CHAPTER 1
INTRODUCTION

1.1 GENERAL

Geopolymers, X-ray amorphous aluminosilicate gels, are produced by the alkali activation of aluminosilicates present in the source material. These gels can be used to bind aggregates, such as sand or natural rocks, to produce mortars and concretes. In simple words, Geopolymers are inorganic binders that function like the better-known Portland cement. French Professor, Davidovits found out that the existence of three-dimensional silicate-aluminium product in the ancient Pyramids had the same structure as Zeolite, and then he designated this man-made rock like product as “Geopolymers”.

Industrialization leads to the generation and release of undesirable pollutants into the environment. In order to keep pace with the rapid industrialization, there is a necessity to select an engineering process, which would cause minimum pollution into environment. On the other hand, construction industry is increasingly turning towards the use of environmentally friendly materials in order to meet the sustainable aspect required by modern infrastructures. Consequently, in the last two decades, the expansion of this concept and the increasing global warming have raised concerns on the extensive use of Portland cement due to the high amount of carbon dioxide associated with its production.

Increasing concern about the environmental consequences of waste disposal has also led to the investigation of new utilization avenues. In
addition to this, the requirements imposed on construction materials are so demanding and diverse that no material is able to satisfy them completely. This has led to a resurgence of the ancient concept of combining different potential materials to satisfy diverse user requirements. So far, some special characteristics of the alkali-activated cementitious material such as high early strength development and excellent resistance to chemical attacks have been recognized and given a lot of interest by scientists in cement and concrete research area.

The development of Geopolymer Concretes offers promising signs for a change in the way of producing concrete. However, to seriously consider Geopolymer binders as an alternative to ordinary Portland cement, various strength related factors of this new material should be evaluated in any comparative analysis format.

Till date, there is no published literature dealing with the mechanical properties and application of Indian fly ash and other constituent materials of Indian origin in the development of Geopolymer concrete.

Every year millions of tons of fly ash are generated worldwide by coal-fired power plants satisfying the large demand for industrial and domestic energy. The management of this by-product is always a matter of concern. Only about 20-30% of the generated fly ash is used, mainly as additive in cement and concrete, filling material and the rest is disposed of. Therefore, strategies are required to deal with this waste safely. Special attention should be paid not only to prevent environmental pollution, but also to treat fly ash as a valuable resource material. In this regard, the synthesis of Geopolymers is foreseen as an interesting approach.

Production of one ton of Portland cement requires about 2.8 ton of raw materials, including fuel and other materials and generates 5% to 10% of
dust. Altogether, 6000-14000m$^3$ dust-containing air streams are generated per ton of cement manufacture and accounts for the release of 0.8 ton of greenhouse gas CO$_2$ into the atmosphere, as a result of de-carbonation of lime in the kiln during manufacturing of cement (Hardjito et al 2004; Buchwald 2005 and Li et al 2004). The reduction in the carbon dioxide emission from cement production can contribute significantly to the turning down of the global thermostat. It is evident that previous research on Geopolymerisation concerning fly ash as the sole source of silica and alumina is quite limited but a lot of unknown factors about the physical and chemical properties of derived products as well as about the factors governing the formation of these Geopolymers have to be explored.

1.2 GEOPOLYMER TECHNOLOGY

1.2.1 Geopolymers

Geopolymers are the synthetic analogues of natural zeolitic materials, which substantially differ from OPC, because Geopolymers use a totally different reaction pathway in order to attain structural integrity. Geopolymers consist of a polymeric silicon-oxygen-aluminium framework with alternating silicon and aluminium tetrahedra joined together in three directions by sharing all the oxygen atoms. The fact that four coordinated aluminium with respect to oxygen creates a negative charge imbalance, and therefore, the presence of cations is essential to maintain electric neutrality in the matrix. Positive ions such as K$^+$ or Na$^+$ that are present in framework cavities, balance the negative charge. For the chemical designation of Geopolymers based on silico-aluminates, the term poly(sialate) that is an abbreviation for silicon-oxo-aluminate has been proposed. Poly(sialates) are chain and ring polymers with Si$_4^+$ and Al$_3^+$ in 4-fold coordination with oxygen and their general formula is $M_n[-(SiO$_2$)$_z$-AlO$_2$]$_n$$•w$H$_2$O, where $z$ is 1, 2 or 3, $M$ is a monovalent cation such as K$^+$ or
Na⁺, n is the degree of polycondensation and z is 1, 2 or >>3. Chains and rings are formed and cross-linked together always through a silicate Si-O-Al bridge.

1.2.2 Geopolymer Concrete

The development of Geopolymer concrete is attributed to Prof. Davidovits who, in 1978, first proposed that a Geopolymer matrix could replace cement as a binder in concrete. Davidovits’ theory was that an alkaline solution could be added to an aluminium-silicon rich source material to produce cement-like binder and termed this as ‘Geopolymer’ binder. Fly ash, a by-product from coal industry, is the most widely used source material for Geopolymer concrete because of its availability, suitable composition and low calcium content with low loss of ignition. However, other materials that are rich in silicon and aluminium can be used including rice husk ash, blast furnace slag, metakaolin and natural Al-Si minerals. Geopolymer concrete is a concrete which does not utilize any Portland cement in its production. The primary difference between Geopolymer concrete and Portland cement concrete is the binder. The silicon and aluminium oxides in the low-calcium fly ash reacts with the alkaline liquid to form the Geopolymer paste that binds the loose coarse aggregates and fine aggregates 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. The influence of aggregates such as grading, angularity and strength are considered to be the same as in the case of Portland cement concrete (Lloyd and Rangan, 2009). Therefore, this component of Geopolymer concrete mixtures can be designed using the tools currently available for Portland cement concrete.
1.3 CONSTITUENTS OF GEOPOLYMER CONCRETE

The main constituent of Geopolymer concrete is low calcium ASTM class F fly ash, alkaline liquid, coarse and fine aggregates. Unlike ordinary cement concrete in which cement is mixed in the range of 350 kg/m$^3$ to 450 kg/m$^3$ depending upon the grade of concrete, an equivalent quantity of fly ash is taken and mixed to obtain Geopolymer concrete. In this research, Class F fly ash obtained from Tuticorin Thermal Power Station is used to manufacture Geopolymer concrete.

1.3.1 Source Material of Geopolymerisation

The source materials may be natural minerals such as kaolinite, Calcined kaolinite (metakaolin) and clays (Davidovits 1991; Barbosa et al 2000; Xu and van deventer 2002). Alternatively, industry waste products such as fly ash, slag, red mud, rice-husk ash and silica fume may be used as feedstock for the synthesis of Geopolymers. It has been proved that calcined materials such as slag, fly ash and metakaolin which are mostly amorphous, undergo high reaction during Geopolymerisation than non-calcined materials (Palomo et al 1999; Xu and Deventer 2000). For fly ash-based Geopolymers, mechanical strength increases due to the formation of an Al-rich alumino-silicate gel during the first stage of alkaline activation of fly ash particles and may further increase as a result of the Si enrichment of the material (Fernández-Jiménez et al 2006). It has also been found that Geopolymers derived from metakaolin may require too much of water due to increase in porosity and therefore become too soft for construction application although metakaolin remains important in the production of Geopolymers for applications such as adhesives, coatings and hydroceramics. Also, the microstructure and properties of Geopolymers depend strongly on the nature of the initial source materials (Duxson et al 2007). As a result, it is important to understand the reactivity and chemistry of raw materials in order to
optimise both cost and technical performance for certain applications. The cement industry seems to have realised the potential of fly ash as a resource and it could be seen from the increased share of fly ash in the blended cement production in recent years. The recent statistics of Cement Manufacturers’ Association indicate that the share of Portland pozzolana cement (PPC) has dramatically jumped from 26.17% to 44.36% between 2000 and 2004, an increase of almost 70 percent within a span of just four years. The responsibility of large-scale utilization of fly ash in concrete construction in India falls on the shoulders of the cement industry. In India, major initiatives are needed to use this resource in large volumes in construction sector especially housing and infrastructure projects and to pursue technologies mentioned in this report to make it a value added product for export and use in India. India should aggressively identify projects that can be registered with World Bank for carbon credits (Malhotra 2005). It is also estimated that only 14 million tonnes of the total 100 million tones of fly ash get utilised (Mallick 2005).

The reactivity of fly ashes is dependent on their glass content and other mineral phases present in it. Indian fly ashes are more crystalline than those obtained in other countries with the glass content ranging from 47.0% to 60.9% (Fournier et al 2004).

1.3.2 Alkaline Liquid

Locally available silicates and hydroxides of sodium are used to prepare alkaline liquid. Though silicates and hydroxides of potassium could be used to prepare alkaline liquid, sodium based silicates and hydroxides are used in this research considering the high cost of potassium based chemicals.

Sodium silicate is the common name for a compound sodium metasilicate, Na$_2$SiO$_3$, also known as water glass or liquid glass. It is available in aqueous solution and in solid form and is used in cements, passive fire
protection, refractories, textile and lumber processing, and automobiles. Sodium carbonate and silicon dioxide react when molten to form sodium silicate and carbon dioxide and the chemical equation reads as $\text{Na}_2\text{CO}_3 + \text{SiO}_2 \rightarrow \text{Na}_2\text{SiO}_3 + \text{CO}_2$.

Sodium hydroxide (NaOH), also known as caustic soda, is a caustic metallic base. It is used in many industries, mostly as a strong chemical base, in the manufacture of pulp and paper, textiles, drinking water, soaps and detergents and as a drain cleaner. Worldwide production of NaOH was approximately 60 million tonnes in 2004, while the demand was 51 million tonnes. Pure sodium hydroxide is a white solid available in the form of pellets, flakes and granules. It is hygroscopic and readily absorbs carbon dioxide from the air and therefore it should be stored in an airtight container. It is very soluble in water and is highly exothermic when it is dissolved in water.

Sodium hydroxide solution will leave a yellow stain on fabric and paper. Care should be taken while handling the sodium hydroxide pellets or flakes. Gloves and masks should be worn while weighing the sodium hydroxide and while dissolving it in water. Sodium silicate and sodium hydroxide are mixed in suitable proportions to obtain the alkaline liquid. In this research, the molarities of sodium hydroxide used were 8M, 12M and 14M.

1.4 CURING OF GEOPOLYMER CONCRETE

The most important operation in the manufacture of Geopolymer concrete is curing. Unlike OPC concrete which needs water for curing, Geopolymer concrete requires heat or temperature to activate the chemical reaction that takes place in Geopolymer matrix. Steam curing, dry curing and
curing at ambient temperature are the types of curing that could be employed to cure the Geopolymer concrete. The steam curing and dry curing are collectively called Heat-curing. In India, the possibility of curing at ambient temperature is high. But, in India only in summer temperature is between 26°C and 40°C. The main drawbacks in adopting ambient temperature curing are found to be the longer time it consumes to cure the concrete to get required compressive strength and the non-availability of required temperature in winter. On the other hand, the advantage of heat-curing is attainment of required compressive strength within several hours and even during all seasons. The requirement of boiler and fire wood to generate steam or electrical energy to produce heat makes it a little expensive.

Throughout this research, dry-curing is adopted to cure the Geopolymer concrete elements between 60°C and 90°C in a heat curing chamber exclusively designed for this experimental work. The heat curing enhances the compressive strength of Geopolymer concrete by 15% (Hardjito and Rangan 2005) than steam curing and also attains its full strength in 24 hours.

1.5 RESEARCH SIGNIFICANCE

This topic is one among the fields of high profile research and commercial interests over the past decade. Geopolymer Technology paved way for conversion of waste by product materials into valuable material. Some reports outside India stated that Geopolymer concrete has good strength and durability aspects. However, till date, no published results could be found using Indian Fly ash based Geopolymer concrete. The results of this extensive work will provide data and information about mixture optimization and application into structural elements for the needy successors. This research
may significantly be accepted and applied in real construction practices as an alternative to OPC concrete.

1.6 RESEARCH OBJECTIVES

The aim of this research is to study the factors ruling the compressive strength of fly ash based Geopolymer concrete and behaviour of both short and slender columns.

The main aims of this research program are:

- To experimentally examine the development and application of “Geopolymer Technology” with Indian fly ash and materials.
- To examine the crack pattern, deflection and load carrying capacity of both short and slender reinforced concrete columns manufactured using dry heat curing process.
- To investigate the thermal behaviour and bond strength of fly ash based Geopolymer concrete.
- To evaluate the cost effectiveness of low calcium fly ash based Geopolymer concrete over OPC concrete.

1.7 SCOPE OF WORK

The scope of the research work is stated below:

- To produce Geopolymer concrete mixtures with target compressive strength for the manufacture of all the columns.
To identify and study the effect of salient parameters that affects the properties of low-calcium fly ash based Geopolymer concrete.

To ascertain various strength aspects of Geopolymer concrete such as tensile strength, flexural strength, bond strength and thermal stability.

To manufacture and test reinforced fly ash-based Geopolymer concrete short columns and slender columns under monotonically increasing load with concrete compressive strength as test variable.

To perform calculation on load carrying capacity of both short columns and slender columns using current code provisions available for Portland cement concrete members.

To study the correlation of the test and calculated results.

The scope of work also involves the following:

- Research utilized ASTM class F low-calcium Indian fly ash as the source material for manufacturing all the Geopolymer concrete specimens. This fly ash was obtained from Tuticorin Thermal Power Station, Tamilnadu, India. The concrete technology currently used to manufacture OPC concrete was followed throughout the work.

- Based on the research described in research report GC1 and GC2, suitable proportions of concrete mixtures have been chosen and tried with class F Indian fly ash.

- To perform calculations to predict the strength and the deflection of Geopolymer concrete test columns using the
methods currently available for Portland cement concrete members.

- To perform cost analysis to ascertain the affordability of this alumino-silicate concrete.

1.8 THESIS STRUCTURE

The thesis is divided into eight chapters.

Chapter 1 introduces the background, research significance and objectives of the thesis.

Chapter 2 gives an overview of fly ash based Geopolymer concrete in general, recent developments, performance criteria of Geopolymer concrete as structural elements and durability of Geopolymer concrete.

Chapter 3 presents the research methodology and different stages of works involved in this research.

Chapter 4 provides data of physical and chemical properties of materials used in this research.

Chapter 5 describes the experimental investigations done in finding mixture proportioning of normal and high strength Geopolymer concretes, studying the response of plain Geopolymer concrete cubes to salient parameters, ascertaining the behaviour of reinforced Geopolymer concrete short and slender columns loaded axially as well as with moment.

Chapter 6 presents results and discussion of the analyses of the data obtained from the experimental work.
Chapter 7 shows the comparison of cost of one cubic metre of Geopolymer concrete with that of OPC concrete.

Chapter 8 outlines the conclusions of this study and presents recommendations for future research that may be carried out in order to enhance the current findings.

The thesis ends with a list of references and appendices detailing the experimental data and other supporting results.