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Studyon High Calcium Flyash Based Geopolymer concrete

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ABSTRACT:*The astronomical growths of Portland cement and hence the concrete industries tend to contribute for environmental pollution particularly the carbon dioxide emission. The contribution of ordinary Portland cement production worldwide is about 7% of the total greenhouse gas emission to the atmosphere. Therefore, for longterm sustainability, rate of emission of greenhouse gases to the atmosphere must be prevented from increasing. It is realized that replacement of cement with suitable alternatives could solve the problem. In this line, research is directed towards the development of GPC. Most of the works reported are based only on low calcium flyashused as the main source material and hardly about the use of high calcium flyash. This article deals with the development of high calcium flyash based GPC. The influence of Molar concentration of the sodium hydroxide in the activating solution anddifferent curing methods on the compressive strength is studied using trials of M30 grade and GM30 concrete.The activator/flyash ratio by mass is taken as 0.35 and the liquid ratio of the activating solution as 2.5. It is observed that, ambient curing is adequate for high calcium flyash based GPC.*

Keywords:*Geopolymer, source material, class C flyash, activator, consistency, setting time.*

I. INTRODUCTION

GPC (GPC) also known as Alkali-activated concrete or Inorganic polymer concrete has shown to possess excellent properties such as a high early strength, low shrinkage, high resistance to freezing and thawing, sulphate attack and corrosion in most of the pioneers work. It necessarily has a source material similar to cement and activating solution instead of water to act as a binder.

There are numerous publications available discussing different properties of geopolymer synthesised from different raw materials and activators. Geopolymer cement hardens rapidly at room temperature and provides compressive strength of 20MPa after only 4 hours at 20^{o}C and the final 28 day strength in the range of 70-100MPa and their unique properties that include high early strength, low shrinkage, freeze and thaw resistance, sulphate resistance and corrosion resistance, make them ideal in long term containment in surface disposal facilities and further these high alkali cements do not generate alkali aggregate reaction[1].The development, the mixture proportions, and the short-term properties of low calcium flyash-based GPC has been described and reported[2] that one ton of low-calcium flyash can produce 2.5 cubic metres of high quality GPC, and the bulk cost of chemicals needed to manufacture this concrete is cheaper than the bulk cost of one ton of Portland cement.

It is concluded that low-calcium flyash based GPC has excellent compressive strength, suffers very little drying shrinkage and low creep, excellent resistance to sulfate attack, and good acid resistance.

The literature survey on GPCs indicating the qualitative information available on the mechanical properties of GPC mixes is presented[3], sufficient to develop GPCs for use in structures. It is reported that it is possible to practically formulate the alkali activating solution for class F flyash, GGBS and in different combination to achieve strength levels useful in civil Engineering application and it is therefore possible to prepare typical structural members such as beams and columns using the GPCs capable of being cured under ambient conditions only for studying the possibility of applicability in existing structural design guidelines to new composites.

A comprehensive summary also presented[4]from the extensive studies conducted on flyash based GPC. Test data are used to identify the effects of salient factors that influence the properties of the GPC in the fresh and hardened states. These results are utilized to propose a simple method for the design of GPC mix proportions. Test data of various short term and long-term properties of the GPC are then presented. Criticaldiscussion[5]on opportunities, limitations, and future needs for the development in GPC for producing a sustainable concrete is made and summarized that the technology of geopolymerization is not new and is believed to have been used in the construction of the Pyramids at Giza, Egypt, (circa 2550 B.C.) and other ancient construction of the Mohenjo-Daro, in Sindh, Pakistan, (circa 2600 BC) and however GPC technology is still mostly confined at laboratory levels.

Explanations on the geopolymers[6] based on, Kaolinite/Hydrosodalite,Metakaolin MK-750, Calcium, Rock, Silica, flyash, Phosphate and organic minerals are also reported on the development of GPC from these source materials as the attempts of scientists from various origins. Apart from other aspects, a good quantum of flyash is available in India, but to date its utilization is limited inspite of the codal recommendations[7].Review on the flyash scenario in India particularly for its generation and utilization in India, characterization and advantages of its applications in concrete and in agriculture are explained and addressed[8,9]. It is reported that flyash generation is expected to increase to 300 million tons per annum by 2017 and 900 million tons per annum by 2031-32.An overall view of the process and parameters which affect the geo-polymer concrete till date is also given[10]. The economic benefits and contribution of GPC to sustainable development have been outlined and it is reported that no Indian Standards are available so a detailed study on the chemistry behind the polymerization is needed.

Experimental investigation made on the performance of class C flyash based GPC subjected to severe environmental conditions and compared with conventional concrete of M30, M40, M50 and M60 grades is presented[11]. Sodium hydroxide solution (8M and 12M) and sodium silicate with ratio of 2.50 and 3.50 were used. The test results indicated that the heat-cured (60°C for 24 hours) flyashbased GPC had an excellent resistance to Sulphuric acid and magnesium sulphate attack when compared to conventional concrete.Relationship between the activator composition and the properties of class C flyash based geopolymer mortar in fresh and hardened states is also establishesd[12]. Scanning electron microscopy, energy dispersive X-ray spectroscopy and X-ray diffraction techniques were also used to characterize the material and indicated thepotential available for the concrete industry to use flyash based GPC as an alternative to Portland cement.

Numerous geopolymer systems have been proposed (many are patented), most are difficult to work with and require great care in their fabrsication. Furthermore, there is a safety risk associated with the high alkalinity of the activating solution, and high alkalinity also requires more processing, resulting in increased energy consumption and greenhouse gas generation. Also the polymerization reaction is very sensitive to temperature and usually requires that the GPC be cured at elevated temperature under a strictly controlled temperature regime. In many respects, these facts may limit the practical use of GPC in the transportation for precast applications. Considerable research to develop GPC that address these technical hurdles, creating a low embodied energy, low carbon dioxide binder that has similar properties to Portland cement is under way. In addition, current research is to focusing on the development of userfriendly GPC.

It is worth to note that only few studies have been made on high calcium flyash based GPC compared to low calcium flyash based GPC. Neyveli Lignite Corporation (NLC) is a lignite based unit generating power through two major thermal Power stations and annually produces 1.20 million tons of high calcium flyash (ASTM class C).As the utilization is very much limited, storing of ash is a hectic problem. Therefore, there is a need of mass utilization of this flyash for structural purpose. As the high calcium flyash is more cementitious compared to low calcium flyash, an experimental study is initiated for promoting high calcium flyash based GPC. In order to simplify the development process, the compressive strength was selected as the benchmark parameter.

Contituents and Design Parameters

In skeleton the important details of production of GPC from the literature are summarized here:

- The source material:flyash, GGBS, Rice husk ash, metakaolin or calcined kaolin, etc.,
- The activating solution (type and silicate/hydroxide ratio): Sodium based (Na_2SiO_3/NaOH) or Potassium based (K_2SiO_3/KOH) having a ratio 1.5 to 3.0 with hydroxide of varying molarities (8-16M).
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$$\text{Water/Geop olymer} = \frac{\text{Mass of water in the solution of silicate, hydroxide and extra water if any}}{\text{Mass of flyash and mass of solids in silicate and hydroxide solutions}}$$

- Curing: After casting, the fresh concrete specimens are placed in the oven for dry curing or in the steam curing chamber for steam curing with a curing temperature ranging from 60^{o}C to 100^{o}C. Ambient curing (at room temperature) is also successfully attempted.

Experimentation

For conventional concrete, ordinary Portland cement having specific gravity 3.14 is used. High calcium flyash (ASTM Class C) from the Neyveli Lignite Corporation (NLC) having specific gravity 2.24 and fineness 325m^2/kg is used as the main source material for GPC. NLC is lignite based thermal power station annually producing 1.20 million tons of class C flyash. The chemical composition of the flyash procured for the research is shown in Table 1.

Table 1 Chemical Composition of Class C Flyash

No	Elements	Mass (%)
1	Silicon dioxide (SiO_2)	47.60
2	Aluminum oxide (Al_2O_3)	21.40
3	Ferric oxide (Fe_2O_3)	07.80
4	Calcium oxide (CaO)	11.90
5	Magnesium oxide (MgO)	01.80
6	Sulphur trioxide (SO_3)	02.80
7	Sodium Oxide (Na_20)	00.70
8	Potassium oxide (K_2O)	00.82
9	Titanium dioxide (TiO_2)	01.88
10	Loss on Ignition	03.30

Conventional aggregates like fine river sand(specific gravity 2.64) and 12.5mm coarse aggregates (specific gravity 2.7)are used. The commonly available sodium hydroxide (Analytical grade in pellets form with 98% purity) and sodium silicate solution(with Na_2O = 12%, SiO_2 = 30%, and water = 58% by mass) in combination is used as the alkaline activator. Mix design for conventional concrete M30 and for GPC GM30 is made based on the material properties and requirements. The views of constituent materials are shown in figure 1.

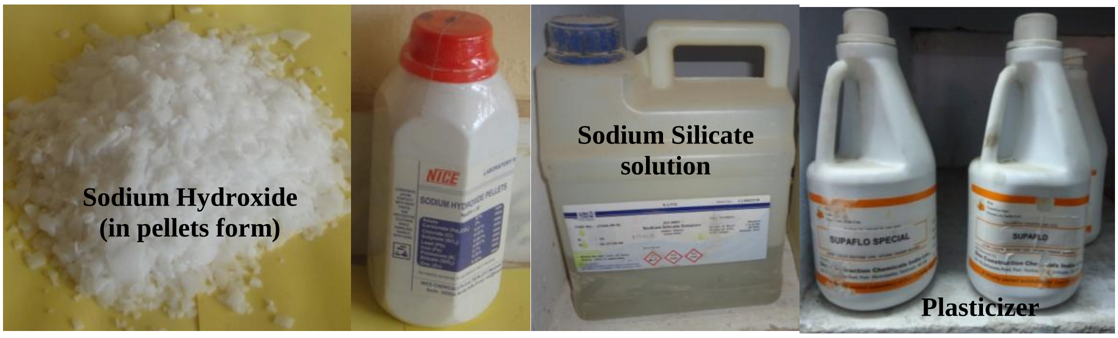

Fig.1 Constituents of Activator in GPC

Preparation of Activating Solution

Themolar concentrations of NaOH considered are 8M, 10M, 12M and 14M.The activator/flyash ratio by mass is 0.35 and the liquid ratio of the activating solution is 2.5. For instance, 8Molar NaOH consists of 8×40 = 320gm of Solid NaOH per litre of solution where, 40 is its molecular weight. The mass of NaOH solids is measured to be 262 gms/kg of NaOH solution. Similarly, the details for other molarities are given in Table 2. The NaOH solution is prepared 24 hours prior to use, because after dissolving flakes of NaOH in water, the temperature of solution can go up to 80^{o}C, hence it is necessary to cool it at room temperature before use. The NaOH solution thus prepared was mixed together with Sodium silicate solution to get desired alkaline solution. These solutions are mixed together one day before adding the liquid to the solid dry constituents.

Table 2 Mass of NaOH Solids in Various Molar Solution(Rangan, 2008)

No	Molarity of NaOH	Mass of NaOH solids per litre of solution (gm)	Mass of NaOH solids per kg of NaOH solution(gm)
1	8M	320	262
2	10M	400	314
3	12M	480	361
4	14M	560	404

Casting and Testing of Specimens

Using the constituents, conventional concrete of M30 grade and equivalent grade of GPC designated as GM30 are designed[4] and trial mixes prepared. The mix proportions for the trial mix and the quantities required for one meter cube of concrete are given in Table 3. The dry materials (flyash and aggregates) are then mixed in the pan mixer for about three minutes and the activating solution premixed with admixture is added to the dry mixture, and mixing continued for another three minutes.

Table 3 Mix Proportions for Conventional Concrete and GPC

No	**Conventional concrete Mix (M30)**				**GPC (GM30)**		
1	Constituents		Ratio	Wt/m^3	Constituents	Ratio	Wt (kg/m^3)
2	Cement		1	476.10	Flyash	1	550
3	Sand		1.24	591.55	Sand	1.09	600
4	Jelly	20 mm		-	Jelly	1.53	838
5		12.5mm	2.26	1079.96	Activator	2.5	239/95
6	Water		0.40	190.44	Activator/FA	0.68	-
7	Admixture		1.5%		Admixture	1.5%	
8			(Supaflo special)		Extra water	Vary w.r.to molarity	
9	Slump		34mm		Made to 40mm by adding water		

After discharge from the mixer machine, workability test was conducted and slump value obtained. The concrete is poured in the cube moulds of 100mm size in three layers and compacted by placing on the table vibrator. After finishing the top, the specimens are wrapped by placing a lid on the mould. Dry curing in the laboratory oven for 24 hours at 65^{o}C as well as ambient curing (at room temperature of 29±1^{o}C that exists) is adopted. The compressive strength of various concrete specimens is obtained by testing these 100mm cubes at appropriate days. The results are presented in Table 4 and the comparison is made in figure 2.

II. DISCUSSION

- The preparation of alkaline solution is very much comfortable and mixing is very convenient. The GPC is also fairly workable. Being 100mm cubes, hot curing is feasible for more number of specimens.

Table 4: Comparison of Compressive Strength

No	Compressive strength of concrete								
	M30 OPCC	GPC-GM30 by Oven*/ Ambient** curing for varying molarity							
		8M		10M		12M		14M	
1	37.6	33.2	35.6	35.4	36.7	42.4	39.7	40.1	38.7
2	38.5	34.7	36.2	34.3	37.1	41.3	38.9	42.3	38.5
3	37.8	36.3	35.3	36.1	36.3	42.2	45.3	40.2	39.6
4	39.4	34.4	36.3	35.4	38.3	43.4	44.3	39.4	38.3
5	40.2	33.1	33.5	35.1	35.5	42.2	41.5	40.2	37.5
6	37.7	34.2	35.5	36.2	37.5	41.4	40.5	40.8	38.4
Average	38.53	34.32	35.4	35.41	36.90	42.15	41.7	40.5	38.5
Fraction of strength of M30 concrete		0.89	0.92	0.92	0.96	1.09	1.08	1.05	0.99
Difference by curing methods		+3.15%		+4.21%		-1.07%		-4.94%	
* For 24 hours at 65^{o}C ** at 28 days									

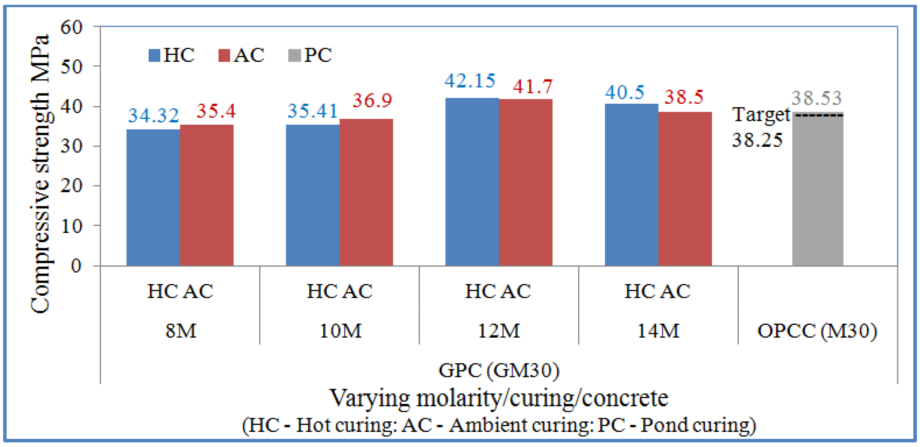

Fig.2 Compressive Strength of GPC and OPCC

- The compressive strength of geopolymer increases generally for oven curing for all molar concentrations (8M-14M) but reduces after 12M in case of ambient curing. Upto 10M concentration, the compressive strength of GPC is less by 5-10% compared to conventional concrete.

- The compressive strength of ambient cured concrete is 3.15% more than the hot cured concrete up to 10M concentration and 1% and 4% less for molar concentrations of 12M and 14M respectively.
- Extra water is required for concrete with higher molar concentrations of sodium hydroxide solution like 12M and 14M to make them workable with a slump of 40mm.

III. CONCLUSIONS

- Confined to the experimental study in developing high calcium flyash based GPC of equivalent M30 grade concrete, ambient curing of concrete at room temperature for 28 days is adequate.
- 12M molar concentration of NaOH is optimum for the designed compressive strength.
- Hot curing is not required under laboratory conditions. However, in case of fabrication of precast elements, steam or hot curing shall be recommended.

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