LIMESTONE CALCINED CLAY CEMENT (LC3)

BY

MOHAMMED, Abdullahi Junior

ENG1704111

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CERTIFICATION

This is to certify that this project was carried out by **MOHAMMED, ABDULLAHI JUNIOR**, with **MAT. NO. ENG170411**, of the Department of Structural Engineering, Faculty of Engineering, University of Benin, Benin City, Edo state, Nigeria.

PROJECT COORDINATOR:

Name: Engr. E. Oria-Osifo

....

Signature Date

SUPERVISOR:

Name: Engr. S.A. Adegbemileke,

....

Signature Date

HEAD OF DEPARTMENT:

Name: Engr. Dr. (Mrs) N. I. Ihimekpen

....

Signature Date

DEDICATION

This project is dedicated to GOD ALMIGHTY for His unending love and perseverance over my life, my family and friends.

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ABSTRACT

This study investigates the properties of limestone calcined clay cement (LC^3) with a water/cement ratio of 0.5 and cement/sand ratio of 1:2.75 produced using clay sourced from Uzebba, Nigeria. The kaolinitic Uzebba clay was calcined at 600°C, 700°C and 800°C to activate it's pozzolanic properties. Mortar cubes were cast and cured in lime water and by air. A total of 120 mortar cubes were prepared for compressive strength testing and water absorption test. For compressive test, 9 cubes were mixed and cured in lime water and air serving as the control, 27 cubes were mixed for LC^3 calcined at 600°C, 700°C and 800°C for 30% and 40% replacement and cured in lime water and by air. Additionally, this study utilized other tests like sieve analysis of fine aggregate, standard consistency test, setting time of cement and bleeding tests.

The average compressive strength for 30% and 40% mortar cubes cured in lime water ranged from $9.44N/mm^2$ - $17.12N/mm^2$ and $7.47N/mm^2$ - $12.16N/mm^2$ respectively, while for 30% cured in air ranged from $5.70N/mm^2$ - $15.91N/mm^2$. For water absorption test, 12 cubes were mixed and cured in lime water to determine the amount of water absorbed by the cubes for the control and replacement.

The results demonstrated that locally available Uzebba clay calcined at a higher temperature (800°C) can be an effective supplementary cementitious material in LC^3 because it showed that the strength of the mortar cubes with LC^3 at 800℃ is comparable to the strength of the OPC produced than those calcined at 600℃ and 700℃. This new blend of cement has been shown to have an improved strength and durability due to the less water absorbed by the cubes when calcined at a higher temperature

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CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND OF STUDY

Development has brought comfort to humans in their daily lives, but it has become an issue on the earth's natural resources, thereupon, it has unfavorably affected the environment. As the demand of cement in the construction industry has increased, it has climbed dramatically globally. More than 10 billion cubic meters of concrete are produced annually around the globe, and it is unlikely that this volume will recede (Alexander et al., 2017). The high demand of cement around the world today has brought about notable rise in the emission of CO_2. According to the UN Environment Program, buildings are responsible for up to 41% of global anthropogenic carbon emissions. Due to the enormous demand for concrete, the cement industry is responsible for 5–8% of the world's greenhouse gas emissions (Schneider, 2019). The major origin of this greenhouse gases exploited for the production of cement is clinker and brings about climate change. Overall, there are numerous issues that the worldwide cement production business is currently dealing with, including a lack of resources, excessive energy use, and environmental contamination (Zhou et al., 2017). The world is on track to exceed carbon dioxide emissions by 2028 because of which the temperature may rise by up to 1.5°C above preindustrial levels as a result (Scrivener, 2019). Hence, we have to work aggressively in all areas of life to slow down the temperature rise. Else, we will have to spend in the future to address problems. The utilization of supplementary cementitious materials (SCMs) to replace part of the clinker in cement has a great possibility to reduce the amount of CO_2 emitted during cement production globally. Although, due to the unavailability of SCMs in many countries or other parts of the world, it is a major barrier to its extensive use. Today more than 80% of SCMs used to reduce the clinker factor in cement are either limestone, fly ash or slag (World Business Council for Sustainable Development (WBCSD) 2009). Due to the limited supply of fly ash and other SCMs available, calcined clay has emerged to be a better supplementary cementitious material. This clay containing kaolinite are abundant worldwide which can be calcined to meet the demand of a useful SCMs. Clays that contain a high percentage of kaolinite have been shown to exhibit strong pozzolanic properties if they undergo calcination (heating) between approximately 700 and 850 degrees Celsius (Fernandez et al., 2011). However, not all types of clay are permitted for the purpose, only clays having kaolinite content of 40% or above holds the properties to be used without having any impact on the hydration and strength of cement, and ultimately replacing cement clinkers which are the main source of CO_2 emission. Furthermore, most geologists focus on high-purity clays, while research has proven that a kaolinite content of around 40-60 percent is sufficient to achieve good reactivity (Alujas et al., 2015; Avet et al., 2018). Calcined clay plays a very important role in yielding as supplementary cementitious material for cement because of its low-cost, widely available and less energy usage in grinding processes and others. It is challenging to lower the clinker percentage in cement below 70% without utilizing combinations of supplementary cementitious materials (Scrivener et al., 2018). For many years, a highly reactive mineral additive called "metakaolin" has been produced through the calcination of high purity clays containing kaolinite (Scrivener et al., 2018). Studies at École polytechnique fédérale de Lausanne (EPFL) (Alujas et al., 2015; Avet et al., 2016) have shown that a kaolinite content of only about 40% in a mixture of LC3 -50 (50% ground clinker, 30% calcined clay, 15% limestone, 5% gypsum) is sufficient to give mechanical properties comparable to the reference plain Portland cement from about 7 days. [(EN 196-1 mortar bars w/c = 0.5, sand/cement = 3 (European Standard EN 196-1 2016)].

Due to the high emission of CO_2 into the atmosphere, which has negative impacts on the environment, the amount of CO_2 can be mitigated by reducing the clinker content in the cement and replacing with a supplementary cementitious material (SCM). It has been reported that the most significant change is the partial replacement of cement with essentially two supplementary materials, calcined clay (metakaolin) and limestone. Since less clinker is needed in the manufacturing processes of limestone calcined clay cement, this replacement helps to minimize financial cost and environmental footprints of this type of cement production as clinker is expensive to produce.

The calcination of clay will be optimized to activate its cementitious properties, allowing increased substitution of clinker. Combining the calcined clay with a percentage of limestone and lower clinker. This research will focus on developing the right formulations, properties and manufacturing process for LC3 to make it a viable eco-friendly construction material. With LC3 technology, the cement industry can retain performance while dramatically lowering its carbon footprint and contributing to climate change mitigation.

1.2 STATEMENT OF THE PROBLEM

The demand of cement is rising globally and this tend to bring about a notable contribution to global CO_2 emissions. Producing ordinary Portland cement necessitates calcining limestone and clay at approximately 1300°C, consuming considerable fossil fuels, this results in high energy usage, carbon emissions, and manufacturing costs. (Monteiro et al., 2017). The manufacturing of cement is an energy consumption process which involves the large utilization of raw materials, energy and heat but also has a great environmental impact. The main effect on the energy consumption process is the heating of cement clinker in a rotary kiln and the energy cost in burning this cement clinker is about 50 – 75% of cement production cost. The global cement industry is facing many challenges at present, these include shortages of raw materials, high energy consumption, and pollution generated during cement production (Damineli et al., 2010; Berriel et al., 2016; Ishak & Hashim, 2015; Zhou et al 2017; Heath et al., 2014).

In regards to the above problem stated above, the cement industry is on careful examination on means to decarbonize cement to reduce the emission of CO_2 globally and thereby attaining similar properties in terms of the strength and durability of the end concrete. In addition, to reduce the energy consumption process that is related with the ordinary Portland cement and thereby making it accessible in terms of cost and a standard material for construction. In summary, resource scarcity, excessive energy utilization, and ecological impacts from emissions and wastes are pressing problems the worldwide cement business must now confront

To overcome this problem, a further research and developments need to be done on how the reduction of CO_2 can be carried out while it still attains the desired properties of the OPC cement, reducing the production process and evaluating the performance. This brings about the advent of the limestone calcined clay cement (LC3) which serves as a supplementary cementitious material in cement clinker. Limestone calcined clay cement (LC3) is a blended cement that is made up of Portland cement clinker, calcined kaolinitic clay and limestone, combining gypsum. This project provides an important opportunity to advance the understanding of LC3 and its outstanding potential as a sustainable and environmental friendly alternative in the construction industry.

1.3 AIMS AND OBJECTIVES

The purpose of this work is to assess the use of limestone ($CaCO_3$), calcined clay at different temperatures (600°C, 700°C and 800°C) obtained from Uzebba town, Edo state, Nigeria and gypsum as supplements for cement production and its effects on the strength of mortar samples cured in lime water and air at 3, 7, 14 and 28 days.

The following objectives are to be considered for the above stated aim;

i. Heat kaolinite clay to a calcination temperature of 600, 700, and 800 degrees Celsius using a muffle furnace.
ii. Determine the compressive strength of mortar cubes of dimension 50 x 50 x 50mm for a 0%, 30% and 40% replacement of cement, cured at 3, 7 ,14 and 28 days in lime water.
iii. Determine the compressive strength of mortar cubes of 50 x 50 x 50mm for 30% replacement of cement cured in air at 3, 7 14 and 28days.
iv. Determination of the variation in compressive strength for different calcination temperatures, curing days for the koalinitic clay used.
v. Determination of the consistency and the setting time of the limestone calcined clay at different temperatures (i.e.600, 700 and 800°C) in comparison with the ordinary Portland cement (OPC).
vi. Determine the amount of water absorbed by the mortar cubes casted with LC3 in comparison with the mortar cubes casted with OPC.
vii. Carrying out a Bleeding Test on the limestone calcined clay cement for the different temperatures in comparison with the conventional Portland cement.

1.4 SCOPE OF STUDY

The scope of this study includes milling kaolinite clay obtained from Uzebba, Edo State, Nigeria and limestone obtained from Ikpeshi, Akoko-Edo local government area, Edo state. It also involves calcining the kaolinite clay at 600°C, 700°C, and 800°C using a muffle furnace.

Additionally, 50 x 50 x 50mm mortar cubes will be fabricated and cured in limewater. Sieve analysis will be conducted on the fine aggregate, and compressive strength tests performed on the cured mortar cubes.

Furthermore, the consistency and setting time of both limestone calcined clay cement (LC3) and ordinary Portland cement (OPC) will be evaluated. Bleeding and water absorption tests will also be carried out. The results will be analyzed and compared, followed by conclusions and recommendations. Overall, this study aims to mill, calcine, and test kaolinite clay as a supplementary cementitious material in LC3 and compare its properties and performance to standard OPC.

1.5. JUSTIFICATION OF STUDY

Due to the current trend in the emission of greenhouses gases like CO_2 which has brought about environmental degradation as a result of the up rise in the production of cement, it is very important to find an alternative that is advantageous to the environment and economic friendly that involves a process of reducing a significant portion of clinker and replacing with calcined clay which has low carbon thereby preserving natural resources, reducing environmental hazards and attaining the properties of OPC in terms of strength, durability as well as being cost effective while they are utilized in the construction industry.

The extensive use of limestone calcined clay cement (LC3) and advent of other supplementary cementitious material that can reduce the amount of clinker which is the major source of CO_2 in cement is a promising solution to eradicate the amount of CO_2 in the cement industry thereby providing a sustainable environment, ecofriendly and the performance benefit of cement globally.

CHAPTER TWO

LITERATURE REVIEW

2.1 INTRODUCTION

The rise in the demand of cement has led to the utilization of the use blended cements, which involves replacing a portion of Portland cement clinker with a supplementary cementitious material (SCMs). Although, most SCMs commonly used in construction such as slag, silica fume and fly ash are industrial by-products, which its availability reduced with a decrease in the production of steel, silicon metal, and coal, respectively (Srivener et al., 2018). The only material that are available in large quantities and that can be easily accessible is clay which can be calcined to act as an effective SCMs. The Portland cement consist of 95% clinker and 5% gypsum. The use of Supplementary Cementitious Materials (SCMs) has been embraced for the reason of not only reducing the amount of CO2 in OPC used in construction but also improving strength and enhancing durability of concrete (Juenger and Siddique 2015). The reduction of CO2 can be achieved by reducing the clinker content in the cement with this supplementary cementitious (Rahla et al., 2019; Juenger et al., 2019).

Limestone calcined clay cement LC3 is a new blend of two materials which are limestone and calcined clay (metakaolin) which are available in large quantities which have a coactive effect. LC3 can reduce CO2 emissions by up to 40%. LC3 uses industrial waste materials which thereby increase resource efficiency and reduce the utilization of the scarce raw materials that are necessary for producing clinker (Avet et al., 2019). Also, LC3 has the potential for applications used in pre-stressed and post-tensioned concrete members, used in masonry mortars and plastering, used in decorative and art structures, used in the manufacture of precast sewage pipes, used under harsh concrete conditions (Krishnan et al., 2018). This ternary blend of limestone, calcined clay and clinker is called LC3 which has set a path to indicates its potential in the cement industry by dealing with the issues of CO2 emissions and conserving natural resources.

2.2 CLAY AND CLAY MINERALS

Clay is a naturally occurring, fine-grained material that is primarily made up of minerals. Clay is generally plastic and moldable when mixed with suitable amounts of water, and it hardens when dried or fired. Clay typically contains phyllosilicate minerals, as well as other materials that provide its plasticity and hardening capabilities. Clay may also contain non-plastic mineral phases and organic matter. The key traits of clay are its fine grain size, plasticity when wet, and its ability to harden when dried or fired due to its mineral composition. Clay can be shaped into any form when it contains water, owing to its plasticity. For clay materials, particle size is an important characteristic, however no definitive upper size limit has been specified. Clays can be differentiated from each other based on their particle size distribution as well as mineralogical composition (Velde 1995)

Clay minerals are phyllosilicates that provide clay its plasticity and hardening abilities upon drying or firing (Guggenheim and Martin 1995). They are formed from weathering of silicate minerals and are found commonly in sedimentary shales. Clay minerals have the ability to adsorb, or attract, water molecules to their surface. This is different from absorption, where molecules would permeate into the mineral. The water attraction is an adsorption process that occurs on the clay surface rather than inside it. In terms of composition, clay minerals resemble micas but are much smaller in grain size, usually only visible under a microscope. Like micas, clay minerals have a plate-like or flaky shape, with one smooth side and irregular edges. The fine grain size, platy shape, and water adsorption abilities differentiate clay minerals from other silicate minerals.

2.2.1 CLASSIFICATION OF CLAY

Clays are primarily classified based on the type of tetrahedral and octahedral silicate sheet combinations and how the sheets stack together. Some examples of classifications are:

i. Kaolinites with a 1:1 ratio of one octahedral and one tetrahedral sheet (e.g. kaolinite, halloysite, serpentine);

ii. Non-expanding 2:1 clays with one octahedral sheet between two tetrahedral sheets (e.g. mica, illite);

iii. Limited expanding 2:1 clays like vermiculite;

iv. Strongly expanding 2:1 clays such as montmorillonite;

v. Uncharged 2:1 clays like pyrophyllite and talc

vi. 2:1:1 clays with a brucite octahedral layer between 2:1 layers like chlorites.

vii. Fibrous clays such as palygorskite and sepiolite. The sheets are held by weak van der Waals forces in the interlayer space. Substitutions in the silicate sheets and pH influence the negative and positive surface charge.

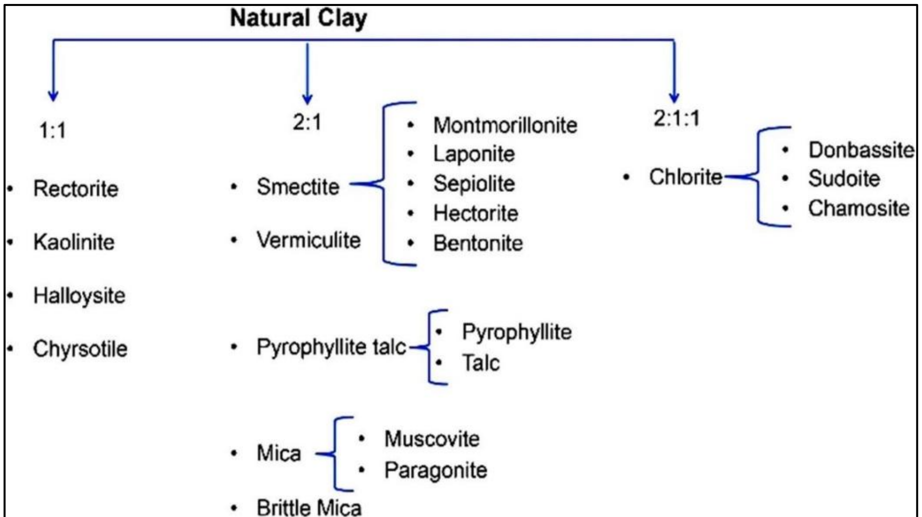

Fig 2.1: Different types of clay and their classifications (Ma et al., 2020)

Many clay minerals have unique structures (Ma et al., 2020; Muhammed et al., 2021; Awad et al., 2019; Del Mar Orta et al., 2020; Tournassat et al., 2015). Kaolinite is a 1:1 phyllosilicate with one tetrahedral silica sheet and one octahedral alumina sheet. It has long been used in ceramics and porcelain. Montmorillonite is an expandable 2:1 clay with a layered structure of two tetrahedral sheets surrounding one octahedral sheet. Metakaolin has the formula Al2Si2O7. Smectite clays like montmorillonite and beidellite have a 2:1 layer of two tetrahedral sheets sandwiching one octahedral sheet. They form from weathering of rocks and soils. Illite is a very common 2:1 clay similar to muscovite in structure. Bentonite mainly comprises smectite clays and forms from altered volcanic ash. Vermiculite is a 2:1 high-charge phyllosilicate clay that arises from weathered micas. In general, clays are fine phyllosilicates with high surface area and contain iron/manganese hydroxides. Smectite and illite make up about 30% of sedimentary rocks (Tournassat et al., 2015). Clays consist of tetrahedral silica sheets fused to octahedral magnesia/alumina/iron sheets. One tetrahedral sheet gives a 1:1 clay while two tetrahedral sheets on either side of one octahedral sheet gives a 2:1 clay structure.

2.2.2 APPLICATIONS OF CLAY

Clays and clay minerals are vital industrial minerals due to their unique properties and numerous applications across sectors. They are utilized in ceramics, cosmetics, biomedicine, healthcare, energy, construction, environmental cleanup, food packaging, textiles, paints, agriculture, radioactive waste disposal, and more. The variety of uses stems from the range of properties clays possess such as plasticity, surface area, ion exchange capacity, and more. Clays are also used to manufacture different composites with tailored properties for specialized functions. For example, polymer-clay nanocomposites are fabricated for applications ranging from flame retardant materials to spill absorption products. The abundance, low cost, and versatility of clays and clay minerals make them extremely valuable industrial minerals. In the construction industry, the following are the most important components;

i. Cement and concrete
ii. Limestone calcined clay cement (LC3)
iii. Geopolymer and concrete
iv. Bricks

2.3 CEMENT

Cement is a dry powdered binding material that undergoes chemical reactions called setting to bind other materials together. It should not be confused with concrete or mortar, although it is a key ingredient in both, acting as the adhesive agent that gives strength. Mortar is a mixture of cement and sand. Concrete also contains coarse aggregates along with the cement and sand. As a major component of concrete and mortar, cement is an extremely important construction material used in modern buildings, bridges, harbors, roads, and more. The worldwide demand for infrastructure drives cement to be the second most consumed resource in the world after water (Francesca 2010).

Cements used for construction can be divided into two categories; hydraulic or non-hydraulic, based on whether the cement is able to harden and cure when mixed with water. Hydraulic cements, such as Portland cement, have the ability to set and harden through a chemical reaction between the dry cement mixture and water. This chemical reaction forms hydrates that are not very soluble in water. As a result, hydraulic cement can cure in wet conditions or even when submerged underwater. The hydrates make hydraulic cement durable when hardened and resistant to degradation from exposure to chemicals, whereas non-hydraulic cement does not cure when mixed with water. Non-hydraulic cement requires air exposure to harden and will not set properly in wet conditions or when submerged under water. The curing process for non-hydraulic cement involves drying and a chemical reaction with carbon dioxide present in the air. Once fully cured, non-hydraulic cement is vulnerable to degradation by certain aggressive chemicals that can damage or deteriorate the cement over time (Blezard 2004)

2.3.1 RAW MATERIALS FOR CEMENT PRODUCTION

The key ingredients used to manufacture cement include sedimentary rocks like limestone and chalk, as well as shale, clay, and sand. These raw materials are quarried and then crushed into a powder to produce the bulk powder used in making cement. But limestone, chalk, shale, clay, and sand are the primary raw materials used in cement production. The table below shows the raw ingredient used to provide each of the main cement element;

Table 2.1: Raw Ingredients Are Used to Provide Each of the Main Cement Element

(Kosmatka et.al 2002)

Calcium	**Silicon**	**Aluminum**	**Iron**
Limestone	Clay	Clay	Clay
Marl	Marl	Shale	Iron ore

Calcite	Sand	Fly ash	Mill scale
Aragonite	Shale	Aluminum	Shale
Shale	Fly ash		Blast furnace dust
Seashells	Rice hull ash		
Cement kiln dust	Slag		

2.3.2 TYPES OF CEMENT

The cement used in construction comes in several varieties that have differing properties, applications and ingredients. The type of cement selected depends on its intended function and the specific construction needs. These are;

a. Ordinary Portland cement (PPC)
b. Portland Pozzolana Cement (PPC)
c. Rapid-hardening cement (RHC)
d. Quick-setting cement (QSC)
e. Low-heat cement (LHC)
f. Sulphate-resisting cement (SRC)
g. Blast furnace slag cement (BFSC)
h. High-alumina cement (HAC)
i. White cement (WC)
j. Coloured cement (CC)
k. Air-entraining cement (AEC) and

l. Hydrophobic cement (HpC)

According to the Bureau of Indian Standards (BIS). These are five certified types of cement and they include Portland cement, Portland blast furnace Cement, Sulphate-resisting Portland cement, Masonry Cement and Portland pulverized fuel ash Cement (BIS 2005).

2.3.3 MANUFACTURE OF CEMENT

Portland cement is made using raw materials that are high in calcium carbonate (calcareous) and aluminum silicates (argillaceous). Common calcareous materials used are cement rock, limestone, marl, chalk and seashells. The argillaceous materials used are typically clays, shales, slates and blast furnace slag. From these raw materials, the key ingredients for cement can be obtained: calcium oxide (lime), silicon dioxide (silica), aluminum oxide (alumina) and iron oxide. Small amounts of other chemicals are also used. There are two main manufacturing processes: the dry process and wet process. Both methods are used to produce the Portland cement clinker which is then ground into the final cement powder.

Dry Process

The dry process for cement making is used when the limestone and clay raw materials are hard and challenging to pulverize. This dry method is slower and yields a costlier final cement product compared to the wet process. In the dry process, limestone and clay are separately crushed into a fine powder. The two powders are then combined together and water is added to form a thick paste containing about 14% water. The paste is formed into cakes which are dried. The dried cakes are fed into a rotating kiln where they undergo calcination at very high temperatures in the range of 1400-1500°C. The cakes are transformed into cement clinker through initial fusion and sintering reactions at this temperature. Ferric oxide acts as a flux to lower the fusion point since its melting point is lower than that of the other oxides. After clinker production, aeration is commonly done which leads to some absorption of moisture and carbon dioxide. Moisture absorption increases cement setting time, while carbon dioxide absorption decreases the setting time.

After clinker is produced in the kiln, it is quickly cooled down. Rapid cooling maintains the unstable compounds and dispersed solids that are formed when heating the clinker to high temperatures. These transient phases occur as some clinker minerals partially dissolve into others at the peak kiln temperatures. The fast-cooled clinker is then sent to tube mills for grinding, where 2-3% gypsum is added during the process. Cement is commonly stored in 50 kg bags after grinding. The purpose of adding gypsum is to coat the surface of the anhydrous cement particles. This coating interferes with the hydration reactions when water is added to cement. It effectively slows down and delays the setting time of the cement. So the gypsum serves to retard and control the set after cement is mixed to make concrete (Duggal 2017).

Wet Process

The main steps in wet process cement production are mixing, burning, and grinding. The crushed raw materials are first mixed with a small amount of water in a ball mill. As the mill rotates, the steel balls inside grind the materials into a slurry with water. This slurry is stored in silos where the proportions of compounds are adjusted to obtain the target chemical composition. The adjusted slurry, containing about 40% water, is fed into a rotary kiln. In the kiln, the slurry loses moisture and forms lumps that are heated to 1500-1600°C. At this high temperature, the lumps transform into cement clinker. After clinkering, the clinker is cooled then ground in tube mills.

During grinding, around 3% gypsum is added to the clinker. The final cement powder is stored in silos until needed for cement or concrete production (Duggal 2017).

2.3.4 ENVIRONMENT IMPACT OF CEMENT

Environmental and health effects of pollutants resulting from the cement industry include;

i. **Gases and VOCs:** Manufacturing cement clinker, which contains calcium carbonate, leads to various gaseous pollutants being released into the air. Inside rotary kilns, the raw materials are fired up to very high temperatures to induce chemical reactions that convert the calcium carbonate to calcium oxide (Gibbs et al., 2023). This process, known as calcination, gives off carbon dioxide as a byproduct. Calcination occurs at the cooler upper end of the kiln in the 600-900°C range. Sulfur oxides and nitrogen oxides are also produced from the kiln heating processes and fuel combustion. The amount of sulfur dioxide depends on the sulfur in the raw materials and fuels. Nitrogen oxides form from the nitrogen in the combustion air and fuel burnt (Zimwara et al., 2012). Volatile organic compounds (VOCs) get directly emitted into the air through evaporation from stored industrial chemicals, fuels, and certain cement production processes. Incomplete fuel combustion also significantly contributes VOC emissions (Gibbs et al., 1997)

ii. **Dust:** Dust emissions in cement production primarily come from the raw material mills, kiln system, clinker coolers, and cement grinding mills. A key feature of these processes is that hot exhaust gases or air pass through crushed material, creating a finely dispersed mixture of gas and particles. The composition of the dust particles produced depends on the source - raw materials, partially heated raw meal, clinker, or cement. For example, dust from the raw mill contains ground limestone and clay particles. Dust is generated at each stage where the material is moved and heated in the gaseous exhaust stream. Controlling dust emissions is important to minimize environmental impact. Common abatement techniques include electrostatic precipitators, baghouse filters, and wet scrubbers (Devi et al., 2017).

iii. **Noise:** Noise is generated throughout cement production from material crushing to product dispatch. Key sources are the heavy machinery and fans used in preparing raw materials, clinker production, cement grinding, and product storage and shipment. Milling, fracturing, screening processes create significant noise. Mitigation methods include equipment maintenance, upgrades, noise barriers and isolation. Monitoring noise levels helps identify issues (Devi et al., 2017)

iv. **Wastewater:** Rainwater running through outdoor petroleum coke, coal, and waste storage areas can collect pollutants. Potential contaminants include sulfates, toxic metals, and high dissolved solids if contacting groundwater. Storm water management like diverting clean runoff, treating contaminated water, and covering piles helps prevent environmental discharges (Arachchige, U.S.P.R. et al 2019).

v. **Bad odour:** The gases emitted during cement production can cause foul odors. Also, since the manufacturing impacts plants and animals, their decay can indirectly cause offensive smells (Devi et al., 2017).

2.4 SUPPLEMENTARY CEMENTITIOUS MATERIALS

SCMs substitute for either cement clinker during cement production or cement during concrete production. SCMs are commonly used in concrete for economic and performance advantages. Lately, interest in SCMs has grown due to their lower carbon footprint compared to cement clinker manufacturing (Van den Heede and De Belie 2012). In some areas, demand for traditional SCMs like fly ash and slag exceeds supply (Scrivener and Kirkpatrick 2008). Global concrete demand is projected to increase substantially, so alternative SCM sources are required along with clinker to meet environmental regulations. Production of fly ash and slag can't satisfy future demand alone. Promising alternative SCMs include industrial wastes and natural minerals. Characterizing and producing new SCMs faces challenges. Empirical testing of diverse materials is inefficient (Scrivener and Kirkpatrick 2008) and standard test methods may not suit some alternatives. This passage provides insights into characterizing SCMs for better performance prediction. Developing alternative SCMs will ensure supply of quality, eco-friendly concrete in the future.

2.4.1 COMMONLY USED SUPPLEMENTARY CEMENTITIOUS MATERIALS

i. FLY ASH

Coal fly ash is a fine powder collected from coal power plant flue gases. It has appealing properties as an SCM and has been used in concrete since the 1930s in the US (Davis et al., 1937). Fly ash use is now standardized worldwide. Composition and properties are governed by standards like ASTM C618, EN 450, AS 3582.1, CSA A3001, and others. ASTM C618 classifies fly ash as Class C or Class F based on oxides. However, fly ash chemistry and properties are complex and variable, requiring detailed analysis to optimize use (Bouzoubaâ et al., 1999). In concrete, fly ash enhances long-term performance but can reduce early strength. Typical substitution rates are up to 30% of cement by fly ash but high volumes up to 70% are possible. Fly ash provides rheology benefits but delays strength development. Detailed characterization is key to fly ash being an effective SCM for modern concrete.

ii. GROUND GRANULATED BLAST-FURNACE SLAG

Blast furnace slag (BFS) is a byproduct from iron production in blast furnaces. It forms by fusion of iron ore silica/alumina gangue compounds with calcium and magnesium oxides from the furnace flux and coke ash. This occurs at 1300-1600°C. The molten slag floats on the iron and is tapped periodically. Slag leaves the furnace around 1450°C and is either air cooled slowly or rapidly water granulated. Air cooled slag is crystalline and poorly reactive. Water granulated BFS is glassy with max 5mm size. The high glass content of granulated BFS enables its latent hydraulic reactivity which makes it an excellent SCM when ground (Hooton 1987). Slow cooling yields crystalline unreactive slag while fast water granulation gives glassy slag that is a reactive SCM precursor.

iii. SILICA FUME

Silica fume, also called microsilica, is a byproduct from silicon and ferrosilicon alloy production in electric arc furnaces using high purity quartz and carbon. It has very high amorphous silica content (>90%) and extremely fine spherical particles (<1 um, avg 0.1-0.2 um). Its surface area is 15-30 m2/g and density 2200-2300 kg/m3. The low bulk density (130-430 kg/m3) necessitates densification for transport. Provided densification isn't excessive (under ~700 kg/m3), particles redisperse in concrete mixers, especially with superplasticizers (ACI 234R-06 2006). Moisture-pelletized silica fume must be ground to cement fineness for use as an SCM, but has been successfully interground in blended cements in Canada. Better characterization of silica fume particle dispersion is needed, as processing impacts performance.

iv. CALCINED CLAY

Metakaolin is costlier than other common SCMs due to limited regional sources and energy-intensive production. Therefore, interest is growing in using non-kaolinite or blended kaolinite clays as a cheaper alternative to metakaolin (Fernandez et al., 2011). While impure clays are widely available, calcined versions have poor pozzolanic reactivity compared to metakaolin (Amboise et al., 1985; He et al., 1995) restricting their use in concrete. Major challenges are determining performance factors and enhancing reactivity. Appropriate characterization is key to addressing both challenges. Though abundant, calcined clays from impure sources react poorly versus metakaolin. Detailed analysis is critical to improve reactivity, identify performance factors, and enable the use of calcined clays as cheaper metakaolin alternatives**.**

2.5 LIMESTONE CALCINED CLAY CEMENT (LC3)

According to research by Zunino et al., 2021, limestone calcined clay cements provides a better chance of reducing the clinker factor of the cement industry at a global scale thereby conserving 40% of CO2 in comparison with the traditional Portland cement. The soundness and wide use of the limestone calcined clay combination presents the chances of use and adoption in markets where blended cements (i.e. LC3) or mineral additions (as LC2) are normally used. The kaolinite content in clay is a very important parameter for determining the suitability of natural clay for LC3 production. In this article, the authors explain the scientific base of the LC3 technology and describe some of its properties and performance as a cement. The earth crust consists of only eight elements which makes up 98% of it (I.e. O, Si, Al, Fe, Ca, Na, K, and Mg). therefore, any suitable material will be based on the SiO2-CaO-Al2O3 ternary diagram. In respect to this, material, such as calcium (sulfo)aluminate cements which requires a high aluminum content in it are not abundant due to cost and availability of minerals containing more alumina than silica thereby making Portland cement based to be dominant. There are three major materials that has proven to be an outstanding SCMs today. Ground-granulated blast-furnace slag (GGBS) and coal fly ash are by-products that can be used to partially replace cement in concrete. However, the total amount of these materials available is only about 15% of the amount of cement currently being produced. So while slag and fly ash can reduce the need for cement to some degree, there is a limit to how much they can offset cement production based on their limited availability (International Energy Agency 2018) and the availability of the SCMs tend to decrease in the future. Coal fly ash availability is declining as coal power plants are replaced by cleaner energy sources (Scrivener et al., 2016) and this leads to less slag as more steel is recycled and more environmentally friendly. The third major SCM is limestone which is available in large quantities but above a substitution level of 10 to 15% tend to reduce the properties of cement. Clay is a very reactive pozzolan when calcined between the range of 700 to 850°C and it is sufficient enough to reduce the clinker content in cement. LC3 refers to a type of cement made by partially replacing clinker with limestone and calcined clay. The calcined clay provides alumina that reacts with the added limestone to form additional hydration products that give strength to the cement. This synergistic reaction between the clay and limestone allows less clinker to be used, resulting in a lower carbon footprint for LC3 cement compared to traditional Portland cement (Zunino and scrivener 2021).

In addition, the high reactivity of calcined clay and the synergy between calcined clay and limestone allow high substitution levels (50%) as well as obtaining similar strength to the traditional Portland cement. There are different types of clay around the world with different quantity of kaolinite in them but among the major types of clay, kaolinite or 1:1 clay is most reactive after it is being calcined (Fernandez et al., 2011). Clay particles are made up of tens to hundreds of layers, composed of alternating silica tetrahedral and alumina octahedral sheets (Sabir et al., 2001; Alujas et al., 2015). The three major abundant clay types are kaolinite, illite, and montmorillonite (smectite). Kaolinite has a layer structure of one silica and one alumina layer while in illite and montmorillonite, the layers are composed of two silica layer.

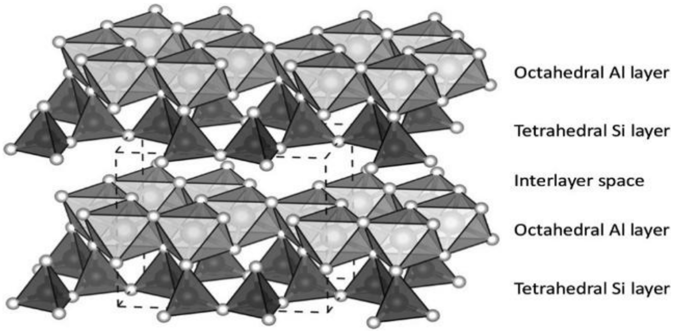

Fig 2.2: Crystal structure of kaolinite, showing layer of octahedral aluminum sites with a layer of tetrahedral silicate in 1:1 structure (Momma and Izumi 2011)

The important factor that influence the strength of LC3 cement is the metakaolin content of the calcined clay used (Avet and Scrivener 2018) while other associated minerals that are found in kaolin do not contribute in the strength of LC3. Also, the fineness of the limestone fraction can be developed to achieve specific strength requirement. Using higher grade clays in LC3 cement provides only a small improvement in performance. This is because even with lower grade clays, there is unused clinker and metakaolin left over due to insufficient space for the hydration products to form. The hydration reactions are limited by the amount of space available, so the reactivity of the clay makes little difference. There is minimal benefit to using scarce high grade clays rather than more abundant lower grade clays in LC3 cement. (Avet and Scrivener 2018; Scrivener et al., 2019; Briki, Y., 2020). Therefore, the metakaolin content should be in the range of 40 to 60% in terms of cost or performance. the ideal range in terms of cost/performance is between 40 to 60% metakaolin content. Clays with lower kaolin contents is enriched by air separation of the finer fraction (Zunino and Scrivener 2020). The grade of a clay depends on its kaolinitic content. The reactivity of other common SCMs compared to calcined clay is very low whereas the combination of limestone and calcined clay results in a reduction of the clinker in cement without affecting the materials properties. The alkali content is another important aspect to look into during the production of LC3. A rise in the total alkali in LC3 can increase the early age strength, so this alkali content was modified by the addition of KOH to the mixing water. The sulfate balance of LC3 is related to the surface area provided by the addition of calcined clay and limestone. Thus, when the LC2 blend is correctly sulfated for its specific surface area, it becomes useful in cement at different substitution level without the risk of undersulfation (Zunino and Scrivener 2019).

An important area that needs attention is the workability. The high specific surface of calcined clays brings about an increase in the demand of water in LC3 compared to OPC. Slump retention is another aspect to be taken into account, as LC3 might tend to lose slump faster than OPC-based materials. While this is also important in other SCMs, there is a chance of providing new technological solutions to unravel this problem by combining two polycarboxylate ether (PCE) molecules with different degrees of grafting allows for obtaining good retention up to 3 hours, compared to a commercial PCE high-range water-reducing admixture, without an increase of the total amount of admixtures that can slow it.

In the United States, the ASTM C595-19 standard for blended cements covers LC3 -50. An LC3 -50 production with a 2:1 clay to limestone ratio would be indicated as type IT(P30) (L15). But in Europe, the situation is different, as the EN 197-122 standard only allows the replacement of 35% of the clinker. Under this standard, an LC3 -65 formulation would be denoted as CEM II/B-Q-L. However, moves are underway to introduce a CEM II/C category in EN 197, allowing commercialization of LC3 -50. But a challenge introduced by ASTM C595 is that the strength test is conducted in samples prepared with an amount of water of 100 to 115 for its flowability, without using admixtures. In the European standard, samples are prepared at a constant water-binder ratio (w/b). Because LC3 has a demand of water than OPC.

2.5.1 HYDRATION REACTIONS IN LC3

Metakaolin react with CH produced obtained from cement hydration to form C-A-S-H (Avet and Scrivener 2018; Antoni et al., 2012) thereby contributing to strength by space filling

$AS_2 + 3CH + 6H \rightarrow C\text{-}A\text{-}S\text{-}H + C_2\ ASH_8$ Eqn. (2.1)

The formation of calcium monocarboaluminate (C_4AcH11, Mc) and hemicarboaluminate ($C_4Ac_{0.5}H_{12}$, Hc) instead of monosulphoaluminate (C_4ASH_{12}) as AFm phases which occur when limestone is mixed with OPC system is related to the bulk molar CO_2/Al_2O_3 and SO_3/Al_2O_3 ratios of the system (Matschei et al., 2007).

$C_3A + 0.5Cc + 0.5CH + 11.5H \rightarrow C_4\ Ac_{0.5}H_{12}$ Eqn. (2.2)

When an additional source of amorphous alumina is introduced in the system, such as metakaolin, calcite can furtherly react with these aluminates to form more Mc and Hc phases. This so-called synergic effect of limestone/metakaolin leads to the formation of an increased number of hydrates (Hc and Mc) which further fills in the porosity, increasing strength and reducing the permeability of the material (Antoni et al., 2011; Scrivener et al., 2019; Antoni et al., 2012).

$AS_2 + 0.5Cc + 3.5CH + 8.5H \rightarrow C4Ac_{0.5}H_{12}$ Eqn. (2.3)

Reactions 1 and 3 consume calcium hydroxide. Although for clinkers with alite contents above 60% and calcined clays with kaolinite in the range of 40 to 60%, calcium hydroxide remains unreacted in the long term. Pore solutions show a pH of more than 13 (Avet and Scrivener 2018).

2.5.2 PRODUCTION OF LC3 CEMENT

Kaolinitic clays calcined between the temperature of 600 and 850°C results in the removal of OH group (dehydroxylation) from its crystalline structure to give a disordered structure metakaolin

(Fernandez et al.,2011; Ambroise et al.,1994). It has been observed that at a temperature between 600 and 700°C, complete removal of OH is achieved, however, full calcination is ideally at a temperature range between 700 and 850°C where the maximum reactivity is achieved is noticed. Beyond this temperature range, there will be a decrease in the specific surface area due to sintering which will have negative impact on the reactivity. Flash calcination exposes the material to much higher temperature gradients (103 –105 °C/s) over short periods of 0.2 to 1 seconds (Teklay et al., 2014), which leads to a higher specific surface area than calcination in a rotary kiln due to the rapid release of water vapor (Bridson et al., 1985). However, flash calcination has been found to produce calcined clay with slightly higher reactivity compared to static or rotary calcination (Salvador 1995) However, this can only be differentiated during the first hours of hydration (Scrivener et al., 2019).

In laboratory conditions, the constituents of LC3 are usually ground separately in open circuit grinding configuration but the common process of grinding cement in cements plants is based on intergrinding of cement constituents in closed circuit units. The difference between separate and intergrinding is that during intergrinding the components interact inside the mill. These interactions are primarily due to their differences in grindability (De Weerdt 2007).

In LC3, calcined clay and limestone have higher grindabilities (softer particles) compared to clinker (harder particles). Upon intergrinding of LC3, clinker tends to remain concentrated in the coarse fraction, which may compromise the early age strength of LC3. Calcined clay and limestone become much finer (Zunino 2020) which may have a negative effect on workability. But generally, the highest reactivity is obtained when clinker is ground separately from limestone and calcined clay. In LC3, grounding aids (Gas) have significantly increased the yield of the grinding process of calcined clays. The use of GAs increases the efficiency of the dry separation process of the material (Zunino and Scrivener 2020). Alkanolamines also promote the formation of Hc and Mc in LC3 systems, increasing strength (Zunino and Scrivener 2020).

The use of LC3 are highly useful for reducing alkali silica reaction (ASR). Conventionally, SCMs reduce ASR in concrete (Shehata and Thomas 2000; Duchesne and Bérubé 1994) due to its lower alkalinity in pore solution (Shehata, et al., 1999). Globally, one of the important factor about the durability of concrete is as a result of steel corrosion due to chemical attack of chloride ions and this is governed by the microstructural features of the cement paste which rely on the solid phase assemblage, the pore structure, and the pore solution's composition (Sui et al., 2019). LC3 concrete behaves in a similar feature as the OPC concrete as carried out using the freezing and thawing resistance tests with deicing salts of LC3 concrete specimens (non-air-entrained) which were conducted following the procedure of the Swiss standard SIA262/1 (immersed in 3% NaCl solution, temperature variation between –15°C and 15°C).

2.6 RECENT PROGRESS IN LIMESTONE-CALCINED CLAY CEMENT (LC3)

In this paper, a comprehensive review of previous research on LC3 is carried out with the purpose of describing the aspects that lacks investigation and the ones prior for the future work which includes nano-modification, fiber reinforcement, and durability enhancement, also and the steps to be undertaken to improve their performance under normal and aggressive environmental conditions, restrictions, challenges related with the new novel cement (i.e. LC3) by Abdelaziz et al., 2023. SCMs are important materials to decrease the amount of CO_2 in the cement industry. LC3 reduces the amount of CO2 emitted by 30% compared with OPC and is feasible alternative for future green cement. thus, it shows the properties of a good and promising cement. At a high substitution level, it sustains a good compressive strength (Yu et al., 2021). The durability and the mechanical properties of LC3 cement is as a result of the reactivity of the calcined clay and the limestone effects (Long et al., 2022; Dhandapani et al., 2018). Clay with high kaolinite content is available in the earth crust and when the calcined clay is combined with limestone it gives physiochemical properties and better durability compared with the traditional portland cement at a substitution of 50% clinker (Scrivener et al., 2018; Avet et al., 2016; Alujas et al., 2015; He et al., 1995; Avet and Scrivener 2018). The four criteria to meet the requirement of any new technology include the economic viability, technical feasibility, raw material accessibility, and cheap capital investment (Baghban and Mahjoub 2020) and the LC3 satisfies the above requirement. Although, the combination of calcined clay and limestone brings about a decrease in the workability of the cement due to the large surface area and the use of superplasticizer and viscosity-modifying admixture could solve this workability issue (Baghban and Mahjoub 2020). The table below summarizes the previous research work investigated the LC3 binder performance.

Table 2.2 Previous research work on LC3 binder performance

Research	**Total Rep. %**	**Mixing Proportions %**				**Water**	**Fiber**	**Compressive Strength [Mpa]**	**Matrix**	**Notes**
		OPC	**C.C**	**L.S**	**GYPSUM**					
Alghamdi et al.	60	40	40	20	0	W/b = 0.5		13:29.8	LW Mortar	Autoclaved aerated concrete waste (AACW) as fine aggregate (LWA).
Lin et al.	45	55	30	15	0	W/b = 0.5		100:128.2	Paste and Mortar	replacement ratio of nanosilica (1 wt% and 2 wt%) of

										the cement content
Long et al.	50	50	40	5	5	W/b = 0.45	1% steel fibres	56	Mortar	
Purushotham et al.	50	50	30	15	5	0.4 w/c		54.57	Mortar	
Wang et al.		50	30	15	5	W/b = 0.192	2% PE fibres	117:136	HSSHCC Mortar	16.67% of total binder was replaced by SF, only OPC in the binder system was substituted by LC3. • The w/b of the LC3 mixes was a bit increased to 0.204. An additional increment of water quantity was avoided to limit the consequential impact on the mechanical properties of the LC3 composite.
Kavya et al.	50	50	30	15	5	w/c = 0.46		42.89	Concrete	
Bernal et al.]	48	52	30	15	3	W/b = 0.4		62	Paste and Mortar	
Santhanam et al.	50	50	31	15	4			45		
	35	65	30:2	3.5:2		W/b = 0.45			Concrete	

	46.6	53.5	5	0	1.5			43:52		
Dhandapani and Santhanam	46	51	31	15	0	W/b = 0.3, 0.4, 0.5		63:30	Concrete	
Pillai et al.	50	50	31	15	4	w/b = 0.4, 0.45, 0.5		56.7: 38.8	Concrete	
Dhandapani et al.	50	50	31	15	4	w/b = 0.42		43.7	Mortar	
	50	50	31	15	4	w/b = 0.4, 0.45, 0.5		55:45	Concrete	
Dhandapani et al.	45	55	30	15	0	w/b = 0.45		42.1	Mortar	

C.C: calcined clay, **LS:** limestone, **w/c:** water to cement ratio, **w/b:** water to binder ratio

The unavailability of other SCMs material cannot be ignored when considering the success of the reduction of C02 in clinker. Although, several sources of this SCM has been looked into but there is no enough quantity that is required for the massive production of cement. Clays with high kaolinitic content has proven to be excellent SCM due to its reactivity after it is being calcined and it is widely available in abundant quantity. Furthermore, Limestone has shown to be a good SCM material due to his high availability, low price and has a very low amount of energy consumption during the grinding process (Scrivener et al., 2021)

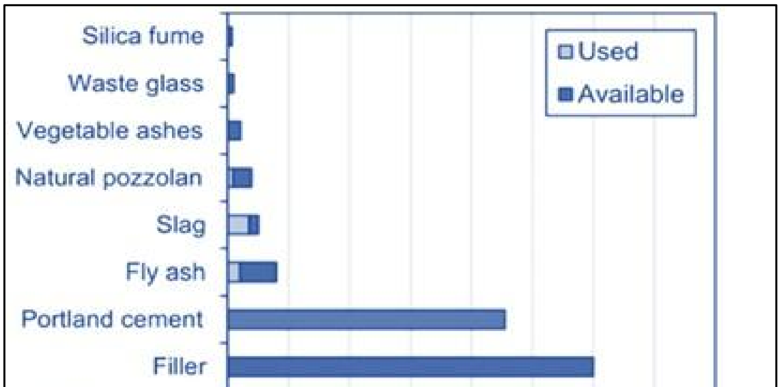

Fig 2.3: Estimated available quantities of SCM and the amount of produced cement per year (UN Environment et al., 2018)

The concepts behind combining limestone with calcined clay is that limestone promotes clinker hydration facilitates hydrate nucleation by providing surface area, and controls hydration reactions in the presence of aluminates (Purushotham Reddy et al., 2021). The amount of the limestone which reacted relates to the purity of the aluminate source. The strength developed in LC3 depends on the high kaolinite content in clay and which not necessary for adequate workability and early-age strength. The combination of calcined clay and limestone have led to the disclosure of a new novel cement, typically consisting of 50% clinker,30% calcined clay, 15% limestone, and 5% gypsum (Scrivener et al., 2018; Yu et al., 2021).

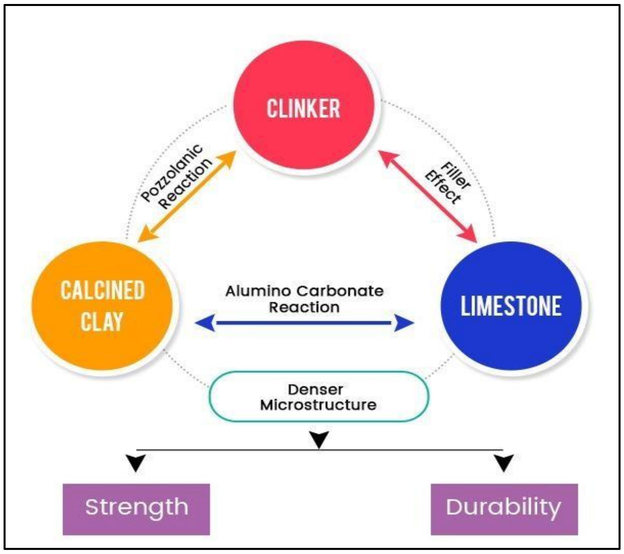

Fig 2.4: The Main Reactions in LC3 Matrix

An interesting analysis was carried out on the rheology of LC3 binder (Ferreiro et al., 2017). They assessed the workability and strength performance of various substitute levels of OPC (up to 65%) and came up with the conclusion that the calcined clay content strongly affects workability. Also the LC3 paste cohesion and viscosity rises as a results of the addition of small quantity of clay (Kawashima et al., 2014) and noted that the clay addition promotes the rate of pastes recovery, usually at early ages. Although, as the hydration process continues, that promoted effect decreases (Kawashima, et al., 2013). Additionally, bleeding is not controlled by only limestone fill and there are no rheological differences between cement paste containing limestone fill and plain OPC that was accounted (Santos et al., 2017). Metakaolin is recommended for obtaining low slump. The influence of different SCM such as clay and fly ash on rheological properties was examined and came to the conclusion that clay improved the stability shape of cement pastes significantly (Tregger et al., 2010).

The use nano admixtures such as nano silica plays a crucial role in improving the early-age strength of LC3 binder. By so doing, a research was carried out on the effect of combining 1% and 2% nano-silica on early strength and carbonation resistance of LC3 binders and came to the conclusion that the nano-silica addition remarkably promotes the hydration of LC3 binder (Lin et al., 2022).

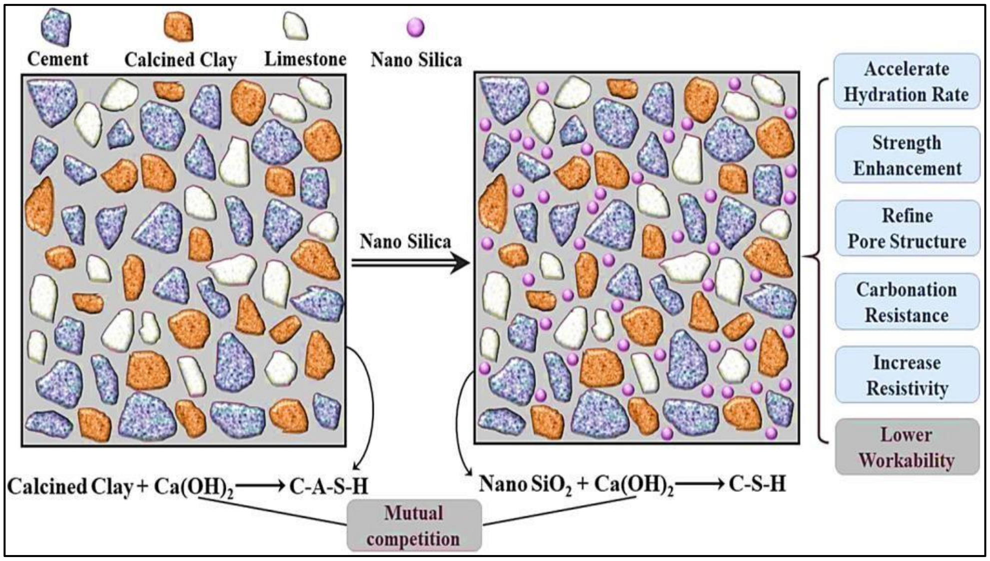

Fig. 2.5: The effect of Nano-silica particles on LC3 matrix (Lin et al., 2022)

The high-strength cementitious composites (HS-CC) are expensive and it is harmful to the environment due to the high cement content. Furthermore, due to the very low w/b ratio, a significant amount of cement clinker remains unhydrated (Wang et al., 2021; Huang et al., 2017; Yu and Leung 2020). High-strength strain-hardening cement-based composites (HS-SHCC) exhibit higher mechanical and durability properties but the high cement content results in increase of the emission of CO2, excessive hydration heat, and serious autogenous shrinkage. Consequently, the applicability, serviceability, and durability of HS-SHCC can be negatively affected. LC3 was used to obtain sustainable HS-SHCC (Yu and Leung 2020). The substitution of LC3 resulted in large energy consumption during mixing and decrease the setting time, plain matrices. Nevertheless, the compressive strength of the plain matrices was slightly reduced with the LC3 substitution, the flexural strength accounted for was improved.

An experimentation was carried out while making SHCC through a combination of basalt fiber with an ultra-high volume LC3 blend and results shows that the enhanced mix has a 1% tensile strain while crack width has been controlled to a low value of 20 microns and below (Das and Leung 2023). The ultrahigh-volume LC3 of 80% by weight of binder was utilized to develop polyvinyl alcohol fiber-reinforced SHCC with sufficient compressive strength and high tensile strength which supports the possibility of producing sustainable fiber-reinforced LC3-SHCC (Yu and Leung 2020).

The usefulness of recycling the waste aggregate such as slags, glass, ceramic, incinerated bottom ash, and recycled concrete have proven to be remarkable in the LC3 without affecting the technical standards. Although, combining waste aggregate should correspond with physical and mechanical standards, such as shape, density, size, and water absorption (Alghamdi et al., 2023; Shoukry et al., 2022). Under severe conditions like fire, LC3 exhibits a distinctive strength retention efficiency. Limestone and calcined clay with 30% total replacement tends to reduce sulfate attack (Favier and Scrivener 2018). A research on the resistance against chloride penetration of clay with intermediate to high kaolinite content was carried out and come to the conclusion that chloride resistance of intermediate kaolinite clay was compared with the high kaolinite clay which shows a promising result of producing LC3 that is developed to resist chloride attack as well as decarbonizing the clinker content by 16 to 30% compared to OPC (Maraghechi et al., 2018). Furthermore, the tested LC3 mixes showed comparable resistance to chloride penetration and reduces CO2 emissions than fly ash binder of similar strength. Consequently, the structures made with LC3 and fly ash systems can have a successful life span compared with only OPC system.

2.7 INFLUENCE OF CALCINED CLAY-LIMESTONE RATIO ON PROPERTIES OF CONCRETE WITH LIMESTONE CALCINED CLAY CEMENT (LC3)

The research explains the validity of the use limestone calcine clay cement in obtaining a durable concrete put together by Dhandapani and Santhanam 2020. In this article, the combination of the low grade calcined clay and limestone was shown to give a strength that is identical to the traditional Portland cement (Dhandapani et al., 2018) and the durability of this binder made of limestone-SCM composition is as a result of the usefulness of the limestone for the dilution and produce a coactive interaction with the aluminosilicate based SCM (Avet and Scrivener 2018) such as fly ashes, slags and calcined clay which are widely recognised (Li et al., 2018). This hydration and hardening properties on cement paste with binary and ternary mixes involving limestone was conducted experimentally as well as the impact of calcined clay-limestone ratio on strength development and durability performance was also investigate.

The research involves the use of ordinary Portland cement (OPC) as a control mix while Limestone and calcined clay (with 50–60%kaolinite content) obtained from Bhuj, Gujarat and Ultratech plant, Ariyalur with a 42% CaO were used to produce the ternary binder compose of OPC, limestone, calcined clay and gypsum as well as the comparison with a combination made of fly ash and limestone.

SCM type	Mix ID	OPC	SCM	LIMESTONE	GYPSUM
OPC	OPC	100	_	_	_

Table 2.3: Binder composition used in the study (Dhandapani and Santhanam 2020)

Class F	FAF30	66	30	3.5	0.5
	FAF42	54.5	42	3	0.5
	FAFL10	54.5	34	11	0.5
	FAFL15	54.5	30	15	0.5
	FAFL20	54.5	25	20	0.5
Calcined clay	CC30	65.0	30	3.5	1.5
	CC42	53.5	42	3	1.5
	CCL10	53.5	34	11	1.5
	CCL15	53.5	30	15	1.5
	CCL20	53.5	25	20	1.5

Limestone content includes calcite content in OPC + limestone amount added

The binder content and w/b were maintained at 360 kg/m^3 and 0.45 respectively across the concrete made of crushed granite as the coarse aggregate with a maximum size of 20mm and a well graded river sand as fine aggregate which is kept at a fixed ratio of 60:40 by weight. A slump of 80-120mm was achieved with the use of a plasticizer made of polycarboxylic ether (PCE).

The total amount of heat release in these binder systems indicates the difference between binary and ternary combinations. An increase in the amount of SCM, i.e. fly ash or calcined clay reduces the total heat release by 7 days and the reduction was higher for increasing fly ash quantity than calcined clay.

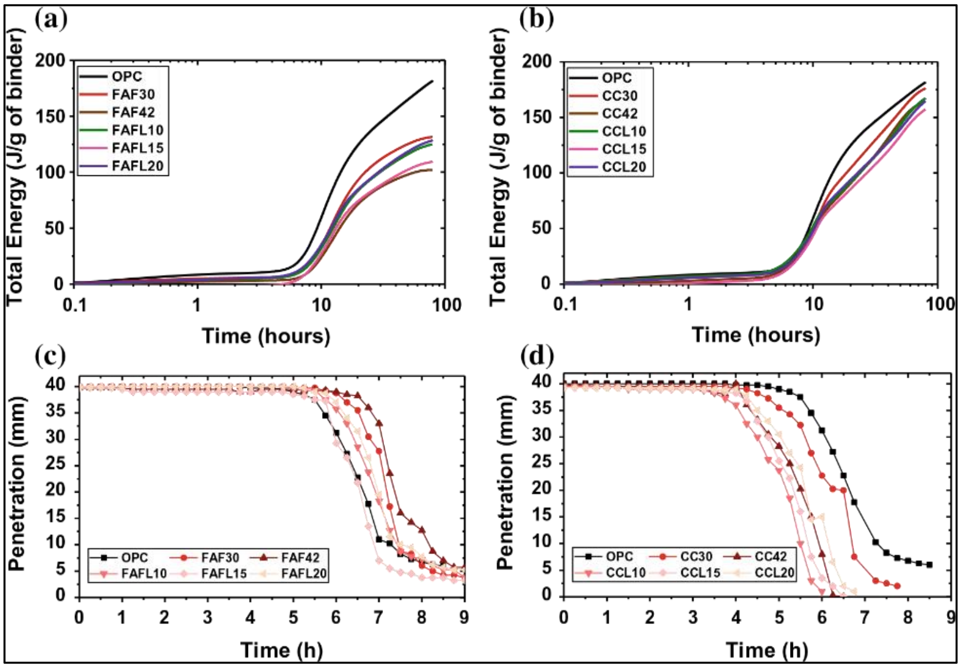

Fig 2.5: Hydration heat of fly ash (a) and calcined clay (b) mixes and setting characteristics of fly ash (c) and calcined clay (d) mixes (Dhandapani and Santhanam 2020)

Limestone-flyash combinations showed higher heat release than FAF42 indicating the positive influence of limestone on early hydration characteristics. The change in heat release was not notable between CC30 and CC42, and only a slight difference was observed in the total heat release due to limestone addition in calcined clay binders. Also in the setting properties, the penetration resistance decreases with increasing quantity of fly ash. The acceleration in hydration properties due to the addition of limestone was able to shift the setting characteristics of fly ash binders close to the plain Portland cement. An increase in calcined clay quantity from CC30 to CC42 resulted in early hardening, and the Vicat resistance was further accelerated in the presence of limestone unlike in the fly ash mixes. In fly ash mixes, the addition of limestone was found to be favorable in decreasing delay in setting characteristics caused by a higher quantity of fly ash addition as a cement substitute. The effect in strength development due to limestone addition was limited and a major influence of the choice of SCM (i.e. calcined clay or fly ash) on the strength development potential can also be noted. The calcined clay-limestone binders could accommodate up to 15% limestone and produce comparable strength development to OPC all ages**.**

The difference in chloride resistance were limited for calcined clay binders irrespective of the quantity of limestone. In fly ash limestone combination, the 28days transport Properties were consistently reduced with the addition of limestone powder. The combined influence of both initial transport resistance and the higher ageing coefficient can be rationalized a slower chloride build-up at steel surface for fly ash and calcined clay concretes compared to OPC.

2.8 IMPACTING FACTORS AND PROPERTIES OF LIMESTONE CALCINED CLAY CEMENTS (LC3)

This paper gives detailed information about the main factors influencing the performance of limestone calcined clay cements by Scrivener et al., 2018**.** The interest in reducing CO2 emissions has led to the development of LC3 or limestone calcined clay cement, which substitutes limestone and calcined clay together to replace Portland cement (Scrivener and Favier 2015; Martirena et al., 2017). Using a clay containing just 40% calcined kaolinite can achieve comparable strength to ordinary Portland cement (OPC) after about 7 days of curing. This paper presents key findings on LC3 cement and concrete from years of research at the Laboratory of Construction Materials, École Polytechnique Fédérale de Lausanne, Switzerland. It begins by examining suitable clays and their characterization. It then continues with critical processing factors, including optimizing calcined clay reactivity through calcination parameters. The paper further explores the hydration, mechanical properties, and durability of LC3 systems.

The kaolinite content is an important factor for choosing appropriate clays. The kaolinite percentage can be determined through thermogravimetric analysis (TGA) using the tangent method (Scrivener et al., 2016). The dehydroxylation of kaolinite AS2H2 takes place in the temperature range of approximately 400°C to 650°C (Shvarzman, et al 2003; Ptáček et al., 2014; Kakali et al., 2001). This dehydroxylation leads to the creation of amorphous metakaolin phase AS2 according to the equation;

$$AS_2H_2 \rightarrow AS_2 + 2H \qquad \text{Eqn. (2.4)}$$

The water released when kaolinite dehydroxylates enables calculating the kaolinite percentage. Thermogravimetric analysis (TGA) is also performed on calcined clays to detect any water loss, which would indicate insufficient calcination. The effect of secondary phases on quantifying kaolinite content was studied to ensure they do not significantly impact the measurement. Some impurities in clays lose water or carbon dioxide during calcination, but most do not interfere with kaolinite dehydroxylation. Of the common impurities in kaolinitic clays, goethite and gibbsite dehydroxylate at lower temperatures (around 250-350°C) compared to kaolinite (Zhu et al., 2010; Ruan and Gilkes 1995; MacKenzie 1957). More than 50 different kaolinitic clays were analyzed by thermogravimetric analysis (TGA) in triplicate for LC3 testing. The average deviation in measured kaolinite content was 1.0% between the three tests for each clay. This demonstrates that TGA provides good reliability and reproducibility for quantifying kaolinite percentage in clays. Another method for determining kaolinite percentage is X-ray diffraction (XRD) with Rietveld refinement. However, quantifying kaolinite by XRD is very difficult due to kaolinite's layered structure and preferred orientation. XRD-Rietveld was performed on 40 clays and compared to TGA results. Although a general 1:1 trend is observed, significant differences exist in some cases. The maximum deviation was 29.8% and average absolute difference was 6.1% between XRD and TGA. Due to these inconsistencies, TGA is preferable over XRD for quantifying kaolinite content.

Thermogravimetric analysis (TGA) can determine the extent of clay calcination but does not give any data on the reactivity of the calcined clay. The R3 pozzolanic test was developed as an indicator of calcined clay reactivity (Avet et al., 2016), also predicting mortar strength well even at later ages. The test evaluates calcined clay reactivity in model systems containing portlandite, calcined clay, and limestone with sulfate and alkali levels simulating blended cements. Two methods can assess the reactivity: monitoring heat release by isothermal calorimetry at 40°C (fastest at 24h, best for strength prediction), or measuring bound water content (slightly longer but only needs an oven).

2.8.1 INFLUENCE OF THE METHOD OF CALCINATION

Calcined clay suitable for industrial use can be produced through different heat-based processes. Rotary kiln calcination and flash calcination seem to be the most viable options for large-scale production. The specific calcination technique chosen will determine the ideal maximum temperature and duration of heating that should be used. These calcination parameters need to be properly calibrated to guarantee the reactivity of the resulting calcined clay is optimized. Flash calcination exposes the clay to incredibly fast heating rates (103 to 105°C per second) over very short timespans between 0.2 to 1 second (Teklay et al., 2016). This generates a larger surface area compared to rotary kiln calcination due to the sudden release of water vapor from the clay (Bridson et al., 1985). The rapid dehydration causes the material to become highly porous.

Research has found that flash-calcined clay demonstrates greater reactivity over clay calcined using static or rotary kiln methods (Salvador 1995). The extremely fast heating and cooling cycles create a calcined clay with enhanced reactivity properties.

Another important consideration that affects the reactivity of calcined clay is by proper grinding. It is critical to finely grind the clinker, limestone, and calcined clays in order to obtain a high degree of fineness. This fine grinding results in improved reactivity and mechanical performance. Proper grinding to achieve a very fine powder is essential for the clinker, limestone, and calcined clays to have optimal reactivity and strength when used in cement. In lab settings, the ingredients in LC3 (clinker, limestone, and calcined clay) are typically ground separately using an open-circuit configuration. However, cement plants most often grind the cement components together in a closed-circuit system. The key distinction between separate grinding and intergrinding is that with intergrinding, the clinker, limestone, and clay interact with each other during the grinding process. In industrial cement production, the LC3 constituents are interground, allowing the materials to influence each other during the closed-circuit grinding. Grinding the clinker separately from the limestone and calcined clay produces clinker with the highest reactivity. When the clinker is ground independently in an open circuit, it achieves optimal reactivity compared to intergrinding where the clinker interacts with the other LC3 components. Although intergrinding is more common in cement plants, separate grinding of the clinker leads to superior reactivity.

2.8.2 OPTIMIZING THE PROPORTIONS OF THE INGREDIENTS IN THE CEMENT MIXTURE

In order to find the ideal ratio of components in the cement blend, there has to be some adjustment in the sulphate and alkali content. In ordinary Portland cement (OPC), the sulfate level is set based on the aluminate content in the clinker. However, in LC3 systems, some of the clinker is replaced by calcined clay, which contains a metakaolin phase rich in aluminates. Therefore, when making LC3, the sulfate dosage used in OPC cannot just be proportionally lowered. Because the calcined clay introduces extra aluminates beyond what is in the clinker, the sulfate content needs to be re-optimized for proper sulfate levels in the LC3 blend. Without adjusting the sulfate level, the silicate and aluminate reactions happen at similar times in LC3, decreasing total heat release and reactivity. But with proper gypsum addition of 1% to the LC3, the silicate and aluminate reactions can be separated. This differentiation of the two peaks by optimizing sulfate leads to optimal properties in the blended LC3 cement (Antoni et al 2017). Also, the alkali concentration which has significant effects on cement hydration, strength development, and durability. It is known that alkalis accelerate early cement hydration (Mota et al., 2015) but reduce later hydration and strength (Smaoui et al., 2005). Some alkalinity is also essential for the pozzolanic reaction in LC3 blends (Lagier and Kurtis 2007; Cyr et al., 2014). From the experiment carried out in the course of optimizing the mix design, it clearly demonstrates that higher alkali content speeds up the silicate and aluminate reactions. The ideal alkali quantity for LC3 provides sufficient alkalinity to improve the pozzolanic reaction without excessively impairing properties at later ages.

Clays with moderate kaolinite content between 40-50% improve the workability of LC3 more than very pure kaolinite clays. The rheological properties of LC3 can be further enhanced by optimizing the particle size distribution of the limestone. The presence of some impurities in the clay and engineering the limestone grading both help to improve the flow characteristics of LC3 cement blends. The optimal workability is achieved through using clays with partial kaolinite content around 40-50% and tailored limestone particle size distribution. Also, clays containing 40-50% kaolinite provide excellent chloride resistance for LC3 paste and mortar, significantly better than ordinary Portland cement and blends with other supplementary cementitious materials (SCMs). This improved chloride transport is mainly due to refined porosity in LC3 systems. Alkali-silica reaction (ASR) is also mitigated by LC3, with LC3-50 performing even better than LC3-65 in this regard. The incorporation of supplementary cementitious materials (SCMs) typically provides effective prevention of alkali-silica reaction (ASR) in concrete (Shehata and Thomas 2000; Duchesne and Bérubé 1994). This ASR mitigation stems from two factors - the lower alkalinity of systems with SCMs compared to plain Portland cement, and the availability of aluminum from the SCMs in the pore solution (Shehata et al., 1999). The combination of reduced alkali levels and the presence of aluminum from the SCMs results in reliable ASR prevention in concrete containing SCMs. The moderate kaolinite clays result in superior durability for LC3, with reduced chloride penetration and ASR compared to OPC and other SCM blends, attributed to the refined pore structure of LC3.

2.9 A FRESH VIEW ON LIMESTONE CALCINED CLAY CEMENT (LC3) PASTES

According to the recent studies carried out by Ez-zaki et al., 2021, this paper presents an insight of the behavior of SCMs from the casting to the setting of binary and ternary systems. Blended cements (w/s 0.5) were evaluated by Vicat apparatus, rheometer, and X-ray imaging to ascertain the setting times, rheological properties and the evolution of early shrinkage for the mew pastes. Binders with SCMs had a higher initial setting time as a result of low clinker content. The use of a highly calcined clay in binary systems led to an overall delay in setting, while the replacement of the clinker content by limestone/calcined clay caused a smaller setting time delay compared to the reference binder. The difference of setting in the presence of SCMs can be explained by chemical equilibria, progressive flocculation, and water demand. Flocculation is increased by the presence of metakaolin while the presence of limestone has the advantage of making an easy of the fresh paste. Limestone calcined clay cement (LC3) is a novel, more sustainable type of cement that has the potential to substantially lower carbon dioxide emissions from cement production, it utilizes supplementary cementitious materials (limestone and calcined clay) that are widely available at low cost by replacing a significant portion of clinker in cement with these SCMs, LC3 can reduce CO2 emissions by around 40% compared to traditional Portland cement production. (Scrivener et al., 2019; Joseph et al., 2016; Maraghechi et al., 2018). Such cements have proven to show a coactive impact of calcined clay and limestone, which has brought a large reduction of high amount of clinker consumption, but also reduced the amount of energy required because calcination of clays occur at a temperature between 700 and 850℃. Although, metakaolin can bring about an increase in the demand of water due to the fineness and large specific surface of the calcined clay, which resulting from the sheet-like structure of kaolinite, thereby causing a reduction in the workability of a new cementitious material (Nair et al., 2020; Chen et al., 2019; Scrivener et al.,2015). The major problem of matekaolin as a SCMs is the water required which is as a result of its non-uniform structure (Cassagnabère et al., 2013). Efforts have been carried out to enhance the workability of metakaolin using viscosity modifying agents to lower the yield stress of fresh slurries. It was shown that calcined clay in LC3 has a high demand for superplasticer and indicates some problems of the flow for a long period of time (Nair et al., 2020).

Alternatively, an understanding of the shrinkage mechanism of a new paste is relevant for ascertaining the distortion after it is being casted and it has shown that clay is more liable to shrinkage in combination with water (Hu et al., 2013).

The materials used for undergoing this study were Portland cement, limestone supplied in the form of waste slurry from marble quarries located in the Apuan Alps in Tuscany (Carrara, Italy) (44°03′08″ N, 10°14′04″ E), and clays obtained from Mûkûrwe'inî- (Nyeri,Kenya) (0.5609° S, 37.0488° E). The chemical compositions of all raw materials are shown in the table below;

Table 2.4: Chemical Composition of Raw Materials by %wt (Ez-zaki et al., 2021)

Material	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	L.O.I
Clay	67.07	0.52	21.43	1.85	0.11	0.13	0.20	0.15	0.44	0.07	6.00
Clinker	23.67	0.35	4.69	4.06	0.10	2.07	61.43	0.69	1.53	0.00	1.41
Limestone	0.00	0.00	0.10	0.00	0.00	0.60	55.90	0.00	0.01	0.00	43.4

The mineral composition of the raw clays was ascertained by X- ray diffraction (XRD) using a Panalytical X'Pert Pro diffractometer (Malvern, UK) with Co radiation provided with an X'Celerator detector, operating within a 2θ range of 5–85°, step size of 0.017°, and a time per step of 100s. The internal standard method was carried out to measure the total amount of the amorphous phase in clays using the Rietveld method (Hill et al., 1987). The clay sample was calcined at 850°C for 3 hours with a heating rate of 10°C/min in the oven. The study involves the use of four binders which comprises of clinker, limestone calcined clay and gypsum. The gypsum was kept constant at a weight 5%. The amount of clinker was different due to the addition of cementitious materials present in it or not. The total replacement of clinker was kept constant at 45% weight, the ratio of the ternary blend (i.e. LC3) of 2:1 and the binary blends contains only 45% of either limestone (KL) or calcined clay (KC). The binder can be composing of both the clinker and gypsum (K) which is shown in the table below;

Table 2.5: Summary of The Proportions of Various Binders by wt% (Ez-zaki et al., 2021)

Binder	Clinker	limestone	Calcined clay	gypsum
K	95			5
LC3	50	30	15	5
KL	50	45		5
KC	50		45	5

The tests carried out include;

i. Setting Time Measurements

The setting time of the cement paste is measured with a Vicat apparatus, as specified by the East African Standard (EAS) 148-3:2000 standard which prescribes that OPC should have setting times between 100 ± 10 min and 170 ± 10 min, while for blended cements, it should be between 180 ± 10 min and 240 ± 10 min for initial and final setting times, respectively as well as ascertaining a considerable range of time at which it deformed or for the rheological measurement. The four different paste containing different binders were mixed and cast into the vicat molds as specified by the adopted standard and placed under the vicat apparatus, provided with a needle of 1.13 ± 0.05 mm diameter and 300g mass, for determining the initial setting time. The samples were carried out at a temperature of 25 ± 2 ◦C and relative humidity than is more than 50%. The precision of the measurement depends mainly on the immersion depth of the needle, the measured mass, and the experimental conditions, such as temperature and relative humidity (Sleiman et al., 2010). The setting time needle was lowered gently into the cement paste surface and was released immediately to penetrate, the timeframe expended during which the water was added to the binder and when the needle ceased to penetrate beyond 4mm was taken as the initial setting time while the final setting time was obtained at the point where the needle only penetrates 0.5mm of the samples. The table below show the initial and final setting time of the different cement paste;

Table 2.6: Initial and Final Setting Time (In Min) Of Blended Cements (Ez-zaki et al., 2021)

Binders	Initial setting time	Final setting time
K	90	174
LC3	114	234
KL	109	224
KC	130	280

The Vicat test does not give a precise results of the rheological properties such as yield stress and viscosity and their extension with time, but it assists to have a clear understanding of the mechanism of the interactions within the sample. It has been shown that the initial setting time corresponds with the elastic modulus of the material (Roussel et al., 2019). These findings suggest different mechanisms influencing the rheological properties of the system: (a) the structure of fresh cement can be controlled mainly by the nucleation and growth of C-S-H, (b) absorbed and entrapped water in the particle agglomerates (flocs) formed by the flocculation of clays causes an increase in yield stress and elastic modulus, and (c) the use of limestone can reduce the yield stress and elastic modulus due to the dilution effect (Muzenda et al., 2020; Roussel et al., 2019; Bentz et al., 2017; Vance et al., 2013). The rheometer is able to detect the changes of structural organization inaccessible to the Vicat needle (Bentz et al., 2017; Sant et al., 2008).

ii. Rheological Properties

The four pastes were prepared with a water-to-solid ratio (w/s) of 0.5. The pastes were mixed in an IKA ULTRA TURRAX Tube Drive mixer (Berlin, Germany) for 3 min at 1700 rpm. The rheological tests start 5min from the time water comes in contact with the binder using a stress-controlled rheometer, Anton Paar MCR

92 (Graz, Austria), provided with a serrated plate-plate geometry (upper plate of 25 mm diameter and lower plate of 50 mm diameter) at 20 ± 1◦C and a gap of 2 mm between two plates. A solvent trap was used to prevent water evaporation. The experiments follow two protocols:

a. Rotational measurements are used to determine yield stress.
b. Amplitude sweep oscillation measurements are used to determine viscoelastic properties.

iii. Plastic Shrinkage

Plastic shrinkage strain was carried out on new samples (w/s 0.5) placed in cylindrical plastic holders (3 cm height × 1.4 cm diameter) immediately after mixing by means of X-ray imaging (Bruker Skyscan 1172 CT, Billerica, MA, USA). X-ray attenuation images of the samples were obtained for three hours, with 10 min intervals. The first set of samples was isolated from the surrounding by covering the upper part of the sample holder with a plastic cap, with the aim of preventing moisture loss, called a bleeding regime while the second sample was left open thereby allowing evaporation known as drying regime (Ghourchian et al.,2018).

2.10 SETTING TIME OF CEMENT

Each and every building job requires cement. It serves as a binding substance to keep a structure's framework in place. Cement is a powdery substance that starts reacting after getting into contact with water. The reaction is commonly known as the hydration process. When cement comes into touch with water, it must be used right away. Setting properties of cement is the most important part in the field of concrete construction (Brooks et al., 2000). It helps in the development of different kinds of concreting operations such as transporting, placing, compacting and finishing of concrete. Placement of concrete in formwork depends on the setting time of concrete, which makes the concrete rigid (Clear and Harrison, 1985).

In the field of concrete building, understanding the setting characteristics is crucial. This will assist in planning the various concrete construction operations stages, such as concrete transport, placement, compacting, and finishing. When choosing whether or not to apply a retarding admixture or accelerator, this information is required.

Many methods have been used to obtain the setting time of concrete, such as penetration resistance, ultrasonic wave, electricity, maturity, the heat of hydration, and nuclear magnetic resonance (Liu et al., 2021). Penetration resistance is the standard test method for setting time. However, the traditional penetration resistance test requires wet screening of concrete, and the coarse aggregates after wet screening cannot be reused. That is, the penetration resistance test consumes a lot of manpower and material resources, which affects the construction progress.

Based on the factors that affect concrete setting time, some researchers have provided prediction equations of concrete setting time by using mathematical techniques to train existing data. (Ahmadi, 2000) proposed the functional dependencies between the initial setting time and additives, ambient temperature, relative humidity, and wind speed by adapting multiple regression analysis. (Mourad et al., 2011) predicted that the key factors affecting the initial setting time of concrete are the type and content of admixtures, air temperature during concrete mixing, average and maximum values of air temperature before initial setting, average and maximum values of air humidity before initial setting, and maximum temperature of concrete. Based on the multiple regression analysis method, a prediction model for the initial setting time of concrete mixture under field conditions was established. In addition, (Hu et al., 2014) provided a comprehensive research study on the influences of retarder dosage, specific surface area of dead burned MgO powder, temperature, and water solid ratio on the setting time of magnesium phosphate cement via Bayes network. Meanwhile, a prediction model for the observation of setting time for magnesium phosphate cement was proposed by means of the regression.

2.10.1 THE RELEVANCE OF SETTING TIME IN CONSTRUCTION

It is essential that cement set neither too rapidly nor too slowly. In the first case there might be insufficient time to transport and place the concrete before it becomes too rigid. In the second case too long a setting period tends to slow up the work unduly, also it might postpone the actual use of the structure because of inadequate strength at the desired age.

1. Initial setting time test is important for transportation, placing and compaction of cement concrete.
2. Initial setting time duration is required to delay the process of hydration or hardening.
3. Final setting time is the time when the paste completely loses its plasticity.
4. It is the time taken for the cement paste or cement concrete to harden sufficiently and attain the shape of the mould in which it is cast.
5. Determination of final setting time period facilitates safe removal of scaffolding or form.
6. During this period of time primary chemical reaction of cement with water is almost completed.

2.11 BLEEDING OF CONCRETE

Plastic cracking of concrete such as plastic settlement and plastic shrinkage cracking is directly related to the bleeding of concrete, which is a natural time-dependent process in a fresh concrete mix. A portion of the mixing water together with very fine materials finds its way to the surface of the concrete during this process (Sri Ravindrarajah, 2003). Bleeding in concrete is a phenomenon in which free water in the mix rises up to the surface and forms a paste of cement on the surface known as “laitance”.

Flowable concretes tend to segregate. The risk of segregation is particularly high when the concrete is vibrated during the compaction process. A well-known segregation phenomenon is the so-called “bleeding”. This is a rise of water to the surface of the freshly poured concrete due to the difference in density between the mixing water and the concrete's denser solid components (aggregates, cement and additives) (Bronk et al., 2020).

The relevance of bleeding for the quality and durability of hardened concrete has been known since the early twentieth century, and the bleeding process has been the subject of numerous studies since then. Powers was one of the first, who studied the phenomenon of bleeding in detail. Powers (1939) as well as Steinour(1945) developed the first equations, based on Poiseuille's Law of capillary flow, to determine the initial constant bleeding rate of cement pastes. Because cement pastes are suspensions with a high solids content, interparticle interactions as well as gravity forces are inextricably linked to the bleeding process. Because of this, several authors claimed that bleeding is more like a self-weight consolidation process than a sedimentation process (Rosquoët et al., 2003). The interparticle forces are taken into account as effective stresses in the paste based on soil mechanics (Tan et al., 1997). Physical and chemical processes also contribute to the mechanism of bleeding in cementitious materials because of the hydration reaction, in addition to gravitational and interparticle forces. Concrete bleeding was described by (Josserand et al., 2006) as an aging consolidation process that primarily comes from the self-weight consolidation of the granular skeleton. The bleeding of cementitious materials corresponds to the settlement of the granular skeleton accompanied by the accumulation of water at the surface (bleed water). Part of this water (internal bleeding) remains trapped under the aggregates (sand or gravel) or the reinforcements. The excess of this trapped water can weaken the bond between the cementitious matrix and the aggregates (or the reinforcements), which affects the mechanical performance and durability of the material (Abadassi et al., 2023). According to Han and Wang (2016), the excessive bleeding makes the concrete more porous, weakens the bond between the cement matrix and the subsurface of aggregates, and induces a non-uniformity of strength.

Some of the implications of bleeding of concrete after placing tends to bring several kinds of defects to hardened concrete in structures: bleeding channels, fissures beneath aggregate particles, weak bond between reinforcement and concrete, heterogeneity with the depth, weak construction joints by laitance.

CHAPTER THREE

METHODOLOGY

3.1 MATERIALS

The materials used for the preparation of limestone calcined clay cement (LC3) includes the following;

a. Calcined clay or metakaolin
b. Limestone
c. Gypsum
d. Portland cement of grade 42.5N
e. Fine aggregate
f. Water

3.1.1 CALCINED CLAY

The clay utilized for this study is rich in kaolinite. The clay is calcined in a muffle furnace although, static or rotary kiln, flash calcination unit or roller hearth kiln can also be used for the calcination process. Flash calcination has been found to provide higher reactivity as compared with rotary calcination (Salvador, 1995). During this process of calcination, the kaolinite clay is heated between a temperature of 600-850 degrees Celsius and results in the formation of a metakaolin. Metakaolin is an aluminosilicate rich compound which reacts with calcium hydroxide as a conventional pozzolana to give hydrated calcium silicate gel and aluminum hydrate. Further reaction of the alumina with limestone will help to enhance the strength and durability of cement products. After the complete calcination of the kaolinite clay, the color is observed to change slightly and very reactive when mixed with clinker.

3.1.2 DESCRIPTION OF CLAY SOURCE

Uzebba is a Town in the Owan local council of Edo State**,** Nigeria. Uzebba, along with its neighbouring towns and villages, Avboisi, Okpuje, Ukhuse-Osi, Ukhuse-Oke in Owan, Etsakor, and Akoko Edo, are known as Afemai. They collectively make up Edo-North Senatorial District.

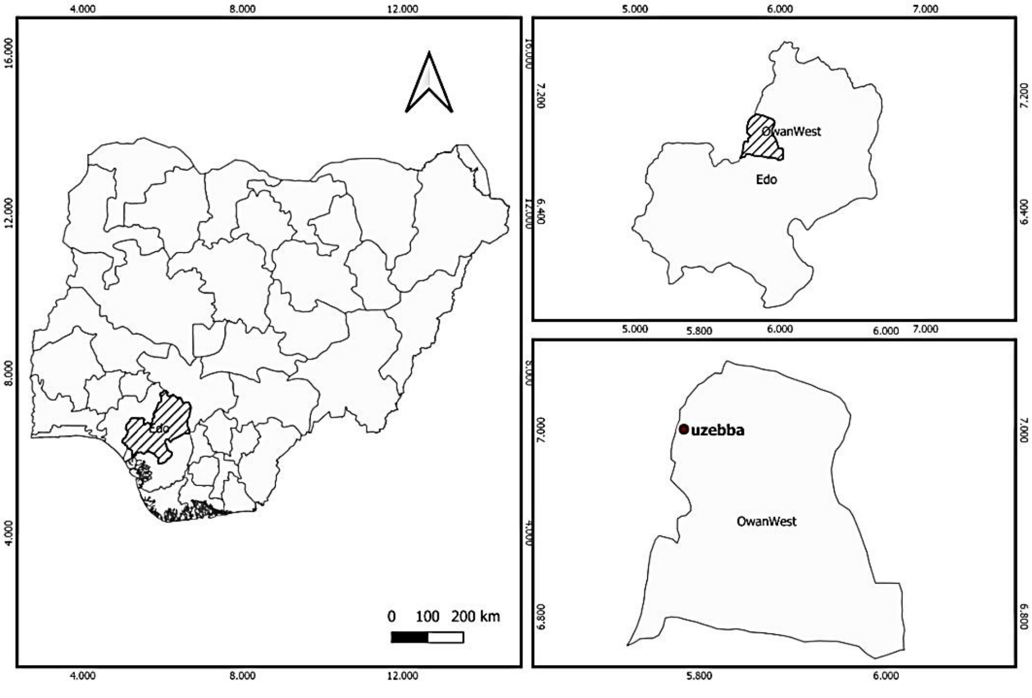

Fig 3.1: Location Map of Uzebba, Edo State

3.1.2 LIMESTONE

Adding limestone to Portland cement was found to speed up the early hydration process and also change the composition of hydrated products formed in the cement paste (Lothenbach et al., 2008). Substituting 5-10% of the cement with limestone accelerates the hydration process. Additionally, the limestone fills in spaces between cement particles as carboaluminate phases are formed (Mohamed et al., 2015). In the hydration of ordinary Portland cement, dissolved sulfate ions react with C_4AF and/or C_3A to first form ettringite. then, the remaining C_3A and C_4AF further react with the ettringite to create monosulfoaluminate (C_4ASH_{12}).

In the course of this research, the limestone used was obtained from Ikpeshi, Akoko Edo local government area, Edo state and the content maintained in the blends are 10% and 13.3%.

3.1.3 GYPSUM

Without the addition of gypsum, cement clinker will rapidly hydrate and generate heat immediately after mixing with water. This is primarily because the C_3A in the clinker quickly dissolves into the water to form calcium aluminate hydrates that accelerate the reaction, causing the cement to not function as intended. Gypsum has the effect of slowing down the hydration rate (Jelenic et al., 1977). It reacts with C_3A during hydration to form hydrated calcium sulfate (calcium sulfate), which has low solubility in water. The calcium sulfate precipitates on the surface of cement particles, forming a protective layer that hinders the hydration of C_3A and prolongs the cement setting time. If the gypsum content is too low, its hydration-slowing effect is insignificant. Conversely, if the gypsum content is too high, it can transform into a substance that accelerates hydration itself, speeding up cement setting. The optimal gypsum ratio depends principally on the C_3A content in the cement and the SO_3 content in the gypsum.

3.1.4 CEMENT/CEMENT GRADE

In this study, Portland cement of grade 42.5N, manufactured by Dangote group was utilized. Portland cement (PC) is generally made in a rotary kiln by heating finely crushed raw materials (such as limestone, clay, marl, and sometimes shale) to approximately 1450°C. The material produced through this heating process is called clinker, which is then cooled, mixed with gypsum, and ground into a fine powder. The clinker contains oxide compounds including CaO (60-70%), SiO_2 (18-22%), Al_2O_3 (4-6%), and Fe_2O_3 (2-4%). These four oxides make up around 95% of the clinker, while the remaining 5% is composed of MgO, Na_2O, K_2O, SO_3, Mn_2O_3, and TiO_2

The cement grade or strength class refers to the minimum compressive strength achieved by cement after 28 days. There are generally three cement grades: grade 33, grade 43, and grade 53, which correspond to strength classes of 32.5MPa, 42.5MPa and 52.5MPa respectively. In other words, grade 33, 43, and 53 represent cements that have minimum compressive strengths of 32.5MPa, 42.5MPa and 52.5MPa at 28 days. For quality control purposes, any cement that demonstrates a compressive strength of 32.5MPa would be considered as meeting the strength criteria for cement grade 32.5. Therefore, a cement manufacturer aiming to produce grade 42.5 cement could easily downgrade the cement to grade 32.5 if its compressive strength does not reach 42.5MPa. In other words, cement grade 32.5 or cement with a strength class of 32.5MPa is the lowest strength cement compared to grades 42.5 and 52.5. Additionally, cement strength can be denoted as 32.5N, 32.5R, 42.5N, 42.5R, 52.5N, 52.5R.

The letters added after the strength grade numbers indicate different types of early strength performance "N" denotes cement with normal early strength gain, while "R" signifies cement with high early strength development

3.1.5 FINE AGGREGATE

The fine aggregate used was river sand that was well-graded and able to pass through a 4.75 mm sieve. Before mixing, the sand was air-dried and sieved to eliminate any unwanted foreign particles. The fine aggregate should be comprised of either natural sand or crushed stone sand. It must have properties like hardness, durability, and be free of organic material and other impurities. The fine sand should not have considerable quantities of clay balls or detrimental contaminants like alkalis, salts, coal, rotted plant matter etc. The experiment utilizes locally sourced river sand.

3.1.6 WATER

Water plays an important role in cement and the mortar mixtures. First, it acts as the medium that allows the cement to bind the other particles together. Second, water reacts chemically with the cement through a process called hydration.

For this experiment, ordinary clean potable water without any particles or added chemicals was utilized. This clean potable water was used for both the initial mixing of the mortar and the subsequent curing of the cast mortar cube specimens. Using regular pure water ensured consistent and controlled conditions for the cement hydration reactions and the overall hardening of the mortar samples over time.

3.2 EXPERIMENTAL PROGRAM

3.2.1 MOULD FABRICATION

The moulds were constructed to enable easy removal of the molded samples without causing any harm. Each mold set, which includes 6 cubes, and fabricated from wood had a base that can easily be screwed for molding or demolding of the mortar cubes The mould was built to prevent leakages while vibrating. The wooden base was intended to have adequate contact with the vibrating table and be stiff enough that it would not produce any extra vibrations. A 50 X 50 X 50mm cube was fabricated for the test of the newly blended cement in accordance with the loading capacity of the available testing machine to crush the cubes and as specified by ASTM C 109M.

Fig 3.2: 50 X 50 X 50mm Wooden Mold

3.2.2 CALCINATION OF KAOLIN (UZEBBA)

A laboratory-scale calcination process was performed on the Uzebba clay samples. An electrically-powered muffle furnace with dimensions of about 0.4m x 0.4m x 0.3m was used. 1kg of the clay sample was weighed using a precise digital scale and placed in a crucible inside the furnace's heating chamber. The sample was steadily heated to 600°C at a heating rate of 10℃ per minute and retained at that temperature for 2 hours to properly calcine. This process was repeated at 600°C, 700°C and 800°C as well.

3.2.3 SIEVE ANALYSIS

According to the BS812-103.1:1985 standards, the fine aggregate (sand) is passed through different sieve sizes after it has been dried for about 24 hours to ascertain the particle size distribution of granular materials. The procedure involves separating a sample of material into different particle size ranges using standard sieves with varying mesh sizes. The test results provide important particle size distribution data that is critical for many applications, such as categorizing soils, quality control of aggregates, and designing mixes for construction materials. The sieve analysis determines how the sample is divided into fine and coarse fractions across the sieves.

The laboratory-scale sieving was performed manually using sieves of sizes 2.36mm, 2.00mm, 1.18mm, 600µm, 425µm, 300µm, 212µm, 150µm, and 75µm. For the analysis, a 500g representative sample was collected and sieved through the arranged sieves. The samples retained on each sieve were gathered and weighed using a precise digital scale. The particle masses obtained were used to compile a detailed particle size distribution. For this study, the aggregate fractions retained on the 600µm sieve were utilized.

The process involved carefully weighing and documenting the quantities retained on each sieve and passed through. These measurements were utilized to determine the percentage of the total sample weight accounted for by each fraction. The obtained values were fastidiously recorded for future reference. Furthermore, the cumulative percentage weight retained was calculated and noted, considering the total retained up to each sieve from largest to smallest openings. This provided extensive particle size distribution data. To visually represent the results, a graph was created plotting the cumulative percent passing on the y-axis, displaying the progressively increasing amounts passing each sieve. The x-axis showed the sieve sizes, presenting an all-encompassing overview of the sample's particle size distribution. This graph was an important visual tool for interpreting and examining the experimental data.

$$\text{Percentage retained} = \frac{weight\ of\ sample\ retained}{Total\ weight}\ X\ 100 \qquad \text{Eqn. (3.1)}$$

Fig 3.3: Set Up of the Sieve Sizes for Sieve

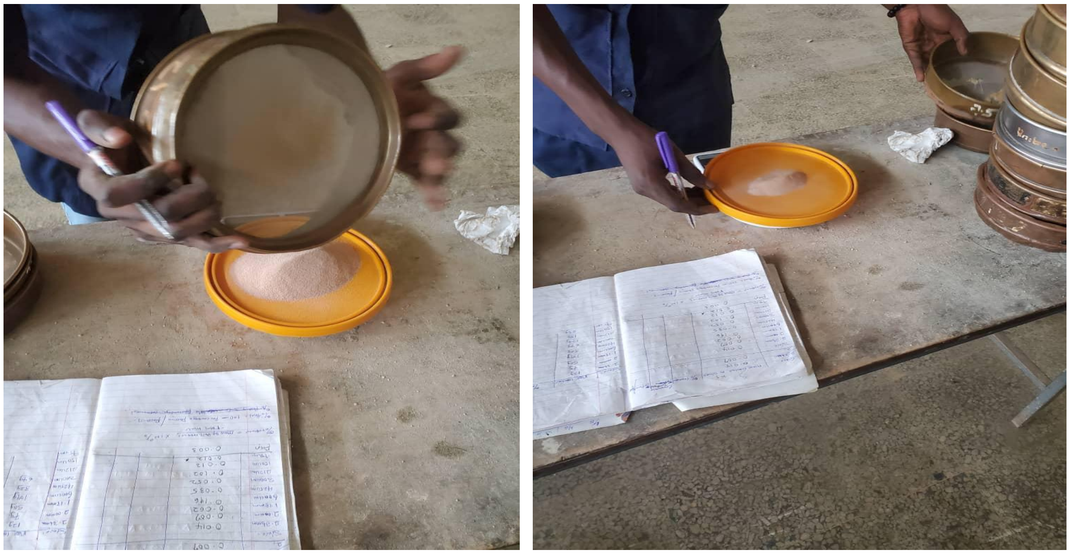

Fig 3.4: Measurement of The Mass Retained in Each Sieve Sizes

3.2.4 CASTING OF MORTAR CUBES

According to ASTM C109 standard, the mortar mix used contains 1-part cement and 2.75 parts sand by mass. Portland cement is mixed at specified water-cement ratios. For other cement types, the water amount is adjusted to obtain a flow of 110 ± 5 in the flow table test over 25 drops. The mortar is compacted into 2-inch or 50mm cube molds using a vibrator.

The mortar mix ratio used in this study was 1-part cement to 2.75 parts sand, and this ratio remained consistent throughout the entire project. A water/cement ratio of 0.5 was also maintained in the mortar mix. A control sample cube was casted for as well as the partial replacement of cement with 30% and 40% of clay and limestone. The equipment and apparatus used include;

a. Weighing device

b. A graduated glass measuring cylinder

c. A laboratory mixing bowl

d. A fabricated wooden mold of 50 X 50 X 50mm dimension

e. Hand trowel and head pan

Casting of control cubes (0% replacement)

The casting of control cubes was carried out by using 1000g of cement, which was mixed with 2750g of fine aggregate (sand) retained on sieve 600µm with a water/cement ratio of 0.5 (i.e. 500g of water). To ensure a uniform mixture, the mortar ingredients were thoroughly blended together prior to use. The mortar was then compacted by vibrating the filled molds on a laboratory vibrating table. This vibration properly consolidates the mortar and to avoid voids.

Once the mortar was adequately compacted in the molds, the specimens were properly labeled for identification. The filled and compacted molds were then allowed to hydraulically cure and harden at room temperature for a minimum of 24 hours before further handling. Allowing the mortar to properly set ensures adequate strength development before demolding and testing the specimens.

Casting of mortar cubes of 30% and 40% replacement

In casting the binary blended mortars, the Portland cement content was partially replaced with supplementary cementitious materials (SCMs) at replacement levels of 30% and 40% by mass.

This replacement is composed of clay and limestone. The exact proportions of the cementitious blends were determined as follows:

Table 3.1: Mix Proportions of LC3 blend at 30% Replacement Level

SAMPLE	OPC (g)	CLAY (g)	LIMESTONE (g)	GYPSUM (g)	WATER (g)	SAND (g)
CONTROL	1000				500	2750
LC^3_{30} 600°C	650	200	100	50	500	2750
LC^3_{30} 700°C	650	200	100	50	500	2750
LC^3_{30} 800°C	650	200	100	50	500	2750

Table 3.2: Mix Proportions of LC3 blend at 40% Replacement Level

SAMPLE	OPC (g)	CLAY (g)	LIMESTONE (g)	GYPSUM (g)	WATER (g)	SAND (g)
LC^3_{40} 600°C	550	267	133	50	500	2750
LC^3_{40} 700°C	550	267	133	50	500	2750
LC^3_{40} 800°C	550	267	133	50	500	2750

The limestone, calcined clay, cement and gypsum were first mix together to obtain a uniform mixture in their specified proportions before mixing with sand prior to adding water. This ensured the dry components were thoroughly mixed. The mortar specimens were then prepared by adding water to the blended dry mix, followed by compacting the mortar in molds similarly to the process for plain mortar.

The key differences were the partial replacement of cement with the limestone and calcined clay additives at designated levels, as well as the use of calcined clays produced at varying temperatures (i.e. 600°C, 700°C and 800°C). Aside from these compositional and processing variations, the same casting procedures applied as for the plain cement mortar.

Fig 3.5: Casting and Compaction of mortar cubes

Fig 3.6: Identification of mortar cubes in mould

3.2.5 DEMOLDING AND CURING OF MORTAR CUBES

Immediately after demolding, the mortar cubes were immediately placed in wet curing to hydrate the cement. Curing was done by fully submerging the cubes in limewater at room temperature and by air for designated periods of 3, 7, 14 and 28 days. The presence of alkali helps to increase the early strength of the cubes. This wet curing method provided sufficient moisture for ongoing cement hydration reactions.

Testing cubes cured for 3, 7, 14 and 28 days allowed comparison of compressive strengths at early, medium and late curing ages for the different mortar blends. The photograph shows an example of mortar cubes undergoing laboratory wet curing in cure tanks and by air curing for the specified duration.

Fig 3.7: Curing of Mortar Cubes

3.2.5 COMPRESSIVE STRENGTH TEST

The compressive strength of the different mortar blends after 3, 7, 14 and 28 days of curing was carried out by crushing the cubes using a Matest digital compression testing machine. The cubes were loaded at a uniform rate of 2kN/sec until failure, as per the cube size. The compressive strengths measured for all the blended mortars were compared to the strength of the plain Portland cement mortar control cubes under identical air and water curing. The blended mortars achieved strengths equal or greater than the minimum criteria specified by standards for Portland Pozzolana Cement (PPC).

Fig 3.8: Crushing of Mortar Cubes on a Digital Compressive

3.2.6 CONSISTENCY AND SETTING TIME TEST

According to ASTM C807 for testing of cement, it specifies the methodology for determining the compressive and flexural strength of hydraulic cement mortar, it provides the procedure for mixing, molding, curing, and testing mortar specimens made with hydraulic cement. The standard is applicable to common hydraulic cements and cement combinations, including Portland, blended, masonry, and more.

In this study, a consistency test and setting time which comprises of the initial and final setting was ascertain for both the control and replacement. The apparatus includes;

a. Vicat apparatus
b. Mold
c. Base plate
d. Plunger for standard consistence
e. Needle for initial set
f. Needle with attachment for final set
g. Water
h. Stop watch

Table 3.3: Mix Proportion for the Consistency and Setting Time Test at 30% Replacement Level

SAMPLE	VOLUME OF WATER (ml)	OPC (g)	CLAY (g)	LIMESTONE (g)	GYPSUM (g)
CONTROL	135	400			

LC^3_{30} 600°C	145	260	80	40	20
LC^3_{30} 700°C	150	260	80	40	20
LC^3_{30} 800°C	155	260	80	40	20

The consistency was determined by preparing a cement paste with specified quantity of cement of 400g and estimated water, this was mixed properly while the time stop watch started counting immediately water was added to the cement. The Vicat apparatus is adjusted by placing the plunger on the base plate and setting the dial to zero. The plunger is raised to a standby position. After leveling the cement paste in the mold, it is placed at the center under the plunger on the base plate and gently lower the plunger until it just touches the paste surface, pausing 1-2 seconds to avoid force. Quickly release the plunger to penetrate vertically into the paste. Do this release exactly 4 minutes ± 10 seconds after the zero time when water was added to cement. Read the depth of penetration from the dial no less than 5 seconds after plunger movement stops, or 30 seconds after releasing it - take the earlier of the two times. This plunger penetration reading is used to determine the setting time of the cement paste sample.

For each penetration test, record the scale reading showing the distance between the bottom of the plunger and base plate, along with the water content of that paste as a percentage of the cement mass. Immediately clean the plunger after each test. Repeat the penetrations on pastes with different water amounts until a distance of 6 ± 2 mm is achieved between the plunger and base plate. Record the water content that gives this plunger distance of 6 ± 2 mm to the nearest 0.5% as the standard consistency water content. This is the water-cement ratio required to produce a cement paste of standard consistence for further testing.

After the consistency is determined from the above procedure, the plunger is replaced with an initial setting time needle. After allowing adequate time for initial set, position the mold with paste on the base plate under the Vicat needle. Carefully lower the needle until it contacts the paste surface, pausing 1-2 seconds to avoid force. Rapidly release the needle to penetrate vertically into the paste. Read the penetration depth from the dial once needle motion has ceased, or 30 seconds after releasing - take the earlier time. This measures how far the Vicat needle sinks into the setting cement paste. Repeat the test periodically to monitor the reduction in needle penetration until it falls between 5mm – 7mm over time as the cement sets. After which, the time is taken at which its sets initially.

Once the initial setting time is determined, the needle is replaced with a final setting time needle to determine the times at which it hardens. To accurately determine the final time, reduce the interval between penetration tests as the cement approaches its final set. Confirm the final setting time by repeating the test at two additional positions on the paste specimen. Ensure the needle fails to mark a complete circle at all three locations. This confirms when the cement has reached its final set point based on the needle attachment unable to imprint the hardening cement paste surface. This test procedure was repeated for the replacement at the different temperatures.

Fig 3.9: Determination of The Consistency and Setting Time of Cement Using Vicat Apparatus

3.2.7 WATER ABSORPTION TEST

The water absorption test was conducted after 28-days of curing the mortar cubes to evaluate porosity and permeability based on ASTM C642. The cured cubes were first dried at 105°C then weighed. They were immersed in water for a time interval of 10mins, 20mins, 30mins, 24 hrs. till the 7 day to fully saturate before reweighing to determine water absorbed. By following the standard test method, the permeation characteristics of the mortar mixes could be assessed. This was carried on the control cube and replacement for the different temperatures. To calculate the percentage absorption, the following equation was used;

$$\text{Percentage Absorption} = \frac{Weight\ of\ Water\ Absorbed}{Dry\ Weight\ of\ Concrete\ Cubes}\ X\ 100 \qquad \text{Eqn. (3.2)}$$

Fig 3.10: Immersion of The Control and Replacement Cube for Water Absorption Test

3.2.8 BLEEDING TEST

According to ASTM C232 which indicate the standard procedure for determining the proportion of mixing water that separates out from a newly mixed concrete specimen. Two similar test techniques are covered, with the primary difference being the level of vibration that is used on the concrete sample during the test and they are not expected to give same result.

For this project, the bleeding test was carried out by consolidating the sample by using a vibrating table. The apparatus used include;

a. Vibrating platform
b. Timer

c. Pippete or syringe

d. Cylindrical container

e. Weighing balance

f. Measuring cylinder

Table 3.4: Mix Proportion for the bleeding test at 30% Replacement

SAMPLE	OPC (g)	CLAY (g)	LIMESTONE (g)	GYPSUM (g)	FINE AGGREGATE (g)	COARSE AGGREGATE (g)
CONTROL	1190				2380	4760
$LC^3{}_{30}$ 600°C	773.5	238	119	59.5	2380	4760
$LC^3{}_{30}$ 700°C	773.5	238	119	59.5	2380	4760
$LC^3{}_{30}$ 800°C	773.5	238	119	59.5	2380	4760

W/C = 0.42

The concrete sample and container was a placed in a stable position, level platform or floor free from any noticeable vibrations. The container is then covered to prevent evaporation of the bleed water. The cover was kept in place over the container throughout the duration of the test, only removing it when drawing off the collected bleed water. The vibration pattern for the test involves turning on power to the vibrator for 3 seconds followed by turning off power for 30 seconds. However, the vibrator motor coasts for a short time after being powered off, so the duration of actual perceptible vibration is approximately 7 seconds per cycle. Time was taken as soon as the motor of the vibrator was turned on. The vibration cycles were done intermittently for about 1 hour. A syringe was used to remove the water that was collected on the surface, every

10 minutes during the first 40 minutes and then every 30 minutes after that until the bleeding stops. To calculate the bleeding percentage, the following equation was used;

$$\text{Bleeding water \%} = \frac{Total\ Quantity\ of\ Bleeding\ Water}{Total\ Quantity\ of\ Water\ in\ the\ Concrete\ Mix}\ X\ 100 \qquad \text{Eqn. (3.3)}$$

Fig 3.11: Determination of The Bleeding of Concrete for The Control and Replacement

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 RESULTS

The practical study of limestone calcined clay cement, produced by combining limestone, calcined clays, and Portland cement, offers a solution that matches the mechanical performance of ordinary Portland cement while better withstanding chloride and alkali-silica reaction and reducing CO2 emissions. This review focuses on mortars made with LC3 binder and compares LC3 and Portland Cement mortars in terms of binder composition, curing processes/hardening mechanisms, and environmental, economic, physical, and mechanical characteristics. The effects of using LC3 are heavily influenced by percentages of limestone, calcined clay, and gypsum; binder/aggregate ratio; and water/binder ratio.

The tables in this chapter present the findings from all of the laboratory experiments conducted for this research study.

4.1.1 COMPRESSIVE STRENGTH

Compressive strength testing on mortar cubes aims to determine the load-bearing capacity of the cubes under two different curing conditions, which are the immersion in a calcium hydroxide water solution and exposure to air. The tests evaluate and compare how well the mortar resists compression after curing in the calcium hydroxide versus curing in air.

$$\text{Compressive strength} = \frac{crushing\ load \times 10^3\ (N)}{crushing\ area\ (mm^2)} \qquad \text{Eqn. (4.1)}$$

The compressive strength results for the mortar cube specimens made with the control design mix and mixes containing 600°C, 700°C, and 800°C of Uzebba calcined clay at 3, 7, 14, and

28 days for both water and air curing are statistically analyzed and summarized in the tables below. The compressive strength testing was conducted with the loading rate of the compression machine set at 2kN/sec. The analysis allows comparison of the compressive strength development over time for the different cube mixes.

Table 4.1: Compressive Strength of the Control Mix Cured in Lime Water

CURING DAYS	WEIGHT (g)	DENSITY (kg/m^3)	FAILURE LOAD (KN)	STRENGTH (N/mm^2)	AVERAGE (N/mm^2)
3	291	2328	29.07	11.63	12.91
	289	2312	35.31	14.12	

	285	2280	32.46	12.98	
7	269	2152	29.03	11.61	14.64
	272	2176	41.42	16.57	
	271	2168	39.38	15.75	
28	273	2184	38.49	15.40	13.24
	273	2184	34.21	13.68	
	271	2168	26.57	10.63	

Table 4.2: Compressive Strength of 30% Replacement Cured in Lime water

UZEBBA TEMP(℃) 30%	CURING DAYS	WEIGHT (g)	DENSITY (Kg/m^3)	FAILURE LOAD (KN)	STRENGTH (N/mm^2)	AVERAGE
600	3	273	2184	22.46	8.98	9.44
		267	2136	25.67	10.27	
		270	2160	22.71	9.08	
	7	269	2152	31.03	12.41	12.07
		273	2184	21.85	8.74	
		268	2144	37.63	15.05	
	28	272	2176	29.78	11.91	10.22
		278	2224	21.96	8.78	
		270	2160	24.92	9.97	
700	3	271	2168	34.17	13.67	12.61
		267	2136	30.03	12.01	
		272	2176	30.39	12.16	
	7	276	2208	40.03	16.01	16.83
		269	2152	44.81	17.92	
		270	2160	41.42	16.57	
	28	274	2192	26.57	10.63	12.05
		270	2160	29.28	11.71	
		272	2176	34.56	13.82	
800	3	274	2192	32.53	13.01	11.09
		268	2144	26.07	10.43	
		268	2144	24.6	9.84	
	7	277	2216	45.67	18.27	16.38
		270	2160	39.99	16	
		271	2168	37.21	14.88	
	28	268	2144	38.13	15.25	17.12
		270	2160	50.13	20.05	
		272	2176	40.17	16.07	

Table 4.3: Compressive Strength of 40% Replacement Cured in Lime water

UZEBBA TEMP(°C) 40%	CURING DAYS	WEIGHT (g)	DENSITY (KG/M3	FAILURE (KN)	STRENGTH (N/MM2	AVERAGE
600	3	319	2552	19.03	7.61	7.47
		281	2248	19.39	7.76	
		280	2240	17.6	7.04	
	7	283	2264	35.13	14.05	9.72
		281	2248	20.85	8.34	
		281	2248	16.89	6.76	
	28	282	2256	19.39	7.76	7.62
		289	2312	19.07	7.63	
		259	2072	18.71	7.48	
700	3	281	2248	21.89	8.76	7.59
		289	2312	15.25	6.1	
		289	2312	19.75	7.9	
	7	282	2256	14.07	5.63	8.77
		287	2296	26.71	10.68	
		287	2296	24.99	10.00	
	28	289	2312	22.75	9.10	7.95
		295	2360	19.57	7.83	
		255	2040	17.32	6.93	
800	3	291	2328	27.17	10.87	9.72
		281	2248	26.32	10.53	
		280	2240	19.42	7.77	
	7	280	2240	32.28	12.91	12.16
		288	2304	28.64	11.46	
		285	2280	30.31	12.12	
	28	283	2264	17.64	7.06	10.19
		289	2312	30.17	12.07	
		290	2320	28.61	11.44	

Table 4.4: Compressive Strength of the Control Mix Cured in Air

CURING DAYS	WEIGHT (G)	DENSITY (KG/M3)	FAILURE LOAD (KN)	STRENGTH (N/MM2)	AVERAGE
3	291	2328	10.28	4.11	5.70
	278	2224	16.53	6.61	
	301	2408	15.96	6.38	
7	281	2248	19.03	7.61	9.87
	282	2256	27.32	10.93	

	282	2256	27.67	11.07	
28	287	2296	42.64	17.06	14.77
	291	2328	36.93	14.77	

Table 4.5: Compressive Strength of 30% Replacement Cured in Air

UZEBBA TEMP (°C) 30%	CURING DAYS	WEIGHT (g)	DENSITY (Kg/m^3)	FAILURE LOAD (KN)	STRENGTH (N/mm^2)	AVERAGE
600	3	285	2280	11.6	4.64	4.37
		284	2272	10.39	4.16	
		291	2328	10.78	4.31	
	7	280	2240	13	5.2	6.79
		275	2200	18.75	7.5	
		277	2216	19.21	7.684	
	28	292	2336	31.69	12.68	13.37
		283	2264	35.17	14.07	
700	3	283	2264	8.64	3.46	4.78
		283	2264	18.85	7.54	
		278	2224	12.5	5.00	
	7	290	2320	10.25	4.1	5.92
		278	2224	13.1	5.24	
		286	2288	21.07	8.428	
	28	281	2248	26.6	10.64	11.66
		284	2272	31.69	12.68	
800	3	260	2080	19.57	7.83	8.09
		280	2240	20.75	8.30	
		283	2264	20.35	8.14	
	7	290	2320	43.81	17.52	15.58
		324	2592	40.88	16.352	
		302	2416	32.14	12.856	
	28	270	2160	27.15	10.86	10.90
		295	2360	22.13	8.85	
		291	2328	32.49	13.00	

4.1.2 SIEVE ANALYSIS

The particle size distribution of the fine aggregate used is presented in the table below. However, a 20-30 standard sand was adopted (ASTM C778-02) in preparing the mortar for the strength test. The table shows the particle size distribution for a 500g of fine aggregate.

Table 4.6: Sieve Analysis of Fine Aggregate of Weight 500g

SIEVE SIZES	MASS RETAINED (g)	% RETAINED	%CUMMULATIVE RETAINED	%FINER/PASSING
2.36mm	12	2.4	2.4	97.6
2.00mm	7	1.4	3.8	96.2
1.18mm	50	10	13.8	86.2
600µm	109	21.8	35.6	64.4
425µm	32	6.4	42	58
300µm	64	12.8	54.8	45.2
212µm	177	35.4	90.2	9.8
150µm	15	3	93.2	6.8
75µm	23	4.6	97.8	2.2

4.1.4 WATER ABSORPTION TEST

The amount of water absorbed by the mortar cubes for the control and the replacement for the different temperatures (i.e. 600°C, 700°C and 800°C) using Portland cement and limestone calcined clay cement respectively after curing in water for 28days are shown in the table below;

Table 4.8: Water Absorption Test for The Control and Replacement

SAMPLE	INITIAL MASS(g)	OVEN DRY WEIGHT (g)	WA1 (10min)	WA (20min)	WA (30mins)	WA (1hr)	WA (24hr)	WA (72hr)
CONTROL	276	259	270	273	273	274	274	275
	276	258	269	272	273	274	274	275
	278	258	270	272	272	273	274	275
LC^3 600°C	256	227	246	249	249	250	251	252
	269	259	264	267	267	268	269	270
	270	257	262	265	265	267	269	270
LC^3 700°C	273	255	261	265	265	270	272	273
	262	241	254	256	256	258	259	259
	268	255	260	263	263	265	267	268
LC^3 800°C	271	260	266	268	270	269	272	272
	273	261	265	269	270	270	272	273
	273	262	267	270	270	271	272	273

WA = Water Absorbed

Table 4.9: Average Value for The Water Absorption Test for The Control and 30% Replacement Mortar Cubes

SAMPLE	OVEN DRY WEIGHT (g)	WA (10mins)	WA (20mins)	WA (30mins)	WA (1hr)	WA (24hr)	WA (72hr)

CONTROL	258.33	269.67	272.33	272.67	273.67	274.00	275.00
LC$^{3}_{30}$ 600℃	247.67	257.33	260.33	260.33	261.67	263.00	264.00
LC$^{3}_{30}$ 700℃	250.33	258.33	261.33	261.33	264.33	266.00	266.67
LC$^{3}_{30}$ 800℃	261.00	266.00	269.00	270.00	270.00	272.00	272.67

Table 4.10: Percentage Water Absorbed for The Control and 30% Replacement Mortar Cubes

SAMPLE	WA (10mins)	WA (20mins)	WA (30mins)	WA (1 hour)	WA (24 hours)	WA (72 hours)
CONTROL	4.39%	5.42%	5.55%	5.94%	6.07%	6.45%
LC$^{3}_{30}$ 600℃	3.90%	5.11%	5.11%	5.65%	6.19%	6.59%
LC$^{3}_{30}$ 700℃	3.20%	4.40%	4.40%	5.59%	6.26%	6.53%
LC$^{3}_{30}$ 800℃	1.92%	3.07%	3.45%	3.45%	4.21%	4.47%

4.1.5 CONSISTENCY AND SETTING TIME

The consistency and setting time (initial and final setting time) results obtained for the control using a Portland cement and limestone calcined clay cement is tabulated below;

Table 4.11: Consistency and Setting Time

SPECIMEN	VOL. OF WATER (g)	INITIAL SETTING TIME	AVG. INITIAL	FINAL SETTING TIME	AVG. FINAL (Min)

		(Min)	(Min)	(Min)	
Control 1	135	88	90.00	222	221.00
Control 2	135	92		220	
LC^3 (600°C) 1	145	124	125.50	222	223.50
LC^3 (600°C) 2	145	127		225	
LC^3 (700°C) 1	150	117	117.50	225	225.00
LC^3 (700°C) 2	150	118		225	
LC^3 (800°C) 1	155	92	91.00	226	225.50
LC^3 (800°C) 2	155	90		225	

4.2 ANALYSIS OF RESULTS

Compressive Strength

The chart shown below in figure 4.1 shows the comparison between the compressive strength of 30% replacement of limestone calcined clay cement at 600°C, 700°C and 800°C and control using ordinary Portland cement cured in lime water. From the experiment, it was observed that the compressive strength shows an inconsistent trend for 3days, 7 days and 28days. At three days, the value for the compressive strength of the control was 12.91N/mm^2 with a decrease of 26.88%, 2.32% and 14.10% for the replacement at 600°C, 700°C and 800°C respectively. At 7 days, the value for compressive strength was observed to be higher than that of 3 days, however, the compressive strength for the control was 14.64N/mm^2 having a decrease of 17.55% for 600°C while it had an increase of 14.96% and 11.89% for 700°C and 800°C respectively.At 28 days, the strength of the control cube was at 13.24N/mm^2 while it had a decrease of 22.81% and 8.99% at 600°C and 700°C respectively with an increase of 29.31% for 800°C.

In summary, the highest strength for 3 days obtained is 12.91N/mm^2 for the control, at 7 days, the highest strength was significant for 700°C with a compressive strength of 16.83N/mm^2 while the highest strength 28days was significant for clay calcined at 800°C with a compressive strength of 21.97N/mm^2 and 17.12N/mm^2 respectively.

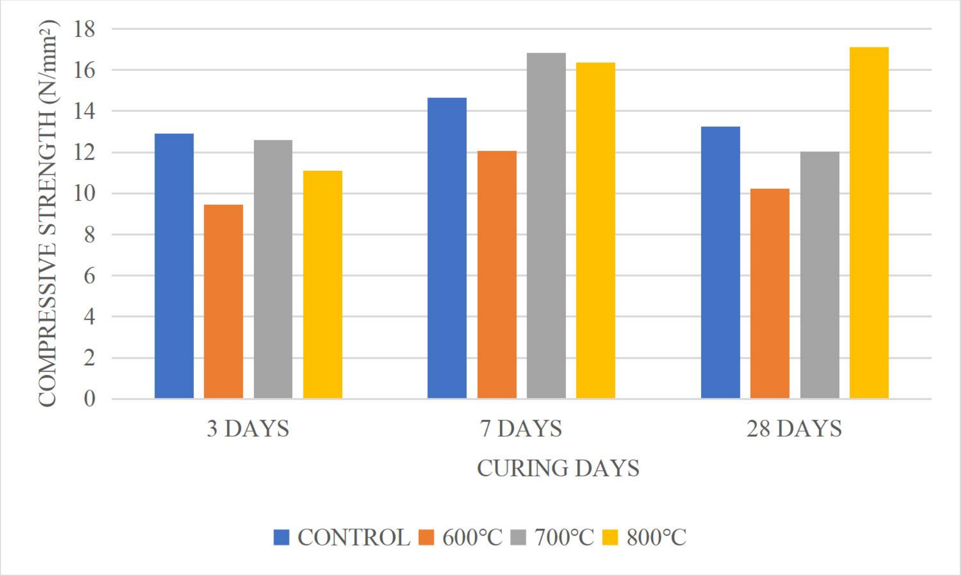

Fig 4.1: Compressive Strength of 30% Replacement of LC3 Mortars calcined at 600°C, 700°C And 800°C Compared with OPC Mortars Cured in Lime Water

From figure 4.2, the results show the comparison between the compressive strength of 40% replacement of limestone calcined clay cement at 600°C, 700°C and 800°C and control using ordinary Portland cement cured in lime water. From the experiment, it was observed that the compressive strength shows an inconsistent trend for 3days, 7 days and 28days similar to that of 30% replacement. At three days, the value for the compressive strength of the control was 12.91N/mm^2 with a decrease of 42.14%, 41.21%, 24.71% for the replacement at 600°C, 700°C and 800°C respectively. At 7 days, the value for compressive strength was observed to be higher than that of 3 days, however, the compressive strength for the control was 14.64N/mm^2 having a decrease of 33.61%, 40.10% and 16.94% for 600℃, 700℃ and 800℃ respectively. At 28 days, the strength of the control cube was at 13.24N/mm^2 while it had a decrease of 42.45%, 39.95% and 23.04% at 600℃, 700℃ and 800℃ respectively.

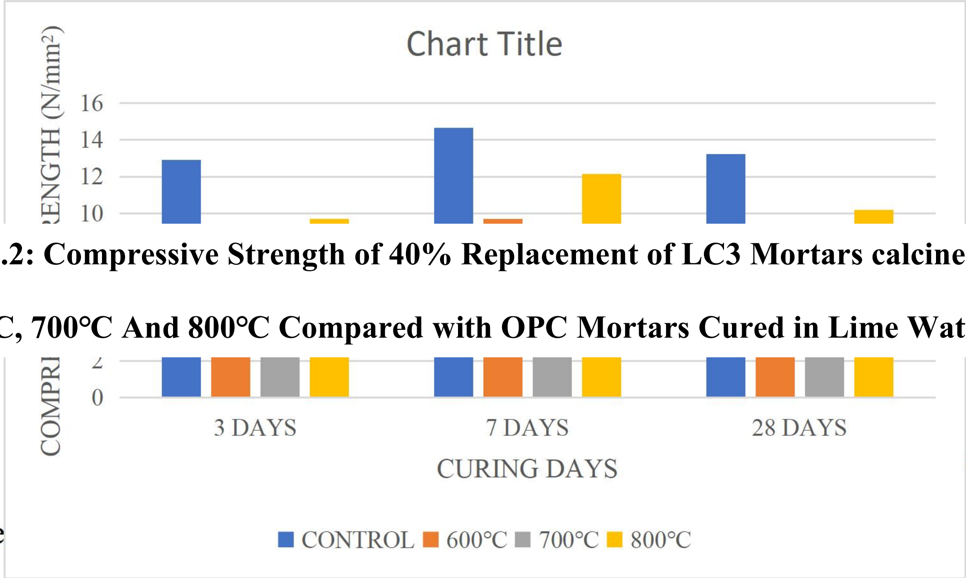

Fig 4.2: Compressive Strength of 40% Replacement of LC3 Mortars calcined at 600℃, 700℃ And 800℃ Compared with OPC Mortars Cured in Lime Water

The chart ive strength of 30% re and control using ordinary Portland cement cured in air. From the experiment, it was observed that the compressive strength shows a consistent trend in the increase in strength for 3days, 7 days until it dropped at 28days. At three days, the value for the compressive strength of the control was 5.70N/mm^2 with a decrease of 23.33% and 6.49% for the replacement calcined at 600℃ and 700℃ respectively and increase in strength by 65.26% for clay calcined at 800℃. At 7 days, the value for compressive strength was observed to be higher than that of 3 days, the compressive strength for the control was 9.87N/mm^2 having a decrease of 31.21% and 40.02% in strength for LC3 calcined at 600℃ and 700℃ respectively while an increase of 57.85% for the strength of LC3 calcined at 800℃. At 28 days, the strength of the control cube was at 15.91N/mm^2 while it had a decrease of 15.96%, 26.71% and 31.49% for LC3 calcined at 600℃, 700℃ and 800℃ respectively.

In summary, there was a consistent trend for the increase in the strength for the control cubes and LC3 calcined at 800℃ for 3 and 7 days until it dropped at 28 days while that of LC3 calcined at 600℃ and 700℃ was inconsistent with the strength.

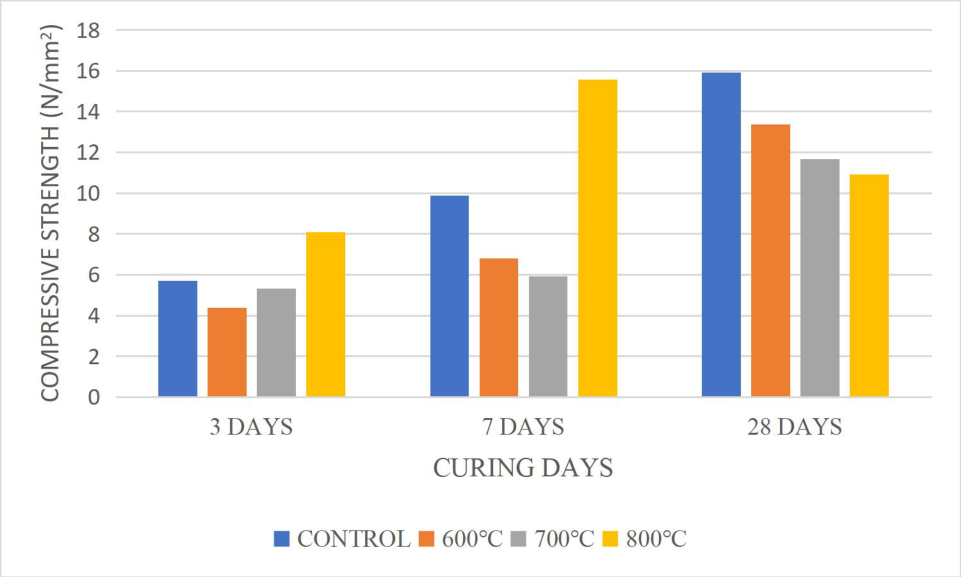

Fig 4.3: Compressive Strength of 30% Replacement of LC3 Mortars calcined at 600℃, 700℃ And 800℃ Compared with OPC Mortars Cured in Air

Sieve Analysis

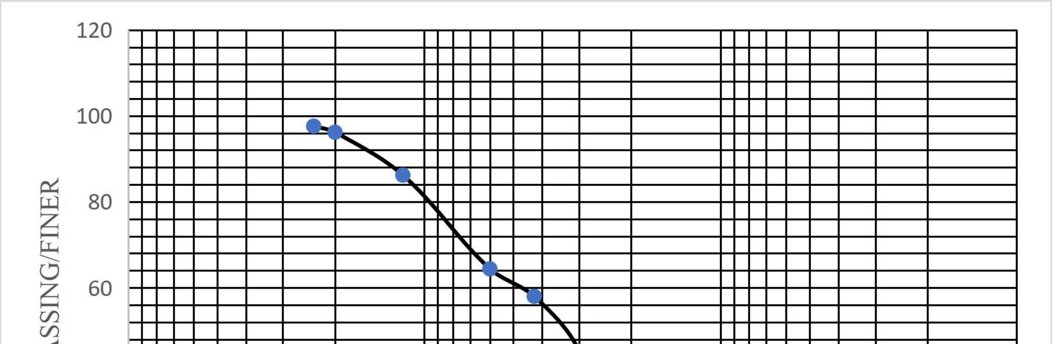

Fig 4.4: Particle Distribution of Fine Aggregate

From Figure 4.4 above, shows the particle size distribution of 500g of fine aggregate passed through different sieve sizes according to BS812-103.1:1985 sieve sizes, from the sieve analysis graph, the particles diameter at 60%, 30% and 10% passing obtained from the graph are 0.46mm, 0.27mm and 0.22mm respectively. The coefficient of uniformity (C_U) and coefficient of curvature (C_C) or gradation obtained from the graph are 2.1mm and 0.72mm respectively. This shows that the fine aggregate is a coarse sand that is non uniform and well graded accordingly because C_U exceed the limit of sand and C_C lied within the accepted range in accordance to BS1377:2:1990.

Consistency and setting time

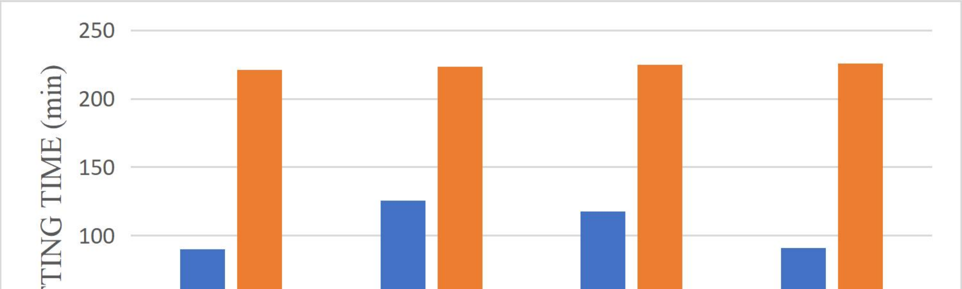

Fig 4.5: Initial and Final Setting Time Result for OPC and LC3 Calcined at 600°C, 700°C And 800°C

The figure shown above shows the comparison between the setting time for Portland cement (control) and 30% replacement of LC3 calcined at different temperatures (600°C, 700°C and 800°C respectively).

The chart shows that the OPC has an initial setting time of 90min. However, for LC3 calcined at 600°C and 700°C, the initial setting time is relative to OPC increased to 125.5min and 117.5min respectively and LC3 calcined at 800C, the initial setting time has an approximate value to that of OPC.

The final setting time of all the samples is observed to all have a close range of values (221min, 223.5min, 225min, 225.5min) for control, LC3 at 600, 700 and 800 respectively.

Water Absorption Test

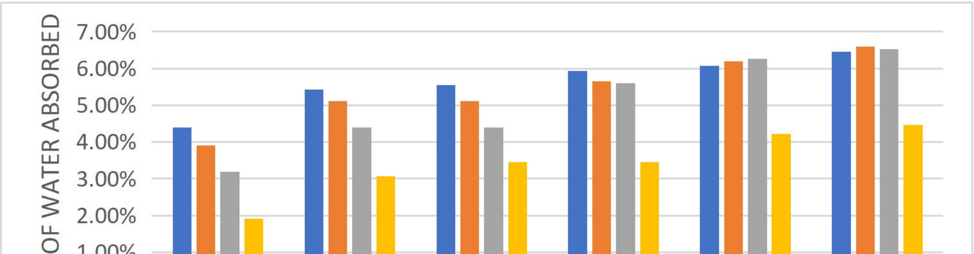

Fig 4.6: Water Absorption Test for The Control and 30% Replacement Calcined at 600℃, 700℃ And 800℃

Fig 4.6 explains graphically the behavioral pattern of the water absorbed by the mortar cubes. it can be seen from the chart that the total percentage of water absorbed by the control and LC3 calcined at 600℃, 700℃and 800℃progresses over time but at 24 hours and 72 hours, the limestone calcined clay cement samples at 600℃ and 700℃ was observed to have an increment in the percentage of water absorbed compared to the control.

The water absorbed by LC3 calcined at 800 progresses over time, but it exhibits a slower absorption rate compared to the control and LC3 calcined at 600 and 700. This behavior indicates that the LC3 calcined at 800 have a higher strength than the other samples as less water permeates into the concrete.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSION

The experimental results shown from the practical study of limestone calcined clay cement in using the calcined clay sample obtain from Uzebba town and limestone from Ikpeshi which serves as a supplementary cementitious material for partially replacing ordinary Portland cement to mitigate the emission of CO_2 from the clinker produce in cement production has shown a remarkable insight about the properties of limestone calcined clay cement.

Based on the conducted experiments and analysis of data, it can be observed that the Limestone calcined clay heated to 800C has similar or better properties than the control.

The following observations and conclusions can be drawn:

1. The compressive strength achieved using calcined clay cured with lime water at 800℃ is higher than that of the Ordinary Portland Cement used in this study compared to the clay calcined at 600℃ and 700℃. Hence, the calcined clay at 800℃ has the ability to withstand more load than any of the samples.
2. The total percentage of water absorbed is lesser for the limestone calcined clay at 800C compared to other samples which indicates less water penetration in the sample. This can also bring about an increased durability of the sample.
3. The initial and final setting time of the LC^3 at 800℃ is an approximate value of the Controls. Hence, it takes approximately same duration for the calcined clay and control to lose their plasticity, be transported, set and gain ultimate strength.

In summary, the Limestone calcined clay cement heated to 800℃ has not only been found to be affordable in terms of the availability of its raw materials, it can also be employed in the construction industry as it can serve same or even better purposes than the Ordinary Portland Cement.

5.2 RECOMMENDATIONS

Based on the findings of the study of limestone calcined clay cement using a clay sample obtained from Uzebba town and limestone from Ikpeshi, here are some recommendations:

1. More research is needed to explore how other types of clay could potentially act as supplementary cementitious materials that can reduce CO_2 emissions from cement production. The goal would be to identify clays that can enhance early strength development in concrete mixes in the way that cement does, while also decreasing the carbon footprint.
2. Additional research is needed to investigate the performance of the LC3 binder in reinforced concrete (RC) beams and other structural members. While the LC3 binder shows promise, further structural testing and evaluation is required before it can be widely adopted for construction applications. Studies should analyze the behavior of RC beams, columns, slabs, and other elements made with LC3 under loading conditions and assess its suitability as a structural binder.
3. Further studies could explore modifying the ratio of clay to limestone, especially for clays with high kaolinite content. Using a combination of calcined clay and limestone as a supplementary mineral admixture when mixing concrete is another area of interest. This blended addition could potentially enhance concrete durability, which is crucial for resistance against chloride ion penetration or alkali-silica reaction.

4. Additional research and testing on the production methods, environmental sustainability, and cost-effectiveness of LC3 is needed. This could provide crucial insights to help develop LC3 into an economically viable and eco-friendly solution for the global cement industry.
5. There is need to study the impact of clay mineralogy and composition on LC3 properties which can be ascertain either by X-ray diffraction (XRD) test or by thermogravimetric analysis.
6. Developing standardized testing methods and specifications for LC3 cements.

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