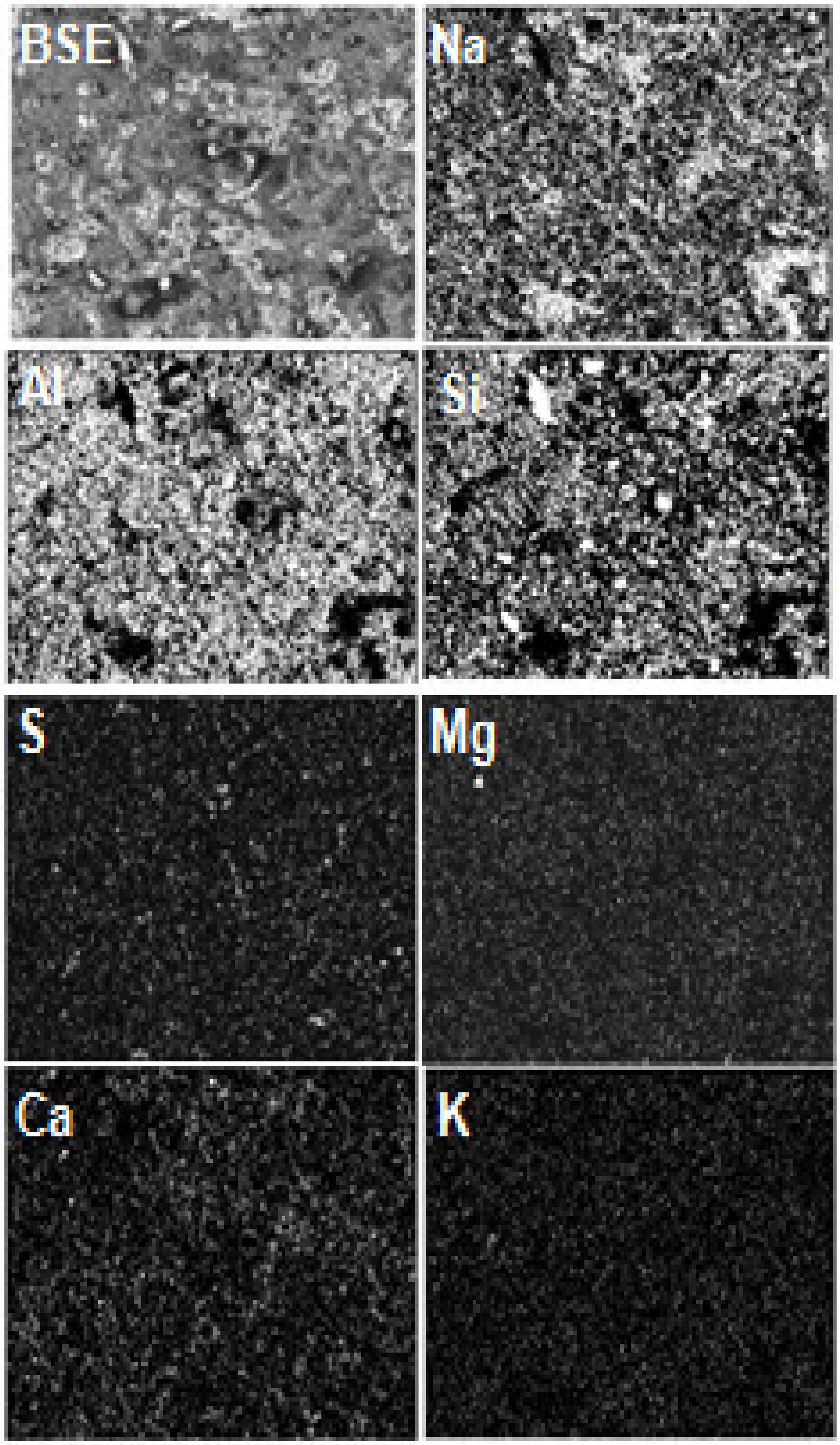


Figure-3.b: Mapping of the geopolymer fly ash sample for Na, Al, Si, S, Mg, Ca & K

DISCUSSION

During the experiment, fly ash has been used up to 87% by weight of the total mix by maintaining $Na_2O/(Al_2O_3+SiO_2)$ ratio between 0.025 and 0.078 in presence of an alkaline activator. In this type of fly ash mix, the solidified product under atmospheric curing attains a crushing strength as high as 48 MPa. The process has been implemented for economic production of high volume (87%) fly ash building bricks by maintaining $Na_2O/(Al_2O_3+SiO_2)$ ratio 0. 0 2 5 to

0.038. The fly ash building bricks of size 230×110×75 mm produced by hydraulic compaction after 25 days of atmospheric curing weigh in the range of 2.80 to 3.20 kg after 8 to 11% of water absorption and attain up to 10 MPa crushing strength, which sartisfies the BIS standard BIS-12894 (IS 12894:2002). It was observed that (Figure-1:a) the under atmospheric curing fly ash mix with $Na_2O/(Al_2O_3+SiO_2)$ ratio between 0.025 to 0.038 are suitable for manufacture of building bricks.

Inter-coordination of the polymerized minerals helps in build-up of the cementation property. Depending upon the crushing strength geopolymerisation process is flexible to make high strength building bricks ranging in crushing strength from 7 to 12 MPa. In geopolymerization process $SO_4^{=}$ is an effective ion of higher hydration energy which promotes hydration of silicates, aluminates and alkalis and enhances the interactions of monomers in formation of crystalline phases (Wang et al., 2006; Desbats-Le Chequer and Frizon, 2011). The Cl^- ion acts as an accilator in gel formation and helps in crystallization (Lee and Van Deventer, 2002; Rattanasak, 2011). The polymerization process involves a substantially fast chemical reaction under alkaline condition with Si and Al bearing minerals that results in the three dimensional polymeric chain and ring structures of Si-O-Al-O monomers. Al and Si co-ordinates with oxygen atoms, and therefore, the presence of cations such as Na^+ is essential to maintain the electric neutrality in the geopolymeric matrix and formation of geopolymer minerals.

From the Scanning Electron Micrograpy study it is observed that Fly ash is fine grain in nature and mostly consists of spheres shaped particles and cenospheres, but in geopolymerized fly ash there is a formation of crystalline structures of sodium assisted cross linked alumino-silicate geopolymer phases. These alkaline phases occur in acicular form and seem to have cross linked into a matrix in the solidified product. The grains are mostly radiating, fibrous and elongated. SEM mapping studies given in Figure- 3.a reveals that the fly ash sample mostly consists of Si and Al with traces of Ca, where as the mapping study of geopolymer fly ash building brick reveals that the sample uniformly consists of Na-Al-Silicate with minor to trace amount of S, Mg, ca and K given in Figure- 3.b. Distribution of different elements of different spectrum of geopolymer fly ash has been shown in Figure- 4 and the elemental distribution of the crystalline acicular structures of Na-crosslinked aluminum silicate of solidified geopolymer fly ash product shows the presence of Na, Al, and Si which correspond to the geopolymer phase of sodium aluminum silicate with minor to trace amounts of Fe, Ti, S, Mg, Ca, and K given in Table- 4 and confirm the compositional analyses

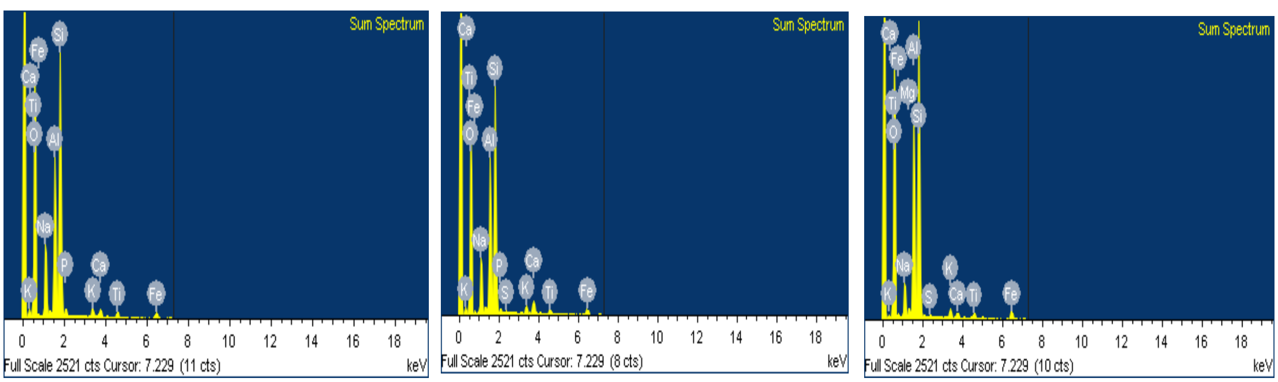


Figure - 4: Elemental analysis of different spectrum of geopolymer fly ash

The SEM mapping study reveals that the sample uniformly consists of Na-Al-Silicate with minor to trace amount of S, Mg, ca and K. These grains are mostly fibrous and elongated. These mineral phases with different cation and anion substitution grow into amorphous to crystalline structures by dissolution and solidification. The basic raw materials play a vital role in the geopolymerization reaction and controlthe chemical composition and microstructure of the final geopolymeric products. It differs basing on their amorphous phases, Si/Al ratios, solubility in alkali solution, reactivity, and even the nonreactive crystalline phases. These factors may result in the variability of curing condition and mechanical properties of geopolymers, which are two important factors, should be considered in practical applications. The knowledge of the micromorphology of these raw materials can help identify those nonreactive and unreacted phases present in the geopolymer binder, as discussed in the text. Development of microstructure with a $Na_2O/(Al_2O_3+SiO_2)$ ratio of 0.078 consists of clear porous, gel like spine-shaped particles while the EDX analyses of selected reveals that both Al, Si, Na with with minor to trace amounts of Fe, Ti, S, Mg, ca and K which are the major elements of the geopolymer backbone. As the fly ash contains very few impurities, other elements should not be expected in the final geopolymeric product. Therefore, it is reasonable to conclude that the continuous, gel-like area is geopolymer. After atmospheric curing some unreacted NaOH may appear.

Conclusion

It is clear that the microstructure of fly ash geopolymer is very difficult to be understood. A series of geopolymer fly ash building brick was manufactured to investigate, the microstructure of fly ash geopolymer. The elemental distribution of the crystalline acicular structures of Na-crosslinked aluminum silicate of solidified geopolymer fly ash product shows the presence of Na, Al, and Si w with ca, Mg, Fe, Ti etc. as minor element, which correspond to the geopolymer phase of sodium aluminum silicate looks mostly fibrous and elongated. As the sodium silicate activator dissolves rapidly and reacts with fly ash particles, the crystalline spine structures are formed by alkaline reaction under atmospheric curing with a high mechanical crushing strength and suitable for manufacture of building brick.

ACKNOWLEDGEMENT

Authors are thankful to Director, CSIR-IMMT Bhubaneswar for giving his kind consent and permission to publish the paper.

REFERENCES

ASTM C618-08, 2008, Standard specification for coal fly ash and raw or calcined natural pozzolan for use as a material admixture in concrete ASTM Annual Books. USA: ASTM.

Davidovits J., 1988b, Geopolymer chemistry and properties. In: Davidovits, J., Orlinski, J. (Eds.), Proceedings of the 1st International Conference on Geopolymer '1988, vol. 1, Compiegne, France, 1–3 June, 25–48,

Davidovits J., 2005, The polysialate terminology: a very useful and simple model for the promotion and understanding of green-chemistry. In Geopolymer, Green Chemistry and Sustainable Development Solutions: Proceedings of the World Congress Geopolymer 2005, Davidovits J., GeopolymerInstitute, Saint-Quentin: France, pp. 9–15, 2005.

Desbats-Le Chequer C. and Frizon F., 2011, Impact of sulfate and nitrate incorporation on potassium and sodium-based geopolymers: geopolymerization and materials properties, Journal of Material Science (46), 5657–5664.

Dimas I., Giannopoulou I. and D. Panias, 2009. Polymerization in sodium silicate solutions: a fundamental process in geopolymerization technology, J. Mater Sci., 44: 3719- 3730.

Duxson P., Provis J. L., Lukey G. C., Mallicoat S. W., Kriven W. M., and Van Deventer, J. S. J., 2005, Understanding the relationship between geopolymer composition, microstructure and mechanical properties. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 269 (1-3), 47-58.

Fernandez-Jimenez A., Monzo M., Vicent M., Barba A. and Palomo, A., 2008, Alkaline Activation of Metakaolin-Fly Ash Mixtures: Obtain of Zeoceramics and Zeocements, Microporous and Mesoporous Materials (108), 41-49.

Fernandez-Jimenez A., Palomo A. and Criado M., 2005, Microstructure development of alkali-activated fly ash cement: a descriptive model. Cement and Concrete Research, 35(6), 1204-1209.

IS 12894:2002 Pulverized Fuel Ash-lime Bricks – Specification, Bureau of Indian Standards.

IS 3495 (Parts 1 to 4): 1992. Methods of tests of burnt clay building bricks, Bureau of Indian Standards.

Lee W.K.W. and Van Deventer J.S.J., 2002, Effects of anions on the formation of aluminosilicate gel in geopolymers. Industrial and Engineering Chemistry Research, (41), 4550-4558.

Nayak B.D., Mishra B.K., Behera S. and Kumar V., 2009, Composition for building material and a process for the preparation there of, Pub. No.: US 2009/0250660 A1.

Petermann J.C., 2010, Saeed Athar and Hammond Michael I., Final Technical Report on Alkali-activated geopolymers: a literature review AFRL-RX-TY-TR-2010-0097, AIR FORCE RESEARCH LABORATORY MATERIALS AND MANUFACTURING DIRECTORATE.

Rattanasak U., Pankhet K. and Chindaprasirt P., 2011, Effect of chemical admixtures on properties of high-calcium fly ash geopolymer, International Journal of Minerals, Metallurgy and materials 18(3), 364-369.

Vara S. k., 2007, Alkali activated material-geopolymer, Department of glass and ceramics, Faculty of Chemical Technology, ICT Prague. Ed., 661-676.

Vijaya Rangan B., 2008, "Fly Ash-Based Geopolymer Concrete", available at: http://www.yourbuilding.org/display/yb/Fly+Ash-Based+Geopolymer+Concrete

Wang L., Shao Y., Zhang J. and Anpo M., 2006, Synthesis of MCM-48 mesoporous molecular sieve with thermal and hydrothermal stability with the aid of promoter anions. Microporous Mesoporous Mater 95(1–3): 17-25