

CHAPTER 1

INTRODUCTION

1.1 Cement and Environment

Cement is a widely used construction material due to its strength, durability and ease of mixing and placing. China, India and United States are the top 3 cement- producing countries. China has produced 2350 million metric tonnes of cement in 2015 followed by India at 270 million metric tonnes. (www.statista.com). Global demand for cement is in the uptrend and expected to rise by 4.5% in the next five years. 5190 million metric tonnes of cement is projected as the global demand in 2019 (www. world cement.com).

Cement is manufactured from limestone and clay mixture heated by an electrical furnace or coal fired furnace. In addition, production of cement emits Carbon dioxide, one of the major green-house gases that cause Global Warming. It is estimated that 1 tonne of cement during production releases approximately, 1 tonne of CO₂ into the atmosphere (Davidovits, 1996). 6 % of the total CO₂ emission is from the cement industry (www.epa.gov). Mankind is facing the wrath of nature, as huge inexplicable natural calamities, it is imperative to keep our environment unpolluted. As manufacture of cement consumes natural resources, energy and leaves a carbon footprint on the environment, (Scrivener, 2007) it is necessary to find an alternative to cement.

1.2 Sustainable Geopolymer

Geopolymers (Davidovits, 1978) are a new class of materials which are being developed as alternative to cement based materials. No cement is used in

geopolymers and it reduces the CO₂ emission by 80% (Davidovits, 1996). Geopolymer comprises of aluminosilicate rich source material and an alkali activator solution. Many materials like Flyash, Kaolinite, Metakaolin, Ground granulated Blast Furnace slag (GGBFS), Rice Husk ash, Biomass ash can be used as source material. Alkaline solutions like Sodium Hydroxide or Potassium Hydroxide are combined with silicate solutions like Sodium silicate or Potassium silicate to form alkali activating solution (Davidovits, 1982).

Geopolymerization is a polycondensation process in which the aluminate and silicate in the source material are combined with alkali activator solution to form a three-dimensional network of polymeric oxide structures (Rahier, 1997). The typical geopolymer composition is given by



where M is an alkali metal, n is the degree of polycondensation and z is 1, 2 or 3. However, the exact mechanism of setting and gaining strength is still to be completely understood. Geopolymers are self-curing at ambient condition though elevated curing results in high early strength. They are durable and being inorganic, Geopolymers exhibit better fire resistance compared to cement-based materials (Davidovits, 1991, Kong Daniel, 2007). Starting materials and processing conditions affect the physical, chemical and mechanical properties of Geopolymer to a great extent (Granizo, 1997).

1.3 Precursors

1.3.1 Flyash

Precursors are compounds that participate in a chemical reaction to result in another compound. The aluminosilicate rich source materials are the precursors upon polymerisation forms geopolymers. A widely used precursor is flyash, which is a finely divided residue from the combustion of coal-fired at

thermal power stations. Flyash is precipitated from flue gases by electrostatic precipitators or fabric filters. The quality of flyash depends on the type of furnace, coal and the precipitator type and location. As thermal power remains to be the major source of power, flyash generation is unavoidable. Disposal of flyash is a huge problem unless effective means to utilise flyash in large quantities are found. Flyash is found to contain pozzolanic properties and 20-40 percentage of cement is replaced with flyash in cement products.

1.3.2 Metakaolin

Kaolin is derived from the Chinese word Gao-ling meaning a high ridge. Rocks that primarily constitute Kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) mineral are named Kaolin. Kaolinite is a hydrous aluminium silicate mineral formed by the decomposition of Feldspar. Kaolin is commonly known as china clay. The structure of Kaolinite is shown in Figure 1.1. Kaolinite contains alternate layers of silicate sheets weakly bonded with aluminium oxide /Hydroxide sheets. The weak bonding causes cleavage and softness to the mineral. The colour of the mineral is white, but sometimes red, blue or brown tints due to impurities. Kaolinite is a naturally available rock mineral in abundance. Table 1.1 shows the major producers of Kaolin in the world as of 2015.

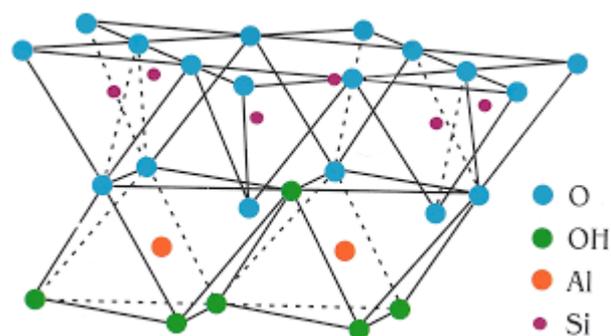


Figure 1.1 Structure of Kaolin

Table 1.1 Major Producers of Kaolin in world-2015

Country	Production in Million Metric Tonnes
Mexico	0.17
Italy	1.0
United Kingdom	1.1
Turkey	1.3
Ukraine	1.4
Brazil	1.7
China	3.3
Czech Republic	3.3
Spain	3.3
Germany	4.3
India	4.48
United States	6.16
Other	8.4

(U. S. Geological Survey: Mineral Commodity Summary 2016)

Though Kaolin is found from China, Kaolin of best quality is found in Georgia, the USA along the Atlantic seaboard fall line between Augusta and Macon. Thirteen counties in middle Georgia form the Kaolin belt. Kaolin belt in the USA is shown in Figure 1.2. The kaolin mining industry has located its processing facilities in the communities near the deposits, primarily in the nine rural counties between Macon and Augusta.



Figure 1.2 Kaolin belt in the USA

China clay resources in India as per United Nations Framework Classification (UNFC) system as on 1.4.2010 have been placed at 2,705.21 million tonnes. The reserves constitute only about 7% of the resources at 177.16 million tonnes. Out of the total reserves, 70% (about 124 million tonnes) reserves are under proved category whereas 30% (about 53 million tonnes) reserves fall under the probable category.

The resources are spread over in a number of states of which Kerala holds about 25%, followed by West Bengal and Rajasthan (16% each) and Odisha and Karnataka (10% each). Out of total resources, about 22% or 608 million tonnes fall under ceramic/pottery grade, 4% are classified under chemical, paper filler and cement grades and about 73% or 1,980 million tonnes resources fall under mixed grade, others, unclassified & not-known categories. The details of reserves are given in Table 1.2.

Table 1.2 Kaolin Reserves in India

State	Reserves in million tonnes
Kerala	66.3834
Rajasthan	43.2517
West Bengal	42.1663
Odisha	28.0926
Karnataka	25.8523
Jharkhand	19.8690
Gujarat	11.2189
Meghalaya	8.8875
Tamil Nadu	5.6897
Uttar Pradesh	2.5065

(Government of India, Ministry of mines, Indian Bureau of mines, Indian minerals yearbook, 2013).

Meta in Metakaolin indicates the transformation of Kaolinite mineral through loss of hydroxyl ions. This process is known as hydroxylation or calcination. Calcining Kaolinite at the temperature range of 700 °C -800 °C (IS 1344-1981) for 4 hours and grinding to have a specific surface area of 20 m²/g makes the clay highly reactive. Metakaolin is rich in Alumina and Silica and it can be ground to have a particle size as low as 2 µm and hence higher specific area of 20 m²/g.



Calcining is traditionally carried out in rotary kilns and takes several hours. The use of a fluidized bed process may reduce calcining time to minutes, although both of these methods require grinding of the agglomerated products. Flash-calcining, which consists of rapid heating, often to 1000 °C, followed by rapid cooling, may reduce the processing time further from minutes to several tenths of a second. Additionally, there is no grinding step required, as the starting material is finely powdered kaolin suspended in a gas [Salvador, 1995]. The MK precursors used in this study were produced using vertical hearth fluid bed calciners, into which the clay was fed at the top and the product collected from the bottom.

While prolonged soak-calcining at lower temperatures is generally quite effective at removing hydroxyl groups, Salvador [Salvador, 1995] showed calcining rate influences the pozzolanic reactivity of MK. In his study, flash-calcined kaolins had higher water absorption capacity and thus required more water to achieve suitable workability, suggesting these had a higher initial reactivity than soak-calcined kaolins. Further, at the same water-to-cementitious materials ratio (w/cm), cylinders made with flash-calcined kaolins always performed better in compression than those made with soak-calcined kaolins.

The smaller particle size and the higher specific area are advantageous in producing strong and durable Geopolymer products. The secondary sources of kaolinite are paper sludge waste and oil sand tailings. Metakaolin is different from other pozzolanic aluminosilicate material like flyash, silica fume, slag in that metakaolin is not a by-product of an industrial process. It is manufactured under controlled conditions for the specific purpose.

1.4 Need for the Study

India is a growing economy. Infrastructure facilities are to be stepped up to compete in the global arena. Boom in the construction activity, escalates the demand for cement as it is the largely used construction material. Production of 1 Tonne of cement releases 1 Tonne of CO₂ into the atmosphere. In this study, geopolymer is presented as an alternate construction material. Synthesis of geopolymer involves no cement. Geopolymers can be synthesised to be as strong as and more durable than cement concrete depending on the starting material. Curing is eliminated as Geopolymers are self-curing at temperate climates. Precast products can be used in colder regions. Geopolymer concrete is a viable alternative to cement concrete considering the abundant availability of raw materials and the carbon footprint left on the environment is very much less compared to cement. Metakaolin is manufactured from Kaolinite under controlled conditions. Kaolinite is abundantly available and the energy involved is less compared to ordinary cement. This research investigates the performance of metakaolin as geopolymer precursor to meet the growing demands of construction industry for a reliable and an efficient material.

Metakaolin is rich in silica and alumina, has smaller particle size and hence higher specific area to react with the activator solution in geopolymer synthesis. As metakaolin can be tailored to meet the purpose for which it is required, it is reliable unlike other commonly used geopolymer precursors like

flyash, GGBFS, silica fume etc. The gain in strength is early as it is highly reactive and Metakaolin based geopolymer concrete reduces the carbon dioxide emission as it replaces cement and gains carbon credit. This is the main need for this study.

1.5 Problem Statement

Economic growth is not acceptable at the cost of compromised quality of living. The increase in infrastructures worldwide pushes the demand for cement year on year. Cement uses Limestone and clay in manufacture, leading to depletion of these natural resources. In addition, fossil fuels are burnt during heating the materials to 1200 °C-1500 °C to form clinkers. At every stage of production, environment is harmed in one way or other. Carbon emissions, release of heavy metals in the air, water pollution are a few. Fine cement dust is the cause for chronic respiratory disorders observed in people working in cement production.

Production of cement emits CO₂ which is harmful to environment. CO₂ emission from cement production has to be curtailed for sustainable living. An alternate building material that can replace cement is being researched for. Geopolymers are evolving as building material with huge saving in carbon footprint.

Flyash based geopolymers are widely researched at present. Flyash is an industrial by-product and hence the properties of flyash vary with the type of coal burnt, furnace used and the place where the precipitators are located. The particle size of flyash is as large as 45 µm. Loss on ignition is more than one as unburnt coal particles also are present. In addition, flyash based geopolymers present porosity problems. Metakaolin is calcined at 700-800 °C, which is less compared to clinkering temperature of 1200 °C-1500 °C and ground to have a particle size as low as 2 µm. Small particle size leads to higher surface area of

around 20 m²/g indicating high rate of reaction. Hence Metakaolin is used for synthesis of geopolymers. Flyash poses disposal problems and hence it is wise to use flyash with Metakaolin to take advantage of both the materials.

1.6 Objectives of the Study

The main objective of this research is to investigate the performance of metakaolin as a precursor in geopolymer. The sub-objectives are

1. To investigate the mechanical and durability properties of metakaolin based geopolymer concrete.
2. To investigate the microstructural property of the metakaolin based geopolymer concrete.
3. To conduct an extensive study on the behaviour of metakaolin based brick prism with varying aspect ratio and compare it with clay brick prism.

1.7 Methodology of the Study

Using the inferences from the review of literatures, problem was identified and the objectives were finalised. Materials were tested for their basic properties and mix design was arrived at. Concrete specimens were cast and tested for compressive strength, split tensile strength, flexural strength, water absorption, volume of permeable voids and rapid chloride permeability. Metakaolin bricks and clay bricks were tested for basic properties like compressive strength, initial water absorption, efflorescence, water absorption, Static and dynamic modulus of Elasticity, and Poisson's ratio. Clay brick prisms and metakaolin geopolymer brick prisms of varying aspect ratio were constructed in cement mortar and tested for compressive strength and modulus

of Elasticity. Behaviour of clay and metakaolin geopolymer brick prisms were compared. Results were interpreted and conclusions were drawn.

1.8 Limitations of the Study

Thermal behaviour of metakaolin based geopolymer is not included in this study. Shrinkage cracks are not studied. Plasticisers are not used in this study. Molarity of the NaOH is maintained at 10M. High temperature curing is not resorted to in this study.

1.9 Organization of the Thesis

The thesis is structured in seven chapters. **Chapter 1** gives an introduction to geopolymer concrete and the sustainability of geopolymer concrete compared to pollution caused by cement production. Global Economy pushed the demand for infra- structure development in all the developing countries worldwide to remain in the fray. Availability and suitability of metakaolin as a precursor in geopolymer synthesis is established. The significance of this study on metakaolin based geopolymer concrete is also explained. The objectives of this study are listed at the end of the chapter. A literature review is presented in **Chapter 2**. Published results of the earlier research on topics connected to this study are presented. Papers are grouped under subheadings like carbon emission of OPC and GPC, flyash based geopolymer concrete, metakaolin based geopolymer concrete, thermal behaviour, porosity and behaviour of masonry prisms.

Materials and their properties needed for metakaolin modified geopolymer are listed in **Chapter 3**. The conformation of the materials used in this study to the appropriate governing standards is established. Study of microstructural properties like particle morphology using Scanning Electron Microscopy, elemental composition of flyash and Metakaolin 1, Metakaolin 2,

Metakaolin 3 using Electron Dispersive Spectroscopy, degree of calcination and presence of moisture in metakaolin using Fourier Transform Infra-red Spectroscopy is detailed in this chapter. Mix design adopted is given followed by a flow chart explaining the methodology of this study.

Chapter 4 elucidates the procedure adopted for experimental investigation on metakaolin modified geopolymer concrete. Preparation procedure for geopolymer synthesis is explained at the beginning of the chapter. Number, type and size of specimens cast and cured to be tested for various intended properties is listed. The procedure for various tests done in this study is explained. **Chapter 5** deals with the casting of geopolymer bricks of desired strength and testing of clay and geopolymer bricks. Construction of clay brick prisms and geopolymer brick prisms with aspect ratio between 2 and 5 and test setup is also presented in this chapter.

Chapter 6 presents the results of all the experimental investigations and the discussion on results follows suit. Comparison of the results of this study with the existing results is presented at the end of the chapter. Summary and conclusion of the investigation and recommendation for extension of the present work are presented in **Chapter 7**.