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Development of Geopolymer Mortar From Fly Ash And Characterization of Its Zeolitic Phases

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ABSTRACT
Geopolymers produced by aluminosilicate source materials with an alkaline activator solution promised an excellent properties akin to the existing construction material. Among the various uses of fly ash, its bulk utilization is possible only in geotechnical engineering applications. This necessitates characterization of the fly ash with reference to geotechnical applications. The development of alkali-activated binders seems to present a greener alternative to OPC. The geopolymer mortar is manufactured by replacing cement fully with processed low calcium fly ash which is chemically activated by alkaline solutions like sodium silicate and sodium hydroxide. The geopolymer mortar has been prepared with ennore sand and Indian fly ash mixed with alkali activator fluid. The effect of curing temperature and duration of curing on compressive strength of geopolymer mortar was studied. 72 hours curing at about 120^{o}C seems to give optimum compressive strength. The Standardize cubes were casted using 50:50 sand and fly ash ratio mixed with alkali activator fluid . All the specimens were cured in oven at 60, 90 and 120 ^{o}C for 12, 24 , 48 and 72 hour's duration respectively . Test results show that the compressive strength increases with increase in duration and temperature of oven curing**.** The characterization of zeolitic phases of alkali activated mortar was done with Fourier transform infrared spectroscopy**(** FT-IR) . The mineralogical transformation was evaluated with the help of X-ray diffraction analysis (XRD). The thermal characteristics of hardened geopolymer mortar was examined with the help of Differential Scanning Calorimeter **(**DSC) .

Keywords – Alkali activator , Compressive Strength , Fly ash, Geopolymer Mortar, Mineralogy , Zeolite.

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I. INTRODUCTION

Fly ash, an industrial by-product, has been one of the most important raw materials for various types of bulk applications (viz., manufacturing of pozzolana cement, filler material for reclamation of low lying areas, manufacturing of fly ash bricks) [1-4]. In the light of increasing quantity of fly ash, with an increase in demand of electrical energy and hence thermal power plants, the major challenges in front of the researchers and planners have been to solve various environmental problems that arise due to unused and surplus quantity of the fly ash [5-9].

With this in view, focus of the researchers has turned to venture into the potential areas of specific and value added applications of the flyash. One of the promising areas in this context is synthesis of Geopolymers containing zeolotic phases from flyash [10-13].

On the other side the manufacturing of cement demand burning of huge quantities of fuel as well as significant emissions of CO_2 resulting from the decomposition of limestone that consequently resulted in severe environmental impact that is estimated by one ton of CO_2 per ton of cement. Geopolymerization technology is an effective method for converting wastes (containing alumina and silica) into useful products. It can reduce CO_2 emissions significantly from the cement industry. The geopolymerization process usually starts with source materials like fly ash based on alumina/silicate in addition to alkaline liquids[14].

Recently, the potential for replacing the OPC with fly ash has been explored extensively by researchers. Geopolymer is a term used to describe inorganic polymers based on aluminosilicate, which can be produced by reacting pozzolanic compounds or aluminosilicate source materials with highly alkaline solutions[15-17]. The alumino silicate source can be a natural mineral or by-product materials, such as kaolinite, clay, fly ash, silica fume, rice husk ash, or slag. These raw materials must be rich in silicon (Si) and aluminum (Al) in order to produce geopolymer.[18].

Fly ash is suitable for use as a geopolymer source material because it consists mostly of glassy, hollow and spherical particles[19]. Fly ash-based geopolymer cement and concrete have been studied extensively, and they are well known for their properties, which are better than those of normal concrete due to their lower creep, lower shrinkage, better fire and acid resistance, and resistance to acid, chlorides and sulfate attack.[20]

Mineralogical and morphological composition were investigated by X-ray diffraction, XRD and Scanning electron microscopy, SEM [21-22]respectively, whereas, the characteristics of zeolite structure was investigated by resorting to Fourier Transform Infra-red Spectroscopy, FTIR [23-25].

This paper presents the synthesis of geopolymer mortar using fly ash as source material and annore sand followed by its characterization by identified zeolitic phases during geopolymerization. The geopolymer was synthesized with fly ash, sodium silicate and sodium hydroxide solutions.

II. MATERIALS AND METHODOLOGY

2.1. Materials

- Fly ash (Obtained from Dadri Thermal Power Plant, Dadri, UP, India)
- Analytical grade chemicals viz. sodium silicate-sodium hydroxide, sodium silicate-potassium hydroxide etc.

Geopolymeric cubes were developed using fly ash, sand and sodium hydroxide solution The chemical composition analysis of fly ash (as per IS 1727-2004) is presented in Table-1.

Table-1 Chemical Composition of Fly ash

Parameters	% by weight
Silica, SiO_2	57.95
Alumina ,Al_2O_3	31.78
Iron Oxide , Fe_2O_3	4.30
Calcium Oxide ,CaO	1.10
Magnesia, MgO	0.51
Sodium Oxide, as Na_2O	0.15
Potassium .Oxide, as K_2O	0.28
Loss on ignition, LOI	2.65
Sulphate as SO_3	0.075

2.2. Experimental

The combination of sodium silicate (Na_2SiO_3) and NaOH solution was used as alkaline activators. The alkaline activator was prepared by mixing a sodium silicate and NaOH solution with a concentration of 10 M. The ratio of fly ash to alkaline activator (Na_2SiO_3/NaOH) ratio were fixed as 2.5 and applied for all samples. The fly ash was then mixed with the alkaline activator in the mixer. Sand is small aggregates in geopolymer mortar. Cubes were casted with taking sand –fly ash ration fixed (50:50) keeping NaOH- concentration 10 M. The Mortar resulting from mixing the fly ash with sand and alkaline solution was poured in to metallic prismatic molds, (Cube Area 14.44 cm2) which were later kept in an oven. The cubes were cured at different temperature for different time intervals in order to achieve optimum compressive strength after curing the specimens cubes were subjected to compressive strength and durability study under different aggressive chemical environment. The experimental steps regarding preparation of alkaline activator mix , casting of cubes and curing are presented in fig.1-3.

Figure.1. Preparation of Geopolymer Mortar Mix.

Figure.2. Casting of Geopolymer Mortar Cubes.

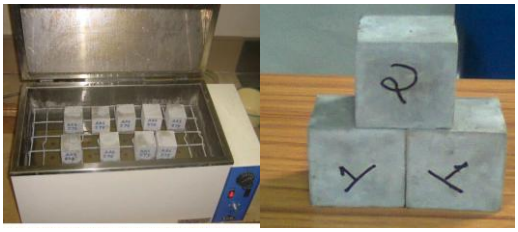

Figure.3.Curing of Geopolymer Mortar Cubes.

Mortar cubes were prepared and cured at different temperature i.e.60, 90 and 120^oC for different time intervals of, 12, 24, 48 and 72 hours duration. The compressive strength were determine using Universal Testing Machine (UTM. (Fig.4)

Figure.4. Compressive Strength Test with UTM.

The sample mix with optimum compressive strength sample was then subjected to Fourier Transform Infrared Spectroscopy analysis(FT-IR) analysis using model IR 200 model of Thermo Nicolet spectrometer with a DTGSBr detector (Fig.5) for understanding the Zeolite phase transformation during geopolymerization.

Figure.5.Fourier Transform Infrared Spectrometer FT-IR.

The mineralogical analysis was done with x ray diffractometer , XRD analysis was done by using GBC Scientific Equipment (Australia), Model - EMMA 125 diffractometer XRD Model (Fig.6)

Figure.6. X-Ray Diffractometer (XRD)

The effect of heat on phase transformation was done with Differential scanning calorimeter equipment (DSC) Mettler Toledo (Fig.7).

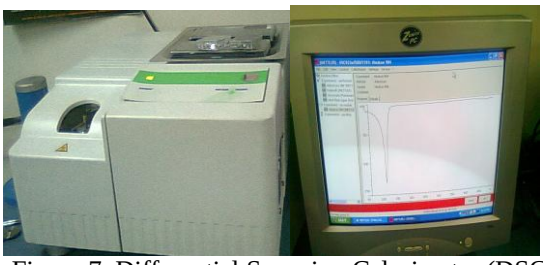

Figure.7. Differential Scanning Calorimeter (DSC).

III. RESULTS & DISCUSSIONS

3.1. Compressive Strength

The results of compressive strength of mortar cubes cured at variable temperatures and for different time intervals are presented in Table-2.

Table 2.Compressive strength Results of Geopolymer Mortar Cubes.

Sl. No.	**Duration of curing in hours**	**Temp. in ^{o}C**	**Compressive strength** (MPa)
C-1	12	60	15.92
C-2		90	16.96
C-3		120	18.00
C-5	24	60	17.17
C-6		90	17.65
C-7		120	19.04
C-8	48	60	21.46
C-9		90	22.50
C-10		120	24.23
C-11	72	60	21.81
C-12		90-	22.80
C-13		120	24.52

The maximum compressive strength of 24.52 Mpa was achieved with geopolymer mortar cube exposed to heat curing at 120^{O}C for 72 hours duration. The

effect of curing time on compressive strength is presented in fig.8.

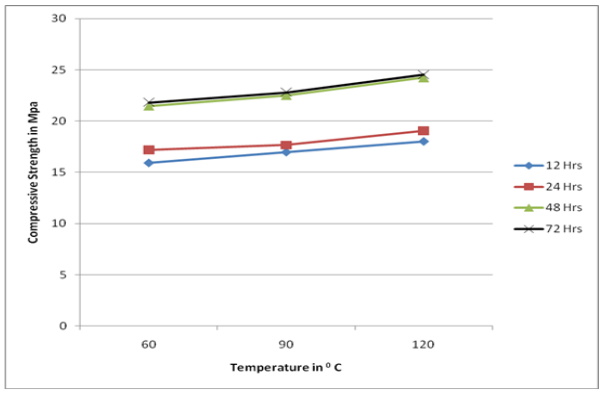

Figure.8.Compressive strength with different curing time and Temperatures.

3.2 XRD Analysis

The XRD pattern of original fly ash mainly represents the presence of crystalline quartz and mullite (Fig.9.). Fly ash, after treatment gives several sharp diffraction peaks, which are different from those present in the untreated one. Different crystalline zeolitic phases present in the treated fly ashes were identified using International Centre for Diffraction Data (ICDD) library . The XRD pattern of geopolymer mortar shows that the amorphous phases originally existing in the fly ash have been apparently altered by the alkali activation reaction, however diffraction lines associated with the presence of quartz appear more intensely which is due to presence of sand particles in the matrix also. The XRD pattern of geopolymer mortar cube (Fig.10) also shows formation of new minor crystalline phases which is similar to Zeolitic phases which contributes improvement in compressive strength.

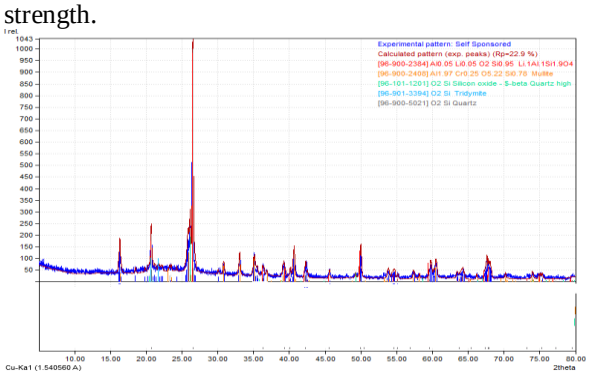

Figure.9. XRD Pattern of Fly Ash.

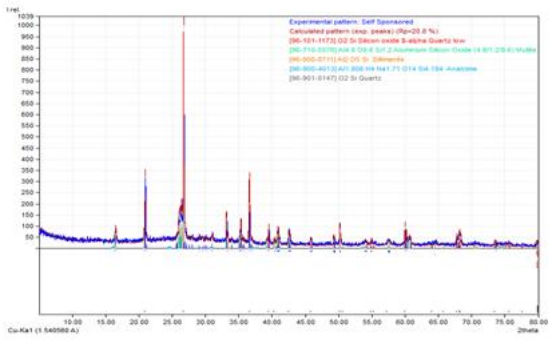

Figure.10. XRD Pattern of Geopolymer Mortar Cube.

3.3. Observation of FT-IR conducted on Fly ash and Geopolymer Mortar Cube.

FT-IR spectroscopic analysis of fly ash and geopolymer mortar cubes are presented in fig.11.

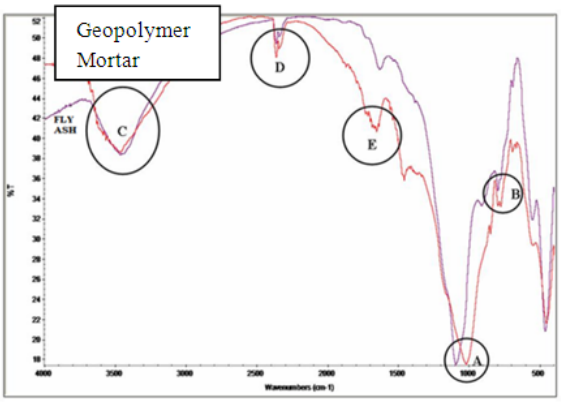

Figure.11.FT-IR Pattern of Fly ash and Geopolymer Mortar Cube.

Using samples in powder form, infrared bands were recorded for wavelengths between 4000 cm^{-1} to 650 cm^{-1} . The specimen for testing was prepared using the KBr pellet technique. Potassium Bromide (KBr) and sample powders were put into a mold and compressed by using cold press machine for 2 minutes at a load of 4 tons. It is observed that there are significant changes in the intensities and the width of various bands due to interaction of fly ash with alkali.

The IR spectrum of fly ash shows main absorption bands at 1004, 1428, 2358, and 3715 cm^{-1}. The absorbance band in between the wave numbers 980–1320 cm–1 in the IR spectrum of fly ash and treated fly ash represents the presence of substituted Al atoms in the tetrahedral forms of silica frameworks. It can be noticed that the there is increase in the intensity and the broadness of the stretching *v*(O-H) band at 3452 cm-1 after the treatment. This can be attributed to an increase in

hydrated products due to the reaction between amorphous silicates (i.e., glass) and the alkali.

In addition, a decrease in the intensity corresponding to the bending *v*(O-H) band from 1605 to 1653 cm-1, reveals loss of adsorbed water and the water of hydration due to the treatment. Moreover, asymmetrical stretching of TO4 (=SiO_4 or AlO_4) band (broad-strong) corresponding to the variation infrequency from 1093 to 1014 cm^{-1} and the increase in its sharpness confirms synthesis of silicates This can be attributed to substitution of Si^{4+} by Al^{3+} in some of the tetrahedral framework of the primary building units of the alumino-silicates and their external linkage with the Na^{+} ions due to their interaction with the alkali. Further, it is observed that there is a significant decrease in the intensity of bending modes of the vibration of the Si-O-Al bonds corresponding to 433 cm^{-1} Hence, it can be opined that fly ash-alkali interaction results in synthesis of a fly ash zeolite compared to the similar structure of quartz present in the fly ash. Based on the FTIR spectrum, it can be observed that there is presence of pore openings corresponding to frequency range from 420 to 400cm-1 in the geopolymer mortar which can be attributed to the dissolution of the minerals (viz., quartz and mullite) present in the flyash and precipitation of zeolite. The broad component at 1004 cm^{-1} is due to the Si-O-Si and Al-O-Si asymmetric stretching vibration and it becomes sharper and shifts towards lower frequencies in lightweight geopolymer. This indicates the formation of a new product (the amorphous aluminosilicate gel phase) due to dissolution of fly in alkaline activator.

3.4. Observation of Differential Scanning Calorimeter Analysis (DSC).

In DSC the plot obtained is known as a DSC curve (Fig.12) and shows the amount of heat applied as a function of temperature or time.

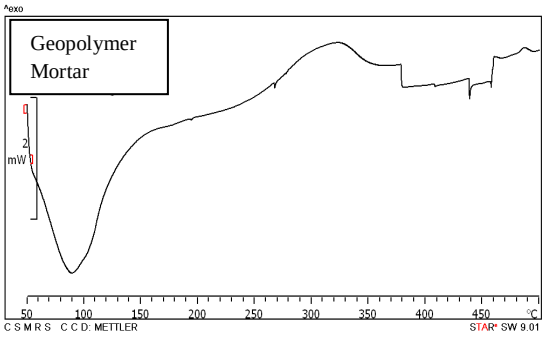

Figure12.DSC Pattern of Hardened Geopolymer Mortar.

Differential Scanning Calorimeter (DSC) are commonly used to monitor the peak formation and enthalpy of geopolymerization process. Geopolymerization consists of several chemical reactions that has been reported widely as an exothermic reaction. The amount of heat released was determined by using Differential Scanning Calorimeter. Only small amount of geopolymer mortar paste (less than 20 milligram) was required and it was directly inserted into a small aluminium crucible with lid in which also referred as sample pan. The weight of empty sample pan and the weight of sample pan with geopolymer paste was weighed to ensure no excessive weight of geopolymer mortar paste contained in the pan as this will cause destruction to the DSC. As shown in figure 12, DSC curves demonstrate a small endothermic peak at 50^{o}C-150°C, corresponding to the evaporation of free water. After that, a stronger exothermic peak appears at the range of 300^{o}C -500°C, which is attributed to the phase transition of mineral compositions. In general, the difference between the width and height of peak can reflect the change of chemical constituent and proportion of geopolymer formulation.

IV. CONCLUSION

- Alkali activated fly ash can be used as an alternative binder system to cement mortar in various structural applications.
- The treatment of fly ash with alkaline activators initiates the geopolymerization reactions which subsequently form various zeolitic phases producing amorphous to crystalline geopolymer system.
- The strength properties of geopolymer mortar is dependent on curing temperature and time period of curing. It was observed that optimum compressive strength was achieved at curing temperature of 120^{O}C for 72 hours.
- The comparative XRD pattern of fly ash and Geopolymer mortar shows that the amorphous phases originally existing in the fly ash have been apparently altered by the alkali activation reaction. Presence of new minor crystalline phases which is similar to Zeolitic phases confirms the geopolymerization reactions and appreciable compressive strength.
- FT-IR pattern also shows significant changes in the intensities and the width of various bands due to interaction of fly ash with alkali. The FT-IR interpretation further confirms the synthesis of silicates and formation of new zeolitic phases in alkali activated fly ash geopolymer mortar.
- Differential Scanning Calorimeter (DSC) study also reveals that initial endothermic peaks related to evaporation of free water which

further followed by exhothermic peak which is attributed to the phase transition of mineral compositions and also confirms the thermal stability of geopolymer mortar.

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