DEVELOPMENT OF SUSTAINABLE CONSTRUCTION MATERIAL FROM FLY ASH C

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ABSTRACT

Environmental issues caused by the production of Portland cement have necessitated its replacement by waste materials like fly ash which has been proven to be quite beneficial environmentally and economically.

Therefore, this research project was focused on the development of sustainable construction materials using 100% of high-calcium fly ash with KOH based alkaline solution. Experimental work was conducted to determine concrete properties like compressive strength, flexural strength, setting time, and slump. In the phase I of the research, CNTs were also used to study its effect on geopolymer mortar.

The results derived from the experiments show that mortar and concrete made with 100% fly ash C needs alkaline solution to reach properties established by Portland cement concrete. However increased amount of KOH generates heat making the concrete to set faster without forming a proper bond. Furthermore, the addition of CNTs makes the mortar sturdier than the one without CNT.

ACKNOWLEDGEMENTS

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DEDICATION

To my Dad, Madhab Lal Shrestha, and Mom, Chandreswori Shrestha.

I am grateful to God for having parents like you. Your unconditional love and support made my

every achievement possible.

I Love You!

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CHAPTER 1. INTRODUCTION

1.1. Background

The development of concrete mix design has become an important concern in the world of construction. Various methods have been employed in different parts of the world to achieve concrete mixes that can sustain any load and to address challenges associated with concrete such as workability, bleeding, and segregation.

In addition to dealing with these challenges, the other biggest concern of the concrete industry is the use of Portland cement. It could be considered as one of the factors contributing to global warming. Harmful gasses like CO_2, NO_2, SO_2 and specks of dust are discharged into the atmosphere during the production of Portland cement due to the calcination of limestone and combustion of fossil fuel (**Hardjito, 2005**). The CO_2 produced in this process is in the order of one ton for every ton of Portland cement produced (**Hardjito, 2008**). Along with environmental issues, Portland cement production also requires a considerable amount of energy, following steel and aluminium (**Hardjito, 2005**). Therefore, it has become important to reduce the cement content in concrete and at the same time maintain the concrete's characteristics such as strength, workability, and durability.

In recent years, geopolymer technology has been developed to reduce the use of Portland cement in concrete (**Davidovits, 1994**). As part of the sustainability movement in the concrete industry, the technology has led researchers to the discovery of a green concrete as a substitute for traditional concrete. Among the different kinds of geopolymer materials, fly ash is the most widely used material and has been seen as an ideal replacement for Portland cement. Fly ash can be considered the world's fifth largest raw material resource (**Ahmaruzzaman, 2009**). Fly ash is an industrial byproduct produced in coal-fueled power

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plants and mainly categorized into two types: class C, and class F. Approximately, 500 million tons of fly ash are produced per year throughout the world (**Ahmaruzzaman, 2009**). The amounts of fly ash used were limited to 10- 30% of its total production (**Chunfeng et al., 2008**). Fly ash particles are considered to be highly contaminating due to their enrichment in potentially toxic trace elements which condense from the flue gas; therefore, there is a need for the disposition of significant amounts of fly ash. However, the disposal of fly ash is becoming a real problem (**Ahmaruzzaman, 2009**). On the other hand, the negative impact associated with the waste disposals has generated some beneficial uses, mainly in concrete application. The recycling of this abundantly available material is also minimizing the environmental impact associated with the production of Portland cement. Geopolymer technology could save up to 80% of CO_2 emissions caused by the cement industries (**Raijiwala et al., 2011**). Nevertheless, to understand fly ash's capacity to improve the performance of concrete and address the issue concerning the disposal of it, various evaluations have been carried out by replacing Portland cement with fly ash.

Prominent characteristics such as high strength have been discovered in fly ash which improves the performance of a wide range of concrete applications such as the construction of roads, embankments, and structural fill (**Ahmaruzzaman, 2009**). The properties of fly ash are very similar to Portland cement. The pozzolanic properties of the fly ash, including its lime binding capacity, make it useful for manufacturing cement, concrete building materials, and concrete-admixed products (**Ahmaruzzaman, 2009**). When used as a partial replacement of Portland cement, in the presence of water and ambient temperatures, fly ash reacts with the calcium hydroxide during the hydration process of Portland cement to form the calcium silicate hydrate (C-S-H) gel (**Hardjito et al., 2005**).

In the process of making concrete more resistant to excessive load, reinforcing materials like steel have been incorporated in concrete. In recent years, nanotechnology is being researched to replace steel in concrete. Fibers in the form of nanomaterials such as carbon nanotubes (CNTs) have been used or thought of as a replacement for reinforcing steel. These nanomaterials have been found to have very high mechanical properties with high strength (i.e. 100 times more than steel), but yet are six times lighter (**Chaipanich et al., 2009**). Furthermore, the usage of CNTs exhibits the phenomenal thermal, chemical, and electrical properties which remarkably increase the comprehensive strength of structural concrete (**Konsta-Gdoutos et al., 2010**). Due to their unique properties and characteristics, carbon nanotubes have been used in several concrete designs to reinforce the matrix (**Chaipanich et al., 2009**). The incorporation of such nanomaterials in concrete will control the matrix cracks at the nanoscale level and possibly create-crack free concrete materials (**Konsta-Gdoutos et al., 2010**). The study of nanomaterials in concrete represents a new research area (**Chaipanich et al., 2009**). Much research and many investigations are required to be carried out to learn the possibilities of the use of such nanomaterials as key constituents in enhancing the strength of concrete (**Chaipanich et al., 2009**).

1.2. Objectives

This study was carried out to investigate the possibility of utilizing fly ash to replace Portland cement in different construction applications. Moreover, this thesis will cover the following objectives;

1. To design concrete mix to replace Portland cement (100%) with class C fly ash based cementitious material while maintaining adequate durability, compressive strength, and flexural strength.

2. The test focuses on the study of concrete characteristics like a slump, setting time along with compressive strength and flexural strength properties.

3. To analyze the use of CNT to make the concrete more durable and crack free.

1.3. Scope of Work

Class C fly ash was used as 100% replacement of Portland cement to develop geopolymer concrete. In addition to the class C fly ash, CNTs were also added to the mixture during the Phase I of the research. The technology and the equipment currently used to produce Portland cement concrete were used throughout the experiments. The concrete properties studied mainly included compressive strength and flexural strength along with early features of fresh concrete such as slump and setting time.

1.4. Research Methodology Layout

This study has been further categorized into four chapters.

1. Chapter 2: Literature Review

2. Chapter 3: Materials and Experimental Design

3. Chapter4: Experiment Analysis: Result and Discussion

4. Chapter 5: Summary, Conclusion, and Recommendations

Chapter two, literature review, reviews the history of the utilization of fly ash replacing Portland cement. It discusses the properties of the geopolymer materials and its application around the world. Chapter three, materials and experimental design, gives the details of the materials and equipment used in the study. It also explains the procedure for the research and the experiments in detail. Chapter four, experiment analysis: result and discussion, presents test results. Also, it analyzes the results of the experiments. In chapter

five, summary, conclusion and recommendation, the summary of the research is presented. In addition, conclusions are derived along with the recommendations for future study.
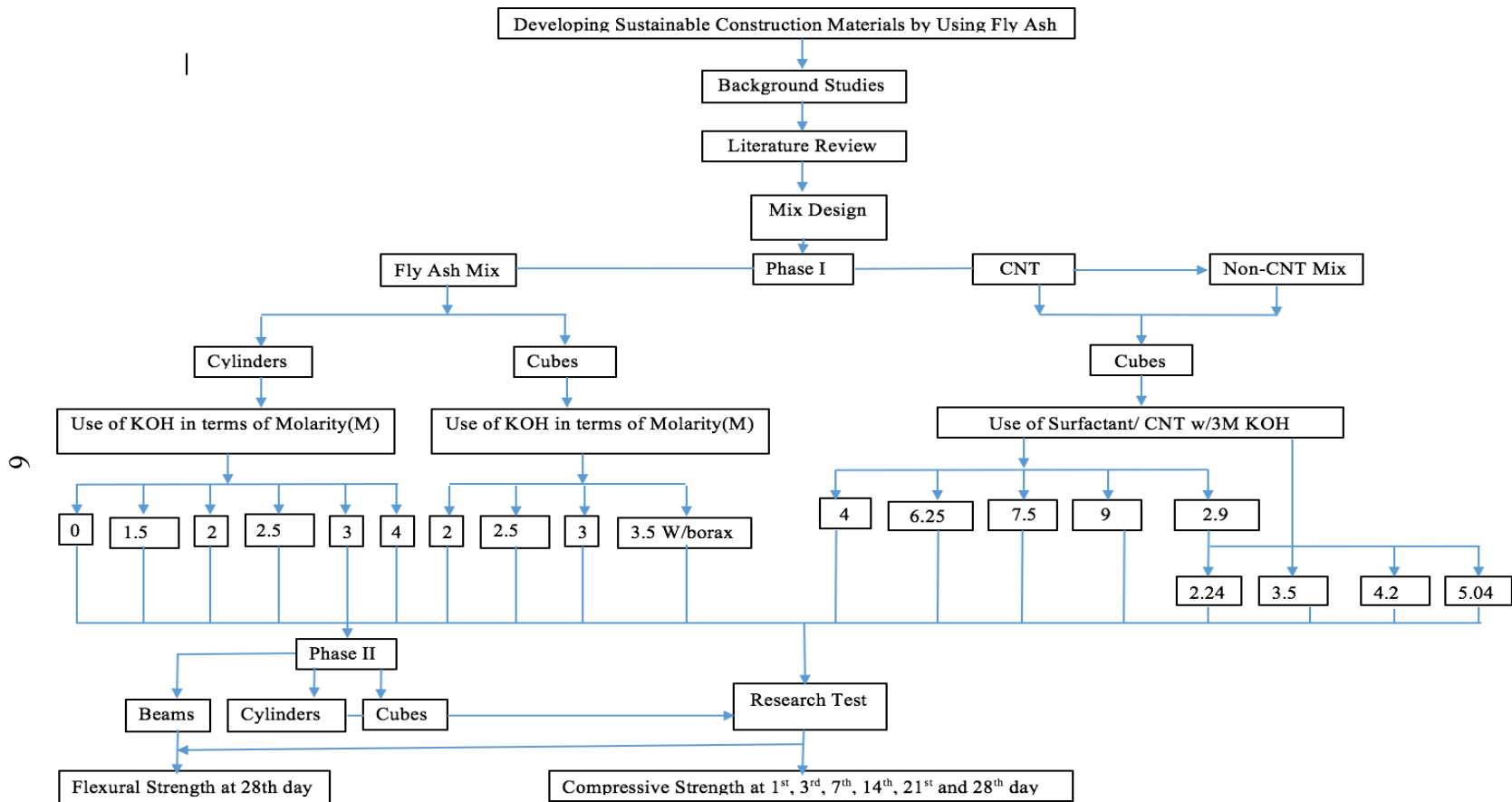
Figure 1.1. Research Layout

CHAPTER 2. LITERATURE REVIEW

2.1. Introduction

The construction industry has practiced the use of fly ash as a key binder in developing concrete-based construction materials for many decades. Due to its environmentally friendly properties, several research studies have been conducted around the world to replace the Portland cement with fly ash. This chapter will include available literature related to geopolymer concrete research. It will also present the current and possible usage of geopolymer in different construction applications and the factors affecting its performance.

2.2. Background

2.2.1. Traditional Cement

2.2.1.1. Introduction

Concrete is the most used construction material in the world. It is required globally for the construction of buildings, bridges, roads, runways, sidewalks, dams and others (**Rubenstein, 2012**). Moreover, its availability has made it more popular as a key binder in developing construction material (**Rubenstein, 2012**). Its application has greatly prompted the development of civilization, enhanced economic progress, and improved quality of life (**Rubenstein, 2012**). However, some of its disadvantages especially its environmental impacts are challenging to mitigate. The major challenge is the CO_2 emissions associated with cement clinker production and its association with climate change.

2.2.1.2. Effect on the Environment

Rubenstein, 2012 reported that single industry is responsible for 5% of global CO_2 emissions. Concrete is the second most consumed substance on earth after water. On average, three tons of concrete are consumed by every person on the planet each year. Thus, cement production is growing by 2.5% annually, and it is expected to rise from 2.55 billion tons in 2006 to 3.7-4.4 billion tons by 2050. Besides, cement manufacturing is highly energy intensive process because of the extreme heat required in its production. Producing a ton of cement requires 4.7 million BTU of energy, equivalent to about 400 pounds of coal, and generates nearly a ton of CO_2. Due to its high emissions and direct impact on society, cement production needs to mitigate to reduce greenhouse gas emissions.

Roskos et al., 2011 indicated in their research study that the demand for cement is increasing, and about 7 billion cubic yards of cement is produced every year, making it the second most used material on earth after water. Its production is an energy intensive process which uses temperature of more than $2500^{o}F$ to heat raw materials. During this process greenhouse gas, i.e. carbon dioxide (CO_2) is emitted into the atmosphere from fuel combustion and decarbonization of limestone. Therefore, traditional cement is responsible for 7% of the world's generation of greenhouse gasses.

Chen et al., 2010 reported that the Portland cement manufacturing industries are under scrutiny these days because of the production of large volumes of CO_2. One industry is thought to represent 5–7% of the total CO_2 anthropogenic emissions. Other emissions such as SO_2 emissions have also been analyzed using life cycle assessment.

Hardjito, 2005 indicated that the production of Portland cement has increased every year to meet the ever increasing demand for infrastructure, and this has contributed to the production

of CO_2 resulting in the greenhouse effect and climate change. Also, the climate change results in global dimming. Global dimming refers to the reduction in the amount of sunlight reaching the earth due to increasing pollution from cement manufacturing and other economic activities.

2.2.2. Fly Ash

2.2.2.1. Introduction

Fly ash is a byproduct of burning finely ground coal in electric generating plants. Fly ash has been defined as "the finely divided residue resulting from the combustion of ground or powdered coal, which is transported from the firebox through the boiler by flue gases" (**ACI Committee 116, 2000**). Physically, fly ash is a very fine and powdery material, and it is light tan to dark gray in color depending on its chemical constituents. Fly ash with high lime content has tan color whereas fly ash with dark gray has increased amount of unburned carbon. Fly ash particles are usually spherical, finer than Portland cement and lime and ranges in diameter from less than 1 μm to no more than 150 μm. Generally, it is captured from the flue gasses by using electrostatic precipitators or other filtration equipment before it is discharged into the atmosphere. Fly ash is a pozzolan, a siliceous material which reacts with an alkaline activator at ordinary temperatures to produce cementitious compounds. Due to its spherical shape and pozzolanic properties, it is useful in cement and concrete applications. Fly ash is mainly composed of the oxides of silica, aluminum, iron and calcium. It also contains different essential elements, including both macronutrients (P, K, Ca, Mg) and micronutrients (Zn, Fe, Cu, Mn, B, and Mo). The chemical composition of fly ash varies according to the type of coal used. Anthracite and bituminous coal produce fly ash classified as Class F. It consists of mainly an aluminosilicate glass, and has less than 10 percent of CaO. Class C or high calcium fly ash is

produced by burning lignite or sub bituminous coal, and it typically contains more than 20 percent of CaO.

Aside from the chemical composition, the other characteristics of fly ash considered are loss on ignition (LOI), fineness and uniformity. LOI is a measurement of unburnt carbon remaining in the ash. The fineness of fly ash mostly depends on the operating conditions of coal crushers and the grinding process of the coal itself. Finer gradation results in a more reactive ash that contains less carbon.

2.2.2.2. Fly Ash Utilization

Fly ash has a great potential to be used in different applications. Its utilization in developing durable construction materials benefits the environment.

Ram et al., 2013 provided an overview of the potential applications of fly ash for soil amelioration. A typical characteristic of fly ash promotes improvement in the physical, chemical and biological qualities of soil. Fly ash application along with various locally available organic and inorganic amendments like lime, gypsum, red mud, farm manure, animal manure, sewage sludge, composts, and press mud can further improve soil quality and lead to higher plant biomass production. Regardless of the significance of using fly ash in amending soils, a collective recommendation from these investigations is difficult due to heterogeneity in fly ash characteristics, soil types, and agro-climatic conditions.

Di et al., 2012 reported that the utilization of fly ash has vital economic significance and environmental value. Fly ash has the same physicochemical property with limestone mineral powder, which makes it possible for replacement of mineral powder. It was further demonstrated

by running experiments that the fly ash can improve the high-temperature stability of concrete, bituminous mixture efficiently by replacing the limestone mineral powder completely.

Ahmaruzzaman, 2009 reported that the utilization of fly ash in construction, as a low-cost adsorbent for the removal of organic compounds, flue gas and metals, lightweight aggregate, mine backfill, road sub-base, and zeolite synthesis. A considerable amount of research has been conducted on the utilization of fly ash for adsorption of NO_x, SO_x, organic compounds, and mercury in air, dyes and other organic compounds in waters. It was found that fly ash is a promising adsorbent for the removal of various pollutants. The unburned carbon content in fly ash plays a key role in its adsorption capacity. The adsorption capacity of fly ash may be increased after chemical and physical activation. Also, it was discovered that fly ash has good potential for use in the construction industry. The conversion of fly ash into zeolites has many applications such as ion exchange, molecular sieves, and adsorbents converting a waste material into a marketable commodity.

Basu et al., 2008 reported that fly ash has high potentiality in agriculture due to its efficacy in modification of soil health and crop performance. The high concentration of all the essential plant nutrients like macronutrients (K, Ca, Mg, P, and S) and micronutrients (Fe, Mn, Zn, Cu, Co, B, and Mo) in fly ash increases the yield of many crops. Fly ash can be utilized for stabilizing erosion-prone soils. There is also an expectation that the use of fly ash instead of lime in agriculture can reduce net CO_2 emission, thus reduce global warming.

Wang et al., 2008 showed that fly ash based adsorbents is proposed as an alternative to more expensive adsorbents such as activated carbon for removal of heavy metals from industrial wastewaters. This process was developed by synthesizing the two pure forms of zeolites (A and X) from fly ash to remove heavy metal (e.g., copper and zinc) ions. The removal mechanism of

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metal ions followed adsorption and ion exchange processes. They also attempted to recover heavy metal ions and regenerate adsorbents. From their experiments, they were able to obtain removal efficiency in the range of 81.45% to 99.73%.

Rao et al., 2005 reported that textile effluents are highly toxic as they contain a large number of complex metal dyes. It can cause many waterborne diseases and increases the Biological Oxygen Demand (BOD) in water. Therefore, in their work, adsorption studies were conducted by treating the textile dye solutions of methylene blue (M-B) and Congo red (CR) by using fly ash. There is an experimentally determination of effects of the quantity of adsorbent, time of contact, initial effluent concentration, pH, and temperature. There is also an observation from the experiments that about 90–100% removal is possible using a lower concentration of fly ash. Therefore, the results showed that fly ash can effectively be used as an adsorbent for the removal of color from dyeing industrial effluents.

2.2.2.3. Use of Fly Ash in Concrete

One of the techniques used to produce environmentally friendly concrete is to replace the Portland cement with fly ash. Fly ash has been found to produce similar levels of concrete strength compared with Portland cement. The advantages of using fly ash in concrete are;

1. Improved workability;
2. Improved sulfate resistance;
3. Increased resistance to freezing and thawing;
4. Increased cohesiveness;
5. Improved long-term strength;
6. Reduced water content of the mix;
7. Reduced heat of hydration;

8. Decrease in permeability; and

9. Increases resistance to alkali-aggregate reaction.

Even after discovering the cementitious characteristics in fly ash, its widespread acceptance is an ongoing research studies on the use of 100% fly ash concrete.

Hardjito et at., 2005 reported that a significant achievement in the use of fly ash in concrete is the development of high-volume fly ash (HVFA) concrete that successfully replaces the use of ordinary Portland cement (OPC) in concrete up to 60% and yet possesses excellent mechanical properties with enhanced durability. HVFA concrete has been proven to be more durable and resource-efficient than OPC concrete.

Cross et al., 2005 explored the feasibility of using 100% of high-calcium lignite fly ash as a concrete binder. Based on their findings, they stated that by just mixing fly ash, aggregates, and water, concrete with strength up to 4000 psi was produced. Moreover, from the experiments they found that the fly ash concrete exhibited behavior comparable to Portland cement.

Yazici et al., 2005 concluded that high-volume Class C fly ash is suitable for use in construction of products like cast-in-place and precast products. However, external factors like steam curing and a superplasticizer were required to develop the sufficient compressive strength from day one.

Papadakis, 2000 investigated the properties of a high-calcium fly ash as an additive in a mortar, replacing part of the volume either of Portland cement or aggregate. The properties of strength, porosity, bound water and calcium hydroxide content were observed. Replacing aggregate resulted in higher strengths from the beginning of the hydration, as well as higher water binding with considerably lower porosity. Whereas while replacing cement, the strength was found to be constant. Furthermore, process describing the chemical reactions of the fly ash C in hydrating Portland cement is proposed.

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Thomas et al., 1999 reports the use of fly ash with the ternary cementitious systems. They presented the results based on the laboratory studies on the durability of concrete using the blends of Portland cement, silica fume, and a wide range of fly ashes. It was presented that replacement levels of up to 60% of some fly ashes were capable of controlling expansion due to alkali-silica reaction (ASR). Nevertheless, blends of relatively small amounts of silica fume (e.g., 3 to 6%) with moderate amounts of fly ash C (20 to 30%) were able to reduce expansion due to ASR significantly along with high level of sulfate resistance. Also, this combination exhibited the excellent fresh and hardened properties of concrete with a very high resistance to the penetration of chloride ions which have a significant effect on the predicted service life of concrete exposed to chloride environments.

2.3. Geopolymer Concrete

2.3.1. Introduction/ History

In today's environmentally-conscious society, geopolymer concrete is a technology that is generating considerable attention in the concrete construction industry. Unlike Portland cement, geopolymer depends on minimally processed natural materials or industrial byproducts to produce binding agents (**Hardjito, 2005**). The chemical compositions of geopolymers are similar to zeolites with amorphous microstructure instead of crystalline. Since the polymerization process occurs during the formation of concrete, Davidovits used the term 'Geopolymer' for these binders (**Rangan, 2008**). It has several advantages such as reducing the production of CO_2, economical, better mechanical properties, and eco-friendliness. Although the cementing properties of geopolymer materials have been known for more than three decades and has been claimed as the building material used in other ancient constructions, there is so much yet to discover. Therefore, many reviews have been done to understand the history and salient features

of geopolymer concrete. Some of the definitions and properties of geopolymer concrete by researchers worldwide are as follows:

Ryu et al., 2013 reported from their review that the active research on this technology was not done in a proper way due to problems related to production and economic efficiency. However, the recent awareness of environment sustainability has encouraged researchers to conduct more research on alkali-activated concrete using industrial byproducts such as fly ash and blast furnace slag of which several practical applications can be found today. In this research, the authors proposed the design of cementless concrete using fly ash as a binder and alkali activator. Microstructural analysis was also conducted to observe strength development mechanism.

Vijai et al., 2010 reported that the hardened geopolymer concrete has an amorphous microstructure which is quite similar to that of ancient structures such as Egyptian pyramids and Roman amphitheaters. Geopolymer, which was pioneered by Joseph Davidovits is an inorganic aluminosilicate polymer synthesized from predominantly silicon (Si) and aluminum (Al) materials of geological origin or byproduct materials like fly ash, metakaolin, Granulated Blast furnace slag and others. The polymerization process involves a substantially fast chemical reaction under the alkaline condition on Si-Al minerals that result in a three-dimensional polymeric chain and ring structure consisting of Si-O-Al-O bonds. The chemical reactions are categorized into following steps:

1. Dissolution of Si and Al atoms from the source material through the action of hydroxide ions.
2. Condensation of precursor ions into monomers.
3. Polymerization of monomers into polymeric structures.

$$n(Si_2O_5,Al_2O_2)+2nSiO_2+4nH_2O+NaOH \text{ or } KOH \rightarrow Na^+,K^+ + n(OH)_3\text{-Si-O-Al}^-\text{-O-Si-(OH)}_3$$

(Si-Al materials)

$$(OH)_2$$

(Geopolymer precursor)

(1)

$$n(OH)_3\text{-Si-O-Al}^-\text{-O-Si-(OH)}_3 + NaOH \text{ or } KOH \rightarrow (Na+,K+)\text{-(-Si-O-Al}^-\text{-O-Si-O-)} + 4nH_2O$$

(OH)₂

O   O   O

(Geopolymer backbone)   (2)
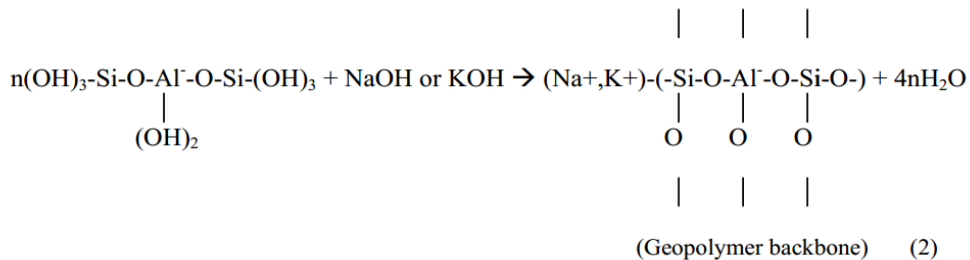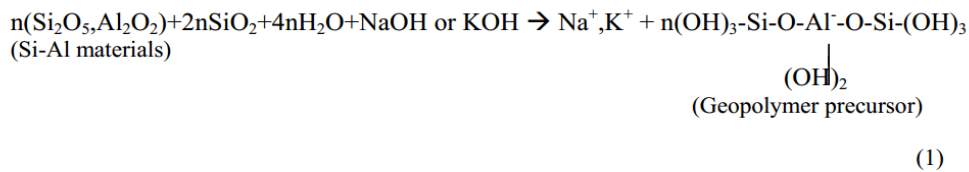
Figure 2.1. Mechanism of Geopolimerisation

Geopolymer concrete exhibits many advantages as compared to Portland cement like good compressive strength, resistance to sulfate attack, good acid resistance, little dry shrinkage and low creep.

Hardjito et al., 2010 asserted that geopolymer technology is one of the new technologies aimed at reducing the use of Portland cement in concrete. Geopolymer concrete is an environmentally friendly material and does not emit greenhouse gases during the polymerisation process. Besides, it needs only moderate energy to produce. Geopolymers are made from source materials with silicon (Si) and aluminium (Al) content; thus, geopolymer concrete can be developed using fly ash, waste product of a coal-fired power station as the source material. Furthermore, geopolymer possesses good mechanical properties which mean it does not dissolve in an acidic solution and does not generate any hazardous alkali-aggregate reaction even with alkali content as high as 9.2%.

Rangan, 2008 researched geopolymers as members of the family of inorganic polymers. The chemical composition of the geopolymers is similar to natural zeolitic materials. It was described that the polymerization process as a substantially fast chemical reaction under alkaline

activators that results in a three-dimensional polymeric chain and ring structure consisting of Si-O-Al-O bonds (**Davidovits, 1994**), as follows:

$$Mn\ [-(SiO2)\ z–AlO2]\ n\ .\ wH2O$$
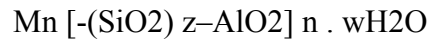
Where: M = the alkaline element or cation such as potassium, sodium or calcium; the symbol – indicates the presence of a bond, n is the degree of polycondensation or polymerization; z is 1, 2, 3, or higher, up to 32.

The schematic formation of geopolymer material as defined by Davidovits (1999) and van Jaarsveld, van Deventer et al. (1997) are presented as Equations (1) and (2) (Figure 2.1). These chemical equations indicate that all materials containing mostly Silicon (Si) and Aluminium (Al) can be processed into geopolymer material.

In the latter equation, water is released by the chemical reaction that occurs during the formation of geopolymers. This water leads to the formation of discontinuous nano-pores in the matrix which provides benefits to the performance of geopolymers. This water has no role in the chemical reaction except providing workability to the mix.

Duxson et al., 2007 concluded from their research that considerable work has been done with geopolymer concrete, yet much work remains to be done. Furthermore, it was explained that only application based research was done previously. Mechanisms controlling the properties and structures of geopolymer concrete have only been given attention in recent years. However, many improvements have been made to the understanding and development of this new technology to produce sustainable construction materials.

Barsoum, 2006 wrote that geopolymers have several advantages compared to Portland cement. Firstly, they can survive for nearly five millennia. Geopolymers are more environmentally friendly. Unlike ordinary portland cement, geopolymer does not consume more

energy and generates 90% less CO_2 with little pre-processing and a simple mixing process. The raw materials used to produce geopolymer cement are commonly found in the Earth's crust and are almost indistinguishable from natural stone.

Nicholson et al., 2005 asserted that geopolymer concrete is an inorganic polymer produced by reaction of an alkali activator and an aluminosilicate source at room temperature. The low energy process results in a fast-setting material exhibiting exceptional hardness and strength. A comparison of the reactions in Figure 2.1 shows that traditional cement is composed of portlandite [$Ca(OH)_2$] and calcium silicate hydrate (C-S-H) phases whereas geopolymer cement is based on an aluminosilicate framework. Aluminosilicate materials are much more resistant to chemical attack, *e.g.* by acids, than calcium-rich Portland cement. In the polymerization process, there is no calcination step (heating to 1450 ºC) which is mitigating the release of CO_2. Therefore, from this, it can be concluded that geopolymers have more advantages than Portland cement.

Portland Cement

1450º   Hydration

$CaO + SiO_2 \rightarrow$ Clincker Phases $\rightarrow$ C-S-H + $Ca(OH)_2$

Geopolymeric Cement

20-90 ºC + alkali
silicate solution   Poly-condensation

$Al_2O_3 + SiO_2 \longrightarrow$ -Si-O-Al-O $\longrightarrow$ Aluminosilicate 3D framework
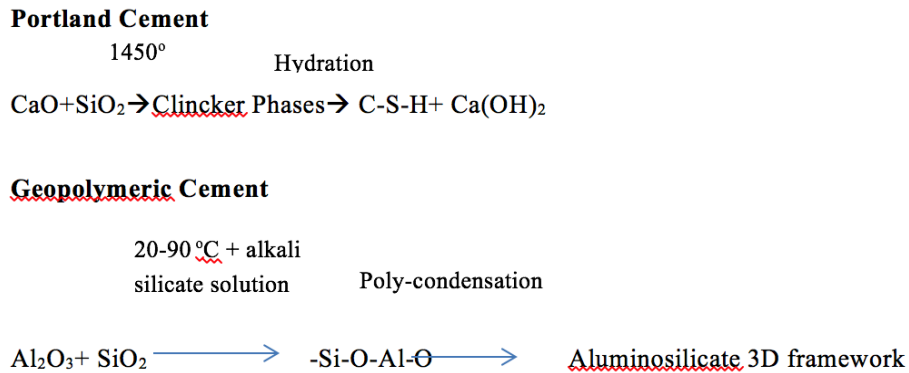
Figure 2.2. Comparison of the Reactions of Portland Cement and Geopolymeric Cement

(**Nicholson et al., 2005**)

Feng et al., 2005 reported that on their review that this technology has attracted the world as a revolutionary technique which is used for three major applications: preparation of

monolithic materials, immobilization of hazardous metals and preparation of nanometer-sized crystallites. This technique is based on polycondensation process rather than hydration process. This technique helps in Solidifying industrial, mining, and urban wastes discharged in the form of dry and wet powders into monoliths as recycling materials.

2.3.2. Components of Geopolymer

Geopolymer has two key components, namely the source materials and the alkaline liquids. The source materials for geopolymers based on alumina-silicate should be rich in silicon (Si) and aluminium (Al). These could be natural minerals such as kaolinite, clays, and others. Alternatively, byproduct materials such as fly ash, silica fume, slag, rice husk ash, red mud, and others could be used as source materials. The alkaline liquids are from soluble alkali metals that are usually sodium or potassium based. The most common alkaline liquid used in geopolymerization is a combination of sodium hydroxide (NaOH) or potassium hydroxide (KOH) and sodium silicate (Na_2SiO_3) or potassium silicate (K_2SiO_3). Alkaline liquid plays a significant role in the polymerization process. Reactions occur at a high rate when the alkaline liquid contains soluble silicate, either sodium or potassium silicate, compared to the use of only alkaline hydroxides.

2.3.2.1. Source Materials

Motorwala et al., 2013 explained from their review that the source materials for geopolymer concrete that are based on alumina-silicate should be rich in silicon (Si) and aluminium (Al). These materials could be natural minerals such as kaolinite clay, and byproduct materials such as fly ash, silica fume, slag, rice husk ash, red mud, and others. The choice of the

source materials for making geopolymers depends on factors such as availability, cost, type of application, and specific demand of the end users.

Petermann et al., 2010 summarized the definition of source materials that it is a finely divided aluminous and siliceous material which reacts chemically with slaked lime at ordinary temperature in the presence of moisture to form strong hardening concrete. For the process of geopolymerization to occur, source materials should be rich in silicon and aluminum. Examples of source materials are fly ash, blast furnace slag, calcined metakaolin, and many more.

Hardjito, 2004 wrote that the source materials for geopolymers based on alumina-silicate should be rich in silicon (Si) and aluminium (Al). Metakaolin or calcined kaolin, fly ash, natural Al-Si minerals, a combination of calcined mineral and non-calcined materials, the combination of fly ash and metakaolin, and a combination of granulated blast furnace slag and metakaolin were found to be source materials for geopolymer concrete. It was stated that high calcined source materials like fly ash and slag were found to exhibit higher final compressive strength than non-calcined ones, like kaolin clay and mine tailings. Among the byproduct materials, only fly ash and slag have been proved to be the potential source materials for making geopolymers.

2.3.2.2. Alkaline Activator

Motorwala et al., 2013 reported that alkaline liquid plays an important role in the polymerization process. After a study of the geopolymerization of sixteen natural Al-Si minerals, they found that mostly the NaOH solution results in a higher extent of dissolution of minerals than the KOH solution.

Hammons et al., 2010 reported that the most common alkaline activators are hydroxides of sodium and potassium (NaOH and KOH). The highest observed mechanical strengths have resulted from the use of KOH in varying concentrations. Since K+ is more basic, it allows a

higher rate of solubilized polymeric ionization and dissolution leading to a dense polycondensation reaction that provides greater overall network formation leading to a better compressive strength of the matrix.

Petermann et al., 2010 reported that the use of alkali activators in geopolymerization process is the most significant factor in producing a mechanically-sound cementitious material by rapid precipitation and crystallization of the siliceous and aluminous species present in the solution. In the reaction, OH- acts as a catalyst for better reactivity, whereas the metal cation serves to form a strong structural element and balance the negative framework carried by the tetrahedral aluminum. For example, when a source material like fly ash is mixed with alkaline solutions, their vitreous component is instantly dissolved with lesser time for the resulting gel to grow into a well-crystallized structure resulting in the formation of a microcrystalline, amorphous or semi-amorphous structure.

Palomoa et al., 1998 stated that the mechanical strength always depends on the type of alkaline activator used in the preparation of geopolymer concrete. Alkali activation of waste materials has become the focused area of research to develop environmentally friendly concrete. The process of the activation of a fly ash with highly alkaline solutions made with NaOH, KOH, and water glass with the common characteristic of having a very high OH⁻ is described in their work. Aluminosilicate gel produced were studied regarding variables like temperature and time of curing. Therefore, they concluded that these variables have a big influence on the development of mechanical strength with values in the 60 MPa range.

2.3.3. Properties of Geopolymer Concrete

It has been discovered from many investigations that the elastic properties, behavior and strength of hardened geopolymer concrete are similar to Portland cement. Different recent

studies on geopolymer concrete and its structures have shown that using the proper methodology one can develop a concrete with desired properties. It also exhibits resistance to sulfate acid attack, has good acid resistance, undergoes low creep, and suffers very little drying shrinkage. **Duxson et al., 2006** stated that depending on the raw material selection and processing conditions, geopolymers can exhibit a wide variety of properties and characteristics, including high compressive strength, low shrinkage, fast or slow setting, acid resistance, fire resistance, freeze-thaw resistance, sulfate resistance corrosion resistance and low thermal conductivity.

2.3.3.1. Strength of Hardened Mortar

Ryu et al., 2013 presented from their experiments that higher compressive strength together with a considerable effect on the early strength was achieved by using higher molarity alkaline activator. The use of a mix of sodium hydroxide and sodium silicate with a mix ratio of 1:1 ($SiO_2/Na_2O = 8$) was shown to activate the geopolymerization of fly ash and achieve remarkable strength development with a compressive strength of approximately 47 MPa. This value is larger than 40 MPa known as the criterion of high-strength concrete, and it verifies the potential of fly ash as a replacement for Portland cement.

Bondar et al., 2010 showed from their experiments that the strength gain of geopolymer concrete is slow in the early phase when compared to Portland cement. However, they reach the same or even higher strengths than Portland cement mixes after long-term aging. They also explained through their experiments that the effect of different curing condition and temperature plays a significant role in developing the strength in geopolymer concretes. Likewise, the tensile strength of the concrete is similar to compressive strength. However, the tensile strength of activated natural pozzolan geopolymer concrete is more sensitive to improper curing than its compressive strength, the same as in Portland cement concrete.

Olivia et al., 2011 stated that the optimal fly ash geopolymer concrete for use in a seawater environment has high compressive, and splitting strength. A gradual increase in strength in geopolymer concrete was observed in all the mixes. Therefore, the results obtained from the experiment showed that the nature of the geopolymer paste has a significant influence on its durability in the seawater environment.

Skvara et al., 2006 concluded from the experiments that strength characteristics of geopolymer concrete are in a long-term rising trend. Depending on the conditions of preparation and composition, the values of compressive strength for pastes, mortars and concretes range between 15-70 MPa after 28 days. The highest strength values obtained were for geopolymers based on fly ash and blast-furnace slag ranging between 100-160 MPa of compressive strength at 28 days after preparation.

Yazici et al., 2005 verified with their experiments that different compressive strength can be developed by replacing Portland cement with different volume of fly ash. Furthermore, it was shown that the use of different curing system can significantly affect the strength properties of a concrete. Test results showed that under standard curing long-term strength of fly ash concrete was satisfactory compared to the 1-day strength. However, steam curing increased the 1-day strength, but long-term strength was not satisfactory.

2.3.3.2. Acid Sulphate Resistance

Ariffin et al., 2013 reported that geopolymer binders have emerged as one of the possible alternatives to Portland cement due to their high early strength and resistance to acid and sulfate attack apart from being eco-friendly. Moreover, the following results were derived from the study:

1. Geopolymer concrete specimens remained structurally intact though their surface turned a little softer while visual observation of OPC concrete specimens showed severe deterioration after 18 months exposure to sulfuric acid. The mass loss for geopolymer concrete specimens was 8%, and that was considerably smaller than the mass loss of Portland cement concrete specimens which exhibited 20% after 18 months of sulfuric acid exposure.

2. Geopolymer concrete specimens had 35% compressive strength loss. In the case of Portland cement, concrete specimens started deteriorating in the first month of the exposure and had 68% strength loss. Furthermore, specimens were severely deteriorated after 18 months of sulfuric acid exposure.The products of the sulfuric attack were poorly cohesive and expansive, leading to dimensional instability and a loss of mechanical performance. Whereas exposure of geopolymer concrete to sulfuric acid did not result in any apparent degradation.

Therefore, it was concluded that the key factor which determined the rate and effects of the processes commonly described as 'sulfuric attack' in concrete are due to the nature of the binder gel system. The C-H-S gel in Portland cement can have severe effects on these materials whereas geopolymer gel systems at the same concentration of acid appeared to have little or no impact on the structure of the material.

Singh et al., 2013 presented the study that showed that geopolymer concrete possessed excellent mechanical properties and durability for an aggressive environment like sea water areas compared to Portland cement concrete. The better performance of geopolymeric materials than that of Portland cement concrete in acidic environment could be attributed to the lower calcium

content of the source material as a main possible factor since geopolymer concrete does not depend on lime like Portland cement concrete.

Thokchom et al., 2009 presented an experimental study to assess the acid resistance of geopolymer mortar specimens having a percentage of Na_2O ranging from 5% to 8% of fly ash. Evaluation of the resistance in terms of surface corrosion, residual alkalinity, changes in weighing and compressive strength at regular intervals were done. There was also an immersion of specimens in solutions of 10% Sulfuric acid and 10% Nitric acid up to a period of 24 weeks. It was discovered that geopolymer mortar specimens did not show any noticeable change in color and remained structurally intact though the exposed surface turned slightly softer. However, through Optical Microscope, the corroded surface could be seen which increased with duration of exposure. Samples almost lost their alkalinity after exposure in the acid solution within 12 weeks and showed very low weight loss in the range from 0.81% to 1.64% in Sulfuric acid and from 0.21% to 1.42% in Nitric acid. Compressive strength loss at the end of the tests varied from 44% to 71% and 40% to 70% in Sulfuric acid and Nitric acid respectively. Therefore, it was concluded that geopolymer concrete are highly resistant to sulphate acid reaction.

Wallah et al., 2006 presented that the heat-cured fly ash-based geopolymer concrete has excellent resistance to sulfate attack. There were no significant damage and changes in the mass and strength of the specimens after acid exposure up to one year. However, the sulfuric acid attack causes degradation in the compressive strength of heat-cured geopolymer concrete but is significantly better than that of Portland cement concrete. Therefore, geopolymer concrete has better ability to resist sulphate acid reaction than Portland cement concrete.

2.3.4. Factors Affecting the Performance of Geopolymer Concrete

There are many different opinions as to which main parameters that affect the properties of geopolymer concrete. This segment presents the review of the research studies done worldwide about the factors influencing the properties of geopolymer concrete.

Aleem et al., 2012 showed that from the optimum mix, the compressive strength of the geopolymer concrete can be increased by increasing the percentage of fine aggregates and coarse aggregates to an optimum level. This may be due to the high bonding between the aggregates and alkaline solution. However, the compressive strength beyond the optimum level decreased. They reasoned that this might be attributable to the increase in the volume of voids between the aggregates.

Bondar et al., 2010 presented the different views of researchers on the factors that affect the properties of geopolymer concrete. From the review, it was found that some researchers stated that the major influences on the compressive strength are the type of alkaline activator; the curing temperature and the curing time. Other researchers have reported that the important parameters for better strength result are the proper amounts of Si, Al, K, Na, and the molar ratio of Si to Al present in solution, the type of alkaline activator, the water content, and the curing temperature.

Van Jaarsveld et al., 2002 reported that interrelationship exists among the different materials that affect the final structure and property of fly ash-based geopolymers. Water content, curing, calcining conditions and clay content affect the properties of a geopolymer. For curing, they suggested that mild curing improves physical properties while curing under higher humidity is not usually beneficial. However, curing at high temperature can cause cracking and have a negative effect on physical properties. Therefore, they concluded that the manufacture of

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a geopolymer product for specific applications requires a careful attention to such factors as, curing temperature and humidity, with the consideration of initial mix design.

Xu et al., 2000 concluded from their study of geopolymerization of sixteen natural Si-Al minerals, that factors like the percentage of CaO, K_2O, the molar Si-to-Al ratio in the source material, the type of alkali liquid, the extent of dissolution of Si, and the molar Si-to-Al ratio in solution significantly influenced the compressive strength of geopolymers.

Barbosa et al., 2000 reported, based on a statistical study of the effect of parameters on the polymerisation process of metakaolin-based geopolymers, the importance of the molar composition of the oxides present in the mixture and the water content. They also confirmed that the cured geopolymers showed an amorphous microstructure and exhibited low bulk densities between 1.3 and 1.9.

2.3.5. Geopolymer Concrete Products

Due to their physical, mechanical and chemical properties, geopolymer concrete could be possibly used in the concrete industry. Its properties like durability, chemical resistance, early development of strength can lead to its 100% use in commercial as well as industrial applications, replacing Portland cement.

Ferdous et al., 2014, proposed a mix design procedure for fly ash based geopolymer concrete. The investigation of the flexural behavior of composite beam filled with geopolymer was used to show the possibility of its application as a light-duty railway sleeper. The results from their study drew the following conclusions;

1. The mix design procedure proposed for fly ash-based geopolymer concrete is useful for designing specific concrete strengths which could overcome many limitations of existing design guidelines.

2. The method proposed for beam analysis showed good reciprocity with the experimental results. This method of analysis will also be useful in determining the behavior of using similar designs having different dimensions and properties without conducting actual experiments.

3. The proposed composite beam satisfied the minimum flexural requirements for railway sleeper specified in the AREMA (The American Railway Engineering and Maintenance of-Way Association) standard. Its performance was found to be better than some existing composite and traditional timber sleepers.

4. Numerical simulation showed the behavior of the composite beam and traditional timber sleeper in a ballast railway track to be similar which increases the acceptability of the proposed beam as a sleeper in light duty railway tracks.

Petermann et al., 2010 reviewed the usage of geopolymer concrete as a structural element, commercial sewer piping, heat resistant pavement, toxic metal immobilization and sub-aqueous seawater applications and drew the following conclusions;

1. From the perspective of material longevity in harsh environments and large operating loads, geopolymer concretes possess high compressive strength, experience very minor dry shrinkage and creep while maintaining excellent resistance to sulfate acid attack.

2. Geopolymer concrete is suitable for commercial sewer piping as it can withstand the effect of a sulfuric and acidic environment. It can offer an economical alternative to

currently used materials and the issues associated with regular damage and repair of the concrete pipe networks.

3. The thermal capacity present in pozzolan based geopolymer concrete can resist the extreme heat environment compared to Portland cement. Fly ash-based cement retain their mechanical properties up to 600 °C, unlike Portland cement. The reason could be geopolymer cement utilize more and store less water from solution during the polymeric reaction, and prevents aged dry shrinkage and strength degradation due to rapid water loss under extreme heat. Therefore, it has the possibility of being used in heat resistant pavement applications.

4. There is a possibility for the use of geopolymer concrete for metal immobilization application. However, much research is needed for the safe use of geopolymers with toxic metals. Geopolymer materials being sulfate resistant makes it a prime candidate for subaqueous marine applications. Mortars and concretes developed with alkali-activated process perform very steadily when immersed in aggressive solutions of various types like deionized water, seawater, sodium sulfate solution, and sulfuric acid.

Lloyd et al., 2010 stated that geopolymer concrete shows excellent resistance to chemical attack and can be used in aggressive environments where the use of Portland cement concrete may be of concern. Therefore, geopolymer concrete can be applicable in aggressive marine environments with high carbon dioxide or sulfate rich soils. Similarly, in highly acidic conditions, geopolymer concrete has shown to have superior acid resistance and may be suitable for applications such as mining, some manufacturing industries, and sewer systems. Therefore, it has been used to produce precast railway sleepers, sewer pipes, and other prestressed concrete

building components and can be used in precast industry where steam curing or heated bed curing is commonly used.

Ahmaruzzaman, 2009 wrote that fly ash can be used for various applications. Mainly, it can be used as a replacement of Portland cement, pozzolanic material in the production of pozzolanic cement and set retardant ingredient with cement as a replacement of gypsum. The use of fly ash in construction, removal of organic compounds, heavy metals, dyes, and zeolite synthesis can help a great deal in the reduction of environmental pollution. For maximum benefit, new technologies for the efficient utilization of fly ash should be developed and used. To improve removal efficiencies and adsorption capacities, chemical modifications of fly ash is needed.

2.4. Use of Carbon Nanotubes in Concrete

Saafi et al., 2013 investigated the effect of multiwalled carbon nanotubes (MWCNTs) on the mechanical and electrical properties of fly ash composites. Different concentrations of MWCNTs were synthesized to determine the mechanical properties, electrical conductivity, and piezoresistive response. SEM was used to observe the distribution quality of MWCNTs within the matrix and determine their crack-bridging mechanism. Therefore, from the results they were able to derive following conclusions;

1. Mechanical properties: MWCNTs increased the flexural strength, Young's modulus and flexural toughness by as much as 160%, 109%, and 275% respectively.

2. Electrical conductivity: MWCNTs enhanced the fracture energy and increased the electrical conductivity by 194%.

3. Piezoresistive response: The geopolymeric nanocomposites presented a piezoresistive response with high sensitivity to micro-crack propagation.

4. Furthermore, the experimental results also showed that the MWCNTs were uniformly distributed within the matrix at 0.1 and 0.5-wt%

Siddique et al., 2013 reported that after various years from its detailed characterization, CNTs have grown from a material of dreams to a real world material with many application possibilities. In addition to their remarkable strength, which is usually quoted as 100 times that of a tensile strength of steel at one-sixth of the weight, CNTs have a wide range of use in various applications including concrete. CNTs have been effectively used in various research works which led to remarkable progress in the mechanical properties of cement mortars. They presented an overview of some of the research published on the use of CNT in concrete/mortars with an effect of CNTs on properties such as compressive strength, tensile strength, modulus of elasticity, flexural strength, porosity, electrical conductivity and autogenous shrinkage.

Shah et al., 2009 presented that the concrete materials are characterized as a quasi-brittle material with low tensile strength and low strain capacity. To overcome these weaknesses, fibers like CNTs are incorporated into the cementitious matrices. These fibers reinforce the concrete in millimeter scale and delay the development of microcracks at the nanoscale level, therefore, creating crack-free concrete material.

Chaipanich et al., 2009 presented the advantages of the use of carbon nanotubes in fly ash-cement system in the form of pastes and mortars. From the results of their experiments higher strength of fly ash mortars were reached (51.8 MPa at 28 days). In addition, scanning electron micrographs (SEM) also showed that good interaction between carbon nanotubes and the fly ash cement matrix is seen where carbon nanotubes are acting as a filler. This resulted in a denser microstructure and higher strength when compared to fly ash mix without CNTs.

CHAPTER 3. MATERIALS AND EXPERIMENTAL DESIGN

3.1. Introduction

This chapter provides the methods and details of the experimental process employed in the research. The present study used 100% high calcium (ASTM Class C) fly ash with technology that is in use for Portland cement mix design and testing (ASTM C496, ASTM C192, ASTM C143, ASTM C109, ASTM C78, ASTM C39). The same technology was used to encourage the use of new material in the concrete industry (Hardjito et al., 2005).

This study is divided into two phases. In Phase I, experiments have been conducted to formulate a mix design to produce fly ash based geopolymer concrete with proper proportioning of the different components of the fly ash concrete mix to achieve the specified properties. Some trial and error experiments were performed using different materials like fly ash F, MgO, CaO. The Phase II was focused on using the best mix, based on the compressive strength, developed in Phase I for testing the various properties of the concrete, for example, slump, setting time, compressive strength, and flexural strength test.

3.2. Material Used

3.2.1. Fly Ash

For all the experiments, 100% class C fly ash (according to ASTM C 618) was used. The fly ash (Figure 3.1) was produced by Green River Energy, Las Vegas, NV. The specific gravity of the Fly Ash is 2- 2.9 g/cc. It has a significant amount of lime. Table 3.1 and Table 3.2 provide a description of the properties of the fly ash used in this research. Figure 3.1 shows the fly ash being weighed.

Table 3.1. *Description of the Properties of the Fly Ash.*

Physical State	Solid (Powder)
Appearance	Brown/ Tan powder which may contain solidified masses
Odor	None
Vapor Pressure	NA
Vapor Density	NA
Specific Gravity	2 – 2.9
Evaporation Rate	NA
pH (in water)	4- 12
Boiling Point	>1000°C
Freezing Point	None (Solid)
Viscosity	None (Solid)
Solubility in Water	Slightly (<5%)

Table 3.2. *Chemical Composition of the Fly Ash.*

Components	Percent	Threshold limit Value (units)
Calcium Oxide	30	2.0 mg/m^3
Silicon Dioxide	35	10 mg/m^3
Aluminum Dioxide	12	10 mg/m^3
Iron Trioxide	8.5	5.0 mg/m^3
Magnesium Oxide	6.5	10 mg/m^3
Potassium Oxide	4.7	15 mg/m^3
Sulfur Trioxide	4.7	15 mg/m^3

Figure 3.1. Weighing Fly Ash

3.2.2. Aggregates

Coarse aggregates used in high-strength concrete should be clean and free of detrimental coatings of dust and clay (ASTM Chapter 17, 2002). Removing dust is important since it may affect the water demand of a concrete mix (ASTM Chapter 17, 2002). Therefore, aggregates were washed with tap water and placed in the oven at 200° F for 24 hours before using for experiments.

Coarse aggregates (Figure 3.2) from a local store in Fargo, ND, were used with a maximum diameter of 19mm (3/4 in) and specific gravity of 2.65 kg/m^3. Table 3.3 and 3.4 gives the detail of gradation of aggregates used for cylinders and beams as according to ASTM C33.

Figure 3.2. Coarse Aggregates

Table 3.3. *Mechanical Analysis of Coarse Aggregates used for Cylinders.*

Sieve Sizes	% Passing
19mm	98.99
12.5mm	58.89
9.5 mm	8.59
4.75 mm	0.39
2.36 mm	0.19
Pan	0.19

Table 3.4. *Mechanical Analysis of Coarse Aggregates used for Beams.*

Sieve Sizes	% Passing
25mm	99.3
19mm	99.3
12.5mm	40.4
9.5 mm	7.2
4.75 mm	0.4
2.36 mm	0.4
Pan	0.4

3.2.3. Fine Aggregates (Sand)

Sand (Figure 3.3) from a local store in Fargo, ND was used. The specific gravity of the sand was 2.63 kg/m^3. Wet sand was placed in an oven at 200° F for 24 hours before using for

experiments. Table 3.5 gives the detail of gradation of aggregates used for cylinders, beams and cubes according to ASTM C33.

Figure 3.3. Fine Aggregates (Sand)

Table 3.5. *Mechanical Analysis of Fine Aggregates.*

Sieve Sizes	% Passing
9.5mm	99.78
4.75mm	98.38
2.36mm	87.08
1.18mm	70.88
600 µm	46.88
300 µm	15.78
150 µm	3.18
75 µm	1.48
Pan	0.48

3.2.4. Potassium Hydroxide (KOH)

Strong alkali activator KOH, was used for strengthening the surface area of the resulting specimens. The addition of KOH generates heat which makes the mix set even faster. A potassium-based activator was chosen as it produces a better strength concrete compared to a sodium-based activator (**Hardjito, 2010**).

3.2.5. Citric Acid

Citric acid is also known as 2-hydroxy-1, 2, 3-propanetricarboxylic acid with chemical formula $C_6H_8O_7$. It is in a solid (crystalline powder) state without any odor and has the taste of strong acid. Its molecular weight is 192.13 g/mole and its density is 1.66 g/cm3. In this research, citric acid is used as the modifying agent. Since the hydration process in class C fly ash takes place in an early phase, the mix tends to set faster after its preparation. The addition of KOH generates heat as well; which makes the mix set even sooner. Therefore, to increase the setting time of the mixture, citric acid was used as a retarder. Since citric acid is a weak acid, it does not affect the acid-base reaction; it only works as a retarder.

3.2.6. Borax

In one mix of the first phase, 20 Mule Team Borax ® (decahydrate borax), was used to see its effect in retarding the setting time. It is a dry powder and it is easily available in stores as a laundry detergent.

3.2.7. Surfactant

To improve the workability of the concrete mix, Surfactant (Figure 3.4) was used as water reducer in all the mixes.

Figure 3.4. Surfactant

3.2.8. Water

Ordinary Fargo city water was used for the experiments.

3.2.9. Carbon Nanotubes

In Phase I of the research, multi-walled carbon nanotubes (MWCNT) were added in some of the mixes. MWCNTS are rolled with diameter ranges from 10-80 nm. The Young's modulus of an individual nanotube should be around 1 TPa and its density is about 1.33 g/cm3 (**Konsta-Godoutos et al., 2010**). Molecular mechanic simulations suggested that CNTs' fracture strains were between 10% and 15%, with corresponding tensile stresses on the order of 65 to 93 GPa (**Konsta-Godoutos et al., 2010**). Their aspect ratios are generally beyond 1000. The major challenge associated with the incorporation of CNTs in cement-based materials is its poor dispersion (**Konsta-Godoutos et al., 2010**). Poor dispersion of CNTs leads to the formation of many defect sites in the nanocomposite and limits the efficiency of the CNTs in the matrix. The

use of CNTs requires ultrasonic energy to achieve effective dispersion (**Konsta-Godoutos et al., 2010**).

3.3. Laboratory Equipment

Different sizes of beakers, flasks, buckets and test tubes were used for the preparation of chemical solutions (Figure 3.5). In Phase I, a medium-sized pan with a medium-sized spatula was used for the mixing of mortar, whereas in Phase II, mortar mixer was used for mixing. Concrete mixer was used for mixing concrete for cylinder and beam molds.

As CNTs tend to stick to each other, their use requires ultrasonic energy to achieve effective dispersion in a solution. Therefore, to disperse CNTs in alkaline solution, a probe sonicator (Figure 3.6) with beaker size of 100 ml was used.

In Phase I, all the specimens were prepared using molds of size 3*6 (cylindrical) and 2*2*2 (cube) whereas in the phase II 4*8 size of cylindrical molds were used due to the unavailability of 3*6 size cylindrical molds (Figure 3. 9- Figure 3.11). In Phase II beam molds of 6*6*20 was used (Figure 3.11). Other lab equipment like a small pump blower, lab spoons, and a water jar were also used for various purposes.

For the slump test, slump cone, rod, and base were used (Figure 3.7). Oven was used for the curing cubes (Figure 3.8). For the determination of strength of the specimens, a concrete compressive strength and tensile strength machine were used (Figure 3.12). Another equipment like demoulding machine was also used (Figure 3.13).

Figure 3.5. Different Lab Equipment

Figure 3.6. Sonicator

Figure 3.7. Slump Cone, Base and Rod

Figure 3.8. Oven for Curing
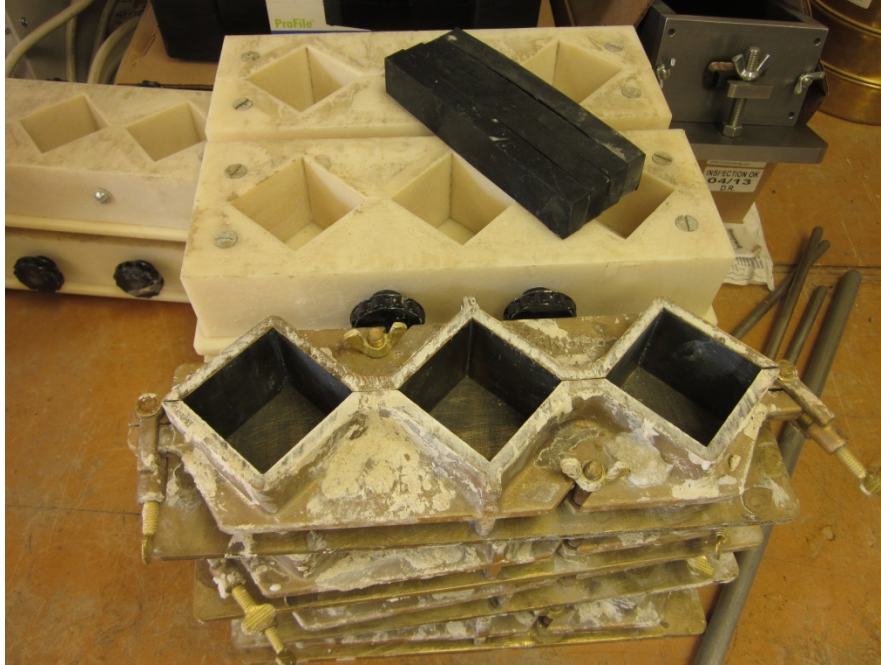
Figure 3.9. Cube Molds (2*2*2)

Figure 3.10. Cylinder Molds (4*8)

Figure 3.11. Beam Mold (6*6*20)
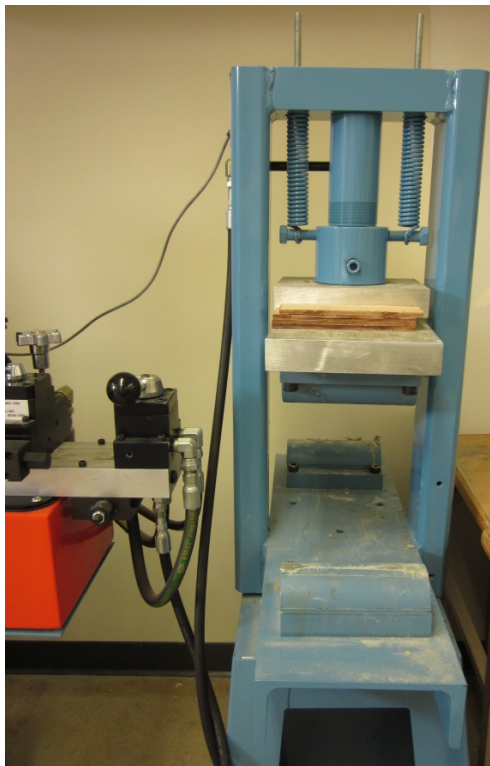
Figure 3.12. Compressive and Tensile Strength Machine

Figure 3.13. Demoulding Machine

3.4. Mix Design

This section describes the basic mix design procedure used to prepare mixes for the research. ASTM C109 and ASTM C192 were followed during the preparation of the mixes.

3.4.1. Water-Cement Ratio`

The water-cement (w/c) ratio is the controlling factor for most of the desirable properties of concrete such as strength, durability, shrinkage potential, and permeability. Durable concrete mixes usually need a w/c ratio of .50 or less (**Sparkman, 2006**). For this research experiments, w/c ratio of 0.40 was used (Table 3.8- 3.13).

3.4.2. Fly Ash-Sand-Coarse Aggregates Ratio

The ratio of fly ash-sand-coarse aggregates is the major factor that influences the properties of mix design. The guiding principle of mix design is to pack as much aggregate into the mix as possible to make the mixes economical, and to reduce the required paste volume

(**Sparkman, 2006**). For this research experiments, fly ash, sand and coarse aggregates was used in 1:2:2 ratio (Table 3.8 and 3.12) for cylinder and beam specimen whereas 1:2.75 ratio of fly ash and sand was used for cube specimens (Table 3.9, 3.10, 3.11 and 3.13) following ASTM C192 and ASTM C109.

3.4.3. Admixture: Surfactant

Of all the admixtures available, surfactant offer the most benefits during the mix design process (**ConcreteNetwork, 2006**). Surfactant is used to reduce the amount of water needed for concrete mix. In Phase I, different quantities of surfactants were used for the experiment, especially for the experiments using CNTs (Table 3.8-3.11). In Phase II, 0.08% of total weight of the fly ash-sand-coarse aggregates were used (Table 3.12 and 3.13).

3.4.4. Chemicals

Alkaline solution is used to increase the strength and durability of geopolymer concrete. In this research, KOH is used to strengthen the mortar and resulting concrete; whereas citric acid is used to retard the setting time of the mix. As alkaline activator is one of the key elements of the geopolymer concrete, in Phase I, different amounts were used regarding the molar value of KOH, and the effects were observed by performing compressive strength tests. The KOH solution was prepared by dissolving KOH pellets in water. The mass of KOH solids in a solution was varied depending on the concentration of the solution expressed in terms of molarity, M. For instance, KOH solution with a concentration of 3M consisted of 3x56 = 168 grams of KOH solids per litre of the solution, where 56 is the molecular weight of KOH (Table 3.8-3.11). In one of the mix, borax was used as a retarder and the setting time was observed (Table 3.9).

In Phase II, the best proportion of KOH and citric acid which exhibited the highest compressive strength in Phase I was used (Table 3.12 and 3.13). Figure 3.14 shows the preparation of KOH and citric acid solution.

Figure 3.14. Preparing the Solution of KOH and Citric Acid

3.4.5. CNTs

CNTs were used in Phase I of the study. Five dispersions were prepared by mixing CNT with alkaline surfactant solution (100 g) at surfactant- CNTs weight ratios of 4, 6.25, 7.5, 9, and 2.9 (**Konsta-Gdoutos et al., 2010**) for the cubes. In five out of six mixes, a constant amount of CNTs, i.e. 0.56 g, was used whereas in the last mix, the amount of CNTs was increased to 1.2 g to observe any changes in the characteristic of cubes (Table 3.6, Table 3.10 and 3.11).

3.4.5.1. Dispersion of CNTs

As CNTs tend to stick to each other, they need ultrasonic energy to achieve effective dispersion in a solution. Therefore, a probe sonicator was used to disperse CNTs in alkaline solution. The dispersions were sonicated at room temperature at the power of 35W-49W for 20 min. with medium intensity tip of diameter .25" (6.4mm). The frequency used for the dispersion was 5 KHz. Figure 3.15 shows the dispersion process of CNT in alkaline solutions.

Table 3.6. *Proportions of Sonicated Solution.*

Alkaline Solution	97.2 g	95.9 g	95.2 g	94.4 g	95.3 g
Surfactant	2.24 g	3.5 g	4.2 g	5.04 g	3.5 g
CNTs	.56 g	.56 g	.56 g	.56 g	1.2 g
SFC/CNT	4	6.25	7.5	9	2.9

*Figure 3.15***.** Dispersing CNT in Alkaline Solution

3.4.6. Mixture Proportion

In order to accomplish the aims of this research, experiments were divided into two phase. This section shows the exact proportion of the materials used for the mixes of both phases. Table 3.7 indicates the number of mix designs prepared in phases I and II.

Numbers of mix designs were prepared in Phase I to observe the results. In Phase II, only one set of mix design, based on the best result achieved in phase I, was prepared. CNT mixes were not repeated in phase II, whereas, one mix design was prepared for the beam. Tables 3.8, 3.9, 3.10 and 3.11 show the proportions of materials used to prepare mix design for cylinders and

cubes in phase I. Tables 3.12 and 3.13 show the proportions of materials, derived from Phase I,

used to prepare mix design for cylinders, beams, and cubes in Phase II. Tables 3.14 and 3.15 give

the detail of the number and sizes of specimen, curing temperature, quantity and type of test used

in Phase I and Phase II. Table 3.16 gives the total amount of concrete used in this research.

Figure 3.16 shows the materials used for the preparation of the concrete.

Figure 3.16. Preparing the Mixture Proportion for Concrete Mix

Table 3.7. *No. of Mixes Prepared.*

Phase	Types of Molds	No. of Mix Designs
I	Cylinders	6
	Cubes	4
	CNT Cubes	5
	Non-CNT Cubes	4
II	Cylinders	1
	Cubes	1
	Beams	1

Table 3.8. *Phase I: Proportions of Materials used for the Experiments (Cylinders). Percentage of the Weight is of Total Weight of Fly Ash, Sand and Aggregate.*

Materials	Mix 1	Mix 2	Mix 3	Mix 4	Mix 5	Mix 6
Fly Ash	20%	20%	20%	20%	20%	20%
Sand	40%	40%	40%	40%	40%	40%
Aggregate	40%	40%	40%	40%	40%	40%
KOH	0	1.5M	2M	2.5M	3M	4M
Citric Acid	0.00%	0.10%	0.30%	0.50%	1.62%	1.62%
Surfactant	0.08%	0.08%	0.08%	0.08%	0.08%	0.08%
Water/FA ratio	.4	.4	.4	.4	.4	.4

Table 3.9. *Phase I: Proportions of Materials used for the Experiments (Cubes). Percentage of the Weight is of Total Weight of Fly Ash and Sand.*

Materials	F1	F2	F3	F3A
Fly Ash	26.6%	26.6%	26.6%	26.6%
Sand	73.2%	73.2%	73.2%	73.2%
KOH	2.5M	3M	3.5M	3.5M
Citric Acid	0.90%	1.02%	1.02%	1.02%
Surfactant	0.08%	0.08%	0.08%	0.08%
Water/FA ratio	.4	.4	.4	.4
Borax	0	0	0	1.68%

Table 3.10. *Phase I: Proportions of Materials used for the Experiments (CNT Cubes). Percentage of the Weight is of Total Weight of Fly Ash and Sand.*

Materials	Mix 1	Mix 2	Mix 3	Mix 4	Mix 5
Surfactant	2.24g	3.5g	4.2g	5.04g	3.5
CNT	0.56g	0.56g	0.56g	0.56g	1.2g
Fly Ash	26.6%	26.6%	26.6%	26.6%	26.6%
Sand	73.2%	73.2%	73.2%	73.2%	73.2%
KOH	3M	3M	3M	3M	3M
Citric Acid	1.62%	1.62%	1.62%	1.62%	1.62%
Water/FA ratio	.4	.4	.4	.4	.4

Table 3.11. *Phase I: Proportions of Materials used for the Experiments (Non-CNT Cubes). Percentage of the Weight is of Total Weight of Fly Ash and Sand.*

Materials	Mix 1	Mix 2	Mix 3	Mix 4
Surfactant	2.24g	3.5g	4.2g	5.04g
CNT	0g	0g	0g	0g
Fly Ash	26.6%	26.6%	26.6%	26.6%
Sand	73.2%	73.2%	73.2%	73.2%
KOH	3M	3M	3M	3M
Citric Acid	1.62%	1.62%	1.62%	1.62%
Water/FA ratio	.4	.4	.4	.4

Table 3.12. *Phase II: Proportions of Materials used for the Cylinder, and Beam Molds. Percentage of the Weight is of Total Weight of Fly Ash, Sand and Aggregate.*

Materials	Mix
Fly Ash	20%
Sand	40%
Aggregates	40%
w/FA ratio	0.4
KOH	3M
Citric Acid	1.62%
Surfactant	0.08%

Table 3.13. *Phase II: Proportions of Materials used for the Cube Molds. Percentage of the Weight is of Total Weight of Fly Ash and Sand.*

Materials	Mix
Fly Ash	26.6%
Sand	73.2%
w/FA ratio	0.4
KOH	3M
Citric Acid	1.62%
Surfactant	0.08%

Table 3.14. *Phase I: Detail of the Mix.*

Molds	Size (Inch)	No. of Specimens	No. of Specimens Curing in Room Temperature at 24hr, 3 day, 7day, 14 day, 21 day, 28 day						Quantity (In3)	Test
			Mix 1	Mix 2	Mix 3	Mix 4	Mix 5	Mix 6		
Cylinder	3*6	108	18	18	18	18	18	18	4644	CS
Cube	2*2*2	72	18	18	18	18	-	-	576	CS
Cube (CNT)	2*2*2	90	18	18	18	18	18	-	720	CS
Cube (Non-CNT)	2*2*2	72	18	18	18	18	-	-	576	CS
Total amount of concrete									6516 In3= 0.13 CY	

Table 3.15. *Phase II: Detail of the Mix with 3M of KOH.*

Molds	Size (Inch)	No. of Specimens with Curing Temperatures at 24hr, 3 day, 7day, 14 day, 21 day, 28 day								Quantity (In^3)	Test
		Room Temp.	Oven (100° F)	Oven (150° F)	Oven (200° F)	Oven (250° F)	Oven (300° F)	Oven (350° F)	Oven (400° F)		
Cube	2*2*2	24	24	24	24	24	24	24	24	1152	CS
Cylinder	4*8	30	-	-	-	-	-	-	-	3012	CS
Beam	6*6*20	3	-	-	-	-	-	-	-	2160	TS
Total amount of concrete										6324 In3= 0.135 CY	

Table 3.16. *Total Concrete.*

Total amount of concrete used	12840 In3= 0.27 CY

3.5. Experimental Design

This section describes the mixing and specimen preparation procedures that were used in this study. The experiments started with numerous trial mixtures of fly ash geopolymer concrete. The mixtures were prepared using different chemicals and materials like MgO, CaO, and Portland cement and then tested for strength. The main objectives of the preliminary laboratory work were:

1. To practice the mixing of fly ash-based geopolymer concrete;

2. To observe the effects of alkaline liquid on the mix;

3. To study the behavior of the mortar and other features like setting time;

4. To develop the process of mixing;

5. To understand the basic mixture proportioning of fly ash-based geopolymer concrete;

6. To study the strength of the concrete and mortar; and

7. To explore the effect of CNT in a mortar.

3.5.1. Experiment Summary

3.5.1.1. Phase I Experiments

The first batch of the mix was prepared without the alkaline solution to observe the strength it could develop after setting. Only 3*6 cylinders were made from this mix. The second batch was prepared using alkaline activator (KOH and citric acid), and surfactant. Concrete and mortar were prepared into a 3*6 cylinder and 2*2*2 cube molds. In one mix for cubes, borax was also added to observe if it can further minimize the setting rate of the fly ash.

The third batch of mixes was prepared for cubes only. The process of mixing was the same, but CNTs were added to the chemicals and surfactant. For the optimal blend, a sonicator with moderate sized tip was used to disperse CNTs in the solution of KOH, citric acid, and surfactant. The power used by the sonicator varied from 35W to 49W with no temperature selection. For each dispersion, a time duration of 20 min. was selected.

A series of compressive strength tests were performed for mixes of each batch. Each mix was tested at time intervals of 24 hr., 3 days, 7 days, 14 days, 21 days, and 28 days. ASTM C192 and ASTM C109 was followed for the mixing of cylinders and cubes. ASTM C39 and ASTM C109 was followed for compressive strength test of cylinders and cubes.

3.5.1.2. Phase II Experiments

The mix with highest compressive strength developed in Phase I was used to prepare the cylinders, cubes and beam specimens using the same mixing process. Tests like slump and setting time were performed for the fresh mortar. ASTM C143 was followed by the slump test. For hardened concrete, compressive strength, flexural strength tests were performed on cylinder and cube specimens at time intervals of 24 hr, 3 days, 7 days, 14 days, 21 days, and 28 days whereas only flexural strength test was done for beam specimens after 28 days. ASTM C39, ASTM C109, and ASTM C78 was followed for the strength test of cylinders, cubes and beams. An oven was used to cure cube specimens at temperatures of room temperature, 100° F, 150° F, 200° F, 250° F, 300° F, 350° F, and 400° F. ASTM C31 was followed for curing cubes.

3.5.2. Specimen Preparation

Before mixing the samples, the interior of the mixer, pan, and all the tools used for mixing and placing concrete was coated with water to minimize moisture loss during the mixing procedure. Mixing was performed according to ASTM C 192, ASTM C109, and ASTM C39. The day before the mixing, KOH and citric acid solutions were prepared with water in separate beakers and made to stand overnight for the KOH solution to cools down. The two solutions were mixed in one beaker and kept covered till the mixing of the concrete.

3.5.2.1. Mixing Procedure

ASTM C192, ASTM C109, ASTM C39 were followed for mixing, drying and curing of the specimens.

### 3.5.2.2. Cylinders and Beams

Coarse aggregates and some of the alkaline solution were added to the mixer. Mixer was started and kept mixing for 30 seconds. Fine aggregate, fly ash and remaining solution were added in the mixer and kept mixing for 3 minutes, followed by 3 minutes' rest and 2 minutes mixing again. The open part of the mixer was covered to avoid evaporation during the rest period. After the mixing process had been completed, mixed concrete was deposited into clean mixing pan. To avoid segregation, the mixture was remixed by scoop until it appeared to be uniform. The concrete was poured in the molds into three layers by using a scoop. Every layer was consolidated by using a rod with rounded ends for 25 times for cylinders and 60 times for beams. Outside of the mold was lightly tapped for 10-15 times with a mallet. It is done to close any holes left by rodding and to release any air bubbles that might be trapped inside. The top

surface of the mold was leveled by using a rod. Figure 3.17 to Figure 3.23 shows the preparation of cylinder and beam specimen.

3.5.2.3. Cubes

The solution was poured into the mixer. Fly ash was added to the solution, and the mixer was started with power level 1 and mixed for 30 seconds. Sand was added, and the mixture was mixed in it for another 30 seconds. The power level of the mixer was changed to level 2, and the mixture was kept mixing it for 60 seconds followed by 90 seconds rest and another 60 seconds of mixing. After the mixing process had been completed, the mortar was poured by using scoop into the molds with two layers. Every layer was consolidated 32 times by using a tamper to avoid the air bubbles in-between. The top surface of the mold was leveled by using a rod. Figure 3.24 to Figure 3.27shows the preparation of fresh mortar.
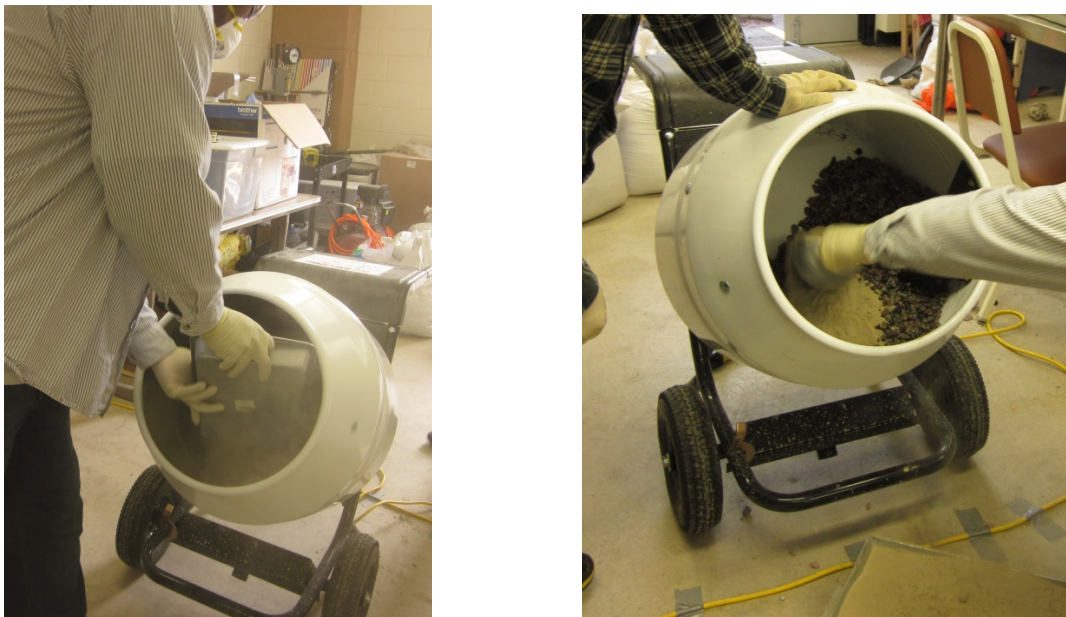
Figure 3.17. Mixing the Concrete in Mixer

Figure 3.18. Mixing the Concrete in Mixer

*Figure 3.19***.** Fresh Concrete Mix

Figure 3.20. Pouring Concrete in Cylinder Molds

Figure 3.21. Consolidating Concrete using Rod

Figure 3.22. Consolidating Concrete using Rod

Figure 3.23. Pouring and Leveling Concrete in Beam Mold

Figure 3.24. Mixing Mortar

Figure 3.25. Fresh Mortar

Figure 3.26. Tamping Fresh Mortar in Cube Molds
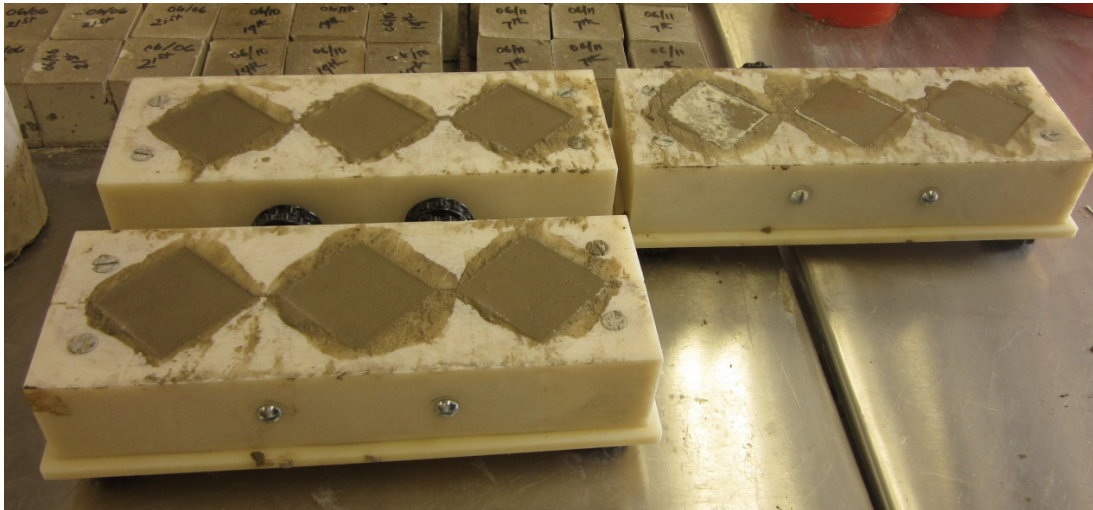
Figure 3.27. Fresh Mortar in Molds

3.5.3. Drying and Curing

After casting, the specimens were kept at room temperature and demoulded after 24±4

hours and marked with the date of mixing. The specimens in Phase I was cured at room

temperature. In Phase II, cube specimens were cured in oven using temperatures like room temperature, 100° F, 150° F, 200° F, 250° F, 300° F, 350° F, and 400° F. whereas cylinders and beams were cured only in room temperature. Figure 3.28 to Figure 3.32 shows the curing process of the specimen.

Figure 3.28. Cylinder Specimens

Figure 3.29. Cube Specimens

Figure 3.30. Demouding Beam

Figure 3.31. Beam Specimens in Room Temperature

Figure 3.32. Curing Cube Specimens in Oven

3.5.4. Properties of Fresh Mortar

3.5.4.1. Slump Test

To analyze the behavior of fresh mortar, the slump test was performed. This test was based on ASTM C143. For the test, a slump cone and a steel rod were used. The slump test gives the vertical distance from the top of the settled concrete to the upper part of the slump cone. The dampened slump cone was placed upright on a flat concrete surface. The cone was filled with concrete in three layers. Each layer was rodded for 25 times to purge air bubbles and make even distribution of concrete in the cone. The cone was removed slowly. Furthermore, the empty slump cone was placed next to the concrete and the distance was measured. Figure 3.33 shows the concrete being rodded.

Figure 3.33. Slump Test

3.5.4.2. Setting Time

The setting of concrete is the gradual transition from liquid to solid. The final setting of concrete relates to the point where stresses and stiffness start to develop in freshly placed concrete. The initial set time is important as it provides an estimate of when the concrete has reached the point where it has stiffened to such an extent that it can no longer be vibrated without damaging it.

The setting time of the fresh concrete/ mortar was analyzed after pouring it into the mold. After each mixture had been poured, specimens were observed for several hours. It was found that the specimens with higher amounts of KOH had shorter setting time than those with comparatively lesser ones.

3.6. Experimental Procedures: Test of Hardened Mortar

The following section provides an overview of the experimental equipment and test procedures that were used in this study.

3.6.1. Compressive Strength Test

The compressive strength test (ASTM C39) is the most common method used to measure the strength and durability of the concrete. The compressive strength was selected as the benchmark parameter as it is the most important parameter considered in the structural design of concrete structures. It is reported in units of pound-force per square inch (psi) in the US, customary units, or pascals (Pa) in SI units.

The results of this test method will be used as a basis for quality control of concrete proportioning, mixing, and placing operations; determination of compliance with specifications; control for evaluating the effectiveness of admixtures; and similar uses (ASTM C39/ C39M - 11a).

In Phase I, the compressive strength was performed in the Structural Lab of the Civil Engineering Department on cylinders and cubes. In phase II, it was done in CME lab on cylinders and cubes. Compressive strength test was conducted at ages of 24 hr., 3, 7, 14, 21, and 28 days. ASTM C39 and ASTM C109 were followed for the compressive test for both cylinders and cubes. Figure 3.34 shows the performance of a compressive strength test on a cylinder.

Figure 3.34. Compressive Strength Test Machine of Cylinder Specimen

3.6.2. Flexural Strength Test

The Three-Point bending test was conducted on a loading frame to calculate, according to ASTM C78, the flexural tensile strength on standard beam specimens of size 6 in*6 in*20 in by using the flexural strength machine in CME lab. The loads were gradually increased at the loading rate of about 100lb/sec. The test was carried out on 28th day. Figure 3.35 shows the flexural test machine for the beam. The modulus of rupture for the flexural strength of the beam was calculated by the following formula:

$$R = PL/bd$$

Where:

R= Flexural strength (psi)

P = the maximum applied load indicated by the machine at failure (lb.)

b = Average width of the specimen (in)

d = Average depth of the specimen (in)

This formula is used if the fracture initiates in the tension surface within the middle third of the

span length.

Figure 3.35. Flexural Strength Test Machine of Beam

CHAPTER 4. EXPERIMENT ANALYSIS: RESULT AND DISCUSSION

4.1. Introduction

This chapter presents the analysis of materials used, experimental design and the results of the experiments. The results are evaluated to compare the relative compressive strength and flexural strength test along with the characteristic tests like slump, and setting time of all the mixtures. All the tests were performed using ASTM standards; compressive strength (ASTM C39), flexural strength (ASTM C78), and slump test (ASTM C143).

4.2. Fresh Mortar Properties

4.2.1. Slump

The results of the slump test performed in Phase II is shown in Table 4.1 and Figure 4.1. Three slump tests, slump 1, slump 2 and slump 3 were done to compare the values obtained. The slump test was repeated at four intervals of time, i.e. immediately, 7 minutes, 12 and 16 minutes after mixing to observe the workability of the mix. The results in Table 4.1 indicates that workability span for all the mixes was short, i.e. the mixes tend to set faster; therefore, the slump value decreased as the time of mixing increased (**Hardjito et al., 2005**). This is because of the presence of high lime and the activation of alkaline solution (**Nicholson et al., 2005**). In Figure 4.1, it can be seen that as the mixing time was increased, the slump value dropped greatly. Comparing all the test results, appropriate workability was achieved at 12 min test with slump value from 6" to 7"

.

Table 4.1. *Slump Test.*

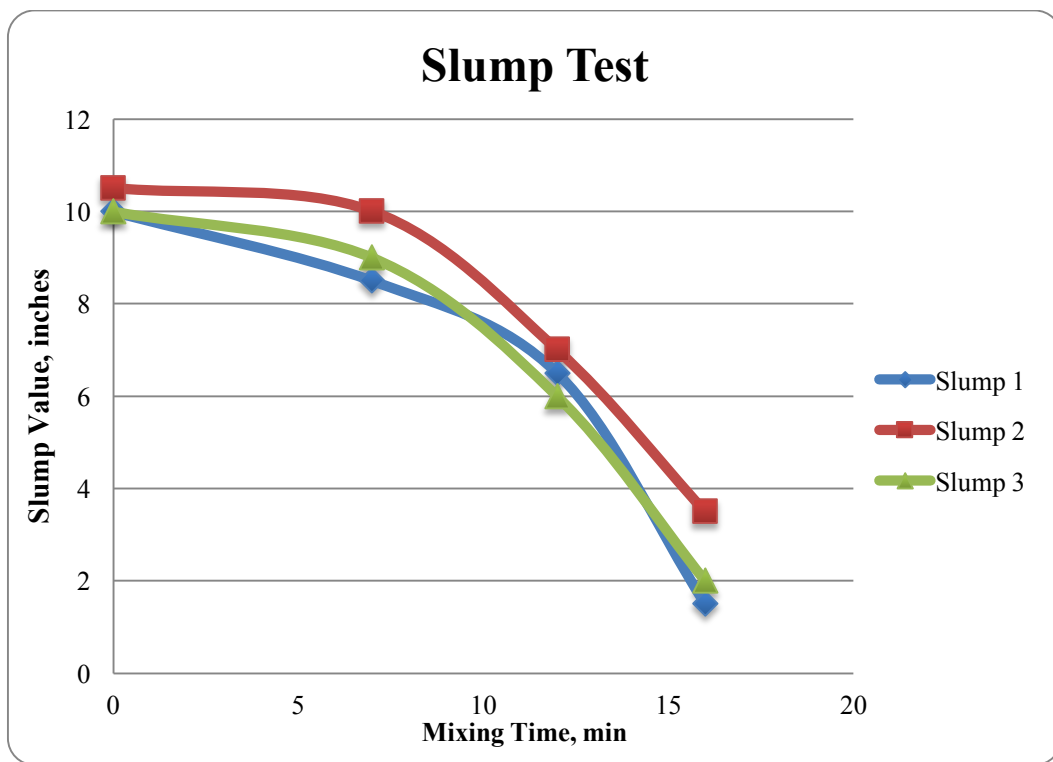| Slump No.	After Mixing	After 7 min	After 12 min	After 16min
Slump 1	10"	8.5"	6.5"	1.5"
Slump 2	10.5"	10"	7"	3.5"
Slump 3	10"	9"	6"	2"

Figure 4.1. Slump Values with respect to Different Mixing Time

4.2.2. Setting Time

The setting time of the mixes was observed throughout the experiments. It was discovered that the specimens with a higher molar value of KOH had shorter setting time compared to those with lesser ones. The overall setting time observed was not more than 30

70

minutes. This is because fly ash C tends to set faster than other geopolymers due to the presence of high amounts of lime. Also, the activation of alkaline solution generates heat which makes the mix set faster. Table 4.2 gives the setting time of the mixes when different molar values of KOH were used. Figure 4.2 shows the graph of setting time concerning the molar values used in the mixes. It can be observed in the figure that as the molar value of the mixes were increased, the setting time was shorter. The lowest molar value, 1.5, gave the setting time of 30 min whereas the highest molar value, 4, gave the setting time of 10 min.

Table 4.2. *Setting Time with respect to Molar Value of KOH.*

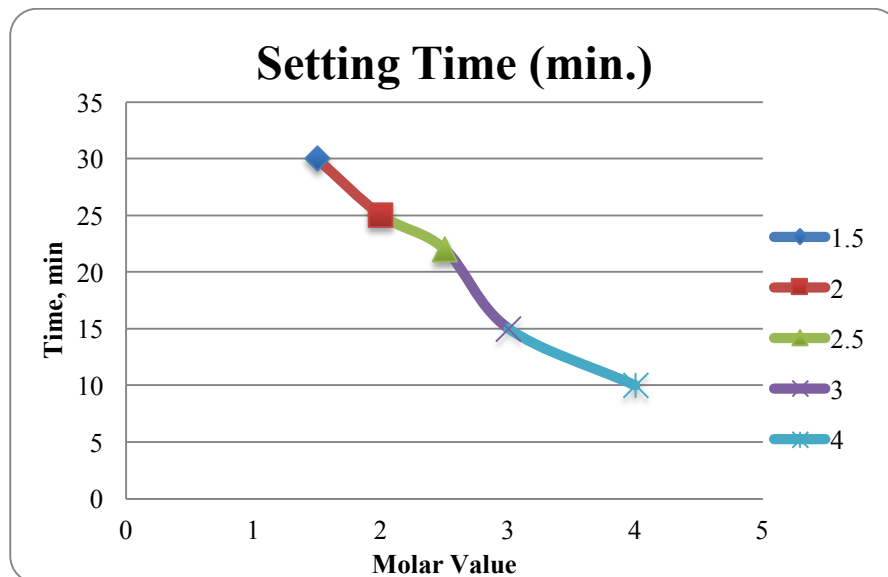| Setting Time (min.)	Molar Value
30	1.5
25	2
22	2.5
15	3
10	4

Figure 4.2. Setting Time with respect to Molar Value of KOH

4.3. Compressive Strength Test

Compressive strength is considered as one of the most important properties of hardened concrete. It is generally the main property value used to investigate the quality of concrete according to ASTM C39. That is why it is important to evaluate whether changes in the mixture composition will affect the early and late compressive strength of concrete. Compressive stress results for cylinders and cubes at age 1, 3, 7, 14, 21, and 28 days are given below.

4.3.1. Phase I Results

4.3.1.1. Cylinders

From the Table 4.3 and Figure 4.3, we can observe that as the age progressed, strength gain can be observed in each mix with slight ups and downs (Figure 4.3). Alkali activators play a key role in strengthening the concrete materials. It can be seen by comparing the results exhibited by each mix (Table 4.3) that mixes without KOH (mix 1) result in lower strength than mixes with KOH. The highest strength of 1498 PSI is exhibited by Mix 1 (Table 4.3), whereas the other mixes with KOH exhibited higher strength. Moreover, significant strength gain can be seen from mix 2 to mix 5 (Table 4.3) as the molarity of KOH was increased. Figure 4.3 shows the lines constantly increasing with slight ups and downs till mix 5. However, as the molarity of KOH was further increased in mix 6 (Table 4.3), there was no gain in the strength. In fact, there was a slight decline in the strength. Figure 4.3 shows the mix 6 being dropped below mix 5. The reason could be after reaching its optimum level in mix 5, the increased amount of KOH produced excessive heat which made the mix set faster without forming a proper bond. Comparing the cracks of the cylinders with ASTM C39, type 3 fracture pattern matched, i.e. columnar vertical cracking through both ends, no well-formed cones (Figure 4.4 and Figure 4.5).

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Table 4.3. *Phase I: Strength of Each Mix (Cylinder) in Different Time Interval.*

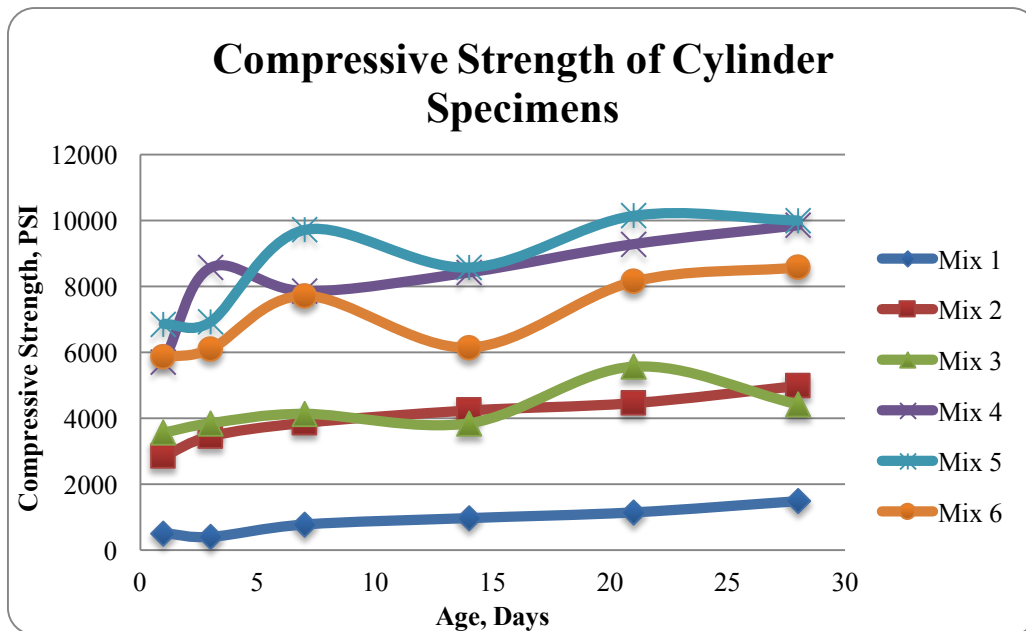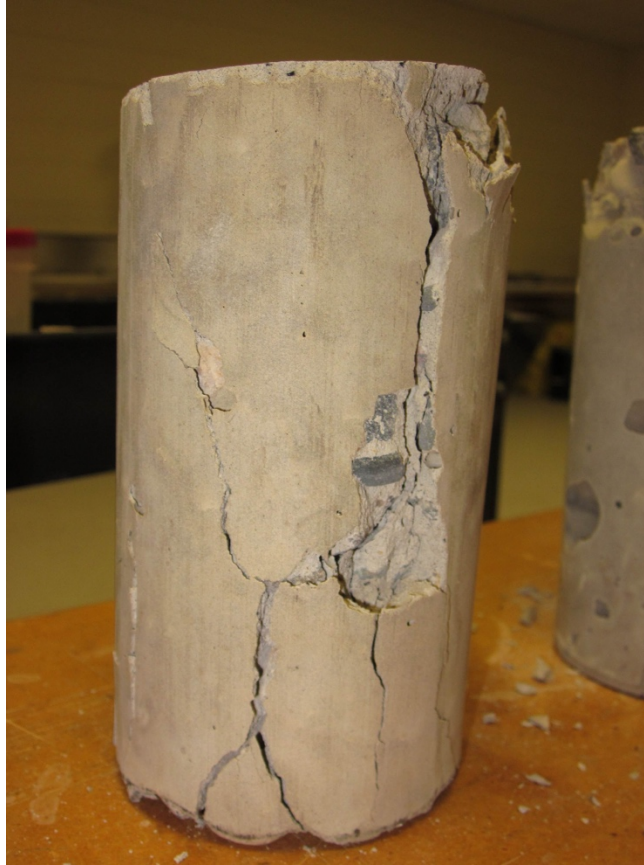| Curing Time/Days	Mix 1	Mix 2	Mix 3	Mix 4	Mix 5	Mix 6
1	523	2859	3571	5714	6857	5857
3	412	3467	3857	8571	6926	6100
7	787	3872	4142	7857	9714	7714
14	982	4246	3857	8428	8571	6143
21	1156	4469	5571	9285	10142	8143
28	1498	4988	4429	9857	10000	8571

(Stress in PSI)

Figure 4.3. Phase I: Compressive Strength Chart

Figure 4.4. Phase I: Cracks formed after Compressive Strength Test

Type 3
Columnar vertical cracking
through both ends, no well-
formed cones

Figure 4.5. ASTM C39 Fracture Pattern (ASTM C39)

4.3.1.2. Cubes

Similar to the results of the cylinder, the compressive strength of cubes also got better with the increase of KOH, from mix F1 to F2 (Table 4.4). As the molarity of KOH was increased in mix F3 and F3A (Table 4.4), a decrease in strength was observed in cube mixes as well. In mix F3A as the borax was added, the setting time was slightly increased. In addition, it also lowered the use of water in comparison to other cubes. Figure 4.6 displays the pattern of the compressive strength gain and loss of the cubes.

Table 4.4. *Phase I: Strength of Each Mix (Cube) in Different Time Interval.*

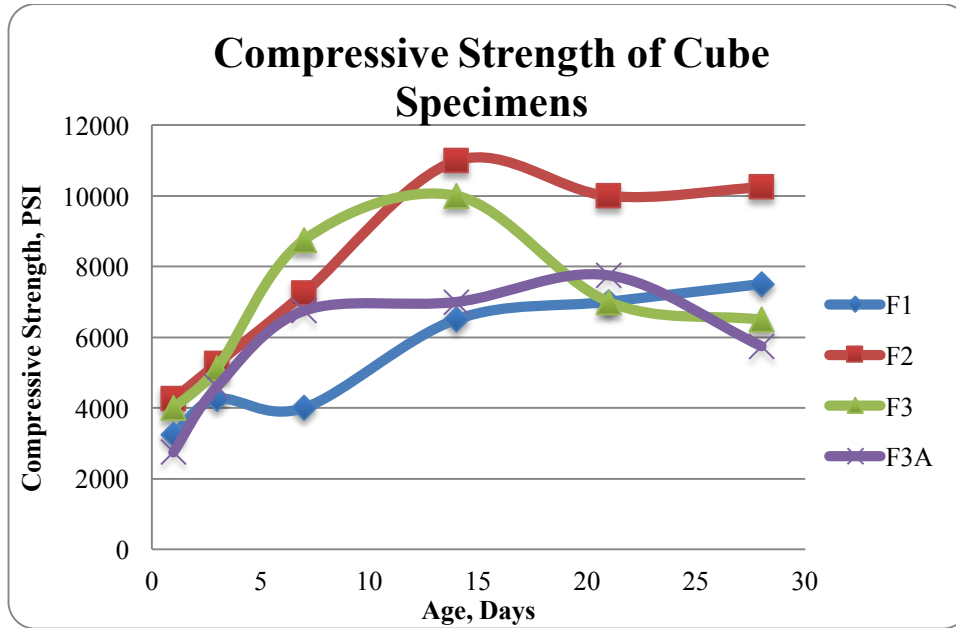| Curing Time/Days	F1	F2	F3	F3A
1	3250	4250	4000	2750
3	4250	5250	5126	4596
7	4000	7250	8750	6750
14	6500	11000	10000	7000
21	7000	10000	7000	7750
28	7500	10250	6500	5750

(Stress in PSI)

Figure 4.6. Phase I: Compressive Strength Chart

4.3.1.3. Carbon Nanotubes

CNT Cubes and Non-CNT Cubes:

From the Table 4.5, Table 4.6, Figure 4.7 and Figure 4.8, it can be observed that; the compressive strength of the cubes with CNT has shown increment compared to the results of non-CNT cubes. Non-CNT cubes were only able to reach the second highest strength established by the CNT cubes. However, early strength gain can be observed in non-CNT cubes compared to CNT cubes. The other observable difference found in-between the mixes with and without CNT is rigidness. CNT cubes were stronger enough to resist the force. The mixes tend to fight back the force till they crushed down totally, whereas the non-CNT cubes were easily crushable once the cracks were formed. Figure 4.9 shows the non-CNT cube being tested in compressive strength test machine.

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Table 4.5. *Strength of Each Mix in Different Time Interval (CNT Cubes).*

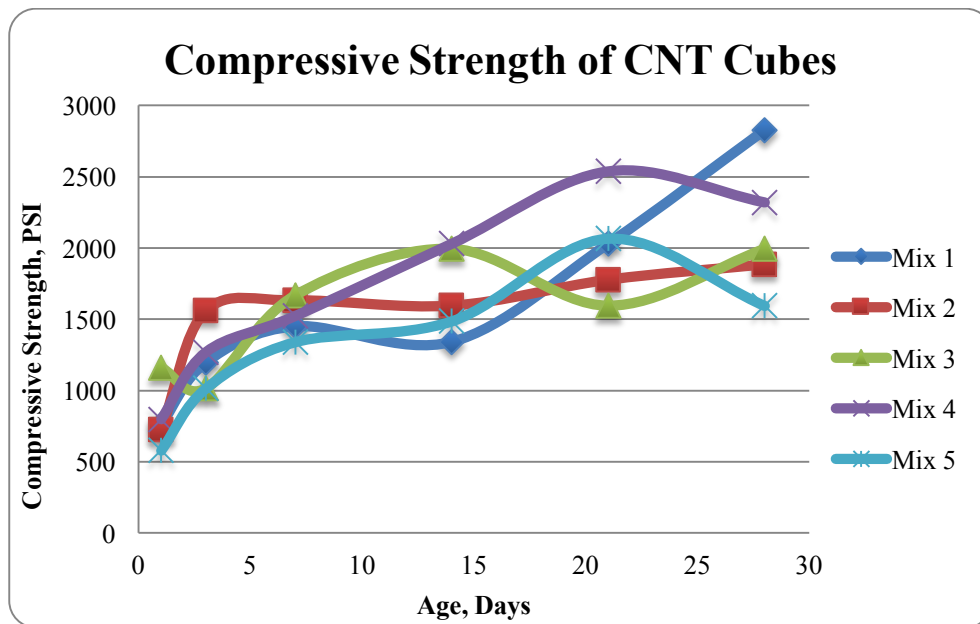| Curing Time/Days	Mix 1	Mix 2	Mix 3	Mix 4	Mix 5
1	762	725	1160	798	580
3	1197	1559	1015	1269	1015
7	1450	1632	1668	1523	1341
14	1341	1595	1994	2030	1487
21	2030	1777	1595	2538	2067
28	2828	1885	1994	2320	1595

(Stress in PSI)

Figure 4.7. Compressive Strength Chart of CNT Cubes

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Table 4.6. *Strength of Each Mix in Different Time Interval (Non- CNT Cubes).*

Curing Time/Days	Mix 1	Mix 2	Mix 3	Mix 4
1	1377	1051	1087	906
3	1595	1120	1522	1305
7	2066	1994	1450	1667
14	2030	1232	2248	2248
21	1776	2538	1559	1450
28	2139	2175	1783	1682

(Stress in PSI)

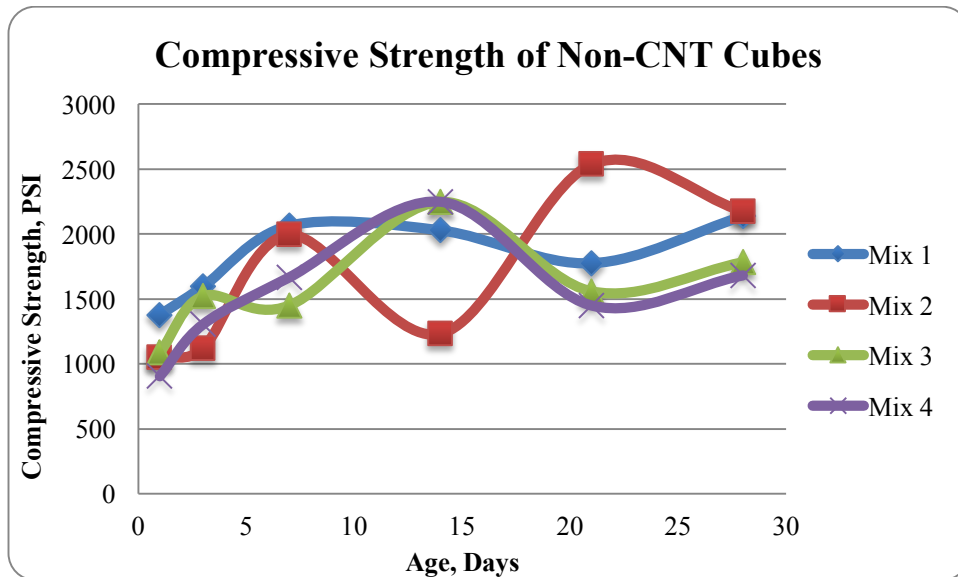*Figure 4.8*. Compressive Strength Chart of Non-CNT Cubes

Figure 4.9. Compressive Strength Test for Cube

4.3.2. Phase II Results

4.3.2.1. Cylinders

It was observed from Table 4.7 and Figure 4.10 that strength was gained gradually with time. After reaching its peak on the 14th day, the strength started to drop significantly on the 21st day, and there was a slight increase on the 28th day. The significant change in the graph of the strength could be because of the presence of moisture in the lab where the experiments were conducted as it rained considerably in Fargo when the experiments were performed.

Comparison of the cracks formed in the cylinders with the given crack types in the ASTM C39, it can be concluded that the cylinders are well formed matching type 1 (Figure 4.12 and Figure 4.13). The vertical cracks at the upper side indicate that there were no well-defined

cones formed. Figure 4.11 shows the performance of a compressive strength test in a cylinder. Figure 4.13 and Figure 4.14 shows the cracks formed in cylinders.

Table 4.7. *Strength of Cylinders in Different Time Intervals.*

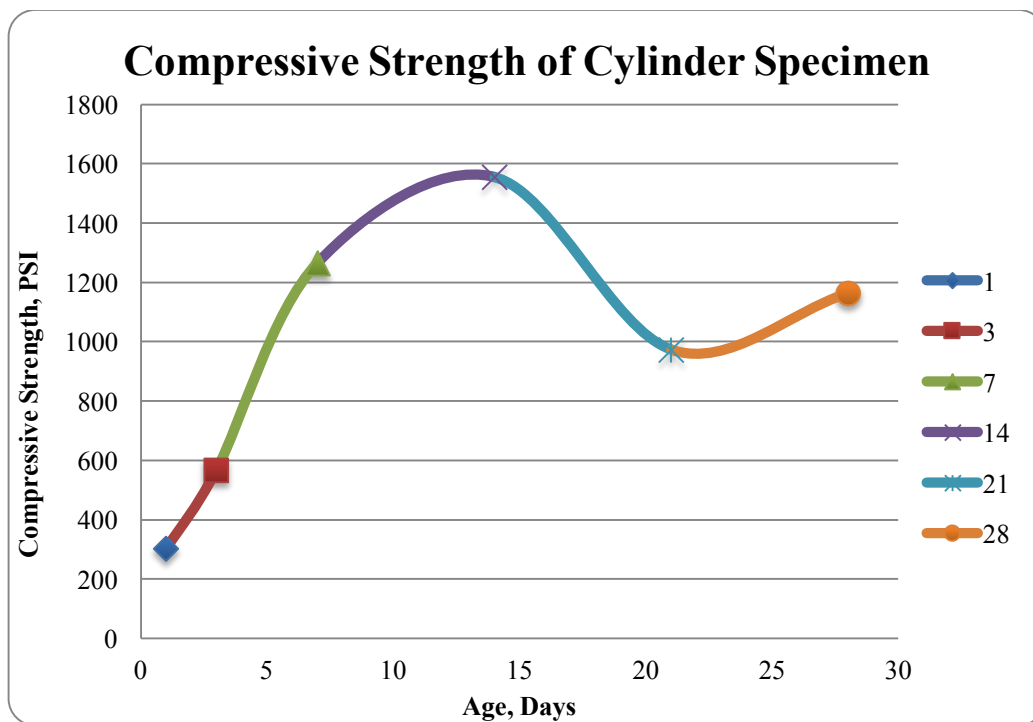| Age	Strength
1	303
3	566
7	1265
14	1555
21	973
28	1163

(Stress in PSI)

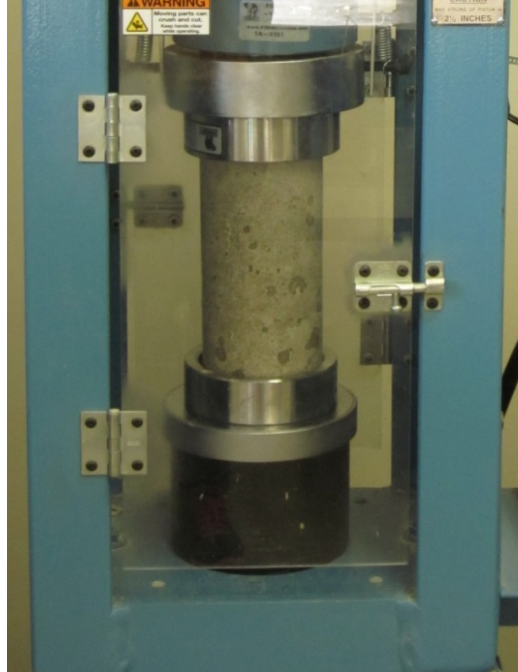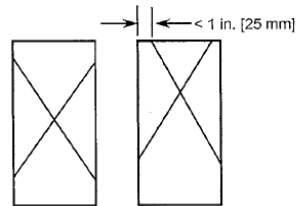*Figure 4.10.* Phase II: Compressive Strength Chart of Cylinders

Figure 4.11. Phase II. Compressive Strength Test of Cylinder

Type 1
Reasonably well-formed
cones on both ends, less
than 1 in. [25 mm] of
cracking through caps

Figure 4.12. ASTM C39 Fracture Pattern (Type 1)

Figure 4.13. Cracks formed after Compressive Strength Test of Cylinders

Figure 4.14. Cracks formed after Compressive Strength Test of Cylinders

4.3.2.2. Cubes

Table 4.8 represents the strength of cubes in a different age regarding different curing temperature. Figure 4.15 and Figure 4.16 are the graphical comparisons of the compressive strength of cubes. Fig. 4.17 to Fig. 4.30 shows the effect of age and temperature on the strength of the cubes. The compressive strength curves are different with respect to age and temperature changes. From the overall comparison shown in Figures 4.15 and 4.16, a gradual decrease in strength was observed as the curing temperature was increased.

On day one, it was observed in Figure 4.17 that the strength declined significantly as the higher temperature was introduced. The reason could be due to the absence of a strong mortar bond. Therefore, as the temperature was increased, the bond started to deteriorate. On day three, the strength remained constant with slight ups and downs (Figure 4.18). However, there was a moderate rise in the strength of the cube cured at 400° F. Slight ups and downs were observed as the curing temperature increased on the 7th day test (Figure 4.19). Significant changes in strength were seen on the 14th and 21st day test (Figure 4.20 and Figure 4.21). There was a decrease in strength as the temperature increased after the 28th day (Figure 4.22). After having its peak at room temperature, the cubes started to lose strength.

Even though many fluctuations in strength can be seen, the strength of the cubes improved as the age progressed. Huge changes of strength gain were observed from day 1 to day 28. Highest peak was achieved at room temperature and 100° F. This could be because of the formation of a stronger bond as the age progresses. However, the strength did not change (increase) a lot with temperature as the specimen aged.

Table 4.8. *Compressive Strength of the Cubes Cured in Different Temperature.*

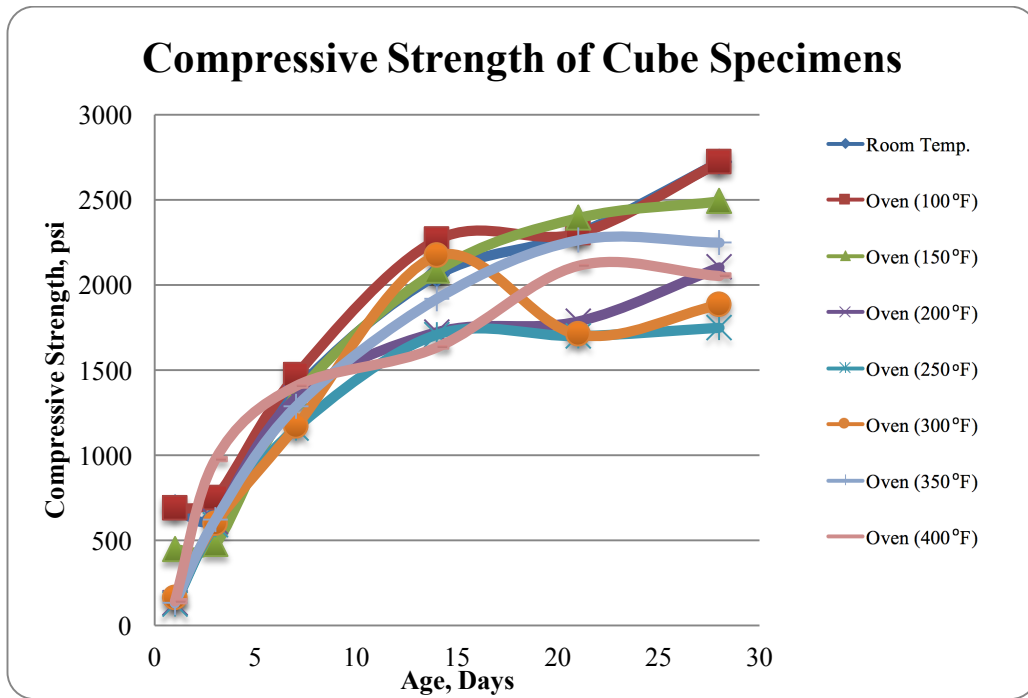| Age	Room Temp.	Oven (100° F)	Oven (150° F)	Oven (200° F)	Oven (250° F)	Oven (300° F)	Oven (350° F)	Oven (400° F)
1	690	687	446	132	122	160	129	139
3	635	747	475	608	588	595	618	972
7	1378	1468	1347	1333	1157	1167	1283	1405
14	2058	2265	2082	1722	1707	2170	1917	1633
21	2303	2302	2392	1785	1698	1708	2260	2112
28	2720	2720	2490	2103	1747	1883	2246	2052

(Stress in PSI)

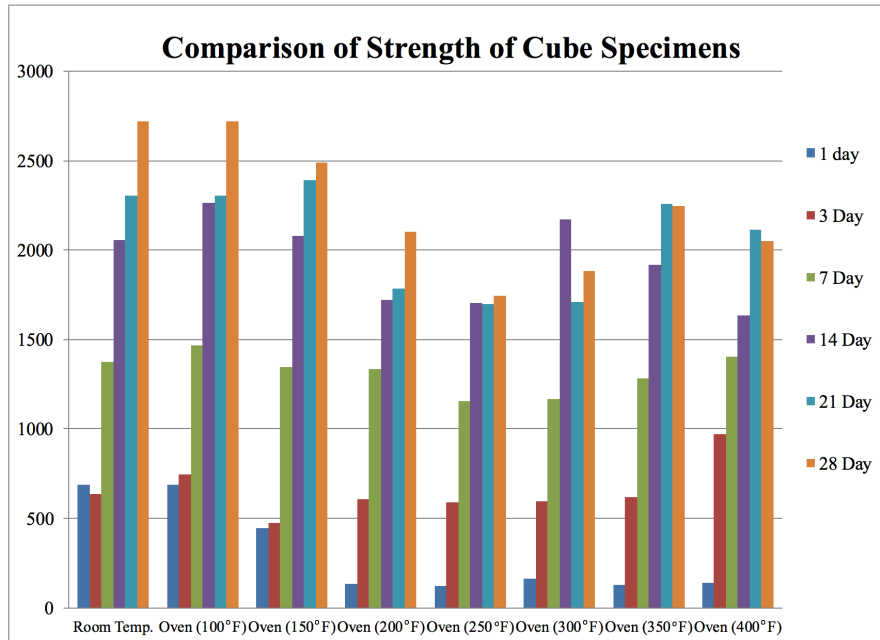*Figure 4.15*. Strength of Cubes Cured in Various Temperatures

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Figure 4.16. Comparison of the Strength of Cubes Cured in Oven with Different Temperatures in Different Time Interval
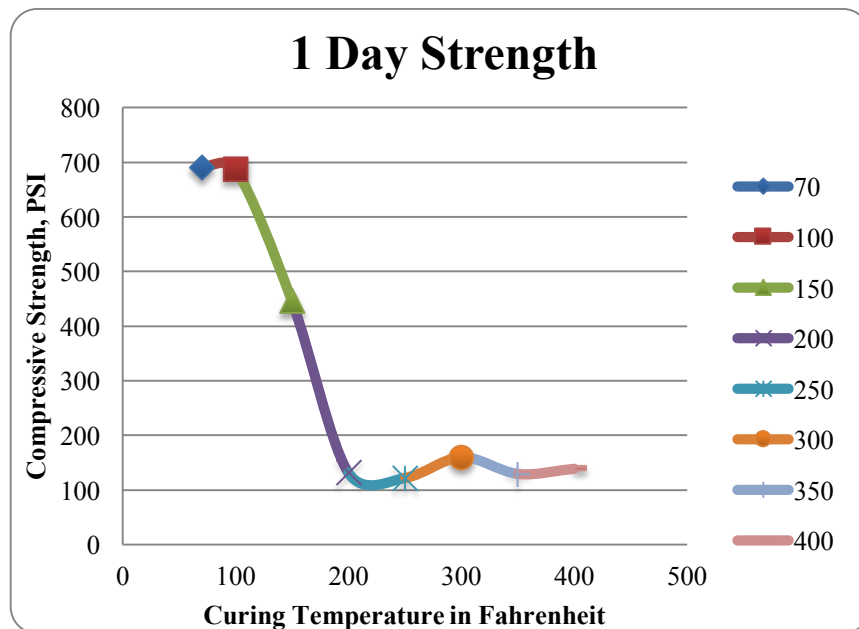

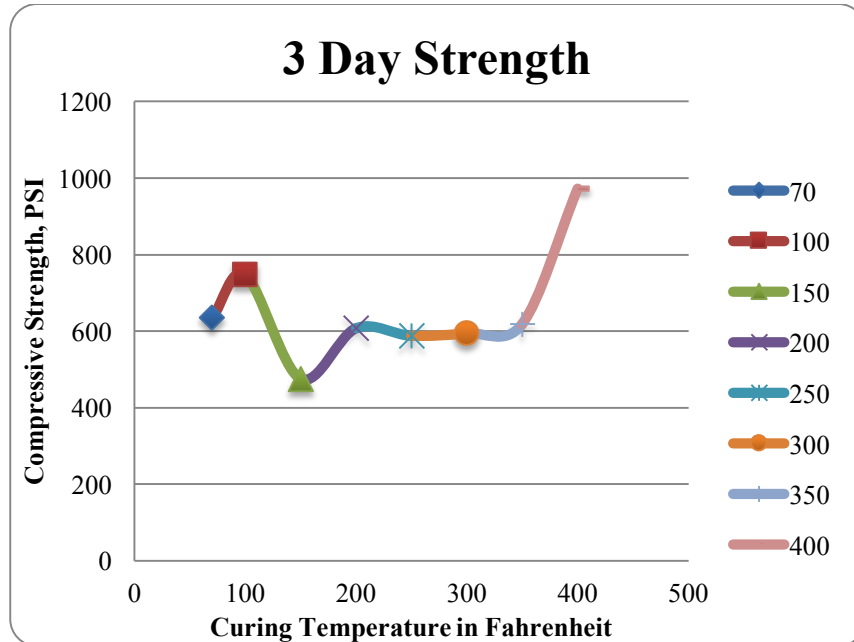*Figure 4.17*. Strength Gain on 1st Day
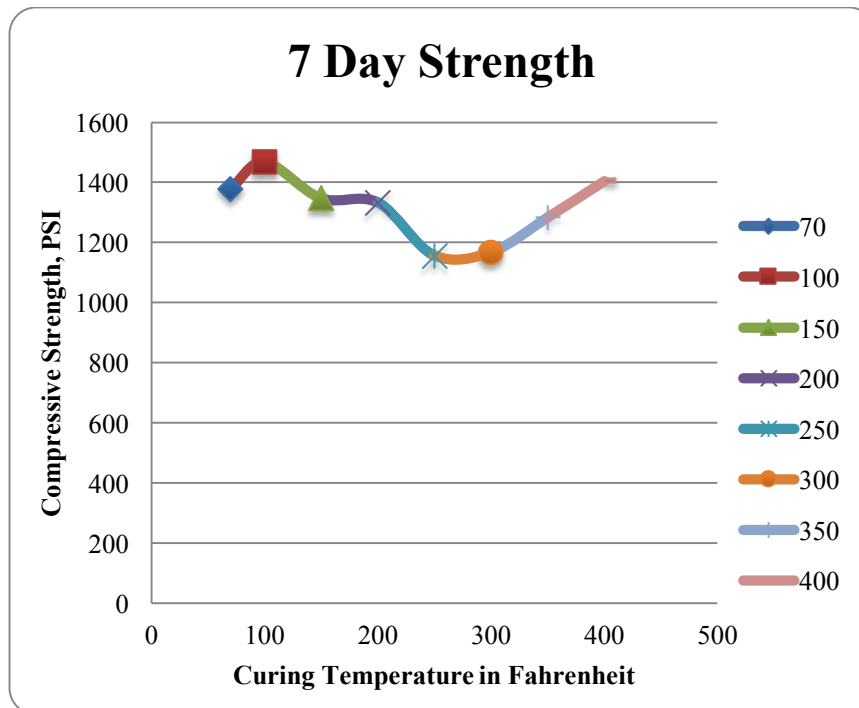
Figure 4.18. Strength Gain on 3rd Day

Figure 4.19. Strength Gain on 7th Day
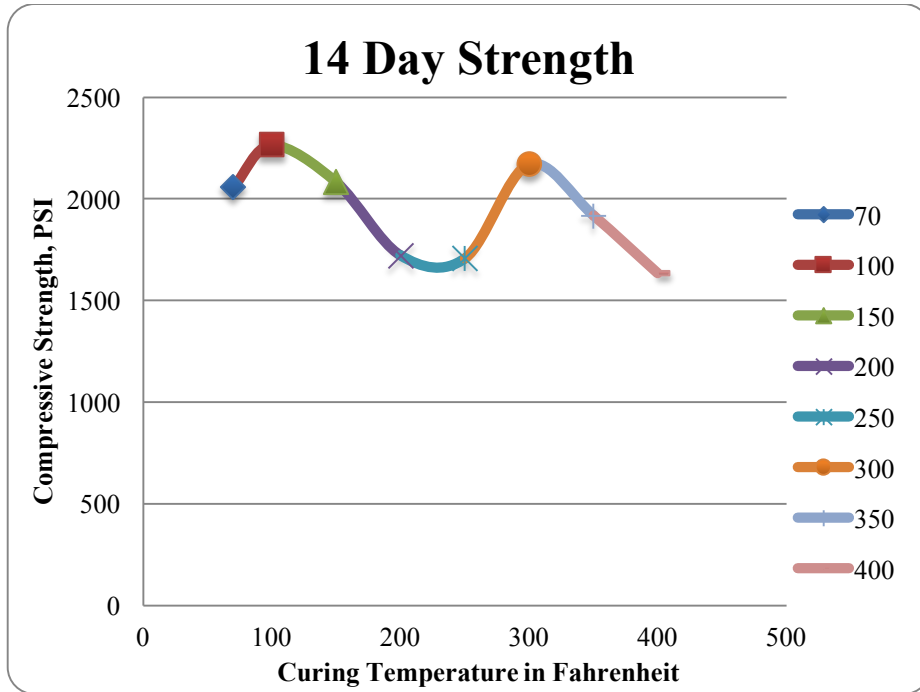
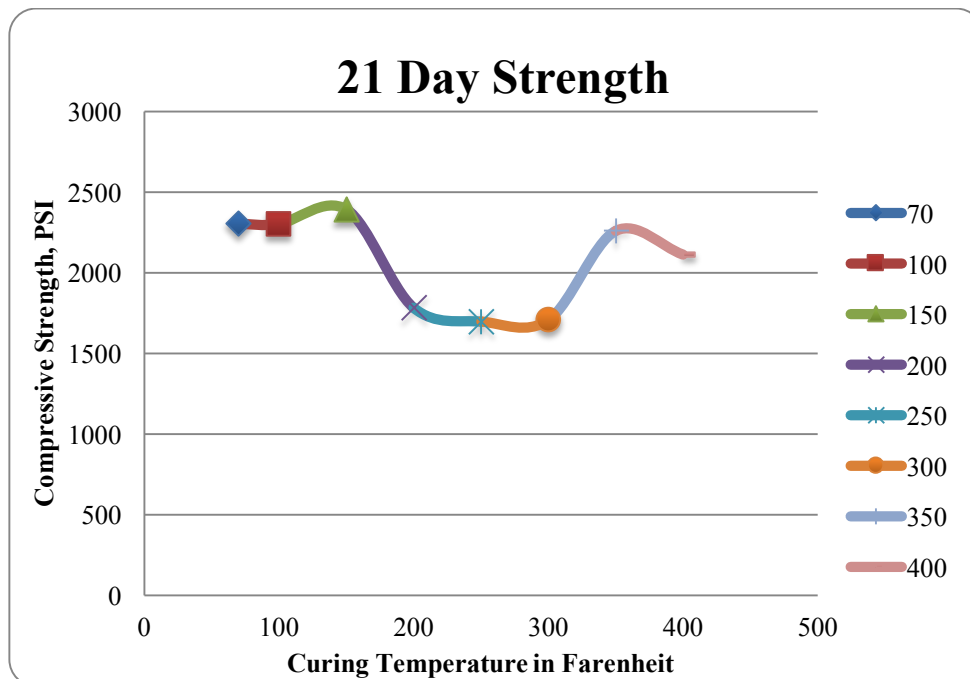*Figure 4.20*. Strength Gain on 14th Day

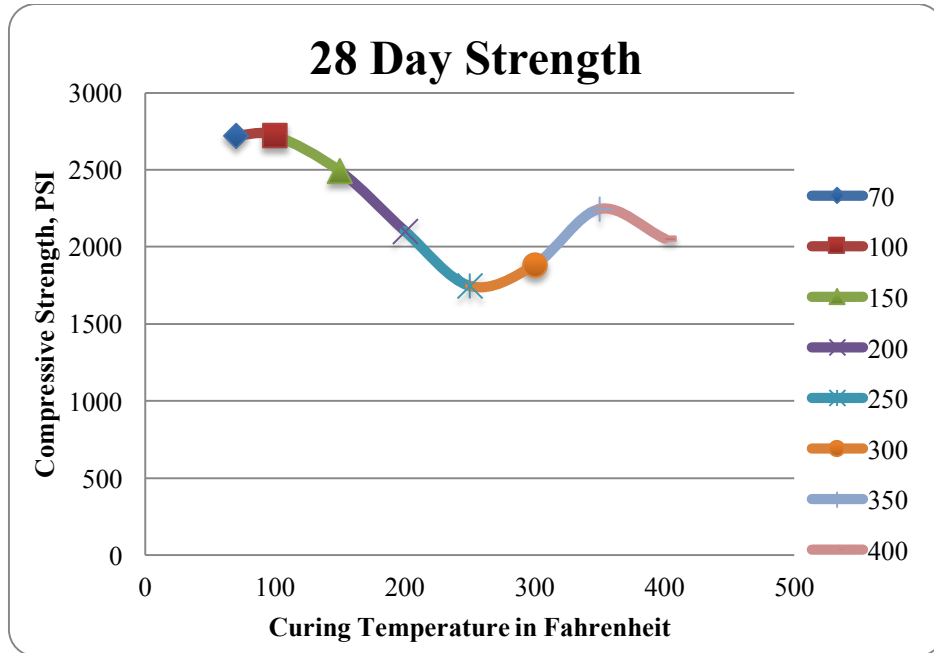*Figure 4.21*. Strength Gain on 21st Day

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Figure 4.22. Strength Gain on 28th Day

Figures 4.23 to 4.30 show the analysis of the strength gained at each temperature. Except for the slight strength loss on the 3rd day, it was observed in Figure 4.23 that room temperature cured cubes gained strength gradually with increase in duration of curing. Strength achieved on the 28th day was the highest amongst all. Steady strength gain was observed along with an age at 100° F (Figure 4.24), except on the 3rd and 21st day test. Similar to room temperature, strength achieved on the 28th day was the highest amongst all. From the 3rd day test, curing at 150° F showed a steady increment in the strength of the cubes (Figure 4.25). At 200° F, the steady increase of strength was disrupted at the duration of 21 days with a slight decrease in the rate of the strength. Strength gain was observed after the age of 28 days (Figure 4.26). At 250° F, compressive strength is increased constantly with age till the 14th day (Figure 4.27). After that, not much strength was gained. At 300° F, a sudden decrease in strength was observed after the 14th day test (Figure 4.28). There was a steady increase in strength for 350° F with a slight

decrease on the 28th day test (Figure 4.29). At 400° F, the gain in strength was disrupted on 14th and 28th days (Figure 4.30).

From the results, it is observed that there is not much effect of temperature on strength. However, with more study, there is a possibility of developing geopolymer concrete with better strength, as some peaks are achieved at different temperatures.

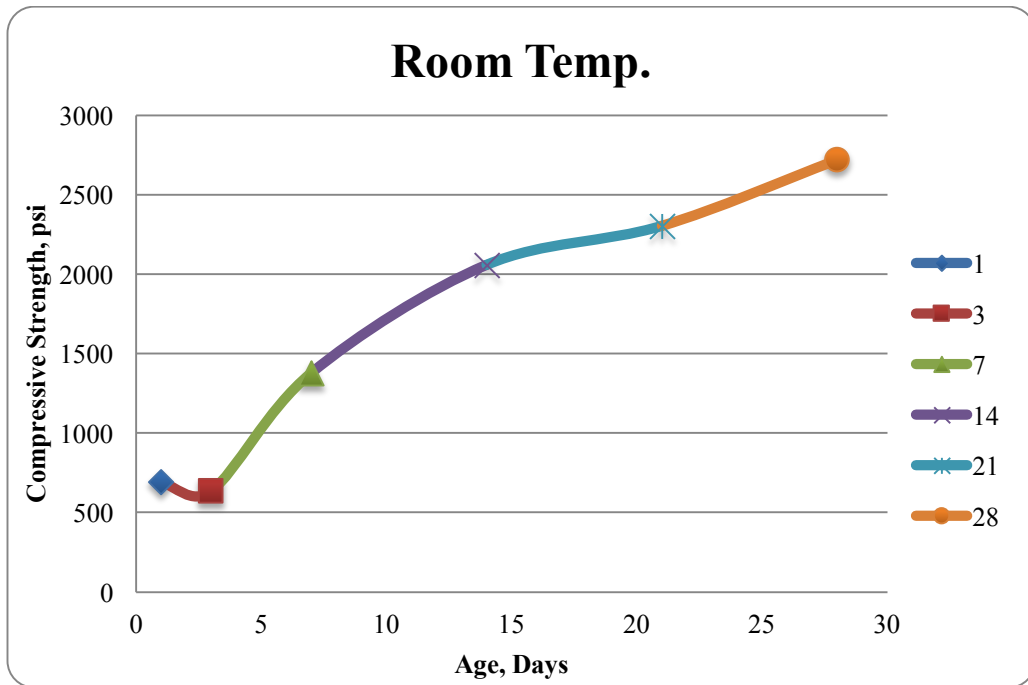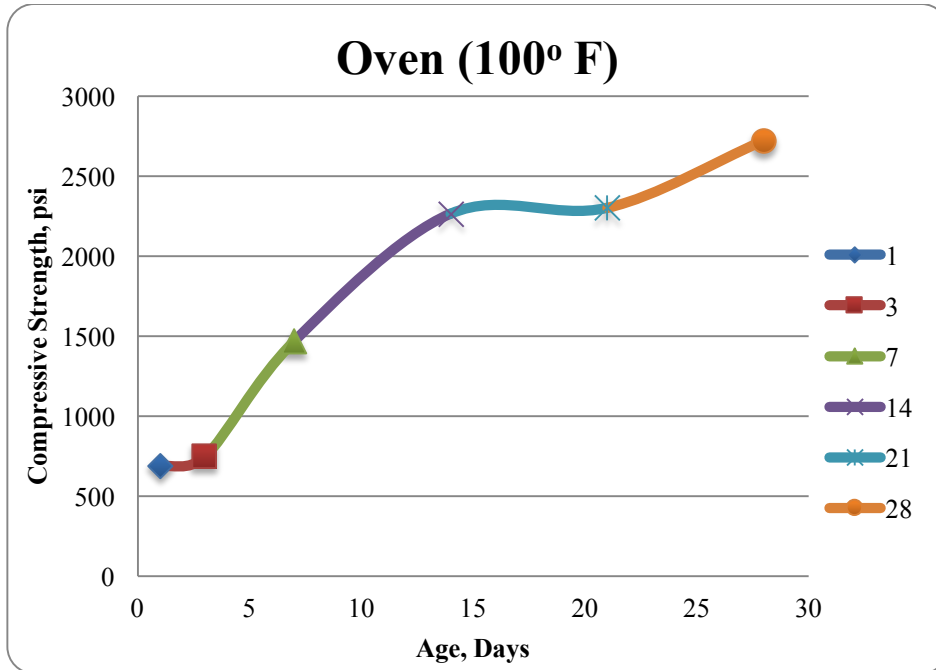*Figure 4.23*. Strength Gain of Cubes Cured in Room Temperature

Figure 4.24. Strength Gain of Cubes Cured in 100° F
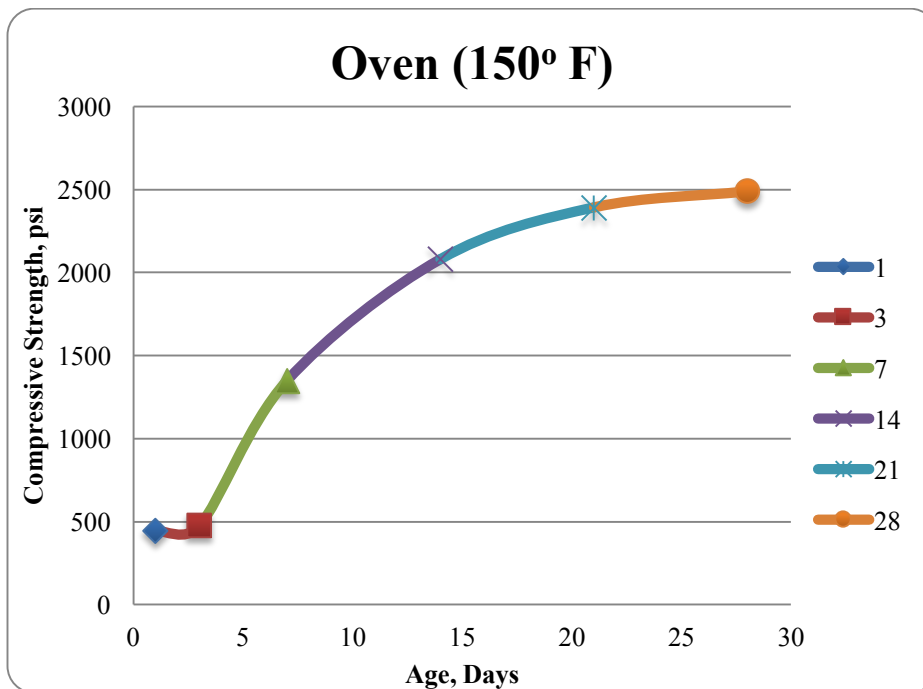
Figure 4.25. Strength Gain of Cubes Cured in 150° F
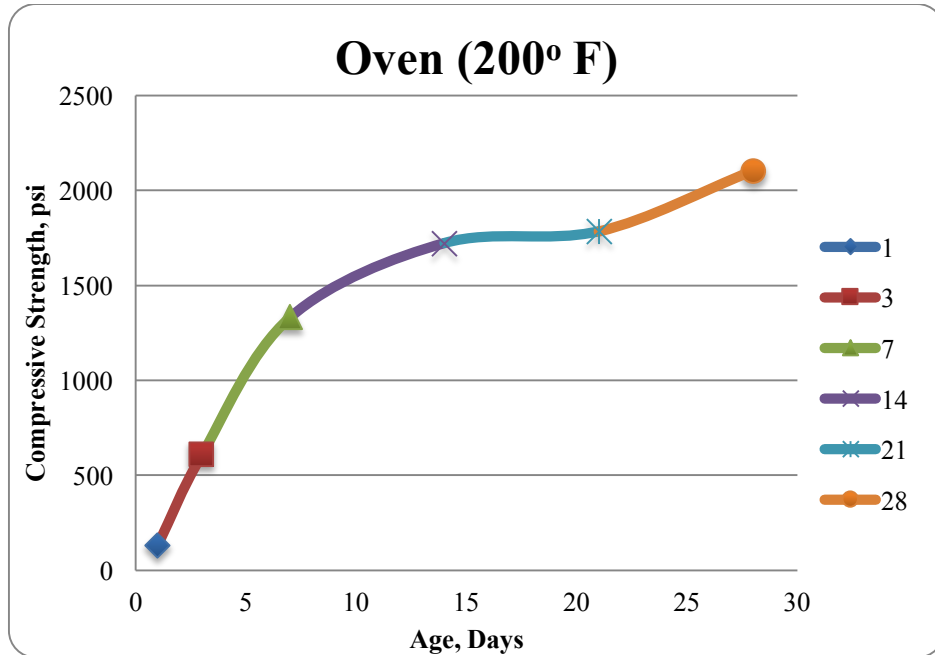
Figure 4.26. Strength Gain of Cubes Cured in 200° F
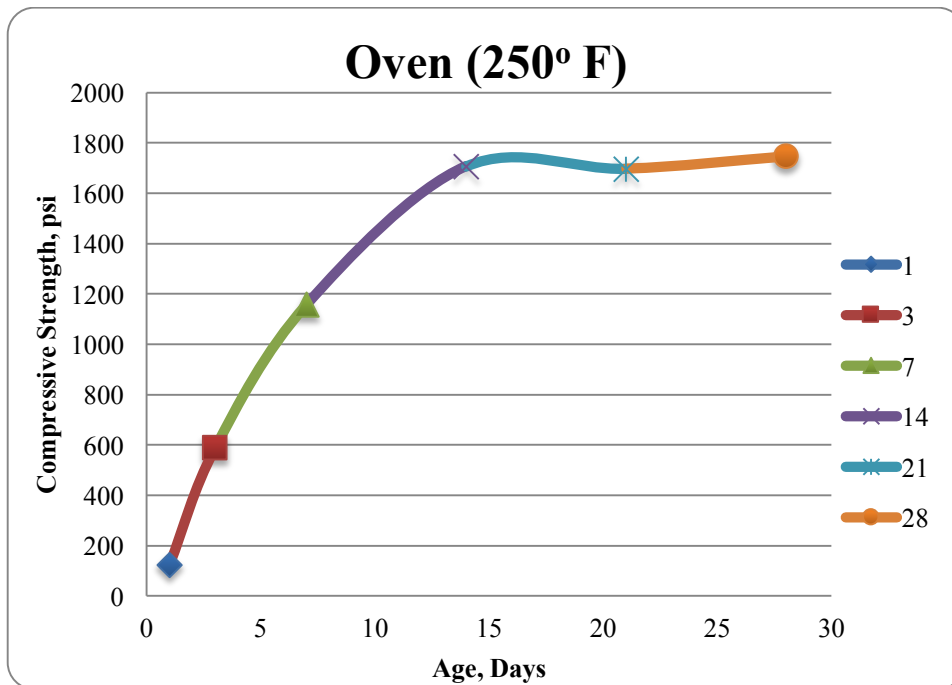
Figure 4.27. Strength Gain of Cubes Cured in 250° F
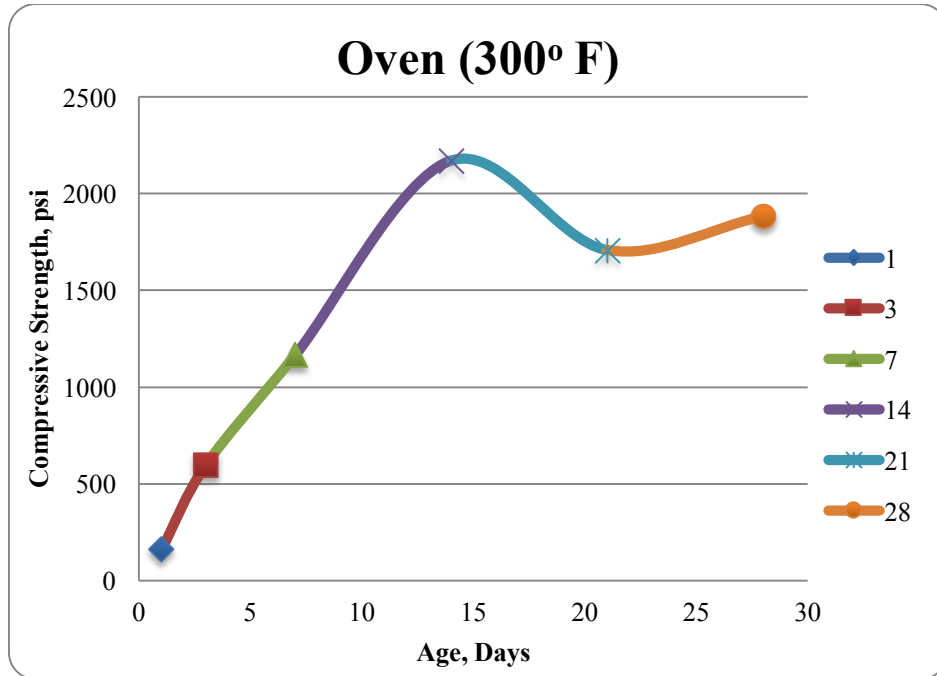
Figure 4.28. Strength Gain of Cubes Cured in 300° F
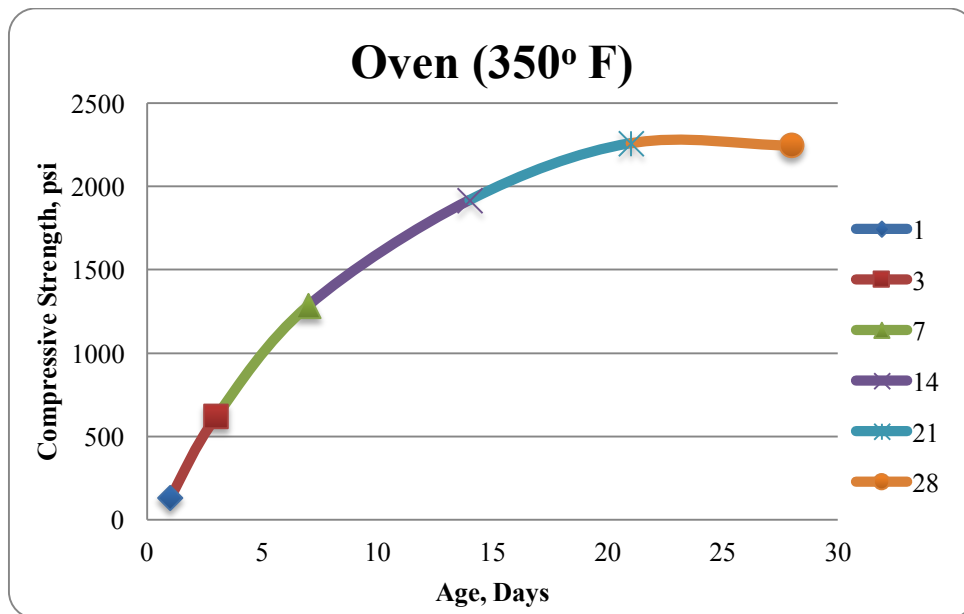
Figure 4.29. Strength Gain of Cubes Cured in 350° F
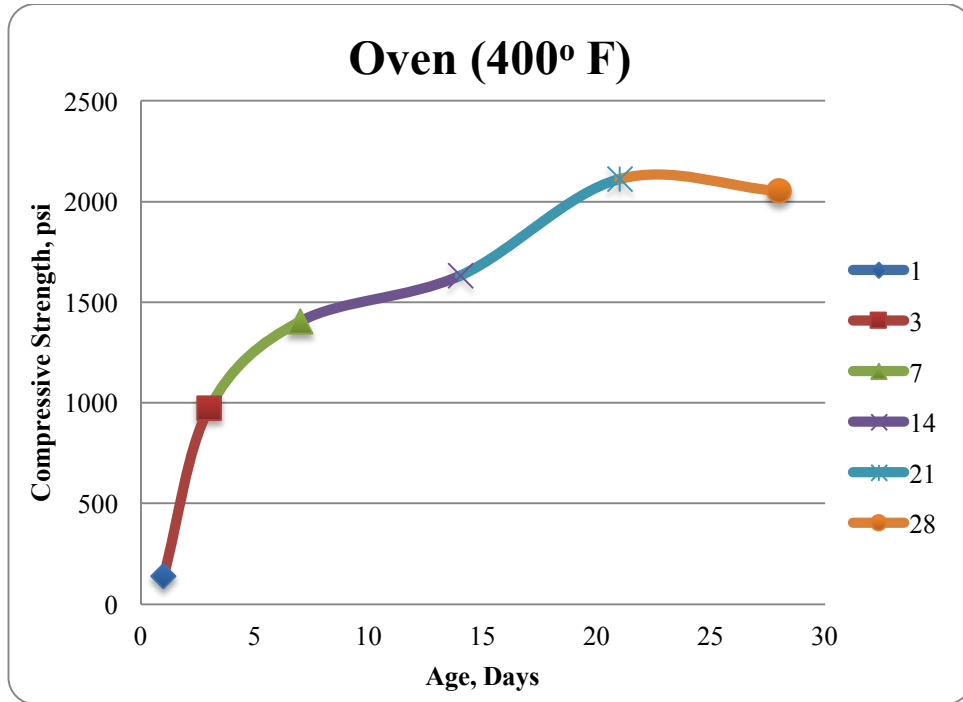
Figure 4.30. Strength Gain of Cubes Cured in 400° F

4.3.3. Flexural Strength Test

It is one of the measure of an unreinforced concrete beam to resist failure in bending. It is one of the properties value used to observe the quality of concrete according to ASTM C78. It is expressed as modulus of rupture in psi. According to the ASTM C78, this test is used for the formulation of the proportioning, mixing and placement process. It is used in testing the concrete which is used for the construction of slabs and pavements (ASTM C78). The flexural strength test for the beam cured in room temperature was performed on the 28th day.

The flexural strength of the beam on the 28th day is given in Table 4.9. From Table 4.9, and Figure 4.31 to Figure 4.34, we can observe that the cracks were formed within the middle third of the span length.

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Table 4.9. *Strength of Beam on 28th Day.*

Age	Strength
28	339

(Stress in PSI)

Figure 4.31. Flexural Strength Test of Beam

Figure 4.32. Flexural Strength Test of Beam

Figure 4.33. Cracks Formed after Flexural Strength Test of Beam

Figure 4.34. Cracks Formed after Flexural Strength Test of Beam

CHAPTER 5. THESIS SUMMARY, CONCLUSION AND RECOMMENDATIONS

5.1. Thesis Summary

The main purpose of this research was to design the mix using green cement to completely replace the use of Portland cement. As a green cement fly ash C was used in the whole experiment. The reason behind choosing fly ash C was its self-cementing properties which is similar to Portland cement (Ahmaruzzaman, 2009). The pozzolanic properties of fly ash C have made it useful for manufacturing a wide range of concrete products (Ahmaruzzaman, 2009). Similar to Portland cement concrete, it also exhibits prominent characteristics such as durability, improving the performance of a wide range of concrete applications such as the construction of roads, embankments, and structural fill (Ahmaruzzaman, 2009). Along with chemicals such as KOH and citric acid, fibers in the form of nanomaterial like CNT were also used as a reinforcing material with the thought of replacing steel with concrete. The main purpose of using CNT was to observe the high mechanical properties in fly ash mortars.

This research focuses on the study of properties like slump, setting time, compressive strength and flexural strength of concrete and mortars. In this process, the research methodology included literature review, experiments, tests and results analysis. Literature review presented the study of the need for the replacement of Portland cement. It also introduced further the study of fly ash and its use in construction industry. It helped to understand the properties of the fly ash based geopolymer concrete which is similar to Portland cement. The study of current trends in using fly ash gave the direction to the research in formulating the mix design and experiments.

In this research, experiments are divided into two phases, I and II. In Phase I, several experiments were performed to understand the basic mixture proportioning of fly ash-based geopolymer concrete until five mixes for cylinders and four mixes for cubes were developed. In

Phase I, CNTs were used only for the mix design of cubes. To compare the design, non- CNT cubes were also prepared using same mixture proportion. Along with experiments, compressive strength tests were also performed in 24 hr, 3rd, 7th, 14th, 21st and 28th day simultaneously. Only one set of mix design was prepared for the cylinder, cube and beam specimens of Phase II which were based on the best result achieved in Phase I. Along with compressive strength and flexural test; tests like slump and setting time test were also performed simultaneously.

Analysis of the results was done along with performing experiments. As fresh mortar properties test, slump and setting time tests were done whereas compressive, and flexural strength tests were done to study hardened concrete properties. Slump test indicated that the mixes tend to set faster resulting in low slump value. This could be the result of the presence of high lime and the activation of alkaline solution (**Nicholson et al., 2005**). From the Figure 4.1 and Table 4.1, it was observed that slump value decreased considerably as the mixing time was increased.

The throughout observation of setting time in all the experiments indicated that the specimens with a higher molar value of KOH had shorter setting time compared to those with lesser ones. The overall setting time observed was not more than 30 minutes due to the fact that fly ash C tends to set faster because of the presence of high amounts of lime. The activation of alkaline solution generates heat which also makes the mix set faster.

In Phase I, results for compressive strength test of cylinders showed that as the age progressed, strength gain was observed in each mix with slight ups and downs. From the results, it was discovered that alkali activators play a key role in strengthening the concrete materials. The higher the amount of the KOH, the higher the strength that was exhibited. Similar results were observed in the results for cubes mix as well. CNT cubes did not showed any significant

increment in the strength but were similar to the strength exhibited by non-CNT cubes. In Phase II, cylinders did not show any significant strength gain. The strength gain for the cubes can be seen with many fluctuations. The strength of the cubes improved as the age progressed. However, the strength did not increase significantly with temperature.

Expected flexural strength of beams was not achieved in Phase II due to different reason including moisture content in mix and lab.

5.2. Conclusion

This study was carried out to design concrete mix using fly ash C as a green cement to replace Portland cement. Developing fly ash products maintaining desired properties like strength, workability has been one of the aims of the research. Therefore, study focuses on the concrete characteristic tests like slump, setting time, compressive strength and flexural strength. Different materials viz. KOH, citric acid, borax, CNT, surfactant were added to the fly ash C mixes, and their effects on the properties of the mixes were observed. The conclusions based on the experimental work done in this study are presented below;

1. Concrete mix was design and tested using 100% class C fly ash.

2. The use of fly ash C as a full replacement for Portland cement needs alkaline activator to produce the strength of Portland cement. Therefore, the use of alkaline activator seems to have a significant effect on the strength of the concrete/ mortar. In Phase I, the results showed that as the molarity of KOH was increased, the fly ash concrete gained strength and become sturdier. However, the problem with the increased molar value of KOH is the generation of heat, resulting in shorter setting time of the specimens and decrease in the strength (Table 4.3 and 4.4, Figure 4.3 and 4.4).

3. Highest strength of 10142 psi was exhibited by mix 5 in phase I (Table 4.3 and Figure 4.3).

4. Though the concrete mix design with the highest strength achieved in Phase I was used in the Phase II, the strength achieved was much less than the Phase I.

5. It can be observed that curing do not have much effect on strength. From the overall comparison of the strength gain, it can be concluded that the key factor in gaining strength is the age of concrete as the highest peak was achieved at room temperature and 100° F on the 28th day (Figure 4.12 and Figure 4.13).

6. Slump test shows that the workability span for the mix was shorter. The slump value decreased as the time of mixing was increased (Table 4.1 and Figure 4.1). The presence of high lime in fly ash and the activation of alkaline solution made the mix set faster.

7. From the observation of the setting time of the mixes, it was found that the mixes with higher value of KOH had shorter time compared to those with lesser ones (Table 4.2 and Figure 4.2).

8. The strength of CNT were higher than non-CNT cubes. The other difference found on CNT cubes were rigidness compared to the non-CNT cubes (Table 4.5 and 4.6, Figure 4.5 and 4.6).

9. Flexural strength achieved for beam was 339 psi.

5.3. Recommendations

1. More studies are recommended to study the different properties of geopolymer concrete/ mortar. Different values of water-cement content, KOH, curing temperatures can be explored to observe the behavior of the concrete.

2. Effects of the factors like alkali-silica reaction, acid reaction, and heat on the long-term sustainability of geopolymer concrete can be investigated.

3. The impact of nanotechnology on the strength gain of the concrete can be further investigated. Characterization methods like STEM, TEM, X-Ray diffraction, X-Ray photoelectron spectroscopy can be used to study the microstructure of CNT and non-CNT concrete.

4. Flexural strength of the beam needs to be studied further with different strength values to compare.

5. Much research must be done to study the use of geopolymer concrete in different construction application.

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