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"GEOPOLYMER BINDER"– AN APPROACH TOWARDS COMPLETE CEMENT REPLACEMENT

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***Abstract*— Construction industry is constantly growing globally hence the raw material required is also in heavy demand. At the same time due to fast industrialization, the industrial waste generation is creating a big threat at its disposal. It leads to a lot of environmental problems due to its hazardous characteristics. Though these are wastes; some are having rich characteristics hidden in them that can be utilized to make these wastes a useful raw material. In this paper, an attempt has been made to analyze the characteristics of the industrial waste and utilize them as a binder in construction by keeping in view the objective of complete cement replacement. As there are no any standard specifications for geopolymer mix the compositions are based on trial and error basis. The study shows variations in the compressive strength due to change in form of chemical and different curing methods.**

Keywords— fly ash, geopolymer, alkaline activators

I. Introduction

The construction industry is one of the biggest industries in the world which plays an important role in the infrastructural and commercial development of any country. Concrete is one of the most important materials in building construction and other infrastructure works. As per the survey was done by "statista" about 2.7 billion m^3 of concrete was manufactured in 2002 worldwide, which is more than 0.4 m^3 of concrete generated per person once a year. It is anticipated that the need for concrete will increase further to almost 7.5 billion m^3 (about 18 billion tons) a year by 2050.Such an enormous utilization of concrete calls for the higher use of natural aggregates and cement, thus taking a toll on the environment. Concrete is the highest consuming material on the global level after water.[3] Increasing rate of urbanization and industrialization lead to overexploitation of natural resources such as river sand and gravels, which is giving rise to sustainability issues.

The concrete contains cement as a binding material majorly Ordinary Portland Cement which is responsible for nearly 5-8 % of the total Carbon Dioxide (CO_2) emission; which is a greenhouse gas; heavily responsible for the Global Warming. [8]

II. Industrial waste generation

The speed of development of any country is depended on its growth of industrialization. Higher the industrialization; higher will the supply of the products but simultaneously the generation of industrial waste is also higher.

As per the "Report on fly ash generation at coal/ lignite based thermal power stations and its utilization in the country for the year 2014-15" by CEA (Central Electricity Authority; New Delhi) 184.14 (Million tons) of fly ash is generated in the year 2014-2015 in 145 thermal power stations throughout India. The application of use is dumping in dead mines, filling material in road work and lake filling etc; which are not the environmentally friendly solutions of disposing of the fly ash.

Table 1- CEA fly ash report

Description	***data***
Nos. of stations	145
Flyash generation(million tons)	184.14
Flyash utilized (million tons)	102.54
Percent utilization	55.69

As per the data received by the central authority, the 44.31% of fly ash remained unused. The quantity whatever is used; adopted in PPC manufacturing and landfilling.

III. Geopolymerization

"Geopolymer" was the firstly introduced by Joseph Davidovits in 1978; he found that the alkaline metals can react with the high valued Si-Al materials and produces 3-dimensional alumino-silicate complexes with having a strong binding property of Al-Si elements. As the coal ash is rich in both aluminum as well as silicon we can utilize the coal ash the replacement for OPC which will help us to reduce the heavy emission of the carbon dioxide (CO2) as well as degradation of the naturally limited sources of the raw material that is required for making the OPC.

The fly ash is generated mainly in steel industries, casting industries and in thermal power plants. This ash is a waste hence it can be collected at free of cost. While saying about the industrial waste utilization we are focusing on the characteristics of fly ash. The main selection of the wastes to be considered in the project will be based on the rate of its generation and quality of the waste generated which may be helpful in the binding process. Based on these parameters we will finalize suitable waste products depending upon the results.

There are no any specifies IS specifications for making the geopolymer mix design; hence research is carried out on trial and error method to achieve the desired strength of minimum 3.5 MPa. Based on these parameters we will finalize the application of the geopolymer binders in the civil engineering area.

A. Geopolymerization Reaction

The process of geopolymerization does not contain any hydration reaction hence there is no any production of heat of hydration which leads to saving of water which is required in the regular cement concrete for curing purpose.

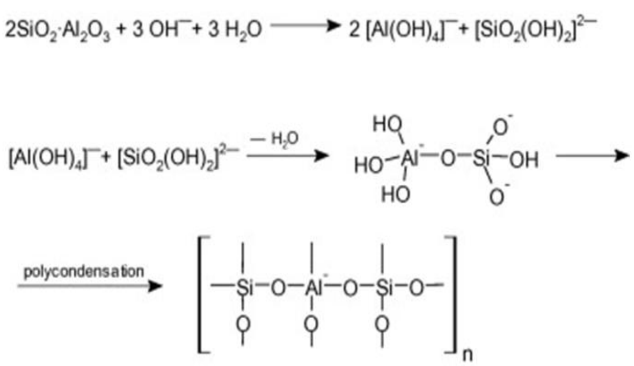

Figure 1- Geopolymerization Reaction

IV. Materials and Methods

For completion of Geopolymerization process, any reactive agent having a high quantity of silica-aluminum is required along with alkali activators which will react with silica to form alumino-silicate binders and water as a byproduct.

Following material is essential for the formation of geopolymer reaction-

Fly ash – It should be having SiO2 (Silica Oxide) content in between 40% to 85% i.e. highly rich in silica content to have better performance in the geopolymer reaction

Catalytic liquid system (CLS) - It is an alkaline activator solution (AAS) for GPCC. CLS is a composition of alkali chemicals such as sodium hydroxides and sodium silicate dissolved in distilled water. The role of AAS is to activate the geopolymeric source materials (containing Si and Al) such as fly ash.

Heat Curator – As Hydration reaction is not taking place in the geopolymer reaction the water curing is not playing any role in gaining the strength. It is recommended in previous studies that steam curing or oven curing is playing a very important role in hardening process.The process of curing should be followed by the aging of at least 24 hours.

Fine and Coarse Aggregate – These are to be selected as per required strength and specifications of the mix design.

A. Characteristics of materials required

Following materials are required for the complete reaction of geopolymerization which will act as a binder and replace the cement 100 %.

Fly ash sample - 1

This sample of ash was collected from the JSW thermal power plant, Jaigad. The physical and chemical characteristics were studied in institute laboratory and NAR Pvt Ltd., Sangli. The obtained results of the sample – 1 fly ash were as follows;

Table 2- Physical characteristics of fly ash-1

Physical tests	***Observations***
Color	Silver grey
Form	Powder form
Sp.Gravity	2.36
Source	JSW thermal power plant, Jaigad

Table 3- Chemical characteristics of fly ash-1

Chemical tests	***Observation***
SiO_2 Content	81.41 %
CaO Content	0.39%
PH (PH Meter)	11.5
Al_2O_3 Content	14.37 %

The analysis reports show that the silica content is high in fly ash sample-1 which is a good sign of having rich characteristics; similarly, the CaO content is very less which will help to avoid expansion after hardening.

Fly ash sample - 2

This sample of ash was collected from the thermal power plant, Ratnagiri. The physical and chemical characteristics were studied in institute laboratory and NAR Pvt Ltd., Sangli. The obtained results of the sample – 2 fly ash were as follows;

Table 4- Physical characteristics of fly ash sample - 2

Physical tests	***Observations***
Color	Muddy Brown
Form	Powder form
Sp.Gravity	2.34
Source	Ratnagiri thermal power plant

Table 5-Chemical characteristics of fly ash sample - 2

Chemical tests	***Observation***
SiO_2 Content	64.97 %
CaO Content	2.32%
PH (PH Meter)	11.2
Al_2O_3 Content	27.98 %

The analysis reports show that the silica content is lower than in fly ash sample-1 which is not helpful for geopolymerization; similarly, the CaO content is higher than fly ash sample-2 which will lead to expansion after hardening.

After analyzing the physical and chemical characteristics of both fly ash samples; sample-1 fly ash was finalized for a binding agent as a raw material.

Natural Sand –

Natural sand is used as fine aggregate in a mixture; it is also known as river sand in a local language.

Followings are the characteristics of natural sand.

Table 6- Characteristics of Natural Sand

Characteristics	***Observations***
Gradation	4.75mm – 150 microns
Shape	Rounded Grains
Sp.Gravity	2.38

For the use of fine aggregates, the naturally available river sand was finalized having a gradation of 4.75mm to 150 microns.

Sodium Silicate –

Sodium silicate is a chemical which is highly used in textile and soap industry. The same chemical is used for the research work. This chemical is also known as "alkaline type sodium silicate" in the local language; the required chemical composition is as follows;

The sodium silicate reacts with the SiO_2 content from fly ash which will start the geopolymerization process. Both forms of sodium silicates are used in the research work.

Table 7- Characteristics of Sodium Silicate

Compound	***% by mass***
Na_2O	14.7
SiO_2	29.4
H_2O	55.9
Form	Gel
Color	Light yellow

The sodium silicate solution can't react alone with fly ash it has to be activated to react. The activator agent is Sodium hydroxide.

Sodium Hydroxide –

Sodium Hydroxide releases the high amount of heat when mixed with water hence it is recommended to prepare the sodium hydroxide solution 24 hours prior to mix with fly ash which will help to get the solution at normal temperature. Followings are the characteristics of the sodium hydroxide solution;

Table 8- Characteristics of Sodium Hydroxide

Characteristics	***Observations***
Color	White
Form	Flakes
Molecular Weight	40
Molarity	16 Molar

Sodium hydroxide activates the sodium silicate and then the geopolymer reaction starts which form alumino-silicate complexes which work as a binding agent.

Sodium hydroxide is available in the market in various ranges of purity up to 99 % which are used in laboratory work. In this reaction, the main task of sodium hydroxide is to activate the sodium silicate solution hence least costing chemical can be used.

B. *Molarity Calculations*

The solids must be dissolved in water to make a solution of required concentration. The concentration of Sodium hydroxide solution can vary in different Molar. The mass of NaOH solids in a solution varies depending on the concentration of the solution.

For instance, NaOH has a molecular weight of 40 hence solution with a concentration of 16 Molar consists of 16 x 40 = 640 grams of NaOH solids per liter of distilled water. Note that the mass of water is the major component in both the alkaline solutions. The mass of NaOH solids was measured as 444 grams per kg of NaOH solution with a Concentration of 16 Molar.

But; while talking about per KG of the solution following table helps in a calculation.

Table 9- Molarity Calculations

Soln. Qty.	*Solid Qty.*	*Water Qty.*	*Concentration*
1 Kg	444 gm	556 gm	16 M
1 Kg	404 gm	596 gm	14 M
1 Kg	361 gm	639 gm	12 M
1 Kg	314 gm	686 gm	10 M

V. EXPERIMENTAL PROGRAMME

The mortar cubes were casted of sizes 70.7 X 70.7 mm. 3 cubes of each sample mix were casted and final results were drawn from their mean values.

The results of compressive strength were checked after 3 days of hot air oven curing and after 7 days of ambient temperature curing.

A. *Preparation of Alkaline activators*

The sodium hydroxide solution of 16 molar concentrations was prepared 24 hours prior to mixing with sodium silicate to normalize its temperature. The ratio of Sodium silicate to Sodium Hydroxide was kept as 2.5 in all mixes. The quantity of alkaline activators was kept as 55% by weight of fly ash.

Both chemicals were mixed together just prior to mixing with the fly ash to avoid improper bonding.

B. *Preparation of Mix*

The ratio of fine aggregate to fly ash was kept 70:30 by weight. The extra water added to the mix was 0.06 times (6%) of the weight of fly ash. Following is the detailed procedure of mix formation;

-Dry mixing of Fly ash and fine aggregate in the required proportion that is 30 % fly ash by weight of the total mass.
-Addition of Alkaline activators in the dry mix slowly without allowing the formation of lumps.
-Addition of water simultaneously while mixing with alkaline activators.
-Wet mixing for 10 minutes.
-Casting by the same method used for the placing of concrete blocks that is by tamping rod.
-Curing the cubes.
-After curing it is required to lower the temperature of the cube to the normal room temperature hence aging of 24 hours after curing is recommended.

C. *Curing method*

As there is no any hydration reaction in the geoplymerization process hence the water curing is not necessary. There are following methods of curing that are acceptable for geopolymerization;

a) Hot air oven curing
b) Ambient temperature curing
c) Steam curing

By considering the availability of the equipment and economy hot air oven curing and ambient temperature curing were selected for the research work.

Rest Day Curing- This is another way of curing in which rest days are introduced between the day of casting and the starting day of curing.

For example; 3 Rest day cured (3RDC) means specimen is casted and kept 3 days as it is in a normal environment and kept in the oven for curing on the 4th day.

Aging- It is the process of allowing the cubes to lower their temperature down to room temperature; it is around of 24 hours after oven curing.

VI. RESULT AND DISCUSSION

There are 2 mix samples were designed with various replacements. These are elaborated in tabular format as below;

Table 10- Material Composition

Mix	*Fly ash Kg/m3*	*Activators %*	*Type of fine aggregate*	*Type of Na_2SiO_3*
Mix A	400	55	Natural Sand	Powder
Mix B	400	55	Natural Sand	Gel

Above table shows the quantity of activators and fly ash per m^3 were kept constant. The quantity of fly ash and the alkali activators is 400 kg/m^3 and 55% of the weight of fly ash respectively.

Table 11- Material Quantity

	Quantities of materials in Kg/m3			
Mix	*Alkaline Activators Kg/m3*	*Natural Sand*	*NaOH*	*Na_2SiO_3*
Mix A	220	1334 Kg	62.857 Kg	157.143 Kg
Mix B	220	1334 Kg	62.857 Kg	157.143 Kg

Above tables show the exact quantities of the various materials in the different mixes. Mix A is composed of pure natural sand with a powder form of sodium silicate while Mix B is composed of pure natural sand with gel form sodium silicate.

Followings are the results of compressive strength test carried out with 3 rest day hot air oven curing and 7 days ambient temperature curing of various mix designs.

Table 12- Compressive strength and weight results

Mix	*Compressive Strength in MPa*		*Weight in Grams*	
	3RDC	*7DAC*	*3RDC*	*7DAC*
Mix A	4.40	5.44	658	740
Mix B	8.40	15.44	645	768

3RDC (3 rest days curing) - The cubes are kept in an open atmosphere for 3 days and then cured in an oven @60^{0}c for 24 hours then kept for aging.
7DAC (7 days ambient curing) - The cubes are kept in an open atmosphere for 7 days and then tested.

Results in above table show large variance; when a change occurs in the curing method and material composition. The Mix B gives the highest strength that is of 15.44 MPa which contains pure natural sand and gel form sodium silicate with fly ash.

The weight comparison of the geopolymer cubes and cement cubes also shows positive results; the weights of geopolymer cubes are affected by the method of curing and change in the form of chemical composition.

VII. CONCLUSION

After carrying out the process of geopolymerization with fly ash and the alkaline activators it is found that the total cement can be replaced (100 % replacement) with an industrial waste fly ash.

The change in the form of the alkaline agent affects the strength as well as the weight of the cubes.

The process of curing directly changes the compressive strengths of the cubes. The ambient temperature curing gives more strength than rest days oven curing.

As the powder formed silicate takes longer time for dissolving in water it creates a problem of saturation which affects the process of geopolymerization; hence liquid form silicate gives higher strength than powder form silicate.

The weights of geopolymer cubes are around 20 % less than that of cement cubes having same proportion.

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