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EFFECT OF SILICA FUME ADDITIONS ON POROSITY OF FLY ASH GEOPOLYMERS

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ABSTRACT

This paper presents the results of an experimental study performed to investigate effect of incorporating silica fume in the fly ash geopolymer on its porosity and compressive strength. Geopolymer specimens were prepared by activating fly ash incorporated with additional silica fume in the range of 2.5% to 5% with a mixture of sodium hydroxide and sodium silicate having Na_2O content of 8%. The characterization of the geopolymer specimens was done with ESEM/EDAX and MIP tests. Addition of silica fume up to 5% enhanced compressive strength of geopolymer mortars. However, further increase of silica fume caused a decrease in compressive strength. SEM micrographs for specimens incorporated with silica fume showed better microstructure and exhibited lesser porosity. MIP results of paste specimens indicate higher pore volume in the specimen prepared with additional silica fume while for mortar specimens; the pore volume was seen lesser in specimens with additional silica fume. Silica fume may be used as an additional material to improve or modify some properties of the resulting geopolymer.

Keywords: fly ash, silica fume, geopolymer, MIP, ESEM, EDAX, compressive strength.

1. INTRODUCTION

Geopolymers are a class of new binder manufactured from an aluminosilicate source material such as fly ash, silica fume, blast furnace slag etc, by activating with a highly alkaline solution with moderate thermal curing. In the recent years, interest in geopolymer is increasing manifold due to their reported advantages over ordinary Portland cements. Geopolymer materials are reported to possess high early strength, better durability and have almost no alkali-aggregate reaction [1]. These materials are therefore projected to be cement for the future [2]. Presently, fly ash based geopolymers have received tremendous attention as fly ash has huge potential and are abundantly available as wastes from thermal power plants. Low calcium fly ash based geopolymer manufactured with different activators have shown high compressive strengths and excellent performance when exposed to different acid and sulphate solutions [3--9]. It has also been reported to be highly resistant to elevated temperatures [10, 11]. Wallah and Rangan [8] noticed that geopolymer concrete specimens exhibit extremely small changes in length and also very little increase in mass after one year of exposure in sulphate solution of varying concentrations. It was found that geopolymer materials manufactured by activation with sodium hydroxide perform better in sulfate solution when compared with those prepared with other activators [15]. It has been observed that geopolymer activated by a mixture of sodium hydroxide and sodium silicate solution yield higher compressive strength [3, 9, 10]. Moreover, the microstructure development depends on alkali content of activating solution. Past investigations have not used silica fume as an additive in manufacturing geopolymers. It can be expected to improve the properties of resulting geopolymers in terms of strength and porosity, with addition of silica fume.

The objective of the present experimental investigation is to study the effect addition of silica fume on the pore characteristics of fly ash based geopolymer composites. Up to 5% of silica fume has been added in increments to the fly ash while manufacturing geopolymer paste and mortars. Porosity, compressive strength, water absorption and micro structural studies have been performed for the resulting geopolymers to investigate the effect of additional silica fume.

2. EXPERIMENTAL

2.1 Materials

Table-1. Chemical composition of fly ash and silica fume.

Chemical composition	Fly ash	Silica fume
SiO_2	56.01	92.00
Al_2O_3	29.8	0.46
Fe_2O_3	3.58	1.60
TiO_2	1.75	Nil
CaO	2.36	0.29
MgO	0.30	0.28
K_2O	0.73	0.61
Na_2O	0.61	0.51
SO_3	Nil	0.19
P_2O_5	0.44	Nil
Loss on ignition	0.40	1.00

Low calcium Class F fly ash used in the present research work was collected 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^2/kg. Silica fume was obtained from Oriental Trexim Pvt Ltd, Mumbai, India. The chemical composition of silica fume is given in Table-1. It has a specific gravity of 2.36 and BET surface area of 18900 m^2/kg. Laboratory grade sodium hydroxide in pellet form (98 percent 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 1410 kg/m^3 was supplied by Loba Chemie Ltd, India. The alkaline activating solution was prepared by dissolving required quantity of sodium hydroxide pellets directly into predetermined quantity of sodium silicate solution. It had Na_2O content and SiO_2 content as 8.0% of fly ash, thereby making SiO_2/Na_2O ratio of 1. Water to fly ash ratio was of 0.33. The activator solution was left at room temperature overnight before being used to manufacture geopolymer specimens.

2.2 Preparation of specimens and testing

In a Hobart mixer, fly ash, with or without silica fume was mixed with predetermined quantity of activator solution for 5 minutes. The geopolymer mix exhibited a thick sticky nature with good workability. In case of mortar specimens, sand in surface saturated condition was gradually introduced at this stage and continued mixing for another 5 minutes. The ratio of fly ash to sand was taken as 1. The mix was then was transferred into 50 x 50 x 50 mm cube moulds. Table vibration was provided for 2 minutes to expel any entrapped air. After 60 minutes, the cubes were cured in an oven for a period of 48 hours at 85^{o}C and then allowed to cool inside the oven [12]. Specimens were removed and stored at room temperature at a dry place before testing. Some data of the present study are given in the Table-2.

After 28 days from casting, the geopolymer specimens were tested for its pore characteristics, water absorption, compressive strength and micro structural properties including energy dispersive X-ray analysis. Micro structural studies and micro-analysis used environmental scanning electron microscope (ESEM) FEI Quanta 200. Pore characteristics were studied by Mercury Intrusion Porosimetry test, using Quanta chrome Pore master 60, at a contact angle 140^o, which measured total intruded volume of mercury into the specimens.

Table-2. Details of geopolymer paste and mortar specimens.

Sample ID	Na_2O content in activator (%)	SiO_2 content in activator (%)	Silica fume (% by wt of fly ash)	Type of specimen	Water / fly ash ratio	Curing temp. and duration
FP	8	8	0	Paste	0.33	85^{0}C and 48 hrs
FP1	8	8	2.5	Paste	0.33	85^{0}C and 48 hrs
FP2	8	8	5.0	Paste	0.33	85^{0}C and 48 hrs
FM	8	8	0	Mortar	0.33	85^{0}C and 48 hrs
FM1	8	8	2.5	Mortar	0.33	85^{0}C and 48 hrs
FM2	8	8	5.0	Mortar	0.33	85^{0}C and 48 hrs

3. RESULTS AND DISCUSSIONS

3.1 Mercury intrusion porosimetry (MIP)

Mercury intrusion porosimetry was used to investigate the total porosity of the geopolymer specimens. The bulk volume of each test specimen was 1cc and maximum applied intrusion pressure during the test was about 53500 psi. Plots of cumulative volume of mercury intruded into specimens and pore diameter of the paste and mortar specimens are shown in Figure-1. From the said Figure, it is evident that most of the mercury intrusion occurred within the pore sizes of 0.2 µm to 20 µm for paste specimens, while for mortar specimens, the range of pore size for maximum intrusion volume is 0.1 µm to 4 µm. This indicates that paste specimens generally have larger pore sizes than the corresponding mortar specimens. Details of average pore diameter; penetrated mercury volume and total porosity (%v/v) are presented in Table-3. The total volume of pores for different specimens was found quite different as observed from Table-3. Average pore diameter calculated from Washburn's equation [13] for the geopolymer specimens ranged from 3.92 nm to 4.02 nm. Similar observations were also made by some other researchers [9, 15, 16]. It can be noticed that addition of silica fume in the mix has a significant influence on the total porosity. A small addition of silica fume (2.5% of fly ash) resulted in improvement of porosity for geopolymer paste specimens. Further increase of additional silica fume causes corresponding increase of total porosity of paste specimens. However, in case of mortar specimens, porosity is seen to improve with additional silica fume, irrespective of the amount of silica fume. Specimens marked FP which does not have silica fume registered a total mercury intrusion of 0.1365cc/g which corresponds

to a porosity of 16.61% v/v. An increase in total porosity (17.05%) was observed for FP1 having silica fume of 2.5%. In contrast, under similar applied intrusion pressure, specimens marked FP2 (5% Silica fume) allowed relatively higher mercury intrusion volume of 17.65%. For geopolymer mortars made without silica fume, the volume of mercury intrusion was found to be 0.1556cc/g, which is equivalent to total porosity of 20.34%. When 2.5% silica fume is added, the porosity reduced to 19.49%. Further addition of silica fume up to 5% resulted in rapid reduction of porosity to 15.56%.

Table-3. Details of pore characteristics.

Specimen	Cumulative volume of mercury intruded (cc/g)	Total porosity (%)	Average pore diameter (nm)
FP	0.1365	16.61	4.00
FP1	0.1445	17.05	4.01
FP2	0.1621	17.65	4.02
FM	0.1556	20.34	3.93
FM1	0.1211	19.49	3.93
FM2	0.085	15.56	3.92

Significant variation in total porosity is noticed due to the different quantities of silica fume added into the geopolymer mix. Skvara *et al*., [14] found that the Na_2O content and SiO_2/Na_2O ratio of geopolymer mix significantly affects pore characteristics and compressive strength. In the present experimental investigation, the least porosity is obtained in FM2 specimen having highest silica fume content. Addition of silica fume which has a high percentage of SiO_2 could have hindered the process of geopolymerisation. This should be attributed to the fact that for increased SiO_2 content, Na_2O required for complete dissolution is not available in the activator solution thereby more unreacted particles remain in the formed geopolymer gel which subsequently makes a porous microstructure. However, in case of mortar specimens, these excess fine silica fume particles could have filled up the voids between the sand particles and must have contributed to improvement of porosity. These significant variations in the total porosity in the geopolymer specimens may affect their mechanical properties.

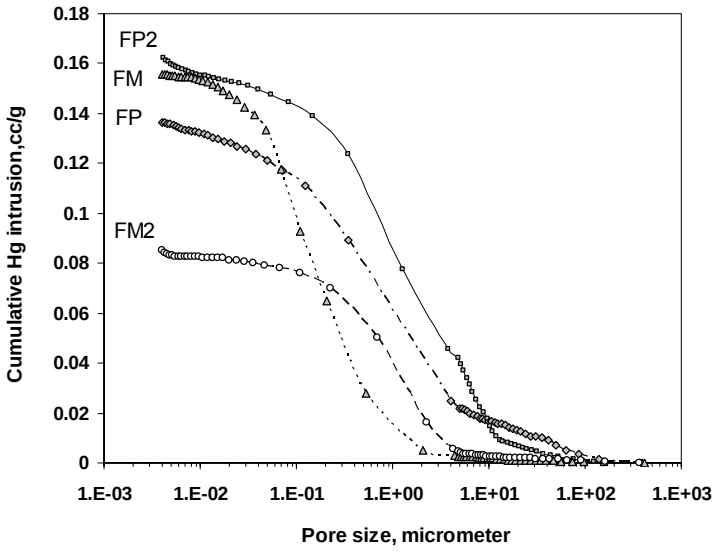


Figure-1. Relationship of cumulative volume of mercury intrusion with pore diameter.

3.2 Compressive strength

The compressive strength of the geopolymer paste and mortar specimens were determined after 28 days from manufacture. Three specimens for each series were crushed in a digital compression testing machine and the average is reported. Compressive strength obtained for the specimens are presented in Figure-2. It is noticed that paste specimens has higher strength in all the cases, with or without silica fume. FP specimen prepared without silica fume has a compressive strength of 37 MPa. With additional 2.5% silica fume (FP1), the strength dropped marginally to 34 MPa. Further increase in silica fume content up to 5% resulted in further decrease in compressive strength (30 MPa). The percentage decrease of strength for FP1 and FP2 were found to be 8.11% and 18.92% respectively. However, addition of silica fume caused an increase in compressive strength of mortar specimens. Mortar specimens prepared with fly ash (FM) recorded strength of 26 MPa after 28 days. Significant increase of strength occurred for FM1 specimen (31 MPa)

which contained 2.5% silica fume. Similarly, the compressive strength further increased (36 MPa) with additional silica fume of 5%. It amounted to a strength increase of 19.23% and 38.46% for FM1 and FM2 respectively. The results clearly indicate successive decrement of compressive strength for paste specimens and successive increment in case of mortar specimens. Porosity has been reported to be chief micro structural variable limiting the mechanical properties of geopolymers [17]. The variation of compressive strength should be due to significant differences in their porosity as noticed from the MIP results. It has been already discussed that total porosity for paste specimens increases with increasing silica fume in the mix. This has subsequently caused a drop in compressive strengths for paste specimens FP1 and FP2. However, it was noticed from the MIP results that porosity improves with addition of silica fume in case of mortar specimens. Hence, the compressive strength shows a corresponding increase. Improvements in microstructure can also be seen in the mortar specimens FM1 and FM2.

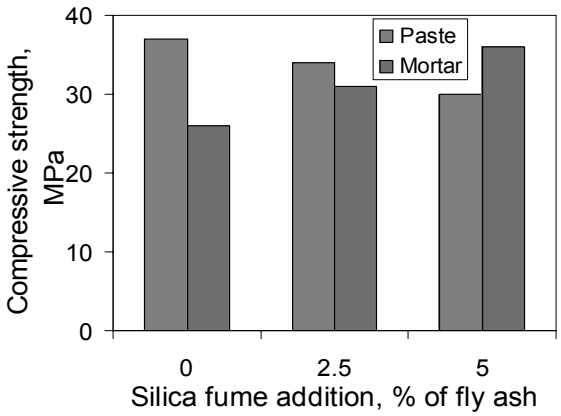
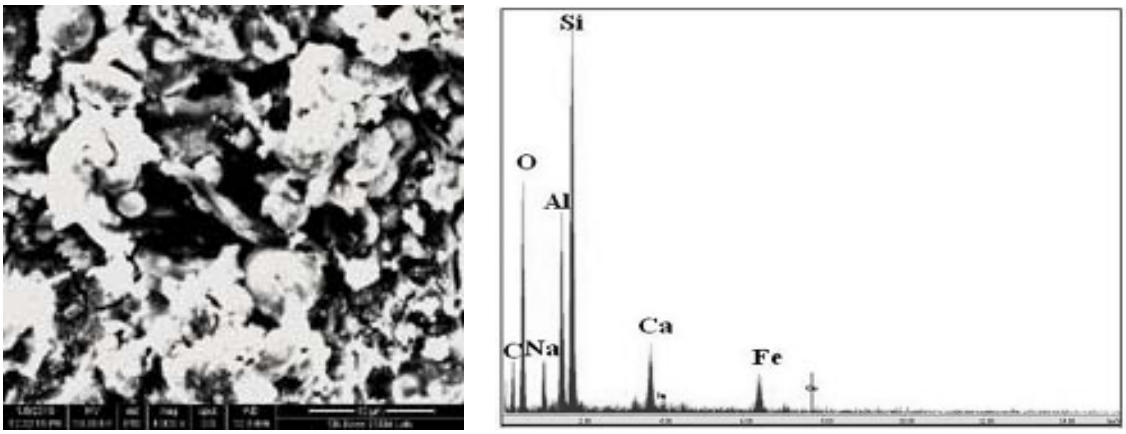


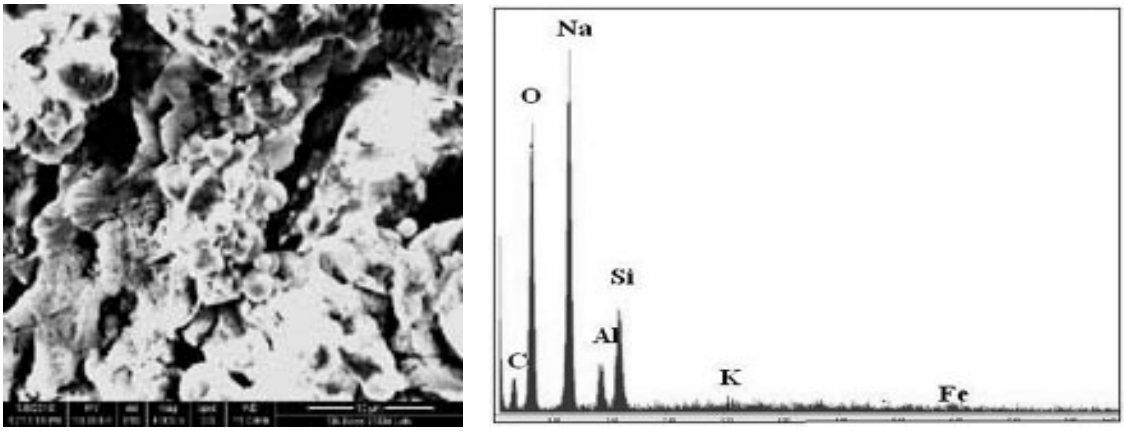
Figure-2. Compressive strength of specimens

3.3 Microstructural investigation with ESEM/EDAX

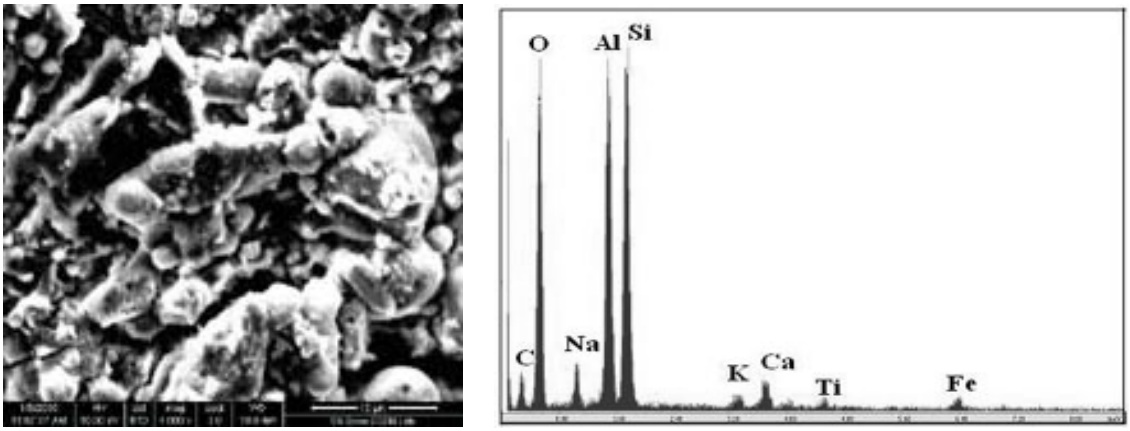
SEM analysis was performed to study the pore morphology and to view the reacted and unreacted regions of the specimens. Figure-3 presents the ESEM micrographs for geopolymer mortar specimens FM, FM1 and FM2 along with their EDAX traces. In all the micrographs of specimens, whether silica fume is added or not, it depicts a microstructure having some unreacted and partly unreacted particles embedded in the geopolymer gel. The micrographs reveal mostly an amorphous phase with pores of various sizes. FM specimen which is prepared without silica fume appear to be more porous than other specimens FM1 and FM2 which contain 2.5% and 5% silica fume. Another significant observation is that formation of gel looks better in specimens where silica fume has been added in the mix. EDAX spectra of FM specimen shows major elements such as carbon (C), oxygen (O), aluminium (Al), silicone (Si), calcium (Ca) and sodium (Na). The weight percentages of some important elements were Si (15.95%), Al (8.38%) and Na (3.71%). The Si/Na and Si/Al ratios are respectively 4.29 and 1.90. FM1 having a silica fume content of 2.5% also has similar elements. However, the weight percentages of important elements are different which shows Si (6.19%), Al (3.44%) and Na (27.99%). There is a noticeably a significant increase in weight percentage of Na. The Si/Al and Si/Na ratios for FM1 were found to be 1.79 and 0.22. In comparison, the ratios of Si/Al and Si/Na decreases in FM1 specimen. For FM2 specimen prepared with addition of 5% silica fume, the weight percentages from EDAX analysis yielded the following: Si (25.67%), Al (20.06%) and Na (5.01%). The Si/Al and Si/Na ratios are calculated as 1.28 and 5.12 respectively. It can be noticed that the Si/Al ratio is further decreased whereas the Si/Na ratio shows a rapid increase. An important observation from the EDAX analysis is the formation of Na-aluminosilicate hydrates.



[A] FM specimen



[B] FM1 specimen



[C] FM2 specimen

Figure-3. ESEM micrographs and EDAX spectra for Geopolymer mortar specimens.

2.4 Water absorption

Water absorption test was conducted for the geopolymer specimens to relate it to the total porosity results obtained from MIP results. Figure-4 presents the variation of water absorption of specimens. As expected, water absorption values for geopolymer paste specimens gradually increased with introduction of silica fume into the mix. FP specimens without silica fume recorded water absorption of 12.23%. In comparison, FP1 (2.5% silica fume) and FP2 (5% silica fume) had water absorptions of 12.58% and 13.47% respectively. It may be noted here that addition of silica fume was observed to increase porosity of paste specimens. This should be the reason for the increased water absorption. However, using silica fume as additives causes a reduction in water absorption for mortar specimens. FM specimen having no silica fume showed 6.5% water absorption. Addition of silica fume resulted in reduction of water absorption to 5.94% and 3.92% for FM1 and FM2 respectively. It is significant to note that FM1 and FM2 specimens had improved porosities when compared to FM. It can be concluded from the results that water absorption is proportionally related to porosity of the specimens.

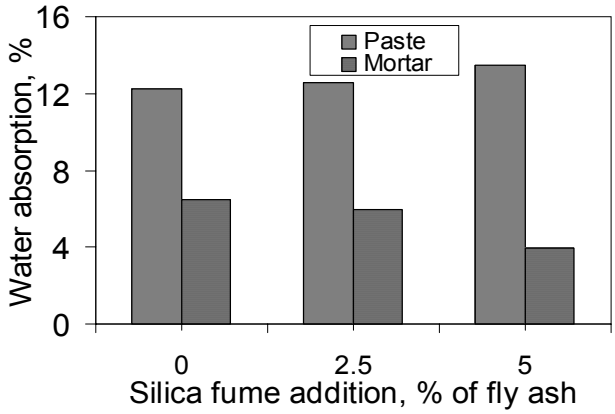


Figure-4. Water absorption of geopolymer specimens.

4. CONCLUSIONS

Following conclusions were made on the basis of the results from the experimental investigation.

a) Addition of silica fume to fly ash based geopolymer mortar specimens improves the total porosity. However, it increases porosity in case of geopolymer pastes.

b) Incorporation of silica fume enhances the compressive strength of mortar specimens whereas it causes a significant drop for the paste specimens. This could be due to the notable variations of porosity between the specimens prepared with or without silica fume.
c) Water absorption values were found directly related to total porosity of specimens. For paste specimens, water absorption gradually increases with introduction of silica fume into mix. In contrast, mortar specimens showed a decreasing trend in water absorption with increasing silica fume content.
d) SEM micrographs of specimens generally reveal an amorphous nature. The microstructures are characterized by the presence of unreacted or partially reacted particles which are embedded in the geopolymer gel.
e) The Si/Al weight ratios showed a decreasing trend with addition of silica fume for geopolymer mortars. This could be reason for improved porosity resulting in lesser water absorption and higher compressive strength.

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