Performance of Geopolymer Concrete in Sulphate Environment

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Abstract— **The present paper focuses the experimental work done in accessing the durability of geopolymer concrete compared to conventional concrete in sulphate media. The molarity used for the preparation of geopolymer specimens is 12. The grade chosen for the investigation was M-30. The alkaline solution used for present study is the combination of sodium silicate and sodium hydroxide solution with the ratio of 2.50. The test specimens were 150x150x150 mm cubes, cured in ambient room temperature. The performance evaluation of the specimens were assessed by immersing geopolymer concretes (GPC1, GPC2) and OPC specimens in 5% magnesium sulphate solution separately, periodically monitoring surface deterioration and depth of dealkalization, changes in weight and strength over a period of 15, 30, 45, 60 and 90 days. The test results indicate that the geopolymer concrete has an excellent resistance to sulphate attack when compared to conventional concrete. Thus we can say that the production of geopolymers have a relative higher strength, excellent volume stability and better durability.**

Index Terms— **geopolymer concrete, fly ash, molarity, sodium silicate, sodium hydroxide, magnesium sulphate**

I. INTRODUCTION

Construction industry is one of the major users of the natural resources like cement, sand, rocks, clays and other soils. The ever increasing unit cost of the usual ingredients of concrete have forced the construction engineer to think of ways and means of reducing the unit const of its production. At the same time, increased industrial activity in the core sectors like energy, steel and transportation has been responsible for the production of large amounts like fly ash, blast furnace slag, silica fume and quarry dust with consequent disposal problem [1].

The geopolymer technology was first introduced by Davidovits in 1978. His work considerably shows that the adoption of the geopolymer technology could reduce the CO2 emission caused due to cement industries. Davidovits proposed that an alkaline liquid could be used to react with aluminosilicate in a source material of geological origin or in by-product materials such as fly ash to make a binder [2]. Geopolymer is synthesized by mixing aluminosilicate- reactive material with strong alkaline solutions, such as sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium silicate or potassium silicate. The mixture can be cured at room temperature or temperature cured [3]. Fly ash is the most common source material for making geopolymers. Normally, good high- strength geopolymers can be made from class F fly ash [4]. Alkaline activating solution is important for dissolving of Si and Al atoms to form geopolymer precursors and finally alumino- silicate material. Bakharev, T. [5] reported that the covalent bonds of Al, Si, and Ca present in GGBFS can be comparatively more easily broken by high alkaline nature of catalytic liquids. Rajamane, N. P, et al. [6] reported that the covalent bonds of Al, Si, and Ca present in blast furnace slag can be comparatively more easily broken by high alkaline nature of catalytic liquid. Break down of glassy surface of fly ash require generally a higher temperature and higher alkaline environment.

The most commonly used alkaline activators are NaOH, since sodium based solutions were cheaper than Potassium based solutions [7-9]. The role of alkaline liquid is to activate the geopolymeric source mater ials (containing Si and Al) such as fly ash and GGBS.

II. EXPERIMENTAL INVESTIGATIONS

Materials

The following materials have been used in the experimental study [12]

A. Fly Ash (Class F) collected form Raichur Thermal power plant having specific gravity 2.00 and confirming to IS:3812 [26].
B. Ground granulated blast furnace slag collected from JSW Steel Ltd., Vidyanagar, Toranagallu, Bellary having specific gravity 2.90 and confirming to IS:3812 [27]..
C. Fine aggregate: Sand confirming to Zone –III of IS:383-1970 [24] having specific gravity 2.51 and fineness modulus of 2.70.
D. Coarse aggregate: Crushed granite metal confirming to IS:383-1970 [24] having specific gravity 2.70 and fineness modulus of 5.85.
E. Water : Clean Potable water for mixing
F. Alkaline liquids: Specific gravity of
    I. Sodium Hydroxide (NaOH) = 1.16
    II. Sodium Silicate (Na2SiO3) = 1.57

Tests were conducted on specimen of standard size as per IS: 516-1959 [25]. For the present investigation two types of mixes were designed, they are designated with the specific identification as given in Table 1.

Table 1: Specimen Identification

Type of mix	Identification	Source Materials used
Geopolymer concrete	GPC1	Fly ash , CA, FA, Alkaline solutions
Geopolymer concrete	GPC2	Fly ash (60%), GGBS (40%), CA, FA, Alkaline
Conventional concrete	OPC	Cement, CA, FA, Water

Mix design of geopolymer concrete

In the design of geopolymer concrete mix, coarse and fine aggregates together were taken as 77% of entire mixture by mass. This value is similar to that used in OPC concrete in which it will be in the range of 75 to 80% of the entire mixture by mass. Fine aggregate was taken as 30% of the total aggregates. The density of geopolymer concrete is taken similar to that of OPC as 2400 kg/m^3 [10]. The details of mix design and its proportions for different grades of GPC are given in Table 2.

Alkaline Solution

In geopolymerization, alkaline solution plays an important role. The most common alkaline solution used in geopolymerization is a combination of sodium hydroxide (NaOH) or potassium hydroxide (KOH) and sodium silicate (Na2SiO3) or potassium silicate (K2SiO3). In this study, a combination of sodium hydroxide and sodium silicate was choosen as the alkaline liquid. Sodium based solutions were choosen because they are cheaper than Potassium based solutions. Generally sodium hydroxide and sodium silicate are readily available in market in the form of pellets and gel (liquid). The pellets of NaOH are dissolved in one liter of water for the required concentration. When sodium hydroxide and sodium silicate solutions mixed together polymerization will take place liberating large amount of heat, which indicates that the alkaline liquid must be used after 24 hours as binding agent.

Table 2: GPC mix design details for 12 Molarity with FA and GGBS

Materials		Mass (kg/m^3)
		M-30
Coarse aggregates	20 mm	277.20
	14 mm	369.60
	7 mm	646.80
Na2SiO3/ NaOH		2.50
Fine sand		554.40
Fly ash		228.41
GGBS		236.52
NaOH solution		48.95
Na2SiO3 solution		122.36
Super Plasticizer		5.70
Extra water		38.06

III. MIXING, CASTING AND CURING OF GEOPOLYMER CONCRETE

GPC can be manufactured by adopting the conventional techniques used in the manufacture of Portland cement concrete. In the laboratory, the fly ash and the aggregates were first mixed together dry on pan for about three minutes. The liquid component of the mixture is then added to the dry materials and the mixing continued usually for another four minutes (Fig.1).

The addition of sodium silicate is to enhance the process of geopolymerization [11]. For the present study, concentration of NaOH solution is taken as 12M with Na2SiO3 / NaOH as 2.5 for all the grades of GPC mixes. The workability of the fresh concrete was measured by means of conventional slump test (Fig. 2). In order to improve the workability, superplasticizer Conplast SP-430 with a dosage of 1.5% by mass of the fly ash was added to the mixture. Extra water (other than the water used for the preparation of alkaline solutions) and dosage of super plasticizer was added to the mix according to the mix design details. The fly ash and alkaline activator were mixed together in the mixer until homogeneous pate was obtained. This mixing process can be handled within 5 minutes for each mixture with different ratios of alkaline solution. After casting the specimens, they were kept in rest period for two days and then they were demoulded. The demoulded specimens were kept for ambient air curing.

Sulphate attack test on concrete specimens

Generally, for any new material used in the construction practices it should be assessed based on its strength and durability characteristics. Among various sulphates, sodium and magnesium sulphates are reported as highly aggressive chemicals for conventional concretes. Hence, in the present investigation we have considered magnesium sulphate as the media, since sulphate is the most common deteriorating agents in the concrete structures.

The magnesium sulphate solution was prepared by dissolving 5 gm of $MgSO_4$ solids in 95 gm of distilled water to get 100 gm of solution.

Fig. 1 Alkaline solution

Fig. 2 Slump cone test

IV. RESULTS AND DISCUSSIONS

Workability

Fresh GPC mixes were found to be highly viscous and cohesive with medium to high slump. The workability of the geopolymer concrete decreases with increase in the grade of the concrete, this is because of the decrease in the ratio of water to geopolymer solids by mass. For a given geopolymer concrete, the total mass of water in the mixture is taken as the sum of the mass of water in the sodium silicate solution, the mass of water in the sodium hydroxide solution and the mass of extra water added to the mixture. The mass of geopolymer solids is the sum of the mass of fly ash, the mass of sodium hydroxide flake and the mass of sodium silicate solids (the mass of Na_2O and SiO_2 in sodium silicate solution). The test data shown in Figure are somewhat analogous to the well-known effect of water-to-cement ratio on the compressive strength of OPC concrete, although the chemical processes involved in the formation of the binders of both these types of concretes are entirely different

Specimens in the sulphate media

The cube specimens of the three mixes (GPC1, GPC2 and OPC) were submerged in sulphate media of known concentration. To perform the sulphate studies, immersion technique was adopted. After 28 days of casting, 150 mm cube specimens were immersed in 5% $MgSO_4$ solution kept in a plastic tubs such that there was a minimum of 30 mm depth of solution over the top surface. The solution was regularly monitored to have the uniformity.

Fig. 3 GPC specimens after 90 days of exposure

Fig. 4 OPC specimens after 90 days of exposure

The cube specimens of GPC and OPC mixes were submerged in sulpahte environment of known concentration. To perform the sulphate studies, immersion techniques was adopted. After 28 days of casting, 150 mm cube specimens were immersed in 5% sulphuric sulphate solution kept in a plastic tubs such that there was a minimum of 30 mm depth of sulphate over the top surface of specimens. To maintain the uniformity of sulphate solution, it was stirred regularly at least twice in a day. Care was taken to maintain the concentration of solution, which was replaced at regular intervals. The results were summarized after 15, 30, 45, 60 and 90 days of curing period.

Visual appearance

There was no change observed in the shape of geopolymer concrete mix specimens and they remained structurally intact without visible cracks. There were white deposits throughout the duration of exposure, which were soft and powdery during early stage of exposure, but it became harder with time. On the other hand, the OPC specimens have received less deposit of white and less deterioration on the surface of concrete. There was no sign of surface erosion, cracking or spalling on the specimens in both the type of concretes.

Weight change

The percentage loss in weight of geopolymer concretes and OPC mixes are presented in Fig. 5. All the specimens observed to increase their weight over duration of exposure. The weight gain or loss is almost similar in the three different series of mixes. Maximum increase in weight was observed in GPC2 specimens and least gain in weight was observed with OPC specimens. As the grade of concrete increases we can notice that the loss of weight for the specimens goes on increasing indicating the stiffness of concrete. On exposure after 90 days GPC1, GPC2 and OPC specimens lost their masses. From these values it can be seen that the geopolymer concrete specimens (GPC1 or GPC2) are highly resistant to sulphate environment and they can sustain the media without losing much of the mass.

There was increase in weight of the specimens, which indicate that there were some white deposits within the surface pores which might have led to the increase in its mass. These white deposits were nothing but the gypsum in the matrix [14]. The change in masses of geopolymer concrete mixes found out to be negligible as observed in the present study. These observations are similar to the investigations done by [15, 16, 17].

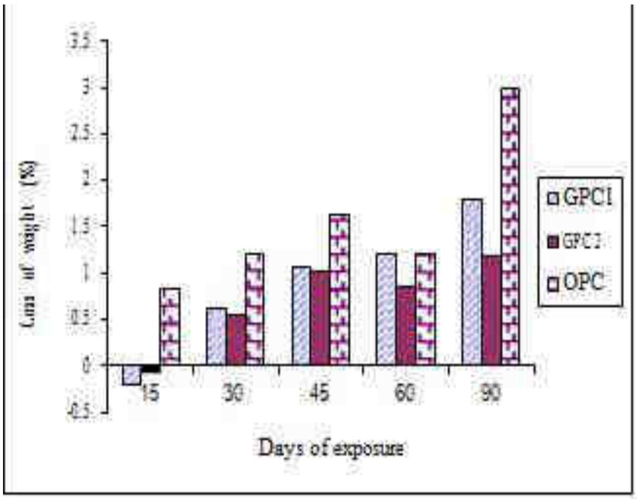

Fig. 5 Loss of weight with days of exposure (M30)

Compressive strength

The compressive strength lost during the period of exposure in sulphate media for the three types of mixes are illustrated in Fig. 6. The reduction in strength for GPC1, GPC2 and OPC mixes with different grades of concrete were varying as illustrated below. From these values it clearly indicates that the geopolymer concrete specimens (GPC1 and GPC2) are superior to OPC specimens in strength also.

As indicated earlier, the choice of $MgSO_4$ has observed the loss of strength in OPC, because of its reaching action compared with other sulphates [18,19]. This solution basically attacks the main part of cement hydration products like C-S-H, C-H and C-A-H to form gypsum, $Mg(OH)_2$ and silica [20,21]. The reaction between these substances, if enough water is present, produces ettringite and gypsum and causes expansion of the ordinary Portland concrete, leading to cracking. At the same time, the attack of magnesium ions and, to a lesser extent, the sodium ions on C-S-H starts, when CH is depleted. This attack leads to gypsum precipitation and decalcification of C-S-H. The decalcification of C-S-H destroys the binding capacity of C-S-H and leads to a loss of adhesion and strength in concrete.

On the other hand, when we observe the strength values of GPC1 and GPC2 there is no significant change in the values, which clearly indicate that the geopolymer concrete mixes are resistant to sulphate attack also.

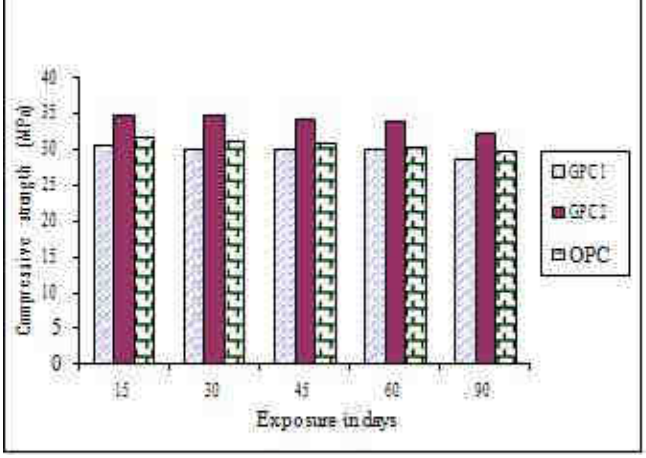

Fig. 6 Compressive strength with days of exposure (M30)

Residual compressive strength

The variation of residual compressive strength with the period of exposure for the concrete mixes in 5% magnesium sulphate solution as shown in Fig. 7. The observation made during the testing of specimens is that the geopolymer concrete specimens produced a cracking sound. The sound occurred may be due to the deposited crystals within the pores. The loss of strength would be mainly due to the formation of gypsum and ettringite in the surface pores. The residual compressive strength was 84.12 to 95.08%, 83.77 to 97.10% and 79.20 to 89.49% respectively for GPC1, GPC2 and OPC mixes for different grades after 90 days of exposure.

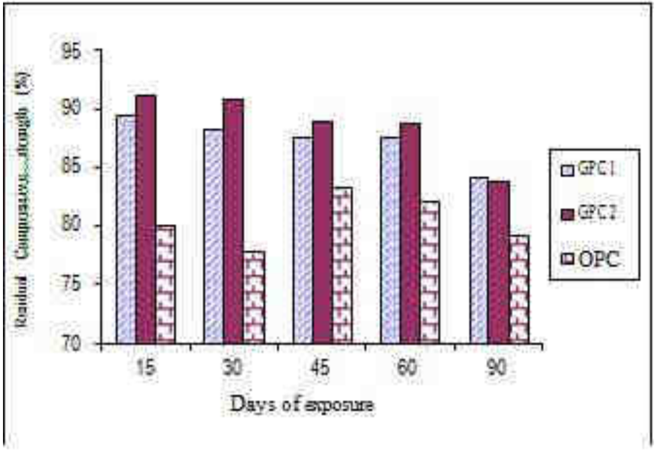

Fig. 7 Residual Compressive strength with days of exposure (M30)

CONCLUSIONS

Based on the experimental investigations carried out, it can be concluded that geopolymeric materials perform much better in acidic environment compared to Portland cement The better performance of geopolymeric materials than that of Portland cement in sulphate environment might be attributed to the lower calcium content of the source material as a main possible factor, since geopolymer concrete does not rely on lime like Portland cement concrete.

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