



EFFECT OF MIX COMPOSITION ON COMPRESSIVE STRENGTH AND MICROSTRUCTURE OF FLY ASH BASED GEOPOLYMER COMPOSITES

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ABSTRACT

Geopolymer is a class of aluminosilicate binding materials synthesized by thermal activation of solid aluminosilicate base materials such as fly ash, metakaolin, GGBS etc., with an alkali metal hydroxide and silicate solution. These binders are currently attracting widespread attention due to their potential utilization as a high performance, environmental friendly and sustainable alternative to Portland cement. The present paper reports results of an experimental study on development of compressive strength and microstructure of geopolymer paste and mortar specimens prepared by thermal activation of Indian fly ash with sodium hydroxide and sodium silicate solution. The effect of main synthesis parameters such as alkali content($\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$), silica content ($\text{SiO}_2/\text{Al}_2\text{O}_3$), water to geopolymer solid ratio and sand to fly ash ratio of geopolymer mixture and processing parameters such as curing time and curing temperature on development of compressive strength and microstructure of fly ash based geopolymer paste and mortar were studied. The compressive strength of 48.20MPa was obtained for geopolymer mixture cured at 85°C for 48 hours with alkali content of 0.62 and silica content of 4.0. The mineralogical and microstructure studies on hardened geopolymer performed by means Scanning electron microscope (SEM) and X-ray diffraction (XRD), showed formation of a new amorphous alumino-silicate phase such as hydroxysodalite and herschelite, which influenced development of compressive strength. The results obtained in the current research will be useful for developing of mix design guidelines for commercial exploitation of the new binding material.

Keywords: fly ash, geopolymer, alkaline activator, thermal curing, microstructure, compressive strength.

1. INTRODUCTION

Geopolymers are inorganic polymeric binding materials, firstly developed by Joseph Davidovits in 1970s. Geopolymerisation involves a chemical reaction between solid alumino-silicate oxides and alkali metal silicate solutions under highly alkaline conditions yielding amorphous to semi-crystalline three-dimensional polymeric structures, which consist of Si-O-Al bonds [1]. The geopolymerisation reaction is exothermic and takes place under atmospheric pressure at temperatures below 100°C . The exact mechanism by which geopolymer setting and hardening occurs is not yet fully understood. However, the most proposed mechanisms for the geopolymerisation includes the following four stages [2-4] that proceed in parallel and thus, it is impossible to be distinguished: (i) dissolution of Si and Al from the solid aluminosilicate materials in the strongly alkaline aqueous solution, (ii) formation of oligomers species (geopolymers precursors) consisting of polymeric bonds of Si-O-Si and/or Si-O-Al type, (iii) polycondensation of the oligomers to form a three-dimensional aluminosilicate framework (geopolymeric framework) and (iv) bonding of the unreacted solid particles and filler materials into the geopolymeric framework and hardening of the whole system into a final solid polymeric structure.

Fly ash, which is rich in silica and alumina, has full potential to use as one of the source material for Geopolymer binder. It is the main solid waste generated from the coal combustion in the power stations. Since the worldwide electric power industry relies heavily on the

use of coal as a primary energy source, enormous quantities of fly ash are generated every year. According to 2000 estimation, the annual global fly ash production was more than 600 million tons. In the India, the annual production of fly ash is approximately 110 million ton and its generation is likely to reach 170 million tons by 2010. Presently, as per the Indian Ministry of Environment and Forest figures, only 20% to 30% of fly ash is used in manufacturing cements, construction, concrete, block and tiles and some disposed off in landfills and embankments, but a huge amount of fly ash is unutilized which causes several environmental problems of the air, soils and surface and ground-water pollution.

The utilization of fly ash in the development of geopolymeric materials for construction purposes has been and continues to be subject of many research studies.

Recent works on the Geopolymerisation of fly ash, reported production of geopolymeric materials with high mechanical strength, low density, less water absorption, negligible shrinkage and significant fire and chemical resistance. Due to these properties, Geopolymeric materials are viewed as an alternative to Portland cement for certain industrial applications in the areas of construction, transportation, road building, aerospace, mining and metallurgy. Significant research work on geopolymer concrete manufactured from fly ash in combination with sodium silicate and sodium hydroxide solution has been carried out by Rangan B.V. *et al.*, [9]. The authors have reported higher strength and better durability of geopolymer concrete than Portland cement



concrete. J. S. J. van Deventer *et al.*, [2] have reported that mechanical properties and microstructure of Na-based metakaolin geopolymers are highly dependent on composition of the aluminosilicate gel particularly, alkali content and silica content. The development of compressive strength of geopolymers is attributed to specific structural transformations of fly ash occurred during geopolymers and especially, due to formation of a new amorphous aluminosilicate gel phase in the geopolymers matrices. The main reaction product of alkali-activated fly ash is an alkaline silico-aluminate gel [7]. The OH⁻ ion acts as a reaction catalyst during the activation process and the alkaline metal (Na⁺) acts as a structure-forming element. The structure of the pre-zeolite gel contains Si and Al tetrahedral randomly distributed along the polymeric chains that are cross-linked so as to provide cavities of sufficient size to accommodate the charge balancing hydrated sodium ions [13]

The present paper describes manufacturing process of geopolymers from an Indian origin class-F fly ash. The effect of geopolymers mix formulation such as alkali content (Na₂O/Al₂O₃), silica content (SiO₂/Al₂O₃), water to geopolymers solid ratio and sand to fly ash ratio of geopolymers mixture and processing parameters such as curing time and curing temperature on compressive strength and microstructure have been investigated. The mineralogical and microstructural characteristics of Geopolymers materials were studied by means of XRD and SEM for explaining the changes in compressive strength of mortar prisms. The results obtained in the present study may be useful for formulating Geopolymers mix of desired engineering performance.

2. EXPERIMENTAL WORK

2.1 Materials

2.1.1 Fly ash

Typical Class-F fly ash from Kolaghat Thermal Power Station located near Kolkata was used in the present study. The chemical composition of fly ash determined by XRF analysis is given in Table-1.

Table-1. Chemical analysis of the fly ash (mass %).

Oxide	Mass (%)
SiO ₂	56.01
Al ₂ O ₃	29.80
Fe ₂ O ₃	3.58
TiO ₂	1.75
CaO	2.36
MgO	0.30
K ₂ O	0.73
Na ₂ O	0.61
SO ₃	Nil
P ₂ O ₅	0.44
LOI*	0.40
* Loss on ignition	

The calcium oxide content of the fly ash is less than 10% hence; it can be classified as Class-F fly ash, according to ASTM standard C6128-03. (Or siliceous pulverised fuel ash conforming to IS 3812(Part-I)-2003 specifications). About 90% of particles were smaller than 45 micron. The Blaine specific surface was 380m²/kg.

According to the XRD diffractograms of fly ash shown in Figure-1, the major crystalline constituents are quartz (SiO₂), mullite and magnetite. The fly ash is also constituted of an X-ray amorphous phase indicated by the broad hump registered between 2θ =20° and 30°. The SEM micrograph of original fly ash also shows that fly ash particles are spherical in shape of different diameters.

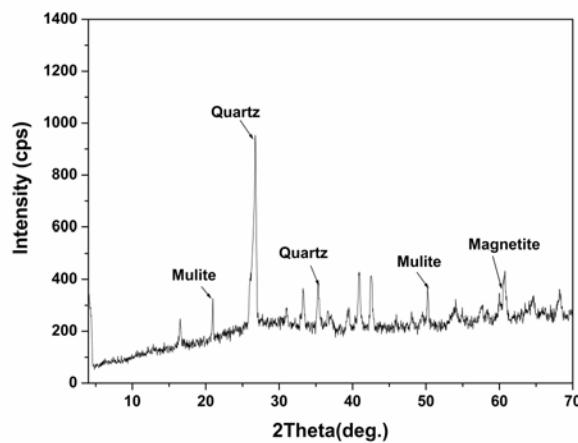


Figure-1. X-ray diffractogram of fly ash.

2.1.2 Alkaline activator

The alkaline activator liquid used was a combination of sodium silicate solution and sodium hydroxide. The sodium silicate solution (Na₂O= 14.7%, SiO₂= 29.4% and 55.9% water) with silicate modulus of 2.0 and a bulk density of 1390 kg/m³ and an analytical grade sodium hydroxide in pellets form (Merck Chemicals Ltd., NaOH with 98% purity) was used to adjust the composition of activating solution. To avoid effects of unknown contaminants in laboratory tap water, the distilled water was used for preparing activating solutions. A commercially available high range water reducing admixture (HRWRA) was used to improve workability of fresh mix. The activator solution was prepared at least one day prior to its use in specimen casting.

2.1.3 Fine aggregate

The fine aggregate was river sand obtained from local source. The specific gravity of sand was 2.54 and fineness modulus of the sand was 2.65. As per IS 383-1976, the particle size distribution of sand shows that it is in zone II. The sand was made saturated surface dry (SSD) before using in geopolymers mix to avoid water absorption from activator solution.



2.2 Preparation of geopolymers specimens

2.2.1 Mix proportions

Six series of geopolymers paste and mortar specimens were prepared by varying their mix composition for studying the effect of alkali content ($\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$), silica content ($\text{SiO}_2/\text{Al}_2\text{O}_3$), water to geopolymers solid ratio and sand to fly ash ratio of geopolymers mix and changing processing parameters such as curing time and curing temperature on development of compressive strength and microstructure. The compositional change in geopolymers mix was obtained by varying amount of sodium hydroxide (NaOH), sodium silicate solution (Na_2SiO_3), and water in the activating solution. In test series-1, the alkali content ($\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$) of the mix was varied from 0.46 to 0.62. The specimens for this test series were prepared with sand to fly ash ratio (S/F) of 1.5 and activator to fly ash ratio (A/F) of 0.5. The chemical composition of geopolymers mixes for this test series is shown in Table-2.

Table-2. Geopolymer mix with different alkali content.

Composition of geopolymers mix			Compressive strength (Mpa)			
Mix No.	$\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$	$\text{SiO}_2/\text{Al}_2\text{O}_3$	H ₂ O/ Na_2O	3day	7day	28day
A1	0.46	4.0	12.40	16.40	20.13	23.73
A2	0.50	4.0	11.08	22.74	28.27	33.47
A3	0.54	4.0	9.96	28.67	34.60	40.50
A4	0.58	4.0	8.49	34.26	39.57	44.75
A5	0.62	4.0	8.17	37.27	43.26	48.20

In test series-2, the effect of silica content ($\text{SiO}_2/\text{Al}_2\text{O}_3$) was studied. The silica content of the mix was 3.7 to 4.3, other parameters of mix i.e. S/F=1.5, A/F=0.5, were kept constant. The mix composition for this series is shown in Table-3.

Table-3. Geopolymer mix with different silica content.

Composition of geopolymers mix			Compressive strength (Mpa)			
Mix No.	$\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$	$\text{SiO}_2/\text{Al}_2\text{O}_3$	H ₂ O/ Na_2O	3day	7day	28day
S1	0.50	3.70	13.21	20.13	23.73	26.73
S2	0.50	3.85	12.14	25.74	30.27	35.47
S3	0.50	4.00	11.08	28.67	34.60	40.50
S4	0.50	4.15	10.07	29.00	33.57	39.75
S5	0.50	4.30	9.10	24.27	29.26	35.20

In test series-3, activator to fly ash ratio (A/F) was varied from 0.4 to 0.6. The alkali content and silica content was kept constant to 0.5 and 4.0 respectively. In test series-4, sand to fly ash ratio was varied from 0.5 to 3.0 and, A/F=0.5, $\text{SiO}_2/\text{Al}_2\text{O}_3=4.0$, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3=0.5$, were kept fixed. The curing temperature and duration for above

four test series was 85°C for 48hours. For test series-5, thermal curing temperature was varied from 6 to 72 hours and other parameters, i.e. S/F=1.5, A/F=0.5, were kept constant. For test series-6, the temperature of thermal curing was varied from 45°C to 120°C keeping S/F=1.5, A/F=0.5 constant. The duration of thermal curing was 48 hours.

2.2.2 Mixing, curing and testing procedure

For making geopolymers mortar specimens of various test series, fly ash and alkaline activating solution in desired proportion were first mixed together in Hobart mixer for five minutes. The sand was then slowly added and mixed for another five minutes. The fresh mortar mix had good consistency and glossy appearance. The fresh mortar was then filled in 50mmx50mmx50mm steel moulds and vibrated for two minutes on vibration table to remove entrapped air. The specimens were left undisturbed to room temperature for 120 minutes before curing in an oven at 85°C for 48 hours under atmospheric pressure and uncontrolled humidity conditions. The samples were demoulded after cooling down to room temperature and left to air curing (drying) until tested for direct compression in a digital compression testing machine at the age of 3, 7 and 28 days. The reported compressive strength is average strength of three specimens. Geopolymers paste specimens were prepared in similar manner with same chemical composition as that of respective mortar specimens for a particular test series. Cylindrical steel moulds of $\Phi 25 \times 50$ mm were used to cast paste specimens. The paste specimens were used to evaluate mineralogical and microstructure characteristics of the materials by means of XRD, and SEM. The X-ray diffractogram of powdered samples were obtained at same age of mortar specimens with a Philips diffractometer PW 1730, using CuK α radiation. A JEOL JSM 5400 scanning electron microscope was used for microstructure study.

3. RESULTS AND DISCUSSIONS

3.1 Effect of alkali ($\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$) content

The 3days, 7days and 28 days compressive strength for geopolymers mortar specimen with different alkali content is shown in Figure-3. It is observed that the compressive strength increased almost linearly with increasing alkali content of the mix. Higher alkali content ($\text{Na}_2\text{O}/\text{Al}_2\text{O}_3=0.62$) yielded highest compressive strength of 48.20MPa. The percentage increase in compressive strength from 3days to 28days after air curing (drying) is 44.69%, 41.26% and 29.32% for alkali content of 0.46, 0.54 and 0.62, respectively.

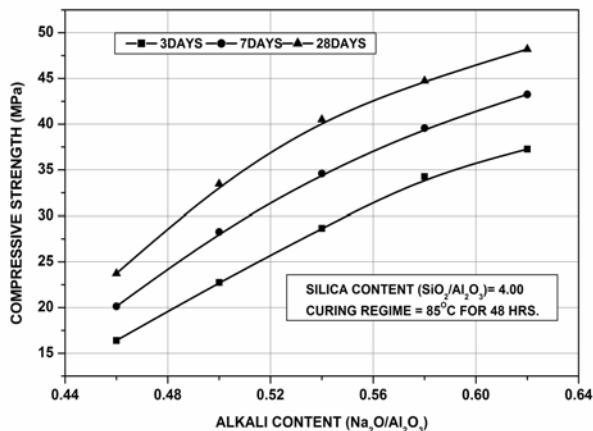


Figure-3. Alkali content vs. compressive strength.

The microstructure of specimens was viewed as geopolymers matrix comprising of gel phase and partially reacted spherical particles. The quantity of resultant alumino-silicate gel and interface between gel and sand particles in the geopolymers matrix is expected to have significant bearing on overall development compressive strength of the material [5]. The micrograph for geopolymers paste specimens were obtained at the age of 28days.

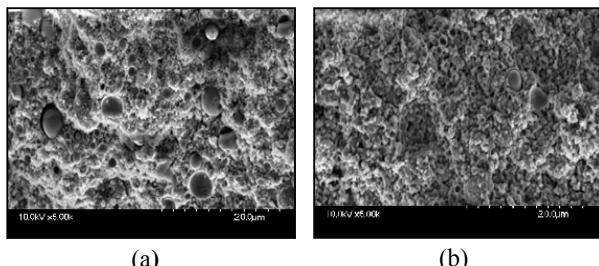


Figure-4. SEM Micrograph with $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratio
(a) = 0.46 and (b) = 0.62.

From micrographs shown in Figure-4, it can be observed that with increasing alkali content of geopolymers mix from 0.46 to 0.62, resulted in decrease of number and size of spherical-shaped un-reacted fly ash particles in the geopolymers matrix indicating formation of more aluminosilicate gel which resulted in increasing of compressive strength from 23.73MPa to 48.20MPa at the age of 28days.

Comparing the XRD spectra of the original fly ash with those of the hardened geopolymers materials shown in Figure-5, it is seen that the crystalline phases originally existing in the fly ash (quartz, mullite, magnetite etc.) have not been apparently altered by the activation reactions. However, the XRD pattern of sample A3, A4 and A5, shows formation of new crystalline phases (zeolites) like hydroxysodalite ($\text{Na}_4\text{Al}_3\text{Si}_3\text{O}_{12}\text{OH}$) and herschelite ($\text{NaAlSi}_2\text{O}_6 \cdot 3\text{H}_2\text{O}$) which contributes improvement in compressive strength.

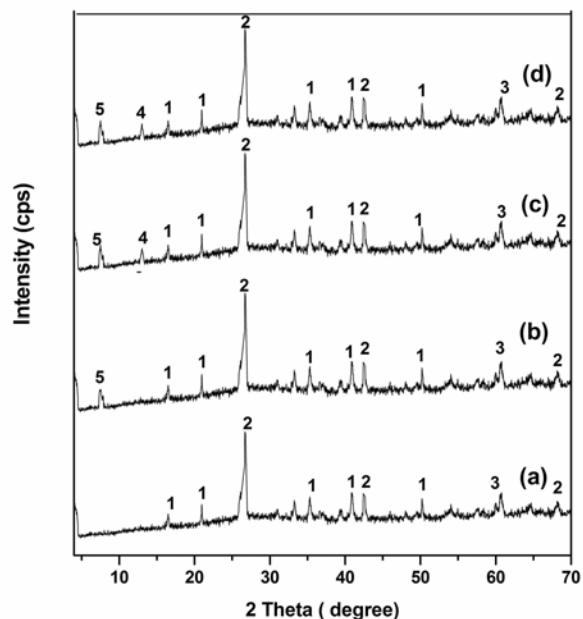


Figure-5. X-ray diffractogram of (a) fly ash and geopolymers specimens (b) A3, (c) A4, (d) A5; (1) quartz, (2) mullite, (3) magnetite, (4) hydroxysodalite, (5) herschelite.

3.2 Effect of silica ($\text{SiO}_2/\text{Al}_2\text{O}_3$) content

In test series-2, Geopolymers mortar specimens were prepared by varying silica ($\text{SiO}_2/\text{Al}_2\text{O}_3$) contents from 3.7 to 4.3. The 3days, 7days and 28days compressive strength for geopolymers mix with different silica content is shown in Figure-6.

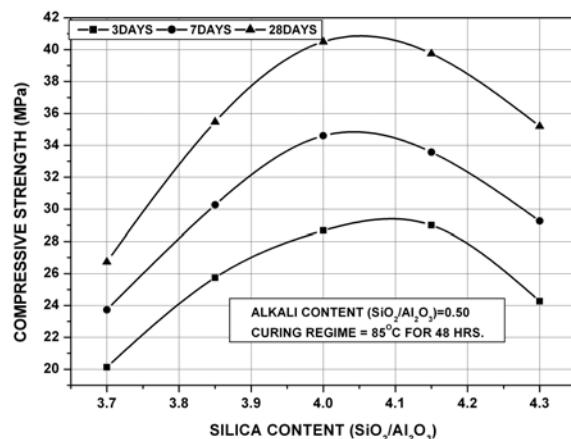


Figure-6. Silica content vs. compressive strength.

It is observed that the compressive strength increases almost linearly with silica content up to 4.0. Further increase in silica content of mix reduced compressive strength. Maximum compressive strength of 40.5MPa was obtained for silica content of 4.0 with



corresponding alkali content was 0.5. The silicate content controls the dissolution and polymerisation of Si and Al in aluminosilicate gel. It is found that the increase of silica content from 3.7 to 4.0 leads to an increase in the compressive strength which suggests a higher degree of reaction has taken place.

It is also found that at higher silica content beyond the threshold value of 4.0, leads to a reduction in reactivity showed by the decrease in the compressive strength. The setting time of geopolymers is also longer at higher silica content, suggested an inhibition in the reaction. It is found that at high silica content, the polymerisation of aluminosilicate gel is not favored. Instead, the dissolved precursors tend to form zeolites which are weaker in compressive strength.

The SEM micrographs of geopolymer composite with silica content ($\text{Si}_2\text{O}/\text{Al}_2\text{O}_3$) = 3.7 and 4.0 are shown in Figure-7. The bigger fly ash particles are almost dissolved or reduced to smaller size at higher silica content showing denser and finer microstructure, which indicates a higher degree of reaction resulted in increasing compressive strength from 26.73MPa to 35.20MPa.

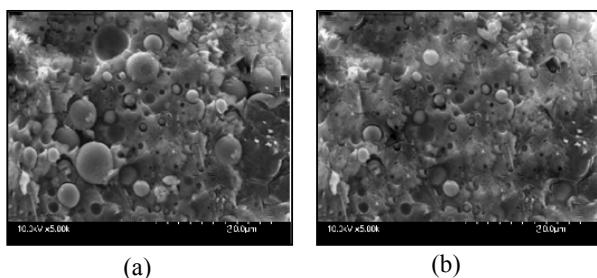


Figure-7. SEM micrograph with $\text{Si}_2\text{O}/\text{Al}_2\text{O}_3$ ratio of (a) = 3.7 and (b) = 4.3.

3.3 Effect of water to geopolymer solid ratio

Water content in initial mix plays a vital role in synthesis of geopolymeric material. It acts as the medium for dissolution and polymerisation of Al and Si precursors. The compressive strengths of geopolymer formulations based on water to Geopolymer solid ratios varying from 0.157 to 0.366 are shown in Figure-8.

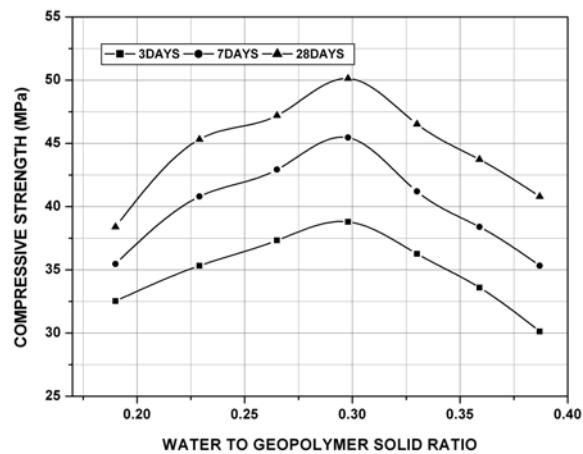


Figure-8. Water solid ratio v/s compressive strength.

Results indicated that lower the water content in the mix, higher was the compressive strength. However, there are practical limitations to reducing water content of mix for obtaining desired workability. Lower water content greatly raises the viscosity of the liquid component reducing dispersal and ease of mixing. The compressive strength continuously improved till water to geopolymer solid ratio of 0.3. However, further decrease in water content reduced compressive strength. It is reasonable to suggest that increasing water content beyond 3.0 will prevent the system from reaching super saturation, thus the dissolution of precursors is likely to be prolonged resulting in slow gel formation and reduction in strength.

3.4 Effect of sand to fly ash ratio

Filler material like sand reduces cracking and improves porosity of the composite. Its addition also reduces the quantity of binder paste making the resultant material more economical. In test series-4, sand content (sand to fly ash ratio) of the geopolymer mix was varied from 0.5 to 3.0. The effect of sand content geopolymer mix on compressive strength is shown in Figure-9.

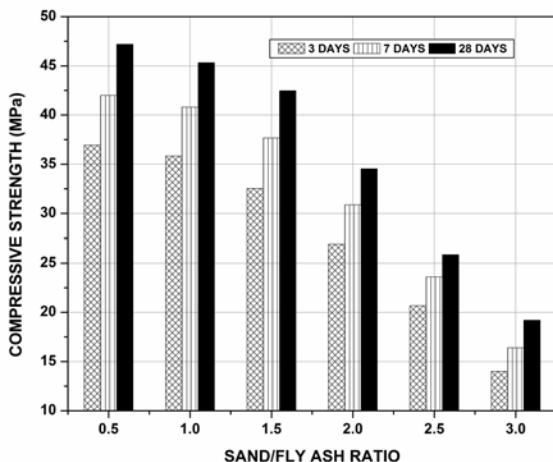


Figure-9. Sand/Fly ash ratio vs. compressive strength.

It is observed that, there is no much variation in compressive strength up to sand to fly ash ratio of 1.5, but further increases in sand content drastically reduced the compressive strength to 18.5MPa at sand to fly ash ratio of 3.0.

3.5 Curing conditions

Curing conditions are defined as the external environmental conditions applied to enhance geopolymerisation. The Effect of curing temperature and duration of heat curing on compressive strength has been investigated.

3.5.1 Effect of curing temperature

For studying the effect of curing temperature on compressive strength, the specimens with alkali content of 0.62 and silica content of 4.0 were cured for 48 hours varying curing temperatures from 45°C to 120°C under atmospheric pressure and uncontrolled humidity conditions. The effect of the curing temperature on compressive strength is shown in Figure-10.

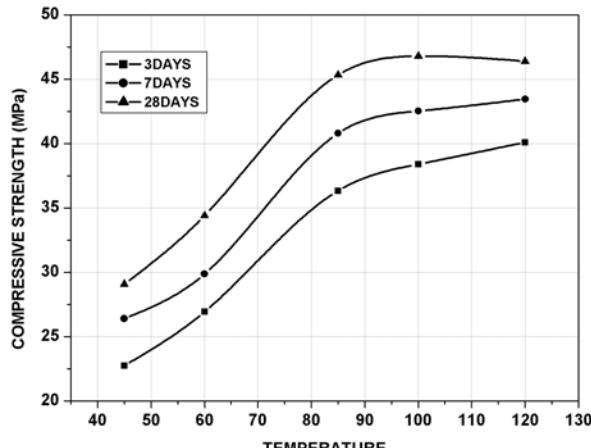


Figure-10. Curing temperature vs. compressive strength.

For optimum temperature of 85°C, the maximum compressive strength obtained was 48.20Mpa. With increase in curing temperature from 45°C to 85°C increased compressive strength almost linearly. However, no substantial improvement in strength was observed beyond 85°C.

3.5.2 Effect of duration of thermal curing

In this trial, test specimens with alkali content, silicate content and water to geopolymer solid ratio of 0.62, 4.0 and 0.228 respectively, were cured in oven under atmospheric pressure and uncontrolled humidity conditions at 85°C for a varying duration of 4 to 72 hours. The effect of duration of heat curing on compressive strength is shown in Figure-11.

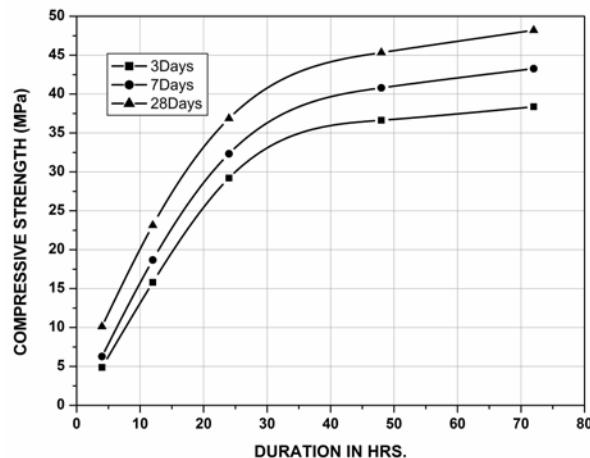


Figure-11. Curing duration vs. compressive strength.

The compressive strength increases with increase in curing time. Maximum compressive strength of 40.8MPa was obtained with 48 hours of thermal curing. Further increase of curing time did not result in appreciable increase of compressive strength.

4. CONCLUSIONS

Based on the results of experimental work following conclusions can be drawn:

- Alkali content, silica content and water content of geopolymer mix was found to affect the compressive strength significantly;
- Water plays important role during dissolution, polycondensation and hardening stages of geopolymerisation. Reduction of water content improved compressive strength;
- The choice of curing temperature and curing time affected final compressive strength of geopolymer. Heat overcomes activation barrier and enhances the dissolution rate of solid aluminosilicate material. The increase in compressive strength was observed with



- increasing duration of heat curing and curing temperature;
- The microstructure of geopolymer specimens may be viewed as composites comprising of aluminosilicate gel phase and partially reacted fly ash particles;
 - The mineralogical studies on hardened geopolymer composite performed by (XRD) indicated formation of a new amorphous alumino-silicate phases like hydroxysodalite and herschelite;
 - Addition of fine aggregate up to 50% did not increase the compressive strength but more than 50% addition of aggregates decreased compressive strength; and
 - The Geopolymer binders may be treated as future environment friendly alternative to Portland cement in certain industrial applications.
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