# STRENGTH CHARACTERISTICS OF CONCRETE CONTAINING HIGH VOLUME METAKAOLIN AS CEMENT REPLACEMENT

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B TECH BUILDING

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OCTOBER, 2016

# DECLARATION

I hereby declare that this work is the product of my own research effort undertaken under the supervision of Dr. O. A. U. Uche and has not been presented anywhere for the award of a degree certificate. All sources have been duly acknowledged by means of references.

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# CERTIFICATION

This is to certify that the research work for this thesis and the subsequent write up by Felix Nkapheeyan Isa (SPS/12/MCE/00012) were carried out under my supervision.

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# APPROVAL PAGE

This thesis has been examined and approved for the award of Masters in Structural Engineering.

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# DEDICATION

To my father and lovely mother, may God grant you long life to reap the fruit of your labour.

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# ABSTRACT

The study examined the strength characteristics of high volume metakaolin concrete sourced from Alkaleri in Bauchi State, Nigeria. Mix ratio of 1:2:4 was adopted for the concrete samples used in the research using 150 x 150 x 150mm moulds with a water/cement ratio of 0.5. The cubes were demoulded after 24 hours and cured in water and chemical solutions (NaCl and $MgSO_4$). Some of the concrete cubes were also subjected to varying elevated temperatures and their compressive strength measured. The research found 50% replacement of cement replacement with high volume metakaolin as adequate. The density of the high volume metakaolin cubes increased with curing age, though at the early curing age some of the specimens had low densities but the cubes finally attained same densities at the later age of curing. The study found that there was an indication in rise and fall in the setting time as the metakaolin content increases however, the setting time for the samples fall within the allowable limits. The compressive strength of the sample increased with curing age. Results of the durability test revealed that the OPC/MK concrete performed best in most of the chemical solutions at 90 days hydration period with compressive strength values of 28.05N/mm$^2$ for B10 and 27.6 N/mm$^2$ for B20 in $MgSO_4$ solution respectively, while the OPC/MK performs best at 90 days hydration period with compressive strength values of 27.2N/mm$^2$ for B10 and 26.8 N/mm$^2$ for B20 in NaCl solution respectively. It was observed that binary blends B10 and B20 had the best performance at a temperature of 600˚C with a 15% and 14% reduction of the compressive strength of the cubes cured in water respectively. The study therefore recommends the replacement of cement with 50% high volume metakaolin having been proven to achieve the compressive strength of $f_{cu}$ = 22.7 N/mm$^2$ at 90 days curing in water for durability purposes while 20% replacement is recommended for improved structural integrity having achieved the compressive strength of $f_{cu}$ = 30N/ mm$^2$ at 28 days curing in water.

# CHAPTER ONE
# INTRODUCTION

## 1.1 BACKGROUND OF STUDY

Concrete is one of the most extensively used construction materials in the world (Mindess, et al. 2003). It is a composite material made of cement, water, fine aggregates and coarse aggregates. It is attractive in many applications because of its considerable strength at a relatively low cost and requires minimal maintenance. According to Gambhir (2005) concrete is the most commonly used man made construction material in the world and is second only to water as the most utilized substance on the planet. The world-wide consumption of concrete is believed to rise exponentially primarily driven by the infrastructural development taking place around the world and it is estimated to be about 8.8 billion tons per year (Mehta, 2001). Conventional concrete is produced by mixing ordinary Portland cement, aggregate (fine and coarse) and water in the right proportion to attain the desirable product. The physical properties and chemical properties of the concrete are determined in parts; by the proportion of these three key ingredients. Sayyad (2012) stated that extreme quality control is needed at many points throughout the process of making concrete in order to make sure these proportions are adequate.

Making cement for concrete involves heating pulverized limestone and clay to a temperature reaching 1450°C. They chemically interact to form the cementitious compounds in Portland cement. The limestone or calcium carbonate ($CaCO_3$) is broken down to carbon dioxide gas and calcium oxide when heated to extreme temperatures (Rosenwald, 2011). The heating of the limestone paired with the use of fossil fuels needed to heat the substance send carbon dioxide gas wafting into the atmosphere, contributing to global warming (Nmai, 2001). According to Mehta (2001), one tone of carbon dioxide is estimated to be released to the atmosphere when one tone of Ordinary Portland cement is manufactured. Hardjito, Cheak, and Ing (2008) also stated that the emission by cement manufacturing process contributes about 7% to the global carbon dioxide emission. Also, about 1.5 tonnes of raw materials is needed in the production of every tone of Portland cement (Davidovits, 1994). Therefore the production of Portland cement is extremely a resource and energy intensive process. The increased use of cement in concrete causing environmental concerns in terms of emission of carbon dioxide during cement manufacture has brought pressure to reduce the cement consumption in the construction industry by the utilization of supplementary materials (Sabir, Wild and Bai 2001). Similarly, Mindess, et al. (2003), opines that environmental concerns, stemming from the high energy expense and Carbon (IV) oxide emission associated with cement manufacture, have brought about pressures to reduce cement consumption through the use of supplementary materials. For a nation that desires to grow, she must look inwards to identify areas where she has comparative advantage over other nations and effort should be geared towards the development of the identified areas. Apart from the crude oil potentials of Nigeria, Nigeria also has absolute advantage in the solid minerals sector owing to the large deposits of minerals scattered in different parts of the country. Kaolin is one of the industrial minerals that can be found in commercial quantity. Kaolin is a soft, lightweight and often chalk-like sedimentary rock. It has an earthy odour with plate-like crystal morphology. The main constituent, kaolinite is a hydrous aluminium silicate of approximate composition $Al_2O_3 \cdot 2SiO_2 . 2H_2O$ (Prasad, Reid and Muoray.,1991). Kaolin also contains quartz, mica and less frequently feldspar, illite, bauxite, zircon and graphite (Varga, 2007). Nigeria has an estimated reserve of about two billion metric tonnes of kaolin deposits scattered in different parts of the country which include Ogun, Edo, Plateau, Bauchi, Gombe and Nasarawa states (Raw Materials Research and Development Council, 2010). The market for kaolin is large, sustainable and expanding because of the numerous applications of the product. Also there is an outright ban on the importation of kaolin into Nigeria in order to stimulate the growth of the local industry.

Supplementary cementitious materials (SCMs) are finely ground solid materials that are used to replace part of the cement in a concrete mixture. These materials react chemically with hydrating cement to form a modified paste microstructure. In addition to their positive environmental impact, SCMs may improve concrete workability, mechanical properties, and durability. One of such SCMs is the Metakaolin (MK). MK is unique in that it is not the by-product of an industrial process nor is it entirely natural; it is derived from a naturally occurring mineral and is manufactured specifically for cementing applications. Unlike by-product pozzolanas, which can have variable composition, MK is produced under carefully controlled conditions to refine its color, remove inert impurities, and tailored particle size (Brooks and Johari, 2001; Ding and Li, 2002). As such, a much higher degree of purity and pozzolanic reactivity can be obtained. MK has great promise as an SCM, as it can improve many properties of concrete while also reducing cement consumption (Sabir, et al., 2001).

Therefore, this study investigated the strength characteristics of concrete containing high volume MK as cement replacement.

## 1.2 STATEMENT OF THE PROBLEM

Concrete, produced from cement is one of the most widely used construction materials but it has a negative effect on the environment as a result of high carbon (IV) oxide emission. There is the need to find a replacement for cement which will produce concrete with low carbon emission while having the required characteristics strength, density and other properties. Production of cement involves high energy consumption involving high temperature around 1450°C.$CO_2$

emission to the environment constituting environmental nuisance. In recent times, the use of Metakaolin (MK) as a partial substitution of cement in concrete has been on the increase. MK is produced from kaolin that is calcined at temperatures of around 800 ± 100°C, which is much lower than that of cement (1450°C); thus reducing $CO_2$ emission and energy requirement. The composition of MK is similar to clay, which is silica and alumina. When replacing cement with MK, the calcium hydroxide is reduced, thus leading to an increase in sulphate resistance in MK concrete as the gypsum and ettringite formation would reduce. Other cement replacement materials such as fly ash or ground granulated blast furnace slag (GGBS) can be used in conjunction with MK in order to refine the pore structure of cement paste. In this work, concrete with high volume MK as partial replacement of cement was produced in order to examine some properties at high MK level including compressive strength, density and durability.

## 1.3 JUSTIFICATION OF THE STUDY

The case of global warming and air pollution suggest the need to provide low energy consumption compared to production of cement alternative binders to cement. The outcome of this research will proffer one of the many desirable replacements for cement. Apart from its low carbon content, MK has increased resistance to chemical attack and reduced permeability (Brooks and Johari, 2001).

## 1.4 AIM AND OBJECTIVES

The aim of the research is to investigate the strength characteristics of concrete containing high volume Metakaolin as cement replacement.

The objectives of this research are:

i. To determine the chemical properties of Metakaolin.
ii. To determine the density of high volume MK concrete.
iii. To determine the optimum percentage of MK that will produce a desired concrete strength.
iv. To investigate the durability of concrete with high volume of MK as cement replacement

## 1.5 SCOPE AND LIMITATION

The scope of the research determined the strength characteristics of concrete produced with metakaolin as cement replacement only. It covers concrete made with 10%, 20%, 30%, 40%, 50%, 60%, 70% and 80% MK as cement replacement. The research is limited to concrete and metakaolin used as the pozolanic material in the production of the concrete. It doesn't apply to other cement based products like mortar and sandcrete blocks.

## 1.6 SIGNIFICANCE OF THE STUDY

Research of this nature is of considerable significance in that it paves ways for producing cement based (concrete and mortar) products that have adequate characteristic strength and durability with less environmental hazards. It will also ensure a healthy environment as $CO_2$ emission which is harmful to the environment is reduced to a minimal amount when using Metakaolin in place of Portland cement.

## 1.7 CONTRIBUTION TO KNOWLEDGE

1. The study assessed the compressive strength of high volume metakaolin, assessed the density of high volume MK concrete, determine the optimum percentage of MK that will

produce a desired concrete strength which was obtained as 50% and also studied the performance and durability of concrete with high volume of MK as cement replacement.

2. The study found out that High Volume Metakaolin cubes increase the structural integrity of concrete structure.

3. The results of the study therefore, could be used by builders, structural engineers, contractors and clients in the production of concrete, with increased strength with durability at elevated temperature and in the presence of chemicals.

# CHAPTER TWO
# LITERATURE REVIEW

## 2.1 PREMBLE

This chapter reviewed some related literatures on cement, aggregates, metakaolin, the workability of the mix and performance from previous works.

## 2.2 CEMENT

Cement is a binder, a substance that sets and hardens independently, and can bind other materials together. The word “cement” trace to the Romans, who use the term “opus Caementicium” to describe masonry which resembled concrete and was made from crushed rock with burn lime as binder (Ismail, 2001). The most important use of cement is the production of mortar and concrete – the bonding of natural or artificial aggregates to form a strong building material, which is durable in the face of normal environment effects. Portland cement is the most common type of cement in general usage. It is a basic ingredient of concrete, mortar, and plastic. English engineer Joseph Aspdin patented Portland cement in 1824. It was named because of its similarity in colour to Portland limestone, quarried from the English Isle of Portland, and used extensively in London architecture. It consists of a mixture of oxides of calcium, silicon, and aluminium. Portland cement and similar materials are made by heating limestone (a source of calcium) with clay, and grinding this product (called clinker) with a source of sulphate (most commonly gypsum) (Ismail, 2001).

### 2.2.1 History of Cement.

It is uncertain where it was first discovered however the combination of hydrated non – hydraulic lime and a pozzolan produces a hydraulic mixture but concrete made from such mixtures was first used on a large scale by Roman engineers (Donald, 2004). They used both natural pozzolans (trass or pumice) and artificial pozzolans (ground bricks or pottery) in these concretes. Many excellent examples of structure made from these concrete are still standing, notably the huge monolithic dome of the pantheon in Rome and massive Baths of Caracalla. The vast system of Roman aqueducts also made extensive use of hydraulic cement. The used as a core fill in stone walls and columns (Bensted and Barnes, 2002).

Modern hydraulic cements began to be developed from start of the industrial Revolution (around 1800), driven by three main needs:

1. Hydraulic renders for finishing bricks building in wet climates.
2. Hydraulic mortars for masonry construction of harbour work such structure in contact with sea water.
3. Development of strong concretes.

According to Ismail (2001), Joseph Aspdin, a British bricklayer, in 1824 was granted patent for a process of making cement which he called Portland cement. His cement was an artificial hydraulic lime similar in properties to the material known as "Roman Cement" (patented in 1796 by James Parker) and his process was similar to that patented in 1822 and used since 1811 by James Frost who called his cement "British Cement". The name "Portland cement" is also recorded in dictionary published 1823 being associated with William Lockwood and possibly other (Taylor, 1997). Aspdin's son William in 1843 made an improved version of this cement and his initially called it "patent Portland cement" although he had no patent. In 1848 William Aspdin further improved his cement and in 1853 moved to Germany where he was involved in cement making. Many people have claimed to have made the first Portland cement in the modern sense, but it is generally accepted that was first manufactured by William Aspdin at North fleet, England in about 1842. The German government issued a standard on Portland cement in 1878 (Ismail, 2001).

Portland cement is the most common type of cement in general use around the world, because it is basic ingredient of concrete, mortar, stucco and most non-specialty grout. It is a fine power produced by grinding cement clinker (more than 90%), a limited amount of calcium sulphate which controls the set time, and up to 5% minor constituents (as allowed by various standards). As define by European Standards EN 197 – 1 (1971) in Neville (2000) "Portland cement clinker is a hydraulic material which shall consist of two-third by mass of calcium silicate ($3CaO.SiO.SiO_2$). The remainder consists of aluminium, iron – containing clinker phases and other compounds. The ratio of CaO to $SiO_2$ shall not be less than 2.0; the magnesium content (MgO) shall not exceed 5.0% by mass "(The last two requirement were already set out in German Standard, issued in 1909). Portland cement is made by heating limestone with small quantities of other materials (such as clay) to $1450^0$C in a kiln, in a process known as calcination. The resulting hard substance, called 'clinker`, is then ground with a small amount of gypsum into powder to make 'Ordinary Portland Cement; the most commonly used type of cement (often referred to as OPC).

### 2.2.2 Classification of Portland cement

There are different standards for classification of Portland cement. The two major standards are the ASTM C150 used primarily in U.S and European EN- 197 – 1 (1971) in Neville (2000).

There are five type of Portland cement with variations of first three according to Ismail (2001)

Type I**:** Ordinary portland cement is known as common or general purpose cement. It is commonly used for general construction especially when making precast and pre-stressed concrete that is not to be in contact with soils or ground water. The typical compound compositions of this type are:

55% ($C_3S$), 19% ($C_2S$), 10% ($C_3A$), 7% ($C_4AF$), 2.8% MgO,2.9% ($SO_3$), 1.0% Ignition loss, and 1,0%free CaO. A limitation on the composition is that the ($C_3A$) shall not exceed 15%.

Ordinary Portland cement Type II**:** is intended to have moderate sulphate resistance with or without moderate heat of hydration. This type of cement costs about the same type I. its typical compound composition is:

51% ($C_3S$), ($C_2S$), 6% ($C_3A$), 11% ($C_4AF$), 2.9 % ($SO_3$), 0.8% Ignition loss and 1.0% free CaO

A limitation on compound is that the ($C_3A$), shall not exceed 8% which reduces its vulnerability to sulphates. This type is for general construction that is exposed to moderate sulphate attack and is meant for use when concrete is in contact with soils and ground water especially in the western United States due to the high sulphur content of the soil. Because of similar price to that of Type I, Type II is much used as general purpose cement, and majority of Portland cement sold in Northern America meets this specification.

Note: cement meeting (among others) the specifications for Type I and II has become commonly available in the world market.

Ordinary Portland cement Type III**:** has relatively high strength. The typical compound composition is:

57% ($C_3S$), 19% C2S), 10% ($C_3A$), 7% ($C_4AF$), 3.0% MgO, 3.1% ($SO_3$), 0.9 Ignition loss and 1.3% free CaO.

This cement is similar to Type I, but ground finer. Some manufacturers make a separate clinker with higher $C_3S$ and or $C_3A$ content, but this is increasingly rare, and general purpose clinker is usually used, ground to specific surface typically 50-80% higher. The gypsum level may also be increased a small amount. This gives the concrete using this type of cement a three days compressive strength equal to the seven days compressive strength of type I and II 28 day's compressive strengths. This only downside is that the six month strength of type III is the same is the same or slightly less than that of type I and III is the same or slightly less than that type of I and II. Therefore the long –term strength is sacrificed a little. It is usually used for precast concrete manufacture, where high 1 day strength allows fast turnover of moulds. It may also be used in emergency construction and repair and construction of machine bases and gate installations.

Ordinary Portland cement Type IV**:** Portland cement is generally known for its low heat of hydration. The typical compound composition is.

28% ($C_3S$), 40% ($C_2S$), 4% (($C_3A$), 12 % ($C_4AF$), 1.8% Mg, 1.9% ($SO_3$), 0.9% Ignition loss, and 0.8 free CaO.

The percentages of ($C_2S$) and ($C_4AF$), are relatively high and ($C_3S$) and ($C_3A$) is seven, and the maximum percentage of ($C_3A$) is thirty five. This cause the heat given off by the hydration reaction of develops at slower rate. However, the strength is higher than the other types after full curing. This cement is used for very large concrete structures, such as dams, which have a low surface to volume ratio. This type of cement is generally not stocked by manufactures but some might consider a large special order. This type of cement has not been made for many years, because Portland – pozzolan cements and ground granulated blast furnace slag addition offer a cheaper and more reliable attractiveness.

Ordinary Portland cement Type V**:** is used where sulphate resistance is important. The typical compound composition is:

38% ($C_3S$), 43% ($C_2S$), 4% ($C_3A$), 9 % ($C_4AF$), 1.9% Mg0, 1.8% ($SO_3$), 0.9% Ignition loss and 0.8% free CaO.

This cement has a very low ($C_3A$) composition which account for its sulphate resistance. The maximum content of ($C_3A$) allowed 5% for type V Portland cement another limitation is that the ($C_4AF$) + 2 ($C_3A$) cannot exceed twenty percent. This type is used in concrete that is to be exposed to soil and ground water sulphate which rate with ($C_3A$) causing disruptive expansion. It is available in many places although its use is common western United State and Canada. As with Type IV, Type V Portland cement is mainly supplemented by ordinary cement with added ground granulated blast furnace slag or tertiary blended cement containing slap and flying ash.

Type Ia, Type IIa and Type IIIa have the same composition as Type I, II and III. The only difference is that in Ia, IIa and IIIa and air entrainment agent in ground into a mix. The air entrainment must meet the minimum and the maximum optional specification found in the ASTM manual. These types are only available in the eastern United State and Canada but can only be found on a limited basis. They are a poor approach to air-entrainment which improves resistance to freezing under low temperatures.

Comprising Portland cement and up to 5% of minor additional.

I. Portland cement Constituents Portland – composite

II. Portland cement and up to 35% of minor additional Cement.

III. Blast furnace Portland cement and high percentage of blast furnace slag.

IV. Pozzolanic Portland cement and up to 55% of pozzolanic Constituent.

V. Composite Portland cement, blast furnace slag and pozzolana or fly ash.

### 2.3 WHITE PORTLAND CEMENT

White Portland cement differs physically from the grey from only in its colour, and as such can fall into many of the above categories. (eg ASTM C150 Type I, II, and or III). However its manufacture is significantly different from that of others.

#### 2.3.1 Non – Portland Hydraulic Cement.

i. Pozzolan – lime cements: This is a mixture of ground pozzolan and lime. These cements were used by the Romans, and are to found in Roman structures still standing (e.g the pantheon in Rome). They develop strength slowly, but their ultimate strength can be very high. The hydration products that produce strength are essentially the same as those produced by Portland cement.

ii. Super –lime cement: Ground granulated blast furnace slag does not hydrate on its own, but is “activated” by addition of alkalis, most economically using lime. They are similar to pozzolan lime cements in their properties. Only granulate slag (i.e. water – quenched, glassy slag) is effective as a cement component.

iii. Super – sulphate cements: these contain about 80% ground granulated blast furnace slag, 15% gypsum or anhydrite and a little Portland clinker or lime as an activator. They produce strength by formation of ettringite, with strength growth similar to slow Portland cement. They exhibit good resistance to aggressive sulphate.

iv. Calciumaluminate cements: these are hydraulic cements made primarily from limestone and bauxite. The active ingredient are monocalcium aluminate’$CaAI_20_4$ (CA in cement chemist notation) and Mayenite $Ca_{12}AI_{14}$ $0_{33}$ ($CaAI_2A_7$ in CCN). Strength form by hydration to calcium aluminates hydrates. They are well- adapted for use in refectory (high temperature resistant) concretes, e.g for furnace linings.

v. Calcium sulfo-aluminate cement: these are made from clinkers ($Ca_4$ $(AI0_2)_6SO_4$or $C_4A_3$ in cement chemists, notation) as a primary phase. They are used in expensive cements in ultra – high early strength cements and in “low-energy cements” hydration produces ettringite, and specialized physical properties (such as expansion or rapid reaction) are obtained by adjustment of availability of calcium and sulphate ions. Their use as a low –energy alternative to Portland cement has been pioneered in China, where several million tonnes per year are produced. Energy requirements are low because of the lower kiln temperatures required for the reaction and the lower amount of limestone (which must be endothermic ally decarbonate) in the mix. In addition, the lower limestone content and lower fuel consumption leads to a $CO_2$ emission around half that associated with Portland clinker. However, $SO_2$ emissions are usually significantly higher.

Vi. “Natural”Cement: correspond to certain type of the pre-portland era, produced by burning argillaceous lime stone at moderate temperatures. The level of clay components in the limestone (around 30 -35%) is such that large amounts of belite (the low-early strength, high –late strength mineral in Portland cement) are formed without the formation of excessive amount free lime. As with any natural material, such cements have very variable properties.

Vii. Geopolymer cement: these are made from mixtures of water-soluble alkali metal silicates and aluminosilicate material powders such as fly ash and Metakaolin.

## 2.4 CONSTITUENTS OF CEMENT

The constituents of cement are classified according to their quantities into major and minor constituents of cements. Four oxides according to Matawal (2005) are usually regarded as the major constituents of cement and are listed in Table 2. The cement chemists describe each oxide by one letter as shown CaO = C; $SiO_2$ = S; $A1_2O_3$ = A and $Fe_20_3$ = F. Likewise $H_20$ in hydrated cement is denoted by H and $S0_3$ by S. The calculation of the potential composition of Ordinary Portland Cement (OPC) is based on the work of Bogue and others, and is often referred to as "Bogue computation". The combined content of the major constituents is approximately 90% of the mass of cement.

In addition to the main compounds listed in Table 1 there exist minor compounds, such as Magnesia (MgO), titanium oxide ($TiO_2$), potassium and sodium oxides ($K_2O$ and $Na_2O$), free lime (CaO), gypsum ($CaSO_4$. $2H_2O$) and phosphorus pent oxide ($P_2O_5$). They usually amount to not more than a few percent of the mass of cement. Table 2 shows the oxide composition of a typical Portland cement and the calculated compound composition obtained by means of Bogue's equation as given by Neville (2000).

Two of the minor compounds, that are $Na_2O$ and $K_2O$ known as the alkalis in cement, react with some aggregates. The product of their reactions causes disintegration of concrete. It has also been said to affect the rate of strength gain (Neville, 2000). The insoluble residue in Table 3 is determined by treating cement with hydrochloric acid. It is a measure of adulteration of cement, largely arising from impurities in gypsum. The loss on ignition shows that the extent of carbonation and hydration of free lime and free magnesia are due to the exposure of cement to the atmosphere. The compounds are summarized by both Neville (2000) and Matawal (2001) in Table 2.1 and Table 2.2

Table 2.1 Main Compounds in Portland cement

| Compound | Oxide composition | Abbreviation |
|---|---|---|
| Tricalcium Silicate | $3CaO.\ SiO_2$ | $C_3S$ |
| Dicalcium silicate | $2CaO.\ SiO_2$ | $C_2S$ |
| Tricalcium aluminates | $3CaO.\ A1_2O_3$ | $C_3A$ |
| Tetra calcium Aluminoferrite | $4CaO.\ A1_2O_3.\ Fe_2O_2$ | $C_4AF$ |

Source: Matawal, 2001in Soji, 2015)

Table 2.2 Oxide and Compound Composition of a Typical Portland cement

| Oxide | Composition Percent (%) | In compound | (Using Bogue's equation in Percent (%)) |
|---|---|---|---|
| CaO | 63 | $C_3A$ | 10.8 |
| $SiO_2$ | 20 | $C_3S$ | 54.1 |
| $A1_20_3$ | 6 | $C_2S$ | 16.1 |
| $Fe_2O_3$ | 3 | $C_4AF$ | 9.1 |
| MgO | 1½ | Minor Compounds | - |
| $SO_3$ | 3 | | |
| $K_2O$ | | | |
| $Na_2O$ | 1 | | |
| Others | 1 | | |
| Loss of ignition | 2 | | |
| Insoluble residue | ½ | | |

(Source: Neville, 2000 in Soji, 2015)

### 2.4.1 Tricalcium Silicate ($C_3S$)

The silicates, $C_3S$ and $C_2S$ are the most important compounds, which are responsible for the strength of hydrated cement paste. In reality, the silicates in cement are not pure compounds but contain minor oxides in solid solution. The impure $C_3S$ is alite and the impure $C_2S$, as belite. They both contain a few percentages of $A1_2O_3$, MgO and $Na_2O$ atomic arrangement, crystal form and hydraulic prosperities of the silicate (Ismail, 2001).

$C_2S$ is primarily responsible for the high early strength of hydrated OPC. The reaction is exothermic giving off large quantity of heat (heat of hydration) attaining most of its strength in 7 days. The $C_3S$ exits in alpha, beta and gamma rays but only the beta is significant. It takes longer days to set, as such produces little strength until after 28 days (Ismail, 2001).

### 2.4.2 Tri calcium Aluminates ($C_3A$)

In the manufacture of cement, $C_3A$ is beneficial in that it facilitates the combination of lime and silica. In its pure form tricalcium aluminates reacts with water almost instantaneously giving a flash set accompanied by the evolution of a large quantity of heat that is, about 850j/g. Normal setting may be achieved in mixes with a high water content by the addition of 15% gypsum. In moist air, most of the strength is developed within a day or two, but the strength, as such, is comparatively low. Thus, it contributes little or nothing to the strength of cement except at early ages, and when concrete is attacked by sulphates, $C_3A$ reacts with gypsum to form calcium sulphoaluminate (ettringite) which may cause disruption of the hardened paste. In Portland cement, $C_3A$ occurs as an impure form. Its content in Ordinary Portland Cement varies from 7 to 15% (Ismail, 2001).

### 2.4.3 Tetra calcium Aluminoferrite ($C_4AF$)

$C_4AF$ is present in cement in small quantities and, compared with the other three compounds, does not affect the behavior significantly. It reacts with water rapidly and setting occurs within minutes. The heat evolution on hydration is approximately 420j/g. It reacts with gypsum to form calcium sulphoferrite and its presence may accelerate the hydration of silicates. In Portland cement, the ferrite phase (celite) occurs as a solid solution, the composition of which varies from about $C_6A_2F$ to about $C_6AF_2$ with the median value being fairly close to $C_4AF$. The calcite content in Ordinary Portland cement ranges from 5 to 10% with an average approximately 8% (Ismail, 2001).

### 2.4.4 Gypsum ($CaSO_4$. $2H_2O$)

During the processes of the manufacture of cement, gypsum is added to cement clinker in order to prevent flash setting time of cement. The amount of gypsum added to the clinker is crucial. It is therefore used as a retarder. There is an optimum content of gypsum added to cement to give maximum strength and minimum shrinkage. This optimum content depends upon the $C_3A$ content and the alkali contents of the cement. Increasing the fineness of cement has the effect of increasing the quantity of $C_3A$ available at early ages and this raise the gypsum level. An excess of gypsum leads to expansion and consequent disruption of the cement paste. This adverse effect is due to the formation of ettringite ($3CaO.Al_2O_3.3CaSO_4.31H_2O$) resulting from reaction between $C_3A$ and gypsum. This type of deterioration of the cement paste is customarily described as an internal sulphate attack. The optimum gypsum content is determined on the basis of the generation of heat of hydration so that a desirable rate of early reaction occurs which ensure that there is little $C_3A$ available for reaction after all the gypsum has combined

Cement standards specify a maximum $SO_3$ content which is, in accordance with BS 12 (1991), to be 2.5% for cement having tricalcium aluminates ($C_3A$) content of 7% or less, and 3% for cement having $C_3A$ content greater than 7%. $SO_3$ exist from cement raw materials and the added gypsum. The amount of $SO_3$ originating from the raw materials is usually 0.1% to 0.5%.

### 2.4.5 Alkali Oxides ($K_2O$ and $Na_2O$)

Potassium oxide ($K_2O$) and sodium oxide ($Na_2O$), alkali oxides, have been found to react with some coarse aggregates in concrete. The product of the alkali-aggregate reaction (AAR) causes disintegration of cement paste. It contains a reactive form of silica which combines with the alkali oxides released from the cement. This reaction results in the formation of alkali silica gel and involves expansive forces, which in turn, may cause cracking and deterioration of the concrete. This effect may be avoided by the use of low alkali cement that is, cements in which the total alkalis content, $K_2O$ and $Na_2O$, does not exceed 0.6% (Ismail, 2001).

### 2.4.6 Free Lime (CaO)

Free or un combined lime in cement may occur when the raw materials used in manufacturing process contain more lime that can combine with the acidic oxides, $SiO_2$, $A1_2O_3$ and $Fe_2O_3$. Free lime may also occur when the amount of lime in the raw materials is not sufficient enough to cause a complete reaction with the acidic oxides during the clinkering process.

The reactions that take place during the burning of cement are essentially solid-solid reactions (SSR). It occurs at the final stage of burning. To achieve complete reactions the materials are finely ground and thoroughly mixed together. However, complete reactions are not achievable as less than 1% free lime does exist in Portland cement (Ismail, 2001).

In determining the quality of cement, the presence of free lime as CaO is the important factor. The CaO present in the cement formed with $CaCO_3$ dissociated on burning of the raw materials. The burning of the cement is carried out at temperature which is much higher than the dissociation temperature of $CaCO_3$ (about $900^oC$). The CaO is very slow to hydrate because it is 'hard burnt'. Furthermore, the lime formed on burning is inter crystallized with other minerals and is, therefore, not readily accessible to water. Consequently, with such lime, the hydration will take place after the cement has set. This hydration causes an expansion of the set cement which in turn causes cracking and deterioration of cement paste. The reason being that hydrated (slaked) lime occupies a larger volume than free CaO. The phenomenon is known as 'unsoundness due to lime'. Cement which exhibits such expansion is said to be unsound (Ismail, 2001).

### 2.4.7 Titanium Oxide ($TiO_2$)

Titanium ($TiO_2$) occurs in cement to a small extent and its content varies from 0.1% to 0.4%. Titanium is introduced into cement through the clay or shale used in its manufacture.

### 2.4.8 Phosphorus Pent oxide ($P_2O_5$)

Phosphorus Pent oxide is usually introduced into cement through limestone used in its manufacture. Generally, $P_2O_5$ content in cement does not exceed 0.2%. Its presence slows the cement hardening because it breaks down the $C_3S$ to $C_2S$, which contains the $P_2O_5$ in solid solution and CaO. Larger amounts of $P_2O_5$ may cause unsoundness because free lime will be formed. This latter effect may be partly overcome by reducing the lime content in the raw materials. Accordingly, sound cement, of $P_2O_5$ content of 2.0 to 2.5% can be produced (Ismail, 2001).

### 2.4.9 Magnesia (MgO)

The raw materials for the cement usually contain a certain amount of $MgCO_3$, which on burning dissociates to magnesium oxide (magnesia) and carbon dioxide.

Magnesia does not combine with the major oxides; some are taken up in solid solution in the clinker minerals while the remainder crystallizes as periclase (MgO). The hydration of periclase, similar to that of the CaO, involves increase in magnesia which may cause unsoundness.

The magnesia content is limited to 4% by BS 12. The magnesia content as such is not a good indication of potential unsoundness. As has been pointed out, some MgO is held in solid solution by the clinker minerals and the remainder crystallizes as periclase. Only the presence of periclase may cause unsoundness.

## 2.5 CONCRETE AND ITS COMPOSITION

Concrete is a construction material composed of cement (commonly Portland cement) as well as other cementatious materials such as fly ash and slag cement, aggregate (generally a coarse aggregate such as gravel, limestone or granite, plus a fine aggregate such as sand), water, and chemical admixtures. The word concrete comes from Latin word “Concretus” meaning compact or condensed), the past participle of “concreso”, from “come –“(together), and “Cresco” (to grow) ASTM C150 (1994). According to Neville (2000) during the Roman Empire, Roman concrete (or Opus caementicium) was made from quicklime, pozzolanic ash/pozzolana, and an aggregate of pumice. Its widespread use in many Roman structures, a key event in history of architecture termed the Concrete Revolution, freed Roman construction from the restrictions of stone and bricks material, and allowed for revolutionarily new designs in terms of both structural complexity and dimension.

Modern tests show Opus caementcium similarly strong as modern Portland cement concrete in its compressive strength. However, due to the absence of reinforced steel, its tensile strength was far lower and its mode of application was different (Neville and Brooks., 1987). The secret was lost for 13 centuries until 1756, when the British Engineer John Smeaton, pioneered the use of hydraulic lime in concrete, using pebbles, and powdered brick as aggregate. Portland cement was first used in concrete in the early 1840s, this version of history has been challenged however, as the Canal du Midi was constructed using concrete in 1670 (Donald, 2004). Recently, the use of recycled materials as concrete ingredients is gaining popularity because of increasingly stringent environmental legislation. The most conspicuous of these is fly ash, a by-product of coal-fired power plants. This has a significant impact by reducing the amount of quarrying and landfill space required, and, as it acts cement replacement, reduce the amount of cement required to produce solid concrete (Bai and Wild, 2002). Concrete additives have been used since Roman and Egyptian times, when it was discovered that adding volcanic ash to mix allowed it to set under water. Similarly, the Roman knew that adding horse hair made concrete less liable to crack while it hardened, and adding blood made in more frose –resistant (Donald, 2004).

### 2.5.1 Properties of Concrete.

Properties of concrete are too numerous. Few of which discussed in this section, include: compressive strength, expansion and shrinkage, cracking, shrinkage cracking, tension cracking and creeps.

### 2.5.2 Compressive and Tensile Strength of Concretes.

According to ACI 318 - 08 (2008), Concrete has relatively high compressive strength, but significantly low tensile strength, it is fair to assume that a concrete samples tensile strength is about 10% - 15% of its compressive strength. As a result, without compensating, concrete would usually fail from tensile stresses – even when loaded in compression. The practical implication of this is that concrete elements subjected to tensile stresses must be reinforced with materials that are strong in tension. Reinforced concrete is the most common form of concrete. The reinforcement is often steel; rebar (mesh, spiral, bars, and other forms). The ultimate strength of concrete is influenced by the water – cementitious ratio (w/cm), the design constituents, and the mixing, placement, and curing methods employed. All things being equal, concrete with lower water – cement (cementitious) ratio makes a stronger concrete than that with a higher ratio. The quantity of cementitious materials (Portland cement, slag cement pozzolans) can affect strength, water demand, shrinkage, abrasion resistance, and density. All concrete will crack independent of whether or not it has sufficient compressive strength. In fact, Portland cement content mixtures can actually crack more readily due to increased hydration rate. As concrete transforms from its plastic state, hydration to solid, material undergoes shrinkage.

### 2.5.3 Expansion and Shrinkage.

Concrete has a very low coefficient of thermal expansion. However, if no provision is made for expansion, very large forces can be created, causing crack in parts of the structure not capable of withstanding the force or the repeated cycles of expansion and contraction. As concrete matures it continues to shrink, due to the ongoing reaction taking place in the material, although the rate of shrinkage falls relatively quickly and keeps reducing over time (for all practical purposes concrete is usually considered not to shrink due to hydration any further after 30 years). The relative shrinkage and expansion of concrete and brickwork require careful accommodation when the two forms of construction interface (Bensted and Barnes, 2002).

### 2.5.4 Cracking

All concrete structures will crack to some extent. Concrete cracks due to tensile stress induced by shrinkage or stresses occurring during setting or use. Various means are used to overcome this. Fibre reinforced concrete uses fine fibres distributed throughout the mix or larger metal or other reinforcement element to limit the size and extent of cracks. In many large structures, joints or concealed saw-cuts are placed in the concrete as it sets to make the inevitable cracks occur where they can be managed and out of sight. Water tanks and highways are examples of structures requiring crack control (Andrew, 1995).

### 2.5.5 Shrinking Cracking

Shrinking cracks occur when concrete members undergo restrained volumetric changes (shrinkage) as a result of drying, autogenously shrinkage or thermal effects. Restraint is provided either externally (i.e. supports walls and other boundary conditions) or internally (differential drying shrinkage, reinforcement). Once the tensile strength of concrete is exceeded, a crack will develop. The number and width of shrinkage cracks that develop are influenced by the amount of shrinkage that occurs, the amount of restraint present and the amount and spacing of reinforcement provide (Ahmadi, et al., 2007). Plastic – shrinkage cracks are immediately apparent, visible within 0 to 2 days of placement, while drying –shrinkage cracks develop over time. Autogenously, shrinkage also occurs when the concrete is quite young and results from the volume reduction resulting from the chemical reaction of the Portland cement (Ismail, 2001).

### 2.5.6 Tension cracking

Concrete members may be put into tension by applied loads. This is most common in concrete beams where a transversely applied load will put one surface into compression and the opposite surface into tension due to induced bending. The portion of the beam that is in tension may crack. The size and length of cracks is dependent on magnitude of the bending moment and design of reinforcing in the beam at the point under consideration. Reinforcement concrete beams design to crack in tension rather than in compression. This is achieved by providing reinforcing steel which yields before failure of the concrete in compression occurs and allowing remediation, repair, or if necessary, evacuation of an unsafe area (Bented and Barnes, 2002).

### 2.5.7 Creep

Creep is the term use to describe the permanent movement of deformation of a material in order to relieve stresses within the material. Concrete, which is subject to long-duration forces, is prone to creep. Short duration forces (such as wind or earthquakes) do not cause creep. Creep can sometimes reduce the amount of cracking that occurs in a concrete structure or element, but it also must be controlled. The amount of primary and secondary reinforcing in concrete structures contributes to a reduction in the amount of shrinkage, creep, and cracking (Bai, et al., 1999).

### 2.5.8 Composition of Concrete

Concrete is mainly composed of aggregates (gravels and sand) water and cement and in some cases reinforcement and admixtures (Job, 2009).

### 2.5.9 Aggregates

Fine and coarse aggregate make up the bulk of concrete mixture. Sand, natural gravel and crushed stone are mainly used for this purpose. Recycled aggregate (from construction, demolition and excavation waste) are increasingly used as partial replacements of natural aggregates, while a number of manufactured aggregates, including air- cooled blast furnace slag and bottom ash are also permitted. Decorative stone such quartzite, small river stones or crushed glasses are sometimes added to the surface of concrete for decorative ‘’exposed aggregate’’ finish, popular among landscape designers. The most important properties of aggregate usually considered in material testing are; sieve analysis, bulk density, specific gravity, aggregate crushing value etc.

### 2.5.10. Reinforcement

Concrete is strong in compression, as the aggregate efficiently carries the compression load. However, it is weak in tension as the cement holding the aggregate in place can crack, allowing the structure to fail. Reinforced concrete solves the problems by adding metal reinforcement bars, glass fibre, or plastic fibre to carry tensile loads.

### 2.5.11. Water

According to Neville (2000), water is an important ingredient of concrete, it actively participate in the chemical reaction with cement. Since it helps to form the strength giving cement gel, the quality and quantity of water is required to be looked into very carefully. A popular yardstick to the suitability of water for mixing concrete is that, if water is fit for drinking it is fit for making concrete. Some specification also accept water for making concrete if $p^H$ value lies between 6 and 8 and water is free from organic matter. Instead of depending on $p^H$ and other chemical composition, the best course to find out whether a particular source of water is suitable for concrete making or not, is to make concrete with this water and compare it 7 days and 28 days strength with companion cubes made with distilled water. If the compressive strength is up to 90percent, the source of water may be accepted (Matawal, 2001).

## 2.6 POZZOLANA

Ambroise, et al.(1994), defines Pozzolanas as materials containing reactive silica and /or alumina which on their own have little or no binding property but when mixed with lime in the presence of water, will set and harden like cement. They are an important ingredient in the production of an alternative cementing material to ordinary Portland cement (OPC). In a similar definition by Lea and Hewlett (2009) the term pozzolana has two distinct meanings. The first one indicates the pyroclasic rocks essentially glassy and sometimes zeolitised, which occur either in the neighborhoods of pozouli (puteoli of the Roman times or around Rome. The second includes all those organic materials, either natural or artificial, which harden in water when mixed which calcium hydroxide (lime) or with materials that can release calcium hydroxide (Portland cement clinker). In our discussion, the term pozzolana will be referring to the later all through.

### 2.6.1 History of Pozzolana

The Greeks and Romans were the first civilizations known to use Pozzolanas in lime mortars. The Romans used not only crushed pottery, bricks and tiles which formed the first artificial pozzolanas but also found that some volcanic soil were excellent for producing a hydraulic mortar. Nowadays, a wide variety of siliceous or aluminous materials are used for producing pozzolanas, the common materials being calcined clays, pulverized fly ash, volcanic ash from agriculture residues such as rice husks. Cement or some form of building agent is an element in all types of construction and in recent years the cement market has been dominated by one product, OPC. In many countries of the developing world, OPC is an expensive and sometimes scarce commodity. This has severely limited the construction of affordable housing. Many of these countries have large supplies of pozzolanic materials readily available. In volcanic areas such as Central Africa, Central America and Indonesia there are enormous deposits of volcanic ash. In India and other Asian countries rice husk (RHA), (the husks can often be difficult to dispose of) and it provides a good source of pozzolana for use in masonry elements. Although still limited in comparison with growth of the use of pozzolanas in Europe and the USA, there is growing number of developing countries now using more and more pozzolanas in combination with lime of OPC.

### 2.6.2 Classification of Pozzolanas

Pozzolanas are mainly classified based on the origins, because a precise classification of pozzolanas prove difficult since this common name include materials which are very different in terms of chemical composition, mineralogical nature and geological and which are related only by the general property.

Neville (2000) classified pozzolanas into two main classes namely:

(i) Natural Pozzolanas and
(ii) Artificial Pozzolanas

1. Natural Pozzolanas: do not require any further treatment apart from grinding. According to Neville (2000), Natural pozzolanas are further classified into two.

(a)Those derived from volcanic rocks in which the amorphous constituents are glass produced by fusions. These are for examples volcanic ashes, pumices, scoria, and obsidian.

(b)The other are derived from rocks or earth for which the silica constituent contains opal, from precipitate of silica from solution or from remains of organism. Examples of these are diatomaceous earth charts, opaline, silica, lava containing substantial amounts of glassy components and clay that has been naturally calcined by heat from flowing lava. In Africa, some of known sources of natural pozzolanas of volcanic origin may be found in Nigeria, Cameroon, Capeverde, Burundi, Ethiopia, Tanzania, Kenya, etc.

2. Artificial Pozzolanas: these result from chemical and /or structural modifications of materials originally having no or only pozzolanic properties. The later can be residues of certain production methods manufactured from selected materials. Neville (2000) also classified artificial pozzolana into that organic and inorganic origin.

(a) Artificial Pozzolana of Inorganic Origin: the most common and important inorganic artificial pozzolanas are obtained from calcined clays and shale, cacined bauxite, calcined bauxite-waste, calcined spen oil, calcined mola, fly ash (pulverised fuel coal and Surki (brick powdered).

(b) Artificial pozzolana of Organic origin: agricultural waste like rice husk, Coffee hub, Coconut shell, Sugarcane Bagasse and Palm nutshells etc. constituent artificial pozzolanas of organic origin. Of these pozzolanas of organic origin, (RHA) has been well investigated and documented (Okpala, 1992).

### 2.6.3 Importance of pozzolana

The importance of the use of pozzolanic materials in concrete is clearly highlighted by Matawal (2001) under the following:

(i) Technological (ii) Economical (iii) Environmental

(i) Technological: technologically, ash – based pozzolan can modify the properties of cement, by increasing or decreasing its durability and resistance to aggressive agent as well as lime. Improved behaviour is the function of activity of the additions and this varies from one pozzolana to another.

(ii) Economical**:** economically, active additions reduce the quantity of cement required.

(iii) Environmental: environmentally, employing such additions utilises waste materials, a central theme that is deliberately expatiated upon later in the text as emphasis is laid on different ashes. These reasons justify the employment of active additions. Matawal (2001) further outlined other advantages of using pozzolanic materials for partial replacement of cement in the production of bricks mortar and concrete as:

- Improved place ability or workability: a vital consideration in the assessment of fresh concrete.
- Improve sulphate resistance, particularly, in marine environment.
- Improved sulphate resistance to freezing and thawing in temperate environment.
- Increase cohesiveness or bonding strength of the concrete.
- In few instances, there is an long-time strength.
- A reduction in water content of mortar and concrete mixes, resulting in less shrinking and cracking.
- A reduction in the heat of hydration, a particularly potent advantage in hot weather concreting.
- Decrease permeability and water tightness
- High resistance to alkaline – aggregate reactions.

These outlined advantages are not universal because they vary from one pozzolanic material to another. Hence, a more comprehensive knowledge is gained by taking the pozzolanas one after the other.

### 2.6.4 Properties of Concrete Made With Pozzolanas

Pozzolana also known as pozzolanic ash (pulvis pute) in latin is a siliceous or siliceous and aluminous material which reacts with calcium hydroxide in the presence of water at room temperature, resulting in pozzolanic reaction (Ghanan, et al., 2012). In this reaction, insoluble calcium silicates hydrate (C – S – H) and calcium aluminate hydrate compounds are formed possessing cementitous properties (Bentz, et al., 1992). According to Chiakaron (1997), the application of pozzolanas in ordinary Portland cement (OPC) is mainly controlled by the local availability of suitable deposits and competition with accessible agricultural wastes and industrial by product cementitious materials resulting in pozzolana – concrete. Compared to normal concrete it has higher strength and has more durability in addition it has ability to minimize cracks in concrete structures. Thus, the utilization of pozzolana in the construction industry will promote waste management at low cost, reduce pollution and increase the life span of concrete structures all at minimal cost (Tsado, et al., 2014). As with other high performance concretes such as (High strength, self compacting concrete, fibre reinforced concrete, rapid hardening concrete etc), concrete made with pozzolana cement equally possesses such special properties and quality which differs from concrete made with ordinary Portland cement only due to the presence of some proportions of the pozzolana in the cement (Neville and Brooks,1987). Pozzolana mixes generally have high content of $SiO_2$, $Al_2O_3$ and lower content of $CaO$ (Taylor, 1997) which accounts for the increase in quality of the cement.

Luding (1986) opines that pozzolana cement possesses the following under listed properties than the conventional concrete:

- The pozzolana cement must be able to react with Ca $(OH)_2$ in the presence of water at room temperature.
- The pozzolana cement must encompass any volcanic materials such as Pumice and Volcanic ash.
- The calcium silicate hydrate and calcium aluminate hydrate compound contained in the pozzolanic cement must possess cementitious properties.
- The pozzolana cement must be able to increase the strength, cracking resistance and durability of concrete structures.

Accordingly, Verlory (1987) recorded that the benefits derived from using pozzolana cement are in threefold viz:

- Increase in economic gain due to the replacement of substantial part of Portland cement which makes it cheaper and reduces pollution.
- Great reduction in the effect of green house gases emitted during the production of Portland cement which would have caused global warming due to uncontrolled burning and non compliance with directives on the disposal of the agricultural waste issued by authorities.
- Increased strength, cracking resistance and durability of the end product.

## 2.7 METAKAOLIN

Kaolin is a product of clay, which upon heating produces metakaolin (MK). The properties of MK pozzolanic material have been reported previously. MK shows a high level of pozzolanic activity, similar to Silica fumes. For this reason, it is very important to quantify the heat evolution during hydration in MK/cement systems. Also, as reported (Gruber, et al., 2001 and Boddy, et al., 2001), the performance of concrete incorporating Meta Kaolin, at appropriate replacement levels, is similar to that of concrete containing silica fume. When used as a partial replacement for OPC, Rice husk ash (RHA) is capable of reacting with portlandite to form supplementary calcium-silicate-hydrate (C-S-H) similar in composition and structure to those obtained from Portland cement. Metakaolin has also been used for making cementitious materials called hydroceramics, i.e. ceramic-like materials synthesized from a solid aluminosilicate and alkali-rich solution at low temperature, $< 100\ ^{o}$ C. It has been reported that metakaolin of high lime reactivity can be produced by thermal decomposition of kaolin, a naturally occurring clay basically containing kaolinite ($Al_2O_3$-$Si_2O_5(OH)_4$) mineral and trace of silica and other minerals which can be blended with high quantity of fly ash (over 45%) lime and industrial gypsum to form strong binder of low leach ability. In the particular case of MK, it appears to have excellent potential as an active addition for producing mortars and concretes (Gruber, et al., 2001). The hydrated phases formed during the pozzolanic reaction at early curing periods, tend to be present as meta stable phases. With longer curing times, the conversion of these hydrates to hydro garnet (stable phase) can be expected. This transformation will depend on different factors (for example, temperature reached inside the specimen). Because of its white colour, high-reactivity MK does not darken concrete as Silica Fumes typically does (the whitecoloured Silica Fumes is very limited in tonnage), which makes it suitable for colour-matching and other architectural applications (Job, 2009).

MK is unique in that it is not the by-product of an industrial process nor is it entirely natural; it is derived from a naturally occurring mineral and is manufactured specifically for cementing applications. Unlike by-product pozzolanas, which can have variable composition, MK is produced under carefully controlled conditions to refine its color, remove inert impurities, and tailored particle size (Brooks and Johari 2001and Ding and Li, 2002).

Metakaolin (MK) has been established as a pozzolanic material (Ambroise, et al., 1994). It is obtained by the calcination of kaolinitic clay at a temperature ranging between 500 °C and 800 °C. The raw material input in the manufacture of metakaolin ($Al_2Si_2O_7$) is kaolin. Metakaolin on reaction with $Ca(OH)_2$, produces CSH gel at ambient temperature and reacts with CH to produce alumina containing phases, including $C_4AH_{13}$, $C_2ASH_8$, and $C_3AH_6$ (Changeling, et al., 1995; Zhang and Malhotra, 1995).

### 2.7.1. Uses of Metakaolin

Researchers have shown that Metakaolin are used in the following areas according to (Batis, et al., 2004)

i. High performance, high strength and lightweight concrete

ii. Precast concrete for architectural, civil, industrial, and structural purposes

iii. Fiber cement and ferrocement products

iv. Glass fiber reinforced concrete

v. Mortars, stuccos, repair material, pool plasters

### 2.7.2. Advantages of using Metakaolin

The advantages derived from using Mk includes

i. Increased compressive and flexural strengths

ii. Reduced permeability

iii. Increased resistance to chemical attack

iv. Increased durability

v. Reduced effects of alkali-silica reactivity (ASR)

vi. Reduced shrinkage due to particle packing, making concrete denser

vii. Enhanced workability and finishing of concrete

viii. Reduced potential for efflorescence

ix. Improved finish ability, color and appearance

### 2.7.3 Compressive Strength of Metakaolin

Inclusion of MK as partial replacement of cement enhanced the compressive strength of concrete, but the optimum replacement level of OPC by MK to give maximum long term strength enhancement was about 20% (Wild, et al., 1996). Brooks and Johari (2001) also reported that compressive strength increased with the increase in the metakaolin content. Similar results were also reported by Li and Ding (2003) that concrete achieved the best compressive strength with 10% MK content.

Cement pastes containing 5% to 20% MK had higher compressive strengths than the control at all ages from 3 to 90 days, with the paste containing 10% MK performing the best (Poon, et al., 2001). Jian and Li (2003) concluded that

(i) incorporation of metakaolin can prompt both the strength and modulus of elasticity development of a young concrete and

(ii) metakaolin showed the best enhancement on the mechanical properties of young concrete.

Poon, et al. (2002) concluded that concrete containing MK (0 to 20%) showed a distinct pattern of strength gain and loss at elevated temperatures up to 800 °C. After an increase in compressive strength at 200 °C, the MK concrete suffered a more severe loss of compressive strength. A sharp reduction in compressive strength was observed for all HSC beyond 400 °C followed by severe cracking and explosive spalling. Within the range 400–800 °C, MK concretes suffered more loss and possessed lower residual strengths than the other concretes.

Badogiannis, et al. (2004) investigated the effect of metakaolin on the compressive strength of concrete. In concrete mixtures, metakaolin replaced either cement or sand in percentages of 10% or 20% by weight of the control cement content. The strength development of metakaolin concrete was evaluated using the efficiency factor (k value). The efficiency factor K was defined as the ratio of the mass of cement to the mass of the metakaolin when they had equivalent effect on the water-to-cement ratio. The produced metakaolin (MK) as well as the commercial one (MKC) imparted a similar behaviour with respect to the concrete strength. Both metakaolin exhibited very high k-values (close to 3.0 at 28 days) and were characterized as highly reactive.

### 2.7.4 Durability Properties of Concrete Containing Metakaolin

#### a) Alkali-silica reaction

Ramlochan, et al. (2000) reported that incorporation of high reactivity metakaolin (HRM) as a partial cement replacement between 10 and 15% may be sufficient to control deleterious expansion due to alkali-silica reaction in concrete, depending on the nature of the aggregate. Amount of High reactivity Metakaolin required to control the expansion to 0.04% at 2 years was found to be between 10 and 15% depending on the aggregate. The mechanism by which HRM may suppress expansion due to alkali-silica reaction appeared to be entrapment of alkalis by the supplementary hydrates and a consequent decrease in the pH of pore solutions (Ramlochan et al., 2000).

b) Chloride-ion diffusion

OPC–MK concrete showed significantly lower conductivity values than the OPC concrete (Zhang and Malhotra, 1995). Thomas, et al. (1997) and Hooton, et al. (1997) determined the chloride penetration resistance of concrete of water to binder ratios 0.3 and 0.4 containing 0, 8 and 12% replacement of PC with 'high-reactivity MK' (HRM). Data were presented in the form of 'apparent diffusion coefficients' calculated using Fick's second law of diffusion from chloride concentration–depth profiles after 28, 90 and 140 days exposure to 1.0 mol/l NaCl solution. Cabrera and Nwaubani (1998) reported that PC–MK and the PC–PFA pastes gave lower chloride diffusion coefficients than the PC paste, and the former gave particularly low values.

Gruber, et al. (2001) determined the chloride diffusion up to 365 and 1095 days. The apparent diffusion coefficients decreased with increasing exposure time and decreasing water to binder ratio, and showed marked decreases with increasing High Resistivity Metakaolin content.

Asbridge, et al. (2001) studied the effect of metakaolin and variations in aggregate volume content on the diffusion kinetics of chloride ions in hydrated Portland cement mortars. 10% metakaolin was used as partial replacement for Portland cement. Chloride diffusion was monitored under steady- and non-steady state conditions, and capillary porosity data were obtained. Results showed that metakaolin reduced the rate of chloride diffusion through the hydrated cement matrix and also tended to enhance the resistance to chloride transport of the material within the mortars.

Bai, et al. (1999) reported that significant reductions in chloride penetration depths were observed when OPC was partially replaced with MK in concrete, exposed to seawater. These reductions increased with both increasing total replacement level and increasing exposure time. This was attributed to the relative changes in intrinsic diffusivity and chloride binding capacity with age exhibited by the different binder compositions; Courard, et al. (2003) measured the chloride diffusion rates of mortars containing 0, 10, 15, and 20% metakaolin as partial replacement of cement. Apparent diffusion coefficient of mortar ($m^2/s$) increased with the increase in metakaolin content from 5 – 15%.

However, no diffusion was observed in mortar with 20% MK even after 1 year. Kaolin had no effect and seemed on the contrary to accelerate the phenomenon of diffusion in comparison with the reference mixture.

Chloride penetrability of the concrete with metakaolin (MK) at water to binder ratios of 0.3 and 0.5 were reported by Poon, et al. (2002).Both the MK concretes showed lower total ion penetration than the control. At water to binder ratio of 0.3, concrete with a 10% MK showed the best performance, while at water to binder ratio of 0.5, 20% replacement was the best.

### 2.7.5. Sulphate Resistance

Khatib and Wild (1998) evaluated the effect of metakaolin on the sulfate resistance of mortar. Inclusion of metakaolin in two types of cements having high $C_3A$ and intermediate $C_3A$ content decreased the expansion of mortar systematically with the increase in MK (5–20%) content. Roy, et al. (2001) reported that substitution of MK increased the chemical resistance of such mortars over those made with plain Portland cement.

### 2.7.6 Comparism between Metakaolin and Other Pozzolans

The use of by-products like fly ash, granulated blast furnace slag, silica fume, rice husk ash, and metakaolin in cement and concrete has gained significant importance because of the requirements of environmental protection and sustainable construction in the future. The use of metakaolin (MK) as partial replacement of cement in mortar and concrete has been extensively investigated in recent years.

The literature reviewed from researches by Asbridge, et al. (2001) and Bai, et al. (2003) clearly demonstrates that MK is an effective pozzolana as:

1. MK helps in enhancing the early age mechanical properties as well as long-term strength properties of cement paste/mortar/concrete.
2. The partial replacement of cement with MK reduces the water penetration into concrete by capillary action.
3. Incorporation of metakaolin, as a partial cement replacement, into OPC pastes causes substantial changes in the chemical composition of the pore solution phase of the hydrated material.
4. MK modifies the pore structure of the cement, mortar, and concrete, and significantly reduces the permeability resulting in resistance of transportation of water and diffusion of harmful ions which led to the deterioration of the matrix.
5. Metakaolin replacement of cement is effective in improving the resistance of concrete to sulfate attack. The sulfate resistance of MK concrete increased with increasing the MK replacement level.Concrete containing 10% and 15% MK replacements showed excellent durability to sulfate attack.
6. Substitution of MK has shown to increase the chemical resistance of such mortars over those made with plain Portland cement. Mortars were relatively little affected by 1% hydrochloric acid, 1% sulfuric acid, and 1% nitric acid environments, but those mortars made from all three series showed poor resistance to higher acid concentrations: 5% sulfuric acid, 5% acetic acid, and 5% phosphoric acid environments.

7. Incorporation of high reactivity metakaolin as a partial cement replacement between 10% and 15% may be sufficient to control deleterious expansion due to alkali-silica reaction in concrete, depending on the nature of the aggregate.

## 2.8 LITERATURES OF RELATED WORKS ON METAKAOLIN

So many research works had been carried out on metakaolin, some of which will be review here for the purpose literature;

Ramezanianpour and Bahrami (2012) carried out a research on the Influence of metakaolin as supplementary cementing material on strength and durability of concretes. They found that the Durability of concrete is an important issue for predicting the service life of concrete structures. They reported that though, the properties of metakaolin as high-quality pozzolanic materials are investigated by several researchers. It is not widely produced and used due to the lack of adequate experiments on the material in the Middle East. The research followed the procedure of heating the kaolin to meta kaolin with high kaolinite content, it was thermally treated by a special furnace at 800°C and 60 min burning time to produce metakaolin and determined the performance of concrete mixtures containing local metakaolin in terms of compressive strength, water penetration, sorptivity, salt ponding, Rapid Chloride Permeability Test (RCPT) and electrical resistivity at 7, 28, 90 and 180 days. In addition, microstructure of the cement pastes incorporating metakaolin was studied by XRD and SEM tests. The percentages of metakaolin that replace PC in the research were 0%, 10%, 12.5% and 15% by mass. The water/binder (w/b) ratios were 0.35, 0.4 and 0.5 having a constant total binder content of 400 kg/m$^3$. They found that concrete incorporating metakaolin had higher compressive strength and metakaolin enhanced the durability of concretes and reduced the chloride diffusion. An exponential relationship between chloride permeability and compressive strength of concrete is exhibited. They reported that there is a significant linear relationship between Rapid Chloride Permeability test and salt ponding test results. Similarly, Khatib and Clay (2003) studied the 'Effect of metakaolin content on the properties self-consolidating lightweight concrete'

Their work presented the fresh, mechanical and transport properties of expanded shale aggregate self consolidating lightweight concrete (SCLC) containing metakaolin assessed by means of slump flow, flow time, V-funnel, L-box, compressive, flexural/splitting/bond strength, water absorption, porosity, sorptivity and rapid chloride permeability tests. Metakaolin content based SCLC mixtures were developed by incorporating 0%, 20%, 40% and 60% of as a replacement by weight of fly ash while keeping a constant cement and mineral admixture content of 450 kg/m$^3$ and 150 kg/m$^3$, respectively. These included four mixtures containing 0%, 5%, 10% and 15% metakaolin content as a partial binder replacement. They observed that expanded shale aggregates SCLC can be produced with the density lower than 2000 kg/m$^3$ which was increased by the addition of metakaolin. They reported that Increase in metakaolin content worsened the filling and passing ability of SCLC and the addition of metakaolin had no positive effect on the strength properties on SCLC. Replacement of 20%, 40% and 60% of metakaolin with fly ash resulted in 3%, 8% and 10% decrease in porosity and water absorption with respect to control mixture, respectively. The initial and secondary sorptivity values of SCLC mixtures with metakaolin replacement were equal or lower than the control mixture without metakaolin. Moreover, increase in metakaolin content showed significant improvement in chloride ion penetration resistance of SCLC. Similarly, a work on 'Impacts of metakaolin on lightweight concrete by type of fine aggregate' by Caldarone, Gruber and Burg (1994) that Metakaolin is a widely used admixture known to be highly effective in enhancing compressive strength and durability. They further state that previous studies mainly focused on comparing metakaolin with other admixtures, with little research being directed toward the correlation between metakaolin and aggregates. Therefore, their study performs experimental research on the impacts of metakaolin on lightweight concrete according to different types of fine aggregate currently available. Three types of fine aggregate, two types of bottom ash (by-product of power plant) and one type of artificial expanded shale were used. Metakaolin was mixed with each fine aggregate at cement replacement ratios of 0%, 5%, 10%, 15%, and 20% by weight. The effects of metakaolin on the workability, density, porosity, compressive strength, and modulus of elasticity of lightweight concrete are addressed in detail. They found that the compressive strength of lightweight aggregate concrete, which had 1790 kg/cm$^3$ density and 1 cm slump, was increased by up to 74.2% when 20% of metakaolin was replaced by metakaolin. The concluded that the effects of metakaolin vary significantly according to the replacement ratio and types of aggregates.

Another article on ‘Strength development of concretes incorporated with metakaolin and different types of calcined kaolins’ by Moulin, et al. (2001) reported an investigation on the effects of metakaolin (MK) and calcined kaolins (CKs) on the compressive strength development of the concrete. Non purified ground kaolins obtained from different sources were thermally treated at specified conditions. Moreover, commercially available metakaolin (MK) of high purity from Czech Republic was also used for comparison. Four replacement levels (5%, 10%, 15%, and 20%) of CK and MK were assigned for concrete production. Also one plain mix without admixture was produced as reference. Compressive strength development of the concretes was observed at 3, 7, 28, and 90 days. The strength development of concretes was evaluated by statistical technique named GLM-ANOVA. Moreover, a prediction model was derived from gene expression programming (GEP) to illustrate and evaluate the parameters affecting the strength. They investigated the $SiO_2$, $Al_2O_3$, kaolinite, and alunite contents, fineness of mineral admixture, age of concrete, and replacement level. They documented that the type of thermally treated kaolin, the replacement level, and age are very effective on the strength development of the concretes. They concluded that the prediction model containing those seven parameters when compared with the experimental results proved to be a handful tool for estimating compressive strength of concrete incorporated with commercial MK and calcined kaolin.

# CHAPTER THREE
# RESEARCH METHODOLOGY

## 3.1 MATERIALS

The materials used in this research are the conventional materials for concrete production (cement, water, fine and coarse aggregates) in addition to metakaolin (MK) which was used as supplementary cementitious materials (SCM).

### Aggregates

Aggregates are classified into fine and coarse aggregates. The fine aggregates are those passing through the 4.75mm BS (British Standard) test sieve, while those that are retained on the 4.75mm BS sieve are classed as coarse aggregates.

### i. Fine aggregates

The fine aggregates used for this research work conforms to the classification of uniformly graded sand; SU and also falls within zone 1. The fine aggregates were gotten from local suppliers in Yola metropolis, Adamawa state with specific gravity 2.66, bulk density of 1899.50 kg/m3 and moisture content of 2.50 percent. The sieve analysis of fine aggregates was conducted in accordance with BS 812(1985) and particle size distribution is shown in 4.1

### ii. Coarse aggregates

Crushed aggregates were used for this study. The coarse aggregate was evaluated according to BS 812: part 110, 1990 specification, the aggregates corresponds to the requirement of the nominal size of graded aggregates of size range of 5mm – 20mm. The coarse aggregates were gotten from local suppliers in Yola metropolis, Adamawa state and the particle size distribution is shown in Table 4.2

iii. Water

Tap water sourced from Yola, Adamawa State free from impurities was used for mixing of concrete and curing of the concrete in the course of this research work.

iv. Cement

The cement used in this research is the Ashaka brand of Ordinary Portland Cement (OPC). Setting time test was conducted on the cement. The setting times of the cement paste which include initial and final setting times, was measured using the Vicat Needle in accordance with ASTM-C 150 (1994). The results obtained for the initial setting time was 105minutes (1hour, 45 minutes) which is in accordance with ASTM - C150(1994) which prescribes a minimum initial setting time of 45minutes for ordinary Portland cement. The final setting time was 235 minutes (3hours, 55minutes) which is also in accordance with ASTM – C 150 (1994) that specified a maximum setting time of 10 hours for ordinary Portland cement as shown in table 4.2

iv. Metakaolin

The kaolin sample obtained from Alkaleri was heated in a laboratory furnace at Material Development Centre, Abubakar Tafawa Balewa University Bauchi to a temperature of 700°C for 3hours to form metakaolin which was the principal source of alumino-silicate used for the study. After heating, the sample was cooled to room temperature at ambient condition to avoid crystallization of amorphous metakaolin. The metakaolin sample was then sieved with 75µm sieve so as to obtain a very fine powder.

### X-Ray Fluorescence (XRF)

X-ray fluorescence was carried out on the metakaolin sample to determine its chemical composition. X-ray fluorescence spectrometry is a method of quantitative analysis that uses X-ray energy. The X-ray obeys the law of electromagnetic radiation which states that a body surface can absorb incident radiation as a mirror with spherical symmetry which can transmit incident radiation and emit the radiation. The XRF was carried out at Nigerian Geological Survey Agency Kaduna using Energy Dispersive X-ray Fluorescence (EDXRF) spectrometer manufactured by PANalytical in Netherlands of model “Minipal 4” version PW 4030.

Based on the result of the X-Ray Fluorescence on the metakaolin, the major oxides present are the Silicon Oxide ($SiO_2$), Aluminium Oxide ($Al_2O_3$) and Iron oxide ($Fe_2O_3$) with a percentage of 54.03, 39.2 and 4.35 respectively. The combined percentage of these oxides is 97.58% which is expected of a good pozzolana since the percentage is greater than 70%. The MK conformed to ASTM C618, Type N pozzolanas specification. As shown in Table 4.4.

## 3.1 EXPERIMENTAL PROCEDURE

The kaolin was sourced from Alkaleri, Bauchi State and was taken to structural laboratory of the Abubakar Tafawa Balewa University (ATBU) Bauchi state was it was heated to a calcined temperature of ranging between 600˚C and 800˚C to produce the metakaolin. The experimental procedure complete then followed by premixing the cement with fine aggregates, with the addition of metakaolin followed by the addition of coarse aggregates and mixing until it became workable in final preparation for blending. Mix ratio of 1:2:4 was used in the production of the cubes. The cubes were cast in 150x150x150 mm cube moulds and were then vibrated for 5 seconds on a vibrating table. All concrete mixes were prepared at a water/ cement ratio of 0.5

(Appendix A1 to A4 shows the mixing, casting and curing of the cubes). Three hundred and twenty two cubes were cast (Appendix A5). All cubes were demoulded after 24 hours and the cured in water and chemical solutions. The densities and compressive strength of the sampled concrete cubes were determined after 3, 7, 28, 56 and 90 days curing. Test cubes were made from fresh concrete in accordance with BS1881-108:1983. Furthermore, the binary mixtures of metakaolin and cement with the different percentage replacement of the total binder, mixed with same fine and coarse aggregates with a water binder ratio of 0.5 was used to produce the metakaolin concrete. The specimen concrete cubes were demoulded after 24 hours and cured by immersion in a water tank kept at 20 + or - 1˚C for a duration of 90days curing (the choice for 90days is to determine the behaviour of the metakaolin concrete at that age of curing), the concrete samples were brought out of water and allowed to dry before subjecting them to various elevated temperature ranges. Three concrete cubes from each category were exposed to 2 hours to varying elevated temperature of 100˚C, 200˚C, 300˚C, 400˚C, 500˚C and 600˚C in an oven the adopted temperature range was based on previous work by Nwankwo (2013). The oven is heated by an electric coil with capacity to attain 1200˚C. The required temperatures were set and maintained on the panel oven without fluctuations. After exposure to the required temperature range, the oven was switched off and the concrete specimens allowed cooling to ambient temperature before crushing.

## 3.2 WORKABILITY TEST ON THE FRESH CONCRETE

Workability test was performed on the fresh concrete. These tests include slump and compacting factor tests. The workability was determined using the slump test. The slump test was performed in accordance with the provisions of BS 1881: part 102 (1983).

## 3.3 DENSITY

The density of a substance is its mass per unit volume. Mathematically expressed as

$$P = M/V. \qquad (3.1)$$

The density was determined in accordance with the provision of BS 1883(part 103). The result is as presented in Table 4.8

## 3.4 COMPRESSIVE STRENGTH TEST ON HARDENED CONCRETE CUBE

The compressive strength test was performed on the hardened concrete cubes immersed in water in accordance with the provisions of BS 1881: Part 115 (1983). The curing or immersion periods were 3, 7, 28, 56 and 90 days. The samples were removed from curing media, and were left in the state polytechnic civil engineering laboratory for 1 hour to allow the samples attain saturated surface dry condition before the test. The weights of the samples were taken using the electrically operated weighing balance. Universal testing machine, an electrically operated compressive strength machine, was used to obtain the failure loads in kilo Newton. The average failure loads were used to obtain the compressive strength, using the relationship in Equation 3.2

$$Compressive\ Strengt = \frac{Average\ Failure\ Load\ (N)}{Surface\ Area\ (mm^2)} \qquad 3.2$$

# CHAPTER FOUR
# RESULTS AND DISCUSSIONS

## 4.1 RESULTS

This chapter presents the results of the research work as observed in the course of the research. This include the initial and final setting times of the cement pastes, workability test, density of the cast cubes, compressive strength test results and durability of the cast cubes. The sieve analysis test carried out on the sample Sand and coarse aggregates are as presented in Tables 4.1 and 4.2 respectively. Table 4.3 shows the physical properties of Ashaka brand of Ordinary Portland cement used in this research, Table 4.4 shows the Chemical composition of Metakaolin, Table 4.5 shows the summary of the mass of constituents per cubic metre of concrete, Table 4.6 shows the workability test on concrete made with cement with different percentage of Metakaolin replacement, Table 4.7 shows the Initial and Final setting time of cement paste and Metakaolin, Table 4.8 shows the density of the cast Metakaolin cubes, Table 4.9 shows the compressive Strength of the Cast Meta kaolin Cubes, Table 4.10 shows the compressive strength of the cast Meta kaolin Cubes cured in Sodium Chloride (Nacl) solution, Table 4.11 shows the compressive strength of the cast Metakaolin cubes cured in Magnesium Sulphate ($MgSO_4$) solution while Table 4.12 shows the compressive strength of the cast Meta kaolin Cubes at elevated temperature.

Table 4.1 Sieve Analysis of Sample Sand

| Sieve size | Weight passing (g) | Percentage passing (%) |
|---|---|---|
| 4.75mm | 999.00 | 100 |
| 2.36mm | 995.50 | 99.50 |
| 1.70mm | 987.60 | 98.70 |
| 1.18mm | 995.40 | 95.50 |
| 600 µm | 749.20 | 74.90 |
| 300 | 144.80 | 14.50 |
| 100 | 8.50 | 0.90 |
| Pan | - | - |

Table 4.2 Sieve Analysis of coarse aggregates

| Sieve size | Weight passing (g) | Percentage passing (%) |
|---|---|---|
| 37.50mm | 997.50 | 100 |
| 19.00mm | 984.81 | 98.73 |
| 13.50mm | 890.56 | 89.23 |
| 9.50mm | 625.06 | 62.66 |
| 6.70mm | 1.86 | 1.86 |
| Pan | - | - |

Table 4.3 Physical Properties of Ashaka Brand of Ordinary Portland Cement

(Tests in Accordance with B.S. 12 and ASTM-C150 (1994)).

| Test | Values for OPC Used | Requirements in Accordance with B.S. 12 |
|---|---|---|
| Standard Consistency | 28.9% | 26%-33% |
| Initial Setting Time | 105 minutes | Minimum of 45 minutes |
| Final Setting Time | 235minutes | Maximum of 600 minutes |
| Specific Gravity | 3.15 | - |
| Bulk Density ($kg/m^3$) | 1440 | - |

Table 4.4 Chemical composition of Metakaolin

| Oxide | Mass % |
|---|---|
| $Al_2O_3$ | 39.20 |
| $Fe_2O_3$ | 4.35 |
| $SiO_2$ | 54.03 |
| CaO | 1.70 |
| MgO | Trace |
| $Na_2O$ | 0.850 |
| $K_2O$ | 0.170 |
| $Eu_2O_3$ | 0.084 |
| CuO | 0.016 |
| $Ga_2O_3$ | 0.041 |
| ZnO | 0.010 |
| NiO | 0.006 |
| $V_2O_5$ | 0.170 |
| LOI | 0.080 |

Table 4.5 Summary of the mass of Constituents per cubic metre of Concrete

| Materials | Cement(kg) | FA(Kg) | CA(Kg) | Water (L) | MK(Kg) |
|---|---|---|---|---|---|
| B0 | 350 | 675 | 1200 | 175 | - |
| B10 | 315 | 675 | 1200 | 175 | 35 |
| B20 | 280 | 675 | 1200 | 175 | 70 |
| B30 | 245 | 675 | 1200 | 175 | 105 |
| B40 | 210 | 675 | 1200 | 175 | 140 |
| B50 | 175 | 675 | 1200 | 175 | 175 |
| B60 | 140 | 675 | 1200 | 175 | 210 |
| B70 | 105 | 675 | 1200 | 175 | 245 |
| B80 | 70 | 675 | 1200 | 175 | 280 |

Table 4.6 Workability test on concrete made with cement with different percentage of Metakaolin replacement

| Percentage Control | Slump (mm) |
|---|---|
| 100%OPC + 0% Metakaolin | 95 |
| 90%OPC + 10% Metakaolin | 85 |
| 80%OPC + 20% Metakaolin | 85 |
| 70%OPC + 30% Metakaolin | 80 |
| 60%OPC + 40% Metakaolin | 75 |
| 50%OPC + 50% Metakaolin | 75 |
| 40%OPC + 60% Metakaolin | 75 |
| 30%OPC + 70% Metakaolin | 70 |
| 20%OPC + 80% Metakaolin | 65 |

Table 4.7 Initial and Final setting time of cement paste and Metakaolin

| Percentage control | Initial setting time (min) | Final setting time(min) |
|---|---|---|
| B0 | 105 | 235 |
| B10 | 201 | 254 |
| B20 | 190 | 256 |
| B30 | 191 | 258 |
| B40 | 209 | 263 |
| B50 | 202 | 268 |
| B60 | 196 | 273 |
| B70 | 185 | 283 |
| B80 | 183 | 293 |

Where: B means Mix number.

Table 4.8 Density of the Cast Metakaolin Cubes (Kg/m$^3$)

| | Density in (Kg/m$^3$) | | | | | |
|---|---|---|---|---|---|---|
| | 3 days | 7 days | 14 days | 28 days | 56 days | 90 days |
| B0 | 2304 | 2370 | 2405 | 2405 | 2405 | 2453 |
| B10 | 2303 | 2355 | 2400 | 2405 | 2405 | 2453 |
| B20 | 2273 | 2324 | 2402 | 2404 | 2403 | 2451 |
| B30 | 2263 | 2315 | 2402 | 2400 | 2403 | 2450 |
| B40 | 2262 | 2275 | 2305 | 2306 | 2303 | 2404 |
| B50 | 2200 | 2272 | 2305 | 2305 | 2302 | 2403 |
| B60 | 2185 | 2200 | 2300 | 2304 | 2300 | 2400 |
| B70 | 2180 | 2205 | 2300 | 2300 | 2300 | 2400 |
| B80 | 2170 | 2190 | 2302 | 2300 | 2300 | 2400 |

Table 4.9 Compressive Strength of the Cast Meta kaolin Cubes (N/mm$^2$)

| | Compressive Strength in (N/mm$^2$) | | | | | |
|---|---|---|---|---|---|---|
| | 3 days | 7 days | 14 days | 28 days | 56 days | 90 days |
| B0 | 16.3 | 17.6 | 19.5 | 22.5 | 24.8 | 27.3 |
| B10 | 8.6 | 13.8 | 15.9 | 18.1 | 25.2 | 30.4 |
| B20 | 7.8 | 12.5 | 14.8 | 16.7 | 24.9 | 29.4 |
| B30 | 7.6 | 12.2 | 14.1 | 16.0 | 24.6 | 24.7 |
| B40 | 7.3 | 11.7 | 13.8 | 15.6 | 19.7 | 23.6 |
| B50 | 7.0 | 8.6 | 12.2 | 14.0 | 18.9 | 22.7 |
| B60 | 6.7 | 6.8 | 9.5 | 10.7 | 15.4 | 16.9 |
| B70 | 6.5 | 6.8 | 9.4 | 10.5 | 15.4 | 16.7 |
| B80 | 6.0 | 6.3 | 8.8 | 9.9 | 12.8 | 16.2 |

Table 4.10 Compressive Strength of the Cast Meta kaolin Cubes cured in Sodium Chloride (Nacl) solution (N/mm$^2$)

| | Compressive Strength in (N/mm$^2$) | | | |
|---|---|---|---|---|
| | 14 days | 28 days | 56 days | 90 days |
| B0 | 15.2 | 20.5 | 22.3 | 24.8 |
| B10 | 12.4 | 16.3 | 22.8 | 27.2 |
| B20 | 11.7 | 15.2 | 22.6 | 26.8 |
| B30 | 10.9 | 14.4 | 22.2 | 24.8 |
| B40 | 10.5 | 13.9 | 17.5 | 21.0 |
| B50 | 9.5 | 12.7 | 17.0 | 20.4 |
| B60 | 7.3 | 9.8 | 14.0 | 15.4 |
| B70 | 7.1 | 9.6 | 13.8 | 15.0 |
| B80 | 6.8 | 8.8 | 11.4 | 14.4 |

Table 4.11 Compressive Strength of the Cast Meta kaolin Cubes cured in Magnesium Sulphate ($MgSO_4$) solution (N/mm$^2$)

| | Compressive Strength in (N/mm$^2$) | | | |
|---|---|---|---|---|
| | 14 days | 28 days | 56 days | 90 days |
| B0 | 17.6 | 22.8 | 24.7 | 25.9 |
| B10 | 14.6 | 18.7 | 25.4 | 28.4 |
| B20 | 14.1 | 17.5 | 25.0 | 27.6 |
| B30 | 13.3 | 16.8 | 24.6 | 26.0 |
| B40 | 13.1 | 16.2 | 19.9 | 22.1 |
| B50 | 11.9 | 15.1 | 19.4 | 21.6 |
| B60 | 9.6 | 12.3 | 14.3 | 16.5 |
| B70 | 9.5 | 11.9 | 14.1 | 15.2 |
| B80 | 9.1 | 10.8 | 12.4 | 14.8 |

Table 4.12 Compressive Strength of the Cast Meta kaolin Cubes at Elevated temperature (N/mm$^2$)

| | Compressive Strength in (N/mm$^2$) | | | | | | |
|---|---|---|---|---|---|---|---|
| | 25°C | 100°C | 200°C | 300°C | 400°C | 500°C | 600°C |
| B0 | 27.3 | 13.9 | 14.8 | 16.8 | 19.1 | 20.8 | 23.5 |
| B10 | 30.4 | 7.4 | 11.6 | 13.5 | 15.6 | 21.2 | 25.7 |
| B20 | 29.4 | 6.6 | 10.5 | 12.7 | 14.2 | 20.9 | 25.4 |
| B30 | 24.7 | 6.5 | 10.2 | 12.0 | 13.8 | 20.7 | 23.7 |
| B40 | 23.6 | 6.3 | 9.8 | 11.7 | 13.4 | 16.5 | 20.0 |
| B50 | 22.7 | 6.0 | 7.2 | 10.5 | 11.9 | 15.9 | 19.5 |
| B60 | 16.9 | 5.7 | 5.8 | 8.1 | 9.4 | 12.9 | 14.4 |
| B70 | 16.7 | 5.5 | 5.7 | 8.1 | 9.1 | 12.9 | 14.4 |
| B80 | 16.2 | 5.2 | 5.5 | 7.5 | 8.5 | 10.8 | 13.8 |

## 4.2 FRESH CONCRETE

### 4.2.1 Setting Time

Table 4.7 shows the result for the setting time of the cement paste made for the various percentage replacements. The results obtained for the initial setting time for the Ordinary Portland Cement (OPC) sample without metakaolin and a water/cement ratio of 0.5 was 1hour 45 minutes and a final setting time of 3hours 55 minutes. The initial setting time for the paste made with a water/cement ratio of 0.50 and metakaolin content of 10% was 3hours 21minutes and a final setting time of 4hours 14minutes. The initial setting time for the paste made with a water/cement ratio of 0.5 and metakaolin content of 20% was 3hours 10minutes and a final setting time of 4hours 16minutes. The initial setting time for the paste made with a water/cement ratio of 0.5 and a metakaolin content of 70% was 3hours 05minutes and a final setting time of 4hours 43minutes. The initial setting time for the paste made with a water/cement ratio of 0.5 and metakaolin content of 80% was 3hours 03minutes and a final setting time of 4hours

53minutes. This indicates a rise and fall in the setting time as the metakaolin content increases these results agree with the findings of Aquino, et al. (2001) who reported increase of setting times of OPC-MK paste over the plain cement paste. However, the setting time for the samples falls within the allowable limits provided by ASTM-C 150 (1994). The table further shows that the final setting times of the cement pastes produced increased with increase in the amount of metakaolin. This indicates that metakaolin increases the setting time of concrete as contained in the findings of Aquino, et al. (2001) when metakaolin was used in concrete as well as the findings of Nwankwo and Job (2014) when crushed calcined waste bricks and fly ash were used in medium strength ternary concrete.

### 4.2.2 Workability

B0 had a slump of 95mm; B10 had a slump of 85mm while B70 and B80 had a slump of 70mm and 65mm respectively. The slump generally reduced as the metakaolin content increased. The results indicate a reduction from 95mm of the control mix ratio to 65mm of B80 indicating about 0.28% reduction of B80. The higher the replacement of cement by the metakaolin increases water demand thus reducing the workability as justified by Yakubu (2012). According to Andrew (1995), the reduction in slump increase may be as a result of increased in the amount of silica. From the study it was found that the silica-metakaolin reaction requires more water in addition to water required during hydration of cement as opined by Nwankwo (2013), while the immediate workability decreases, the adsorbed water might be partially released during the hardening process (Nwankwo, et al., 2014). This phenomenon may be attributed to the physical characteristics of the metakaolin as reported by Ordinez (2002) and Thomas (2002). However, all the mixes fall within the range of good workability and ideal for structural concrete.

### 4.2.3. Density

Table 4.8 shows the densities of the concrete cubes used for the research. At the early ages of curing, the control samples had greater densities as compared with the metakaolin samples. However, at 14 to 56days of curing B10, B20 and B30 had the same densities with the control. It was further observed that there was an increase in the density of the samples with age. The densities of the concrete samples were influenced by the density of the aggregates and method of curing as stated by Douglas (2004) as well as Ede and Adegbite (2013)

### 4.2.4 Compressive Strength

From Table 4.9, the research observed that the control samples had greater early strength as compared with that of the metakaolin samples. B0 had a compressive strength of 16.3N/mm$^2$, B10 had a compressive strength of 8.6 N/mm$^2$, and B20 had a compressive strength of 7.8 N/mm$^2$, while B70 and B80 concrete samples had lower compressive strength at the early ages. This slow rate of strength development is as a result of the presence of metakaolin as a replacement of cement in concrete, as pozzolanas are known to reduce the early strength of concrete due to its slow rate of hydration. In both cases, there was an increase in strength with the age of curing. However, at 56days, the control samples showed very little increase in strength as compared with the metakaolin concrete samples. B0 had a compressive strength of 24.8 N/mm$^2$, B10 had a compressive strength of 25.2 N/mm$^2$, and B20 had a compressive strength of 24.9 N/mm$^2$. B30 had a compressive strength of 24.7 N/mm$^2$, B40 had a compressive strength of 19.7 N/mm$^2$, B50 had a compressive strength of 18.9 N/mm$^2$, B60 had a compressive strength of 15.4 N/mm$^2$, B70 had a compressive strength of 15.4 N/mm$^2$ and B80 had a compressive strength of 12.8 N/mm$^2$, which is a marked increase in strength. The difference in strength gain between the metakaolin concrete and the control is as a result of the metakaolin content present in the concrete matrix which improves the properties of concrete at the later age of curing as stated by Neville (2000). This result also agrees with the findings of Aquino, et al. (2001) and Ahmadi, et al. (2007) which states that pozzolan mixes developed higher strength at later age of curing. The compressive strength against the age of curing in days shows that the rate of strength gain was not linear as shown in figure 4.2. The compressive strength of the produced metakaolin was slightly higher than the values gotten by Aquino, et al. (2001) and Ahmadi, et al. (2007). From the above results for the density and compressive strength test carried out in this research it was found that B50 having achieved $f_{cu}$ = 22.7 $N/mm^2$ produced densified concrete with increased structural integrity.

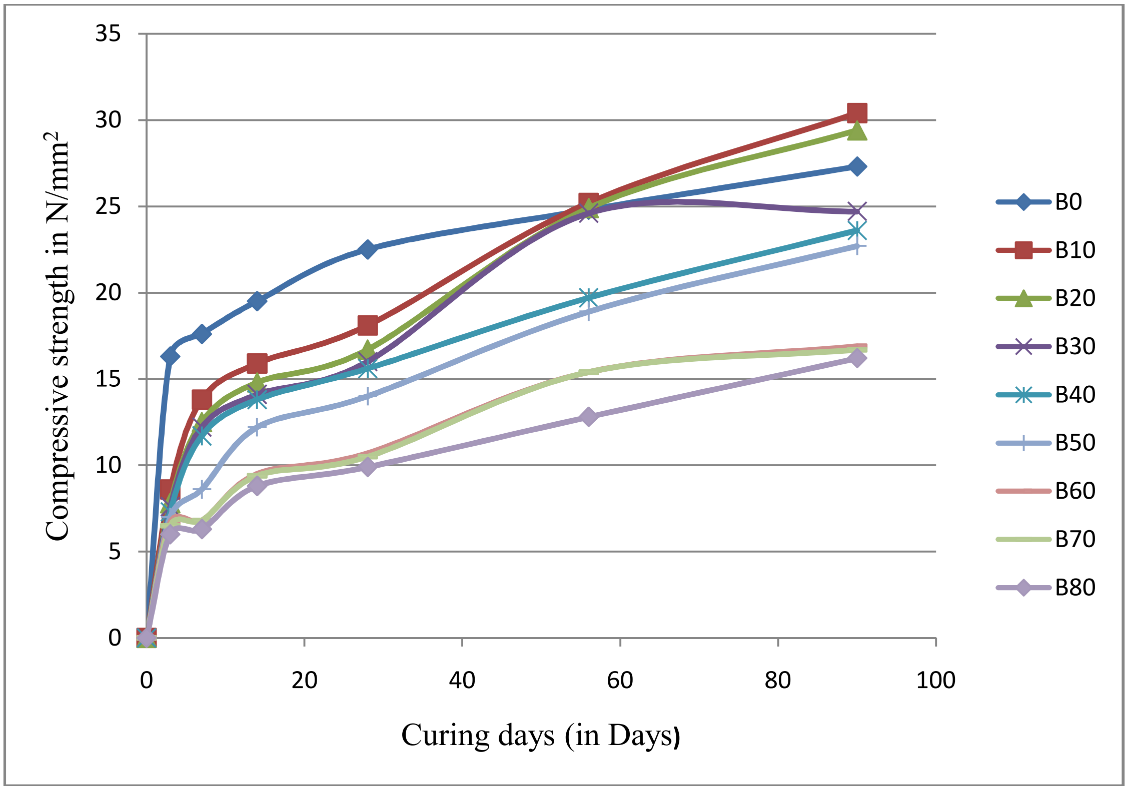

Fig 4.1 Compressive Strength against days of Curing.

## 4.3 DURABILITY OF THE METAKOLIN CUBES

The durability of the metakaolin cubes used in this research was considered in two conditions:

Harsh chemical condition (i.e subjecting the cubes to Magnesium Sulphates and Sodium Chloride) and Elevated temperatures.

### 4.3.1 Chemical Conditions

The concrete mix of ratio 1:2:4 was adopted for the production of concrete cubes at water / cement ratio of 0.5. Cement content was replaced at 10% to 80% with Metakaolin with a control cube of 0%. Batching by volume was adopted. 150mm x 150mm x 150mm cubes were produced for the tests. They were subsequently cured in different media of magnesium sulphate at 15% concentration and sodium chloride at 15% concentration. The choice of the percentage concentration of chemicals used as curing media was based on a similar research carried out by Kamang, et al. (2001). Some of the cubes were cured in water and used as reference point for comparison. All the cubes were cured for hydration period of 14, 28, 56 and 90 days respectively adopted from works by Adole, et al. (2010). Average of three cubes was crushed for each test. The results of the compressive strength of the cubes were then measured to determine its resistance to sulphates and chlorides. Table 4.10 and 4.11 show the effects of chemicals on the properties of concrete with cement partially replaced by metakoalin. The compressive strength of Ordinary Portland Cement (OPC) concrete and OPC/MK concrete after curing in two chemical solutions ($MgSO_4$ and NaCl) were measured at 14, 28, 56 and 90 days hydration periods. The results revealed that the OPC/MK concrete performance in $MgSO_4$ solution at 90 days hydration period had compressive strength values of 28.4N/mm$^2$ for B10 and 27.6 N/mm$^2$ for B20 in respectively. While the OPC/MK at 90 days hydration period in NaCl solution had compressive strength values of 27.2N/mm$^2$ for B10 and 26.8 N/mm$^2$ for B20 respectively. From the study, it can be said that OPC/MK concrete has resistance to magnesium sulphate and sodium chloride media. However, the OPC/MK concrete performs better in $MgSO_4$ solution than in NaCl solution. This result disagrees with the findings of Adole, et al. (2010) in a related study on chemical resistance of Groundnut shell ash concrete. But agrees with the findings of Kamang, et al. (2001) that reported reductions in compressive strength of OPC cured in magnesium sulphate solution and sodium chloride solution at 28 days over that of OPC cured in water. The OPC/MK showed no sign of strength loss in chemical solutions rather there was increased in its values at 90 days.

### 4.3.2 Concrete Subjected to Elevated Temperature

Table 4.12 shows the compressive strength against the temperature though the compressive strength increased with curing days when subjected to elevated temperature, the compressive strength when compared with the cubes cured in water decreases. It could be observed that binary blends B10 and B20 had the best performance at a temperature of 600˚C with a 15% and 14% reduction of the compressive strength of the cubes cured in water which suggests that low content of the metakaolin was responsible for the thermal stability of the composite. This may be attributed to the chemical decomposition of the already depleted calcium silicate hydrates (CSH) in the blend as reported by Nwankwo and Achuenu (2014). At 100˚C to 400˚C the specimens recorded lower densities which were recovered at 600˚C. Therefore, it is safe to conclude that thermal stability of metakaolin composite could be achieved at 10%, 20% and 30% replacement.

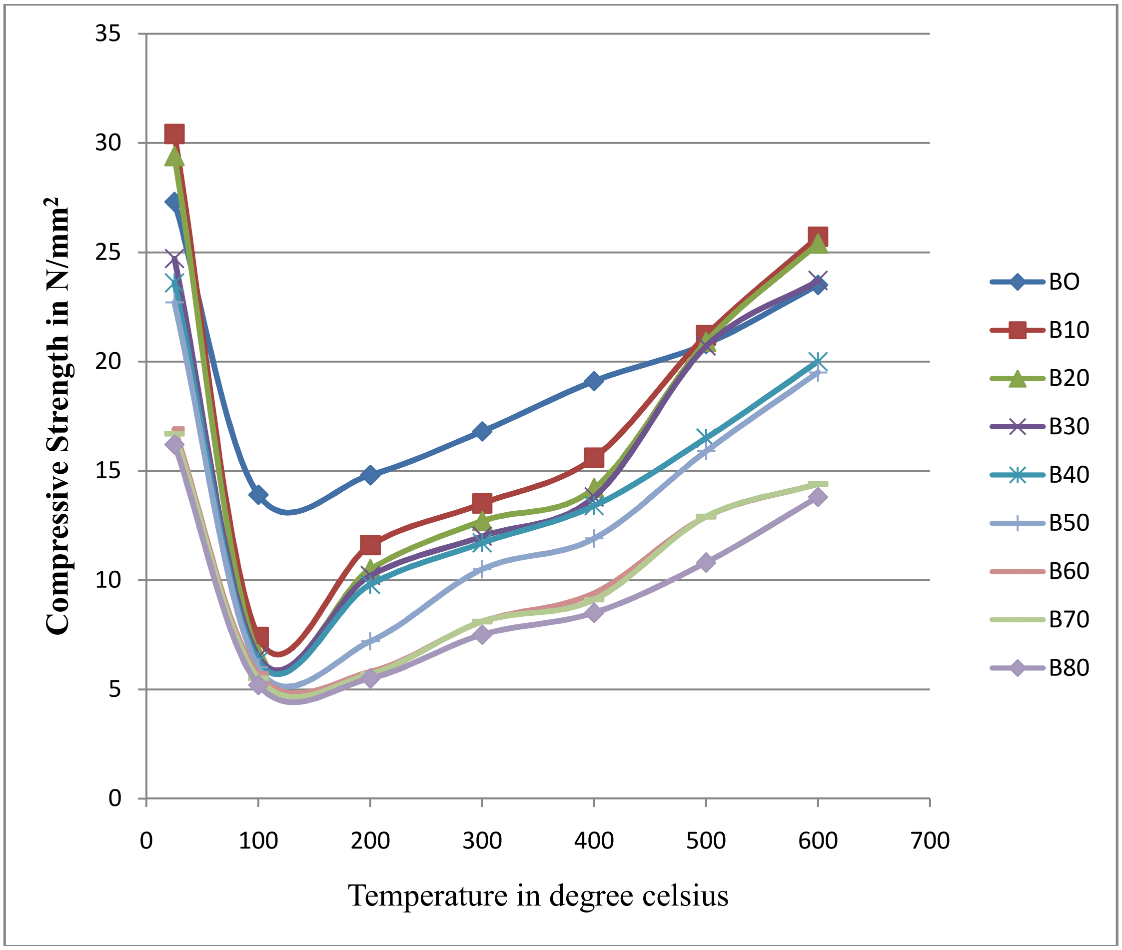

Fig 4.2 Compressive Strength against temperature

Figure 4.2 shows the compressive strength against the temperature though the compressive strength increased with curing days when subjected to elevated temperature, the compressive strength when compared with the cubes cured in water decreases. It could be observed that binary blends B10 and B20 had the best performance at a temperature of 600˚C with a 15% and 14% reduction of the compressive strength of the cubes cured in water which suggests that the lower content of the metakaolin was responsible for the thermal stability of the composite. This may be attributed to the chemical decomposition of the already depleted calcium silicate hydrates (CSH) in the blend as reported by Nwankwo and Achuenu (2014). The graph showed that at 25˚C the compressive strength equals that of the 90days. Similarly, at 100˚C to 400˚C the specimens recorded lower densities which were recovered at 600˚C. Therefore, it is safe to conclude that thermal stability of metakaolin composite could be achieved at 10%, 20% and 30% replacement.

# CHAPTER FIVE

# CONCLUSION AND RECOMMENDATION

## 5.1 CONCLUSION

From the results of the analysis, the following findings were made:

The study of the strength characteristics of high volume metakolin concrete suggested that:

1. The metakaolin sourced from Alkaleri in Bauchi state is a good pozzolana having met the requirements as stipulated by ASTM C (618).
2. The compressive strength of the HVMK cubes increased with curing age though not linearly.
3. The density of the HVMK cubes increased with curing age, though at the early curing age some of the specimens had low densities but the finally attained same densities at the later age of curing.
4. The optimum percentage of cement replacement with pozzolana is 50%, having been proven to increase the structural integrity of the metakaolin concrete cubes when compared with the control.
5. The durability of the HVMK measured in terms of subjecting the cubes to $MgSO_4$, Nacl and elevated temperatures shows that the HVMK performed satisfactory.

## 5.2 RECOMENDATIONS

Based on the findings in this study, the following recommendations were made:

1. The recommended percentage of cement replacement with High volume metakaolin concrete is 50%, having been proven to increase the structural integrity and attained $F_{CU}$ of 22.7 N/mm$^2$.

2. High Volume Metakaolin cubes can be used in soils containing $MgSO_4$ and Nacl because of its resistance to such chemicals.

3. High Volume metakaolin cubes are recommended for use to regulate fire outbreak because of its satisfactory performance under elevated temperature.

## 5.3 PROPOSALS FOR FURTHER RESEARCH

From the results of this work arose other problems for which further research could be carried out:

1. The impact resistance, abrasion and permeability of the high volume metakaolin cubes need to be studied further, in order to ascertain its suitability for structural elements subjected to impact load and abrasion.
2. Investigation into long – term curing of HVMK cubes should be studied, to determine the compressive strength, flexural strength and water absorption rate to check the variation in the properties of the composites.

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# APPENDIX

## TABLES

Appendix A1 Bulk Density Calculation for Sand

| Description | TEST 1 (kg) | TEST 2 (Kg) |
|---|---|---|
| Weight of cylinder only (W1) | 4.55 | 4.55 |
| Weight of cylinder + water ( W2) | 11.38 | 11.35 |
| Weight of cylinder + loose sand (W3) | 15.10 | 15.05 |
| Weight of cylinder + compacted sand (W4) | 15.65 | 15.60 |
| Weight of loose sand (A) = W3 – W1 | 10.55 | 10.50 |
| Weight of compacted sand (B) = W4 – W1 | 11.10 | 11.05 |
| Volume of water (V) = $\frac{W2 - W1}{1000}$ | $6.83 \times 10^{-3} m^3$ | $6.8 \times 10^{-3} m^3$ |
| Density of loose sand $\frac{A}{V}$ | $1544.6 kg/m^3$ | $1544 kg/m^3$ |
| Density of compacted sand ℓ $= \frac{B}{V}$ | $1625.2 kg/m^3$ | $1625 kg/m^3$ |

Average bulk density of loose sand $= \frac{1544.6 + 1544}{2} = 1544.3 kg/m^3$

Average bulk density of compacted sand $= \frac{1625.2 + 1625}{2} = 1625.1 kg/m^3$

Appendix A2 Specific Gravity of Sample Sand

| Description | Test 1 (g) | Test 2 (g) |
|---|---|---|
| Weight of bottle ($w_1$) | 34.0 | 34.0 |
| Weight of bottle + sand ($w_2$) | 133.5 | 131.5 |
| Weight of bottle + sand + water ($w_3$) | 198.0 | 196.5 |
| Weight of bottle + water ($w_4$) | 126.5 | 126.0 |
| Weight of dry sand ($w_5$) = $w_2 - w_1$ | 99.5 | 97.5 |
| Submerged weight = $w_3 - w_4$ | 71.5 | 70.5 |
| Specific gravity = $\frac{w5}{W_3 - w_4 - w_1}$ | 2.65 | 2.67 |

Average specific gravity of sand = $\frac{2.65 + 2.67}{2} =$ 2.66

Appendix A3 Bulk density test of coarse aggregate

| Description | TEST 1 (kg) | TEST 2 (Kg) |
|---|---|---|
| Weight of cylinder only (W1) | 4.55 | 4.55 |
| Weight of cylinder + water ( W2) | 11.48 | 11.45 |
| Weight of cylinder + loose sand (W3) | 16.10 | 16.05 |
| Weight of cylinder + compacted sand (W4) | 17.65 | 17.50 |
| Weight of loose sand (A) = W3 – W1 | 11.50 | 11.50 |
| Weight of compacted sand (B) = W4 – W1 | 13.10 | 12.95 |
| Volume of water (V) = $\frac{W2 - W1}{1000}$ | $6.93 \times 10^{-3} m^3$ | $6.9 \times 10^{-3} m^3$ |
| Density of loose sand $\frac{A}{V}$ | $1659.5 kg/m^3$ | $1666.7 kg/m^3$ |
| Density of compacted sand $\ell = \frac{B}{V}$ | $1890 \ kg/m^3$ | $1876.8 kg/m^3$ |

Average loose coarse aggregate bulk density = $\frac{1659.5 + 1666.7}{2} = 1663.1 kg/m^3$

Average compacted coarse aggregate bulk density = $\frac{1890 + 1876.8}{2} = 1883.4 kg/m^3$

Appendix A4 Specific Gravity of coarse aggregate

| Description | Test 1 (g) | Test 2 (g) |
|---|---|---|
| Weight of bottle ($w_1$) | 34.0 | 34.0 |
| Weight of bottle + stone ($w_2$) | 134.5 | 131.5 |
| Weight of bottle + stone+ water ($w_3$) | 198.0 | 196.5 |
| Weight of bottle + water ($w_4$) | 126.5 | 126.0 |
| Weight of dry stone ($w_5$) = $w_2 - w_1$ | 100.5 | 97.5 |
| Submerged weight = $w_3 - w_4$ | 71.5 | 70.5 |
| Specific gravity = $\frac{w5}{W_3-w_4-w_1}$ | 2.68 | 2.67 |

Average specific gravity of stone = $\frac{2.68 + 2.67 =}{2}$ 2.68

APPENDIX A5 DETAILED RESULTS OF THE DENSITIES OF THE CAST CUBES (Kg/m$^3$)

| | 3 DAYS | | | 7 DAYS | | | 14 DAYS | | | 28 DAYS | | | 56 DAYS | | | 90 DAYS | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| B0 | 2304 | 2303 | 2304 | 2370 | 2370 | 2372 | 2405 | 2406 | 2404 | 2405 | 2405 | 2405 | 2404 | 2405 | 2406 | 2452 | 2453 | 2453 |
| B10 | 2304 | 2304 | 2302 | 2355 | 2354 | 2355 | 2400 | 2401 | 2401 | 2405 | 2405 | 2404 | 2404 | 2405 | 2405 | 2453 | 2452 | 2453 |
| B20 | 2273 | 2272 | 2273 | 2324 | 2323 | 2324 | 2401 | 2402 | 2402 | 2405 | 2403 | 2403 | 2404 | 2403 | 2403 | 2451 | 2451 | 2452 |
| B30 | 2263 | 2264 | 2263 | 2315 | 2314 | 2314 | 2403 | 2402 | 2402 | 2400 | 2400 | 2400 | 2403 | 2404 | 2403 | 2450 | 2451 | 2451 |
| B40 | 2262 | 2263 | 2262 | 2276 | 2274 | 2276 | 2304 | 2305 | 2305 | 2306 | 2306 | 2304 | 2303 | 2304 | 2303 | 2401 | 2401 | 2400 |
| B50 | 2200 | 2202 | 2203 | 2272 | 2272 | 2272 | 2304 | 2306 | 2304 | 2305 | 2305 | 2305 | 2302 | 2300 | 2302 | 2403 | 2403 | 2402 |
| B60 | 2186 | 2185 | 2182 | 2200 | 2200 | 2200 | 2302 | 2300 | 2300 | 2303 | 2404 | 2404 | 2300 | 2300 | 2300 | 2400 | 2400 | 2400 |
| B70 | 2180 | 2182 | 2180 | 2205 | 2205 | 2205 | 2300 | 2302 | 2300 | 2300 | 2300 | 2300 | 2302 | 2300 | 2300 | 2402 | 2400 | 2400 |
| B80 | 2170 | 2172 | 2170 | 2192 | 2190 | 2190 | 2300 | 2302 | 2304 | 2300 | 2301 | 2300 | 2300 | 2300 | 2300 | 2401 | 2400 | 2400 |

## APPENDIX A6 DETAILED COMPRESSIVE STRENGTH RESULTS OF CAST CUBES (N/mm$^2$)

| | 3 DAYS | | | 7 DAYS | | | 14 DAYS | | | 28 DAYS | | | 56 DAYS | | | 90 DAYS | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| B0 | 16.4 | 16.3 | 16.3 | 17.6 | 17.5 | 17.6 | 19.5 | 19.5 | 19.4 | 22.5 | 22.5 | 22.6 | 24.8 | 24.8 | 24.7 | 27.3 | 27.3 | 27.2 |
| B10 | 8.6 | 8.7 | 8.6 | 13.7 | 13.8 | 13.8 | 15.9 | 16.0 | 15.9 | 18.2 | 18.1 | 18.1 | 25.3 | 25.2 | 25.3 | 30.5 | 30.4 | 30.4 |
| B20 | 7.7 | 7.8 | 7.7 | 12.6 | 12.5 | 12.5 | 14.7 | 14.8 | 14.9 | 16.7 | 16.7 | 16.8 | 24.9 | 25.0 | 24.9 | 29.5 | 29.4 | 29.4 |
| B30 | 7.6 | 7.5 | 7.6 | 12.3 | 12.2 | 12.3 | 14.1 | 14.2 | 14.1 | 16.0 | 16.1 | 16.0 | 24.6 | 24.6 | 24.5 | 24.6 | 24.6 | 24.7 |
| B40 | 7.3 | 7.2 | 7.3 | 11.5 | 11.7 | 11.6 | 13.7 | 13.7 | 13.8 | 15.7 | 15.6 | 15.6 | 19.7 | 19.6 | 19.8 | 23.7 | 23.6 | 23.6 |
| B50 | 7.1 | 7.1 | 7.0 | 8.6 | 8.6 | 8.4 | 12.2 | 12.1 | 12.3 | 14.0 | 14.1 | 14.1 | 18.9 | 19.0 | 19.0 | 22.8 | 22.7 | 22.7 |
| B60 | 6.7 | 6.7 | 6.6 | 6.8 | 6.7 | 6.6 | 9.5 | 9.6 | 9.4 | 10.7 | 10.7 | 10.8 | 15.4 | 15.5 | 15.2 | 16.9 | 17.0 | 16.9 |
| B70 | 6.5 | 6.5 | 6.6 | 6.8 | 6.8 | 6.9 | 9.5 | 9.4 | 9.3 | 10.7 | 10.5 | 10.6 | 15.3 | 15.2 | 15.4 | 16.7 | 16.7 | 16.6 |
| B80 | 6.0 | 5.9 | 6.0 | 6.2 | 6.4 | 6.3 | 8.9 | 8.8 | 8.7 | 10.0 | 9.9 | 9.8 | 12.8 | 13.0 | 12.7 | 16.3 | 16.2 | 16.2 |

## APPENDIX A7

### DETAILED RESULTS COMPRESSIVE STRENGTH OF CAST METAKAOLIN CUBES CURED IN SODIUM CHLORIDE (Nacl) SOLUTION ($N/mm^2$)

| | 14 days | | | 28 days | | | 56 days | | | 90 days | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| B0 | 15.1 | 15.2 | 15.1 | 20.4 | 20.6 | 20.5 | 22.3 | 22.2 | 22.1 | 24.8 | 24.7 | 24.8 |
| B10 | 12.4 | 12.5 | 12.3 | 16.3 | 16.2 | 16.3 | 22.7 | 22.8 | 22.7 | 27.3 | 27.2 | 27.3 |
| B20 | 11.7 | 11.7 | 11.7 | 15.3 | 15.4 | 15.1 | 22.7 | 22.6 | 22.6 | 26.7 | 26.8 | 26.8 |
| B30 | 10.9 | 10.8 | 10.9 | 14.4 | 14.5 | 14.3 | 22.3 | 22.2 | 22.2 | 24.8 | 24.8 | 24.8 |
| B40 | 10.6 | 10.4 | 10.5 | 13.9 | 14.0 | 13.9 | 17.5 | 17.5 | 17.5 | 21.1 | 21.0 | 21.1 |
| B50 | 9.5 | 9.5 | 9.5 | 12.8 | 12.6 | 12.8 | 17.0 | 17.1 | 17.1 | 20.4 | 20.3 | 20.4 |
| B60 | 7.3 | 7.3 | 7.2 | 9.8 | 9.8 | 9.7 | 13.8 | 13.8 | 13.7 | 15.1 | 15.1 | 15.0 |
| B70 | 7.2 | 7.0 | 7.2 | 9.6 | 9.5 | 9.5 | 13.7 | 13.8 | 13.6 | 15.0 | 15.1 | 15.1 |
| B80 | 6.8 | 6.7 | 6.8 | 8.9 | 8.8 | 8.7 | 11.5 | 11.4 | 11.4 | 14.4 | 14.4 | 14.4 |

## APPENDIX A8

### DETAILED RESULTS COMPRESSIVE STRENGTH OF CAST METAKAOLIN CUBES CURED IN MAGNESIUM CHLORIDE (Mgcl$_2$) SOLUTION (N/mm$^2$)

| | 14 days | | | 28 days | | | 56 days | | | 90 days | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| B0 | 17.6 | 17.7 | 17.5 | 22.8 | 22.8 | 22.6 | 24.6 | 24.7 | 24.7 | 25.8 | 25.9 | 25.8 |
| B10 | 14.6 | 14.6 | 14.4 | 18.7 | 18.6 | 18.8 | 25.4 | 25.6 | 25.3 | 28.4 | 28.4 | 28.4 |
| B20 | 14.1 | 14.0 | 14.2 | 17.5 | 17.4 | 17.6 | 25.0 | 25.1 | 25.0 | 27.7 | 27.6 | 27.5 |
| B30 | 13.3 | 13.2 | 13.3 | 16.8 | 16.8 | 16.8 | 24.5 | 24.4 | 24.4 | 26.0 | 25.9 | 26.0 |
| B40 | 13.1 | 13.1 | 13.1 | 16.3 | 16.2 | 16.2 | 20.0 | 19.9 | 19.9 | 22.3 | 22.1 | 22.2 |
| B50 | 11.9 | 11.8 | 11.9 | 15.1 | 15.1 | 15.1 | 19.4 | 19.3 | 19.4 | 21.6 | 21.7 | 21.6 |
| B60 | 9.7 | 9.6 | 9.5 | 12.3 | 12.3 | 12.3 | 14.4 | 14.3 | 14.2 | 15.2 | 15.1 | 15.4 |
| B70 | 9.6 | 9.7 | 9.5 | 11.9 | 12.0 | 11.8 | 14.1 | 14.2 | 14.1 | 15.0 | 15.2 | 15.3 |
| B80 | 9.1 | 9.1 | 9.1 | 10.9 | 10.8 | 10.7 | 12.4 | 12.5 | 12.3 | 14.9 | 14.8 | 14.8 |

APPENDIX A9 DETAILED RESULTS OF THE COMPRESSIVE STRENGTH OF THE CAST CUBES AT ELEVATED TEMPERATURE (N/mm$^2$)

| | 25$^{o}$C | | | 100$^{o}$C | | | 200$^{o}$C | | | 300$^{o}$C | | | 400$^{o}$C | | | 500$^{o}$C | | | 600$^{o}$C | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| B0 | 27.2 | 27.3 | 27.3 | 14.0 | 13.9 | 13.8 | 14.8 | 14.8 | 14.8 | 16.9 | 16.7 | 16.8 | 19.2 | 19.3 | 19.1 | 20.8 | 20.7 | 20.8 | 23.5 | 23.6 | 23.4 |
| B10 | 30.3 | 30.4 | 30.4 | 7.6 | 7.4 | 7.2 | 11.6 | 11.7 | 11.5 | 13.6 | 13.4 | 13.5 | 15.6 | 15.6 | 15.6 | 21.2 | 21.1 | 21.1 | 25.8 | 25.5 | 25.6 |
| B20 | 29.5 | 29.4 | 29.3 | 6.7 | 6.6 | 6.6 | 10.5 | 10.5 | 10.5 | 12.6 | 12.7 | 12.8 | 14.3 | 14.1 | 14.2 | 21.0 | 20.9 | 21.0 | 25.5 | 25.3 | 25.4 |
| B30 | 24.7 | 24.7 | 24.6 | 6.4 | 6.5 | 6.7 | 10.2 | 10.2 | 10.2 | 12.1 | 12.1 | 12.0 | 13.9 | 13.6 | 13.7 | 20.6 | 20.7 | 20.7 | 23.7 | 23.6 | 23.6 |
| B40 | 23.6 | 23.6 | 23.6 | 6.3 | 6.4 | 6.2 | 9.7 | 9.8 | 9.9 | 11.6 | 11.7 | 11.7 | 13.4 | 13.4 | 13.3 | 16.5 | 16.4 | 16.5 | 20.0 | 19.5 | 20.0 |
| B50 | 22.7 | 22.6 | 22.7 | 6.0 | 6.1 | 6.0 | 7.1 | 7.2 | 7.2 | 10.5 | 10.4 | 10.5 | 12.0 | 11.9 | 11.9 | 16.0 | 15.9 | 15.7 | 19.5 | 19.4 | 19.5 |
| B60 | 16.8 | 16.9 | 16.9 | 5.7 | 5.7 | 5.7 | 5.6 | 5.8 | 5.8 | 8.0 | 8.1 | 8.0 | 9.5 | 9.2 | 9.4 | 13.0 | 12.9 | 12.8 | 14.4 | 14.4 | 14.4 |
| B70 | 16.7 | 16.6 | 16.6 | 5.5 | 5.4 | 5.5 | 5.7 | 5.9 | 5.6 | 8.0 | 8.1 | 8.1 | 9.1 | 9.0 | 9.2 | 13.0 | 12.9 | 12.9 | 14.4 | 14.4 | 14.4 |
| B80 | 16.2 | 16.1 | 16.3 | 5.2 | 5.2 | 5.0 | 5.6 | 5.3 | 5.5 | 7.5 | 7.5 | 7.5 | 8.5 | 8.4 | 8.5 | 10.7 | 10.8 | 10.7 | 13.6 | 13.9 | 13.8 |