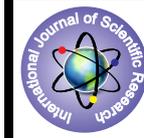


Chemical Analysis of Low Calcium Fly Ash Based Geopolymer Concrete



Engineering

KEYWORDS: Geopolymer, Residual alkalinity, Durability, Absorption study

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ABSTRACT

Geopolymer concrete offers a solution for the need of 'greener' construction material in the midst of environmental concern on the production of Ordinary Portland Cement (OPC). An experimental investigation was conducted to study the chemical properties of fly ash-based geopolymer concrete. Geopolymer was prepared with sodium silicate and sodium hydroxide as activators. The performance of these concretes in aggressive environments was studied using tests on absorption and acid resistance. In addition, performance of the specimens was evaluated in terms of visual appearance, variation of pH of solution and residual alkalinity over the exposure period. A microstructure characteristic of geopolymer concrete was studied using Scanning Electron Microscopy (SEM). pH of solution increased noticeably during the initial weeks which indicate migration of alkalis from mortar specimens. At the end of 18th weeks samples experienced very little weight gain. This research concludes that geopolymer concrete possesses excellent durability for aggressive environments.

1. INTRODUCTION

Geopolymer is a new material which is being used for construction all over the world (Davidovits 1988). Fly ash based geopolymers are one branch in the geopolymer family and this has attracted more attention since the 1990s. As a binder, the performance of fly ash based geopolymers is promising; especially in some aggressive situations where Portland cement concretes are vulnerable Song (2005). Davidovits (1994) found that metakaoline based geopolymer has very low mass loss when samples were immersed in 5% sulphuric acid solutions for 4 weeks. Wallah and Rangan (2006) have shown that the geopolymer composites possesses excellent durability properties in a study conducted to evaluate the long term properties of fly ash based geopolymers. The durability of concrete is a major and important requirement for the performance of the structure in aggressive environments. The durability of concrete depends upon its permeability characteristics. Impermeable concretes can resist the ingress of aggressive ions into the concrete and thereby reduce the damages occurring due to the deterioration of concrete and the corrosion of steel in concrete. The present study aimed to evaluate the performance of low calcium fly ash based geopolymer concrete in aggressive environments. The study comprised of variation of pH of solution, visual appearance, alkalinity, resistance of fly ash based geopolymer concrete in sulphuric acid and analysis of exposed specimen using SEM. The findings of the study shall be useful in determining the applicability of geopolymer materials for use in acid environments.

2. MATERIAL CHARACTERIZATION

Fly ash was obtained from Ennor Thermal Power Plant near Chennai (Southern part of India) and had mineral and chemical composition as shown in Table 1. For the preparation of geopolymer concrete locally available river sand was used as fine aggregate and coarse aggregate ranging from 6 mm to 12 mm sized aggregates is used. Fly ash is a slowly reactive material and has a strong silica alumina chain. In order to enhance the reaction process the strong chain has to be broken; hence, the alkali activators are used to enhance the reaction process. The OH⁻ concentration of the activators is an important constituent which is primarily necessary for the disintegration of the strong silica - alumina glassy chain. Higher the OH⁻ concentration of the activators, more rapid is the disintegration of the chain.

The choice of the activators mainly depends upon the reactivity and the cost of the activators (Dinakar and Ganesh Babu 2004). Literature indicates that sodium silicate solution in combination with sodium hydroxide and potassium hydroxide is an effective activator. Compared to potassium hydroxide, sodium hydroxide is cheaper and equally reactive. Sodium hydroxide solution of 10M was prepared by mixing the pellets with distilled water.

Table -1 Chemical Compositions of Flv Ash

Oxides	Silica	Alumina	Lime	Iron	Sulphur	Magnesia	Alkaline	LOI	Specific Gravity
% by Mass	52.8%	22.3%	Trace	9.2%	0.7%	0.5%	0.2%	3.7	2.30

3. MANUFACTURE OF GEOPOLYMER CONCRETE

Geopolymer concrete were made with low calcium fly ash. A combination of sodium hydroxide and sodium silicate solution was used to activate the fly ash. The sodium hydroxide solids were technical grade in flakes form (3 mm), with a specific gravity of 2.130, 98% purity or a commercial grade in pellets form with 97% purity. All the concretes were designed similar to normal concrete, such that the density was approximately equal to 2400 kg/m³ (Rangan and Hardjito 2005). The total aggregate content normally occupies about 60 - 80 % of the mass of the concrete. The sodium silicate solution and the sodium hydroxide solution were mixed together at least one day prior to use to prepare the alkaline liquid. On the day of casting of the specimens, the alkaline liquid was mixed together with the super plasticizer to prepare the liquid component of the mixture. In the experimental work the optimum activator to fly ash ratio was kept as 0.4 as suggested by Hardjito (2008). The Fly Ash and the aggregates are first mixed together in a mixing pan for about 5 minutes in hand mixing. After the dry mix is made, the prepared alkaline solution is thoroughly mixed with the dry mix for another 5 minutes to make the fresh geopolymer concrete. The fresh concrete was cast in solid cube specimens of size 150mm x 150mm x150mm. This was followed by an additional vibration using a vibrating table. The concrete specimens were left for air curing.

4. CHEMICAL ANALYSIS

4.1 Absorption studies

This study was done to know the relative porosity or permeability characteristics of the concretes. The concrete specimens used in this study are named as GM1, GM2 and GM3 for the discussions. The percentage of absorption was calculated using the equation (1).

$$\text{Absorption (\%)} = [(w_2 - w_1) / w_1] \times 100 \dots (1)$$

Where,

w₁ = weight of specimen after complete drying.

w₂ = final weight of surface dry sample after immersion in water for 3days.

The initial absorption values at 30 minutes were compared with recommendations given by Concrete Society Board (CEB-FIP 1989), and this comparison is presented in Table 2. From the

results shown in Table 3, it can be seen that absorption values of the geopolymer concrete were lower than the limit of 3% specified for good concrete. The geopolymer concretes were having lower absorption rate compared to normal concretes

Table -2
Assessment criteria for absorption Concrete Society Board (CEB-FIP 1989)

Absorption (%) At 30 Minutes	Absorption Rating	Concrete Quality
<3.0	Low	Good
3.0 to 5.0	Average	Average
>5.0	High	Poor

Table -3
Tabulation of w1, w2 and absorption%

S.No	Specimen	Initial Weight W1(Kg)	Final Weight W2(Kg)	Absorption %
1	GM1	7.79	7.86	0.89
2	GM2	7.45	7.50	0.67
3	GM3	7.50	7.57	0.93

4.2. Microstructure of the geopolymer cement

Unlike ordinary Portland pozzolanic cements, geopolymer do not form Calcium Silicate-Hydrates (CSHs) for matrix formation and strength, but utilize the polycondensation of silica and alumina precursors and a high alkali content to attain structural strength. Composition of the geopolymer is similar to natural zeolitic materials, but the microstructure is amorphous instead of crystalline. SEM was used to investigate the surface of fly ash, before and after reacting with NaOH. Fly ash before reacting with NaOH as shown in Fig. 1 appears to be smooth but after reacting with NaOH the surface roughened as a result of leaching of ions (see Fig. 2).



Fig. 1 Fly ash before reacting with reacting NaOH

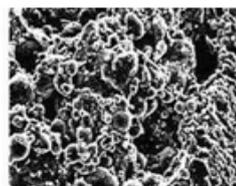


Fig.2 Fly ash after reacting with reacting NaOH

4.3 Acid attack study

To study the effects of exposure to acidic environment, specimens were immersed in 3% solution of sulphuric acid. Test was carried out at regular intervals after 28 days for a period of 18 weeks. The volume of acid solution was kept as 4 times the volume of specimens immersed and stirred every week. The solution was replaced at regular intervals to maintain concentration of solution throughout the test period. The evaluations were conducted after 0, 3, 6, 9, 12 and 18 weeks from the date of immersion. After removing the specimens from the solution, the surfaces were cleaned with a soft nylon wire brush under the running tap water to remove weak products and loose material from the surface. Then the specimens were allowed to dry and measurements were taken. From the initial measurement and measurements at particular intervals, the loss/ gain of the weight were studied. The geopolymer concrete shows percentage of mass loss less than 0.5 % (see Table 4). The percentage of mass loss for geopolymer concrete was only a fraction compared to the normal concrete of equal strength grades. Hence

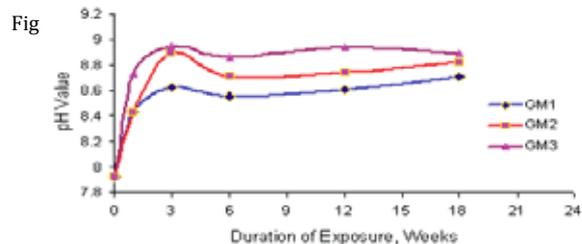
geopolymer concrete showed an excellent resistance to acid attack.

Table- 4
Change in mass of concrete exposed to sulphuric acid solution (3%)

S.No	Duration of Exposure weeks	Weight of Geopolymer Material (G1), Kg	Weight % = ((W2-W1)/W1) X 100
1	0	7.79(W1)	-
2	3	7.90	1.41
3	6	7.95	2.05
4	9	7.98	2.43
5	12	7.99	2.56
6	18	8.01	2.82

4.3.1. pH of Solution

The variation in pH of the solutions containing the geopolymer specimen is shown in Fig. 4. The increase in pH was rapid for few days and there after it showed a gradual reduce. Since the Na2O content in the specimen was very less, the pH of the solution was not increased further. The increase in pH may be attributed to migration of alkalis from specimen into the solution. Rate of migration of alkali appears to be higher within the initial days as indicated by the rapid rise in pH value. After 18 weeks exposure, pH increased considerably to about 9 in specimen GM3. The increase in pH was rapid during first three weeks and thereafter it was not appreciable. Continuous exposure beyond 18 weeks did not result in notable increase which suggests that further migration of alkali from the specimen has diminished or rather stopped. Fig. 3 presents the variation of pH.



4.3.2 Residual Alkalinity

The residual alkalinity of the geopolymer mortar specimens were examined roughly by spraying 1% phenolphthalein solution on the freshly cut surface (Rendell and Jauberther 1999). On spraying, dealkalinized part of specimen showed colourless while remaining part exhibited a magenta color indicating its residual alkalinity which is shown in Fig. 4. It was noticed that the process of dealkalinization progressed inwards with time. Alkalinity were seen to have lost almost in 12 weeks, 15 weeks and 18 weeks, respectively indicating the faster rate of dealkalinization in specimen with lower content of Na2O.

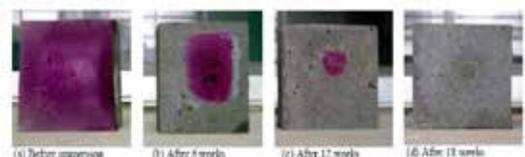


Fig. 4 Residual alkalinity in sulphuric acid

5. ANALYZING GEOPOLYMER SAMPLE IN SEM

Fig. 5 shows typical SEM micrograph of fly ash based geopolymer concrete. This micrograph shows the geopolymer gel with partially or completely unreacted fly ash particles. Geopolymer product has unshaped and uniform microstructure. Some cracks were observed in the surface that might be due to mechanical damage during the sample preparation. The geopolymer microstructure from this research looks like many types of geopolymer from similar observations by Fernandez-Jimenez (2005) and Skvara. (2006).

Fig.6 shows the holes in the microstructure resulted from air bubbles in the mixture. Those voids are distributed around the layer of geopolymer matrix. It is also found that there are some unreacted fly ash particles in the microstructure. Fly ash is known to have a significant proportion of particles with hollow spheres that possible to create porosity when they partially dissolved. As the result, the geopolymer matrix contains more dispersed small sized pores that can contribute to the overall porosity.

Fig.5 Typical SEM micrograph of geopolymer concrete

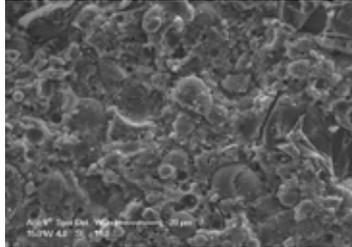
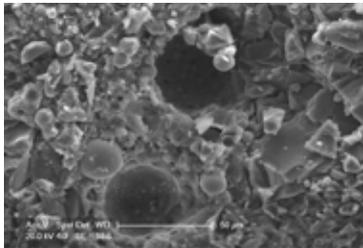


Fig. 6 Air bubbles and unreacted fly ash of geopolymer concrete



6. CONCLUSIONS

The absorption characteristics, which indirectly reflects the permeability, show that the initial 30 minutes absorption values for all the concretes was lower than the limits specified for "good concrete" by Concrete society. The deterioration of geopolymer concrete assessed in 3% H₂SO₄ solution shows that there is no significant variation in weight loss with increasing fly ash content. All the concrete showed weight loss of less than 0.5 %. Exposure solutions recorded considerable increase in pH value which can be attributed to migration of alkalis from specimen to solution. Maximum increase in pH occurred in solution containing specimen with highest Na₂O content which suggests that more alkalis migrated from these specimens. Geopolymer mortar specimens manufactured from fly ash with alkaline activators were structurally intact and did not show any recognizable change in colour after 18 weeks exposure in 3% sulphuric acid solution. Geopolymer samples almost lost its alkalinity within 15 weeks in 3% sulphuric acid solution. From the micro structural analysis, the partially dissolved fly ash particles with hollow spheres mainly contribute to the porosity of the geopolymer matrix. It can thus be concluded that geopolymer concrete possesses excellent durability for aggressive environment.

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