EFFECTS OF METAKAOLIN AS SUPPLEMENTARY CEMENTITIOUS MATERIAL IN MORTARS FOR CONSTRUCTION APPLICATIONS

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A THESIS SUBMITTED TO THE SCHOOL OF GRADUATE STUDIES OF THE UNIVERSITY OF GHANA IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF MASTER OF PHILOSOPHY DEGREE IN MATERIALS SCIENCE AND ENGINEERING.

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JULY 2018

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DECLARATIONS

Candidate's Declaration

I hereby declare that this MPhil thesis which has results of my own original research was prepared in accordance with the University of Ghana's academic regulations and that no part of it has been presented for another degree in this University or elsewhere.

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Signature..... Date.....

Supervisor's declaration

I hereby declare that the preparation and presentation of the thesis were supervised in accordance with the guidelines on supervision of thesis laid down by the University of Ghana.

Supervisor's name: Dr. David Dodoo-Arhin

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Head of Department's declaration

I hereby declare that this thesis has been prepared, supervised and accepted in accordance with the guidelines on the project works laid down by the University of Ghana.

Head of Department's name: Dr. Lucas Damoah

Signature..... Date.....

ABSTRACT

This work presents the effects of metakaolin as a supplementary cementitious material in mortars for construction applications. Kaolin from Teleku Bokazo was calcined at 650^{o}C and partially used to replace Portland limestone cement to produce mortars and paste. The metakaolin was successfully used in a cement paste and its effect observed in the different cement replacements proportions. The replacements ranged from 10% - 35% by mass and characterised after 3, 7, 14 and 28 days of curing. Kaolin was characterized using X-ray diffractometer (XRD) with illite, kaolinite and quartz as the main crystalline phases. The metakaolin was also characterised using XRD with quartz as the main crystalline phase. Calcium silicate hydrate, calcium aluminium silicate hydrate, portlandite, calcite and ettringite were some of the hydrated compounds formed in the hydrated pastes. Fourier transform infrared spectroscopy was used to determine the functional groups of the hydrated cement products formed from the metakaolin cement paste. Other test including initial setting and water consistency were also carried out. Water consistency and setting times generally increased with increase in metakaolin addition. The optimum metakaolin replacement for flexural strength after 28 days curing was 15 and 20% whereas the compressive strength after 28 days curing was 20% metakaolin replacement. Generally, the metakaolin reduced the amount of water absorbed by capillary action for the 28 days cured mortar bars.

The results suggest that 20% metakaolin replacements of Portland limestone possess characteristics that can be adopted for use in mortars for construction applications.

DEDICATION

This work is dedicated to my family and my church.

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LIST OF ABBREVIATIONS

PC	Portland Cement
SCMs	Supplementary Cementitious Materials
CK	Calcined Kaolin
MK	Metakaolin
XRD	X-Ray Diffraction
FTIR	Fourier Transform Infrared Spectroscopy
SF	Silica Fume
RHA	Rice Husk Ash
GS	Ghana Standard
BS	British Standard
PLC	Portland Limestone Cement
ASTM	American Society for Testing Materials
PPC	Portland Pozzolana Cement
C-S-H	Calcium Silicate Hydrates
C-A-S-H	Calcium Aluminium Silicate Hydrate

CHAPTER ONE

1.0 INTRODUCTION

1.1 Background of study

Portland cement has gained widespread acceptance as the choice construction material due to its reassuring properties and price value [1]. Portland cement (PC), is the conventionally used binder in mortars and concrete production due to its durability, versatility and adaptability in forming varying structural shapes [2].

As a binder the availability and abundance of the raw materials used in its production makes it difficult to be competed against or replaced. However, its production process poses serious environmental threats; the clinkering process leads to the emission of carbon dioxide (CO_2) gas which contributes to the global warming phenomenon [3].

Global discussions on the adverse effects of human activities on the environment have shown clearly that there are urgent concerns towards environmental sustainability through change of attitudes and activities. The construction sector therefore recognizing the effects such quick depletion of raw materials and air pollution resulting from its activities, have expand their raw materials base to include other sustainable materials. A class of materials with the potential to minimize the emission of the CO_2 as in the case of Portland cement is the supplementary cementitious materials (SCMs). SCMs are materials when added to Portland cement contribute to the properties of concrete through hydraulic activity or pozzolanic activity or both [4].

Prior works on the use of SCMs have been reported in literature [1], [5]–[7]. SCMs such as zeolites, calcined clays, agricultural waste by-products and industrial waste have been used to reduce the demand for PC [1, 5–7]. Zeolites are aluminosilicates based materials with

physiochemical properties that make them suitable as pozzolans. Industrial waste such as silica fume, fly ash and blast furnace slag have also been used as binders and agro waste such as rice husk ash, sugarcane bagasse ash and palm oil fuel ash among other product have also been used as binders and supplements to cement.

The use of calcined clays and agro-based by-products as SCMs is a well suited alternative that require attention especially in countries with numerous deposits of clay. Therefore, the large deposit of clays in Ghana, including kaolin can be exploited as SCM. Kaolin is a clay containing kaolinite mineral, which when heat treated forms a product called metakaolin ($Al_2Si_2O_7$) which exhibits strong pozzolanic reaction. That is, the active silica and alumina in the metakaolin react with portlandite ($Ca(OH)_2$) to form cementing compounds which improve the properties of mortars and concretes [2].

Metakaolin (MK) as a pozzolan in mortars and concretes improves mechanical properties at early ages, reduce hydration heat of cement, shrinkage, permeability, increase in the freezing and thaw resistance, resistance against chemical effects, decrease in alkali silica reactivity and many more [8]. These properties are possible due to the combination of pozzolanic reaction, accelerated cement hydration and the filler effects of the metakaolin [9].

In this work, Kaolin from Teleku Bokazo in the Western Region has been explored as an SCM in the production of mortars. The hydration product between Portland limestone and metakaolin was studied. The kaolin was heat treated to form metakaolin and partially used to replace Portland limestone cement in mortars to explore the optimum replacement and the mechanical characteristics of the composite mortar products. The pastes and mortars produced were tested for setting time, water absorption, flexural and compression strength. The samples were characterized using X-ray diffraction (XRD) for content and crystallinity of the kaolin. Fourier Transform Infrared Spectroscopy (FTIR) was adopted to study the

functional groups formed during the hydration. Scanning Electron Microscopy (SEM) was used for surface morphological studies of the paste.

1.2 Problem Definition

Kaolin from Teleku Bokazo is one of Ghana's natural kaolin deposits formed in situ. They are usually white (pure) in colour because of the little or low iron and organic matter contents. Therefore, the kaolin from Teleku Bokazo has found wide applications in the paint and dental industries. However, little or no information is known on the use of Teleku Bokazo kaolin as a supplementary cementitious material for construction applications. Hence, if Teleku Bokazo kaolin is well explored, its potential as sustainable construction material could reduce the demand for Portland cement to achieve equal or better characteristics as the pure Portland cement based mortars and also reduce the environmental effects.

1.3 Hypothesis

As a guide to this study, it was necessary to be guided by the scientific basis that the replacement of cement with different proportions of calcined kaolin from Teleku Bokazo can improve the mechanical characteristics of metakaolin-cement mortar composites as a suitable supplementary cementitious material for construction applications.

1.4 Aims and Objectives

The following activities carried out to investigate Teleku Bokazo kaolin as a reliable supplementary cementitious material.

- Characterize the compositional properties of the raw and calcined kaolin from Teleku Bokazo kaolin.
- Produce different mortar composites of calcined kaolin and study the nature of hydration products and their mechanical characteristics.

- Evaluate the mechanical characteristics (compressive and flexural strength results of the mortars produced) and determine the optimum metakaolin replacement.

1.5 Significance of study

The discovery of reliable and sustainable materials for the construction industry cannot be overemphasized. Portland cement, the widely used binding material poses huge environmental concern during their production. The manufacturing process of Portland cement emits large quantities of CO_2 into the atmosphere which contributes to global warming. Any material which can partially or totally replace Portland cement and perform its function as a green material will be embraced by the construction industry. The study investigated the effects of metakaolin produced from Teleku Bokazo kaolin in partially replacing Portland limestone cement. The results from the study showed that, it is feasible to produce metakaolin from Teleku Bokazo kaolin and the improved mechanical properties of the composite mortar samples hence, a reliable supplement to Portland limestone cement.

1.6 Limitation of study

This study characterized metakaolin based mortar composites largely captures all conditions. However, there were few limitations to this study and are recommended for future work. They are as follows:

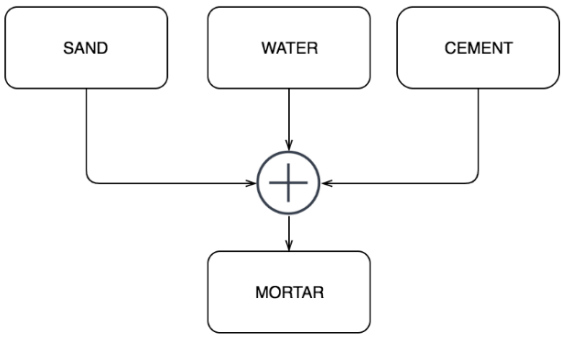
- The study does not include information on the final setting time of the cement paste.
- The study did not include hydration reactions via TGA/DSC to measure heat of hydration and determine pozzolanic reactions and their rates.
- No information on the mineralogical and chemical composition of Portland limestone cement.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Mortars and Concrete

Mortar is a mixture formed from the mixing of cement, fine aggregates (sand), and water whereas concrete is a composite of cement, fine aggregates (sand), coarse aggregate (stones or gravels) and water *(Figure 2.1)*. Mortars and concretes are widely used in building construction. Mortar is used to hold together bricks and blocks in construction works, while concretes in their reinforced form are generally used in structural applications or products where structural integrity is important. Although these construction materials are very important, the production of cement poses numerous environmental challenges. The manufacturing of cement alone contributes approximately 5 - 10% of global CO_2 emissions [10]. This problem has led to the use of supplementary cementitious materials (SCMs) as potential materials in effectively reducing the demand for Portland cement [11]. The introduction of SCMs in mortars and concretes as illustrated in *figure 2.1 (c) and (d)*, can make mortars and concretes sustainable, environmentally friendly, improve durability and reduce cost [12].



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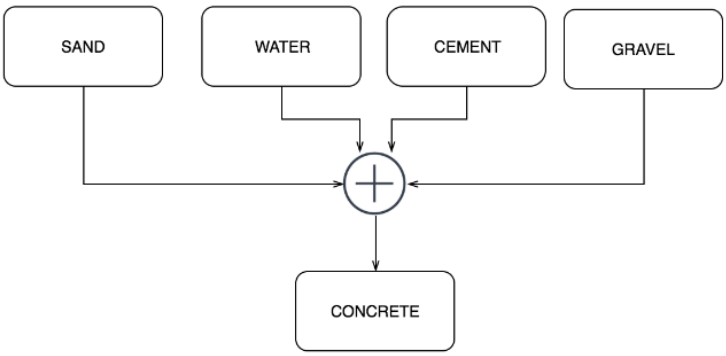

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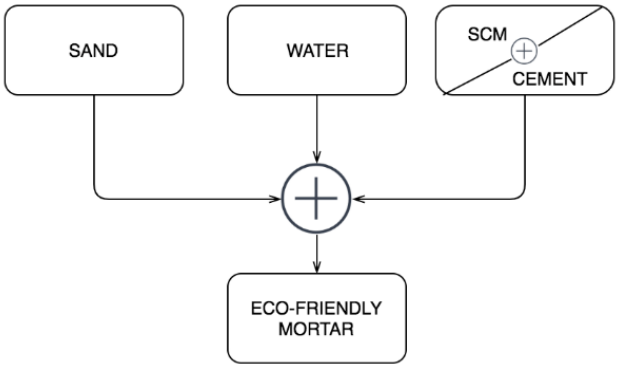

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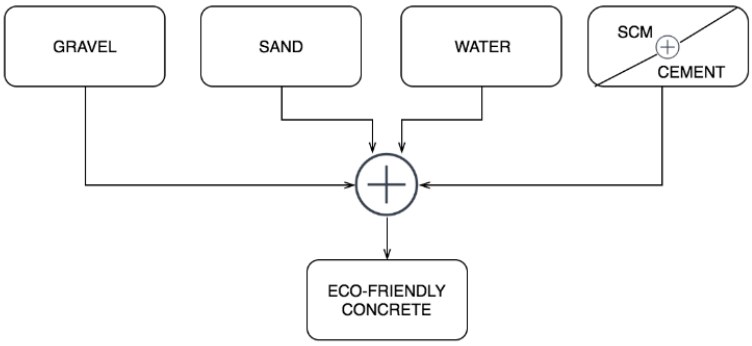


(d)

Figure 2. 1 *Composition of mortar and concrete*

2.2 Supplementary Cementitious Materials (SCMs)

SCMs are materials that add value to the properties of mortar and concrete through hydraulic reactivity or pozzolanic reactivity or both, when added to Portland cement [4]. The principal ingredient of SCMs are usually reactive silica in an amorphous form [9]. SCMs can be obtained from a number of varied sources. Fly ash, silica fume and ground granulated blast furnace slag are the most common SCMs from industry, these are waste products from the combustion of crushed coal, production of silicon and production of Iron respectively[10], [12]. Zeolites, kaolin and clays are also another source of SCMs but these are products of mining. Rice husk ash, sugarcane bagasse ash and palm oil fuel ash, which are sources of SCMs as well, are waste from the agricultural industry [13].

All these materials though are not purely cement materials, produce cementing products during their reactions with cement. The advantages of SCM include, protection of the environment from the dangers of both agro and industry by-products, enhanced performance of fresh or hardened mortars and concretes, low cost of construction and tailored batch mixes to meet different applications [13].

2.3 Pozzolans

In years gone by, pozzolana or pozzolan was a term used to describe naturally formed volcanic ashes and calcined earths, which react with lime at ambient temperatures in the presence of water [2]. In recent times the term is described by ASTM C595 [14] as all siliceous/aluminous materials which, in finely divided form and in the presence of water, will react chemically with calcium hydroxide (CH) to form compounds that possess cementitious properties. Therefore, pozzolans can be classified as SCMs. The importance of pozzolans has to do with their affinity to react with portlandite (a by-product from the hydration of cement) and form hydration products or cementitious materials. Typical sources of pozzolans are industries where fly ash, silica fume and granulated blast furnace slag are produced as waste,

agricultural sources where rice husk can be found. There are various locations in Ghana where different clays and kaolin deposits can be found. The properties of pozzolans-based products include enhanced strength, durability and decrease in rate of temperature rise. For centuries now, calcined earth materials has been blended with lime to form cementitious materials and they have been used in construction of water tanks, aqueducts, walls and bridges [2].

2.3.1 Silica Fume (SF)

Silica fume also known as micro silica is a by-product formed during the manufacturing of silicon or ferrosilicon. Silica fume is produced when coal reduces pure silica in an electric furnace[15], [16]. Micro Silica is predominantly composed of silica (90% SiO_2) with trace amounts of alkali oxides, iron oxide and magnesium oxide. They are generally amorphous with spherical shapes and particle sizes less than 1μm with average diameter of 0.1μm [15]. The relative density of SF is between 2.20 and 2.5 whereas that of Portland cement is 3.15. Their large surface area which is between 15 and 28 m^2/g make them very reactive and a good pozzolan. For applications where an admixture is required, a water reducing admixture is recommended because SF increases the water consistency of cement mixtures [13]. As an SCM, silica fume replaces ordinary Portland cement (OPC) between 9 to 15% by mass [13]. The reward for using micro silica include increased pore refinement, high pozzolanic reactivity, enhanced strength at early age, alkali-silica reaction resistance and improved sulphate resistance [13]. A disadvantage being high cost. SF is used in applications where high concrete strength and impermeability is required [17].

2.3.2 Zeolites

Zeolites have been present in the concrete industry since ancient civilizations [18]. Their properties make them versatile to be used as supplementary cementitious materials and

aggregates [19]. Zeolites are crystalline aluminosilicates or silica polymorphs formed by an interlinked network of silicon and aluminium tetrahedrals to form a three dimensional framework with uniform pore sizes of molecular dimension [20]. The micro-porous structure of zeolites makes them unique and very important; they have been found useful in ion exchange, drug delivery, detoxification, water softening and catalytic cracking processes [21], [22].

Zeolites are natural pozzolans, in spite of their crystalline aluminosilicates structure [23]. Their properties make them very suitable in substituting approximately 40% by weight of Portland cement to form lightweight concrete with specific properties. The compressive strength of concrete made with zeolites ranges from ~5 to ~30 MPa, and density from 500 to 1500 kg/m^3. Zeolite porous structures make them good molecular sieves; this structure helps them retain water which increases curing time and hence, strength during curing. Zeolites also have much higher cation exchange capacities than other natural pozzolans and this limits, or totally prevents the alkali-silica reaction hence earning them a wide range of use in the concrete industry [24]. Many countries including China, Russia, USA, Germany, Bulgaria, Iran, Serbia, and Greece have used zeolitic tuff as supplementary cementitious materials due to its benefit and availability [18], [25].

Perraki *et al*. [26] studied the effects of zeolite on the properties and hydration of blended cements. Zeolite from the Metaxades area in Greece was used for this study and the main aim was to explore Greek zeolites in construction technology with the heulandite type II being the dominant zeolite. Ten and twenty percent (10 and 20%) zeolite replacements were made with ordinary Portland cement and their compressive strengths were measured for 1, 2, 7, 28, 90, 180 and 360 days. It was observed that sample zeolite blended cement (ZBC) had lower compressive strength as compared to the reference cement CEM I 52.5 N for the first 28 days

but developed higher strength than the reference after 90, 180 and 360 days. From the Chapelle test, ZBC exhibited a good pozzolanic activity of 0.64 g of portlandite ($Ca(OH)_2$). The initial and final setting times observed were also similar to the reference cement. Sample ZBC made up of 20 %w/w replacement delayed in strength development during the first 28 days for both CEM 42.5 N and 52.5 N. Perraki et al. [26] concluded that sample ZBC contributes to the consumption of portlandite formed during the hydration and formation of cement products, making zeolites important pozzolans [26].

2.3.3 Rice Husk Ash (RHA)

Rice husk is the natural covering that envelopes rice grains during their growth. Rice husk is also readily available in rice producing countries since it is one of the most consumed meals worldwide and there are large industries growing rice to meet the demand. The rice husk is a constant source of environmental pollution in countries where they are produced, they are difficult to recycle. However, the silica produced from their combustion has the potential to be used in the construction industry since it has the potential to contribute to strength enhancement in mortars and concrete [7].

RHA is produced by either open burning or controlled burning between 500 °C and 800 °C followed by gradual or rapid cooling [7]. Burning under controlled conditions in a furnace/incinerator is preferred due to the production of high quality amorphous silica as compared to a crystalline silica which has low reactivity and a high carbon content when combusted under uncontrolled condition. Uncontrolled burning of RHA negatively impacts concrete performance[6], [27].

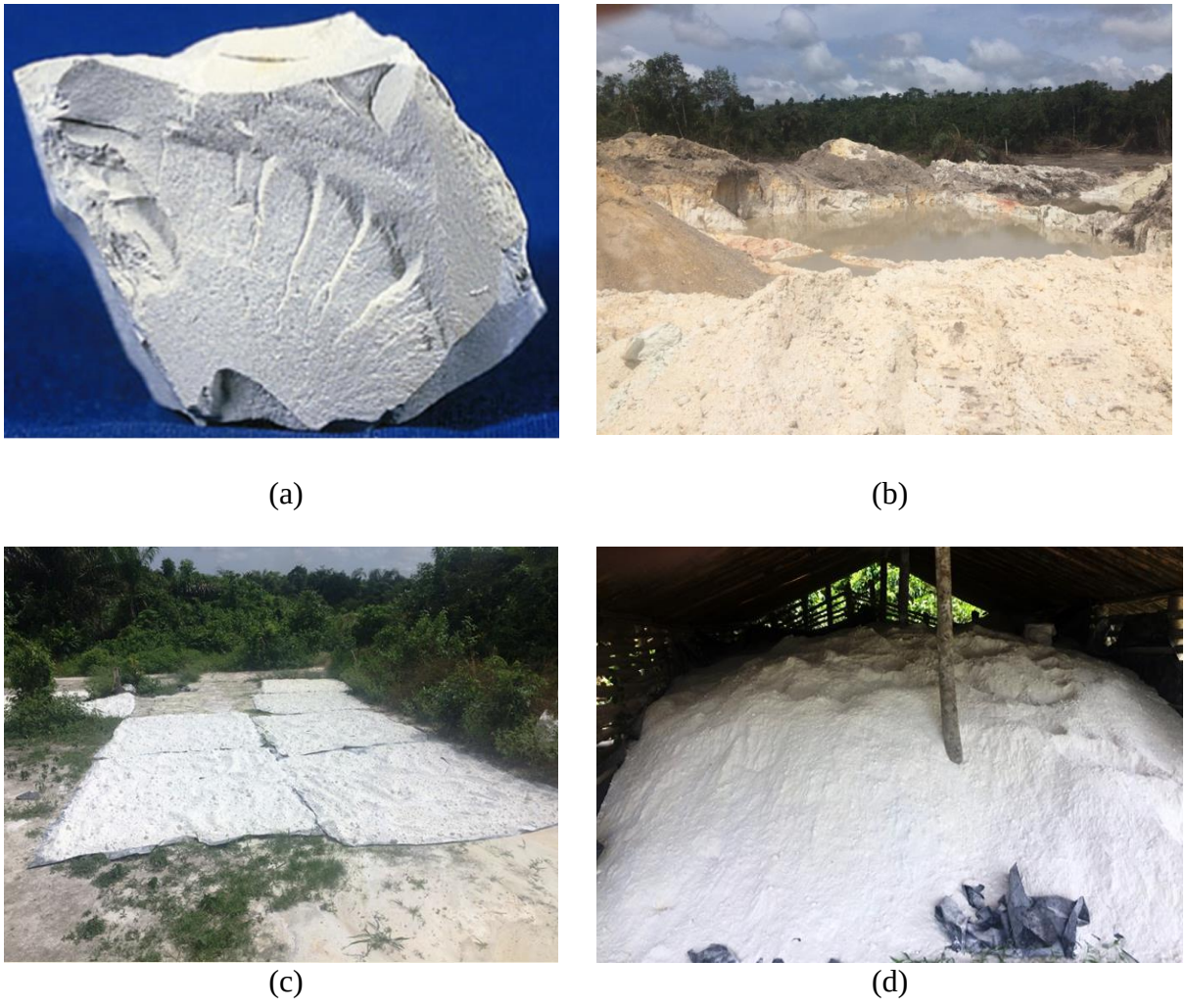
Rice husk is made up of 50% cellulose, 25 - 30% lignin and 15 - 20% silica. Upon burning, cellulose and lignin burn off leaving behind amorphous silica [27]. RHA suitable for construction applications are produced when combustion of rice husk is done at a temperature

below 700°C and milled into very fine particles [6, 24]. RHA contains around 85 - 90% of amorphous silica; the average particle size of RHA is 5 - 10 μm [7]. RHA grains are often porous and come in different shapes. Their structure allows them to absorb water when mixed with cement thereby reducing both their slump and workability values [7]. Finer RHA particles give rise to large surface areas and greater strength of concrete as a result of their fine particles filling the voids in the concrete in an optimum manner. They can be described as super pozzolans due their high silica content [7]. Studies show that RHA concrete have high strengths at various ages compared to concrete without RHA. The introduction of RHA into concrete also reduces chloride ion penetration, which enhances its durability [6, 24].

2.3.4 Kaolin

Centuries ago, a clay was mined in Asia specifically China, which contained kaolinite ($Al_2(OH)_4Si_2O_5$) as the main mineral constituent [28]. It was named Kao-ling which translates high ridge and found its application in the ceramic industry due to its characteristics [28].

Kaolin is mainly made up of hydrated aluminosilicate (kaolinite) and quartz (SiO_2). Its structure can be described as alternating octahedral and tetrahedral sheets of alumina and silica stacked together to form long range crystalline structure with plate-like morphology. Kaolin are generally white, yellow in colour as illustrated in *figure 2.2 (a)* , chemically inert, electrically neutral and have fine particles ranging from ~0.15 to ~0.2 μm [28]. These properties make them suitable for numerous applications including production of ceramics, filler in paints and a coating material, etc. [28]. *Figure 2.2 (b)* shows the Teleku bokazo kaolin deposit in the Western Region of Ghana, the kaolin is excavated and dried in open air *(Figure 2.2 c)* and stored under wooden structures *(Figure 2.2 d).*



(a) (b)

(c) (d)

Figure 2. 2 *The extraction and processing of kaolin; (a) kaolin rock* [20]

(b-d) drying and stockpiling of kaolin

2.3.4.1 Production of Metakaolin

Metakaolin (MK), is the product of thermal activation of kaolin and was discovered before 1960 [29], its use as a pozzolan in the manufacturing of cement and as SCM in mortar and concrete was discovered in the 1980s as a result of its properties [29]. When kaolin is calcined at temperatures ranging between 600 °C and 900°C in a kiln for a suitable period, the kaolinite mineral in the kaolin decomposes by losing hydroxyl ions in the form of water vapour to form a metastable compound known as metakaolin ($Al_2O_3{\cdot}2SiO_2$) which is amorphous and very reactive [30]–[32]. The metakaolin formed can be classified as a

pozzolan and can be used as an SCM. Different calcination temperatures have different effect on the metakaolin produced. For example, calcinations above 900 °C, there could be recrystallization and less pozzolanicity [33]. Using calcination temperatures below 450 °C, kaolin shows little dehydroxylation, less than ~0.18 [31]. In the range from 450 to 570 °C, the degree of dehydroxylation sharply increases up to ~0.95, and finally between 570 and 700 °C, the kaolinite is fully dehydroxylated [31].

The high reactivity characteristic of metakaolin makes it very useful it because helps in consuming the portlandite thereby reducing efflorescence, filler effect; which enhance cement hydration at especially early ages and accelerated cement hydration which produces cementitious materials which fills pores in the pore system [9]. Using MK is also eco-friendly due to the low CO_2 emissions during its production process [9], [29]. Incorporating metakaolin can reduce up to 127 kg of CO_2 per tonne of Portland cement produced [34]. In the construction industry, metakaolin in addition to cement is used in high performance, high strength and lightweight concrete, precast concrete, fiber cement and ferrocement products, glass fiber reinforced concrete, mortars, stuccos, repair material, and pool plasters [31]. Metakaolin has been used to replace Portland cements from 5% to 60% [8], [35], [36]. For mixtures containing up to 15% metakaolin, pozzolanic reactions occur rapidly, thus, within a fortnight leading to an increase in strength and refinement in pore structure of the cement paste [8]. After the fortnight, the rate of pozzolanic reaction decreases glaringly with a corresponding decline in the compressive strength [8]. During the early ages of hydration, thus in a week of curing, the sample becomes more closely packed, forming a compact mass with few pores. For kaolin based composites there is a rapid reduction in the total porosity in the first week and a gradual reduction in the total porosity afterwards [9].

In comparing metakaolin to agro-waste SCMs, very little amount of energy and time is

required in calcining metakaolin. Also, water vapour is often released as compared to the various agro waste which often require high energy for burning for long periods and also the release of CO_2 gas [32]. In an investigation by Poon *et al.* [37], [38], the rate of pozzolanic reaction of metakaolin blended cement was observed to be higher at early ages compared to silica fume blended cement [38]. Tagbor *et al*. [39] studied the pozzolanic properties of Anfoega kaolin from the Volta region of Ghana. The authors reported that the kaolin was calcined at 700^{o}C and used to replace 5 to 40% ordinary Portland cement. They also concluded the optimum metakaolin replacement was 25% and Anfoega kaolin had good pozzolanic properties and suitable for use as a mineral admixture [39].

Bediako *et al.* [35] also reported an optimum replacement of 20% by weight, gave best compressive strength values when calcined low grade kaolin from the Ashanti region was blended with Portland cement. They concluded low grade kaolin influenced mortar strength by both filler and pozzlanic effect [35]. Poon *et al* [37], reported that cement pastes incorporating metakaolin from percentages of 5 to 20% had higher strength in compression than the control at all ages from 3 to 90 days, with 10% metakaolin replacement strength unrivalled [31]. Wild *et al.* [40] also reported incorporation of metakaolin enhanced concrete compressive strength with 20% replacement the optimum [31]. Courard *et al.* [41] studied the flexural strength of mortars by replacing 5 - 20 % of CEM I 42.5 by mass with metakaolin. There was a slight decrease in flexural strength for 3 and 7 days. However, after 14 and 28 days, the mortar containing metakaolin attained higher strength [31].

Brooks *et al* [42], also reported that metakaolin retarded the setting as metakaolin percentage increased. It was observed that, 15% metakaolin replacement showed a significant delay in the setting time. A decrease in the initial setting was as a result of an increase in water demand for forming a dense binding phase [8].

High reactivity, large surface area and amorphous structure of metakaolin gives pastes incorporated with metakaolin higher water consistency in comparison to its control [9]. Badogiannis *et al.* [43] reported that pastes incorporating metakaolin demanded more water than relatively pure cement [31].

Water absorption in normally vibrated concretes (NVC) systems were also investigated and it was found out that there was a reduction in water penetration for concentrates with 20% replacement of cement with metakaolin as reported by Khatib and Clay [29], [44]. Benefits associated with the incorporation of metakaolin in concrete include superior mechanical properties at early ages, reduction of the high hydration heat of cement, improvement of compressive, tensile and flexural strengths, reduction of shrinkage, increase in the freezing and thaw resistance, reduction of permeability, resistance to chemical effects, decrease of alkali-silica reactivity and allowing for denser concretes [8].

2.4 Pozzolanic Reaction

Pozzolanic reactions occur during the hydration of cement in the presence of water. Pozzolanic reaction is a reaction between a pozzolan and portlandite ($Ca(OH)_2$) from Portland cement to form cementitious compounds including calcium silicate hydrates (C-S-H), calcium aluminium hydrate (C-A-H) and calcium aluminium silicate hydrate (C-A-S-H) [2].

$$H_4SiO_4 + Ca(OH)_2 \rightarrow CaH_2SiO_4 \cdot 2H_2O \quad \text{----------(1)}$$

The reaction between the active silica and alumina from the metakaolin with portlandite produced during the hydration of Portland cement is known as the pozzolanic reaction [2], this reaction is represented in equation (1).

During the hydration of Portland metakaolin composite, there is an increase in the amount of C-S-H gel and a decrease of portlandite crystals causing a decrease in micro-cracks as a result of portlandite dehydroxylation [45]. The rate at which pozzolans react with portlandite in the presence of water is termed pozzolanic activity. From literature, metakaolin consumes a significant amount of portlandite in mortar pastes. The quantities of lime ($Ca(OH)_2$) produced during cement hydration and lime consumed can be measured using TG/DTA. Wild and Khatib [46] found out that portlandite was significantly consumed at 14 days of curing for cement replacement of 5,10 and 15% with MK [2].

2.5 Production of Portland cement

2.5.1 Types and varieties of Portland cement

Portland cement is a binder in mortars and concrete that is globally used in the construction industry [47]. Cements are classified into two groups namely Hydraulic and Non-Hydraulic [48]. Hydraulic cements require the presence of water to complete a reaction between the cement components and water to set and bond, whereas non-hydraulic cements do not require water but rather set and bond by drying and reacting with carbon dioxide in its surroundings [48]. There are currently five main types of cement CEM I, CEM II, CEM III, CEM IV and CEM V. Under the main five we have eleven different varieties namely Portland cement, Portland-slag cement, Portland silica fume cement, Portland pozzolana cement (PPC), Portland fly ash cement, Portland burnt shale cement, Portland limestone cement, Portland composite cement, blast furnace cement, pozzolanic cement and composite cement. These eleven varieties produce 27 different cement products of varying mineral compositions [49].

2.5.2 Portland cement manufacturing

The cement manufacturing process involves mining, crushing, grinding, blending of raw materials, calcining, cooling, mixing and milling, and finally storing and bagging this process

is graphically demonstrated in *figure 2.3*. The wet process and the dry process are the two main ways of manufacturing cement. Regarding the wet process, water is added to the raw materials before been fed into the rotary kiln whereas with the dry the raw materials are ground mixed and fed into the kiln [50].

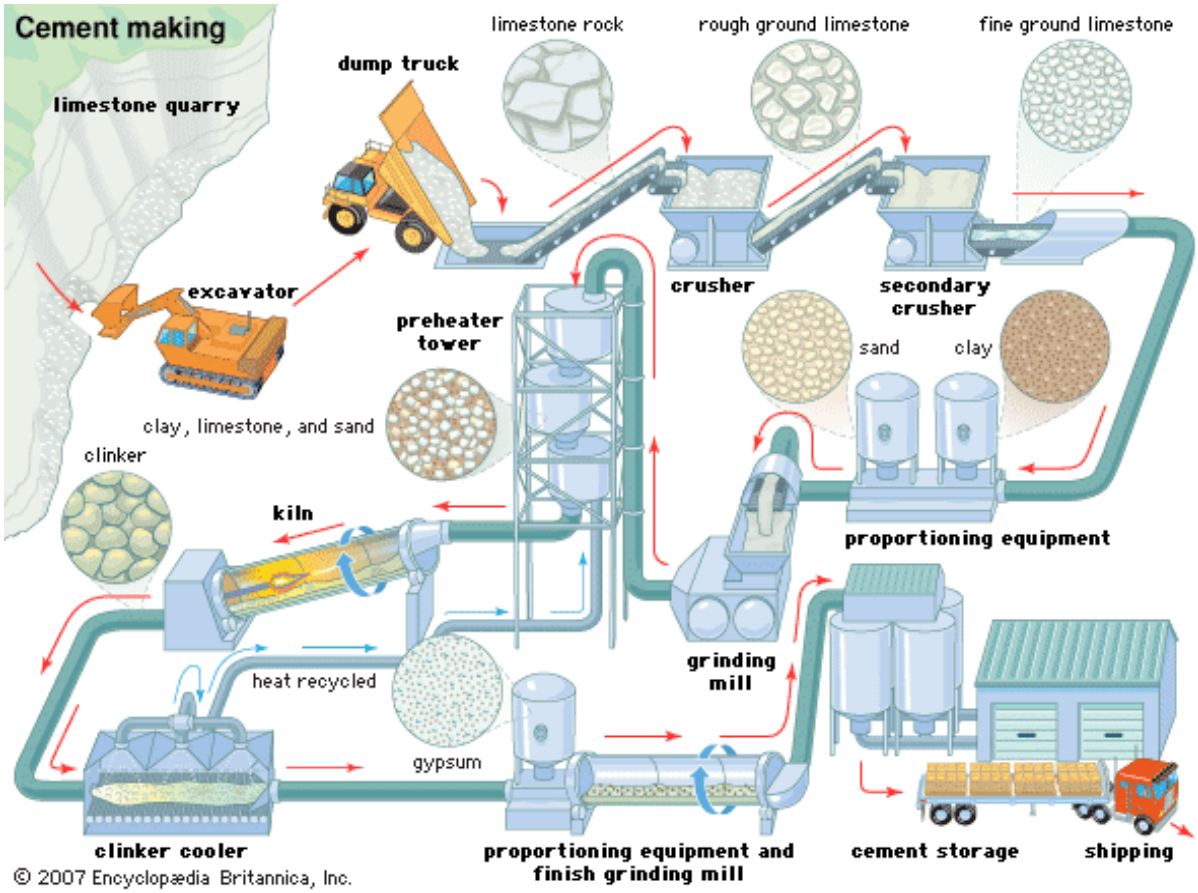


Figure 2. 3 *Shows the process flow sheet for the manufacturing of cement* [51]

In the manufacturing of cement, four basic raw materials are required

i. Lime (calcareous) obtained from a calcareous rock e.g. Limestone [50], [52].

ii. Silica (siliceous) obtained from clays and shales e.g. Kaolin [50], [52].

iii. Alumina (argillaceous) obtained from clays and shales e.g. Bauxite [50], [52].

iv. Iron Oxide (ferriferous) obtained from clays and shales e.g. red mud [50], [52].

Limestone ($CaCO_3$), clay, sand and iron ore are pulverised and mixed together to form a homogenous bulk oxide composition. The mix is then fed into a rotary kiln for calcination. During the calcination, $CaCO_3$ decomposes into CaO and CO_2 at 900°C [50], [52][50], [52].

The clinkering process follows and CaO reacts at high temperatures (1400°C –1500°C) with silica, alumina and ferrous oxide to form tricalcium silicate (Ca_3SiO_5 or C_3S), dicalcium silicate (Ca_2SiO_4 or C_2S), tricalcium aluminate ($Ca_3Al_2O_6$ or C_3A) and tetracalcium aluminoferrite ($Ca_4Al_2Fe_2O_{10}$ or C_4AF) [50], [52].

Different additives are added to the mix depending on the preference of the manufacturer (e.g. silica sand, foundry sand, iron oxide alumina residues and blast furnace) can be added to the mix to meet required slag specification [50].

The clinker formed in the kiln is cooled immediately. The cooled clinker is ground together with gypsum ($CaSO_4 \cdot 2H_2O$) and limestone to form Portland cement. The cement is then stored in silos and bags [50].

2.5.2.1 Portland limestone cement

The gradual move of cement manufacturers to produce green and sustainable cement, led to the replacement of ordinary Portland cement clinker with limestone. This cement is produced when limestone is fused with cement clinker in different proportions. The binder formed in comparison to OPC uses less amount of energy in the clinkering process, less amount of raw materials and reduces CO_2 emissions. Under the European standard Portland limestone cement are classified under CEM II/ A-L, CEM II/ A-LL with clinker composition 6 - 20% by mass and CEM II/ B-L, CEM II/ B-LL with clinker composition 21 - 35% by mass[49], [53].

2.6 Hydration

Hydration is a series of reactions between water and cement compounds which ends in forming a compact and hard mass. Cement contains four main minerals namely; alite (C_3S), belite (C_2S), celite (C_3A), brown-millerite (C_4AF) and gypsum ($CaSO_4 \cdot 2H_2O$). These minerals react at different rates and form different phases when hydrated [54].

The hydration of cement is generally explained as dissolution and precipitation process. The process begins with dissolution of compounds followed by precipitation of new compounds [54]. Immediately cement is mixed with water, a series of reactions occur leading to the dissolution of the cement releasing ions into the mixture. The paste formed is an aqueous solution of different ionic species known as pore solution. Gypsum, alite and celite are highly soluble and they increase the concentration of ionic species in the pore solution immediately cement and water are mixed. The concentration continues to increase till the pore solution is supersaturated making it thermodynamically suitable for ions in solution to precipitate and form stable solid phases [54].

The new phases are formed through precipitation which is the beginning of the second stage. The transformation of one phase to another phase causes an exothermic reaction with large amounts of heat released [54]. The heat evolution with time can also be described in stages. From the onset of hydration there is an evolution of heat for a short period and this is due to a rapid reaction occurring in less than a minute after mixing. This reaction occurs to protect cement particles by forming a layer (an amorphous hydrated product) around the cement particles to prevent an interacting with the pore solution [54]. This shielding prevents further dissolution and is considered stage one. Stage two is the induction period during which there is little or no reaction. After the induction period, there is a rapid reaction period known as stage three, the rate of reaction increases rapidly reaching a maximum at a time that is usually 24 hours after initial mixing and decreases rapidly to less than half of its maximum

value. This behaviour is as a result of the hydration of alite and the rate is controlled by the nucleation and growth of the hydrated products [54].

At the end of stage three, about 30% of the initial cement has hydrated and the paste has undergone both initial and final setting. The primary hydration products calcium silicate hydrate gel and calcium hydroxide fill the capillary pores which were originally occupied by the "mix water", and this causes a decrease in the total pore volume and simultaneously increase the strength [54].

For further hydration, dissolved ionic species from the cement must diffuse outward and precipitate into the capillary pores or water must diffuse inward to reach unreacted cement particles. This diffusion retards as the layer of the hydration products around the cement particles become thicker. This period is the diffusion limited reaction period and it forms the fourth stage of Portland cement hydration [54]. The rate of hydration of the various cement compound at early ages is ranked from the quickest to slowest as follows [55]:

$$Ca_3Al_2O_6 > Ca_3SiO_5 > Ca_4Al_2Fe_2O_{10} > Ca_2SiO_4$$

Increasing rate of hydration

The strength of concretes is solely attributed to calcium silicate hydrates. Alite is responsible for the early strength (generally the first 7 days) while belite adds to the strength at a later age (28 days) [54].

2.6.1 Hydration of C_3S and C_2S

The hydration of Alite and Belite are represented by the reactions in equations (2) and (3) [56] respectively.

$$2Ca_3SiO_5 + 6\,H_2O \rightarrow Ca_3Si_2O_7 \cdot 3H_2O + 3Ca(OH)_2 \quad \text{----------(2)}$$

Immediately water is added to cement, alite reacts with water to release calcium ions and hydroxyl ions, generating a large amount of heat, this continues until the paste is saturated

with calcium and hydroxyl ions, then calcium hydroxide and calcium silicate hydrate begin to crystallize and grow simultaneously. Calcium silicate hydrate continues to grow and become thicker meanwhile making it difficult for unhydrated calcium silicate to come into contact and react with water hence slowing down the production of calcium silicate hydrates [55].

i. C_3S and C_2S make up 80% of Portland cement.
ii. C_3S is responsible for the early strength development of cement.
iii. The hydrated calcium silicate or calcium silicate gel is amorphous.
iv. The formed $Ca(OH)_2$ increases the pH of the paste between 12.5 and 13.

$$2Ca_2SiO_4 + 4H_2O \rightarrow Ca_3Si_2O_7 \cdot 3H_2O + Ca(OH)_2 + 173.6\ kJ \text{----------(3)}$$

i. C_2S is less soluble in water compared to C_3S hence a low hydration rate.
ii. C_2S contributes little to early strength of cement but make significant impact on final strength.

2.6.2 Hydration of C_3A and C_4AF

The hydration of Celite is represented by the reaction in equations (4) [56].

$$2\ C_3Al_2O_6 + 21\ H_2O \rightarrow 2\ [Ca_3(Al(OH)_6] + 9\ H_2O + 58.6\ kJ \text{ ----------(4)}$$

i. C_3A is highly soluble than C_3S in water.
ii. Calcium Aluminate hydrate is crystalline.
iii. C_3A do not form a protective layer around aluminate grain surfaces.

In the hydration of celite the initial reaction is rapid and the next is slower before the formation of hydrogarnet (C_3AH_6). Most often the initial reaction is not allowed to occur in Portland cement due to the large amounts of energy that it releases, which could also cause the cement paste to set shortly after mixing. For that reason, gypsum is added. Gypsum is highly soluble and releases calcium and sulphate ions into the pore solution. The presence of the sulphate ions causes celite to undergo a different hydration reaction forming ettringite.

The formation of ettringite, and monosulphoaluminate are represented by the reactions in equations (5) and (6) respectively [56].

$2[Ca_2Al(OH)_7 \cdot 3H_2O] + 3[CaSO_4 \cdot 2H_2O] + 14H_2O \rightarrow (Ca_6[Al(OH)_6]_2 (SO_4)_3 \cdot 26H_2O + Ca(OH)_2]$ ---------- (5)

If the gypsum in the cement reacts completely before the C_3A then the concentration of sulphate ions in the pore solution decreases drastically and the ettringite becomes unstable and converts to a different solid phase with less sulphate. Gypsum contents in cements are usually not enough to react with all the C_3A and as a result most or all the ettringite is converted to monosulfoaluminate during the first two days.

$Ca_6[Al(OH)_6]_2 (SO_4)_3 \cdot 26H_2O + 4 [Ca_2Al(OH)_7 \cdot 3H_2O] \rightarrow 3(Ca_4[Al(OH)_6]_2 SO_4 \cdot 6H_2O) + 2Ca(OH)_2 + 20 H_2O$ ----------(6)

Formation of monosulfoaluminate and ettringite are both exothermic reactions and contribute to the heat of hydration of cement.

The early hydration of C_3A to form ettringite is quite rapid, C-S-H formation separates the C_3A particles from the pore solution slowing their dissolution. After a period of several hours the early forming ettringite converts to monosulfoaluminate allowing C_3A to undergo renewed rapid hydration with kinetics that are roughly similar to the main hydration peak of C_3S.

Brownmillerite reacts in a similar way to celite but more slowly. The significant difference has to do with the substitution of aluminium with iron. Brownmillerite hydration is represented by equation (7) [56].

$Ca_2AlFeO_5 + 2Ca(OH)_2 + 11H_2O \rightarrow 2 [Ca_2Al_{0.5}Fe_{0.5}(OH)_7 \cdot 3H_2O]$ ----------(7)

A combination of monocarboaluminate, hemicarboaluminate, ettringite and C-S-H in a pozzolanic reaction lead to increase in strength during compression and refinement of pores

in mortar also the limestone grains serve as nucleation sites for the cement hydration process [57], [58].

2.7 Curing

Curing is the process of conserving enough moisture and controlling temperature in a newly cast mortar or concrete to allow hydration to fully take place and gain required properties [55], [59]–[61]. After mortars have been moulded, the curing process follows immediately.

The best curing method takes into consideration the materials to be used, method of construction and planned application of concrete or mortar [62]. Right curing method improves strength, durability, and increases abrasion resistance as illustrated in *figure 2.4.* [62].

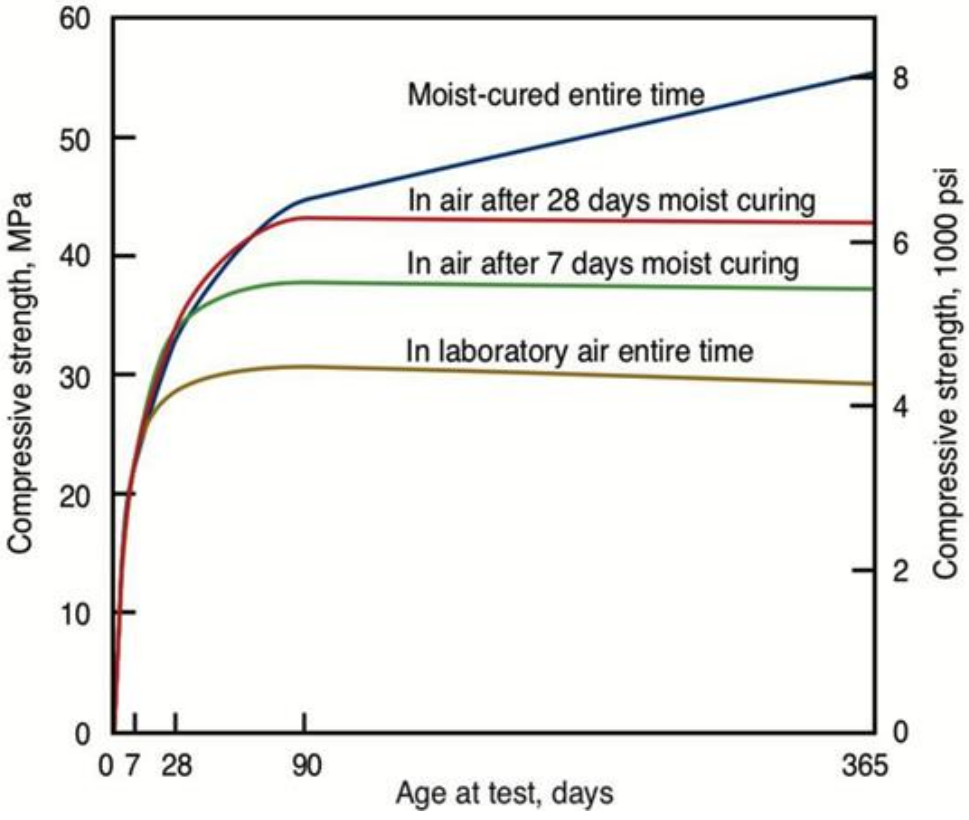


Figure 2. 4 *Effect of curing time on concrete strength* [62]

2.7.1 Types of curing

The Curing methods can generally be classified into three:

i. prevention of moisture loss,
ii. addition of supplemental moisture and
iii. keeping surfaces moist and regulation of temperature of mortars and concrete [59], [61], [62].

2.7.1.1 Immersion, sprinkling and wet covering

These are techniques that add moisture to mortars and concretes while keep mixing water intact. Immersion technique uses a curing pond in which the mortar or concrete surfaces are flooded with water and a uniform temperature maintained in the pond. Unfortunately, this method is used often in laboratories where small quantities are to be cured [59], [62].

The sprinkling method employs sprinklers to keep the concrete moist by spraying water on concrete surface at different time intervals. This is usually effective during hot weather conditions since it reduces concrete temperature [59]. Using this technique requires good supervision to ensure sample surfaces are thoroughly wet and winds do not interfere with sprinkler directions [59], [61], [62].

The wet coverings technique uses fabrics soaked with water such as burlap, cotton mats and hessian to cover the surfaces of mortar or concrete samples. Wet coverings (*figure 2.5*) are used immediately concrete is sufficiently hard and should not be allowed to dry up during use since it can draw water out of the sample. When in use for the first time it must be thoroughly rinsed to prevent staining [59], [61], [62].

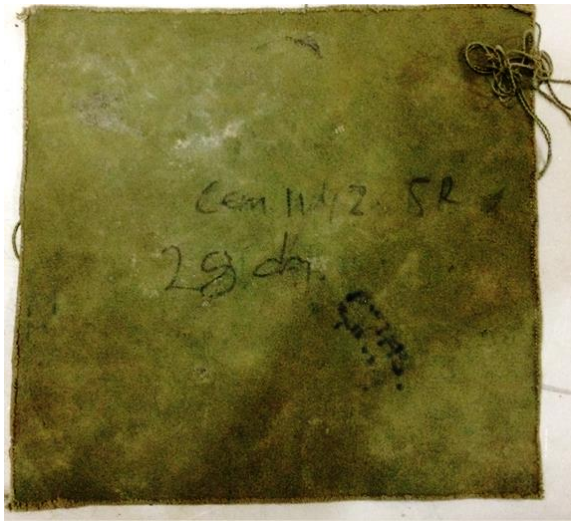


Figure 2. 5 *Wet covering for curing mortar and concrete cubes*

2.7.1.2 Plastic sheeting, membrane forming curing compounds and internal curing compounds.

These are curing methods that prevent moisture loss in mortar. Plastic sheets that conform to American Society for Testing Materials (ASTM C171) [63] are used, an example is polyethylene film, which must be 0.1mm thick is used to cover simple as well as complex shapes. When using plastic sheets, mortars must be fully covered and sealed with wrinkles straightened if used to cover large samples otherwise there maybe partial hydration. Generally plastic sheets (*figure 2.6*) come as either coloured or clear, black and white sheets can be used in the appropriate conditions. Care must be taken when using coloured plastic sheets as they may discolour the sample. Black sheets are appropriate in cool weather conditions since they are able to retain the moisture in concretes whereas white and lightly coloured sheets are suitable under hot conditions since they reflect sun rays [59], [61].

Figure 2. 6 *Plastic Sheet for curing of mortar and concrete cubes*

Membrane forming compounds usually come as liquids derived from wax, resin, and chlorinated rubber [59], [61]. They are sprayed uniformly unto the sample surface which dry and form impermeable membranes that slow down the loss of moisture from the sample. When membrane forming compounds are used it must be noted that their by-products prevent their surfaces from been adhered to, therefore, flooring products and tiles cannot be laid on their surface; if flooring products are to be used the membrane products need to be removed [59], [61]. Membrane curing compounds should be applied as soon as free water on the surface has evaporated or dried. Too early or late application may cause it to lose its effectiveness. They usually come in two varieties clear or white pigmented, with each applied under specific conditions. White is applied during sunny or hot conditions where it is able to reduce concrete temperature by reducing solar heat gain [59], [61].

Internal curing compounds are the only known compounds whose effect on the concrete are from within because they are added as admixtures to concrete before placing. They retard moisture loss and provide moisture for the concrete from within hence producing a fully hydrated concrete over time [59], [61].

2.7.1.3 Steam curing

Steam curing technique is applied when early strength in mortars is needed or in cold conditions where additional heat is required for hydration. This method accelerates strength of mortars and concretes while adding heat and moisture [60], [62]. Live steam curing and high pressure steam curing are the notable steam curing methods. Live steam is used in applications such as large precast concrete as opposed to high pressure steam curing where small concrete products are cured in an autoclave [62].

2.8 Characterization techniques for mortars containing pozzolans

After pastes and mortars are formed and cured, tests are carried out to determine their structure and properties. Characterization gives an idea of how they are likely to perform or behave during application. The test includes mechanical, thermal, optical, etc. The characterizations in this work include XRD, FTIR, SEM, setting time, water of absorption compressive and flexural test.

2.8.1 X-ray Diffractometer (XRD)

This instrument is used to determine the molecular structure of a crystalline material. The working concept is to generate x-rays and diffract the x-rays through a sample; the reflected rays that interact with the crystal planes of the samples are picked up by a detector as a pulse and plotted as a graph to determine the crystallinity of the material. After the data has been plotted on the screen, the software indexes the peaks and compares it with a database to determine the phase transition and crystal structure of the material based on the knowledge of the material. Kaolin and metakaolin mineralogical compositions can be determined using XRD.

Kaolinite and quartz were the main phases present in Anfoega kaolin when characterised with XRD, while pyrophillite, quartz and magnetite were identified after calcination [39]. The

minerolgical composition of kaolin and metakaolin were studied using XRD by El-Diadamony *et al*, Badogiannis et al, Subasi *et al*. and Moodi *et al.* [8], [9], [29], [64]. Kaolinite, illite and quartz were the main crystal phases present in kaolin [29], whereas kaolinite, quartz, muscovite, calcite and mullite were present in different metakaolins [64]–[66].

In identifying and studying the hydrated phases present in cement paste, XRD is used. Ramezianpour and Hooton [57] replaced PLC with 10% MK and identified portlandite, calcite and ettringite as the main mineral phases [57].

Subasi *et al*. [8] examined the hydrated phases of white Portland cement and MK replaced pastes after 28 days and revealed the presence of portlandite, C-S-H, alite, belite and quartz. There was a decrease in portlandite content as MK increased in the paste, in comparison to the control paste [8]. The XRD patterns of ordinary Portland cement (OPC) and MK paste were also studied after 28 days by El-Diadmony *et al*. [9]. The authors observed a decrease in the intensities of portlandite in MK paste in comparison to OPC pastes, also calcite peak intensities decreased as MK contents increased. Finally, alite and belite intensities decreased with increasing time due the continuous hydration of these clinker minerals [9]. Cyr *et al*. [36] also observed the formation of ettringite in cement pastes replaced with 60% MK after 14 and 28 days hydration [36].

2.8.2 Fourier Transform Infrared Spectroscopy (FTIR)

This is a technique used to determine the functional groups present in a material or substance. The instrument uses the concept of transforming time varying signals to frequency domain to produce a spectrum. Molecules are irradiated with infrared radiations and these radiations interfere with each other to produce to produce an interferogram. The application of the Fourier transform mathematical model to the signal from interferogram produces a spectrum of transmission against wavenumber. This data is then analyzed to interpret the functional groups of the substance. [67], [68].

Horgnies *et al*. [69] used FTIR spectroscopy to study the clinker and hydrated phases of cementitious materials. They observed Si-O asymmetric stretching vibrations of belite and alite peaks from 900 - 995 cm^{-1} and 883 - 938 cm^{-1} respectively. Celite phases were present at 898, 786, 739 and 704 cm^{-1}. The main hydrated cement phases such as portlandite and C-S-H were also studied and assigned. Portlandite was found to have a characteristic position of 3640 cm^{-1}. Peaks characterizing calcium silicate hydrates were assigned as follows, O-H bands associated with capillary water from C-A-S-H were found between 3352 and 3356 cm^{-1} and 1640 - 1660 cm^{-1}. Asymmetric stretching vibrations of Si-O bonds were located between 911 - 1000 cm^{-1}, Afwillite a crystalline hydrated calcium silicate was located at 911, 963 and 985 cm^{-1} while C-S-H with gel like structures were located at 950 and 1000 cm^{-1} [69].

Ylmen *et al*. [70] used an in situ attenuated total reflectance (ATR) FTIR method to monitor the hydration of cement paste. At 3640 cm^{-1} an O-H stretching mode was observed which represented portlandite. Bulk water was also represented at 1650 cm^{-1} and 3000 - 3600 cm^{-1}. Gypsum peak appeared at 1100 - 1200 cm^{-1}. From 800 - 1000 cm^{-1} peaks representing alite were also identified. Bands characteristic of hydrated cement compounds (Calcium silicate

hydrates) were present at 900 -1200 cm^{-1} and at 1350 cm^{-1}, representing both Si-O stretching and Si-OH bending modes [70].

Govindarajan *et al*. [71] studied the hydration of Indian Portland cement hydrated in sea and distilled water with FTIR using the KBr pellet technique. They observed sharp bands at 3630 cm^{-1} which was attributed to O-H stretching vibrations of portlandite ($Ca(OH)_2$), bands at 3410 and 1610 cm^{-1} were assigned to water of crystallization from gypsum. At 1425 cm^{-1} carbonate peaks were also detected. Bands present from 1100 - 1160 cm^{-1} were also associated with sulphates SO_4^{2-} vibration modes. Si-O asymmetric stretching vibration of Alite was represented at 919 cm^{-1} [71].

2.8.3 Standard Consistency

The standard consistency is the amount of water required by a cement paste to resist penetration by a standard plunger. Cement paste of standard consistence is one that has a specified resistance to penetration. This test is carried out using a Vicat apparatus with a standard plunger, the plunger is allowed to penetrate the cement paste at different water contents until the scale reads a specified penetration value [72].

The water demand of OPC-MK paste increased from 29 to 36.5% as metakaolin was increased from 5 to 40% in Tagbor et al. [39] studies of the pozzolanic properties of Anfoega kaolin. The increase was attributed to the small particle sizes of metakaolin which increased the overall surface area of the mix hence increasing the water demand [39].

Bediako [73] also reported increase in water consistency of paste containing PLC-CP mixes. The control paste had a water consistency of 26%, with 10% to 40% PLC-CP mixes increasing from 29% to 37% [73]. Bediako [73] attributed the increase in water consistency to the porous nature of the pozzolan. El-Diadamony *et al* [9] reported 5 and 10% metakaolin substitution with cement gave 30% and 50% water consistency respectively [9]. El-

Diadamony *et al.* [9] also concluded the increase in water consistency was due to the amorphous nature, high surface area and high reactivity [9]. Atiemo *et al*. [74] added calcined clay and limestone to Portland cement and observed an increase in the water demand. The increase in water demand was explained as a result of increase in effective surface area when the pozzolans were added and corresponding decrease in the cement content thereby increasing the effective cement water ratio causing an increase in water consistency [74].

2.8.4 Setting Time

It can be simply explained as the time between which cement is mixed with water until it hardens. Setting time is generally categorised in two, initial setting and final setting. The initial setting is the time within which the cement paste mixed with water begins to lose its plasticity while the final setting is the time at which cement paste loses its plasticity. Setting information is important because it gives information on the time required for a cement paste to harden, for cases where cement pastes are to be transported over long distances one can easily monitor and remix when necessary. The initial and final setting of cement paste is determined using a Vicat Apparatus. In determining the initial setting, a standard needle is inserted into the vicat apparatus and allowed to penetrate the cement paste until it is no longer able to penetrate the paste.

Generally, cement paste containing metakaolin prolongs setting time. Brooks et al [42]. observed delays in setting time as metakaolin was increased in cement paste although there was a retardation at 15% metakaolin replacement, this retardation was as a result of the formation of a denser binding phase when the water demand increased [8]. El-Diadamony *et al.* [9]. reported cement paste (OPC) containing metakaolin between 5 to 20% by replacement, prolonged setting as a result of the coating effect of MK particles on the OPC grains, formation of ettringite and dilution of the OPC [9].

In studying the influence of clay pozzolans on Portland limestone cement, Bediako [73] studied the setting time of PLC-CP pastes, 116 minutes was recorded for the initial setting time of the control paste and gradual increase in setting time thus 137 to 172 minutes with clay pozzolana (CP) addition between 10% and 40% [73]. The initial setting time increased from 173 to 210 minutes as Anfoega metakaolin was increased from 5 - 40% whereas the control recorded 160 minutes. The delay in setting was attributed to the low celite content of the OPC [39].

2.8.5 Flexural strength

This test is carried out on samples when information on the stress-strain behaviour of a material under transverse bending conditions is required. A sample with either a rectangular or circular cross-section is bent until it fractures using a three or four-point bending technique as illustrated in *Figure 2.7*. At the point of loading, the surface of the sample is under compression, while the bottom surface is under tension. The thickness of the specimen, moment of inertia and bending moments are used in determining the stress. The stress at fracture is known as the flexure strength or modulus of rapture [75].

The flexural strength is determined using the formula in equation (8)

$$R_f = \frac{1.5 \times F_f \times l}{bd^2} \text{----------(8)}$$

Where,

R_f is the flexural strength, in mega Pascals;

b is the side of the square section of the prism, in millimetres;

F_f is the load applied to the middle of the prism at fracture, in Newtons;

l is the distance between the supports in millimetres;

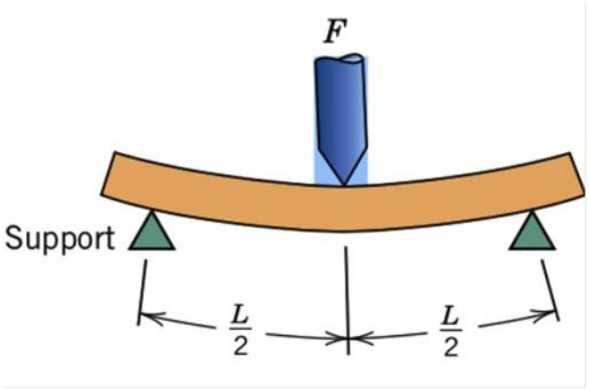


Figure 2. 7 *Three-Point Bend test scheme showing the compression at the top part and tension in the bottom region* [75].

Qian and Li [76] observed an increase in flexural strength in comparison to the control when 5,10 and 15% MK was used in partially replacing cement after 28 days [31]. Courard *et al*. [41] replaced cement with metakaolin from 5 - 20% by mass and studied the bending effects of the metakaolin cement mortar. They observed the replacement of cement with metakaolin slightly lagged behind after 3 and 7 days but gained higher strength after 14 and 28 days [31].

Subasi *et al*. [8] investigated the flexural strength of white Portland cement mortars partially replaced with metakaolin and observed a general decrease in flexural strength after 2, 7, 28, 56 and 90 days. Although, remarkable strength increase were observed after 90 days curing, the significant increase was attributed to the pozzolanic effect of metakaolin [8].

2.8.6 Compressive strength

The maximum uniaxial stress a sample can withstand before fracture is its compressive strength. Compressive strength test *(Figure 2.8)* is carried out on the sample after curing. The compressive strength is determined using the formula in equation (9)

$$R_c = \frac{F_c}{A_c} \text{----------(9)}$$

Where,

R_c is the compressive strength, in megaPascals;

F_c is the maximum load at fracture, in Newtons;

A_c is the area of mortar/concrete cube (72 mm×72 mm);

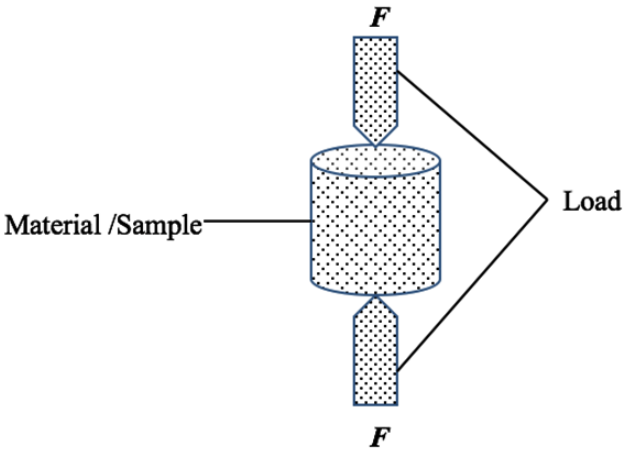


Figure 2. 8 *Schematic representation of a sample under compressive loading*

Generally, incorporating MK in mortars or concrete enhances their strength. The main factors associated with this strength development are accelerated Portland cement hydration, pozzolanic reaction and filler effect. The filler effect contribution is instantaneous whereas accelerated PC hydration occurs within a day and pozzolanic effect occur between the first and second week for 5 - 30% MK replacement [2]. Filler or micro filler effect is when pozzolan fills the voids in the cement mixture and reduces porosity [73]. Accelerated hydration also occurs when pozzolan acts as nucleating agents causing quick hydration of cement at the sites where they are positioned [73]. Dilution effect is simply when there is a decrease in the cement quantity in the mixture [73].

Bediako [73] studied the compressive strength of mortars made from Ghacem class 32.5R Portland limestone cement (PLC) and clay pozzolana (CP) using EN 197-1 standard, results recorded showed strength less than 30 MPa for control and all different PLC-CP mixes after

28 days curing [73]. Bediako *et al*. [35] and Tagbor *et al*. [39] reported the optimum metakaolin replacement for good compressive strength was 20 and 25% MK when they used metakaolin from Ghana [35], [39].

Cement paste containing 5% MK was reported by El-Diadamony *et al*. [9] to have the highest compressive strength among OPC and MK mortars. The strength value observed by the 5% MK was as a result of the accelerated hydration of OPC by the MK. Also the increase in strength by the MK paste was attributed to the MK providing more nucleating sites for enhanced pozzolanic reactivity and packing. The decrease in strength associated with 10 - 20 MK mortars was also attributed to the dilution of OPC with MK [9].

Poon *et al*. [31], [37] reported an increase in compressive strength in all MK paste after 3 to 90 days curing. All MK paste (5-20%) had greater strength than the control while 10%MK provided the best substitution [31].

Subasi *et al.* [8] observed contradictory compressive results to Poon *et al*. [31], where the control mortars recorded higher strength values than the MK mortars for all ages when MK was replaced with white Portland cement. However, 5% MK had compressive strength value greater than 52.5 MPa after 28 days as expected by the standard [8].

2.8.7 Water Absorption

Water absorption is a property of a material to retain some amount of water in its pores when it comes into contact with a material. Mortars and concretes are naturally porous hence they have the ability to absorb water. Although water initiates the hydration process in mortars and concrete, retention of water in mortars for long periods can reduce its durability [77]. Water can be retained in a building by several means and capillary suction is one of such means. Capillary rise is one the principal means by which water gains access into building materials [78]. Water absorption can be determined in a material by initially drying the material,

measuring its weight, followed by immersion in water for 24 hours and measuring its weight. The water absorption is calculated by subtracting the dry weight from the immersed weight.

Badogiannis *et al*. [29] also studied the water absorption by capillary action of metakaolin self-compacting concretes and concluded an increase in metakaolin content improved the sorptivity of the concrete. A partial replacement of cement with 20% metakaolin produced 0.12 $mm/min^{0.5}$, the best sorptivity value among the MK replacement [29]. Torres and Matias [79], measured water absorption by capillary action for mortars produced with white and red ceramic residues. The authors concluded that mortars which incorporated white ceramic residues absorbed much water to mortars incorporating red ceramic residues. They explained the observation for mortars containing white ceramic residues as, having larger particles in comparison to red ceramic residues, resulting in a porous internal structure with small dimension pores while the red ceramic residue mortars had finer particles that produced a more compact structure [79]. Tafraoui *et al*. [80] reported a maximum of 0.5 kgm^{-2} as the water absorbed by ultra-high performance concrete containing 25% metakaolin [80].

CHAPTER THREE

3.0 METHODOLOGY

This chapter gives a detailed description of the procedures and methods used to produce mortar blocks using the supplementary cementitious materials (SCMs).

3.1 Materials used

In this work, kaolin was obtained from Teleku Bokazo deposits in the western region of Ghana, Ghacem Portland limestone cement (32.5R) CEM II / B-L which meets Ghana standard GS 1118:2016 [49] was used as the binder, river sand was collected from Bessblock company and tap water from the Civil Engineering Laboratory of Ghana Standards Authority was used.

3.2 Production of metakaolin

150 g of kaolin (*Figure 3.1a*) was weighed into a crucible using a beam balance and placed into an electric furnace (Carbolite RWF 1200). The kaolin was calcined at 650^{o}C for two hours to form metakaolin (*Figure 3.1b*), followed by sieving using a 90 μm sieve. The metakaolin was then stored in zip lock containers.

(a) (b)

Figure 3. 1 shows the raw and processed kaolin from Teleku Bokazo in the Western Region: (a) unprocessed kaolin and (b) calcined kaolin (metakaolin) at 650^{o}C

3.3 Characterization of Raw and Calcined Kaolin using X-ray Diffraction (XRD)

The mineralogical composition of Teleku Bokazo kaolin before and after calcination was analyzed using X-ray diffractometer (XRD). Small quantities of dried powdered kaolin and metakaolin were subjected to an Empyrean PANalytical X-Ray diffractometer analysis at the Department of Physics, University of Ghana. The analysis was done using a current of 40 mA and 45 kV, and a scan range from 5 to 90° (2 theta) angles. The X-rays were generated from the X-ray tube using a copper anode material (CuKα) of wavelength 1.54060 nm which interacted with the sample and the X-rays were reflected unto the detector, the rays were then plotted as graph and analysed using a X'Pert HighScore software.

3.4 Mortar Preparation

The mortars were prepared and cast at the Civil Engineering Laboratory at the Ghana Standards Authority. The preparation of the mortar was performed according to British Standard (BS EN 196-1:2016) [81]. Metakaolin was replaced with PLC by weight in percentages of 10 to 35 using a 5% step size as shown in **Table 3.1.** The river sand was sieved using a 1.70 mm sieve and used in the production of the mortars. The mortar was produced using 1:3 cement-to-sand and 1:2 water-to-cement ratios respectively. In a typical mortar mix, ~ 1800 g of river sand and ~ 600 g of cement were weighed and mixed in machine (*Figure 3.2 b*) at low speed for a minute followed by the addition of ~ 300 ml of water and further mixing at higher speed for two minutes. The **Table 3.2** shows the batch formulation for the all the other mortar samples. After mixing, the mortar was transferred into a 72 mm^3 mould fastened unto a jolting table (*Figure 3.2 c*). The first layer of mortar was uniformly spread within the mould and vibrated followed by a second layer. The second layer was vibrated and levelled with excess mortar cleared off, this represented the control. For the other batches, the metakaolin gradually replaced Portland limestone cement. The samples were then demoulded after twenty-four hours and cured by immersion in a curing pond

(Figure 3.2 c) at room temperature for three, fourteen and twenty-eight days. Prior to curing, the weights of the samples measured and three samples each of the cured mortar were tested for their compressive strengths. The procedure was repeated in casting the mortars for flexural analyses; the variation was the quantity of materials weighed and dimensions of the prismatic mould which was $40 \times 40 \times 60$ mm (*Figure 3.2 d*). **Table 3.3** shows the batch formulation for the mortar preparation for the flexural test.

Table 3.1 Batch formulations of kaolin-metakaolin-cement mortars

Sample code	Compositions	PLC (%)	MK (%)	Remarks
0MK	CEM II 32.5R (PLC)	100	0	Control
10MK	CEM II 32.5R (PLC) + 10%MK	90	10	10%MK
15MK	CEM II 32.5R (PLC) + 15%MK	85	15	15%MK
20MK	CEM II 32.5R (PLC) + 20%MK	80	20	20%MK
25MK	CEM II 32.5R (PLC) + 25%MK	75	25	25%MK
30MK	CEM II 32.5R (PLC) + 30%MK	70	30	30%MK
35MK	CEM II 32.5R (PLC) + 35%MK	65	35	35%MK

Table 3.2 Batch formulation for mortar cubes with metakaolin replacement

Samples	Cement (g)	Sand (g)	Metakaolin (g)	Water (g)
0MK	600	1800	0	300
10MK	540	1800	60	300
15MK	510	1800	90	300
20MK	480	1800	120	300
25MK	450	1800	150	300
30MK	420	1800	180	300
35MK	390	1800	210	300

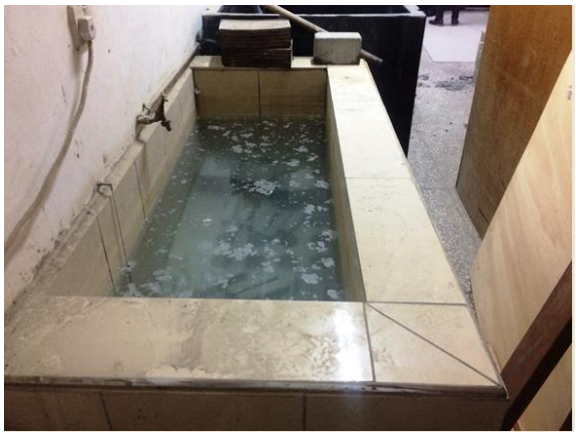
Table 3. 3 Presents the batch formulation for mortar prisms

Samples	Cement (g)	Sand (g)	Metakaolin (g)	Water (g)
0MK	411	1235	0	206

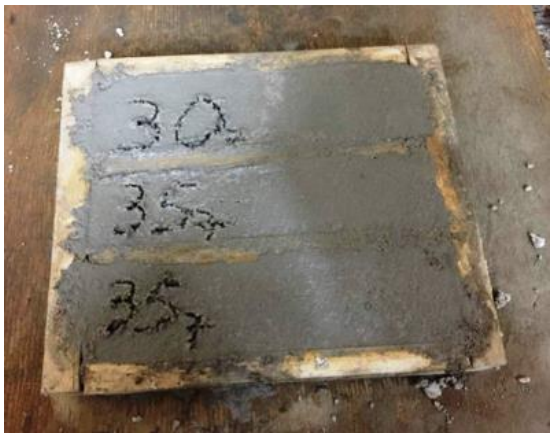
10MK	369.9	1235	41.1	206
15MK	349.35	1235	61.65	206
20MK	328.8	1235	82.2	206
25MK	308.25	1235	102.75	206
30MK	287.7	1235	123.3	206
35MK	267.15	1235	143.85	206

(a)

(b)



(c)



(d)

Figure 3. 2 shows the different steps involved in mortar preparation

3.5 Water Consistency

This test was carried out using British Standard, BS EN 196-3:2016 [72]. **Table 3.4** shows the batch formulation used in the preparation of paste for water consistency and setting time. 500 g of cement and varying quantities of water were used. The weighed cement and measured water were mixed using the mechanical mixer at low speed. After a minute and half, the mixer was stopped and excess mortar paste adhered to the bowl cleaned. The mixer was then restarted for three minutes and transferred into a lightly oiled Vicat mould. Voids in the paste were removed by gently tapping the overfilled mould slightly with the hand. The plunger of the Vicat apparatus was lowered to rest on the base plate and used to adjust the scale on the Vicat apparatus to the zero reading (*Figure 3.3 a*). The plunger was then raised to its standby position, and the mould with the cement paste was placed centrally below the plunger. The plunger was gently lowered to the surface of the paste until it penetrated and the reading on the scale was recorded when the penetration ceased (*Figure 3.3 b*). The plunger was released a minute after mixing cement paste in the mixer. The scale reading together with the water content was recorded as the water content of the paste and expressed as a percentage by mass of the cement. The test was repeated with different water contents until a water content was found to produce a distance between plunger and base plate of (6 ± 2) mm. The water content is recorded to the nearest 0.5% as the water for standard consistence. The Vicat mould, which contained the cement paste under test, was cylindrical in shape with a depth of 40 mm, internal diameter of 85 mm, a base plate of 120 mm^2 and made of polyvinylchloride.

Table 3. 4 Batch mix proportion for water consistency and initial setting time

Sample	Cement (g)	Metakaolin (g)
0MK	500	0
10MK	450	50
15MK	425	75
20MK	400	100
25MK	375	125

30MK	350	150
35MK	325	175

(a)

(b)

Figure 3. 3 Procedure for determining water consistency

3.6 Initial Setting Time

The initial setting time was determined by replacing the plunger of the Vicat apparatus with a needle (*Figure 3.4 a*) and adjusting the needle to the zero reading. The filled Vicat mould together with its base plate, containing cement paste of standard consistence which was made in sub heading 3.5 was put in a water bath. Water was added to submerge the surface of the paste to a depth above 5mm. At the time of the measurement, the Vicat mould filled with cement paste was positioned centrally below the Vicat apparatus. The needle was gently lowered until it was in contact with the paste, then the moving part was gently released and the needle penetrated the paste. The reading on the scale was recorded after 30 seconds when the penetration had ceased (*Figure 3.4 b*). The paste was then placed back in the water bath and penetrations repeated at different time intervals (*Figure 3.4 c*). The penetration continued until the reading on the scale was (6±3) mm, the time at which the scale recorded (6±3) mm

was noted as the initial setting time (*Figure 3.4 d*). This procedure was followed for the different metakaolin replacements. **Table 3.4** shows the mix proportion for the setting time.

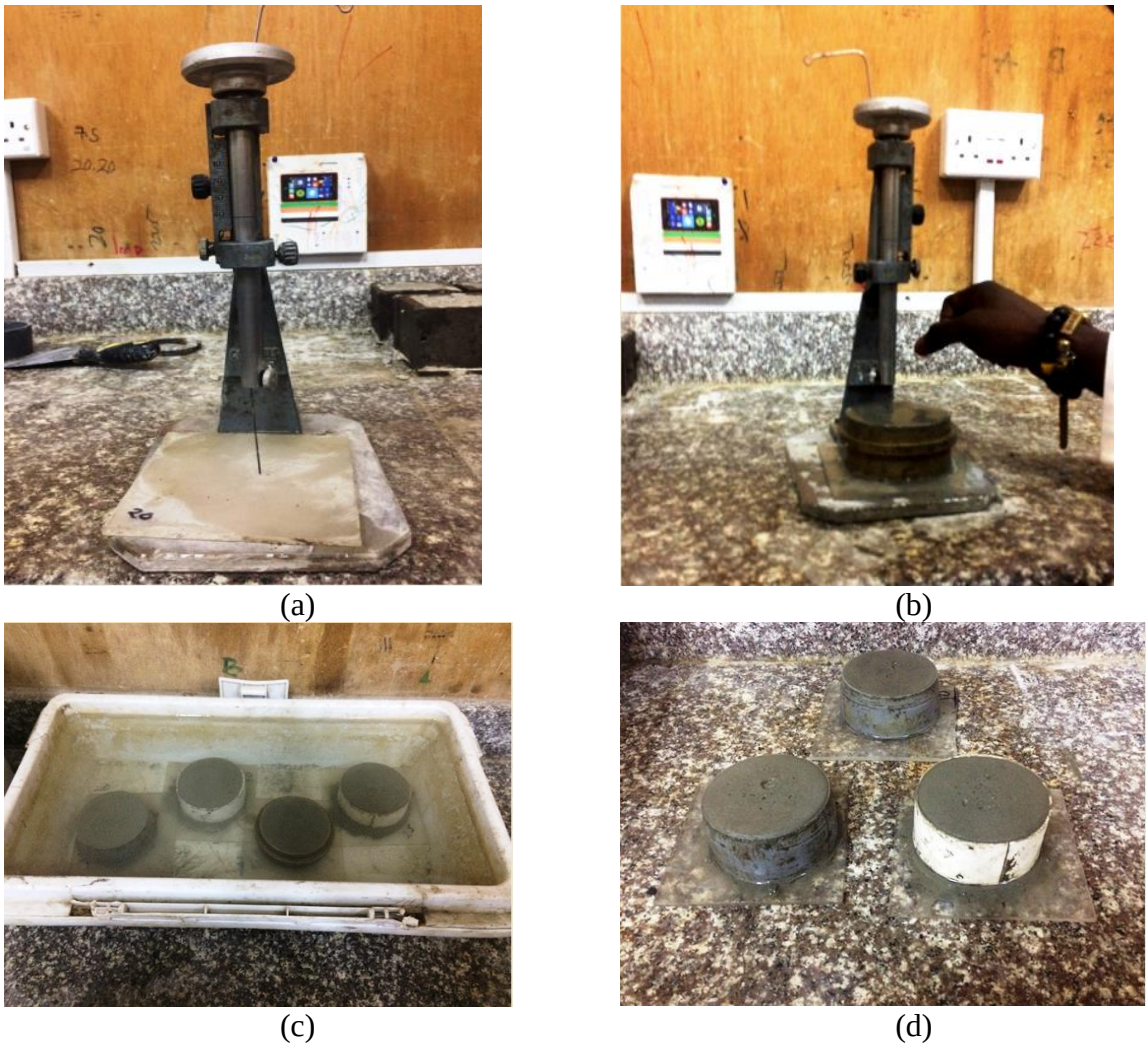


Figure 3. 4 Procedure for determining initial setting time

3.7 Water absorption by capillary action

This test was done in accordance with BS EN 1015-18 [82]. One of the halves from the modulus of rapture test was used for this experiment. All the faces of the mortar prism were coated by dipping in paraffin wax, except the broken face from the flexural test which was rough. The sample was then put in an oven and dried at 60^{o}C until constant mass was reached. The test sample was placed on sample supports and partially immersed in a water

bath containing water of 1 cm depth and weighed at different time intervals for 24 hours (*Figure 3.5*). The water absorption coefficient was determined by curve fitting the sample data points. Water absorption is plotted against square root of time and the gradient of the line of best fit determined, represents the water absorption coefficient. Water absorbed is represented by equation (10).

$$I = \frac{m_t}{a \times d} \quad \text{----------(10)}$$

Where,

m_t is the difference in sample mass in grams at a time t,

I is the water absorbed in mm,

a is the exposed surface area of the sample in mm^2

d is the density of water thus $0.001 g/mm^3$

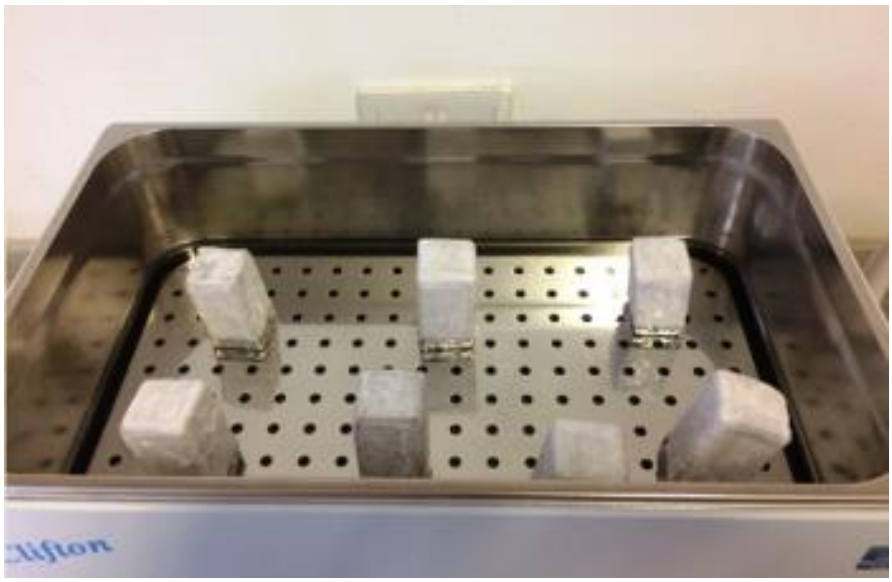


Figure 3.5 Water absorption test

3.8 Flexural testing

A three-point loading technique was used for this test in accordance with BS EN 196-1:2016 [81]. Mortar specimens were tested for strength at 3, 7 and 28 days and result recorded was an average of three mortar specimens. The mortar prisms were carefully placed on the rollers of the machine with the longitudinal axis normal to the supports (*Figure 3.6).* The load was applied vertically by the loading roller to the transverse face of the prism until there was fracture. The load that caused failure was recorded. The bending strength was determined using equation (8).

$$R_f = \frac{3 \times F_f \times L}{2bd^2} \quad \text{----------(8)}$$

Where,

R_f is the flexural strength, in MPa;

b is the side of the square section of the prism, in millimetres;

F_f is the load applied to the middle of the prism at fracture, in Newtons;

l is the distance between the supports in millimetres;

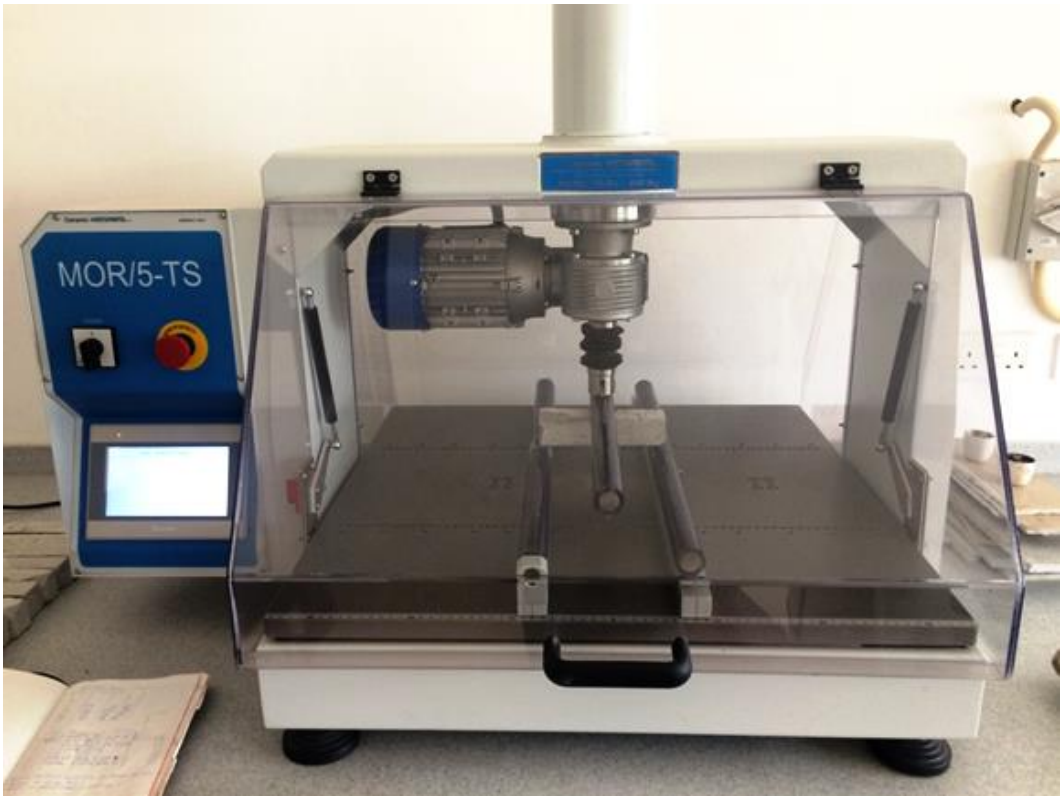


Figure 3. 6 shows the Flexural testing machine used in measuring the modulus of rupture of the kaolin-metakaolin-cement based mortars at the Department of Materials Science and Engineering, UG.

3.9 Compressive Strength Testing

The compressive strength test was performed in accordance with BS EN 196-1:2016 [81]. Mortar specimens were tested for strength at 3, 14 and 28 days and result recorded was an average of three mortar specimens. *Figure 3.7* shows the compressive strength machine that was used for the test. Mortar specimens were centrally placed on sample stage, and load was gradually increased until fracture. The load that caused fracture was recorded.

The compressive strength was determined using equation (9)

$$R_c = \frac{F_c}{A_c} \quad \text{----------(9)}$$

Where,

R_c is the compressive strength, in megaPascals;

F_c is the maximum load at fracture, in Newtons;

A_c is the area of mortar cube (72 mm×72 mm);

Figure 3. 7 Compressive Strength testing machine

3.10 Fourier Transform Infrared Spectroscopy

Fourier transform infrared spectroscopy (FTIR) was carried out on the 14 days cured paste to determine the chemical bonds formed in the hydrated material. PerkinElmer Spectrometer version 10.5.2 was used. The sample stage was cleaned with acetone and the background scanned to determine any contaminations. Fine particles of the various mortar proportions were placed on the sample stage and the force gauge gently dropped on the sample to hold in place. The sample was then scanned and results plotted as a graph of percentage transmission against wave number. *Figure 3.8* shows the FTIR spectrometer that was used for the test.

Figure 3. 8 Fourier Transform Infra-Red Spectrometer (FTIR)

CHAPTER FOUR

4.0 RESULTS AND DISCUSSIONS

4.1 X-ray diffraction analysis of kaolin and metakaolin

Figure 4.1 presents the X-ray diffraction (XRD) patterns of kaolin and metakaolin from Teleku Bokazo. The figure shows three main crystalline minerals present in the kaolin. They are kaolinite, quartz and illite. These minerals occur at 2 theta angles of 9^{o} (Illite), 12.5^{o} kaolinite and 26.5^{o} (Quartz). The metakaolin showed the presence of quartz at 26.5° (2 theta degrees) and the dehydroxylation of kaolinite causing an increase in the quartz intensity. The metakaolin looked crystalline but similar XRD was observed in [64] which had similar features after calcining kaolin at 750, 800 and 850^{o}C.

Studies by Badogiannis *et al.* [29] and Moodi *et al*. [64] have shown that XRD peaks of kaolin contain illite, quartz and kaolinite. El-Diadamony *et al.* also showed quartz as the main mineral in the XRD pattern of metakaolin after calcining at 800^{o}C for two hours [9]. This studies have also been confirmed by Ramli *et al*. and Moodi *et al.* [64], [66].

The reference codes of the various mineral phases present in the mortars using X'Pert High score plus software is (Illite, card no. 09-0334) (kaolinite, card no.98-008-0082) and (quartz, card no.01-087-2096)

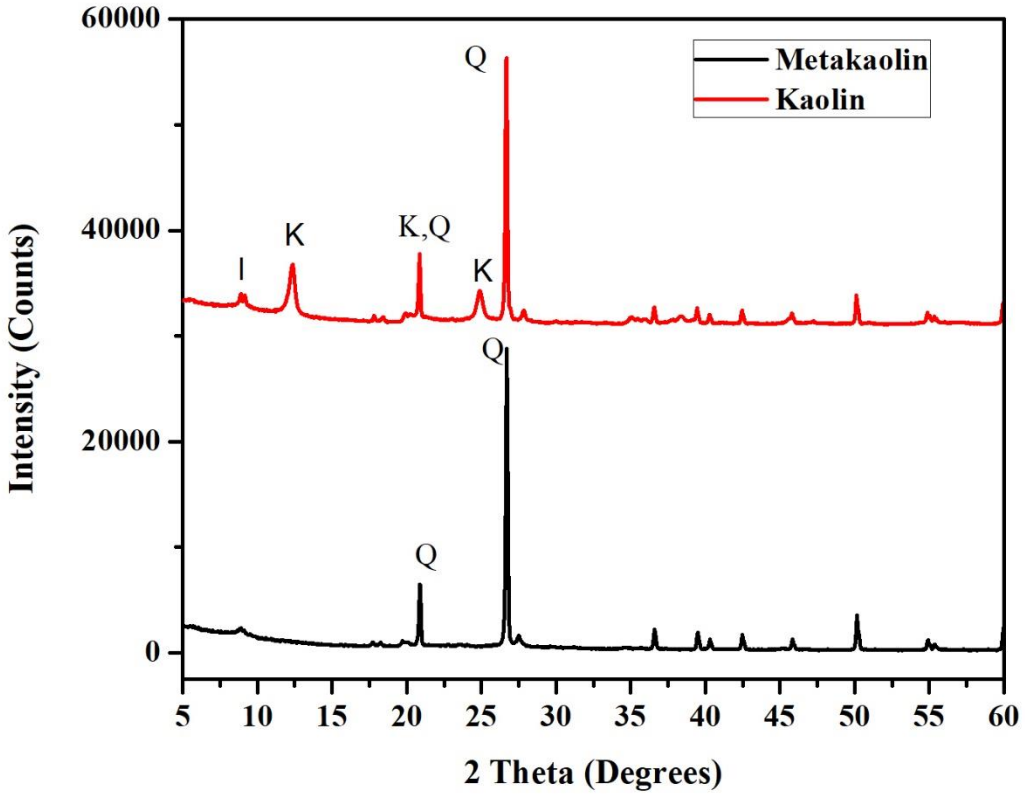


Figure 4. 1 XRD of Teleku Bokazo kaolin and metakaolin (I: illite, K: kaolinite, Q: quartz)

4.1.1 X-ray diffraction analysis of metakaolin based mortars

The main compounds identified in the control and different metakaolin replaced mortars after 14 days curing are presented in *Figure 4.2*. The X-ray diffractions of MK replaced mortars were compared with the control mortar (Portland limestone cement mortar). Calcium silicate hydrate (C-S-H), calcium aluminium silicate hydrate (C-A-S-H), portlandite ($Ca(OH)_2$), ettringite [$Ca_6Al_2(SO_4,SiO_4,CO_3)_3(OH)_{12}\cdot 26H_2O$], quartz ($SiO_2$), calcite ($CaCO_3$) and gypsum ($Ca(SO_4)(H_2O)_2$) were the identified mineral phases in the mortars.

In the control mortar, the XRD revealed peaks of C-A-S-H, C-S-H, portlandite, quartz, gypsum, and calcite as the main phases. Although, ~ 10 – 35 %MK mortars were also composed of C-A-S-H, C-S-H, portlandite, quartz, gypsum, and calcite, a new product known

as ettringite was formed. Ettringite is the distinguishing mineral phase formed between the control and MK mortars through the reaction of metakaolin, celite, portlandite and sulphates [9], [56], [83].

At diffraction angles of ~18.6° and ~34°, it can be seen that, there was a gradual decrease in the intensity of portlandite peaks compared to the control, 10 – 30 %MK and a disappearance of the peak at 35 %MK replacement. This observation could be attributed to the pozzolanic reaction between portlandite and metakaolin in the various MK mortars [57]. Haturite, a hydrated calcium silicate is also a cementitious compound formed in the 15 %MK replacement. The quartz found in all the mixes was from the sand and metakaolin used in the mix whereas gypsum and calcite were from the Portland limestone cement.

The formation of ettringite in MK mortars agree with Ramezanianpour *et al*. and Cyr *et al.* studies [36], [57]. The decrease in portlandite intensity in comparison to the control as the metakaolin content increased was as a result of the pozzolanic reaction between portlandite and metakaolin. Subasi *et al*. [8] and El-Diadamony *et al*. [9] reported similar observations in their studies.

In using the X'Pert High score plus software, the reference codes of the various mineral phases present in the mortars using were for the following: C-A-S-H, card no. 76-0620, C-S-H, card no.72-1907, (portlandite, card no.87-0673), (ettringite, card no.72-0646), (quartz, card no.46-1045), (gypsum, card no.70-0982), (calcite, card no.88-1807) and (hatrurite, card no. 98-006-4759).

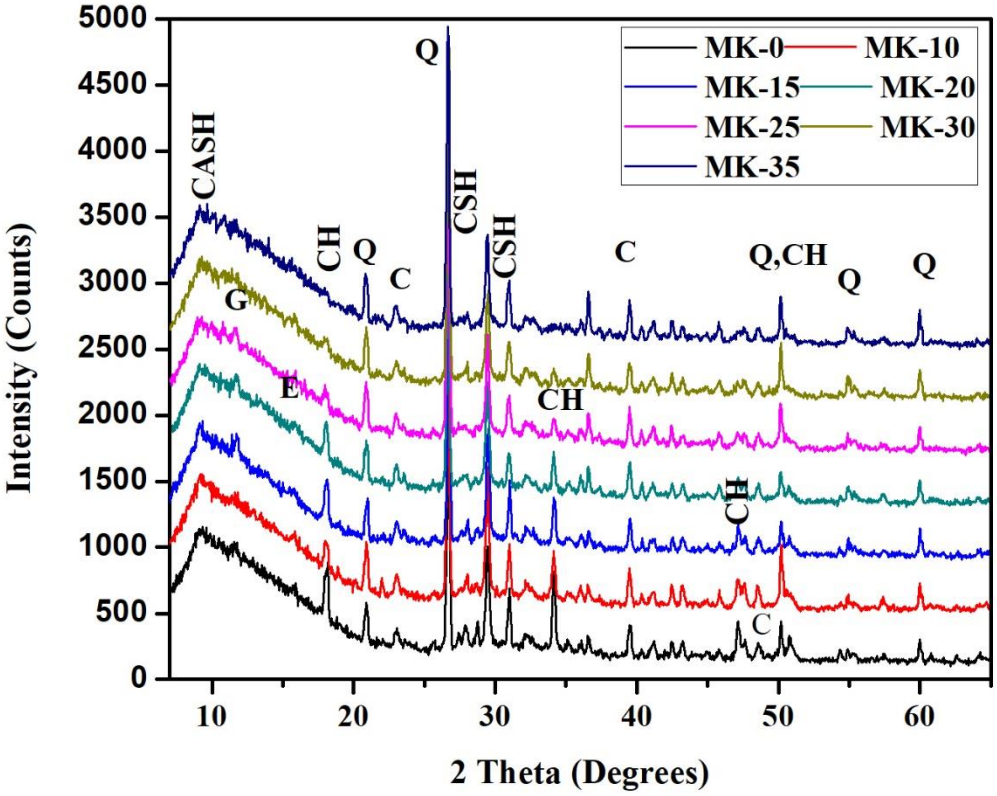


Figure 4. 2 XRD of mortar cubes with different metakaolin proportions after 14 days (C: calcite, CH: portlandite, Q: quartz)

4.2 Determination of hydrated products with FTIR analysis

The FTIR results in *Figure 4.3* and *4.4* show the different chemical bonds formed in the hydrated cement and metakaolin paste. A characteristic peak for portlandite, a by-product of the hydration of cement is located at ~3640 cm^{-1} [69]–[71]. At ~ 3403 to ~3410 cm^{-1}, there is a broad OH stretching band which could be described as free water in the hydrated paste [70], [71], [84]. At ~1739 and ~1741 cm^{-1} vibrations of C=O present [85]. Infrared spectra from ~1415 to ~1419 cm^{-1} and ~873 to ~875 cm^{-1} represents C-O stretching vibration of CO_3^{2-} ion [70], [71], [84] which is observed in all the pastes. Si-O stretching and Si-OH bending modes of calcium silicate hydrate are observed between ~1350 and ~1370 cm^{-1} [70], these peaks are observed in 25, 30 and 35% metakaolin paste. The S-O stretching vibration of SO_4^{2-} is also

found in the control paste at ~1109 cm^{-1} [84] whereas the Si-O vibrations of calcium silicate hydrate is present simultaneously at ~1087 cm^{-1} and from ~956 to ~963 cm^{-1} [69], [70]. The peak at ~1087 cm^{-1} was found in all the metakaolin paste excluding the control sample. However, Si-O asymmetric vibration of calcium silicate hydrate represented from ~956 to ~963 cm^{-1} is seen in all the pastes. At ~963 cm^{-1} a characteristic peak of Afwillite a hydrated calcium silicate mineral [69] is also seen in all metakaolin paste.

It was largely observed that the control, 10 15, 20, and 25% metakaolin paste replacement after 14 days curing had portlandite however, it was not observed in the 30 and 35% metakaolin paste. This absence could be due to the pozzolanic reaction which consumes all the portlandite present. In addition, the O-H band is observed in all cement and metakaolin paste and could be due to the amount of water used in hydration process. The carbonate peak was as a result of the decomposition of calcium carbonate from the Portland limestone cement whereas the sulphate is due to the gypsum in the Portland limestone cement. The Si-O peak present at ~1087 and ~963 cm^{-1} could be from the quartz in the metakaolin. Based on the different compounds identified using the FTIR, the contribution of each mineral phase to the pozzolannic reaction and the hydration process has been greatly explored.

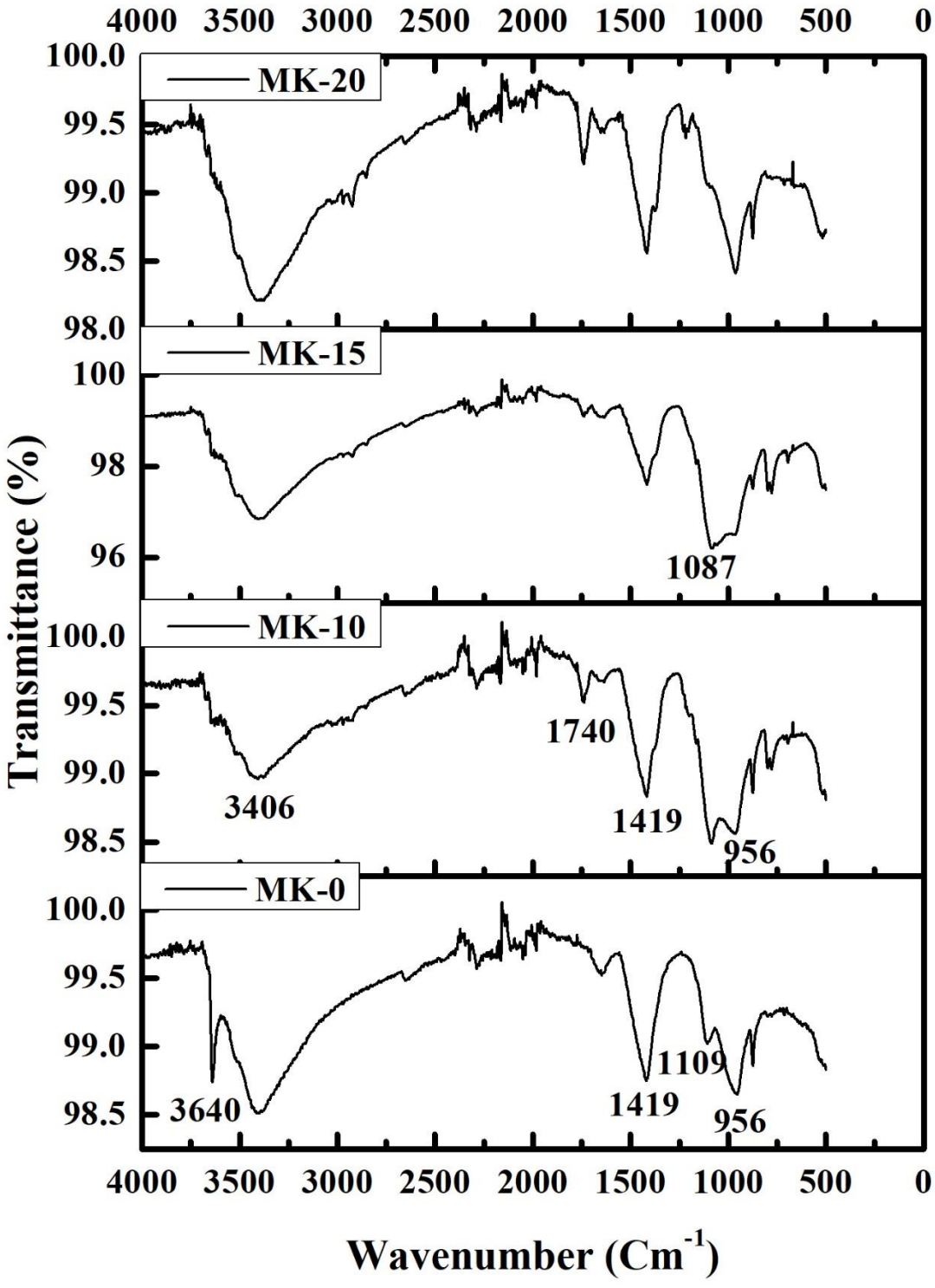


Figure 4. 3 FTIR of mortar paste with different metakaolin proportions after 14 days curing

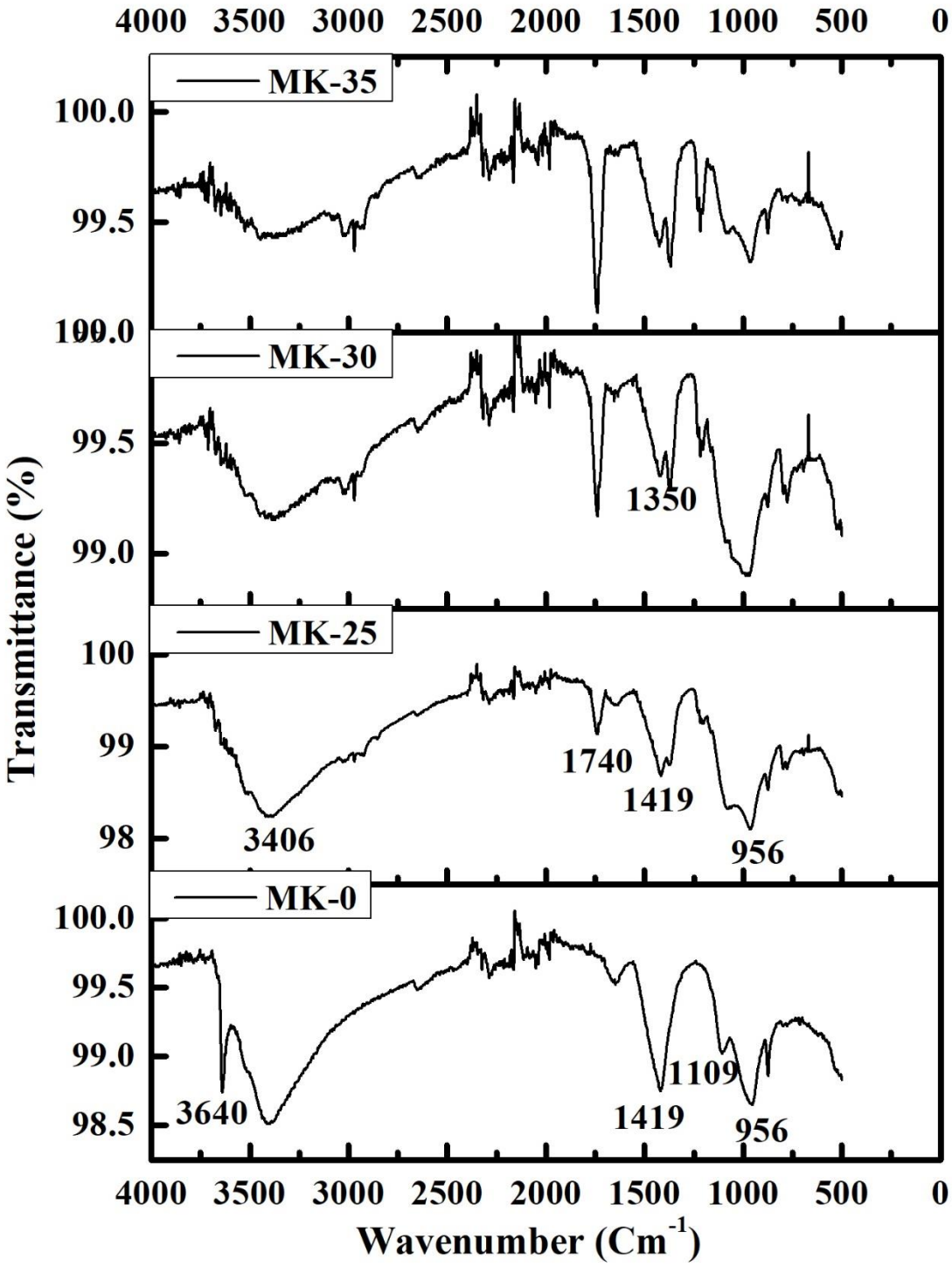


Figure 4. 4 FTIR of mortar paste with different metakaolin proportions after 14 days curing

4.3 SEM of kaolin and metakaolin

Figure 4.5 presents the SEM analysis of kaolin and metakaolin. The surface morphology of kaolin occurs as plate like structures stacked in layers to form a compact structure. Metakaolin occur as a cluster of layered plates stacked over each other. The plate-like structures are indicative of kaolin and metakaolin. This observation is supported by Rashad [28] and Ramli et al. [66].

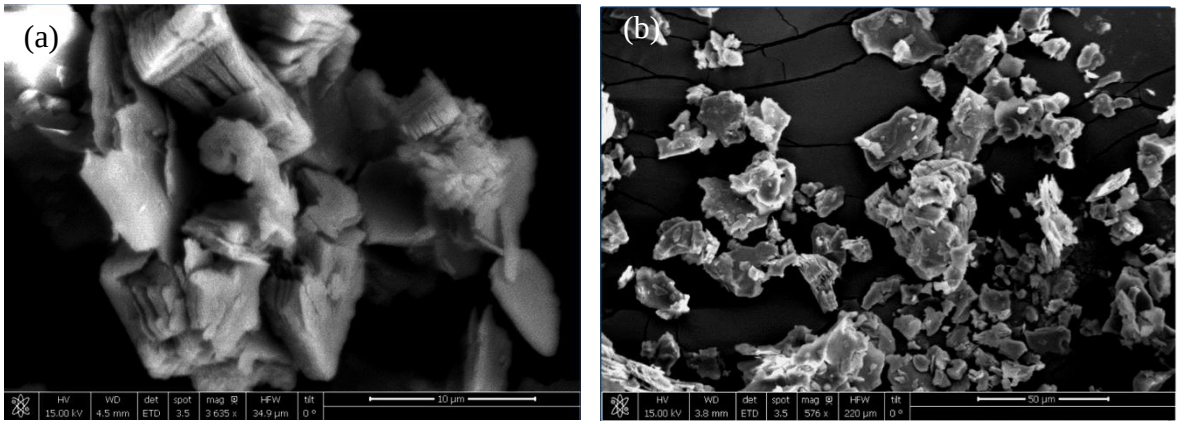


Figure 4. 5 SEM images of (a) kaolin and (b) metakaolin

4.3.1 SEM of PLC and metakaolin mortars

Figure 4.6 presents the structure of the PLC mortar and the different metakaolin mortars after 14 days curing. It can clearly be seen that the control paste is homogenous mixture with pores. The different metakolin mixtures also form homogenous mixtures with few pores.

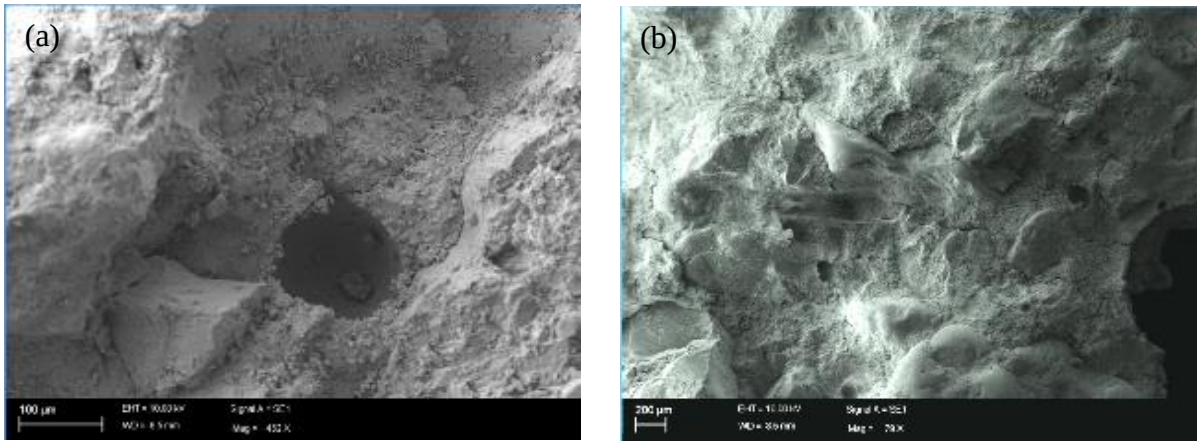


Figure 4. 6 SEM images of (a) control and (b) 10 %MK

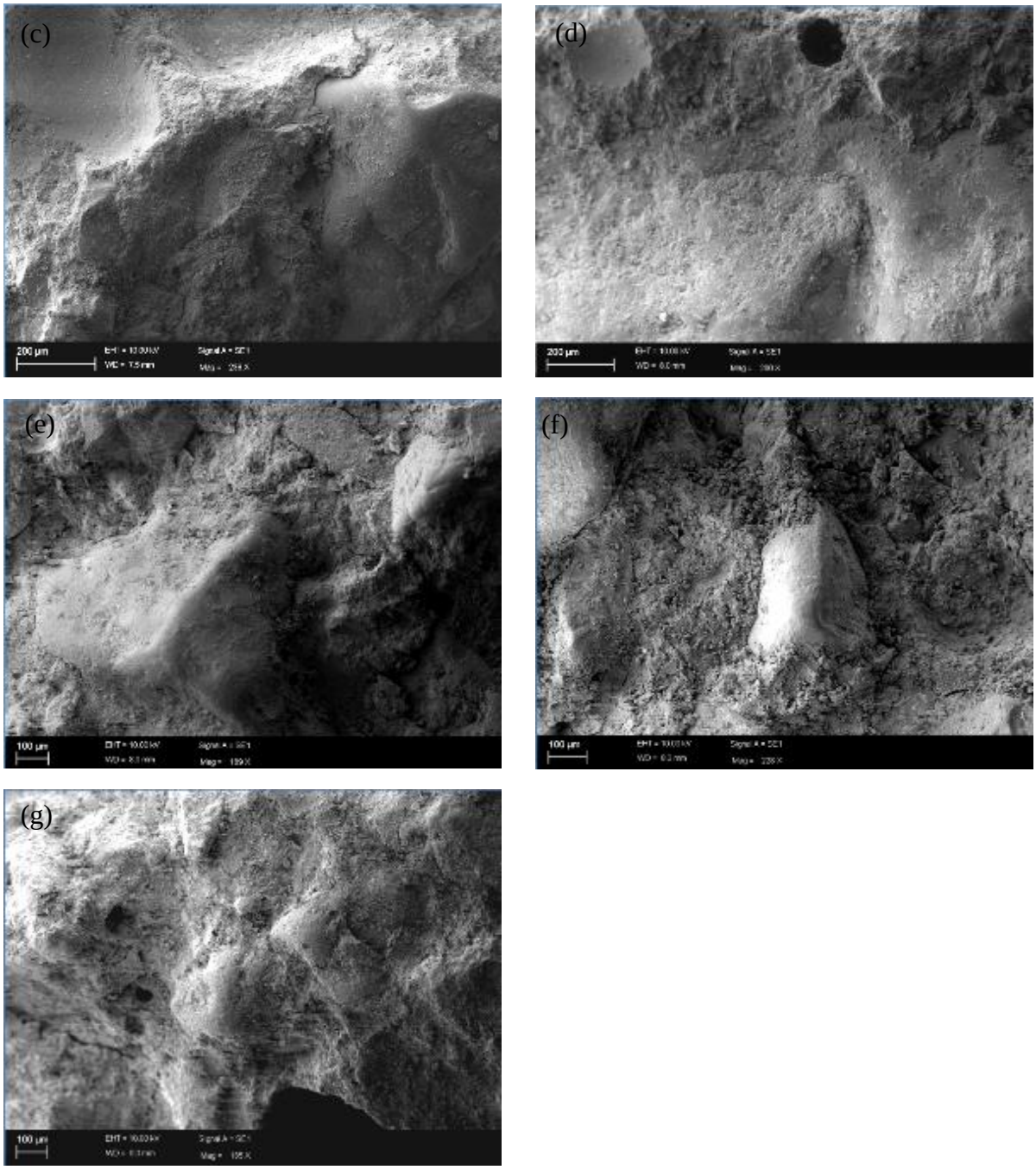


Figure 4. 6 *SEM images of (a) control, (b) 10% MK (c) 15% MK, (d) 20% MK, (e) 25% MK, (f) 30% MK and (g) 35% MK.*

4.4 Water consistency analysis

*Figure 4.*7 presents the water consistency results of cement paste containing 10 - 35% replacement of metakaolin. From the results, there was a progressive increase in the water consistency as the metakaolin content in the cement paste increased. The consistency value of the control paste was 26% whereas that of 10% and 15% metakaolin content were ~30 and ~33% respectively. Mortar paste containing 20% and 25% metakaolin had consistency values of ~40% and ~43% respectively whereas that of 30% and 35% content of metakaolin were also ~47% and ~55% respectively. The addition of metakaolin increased the water demand from ~26% to a maximum of ~55%. This increase in water demand in PLC-MK could be as a result of the porous nature and the high reactivity of metakaolin. As the metakaolin was gradually increased the amount of PLC decreased, increasing the effective surface area and affinity of the paste to absorb water hence the observation in an increase in water consistency.

The results largely agree with the findings observed by El-Diadamony *et al* [9], Bediako [73] and Atiemo *et al.* [74] that cement paste containing metakaolin clays increase the water demand for forming homogenous cement paste [9], [73], [74].

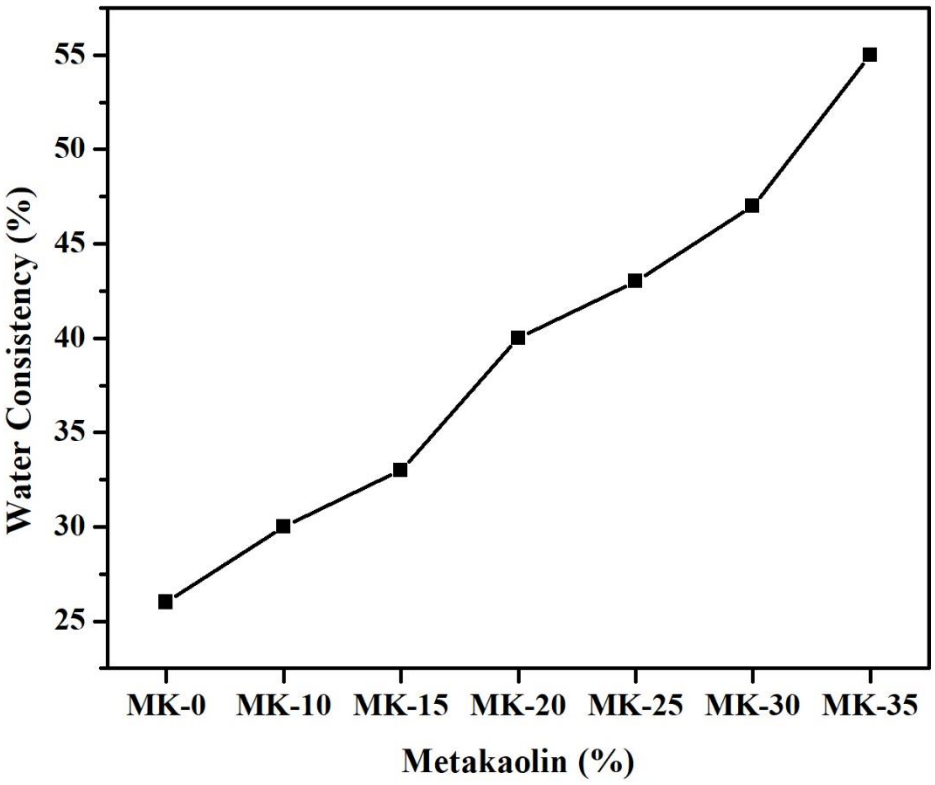


Figure 4. 7 Water consistency of mortar paste

4.5 Setting time of limestone Portland and metakaolin pastes

Figure 4.8 shows the results of the initial setting time of cement paste containing 10 - 35% metakaolin. The initial setting time of the control paste was at 167 minutes. The addition of metakaolin from 10 - 35% prolonged the initial setting time to ~199, 212, 220, 217, 255 and 251 minutes respectively to set. The control sample recorded the lowest initial setting time while 30% metakaolin had the highest initial setting time. The increased setting time could be due to coating of cement particles by metakaolin and dilution of PLC with metakaolin. For example, the 25% and 35% MK that showed a lower setting time in comparison to 20 and 30 %MK respectively, the observation can be attributed to the formation of a dense binding phase as reported by Brooks *et al*. [8], [42].

The trend in the results also agree with prior studies conducted by Bediako [73], Brooks *et al*. [8], [42] and El-Diadamony *et al*. [9]. All pastes had their initial setting time greater than the minimum 75 minutes required for CEM II/B-L 32.5R in GS 1118:2016 [49].

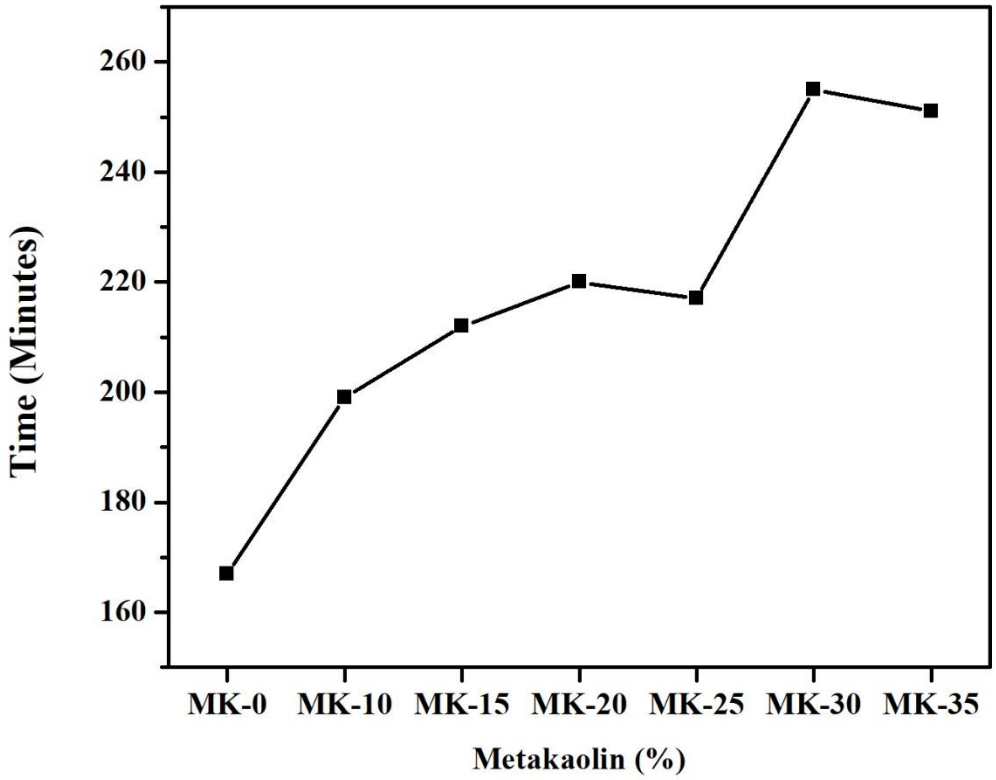


Figure 4. 8 Initial setting time for metakaolin replaced with cement

4.6 Mechanical characterization of mortar paste

4.6.1 Flexural strength analysis

The effect of metakaolin on the bending characteristics of the mortar bars is shown in *Figure 4.9*. There is an appreciable increase in flexural strength of the mortar bars from 3 to 28 days. After three days of curing, the control mortar recorded a flexural strength of ~ 4.31 MPa with the 10 to 30% metakaolin replacement showing a gradual increase from ~ 4.22, ~ 4.26, ~ 4.37, ~ 4.71 and ~ 5.23 MPa. At 35% replacement, there was a decrease in strength to ~4.42

MPa. However, the decrease in strength for mortar bar containing 35% metakaolin is greater than that observed for the control.

The mortar bars cured for seven days showed a reasonable increase in strength in relation to the three days cured bars. The strength of the control was ~ 5.08 MPa. There was an increase in strength from 10 to 20% metakaolin replacement, with a gradual decrease in strength from 25 to 35% replacement. The modulus of rapture of mortar bars containing 10 - 20% MK was ~4.93, ~6.30 and ~6.46 MPa, while 25-30% MK was ~5.43, ~5.29 and ~4.56 MPa.

A similar trend in the seven days cured mortar was observed for the twenty-eight days cured, there was an increase in flexural strength from 10 - 20% MK and a decline from 25 - 35% metakaolin replacements. Two samples, 15 and 20% MK replacement recorded flexural strengths greater than that of the control (~6.05 MPa) meanwhile the strength in 10 - 35% MK was ~4.97, ~6.68, ~6.90, ~5.95, ~5.34, and ~4.94 MPa respectively.

The flexural strength of the mortars bars after 3 days can probably be attributed to the accelerated hydration and filler effect of the metakaolin [2]. The metakaolin particles serve as nucleating sites for formation of cementitious products while also reducing pores to form a compact and dense mass which enhances the strength [9].

After 7 days aging, the pozzolanic effect adds to the 3 days attained strength [2]. The portlandite reacts with the metakaolin to produce C-S-H gels which fill, grow and add strength to mortars. At 20% metakaolin replacement, this effect has probably reached the optimum and hence the strength is greatly enhanced. Beyond 30% replacement, there was a reduction in the strength which could be as a result of the dilution effect of the metakaolin; that is the cement content is reduces and the metakaolin content increases hence reducing the overall strength.

For the 28 days cured mortar the increase in strength is as a result of the continuous hydration of clinker minerals and pozzolanic reactivity of metakaolin. For 15 and 20% metakaolin replacement there is a balance for which enough clinker minerals have hydrated to produce portlandite for which metakaolin can react with. This balance gives 20% metakaolin replacement the highest strength among the batch formulations. Generally, when an SCM partially replaces cement it is known as dilution and when the SCM causes a pozzolanic reaction it is known as compensation. The balance of the dilution and compensating effect is responsible for the overall strength of a mortar or concrete mix [86]. The decrease in strength observed in 25 - 35%MK can be as a result of the dilution of cement with MK and slow hydration of the remaining PLC [2], [9]. The results obtained however contradicts with the observations reported by El-Diadamony *et al* [9].

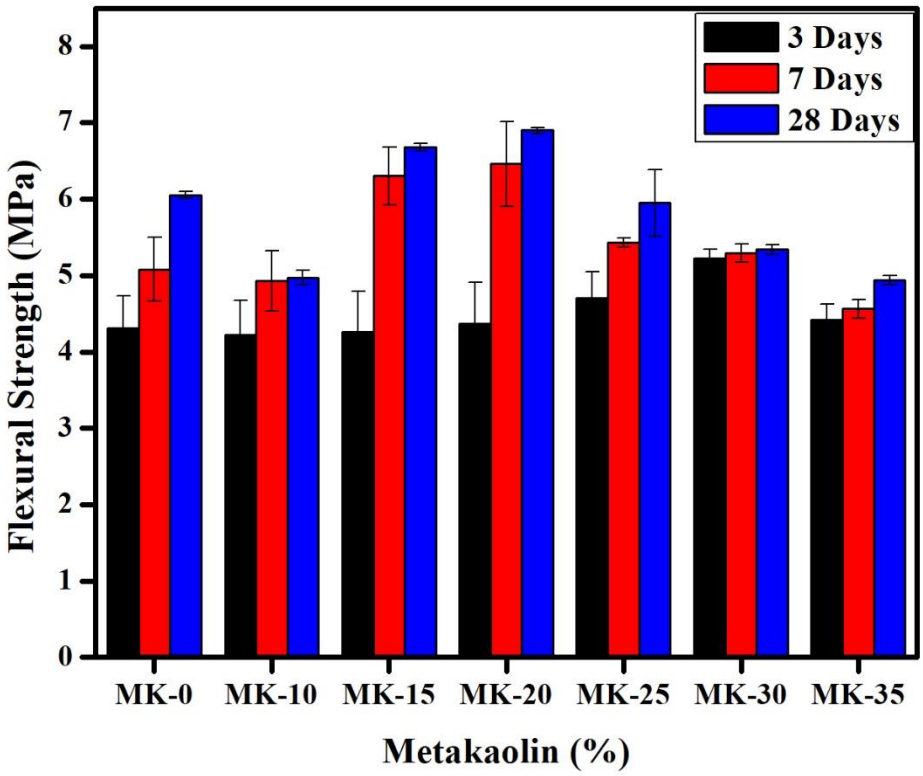


Figure 4. 9 MOR of mortar prism

4.6.2 Compressive strength of mortar cubes

Figure 4.10 presents the compressive strength results of the control and metakaolin replaced mortars. The strength values at 3 days of curing showed that aside 35% metakaolin replacement, all the pozzolan mortars gained higher strength than the control. The recorded strength of the different metakaolin proportions from 10 - 35% is ~18.32, ~20.58, ~21.45, ~19.77, ~16.40 and ~14.47 MPa. The control recorded a compressive strength of ~15.91MPa.

After 14 days of curing, the control strength increased to ~24.11 MPa whereas the 10 and 35% metakaolin mortars obtained lower strength values of ~22.18 and ~20.25 MPa respectively, in comparison to the control. However, the strength values of 15, 20, 25 and 30% metakaolin content were ~24.11, ~26.34, ~28.29 and ~27.51 MPa respectively, which were all higher than the control mortar.

For the 28 days curing strength, the control mortar, 10 and 25% metakaolin mortars had strength values of ~29.0 MPa whereas 15 and 20% metakaolin mortars had strength values of ~30.86 and ~35.69 MPa which were greater than the control strength value. Lower strength values were recorded for 30 and 35% metakaolin replacement in comparison to the control, ~ 27.97 and ~22.51 MPa respectively.

The early strength observed after 3 days curing can be attributed to the accelerated hydration of PLC and filler effect of metakaolin. As the metakaolin content increases, a decrease in compressive strength is expected. The decrease in 30 and 35% MK mortar strength can be attributed to the dilution effect of metakaolin. The strength gained at 14 and 28 days can also be attributed to the pozzolanic effect of metakaolin [2], [9], at this stage enough or all portlandite has been consumed by metakaolin in the mixture to produce hydrated products which grow and fill pores producing a more dense mortar with increased strength. The highest strength gained by the 20% MK could be due to a balance between the accelerated

hydration and pozzolanic effect of metakaolin. The decreased strength observed at 35% MK is as a result of the dilution effect of MK, the quantity had probably surpassed the minimum replacing threshold [2], [9]. This results agrees partially with observations that after 14 days there is no significant increase in compressive strength for samples that contain metakaolin up to 15% [8], in contrast, 20% MK continued to increase in strength.

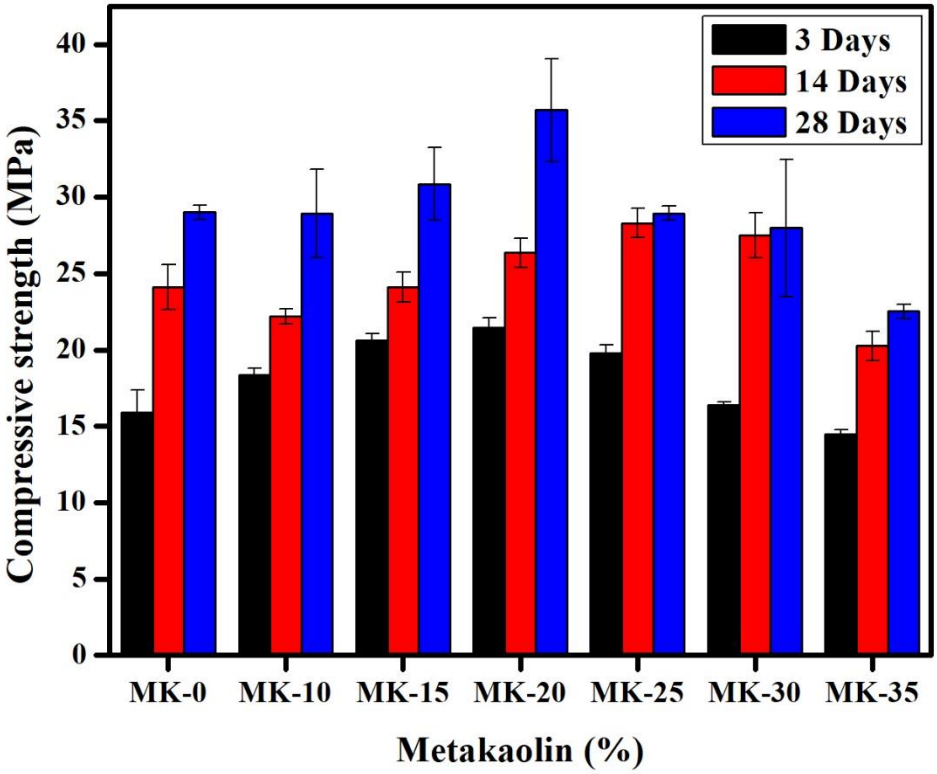


Figure 4. 10 Compressive strength of mortar cubes

4.7 Water absorption of metakaolin mortars

The water absorption by the metakaolin mortar bars cured for 1 3, 7 and 28 days are presented in *figure 4.11* to *4.13* while the water absorption coefficient (WAC) values are

presented in **Table 4.1** to **Table 4.3**. This absorption is mainly due to the capillary action on a cross-sectional area of ~ 1,600 mm^2. The results showed a general decrease in the water absorption and water absorption coefficient from the 3 days to 28 days cured samples.

The different metakaolin replacement proportions showed a high absorption of water compared to the control for 3 days cured mortar bars. The control after a day absorbed water to a depth of 6.25 mm with WAC of 1.22 $mm/hours^{0.5}$ while the metakaolin replacement proportions absorbed water to an average depth of ~8 mm per day. There was a gradual increase in water absorbed and WAC from 10 to 15% MK and a decrease from 20 to 35% MK. For mortar bars cured for 7 days there was a general decrease in absorbed water and WAC in comparison to the 3 days cured mortar. The water absorbed by control was less than the different metakaolin replacement proportions except for 10% MK. The water absorbed by the control mortar was 6.2 mm per day and 7.2 mm per day for 10% MK. The other mortars, 15 – 35 % MK absorbed ~ 6.18, ~ 4.57, ~ 5.49, ~ 4.6, and ~ 4.8 mm per day with their corresponding WAC presented in **Tables 4.2(a)** and **4.2(b)**.

Tables 4.3(a) and **4.3(b)** present the WAC values for the 28 days aged mortars. All mortars showed a significant decrease in absorbed water in comparison to the 3 and 7 days cured prisms. The amount of water absorbed by the control after 28 days curing was less than half the water absorbed at 7 days, thus 3.0 mm per day. 10% MK absorbed 2.1 mm per day, 15% MK absorbed 2.5 mm per day, 20% MK absorbed 3.26 mm per day, 25% MK absorbed 2.5 mm per day, 30% MK absorbed 2.6 mm per day and 35% MK absorbed mm 1.6 mm per day. 35% MK had the lowest WAC, with all the different MK mortars performing better than the control, except 20% MK which had a WAC of 1.55 $mm/hours^{0.5}$.

The overall improvement in water absorption by capillary action can probably be attributed to the filler effect of MK, and the formation of cementitious products by the hydration of PLC and MK, which grow and refine pores leading to a more compact mass with less pores to

absorb water. The general decrease in water absorbed by capillary action agrees with Badogiannis *et al*. [29] that increasing MK content improves sorptivity.

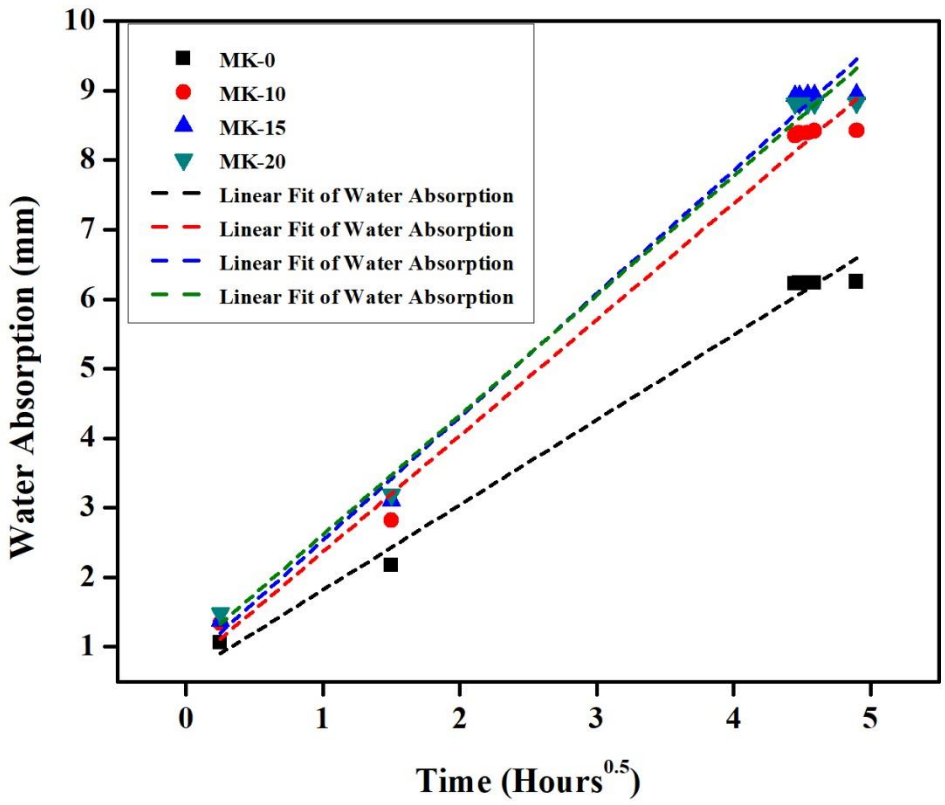


Figure 4. 11 (a) Water absorption after 3 days curing

Table 4. 1 (a) Water absorption coefficient after 3 days curing

Samples	Equation of the linear fit line	Water absorption coefficient (mm/hours$^{0.5}$)	Adj. R^2 Value
0MK	$y = 1.22252X + 0.59822$	1.22252	0.98948
10MK	$y = 1.666945X + 0.69913$	1.666945	0.98927
15MK	$y = 1.77369X + 0.75961$	1.77369	0.99053
20MK	$y = 1.71948X + 0.89692$	1.71948	0.99048

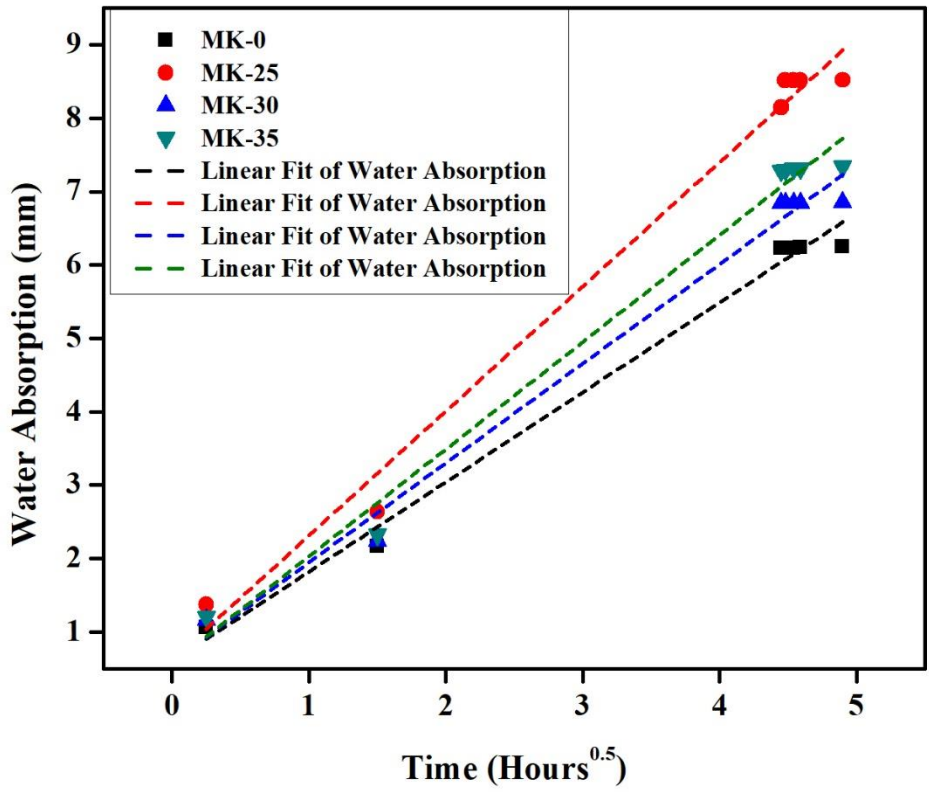


Figure 4. 11(b) Water absorption after 3 days curing

Table 4. 1(b) Water absorption coefficient after 3 days curing

Samples	Equation of the linear fit line	Water absorption coefficient (mm/hours$^{0.5}$)	Adj. R^2 Value
0MK	$y = 1.22252X + 0.59822$	1.22252	0.98948
25MK	$y = 1.69609X + 0.61685$	1.69609	0.98609
30MK	$y = 1.35473X + 0.59253$	1.35473	0.98642
35MK	$y = 1.45975X + 0.57144$	1.45975	0.98631

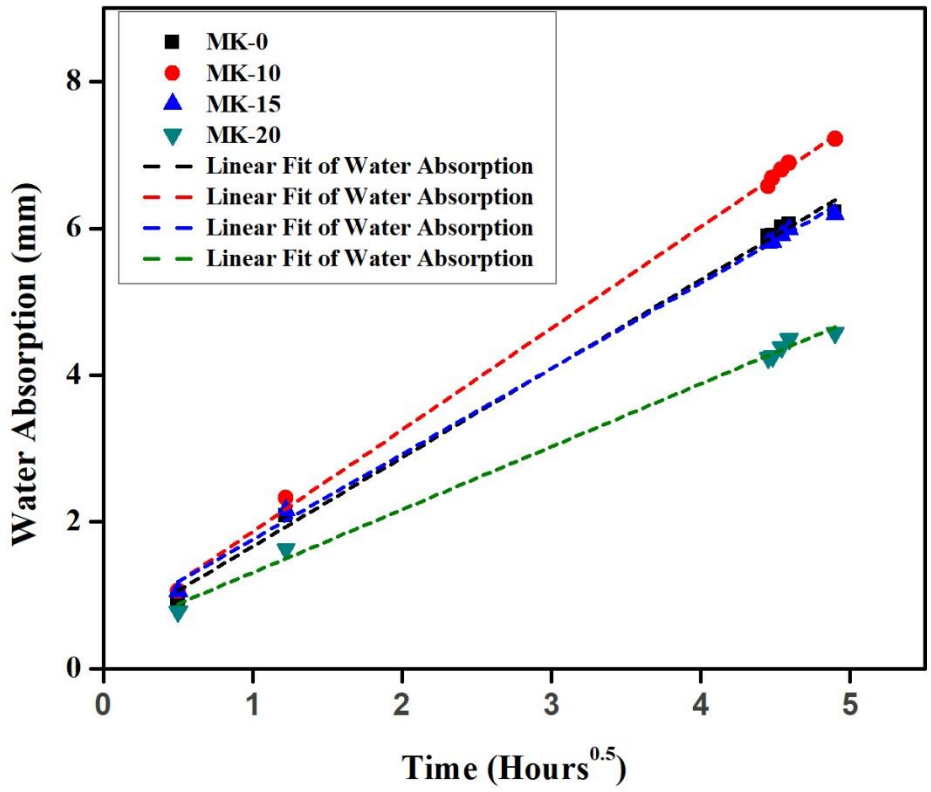


Figure 4.12(a) Water absorption after 7 days curing

Table 4. 2(a) Water absorption coefficients after 7 days curing

Samples	Equation of the linear fit line	Water absorption coefficient (mm/hours$^{0.5}$)	Adj. R^2 Value
0MK	$y = 1.20969X + 0.46086$	1.20969	0.99698
10MK	$y = 1.38304X + 0.48896$	1.38304	0.9985
15MK	$y = 1.16295X + 0.60155$	1.16295	0.99771
20MK	$y = 0.85714X + 0.45385$	0.85714	0.99612

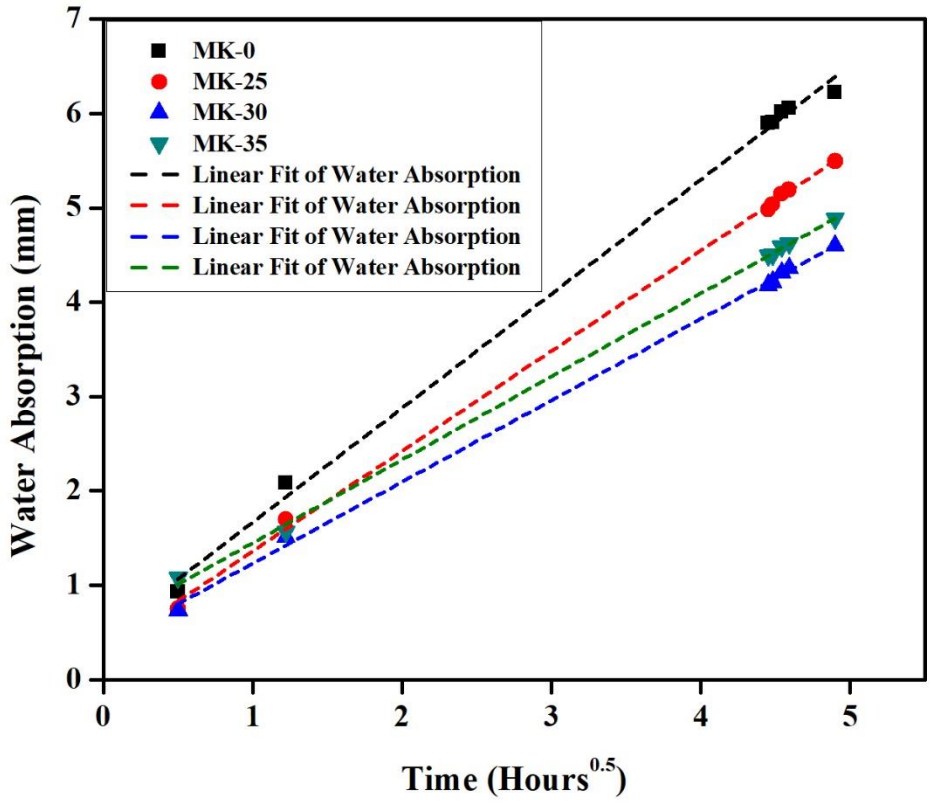


Figure 4.12(b) Water absorption after 7 days curing

Table 4. 2(b) Water absorption coefficient after 7 days curing

Samples	Equation of the linear fit line	Water absorption coefficient (mm/hours$^{0.5}$)	Adj. R^2 Value
0MK	$y = 1.20969X + 0.46086$	1.20969	0.99698
25MK	$y = 1.06098X + 0.30303$	1.06098	0.99889
30MK	$y = 0.86347X + 0.37081$	0.86347	0.99877
35MK	$y = 0.88099X + 0.57156$	0.88099	0.99903

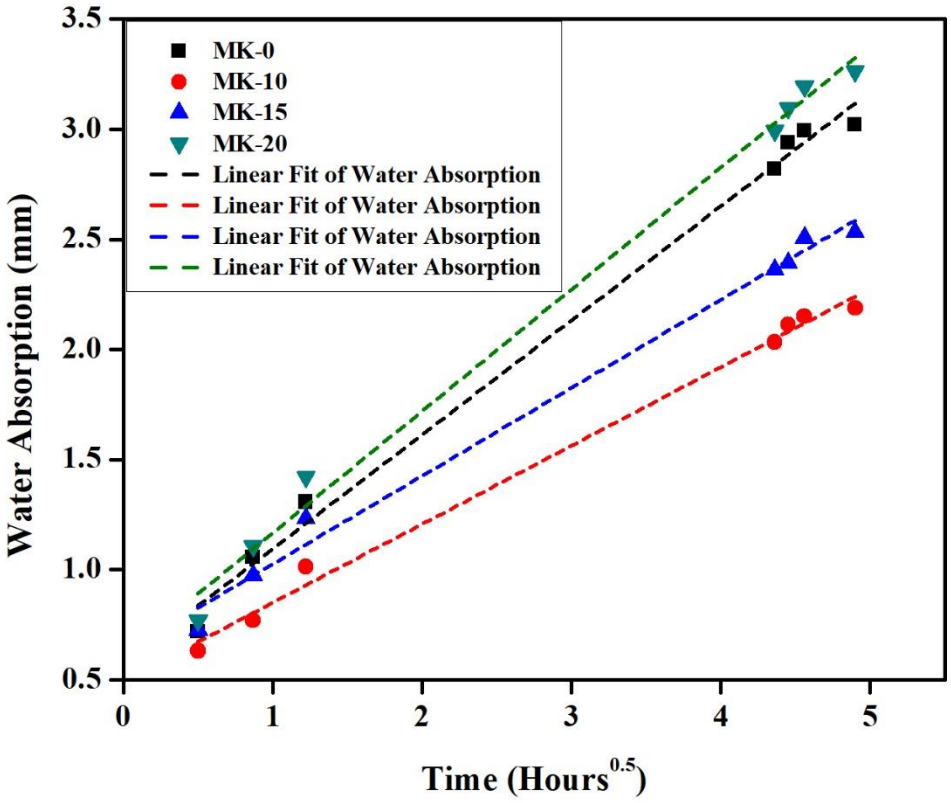


Figure 4.13(a) Water absorption after 28 days curing

Table 4. 3(a) Water absorption coefficient after 28 days curing

Samples	Equation of the linear fit line	Water absorption coefficient (mm/hours$^{0.5}$)	Adj. R^2 Value
0MK	$y = 0.5186X + 0.57631$	0.5186	0.99264
10MK	$y = 0.35631X + 0.49464$	0.35631	0.99415
15MK	$y = 0.39975X + 0.62683$	0.39975	0.99057
20MK	$y = 0.55315X + 0.61443$	0.55315	0.99343

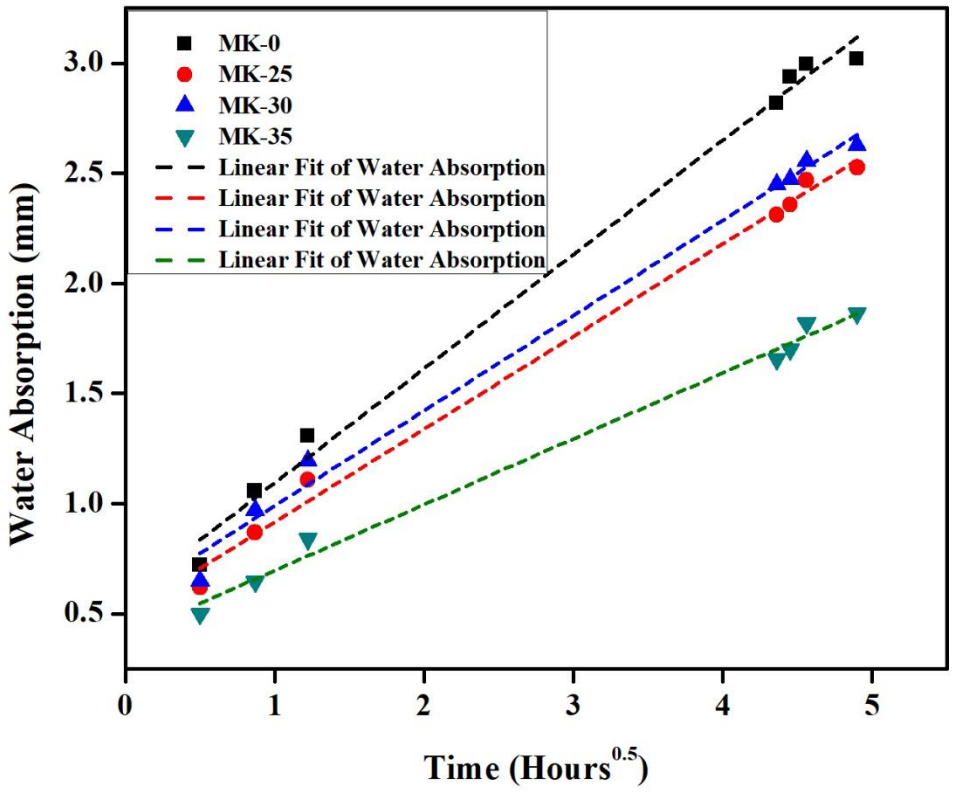


Figure 4.13(b) Water absorption after 28 days curing

Table 4. 3(b) Water absorption coefficient after 28 days curing

Samples	Equation of the linear fit line	Water absorption coefficient(mm/hours$^{0.5}$)	Adj. R^2 Value
0MK	$y = 0.5186X + 0.57631$	0.5186	0.99264
25MK	$y = 0.42113X + 0.49615$	0.42113	0.99393
30MK	$y = 0.43165X + 0.55946$	0.43165	0.99148
35MK	$y = 0.29896X + 0.39767$	0.29896	0.99211

CHAPTER FIVE

5.0 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The effects of partially replacing Portland Limestone Cement with metakaolin produced from Teleku Bokazo kaolin in the Western region of Ghana has been reported in this project. The kaolin was calcined at ~650^{o}C into the reactive metakaolin with a dehydroxlation of the kaolinite. The metakaolin became reactive and hence its suitability as a supplementary cementitious material.

Calcium silicate hydrate, calcium aluminium silicate hydrate, portlandite, calcite and ettringite were the major the hydrated compounds formed in the hydrated pastes. The water demand increased with the addition of metakaolin to the cement paste in the water consistency test. The water demand increased from ~30% to ~55% in the 10% MK - 35%MK replacement in comparison to 26% by 0% MK. The addition of metakaolin decreased the amount of PLC and increased the effective surface area and potential of the paste to absorb water hence the observation in the reported increase in water consistency.

The study again shown that, the addition of metakaolin generally increased the setting time of the cement pastes. For instance, supplementing PLC with metakaolin increased the setting time of the cement paste by ~35%, i.e. from ~167 minutes in the reference sample to ~255 minutes in the 30% MK replacement. It was also discovered that all the cement pastes met the ~75 minutes' minimum requirement for setting according to the Ghana standards for mortar pastes.

The mechanical properties were observed to increase with increasing metakaolin replacements. For instance, a 20% replacement of Portland limestone cement recorded the highest bending strength of ~ 6.9 MPa after 28 day of curing whereas the compressive

strength of the mortar cubes increased to ~36 MPa. According to Ghana Standards (GS 1118:2016), the minimum compressive strength is ~32.5 MPa after 28 days.

Therefore, from the results obtained, it is suggested that ~20% replacement of Portland limestone cement with Teleku Bokazo metakaolin can be very suitable for construction applications.

5.2 Recommendations for future work

This study covers largely the influence of the metakaolin replacements in Portland limestone cement mortar pastes. The calcination of the kaolin was carried out at 650^{o}C. However, an increase in the calcination temperature of the kaolin could affect the extent of the reactivity and their effects on the mortars. Thermogravimetric analysis (TGA) of the metakaolin based mortars could also present useful information on the thermal stability of the different hydrated products formed from the reaction between PLC and metakaolin. Also higher grade cement such as 42.5R or 42.5N should be used for the study to assess the effects of the flexural, compressive and water of absorption. These are clearly suggestions to be considered for further work.

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