To Study the Mechanical Properties of Limestone Calcined Clay Cement Concrete (LC^3-Concrete) at Elevated Temperatures

Submitted By

Usama Zahid
00000273634

A Thesis Submitted in Partial Fulfillment of
the Requirements for the Degree of

Master of Science

in

Structural Engineering

NUST INSTITUTE OF CIVIL ENGINEERING (NICE)
SCHOOL OF CIVIL & ENVIRONMENTAL ENGINEERING
(SCEE)
NATIONAL UNIVERSITY OF SCIENCES AND TECHNOLOGY
(NUST), ISLAMABAD
2022

To study the mechanical properties of Limestone Calcined Clay Cement Concrete (LC^3-Concrete) at elevated Temperatures

By

Usama Zahid

This is to certify that we have examined the above MS thesis and found that it is complete and satisfactory in all respects.

Dr. Hammad Anis Khan

Assistant Professor

Dr. Rao Arsalan Khushnood

Associate Professor

Dr. Azam Khan

Assistant Professor

Dr. Junaid Ahmad

Assistant Professor

THESIS ACCEPTANCE CERTIFICATE

“Certified that final copy of Master thesis written by **Usama Zahid** Registration No. **00000273634** from **2018** Batch of **NUST INSTITUTE OF CIVIL ENGINEERING (NICE)**, has been vetted by undersigned, found completed in all respects as per NUST Statutes/Regulations, is free of plagiarism, errors, and mistakes and is accepted as partial fulfillment for the award of **MS degree in Structural Engineering**.”

Signature: ___________________________

Thesis Supervisor: Dr. Hammad Anis Khan

Date: ________________________________

Signature (HOD):______________________

Date: ________________________________

Signature (Dean/Principal): _____________

Date: ________________________________

Declaration

“I certify that this research work titled **“To study the mechanical properties of Limestone Calcined Clay Cement Concrete (LC^3-Concrete) at elevated temperatures”** is my work. The result has not been presented elsewhere for assessment. The material that has been used from other sources has been appropriately acknowledged/referred to.”

Usama Zahid
00000273634

DEDICATION

“I dedicate this research to my parents, respected teachers, and friends who were always there to help me

ACKNOWLEDGEMENTS

“First of all, I am very thankful to Allah almighty who gave me the strength and courage to accomplish this research. Without the help of my respected teachers and friends, this thesis would not have been finished. I want to express my gratitude to everyone who helped make my thesis a success.

I want to publicly thank my supervisor, Dr. Hammad Anis Khan, for his assistance and guidance at every step that helped me complete the project's objectives. I want to express my gratitude to the entire faculty for their cooperation and sincere advice. I am thankful to my teachers Dr. Rao Arsalan Khushnood, Dr. Azam Khan, and Dr. Junaid Ahmad for their exceptional support and encouragement. My profound gratitude to my family for their never-ending support and love. My siblings have always been there for me as family and friends. I will always be grateful to my parents for providing me with the chances and life experiences that have shaped me into who I am today. They unselfishly inspired me to pursue my journey toward my destiny. Without them, this journey would not have been possible, and I dedicate this accomplishment to them.

I would also like to thank my friends who helped me at every step of this research. I am grateful to Khawar Tufail, Muhammad Farhan Saleem, Muhammad Talha Rasul, Muhammad Haseeb, Muhammad Baqir, and Laraib Majid Satti for their continuous support.”

ABSTRACT

Carbon dioxide (CO_2) is a byproduct of a chemical conversion process limestone ($CaCO_3$) is converted to lime (CaO) to produce clinker, causing global warming. As per a report in the year 2018, 4 billion tons of cement is made for construction purposes annually which results in 8% of the worldwide CO2 emissions. A percentage of cement clinker should be replaced by some other cementitious material to lower CO_2 emissions for example Fly ash, Silica Fumes, and Slag. The sources of these SCMs may be compromised in near future, as the world is moving toward renewable energy production, so coal power stations are being replaced by environment-friendly processes.

Around 74% of the Earth's crust is made up of clay having alumina and silicate minerals. There are over thirty types of clay, Major clay minerals include kaolinite and bentonite. The kaolinite can be converted into metakaolin by calcination. Metakaolin has an amorphous structure, smaller particle size, and increased specific surface area. So, it will result in more pozzolanic metakaolin. Clay is used to substitute cement in concrete after calcination in combination with limestone and it acts as pozzolanic material in concrete. At room temperature, concrete samples with low kaolinite clay show less strength as compared to control samples having no cement replacement.

The samples with more clay proportion show less compressive and tensile strengths at room temperature. The rate of heat transfer in samples having more clay content is less as compared to samples having greater cement content. LC^3-30 fails when the temperature rises above 600°C, and samples with more clay content fail earlier at high temperatures. The strength at a specific temperature decreases with the decrease in cement content in concrete. As we move toward high temperatures, the compressive and tensile strength of all clay samples decreases.

Table of Contents

List of Figures

List of Abbreviations

ASTM	American Society for Testing and Materials
ACI	American Concrete Institute
C-A-S-H	Calcium Aluminate Silicate Hydrates
SCMs	Supplementary Cementitious Materials
CH	Calcium Hydroxide or Portlandite
CSH	Calcium Silicate Hydrate
LC^3	Limestone Calcined Clay Cement
EDX	Energy Dispersive X-Ray
CC	Calcined Clay
OPC	Ordinary Portland Cement
C_3A	Tricalcium Aluminate
AS_2	Metakaolin
H	Water Molecules
TGA	Thermogravimetric Analysis
SEM	Scanning Electron Microscope
XRD	X-ray Diffraction
w/b	Water Binder Ratio
Cc	Calcium Carbonate

List of Tables

CHAPTER 1

Introduction

1.1 Background

Due to its prevalence as a raw material in the building industry, cement will continue to be an important material to meet national and global economic growth [1]. In the process of turning limestone ($CaCO_3$) into lime (CaO) to make cement, carbon dioxide (CO_2) is produced as a byproduct, which contributes to global warming [2]. Cement production as of 2018 was over 4 billion tons per year. Nearly 8% of all CO_2 emissions worldwide come from this industry [3]. Consequently, preserving material and energy resources and lowering CO_2 emissions are becoming more and more difficult tasks for the cement industry globally.

In the history of humanity, concrete has played a remarkable and important structural role. With the advancement of human civilization, concrete will without a doubt remain a key building material in the years to come. But the modernization of the concrete industry also brings with it a host of environmental issues, including pollution, waste disposal, the release of hazardous gases, the depletion of natural resources, etc. The cheapest binders that currently sustain or improve the performance of concrete are Portland cement and other cementitious ingredients. However, Portland cement manufacture requires the most energy out of all of these binders, as well as producing a lot of CO_2. Each ton of Portland cement produced during production emits around 1 ton of CO_2 (PC)[3]. Consequently, around 5% of all worldwide CO_2 emissions are attributed to the manufacture of cement. On the opposite end of the scale, the Kyoto Protocol in 1997 established a worldwide goal of an 8% reduction in greenhouse gas emissions by 2010 in order to slow the pace of climate change[2]. Developed nations are much more conscious of their need and a climate change tax was imposed on them. In this regard, in order to meet its domestic objective of a 20 percent reduction in CO_2 emissions by 2010, the UK government likewise implemented the same kind of tax on April 1, 2001. The government's aim was a 12.5% decrease in greenhouse gas emissions. The concrete industry's business model must be changed to emphasize "sustainability" in order for concrete to maintain its position as a dominating material in the future.

1.2 Level of Research Already Carried Out on the Proposed Topic

The mechanical and physical characteristics of limestone calcined clay cement have been the subject of much research in recent years. For different mixtures of LC^3, the compressive strength and flexural characteristics are being investigated. The fire characteristics of LC^3 cement have not yet been estimated.

1.3 Problem Statement

Most of the clay reserves have low kaolinite content. Calcined-Clay has the capability to replace cement content in the concrete. So, low kaolinite clay should be tested in LC^3-Concrete and its mechanical properties need to be analyzed at elevated temperatures.

1.4 Objectives

The objectives of this research are as follows:

- To investigate the mechanical properties of LC^3-Concrete at elevated temperatures.
- To compare the mechanical properties of low-kaolinite clay LC^3-Concrete with normal cement concrete.
- To analyze the mechanical properties of LC^3-Concrete having different percentages of clay.

1.5 Relevance to National Needs

Alternative binders have long been the subject of research to lessen the negative effects of cement manufacturing on the environment and the related carbon footprint. The large supply of calcined clay can meet the increasing demand for cement replacement materials. Many experiments in the past year have been carried out on the impact of composite binders on the efficiency of concrete systems. The performance of concrete is primarily responsible for any new cementitious system's sustainability in use. Various structural and non-structural concrete uses in multiple service conditions indicate that concrete qualities should satisfy several distinct criteria, including compressive strength development, elastic modulus, and thermal properties.

1.6 Advantages

The development of novel cementitious materials that can provide good mechanical performance at an early age, like Ordinary Portland Cement (OPC), and stay durable in multiple service environments is required to satisfy the needs of sustainable cement production and application. In this approach, limestone calcined clay cement (LC^3) has shown interest. Calcined clay and limestone are used in the ternary binder system known as LC^3 to develop composite cement.

1.7 Areas of Application:

There are several domestic constructions where the addition of LC^3 to concrete is used to reduce CO_2 emissions. Concrete's heat of hydration is significantly reduced by LC^3. The concept behind utilizing LC^3 is not novel, but it is becoming more popular as energy consumption rises in all areas of our lives. Fly ash from coal power stations has been the most broadly utilized SCM so far. However, according to the ongoing decommissioning of coal and lignite power plants, this component, which is essential to produce cement and concrete, is gradually losing its top priority. Therefore, the availability of fly ash will shortly be considerably reduced. Granulated blast furnace slag is also another cement addition that lowers the amount of clinker. It cannot, however, replace fly ash, not least because the worldwide supply is far lower than the demand that might be met. Additionally, it can only be found in nations with steel industries. Even yet, its contribution to the manufacturing of mixed cement is minimal. The need for new sources of pozzolan additives for cement and concrete production is being triggered by the declining availability of fly ash from the power sector.

CHAPTER 2

Literature Review

2.1 Supplementary Cementitious Materials

Supplementary cementitious materials (SCMs) are utilized in conjunction with blended or Portland cement that impart the characteristics of concrete through the pozzolanic or hydraulic reaction or both. The cementitious compounds are produced by the reaction of hydraulic material and water [4],[5]. Calcium silicate hydrates and other cementing products are also formed because of the chemical reaction of pozzolanic material with Ca(OH) in the presence of moisture. A pozzolanic material consists of finely divided forms of siliceous, aluminosilicates, and aluminosiliceous compounds[6]. An effective approach to reducing the clinker need in cement production is the application of SCMs, which respond to the hydration products of clinker to make an extra amount of cementitious material such as calcium silicate hydrate (CSH) gel [7]. Generally speaking, pozzolanic materials can be divided into natural or artificial cementitious materials based on their origins. The most common artificial pozzolanic materials are named as fly ash, slag cement, and silica fume. Examples of natural pozzolanic materials are burnt clay, calcined diatomaceous earth, rice husk ash, volcanic ash, pumice, and calcined shales[8].

Natural pozzolanic materials are produced from natural mineral deposits. Some of these SCMs need heat treatment, called calcining, to produce their pozzolanic nature. Various other materials such as volcanic ash can be utilized with minimal treatments (Such as grinding, dehydrating, and drying) [9]. The North American region has knowledge of natural pozzolanic materials date back to 20th public-sector developments such as roads, dams, and bridges, where they were utilized to mitigate elevated temperature effects in large quantity of concrete. Furthermore, natural pozzolanic materials have been used to reduce the alkali-silica reaction, and to enhance endurance to sulfate attack. The applications of natural pozzolanic materials have increased in recent decades. The availability of artificial pozzolanic materials has been reduced due to the utilization of alternative energy sources and technological variations in industrial practices [10].

Since 1970s, the use of SCMs in concrete blends has been growing in North America. Various SCMs have been acquired from other industrial processes as the byproducts of metallic compounds. Environmental sustainability and energy conservation are largely dependent on the desirable requirement and judicious use of SCMs [11]. These materials have been utilized in minimum 60 percent of ready blended concrete to achieve performance benefits. Specific concrete properties, for instance, providing endurance to alkali-silica reactivity or controlling the heat produced during the hydration in mass concrete are improved through the utilization of SCMs. The amount utilized depends on the desired impact on the concrete performance and materials' characteristics. The proper quantity to use should be established on the field performance or based on detailed testing practices to evaluate the exact dosage rate and to validate whether supplementary cementitious material is enhancing the concrete performance. The exceptional chemical and physical qualities of SCMs can considerably enhance the newly mixed and solidified properties of concrete. In the current century, sustainable development has become significantly important because of the large volume of carbon productions related to concrete development. Furthermore, the requirement for natural resources and power has been increasing exponentially. SCMs have been decreasing the usage of raw materials used in concrete production, reducing energy consumption, substituting clinker, replacing the existing materials with less impactful ones, improving the concrete performance, and enhancing service life[12].

Fly ash has been acquired from electric energy generating facilities through the combustion of bituminous/sub-bituminous pulverized coal, lignite, or burning anthracite as a byproduct of industrial processes[13]. The coal's mineral impurities (for instance shale, quartz, feldspar, and clay) smelted in suspension and moved towards the combustion chambers through the exhaust gases. In this method, the fused matter cools and consolidates into solid finely divided, and non-crystalline grains of aluminous silicate are known as fly ash. Its particles are finely divided solid spheres with a mean size of measuring less than 20 micrometers. Then, bag filters or electrostatic precipitators have been used to collect fly ash from the exhaust gases. The dosage rate usually depends on the desired effects on concrete, and the reactivity of fly ash. The values of specific gravity lie between the range of 1.90 and 2.80. Fly ashes are categorized into further two classes known as Class C and Class F. Fly ash having pozzolanic characteristics and some cementitious characteristics is classified as Class C Fly ash. The sum of SiO_2, Al_2O_3, and Fe_2O_3 needs to be larger than or equal to 50 percent for Class C fly ash. Fly ash has only pozzolanic properties and is classified as Class F fly ash. The sum of iron oxide, silicon dioxide, and aluminum oxides requires to be greater than or equal to 70 percent for Class F fly ash. Magnesium, carbon, calcium, potassium, sulfur, and sodium are present as minor constituents.

Fly ash is widely used to lower water demand, increase setting time, enhance workability by decreasing air content, and decrease the heat of hydration, bleeding, and segregation. It has been generally found its application to gain long-term strength and decrease permeability and absorption. The addition of fly ash in the concrete has no impact on abrasion resistance, freeze, and thaw phenomenon.

Slag cement is non-crystalline matter produced from the molten slag formed in the blast kilns as a byproduct of the manufacturing of iron used in the steel production processes. Slag cement is formerly know as ground, granulated blast-furnace slag [14]. The melted slag is produced as the constituents utilized to manufacture iron melt at the standard temperature of 1300-1500°C and float above the denser smelted iron. Molten slag has been transformed into cementitious material through the rapid quenching of slag in water to produce non-crystalline, granulated material. This sand-like material is ground into a fine powder form. Slow air-cooling of slag will result in the formation of crystalline products having no cementitious characteristics. Air-cooled slag is non-reactive and utilized as aggregate for structural backfill applications. The fineness of slag is approximately equal to or greater than the ordinary PC. The particles of slag cement are angular-shaped, rough, and finely divided ground powder. More than 95% of the chemical structure of slag cement is usually makeup of oxides of magnesium, calcium, alumina, iron, and silica. The values of specific gravity lie between the range of 2.85 and 2.95. Slag cement has been widely used to decrease water demand, minimize the heat due to the hydration reaction, and increase workability and setting time. In the presence of an activator and water, slag cement will hydrate in the similar way like the hydration of Portland cement. In the absence of an activator (such as hydrates of Sodium and Calcium), the hydration process of slag cement will be very low. Slag cement has been found its application to increase corrosion and sulfate resistance and enhance long-term strength.

Silica fume or condensed silica fume or micro-silica consists of ultrafine glassy silica particles formed in electric-arc kilns as an industrial byproduct of the manufacture of ferrosilicon alloys and silicon metals. Silica fume is generally utilized in quantities ranging from 5 to 10 % by mass of the net cementing material. Silica fume consists of extremely fine spherical non-crystalline predominantly silicon dioxide particles with particles diameter less than 1 micrometer having an average diameter of about 0.1 micrometers. The specific gravity of silica fume is approximately 2.20 and its color is gray. The amount of silica content formed by the production of silicon metal is generally greater than 90 percent by weight. The amount of silica content formed by the production of ferrosilicon is generally less than 85 percent by weight. Silica fume is generally used to increase water demand, and decrease workability and air content. The addition of silica fume has no impact on the heat of hydration and setting time. The potential for bleeding and segregation may be reduced through the addition of silica fume content. It is widely used in the production of high-strength and low-permeable concrete. It has been used to gain long-term and early age strength of concrete.

The most typical calcined clay is extracted from clay that is heated or calcined to a standard temperature enough for the transformation of the clay framework into a disordered non-crystalline aluminosilicate structure with pozzolanic characteristics. This method is usually known as thermal activation and the optimum heat treatment depends on the nature of the materials. Calcined clays are utilized for general-purpose concrete construction much similar to the other pozzolans. The values of specific gravity for calcined clays have lie ranging from 2.40 to 2.61. Calcined clays have been used as SCMs due to their wide accessibility, and it has been noticed that under optimal conditions, they show excellent pozzolanic characteristics. Calcined clays have been used to decrease early age strength gain and increase long-term strength gain. Calcined shales and calcined shale have a negligible impact on segregation and bleeding. Similarly, calcined shales and calcined clays have a negligible impact on the setting time unless these SCMs have been utilized at high substitution rates with high dosages for the Portland cement. Calcined clay releases the same amount of heat of hydration as moderate heat cement. Calcined clays and calcined shales have no effect on the drying shrinkage and creep phenomenon. They can be utilized as a constituent usually in the range of 15-35 percent of the total cementing material. Calcined clays mitigate alkali-silica reaction, increase the degree of impermeability, improve resistance to sulfate attack, and enhance strength development.

Calcined shales have been utilized as the replacement of conventional SCMs such as silica fume and fly ash and have the economic benefit, that they can be extracted as by-products of mining activities[15]. The most typical calcined shale is extracted from shale that is heated or calcined to a standard temperature enough for the transformation of the shale framework into a disordered non-crystalline aluminosilicate structure with pozzolanic characteristics[16]. Calcined shale may consist of calcium ranging from 5% to 10% of the total weight, which leads to the material with some hydraulic or cementitious characteristics[17]. Due to the quantity of surplus calcite which isn't completely calcinated, and the entrapped water molecules in the clay molecules, calcinated has values of loss on ignition of nearly 1% to 5%. SCMs usually mitigate chemical attacks by improving hydraulic characteristics to secure the concrete structures from aggressive exposures and chemicals[18]. Calcined shales and calcined clays usually have negligible impacts on water requirement at normal dosages. Other natural pozzolanic materials can substantially decrease or increase water requirements. Calcined shales and calcined clays have no influence on the freezing and thawing phenomenon[19].

2.2 Limestone Calcined Clay Cement

Clay, consisting of the alumina-silicate mineral deposits, incorporates 74% of the Earth's surface. Clays are aluminum silicates that are the ultimate common hardening outcome of feldspar and other fundamental elements and usually existed in sedimentary rocks[20]. Clay has been used in refractory, brick, chemical filter, pottery, paint, ceramic, and paper industries. Clay minerals consist of necessarily of silica, alumina or magnesia, or both, and water, but iron substitutes for aluminum and magnesium in varying degrees, and appreciable quantities of sodium, potassium, and calcium are usually available as well[21].

Clays are divided into three major groups such as montmorillonite, kaolinite, and, illite. These minerals become reactive after the calcination at the standard temperatures. Metakaolin is the most reactive calcined product produced by de-hydroxylation of kaolinite above 600°C. The de-hydroxylation reaction of metakaolin is expressed as follows:

$$Al_2Si_2O_5(OH)_5 \rightarrow Al_2Si_2O_7 + 2H_2O$$

This reactivity loses the crystallinity of the structure and is converted to a hydraulic product having an amorphous structure that will act as pozzolanic material due to increased specific surface area. Kaolinite and metakaolin are clay minerals, having the chemical formulae $Al_2Si_2O_5(OH)_5$ and $Al_2Si_2O_7$ respectively[22].

The activation of clay happens to range the temperature between 700 and 1200°C. The calcination temperature depends upon the mineralogical composition of the clay structure. However, calcination processes of clays will be uneconomical if fly ash or slag cement are locally available. Calcined clays result in the production of Calcium Silicate Aluminate Hydrates (C-A-S-H) and AFm phases having longer chains[22].

Pozzolans have non-crystalline silica which reacts to calcium hydroxide or portlandite (CH) which is advantageous because pozzolanic materials generate a small amount of CH that can be shattered through the chemical attack, consequently minimizing the voids of the final creation, and developing the more dense substance. This phenomenon has been classified into three reactions.

In the first phase, the metakaolin (AS_2) will be combined with calcium hydroxide formed throughout the cement hydration process to produce C-A-S-H, thus developing the strength by filling the pores of the structure. This is called a classic pozzolanic reaction.

$$AS_2 + 3CH + 6H \rightarrow C - A - S - H + C_2ASH_8$$

In the second phase, the alumina in the tricalcium aluminate (C_3A) can react with Ca(OH) and Cc from limestone to produce monocarboaluminate and hemicarboaluminate as AFm phases, and these products contain more available sulfates for the formation of ettringite.

$$C_3A + 0.5\ Cc + 0.5\ CH + 11.5\ H \rightarrow C_4Ac_{0.5}H_{12}$$

In the last phase of the reaction, metakaolin reaction with limestone and portlandite in the presence of moisture leads to the production of additional hemicarboaluminate[23].

$$AS_2 + 0.5\ Cc + 3.5\ CH + 8.5\ H \rightarrow C_4Ac_{0.5}H_{12}$$

Clay minerals belong to the kaolinite group, and these minerals are considered the most reactive SCMs when they are completely activated. The kaolinite group of clay has various advantageous factors such as its low initiation temperature, abundance, and large thermal stimulation range as compared with other clay minerals. Calcination products obtained from kaolinite groups are considered an exceptional source of reactive alumina, a specific aspect that permits to enhance the amount of clinker replacement while sustaining the durability and mechanical performance by the combination of products having alumina with calcium carbonate.

LC^3 is an enhanced type of ternary incorporation of clinker, ground calcined clay, inter-ground gypsum, and limestone. It has been considered an attractive option for cement replacement to decrease carbon emissions from cement production. Although limestone and calcined clay have been utilized for various years in blended cement, the novelty of LC^3 is to utilize the synergy of the combined usage of limestone and calcined clay. LC^3 has the same or better characteristics than Ordinary Portland Cement (OPC) even utilizing much smaller amounts of clinker[21].

2.3 Previous Research Work

Metakaolin is a type of calcined clay which is formed by the calcination process of kaolin clay at low temperatures[24]. As contrary to other calcined clays, Metakaolin is made pure by water treatment before very cautious controlled thermal activation at comparatively low temperature lies in the range of 650°C to 800°C [25]. It is finely grounded particles with high fineness having a mean particle diameter of approximately 1 to 2 micrometers. Metakaolin is consist of kaolin clay containing mainly oxides of silicon and aluminum. The sum of aluminum oxide and silicon dioxide is usually equal to or greater than 95 percent by weight. Metakaolin has been used to produce low permeable or very high strength concrete[26]. It has been used as an additive to concrete rather than a replacement for cement. Around 10 percent of the total weight of cement has been typically used as an additive[27]. Metakaolin has been distinguished as a highly reactive pozzolanic material as compared to other calcined clays which are normally less reactive. The remaining portion consists of minute quantities of alkalis, calcium, and iron. Metakaolin has been used to produce low permeable or very high strength concrete. It has been used as an additive to concrete rather than a replacement for cement[26]. The application of Metakaolin may increase the water requirement at higher dosages. The enhanced water demand may be offset by the application of superplasticizers and water-reducing chemical admixtures. The effect of metakaolin on segregation and bleeding is largely dependent on the level of replacement and degree of fineness. Metakaolin has been considered a highly effective pozzolanic material in alkali-silica reactions due to its high reactivity. Strengths related to early age and long term have been increased. The permeability and absorption rate have been reduced to a large extent. Metakaolin has a negligible impact on the creep and drying shrinkage phenomenon. Metakaolin products also find their application in ceramic, refractory, and paper industries.

Concrete is primarily used in infrastructure and construction industries all over the world. Mainly OPC has been used as a binder to make concrete. The generally used SCMs are cement slag, fine limestone, fly ash, and silica fume. However, the combined use of optimum fly ash and cement slag reduced the carbon footprint emission by up to 15 percent during OPC production[28].

LC^3 mortars had higher compressive strength than ordinary pozzolanic Portland cement. It had been observed that LC^3 is a potentially more feasible cementing materials as compared to volcanic ash.[29].Pozzolanic reactivity of calcined clays was determined by compressive strength tests on the specimens that pozzolanic reactivity is proportional to kaolinite content[30].

It was observed that calcined clay accelerates the rate of hydration. The peaks of the heat of hydration associated with C_3A and overall reaction had increased after 28 days. The CH content in specimens with calcined clay was also considerably less as compared to specimens with 100 percent conventional OPC [31]. Calcareous clays have been utilized as SCMs in the production of cement. Clays with a calcite amount ranging from 15 to 25 percent formed reactive amorphous structures during the calcination process. The reactivity of the montmorillonite and illite groups can be increased with the increasing amount of calcite content [32].

Exceptional characteristics were observed using LC^3-50 concrete. LC^3 had similar performance properties as compared to conventional OPC with improved sustainability. LC^3 needs a lesser amount of superplasticizer than silica fume, for better environmental conditions and comparable mechanical properties[33]. LC^3 has better performance than slag cement [34]. The increasing temperature accelerates the pozzolanic reaction and rapid hydration of clinker leading to an improvement in the strength gain of LC^3 at the initial stages. However, the increasing temperature doesn’t influenced significantly on the characteristics of LC^3 [35].

CHAPTER 3

Experimental Investigation

3.1 Collection of Clay Material:

Four Clay samples from different regions were picked in raw form to select a clay having a kaolinite percentage of less than 40%. Clays having low kaolinite content are brownish in appearance while high kaolinite clays appeared to be whitish in nature. 50g of each sample was taken into a laboratory to calculate the kaolinite percentage by weight.

3.2 Calculation of Kaolinite Content

To find out the percentage of kaolinite in clay, an experiment was carried out under the protocol provided by François Avet from the EPFl (Swiss Federal Institute of Technology Lausanne, Switzerland). The main purpose of this experiment was to calculate the weight percentage of kaolinite in the clay with the help of a weighing balance and furnace/oven.

The weight of each clay sample was 10g. The particle size of clay was less than 4mm. there is no need to remove the moisture from the clay or to oven-dry the sample.

Figure 3.1 Clay Selection

In the first step, the crucibles were washed keenly, and then they were placed in the oven for one hour at 800°C to remove any kind of impurity or moisture.

Figure 3.2 Placement of Crucibles in Furnace

Then the weight of each crucible was noted with the help of weighing balance, and it was noted against wt_i. The clay samples weighing 10g were placed in each crucible separately. The crucibles were placed in the furnace with the help of a clamp and were heated at 200°C for one hour. The crucibles were left in the furnace for some time to cool down and then the weight was measured and noted as $wt_{200°C}$. These crucibles were then placed in the furnace for one hour at 400°C, and the weight was noted of each crucible after cooling down as $wt_{400°C}$. Then again, the crucibles were heated for one hour at 600°C, and the weight was noted after cooling down as $wt_{600°C}$.

$$wt\%_{Kaolinite} = \frac{wt_{400°C} - wt_{600°C}}{wt_{200°C} - wt_i} \times 7{,}17 \times 100$$

Here, the factor was obtained by dividing the molecular weight of kaolinite i-e 256.16g/mol by the molecular weight of two water molecules i-e 36.03g/mol.

Figure 3.3 Heating in Controlled Furnace

The same procedure was repeated three times for each sample of clay and the average value of kaolinite weight percentage was taken. The clay sample having $wt\%_{kaolinite}$ of 16.67 was selected for further testing and experimentation.

3.3 Thermo-Gravimetric Analysis (TGA)

The TGA test was performed on the raw clay to check its stability at different temperatures. The DTG 5500-0304 TGA equipment was used to perform this test. The clay sample was put in the equipment and the temperature ramp of 20°C per minute was applied. The temperature range of the TGA test was from 30°C to 850°C. The output of this test was in the form of a graph plotted between the mass loss percentage at Y-axis and temperature at X-axis. This showed the percentage loss in weight of clay as we move from 30°C to 850°C.

3.4 Calcination of Clay

The selected clay having low kaolinite content was oven dried for 24 hours. Then, it was pulverized into fine particles and passed through sieve #200. Around 50kg of the clay was put in the furnace and then heated at 850°C for 3 hours. The clay was placed in a tray made of steel having sides 24” ×36”×12” and a melting point of 1500°C. The furnace chamber used for calcination has a capacity of 1000L, its internal dimensions are 35”×50” ×35”, and its maximum temperature limit is 1200°C.

This process was repeated five times to get desired quantity of 250kg of calcined clay.

Figure 3.4 Temperature Controlled Furnace

3.6 Mix Design of Various Regimes

The calcined clay and limestone were used in the ratio of 1:2 by weight. The concrete ratio selected was 1:1.5:2 and the water to cement ratio, known as W/C or W/B ratio, was 0.45. The control samples were made of cement only and then cement was replaced by different proportions of calcined clay and limestones. Following are the material quantities calculated for different regimes based on mixed design.

Regime	**Cement**	**Calcined-Clay**	**Limestone**	**Sand**	**Aggregates**
	(kg/m^3)	**(kg/m^3)**	**(kg/m^3)**	**(kg/m^3)**	**(kg/m^3)**
Control	485.84	-	-	728.77	971.69
LC^3-80	388.68	64.78	32.39	728.77	971.69
LC^3-65	315.8	113.36	56.68	728.77	971.69
LC^3-50	242.92	161.95	80.97	728.77	971.69
LC^3-30	145.75	226.73	113.36	728.77	971.69

Table 3.1 Material Quantities of Different Regimes

3.6 Sampling of Concrete Specimen

Properties	**Temperature**	**Compressive**	**Tensile**	**Thermal Conductivity**	**Weight Loss**	**Total Samples**
Control	29°C	3	3	1	-	
	100°C	3	3	1	-	
	200°C	3	3	1	-	42
	400°C	3	3	1	-	
	600°C	3	3	1	-	
	800°C	3	3	1	-	
LC^3-80	29°C	3	3	1	-	42
	100°C	3	3	1	-	
	200°C	3	3	1	-	
	400°C	3	3	1	-	
	600°C	3	3	1	-	
	800°C	3	3	1	-	
LC^3-65	29°C	3	3	1	-	42
	100°C	3	3	1	-	
	200°C	3	3	1	-	
	400°C	3	3	1	-	
	600°C	3	3	1	-	
	800°C	3	3	1	-	
LC^3-50	29°C	3	3	1	-	42
	100°C	3	3	1	-	
	200°C	3	3	1	-	
	400°C	3	3	1	-	
	600°C	3	3	1	-	
	800°C	3	3	1	-	
LC^3-30	29°C	3	3	1	-	42
	100°C	3	3	1	-	
	200°C	3	3	1	-	
	400°C	3	3	1	-	
	600°C	3	3	1	-	
	800°C	3	3	1	-	

Table 3.2 Sampling of Various Concrete Regimes

3.7 Casting of Concrete Specimens:

The concrete cylinders of 4” x 8” were made for each regime. The materials were mixed according to the calculated quantities using the mixer. Following ASTM C305, the material was mixed at 140rpm for 5 minutes. The concrete in the mixer was then poured into the molds of cylinders in three different layers and each layer was compressed by 25 blows of a damping rod. These molds were opened after 24 hours and then soaked in a curing tank having filtered water for 28 days to achieve concrete’s ultimate strength. After 28 days, the samples were moved out of the water tank and dried at room temperature for 24 hours.

Figure 3.5 Casting of Concrete Specimens

3.8 Elevated Temperature:

Some cylinders were tested at room temperature and some samples were exposed to elevated temperature and tested after these samples cooled down. The temperatures at which the samples were heated in the furnace were 100°C, 200°C, 400°C, 600°C, and 800°C. The cylinders were kept in a steel cage before placing them in the furnace so that they may not do any harm to the furnace. The samples were exposed to each temperature for 2-4 hours based on the time taken by the core to reach that specific temperature. After heating, the furnace was kept open for some hours to let the samples cool down, and then these samples were taken out for further testing.

Figure 3.6 Heating Specimens in Furnace

3.9 Visual Appearance:

The samples were visually inspected at every temperature to see the changes that occurred at elevated temperatures. This observation was done with the naked eye in daylight and the samples were looked for any changes in color or cracks that appeared on the surface of samples at elevated temperatures.

3.10 Compressive test:

ASTM C39 was followed to check the compressive strength of these 4”x 8” cylinders. Prior to the compression test, capping was done. Capping is done to make the top and bottom surface of the cylinder smooth so that the compressive stress that is applied to the cylinder will be distributed uniformly.

Capping was done with the help of gypsum paste. After capping, the samples were placed in Compression Testing Machine (CTM).

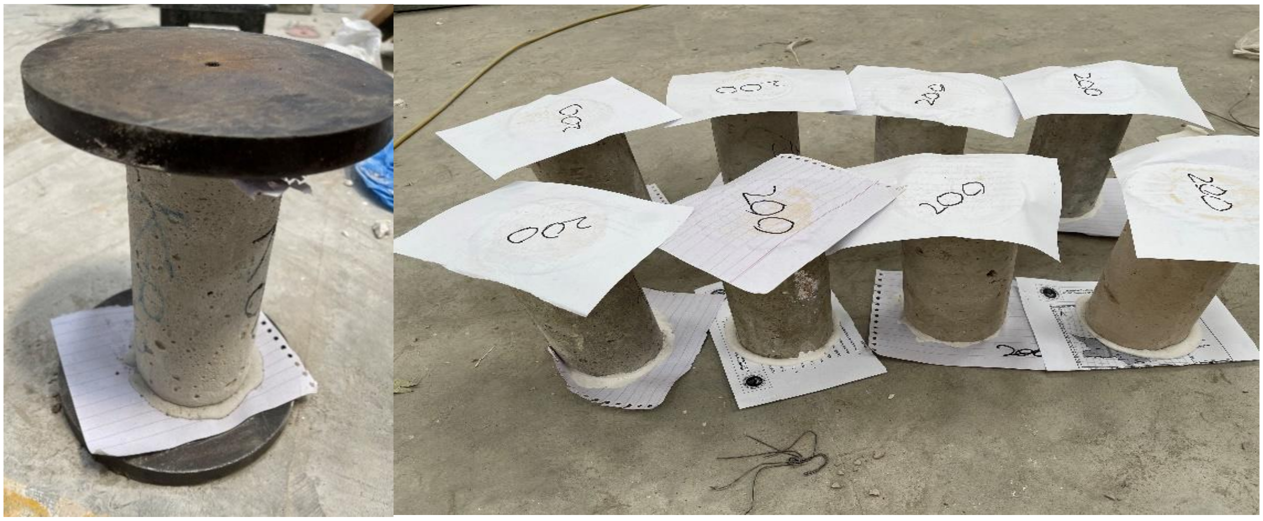

Figure 3.7 Capping Procedure of Concrete Specimens

It was strain-controlled compressive strength, and a constant strain of 0.002/s was applied. Stress-strain curve for each sample was obtained.

Figure 3.8 Concrete Compressive Apparatus and Failure Pattern

3.11 Elastic Modulus:

Following ASTM C128, elastic modulus can be calculated for each sample. The stress-strain curve was taken directly from the strain-controlled compression testing machine and the elastic modulus was calculated by finding the slope of the initial straight portion of the stress-strain curve.

3.12 Split Tensile Strength:

The cylinders were tested for split tensile strength by following ASTM C496. Universal Testing Machine was used to perform this test.

Figure 3.9 Spilt Tensile Strength Test Assembly

The stress was applied along the length of the cylinder. The failure load was taken from the CTM at a point where the sample was split in half as shown in figure.

Figure 3.10 Split Tensile Failure Pattern

The tensile strength of the cylinder was then calculated by using the equation given in ASTM standard.

$$T = 2P/\pi Ld$$

Where,

P = Load at which the cylinder failed

L= Length of the cylinder

d= Diameter of the cylinder

3.12 Thermal Conductivity:

The thermal conductivity of all the regimes was calculated with the help of temperature observation at different intervals at the surface and core of cylinders. For this purpose, the samples were drilled, and thermocouples were inserted in the core of samples from different regimes. Thermocouples were also attached to the outer surface of the samples. The temperature at the surface of each cylinder was compared with the temperature at the core at different time intervals.

Figure 3.11 Thermal Conductivity of Concrete Specimens

3.13 Weight Loss:

The weight of samples from every regime was noted down at room temperature. Then these samples were heated at elevated temperature and again put on the weighing balance to note the changes in mass after exposing to each temperature. These weights were subtracted from the initial weight of the samples to calculate the weight loss. After that, a graph was plotted that showed the mass loss curve for each sample at every temperature.

CHAPTER 4

Results and Discussions

4.1 Mechanical Properties:

The results from the testing discussed in the previous chapter are explained in this section. The mechanical properties of different variants of LC^3-Concrete are as under:

4.1.1 Compressive Strength:

The compressive strength of the LC^3-Concrete was analyzed with the help of the Compressive strength test explained in the previous chapter. The samples were tested at room temperature first.

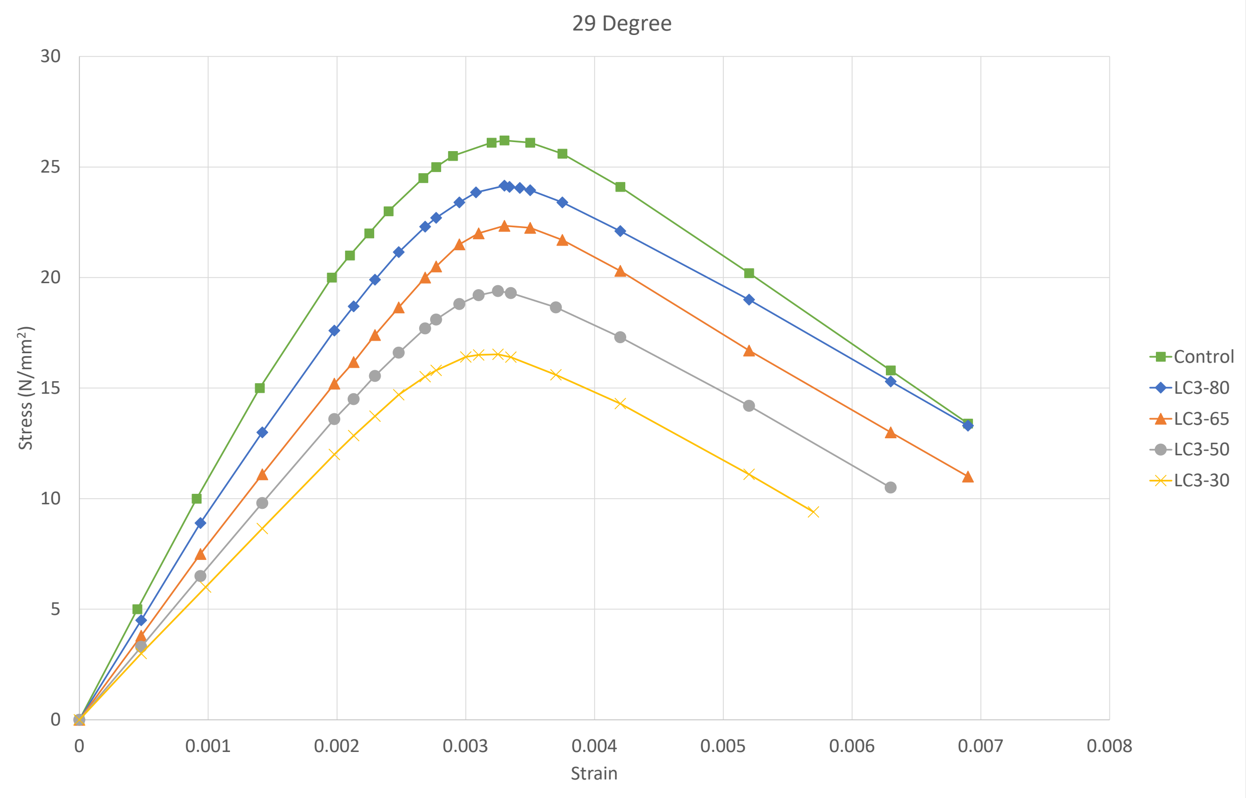

Figure 4.1 Stress Strain Curve for 29°C temperature

It can be seen from the figure that the sample having 100% cement shows the highest compressive strength. While the compressive strength of the LC^3-30 cylinder, having 30% cement and 70% calcined clay with limestone, is the least at room temperature. LC3-50 shows 26.03% strength reduction and LC3-30 shows 36.91% strength reduction as compared to the Control sample. The overall trend of all the samples is the same. As we move towards the low cement content and high clay content, the compressive strength of the samples decreases. This is due to the low kaolinite clay, as the amount of metakaolin in the calcined clay to react with limestone is less. The samples were then heated at 100°C and their compressive strength was performed after letting them cool down for some time. The result of the compressive strength test for samples heated at 100°C is shown in the following graph.

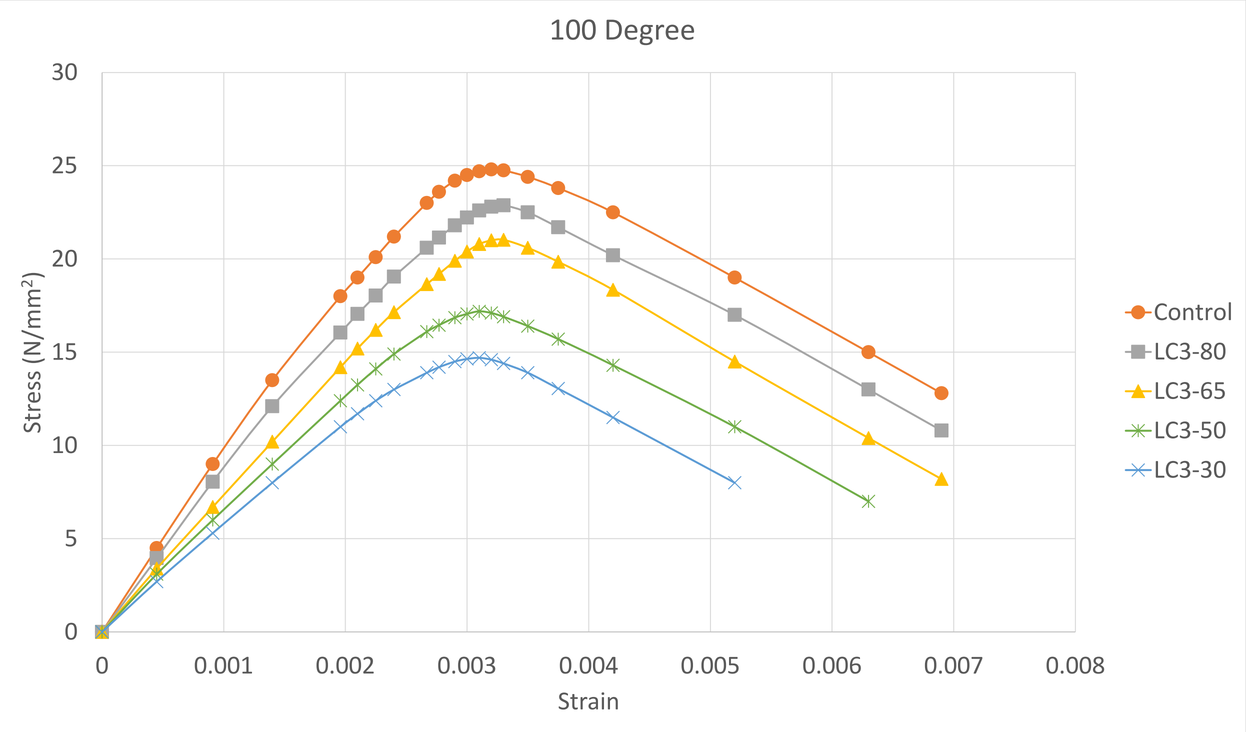

Figure 4.2 Stress Strain Curve for 100°C temperature

When the samples were heated at 100°C, the compressive strength decreases. From the above graph, the comparison of the control sample and different LC^3-Concrete samples can be seen. The control sample shows the highest compressive strength which is 24.8 N/mm2. The LC^3-50 peak value is 17.49 N/mm2, a 29.47% reduction as compared to the control sample. LC^3-30 shows the least strength of 14.7 N/mm2, 40.73% reduction as compared to the control sample at 100 degrees.

The samples were then heated at 200°C in the furnace and the compressive strength tests were performed on the samples after cooling down to draw the comparison of the compressive strengths of the control sample and LC^3-Concrete samples. The graph plotted for compressive strengths at 200°C is shown below.

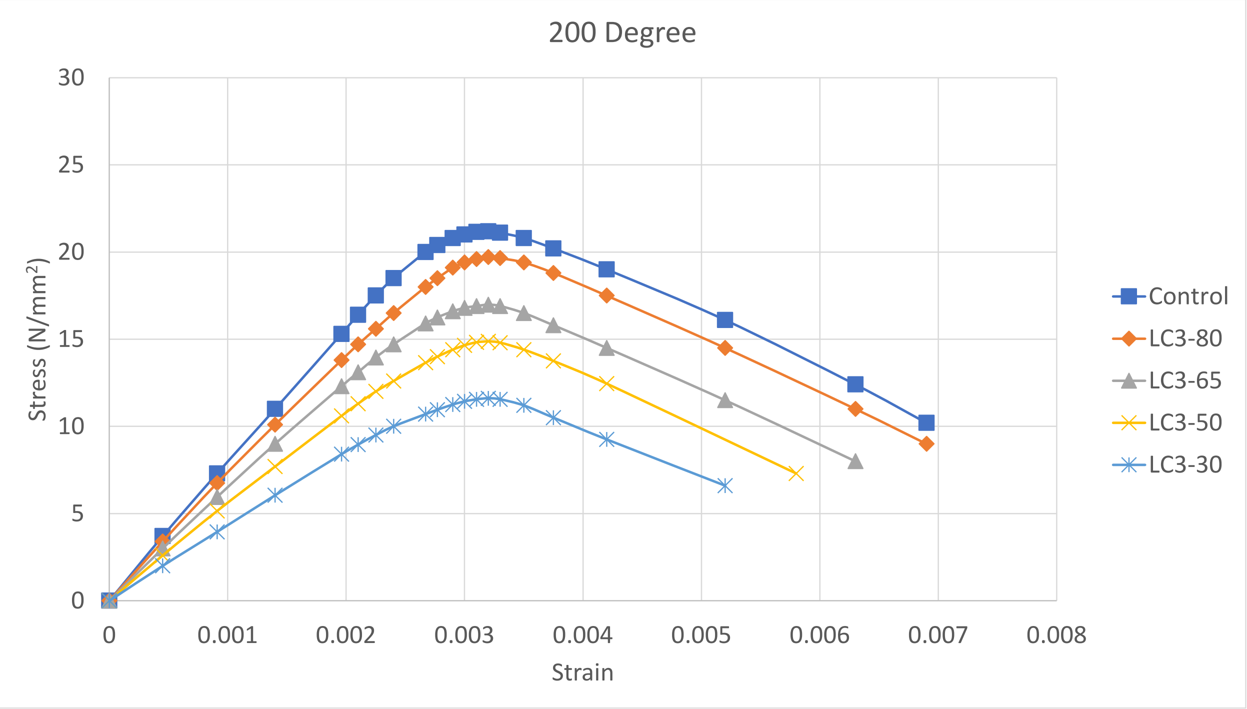

Figure 4.3 Stress Strain Curve for 200°C temperature

From the above graph, it can be seen the compressive strength of the samples was reduced as compared to the compressive strengths at room temperature and 100°C. The control sample shows the highest compressive strength which is 21.17 N/mm^2. While the compressive strength of LC^3-30 is 11.61 N/mm^2, it is reduced by 45.2% as that of Control at 200°C. The peaks of the compressive strengths drop gradually when we move from high cement content to low cement content.

After 200°C, the samples were exposed to 400°C in the furnace. The samples were cooled down for some time and then the compressive strength tests were performed on the samples. These test results were plotted on a graph to build a comparison between different types of samples. The graph is shown below.

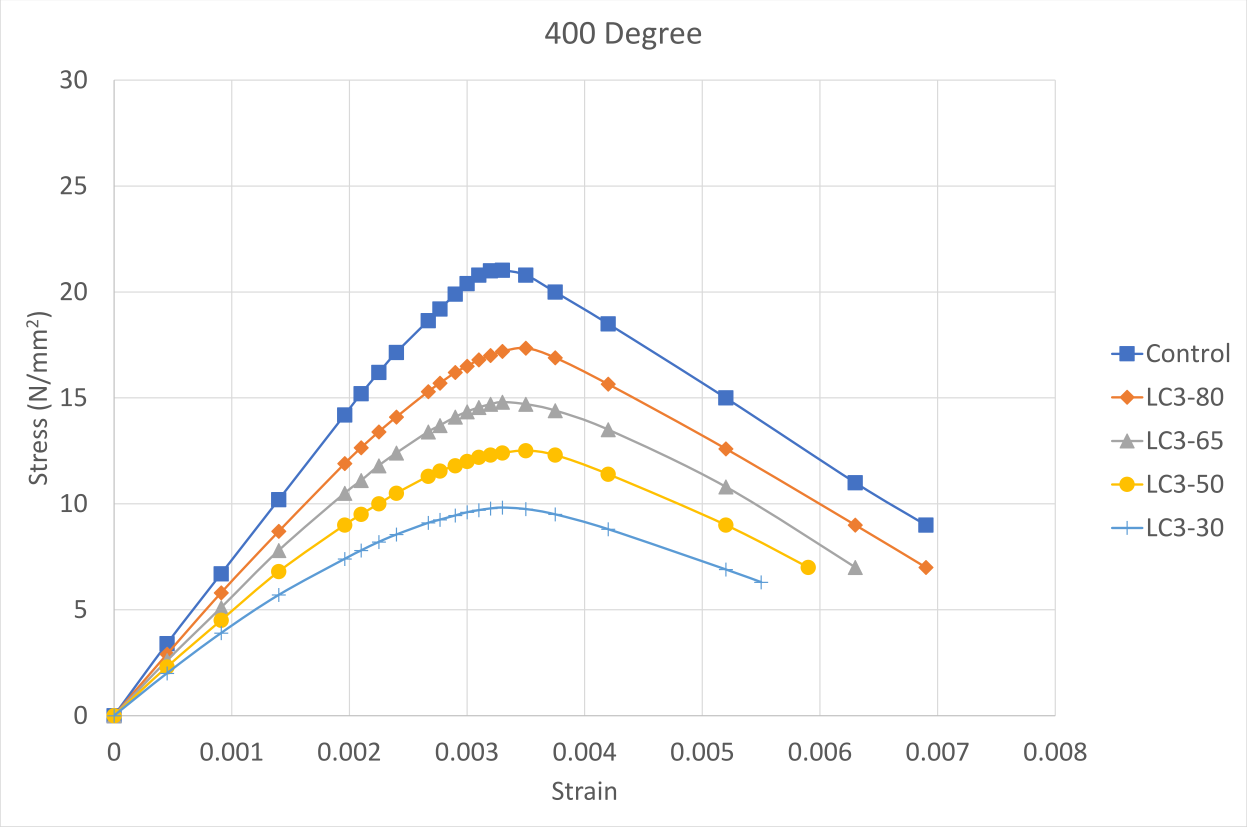

Figure 4 4 Stress Strain Curve for 400°C temperature

The same trend can be seen for the stress-strain curve as it was observed in graphs for 100°C and 200°C. The control sample having no clay content shows the highest compressive strength at 400°C. The control sample shows the highest compressive strength of 19.5 N/mm^2. The LC^3-30 sample shows the least strength of 9.82 N/mm^2, 49.64% less than the compressive strength of the control at 400 degrees.

The samples were placed in the furnace and heated at 600°C. Then, the samples were removed and cooled down. After that, the compressive strength tests were performed on the samples and a graph was plotted between the stress-strain curves of each sample after heating at 600°C. The graph is shown below.

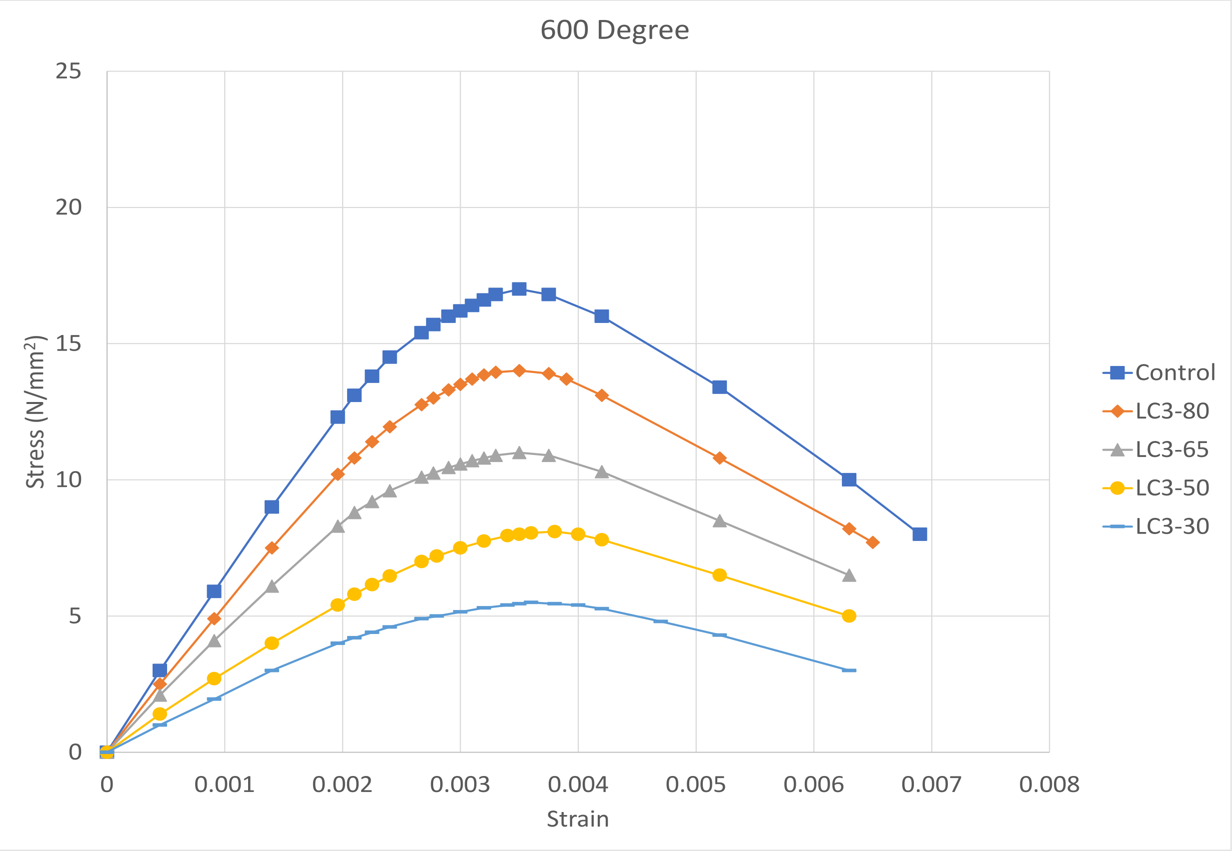

Figure 4.5 Stress Strain Curve for 600°C temperature

It can be seen from the graph that the compressive strength decreased significantly at 600°C. The graphs become flattered when we move towards high temperatures, which means that low stresses induce high strains when samples are exposed to elevated temperatures.

The control sample shows the highest compressive strength which is 17 N/mm^2. The LC^3-30 sample shows the least strength of 5.5 N/mm^2, a 67.65% reduction in the strength of the sample having cement only.

These were the stress-strain curves of samples at each temperature. After that, a comparison was plotted on a graph to observe the overall trend at every temperature. For that purpose, the peak values of the stress-strain curve i-e maximum compressive strength values were picked for each sample and plotted again temperature as shown in the figure below.

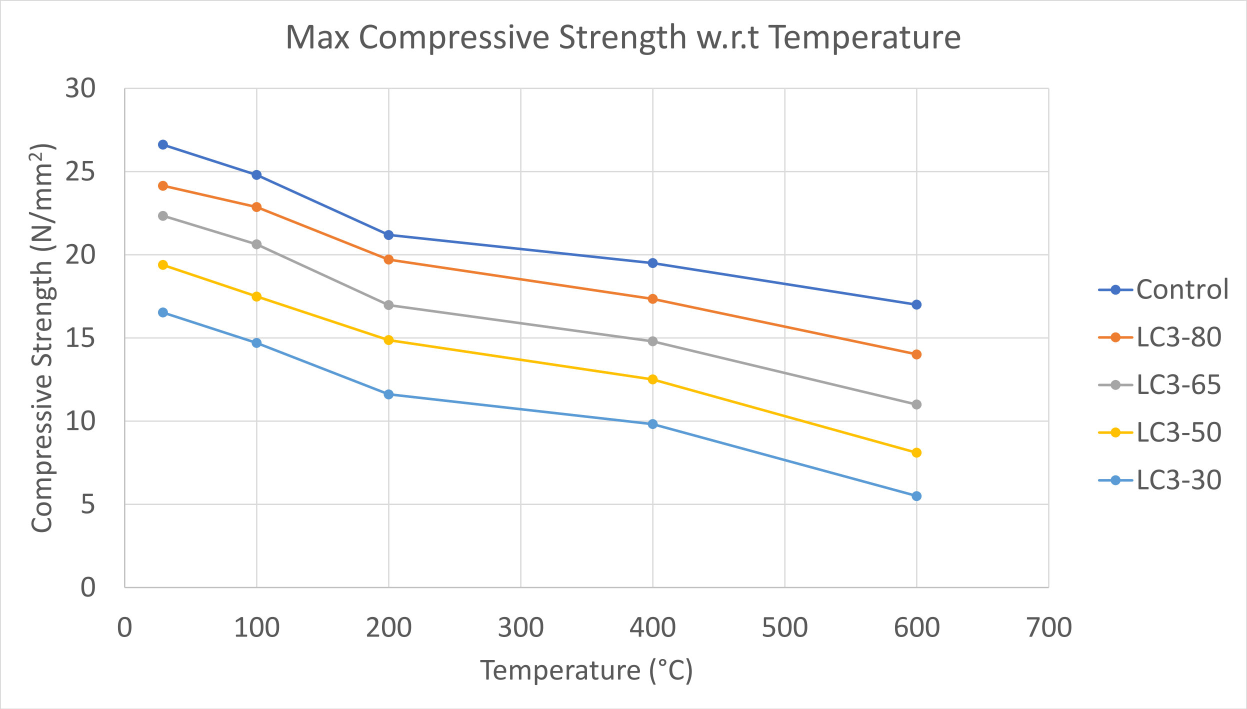

Figure 4.6 Maximum Compressive Strength vs Temperature (°C)

It can be seen from the above graph that the compressive strength decreases when we move toward high temperatures. And at a specific temperature, the difference in the compressive strength of different samples can be observed from the graph. The strength reduction in LC^3-Concrete is less than the normal cement concrete at 200°C. LC^3-80 shows a 17% strength reduction while the control sample shows a 19.8% strength reduction.

4.1.2 Elastic Modulus:

The elastic modulus can be easily calculated from the stress-strain curves for each sample. The stress-strain curve was plotted with the help of the Compression Testing Machine. The area under the curve, in the elastic region where stress is directly proportional to the strain, gives the value of elastic modulus. A graph was plotted for the elastic modulus of each sample at every temperature is shown below.

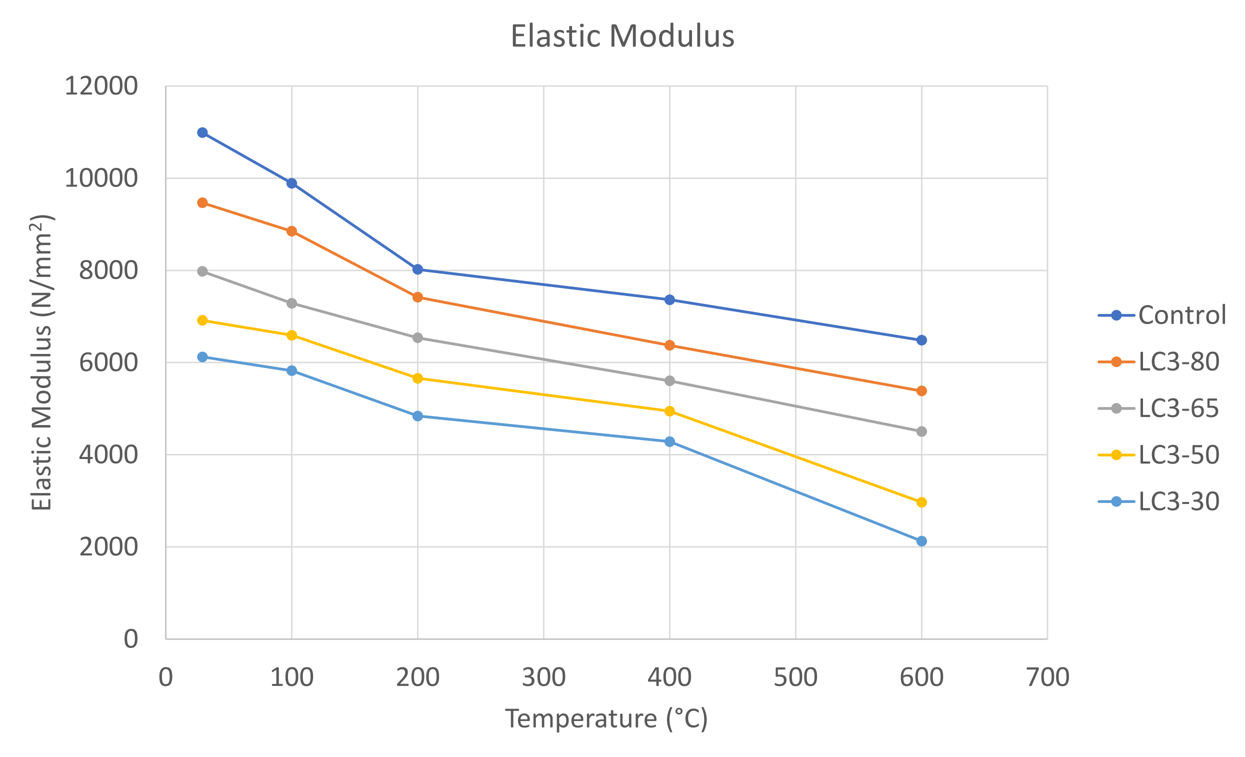

Figure 4.7 Elastic Modulus vs Temperature (°C)

The elastic modulus of each sample decreases with the increase in temperature. A decreasing trend can be seen for the elastic modulus of each sample over increasing temperature. The difference in the elastic modulus of the control sample and different LC^3-Concrete samples can also be seen at a specific temperature. The elastic modulus of the control sample at 600 degrees is 6483.52 N/mm^2 and that of LC^3-30 is 2124.86 N/mm^2, which means it is reduced by 67.23%. When the temperature was raised from 400°C to 600°C, an abrupt decrease in the elastic modulus of the LC^3-50 and LC^3-30 samples was observed. The low value of elastic modulus means that the small stress applied to the sample will result in large strains.

4.1.3 Tensile Strength:

The tensile strength for each cylinder was calculated from the split tensile test. The test procedure is explained in the previous chapter. The tensile test of each sample was calculated for every temperature, and it was plotted on the graph to get a comparison between the control sample and the LC^3-Concrete samples. The graph for the tensile strength is shown below.

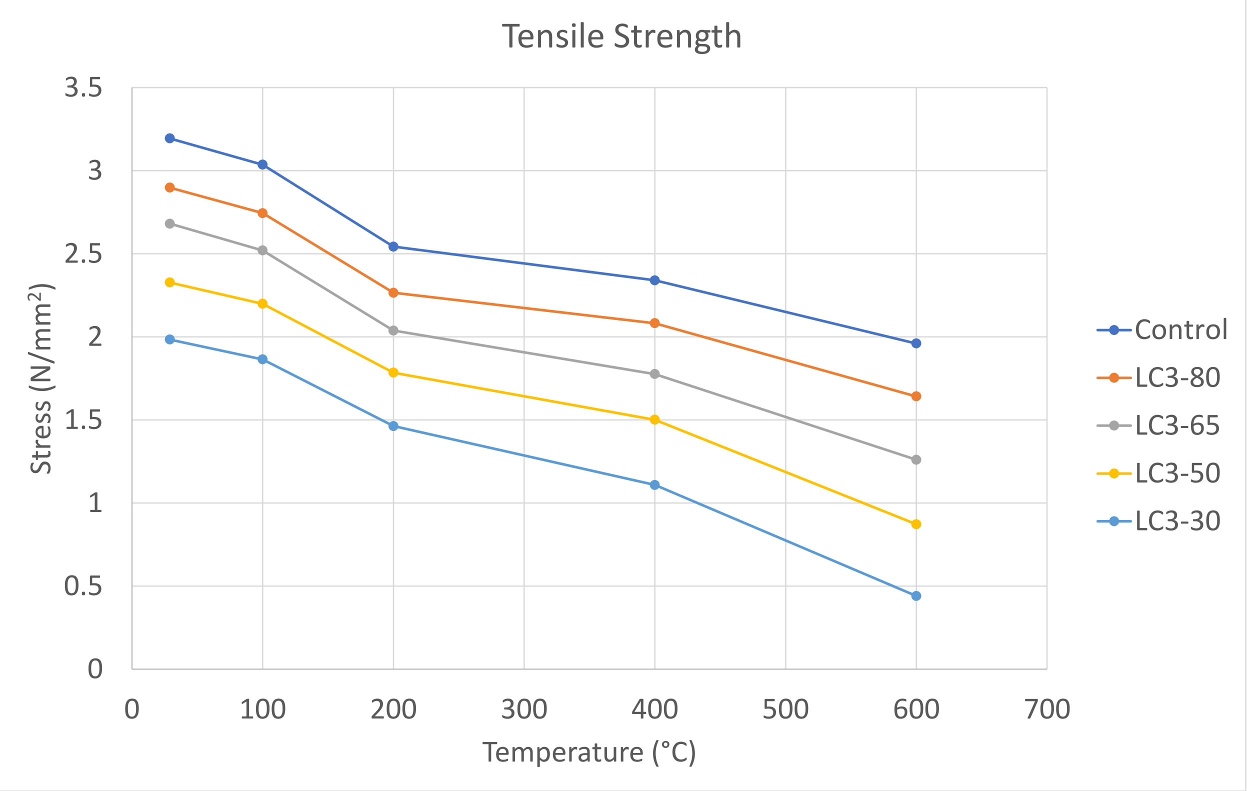

Figure 4.8 Tensile Strength vs Temperature (°C)

The graph starts at 29°C and ends at 600°C. The difference in tensile strength of every sample can be seen against each temperature. The control sample showed the maximum tensile strength while the samples having calcined clay and limestone showed a reduction in tensile strength. The strength at room temperature was the maximum and it was reduced when the temperature was raised to 600°C. The tensile strength of LC^3-30 is 0.44 N/mm^2, the lowest at 600°C, 77.55% reduction as compared to the control sample. At room temperature, the tensile strength of the control is the highest, which is 3.19 N/mm^2. The LC^3-30 concrete sample has a tensile strength of 1.96 N/mm^2. A reduction of 38.64% in the LC^3-30 concrete cylinder was noted as compared to the control sample at 29°C.

4.2 Thermal Conductivity:

The thermal conductivity was necessary to calculate the time at which the surface and core temperature of each sample will be equal to the temperature of the furnace. It is defined as the rate of heat transfer in a solid cross-section by conduction against the temperature gradient held at a right angle to the substance. The sensors were placed in the core and on the surface of each cylinder and the temperature was observed with the rise in furnace temperature. The graph plotted between the control sample, LC^3-80, and LC^3-30 is shown below.

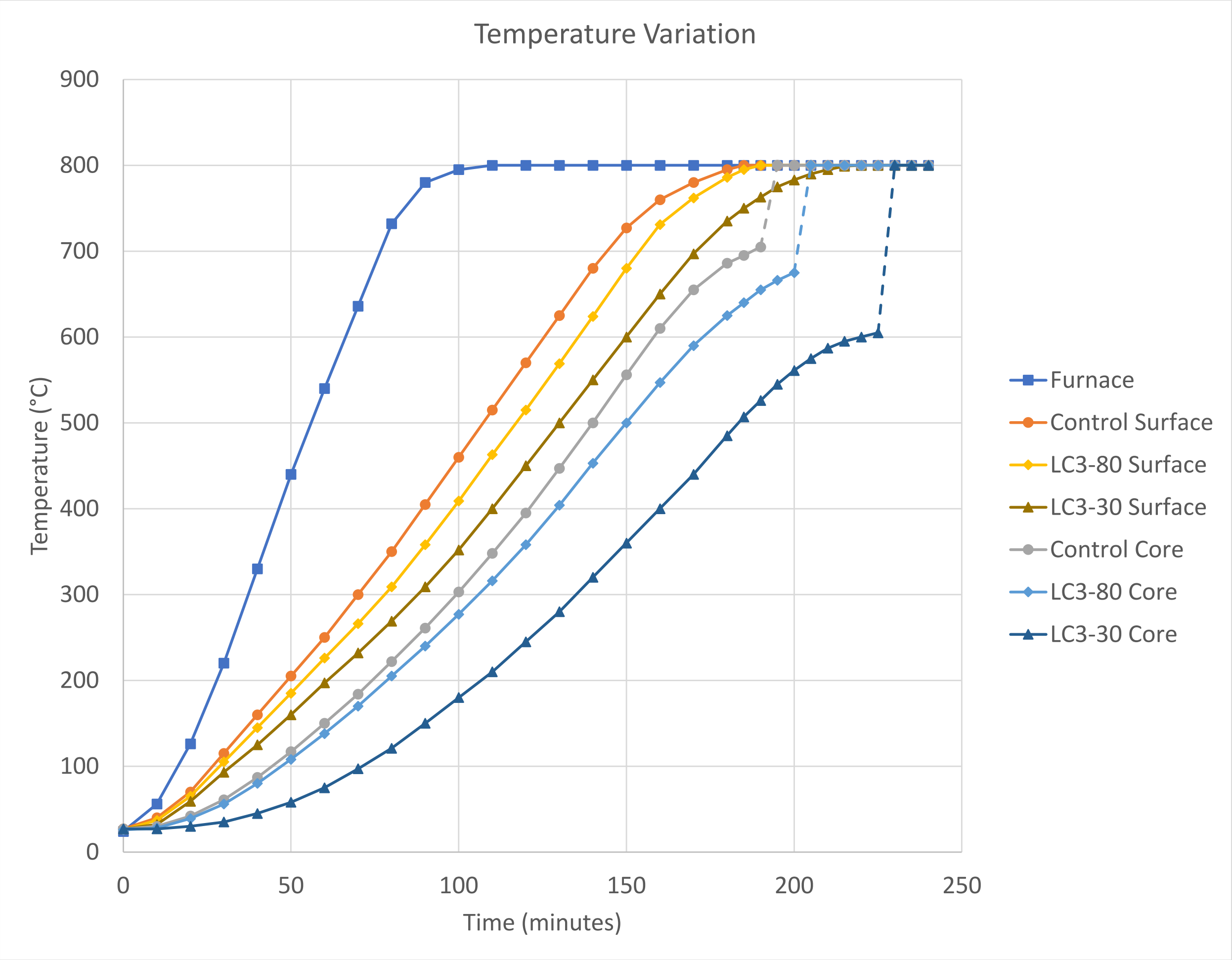

Figure 4.9 Temperature Variation (°C) vs Time (minutes)

It can be seen from the graph, the temperature of the surface changed quickly while it took some extra time for the core of samples to reach the outer temperature. The control sample took the least time to reach the furnace temperature while the time taken by the LC^3-30 sample was the longest. It means that the rate of heat transfer in the samples having more clay content and less cement content is less as compared to the samples having greater cement content. The curves for the core temperature of each sample become straight at the end because of the failure of cylinders. The control cylinder failed at 705°C, the LC^3-80 cylinder failed at 675°C, and the LC^3-30 cylinder failed at 610°C.

4.3 Mass Loss:

The weight of each sample was calculated before heating and after heating in the furnace. The difference in the mass at each temperature was calculated. The graph was plotted showing the mass loss percentage with the rise in temperature of the control samples and LC^3-Concrete samples.

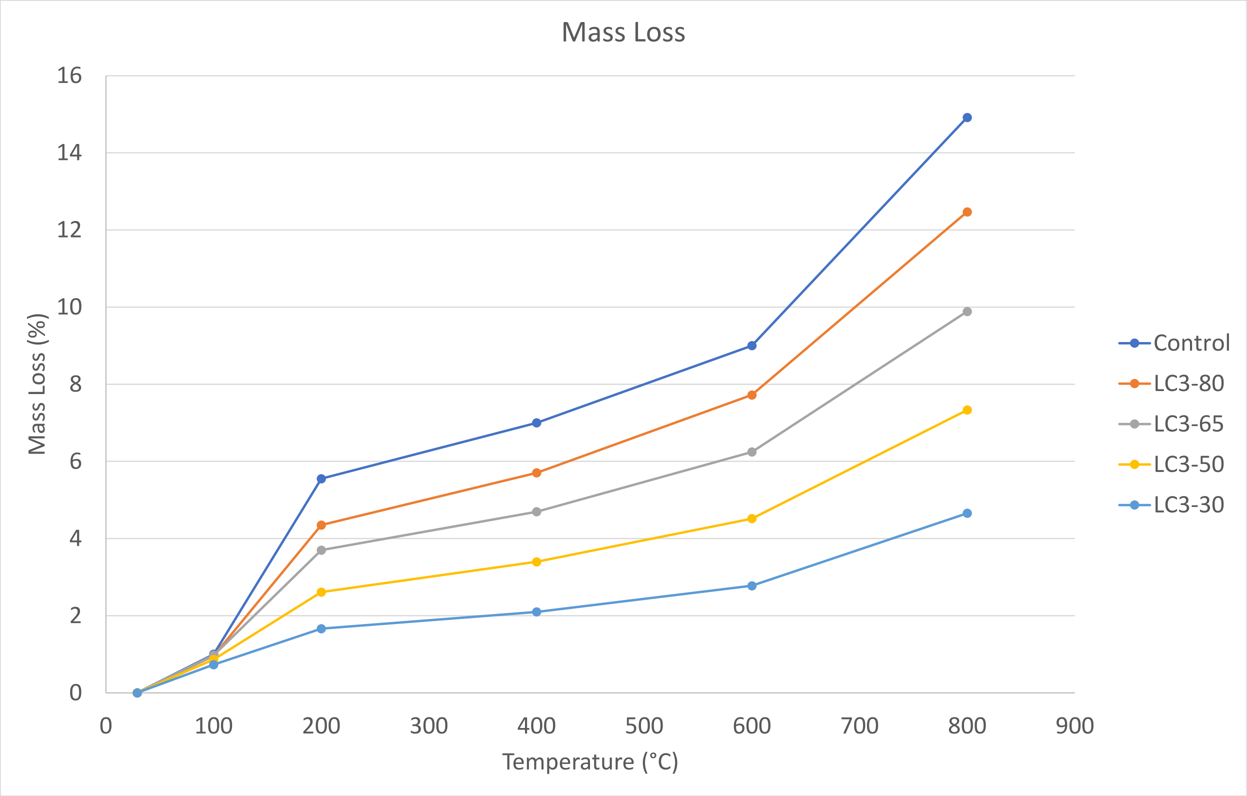

Figure 4.10 Mass Loss (%) vs Temperature (°C)

The trend in the graph above shows that the mass loss percentage increases with the increase in temperature. While the mass loss in the sample having 100% cement content is greater as compared to the samples having calcined clay and limestone. It can also be seen that the mass loss percentage decreases with the increase in the clay content in the samples. The LC^3-30 has shown the least mass loss of around 4.6% and the control sample has shown the maximum mass loss of around 15%.

4.3 Visual Analysis:

The samples were visually analyzed to see the effect of temperature on each sample. The table below includes the pictures of the control sample and all LC^3-Concrete samples at room temperature as well as after each temperature rise.

	Control	LC^3-80	LC^3-65
29°C			
100°C			

200°C			
400°C			
600°C			
	Control	LC^3-80	LC^3-65

800°C			
	Control	LC^3-80	LC^3-65

Table 4.1 Visual Analysis of Control, LC^3-80, LC^3-65

	LC^3-50	LC^3-30
29°C		

100°C		
200°C		
400°C		
	LC^3-50	LC^3-30

600°C		
800°C		
	LC^3-50	LC^3-30

Table 4.2 Visual Analysis of LC^3-30 and LC^3-50

Visual Analysis of Control, LC^3-80, LC^3-65The changes in the physical appearance of the sample can be seen in the above table. The color of the sample becomes faint at temperatures of 100°C and 200°C. This is due to the escape of moisture entrapped in cylinders. No surface deterioration was observed till 200°C. But when the temperature reached 400°C, small cracks were seen on the surface of the samples. These cracks were more visible when the temperature reaches 600°C. At 800°C, all the samples failed.

4.4 Thermogravimetric Analysis:

To check the stability of the substance under high temperatures, the TGA test is performed. The test was performed on the raw clay to check its behavior under rising temperatures. The TGA test gives us the value of mass loss of the substance with respect to temperature. The ramp for temperature was 20°C per minute following ASTM E1131. The graph, plotted for clay, is shown under.

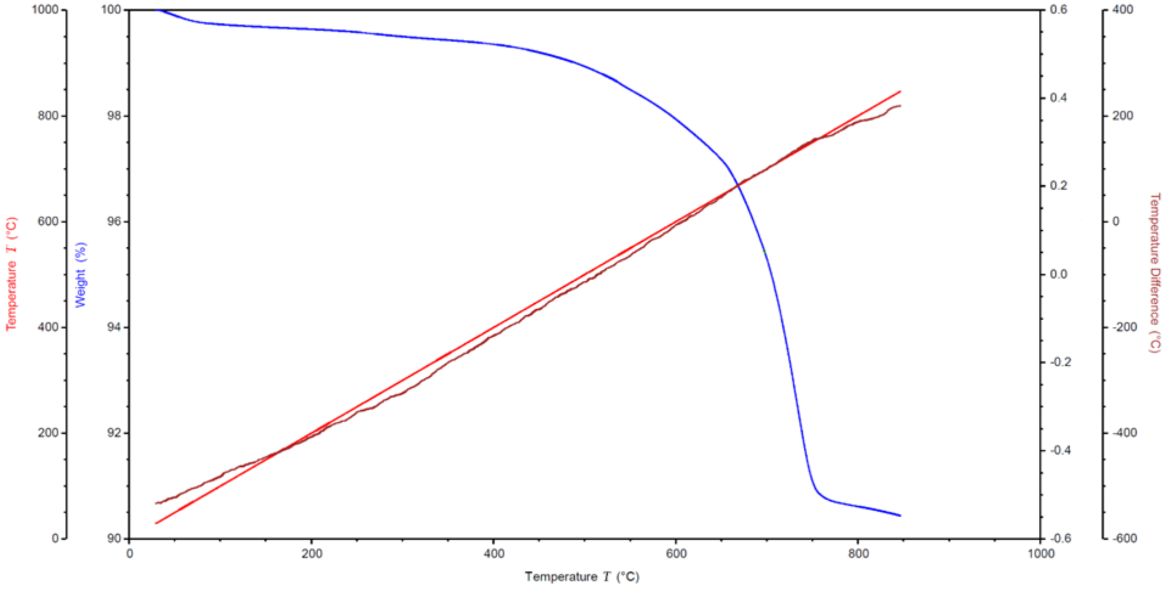

Figure 4.11 Thermo-Gravimetric Analysis Chart

The blue line represents the weight of the clay. And the red lines show the temperature of the sample and the instrument. Slight mass loss occurs at 450-650 degrees, due to the decomposition of organic matter present in the clay. Abrupt mass loss (around 6%) occurs at 650-750 degrees, due to dihydroxylation of kaolinite in the clay.

CHAPTER 5

Conclusions and Recommendations

This research deals with the use of low-kaolinite clay in concrete and its testing at elevated temperatures. The conclusions drawn from this research and recommendations for future research are explained in this chapter.

5.1 Conclusions

- The Calcined-Clay can be used to replace cement content in concrete in combination with limestone.
- The low kaolinite concrete can also be used in LC^3-Concrete. The mechanical properties of the concrete will be compromised when we move below 40% kaolinite content.
- At room temperature, concrete samples with low kaolinite clay show less strength as compared to normal cement control samples. The strength reduction in LC^3-50 is 26.03% as compared to the compressive strength of the control sample.
- The samples with more clay proportion show less compressive strength at room temperature. LC^3-80 shows 7.82% strength reduction while LC^3-30 shows 36.91% strength reduction as compared to the normal cement concrete sample.
- The rate of heat transfer in a sample having calcined clay is lower than the sample having no cement replacement.
- The thermal conductivity of the samples with greater clay proportions is less and it takes more time for their core temperature to reach the outer temperature.

- The LC^3-Concrete shows less mass loss at elevated temperatures. LC^3-30 shows the least mass loss of around 4.6% and the sample having normal cement shows the maximum mass loss of around 15%.
- The strength reduction in LC^3-Concrete is less than normal cement concrete at 200 degrees. LC^3-80 shows a 17% strength reduction while the control sample shows a 19.8% strength reduction.
- At 600 degrees, the control sample shows more strength as compared to calcined-clay samples. The control sample shows 46.11% strength loss while LC^3-30 shows 66.73% strength reduction.
- The control sample showed the maximum tensile strength while the samples having calcined clay and limestone showed a reduction in tensile strength.
- The strength at room temperature was the maximum and it was reduced when the temperature was raised to 600°C. The tensile strength of LC^3-30 is 0.44 N/mm2, the lowest at 600°C, 77.55% reduction as compared to the control sample.
- At room temperature, the tensile strength of the control is the highest, which is 3.19 N/mm^2. The LC^3-30 concrete sample has a tensile strength of 1.96 N/mm^2. A reduction of 38.64% in the LC^3-30 concrete cylinder was noted as compared to the control sample at 29°C.
- The samples with more calcined clay fail at comparatively low temperatures. LC^3-30 fails when the temperature reaches 610 degrees while LC^3-80 fails at around 675 degrees.

5.2 Recommendations

For future research, the following recommendations are suggested based on this research:

- The behavior of low kaolinite LC^3-Concrete again sulfate attack should be studied.
- The structural properties of low kaolinite LC^3-Concrete needs to be analyzed.

References

[1] M. Schneider, M. Romer, M. Tschudin, and H. Bolio, “Sustainable cement production—present and future,” *Cem. Concr. Res.*, vol. 41, no. 7, pp. 642–650, 2011.

[2] J. Lehne and F. Preston, “Making concrete change: Innovation in low-carbon cement and concrete,” 2018.

[3] H. Justnes, “How to make concrete more sustainable,” *J. Adv. Concr. Technol.*, vol. 13, no. 3, pp. 147–154, 2015.

[4] S. H. Kosmatka, W. C. Panarese, and B. Kerkhoff, *Design and control of concrete mixtures*, vol. 5420. Portland Cement Association Skokie, IL, 2002.

[5] R. Snellings, G. Mertens, and J. Elsen, “Supplementary cementitious materials,” *Rev. Mineral. Geochemistry*, vol. 74, no. 1, pp. 211–278, 2012.

[6] A. M. Neville, *Properties of concrete*, vol. 4. Longman London, 1995.

[7] P. K. Mehta and P. J. M. Monteiro, *Concrete: microstructure, properties, and materials*. McGraw-Hill Education, 2014.

[8] E. G. Nawy, *Concrete construction engineering handbook*. CRC press, 2008.

[9] M. C. G. Juenger, R. Snellings, and S. A. Bernal, “Supplementary cementitious materials: New sources, characterization, and performance insights,” *Cem. Concr. Res.*, vol. 122, pp. 257–273, 2019.

[10] G. S. Barger *et al.*, “Evaluation of a blended cement and a mineral admixture containing

calcined clay natural pozzolans for high performance concrete," in *International Purdue Conference on Concrete Pavement Design and Materials for High Performance, 6th, 1997, Indianapolis, Indiana, USA*, 1997, vol. 1.

[11] B. Lothenbach, K. Scrivener, and R. D. Hooton, "Supplementary cementitious materials," *Cem. Concr. Res.*, vol. 41, no. 12, pp. 1244–1256, 2011.

[12] S. K. Reinert, *Optimizing Portland cement concrete mix design to environmental and construction variables with the aid of computer design software*. Iowa State University, 2007.

[13] M. D. A. Thomas, *Optimizing the use of fly ash in concrete*, vol. 5420. Portland Cement Association Skokie, IL, USA, 2007.

[14] M. Otieno, H. Beushausen, and M. Alexander, "Effect of chemical composition of slag on chloride penetration resistance of concrete," *Cem. Concr. Compos.*, vol. 46, pp. 56–64, 2014.

[15] K. Scrivener, F. Martirena, S. Bishnoi, and S. Maity, "Calcined clay limestone cements (LC3)," *Cem. Concr. Res.*, vol. 114, pp. 49–56, 2018.

[16] M. Sharma, S. Bishnoi, F. Martirena, and K. Scrivener, "Limestone calcined clay cement and concrete: A state-of-the-art review," *Cem. Concr. Res.*, vol. 149, p. 106564, 2021.

[17] B. B. Sabir, S. Wild, and J. Bai, "Metakaolin and calcined clays as pozzolans for concrete: a review," *Cem. Concr. Compos.*, vol. 23, no. 6, pp. 441–454, 2001.

[18] F. Avet and K. Scrivener, "Investigation of the calcined kaolinite content on the hydration of Limestone Calcined Clay Cement (LC3)," *Cem. Concr. Res.*, vol. 107, pp. 124–135, 2018.

[19] R. Fernandez, F. Martirena, and K. L. Scrivener, “The origin of the pozzolanic activity of calcined clay minerals: A comparison between kaolinite, illite and montmorillonite,” *Cem. Concr. Res.*, vol. 41, no. 1, pp. 113–122, 2011.

[20] F. Avet, E. Boehm-Courjault, and K. Scrivener, “Investigation of CASH composition, morphology and density in Limestone Calcined Clay Cement (LC3),” *Cem. Concr. Res.*, vol. 115, pp. 70–79, 2019.

[21] Y. Dhandapani, T. Sakthivel, M. Santhanam, R. Gettu, and R. G. Pillai, “Mechanical properties and durability performance of concretes with Limestone Calcined Clay Cement (LC3),” *Cem. Concr. Res.*, vol. 107, pp. 136–151, 2018.

[22] G. M. Ayininuola and O. A. Adekitan, “Characterization of Ajebo Kaolinite Clay for production of natural pozzolan,” *Int. J. Civ. Environ. Eng.*, vol. 10, no. 9, pp. 1233–1240, 2017.

[23] F. Zunino and K. Scrivener, “The reaction between metakaolin and limestone and its effect in porosity refinement and mechanical properties,” *Cem. Concr. Res.*, vol. 140, p. 106307, 2021.

[24] F. Zunino and K. Scrivener, “Increasing the kaolinite content of raw clays using particle classification techniques for use as supplementary cementitious materials,” *Constr. Build. Mater.*, vol. 244, p. 118335, 2020.

[25] F. Zunino and K. Scrivener, “Factors influencing the sulfate balance in pure phase C3S/C3A systems,” *Cem. Concr. Res.*, vol. 133, p. 106085, 2020.

[26] S. Aiswarya, G. Prince Arulraj, and C. Dilip, “A review on use of metakaolin in concrete,” *Eng. Sci. Technol.*, vol. 3, no. 3, pp. 592–597, 2013.

[27] J.-T. Ding and Z. Li, “Effects of metakaolin and silica fume on properties of concrete,” *Mater. J.*, vol. 99, no. 4, pp. 393–398, 2002.

[28] K.-H. Yang, Y.-B. Jung, M.-S. Cho, and S.-H. Tae, “Effect of supplementary cementitious materials on reduction of CO2 emissions from concrete,” *J. Clean. Prod.*, vol. 103, pp. 774–783, 2015.

[29] J. M. Marangu, K. Riding, A. Alaibani, A. Zayed, J. K. Thiong’o, and J. M. Wachira, “Potential for Selected Kenyan Clay in Production of Limestone Calcined Clay Cement,” in *Calcined Clays for Sustainable Concrete*, Springer, 2020, pp. 19–25.

[30] R. S. Almenares Reyes *et al.*, “Clay Deposits from the Northeastern of Cuba: Characterization, Evaluation, and Use as a Source of Supplementary Cementitious Materials,” in *Calcined Clays for Sustainable Concrete*, Springer, 2020, pp. 49–56.

[31] M. Antoni, “Investigation of cement substitution by blends of calcined clays and limestone,” EPFL, 2013.

[32] T. Danner, G. Norden, and H. Justnes, “The effect of calcite in the raw clay on the pozzolanic activity of calcined illite and smectite,” in *Calcined clays for sustainable concrete*, Springer, 2020, pp. 131–138.

[33] D. P. Bentz, P. E. Stutzman, and F. Zunino, “Low-temperature curing strength enhancement in cement-based materials containing limestone powder,” *Mater. Struct.*, vol. 50, no. 3, pp. 1–14, 2017.

[34] T. R. Muzenda, P. Hou, S. Kawashima, T. Sui, and X. Cheng, “The role of limestone and calcined clay on the rheological properties of LC3,” *Cem. Concr. Compos.*, vol. 107, p. 103516, 2020.

[35] K. Scrivener *et al.*, “Impacting factors and properties of limestone calcined clay cements (LC3),” *Green Mater.*, vol. 7, no. 1, pp. 3–14, 2018.