



DURABILITY OF FLY ASH GEOPOLYMER MORTARS IN NITRIC ACID – EFFECT OF ALKALI (Na₂O) CONTENT

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Abstract. Durability of fly ash based geopolymer mortar specimens in Nitric acid solution was investigated on three different series of specimens manufactured by activating fly ash with a mixture of sodium hydroxide and sodium silicate solution containing Na₂O ranging from 5% to 8% of fly ash. Specimens were exposed in 10% by weight Nitric acid solution up to 24 weeks. The effect of alkali (%Na₂O) content on durability of geopolymer mortar specimens were studied in terms of visual appearance, change in weight and change in compressive strength. Mineralogical and microstructure changes due to nitric acid attack were also investigated. Geopolymer mortar specimens showed excellent durability in terms of extremely less weight loss as well as high retention of compressive strength. Specimens with higher alkali content exhibited better durability in nitric acid.

Keywords: fly ash, Geopolymer, durability, weight change, compressive strength, scanning electron microscopy, porosity, XRD.

1. Introduction

Ordinary Portland cement concrete is known to be susceptible to acid attack. The high content of CaO in OPC makes it vulnerable as it is readily soluble in acid environment (Pavlík 1996; Beddoe and Dorner 2005; Dan and Janotka 2003). In this scenario, alkali activated fly ash cementitious materials are a promising alternative for the reasons that fly ash contain very less CaO.

Normal cement concrete when exposed to acids suffers from severe corrosion (Pavlík 1996; Chang *et al.* 2005) and often leads to decrease of their service life (Kamaitis 2008). Geopolymer are a new binder generally manufactured by activating an aluminosilicate source material such as fly ash, silica fume, blast furnace slag, etc. in a highly alkaline medium. It is reported that geopolymer possesses high early strength, better durability and has no dangerous alkali-aggregate reaction (Davidovits 1994). Of late, fly ash based geopolymers have received tremendous attention as an alternative to Portland cement binders for the above reasons. Low calcium fly ash based geopolymer manufactured with various activators have shown excellent performance when exposed to different acids with varying concentrations and exposure durations (Davidovits 1994; Bakharev 2005a; Song *et al.* 2005; Jimenez *et al.* 2007; Thokchom *et al.* 2009a, b).

Wallah and Rangan (2006) investigated long term properties of geopolymer concrete and showed the superior durability of geopolymer over portland cement concrete in both acid and sulfate environment. Durability of geopolymer materials manufactured with uniform Na₂O content but with different activating solutions was studied by Bakharev (2005a, b). The author found that geopolymer materials manufactured by activation with sodium hydroxide performed better in both acid and sulphate solution when compared with those activated by sodium silicate or potassium hydroxide. Allahverdi and Škvára (2001a, b) examined the mechanism of nitric acid attack on geopolymer cements prepared from a mix of fly ash and slag in equal proportions. The authors also performed a similar study on geopolymer cements for sulfuric acid attack (Allahverdi and Škvára 2005, 2006).

The objective of present experimental program was to study effect of alkali content (%Na₂O) of fly ash based geopolymer mortar specimens on its performance in nitric acid solution. Geopolymer mortars manufactured with varying alkali (%Na₂O) were immersed in 10% nitric acid solution and its performance was evaluated on the basis of appearance, changes in weight and compressive strength at regular intervals over the exposure duration. Porosity of specimens is correlated to their performance in addition to identifying mineralogical and microstructure changes using XRD and SEM.

Table 1. Chemical composition of fly ash by XRF

Chemical composition	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	K ₂ O	Na ₂ O	SO ₃	P ₂ O 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

2. Experiment

2.1. Materials

Low calcium Class F fly ash used in the present experimental program was sourced from Kolaghat Thermal Power Plant near Kolkata, India. It had a chemical composition as given in Table 1. About 75% of particles were finer than 45 micron and Blaine's specific surface was 380 m²/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 (98 percent purity) and sodium silicate solution (Na₂O = 8%, SiO₂ = 26.5% and 65.5% water) with silicate modulus ~ 3.3 and a bulk density of 1410 kg/m³ was supplied by Loba Chemie Ltd, India. A mixture of sodium hydroxide pellets, sodium silicate solution and water was prepared one day ahead, having Na₂O in the mix as 5% to 8% of fly ash and used as the activating solution to manufacture the geopolymer mortar. Water to fly ash ratio was maintained at 0.33 by using required additional water. For the exposure solution, concentrated nitric acid was directly mixed with tap water to make a 10% concentrated solution by weight. Nitric acid was used as it is a strong and corrosive acid.

2.2. Preparation of specimen

Fly ash geopolymer mortar samples contained equal proportions of fly ash and sand. The mixing procedure and curing regime adopted was after Thakur and Ghosh (2007). In a Hobart mixer, fly ash was first mixed with required quantity of activator solution for 5 minutes. The geopolymer 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 for 2 minutes. Specimens were cured along with the moulds (covered with a polythene sheet) in an oven for a period of 48 hours at 85 °C and allowed to cool inside the oven before being removed to room temperature. The details of the samples used in the present study are given in the Table 2. The compressive strength determined at 28 days was found to be 22 Mpa, 37 Mpa and 40 Mpa for specimens manufactured with 5%, 6.5% and 8% Na₂O (alkali) respectively.

Table 2. Details of geopolymer mortars (Quantities per kg of fly ash)

Sample ID	Alkali content (Na ₂ O)	NaOH pellets (gm)	Na ₂ SiO ₃ solution (gm)	Extra water (gm)	28 days comp. strength (Mpa)
GM1	5%	39	245	161	22
GM2	6.5%	58	245	156	37
GM3	8%	78	245	152	40

2.3. Test procedure

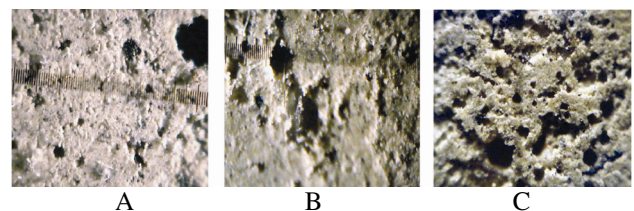
To study the effect of alkali (Na₂O) content on performance of geopolymer mortar samples in nitric acid, specimens were soaked in 10% nitric acid solution after 28 days from manufacture for 24 weeks. The volume of acid solution was taken as four times the volume of specimens and refreshed after 12 weeks. The effects of nitric acid on the geopolymer mortar specimen were constantly monitored through visual inspection, weight measurements and strength tests at predetermined intervals during the exposure period. For investigating the surface changes, an optical microscope was used to observe the surfaces after removal from solution at regular intervals. Samples 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. Average values of minimum three specimens have been reported for weight changes and residual compressive strengths. A JEOL JSM 6360 scanning electron microscope equipped with Inca Oxford EDX analyzer was employed to examine changes in microstructure as well as for micro-analysis of specimens. For mineralogical investigation, Rigaku Miniflex XRD machine was utilised at a scanning rate of 1° per minute for scanning angle 2θ ranging from 5° to 65°. Mercury intrusion porosity of specimens was determined with a Quantachrome Poremaster 60 at a contact angle of 140°.

3. Results and Discussion

3.1. Surface corrosion and depth of dealcalization

Geopolymer mortar specimens remained unaffected in shape and showed no signs of cracks. Some corrosion could be observed when seen through the optical microscope. The magnitude of corrosion appeared to be greater in the specimen with lower Na₂O content. Photographs taken for the corroded surfaces of specimens at various ages of exposure are shown in Fig. 1.

A phenolphthalein solution was used to check the depth of loss of alkali in the specimen termed as 'depth of dealcalization' by spraying it on freshly cut surface of specimen. Fig. 2 shows a typical photograph of the specimen tested. The depth of dealcalization became

**Fig. 1.** Surface corrosion of geopolymer mortar specimen GM1: A – unexposed specimen; B – after 3 weeks; C – after 9 weeks

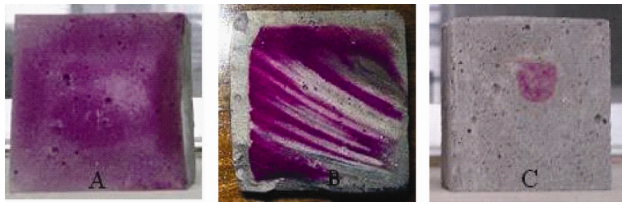


Fig. 2. Depth of dealcalization of specimen GM3: A – unexposed specimen; B – after 3 weeks; C – after 9 weeks

greater with time in all specimens. However, the ones manufactured with higher alkali (8% Na₂O) sustained longer than those prepared with lesser alkali content. Within 15 weeks GM3 specimens were fully dealcalized. In contrast specimens of GM1 (5% Na₂O) needed only 6 weeks for complete dealcalization.

3.2. Total porosity by Mercury intrusion porosity

Porosity of geopolymer specimens were measured with the help of mercury intrusion porosimetry test. Fig. 3 presents the results of porosity tests for the three series of specimens. It shows the cumulative volume of mercury intruded in cc/g versus pore size in micrometer. Total porosity expressed in terms of cumulative volume of mercury intruded was found to be significantly affected by alkali content of specimens.

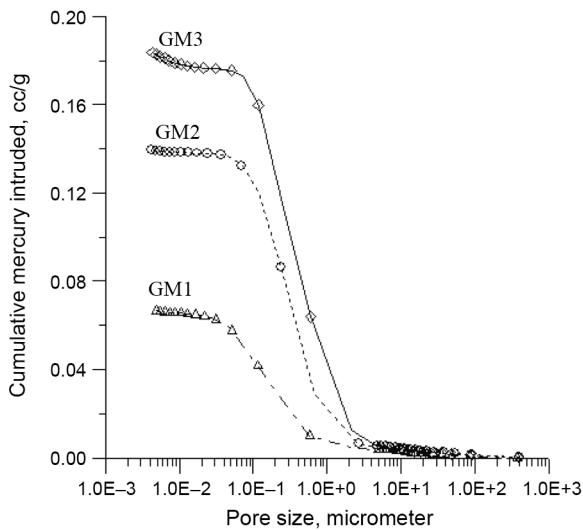


Fig. 3. Total porosity of fly ash geopolymer mortar specimens by MIP

Higher alkali content in the specimen caused decrease in porosity. GM3 (8% Na₂O) showed a total penetrable pore of 0.067 cc/g whereas specimens of GM2 (6.5% Na₂O) and GM1 (5% Na₂O) recorded porosity volume of 0.14 cc/g and 0.18 cc/g respectively. However, the maximum pore size in all three series of specimens remained more or less the same at around 0.38 mm.

3.3. Variation in weight

The variation of weight of geopolymer mortar specimens with varying alkali content after 24 weeks in nitric acid solution is presented in Fig. 4. Though loss in weight was

found to be quite less across the geopolymer mortar specimens, it is important to note that specimens manufactured with lower alkali content showed greater loss. In fact, when GM3 specimen lost 0.21% after 24 weeks of exposure, the corresponding weight loss for GM1 and GM2 were found to be 0.54% and 1.42% respectively. With respect to loss in weight, GM3 with highest alkali (8% Na₂O) among the three remained most stable in nitric acid solution.

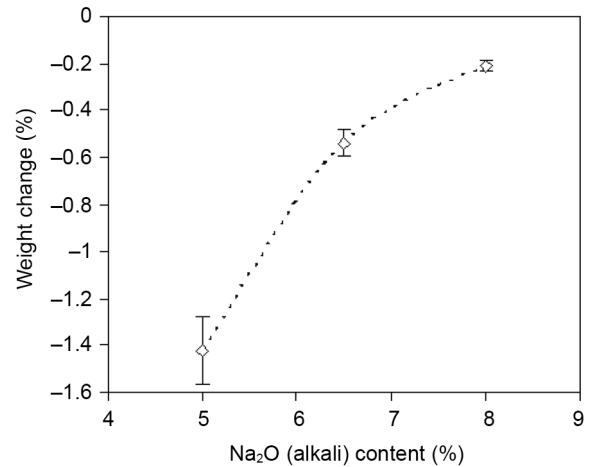


Fig. 4. Weight changes of specimens after 24 weeks in Nitric acid solution

3.4. Variation in compressive strength

At predetermined intervals during the exposure period geopolymer mortar specimens were removed from solutions and compressive strength determined after 3 days of ambient drying. Fig. 5 gives variation of compressive strength with time of exposure. Geopolymer mortar specimens declined in strength throughout the exposure period though magnitude of loss in strength varied in the specimens. For GM1 and GM2 specimens there was rapid loss of strength during the first 12 weeks and thereafter remained stable. However GM3 specimens exhibited a uniform decline in strength till the end of 24 weeks. GM3

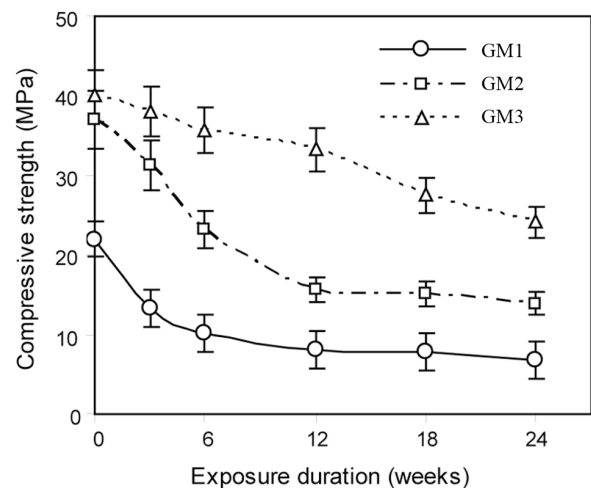


Fig. 5. Compressive strength evolution of geopolymer mortars in nitric acid solution

mortar specimens which initially had a strength of 40 Mpa before immersion returned a final strength of 24 Mpa which accounted for a loss of ~40%. In the GM1 and GM2 specimens the loss of compressive strength recorded were considerably higher at ~70% and ~63% respectively. On the basis of retention of compressive strength, specimen with higher alkali content performed much better than those with lesser alkali.

3.5. Microstructure study by scanning electron microscopy (SEM) and micro-analysis by EDX

Samples removed from the surface of specimens exposed to nitric acid solution were subjected to scanning electron microscopy to identify the changes in microstructure due to interaction of geopolymer mortars with nitric acid. In addition micro-analysis of selected spots was performed with EDX technique. Fig. 6 shows the SEM micrographs along with EDX spectrum at selected spots A, B and C indicated by arrows for geopolymer mortar specimen GM2. Initially, SEM image exhibited comparatively porous microstructure with amorphous aluminosilicate phases including some unreacted fly ash particles.

After 12 weeks exposure in 10% nitric acid solution, there seems to be an improvement in the microstructure with lesser pores which could be due to presence of products of degradation caused by nitric acid attack. More precipitates are observed in the microstructure of specimen after 24 weeks exposure which might be due to continuous deterioration of the geopolymer materials. In Fig. 7, SEM images of GM1 and GM3 mortar specimens after 12 weeks of nitric acid interaction are shown accompanied by corresponding EDX spectrum at indicated spots D and E. GM1 specimens still abound with numerous pores besides resembling a highly deteriorated microstructure. In contrast, GM3 mortars seem to remain apparently unaffected. EDX spectrum on spot A for unexposed GM2 mortar specimen revealed presence of Al, Si, Na, and Fe as the main elements with traces of K, Ca among others. However for the exposed specimens, analysis conducted on similar spots indicated depletion or disappearance of Na, Ca and K as observed clearly in EDX spectra.

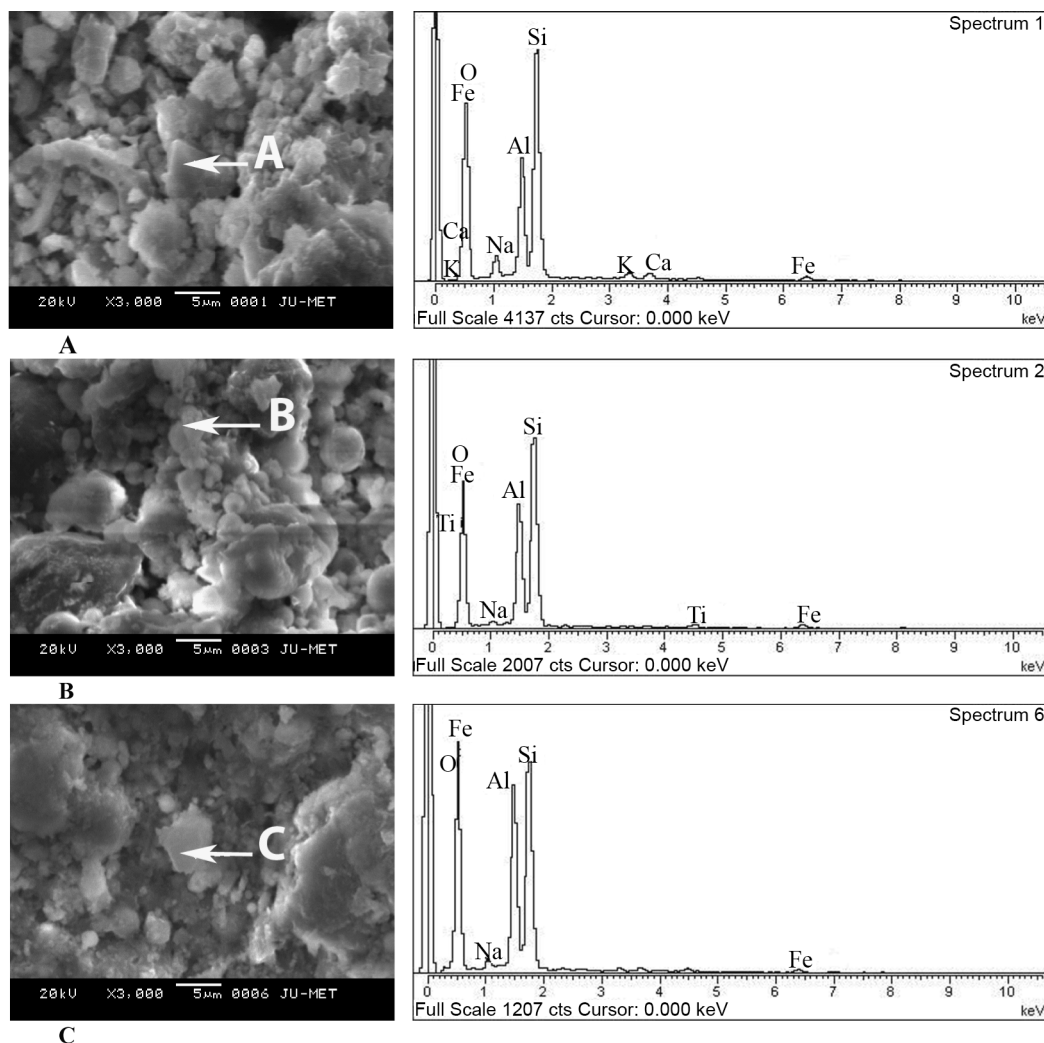


Fig. 6. SEM images and EDX spectrum at arrow spot for GM2(6.5% Na_2O) specimen: A – unexposed specimen; B – after 12 weeks; C – after 24 weeks exposure

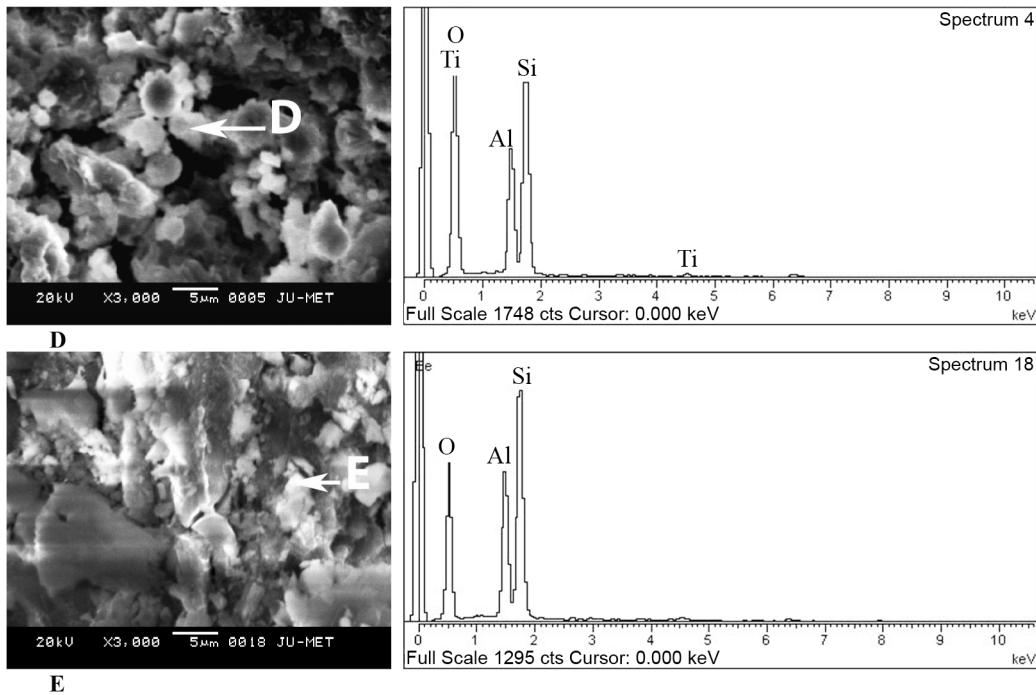


Fig. 7. SEM images and EDX spectrum of geopolymer mortar specimens after 12 weeks in nitric acid solution: A – GM1 and B – GM3

3.6. Mineralogical investigation by XRD

Fig. 8 shows XRD spectra of fly ash and its comparison with those of exposed specimens GM2 and GM3 geopolymer mortars. For fly ash, peaks of quartz and mullite dominate the XRD spectra. While appreciable phase changes were not observed in the specimens exposed to nitric acid attack, new peak of chabazite developed along with diminishing peaks of few other phases. In the spectra of exposed specimens, peaks due to gismondine be-

came quite prominent including those of albite and chabazite. Peaks due to mullite and hematite which were prominent in the spectra of fly ash became depleted in those of GM2 and GM3 mortar specimens after 12 weeks exposure in nitric acid media. However, phase changes due to interaction of geopolymer mortars with nitric acid were almost identical in both GM2 and GM3 specimens though they were manufactured with alkaline solutions differing in Na₂O content.

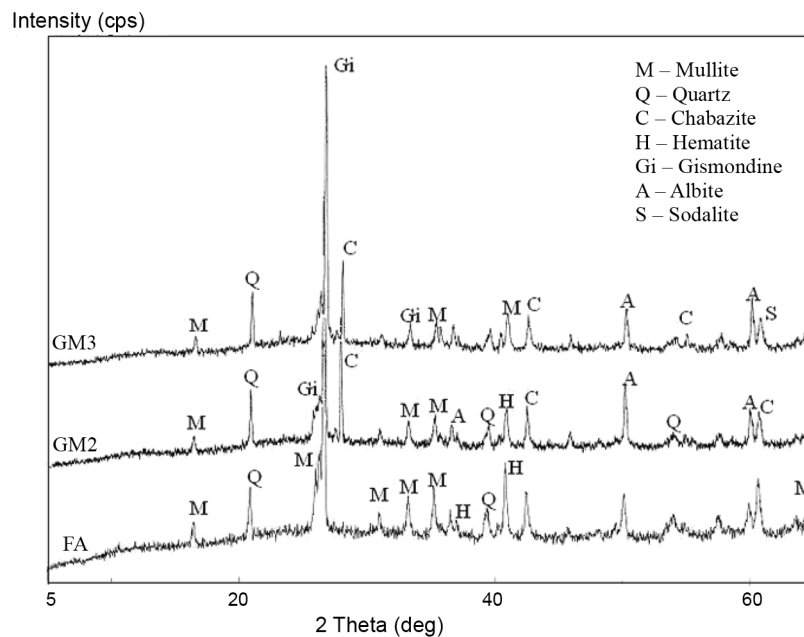


Fig. 8. XRD spectra of geopolymer mortar specimens after 18 weeks in nitric acid

4. Discussion

On the basis of results obtained, geopolymer mortars made by alkali activation of fly ash remained highly durable in such a high concentration of 10% nitric acid solution even up to 24 weeks. Very less weight loss and high retention of compressive strength as observed through results of the present investigation are a significant proof of resistance to acid attack. These were again supported by the microstructure images as well as by very little mineralogical changes indicated in XRD spectra of exposed specimens. Moreover, geopolymer mortar specimens remained structurally unaffected though the surface became slightly corroded which was hardly visible to naked eye. The loss in weight and compressive strength could be attributed to leaching of sodium and calcium present in the geopolymer matrix. Allahverdi and Škvára (2001a) reported that the process of acidic corrosion results in leaching of both sodium and calcium. The authors also pointed out insignificant changes in concentration of silicon and aluminum in the corroded layer. Though loss in weight was small, the fact that geopolymer mortars manufactured with 5% Na₂O (GM1) recorded maximum loss among the three different series of specimens could then be attributed to its higher volume of porosity as obtained through mercury intrusion porosimetry test. Higher volume of porosity allows more quantity of acid solution to penetrate into the specimen thereby exposing greater surface area to acid attack. This in turn could have possibly caused increased leaching of sodium and calcium in such specimens affecting its weight as well as strength. In the EDX spectrum of unexposed GM2 specimen shown in Fig. 6 – A, traces of sodium and calcium could be observed among high concentrations of silicon and aluminum. However, after exposure in 10% nitric acid solutions, EDX spectra did not exhibit any traces of both sodium and aluminum (Fig. 6 – B and C). Similar spectrum was also obtained for GM1 and GM3 specimens shown in Fig. 7. Bakharev (2005a) also found that migration of alkalis occur from specimen to acid solution. The electrophilic attack by acid protons on polymeric Si-O-Al bonds are reported to result in destruction of aluminosilicate framework and therefore the corroded layer could be considered as a partially dealcalized and decalcified Si/Al residue which has the potential to inhibit further corrosion by acting as a barrier to the acid ions (Allahverdi and Škvára 2001a, b). Probably, this might be the reason behind the slower rate of strength loss of geopolymer mortar specimens at later stages of exposure in nitric acid solution. In the present investigation, it has been observed that fly ash based geopolymer mortar activated by alkaline solution containing higher alkali perform much better than those with lesser alkali content. Microstructure and porosity of specimen with higher Na₂O content was comparatively better and this should be considered as primary reason for its superior performance in nitric acid.

5. Conclusions

1. Geopolymer mortar specimens remained structurally sound even after prolonged exposure in a high

concentration of nitric acid solution. Corrosion of exposed surface was more in specimens manufactured with lower alkali content.

2. Volume of penetrable pores as determined by mercury intrusion porosimetry was found greater in the specimens with lesser Na₂O content

3. Mortar specimens manufactured by activation with alkaline activator of higher alkali content exhibited better performance in nitric acid on the basis of weight loss and retention of compressive strength.

4. Loss in weight and compressive strength of specimens in nitric acid could be attributed to leaching of sodium and calcium from specimens which were clearly observed through EDX spectra of exposed specimens.

5. The fact that specimens continue to retain its shape and integrity along with high residual compressive strength even after 24 weeks in 10% nitric acid proves the earlier reports of superior durability of geopolymer materials.

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GEOPOLIMERINIO SKIEDINIO, PAGAMINTO NAUDOJANT LAKIUOSIUS PELENUS, ILGAAMŽIŠKUMAS AZOTO RŪGŠTYJE: ŠARMŲ (Na_2O) KIEKIO POVEIKIS

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Santrauka

Buvo tiriamas geopolimerinio skiedinio bandinių, pagamintų naudojant lakiuosius pelenus, ilgaamžiškumas azoto rūgšties tirpale. Buvo tiriami trijų skirtingų partijų bandiniai, pagaminti pridėjus lakiųjų pelenų, kurie turi natrio hidroksido ir natrio silikato mišinį, jo sudėtyje Na_2O svyruoja 5–8 % nuo lakiųjų pelenų kiekio. Bandiniai 24 savaites buvo veikiami 10 % (pagal masę) azoto rūgšties tirpalu. Šarmų (% Na_2O) kiekio poveikis geopolimerinio skiedinio bandinių ilgaamžiškumui buvo tiriamas įvertinant išvaizdą, nustatant masės ir gniuždomojo stiprio pokytį. Taip pat buvo nustatyti mineraloginiai ir mikrostruktūriniai pokyčiai veikiant azoto rūgštimi. Geopolimerinio skiedinio bandinių ilgaamžiškumas buvo labai didelis, masės nuostoliai nedideli ir didelis gniuždomasis stipris. Bandiniai su didesniu šarmų kiekiu buvo ilgaamžiškesni azoto rūgštyje.

Reikšminiai žodžiai: lakieji pelenai, geopolimeras, ilgaamžiškumas, masės pokytis, gniuždomasis stipris, skenuojanti elektroninė mikroskopija, poringumas, rentgenografinė analizė.

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