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FLY ASH BASED GEOPOLYMER CONCRETE

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ABSTRACT

Geopolymer are inorganic polymeric materials with a chemical composition similar to zeolites but possessing an amorphous structure. In a simple way geopolymer may be seen as man-made rocks. Unusually, geopolymer are synthesized at relatively low temperature from metakaolinite, whereby the geopolymerization reaction is favored by its amorphous state. The smaller the particle size of the starting material the higher the reactivity and the geopolymerization rate will be. Due to their low porosity highly-packed microstructure, high temperature resistance, water resistance, acid resistance, low thermal expansion and fire-proofness, geopolymer can be used in many applications, among which binders in certain specialty cements and for immobilization, stabilization and solidification of a large number of materials are best known.

The ration of silica and aluminum i.e. Si/Al ratio, the predominant amorphous structure, and the fine particle size of fly ashes, are appropriate for the synthesis of geopolymer. This paper reviews previous work in which fly ash were successfully used as starting material for the production of geopolymer. Further the first result will be presented from a new EC-sponsored project, investigating the possibilities of the production of geopolymer from co-combustion residues. Coal / Biomass co-combustion fly ashes are selected because of the relatively high amount of submicron particles. Particle size distribution maybe further enhanced by separation and micro-grinding technologies. The aim is to use the produced geopolymer as new matrices for the immobilization of toxic wastes

I. INTRODUCTION

1.1. General

The global use of concrete is second only to water. As the demand for concrete as a construction material increases, so also the demand for Portland cement. It is estimated that the production of cement will increase from about from 1.5 billion tons in 1995 to 2.2 billion tons in 2010 (Malhotra, 1999). On the other hand, the climate change due to global warming has become a major concern. The global warming is caused by the emission of greenhouse gases, such as carbon dioxide (CO2), to the atmosphere by human activities. Among the greenhouse gases, CO2 contributes about 65% of global warming (McCaffery, 2002). The cement industry is held responsible for some of the CO2 emissions, because the production of one ton of Portland cement emits approximately one ton of CO2 into the atmosphere (Davidovits, 1994; McCaffery, 2002).

Several efforts are in progress to reduce the use of Portland cement in concrete in order to address the global warming issues. These include the utilization of supplementary cementing materials such as fly ash, silica fume, granulated blast furnace slag, rice-husk ash and metakaolin, and the development of alternative binders to Portland cement. In this respect, the geopolymer technology proposed by Davidovits (1988) shows considerable promise for application in concrete industry as an alternative binder to the Portland cement (Duxson et al, 2007). In terms of global warming, the geopolymer technology could significantly reduce the CO2 emission to the atmosphere caused by the cement industries as shown by the detailed analyses of Gartner (2004).

1.2. Objectives

The primary objectives of this research are to conduct experimental and analytical studies to establish the following:

a) The flexural behavior of reinforced geopolymer concrete beams including flexural strength, crack pattern, deflection, and ductility.

b) The behavior and strength of reinforced geopolymer concrete slender columns subjected to axial load and bending moment.

c) The correlation of experimental results with prediction methods currently used for reinforced Portland cement concrete structural members.

1.3 Scope of Work

The scope of work involved the following:

i. Based on the research described in Research Reports GC1 and GC2 (Hardjito and Rangan 2005, Wallah and Rangan 2006), select appropriate geopolymer concrete mixtures needed to fabricate the reinforced test beams and columns.
ii. Manufacture and test twelve simply supported reinforced geopolymer concrete rectangular beams under monotonically increasing load with the longitudinal tensile reinforcement ratio and the concrete compressive strength as test variables.
iii. Manufacture and test twelve reinforced geopolymer concrete square columns under short-term eccentric loading with the longitudinal reinforcement ratio, the load eccentricity and the concrete compressive strength as test variables.
iv. Perform calculations to predict the strength and the deflection of geopolymer concrete test beams and columns using the methods currently available for Portland cement concrete members.

II. GEOPOLYMER MATERIALS

2.1 General

Davidovits (1988) introduced the term ‘geopolymer’ in 1978 to represent the mineral polymers resulting from geochemistry. Geopolymer, an inorganic alumina-silicate polymer, is synthesized from predominantly silicon (Si) and aluminium (Al) material of geological origin or by-product material. The chemical composition of geopolymer materials is similar to zeolite, but they reveal an amorphous microstructure (Davidovits 1999). During the synthesized process, silicon and Aluminium atoms are combined to form the building blocks that are chemically and structurally comparable to those binding the natural rocks.

2.2 Use of Fly Ash in Concrete

Fly ash has been used in the past to partially replace Portland cement to produce concretes. An important achievement in this regard is the development of high volume fly ash (HVFA) concrete that utilizes up to 60 percent of fly ash, and yet possesses excellent mechanical properties with enhanced durability performance. The test results show that HVFA concrete is more durable than Portland cement concrete (Malhotra 2002).

Recently, a research group at Montana State University in the USA has demonstrated through field trials of using 100% high-calcium (ASTM Class C) fly ash to replace Portland cement to make concrete. Ready mix concrete equipment was used to produce the fly ash concrete on a large scale. The field trials showed that the fresh concrete can be easily mixed, transported, discharge, placed, and finished (Cross et al 2005).

2.3 Fly Ash-Based Geopolymer Concrete

Past studies on reinforced fly ash-based geopolymer concrete members are extremely limited. Palomo et.al (2004) investigated the mechanical characteristics of fly ashbased geopolymer concrete. It was found that the characteristics of the material were mostly determined by curing methods especially the curing time and curing temperature. Their study also reported some limited number of tests carried out on reinforced geopolymer concrete sleeper specimens. Another study related to the application of geopolymer concrete to structural members was conducted by Brooke et al. al (2005). It was reported that the behaviour of geopolymer concrete beamcolumn joints was similar to that of members made of Portland cement concrete.

III. INGRIDIENTS, MIXTURE PROPORTIONS, COMPACTION AND CURING OF GEOPOLYMER CONCRETE

3.1 Constituents of Geopolymer Concrete

Geopolymer concrete can be manufactured by using the low-calcium (ASTM Class F) fly ash obtained from coal-burning power stations. Most of the fly ash available globally is low-calcium fly ash formed as a by-product of burning anthracite or bituminous coal. Although coal burning power plants are considered to be environmentally unfriendly, the extent of power generated by these plants is on the increase due to the huge reserves of good quality coal available worldwide and the low cost of power produced from these sources. Therefore, huge quantities of fly ash will be available for many years in the future (Malhotra, 2006). The chemical composition and the particle size distribution of the fly ash must be established prior to use. An X-Ray Fluorescence (XRF) analysis may be used to determine the chemical composition of the fly ash.

3.1.1 Fly Ash

Low-calcium fly ash has been successfully used to manufacture geopolymer concrete when the silicon and aluminum oxides constituted about 80% by mass, with the Si-to-Al ratio of about 2. The content of the iron oxide usually ranged from 10 to 20% by mass, whereas the calcium oxide content was less than 5% by mass. The carbon content of the fly ash, as indicated by the loss on ignition by mass, was as low as less than 2%. The particle size distribution tests revealed that 80% of the fly ash particles were smaller than 50 μm (Gourley, 2003; Gourley and Johnson, 2005; Hardjito and Rangan, 2005; Wallah and Rangan, 2006; Sumajouw and Rangan, 2006; Fernandez-Jimenez et al, 2006a; Sofi et al, 2006a; Siddiqui, 2007). The reactivity of low-calcium fly ash in geopolymer matrix has been studied by Fernandez-Jimenez, et al (2006b).

3.1.2 Aggregate

Coarse and fine aggregates used by the concrete industry are suitable to manufacture geopolymer concrete. The aggregate grading curves currently used in concrete practice are applicable in the case of geopolymer concrete (Hardjito and Rangan, 2005; Wallah and Rangan, 2006; Sumajouw and Rangan, 2006; Gourey, 2003; Gourley and Johnson, 2005; Siddiqui, 2007).

3.1.3 Alkaline Liquide

A combination of sodium silicate solution and sodium hydroxide (NaOH) solution can be used as the alkaline liquid. It is recommended that the alkaline liquid is prepared by mixing both the solutions together at least 24 hours prior to use. The sodium silicate solution is commercially available in different grades. The sodium silicate solution A53 with SiO2-to-Na2O ratio by mass of approximately 2, i.e., SiO2 = 29.4%, Na2O = 14.7%, and water = 55.9% by mass, is recommended.

The sodium hydroxide with 97-98% purity, in flake or pellet form, is commercially available. The solids must be dissolved in water to make a solution with the required concentration. The concentration of sodium hydroxide solution can vary in the range between 8 Molar and 16 Molar. The mass of NaOH solids in a solution varies depending on the concentration of the solution. For instance, NaOH solution with a concentration of 8 Molar consists of 8x40 = 320 grams of NaOH solids per litre of the solution, where 40 is the molecular weight of NaOH. The mass of NaOH solids was measured as 262 grams per kg of NaOH solution with a concentration of 8 Molar. Similarly, the mass of NaOH solids per kg of the solution for other concentrations was measured as 10 Molar: 314 grams, 12 Molar: 361 grams, 14 Molar: 404 grams, and 16 Molar: 444 grams (Hardjito and Rangan, 2005). Note that the mass of water is the major component in both the alkaline solutions. In order to improve the workability, a high range water reducer super plasticizer and extra water may be added to the mixture.

3.2 Mixture Proportions of Geopolymer Concrete

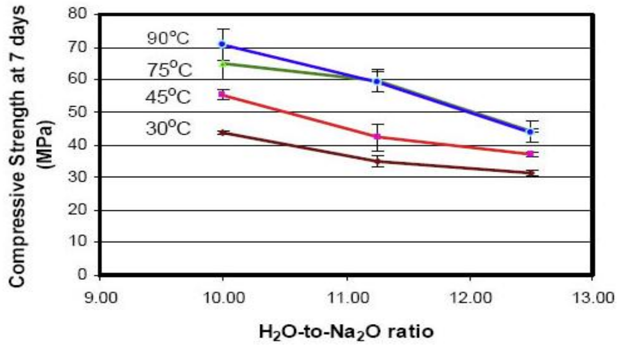
The primary difference between geopolymer concrete and Portland cement concrete is the binder. The silicon and aluminum oxides in the low-calcium fly ash reacts with the alkaline liquid to form the geopolymer paste that binds the loose coarse aggregates, fine aggregates, and other un-reacted materials together to form the geopolymer concrete.

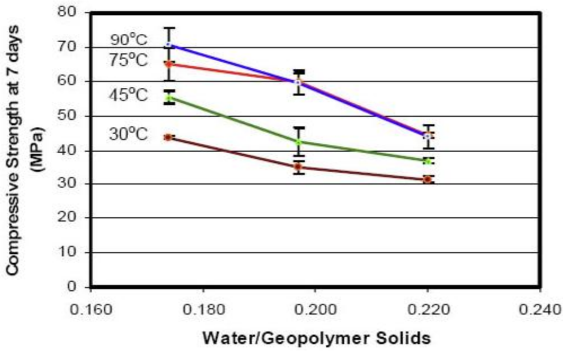
As in the case of Portland cement concrete, the coarse and fine aggregates occupy about 75 to 80% of the mass of geopolymer concrete. This component of geopolymer concrete mixtures can be designed using the tools currently available for Portland cement concrete.

The compressive strength and the workability of geopolymer concrete are influenced by the proportions and properties of the constituent materials that make the geopolymer paste. Experimental results (Hardjito and Rangan, 2005) have shown the following:

- Higher concentration (in terms of molar) of sodium hydroxide solution results in higher compressive strength of geopolymer concrete.
- Higher the ratio of sodium silicate solution-to-sodium hydroxide solution ratio by mass, higher is the compressive strength of geopolymer concrete.
- The addition of naphthalene sulphonate-based super plasticizer, up to approximately 4% of fly ash by mass, improves the workability of the fresh geopolymer concrete; however, there is a slight degradation in the compressive strength of hardened concrete when the super plasticizer dosage is greater than 2%.
- The slump value of the fresh geopolymer concrete increases when the water content of the mixture increases.
- As the H2O-to-Na2O molar ratio increases, the compressive strength of geopolymer concrete decreases (Figure).

Tests were performed to establish the effect of water-to-geopolymer solids ratio by mass on the compressive strength and the workability of geopolymer concrete. The test specimens were 100x200 mm cylinders, heat-cured in an oven at various temperatures for 24 hours. The results of these tests, plotted in Figure , show that the compressive strength of geopolymer concrete decreases as the water to- geopolymer solids ratio by mass increases (Hardjito and Rangan, 2005). This test trend is analogous to the well-known effect of water-to-cement ratio on the compressive strength of Portland cement concrete. Obviously, as the water-to-geopolymer solids ratio increased, the workability increased as the mixtures contained more water.





Materials		**Mass In Kg/M^2**	
		Mixture-1	**Mixture-2**
Coarse Aggregate	**20 Mm**	277	277
	14 MM	370	370
	7 MM	647	647
Fine Sand		554	554
Fly Ash (Low-Calcium ASTM Class F)		408	408
Sodium Silicate Solution (Sio$_2$/Na$_2$o = 2)		103	103
Sodium Hydroxide Solution		41 (8 MOLAR)	41 (14 MOLAR)
Super Plasticizer		6	6
Extra Water		NONE	22.5

3.3 Mixing, Casting, and Compaction of Geopolymer Concrete

Geopolymer concrete 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 in 80-litre capacity pan mixer for about three minutes. The aggregates were prepared in saturated-surface-dry (SSD) condition, and were kept in plastic buckets with lid.

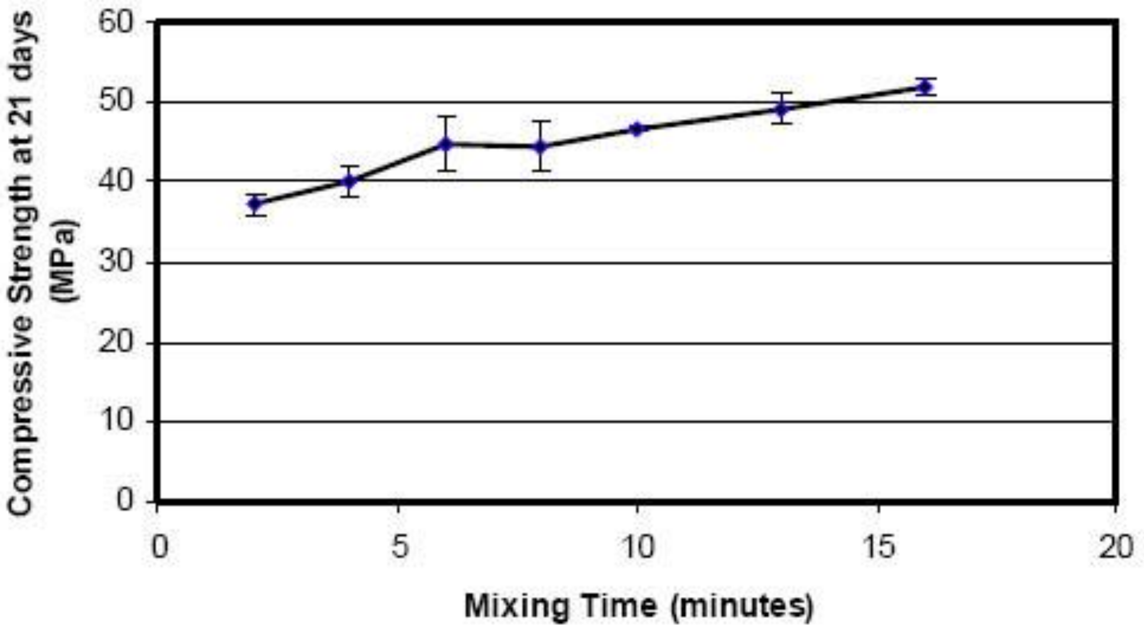
Mixing of Ingredients

The alkaline liquid was mixed with the super plasticizer and the extra water, if any. The liquid component of the mixture was then added to the dry materials and the mixing continued usually for another four minutes. The fresh concrete could be handled up to 120 minutes without any sign of setting and without any degradation in the compressive strength.

The fresh concrete was cast and compacted by the usual methods used in the case of Portland cement concrete (Hardjito and Rangan, 2005; Wallah and Rangan, 2006; Sumajouw and Rangan, 2006). Fresh fly ash-based geopolymer concrete was usually cohesive. The workability of the fresh concrete was measured by means of the conventional slump test .

Slump Cone Test

The test specimens were 100x200 mm cylinders, steam-cured at 60oC for 24 hours and tested in compression at an age of 21 days. Figure shows that the compressive strength significantly increased as the wet-mixing time increased. The slump values of fresh concrete were also measured.

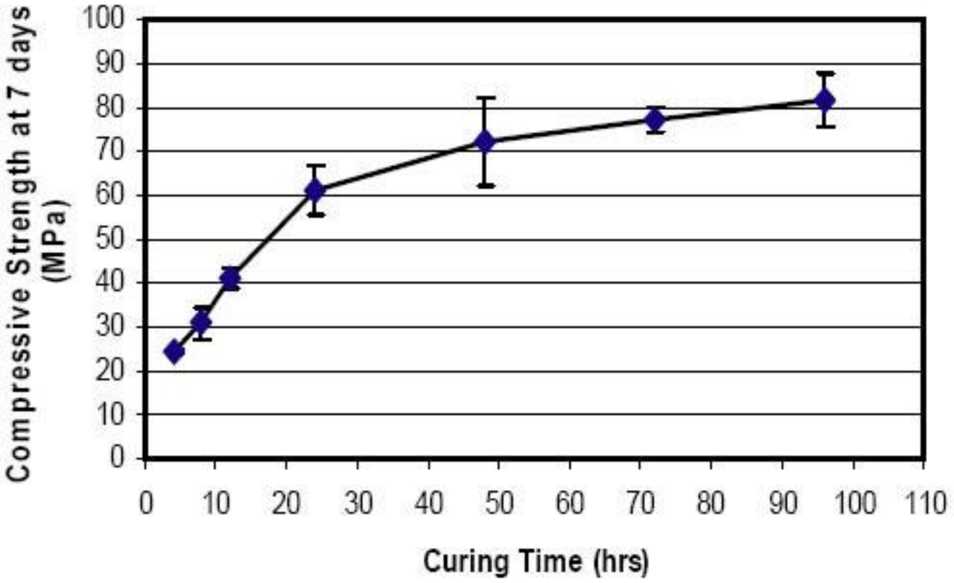


Mixing Time vs. Strength

3.4 Curing of Geopolymer Concrete

Heat-curing of low-calcium fly ash-based geopolymer concrete is generally recommended. Heat-curing substantially assists the chemical reaction that occurs in the geopolymer paste.

Both curing time and curing temperature influence the compressive strength of geopolymer concrete. The effect of curing time is illustrated in Figure (Hardjito and Rangan, 2005). The test specimens were 100x200 mm cylinders heat-cured at 60oC in an oven. The curing time varied from 4 hours to 96 hours (4 days). Longer curing time improved the polymerization process resulting in higher compressive strength. The rate of increase in strength was rapid up to 24 hours of curing time; beyond 24 hours, the gain in strength is only moderate. Therefore, heat-curing time need not be more than 24 hours in practical applications.



Curing Time vs. Strength

Figure shows the effect of curing temperature on the compressive strength of geopolymer concrete (Hardjito and Rangan, 2005). Higher curing temperature resulted in larger compressive strength.

IV. DESIGN, PRECAST PRODUCTS AND ECONOMIC BENEFITS OF GEOPOLYMER CONCRETE

4.1 Design of Geopolymer Concrete Mixtures

Concrete mixture design process is vast and generally based on performance criteria. Based on the information explained earlier, some simple guidelines for the design of heat-cured low calcium fly ash-based geopolymer concrete are proposed. The role and the influence of aggregates are considered to be the same as in the case of Portland cement concrete. The mass of combined aggregates may be taken to be between 75% and 80% of the mass of geopolymer concrete.

The performance criteria of a geopolymer concrete mixture depend on the application. For simplicity, the compressive strength of hardened concrete and the workability of fresh concrete are selected as the performance criteria. In order to meet these performance criteria, the alkaline liquid-to-fly ash ratio by mass, **water-to-geopolymer solids ratio** by mass, the wet-mixing time, the heat-curing temperature, and the heat-curing time are selected as parameters. With regard to alkaline liquid-to-fly ash ratio by mass, values in the range of 0.30

and 0.45 are recommended. Based on the results obtained from numerous mixtures made in the laboratory over a period of four years, the data given in Table are proposed for the design of low-calcium fly ash-based geopolymer concrete. Note that wet-mixing time of 4 minutes, and steam-curing at 60oC for 24 hours after casting are proposed. The data given in above Figures may be used as guides to choose other curing temperatures, wet-mixing times, and curing times.

Sodium silicate solution is cheaper than sodium hydroxide solids. Commercially available sodium silicate solution A53 with SiO2-to-Na2O ratio by mass of approximately 2, i.e., Na2O = 14.7%, SiO2 = 29.4%, and water = 55.9% by mass, and sodium hydroxide solids (NaOH) with 97-98% purity are recommended. Laboratory experience suggests that the ratio of sodium silicate solution-to-sodium hydroxide solution by mass may be taken approximately as 2.5 (Hardjito and Rangan, 2005).

The design data given in Table assumes that the aggregates are in saturated-surface-dry (SSD) condition. In other words, the coarse and fine aggregates in a geopolymer concrete mixture must neither be too dry to absorb water from the mixture nor too wet to add water to the mixture. In practical applications, aggregates may contain water over and above the SSD condition. Therefore, the extra water in the aggregates above the SSD condition must be included in the calculation of water-to geopolymer solids ratio given in Table.

Calculation of Water-To Geopolymer Solids Ratio

Water-to-geopolymer solids ratio, by mass	**Workability**	**Design Compressive Strength (Wet-Mixing time of $ Min, steam curing at 60^0**
0.16	Very Stiff	60
0.18	Stiff	50
0.20	Moderate	40
0.22	High	35
0.24	High	30

4.1.1 Short-Term Properties of Geopolymer Concrete

a. **Behavior in Compression:** The behavior and failure mode of fly ash-based geopolymer concrete in compression is similar to that of Portland cement concrete.

b. **Indirect Tensile Strength:** The tensile strength of fly ash-based geopolymer concrete was measured by performing the cylinder splitting test on 150x300 mm concrete cylinders.

Short term properties

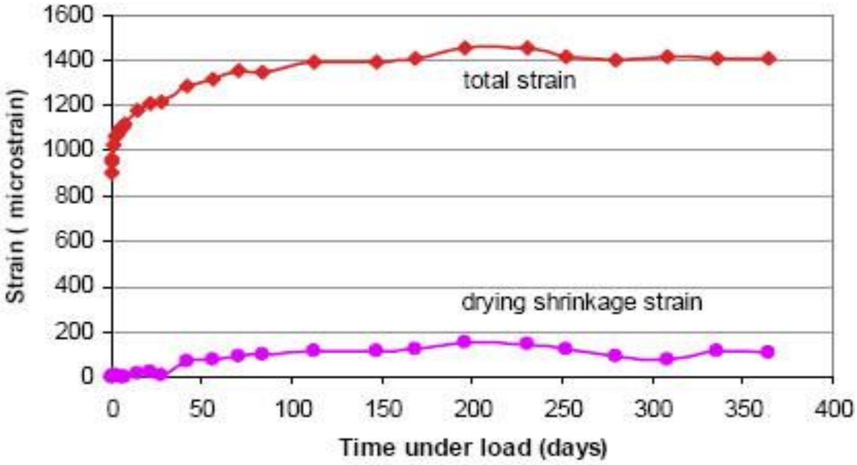
Mean Compressive Strength (MPa)	**Mean Indirect Tensile Strength (MPa)**	**Characteristics Principal Tensile Strength Equation (MPa)**	**Splitting Strength Equation**
89	7.43	3.77	5.98
68	5.52	3.30	5.00
55	5.45	3.00	4.34
44	4.43	2.65	3.74

c. **Unit-weight: -** The unit-weight of concrete primarily depends on the unit mass of aggregates used in the mixture. Tests show that the unit-weight of the low-calcium fly ash-based geopolymer concrete is similar to that of Portland cement concrete.

4.1.2 Long-Term Properties Of Geopolymer Concrete

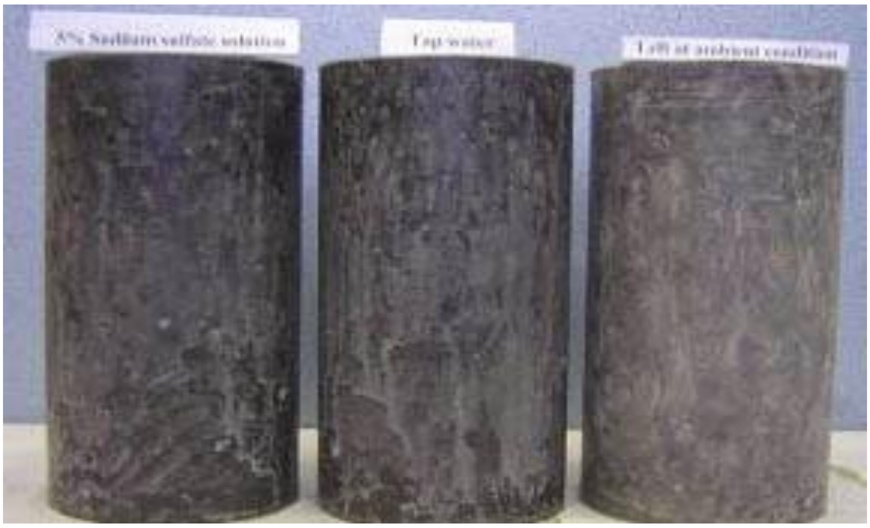
a. **Compressive Strength: -** The compressive strength of ambient-cured geopolymer concrete significantly increased with the age (Wallah and Rangan, 2006).

b. **Creep and Drying Shrinkage: -** The creep and drying shrinkage behavior of heat-cured low-calcium fly ash-based geopolymer concrete was studied for a period of one year (Wallah and Rangan, 2006). Test results show that heat-cured fly ash-based geopolymer concrete undergoes very little drying shrinkage in the order of about 100 micro strains after one year. This value is significantly smaller than the range of values of 500 to 800 micro strains experienced by Portland cement concrete.



Drying Shrinkage Strain

Figure No.3.1: Visual Appearance of Heat-cured Specimens after One Year of Exposure (Wallah and Rangan, 2006)



Visual Appearance of Heat-cured Geopolymer Concrete after One Year Exposure in Sulfuric Acid Solution (Wallah and Rangan, 2006)

c. **Sulfate Resistance: -** Tests were performed to study the sulfate resistance of heat-cured low-calcium fly ash-based geopolymer concrete. Test results showed that heat-cured low-calcium fly ash-based geopolymer concrete has an excellent resistance to sulfate attack. There was no damage to the surface of test specimens after exposure to sodium sulfate solution up to one year.

d. Sulfuric Acid Resistance:- Tests were performed to study the sulfuric acid resistance of heat-cured low-calcium fly ash-based geopolymer concrete. The concentration of sulfuric acid solution was 2%, 1% and 0.5%. The sulfuric acid resistance of geopolymer concrete was evaluated based on the mass loss and the residual compressive strength of the test specimens after acid exposure up to one year.

The visual appearance of specimens after exposure to sulfuric acid solution showed that acid attack slightly damaged the surface of the specimens. Figure compares the visual appearance of the geopolymer concrete specimens after soaking in various concentrations of sulfuric acid solution for a period of one year with the specimen without acid exposure and left in ambient conditions of the laboratory.

4.2 Geopolymer Precast Concrete Products

Gourley and Johnson (2005) have reported the details of geopolymer precast concrete products on a commercial scale. The products included sewer pipes, railway sleepers, and wall panels. Reinforced geopolymer concrete sewer pipes with diameters in the range from 375 mm to 1800 mm have been manufactured using the facilities currently available to make similar pipes using Portland cement concrete. Tests performed in a simulated aggressive sewer environment have shown that geopolymer concrete sewer pipes outperformed comparable Portland cement concrete pipes by many folds. Gourley and Johnson (2005) also reported the good performance of reinforced geopolymer concrete railway sleepers in mainline tracks and excellent resistance of geopolymer mortar wall panels to fire.

Siddiqui (2007) demonstrated the manufacture of reinforced geopolymer concrete culverts on a commercial scale. Tests have shown that the culverts performed well and met the specification requirements of such products.

4.3 Economic Benefits of Geopolymer Concrete

Heat-cured low-calcium fly ash-based geopolymer concrete offers several economic benefits over Portland cement concrete. The price of one ton of fly ash is only a small fraction of the price of one ton of Portland cement. Therefore, after allowing for the price of alkaline liquids needed to the make the geopolymer concrete, the price of fly ash-based geopolymer concrete is estimated to be about 10 to 30 percent cheaper than that of Portland cement concrete.

In addition, the appropriate usage of one ton of fly ash earns approximately one carbon-credit that has a redemption value of about 10 to 20 Euros. Based on the information one ton low calcium fly ash can be utilized to manufacture approximately 2.5 cubic meters of high quality fly ash based geopolymer concrete, and hence earn monetary benefits through carbon-credit trade. Furthermore, the very little drying shrinkage, the low creep, the excellent resistance to sulfate attack, and good acid resistance offered by the heat-cured low-calcium fly ash-based geopolymer concrete may yield additional economic benefits when it is utilized in infrastructure applications.

V. CONCLUSION

Low-calcium fly ash (ASTM Class F) is used as the source material, instead of the Portland cement, to make concrete. Low-calcium fly ash-based geopolymer concrete has excellent compressive strength and is suitable for structural applications. The salient factors that influence the properties of the fresh concrete and the hardened concrete have been identified.

The elastic properties of hardened geopolymer concrete and the behavior and strength of reinforced geopolymer concrete structural members are similar to those observed in the case of Portland cement concrete.

Heat-cured low-calcium fly ash-based geopolymer concrete also shows excellent resistance to sulfate attack, good acid resistance, undergoes low creep, and suffers very little drying shrinkage.

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