

# Fly Ash Geopolymer Pastes in Sulphuric Acid

Suresh Thokchom

Email: thok\_s@rediffmail.com

**Abstract** – Results of an experimental investigation conducted to study the performance of fly ash based geopolymer paste specimens in sulphuric acid are presented. Class F fly ash was activated with a mixture of sodium hydroxide and sodium silicate solution containing Na<sub>2</sub>O in the range 5% to 8% of fly ash. Specimens were exposed to 10% sulphuric acid solution up to a period of 24 weeks. Performance of geopolymer paste specimens was evaluated in terms of visual appearance, residual alkalinity, changes in weight and compressive strength at regular intervals. There were no changes in colour and specimens maintained structural integrity. Surface corrosion was observed to increase with time of exposure. SEM micrographs showed deterioration of specimens due to acid attack. Formation of gypsum and ettringite was identified through X-ray diffractogram of exposed specimens. Loss of alkalinity was faster for geopolymer specimen having lesser Na<sub>2</sub>O content. Specimens revealed very low weight loss in the range of 0.52% to 1.43v%. However, residual compressive strengths were observed to be significantly low for the specimen with least Na<sub>2</sub>O content. Results obtained in the present study indicate that geopolymer manufactured with higher Na<sub>2</sub>O content perform much better on exposure to sulphuric acid.

**Keywords** – Fly Ash, Geopolymer, Residual Alkalinity, Compressive Strength, SEM/EDX, XRD.

## I. INTRODUCTION

Ordinary Portland Cement (OPC) continues to be the most commonly used binder in construction industries. However, its resistance to chemical attacks such as acids and sulphates are of concern. Cement composites gets severely damaged in acids due to dissolution of calcium hydroxide and decomposition of hydrated silicate and aluminium phases. In recent years, geopolymers have emerged as possible alternative to OPC binders due to their reported superior properties and environmental friendliness [1].

Geopolymers are novel binder manufactured by activating a source material rich in alumina and silica with a highly alkaline solution. Fly ash, silica fume, blast furnace slag and metakaolin are major source materials used for producing geopolymers. Since Geopolymers relies on alumina-silicate rather than calcium silicate hydrate bonds for structural integrity, they have been reported as being acid resistant. Davidovits [2] found that metakaolin based Geopolymer has very low mass loss in 5% sulphuric acid solutions. Bakharev [3] studied the resistance of geopolymer materials prepared from fly ash in 5% sulphuric acid up to 5 months exposure and concluded that geopolymer materials have better resistance than ordinary cement counterparts. Song et al [4] reported good durability of geopolymer concrete in a 10% sulphuric acid solution for 56 days. Fly ash based geopolymer composites possesses excellent long term

properties [5]. Durability of geopolymer materials in acid and sulphates have been also investigated by many authors [6-8]. Mechanisms of corrosion in low to high concentrations of acids are different [9-12]. Absence of standard methods to evaluate the performance of cements in acid environments has led to research in different exposure conditions and procedures by various authors making it difficult to correlate the results.

The objective of the present study is to assess the performance of fly ash based geopolymer pastes in sulphuric acid in an accelerated test condition. The study comprises determination of changes in weight, residual alkalinity, compressive strength and visual appearance as a measure of resistance against sulphuric acid. In addition, SEM/EDX and XRD has been extensively used to investigate the changes in microstructure and mineralogy of the exposed specimens.

## II. EXPERIMENTAL PROGRAM

### A. Materials and Preparation of specimens

Low calcium Class F fly ash used in the present experimental program was procured from Kolaghat Thermal Power Plant near Kolkata, India. It had chemical composition as given in Table-1. About 75% of particles were finer than 45 micron and Blaine's specific surface was 380m<sup>2</sup>/kg. Laboratory grade sodium hydroxide in pellet form (98 percent purity) and sodium silicate solution (Na<sub>2</sub>O= 8%, SiO<sub>2</sub> =26.5% and 65.5% water) with silicate modulus ~ 3.3 and a bulk density of 1410 kg/m<sup>3</sup> was supplied by LobaChemieLtd,India. For preparation of exposure solution, Sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) in liquid form (98% purity) was directly dissolved in water to make 10% sulphuric acid solution by weight.

The alkaline activating solution was prepared by dissolving required quantity of sodium hydroxide pellets directly into predetermined quantity of sodium silicate solution to make three solutions having Na<sub>2</sub>O content as 5%, 6.5% and 8% of fly ash. At the same time, water was added so as give water to fly ash ratio of 0.32. The activator solution was left at room temperature overnight before being used to manufacture geopolymer pastes. In a Hobart mixer, fly ash was mixed with measured quantity of activator solution for 5 minutes. The geopolymer mix exhibited a thick sticky nature with good workability. The mix was then transferred into 50 mm steel cube moulds and vibrated for 2 minutes. These were cured along with the moulds in an oven for a period of 48 hours at 85°C and allowed to cool inside the oven [16]. Specimens were then removed and stored at room temperature at a dry place before subjecting to various tests. The details of the samples used in the present study are given in the Table.2.

Table-1: Composition of Fly Ash (mass %)

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	SO <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	LOI*
56.01	29.8	3.58	1.75	2.36	0.30	0.73	0.61	Nil	0.44	0.40

### B. Test Procedure

Geopolymer paste specimens were exposed to 10 % sulphuric acid solution after 28 days from casting for a total period of 24 weeks. The ratio of volume of acid solution to volume of immersed specimens was taken as four which ensured the specimens to remain fully immersed in the solution. The solution was refreshed after 12 weeks while being stirred every week. The effects of sulphuric acid on the geopolymer paste specimen were constantly monitored through visual inspection, weight changes and strength tests after 1,3,6,12 and 24 weeks. For investigating the surface changes, specimens were taken out from the solution at regular intervals and observed

through an optical microscope. Specimens used for weight change measurements were initially primed in water for 3 days and its weight in saturated surface dry condition was taken as initial weight. These were washed in water using a soft brush after removal from the solution at predetermined intervals and its weight was determined in surface saturated condition. Mineralogical changes due to interaction of geopolymer paste with Sulphuric acid were determined using RigakuMiniflex XRD machine at scanning rate of 10 per minute with 2θ ranging from 50 to 650. SEM analysis utilized JEOL JSM 6360 equipped with Inca Oxford EDX analyzer to examine changes in microstructure as well as for micro-analysis of specimens.

Table 2: Mix proportion of geopolymer pastes

Sample ID	Na <sub>2</sub> O percent	Water/Fly ash ratio	Curing temp. and Duration	28 day Compressive Strength(MPa)
GP1	5.0%	0.32	85 <sup>0</sup> C & 48 hrs	19.47
GP2	6.5%	0.32	85 <sup>0</sup> C & 48 hrs	30.53
GP3	8.0%	0.32	85 <sup>0</sup> C & 48 hrs	34.93

## III. RESULTS AND DISCUSSIONS

### A. Visual Appearance

Fly ash based geopolymer paste specimens showed no change in colour and remained structurally intact without any signs of disintegration. With time, the exposed surfaces became a little softer. Deterioration of surfaces due to acid attack were observed under Optical microscope, some of which are shown in Fig. 1. Surface corrosion increased with time though magnitude of deterioration among the three series of samples could not be easily differentiated. However, it appeared that GP1 specimen having least Na<sub>2</sub>O content of 5% has most corrosion while GP3 specimen having maximum Na<sub>2</sub>O content (8%) had the least surface corrosion. Higher Na<sub>2</sub>O content in the activator solution helps in better formation of geopolymer gel thereby reducing the porosity. The lesser porosity for GP3 specimen is the reason for its lesser surface corrosion due to sulphuric acid. However, continuous action of sulphuric acid increases the corrosion with time.

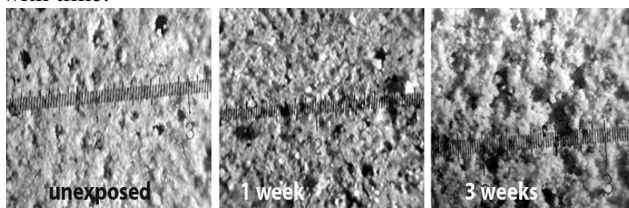


Fig.1. Surface changes of GP3 specimen

### B. Residual Alkalinity

After removal from sulphuric acid solution, specimens were cut into halves using an electrically operated concrete cutter and 1% phenolphthalein solution is sprayed

on the freshly cut surface to study the residual alkalinity and depth of dealcalization. On spraying with phenolphthalein solution, regions still unaffected by acids show a magenta colour whereas dealcalized region indicate colourless. Figure 2 presents a group of paste specimens tested for residual alkalinity after 3 weeks of exposure. GP1 specimens exhibit almost no traces of magenta colour which shows that the specimen is mostly dealcalized. On the other hand, GP2 specimens reveal clearer region having magenta colour which signify higher residual alkalinity. However, GP3 specimen shows a distinct region which looks quite different from the rest. This region is still unaffected by acid and continues maintaining the alkalinity. The depth of dealcalization as measured perpendicularly from the surface towards the inside present significantly different values for the paste specimens containing varying Na<sub>2</sub>O. The complete dealcalization took 6 weeks for GP1 specimens whereas GP2 specimen almost lost its alkalinity by 9 weeks. However, GP3 specimen showed complete dealcalization at 12 weeks. It may be noted herethat process of dealcalization begin from the surface and proceed inwards with time. Specimens having higher Na<sub>2</sub>O contents took longer time for complete dealcalization. This is due to the improved pore structure in the specimens prepared with higher Na<sub>2</sub>O content.

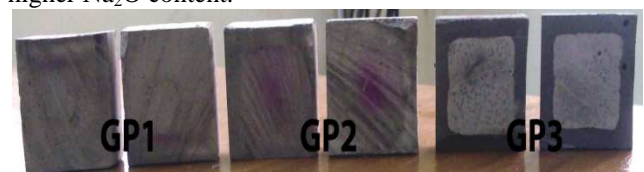


Fig.2. Residual alkalinity test on specimens after 3weeks exposure

### C. Change in Weight

Weight changes for specimens exposed to 10% sulphuric acid are shown in Figure 3. After 3 weeks, a sudden decrease in weight is noticed in all the specimens. The sudden loss of weight could be due to high rate of migration of alkali from the specimen into the solution in addition to dissolution of some material. It may be noted that, specimens having higher Na<sub>2</sub>O content loses more alkalis into the specimen. However, increase in weight occurred beyond 3 weeks up to 12 weeks. As the acid solution continues to enter and form reaction products, increase in weight takes place. After 12 weeks, further exposure caused decrease in weight of the specimens. This indicates that at later stages, the reaction process involving geopolymer material and sulphuric acid has subsided though dissolution continued. For paste specimens, the weight loss determined after 3 weeks are found to be 1.44%, 1.67% and 2.19% for GP1, GP2 and GP3 respectively. Loss of weight has been observed to be more for specimens with higher Na<sub>2</sub>O content. After 24 weeks in 10% sulphuric acid, the paste specimens showed weight losses of 0.52%, 1.29% and 1.43% for GP1, GP2 and GP3 specimens.

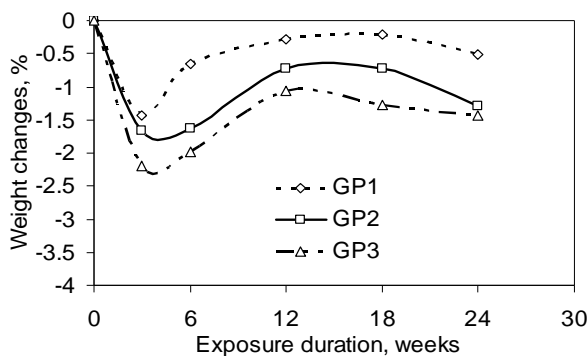


Fig.2. Evolution of Weight of geopolymer specimens

### D. Residual Compressive strength

28 days compressive strengths were found to be 19.47 MPa, 30.53 MPa and 34.93 MPa respectively for GP1, GP2 and GP3 specimens. During exposure to 10% sulphuric acid, residual strength of specimens were determined after predetermined intervals. After removing from solution, the specimens were dried in ambient conditions for 2 days before subjecting to compression tests. Residual compressive strength has been calculated on the basis of the 28 days compressive strength of unexposed specimens. Figure 4 shows the variation of residual strength with time for the geopolymer pastes. Fly ash based geopolymer paste specimens shows loss in strength with time when exposed to sulphuric acid. It is also noticed that the trend of variation of residual strength for different specimens are almost similar. GP1 specimen exhibit rapid loss of strength after 1 week of exposure, whereas GP2 and GP3 specimen reveal gradual loss of strength. After 1 week of exposure, GP1 specimen recorded a low residual strength of 47.92%. At the same level of exposure, GP2 and GP3 specimens maintained a residual strength of 87.78% and 95.51% respectively.

After 24 weeks exposure, GP1, GP2 and GP3 specimens yielded residual strengths of 23.64%, 38.88% and 51.53% respectively. This corresponds to strength losses of 72.36%, 61.12% and 48.47% for GP1, GP2 and GP3 specimens. The better performance for specimens with higher Na<sub>2</sub>O content can be attributed to their better microstructure.

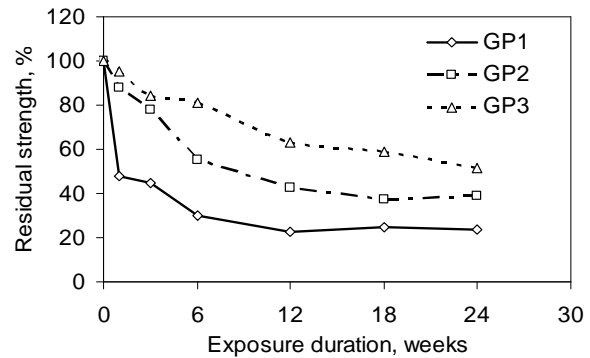


Fig.4. Residual compressive strength of geopolymer specimens

### E. SEM/EDX Analysis

Samples for scanning electron microscopy (SEM) were taken from the surface, both for unexposed and exposed specimens. SEM micrographs of specimens before exposure to sulphuric acid solution are shown in Figure 5. In all the specimens, SEM images show a relatively amorphous microstructure with some crystalline phase. Many unreacted fly ash particles are observed in the SEM micrograph of GP1 specimen, thereby depicting a highly porous microstructure with large pores. However, better and uniform microstructures are noticed in the micrographs of GP2 and GP3 specimens. The low Na<sub>2</sub>O content is the reason for such a poor microstructure in GP1 specimen. In comparison, GP2 specimens reveal an improved microstructure due to formation of more gel. Elongated tubular structures dominate the microstructure of unexposed GP3 specimen. In both GP2 and GP3 specimen, significant improvements in pore characteristics can be observed with regard to pore size and volume. Energy dispersive X-ray (EDX) analysis of specimens indicate the presence of elements such as silicon (Si), aluminium (Al), oxygen (O), calcium (Ca), and sodium (Na) among a few minor elements. Si/Al ratio (at. %) in the three specimens obtained from EDX micro-analysis ranged from 1.39 to 2.57.

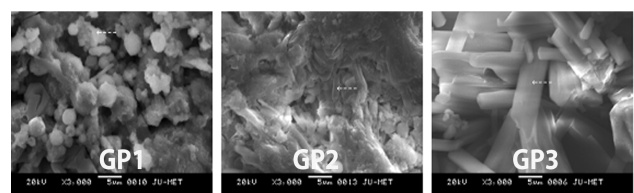


Fig.5. SEM micrographs of specimens before exposure

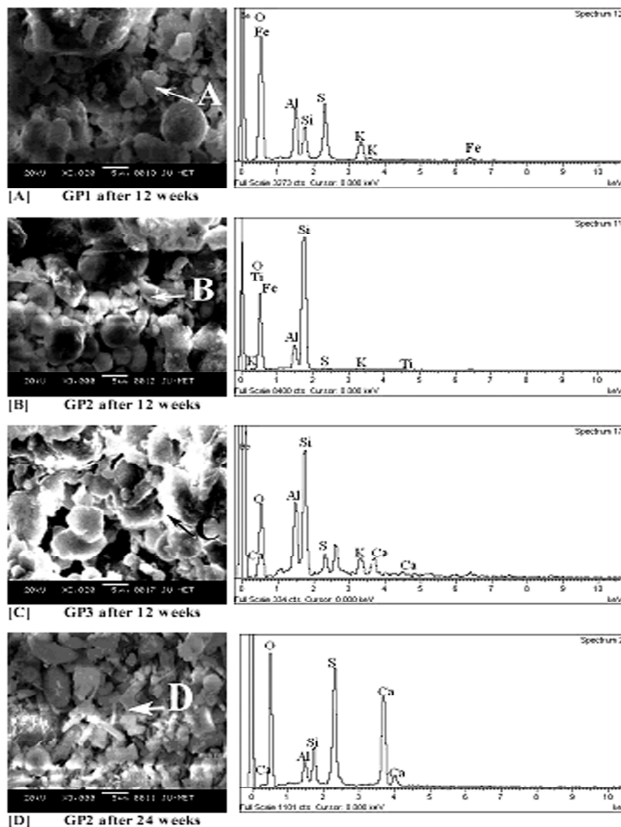


Fig.6. SEM/EDX for exposed geopolymer paste specimens

SEM micrographs and EDX spectra of paste specimens after 12 weeks and 24 weeks in 10% sulphuric acid solution are given in Figure 6 which shows occurrence of precipitates in the specimens irrespective of the Na<sub>2</sub>O content. Major elements detected from EDX microanalysis are Si, Al and oxygen. Fe, Ti and S have also been detected in some spectra. However, in the micrograph of GP2 specimen after 24 weeks of exposure, some elongated formations are observed. Such formations have also been reported by few authors [12, 17]. EDX spectra at spot D shows a high content of sulphur, oxygen and calcium. The weight (%) determined from EDX microanalysis gave values of 13.44%, 64.91% and 15.57% for S, O and Ca respectively. This indicates formation of gypsum (CaSO<sub>4</sub>). Si/Al ratios for exposed specimens increased remarkably in most cases. The increase in Si/Al ratio is due to dealumination of geopolymer framework while Si remains unaffected by action of sulphuric acid.

#### F. Mineralogical investigation with XRD

Figure 7 presents XRD traces of GP2 specimens before exposure and after regular intervals of exposure. Unexposed specimen indicates presence of some crystalline components such as mullite, quartz, hematite etc., and gismondine zeolites. Amorphous phases characterized by the broad hump between  $2\theta=20-30^\circ$  can also be seen. After 1 week of exposure in 10% Sulphuric acid solution, the diffractogram does not show significant changes when compared to that unexposed specimen. However, few minor peaks associated with

gypsum and ettringite are noticed. In the diffractogram of specimen after 6 weeks of exposure, some changes are observed. The peaks of gypsum and ettringite remain unaffected. Compared to the diffractogram of specimen after 1 week exposure, minor changes has taken place in the regions  $2\theta=20-30^\circ$ ,  $2\theta=40-50^\circ$  and  $2\theta=50-60^\circ$ . Even after 12 weeks of exposure, the peaks of mullite, quartz, hematite and gismondine continue to remain though slightly less prominent. Overall, the diffractogram shows a marginally flattened trace along with reduced peaks which indicates lesser intensity. Compared to the XRD traces of unexposed specimen, there are significant changes in most of the regions. It can be concluded that exposure to sulphuric acid causes formation of gypsum and ettringite phases while crystalline phases are least affected.

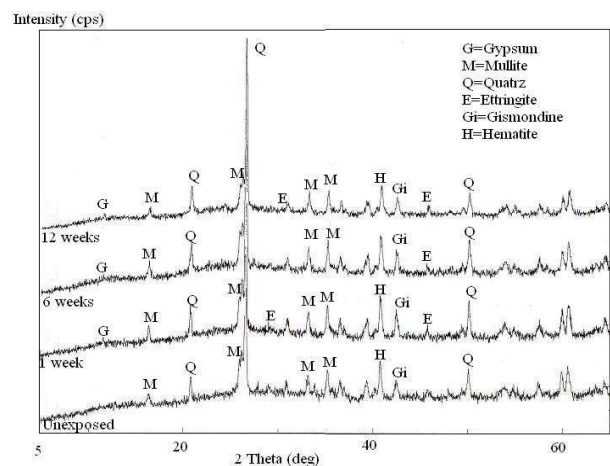


Fig.7. XRD traces for unexposed and exposed GP2 specimen

## IV. CONCLUSION

Based on the results obtained from the study, following conclusion can be drawn:

1. Compressive strength of fly ash geopolymers increases with Na<sub>2</sub>O content.
2. Geopolymer pastes manufactured with higher Na<sub>2</sub>O content exhibit better microstructure with lesser pores.
3. Even after 24 weeks in strong sulphuric acid solution, geopolymer specimens maintained structural integrity, though some corrosion occurred on the surfaces.
4. Residual alkalinity of geopolymer specimens was observed to be more for specimens made with higher Na<sub>2</sub>O content.
5. Weight losses of specimens on exposure to 10% sulphuric acid solution are very low.
6. Geopolymer specimens with higher Na<sub>2</sub>O content recorded higher residual strength indicating better performance.
7. Formation of gypsum due to sulphuric acid attack is evident from EDX spectra and XRD traces.

## REFERENCES

- [1] A Palomo, M.W Grutzeck, M.T Blanco, “Alkali activated fly ashes a cement for the future”, Cement and Concrete Research, vol.29, 1999, pp.1323– 1329.
- [2] J Davidovits, “Properties of geopolymer cements”, Proceedings of the First International conference on Alkaline Cements and Concretes, Vol. 1, SRIBM, Kiev, Ukraine, 1994, pp. -131 -149.
- [3] T Bakharev, “Resistance of geopolymer materials to acid attack”, Cement and Concrete Research. Vol.35, 2005 pp.658 – 670.
- [4] X.J Song, M Marosszeky, M Brungs, R Munn, “Durability of fly ash based Geopolymer concrete against sulphuric acid attack”, 10 DBMC International Conference on Durability of Building Materials and Components, Lyon, France, 17- 20 April 2005.
- [5] S.E Wallah, B.V Rangan, “Low Calcium Fly ash based Geopolymer Concrete : Long term properties, Research report GC 2”, 2006, Curtin University of Technology, Australia.
- [6] A Fernandez-Jimenez, I Garcia-Lodeiro, A Palomo, “Durability of alkali activated fly ash cementitious materials,” J. Mater Sci vol. 42, 2007, pp. 3055-3065.
- [7] T Bakharev, “Durability of geopolymer materials in sodium and magnesium sulphate solutions,” Cement and Concrete Research vol. 35, 2005, pp.1233-1246.
- [8] S Thokchom, P Ghosh, S Ghosh, “Performance of Fly ash Based Geopolymer Mortars in Sulphate Solution,” Journal of Engineering Science and Technology Review vol. 3 (1), 2010, pp.36-40.
- [9] S Thokchom, P Ghosh, S Ghosh, “Resistance of fly ash based geopolymer mortars in sulphuric acid,” ARPN Journal of Engineering and Applied Sciences vol. 4(1), 2009, pp. 65-70.
- [10] S Thokchom, P Ghosh, S Ghosh, “Durability of Fly Ash Geopolymer Mortars in Nitric Acid—effect of Alkali (Na<sub>2</sub>O) Content”, Journal of Civil Engineering and Management, vol. 17(3), 2011, pp. 393-399.
- [11] S Thokchom, P Ghosh, S Ghosh, “Effect of Na<sub>2</sub>O content on Durability of Geopolymer pastes in Magnesium sulfate solution”, Canadian Journal of Civil Engineering, vol. 39, 2012, pp. 1-10.
- [12] A Allahverdi, F Skvara, “Sulfuric acid attack on hardened paste of Geopolymer cements, Part 1. Mechanism of corrosion at relatively high Concentrations”, Ceramics – Silikaty vol. 45 (3), 2001, pp.81 – 88.
- [13] A Allahverdi, F Skvara, “Sulfuric acid attack on hardened paste of Geopolymer cements, Part 2. Corrosion mechanism at mild and relatively low concentrations”, Ceramics–Silikaty vol. 50 (1), 2006, pp.1 – 4.
- [14] A Allahverdi, F Skvara, “Nitric acid attack on hardened paste of Geopolymer cements, Part 1. Corrosion mechanism at mild and relatively low concentrations”, Ceramics–Silikaty vol. 45 (3), 2001, pp.81-88.
- [15] A Allahverdi, F Skvara, “Nitric acid attack on hardened paste of Geopolymer cements, Part 2”.Ceramics–Silikaty vol. 45 (4), 2001, pp.143-149.
- [16] R Thakur, S Ghosh, “Fly ash based Geopolymer composites”, Proceedings of 10<sup>th</sup> NCB International seminar on cement and building materials, NEW Delhi, India, Vol.3, Nov,2007,pp.442 - 451.
- [17] F Rendell, R Jauberthie, “The deterioration of mortar in sulphate environments” Construction and building materials, vol. 13(6), 1999, pp. 321-327.

## AUTHOR'S PROFILE



### Dr. Suresh Thokchom

was born at Imphal, Manipur in 1966. He obtained his B.E (Civil Engineering) from KREC, Surathkal, M.E (Structural Engineering) from University of Roorkee and Ph.D from Jadavpur University, Kolkata.

He has over 25 years of experience in teaching and research. He has published more than 18 papers in international journals and conferences including a book. Presently, he is serving as Associate professor in the Department of Civil Engineering, Manipur Institute of Technology, a constituent college of Manipur University, Imphal. Dr. Thokchom is a member of ICI, ACI (India Section), ASCE (India), and ISCMS.