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Effect of Aggressive Chemical Environment on Durability of Green Geopolymer Concrete

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Abstract: - This paper presents an innovative approach towards thedevelopment of a green concretes, the geopolymersan environmental friendly construction/repairing materials. The Study based on the use of fly ash in synthesizing cement free geopolymer and subsequent study on the durability of geopolymerconcrete. The geoploymers manufactured by geopolymerization between class F fly ash (FA), with alkali activator fluid (Sodium silicate and sodium hydroxide). The optimum compressive strength was obtained at curing temperature of 120^{0}C for 72 hrs. The geopolymer concretes (GPC) consist of an inorganic polymer of alumino-silicates as the binder whereas the conventional concretes have Portland cement (P-C) generated C-S-H gel. The newly synthesized geopolymer then subjected to durability studies under different aggressive chemicalenvironment with particular reference to the effect of Acid, Sulphatesand Chloridesaltsand compare the effect with ordinary Portland cement (OPC). The precast cubes of geopolymers were immersed in different solutions for different time duration (30, 60& 90 days) and then the specimens were subjected to evaluation of the tests results of compressive strength and other physico-chemical and mineralogical changes. It was observed that fly ash-based geopolymer concrete has an excellent resistance to acid and sulphate attack when compared to conventional concrete. It is well known that mechanisms of attack by sulphuric acid and sulphates are different in both the case (GPC& OPC), The conventional concretes are generally not resistant to prolonged exposure to very high concentrations of these solutions because decalcification of C-S-H will occur. The effect on compressive strength and other parameters including structural and mineralogical changes was further evaluate and confirm with the help of X-ray diffraction study (XRD.

Keywords: **Alkali activator fluid , Aggressive chemical environment, Acid attack, Compressive Strength, , Durability, Fly Ash, Geopolymer Concrete,(GPC), Sulfate resistance.**

I. INTRODUCTION

Concrete is one of the most widely used construction materials in the world and ordinary Portland cement is the main binding material in concrete.The consumption of energy during the manufacturing of OPC, which releases a large amount of greenhousegases into the atmospherecausing global warming. Among the greenhouse gases, CO_2 contributes about 65% to global warming.The cement industry is responsible for about 6% of all CO_2 emissions, because the production of one ton of Portland cement emits approximately one ton of CO_2 into the atmosphere.[1-2]. Coal-based thermal power plants all over the world face serious problems of handling and disposal of the ash produced. The high ash content (30–50%) of the coal in India makes thisproblem morecomplex. Safe disposal of the ash without adversely affecting the environment is also big challenge. Hence attempts are being made to utilize this fly ash rather than dump it. The coal ash can be utilized in bulk in geotechnicalengineering applications such as construction of embankments, as a backfill material, and as a sub-base material [3] Geopolymers are inorganic polymeric bindingmaterials, firstly developed by Joseph Davidovits in1970s. Geopolymerisation involves a chemical reactionbetweenan alumino-silicate (Al-Si) material and a strong alkaline solutionyieldingamorphous to semi-crystalline three-dimensionalpolymeric structures, which consist of Si-O-Al bonds [4]. In 1978 Davidovits proposed that an Al-Si compound could polymerise with an alkaline solution. Davidovits (1988) discovered that the concrete used in ancient structures is alkali-activated alumino-silicate binders and named it as geopolymer concrete because of polymerisationreaction;This led to the idea of cement replacement and the subsequent creation of 'Geopolymer Concrete'. Ever since the introduction of geopolymer binders by Davidovits in 1978, it has generated a lot of interest among engineers as well as in the field of chemistry. In the past few decades, it has emerged as one of the possible alternative to OPC binders due to their reported high early strength and resistance against acid and sulphate attack apart from its environmental friendliness. Though geopolymers can be manufactured from various source materials rich in silica and alumina such as fly ash, silica fume, ground granulated blast furnace slag and metakaolinetc, fly ash based geopolymers have attracted more attention. Geopolymer binders might be a promising alternative in the development of acid resistant concrete since it relies on alumina-silicate rather than calcium silicate hydrate bonds for structural integrity [5]. Geopolymersis a type of inorganic polymer composite, that are produced and hardened even at ambient temperature under highly alkaline conditions, in the presence of alkali hydroxide and silicate solution.Polymerization takes place when reactivealuminosilicatesare rapidly dissolved and free SiO_4 and AlO_4 tetrahedral units are released in solution. The tetrahedral units are alternatively linked to polymeric precursors by sharing oxygen atoms thus forming amorphous geopolymers. Positive ions Na+ that are present in framework cavities, balance the negative charge [6]. There are lots of literatures has focused the main attributes of Geopolymer concrete such as strength and durability against aggressive environments like sulphate ,durability of reinforced geopolymer concrete in a seawater and sewage environments. Ordinary Portland

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cement concrete is known to be susceptible to acid attack. The high content of CaO in OPC makes it vulnerable as it is readily soluble in acid environment [7-9].Alkali activated fly ash cementitious materials (Geopolymer Concrete) are a promising alternative for the reasons that fly ash contain very less CaO. Geopolymerconcrete cube manufactured using low calcium class F Indian fly ash and thesame is investigated with the support of SEM and XRD reports. The resistance of geopolymer materials prepared from fly ash against 5% sulphuric acid up to 5 months exposure and concluded that geopolymer materials have better resistance than ordinary cement counterparts [10]. The geopolymer composites possesses excellent durability properties in a study conducted to evaluate the long term properties of fly ash based geopolymers [11-14] . The geopolymer has a very good resistance in acid media in terms of weight loss and residual compressive strength [15] .The performance of geopolymer concretes in aggressive environments was studied using tests on absorption and acid resistance [16]. Results indicated that the water absorption decreased with an increase in the strength of the concrete and the fly ash content. Based on summary of extensive studies conducted, simple trial and error methods were suggested to design the geopolymer concrete mixes [17-19]. The geopolymer concrete (GPC) was superior to plain Portland cement concrete (PPCC) when these mixes were subjected to sodium sulphate and magnesium sulphate solutions [20]. In the present study a class F, fly ash was used to synthesize an alkali activated concrete (Zeopolymer concrete, GPC) without use of OPC, and study its strength and durability properties under different chemical environment.

II METHODOLOGY

A. *MATERIALSAND SAMPLE PREPARATION:*

Fly ash sample collected from Thermal power plant located in the state of Haryana, (India) was used for study. It was low calcium based type F, fly ash. The chemical composition of the fly ash is listed in Table-1

B. *SYNTHESIS OF GEOPOLYMERS CONCRETE*

Geopolymer can be synthesized by polycondensation reaction of geopolymeric precursor (Fly ash), and alkali polysilicates. The process of alkali activation of fly ashes produces a material with similar cementing features than those characterizing ordinary Portland cement. Fly ash mixed with alkali activators and sand and then the mixture is cured under certain temperature to carry out polymerization and condensation reactions which transformed the glassy constituent of the fly ash into well compacted cementitious material. The production of geopolymers has a relative higher strength, excellent volume stability, better durability.

C. *MECHANISM*

Parameters	% by weight
Silica, SiO_2	57.95
Alumina ,Al_2O_3	31.78
Iron Oxide , Fe_2O_3	4.30
Lime,CaO	1.10
Magnesia, mgo	0.51
Sodium Oxide, Na_2O	0.15
Potassium .Oxide, K_2O	0.28
Loss on ignition, LOI	2.65
Sul.anhydride,SO_3	0.075

The most proposed mechanisms for the geopolymerisation include the following four stages. [21-24].

- Dissolution of Si and Al from the solid aluminosilicate materials in the strongly alkaline aqueous solution,
- Formation of oligomers species (geopolymers precursors) consisting of polymeric bonds of Si-O-Si and/or Si-O-Al type,
- Polycondensation of the oligomers to form a three-dimensional aluminosilicate framework geopolymeric framework)
- Bonding of the unreacted solid particles and filler materials into the geopolymeric framework and hardening of the wholesystem into a final solid polymeric structure.

D. *EXPERIMENTAL*

The combination of sodium silicate (Na_2SiO_3) and NaOH solution was used as alkaline activators. The alkaline activator was prepared by mixing a sodium silicate and NaOH solution with a concentration of 10 M. The ratio of fly ash to alkaline activator (Na_2SiO_3/NaOH) ratio were fixed as 2.5 and applied for all samples.The fly ash was then mixed with the alkaline activator in the mixer. Sand is small aggregates in geopolymer mortar.Cubes were casted with taking sand –Fly ash ration fixed (50:50) keeping NaOH- concentration 10 M.The Mortar resulting from mixing the fly ash with sand

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and alkaline solution was poured in to metallic prismatic molds,(Cube Area 14.44 cm^2)which were later kept in an oven. The cubes were cured at different temperature for different time intervals in order to achieve optimum compressive strength after curing the specimens cubes were subjected to compressive strength and durability study under different aggressive chemical environment. The maximum compressive strength (36.50 Mpa) was observed at 72 hours curing at 120^0C. Fig.1-4.

Sample Preparation (Casting of GPC Cubes and Curing Fig.1-4)

Fig.1

Fig. 2

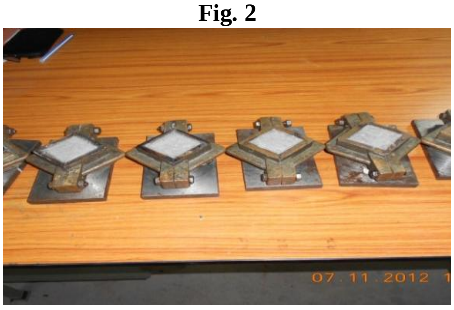

Fig.3

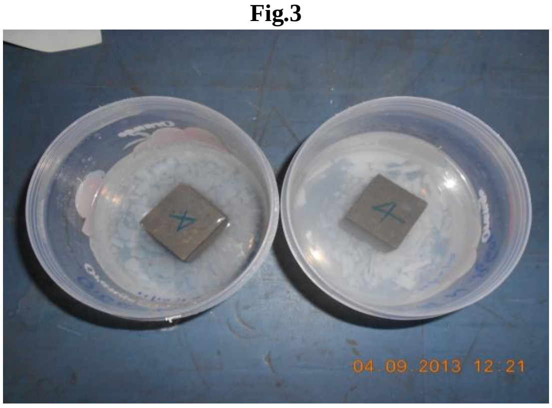

Fig.4

The counterpart OPC concrete specimens were preparedwith43 grade Ordinary Portland cementOPC. The concrete cubes were allowed to set for 24 hours, demoulded and placed in water pond for 28 days foreffective curing. Unlike ordinary Portland/pozzolanic cements, geopolymer do not form calciumsilicate-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.

E. DURABILITY STUDY:

The Geopolymer cubes were then subjected to durability study in different chemical environment.(Fig.5-10) GPC & OPC cubes were immersed in 0.05 & 0.005 Molar Sulphuric acid solution in one liter container for 30, 60& 90 days respectively to study the effect of acid on weight loss, compressive strength and other physical and chemical changes . The concentrated sulphuric acid of 98% purity and density of 1.85 g/cc was utilized to prepare the sulphuric acid solution. The GPC and OPC cubes were also immersed in 10% solution of Sodium Sulphate(Na_2SO_4) and 10% solution of Sodium Chloride (NaCl) for 30, 60& 90 days of duration to observe the effect of these deleterious salts on both types of concrete and compare their resistance power in such aggressive environment.

GPC-cubes after curing in different environment (Fig.5-10)

Fig.5

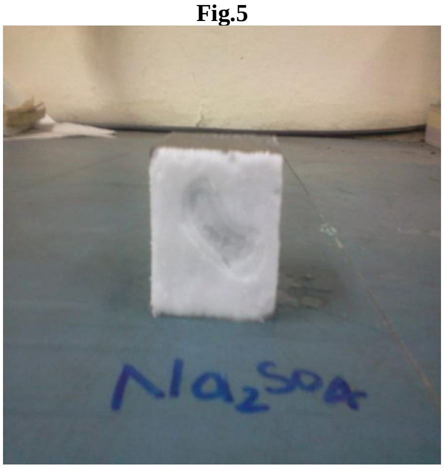

Fig.6

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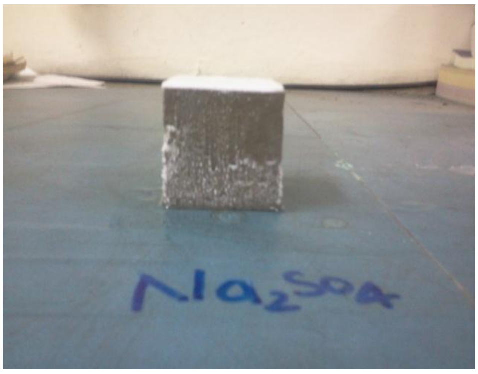

Fig.7

Fig. 8

Fig. 9

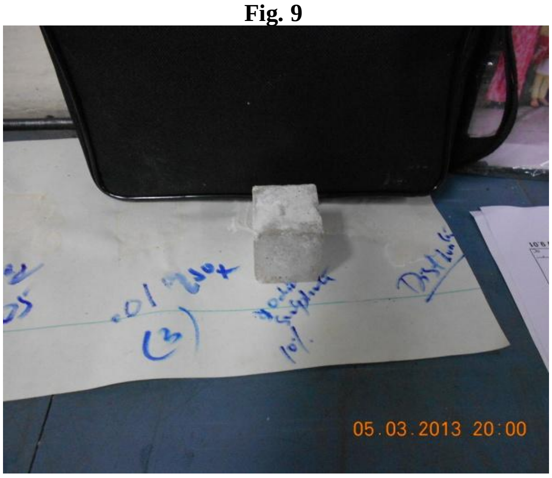

Fig.10

The compressive strength of the cubes was measured with the help of Universal Testing Machine (UTM) and the change in mineralogy due to ingress of aggressive solution was also studied by X-ray diffraction (XRD). XRD analysis was done by using a GBC Scientific Equipment (Australia), Model - EMMA 125 diffracto meter.

III. RESULTS AND DISCUSSIONS

A. CHANGE IN WEIGHT

Cubes each GPC and OPC wereimmersed in 0.005 & 0.05 M sulphuric acid, 10% sodium sulfate solution and 10% sodium chloride solution fortest period of 30,60 and 90 days. The change in weight of geopolymerconcrete cubes exposure to sulphuric acid, sodium chloride and sodium sulphatesolution were observed for GPC concrete cubes and were compared with the weight of unexposed/untreated GPC cube. All the exposedspecimens recorded weight loss and it was observed that the weight loss in case of acid attack was more in compare to sulphate and chloride. The results of change in weight is presented in fig.11

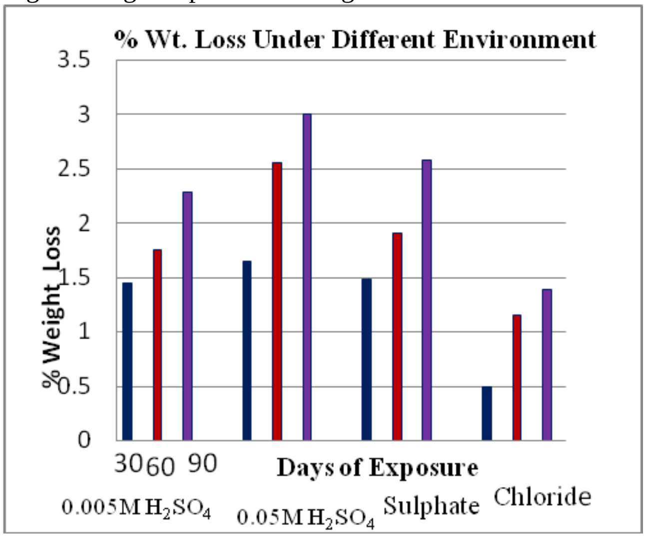

Fig. 11

B. EFFECT ON COMPRESSIVE STRENGTH

Cubes each GPC and OPC wereimmersed in0.005 & 0.05 M sulphuric acid, 10% concentration of sulphuric acid, sodium sulfate solution and sodium chloride solution for the test period of 30,60 and 90 days. The results of compressive strength after 30, 60&90 days are presented in Table-2& 3(Fig.12-17)

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Sl. No.	Type of chemical environment	GPC , Compressive strength,(MPa)		
		30 Days	60 Days	90 Days
1.	Distilled water	36.10	35.55	35.02
2	0.005M Sulphuric acid, H_2SO_4	34.52	32.72	31.22
3	0.05 M Sulphuric acid	33.68	30.55	27.64
4	10% Solution of Sodium Chloride, NaCl	34.90	33.45	32.85
5	10% Solution of Sodium sulphate, Na_2SO_4	33.25	30.15	27.21

Sl. No.	Type of chemical environment	OPC, Compressive strength, (MPa)		
		30 Days	60 Days	90 Days
1	Distilled water	42.85	42.15	41.75
2	0.005M Sulphuric acid, H_2SO_4	41.00	38.68	36.05
3	0.05 M Sulphuric acid	39.75	35.28	30.87
4	10% Solution of Sodium Chloride, NaCl	41.88	39.12	37.92
5	10% Solution of Sodium sulphate, Na_2SO_4	38.54	34.04	29.68

Table-3

C. EFFECT OF AGGRESSIVE ACID NVIRONMENTS ON COMPRESSIVE STRENGTH

The effect on compressive strength on both GPC and OPC sample cubes exposed to 0.005& 0.05 Molar solutions of sulphuric acids for 30 , 60& 90 days were compared.The deterioration observed was connected to depolymerisation of the aluminosilicate , which in some cases lead to a significant loss of strength. Due to low calcium content in fly ash, thegeopolymer concrete exhibits high resistance to acid immersion. The compressive strength of OPC cubes were found decreases more in comparison to GPC. (Fig.12-14).The GPC cubes exposed to sulphuric acid undergoes erosion of the surface while in case of ordinary Portland cement; sulphuric acid attack leads to deposition of a white layer of gypsum crystals on the acid-exposed surface of thespecimen. Whereas, geopolymer cement tested, unlike Portland cement, no gypsumdeposition can be detected visually (Fig.6, 7, 10)

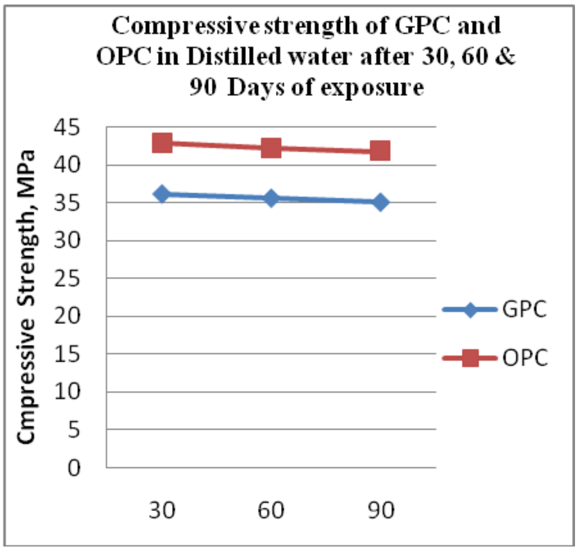

Fig.12

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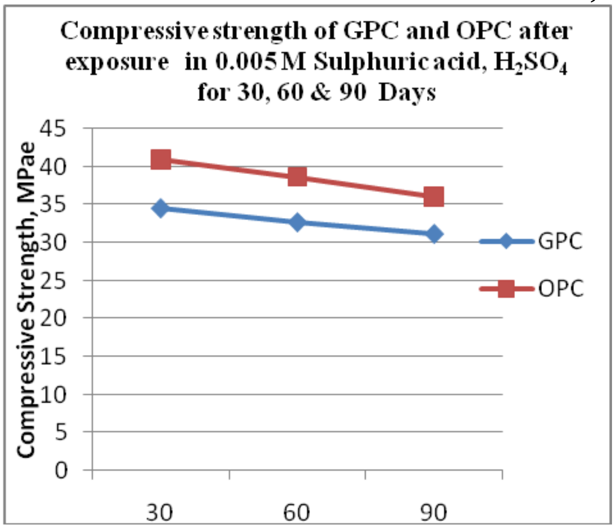

Fig.13

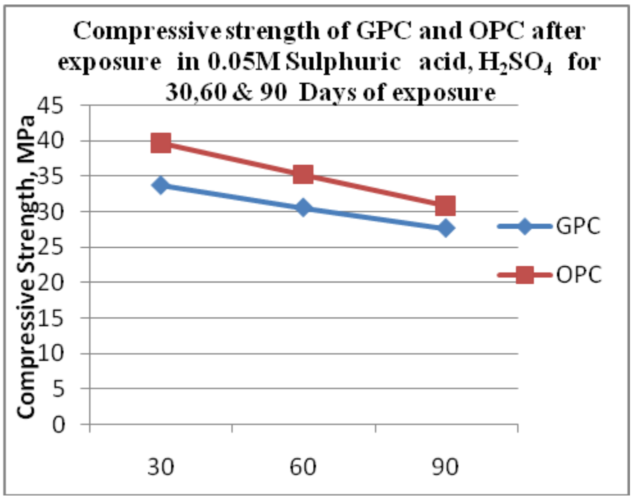

Fig.14

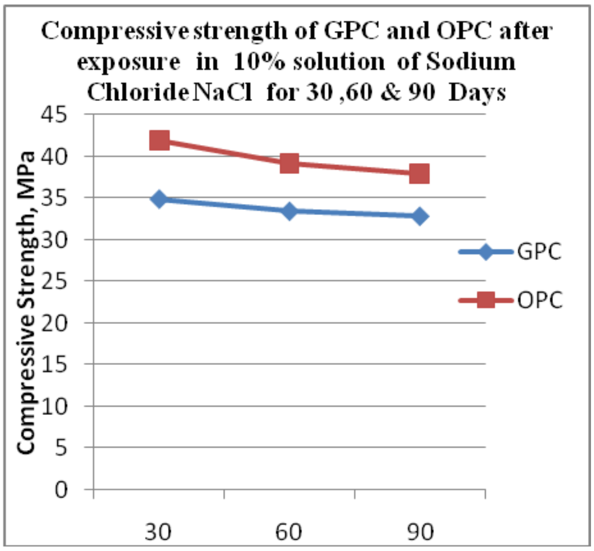

Fig.15

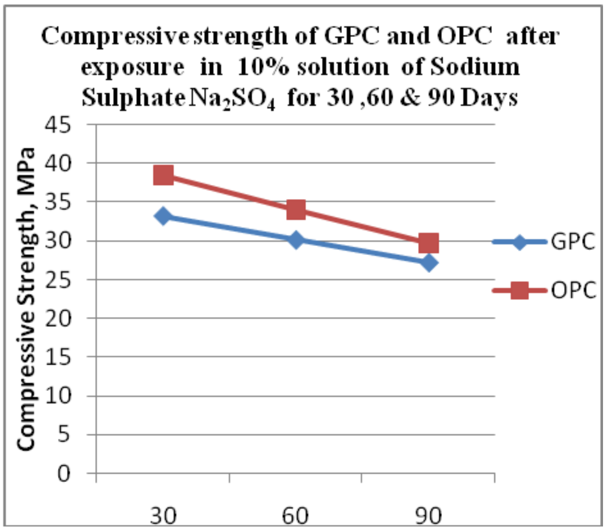

Fig.16

D. EFFECT OF SULPHATE & CHLORIDE SALTS

The effect of sulphate and chloride salts on compressive strength of both GPC and OPC cubes were presented in table-2& 3. Results shows that compressive strength for both types decreases on exposure of 30, 60 &90days duration while the decrease in case of OPC is more in comparison to GPC which shows that Geoploymer concrete exhibit significant resistance to sulphate and chloride attack. (Fig. 15-16) The surface deterioration was observed in both sulphate and chloride immersion for GPC as well as OPC cubes but it was more prominent in case of cubes immersed in Sodium Sulphate solution. The expansion of surface clearly shows the formation of ettringite in case of OPC.

E. X-RAY DIFFRACTION ANALYSIS

The XRD pattern of original fly ash(Fig. 17) mainly representsthe presence of crystalline quartz and mullite.Fly ash, after treatment gives several sharp diffractionpeaks, which are different from those present in the untreated fly ash. The XRD pattern of GPC (Fig. 18) shows that the amorphous phases originally existing in the fly ash have been apparently altered by the alkali activation reaction, however diffraction lines associated with the presence of quartz appear more intensely which is due to presence of sand particles in the matrix also.The XRD pattern of GPC alsoshows formation of new minorcrystalline phases which is similar to Zeolitic phases which contributes improvement in compressive strength. XRD patterns of sulphuric acid immersed cubes (Fig. 19) were shown that several peaks were shorten and disappear possibly due to weathering and dissolution of mineral composites.XRD pattern of GPC cubes immersed in Sodium sulphate and sodium chloride solutions shows that peaks for Zeolitic phases have reduced and new peaks were arising from aluminoilicategelwhichindicates eruption by sulphur. Also new hematitecrystal peak appeared2Θat78^{0}.(Fig.20)

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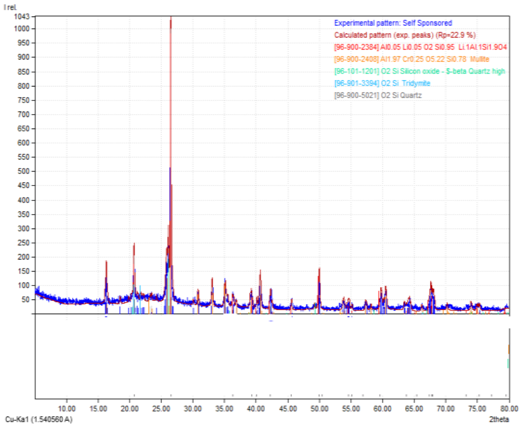

Fig.17, XRD Pattern of Fly Ash

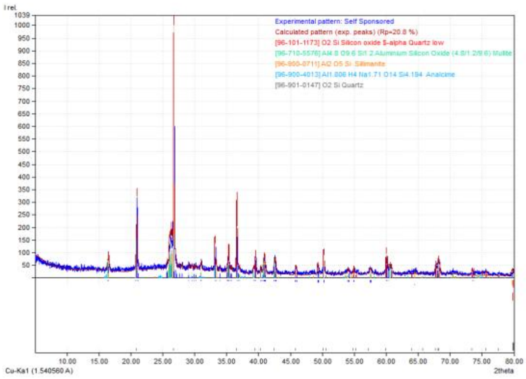

Fig.18, RD Pattern of GPC

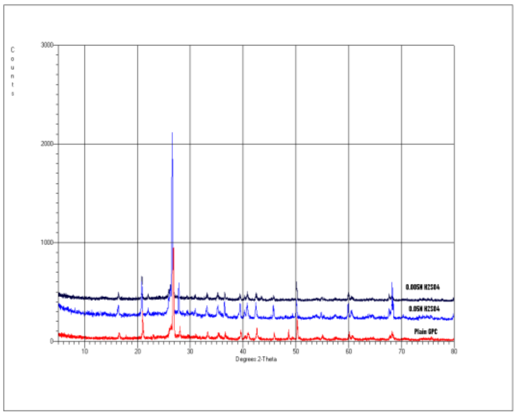

Fig.19, XRD Pattern of Plain GPC, and Acid exposed GPC

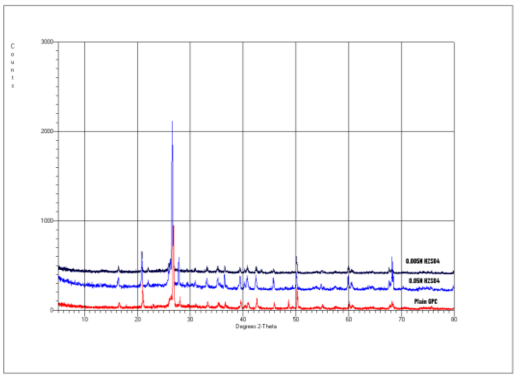

Fig.20, XRD Pattern of Plain GPC, and salts

IV. CONCLUSION

1. Fly ash based Geopolymer concrete has excellent compressive strength and is suitable for structural applications.
2. Fly ash based geopolymer concrete have no visible signs of surface deterioration, formation of pores on the surface and spalling of concrete after immersion in aggressive solution for 30,60 and 90 days of exposure.
3. The loss in weight was observed in all specimens at the end of study period.
4. The sulfuric acid attack causes degradation in the compressive strength of Geopolymer concrete and the extent of degradation depends on the concentration of the acid solution and the period of exposure. However, the sulfuric acid resistance of Geopolymer concrete is significantly better than that of ordinary Portland cement concrete.
5. Observation of the mass changes of the samples exposed to acidic solutions and results obtained from XRD analyses shows the depolymerisation of aluminosilicate polymer gel.
6. The better performance of geopolymeric materials than that of Portland cementconcrete in acidic environment might be attributed to the lower calcium content of thesource material as a main possible factor since geopolymer concrete does not relyonlime like Portland cement concrete.
7. The test result shows that heat-cured fly ash based Geopolymer concrete has an excellent resistance to sulfate attack. There is no damage to the surface of test specimens after exposure to sodium sulfate solution up to 90 days. There are no significant change in the mass and the compressive strength of test specimens after an exposure period of 90 days.
8. Heat cured Geopolymer concrete has an excellent resistance to chloride attack. This proves Geopolymer concrete can be used in sea water area.
9. It can thus be concluded that Geopolymer concrete possesses excellent mechanical properties and durabilityfor aggressive environment compare to OPC.

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AUTHOR'S PROFILE

Dr. Neetu Singh:
Obtained Ph.D. in Chemistry from University of Allahabad (U.P., India). The topic of research was "Studies on Chemical Sensors". Area of research focused on the application of electrochemical sensors in environmental analysis. Presently works at Central Soil and Materials Research Station, a research organization under Ministry of Water Resources, Govt. of India, New Delhi. Works in Concrete Chemistry Discipline, associated with the characterization of construction materialsrelated to mass concrete structureswith particular reference tochemical analysis of constructionmaterials such as concrete, cement, Microsilica (Silica fumes), aggregates,water quality, Fly ash, admixtures, and involved in the study related to associated R&D issues.