CHAPTER 1: INTRODUCTION

1.1 General

The increasing demand on energy conservation and environmental protection issues which has led to development of alternative building materials. Concrete has been used as a worldwide construction material. Ordinary Portland Cement (OPC) has been traditionally used to produce the concrete in the construction industry. It was assessed that quantum of cement production equally emits carbon dioxide gas by the calcination process of limestone and the burning of fossil fuels every year. This emission of CO₂ gas leading to the several environmental issues such as greenhouse effect, global warming, etc., into the earth’s atmosphere will result in global climatic change.

Therefore, researchers started to work in finding an alternate material for cement preferably from waste products from industries. Due to the partial substitution of other materials to cement in production of concrete emission of CO₂ gas into the atmosphere will be reduced. The alternate materials can be a waste product namely fly ash (FA) (from thermal power stations), silica fume (SF) (from ferro silicon industries), ground granulated blast furnace slag (GBFS) (from steel industries), rice husk ash (RHA) (from rice industries) etc. These materials can be used as a partial replacement of cement from 10% to 30% in the concrete mixtures depending upon material type used [1].

A binding material from polymerization process in the presence of alkaline solution along with the byproduct materials such as fly ash, silica fume, ground granulated blast furnace slag, rice husk ash etc., and named this binder as Geopolymer [2]. The geopolymer concrete can be produced from mineral admixtures which are rich in silica and alumina, and when this mineral admixture reacts with alkaline
solution such as sodium hydroxide and sodium silicate solution along with high range water reducer under room temperature produces calcium silicate hydrate (C-S-H) gel. The term geopolymer emphasizes in amorphous to crystalline formation of products with the help of alkali alumina silicates in the presence of alkaline environment. Geopolymers are new class of inorganic polymers. This geopolymers has been used in the manufacture of bricks, ceramic and fiber glass composites, fire protection works and as a sealant in the radioactive and toxic waste disposal for the industrial works. This ecofriendly material possesses a good binding property along with excellent mechanical properties and increases durability of the concrete structures [3-5].

1.2 Chemical composition of Geopolymers

Geopolymers are produced from mineral admixtures and the silicon dioxide present in these admixtures reacts chemically with sodium hydroxide and undergoes hydration process to form calcium silicate (C-S-H) gel. Geopolymers exist in the amorphous form and not crystalline. The geopolymerization process involves chemical reaction under alkaline environment on silica and alumina compounds to form a three-dimensional ring structure with Si-O-Al-O bonds. The rheology of the materials also helps in the workability of the green concrete and its particle size helps in the filling of pores in the concrete thereby increasing the strength and life of the concrete structures [6].

1.3 Use of alternate binders in concrete

Ordinary Portland cement (OPC) has been used worldwide for more than 18 decades and it is one of the predominant binders used in concrete. However, this binder is having some problems depending on the site conditions. Due to some environmental conditions deterioration problems exist in OPC. The construction industry is having lot of pressure to reduce both energy usage and carbon foot print and is seeking
alternatives to this binder. In conjunction with that, number of attempts was done to produce concrete with low CO₂ emission by using waste product from industries.

1.3.1 Fly ash

Fly ash is being used in researches in two forms namely high-calcium (15-35%) or low-calcium (<10%) depending upon the CaO content. It is to be noted that the unburnt carbon content in fly ash should be less than 5%. The use of fly ash is recommended due to characteristics such as better durability, economy and energy saving conditions. Since most of the particles in fly ash are of 20 µm size which is much lesser than the size of cement particles, it can act as a better filler material too. But there are chances that the hydration process of concrete can get slower by the addition of fly ash and the early age strength is low when compared with normal concrete.

1.3.2 Silica fume

Silica fume, because of its finely divided state and very high percentage of amorphous silica, proved to be a most useful mineral admixture which was responsible for filling up of pores in concrete as well for pozzolanic nature the properties required by the concrete to achieve very high strength and long durability. Silica-fume is very fine non-crystalline SiO₂ and is a byproduct of ferro-silicon industry. It was obtained at a temperature of approximately 2000°C. Its size was about 0.1µm and the specific surface area is about 13000 to 30000 m²/kg. Average size of silica-fume was almost 500 times finer than cement. It can act as an excellent pore filling material and can be used in proportions of 5-10% of cement in a mix.
1.3.3 Ground Granulated Blast Furnace Slag (GGBFS)

GGBFS is a mineral admixture obtained from iron and steel industries. During the different stages of steel production blast furnace slag comes as a byproduct of pig iron production. In spite of the disadvantages such as gaining of strength at lower rate especially at lower temperatures, requiring longer curing period, GGBFS is preferred as a partial replacement for cement in concrete as its chemical composition is similar to that of cement composition with higher amount of Silica, aluminum and ferrous oxides and also due to its fineness which helps in filling up of pores in concrete resulting in better strength improvement and resistance to permeability action in concrete. In the present context, production of GGBFS based geopolymer concrete with alkaline solution as activator (0.25 to 0.40) is highly encouraged. Earlier studies indicate that the exact mechanism responsible in the geopolymerization process is yet to be studied a lot [7-15].

1.3.4 Rice Husk Ash (RHA)

Rice husk ash is obtained by incinerating rice husk under controlled conditions. The rate of formation of C-S-H is dependent upon the ash/lime ratio, reactivity and fineness of the ash. Rice husk ash is a super pozzolana in terms of lime reactivity. It has high specific surface and contains amorphous silica and can be ground with high fineness. Earlier studies performed with rice husk ash report that the addition of RHA up to 30% show substantial strength improvement in concrete compared with unblended normal concrete.

1.3.5 Metakaolin

Metakaolin is finer than cement particles but coarser than silica fume. It is obtained by calcinations of pure or refined clay at temperatures of 650-850°C and by grinding it to achieve a fineness of 700-900 m²/kg. It is a highly reactive pozzolana. It contains
highly reactive alumina (around 45%) and silica (around 55%). The thing which makes metakaolin different from other natural or artificial pozzolanas is that metakaolin is a primary product, while Silica fume, fly ash, GGBFS, Rice husk ash are secondary products or by-products.

A new binder material using byproduct from industries to reduce environmental issues and to improve the performance of concrete is emerging. One of such material adopted in the present research work called as geopolymer binder. Furthermore, this new technology has some problem in acceptance in the construction industry to make this concept into real world implementation.

1.4 Scope of the work

The industrial byproduct materials such as silica fume and ground granulated blast furnace slag were used as base materials to produce geopolymer concrete. The methods and instruments which are used for manufacture of OPC were used to produce geopolymer concrete. The properties of hardened concrete such as compressive strength, sorptivity, porosity and load deflection characteristics were studied. Statistical analysis to ensure the quality of concrete produced, cost analysis in terms of economy index (ration between strength and cost) and carbon foot print analysis was made to understand the utilizing potential of mineral admixture based geopolymer concrete.

1.5 Mechanism of Geopolymerization process

The main stages involved in the polymerization process are a) Dissolution of mineral admixture compound or silica and alumina undergoes dissolution in alkaline solution with the formation of alumino - silicate oxide compounds with the action of hydroxide ions, b) Partial condensation or reorientation or transportation of ions to form monomeric compounds of alkali poly sialate structure and c) Conversion of monomers into inorganic polymers by polycondensation or polymerization process.
1.6 Geopolymer - Concept
Geopolymerization is a geosynthesis chemical reaction with alumina silicate materials such as fly ash, silica fume, rice husk ash ground granulated blast furnace slag which can be activated to high alkaline condition (hydroxide and silicates) under thermal curing from 60°C to 90°C gives the formation of geopolymers. It enhances the mechanical properties of concrete [16-24]. These geopolymers will form a two or three-dimensional ring structure which comprises of –Si-O-Al-O- bonds. These polymeric materials will form a cementitious product which will provide zeolitic properties which is not present in OPC.

1.7 Geopolymer development
During polymerization process, initially the pozzolanic admixture gets activated to the development of densified microstructure. These pozzolans form a matrix binder tends to be more environmental friendly, economical and more repellent of liquids which produces an alumina silicate compounds. The dissolution process of alumina silicate compounds with highly alkaline solution polymerize into geopolymeric gel formation to form natural zeolites. Then finally the matrix gets hardened, excess water excludes and growth of crystallization begins [25-26]. The Figure 1.1 shows the process of polymerization.

1.8 Dissolution
The dissolution process will take place between silica and alumina minerals which are present in the source material react with the help of hydroxide ions. This reaction involves a complex process. The larger molecules will condense to form gel structure and undergoes alkali attack on the surface and it has been exposed to larger hole, the exposed smaller size particles either hollow or partially filled with other smaller material to two directional attacks by alkaline solution yet to form in and out shell
until the whole material is completely consumed [27-28]. The dissolution occurs when mineral admixture reacts with alkaline solution and forms an ionic interface between Al and Si and breaking of covalent bonds between silica, alumina and oxygen atoms. These frameworks are called as poly sialates. The rate of dissolution directly depends upon pH value in the activator solution.

Figure 1.1 Process of polymerization [29]
1.9 Polymerization

This process involves fast chemical reaction with Si – Al compounds under the presence of alkaline solution, resulting in the formation of 3D ring structure. The gel formation contains alkaline sodium or potassium ions which rearranges with alumina and silica compounds. The chemical reaction directly depends upon curing condition and the type of activator used to promote the phase of the reaction. The first stage of reaction is controlled by alkaline compounds makes to dissolution of solid mineral network to produce small reactive compounds of silicates and aluminates. The potassium based solution has higher level of dissolution due to greater alkalinity but sodium based solution has capacity to produce more silicate and aluminate monomers. The size of the ions is the main factor in determining the kinetics of the chemical reaction. The sodium ions have better zeolitic capacity because it is smaller and having high charge density than potassium ions and able to move through moist gel framework. This will help to form zeolites in hydrothermal synthesis. During this stage, slow growth of formation of crystalline phases until the size of the polymerized gel becomes critical. This crystalline matrix undergoes fast reaction between the alkalis and does not allow forming a well crystalline structure called as zeolites. The hardened geopolymer concrete are called as zeolite precursors. The final compound of polymerization is an amorphous, semi crystalline cementitious compound.

1.10 Heat of hydration

The several parameters which influence the degree of polymerization are particle size distribution, chemical composition, activator type, activator concentration, ratio of liquids to solids, curing temperature and time. Geopolymers will form amorphous to semi crystalline structure and this structure will depend upon curing temperature. Higher temperature and higher pH concentration makes the process bit faster.
1.11 Factors affecting the usage of alternative binders in producing GPC

In producing geopolymeric binder, its properties highly depend upon the following factors:

1. Type of source material
2. Ratio and concentration of activator solution
3. SiO₂/Na₂O ratio (Modular ratio)
4. Source material to activator ratio
5. Silicate to hydroxide ratio

The most significant factor for the successful production of geopolymer concrete is the choice of the source material. The silica to alumina ratio in the source material decides the rate of dissolution of ions in the chemical reaction. The quantity of calcium is high which will interrupt the polymerisation and changes in the microstructure [30]. Activator solution is the critical parameter in the development of compressive strength. The type of activator solution enhances the faster chemical reaction with the source material. More the concentration of activator solution, lesser the volume of pore spaces and hence there will be an increase in high early strength of concrete [31-33].

1.12 Organization of the thesis

Chapter 1 discusses an overview of geopolymeric materials, various processes involved in the polymerization, mechanism behind the development of strength of concrete. The various byproduct materials that can be effectively used in the production of geopolymer concrete are discussed. The applications of geopolymer in the construction industry are also included in this chapter.
Chapter 2 reviews the literature on geopolymer concrete in detail. Literature reviews on physical and mechanical properties of geopolymer are discussed. At the end of this chapter, the objectives of the present research work are given.

Chapter 3 describes the detailed methodology adopted in this research work. It deals with properties of various materials used and methods adopted (in accordance with codal provisions) towards conduct of experimental investigations from mix design to testing specimens.

Chapter 4 presents the results of various experimental investigations regarding the mechanical and durability properties of silica fume and GGBFS based geopolymer concrete carried out and detailed discussion of results. The optimum values of various parametric studies on silica fume and GGBFS based geopolymer concrete are also given. It also discusses the results on load deflection characteristics of beams tested.

Chapter 5 summarizes the work done in the present work and discussed the conclusions obtained on silica fume and GGBFS based geopolymer concrete.