Int. J. Chem. Sci.: 12(3), 2014, 1086-1094
ISSN 0972-768X
www.sadgurupublications.com

GEOPOLYMER FLY ASH BUILDING BRICK BY ATMOSPHERIC CURING

S. D. MUDULI*, B. D. NAYAK and B. K. MISHRA

Environment & Sustainability Department, CSIR-Institute of Minerals and Materials, Technology, BHUBANESWAR – 13 (Orissa) INDIA

ABSTRACT

In the current research work effort has been made to develop geopolymer fly ash building brick under atmospheric curing. Geopolymer building bricks are manufactured by using fly ash and alkaline soda based chemical activator solution in presence of sodium silicate and water by maintaining different $Na_2O/(Al_2O_3 + SiO_2)$ ratio. During this work 230 × 110 × 75 mm size fly ash building bricks are manufactured under atmospheric curing. After 25 days of atmospheric curing the results shows that the geopolymer fly ash building bricks with $Na_2O/(Al_2O_3 + SiO_2)$ ratio of 0.038 attain a crushing strength of 8.5 Mpa, which is approximately equal to the strength achieved by hot air curing at 90°C for 4 hrs.

Key words: Geopolymer, Fly ash, Atmospheric curing.

INTRODUCTION

Geopolymerization depends, on the ability of the aluminium ion to induce crystallographic and chemical changes with a silica backbone[1]. Several reports are found in the literature on the synthesis, properties and applications of geopolymers[2]. It is observed that fly ash is one of the possible resource for making geopolymer binders, which is available abundantly[3]. Different potential applications of geopolymer includes manufacture of fire resistant materials, thermal insulation, low-tech building materials, low energy ceramic tiles, refractory items, cements and concretes[4]. Several research works has been carried out on manufacture of geopolymer building bricks by a wide range of hot air curing. Geopolymers produced by using metakaolin have been reported to set at ambient temperature in a short time period[5]. However, curing temperature and curing time have been reported to play important roles in determining the properties of the geopolymer materials made from industrial by-products like fly ash. It is observed that increase in curing temperature resulted into higher compressive strength[6]. It is described that in geopolymerization process fresh mixtures allowed at room temperature for 60 mins,

---

*Author for correspondence; E-mail: surabhidipali@gmail.com

followed by curing at 65°C for 90 mins, and then drying at 65°C for complete reaction[7]. It is also observed that long curing time improves the polymerisation process resulting into higher compressive strength but an increase in the curing temperature beyond 60°C did not increase the compressive strength substantially[8] and longer curing time did not decrease the compressive strength of geopolymer product[9]. In this research work, the most important factor is to manufacture fly ash building brick by using geopolymerization process under atmospheric curing.

EXPERIMENTAL

Preparation of geopolymerization activator

The process of geopolymerization requires alkaline chemical activator for initiation of reaction in formation of mineral polymer structures. This chemical activator is a synthetically prepared commercial grade sodium hydroxide in pellet form with water and sodium silicate solution in presence of alkaline base chemicals consisting of anions of O^{2-}, $[OH]^{-}$, Cl^{-} and $[SO_4]^{2-}$ in different concentrations[10]. The pH of chemical activator is maintained within 11-12 for suitable geopolymerization reaction.

Manufacturing process

In the current research work, fly ash; the inorganic solid residue generated from thermal power plant is used as raw material for manufacture of building brick through geopolymerization technology. Alumina and silica are the major chemical constituents of fly ash with minor amounts of other oxides such as Fe, Na, Ca, Mg, and K, etc. The chemical analysis of fly ash has given in Table 1. Fly ash with a suitable weight proportion of alkaline activator is mixed in a pan mixer in presence of the synthetically prepared alkaline activator and water. The manufacturing process of geopolymer fly ash building brick has been designed as: weighing of raw material, preparation of chemical activator, mixing, casting and demoulding followed by curing[11]. The mixtures are used for casting of (230 × 110 × 75 mm) size building brick by applying 20 ton compaction pressure. The cast products are cured under normal atmospheric condition upto 25 days. The crushing strength of the bricks are measured in 5, 10, 15, 20, and 25 days interval. The cast products are also cured under hot air curing at 90°C for 2-10 hrs for a comparison.

Table 1: Chemical analysis of fly ash

Constituent %	Na_2O	MgO	P_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

RESULTS AND DISCUSSION

The principle of geopolymerization has been adopted by making different mix designs of fly ash. The mix design composition of fly ash geopolymer building brick along with the cold crushing strength are presented in the Table 2. The results show that geopolymerization is a temperature dependent reaction. The geopolymer fly ash bricks prepared with $Na_2O/(Al_2O_3 + SiO_2)$ ratio 0.025 is showing crushing strength of 6 MPa, in 25 days of atmospheric curing, which does not satisfy the BIS specification of 12894 (2002) where as in 25 days of atmospheric curing fly ash bricks manufactured with $Na_2O/(Al_2O_3 + SiO_2)$ ratio 0.038 is showing crushing strength of 8.5 MPa.

Table 2: Raw material mix design and crushing strength of building brick

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
Days	**Crushing strength (Mpa)**				
5	2.0	3.0	4.0	6.0	8.0
10	2.5	4.0	6.0	10.0	15.0
15	4.0	6.0	10.0	18.0	28.0
20	5.5	7.0	14.0	31.0	32.0
25	6.0	8.0	18.0	38.0	43.0

The hardening of fly ash mix in presence of alkaline activator generally takes a longer duration to attend the desired strength by atmospheric curing. Therefore, conditions of curing are the major aspects to develop a high quality geopolymer product. The results of the geopolymer fly ash bricks prepared with different $Na_2O/(Al_2O_3 + SiO_2)$ ratio cured under hot air curing of 90^oC are presented in Fig. 2b. Results show that in hot air curing also fly ash bricks prepared with $Na_2O/(Al_2O_3 + SiO_2)$ ratio 0.25 shows the crushing strength of 6.5 MPa, and 10 MPa with $Na_2O/(Al_2O_3 + SiO_2)$ ratio 0.38. From both the Figs. 2 (a) and (b) it is observed that the strength achieved by hot air curing at 90°C for 4 hrs can be achieved by 25 days of atmospheric curing, which mostly depend upon the alkaline activator solution. The concentration of SiO_2 and Al_2O_3 with respect to alkali (Na_2O) in the fly ash mix governs the geopolymerization reaction. The anion group chemicals act as the reactant in presence of sodium silicate as a set-modifier. The pH of the chemical activator consisting of sodium and anion group chemicals in water is above 11.0. The concentration of anion group chemicals in the activator is maintained depending on the chemical constitution of the oxides and silicates of aluminum, calcium, magnesium, iron bearing mineral phases, which is needed for effective reaction. The substantial increase in strength of fly ash geopolymer brick is due to the increase of alkali concentration.

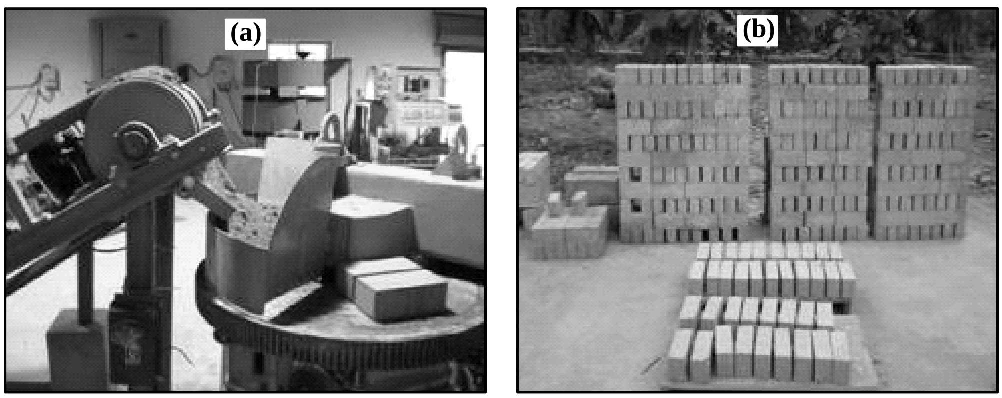

Fig. 1: (a) Casting of fly ash brick, (b) Bricks exposed for atmospheric curing

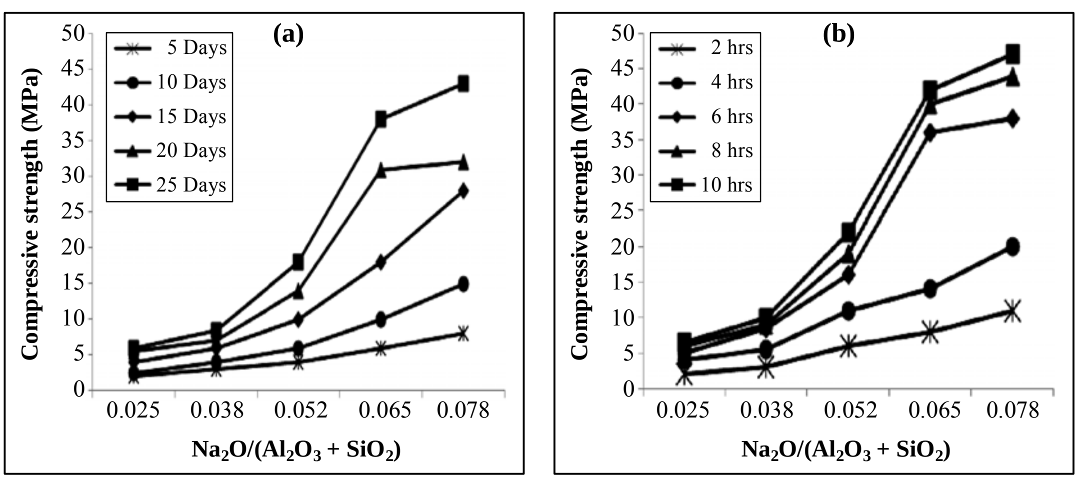

Fig. 2: (a) Bricks under atmospheric curing; (b) Bricks under hot air curing at 90°C

The electron micrograph mapping of fly ash is shown in Fig. 3. It reveals that the fly ash sample mostly consists of Si and Al with traces of Ca, but The electron micrograph of a reacted solidified fly ash product under atmospheric curing having $Na_2O/(Al_2O_3+SiO_2)$ ratio 0.38 mixture is presented in Fig. 4. The micrograph shows the 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 micrograph also shows that the reaction of fly ash in alkaline activator consisting of anions of Cl^- and SO_4^{2-} form crystalline grains of sodium aluminum silicates. The elemental distribution of crystalline phases of acicular structure of solidified fly ash product of $Na_2O/(Al_2O_3 + SiO_2)$ ratio 0.38 is presented in Fig. 5. The results indicate the presence of Na, Al, and Si, which correspond to form the geopolymer phases with minor to trace amounts of Fe, Ti, S, Mg, Ca, and K. These amorphous to crystalline structures grow in presence of different cation and anion by substitution dissolution and solidification.

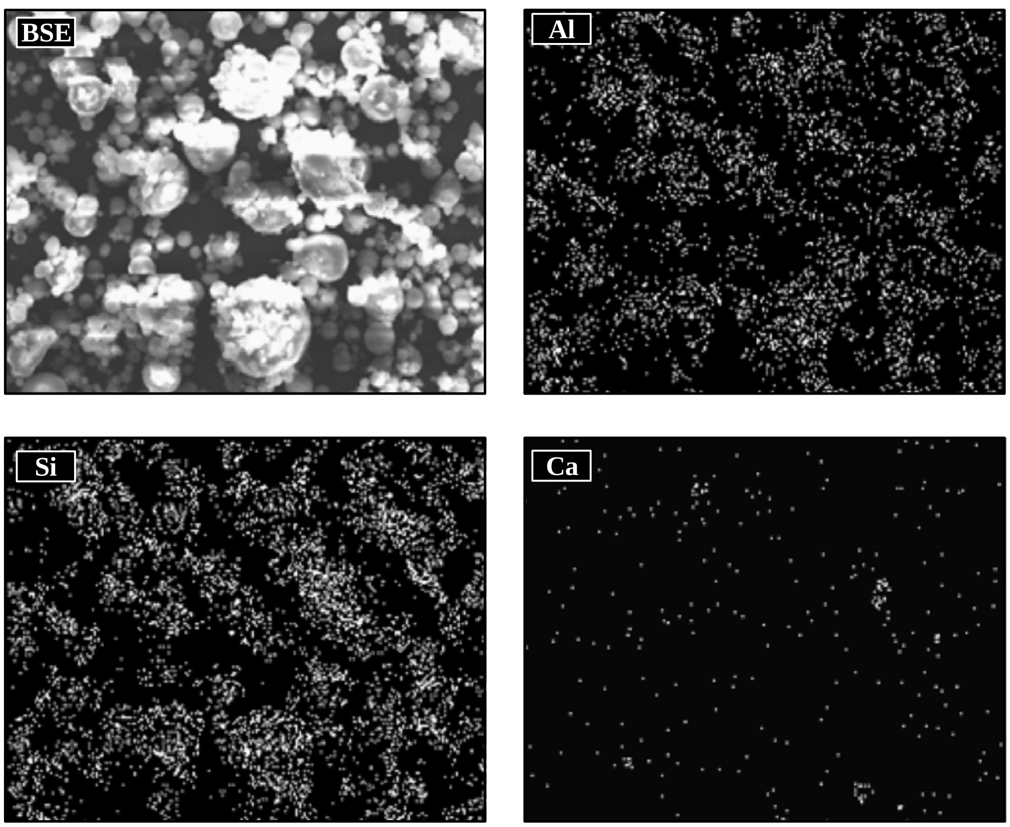

Fig. 3: Mapping of fly ash sample for Al, Si and Ca

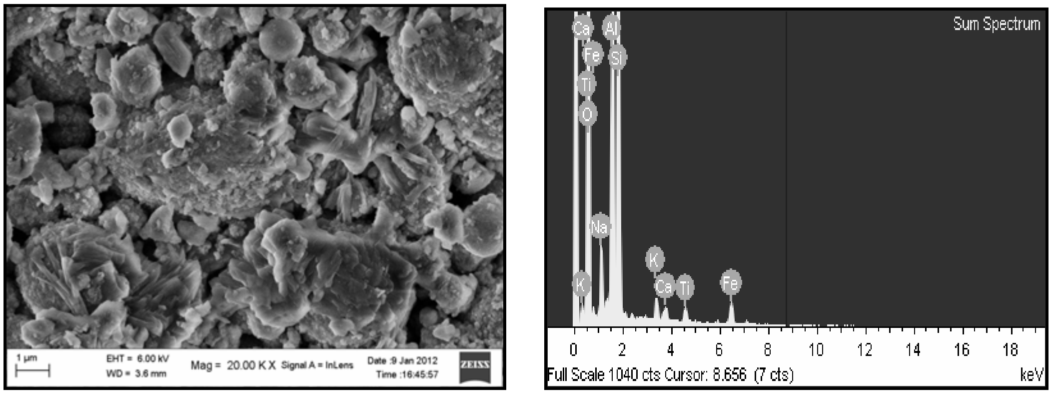

Fig. 4: SEM of fly ash geopolymer brick with $Na_2O/(Al_2O_3 + SiO_2)$ ratio 0.038

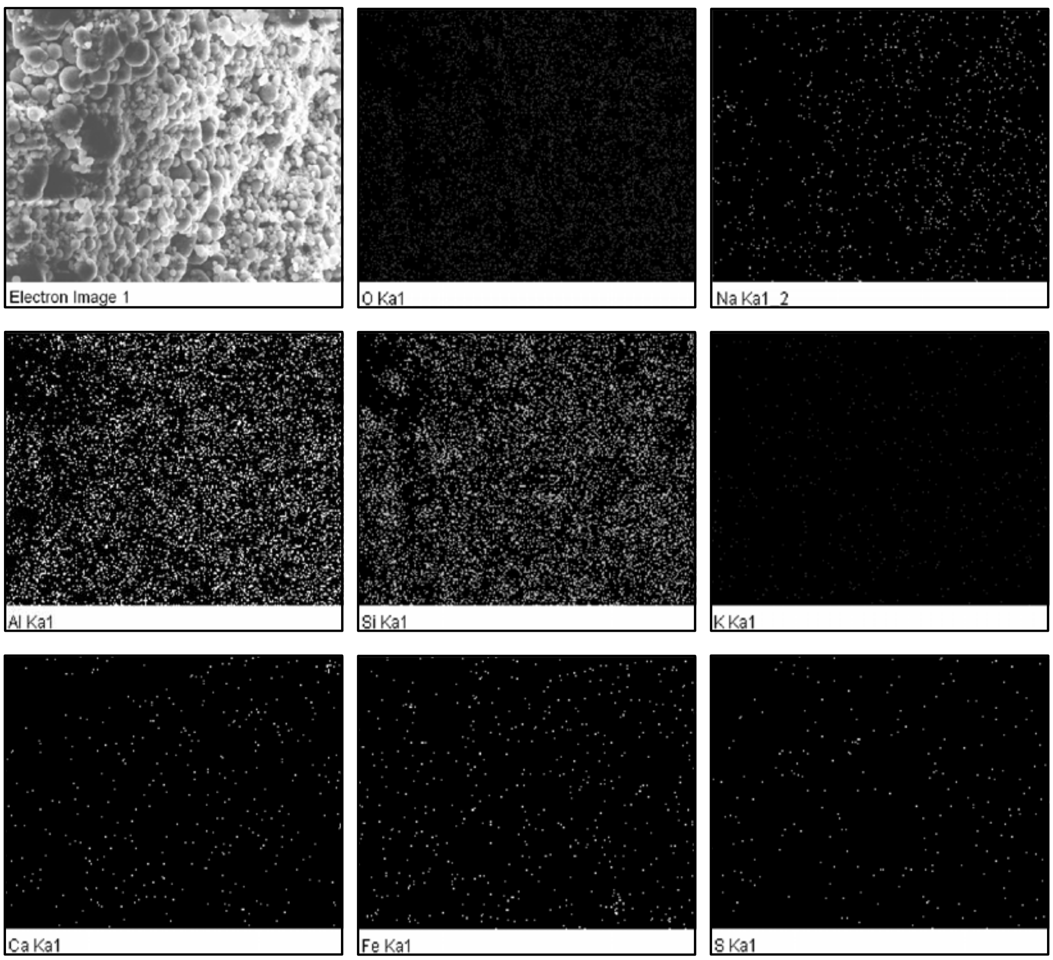

Fig. 5: Mapping of geopolymer fly ash sample for Al, Si and Ca, Fe, S, K and Na

The fly ash mix consisting of $Na_2O/(Al_2O_3 + SiO_2)$ ratio above 0.038 shows a remarkable increase in the strength under atmospheric curing. The geopolymer fly ash bricks manufactured with $Na_2O/(Al_2O_3 + SiO_2)$ ratio 0.078 are cured by exposing to the atmospheric temperature shows a high crushing strength (43 MPa), which mix design may be used for manufacture of concrete. It is observed that with the increase in alkaline activator and $Na_2O/(Al_2O_3 + SiO_2)$ ratio the strength of fly ash product gradually increases. The findings on development of strength indicates that alkaline activator consisting of anions of Cl^- and SO_4^{2-} is effective for geopolymer reaction under atmospheric temperature. The SO_4^{2-} 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[12,13]. The Cl^- ion acts as an accilator in gel formation and helps in crystallization[13,14]. In this process, the silica and alumina bearing minerals of fly ash react with the soluble alkalis at ambient temperature to form the geopolymer minerals in presence of anions of Cl^- and SO_4^{2-}. Chemical reactions between oxide phases of silica and alumina under alkaline condition form OH bearing sodium-aluminium-silicate structures, which on solidification develops the binding strength[11].

The dissolution of Al and Si from fly ash occurs in presence of sodium hydroxide, and also the optimum reaction takes place in presence of Cl^- and SO_4^{2-} ions in atmospheric temperature to form a compact and strong structure. Inter-coordination of the polymerized minerals helps in the build-up of the cementation property. Depending upon the binding strength the geopolymerisation process is flexible to make high strength building material under atmospheric curing.

ACKNOWLEDGEMENT

Authors are thankful to Dept. of Science and Technology, New Delhi for financial support and to the Director, CSIR-IMMT, Bhubaneswar for giving his kind consent and permission to publish this paper.

REFERENCES

1. J. Davidovits, 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, Davidovits J., Geopolymer Institute, Saint-Quentin, France, 9-12 (2005).

2. M. Stevenson and K. Sagoe-Crentsil, Relationship between Composition, Structure and Strength of Inorganic Polymers: Part 1 – Metakaolinderived Inorganic Polymers, J. Mater. Sci., **40**, 2023-2036 (2005).

3. D. Hardjito, S. E. Wallah, D. M. J. Sumajouw and B. V. Rangan, Brief Review of Development of Geopolymer Concrete, George Hoff Symposium, American Concrete Institute, Los Vegas, USA (2004a).

4. J. Davidovits, Geopolymer Chemistry & Applications, 2nd Ed., Chapters 15-16, Institute Ge´opolyme`re, Saint-Quentin (2008) pp. 333-365.

5. J. Davidovits, Chemistry of Geopolymeric Systems, Terminology, Geopolymer '99 International Conference, France (1999).

6. A. Palomo, M. W. Grutzeck and M. T. Blanco, Alkali-Activated Fly Ashes, A Cement for the Future, Cement and Concrete Research, **29(8)**, 1323-1329 (1999).

7. V. F. F. Barbosa, K. J. D. Mackenzie and C. Thaumaturgo, Synthesis and Characterization of Sodium Polysialate Inorganic Polymer Based on Alumina and Silica, in, Davidovits, J., Davidovits, R., James, C. (Eds.), Proceedings of the 2nd International Conference on Geopolymer '99, Saint Qunentin, France, June 30–July 2 (1999)pp. 65-78.

8. D. Hardjito and B. V. Rangan, Development and Properties of Low-calcium Fly Ash-based Geopolymer Concrete, Research Report GC1, Faculty of Engineering, Curtin University of Technology, Perth, Australia (2005).

9. J. G. S. Van Jaarsveld, J. S. J. Van Deventer and G. C. Lukey, The Effect of Composition and Temperature on the Properties of Fly Ash and Kaolinite-based Geopolymers, Chemical Engg. J., **89(1-3)**, 63-73 (2002).

10. B. D. Nayak, B. K. Mishra, S. Behera and V. Kumar, Composition for Building Material and a Process for the Preparation there of, Pub. No.: US 2009/0250660 A1 (2009).

11. S. D. Muduli, J. K. Sadangi, B. D. Nayak and B. K. Mishra, Effect of NaOH Concentration in Manufacture of Geopolymer Fly Ash Building Brick, Greener J. Phys. Sci., **3(6)**, 204-211 (2013).

12. L. Wang, Y. Shao, J. Zhang and M. Anpo, 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 (2006).

13. C. Desbats-Le Chequer and F. Frizon, Impact of Sulfate and Nitrate Incorporation on Potassium and Sodium-based Geopolymers, Geopolymerization and Materials Properties, J. Mater Sci., **46**, 5657-5664 (2011).

14. W. K. W. Lee and J. S. J. Van Deventer, Effects of Anions on the Formation of Aluminosilicate Gel in Geopolymers, Industrial and Engg. Chem. Res., **41(18)**, 4550-4558 (2002).

Accepted : 11.06.2014