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Effect of Na_2O Content on Durability of Geopolymer Mortars in Sulphuric Acid

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***Abstract*—**This paper presents the findings of an experimental investigation to study the effect of alkali content in geopolymer mortar specimens exposed to sulphuric acid. Geopolymer mortar specimens were manufactured from Class F fly ash by activation with a mixture of sodium hydroxide and sodium silicate solution containing 5% to 8% Na_2O. Durability of specimens were assessed by immersing them in 10% sulphuric acid solution and periodically monitoring surface deterioration and depth of dealkalization, changes in weight and residual compressive strength over a period of 24 weeks. Microstructural changes in the specimens were studied with Scanning electron microscopy (SEM) and EDAX. Alkali content in the activator solution significantly affects the durability of fly ash based geopolymer mortars in sulphuric acid. Specimens manufactured with higher alkali content performed better than those manufactured with lower alkali content. After 24 weeks in sulphuric acid, specimen with 8% alkali still recorded a residual strength as high as 55%.

***Keywords*—**Alkali content, acid attack, compressive strength, geopolymer

I. Introduction

BESIDES good strength, durability is an important property of construction materials. Though Ordinary Portland cement (OPC) possesses good strength, its performance is doubtful in conditions of extreme exposure. Literatures abound in study of durability of ordinary Portland cements which invariably reports about its poor performance with regard to acid attack, sulphate attack and also to high temperatures. In case of acid attack, it gets severely damaged due to dissolution of calcium hydroxide and decomposition of hydrated silicate and aluminium phases. Many attempts had been made to improve the performance of ordinary Portland cement by incorporating different admixtures like fly ash and silica fume and have been reported to be advantageous.

Ever since the introduction of geopolymer binders by Davidovits in 1978, it has generated a lot of interest among engineers as well as in the field of chemistry. In the past few decades, it has emerged as one of the possible alternative to OPC binders due to their reported high early strength and resistance against acid and sulfate attack apart from its environmental friendliness.

Though geopolymers can be manufactured from various source materials rich in silica and alumina such as fly ash, silica fume, ground granulated blast furnace slag and metakaolin etc, fly ash based geopolymers have attracted more attention. Geopolymer binders might be a promising alternative in the development of acid resistant concrete since it relies on alumina-silicate rather than calcium silicate hydrate bonds for structural integrity. Davidovits [1] found that geopolymer cements has very low mass loss of 5%-8% when samples were immersed in 5% sulphuric acid and hydrochloric acid solutions. In contrast, Portland cements were completely destroyed in the same environment. Bakharev [2] studied the resistance of geopolymer materials prepared from fly ash against 5% sulfuric acid up to 5 months exposure and concluded that geopolymer materials have better resistance than ordinary cement counterparts. In an accelerated test to assess the durability of geopolymer concrete in a 10% sulfuric acid solution for 56 days, Song et al. [3] noticed the superior performance of fly ash based geopolymer concrete over ordinary Portland cement concrete. Wallah and Rangan [4] have shown that geopolymer composites possesses excellent durability properties in a study conducted to evaluate the long term properties of fly ash based geopolymers. In more recent publications on performance of fly ash based geopolymer mortars, it was confirmed that geopolymer has a very good resistance in acid media in terms of weight loss and residual compressive strength [5], [6]. The mechanism of corrosion of hardened geopolymer pastes manufactured from fly ash in sulphuric acid ranging from low to high concentration was investigated and found to behave differently in different concentrations [7],[8]. The same authors also carried out a similar study by immersing the geopolymer pastes in nitric acid and reported that corrosion by nitric acid starts by leaching of soluble contents of the material [9],[10]. The absence of standard methods to evaluate the performance of cements in acid environments has made it difficult to correlate the results of different authors..

The present experimental program was aimed to study the effect of alkali content (%Na_2O) of fly ash based geopolymer mortar specimens against exposure to high concentration of sulphuric acid. Geopolymer mortar manufactured with varying contents of alkali were immersed in sulphuric acid solution and its performance studied on the basis of change in surface characteristics, changes in weight, compressive strength and changes in microstructure through SEM and EDAX. The findings of the present study could help in deciding the

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suitability of geopolymer materials in sulphuric acid environments.

II. Experimental

A. Materials

Low Calcium Class F fly ash used in the present experimental program was obtained from Kolaghat Thermal Power Plant near Kolkata, India. It had a chemical composition as in Table-1. About 75% of particles were finer than 45 micron and Blaine's specific surface was 380 m^2/kg. Fine sand was local river sand having specific gravity of 2.5 and fineness modulus of 2.65. Laboratory grade sodium hydroxide in pellet form with 98 % purity and Sodium Silicate solution (Na_2O= 8%, SiO_2 =26.5% and 65.5% water) with silicate modulus ~ 3.3 and a bulk density of 1410kg/m^3 was supplied by Loba Chemie Ltd. The alkaline activating solution was a mixture of Sodium hydroxide and Sodium silicate solution having Na_2O in the mix as 5% to 8% of fly ash. Extra water was added in the activator solution so as to result a water to fly ash ratio of 0.33.

TABLE I: CHEMICAL COMPOSITION OF FLY ASH

Chemical composition	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	SO_3	P_2O_5	LOI*
Percentage	56.01	29.8	3.58	1.75	2.36	0.30	0.73	0.61	Nil	0.44	0.40

*Loss on ignition

A. Specimen preparation

The geopolymer mortar samples were prepared taking equal proportions of fly ash and sand. The mixing procedure and curing regime adopted was after Thakur and Ghosh [11].Fly ash was first mixed with the activator solution in a Hobart mixer for 5 minutes. The mix exhibited a thick sticky nature with good workability. Sand was then gradually introduced and further mixed for another 5 minutes. The mix was then transferred into 50 mm cube moulds and vibrated on a vibrating table for 2 minutes. Specimens were cured along with the moulds in an oven for a period of 48 hours at 85^oC and allowed to cool inside the oven before being removed and stored to room temperature until tested. The details of the samples used in the present study are given in the Table.2.

TABLE II: DETAILS OF GEOPOLYMER MORTAR SPECIMENS

Sample	Na_2O, percent	Water/Fly ash	Curing temp &Duration	28 day compressive strength (MPa)
1	5.0%	0.33	85^{0}C&48 hrs	22
2	6.5%	0.33	85^{0}C&48 hrs	37
3	8.0%	0.33	85^{0}C&48 hrs	40

B. Test Procedure

To study the performance of geopolymer mortar samples in sulphuric acid, specimens were soaked in 10 % sulphuric acid solution after 28 days of manufacture. The specimens were kept fully immersed in the acid solution having total volume as four times the volume of specimens for a duration of 24 weeks. The effects of sulphuric acid on the geopolymer mortar specimen were regularly monitored through visual inspection, measurement of weight changes and strength tests. An optical microscope was used to study the surface deterioration of specimens at predetermined intervals. Depth of dealkalization of specimen was roughly found out by spraying a 1% phenolphthalein solution on the freshly cut surface after removal from the acid solution. Samples for weight change test were primed in water for 3 days prior to immersion in sulphuric acid solution and its saturated surface dry weight considered as initial weight. These samples were removed from the solution and weighed at various stages of exposure in similar conditions as the initial weight. Samples for determining residual strength were stored in room temperature for 3 days before crushing for compressive strength.

Microstructure changes due to acid attack were examined after 12 weeks of exposure with the help of JSM-6360 Scanning Electron Microscope fitted with Inca Oxford EDAX analyzer.

III. Results And discussion

A. Surface deterioration and depth of dealkalization

Continuous exposure of fly ash based geopolymer mortar specimens in sulphuric acid solution did not show any visible structural disintegration. Though significant deterioration of specimen surface could not be observed with naked eyes, the same was clearly seen through an optical microscope as given in Fig.1 and Fig.2. Before exposure to acid solution specimens possessed a fairly smooth surface with some pores distributed all over. As the acid solution starts attacking the specimen, deterioration of the surfaces begins which appeared to be predominant in the specimen manufactured with lowest alkali content of 5%. Specimen prepared with 8% alkali showed

minimum deterioration which suggests its better resistance against sulphuric acid. Throughout the duration of exposure specimens were removed periodically and checked for depth of dealkalization. Specimen was cut across through the middle and phenolphthalein solution was sprayed on it. The region still unaffected by the acid shows pink colour whereas dealkalized region was colourless. Depth of dealkalization was measured as the depth of the colourless portion from surface towards the middle. A typical sample tested is presented in Fig. 3. The depth of attack increased with time and rate of attack was faster in specimen containing lesser alkali. Within 12 weeks specimens of both 5% and 6.5% Na_2O were fully dealkalized; however specimen manufactured with 8% Na_2O took 18 weeks to do so. Hence with regard to surface deterioration and depth of dealkalization, specimen of 8% Na_2O had the best performance and those with 5% showed least performance.

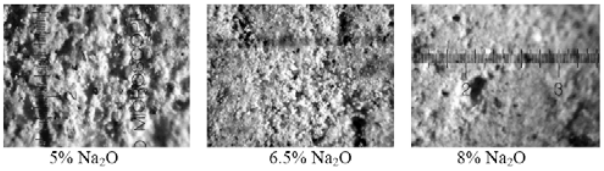

Fig. 1 Surface appearance of geopolymer mortars after 3 weeks in 10% sulphuric acid solution

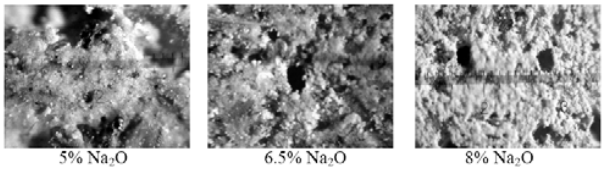

Fig. 2 Surface appearance of geopolymer mortars after 12 weeks in 10% sulphuric acid solution

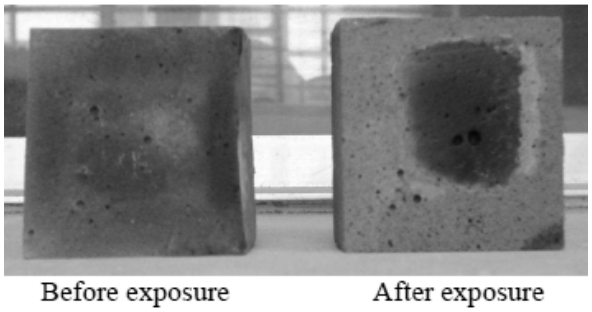

Fig. 3 A sample tested for depth of dealkalization by phenolphthalein method

. *B Change in Weight*

The weight changes of geopolymer mortar specimens at different exposure durations are related to %Na_2O content in Fig. 4. All the specimens recorded loss in weight over the entire duration of exposure. There was a sudden decrease in weight at 3 weeks for all the specimens and thereafter a gradual gain of weight was noticed up to 12 weeks. At 24 weeks the loss in weight was greater for specimen with 8% Na_2O and minimum for 5% Na_2O. The loss of weight was observed to be lower in geopolymer mortar specimen manufactured with lesser alkali content (5% Na_2O) than those manufactured with 6.5% Na_2O and 8% Na_2O. When specimen of 5% alkali recorded loss of weight as 0.91%, the corresponding loss for specimens of 6.5% alkali and 8% alkali for the same duration of exposure was found to be 1.31% and 1.64% respectively.

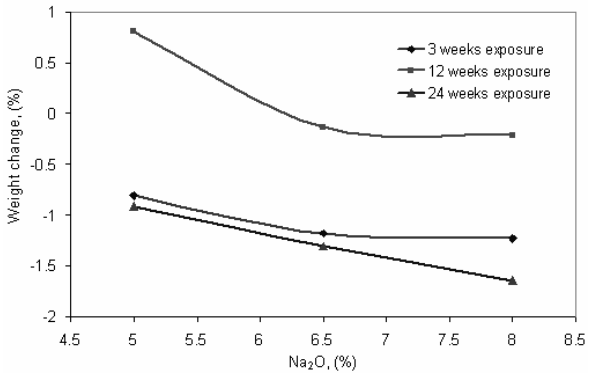

Fig. 4 Variation of weight with % Na_2O

C. Residual compressive strength

Figure 5 represents the variation of residual compressive strength with % Na_2O at various exposure durations for geopolymer mortar specimens in 10% sulphuric acid solution. Throughout the test duration, specimens yielded lower residual strength and exhibited quite a lot of variation among the three of them. Geopolymer mortar specimen prepared by activation with 5% alkali was most affected in sulphuric acid with a residual compressive strength of 29.4% after 24 weeks. The same specimen had retained strength of 57.07% and 48.7% at 3 weeks and 12 weeks respectively. In contrast, geopolymer mortar specimens manufactured with 6.5% Na_2O and 8% Na_2O showed relatively better resistance against degradation of strength in sulphuric acid recording a residual strength of 42.9% and 54.8% respectively after 24 weeks. It is clear that specimen with higher alkali content perform better in sulphuric acid environment.

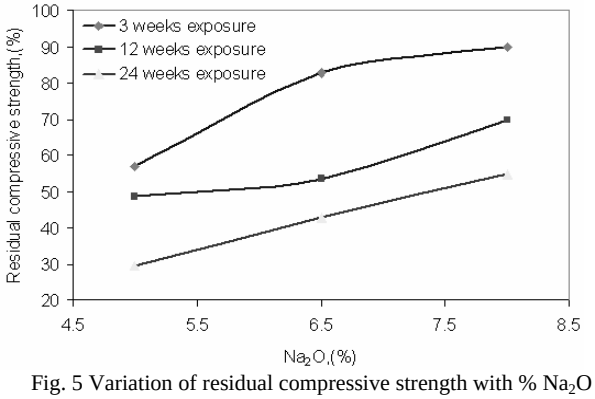

Fig. 5 Variation of residual compressive strength with % Na_2O

D. Scanning electron microscopy (SEM) and EDAX

Samples for scanning electron microscopy (SEM) and EDAX analysis was taken from near the surface of specimen. SEM micrographs with accompanying EDAX spectrum are shown in Fig. 6 to Fig. 10. Fig. 6 and Fig. 7 give the microstructure of unexposed geopolymer mortar specimen for 5% Na_2O and 6.5% Na_2O along with EDAX spectrum at selected spots. In the micrograph of specimen activated with 5% Na_2O, unreacted fly ash particles could be noticed rendering it a comparatively amorphous and less denser microstructure than the one activated with 6.5% Na_2O (Fig.7) where it reveals far denser microstructure. This shows the effect of alkali content in microstructure of fly ash based geopolymer mortars. EDAX spectrum of the spot indicated with the arrow in the micrograph of specimen with 5% Na_2O revealed presence of Si, Al, Ti and O as the main elements. After 12 weeks in sulphuric acid solution specimens appeared to have deteriorated by the acid attack and at the same time EDAX spectrum also showed a change in the presence of elemental traces. In the SEM micrograph of specimen with 5% Na_2O, along with spherical shaped un-reacted fly ash particles, it showed presence of light precipitates which might be a product of degradation. Though specimen prepared with activator containing 8% Na_2O looked relatively denser than those with 5% Na_2O and 6.5% Na_2O, presence of light precipitates appeared in the SEM micrograph (Fig.10) just as in the case of the other two specimens. A notable change was observed in specimen of geopolymer mortar specimen manufactured with 6.5% Na_2O.It revealed presence of elongated crystalline structures which could be gypsum as indicated by EDAX spectrum which shows traces of Ca, S and O among others. Rendell and Jauberthie [12] also reported such similar formations and concluded that these new substances are gypsum. A noticeable difference was the degree of deterioration among the three specimens manufactured with varying alkali content. Geopolymer mortar specimen with least alkali suffered most which could be readily observed from the SEM micrographs taken after 12 weeks of exposure.

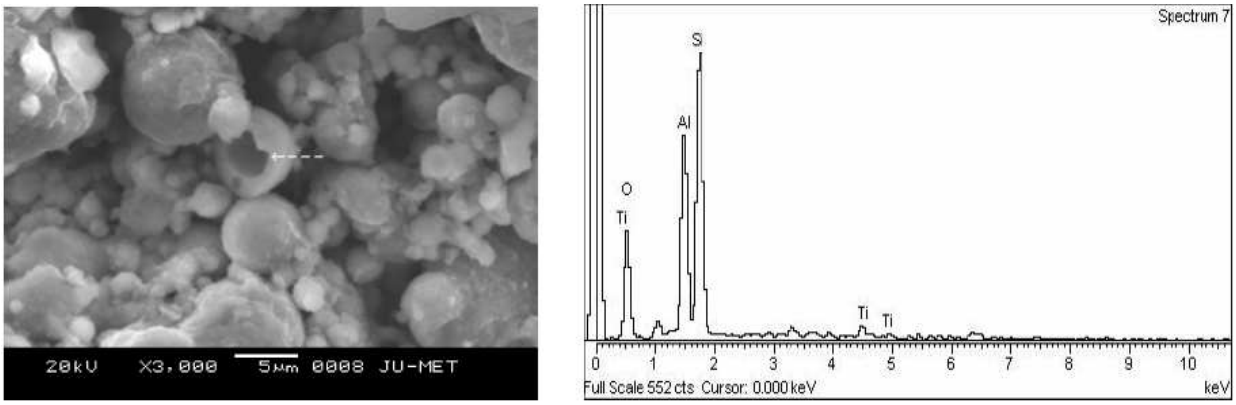

Fig. 6 SEM image of geopolymer mortar with 5% Na_2O and EDAX spectrum at the arrow point before exposure

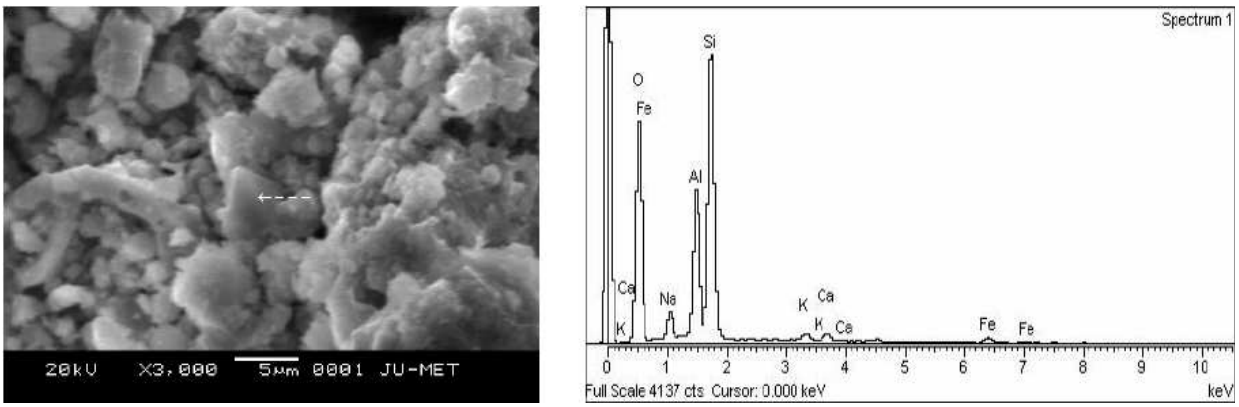

Fig. 7 SEM image of geopolymer mortar with 6.5% Na_2O and EDAX spectrum at the arrow point before exposure

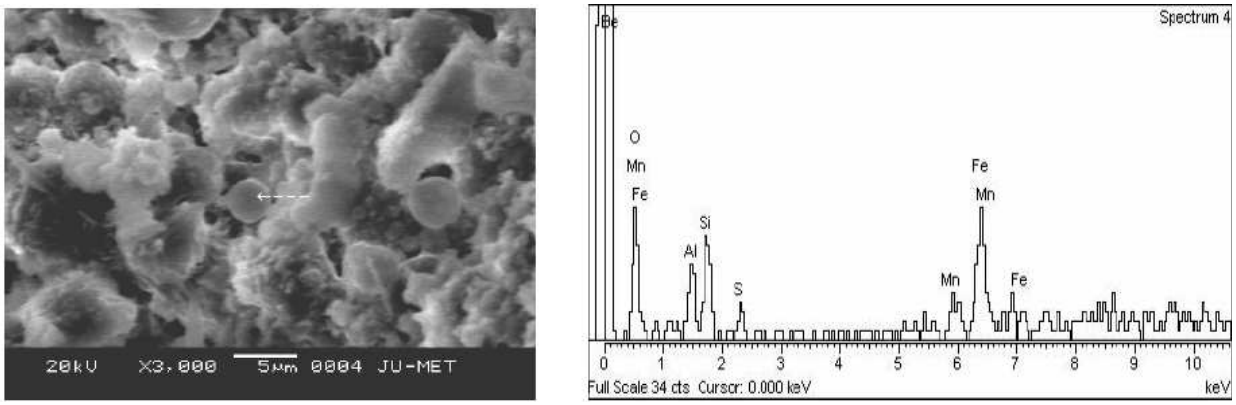

Fig. 8 SEM image of geopolymer mortar with 5% Na_2O and EDAX spectrum at the arrow point after 12 weeks in 10% sulphuric acid

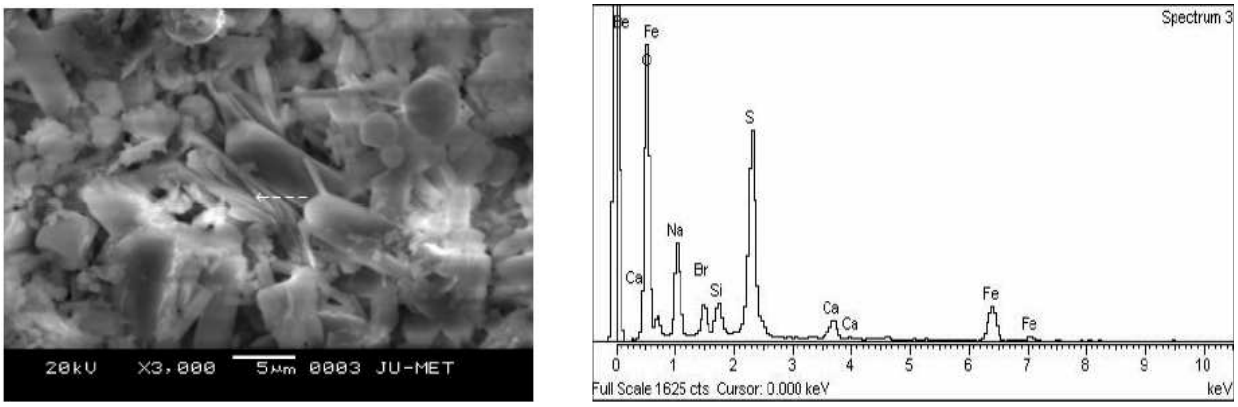

Fig. 9 SEM image of geopolymer mortar with 6.5% Na_2O and EDAX spectrum at the arrow point after 12 weeks in 10% sulphuric acid

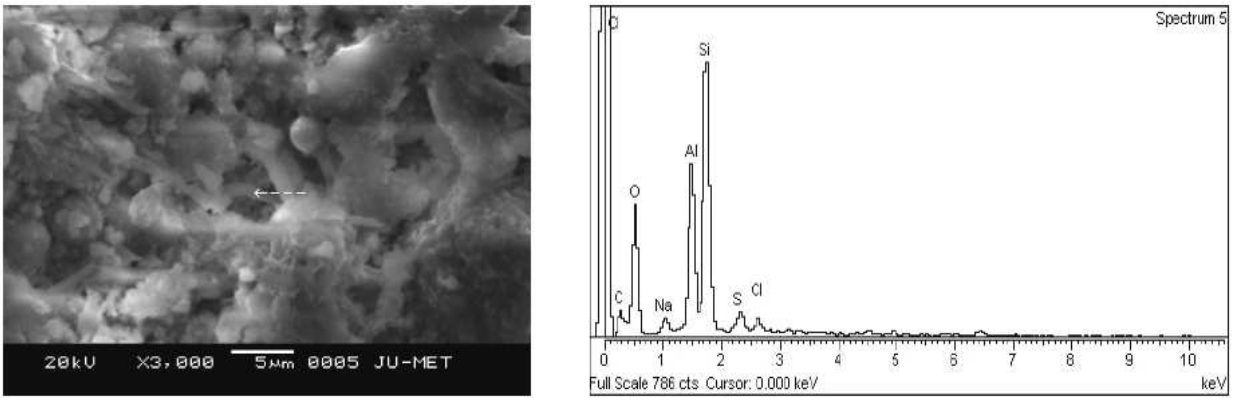

Fig. 10 SEM image of geopolymer mortar with 8% Na_2O and EDAX spectrum at the arrow point after 12 weeks in 10% sulphuric acid

IV. CONCLUSIONS

On the basis of results obtained during the experimental investigation, following conclusions were drawn:

1. Fly ash based geopolymer mortar specimens manufactured with varying alkali content showed varying degree of deterioration when exposed to sulphuric acid.
2. Though mortar specimens revealed no visible signs of structural disintegration, surface deterioration was clearly visible under an optical microscope and these appeared to be severe in specimen manufactured with lesser alkali content.
3. Loss in weight though observed in all specimens, those with higher alkali content recorded higher weight loss. There was a sudden loss in weight for the specimens at 3 weeks.
4. Geopolymer mortar specimen experienced loss in strength which was highest in the specimen manufactured with minimum alkali content. However even after 24 weeks in 10% sulphuric acid the least residual compressive strength measured was 29.4%.
5. SEM micrographs showed different microstructures of mortar specimens before and after exposure in sulphuric acid solution. Microstructure of specimen appeared to be denser after exposure due to formation of light coloured precipitates.
6. Specimen with higher alkali content performed much better than those with lower alkali content in terms of residual compressive strength.

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