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Strength Improvement of Geopolymer Concrete Treated with GGBS over Conventional Concrete

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Abstract

Portland cement production is under critical review due to the high amount of carbon dioxide gas released to the atmosphere. But at the same time, disposal of huge quantity of fly ash generated from the power plants is also becoming a big burning problem. This is detrimental to animal and plant life, since it pollutes the environment as well as it requires large area for its disposal, when availability of land get scarce day by day. Most of the plants now are facing shortage of dumping space of these waste materials. Most of this by product material is a currently dumped inland fill, thus creating a threat to the environment. In recent years attempts to increase the utilization of fly ash to partially replace the use of Portland cement in concrete are gathering momentum.

Efforts are urgently underway all over the world to develop environmentally friendly construction materials, which make minimum utility of fast dwindling natural resources and help to reduce greenhouse gas emissions. In this connection, Geopolymers are showing great potential and several researchers have critically examined the various aspects of their viability as binder system. Geopolymer concretes (GPCs) are new class of building materials that have emerged as an alternative to Ordinary Portland cement concrete (OPCC) and possess the potential to revolutionize the building construction industry. Considerable research has been carried out on development of Geopolymer concretes (GPCs), which involve heat curing. A few studies have been reported on the use of such GPCs f or structural applications.

An experimental investigation was carried out to study the material and mixture proportions; the manufacturing processes, the fresh and hardened state characteristics of fly ash based geo polymer concrete are evaluated. In the present study the compression behaviour of geo polymer concrete was assessed and the behaviour was found to be considerably more than that of conventional concrete.

Keywords: ***Geopolymer concrete, Alkaline Solutions, Portland Cement, Fly ash.***

Introduction

Concrete usage around the world is second only to water. Ordinary Portland cement (OPC) is conventionally used as the primary binder to produce concrete due to its availability of the raw materials over the world, its ease for preparing and fabricating in all sorts of conceivable shapes. The application of concrete in the realms of infrastructure, habitation, and transportation has greatly promoted the development of civilization, economic progress, and stability and of quality of life. Nowadays with the occurrence of high performance concrete (HPC); the durability and strength of concrete have been improved largely.

However, due to the restriction of the manufacturing process and the raw materials, some inherent disadvantages of Portland cement are still difficult to overcome.

The environmental issues associated with the production of OPC are well known. The amount of the carbon dioxide released during the manufacture of OPC due to the calcinations of limestone and combustion of fossil fuel is in the order of one ton for every ton of OPC produced. In addition, the extent of energy required to produce OPC is only next to steel and aluminum.

When used as a partial replacement of OPC, in the presence of water and in ambient temperature, fly ash reacts with the calcium hydroxide during the hydration process of OPC to form the calcium silicate hydrate (C-S-H) gel. The development and application of high volume fly ash concrete, which enabled the replacement of OPC up to 60% by mass is a significant development.

On the other hand, the abundant availability of fly ash worldwide creates opportunity to utilize this by-product of burning coal, as a substitute for OPC to manufacture cement products.

The geopolymer technology is proposed by Davidovits and gives considerable promise for application in concrete industry as an alternative binder to the Portland cement. In terms of reducing the global warming, the geopolymer technology could reduce the CO2 emission in to the atmosphere, caused by cement and aggregate industries about 80%. In this technology, the source material that is rich in silicon (Si) and Aluminum (Al) is reacted with a highly alkaline solution through the process of geopolymerisation to produce the binding material. The term "geopolymer‟ describes a family of mineral binders that have a polymeric silicon-oxygen-aluminum framework structure, similar to that found in zeolites, but withoutthe crystal structure. The polymerization process involves a substantially fast chemical reaction under highly alkaline condition on Si-Al minerals that result in a three-dimensional polymeric chain and ring structure consisting of Si-O-Al-O bonds. Geopolymer concrete is emerging as a new environmentally friendly construction material for sustainable development, using flash and alkali in place of OPC as the binding agent. This attempt results in two benefits. i.e. reducing CO2releases from production of OPC and effective utilization of industrial waste by products such as flash, slag etc by decreasing the use of OPC.

Low-Calicum Fly Ash-Based Geopolymer Concrete
In the present work, low-calcium (ASTM class F) fly ash-based geopolymer is used as the binder, instead of Portland or other hydraulic cement paste, to produce concrete. The fly ash-based geopolymer paste binds the loose, fine aggregates and other un-reacted materials together to form the geopolymer concrete, with or without the presence of admixtures. The manufacture of geopolymer concrete is carried out by using the usual concrete technology methods.

As in the case of ordinary Portland cement concrete, the aggregates occupy about 75-80% by mass, in geopolymer concrete. The silicon and aluminium in the low-calcium (ASTM class F) fly ash react with an alkaline liquid that is a combination of sodium silicate and sodium hydroxide solutions to form the geopolymer paste binds the aggregates and other un-reacted materials.

Objectives of the Work

As mentioned earlier, most of the published research on geopolymers studied the behaviors of pastes using various types of source materials. The present study dealt with the manufacture and the short-term properties of low-calcium (ASTM Class F) fly ash based geopolymer concrete.

The aims of the study are:

- To study the short term engineering properties of low calcium fly ash based geopolymer concrete when fly ash is partially replaced by cement.
- To study the compression strength of geo polymer concrete

Literature Review

This chapter presents the background to the needs for the development of alternative binders to manufacture concrete and the use of fly ash in concrete. The available published literature on geopolymer technology is also briefly reviewed in this chapter

Concrete and Environment

The trading of carbon dioxide (CO2) emissions is a critical factor for the industries, including the cement industries, as the greenhouse effect created by the emissions is considered to produce an increase in the global temperature that may result in climate changes.

The "tradable emissions" refers to the economic mechanisms that expected to help the countries worldwide to meet the emission reduction targets established by the 1997 Kyoto protocol. Speculation has arisen that one ton of emissions can have a trading value about US$10 (Malhotra 1999; Malhotra 2004)

The climate change is attributed to not only the global warming, but also to the paradoxical global dimming due to the pollution in the atmosphere. Global dimming is associated with the reduction of the amount of sunlight reaching the earth due to pollution particles in the air blocking the sunlight. With the effort to reduce the air pollution that has been taken into implementation, the effect of global dimming may be reduced; however it will increase the effect of global warming (Fortune 2005).

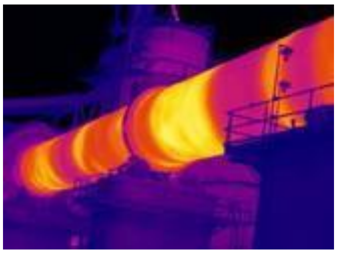
From this point of view, the global warming phenomenon should be considered more seriously, and any action to reduce the effect should be given more attention and effort.

The production of cement is increasing about 3% annually (McCaffrey 2002). The production of one ton of cement liberates about one ton of CO2 to the atmosphere, as the result of de-carbonation of limestone in the kiln during manufacturing of cement and the combustion of fossil fuels (Roy 1999).

In order to produce environmentally friendly concrete, Mehta (2002) suggested the use of fewer natural resources, less energy, and minimize carbon dioxide emissions. He categorized these short-term efforts as „industrial ecology" the long-term goal of reducing the impact of unwanted by-products of industry can be attained by lowering the rate of material consumption. Likewise, McCAFFREY (2002) suggested that the amount of carbon dioxide (CO2) emissions by the cement industries could be reduced by decreasing the amount of calcined material in material in cement, by decreasing the amount of cement in concrete, and by decreasing the number of buildings using cement.

An important ingredient in the conventional concrete is the Portland cement. Actual production of Portland cement contributes 13.5 billion tons of carbon dioxide per year (1 ton of carbon dioxide for each ton of produced cement) which is equivalent to 7% of the total global emission of carbon dioxide to the atmosphere. Geo polymer is made out of waste materials like fly ash, therefore does not have an industry of it and does not contribute to carbon dioxide emissions. The Portland cement production process is one of the most energy consuming mass production processes.

A mixture of powdered raw materials requires heating to over 14000 C to obtain cement powder, with its corresponding high use of fuels. Geo polymer, on the other hand, can be produced out of waste products like fly ash, or out of claimed kaolin (meta-kaolin) which consumes significantly less energy. In order to produce environmentally friendly concrete, Mehta (2002) suggested the use of fewer natural resources, less energy, and minimize carbondioxide emissions. He categorized these short-term efforts as „industrial ecology". The long-term goal of reducing the impact of unwanted by-products of industry can be attained by lowering the rate of material consumption. Likewise, McCaffrey (2002) suggested that the amount of carbon dioxide (CO2) emissions by the cement industries can be reduced by decreasing the amount of claimed material in cement, by decreasing the amount of cement in concrete, and by decreasing the number of buildings using cement.



Geopolymer concrete

The term „geo polymer‟ was first introduced by Davidovits in 1978 to describe a family of mineral binders with chemical composition similar to zeolites but with an amorphous microstructure. Unlike ordinary Portland/pozzolanic cements, geo polymers do not form calcium- silicate-hydrates (CSHs) for matrix formation and strength, but utilize the polycondensation of silica and alumina precursors to attain structural strength. Two main constituents of geo polymers are: source materials and alkaline liquids. The source materials on alumino-silicate should be rich in silicon (Si) and Aluminium (Al).They could be by-product materials such as fly ash, silica fume, slag, rice-husk ash, red mud, etc.

It is the inorganic alumino-silicate polymer synthesized from predominantly silicon (si) and Aluminum (Al) materials (or) by products such as fly ash. The term geo polymer represents the mineral polymers resulting from the geochemistry. The process involves a chemical reaction under highly alkaline conditions on Si-Al minerals, yielding polymeric Si-O-Al-O bonds in amorphous form. It has been reported that geo polymer material does not suffer from alkali-aggregate reaction even in the presence of high alkalinity, and possesses excellent fire resistant.

The silicon and the aluminium in the fly ash are activated by a combination of sodium hydroxide and sodium silicate solutions to form the geo polymer paste that binds the aggregates and other un-reacted materials.

The polymerisation process involves a substantially fast chemical reaction under alkaline condition on Si-Al minerals, that results in a three-dimensional polymeric chain and ring structure consisting of Si-O-Al-O bonds, as follows (Davidovits 1999):

Mn [-(SiO2) z–AlO2] n. wH2O --------------------- 26

Where: M = the alkaline element or cation such as potassium, sodium or calcium.
The symbol "–"indicates the presence of a bond.
"n" is the degree of poly condensation or polymerisation.
"z"is1, 2, 3, or higher, up to 32.

The schematic formation of geo polymer material can be shown as described by Equations

- The chemical reaction of geopolymerisation process comprises the following steps -
- Dissolution of Si and Al atoms from the source material through the action of hydroxide ions.
- Transportation or orientation or condensation of precursor ions into monomers.
- Setting or polycondensation/polymerization of monomers into polymeric structures. However, these three steps can overlap with each other and occur almost simultaneously, thus making it difficult to isolate and examine each of them separately Palomo et al. 1999

A geopolymer can take one of the three basic forms

- Poly (sialate), which has [-Si-O-Al-O-] as the repeating unit.
- Poly (sialate-siloxo), which has [-Si-O-Al-O-Si-O-] as the repeating unit.
- Poly (sialate-disiloxo), which has [-Si-O-Al-O-Si-O-Si-O-] as the repeating unit. Sialate is an abbreviation of silicon-oxo-aluminate

The last term in Equation 26.2 reveals that water is released during the chemical reaction that occurs in the formation of geo polymers. This water, expelled from the geo polymer matrix during the curing and further drying periods, leaves behind discontinuous nano-pores in the matrix, which provide benefits to the performance of geo polymers.

The water in a geo polymer mixture, therefore, plays no role in the chemical reaction that takes place; it merely provides the workability to the mixture during handling. This is in contrast to the chemical reaction of water in a Portland cement concrete mixture during the hydration process.

Davidovits (1999) proposed the possible applications of the geopolymers depending on the molar ratio of Si to Al, as given in table

Table 2.1: Applications of geopolymers based on (Si/Al) ratio

`	Application
1	Bricks, ceramics, fire protection
2	Low CO_2 cements, concrete, radioactive & toxic waste encapsulation
3	Heat resistance composites, foundry equipments, fiber glass composites
>3	Sealants for industry
20<Si/Al<35	Fire resistance and heat resistance fiber Composites

Fly ash

According to the American concrete Institute (ACI) committee 116R, fly ash is defined as „ the finely divided residue that results from the combustion of ground or powdered coal and that is transported by flue gasses from the combustion zone to the particle removal system"

(ACI committee 232 2004) .fly ash is removed from the combustion gases by the dust collection system, either mechanically or by using electrostatic precipitators, before they are discharged to the atmosphere. Fly ash particles are typically spherical, finer than Portland cement and lime, ranging in diameter from less than 1 µm. to not more than 150 µm.

The types and relative amounts of in combustible matter in the coal determine the chemical composition of fly ash the chemical composition is mainly composed of the oxides of silicon (SiO2) , aluminum (Al2O3) , iron (Fe2O3) , and calcium (Cao) whereas magnesium, potassium, sodium, titanium, and sulphur are also present in a lesser amount. The major influence on the fly ash chemical composition comes from the type of coal. The combustion of sub-bituminous coal contains more calcium and less iron than fly ash from bituminous coal. The physical and chemical characteristics depend on the combustion methods, coal source and particle shape. The chemical compositions of various fly ashes show a wide range, indicating that there is a wide variations in the coal used in power plants all over the world.

Fly ash that results from burning sub-bituminous coals is referred as ASTM class C fly ash or high-calcium fly ash, as it typically contains more than 20 percent of CaO. On the other hand, fly ash from the bituminous and anthracite coals is referred as ASTM class F fly ash or low-calcium fly ash. It contains of mainly an alumino-silicate glass, and has less than 10 percent of CaO . The color of fly ash can be taken to dark grey, depending upon the chemical and chemical and mineral constituents (Malhotra and Ramezanianpour 1994; ACAA 2003). The typical fly ash produced from Australian power stations is light to mid-grey in color, similar to the color of cement powder. The majority of Australian fly ash falls in the category of ASTM Class F low calcium fly ash, and contains 80 to 85 % of silica and alumina (Heidrich 2002).

Pozzolanic Action of Fly Ash

Fly ashes exhibits pozzalanic activity. The American society for testing and Materials (ASTM) defines a pozzolans as a siliceous and aluminous materials which in itself possesses little or no cementious value but which will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperature to form compounds possessing cementious properties. Fly ash containing metastable alumino silicates reacting with calcium ions in the presence of moisture to form calcium silicates hydrates.

The inclusion of fly ash in concrete affects all mechanical properties of concrete both at green state and hardened state. As a part of the composite concrete mass, fly ash acts both as a fine aggregate and as a cementious component. It influences the rheological properties of the fresh concrete and the strength, finish, porosity and durability of the hardened mass, as well as the cost and energy consumed in manufacturing the final product.

Geopolymer Binders and Applications

The term "Geopolymers" was coined by Davidovits to represent the mineral polymers resulting from geochemistry or in describing synthetic minerals similar to those that form in the earth's crust. Geopolymer is an inorganic alumino-silicate polymer synthesized from predominantly silicon and aluminum materials of geological origin or by-product materials such as fly ash. First scientific studies of geopolymeric materials indicated a certain potential for these material to become cement for the future. The polymerization process involves a chemical reaction under highly alkaline conditions on al-si minerals, yielding polymeric Si-O-Al-O bonds, as in equation 26.

The polymerization process may be assisted by applied heat, followed by drying. The chemical composition of geopolymer is similar to zeolites, but shows an amorphous microstructure (Xu& Van Deventer 2000). The reaction mechanism of geopolymerisation may consist of dissolution, transportation or orientation, and polycondensation (Xu and Van Deventer 2000), and takes place through an exothermic process (Palomo, Grutzeck& Blanco 1999; davidovits 1999). In the first step, dissolution of alumino-silicate under strong alkali solution is going to occur and after that reorientation of free ion cluster takes place. The last step is polycondensation. But in each step there are so many pathways. For example considering dissolution step, it includes 8 pathways according to the thermodynamics. Different pathway can create different ion clusters. But these three steps take place almost at the same time, which make the kinetics of these three steps inter-dependent. Thus it is impossible to separate these steps in experimental studies.

Coming to the microstructure characterization, the structure characteristics of products directly determine the final mechanical and durability properties. The case is also true for geopolymer. Many researchers have investigated its microstructure using different advanced techniques. Since geopolymer is a amorphous 3D material with complex composition, it is very difficult to quantitavely measure the exact arrangement and chemical atmosphere in geopolymer. To solve this difficulty, we should have to turn to statistical theories for establishing its molecular model. But unfortunately, until now, these studies are not still been done. Therefore, the structural nature of geopolymers is not yet understood thoroughly and hence the exact mechanisms by which geopolymer setting and hardening occur is not yet clear (Davidovits 1999; Van jaarsveld, Van Deventer &Lukey 2002).

For the chemical designation of geopolymers based on silico-aluminates, a term "poly" (sialate) was suggested. Sialate is an abbreviation for silico-oxo-aluminate. The sialate network consists of SiO4 and AlO4 tetrahedra linked alternately by sharing all the oxygen atoms. Positive ions (Na+,K+,Li+,Ca++,Ba++,NH4+,H3O+) must be present in the framework cavities to balance the negative charge of Al3+ in IV-fold coordination. Poly(siliates) has the empirical formula as shown in Equation 3.1. Poly (Sialates) are chain and ring polymers with Si4+ and Al3+ in IV-fold coordination with oxygen and range from amorphous to semi-

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crystalline. Some related frameworks are displayed in Figure

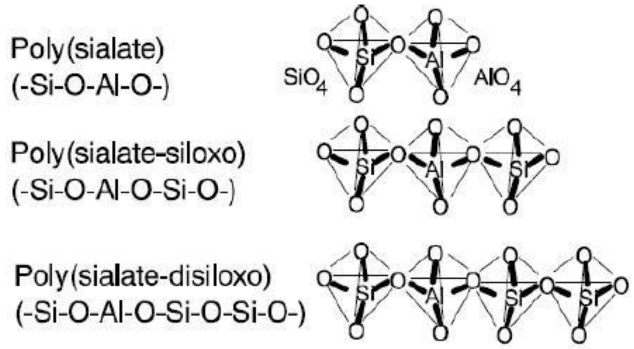

Figure 3.1: Diagrammatic representation of poly (Sialate)

Geo polymeric compounds involved in materials developed for industrial applications are non-crystalline (amorphous or glassy structure). In the non-crystalline state, diffraction of X-rays results in a broad diffuse halo rather than sharp diffraction peaks. Several Geo polymeric materials of practical interest like geo polymer cements are non-crystalline. This structure cannot be investigated from X-ray diffract grams alone. Nuclear Magnetic Resonance (MAS-NMR) spectroscopy provides some insight into their molecular framework.

The Geopolymers chemistry concept was invented in 1979 with the creation of a non-for profit scientific organization , (Geopolymer Institute). The following geopolymer applications were developed since 1972 in france, Europe and USA. The application were based on 30 patents filed and issued in several countries. Several patents were now in the public domain, but others were still valid. The following applications show genuine geopolymer products having brilliantly withstood 25 years of use and that were continuously commercialized.

- Geopolymer
- Low-tech building materials,
- Energy low ceramic tiles,
- Aluminum foundary applications
- Fire resistant wood panels
- Insulated panels and walls,
- Decorative stone artifacts,
- Refactory items,
- Thermal shocks refractory,
- High-tech resin systems
- Fireproof high-tech applications, aircraft interior, automobile,
- Fire resistant and fire proof composite for infrastructures repair and strengthening,
- Foamed (expanded) geopolymer panels for thermal insulation

EXPERIMENTAL PROGRAM

Based on the extensive literature review an attempt has been made to verify the possibility of preparing low calcium (ASTM Class F) fly ash based geopolymer concrete economically to suit the Indian conditions.

In order to develop the fly ash based geopolymer concrete technology, therefore, a rigorous trail-and error process was adopted. In order to simplify the development process, the compressive strength was selected as the benchmark parameter. The focus of the study was mainly on the engineering properties of fly ash based geopolymer concrete and also for partial replacement of fly ash with cement. The current practice used in the manufacture and testing of Ordinary Portland Cement (OPC) concrete was followed, even for geopolymer concrete. It is to ease the promotion of this „new‟ material to the concrete construction industry.

Materials

Fly ash& GGBS

Fly Ash: The Fly ash was used as a partial replacement for cement. The fly ash used in the experiments was from Ramagundam thermal power station (NTPC). The specific gravity was 2.17. The fly ash had a silica content of 63.99%, silica+ alumina +iron oxide content of 92.7%, Calcium oxide of 1.71% , Magnesium oxide of 1.0%, Sulphuric anhydride of 0.73% , water and soluble salts of 0.04%, ph value of 10 and a loss on ignition of 2.12

Here we are using ground granulated blast furnace slag(GGBS) about 4 to 5 % for 1 cube.

Alkaline Liquid

In the present study we have used a combination of sodium hydroxide (NaOH) and sodium silicate (Na2SiO3) solutions. The sodium hydroxide solids were either a technical grade in flakes form (3 mm), 98% purity, and obtained from National scientific company, Vijayawada, or a commercial grade in pellets form with 97% purity, obtained from National Scientific centre, Vijayawada.

Figure 4.1: Sodium Silicate and Sodium Hydroxide Solution

The sodium hydroxide (NaOH) solution was prepared by dissolving either the flakes or the pellets in the Potable water. The mass of NaOH solids in a solution varied depending on the concentration of the solution expressed in terms of molar, M. Molar concentration or molarities is most commonly in units of moles of solute per litre of solution. For use in broader applications, it is defined as amount of solute per unit volume of solution.

Aggregates

Fine aggregate: The fine aggregate conforming to Zone-2 according to IS: 383[1970] was used. The fine aggregate used was obtained from a nearby river source. The bulk density, specific gravity and fineness modulus of the sand used were 1.43g/cc, 2.62 and 2.59 respectively.

Water

Potable water was used in the experimental work for both mixing and curing.

Galvanized Iron mesh:

Galvanized Iron Wire mesh: The galvanized iron wire mesh of square grid fabric is used in the Ferro cement. The properties of the wire mesh are

Table 4.1: Galvanized Iron mesh Properties

Diameter of wire mesh (mm)	Grid spacing of mesh wire (mm)		Yield strength of mesh wire (Mpa)	Ultimate strength (Mpa)
	Longitudinal	Transverse		
0.46	2.80	2.80	350	450

Mould

Cubes: Standard cube moulds of 150mmx150mm x 150mm made of cast iron were used for casting and testing specimens in compression.

Casting

For casting the specimens of geopolymer concrete, the following procedure was adopted. The fine aggregate were prepared in saturated-surface-dry condition, and were batched and were kept in the gunny bags just before casting.

The solids constituents of the fly ash-based geopolymer concrete, i.e the fine aggregate and the fly ash, were dry mixed in the pan mixer for about three times. Then the liquid part of the mixture, the alkaline solution was added to the initially mixed fly ash and the fine aggregate. The whole mix is thoroughly mixed for about 5 to 10 minutes. The above procedure is done casting the geopolymer specimens when fly ash was partially replaced by cement.

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The fresh fly ash-based geopolymer concrete was dark in color and shiny in appearance. The mixtures were usually cohesive. The fresh concrete in the moulds was compacted by applying sixty manual strokes per layer in three equal layers.

The ferrocement mesh was kept in the layers along with mortar. After compaction the top surface was leveled with a trowel. Then the specimens were cured at room temperature.

Curing

Preliminary tests also revealed that fly ash based geo polymer concrete did not harden immediately at room temperature was less than 300c, the hardening did not occur at least for 24 hours. The handling time is a more appropriate parameter (rather than setting time used in case of OPC concrete) for fly ash based geo polymer concrete.

The demoulded specimens were left in sunlight until tested without any special curing regime. For each set of parameter, 3 prisms were cast, three each for determining 28 days strengths.

RESULTS AND DISCUSSIONS

3 Days compression test For Fly Ash:

Date of Casting	Date of curing	Date of testing	Result
10/3/2015	11/3/2015	14/3/2015	27.11 N/mm2

7 days compression test For Fly Ash:

Date of Casting	Date of curing	Date of testing	Result
12/3/2015	13/3/2015	20/3/2015	39.39 N/mm2

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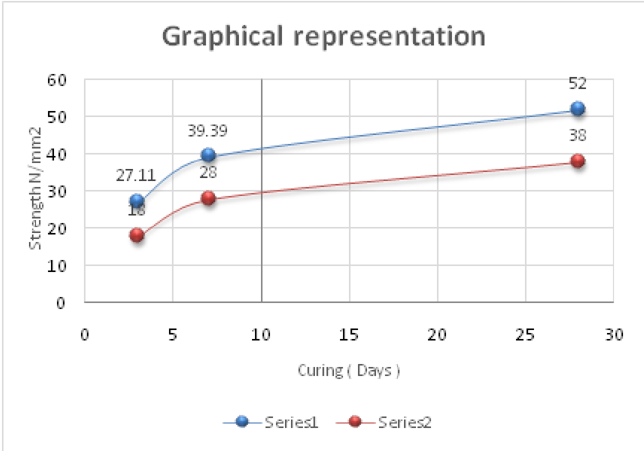
28 days compression test For Fly Ash:

Date of Casting	Date of curing	Date of testing	result
25/2/2015	26/2/2015	26/3/2015	52 N/mm2



CONCLUSIONS

From the experiments conducted on the geopolymer concretes developed in the concrete technology lab

- The geopolymerconcrete specimens load carrying capacity is more than cement mortar specimens
- The cost of fly ash based geopolymer concrete is high compared to Ordinary Portland Concrete.
- Workability of geopolymermortar decreases with the increase in concentration of sodium hydroxide.
- All geo polymer concrete mixes does not exhibited similar nature as that of ordinary Portland cement concrete 28 day for compression strength.

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