AN ASSESSMENT OF JOS PLATEAU VOLCANIC DEPOSITS AS POZZOLANS AND ITS EFFECT ON BLENDED ORDINARY PORTLAND CEMENT CONCRETE

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A DISSERTATION SUBMITTED TO THE POSTGRADUATE SCHOOL, AHMADU BELLO UNIVERSITY, ZARIA, NIGERIA. IN PARTIAL FULFILLMENT FOR THE AWARD OF DOCTOR OF PHILOSOPHY IN CONSTRUCTION TECHNOLOGY

DEPARTMENT OF BUILDING FACULTY OF ENVIRONMENTAL DESIGN AHMADU BELLO UNIVERSITY, ZARIA, NIGERIA.

FEBRUARY, 2012

DECLARATION

I declare that this dissertation entitled 'AN ASSESSMENT OF JOS PLATEAU VOLCANIC DEPOSITS AS POZZOLANS AND ITS EFFECT ON BLENDED ORDINARY PORTLAND CEMENT CONCRETE' has been prepared by me in the Department of Building under the supervision of Prof M M Garba, Prof I K Zubairu and Dr S A Bustani.

The information derived from literature has been duly acknowledged in the text and a list of reference provided. No part of this dissertation has been submitted previously for award of any degree at any University.

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DADU, Danjuma Wurim Date

CERTIFICATION

This dissertation entitle 'AN ASSESSMENT OF JOS PLATEAU VOLCANIC DEPOSITS AS POZZOLANS AND ITS EFFECT ON BLENDED ORDINARY PORTLAND CEMENT CONCRETE' meets the regulations governing the award of the degree of Doctor of Philosophy of Ahmadu Bello University Zaria, Nigeria, and is approved for its contribution to knowledge and literary presentation.

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DEDICATION

This work is dedicated to my wife and children.

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To God be the glory and honour. My appreciation goes to the Head of Building Department, Prof K Bala with whom the idea of undertaken a PhD research work was muted. I wish to express my sincere appreciation and indebtedness to the members of my supervisory committee; Prof M M Garba, Prof I K Zubairu and Dr S A Bustani of the Department of Building who despite the numerous challenges put in immeasurable efforts in making the work a success.

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ABSTRACT

An enormous gap exists between the production capacities of the Cement Manufacturing Plants and the demand for cement in Nigeria. Prior to 2010, Nigeria could only produce between 4 and 6.5 million tons annually as against the domestic demand of about 18 million tons. There is the need therefore to augment the local cement production by the introduction of Natural Pozzolans of volcanogenic origins as partial replacements of the Ordinary Portland Cement (OPC) in concrete mixtures. The study thus focused on experimental works on the pozzolanic characteristics of Jos Plateau volcanic deposits as potential pozzolans for partial replacements of the OPC in concrete mixtures. The laboratory experimental studies evaluated the chemical characteristics of the volcanic materials and the pozzolanic characteristics of concrete made with the volcanic materials in partial replacement of the Portland cement in the concrete mixtures. The results of the chemical analysis indicated that the oxides of SiO_2, Al_2O_3 and Fe_2O_3 are substantially present in all the samples tested. The sum of these oxides varied from 71.45 (JP14) to 95.31% (JP3). The average sum of the minor oxides obtained was 3.16%. However ASTM C (2001) recommends that sum of the minor oxides should not be more than 5% by weight. The average values of CaO, MgO, and SO_3 were 0.29 %, 1.81 %, 0.53 % respectively of the 20 samples of materials tested. Furthermore alkalis (Na_2O and K_2O) average values were 0.25 % by weight of the samples tested. All the materials samples studied have no trace of carbon in any of the samples investigated. The results of test indicated that the LOI and the MC of the 12.3 and 2.3 % respectively. The MC values were within the ASTM C 109/C 109M (2001) maximum recommendations of 3%. While those of the LOI were slightly above the 10% recommendation of ASTM C 618 (2005).The result of the study further indicated that the Initial Setting and Final Setting Times were 2 hours 35 minutes and 3hours 30 minutes respectively. The result of soundness test tests of the Portland pozzolan cement paste showed the changes in volume varied from zero to 0.40%. ASTM C 618 (2005) recommended a maximum of 0.80%. The control cube had compressive strengths of 26.0 N/mm^2 at 28 days curing. The results of the partial replacements of 5, 10, 15 and 20% of OPC with the volcanic materials were all above 75% of the control strength. The investigation established that Pozzolanic Activity Index with Portland Cement (PAIC) at 28 days for 5% to 20% replacement of OPC showed a sliding from an average index of 105 to 81.ASTM C 595(2006) minimum specification is an index of 75 for a pozzolan to be used Portland Pozzolana Cement in concrete mixtures. The volcanic materials can be used for cement Type IP Type P and (ASTM C 595 (2006).It is conclusive that the volcanic deposits possess pozzolanic characteristics as natural pozzolans for use in concrete.

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND TO THE STUDY

Concrete globally, is a crucial material for infrastructural development due to its versatility and flexibility in usage and application making it superior to other building materials such as wood and steel (Hossain *et al*, 2011).The versatile nature of the concrete makes its universal usage in construction next only to water. Altwair and Kabir (2010) averred that though concrete is superior to other materials, the production cost of its main constituents (cement) is excessive. European Commission (EC, 2001) stated that the average energy cost on the production of one ton of cement is 50% the total cost of the production; with the electricity demand at about 90-1300Kwh per ton of cement produced. Horst (2001) asserted further that about 1 barrel of fuel or ¼ ton of coal is needed for the calcinations of the limestone alone to produce 1 ton of cement. Jha and Prasad (2004) affirmed that low-cost or large scale housing can best be achieved by the replacement of costly conventional cementitious materials such as Portland Cement (PC) with innovative and sustainable materials such as the pozzolans. Hashmi (2008) stressed that even though the various cementitious alternatives may not be capable of replacing totally the PC at the moment, but they can however partially be replaced in a variety of construction applications such as in mortar and concrete mixtures.

In line with the concept of producing cheaper alternative cementitious materials, an

assessment of pozzolans of volcanogenic origins for partial replacements of the OPC in the concrete mixtures is earmarked. Thus the object of this study is to investigate the potentials of the volcanic deposits from Jos Plateau as pozzolanic materials for partial replacements of Portland cement in concrete mixtures. Wright (1989) had established that the Jos Plateau is within the historic volcanic deposits of Nigeria (Appendix 'D').The utilisations of the volcanic deposits from the Jos Plateau as raw materials for the production of alternative cements will reduce the OPC contents in concrete mixtures and also improve its engineering properties. Neuwald (2004) affirmed that pozzolans are such materials that can be used in partial replacements of Portland Cement (PC) in concrete mixtures or in cement blending.

The word "pozzolana" according to Jackson (2003), is derived from the Latin words "Pulvis Puteolamus", meaning the *powder* from *Puteoli* or the *dust of Puteoli.* These were a direct reference to the unconsolidated pyroclastic (ash) deposits of Campi flegrei and Vesuvius volcanic fields were the Romans first discovered the unique characteristics of the Natural Pozzolans. Wilson and Ding (2007) stated that, the Romans, while mixing lime and the volcanic ash quarried from Pozzuoli (believing it was sand) found out that the mixtures produced much stronger end results, than the previously mixed materials. This discovery significantly altered the use of construction materials by Builders of the famous Roman historic structures such as the Theatre at Pompeii (seating 200,000 spectators), the Romans walls, aqueducts

and several structures. Pozzolanas are thus cements of antiquities. Shetty (1982) positioned that this pozzolanic reactivity of the natural Pozzolanas accounts for the existence of ancient structures such as The Wharf of Caligula constructed with volcanic ash from Mt Vesuvius in Pozzuoli.

The American Society for Testing and Material (ASTM) C 618 (2005) defined the pozzolans as siliceous or siliceous and aluminous materials, which in themselves possess little or no cementitious values but when, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties. Parhizkar *et al* (2010) has also defined Pozzolanas as materials containing reactive silica and/or alumina, which, alone have little or no binding property, but when mixed with portland cement, react with calcium hydroxide (produced from the hydration of the cement) to form a strong gel.

Pozzolana cement is widely used in countries such as Europe, America, China and India for massive structures such as dams, bridges, roads and high rise buildings; and the volcanic materials in particular has been used in Europe, North America for partial replacement of the OPC in concrete mixes or for the production of a Blended Cement (Detwiler *et al.*, 1996). Day (1990) reported that 32 countries (Appendix 'AE') have so far officially permitted the use of the pozzolans in partial replacement of the Portland cement; a replacement varying from 10% (Ice Land) to 50 % (Argentina, China and Indonesia). But on the African continent, the report indicated

that only South Africa and Morocco made the list with each allowing a replacement up to 15 % of the OPC. Citifmonline (2011) reported recently that the Ghana Standard Board has specified the use of pozzolan cement as a building material; and its use is compulsory for all government infrastructural projects. A growing economy such as Nigerian needs enormous amount of this cement to prop up its housing and other infrastructural developments. Armstrong (2009) reported that in 2008, Nigeria was third largest importer of cement in the world. Fiakpa (2008) reported that Nigeria imports about 11 million tons of its cement demands annually to meet up the domestic demand of the commodity. The Jos Plateau volcanic deposits are accordingly potential pozzolanic materials for cement blending or partial replacement of the PC in concrete mixtures. The prerequisite to the application is the assessment of the pozzolanic characteristics of the deposits with Standards such the ASTM C 618 (2005): Specification for Fly Ash and Raw or Calcined Natural Pozzolana or Use in as a Mineral Admixture in Portland cement Concrete.

1.2 THEORETICAL FRAMEWORK

The Theoretical Framework of this study is based on the assertions of researchers such as Detwiler (1996) and Day (1990) that primarily, the natural pozzolan originates from volcanogenic activities resulting from violent eruptions and ejections of melted magma from the molten earth; and that these rocks of volcanogenic origins posses cementitious properties once in finely divided form.

Neuwald (2004) explained further that these materials react chemically with the calcium hydroxide $Ca(OH)_2$ to form the compound possessing cementitious properties through what is referred to as the pozzolanic activity of the pozzolan. Further theory is that the chemistry of natural pozzolans varies from deposit to deposit because of the variable proportions of the constituents and the variable mineralogical and physical characteristics of the reactive oxides of silica, alumina and iron; and additional constituents, such as alkalis [sodium oxides (Na_2O) and potassium oxides (K_2O)] and other trace elements in varying degrees [ACI (2000), Intermediate Technology Development Group (ITDG, 2000)]. In addition to this theory, Day (1990) and Detwiler (1996) affirmed that virtually with all pozzolans; there has always been no clear correlation between the chemical characteristics of the pozzolan and the respective Pozzolanic Activity of the material. The pozzolan activity of the Jos Plateau volcanic materials is therefore evaluated by assessing the oxides composition and the Pozzolanic Activity Index (also referred to as the Strength Activity Index) of each of the samples of the volcanic deposits in the location to ascertain its pozzolanic characteristics. The philosophy of this study is thus; if the existence of volcanogenic deposits on the Jos Plateau is established, then the deposits would exhibit pozzolanic concrete mix. Consequently it can be predicted that the Jos Plateau volcanic materials would have some levels of pozzolanicity such that its partial replacement of the OPC in concrete mixtures would achieve cheaper cementitious materials which invariably could result in a reduction of the overall cost of housing construction.

1.3 STATEMENT OF RESEARCH PROBLEM

Andrew (2007) stated that the provision of affordable housing has continued to pose a challenge to the developing countries, particularly the Sub-Saharan Africa. Oluwakiyesi (2011) reported that Nigeria for instance has a housing shortfall of between 16 and 18 million units which needs about ₦60 trillion to remedy deficit. This is so as housing production and its affordability are major challenges Nigeria faces as consequence of deficiencies in primary infrastructures such as roads, water and electricity (Sanusi, 2003). The housing short falls in Nigeria is intense. Okeke (2002) reported that the country can boast of only two to three dwelling units per thousand as against the United Nations recommendations of eight to ten units. The magnitude of the housing deficit in Nigeria according to Ajanlekoko (2001) is enormous and had defied solutions by government; the Federal Government of Nigeria (FGN) between 1979 and 1995 set out four National Housing Programmes to boost housing situation in the country as shown in Table 1.1 but with but to no respire. Okeke (2002) reported that out of the 120,000 units proposed by the FGN to be constructed between 1994 and 1995, only 1,014 were actually built.

Table 1.1: National Housing Programmes; 1979 – 1995

PERIOD	HOUSING PROGRAMME	REMARKS
1979-1983	Federal Housing Scheme	400,000 units for four years
1986-1991	National Site and Services Scheme	Site and Services only
1991-1993	National Prototype Housing Scheme	Selected states only
1995	National Housing Scheme –Materials Provision to Contractors	Aimed at addressing raising cost of materials

Source: Okeke (2002)

About two billion additional people are estimated to populate the earth in the next two decades, with 95% of this growth predicted to take place in the developing countries such as Nigeria; it is assertive that this type of growth in population would create an unprecedented demand for Housing and other Basic Infrastructures for the developing countries (Amadei, 2003). Thus the demand for housing will require enormous quantity of cement. The Nigerian Building and Road Research Institute (NBRRI, 2003) asserted that with the exception of doors and windows for a simple residential building, all the building components as shown in Table 1.2 use cement in one form or the other.

Table 1.2: SOME LOCAL BUILDING MATERIALS

S/NO	Building Component	Building materials	Raw materials
1	Foundation	- Soil, concrete	- Soil profile, sand, cement aggregates
2	Building frame	- Reinforced concrete (columns and beams)	- Cement, aggregate, sand, steel reinforcement
3	Walling	- Sand Crete blocks - Cement Stabilized Blocks - Stone Crete blocks	- cement, sand - clay, cement - stone, cement
4	Floors	- Mass Concrete (ground floor) - Reinforced concrete - Reinforced concrete with hollow	- cement, sand, aggregate - as above with steel reinforcement - as above with clay pot
5	Roofing covering	- Corrugated Asbestos - Fiber concrete roofing titles and sheet	- asbestos - cement, sand vegetable/chemical fiber
6	Ceiling	- Ceiling Board	- Asbestos - Cement - Wood particles, cement - Clay (Kaolin) binders
7	Finishes	- Mortars - Terrazzo - Concrete Ceramic tiles	- soft sand, cement - pozzolanas, sand cement - lime, sand, cement, - appropriate chemicals, aluminum separate, titanium oxide, cement, extenders and pigment, etc. - aggregates, cement, pigment, polishing - cement clays, mortar - polyvinyl chloride

Source: Nigerian Building and Road Research Institute (2003)

It is obvious that any prospective extensive housing activities for the country would require enormous financial commitments because the high costs of conventional materials such as cement. Cement for example has always a shortage of cement as a building material in Nigeria. This is as a result of the wide gap that exists between production capacity of the manufacturing plants and the high demand of the

commodity (Fiakpa, 2008).The Raw Materials Research Development Council (RMRDC, 2003) reported that the Local Cement Manufacturers are faced with production challenges such as soaring energy costs, poor infrastructures (such as roads, power/energy). In addition to the economic disadvantages of the PC over other alternatives, Naik (2005) stated that the manufacture of OPC is not environmentally friendly as it generates Green House Gas (GHG) emissions (accounting to 5-8% of harmful gases to the atmosphere); and the mining of lime stone deplete the environment as 1.6 tons of raw materials are needed to produce 1 ton of PC. The natural pozzolan of volcanogenic origins provides a window of opportunities for the argumentation of the local cement production with the volcanic deposits as potential cementitious materials. The Jos Plateau Volcanic deposits are thus potential cementitious material for partial reduction of Portland cement contents in concrete mixtures.

1.4 NEED FOR THE STUDY

There is a need for adequate cementitious materials for the infrastructural development of Nigeria in view of its deficits in housing and other basic infrastructures. Amadei (2000) asserted that in the next decade there will an unprecedented demand for basic needs such as health, food, energy, additional housing and other infrastructures particularly in the sub-Saharan Africa. Jha and Prasad (2004) then stressed that large scale housing for example are inevitable; and that to address such housing shortfalls, there is the need for the replacement of the

costly conventional building materials such as the PC with alternative cementitious materials for instance the pozzolans for housing construction. The Jos Plateau volcanic deposits are thus potential materials for pioneering the alternative to Portland cement production. Detwiler et al (1996) reported that a major economic benefit in the use of these alternatives is that it would substantially increase the capacity of a Cement Manufacturing Plant without an installation of a new kiln. The report also explained further that blending of PC with the Pozzolanas saved power and energy as little or no energy inputs are required prior to their utilisations. This is in contrast to the Manufacturing of OPC in which the energy utilisation is intense European Commission (EC, 2001). The applications of the volcanic materials for cement blending or for partial replacement of the OPC would reduce the cement content in the concrete mixtures and invariably reduce the cost of housing in Nigeria. In addition it will lower GHG emissions associated with the Portland cement productions. Therefore the study of the potential utilisation of volcanic deposits from Jos Plateau will not only transform the volcanic materials into an alternative cheaper cementitious material for the production of low-cost housing but will also yield social-economic benefits. Harris (2005) elucidated that cheaper cement, means more construction activities; and that construction activities are an employment generation source, particular in developing countries (second only to agriculture); with emphases that the utilisations of the Natural Pozzolanas for partial replacements of Portland cement would save as further local employment generate where these deposits are located (in mining and processing of the materials).

1.5 AIM AND OBJECTIVES

1.5.1 Aim

The study aims at assessing the effect of Jos Plateau volcanic deposits as natural pozzolans on blended ordinary portland cement concrete.

1.5.2 Objectives

i. To ascertain from literature and field survey the presence and the locations of volcanic deposits on the Jos Plateau.

ii. To determine the chemical and physical characteristics of the volcanic materials.

iii. To investigate the compressive strengths of concretes containing volcanic materials in partial replacements of the OPC in 5 %, 10 %, 15 %, 20 %, 30 % and 40 % replacements..

iv. To evaluate the durability of concrete containing the natural pozzolan using Autoclave Standard Test Method.

v. To evaluate the pozzolanic activity of volcanic deposits in concrete containing the Jos Plateau volcanic materials.

vi To identity a relationship between the chemical composition of the volcanic deposits and the pozzolanic activity of volcanic materials.

1.6 RESEARCH METHODOLOGY

1.6.1 Identification of the Volcanic Deposits

The study was divided into field and laboratory works. A rigorous literature review

was carried out to obtain indebt knowledge in the field of study. The field work consisted of a number of trips to various sites to spot out the locations of the volcanic deposits based on the following;

i. Volcanic conical hills and outstanding volcanic landmarks.

ii. Volcanic materials exposed of as results of soil erosion.

iii. Volcanic deposits exposed of as results of mining activities.

iv. Volcanic materials exposed due to road construction exploits.

The number of the volcanic complexes were identified and clustered into nine groups according the Local Government Areas (LGA) which the materials are located as follows:

Group I: Bassa LGA-three locations.
Group II: Jos North LGA- one location
Group III: Jos East LGA- two locations
Group IV: Jos South LGA- two locations
Group V: Riyom LGA- two locations
Group VI: Barkin Ladi LGA - two locations
Group VII: Bokkos LGA- two locations
Group VIII: Mangu LGA- five locations
Group IX: Pankshin LGA- one location

Pictures of volcanic hills; eroded volcanic soils; and soils exposed by relics of tin mining activities are shown in Appendix ‘H’ to ‘L’. Materials from various locations were thus collected for the study.

1.6.2 Assessing the Pozzolanic Characteristic of the Volcanic Deposits

The pozzolan activity of the Jos Plateau volcanic materials were evaluated by assessing the chemical characteristics and the Pozzolanic Activity (referred to as the Strength Activity) of the volcanic deposits to ascertain its pozzolanic characteristics and consequently the levels of pozzolanicity of each of the volcanic samples.

1.6.2.1 Chemical characteristics

The evaluation of the chemical characteristics of the volcanic materials and Compressive Strength Tests of Portland Volcanic Materials Cement concrete were evaluated to ASTM C 618 (2005) Standard Specifications for fly ash and the natural pozzolan to use in concrete Mixtures. The oxides composition of the volcanic deposits were evaluated by the Wet Chemistry and the Energy Dispersive X-Ray Fluoresce (EDXRF); and the Neutron Activation Analysis (NAA) methods were under taken at the National Metallurgy Development Centre (NMDC), Jos and the Centre for Energy Research and Training (CERT), Ahmadu Bello University (ABU) Zaria. The Loss on Ignition (LOI) and the Moisture Content (MC) determinations were also carried out at the NMDC, Jos. The grounding of the volcanic materials and the Specific Gravity (SG) were determined at the Building Department ABU, Zaria. The chemical characteristics (Oxides composition, LOI and the MC) and the SG of the *Dangote* brand of PC; sieve analysis of the fine and coarse aggregates were also performed.

1.6.2.2 Pozzolanic Activity of concrete containing volcanic materials

The pozzolanic Activity of concrete containing volcanic materials from Jos Plateau volcanic deposits was determined according to the Standard Testing Procedure of ASTM 311 C (2005): Standard Test Methods for Sampling and Testing Fly Ash or Natural Pozzolans for Use in Portland-Cement Concrete. The evaluation of the physical characteristics of and Compressive Strength Tests of concrete containing the Volcanic Materials were evaluated to specifications of ASTM C 618 (2005): Standard Specifications for fly ash and the natural pozzolan to use in concrete mixtures. The setting time, the compressive strengths tests and the pozzolanic activity index with *Dangote* cement were evaluated at the Building Department. While the soundness of the materials and Pozzolanic Activity with lime was investigated at the Chemistry Departments, ABU Zaria.

1.6.2.3 Appraisal of the potentiality of the Jos plateau volcanic deposits

The data obtained from the literature review, field works and laboratory investigations were used in evaluating the pozzolanic characteristics of concrete containing Jos Plateau volcanic deposits as a partial placement of OPC in concrete mixtures or in cement blending.

1.7 SCOPE AND LIMITATION

1.7.1 Scope

The scope of the research is to evaluate the pozzolanic characteristics volcanic

materials selected from 20 volcanic sites from Jos Plateau by utilising ASTM 311 C (2005) standard tests procedures and other standards. The extents of the tests evaluation is to the recommendation of the Standard Test Methods for Sampling and Testing Fly Ash or Natural Pozzolans for Use in Portland-Cement Concrete of ASTM C 618 (2005).

The materials obtained for the study were excavated from the top surfaces of the volcanic hills; and exposed materials resulting from soil erosion, mining and road construction activities. The following laboratory analyses were carried out;
Oxides composition, Loss on Ignition and Moisture Content and the Specific Gravity of each sample of the volcanic materials were evaluated. The compressive strengths of the concrete made with Portland Volcanic Material Cement (PVMC) and its respective Pozzolanic Activity Index of the pozzolans with the PC; the Setting Time; Pozzolanic Activity Index with Lime; and the durability checked by Autoclave expansion Standard Test Method (Soundness) of mortar containing the volcanic materials were also studied. The chemical and some physical properties of the Dangote cement used for the study were also investigated.

1.7.2 Limitations

The major limitations were the non-availability of land maps and aerial photographs to depicting specific volcanic areas of the Jos Plateau Volcanic Province. These limitations were also reported by Olowolafe (2000) while evaluating the data for its soil mappings of the Jos Area. The information from literature review land marks

Volcanic features and the exposal's of the volcanic materials, as results of physical activities such as soil erosion, mining and road construction exploits in the area of the study was used. Consequently, the exact or accurate boundaries of the volcanic Sites or locations or grouping would not be definite.

The characteristics of historic volcanic eruptions are that they occur in stratified deposits layers depending on the volcanic activity; they are made up of fresher overlying (overburden) materials and other strata. The materials samples were collected from the overburden (top layer) strata in all the locations. Thus results of the samples tested may not reflect the true characteristics of the other layers of the deposits as the other layers may produce varying pozzolanic characteristics.

The effect of silica-alkali reaction, freezing-thawing, permeability (porousity) and exposal to other harsh environment (are related to long term related durability issues) on concrete containing the Jos Plateau volcanic materials were not evaluated; first as the ASTM C 618 (2005) limits the assessment of the pozzolanic activity at 28 days; and concept of the study *ab initio* is to assess the availability and potentiality of the volcanic deposits as Supplementary Cementitious Materials for partials replacement of the costly Portland cement in concrete mixtures.

The chemical evaluation of *Dangote* cement showed that SiO_2 and AI_2O_3 were 49.6 and 43.3 % respectively by weight below the recommended values of ASTM C 150 (2004). CaO were also found in excess 18.6% above the upper limits and the LOI

was 8.8 % as against the recommendations of 0.3 % of the ASTM C 618 (2005). These might have affected the compressive strengths of both the control cubes and the cubes containing the volcanic materials.

CHAPTER 2

LITERATURE REVIEW

2.1 PORTLAND CEMENT

The most widely use cement in the world today as asserted by Shetty (2005) is the Ordinary Portland Cement (OPC), manufacture from modern pre-calcinating plants. According to Draggan (2008), the name 'cement' is derived from the Latin word *caementa* meaning 'rough stone'. Maerschel (2008) asserted that 'cement is simply something that sticks things together'. But for the purpose of this work cements are restricted to calcareous cements containing compounds of lime with the primary function of binding the fine and coarse aggregates particles together. It is thus, the binder in concrete, and, depending on the strength of the concrete, cements usually accounts for 12% to 15% of a concrete mix.

Sharma (2008) asserted that Portland cement derived its name from the Portland stone, a type of building stone that was quarried on the Isle of Portland in Dorset, England during the building of London. Many technologists and researchers have claimed to have made the first Portland cement in its modern sense; but it is generally accepted that it was first manufactured by William Aspin at North fleet, England in 1842. Portland cement is a product obtained by finely pulverising clinker produced by calcining to incipient fusion, an intimate and properly proportioned mixture of argillaceous (clay/shale) and calcareous (lime stone) materials (Duggal,

2010). The European Standard - EN197.1 (1992) prescribed that the proportioned mixture of Portland Cement be thus; that it should consist of calcium silicates (C_3S and C_2S) constituting at least two-third by mass and with the aluminum-iron the compounds consist the balance; it state also the ratio of CaO to SiO_2 shall not be less than 2; and with MgO shall not be not exceeding 5.0% by mass.

There are different standards and classifications of Ordinary Portland Cement varying from country to country each with a particular characteristic suited for a particular purpose. The two major standards in the world today are the American Society for Testing and Material (ASTM) 150 (2005) and European EN-197-1(1992) standards used in the United States of America and Europe respectively. The base materials use in the manufactured of cement determines the type of cement. Natural stones such as volcanogenic substances are used in the production of Roman and Puzzolana cements. Artificial materials of argillaceous and calcareous materials such as lime are used in the manufacture of Portland and Special Cements.

2.1.1 Various Types of Cement

The types of cement have increased over the years with the advancement in processing techniques. Various types of cement produced are as follows:

i) Ordinary Portland cement

ii) Portland Pozzolana Cement

iii) Portland Blast Furnace Slag Cement

iv) Oil Well Cement

v) Rapid Hardening Portland cement

vi) Sulphate Resisting Portland cement

vii) White Cement

viii) Clinker Cement

2.1.2 Standard Specification for Portland Cement

Different types of Portland cement are manufactured to meet various physical and chemical requirements for specific purposes. Portland cements manufactured in the United State of America for example are to meet the specifications of ASTM C 150 (2000) or ASTM C 1157 (2000); while European countries produced cements to meet EN-197-1(1992).The ASTM C 150 Standard Specification for Portland Cement provides for eight types of Portland cement designations as follows: -

i) Type I Normal; for use when the special properties specified for any other type are not required.

ii) Type IA Normal, air-entraining; Air-entraining cement for the same uses as

iii) Type I, where air-entrainment is desired.

iv) Type II Moderate sulfate resistance; for general use, more especially when moderate sulfate resistance is desired.

v) Type IIA Moderate sulfate resistance, air-entraining; air-entraining cement for the same uses as Type II, where air-entrainment is desired.

vi) Type II (MH) for general use, more especially when moderate heat of hydration and moderate sulfate resistance are desired.

vii) Type II (MH) An Air-entraining cement for the same uses as Type II (MH), where air-entrainment is desired.

viii) Type III High early strength; for use when high early strength is desired.

ix) Type IIIA High early strength; air-entraining; air-entraining cement for the same use as Type III Where air-entrainment is desired.

x) Type IV Low heat of hydration; for use when a low heat of hydration is desired.

xi) Type V High sulfate resistance; for use when high sulfate resistance is desired.

2.1.3 Manufacture of Portland cement

Historically, the development of the cement manufacturing processes are categorized in four routes namely dry, wet, semi wet and semi dry processes. From these techniques, the dry process Day (1990) is most economical and advanced technique. This process grinds and dry in tube mills or vertical roller mills, in presence of hot kiln exhaust gases or cooler exhaust air for drying. Prior to being fed to the kiln, the raw meal is homogenized or blended either in batch type or in continuously operating homogenizing silo systems.

According to Altwair and Kabir (2010) though concrete is superior to the other construction materials such as wood and steel, the production of its main

constituents – cement is not only highly energy intensive, it is also a major contribution to CO2 emissions and other GHG to the atmosphere. Wilson and Ding (2007) stated further that Portland cement is produced by pulverizing clinker which consists primarily of hydraulic calcium silicates. Clinker also contains some calcium aluminates and calcium aluminoferrites, and one or more forms of calcium sulfate (gypsum) are inter-ground with the clinker to make the finished product. Materials used in the manufacture of Portland cement must contain appropriate amounts of calcium, silica, alumina, and iron components. During manufacture, chemical analyses of all materials are made frequently to ensure uniformly high quality cement. While the operations of all cement plants are basically the same; but a typical flow diagram ought to adequately illustrate all plants in the production line. Thus there is no typical Portland cement manufacturing facility and every plant has significant differences in layout, equipment, or general appearance. Selected raw materials are transported from the mine quarry, crushed, milled, and proportioned so that the resulting mixture has the desired chemical composition. The raw materials are generally a mixture of calcareous (calcium carbonate bearing) materials, such as limestone, and an argillaceous (silica and alumina) material such as clay, shale, fly ash, natural pozzolan or blast-furnace slag; either a dry or wet process is used. In the dry process the grinding and blending are done with dry materials. In the wet process, the grinding and blending operations are done with the materials mixed with water in a slurry form. In other respects, the dry and wet processes are very much alike. Important technological developments have taken place in recent times

that has improved significantly the productivity and energy efficiency of dry-process plants. Selected raw materials for the production of cement are transported from the mine quarry, crushed, milled, and proportioned so that the resulting mixture has the desired chemical composition.

Day (1990) explained that the raw materials are a mixture of calcareous material, such as limestone, and an argillaceous (silica and alumina) material such as clay, shale, flies ash and natural pozzolans; and there are two types of processes in the cement plant manufacturing process; the dry or the wet process. In the dry process the grinding and blending are done with dry materials. While the wet process, the grinding and blending operations are carried out with the materials mixed with water in a slurry form. After blending, the ground raw material is fed into the upper end of a kiln where the raw mix passes through the kiln at a rate controlled by the slope and rotational speed of the kiln. Burning fuel (powdered coal, new or recycled oil, natural gas, rubber tires, and byproduct fuel) is forced into the lower end of the kiln where temperatures of 1400^{o}C to 1550°C change the raw material chemically into cement clinker of grayish-black pellets predominantly the size of marbles. The clinker is cooled and then pulverized. The burning fuel (powdered coal, new or recycled oil, natural gas, rubber tires, and byproduct fuel) is forced into the lower end of the kiln where temperatures of 1400^{o}C to 1550°C change the raw material chemically into cement clinker of grayish-black pellets predominantly the size of marbles. The clinker is cooled and then pulverized. During this operation a small

amount of gypsum is added to regulate the setting time of the cement and to improve shrinkage and strength development properties. In the grinding mill, clinker is ground so fine that nearly all of it passes through a 45 micron (No. 325) sieve.

In Portland cement Production, Limestone ($CaCO_3$) is calcined to at about 1500^oC; this, product of the calcinations is a mixture of tri-calcium silicate ($3CaO.SiO_2$)-C_3S, di-calcium silicate ($2CaO.SiO_2$)-C_2S, tri-calcium aluminates ($3CaO.Al_2O_3$)-C_3A and tetra calcium aluminoferrites ($4CaO.Al_2O_3Fe_2O_3$) - C_3AF. The clinker is interground with approximately 5% of gypsum to about 350m^2/kg Blaine fineness, to obtain Portland cement (Bhatty, 1995). Gypsum ($CaSO_4.2HO$) is then is added between 2-5% for the preservation the Cement (Neville, 1998). Thus, the main components of Portland cement as affirmed by Lawler *et al* (2007) are calcium silicates, calcium aluminates with calcium sulphate (gypsum) added to control the setting of the cement**.** Maerschel (2008) reported that It took about 2000 years for engineers and architects to agree on one type of cement (Portland cement) suitable for a wide range of constructions with the following optimum proportions; calcium oxide CaO (70%), Silica SiO_2 (20%), Alumina Al_2O_3 (5%), Ferric oxide Fe_2O_3 (3%) and 2% gypsum $CaSO_4.2H_2$. In addition to the main compounds there exist minor compounds such as Magnesia (MgO), Titanium (TiO_2), Manganese (Mn_2O_2) and Alkalis [Potassium K_2O_3 and Sodium (Soda) Na_2O] (Neville, 1996).

Production of Ordinary Portland Cement (OPC) is a recent development. It was conceived in 1824 by William Aspin while Charles Johnson in 1845 developed the

OPC to this form in used today. Prior to this development and as early as 2560 BC the Egyptians used lime and gypsum in building of the great pyramids. Thus the use of these materials is as old as the art of concrete and concrete technology exploited particularly by the Builders of Ancient Greeks and the Romans. Romans and the Greeks also used calcined lime stone for their building works. These cements were produced basically by combining the lime, gypsum and the calcined lime stone with volcanic ash quarried from Mt Vesuvius in Pozzuoli. The cement was thus called pozzolanic cement because the volcanic materials were mined from Pozzuoli, a town North East of Napoli.

2.1.4 Setting time, Soundness, Specific gravity

2.1.4.1 Setting time

The Standard Test Method of ASTM C 451 (2005) by means of the Vicat Apparatus is used to determine the initial and the final settings time of the cement pastes. The initial setting time is the time that elapses between the moment water is added to the cement to the time that the paste loses its plasticity. The Final Settings is the time that elapsed between the moment water is added to cement and the time the paste has completely lost its plasticity and has attained sufficient firmness to resist certain definite pressures.

2.1.4.2 Soundness

When referring to Portland cement, "soundness" refers to the ability of a hardened

cement paste to retain its volume after setting without undergoing delayed destructive expansion. This expansion is caused by slow hydration (or other reaction) of some compounds present

2.1.4.3 Specific gravity

The specific gravity of the volcanic materials is determined in accordance with the Standard Test Method for Specific Gravity (ASTM C 127, 2004); defined as the ratio of mass (weight in air) of a unit volume of material to the mass of the same volume of water at a stated temperature. The specific gravities of the material are determined in accordance with the Standard Test Method for Specific Gravity recommended by ASTM C 127 (2004).

2.1.5 Cement Hydration

Hydration is the result of chemical reactions that occur between water and the chemical compounds present in Portland cement. Portland cement is predominately composed of two calcium silicates: calcium silicates are Dicalcium silicate (C_2S) and Tricalcium silicate (C_3S).These account for 70 percent to 80 percent of the cement. The other compounds present in Portland cement are tricalcium aluminate (C_3A), tetra-calcium-aluminoferrites C4AF) and gypsum. In cement hydration, it is the tri-calcium silicate and the di-calcium silicate that take part in the chemical reaction producing calcium silicate, water and calcium hydroxides - {$CaO.SiO_2.H_2O$ and $Ca(OH)_2$} presented thus;

$$CaO.SiO_2 - 2CaO.SiO_2 + H_2O \Rightarrow CaO.SiO_2.H_2O + Ca(OH)_2.$$

The reaction of Calcium silicate and Tricalcium silicate with water produces calcium silicate hydrate (C-S-H) and calcium hydroxide-$Ca(OH)_2$, as illustrated in the following chemical equation.

$$2C_2S + 9H(water) \dashrightarrow C_3S_2H_8 + CH$$

$$2C_2S + 11H(water) \dashrightarrow C_3S_2H_8 + 3CH$$

On hydration of the Tricalcium Silicate (C_3S) and Dicalcium Aluminate (C_2S)-a gel of calcium silicate plus water ($CaO.SiO_2.H_2O$+ $Ca(OH)_2$ is produced.

$$3CaO.SiO_2 - 2CaO.SiO_2 + H_2O \Rightarrow CaO.SiO_2.H_2O + Ca(OH)_2$$

C-S-H is a poorly crystalline material with a variable composition that forms extremely small particles less than 1.0 μm in size. C-S-H is the main cementitious compound; 'glue' that gives concretes its inherent strength. The structure of C-S-H becomes much more stable and resistant to subsequent environmental changes upon and prolonged moist curing or curing at elevated temperatures. Calcium hydroxide - $Ca(OH)_2$ in contrast, is a well-crystallized material with a fixed composition. $Ca(OH)_2$ contributes somewhat to concrete's inherent strength because it will form large crystals inside concrete voids, thereby reducing the concrete porosity.

2.2 SUPPLEMENTARY CEMENTITIOUS MATERIALS

The OPC is very expensive and its production is harmful to the environment. The global trend is the reduction of the Portland cement contents in the concrete mixtures with cheaper SCM to improve certain properties of concrete. Neuwald (2004) classified SCM as hydraulic and pozzolanic; this is based on their reacting

mechanisms Blended cements more common in Europe and South America. Generally they are less expensive than cement.

Standards in use in SCM blended cement and concrete are the ASTM C 618 (2005): Specification for Fly Ash and Raw or Calcined Natural Pozzolana or Use in as a Mineral Admixture in Portland cement Concrete and the ASTM C1240 (2004):Standard Specification for Silica Fume Used in Cementitious Mixtures. The European committee for standardization standard is EC- ENV 197-1(1992): Types and composition requirements for European cements also set requirements for chemical and physical characteristics for use in blended cements.

2.2.1 Hydraulic Supplementary Cementitious Materials

The Hydraulic SCMs react directly with water to form compounds possessing cement properties. Slag, a by- product of iron production is an example of such material.

2.2.2 Pozzolanic Supplementary Cementitious Materials

The pozzolanic materials such as volcanic ash, materials react chemical with calcium hydroxide $Ca(OH)_2$ to form compound possessing cementitious properties. According to Hossain and Mohammed (2006), as early as the first century the Romans had discovered that the Powder from Puteoli enabled cements and concretes to set in the presence of sea water. It also produced structures stronger than those built with lime alone; thus a Roman Architect/Engineer Vitruvius wrote that “There

is a kind of powder which by nature produces wonderful results. It is found in the neighborhood of Baiae (near Puteoli) and in the lands of the municipalities around Mount Vesuvius. This, when mixed with lime and rubble, not only furnishes the strength to other buildings, but also, when piers are built in the sea, they set underwater". In the construction of breakwaters) the masonry which is to be in the sea must be constructed in this way. Earthly material is to be brought from the district which runs from Cumae to promontory of Minerva (Sorrento), and mixed in the mortar, two parts of it to one of lime". Siddal (2000) stated that Vitruvius wrote that further that 'this powder' when mixed with lime did strengthened buildings and concrete of mortar mix of 2:1; Pozzolana-lime that was used in concrete with set underwater.

2.2.2.1 Portland Pozzolana Cement

According Neville and Brooks (2008) Portland Pozzolan Cement is an interground or a blended mixture of PC with a pozzolans. As earlier defined a pozzolan is a natural or artificial material containing silica, aluminium and iron in reactive and finely divided forms. But prior to the utilisation of a pozzolan in concrete either in partial replacement or in cement blending, Neville stated that the pozzolanic activity of the pozzolan with the PC be first be assessed by the determining the compressive strength of the mixtures with the specified replacement of the cement with the pozzolana.

American Society for Testing and Material C 618 (2005) specified the measurement of pozzolanicity of the pozzolan by evaluation of the pozzolanic activity index with cement and lime. The Pozzolanic Activity Index (PAIC) with Portland cement as explained by Neville and Books (2008) is the ratio of the compressive strength of the mixture with a specific replacement of cement by the pozzolana to the strength of the mix without replacement. While the pozzolanic activity index with lime is the determination of the total activity of the pozzolan. BS EN 196-5(1995) compares the quality of $Ca(OH)_2$ present in the liquid phase in contact with the hydrated pozzolanic cement.

2.2.2.2 Classification of pozzolans

Kurtis (2002) classified the pozzolans into Natural and Artificial. Day (1990) affirmed that the Artificial Pozzolanas are residues of waste products of Industrial Manufacturing Processes while the natural pozzolans are main products of volcanogenic activities. The Natural and Artificial pozzolans are analysed by researchers such as Detwiler *et al* (1996); Neuwald (2004); Day (1990); and Kurtis (2002) as follows:

(a) Artificial pozzolans

The Artificial Pozzolanas can further be group into two; are residues of waste

products of major Manufacturing Industries and those from Agricultural processes. The artificial pozzolans as defined above include the following industrial pozzolans:

i) Fly ash**;** this is a by-product from the burning of pulverized coal in power plants in electricity generation. During the combustion of coal in power plants the volatile matter and carbon are burned off while most of the mineral impurities such as clays, quartz, and feldspar, melt at the high temperature. Known to be much inferior to natural pozzolan, fly ash normally contains excess amounts of carbon dioxide and sulfur trioxide, which are trapped inside the spherical envelope while the coal powder burns.

ii) Slags; In the production of cast iron (also called pig iron) if the liquid slag is rapidly quenched from a high temperature by either water or a combination of air and water, most of the lime, magnesia, silica, and alumina are held in a non-crystalline or glassy state. The water-quenched products are referred to as Granulated blast furnace slag (GBSF).These slags must be violently cooled so that they can amorphous structure can be formed. Good quality granulated blast furnace slag is a good cementitious material. It containing 30% to 40% silicate and about the same amount of calcium oxide, slag is far inferior to natural pozzolan in reactivity with the calcium hydroxide produced by cement hydration.

iii) Activated, burnt or calcined clays; the clay and shales will not show appreciable reactivity with lime unless the crystal structures of the clay minerals present are destroyed by heat treatment. A temperature on the order of 600 to 900^{o}C, in kilns is required for this purpose. The Roman in alternatives to the 'Pulvis Puteolamus' (powder from Pozzuoli) and other

pozzolanas often used these crushed, fired clays, essentially of similar composition to the clays in volcanic ash. The pozzolanic activity of the product is due mainly to the formation of an amorphous or disordered aluminosilicate structure as a result of the thermal treatment.

iv) Silica fume; this is by-product of the induction arc furnaces in the silicon metal and ferrosilicon alloy industries. Reduction of quartz to silicon at temperatures up to 2000^{o}C produces SiO_3 vapors, which oxidize and condense in the low-temperature zone to tiny spherical particles consisting of non-crystalline silica.

v) Bauxite wastes**;** Bauxite waste is an artificial pozzolan obtained by firing the waste material from the manufacture of aluminium. The minerals present are meta-kaolinite, anatase, hematite, titanium oxide, aluminium oxides and hydroxides

vi) Rice husk ash; Rice husk ash (RHA) which is also referred to as rice hulls are produced from rice husks. The husks are the shells produced during the de-husking operation of rice. As they are bulky, the husks present an enormous disposal problem for centralized rice mills. A highly pozzolanic ash can is produced by controlled combustion when silica is retained in non-crystalline form and a cellular microstructure. Each tone of paddy rice produces about 200 kg of husk, which on combustion yield approximately 40 kg of ash.

Rice husks approximately consist of 40-45% cellulose, 25-30% lignin, 15-20% silica and 8-15% moisture. When ignited at the correct temperature an

ash of almost pure silica is produced. To reduce the amount of waste materials, rice husks are incinerated by controlled combustion to remove the lignin and cellulose, leaving behind an ash composed mostly of silica (retaining 20% of the mass of rice husks. To obtain lower-permeability concrete, RHA can be added in amounts of 5 to 15% by mass of cement. The benefits of using RHA are higher compressive strength, decreased permeability, resistance to sulfate attack, resistance to acid attack, reduction of surface cracking in structures, excellent resistance to chloride penetration, and excellent performance under freezing-and-thawing cycling.

vii) Other artificial pozzolans agricultural wastes products include materials such as, burnt banana leaves, ground nut shell ash, burnt sugar cane stalks and bagasse ash which require firing to induce its pozzolanicity.

(b) Natural Pozzolanas

The natural pozzolans are products of volcanic eruptions and a made up of pumice ash, volcanic ash, volcanic dust, Rheinish trass**.** Volcanic tuffs, pumicite, diatomaceous earth, cherts and opaline shales, diatomaceous earth, and opaline shales all as products of volcanogenic activities. The property of each volcanic deposit therefore, depends on the nature and type of eruptions. Their chemistry consequently differs from deposit to deposit containing oxides of silica, alumina, calcium, magnesium, trace elements and alkalis in varying degrees and characteristics as reported by Intermediate Technology Development Group(ITDG,

2004).There are two forms of the natural pozzolans; Natural pozzolan requiring no energy inputs and those that energy inputs are necessary.

i) Natural pozzolan requiring no energy inputs prior to grinding.

Those derived from volcanic rocks in which amorphous glass is produced from fusion: these include volcanic ashes (pumicite), pumice, pumice stone, obsidian, scoria, tuffs (Italian pozzolans and German trass) and andesites. Trass is a "light coloured, silicified trachytic tuff".

Volcanic glasses; Santorin earth are volcanic (glasses) deposits produced from a natural deposit of volcanic ash which was formed at about 1600-1500 B.C. after a tremendous explosive volcanic eruption on the Island of Thera in the Agean Sea. They are also found in Greece, Bacolis (Italy) and the Shirasu Pozzolan of Japan. These pozzolan derive their lime-reactivity characteristic mainly from the unaltered aluminosilicate glass.

Volcanic tuffs**;**The unconsolidated pyroclastic (ash) deposits of Campi flegrei and Vesuvius volcanic fields, Rheinish trass is one of the early known natural pozzolan of volcanogenic origin found in the Valley of the Rhine River in Germany independent of the pozzolan from Pozzuoli.

Rheinish trass; this is one of the early known natural pozzolan of volcanogenic origin found in the Valley of the Rhine River in Germany independent of the pozzolan from Pozzuoli. The pozzolanic materials

compose of is a trachytic tuff (this is volcanic glass).

Pumice ash or the tuff; this comprised of trachyte and are found near Naples and Segni in Italy. This Pozzolana is a product of an explosive volcanic eruption in 79 A.D. at Mount Vesuvius, which engulfed Herculaneum, Pompeii, and other towns along the bay of Naples. The deposit near Pozzuoli is the source of the term "pozzolan" given to all materials having similar properties.

ii) Natural pozzolan requiring energy inputs prior to grinding.

Those derived from rocks or earths which contain opal. The opal is formed from precipitation of silica from solution or from the remains of organisms. researchers such as Bhatty (1955), Day (1990), Detwiler *et al* (1996),Hashmi (2008), Neville (1996) and Kurtis (2002) described the classes of the materials as follows;

Gaize pozzolan; this is a porous sedimentary rock consisting mainly of opal. The material is usually calcined at temperatures around 900 ^{O}C before it is used as a pozzolan. Gaize is found in France.

Metakaolin; Metakaolin ($Al_2O_3.2SiO_2$) is a product of kaolin (containing clay) produced by heating the material over a temperature range of about 600 to 900^{o}C. This keep silica and alumina in amorphous state then pulverized to particles smaller than 2 microns. The product is a highly reactive pozzolan of white color that is especially suitable for use in architectural concrete.

Reactivity of Metalkaolin is dependent upon the amount of kaolinite contained in the original clay material. The use of Metalkaolin as a pozzolanic mineral admixture has been known for many years, but has grown rapidly since approximately 1985. The average particle of high-reactivity size of Metalkaolin of high-reactivity Metalkaolin ranges from 0.5 to 20 mm.

Diatomaceous earths**;** these are pozzolans characterised by hydrated amorphous silica this composed of skeletal shells from the cell walls of many varieties of microscopic aquatic algae. The largest known deposit is in California. Calcined clays and shales; these will not show appreciable reactivity with lime unless the crystal structures of the clay minerals present are destroyed by heat treatment.

2.2.3 Cement Blending

Wang (2003) defined Blended Cement (BC) as cement mixtures containing Portland cement and one or more SCM with the potential benefits of reducing the overall concrete costs; and improving concrete workability, durability and long term strengths. ASTM C 150 (2005) classified BC as cement containing SCM. Horst (2001) elucidated further that BC as a technical term, often refers to cement products that are factory blended by cement companies. For specification purposes BC are designated by type depending on their chemical composition and or performance requirements.

2.2.3.1 Blended cement standards

The American Society for Testing and Material C 595 (2006) recognises the following primary classes of blended cements referred to as modified Portland cements. The term "modified Portland cement" usually refers to blended cement containing mostly Portland cement along with a small amount, less than 15%, of mineral additive.

i) Slag cement; Type S - consist of slag and PC and/ or hydrated lime; the slag content ≥70% by mass. Type S-A - air entraining slag

ii) Portland blast-furnace slag cement; Type IS - Portland blast-furnace slag cement for use in general concrete construction. Slag use for the cement is less than 25% by mass of the finished cement.

iii) Slag - Modified Portland cement: Type I(SM); this is used in general construction. The cement is manufactured by combining Portland cement or Portland blast-furnace slag cement and a fine pozzolan. The pozzolan content is less than 15% by mass of the finished cement.

iv) Portland Pozzolan cements; Type IP- Portland Pozzolan cement for use in general Concrete construction. This type of cement is made from either from Portland cement or from Portland blast furnace slag cement blended and/ or interground with finely divided pozzolan. The pozzolana constitutes is 15-40% by mass of Type IP cement.

Type P- Portland Pozzolan cement for used in general construction where high strengths at early ages are not a requirement. The pozzolana constitutes is 15-40% by mass of Type P cement.

v) Portland- modified Pozzolan cement; Type I (PM) - Portland- modified Pozzolan Cement for use in general concrete construction. This type of cement is produced the same way as Type IP except that the pozzolan content is less than 15% by mass of cement.

2.2.3.2 Industry waste products as additives for blended cement

The use of blended cements in Europe is very common and is continuing to increase. Stiff competition and strict environmental regulations have forced European cement manufacturers to focus their attention on blended uses and promotion specific types of blended cements according to the SCMs available. For instance Slag is widely used in Germany, the Netherlands, and Belgium. While Norway, Iceland, and France, manufacture Blended Cements with silica fume. The most commonly used additives to manufacture blended cement today are waste products from industry processes;

(a) High-Calcium Fly Ash (Class C) HCFA is the residue collected from the smokestacks of coal-fired power plants generally using lignite and/or sub bituminous coals. Class C fly ashes are in themselves mildly cementitious, and have been combined with lime or even calcium carbonate soils to produce moderately strong concrete.

(b) Ground Granulated Blast Furnace Slag is the ground residue from iron smelters, and is also mildly cementitious in itself, but hugely pozzolanic in combination with water and cement. Its usage dates back more than 200 years and is widely used in Europe.

(c) Highly Active Pozzolans Condensed Silica Fume; this is a waste product of the silicon metal industry, and is a super-fine powder of almost pure amorphous silica. Though difficult (and expensive) to handle, transport, and mix, it has become the chosen favorite for very high-strength concretes (such as for high rise buildings). It is often used in combination with both cement and fly ash.

(d) Rice Hull (or Husk) Ash; RHA is the least known of the four pozzolans discussed, but considered promising on a global scale. The world's primary staple crop is rice, the milling of which generates 100 million tons of hulls, or chaff, annually. Like the straw, hulls have historically been burned in the fields, but the resulting pollution is increasingly causing health problems. Research in India and the United States of America (USA) has shown that if the hulls (or straw) are burned at a controlled low temperature, the ash collected can be ground to produce a pozzolan very similar to (and in some ways superior to) silica fume.

2.2.3.3 Use of natural pozzolan as additives for blended cement

Volcanic deposits and materials resulting from volcanic activities (during the volcanic eruption), the magma and the lava produced with rich silica have

excellent pozzolanic characteristics. In the USA and Italy and some European countries, experts in concrete research are now recommending the increase use of the pozzolans in cement blending or partial replacement of the OPC in concrete mixtures.

In the light of economic conditions and the abundant evidence both from research and in the field, it seems inevitable that regular and high-volume usage of pozzolans will become standard practice in cement blending in the concrete industry (Detwiler et al, 1996); as the utilisations of the SCM in the concrete mixtures do have economic, technical and environmental benefits.

2.2.4 Benefits Cement Blending

2.2.4.1 Economics Benefits

(a) Increase production capacity;

Detwiler *et al* (1996) reported that a major economic benefit in the use of the SCM is that substantial increased in the capacity of a cement manufacturing plant can be achieved without the installation of a new kiln; furthermore the production of alternative cements incorporating the SCM saved power and energy as little or no energy inputs are required prior to the utilisations. Whereas in the Manufacturing of Ordinary Portland, European Commission (2001) affirmed that an average energy cost on the production of one ton of cement is 50% of the total cost of the cement production. This is because as Day (1990) stated, Portland cement, the primary

"glue" for structural concrete, is expensive and unaffordable for a large fraction of the world's population. Most abundant pozzolans, are widely available, and could typically costs about half as much by weight as cement. Blended cements that replace up to 60% of the Portland cement with fly ash are successfully used in structural applications. Since Portland cement is typically the most expensive constituent of concrete, the application of natural pozzolans to partially replace the OPC do have economic benefits as they are cheaper to process (with low technological inputs and capital out lay) and requiring no burning of any sort (except grinding)prior to their applications. The volcanic deposits could thus, argument the local cement productions and also reduce the cost of cement particularly a developing communities.

There are other Commercial Cementitious and Pozzolanic Materials. The most commonly used additives to manufacture blended cement today are waste products from industry such as High-Calcium Fly Ash, Ground Granulated Blast Furnace Slag. Its usage dates back more than 200 years and is widely used in Europe. The degree of economic savings that can be achieved with the use of Portland pozzolan cements is enormous.

In the United States of America (USA), Europe and some other countries many

experts in concrete research are now recommending the increase use of pozzolans, especially the readily available fly ash. In the light of the economic advantages and to also meet up the demand of the commodity in the developing communities

particularly of the African continents, it is inevitable that regular and high-volume usage of pozzolans will become standard practice in the concrete industry world over. But the developing nations lag behind in the use of the SCM. Portland cement.

(b) Carbon reduction initiative

As stated earlier, the cement industry is one of the most energy intense sectors and a significant source of greenhouse gas (GHG) emissions. Econoler International (2009) reported that this industry accounts for about 5% of the annual global anthropogenic carbon dioxide emissions; representing about 1,800 million tons of CO_2 emissions in 2005 from the use of fossil fuels, the chemical reaction during clinker processing and the use of electricity to grind raw materials and finished cement product. Thus according to Econoler International (2009), the World Bank in 2006 introduced and launched an incentive program entitled 'Carbon Finance Assistant (CF- Assistant) initiative' to implement offsets for carbon dioxide emissions in excess of carbon dioxide standards; this is in order to control pollution from the GHG emissions from the manufacturing industries. This capacity building and technical assistance programme is to enable full participation of developing countries in the Carbon Market Initiative (CMI). Econoler International (2009) explained further the CMI is an emission trading market-based approach used to control pollution by providing economic incentives for achieving reductions in the emissions of pollutants in the manufacturing industry. The ultimate goal of this effort is to expand business opportunities for cost-effective energy savings and clean technology transfer that will be of benefit to the economic sectors of the developing

countries and emerging economics in the Carbon Market. The initiative is to look at the existing investments in the cement industry and identified new carbon mitigation opportunities that can decipher the GHG) emissions can be by fuel switching with biomass and clinker substitution (partial replacement) with alternative raw materials in cement production (such as the natural pozzolans).

Econoler International (2009) reported that as 2009, 203 projects initiated by the cement industry globally in adopting what is referred to as 'cleaner, sustainable CO_2 emission mitigation' options. Only three of such in the offing in three African countries, these are Senegal, Kenya and Nigeria. In Nigeria, is Lafarge - West African Portland Cement Company (WAPCO) proposing a Blended Cement Project at the Shagamu and Ewekoro Cement Plants? The blended cement project intends to gradually reduce the clinker content of WAPCO's Shagamu cement production and that of Ewekoro Cement Works by about 86.6% and 84.7% in 2005 to 75% in 2017. The project aims to manufacture and sell a new type of cement referred to as blended cement categorized under new cement Standard-Nigerian CEM II/A-L 32.5N. The project is being implemented at the two WAPCO Cement production sites located in Shagamu and Ewekoro in South West Nigeria. The production capacities of the two cement works are 1.32 million tones and 1.0 million tons of cement per year for Shagamu and Ewekoro respectively. Presently the baseline emissions for the companies are 0.8483 ton CO_2 emission for every ton of Blended Cement (BC) and 0.8185 ton CO_2- emission /tone BC for the Shagamu and Ewekoro

plants respectively. The clinker-to-cement ratio in the project scenario is 0.75. The projects emissions are estimated at 0.3688 ton CO_2/ton for Shagamu and 0.4603 ton CO_2- emission per ton for Ewekoro blended cements. The expected emissions reduction from the project is 1,324,140 ton CO_2- emissions per year with respectively 865,789 ton CO_2 - emissions and 458,351 ton CO_2 - emissions for Shagamu and Ewekoro.

2.2.4.2 Energy benefits

Day (1990) reported that the cement industry consumes about 2% of the global primary energy production which is almost 5% of the total industrial energy consumption. The benefits of the use of SCMs into concrete production or cement blending are thus, viewed first in the direct reduction of the cost of cement and the overall cost of housing products. Struble and Godfrey (2004) reported that a total energy demand of 4.88MJ to produce 1 kg of Portland Cement (4,880MJ per ton).The pyroprocessing (calcinations) stage alone gulps for 4.041MJ (4,041MJ per ton), about 83%. The use of the Natural Pozzolans which requires no burning of any sort will require only 17 % of the energy; thus the extra energy can be converted to other uses. The European Commission (EC, 2001) puts the average energy cost on the production of one ton of cement at 50% of the total cost of the production per ton of Portland cement. Jha and Prasad (2004) stated that by the use of Fly Ash (25%) in cement blending for Portland pozzolana cement in India, the Energy Savings was 20 % .

2.2.4.3 Technical benefits

The technical benefits as reported by Azmar International (2003) are increased in compressive strength, fluidity and resistant of concretes to abrasions, sulphate, and chloride attacks freezing and thawing. There are also reductions in expansions, heat of hydration, permeability and voids, in concretes. Alkali-aggregate reactions and micro cracking in concretes also decrease. Furthermore, autogenous activities and concrete durability are enhanced. Neuwald (2004) stated in his works that the materials are blended into concretes to improve workability, increase strength and enhance durability of concretes. Detwiler *et al* (1996), asserted further that other advantages in include the control over the potential for alkali-silica reactivity, improved concrete performance and performance standards (due to more flexibility to the producer); and would also extends plant capacity without an addition of a kiln.

2.2.4.4 Environmental benefits

The environmental benefit according to Horst (2001) is that CO_2 emissions release to the atmosphere is reduced. This is because in every ton of Portland cement produced, the CO_2 released to the atmosphere by the burning fuel is between 1 to 1.25 tons. Thus, a replacement of any quantity of the OPC directly reduces the emissions of CO_2 to the atmosphere.

A number of environmental issues, especially carbon dioxide emissions, can potentially affect the cement industry. Carbon dioxide reduction strategies by the

cement industry are aimed at lowering emissions per ton of cement product. These strategies include installation of more fuel-efficient kiln technologies, partial substitution of non carbonate sources of calcium oxide in the kiln raw materials, and partial substitution of supplementary cementitious additives, such as pozzolans, for Portland cement in the finished cement products such as concrete. The use of SCM will lessen the burden of the green gasses release cement calcinations. The use of waste materials from burning fossil fuels and the manufacturing of steel are generally in plentiful supply in certain regions of the globe. However, where these waste products of industrial processes are not available; substitutes such as natural pozzolans are potential cementitious materials, particularly in developing communities with historic volcanic deposits.

Altwair and Kabir (2010) affirmed further that the benefits of using these pozzolanic materials include reduction in greenhouse gas releases, and other pollutant emissions from the mining of limestone to calcinations and grinding. Pozzolana cement manufacturing is environmental friendly as it has little or no green house gases. in ordinary portland cement, production half a ton of CO_2 is release by burning fuel for every ton of cement produced (Lynne and Adam, 2000; Azmar; 2003).Thus it is environment friendly for any cement production that will reduce the emission of CO_2 to the atmosphere. Thus, blending of OPC with the Pozzolans has the benefits of reducing CO_2 emissions (the green house impacts are large) and energy consumption. Day (1990) stated that further environmental advantage of natural

pozzolan applications in cement blending or partial replacement of OPC in concrete mixes is that the volcanic deposits mining need no blasting.

Mining pozzolan is generally easy due to the youthfulness of the rock and closeness of it to the surface. Pozzolan is usually mineable by open pit methods- at or near the surface- over broad areas. Usually Pozzolan mining generally takes place in remote areas, and its environmental impact is not severe. The green gas effects on the environment can be reduced by the addition of supplementary cementitious materials ground and mixed to reduce the amount of Portland cement in a concrete mix.

2.3 CHARACTERISTIC OF POZZOLANS

2.3.1 Pozzolanic Activity

Neville (1996) appraisal of cement hydration affirmed that $Ca(OH)_2$ is a soluble compound; meaning it will move throughout the pore system in the presence of water, making it extremely vulnerable to chemical attack; stressing that C-S-H is a superior reaction product because it creates a denser microstructure that increases strength, reduces the permeability of the concrete and improve its resistance to chemical attack. But the formation of $Ca(OH)_2$, on the other hand, increases the porosity and is susceptible to sulphate attack. Neville and Books (2008) stated that when the pozzolana is added to the hydrating cement; Silicate- Pozzolana + $Ca(OH)_2$ + H_2O a gel of the cementitious substance of Calcium (a strong gel) is produced. Neville (1996) stated that the reaction is referred to as the Pozzolanic

Reaction of the Pozzolan**.** Thevash (1979) averred that the Pozzolanic Activity of a pozzolan is due to the siliceous compounds in the pozzolana reacting with the $Ca(OH)_2$ to form stable substances. The pozzolanic reaction converts the soluble $Ca(OH)_2$ to C-S-H increasing the overall strength and durability of the concrete.

Pozzolana + $Ca(OH)_2$ + H_2O => C-S-H (a strong gel).

Uniquely with the pozzolanas, this reaction continues to produce additional Calcium Silicate Hydrate(C-S-H).The formation of this *gel* prevents the water soluble compounds from migrating out of the concrete and thus makes the cement paste denser; with no voids and invariably a reduction in the permeability of the concrete and thus stronger concrete. The continued reaction of the pozzolana with the liberated $Ca(OH)_2$ as asserted by (Zhanng *et al*, 1996) is termed The Pozzolanic Activity of the pozzolan. The formation of this *gel* prevents the water soluble compounds from migrating out of the concrete and thus makes the cement paste denser - with no voids and invariably a reduction in the permeability of the concrete and thus stronger concrete. When water is mixed with Portland cement, the product sets in a few hours and hardens over a period of weeks. These processes can vary widely depending upon the mix used and the conditions of curing of the product, but a typical concrete sets; that is, it becomes rigid in about 6 hours, and develops a compressive strength. The compressive strength and hardening time period is shown in the Table 2.1.

Table 2. 1. Compressive Strength and Hardening Time Period of Concretes

Hardening Time period (Hours)	Compressive Strength (MPa)
24	8
72	23
168	35
672	41

Source; Sharma (2008).

In principle, according to various researchers for examples Sharma (2008), Neville (1996), and Neville and Books (2008), the strength continues to rise slowly as long as water is available for continued hydration, but concrete is usually allowed to dry out after a few weeks, and this causes strength growth to stop. Setting and hardening of Portland cement is caused by the formation of water containing compounds, forming as a result of reactions between cement components and water. Usually, cement reacts in a plastic mixture only at water/cement ratios between 0.25 and 0.75. The reaction and the reaction products are referred to as hydration and hydrates or hydrate phases, respectively. As a result of the reactions stiffening can be observed which is very small in the beginning, but which increases with time. The point in time at which it reaches certain level is called the initial setting. The final consolidation is called final setting, after which the phase of hardening begins. Stiffening, setting and hardening are caused by the formation of a microstructure of hydration products of varying rigidity which fills the water filled interstitial spaces

between the solid particles of the cement paste, mortar or concrete. The behaviour with time of the stiffening, setting and hardening therefore depends to a very great extent on the size of the interstitial spaces that is on the water/cement ratio.

The hydration products primarily affecting the strength are calcium silicate hydrates (C-S-H).Calcium silicates or silicate constituents make up over 70 % by mass of silicate-based cements. The hydration of these compounds and the properties of the calcium silicate hydrates produced are therefore particularly important. Calcium silicate hydrates contain less CaO than the calcium silicates in cement linker, so calcium hydroxide is formed during the hydration of Portland cement. This is available for reaction with supplementary cementitious materials such as ground granulated blast furnace slag and pozzolana. The simplified reaction with water may be expressed as:

$$2Ca_3OSiO_4 + 6H_2O \rightarrow 3CaO.2SiO_2.3H_2O + 3Ca(OH)_2$$

This is a relatively fast reaction, causing setting and strength development in the first few weeks. The reaction is expressed as;

$$2Ca_2SiO_4 + 4H_2O \rightarrow 3CaO.2SiO_2.3H_2O + Ca(OH)_2.$$

This reaction is relatively slow, and is mainly responsible for strength growth after one week. Tricalcium aluminate hydration is controlled by the added calcium sulfate, which immediately goes into solution when water is added. To begin with, ettringites is rapidly formed, causing a slowing of the hydration.

2.3.2 Unique Characteristics of Natural Pozzolans

Unique characteristic of Azmar (2000) natural pozzolan is the autogenous healing of concrete structures produced with the Portland Pozzolan Cement; this its inherent ability to heal or reduce cement cracks within the concrete. This is achieved by means of its continued pozzolanic reaction with the calcium hydroxide freed from the hydration of Portland cement.

Furthermore pozzolanic characteristic of the Azmar (2000) natural pozzolan is that it reacts quickly with calcium hydroxide and formed additional C-S-H. Thus, preventing the water soluble compound from migration out of the concrete (this increases the fluidity of concrete), thereby making the cement paste denser (with no voids).The result is that reductions permeability and voids were achieved. This moderation of the water content of the fresh was found not only to aids the to lower the water content of the fresh concretes, but also the reduction in the expansions and shrinkage of concrete; therefore, the creep and micro-cracking were significantly reduced without the process of water cooling (Practical Action, 2007).The lower water requirement with high fluidity, self-leveling and compression in normal operations, the bulk volume of concrete in the constructions are placed and compacted by use of high frequency poke vibrators. The rapid vibration induces segregation phenomena in all orders of magnitude in the fresh concrete for example, stone segregation, internal bleeding giving bonding failures in homogeneous cement paste and air void systems' natural pozzolan Portland cement mixture can achieve

high concrete fluidity with low w/c ratio. Thus, the resulting concrete can be self-leveled and self-compressed without the use of a vibrator.

The pozzolanic reaction between natural pozzolan and calcium hydroxide happens after the lime and di-calcium silicate ($2CaO.SiO_2$) in the cement begins to hydrate (Neville and Brook, 2008). At the early stage of curing, the compressive strengths of concrete made with natural pozzolan (from Pagan Island) substituting Portland cement mixture were slightly lower than reference OPC. As time went up, natural pozzolan kept on reacting with the calcium hydroxide produced by cement hydration and increasing the compressive strength.

Another unique characteristic of the addition of the natural pozzolan in concrete that have increased the engineering applications of the pozzolans is its increases resistance to chloride attack. Concrete deterioration caused by the penetration of chloride occurs quickly when chloride ions react with calcium hydroxide to form hydrated calcium hydroxide. The expansion of hydrated calcium hydroxide enlarges the micro-cracks in concretes and increases the permeability that causes quicker chloride penetration and more damage from freezing and thawing action. But the natural pozzolan added into cement can react with almost all the free calcium hydroxide and form a much denser paste. Thus, the penetration of chloride can be minimized and the penetrated chloride ions cannot find calcium hydroxide with which to react (Neville, 1998).

2.4 EFFECTS OF NATURAL POZZOLAN ON CONCRETE PROPERTIES

The most effective method for evaluating the performance of a concrete containing a natural pozzolan and establishing proper mixture proportions for a specific application is the use of trial batches and a testing program. Because some natural pozzolans perform better than others and project requirements differ, optimum proportions for a given combination of pozzolan and Portland cement cannot be predicted. When used as a replacement for a portion of Portland cement, natural pozzolan replaces an equal volume or equal mass of the cement. For the reason that the density of natural pozzolans is typically less than the density of Portland cement, mass replacement results in a greater volume of total cementitious materials than when volume replacement is used at a given percentage. The mass of natural pozzolan employed may be greater than that of the replaced cement if the concrete is proportioned for optimum properties and maximum economy.

2.4.1 Effect on Fresh Concrete

A number of finely divided mineral admixtures cause a major increase in water requirement; others have little or no effect on water requirement, and still others typically reduce the water requirement of concrete in which they are used .Natural pozzolans affect the water requirement of the concrete and therefore the cement content. A natural pozzolan should be considered as part of the cementitious material. The amount of natural pozzolan used varies significantly based upon the

activity of the pozzolan. Day (1990) asserted that some natural pozzolans are used in a range of 15 to 35% based upon the mass of the total cementitious material in the concrete; also more reactive natural pozzolans can be used in lower concentrations of 5 to 15% by mass of total cementitious material; however, such low concentrations may increase expansion resulting from the altered silica reaction in the presence of some alkali-reactive aggregates. The optimal amount of natural pozzolan depends on where the concrete is used and the specifications for the work. Most natural pozzolans produce a cohesive mixture that maintains a plastic consistency (no increase in total water content of the concrete is required), improving the workability of concretes. Azmar International (2000) asserted that blending of Ordinary Portland Cement with Natural Pozzolana for the production of concrete hah higher workability. Typically, natural pozzolans absorb water from the mixture and hold this water in the system allowing for improved finishing.

The use of the natural pozzolan can also reduce bleeding and segregation, and increase the strength of concrete. Drying shrinkage and absorption of the hardened concrete are not greatly affected. Low water content is also achieved without use of a water-reducing admixture. For example, coarse pozzolan of poor particle shape, such as finely divided pumicite, may require an increase in water content of the concrete for a given slump. This may contribute to increased bleeding and segregation of the fresh concrete. Therefore, with such mixtures, bleeding tends to reduce homogeneity of the concrete. This lack of bond between paste and aggregate

reduces the potential strength of concrete and increases permeability and absorption. These undesirable effects can be reduced by increasing the ratio of surface area of solids to volume of water in the paste. This generally increases the stiffness of the paste and, at a given slump, effects a wider separation of the aggregate particles in the concrete. Increasing the amount of a suitable pozzolan usually increases the ratio of surface area of solids to volume of water.

The setting-time characteristics of concrete are influenced by ambient and concrete temperature; cement type, source, content, and fineness; water content of the paste; water soluble alkalis; use and dosages of other admixtures; the amount of pozzolan; and the fineness and chemical composition of the pozzolan. When these factors are given proper consideration in the concrete mixture proportioning, an acceptable time of setting can usually be obtained. The actual effect of a given natural pozzolan on time of setting may be determined by testing, when a precise determination is needed, or by observation, when a less precise determination is acceptable. Pressures on formwork may be increased when concrete containing a natural pozzolan is used if increased workability, slower slump loss, or extended setting-time characteristics are encountered.

2.4.2 Effect on Hardened Concrete

2.4.2.1 Compressive strength

Concrete containing a pozzolan typically provides lower permeability, reduced heat of hydration, reduced alkali-aggregate-reaction expansion, higher strengths at later

ages, and increased resistance to attack from sulfates from seawater or other sources than concrete that does not contain pozzolan. The effect of a natural pozzolan on the compressive strength of concrete varies with properties of a particular pozzolan and with the characteristics of the concrete mixture in which it is used. The compressive strength development is a function of the chemical interaction between the natural pozzolan and $Ca(HO)_2$ from Portland cement hydration. The cements and pozzolans contribute to strength not only because of their chemical composition but also because of their physical character in terms of particle packing. Early strengths can be increased by substituting the pozzolanic material for the cement on an equal mass basis or -to-one for the cement replaced, provided that the increase in the amount of pozzolanic materials does not significantly increase the w/c so that the required strength of the concrete is not achieved. A natural pozzolan of high chemical activity, such as metakaolin, can sometimes increase early-age strengths, even when used as a replacement for cement, either by an equal mass or by volume in an amount greater than one-to-one for the cement replaced.

2.4.2.2 Durability of concretes

The compressive strength and flexural strength will continue to increase for a long time. Jackson *et al*(2003) asserted that this unique characteristic of the pozzolan is one of the main reasons why many great ancient structures have lasted for over two thousand years. The increases the compressive strength of concrete and makes the concrete matrix denser and stronger. Addition or partially replacements of portland

cement in concrete or mortar also prevents the formation of pulpy, crispy or water soluble materials in the finished concretes thus increase the durability of the concretes. Furthermore, partial replacements or addition of natural pozzolans to Portland cement in concrete do increase resistance of concretes to aggressive attack by seawater, sulfate-bearing soil solutions, and natural acid waters. The relative improvement is greater for concrete with low cement content. The use of a pozzolan with sulfate-resistant Portland cements may not increase sulfate resistance and, if chemically active aluminum compounds are present in the pozzolan, a reduction in sulfate resistance of the concrete may result.

Addition of a pozzolan such as the natural pozzolan of volcanogenic origin promotes a healing mechanism of fractures within concretes; reduction in alkali-aggregate reaction and cement carbonation; thus invariably boosting of the concrete durability. Experiments by Azmar (2000) show that substituting only 25% of Pagan natural pozzolan for OPC can reduce alkali-silica expansion by 70%. This is attained by the trapping the alkalis within the paste in the form of alkali-silica gel, the silica in nature pozzolan renders the alkalis in the Portland cement unavailable for further reaction. According to Jackson *et al* (2003), it is this chemistry of the Natural Pozzolanas that account for the unique characteristics of the pozzolan when used in production of portland pozzolan concretes using the natural pozzolan as mineral additives or in partial replacements of the portland cement in the concretes and mortars production.

Azmar International (2000) thus reported that based on its works on natural pozzolans of Pagan Island and the Millows the enhancement of concrete strengths and durability are achieved on blending of Ordinary Portland Cement with Natural Pozzolana in concretes production. Once the natural pozzolan and the $Ca(OH)_2$ activity starts, pozzolanic reaction begins and will continue many years leading to the lithification of the structure forming a rocky mass. Therefore, it helps the concrete to durably resist abrasion. Concrete durability is also enhanced by reduction in chlorine penetration due to the reaction of the free calcium hydroxide (produced by cement hydration) with the Natural pozzolana. Cement carbonation due to the continued reaction of part of the sodium hydroxide with silica to form water soluble alkali-silica gel and part with carbon dioxide is also reduced. The blending of Portland boosted resistant to sulfate attack and frost action, reduction in alkali-aggregate reaction and the eliminations of the formation of the ettringites and thaumsites. Ettringites are formed as a result of reactions between gypsum and calcium aluminate hydrate Gypsum; Gypsum ($CaSO_4.2H_2$) + calcium aluminate hydrate (C-A-H) → $C3A\text{-}3CaSO_4\text{-}3H_2O$ (effringite). While thaumasites are as results of the combination of gypsum, calcium carbonate and calcium-silicate-hydrate; - Gypsum ($CaSO_4\text{-}2H_2O$) + calcium carbonate + C-S-H → $CaCO_3\text{-}CaSiO_3\text{-}CaSO_4\text{-}15H_2O$ (thaumasites).Ettringites and thaumasites are harmful as they expand concretes. All these reactions result in an expansion and disruption of concrete. Azmar (2000) reported that thaumasites in particular was accompanied by a very severe damaging effect which is able to transform hardened concrete into a pulpy

mess. Natural pozzolan that contains virtually no sulfate in itself and can quickly react with free calcium hydroxide to form additional C-S-H which makes the paste much denser. Therefore, it eliminates the formation of gypsum, ettringites and thaumasites.

The importance of the minerals that are present in small proportions has not been clearly determined. Although any siliceous material, if fine enough, will react with lime, the other impurities, especially aluminates and alkalis may play a critical role in determining the rate and extent of reaction. The nature of the gases liberated during the solidification of the pozzolans at the time of volcanic eruption may play a key role in determining the amount and nature of these "impurities", and thus the reactivity of the material.

2.5 SPECIFICATIONS, REQUIREMENTS AND TESTS FOR POZZOLANS

2.5.1 Standard Specifications

Where a natural pozzolan is to be used with Portland cement in concrete,
ASTM C 618 (2005) sets chemical, physical and performance requirements to be attained for the materials prior to their utilisation; and classified the Natural pozzolans are as Class N pozzolans. The American Concrete Institute (2001) defined this class of pozzolan as raw or calcined natural material (volcanic ash or pumicite, opaline chert and shales, tuffs, and some diatomaceous) that has pozzolanic properties. The ASTM C 618 (2005) provides specifications for Type N pozzolan

which include further the natural pozzolans which may or may not be processed by? calcinations to induce satisfactory properties such as clays and shales.

Specifications of Pozzolan Materials for use in the Cement Industry because of the importance of quality control on cements used in the construction industry, standard tests and certification requirements have been developed over the years in Europe, USA and other industrialized nations of the world. Day (1990) reported that the specifications for the use of natural pozzolans in OPC concrete also exist in other countries such as Bulgaria, Czechoslovakia, Iceland and South Africa, and Morocco, Portugal *et cetera;* countries which officially permit pozzolans: cement blends to be specified according to the standard for cement allow anywhere from 10% replacement 50% replacement with Italy adhering strictly to performance specification and had no set limits on the amount of pozzolan that can be used. There are however no specific or standard percentage of replacement of OPC with the pozzolan. Horst (2001) asserted further that it is possible to specify up to 70% replacement of Portland cement with some specific pozzolanic materials.

Lava Mining and Quarrying International Company (2005) based on its experiences on the Pagan and Millows Islands came up with its recommendation of a good volcanic rocks thus; that the sum oxides of silica, alumina and iron should not be less 70% by weight; those of magnesium, soda, magnesium, potash, calcium, titanium and other trace elements should not be more than 15%; the carbon content should be less than 1% ; and the Loss on Ignition (LOI) and the moisture content

(MC) should not exceed 15% and 5 % of the material respectively. Practical Neville and Brooks (2008) stated the MgO should not exceed 4%. But, Gupta and Gupta (2004) recommended 6% as a maximum value. However, Gambhir (2004) suggested that to reduce unsoundness in cement, the MgO should not exceed 0.5% by weight of the material.

American Standard of Testing Materials C 618 (2005) principally recommends 70% and 50% as a minimum value by weight of the sum of these oxides silica, alumina and iron for any material to be utilised as a pozzolanas natural pozzolans and class F fly ash, and those of and those of class C fly ash respectively. ASTM C 618 (2005) also recommended with Loss on Ignition (LOI) for Natural Pozzolan as 10 %; 6 % for class F and C fly ash; the Moisture Contents (MC) of the potential natural pozzolan and those of fly ash (class F and class C) should not exceed 3 and 5 % respectively; and fineness (max. % retained when wet sieved on 45 μm sieve).

The ASTM C 618(2005) stated further that for a pozzolan to be used in partial replacements of Portland cement concrete, the Pozzolanic Activity of the pozzolan has to be determined. This determination is carried out by the Strength Activity Index (pozzolanic activity index) of the pozzolan with the Portland cement and should not be less than 75%. The Pozzolanic Activity Index (PAIC) with Portland cement as explained by Neville and Books (2008) is the ratio of compressive the strength of the mixture with a specific replacement of cement by the pozzolana to strength of the mix without replacement and expressed thus:-

Strength Activity Index (SAI) = $\frac{A}{B} \times 100 \geq 75\%$

Where A=f'c -average compressive strength at 28 days of the test mixture % replacement.

B=f'c- average compressive strength at 28 days of the control mixture

2.5.2 Requirements

According to the ASTM C 618 requirements for Portland pozzolana cement as presented in Table 2.2

Table 2.2 Requirements for Portland pozzolans cement

Characteristic	Requirements
Chemical	
$SiO_2 + AL_2O_3 + Fe_2O_3$	70.0 min %
Maximum of Sulfur Trioxide, SO_3	4.0 max %
Magnesium oxide MgO	6.0 max %
Moisture Content (105^oC)	3.0 max%
Loss on Ignition at 950^oC	10.0 max%
Mechanical	
Pozzolanic activity index with Portland cement at 28 days	75 min %
Pozzolanic activity index with lime MPa	5.5 % MPa
Physical	
Water requirement, max,	115 max % control
Fineness	3000 cm2/g
Setting time; Initial Setting Time	30 minutes min.
Final Setting Time	600 minute max
Autoclave expansion	0.8min%

ASTM C 618 (2005)

2.5.3 Early Tests Methods for prediction of reactivity of Pozzolans

Day (1990) reported that many chemical test methods had been developed with the intention of producing "the method" in which could be used for the prediction of reactivity of a variety of pozzolans for use in concretes mixtures for some years. Some of the early tests methods for the predicting and assessment of the pozzolanic activity of potential pozzolans included the following;

2.5.3.1 Lime absorption test

This is earliest test to estimate pozzolanic activity was the proposed by Vicat in 1837. In this test lg sample of the material is added to 75m1 of saturated limewater and shaken. 25m1 of solution is extracted and titration is performed to determine the lime absorption.

2.5.3.2 Rivotin test method and Florentin method

Rivotin in 1862 proposed the estimation of the reactivity of the pozzolan by the determination of the residue of a pozzolan after heating with nitric acid and then treating overnight with 10% potassium hydroxide (KOH) solution. While the Florentin method measured the mass of SiO_2 + Fe_2O_3 + AI_2O_3 soluble in cold hydrochloric acid (HCl). These are then related to the amount of SiO_2 + Fe_2O_3 + AI_2O_3 in the pozzolan that has reacted with lime and therefore provide the measure of the pozzolanicity of the pozzolan.

2.5.3.3 Raask & Baskar method

This method was developed by Raask and Baskar in 1975; the amount of pozzolan

dissolved by hydrofluoric acid (HF) and nitric acid (HNO_3) is measured by monitoring the electrical conductivity of the dissolving solution. The conductivity is related to the reactivity of the pozzolan.

2.5.3.4 Surana and Joshi method

Surana and Joshi in 1988 proposed a modern test method is based upon the reaction of monomeric silica with a molybdate reagent. This fairly complex chemical procedure depends on "the complexation of silica and molybdate to give silica-molybdate complex that is sensitive to light. The amount of complex is monitored by spectrophotometric means. This method requires that a suitable calibration curve is established for a particular type of pozzolan which gives reasonable correlations between spectrophotometer absorbance and compressive strength.

In addition to these tests highlighted, three sophisticated chemical methods that could also give a general indication of the pozzolanic potential of a raw material are the Petrographic examination (estimating of the glass content of the pozzolan), the X-ray analysis (using X-ray diffractograms which gives correlation with mechanical strength) and differential thermal analysis of the pozzolan. But their results are hardly positive enough to justify costing of the equipment if not already available. Day (1990) assertion thus is that most natural pozzolans contain more than one active ingredient and the proportion of active and inert material can vary widely within a deposit; this is because the activity of a pozzolan is a function of many factors, including chemical composition, mineralogy, and particle size distribution,

specific surface and total surface area of the materials. conclusion is that the outcomes of these chemical tests methods could not be used for the prediction of the pozzolanicity of the pozzolan; stressed rather that exhaustive testing of the prospective pozzolans are always required; thus attempt to relate reactivity of the pozzolan with the chemistry or mineralogy of the materials proved fruitless.

2.5.4 Standard Tests Methods for Selection of Pozzolans

The most important test in respect to the determination of the performance of the pozzolan is the assessment of its pozzolanic activity Day (1990) and Meral (2004); this tests are carried out according to the tests methods of ASTM C 109/C 109M (2002).The pozzolanicity of the Natural pozzolan according to Meral (2004) is determined by finding its strength activity index (this is the pozzolanic activity index with the Portland cement);this is the ratio of the specimen of concrete cubes' compressive strength with partial replacement of PC to control specimens prepared by 100% PC according to ASTM C 311 (2005):Standard Test Methods for Sampling and Testing Fly Ash or Natural Pozzolans for Use as a Mineral Admixture in Portland-Cement Concrete.

The strength activity index calculated as follows:

Strength activity index (SAI) = –100 and be at least 75(ASTM C 618)

Where: A - Average compressive strength of test cubes.

B - Average compressive strength of control cubes.

One of the most widely used set of standards specification for selection of pozzolanic materials in the world today is the ASTM C 618 (2005); Standard

Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolans for use as a Mineral Admixture in Concrete. The standard test method used is the ASTM C 311 (2005).

2.5.4.1 Chemical characteristics of volcanic materials

(a) Oxides composition of pozzolanic materials

Pozzolanas are materials containing reactive silica, iron and or alumina. Table 2.2 shows the chemical and mineralogy of some global well-known natural pozzolans. The chemical composition of pozzolanas varies considerably, depending on the source but generally, they contained silica, alumina, iron oxide and a variety of oxides and alkalis, each in varying degrees.

Table 2.3: Typical chemical and mineralogical analysis of some natural pozzolanas

	Oxides % by weight							LOI
Pozzolana	SiO_2	AI_2O_3	Fe_2O_3	∑SAF	CaO	MgO	Alkalis†	
Santorin earth*	65.1	14.5	5.5	85.1	3.0	1.1	6.5	3.5
Rhenish trass*	53.0	16.0	6.0	75.0	7.0	3.0	6.0	-
Phonolite*	55.7	20.2	2.8	78.7	4.2	1.1	10.5	3.6
Roman tuff *	44.7	18.9	10.1	68.2	10.3	4.4	6.7	4.4
Neapolilian glass*	54.5	18.3	4.6	76.9	7.4	1.0	11.0	3.1
Opaline shale*	65.5	10.1	4.2	79.6	4.6	2.7	1.4	6.3
Diatomite*	86.0	2.3	1.8	90.1	-	0.6	0.4	5.2
Rhyolite*	65.7	15.9	2.5	70.1	3.4	1.3	6.9	3.4
Jalisco pumice**	68.7	14.8	2.3	85.8	-	0.5	9.3	5.6
Pudahuel glass**	68.8	12.7	2.3	83.8	2.4	0.7	7.5	4.3
Chilean pozzolan**	70.0	16.4	1.1	87.5	1.0	0.3	7.2	5.1
Bolivian pozzolan**	66.5	15.4	0.7	68.6	10.3	0.3	7.2	4.0
Turkish pozzolan**	68.5	11.5	0.5	80.5	-	-	2.7	14.7
Pagan Island Pozzolan***	51.28	15.41	12.97	79.68	10.27	5.31	2,57	0.09

† Na_2O +0.658% K_2O , ∑SAF –Sum Oxides of Silica, Aluminium and Iron

SOURCES: * ACI (2001) ** Detwiler al (1996) ***Azmar International (2000)

The elements that are more abundantly present greater than 5 % are the major elements; these are calcium (Ca), silicon (Si), aluminum (Al) and iron (Fe). Of these oxides silica is considered the most important Centre for Technology and Development (CTD, 2007), stated that the oxide of silica should not be less 40% by weight of the pozzolan. Lesser or minor elements are sodium (Na), potassium (K), magnesium (Mg), and sulfur (S), with concentration l-5 %. While elements occurring at less than 0.02% each as the trace elements or elements present at levels less than 100 ppm are classified as trace elements (Bhatty, 1995). Calcium is an essential component of cement, which comes from the decomposition of the primary raw material such as limestone, chalk, marl or cement rocks.

Though the chemical content of a raw material will not determine whether or not it is pozzolanic and will react when mixed with lime or OPC, the chemical test is the first assessment of the viability of a new potential pozzolanic deposit. The equipment required to perform such testing is, however, very costly and sophisticated. It is simply not possible in some developing countries to carry out such tests, and where the application of the pozzolana is such that knowledge of the characteristics on such a level is not critical, then tests of this complexity are not suitable or necessary. This presents problems for small-scale manufacturers wishing to use pozzolanas in a lime or OPC - pozzolana mix. But many of the standard tests specified in the relevant literature which cover testing of pozzolanas (in India and USA for example), require sophisticated and expensive laboratory equipment to

evaluate the pozzolanicity of a particular material. In developing countries where such equipment is beyond the reach of small-scale producers and in some instances where such laboratory facilities are often non-existent.

The determination of the oxides composition will look at three methods available and the analysis of major, minor and trace elements of the oxides composition of twenty samples as to the economy or not the necessity of undertaken complicated laboratory works in preliminary selection of potential pozzolans. Day (1990) stated that it is highly unlikely that any single test and indeed the property of a pozzolan have an overwhelming influence on its reactivity. It is important to note that good chemical reactivity may mean good performance with respect to strength but does not guarantee a durable building product.

i) The Neutron Activation Analysis method

In chemistry, Neutron Activation Analysis (NAA) is a nuclear process used for determining the concentrations of elements in a vast amount of materials; it allows discrete sampling of elements as it disregards the chemical form of a sample, and focuses solely on its nucleus (Dim ,2005). The method is based on neutron activation and therefore requires a source of neutrons. To carry out an NAA analysis the specimen is placed into a suitable irradiation facility and bombarded with neutrons, this creates artificial radioisotopes of the elements present. Following irradiation the artificial radioisotopes decay via the emission of particles or more importantly gamma rays, which are characteristic of the element from

which they were emitted. The sample is bombarded with neutrons, causing the elements to form radioactive isotopes. The radioactive emissions and radioactive decay paths for each clement are well known. Using this information, it is possible to study spectra of the emissions of the radioactive sample, and determine the concentrations of the elements within it. This theory of NAA which makes exposed material to neutron to become radioactive according to Glascock (2004) is very useful for both the qualitative and quantitative multi- element analysis of elements in sample from almost every conceivable scientific or technical fields and the application on elements are accurate, reliable and a referee method of choice when new procedures are being developed in tracing elements in samples.

The NAA has numerous advantages over other chemical analyses with includes a nondestructive process of determining the chemical composition of a sample, as the sample is not changed in any manner by chemical manipulation or the introduction of any material prior to irradiation. The technique is also time efficient for a large number of samples can be irradiated at a given time and/or counted later on a given decay schedule utilisation small amount of the sample; a 50mg is sufficient for the analysis. Furthermore it measures the total amount of the element in a material without regard to its chemical or physical form; highly precise and accurate and extremely sensitive to trace elements.

Win (2004) explained that the neutron source and gamma rays detection for the analysis of samples is the nuclear reactor; the reactor has fluxes of neutrons from

uranium fission with interacts with the target nucleus of the element and when neutron energy bombard the sample it promotes a radioactive nuclei of the target element; the radioactive nuclei then emit characteristic gamma rays, the detection of these rays indicates the presence of a particular element.The theory of the NAA is that when a material is exposed to neutron and the neutron interacts with the materials they become radioactive. This technique according to Glascock (2004) is very useful for both the qualitative and quantitative multi- element analysis of elements in sample from almost every conceivable scientific or technical fields and the application on elements are accurate, reliable and a referee method of choice when new procedures are being developed in tracing elements in samples. The identification of gamma-ray products of radio nuclides through their energies and quantitative analysis of their concentrations were achieved using the gamma-ray spectrum analysis software WINGSPAN 2004.

(ii) The energy dispersive x-ray fluorescence (EDXRF) method.

According Omotola and Onojah(2009) the X-Ray Fluorescence(XRF) technique provides one of the simplest, most accurate and economic analytical methods for the determination of the oxides of glass, ceramics and building materials; it is none-destructive and reliable for solids, liquids and powdered samples analysis. Simabuco and Filho (1994) further asserted that the XRF method is based on the measurement of x-rays intensities emitted by components of a target sample when excited by Silver-Potassium (Ag-K) X-rays (22.1 keV) from an annular excitation source of 25

mC_i Cadmium 109 (^{109}Cd).The system consists of the excitation source and a Silicon (Si) - Lithium (Li) semiconductor detector coupled to a computer controlled Analog to Digital Control (ADC) Card.

The samples are ground manually to powder with an agate mortar and pestle to grain size of less than 125µm. Pellets of 19mm diameter are then prepared from 0.3-0.5g powder with three drops of organic liquid binder and pressed afterwards at 10 tons with a hydraulic press. The measurement of the elements are performed using the Excitation Source by introducing the pellets of each of the samples into the x-ray fluorescence generator detector source emitting Silver (Ag)-Potassium(K) X-ray (22.1keV) in which all elements with lower characteristic excitation energies were accessible for detection in the samples for the analysis. The measurements of the elements are performed using the Excitation Source. The elements with the characteristic excitation energies are then accessible for detection in the samples.

The quantification of the elements is then carried out using the Emission-Transmission Method. This method involved the use of Molybdenum (Mo) as a target material as the source of monochromatic X-rays, which is excited through the sample by primary radiation and then penetrate on the way to the detector. The spectra for the samples were collected with the Cadmium 109 source and evaluated using the analysis of X- ray Spectra by Iterative Least Squares Fitting (AXIL) a soft ware program used for the analysis of the oxides of SiO_2, Fe_2O_3, Al_2O_3, MgO, CaO, SO_3, TiO_2, Na_2O, Mn_2O_3, CrO, Y_2O_3, and SrO.

According Omotola and Onojah (2009) the X-Ray Fluorescence(XRF) technique provides one of the simplest, most accurate and economic analytical methods for the determination of the oxides of glass, ceramics and building materials; it is non-destructive and reliable for solids, liquids and powdered samples analysis. Simabuco and Filho (1994) further asserted that the XRF method is based on the measurement of x-rays intensities emitted by components of a target sample when excited by Silver-Potassium (Ag-K) X-rays (22.1 keV) from an annular excitation source of 25 milicurie (25 mC_i) Cadmium 109 (^{109}Cd).The system consists of the excitation source and a Silicon (Si) - Lithium (Li) semiconductor detector coupled to a computer controlled Analog to Digital Control (ADC) Card.

(iii) Wet Chemistry (old chemistry) method

Wet chemistry is the technique of analysis involves a scientist working with liquids by hand and physically observing the results of the experiment; it is wet chemistry. This includes basic experimentation techniques like measuring, mixing, and weighing chemicals, as well as testing concentration, conductivity, density, pH, specific gravity, temperature, viscosity, and other aspects of liquids. Analytical techniques in wet chemistry are usually qualitative in nature, meaning that they attempt to determine the presence of a specific chemical rather than the exact amount. Some quantitative techniques are used in wet chemistry, however, and include gravimetric (weighing) and volumetric (titrimetric) analysis (measuring).

The Gravimetric method of Analysis is used to determine the oxides of SiO_2, Al_2O_3, SO_3 and Fe_2O_3. While the Titrimetric Analysis technique are used to determine CaO and MgO oxides of the samples. The method measure the volume occupied by the compound using a solution of known reagent, which reacts in certain way with the component under analysis.

(b) Determination of Loss on Ignition

The determinations of Loss on Ignition of the samples are undertaken by the gravimetric method of analysis. The loss on ignition, report is a part of an elemental or oxide analysis of a mineral. The volatile material lost usually consists of "combined water" (hydrants and labile hydroxyl-compounds) and carbon dioxide from carbonates. It may be used as a quality test, commonly carried out for minerals such as iron ore. For example, the loss of ignition of a fly ash consists of contaminant unburnt fuel.

The loss on ignition (LOI) is the escape of volatile substances until the mass of the substance ceases to change; resulting from strong heating (igniting) of the material at a specified temperature. The volatile materials lost usually consist of "combined water" (hydrates and labile hydroxyl-compounds) and carbon dioxide from carbonates; the residue on the ignition is referred to as a dry the mass (European Standard, 2003) and the weight lost is subsequently calculated. Loss of ignition is a test used in inorganic analytical chemistry, particularly in the analysis of minerals. It

consists of strongly heating ("igniting) a sample of the material at a specified temperature, allowing volatile substances to escape, until its mass ceases to change.

In processing industries such as lime, calcined bauxite, refractories or cement manufacture, the loss of ignition of the raw material is roughly equivalent to the loss in mass that it will undergo in a kiln. The simple test typically consists of placing a few grams of the material in a tarred, pre-ignited crucible and determining its mass, placing it in a temperature controlled furnace for a set time, cooling it in a controlled (for example water-free, CO_2-free) atmosphere, and predetermining the mass.

(c) Determination of Moisture Content

The Gravimetric method of analysis is used in determination of the Moisture content of the materials. In this method, the sample is dried in an oven at various temperatures and weight loss at each temperature is subsequently measured until constant weight is obtained. According to Anonymous (2002), the moisture contained in a material is all the substances (including water, organic solvents, decomposable and combustible products) in the samples that evaporates on heating leading to weight lost of the material; this weight is referred to as the Moisture Content of the materials.

2.5.3.2 Characteristics of portland pozzolanic cement concrete

(a) Determination of the compressive strength

The production and the testing of the compressive strength of Portland Pozzolana Concrete are undertaken in accordance with the procedure
set out in ASTM C 311(2005).

(b) Pozzolanic activity index with Portland cement

American Society for Testing and Material C 618 (2005) provides for the measurement of the Pozzolanic activity index with Portland cement concrete. These are used for the evaluation of the strength of the concrete with zero pozzolan with the specific replacements at 28 days for all the samples investigated.

(c) Pozzolanic activity index with lime

The Portland pozzolana cement pastes of partial replacements of the OPC in the concrete mixtures were used for the Pozzolana Portland Cement pastes samples investigated.

(d) Soundness of the Portland pozzolana cement

Soundness of Portland pozzolan cement materials are investigated using the Autoclave Standard Test Method of the ASTM C 151 (2005) for Autoclave Expansion of hydraulic cement. The Portland pozzolana cement pastes of percentage of partial replacements of the OPC in the concrete mixtures were used.

2.5.4.2 Selection of pozzolans

Day (1990) asserted that the selection of the pozzolans be based on performance of the materials in concrete mixtures rather than specifications of limits based on the properties such as the chemical characteristics of the materials; and that the performance (quality) of natural or artificial pozzolans for pozzolanic cement be evaluated by the strength activity analysis (pozzolanic activity index with portland cement) of the pozzolans. Performance Standards are recognised because more diverse materials and combinations of materials are being used as pozzolans to produce satisfactory building products today. Day (1990) thus, asserted that for a pozzolan to be used in partially replacing the Portland Cement (PC) in concretes, the Strength Activity Index (SAI) (the most important performance test) of the material with the PC ought to first be evaluated prior to its application. In this test (also referred to as the test on the Pozzolanic Activity of the pozzolan with PC), test the mortar specimens are moulded from a control mix and from a test mix and the concrete mixes are tested according to ASTM C 109/C 109M (2002) test method.

2.6 ENGINEERING APPLICATIONS OF NATURAL POZZOLANS

The pozzolanic reactivity of the Natural Pozzolanas has accounted for the continued existence of ancient structures to date. According to Shetty (2006) the economic attraction in the use of pozzolanic materials (with significant reduction in cost of construction) was one of the major economic drives as both the ancient and the modern structures of portland pozzolanic cement concrete showed that the pozzolans

were generally located in the vicinity of the structure, and the large amounts of concrete involved were sufficient to support the extraction costs for the partial replacement of the OPC in the concrete mixtures. In addition to economic benefits, addition of the pozzolan was found to decrease the permeability and increase the resistance to sulphate waters of concrete; reductions in expansion due to alkali-aggregate reaction, higher ultimate strength and providing an overall enhancement in the durability of the concretes were also achieved with the utilisation of the pozzolans in the concrete mixtures.

Research work by Azmar (2000) showed that adding natural pozzolan to Portland cement assisted the concrete in resisting freeze/thaw damage by minimizing the permeability, voids, cracks induced by chemical expansion and attack; and furthermore protected the steel reinforcement in an alkaline environment that is so densely sealed no liquids and gases can penetrate to cause corrosion of the steel. The paste made from the natural pozzolan-Portland cement mixture was so dense and closely cohered with aggregate that moisture only minimally penetrates its matrix, thus providing stronger concretes and durable engineering structures. These explain why the ancient structures built by the Greeks and the Romans have survived more than 2000 years of weathering. Shetty (1982) reported that the Wharf of Caligula for instance was constructed with volcanic ash from Mt Vesuvius in Pozzuoli over 2000 thousand years ago. Wilson and Ding (2007) stated further that the Romans, while mixing lime and the volcanic ash, quarried from Pozzuoli (thinking it was sand)

found out that the mixtures turned out much stronger end results, than the previously mixed materials. This discovery significantly altered the use of construction materials by Builders of the Roman Empire; but the ancient Greeks Pre-400 BC were the first civilisation to use pozzolan in their building works; and use natural pozzolana-lime mixtures to construct water-storage tanks between 700 BC and 600 BC and passed their techniques to the Romans at about 150 BC. Thus the use of The Natural pozzolanic materials is as old as the art of concrete, particularly by the Ancient Greeks and the Romans. The oldest concrete discovered so far during a road construction in 1985 in Yiftah EI-Galilee is a concrete floor date back to 7000 BC.

Detwiler *et al* (1996) affirmed that making of the hydraulic binders using natural pozzolans is not new to mankind but date back to ancient times; and reported further that Cisterns plastered with hydraulic mortars have been found in Jerusalem dating back to the times of King Solomon (10 century BC). But according to Mehelcic (2003) the natural pozzolans (binders) were abandoned for Western based Portland Cements only in the early 1900s due to market strategy rather than cost. Shetty (1982) positioned that, there exist ancient structures such as The Wharf of Caligula constructed with volcanic ash from Mt Vesuvius in Pozzuoli during the time of Julius Caesar over 2000 thousand years which are still standing to date. Pumice a light weight volcanic materials was utilised in the construction of the Dome of Pantheon (Plate I; Appendix 'A') in Rome by 125 (Jackson *et al*, 2003); the Roman

Colosseum (Plate II; Appendix ‘A’) and the aqueduct built between 38 and 52 AD (Plate III; Appendix ‘A’).

In modern times Detwiler *et al* (1996) reported that natural pozzolanas were first used in the United States of America as SCMs, by the Los Angeles Flood Control District Authority in the 1920s; in which the OPC was replaced with 20% of rhyolite pumicite in the construction of one of the abutments of the dam. Shetty (2005) also reported that high volume of fly ash was used for the construction of the shear walls of the Barker Hall Project at the University of California (Plate IV; Appendix ‘A’) here High volume fly ash was used for the construction of the shearwalls in the United States of America. Other projects include the Los Angeles Aqueduct in 1912 (Plate V; Appendix ‘A’), California Aqueduct (Plate VI; Appendix ‘A’); the Golden Gate Bridge (Plate VII; Appendix ‘A’) and the Bhakra Nangal Dam (Plate VIII; Appendix ‘A’).

Shetty (2005) reported that the Bhakra Nangal Dam is one of the biggest dams in India built with concrete containing 20% burnt clay Surkhi pozzolan replacing the OPC. China in 1984 produced 20 million tons of cements containing 5 million tons of Leotitic (a volcanic rock) and 6 million calcined coal shale; Mexico same year produced 6.30 million tons of cement containing natural pozzolans out of the 18.3 million ton by the country(Detwiler *et al*, 1996). Day (1990) reported furthermore that in Northern Europe, Portland: Pozzolan Cements, rather than lime: pozzolan cements, have developed because of the colder climate; the lime: pozzolan cements

do not harden fast enough. In Germany, concretes with the proportions 1 OPC: 1.25 limes: 2 trass: 6.75 sand: 13.5 ballast, have been used for lock construction. In Italy pozzolanic cements (OPC + pozzolan) have become common, where 30-40% of for pozzolanic cement is widely used, in the same mix proportions as Portland cement general construction purposes.

2.7 POZZOLANS AND DEVELOPING COUNTRIES

Centre for Technology and Development (CTD, 2007) reported that with the exception of few developing countries such as Oman, India and China, the commercial exploitation of pozzolans in the developing counties is very low despite its needs for Low-Cost construction materials for these communities. The report stated further that only Kenya, Tanzania on the African Continent that has initiated projects to develop the pozzolans for used in concrete mixtures. Citifmonline (2011) reported recently that Ghana started a Pozzolana Cement Blending Plant but had to close earlier 2011 because of lack of patronage the Ghanaians in preference to the conventional portland Cement. There are other factors affecting the utilisation of alternative cements in the developing countries.

According to Day (1990), these impediments which are both technical and non-technical to the developing countries production of alternative cements has come about due to ignorance on the part of engineers, developers, and government about the availability and the properties of alternative cementitious materials resulting

from lack of macro studies of alternative cements raw materials availability in the communities; for these reasons builders, engineers, architects and other construction industry players tend to turn automatically to Portland cement whose 'quality can normally be trusted'. Day (1990), lamented that Portland cement has become "enormously-powerful status value" cement with omnipresence in the poor countries.

This has two effects: it deters the development of intermediate technology development and the provision of low-cost housing; further dynamics militating against the use of the pozzolans in the developing communities are that subsidies or incentives on OPC productions do exist; thus, new technologies or alternatives cannot complete with such subsidies.

Further roadblocks to the alternative cements in developing countries (including Nigeria) are that standard specifications on cement in developing counties are single standard and recognitions of alternative cementitious materials are not provided for in its construction contracts documents. This is sequel to the adoption of standards from the developed economics. But the well known standards of developed countries do not have the provision to deal with the lower requirements and quality of indigenous building materials such as alternative to the OPC to meet the need of the developing communities. Ghana recognised the pozzolan cement as parts of its Standard Specifications in 2011(Citifmonline, 2011) after the closer of its Pozzolan Plant in Kumasi due lack of patronage as stated earlier. India is about the only

developing country that has recognized this and has established standards for a variety of lime pozzolan mixtures (Day, 1990).

In developing countries, the Construction sectors are sources of employment provision second only to the Agricultural in these Developing Communities. The use of Natural Pozzolanas in the industrialized world may not be cost effective due to the costs of inherent in mining and on the abundance of industrial by products Pozzolanas, but in developing counties especially those with active or historic volcanism there are rays of opportunities and potential markets that need exploitation. But the developing world according to Harris *et al* (2007) is far from embracing these cementitious materials. The identification of a reliable market for the Portland pozzolan cement will depend upon the consistency and quality of the pozzolan and the ultimate overall cost to deliver the mined material to the blended cement producers in industrial countries where deep water shipping costs are not prohibitive. Considering that an investor interested in developing the Pagan pozzolan will be required to incur significant capital investment to develop the project on an island with no infrastructure and located some considerable distance from major markets, it is obvious that to make an adequate return on investment will necessitate focusing on higher price markets as close as possible to Pagan Island. Countries such as China, Taiwan, Philippines, South Korea and possibly Indonesia and India, would appear to be the countries that may show an interest in this pozzolan deposit. Consumer demand for cement also will expand at an above-

average rate, stimulated by higher personal income levels in developing areas, where consumer sales can account for half or more of all cement demand, and by new product introductions in mature developed world markets.

Econoler International (2009) asserted that the main barrier to a successful introduction of blended cement into the Nigerian cement market has been identified as an aversion of consumers to a change to any cement other than OPC, which has been the only type on the market. West Africa Portland Cement Company (WAPCO) has developed and successfully implemented a significant marketing effort to reduce this barrier. The baseline scenario is the current practice in Nigeria where the amount of non-gypsum additive materials in OPC is limited to 6%, thus resulting in a clinker factor above 89% for the Nigerian cement type CEM I brand (where the gypsum content is about 5–6%). WAPCO worked jointly with the Nigerian Cement Manufacturing group, the Standard Organisation of Nigeria, relevant governmental agencies, cement users is proposing a new blended cement standard to raise the baseline benchmark of clinker-to-cement ratio of 0.908 for the two plants and the country benchmark is 0.89. Econoler International (2009) reported further GHG emissions baselines of 0.8483 ton CO_2 per ton and the respective emissions are estimated at 0.3688 ton CO_2 per ton for Shagamu and 0.4603 on CO_2 per ton for Ewekoro project of Changing Blending of portland cement with the has further dual benefits; principally 1 ton of Pozzolana Portland

Cement reduces gross CO_2 emissions by 20% and with the corresponding carbon credit for the CO_2 abatement-ranging from USD 4.38 to 6.24 per ton of CO_2.

2.8 RESERVES OF NATURAL POZZOLAN

2.8.1 Global Volcanic Deposits

The products of volcanic eruptions are very much pronounced in the Mediterranean, Pacific, Central and East African Regions of the world as reported by the Library of Congress (1991).Africa has its own share of the volcanic deposits (Plate IX; Appendix 'B').

Day (1990) asserted that many countries including have reactive volcanic materials; and that five percent of the solid surface of the earth consists of volcanic rocks. These deposits are spread among the on six continents; but stated that the existence of volcanic rocks origin within any country does not automatically make that country's volcanic deposits suitable for use as a natural pozzolan. The pozzolanic reactivity of the deposits must be studied prior to its utilisation. Day (1990) reported that there are 132 volcanic pozzolans from 32 countries of the world which the oxides composition and the physical properties of the pozzolans have been analysed; only a few African countries such as Ghana, Tanzania and Morocco are noted as countries with natural pozzolans have been analysed.

2.8.2 Nigerian Volcanic Deposits

According to Wright (1998) the Nigeria volcanism took place during the Cenozoic

period and covers a wide area of the country (Plate IX; Appendix 'C'). Though Nigerian volcanic deposits' reactivity is yet to reach knowledge of the global Pozzolana Community, Wright (1998) reported there are two main lines of volcanic formations in Nigeria; they are the Jos and the Biu Plateaux (the Biu line extends along the border with Cameroon in the Eastern part of the country) with approximate areas are represented in shown in Plate X; Appendix 'C'. The details of this coverage are within the Benue Trough Plate XI; Appendix 'D'. This area covers approximately the Benue trough Valley, Adamawa Highlands-extending to the Cameroonian High Lands. Wright (1998) then grouped these volcanic activities in the country into four Volcanic Sub- Regions namely:

i) The Jos Plateau Region; Wright (1975) reported that the Jos Plateau Volcanic Region is one of the major volcanic formations in Nigeria and it is situated within Benue Trough Plate XI Appendix 'D'.

ii) North East and South East of the Benue River Region; This is made up of Mambillla Plateau extending to the Cameroonian line, bordering to the far East of the country - with scattered occurrences of volcanic rocks in this region.

iii) The Upper Benue Valley Region; This sub-region consists of Biu Plateau and Longuda Peak covering 500 km^2 and 250 km^2 respectively.

iv) The Middle and Lower Benue Valley; The Agrilla and Oban Hills, the Wase plug makes up this sub-region volcanic formation covering a large area of land.

2.8.3 Jos Plateau Volcanic Deposits

The Jos Plateau it is made up of volcanic deposits of complex rock formations with standing land marks of the volcanic features. There are complex formations covering a land area of about 1,800 km^2 with some standing features at about 1,300 metres above approximately 4.3 billion cubic metres (Lekmang, 2006).These volcanic deposits are found in substantial quantities in Pankshin, Mangu, Bokkos, Barkin-Ladi, Riyom, Bassa, Jos North Jos South and Jos East Local Government Areas (LGA) in the present Plateau State of Nigeria.

The Jos Plateau lies within the water shade of the Niger, Benue and Lake Chad drainage system with innumerable small hills; granite kopjes flat-topped low hills of fluvio-volcanic origin and small extinct volcanoes covering 3,000 square miles (Hodder, 1959) in North Central Nigeria along the Benue Trough PlateXI; Appendix 'D' and it is made up of Pyroclastic falls volcanic deposits covering nine Local Government Areas of Plateau State.

CHAPTER 3

MATERIALS AND METHODS

3.1 RESEARCH APPROACH

The research was carried out by an extensive field visits and laboratory works. The field surveys were to ascertain the approximate locations of the volcanic deposits in view of the fact that there were no specific aerial land maps depicting the boundaries of the volcanic deposits. The guides to the identification of the volcanic deposits were land marks of volcanic conical hills and exposed materials resulting from soil erosion, mining, and road construction activities.

Laboratory investigations to evaluate the pozzolanic characteristics of the volcanic deposits were performed using appropriate test equipment and experimental procedures for the analysing of the samples. Furthermore, a literature review was under taken for indebt knowledge in the subject matter; utilisations of the pozzolans as supplementary cementitious materials in concrete mixtures.

3.2 THE STUDY AREA

The Study Area is the Jos Plateau Plate XI; Appendix 'E') located in Central Nigeria; situated between latitudes 8^{o}.3' and 10^{o}.10' and longitudes 80^{o}.20' and 90.30'E and consist of innumerable small hills; granite kopjes flat-topped low hills of fluvio-volcanic origin and small extinct volcanoes covering about 3,000 square kilometers (Olowolafe, 2000).Wright (1996) stated that, the Jos Plateau lies within

the water shade of the Niger, Benue and Lake Chad drainage system known as the Benue Trough. The Jos Plateau administratively covers nine Local Government Areas in Plateau State Plate XIII; Appendix 'E', namely Pankshin, Mangu, Bokkos, Barkin-Ladi, Riyom, Bassa, Jos North, Jos South and Jos East Local Government Areas (LGA).

3.3 SOME LAND MARKS AND VOLCANIC FEATURES OF JOS PLATEAU

The Jos Plateau is made up of pyroclastic falls volcanic deposits made up of variety of volcanic hill with eroded but traceable outstanding cones features spread all across the volcanic region. These formations according to Olowolafe (2000) and Wright (1998) are presented further by volcanic materials exposed as results of soil erosion, mining and road construction activities The field surveys established the assertions of Olowolafe (2000) and Wright (1998) that the Jos Plateau up of variety of volcanic hills and other volcanic features with a range of materials shots from various locations in a historic volcanism.

3.4 Volcanic Deposits of the Jos Plateau

According to Wright (1998) the Jos Plateau is made up of pyroclastic falls. The volcanic materials are piles and or layers of fallen materials by one or more eruptions; which formed into hardened and compressed versions of the original loose pyroclastic deposits. The materials could be of mixed origin (formed by various methods at the same time or at various times) (Meral, 2994). In the course of

the study some of the volcanic materials were found in such forms loose Plate XV; Appendix 'F' and hardened Plate XXV; Appendix 'K' forms. The materials on the Jos Plateau are of volcanic tuff of altered materials such as siliceous glass, pumice, and trachyte. The materials are presented in form of volcanic bombs and pumice Plate XXV; Appendix 'K'.

3.5 SAMPLING LOCATIONS AND COLLECTIONS

3.5.1 Sampling Locations

The field survey identified 20 volcanic deposits located in eight LGA (Table 3.1) of Plateau State which samples were collected for the research work.

Table 3.1 Grouping of Jos Plateau Volcanic Deposits by LGA

Group	LGA	No. of sites
I	Bassa	3
II	Jos North	1
III	Jos East	2
IV	Jos South	2
V	Riyom	2
VI	Barkin Ladi	2
VII	Bokkos	2
VIII	Mangu	5
IX	Pankshin	1

3.5.2 Samples Collections

Volcanic materials were collected in ethylene bags from the 20 locations; the dept varying from zero to 1.0m ; documented and assigned Identification Marks (ID).

3.6 RESEARCH INSTRUMENTS

The Materials, Equipment, Glassware and Chemicals used for the Chemical, Mechanical and Physical analysis are detailed in Appendix 'N'.

3.7 EXPERIMENTAL PROCEDURES

3.7.1 Chemical Characteristic of Volcanic Deposits

For the study the oxides composition of the volcanic materials were analysed by the Traditional Wet Chemistry technique, Energy Dispersive X-Ray Fluorescence (EDXRF) and the Neutron Activation Analysis (NAA).The Traditional Chemistry technique was used in determining oxides 5% and above by weight; these are calcium (Ca), silicon (Si), aluminum (Al) and iron (Fe). The EDXRF further analysed minor elements are sodium (Na), potassium (K), magnesium (Mg), and sulfur (S), with concentration l-5 % : While elements occurring at less than 0.02% each as the trace elements or elements present at levels less than 100 ppm classified as trace elements are determined by (Bhatty, 1995) were also evaluated by NAA technique.

The Loss on Ignition and the Moisture Contents of the materials were investigation by the Wet Chemistry techniques also referred to as the Old Chemistry techniques. ASTM C 311 (2005) Standard Test Methods for Sampling and Testing Fly Ash or Natural Pozzolans for Use as a Mineral Admixture in Portland-Cement Concrete and ASTM C 618(2005) Standard Specification for Coal Fly Ash and Raw or Calcined

Natural Pozzolans for Use as a Mineral Admixture in Concrete were used.

3.7.1.1 Oxides composition

(a) Wet Chemistry (old chemistry) method

The evaluations of the chemical composition of the ordinary cement used were determined in accordance to the ASTM C 114 (2004) Standard test methods for chemical analysis of hydraulic cement and BS EN 196-2 (2005) Chemical analysis techniques. The details of the step by step procedure in the oxides determination of the oxides by volumetric (titrimetric) and the Gravimetric methods are provided in detail Appendix 'N'.

(i) Silica (SiO_2), Aluminium (Al_2O_3) and Iron Fe_2O_3

The Gravimetric method with the chemical reaction separates the elements from sample solution) of Analysis were used to determine the oxides of Silica (SiO_2). 1gm of the volcanic materials with a mixture of $Na_2CO_3 + K_2CO_3$ in a ratio 1:1 heated at a temperature of 950 ^oC in the Furnace and followed by other process resulting to the termination of the SiO_2. Other oxides determined by the gravimetric technique are Sulphur.

(ii) Aluminium (Al_2O_3), Calcium (CaO) and magnesium (MgO) oxides.

Titrimetric Analysis measure the volume occupied by the compound using a solution of known reagent, which reacts in certain way with the component under analysis. Al_2O_3 for example was determined by titrimetric analysis. Ethylene

Diamine Tetra Acetic Acid Complexometry Method was used. The bauxite sample was fused with sodium hydroxide and a pine of sodium carbonate on Hot Plate and the resultant sodium aluminate extracted with water. An excess of Ethylene Diamine Tetra Acetic Acid (EDTA) solution added and boiled to form a stable complex. After cooling, the excess of EDTA is determined by titrating with a solution of zinc acetate and the percentage of Al_2O_3 was calculated from the amount of actual EDTA used up. The method applied in evaluating the oxides of Calcium (CaO) and magnesium (MgO) oxides.

(b) The energy dispersive x-ray fluorescence (EDXRF) method

The samples were ground manually to powder with an agate mortar and pestle to grain size of less than 125μm. Pellets of 19mm diameter were then prepared from 0.3-0.5g powder with three drops of organic liquid binder and pressed afterwards at 10 tons with a hydraulic press. The measurement of the elements were performed using the Excitation Source by introducing the pellets of each of the samples into the X-Ray Fluorescence generator detector source emitting Silver (Ag)-Potassium(K) X-ray (22.1keV) in which all elements with lower characteristic excitation energies were accessible for detection in the samples for the analysis. The measurements of the elements were then performed using the Excitation Source. The elements with the characteristic excitation energies were accessible for detection in the samples.

(d) Neutron activation analysis method

The volcanic materials samples were placed the reactor. The reactor's flux of

neutrons from uranium fission interact with the target nucleus of the element and when neutron energy bombards the sample it promotes radioactive nuclei of the target element. The radioactive nuclei then emit characteristic gamma rays; the detection of these rays indicates the presence of a particular element. The elements are then measured with a specifically design soft ware; the gamma-ray spectrum analysis Wingspan 2004 computer software for neutron activation analysis measurement of elements.

3.7.1.2 Loss on ignition

The determinations of the LOI of the samples were carried out according to ASTM C 114 (2004) Standard Test Methods for Chemical Analysis of Hydraulic Cement. A furnace capable of reaching a temperature of 1500^{o}C was utilised. The materials were placed in a porcelain crucible and were fired a furnace at 950^{o}C for a period of 1 hour after which they were cooled in a silica gel desicator and the weight losses of the samples were subsequently measured.

3.7.1.3 Moisture content

The total moisture contents of the materials were determined by means of the oven-drying techniques described by BS 812-109 (1990): Methods for determination of moisture content and BS EN197.1-5 (1999): Tests for mechanical and physical properties of aggregates. The determination of water contents were carried out by

drying the samples in a ventilated oven. An Oven capable of reaching a temperature of 120^0 C was utilised.

The samples were placed and dried in an Oven at 105^0C temperatures. The differences in weights before and after the materials were heated were subsequently measured as the moisture contents of each of the samples. This weight is referred to as the Moisture Content of the materials.

3.7.2 Chemical analysis of *Dangote* cement

The test on chemical composition of cement are carried out in accordance with ASTM C 114 (2004) Standard test methods for chemical analysis of hydraulic cement and cement and BS EN 196-2 (2005).

3.7.2.1 Oxides composition

The determination of the oxides of SiO_2, Fe_2O_3, Al_2O_3, MgO, CaO, SO_3, Mn_2O_3, and alkalis (Na_2O) were carried out by the use of Energy Dispersive X-Ray Fluorescence (EDXRF) techniques. This method is based on the measurement of x-rays intensities emitted by components of a target sample when excited by Silver-Potassium (Ag-K) X-rays (22.1 keV) from an annular excitation source of 25 milicurie (25 mC_i) Cadmium 109 (^{109}Cd) (Simabuco and Filho, 1994). The system consists of the excitation source and a Silicon (Si)-Lithium (Li) semiconductor detector coupled to a computer controlled Analog to Digital Control (ADC) Card.

3.7.3 Physical Characteristics Aggregates

3.7.3.1 Preparation of aggregates

The sands were quartzite river sands; and the crushed granite stones were obtained from a Local Quarry in Zaria. The crushed stones and sands sieve analysis were

evaluated as described in B.S. 812 (1960) to remove the impurities and to ascertain their particle size distribution to grading zone 3 of BS 4550: part 6(1991). The aggregate met the specifications of BS 4550 and ASTM C 33(2003).Tap water was used for the production and the curing of the concrete cubes.

3.7.3.2 Specific gravity

The specific gravity tests were in accordance with Standard Test Method for Density, Relative Density (Specific Gravity), and Absorption of Coarse Aggregate ASTM C 127 (2004). In this method 20 gms of the volcanic materials samples were used for each of the samples. The weighed materials were placed in a calibrated cylinder containing 20 mls (v_1) of water with a density of 1.0 (g/cm3).The contents were allowed to settle to a new volume (v_2).The displacements (v_2-v_1) of the water were thus calculated for each of the samples studied.

3.7.4 Physical Characteristic of Volcanic Materials

3.7.4.1 Specific gravity

The specific gravity of the fine and coarse aggregates were determined in accordance with the Standard Test Method for Specific Gravity recommended (SG) by ASTM C 127 (2004). 20 gms of the cement sample was used and the SG of the cement was evaluated.

3.7.4.2 Sieve analysis of volcanic materials

The volcanic materials samples were separately ground manually into powdered form with an agate mortar and pestle in the laboratory. 500g powder of each of the samples was then sieved in accordance with BS 812-103.1 (1985). Only powder particles which passed the 75 μm standard BS sieve No 200 were collected and kept back in their respective poly ethylene bags for used for the experiment.

3.7.5 Physical Characteristic Portland Pozzolana Cement Concrete

3.7.5.1` Consistency test

The consistency standard test was carried out by the use of Vicat Apparatus. Using a 10 mm diameter plunger fitted into the needle holder. Trial mixes with water cement ratios of 0.4, 0.45, 0.5, 0.55 and 0.6 paste of cement and water was mixed in a prescribed manner and placed in the mould. In releasing the plunger to the mould, the penetration of the plunger from the bottom is measured and expressed as a % of mass of the dry cement.

3.7.5.4 Setting time of portland volcanic materials cement concretes

The Initial Setting and Final Setting Times were determined according to American Society for Testing and Material ASTM C 451 (2005).The tests were conducted using Vicat's Apparatus'. A need is size 1 mm^2 was used to measure the penetration of on cement paste (prepare partially replacing OPC with 15% volcanic materials).The Initial Setting Times were recorded when the needle stood 5mm (+0.5 mm) above the bottom of the paste mould. The Final Setting Times of the

pastes were respectively recorded (the time from the addition of water) when the needle failed to make an impression on the paste.

3.7.5.5 Durability test on mortar containing volcanic materials

The durability of concrete containing the volcanic materials was assessed by testing the soundness of cement paste (containing volcanic materials) according to the ASTM C 151 (2005): Standard Test Method for Autoclave Expansion of Hydraulic Cement. Small bars of 50 mm of Portland pozzolana cement paste were place in an autoclave for a period of 3 hours each to a temperature of 120^{o}C. The change in length of the specimens were calculated by evaluating distances(mm) between the pointers before heating and the distances between the pointers after heating for all the materials studied.

3.7.5.6 Pozzolanic activity index with lime

The Portland pozzolana cement pastes of 15% partial replacements of the OPC in the concrete mixtures were used for the Pozzolana Portland Cement pastes samples investigated. The determination of the percentage of lime as CaO in the Portland pozzolan cement sample, about 0.5 g was treated with 2g/50 ml H_2O ammonium octane under acidic condition at 80^{o}C. The resultant precipitate of calcium and monohydrate was (Ca^{+2} + Ca_2O^{+3} + H_2O->Ca_2O_4.H) ignited at about 900^{o}C calcium oxide. Thus the percentages of lime as CaO in the samples in form of $CaO.SiO_2$ were gravimetrically determined for each of Portland Pozzolana Cement paste.

3.7.6 Mechanical characteristics of Portland Pozzolan Cement Concrete

3.7.6.1 Compressive strength of Portland cement concrete

The British Standard 1881: part116 (1983) method for compressive strength tests were used for the production of the control concrete cubes with zero replacements of the OPC in the concrete mixtures. Cement, sand and coarse aggregates were used. The 'Dangote' brand of Portland cements were obtained from Dangote Cement Warehouse in Zaria. The sands were quartzite river sands; and the crushed granite stones were obtained from a Local Quarry. The coarse aggregates and sand met the specifications of BS EN882 (2004): Specification for aggregates from natural sources for concrete. Tap water was used for the production and the curing of the concrete cubes. The workability was evaluated through slump test which varied from zero to 0.5. The concrete cubes were prepared in 150 mm x150 mm x150mm steel moulds with water/cement ratio of 0.65 were used. The control cubes specimens were evaluated at 7, 14 and 28 days.

3.7.6.2 Compressive Strength of portland pozzolana cement concrete

The standard and specification and sourcing of the Portland cement and aggregates were same as for the control cubes. Each set of concrete cubes with the replacement of the OPC with 5, 10, 15, 20, 30 and 40% of the volcanic materials was mechanically mixed using a concrete mixer. Using the water cement ratio 0.65 based on the trial mixes. The PC and the volcanic materials were each batch separately.

The concrete cubes were subsequently prepared in 150 mm x 150 mm x 150 mm steel moulds. The moulds were kept in the laboratory for 24 hours and demoulded; curing was made by submerging the cubes in waters and the compressive strengths were taken at 7, 14 and 28 days. At each date of the tests the cubes were withdrawn from the tanks and kept for about 30 minutes preceding the tests. The cubes were each tested to destruction using a manually operated compressive test machine and the failure loads for each sets of cubes recorded in Newtons.

3.7.6.3 Pozzolanic activity index with Portland cement

American Society for Testing and Material C 618 (2005) provides for the measurement of the Pozzolanic activity index with Portland cement concrete. These were established by evaluating of the strength of the concrete with zero pozzolan with the specific replacements of the volcanic materials at 28 days for all the samples using the expression;

The determination as Pozzolanic Activity Index with Cement = $-$ 100.

Where A - average compressive strengths of test mix cubes (N/mm^2).

B - average compressive strengths of control mix cubes (N/mm^2).

3.8 DATA ANALYSIS

3.8.1 Field Survey

The field information were to be use to ascertain the approximate locations of the volcanic deposits using land marks of volcanic conical hills and exposed materials due to physical activities. Some of the materials are presented in plates and tables.

3.8.2 Laboratory Samples

The purposes of the various laboratory experiments were to ascertain the pozzolanic characteristics of the volcanic materials and compare same with other characteristic of volcanic deposits elsewhere; and secondly to evaluate to suitability of the volcanic materials in concrete mixtures by assessing the level of partial replacement of the OPC in the concrete mixtures. These results are presented in figures and tables.

CHAPTER 4

DATA PRESENTATION, ANALYSIS AND DISCUSSION

4.1 DATA PRESENTATION

4.1.1 The Volcanic Landscape of Jos Plateau

The Jos Plateau is characterised by a landscape of volcanic deposits. The occurrence of these volcanic materials across the study area presence a variety of complex features. The distribution of these deposits on Local Government bases is presented in Table 4.1.

Table 4.1: Distribution of Jos Plateau volcanic deposits by Local Government Areas

LGA	Location	Identified feature(s)	Mark
Bassa	Mista-Ali	Materials Exposed by mining activities	JP 1
	Kaskadi	Conical hill /Materials exposed by mining activities	JP 2
	Miango	Twin conical hills	JP 3
Jos North	Gwafan	Materials Exposed by road construction activities	JP 4
Jos East	Furaka	Materials Exposed by soil erosion	JP 5
	Fobur	Materials Exposed by soil erosion	JP 7
Jos South	Lobel	Materials Exposed by soil erosion	JP 6
	Vwang	Materials Exposed by road construction activities	JP 8
Riyom	Kwi	Outstanding conical hill	JP 9
	Danwal	Volcanic hills and eroded visible materials	JP 13
Barkin Ladi	Bang	Materials exposed by construction activities	JP 14
	Kwok	Materials exposed by soil erosion	JP 11
Bokkos	Kuba	Materials exposed by erosion activities	JP 15
	Wunat	Materials exposed; road construction /erosion activities	JP 17
Mangu	Kombun	Volcanic hills and eroded visible materials	JP 10
	Kuben	Materials exposed by road construction activities	JP 12
	Niyes	Volcanic hills and loose materials including pumice	JP 16
	Kerang	Massive volcanic complex and change of conical hills	JP 18
	Larpia	Volcanic crater and materials by soil erosion activities	JP 19
Pankshin	Kuras	Materials Exposed by road construction activities	JP 20

Source; Field survey (2008)

4.1.2 Chemical Characteristics of Jos Plateau Volcanic Materials

The purposes of the various laboratory experiments were to ascertain the pozzolanic characteristics of the volcanic materials and compare same with other characteristic of volcanic deposits elsewhere; and secondly to evaluate to suitability of the volcanic materials in concrete mixtures by assessing the level of partial replacement of the PC in concrete mixtures. These results are presented in figures and tables.

4.1.2.1 Oxides Composition

i. Old Chemistry Method: The results of the oxides composition of the volcanic deposits by Wet Chemistry Method presented in Table 4.2.

Table 4.2: Oxides composition by Wet Chemistry Method

Sample	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	MgO (%)	SiO_2 (%)	SO_3 (%)
Mista-Ali (JP1)	25.82	21.36	0.28	3.43	29.30	0.45
Kaskadi (JP2)	24.07	18.98	0.28	3.43	31.90	0.07
Mingo (JP3)	26.13	8.98	0.28	1.71	60.20	0.48
Gwafan (JP4)	13.19	25.15	0.28	1.71	52.50	0.07
Fobour (JP5)	20.69	20.96	0.28	0.40	32.80	ND
Furaka (JP6)	20.25	14.17	0.28	ND	51.10	0.27
Lobel (JP7)	20.51	30.54	0.28	ND	32.40	0.76
Vwang (JP8)	20.97	9.78	0.28	0.81	37.0	0..07
Kwi (JP9)	19.13	48.12	0.28	ND	16.80	ND
Danwal (JP10)	23.25	8.18	0.28	1.11	51.80	0.21
Bang (JP11)	21.75	38.14	0.28	1.71	23.30	ND
Kwok (JP12)	29.63	8.17	0.28	2.20	38.90	ND
Wunat (JP13)	20.88	14.57	0.28	1.31	36.00	4.05
Kuba (JP14)	20.50	41.93	0.56	0.91	19.20	0.41
Kerang (JP15)	14.63	13.18	0.84	1.23	36.20	0.21
Kuben (JP16)	18.88	48.12	ND	2.02	20.60	1.99
Niyes (JP17)	18.00	11.78	0.28	9.88	32.90	ND
Larpia (JP18)	25.38	25.35	ND	1.92	63.80	0.21
Kombun (JP19)	21.88	22.37	0.28	1.31	33.80	0.34
Kuras (JP20)	18.38	29.96	0.28	1.01	27.70	0.96

ND; Nothing Dictated

ii. EDXRF method: The results of the oxides composition by EDXRF (Table 4.3).

Table 4.3(a): Oxides composition of the Jos Plateau volcanic materials by EDXRF method

Element	JP1	JP2	JP3	JP4	JP5	JP6	JP7	JP8	JP9	JP10
SiO_2 (%)	29.80	29.40	41.10	40.90	31.60	39.70	27.30	31.40	44.50	44.60
Al_2O_3 (%)	25.70	24.40	35.50	17.00	24.80	25.58	21.20	40.60	25.98	30.10
Fe_2O (%)	35.75	38.23	13.56	36.39	35.23	29.09	44.42	24.19	19.83	16.37
MgO (%)	0.08	0.27	0.05	0.03	0.15	0.07	0.06	0.06	0.05	0.09
K_2O (%)	ND	0.19	ND	0.08	0.04	0.14	0.17	ND	0.48	1.51
CaO (%)	0.18	0.35	0.16	0.15	0.17	0.27	0.15	0.19	0.28	0.17
SO_3 (%)	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Mn_2O_3 (%)	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Na_2O (%)	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
CO_2 (%)	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
TiO_2 (%)	4.53	5.95	5.46	0.56	3.66	1.02	1.90	1.54	3.39	1.18
NiO (%)	0.02	0.06	0.01	ND	0.03	ND	ND	0.02	0.11	ND
Cr_2O_3 (%)	0.14	0.08	0.12	0.11	0.11	0.10	0.14	0.11	0.05	0.07

Table 4.3(b): Oxides composition of the Jos Plateau volcanic materials by EDXRF method

Element	JP11	JP12	JP13	JP14	JP15	JP16	JP17	JP18	JP19	JP20
SiO_2 (%)	19.50	32.30	35.00	19.00	32.80	17.00	36.06	29.20	31.80	27.70
Al_2O_3 (%)	17.70	40.10	27.60	18.60	18.00	14.60	16.00	24.10	24.00	18.38
Fe_2O_3 (%)	53.11	19.66	29.34	58.08	32.40	59.37	28.14	37.96	35.16	29.96
MgO (%)	0.06	0.05	0.06	0.07	0.35	ND	0.40	0.06	0.11	0.73
K_2O (%)	0.05	0.26	ND	ND	0.15	ND	1.55	ND	0.34	ND
CaO (%)	0.15	0.31	0.20	0.11	7.42	0.10	8.24	0.14	0.31	0.28
SO_3 (%)	ND	ND	ND	0.03	ND	ND	ND	ND	0.35	0.43
Mn_2O_3 (%)	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Na_2O (%)	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
CO_2 (%)	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
TiO_2 (%)	2.10	0.90	2.96	2.31	5.01	1.09	4.74	2.70	2.04	3.08
NiO (%)	0.01	ND	ND	0.02	0.14	ND	0.10	0.02	0.02	1.98
Cr_2O_3 (%)	0.20	0.10	0.09	0.20	0.22	0.18	0.16	0.13	0.16	0.67

Note-ND; Noting Dictated

iii. **NAA** Method: The results of the oxides composition by NAA Table (4.4).

Table 4.4(a): Oxides Composition of the Jos Plateau volcanic materials; NAA Method

Element	Mista-Ali JP1	Kaskadi JP2	Miango JP3	Gwafan JP4	Fobour JP5	Furaka JP6	Lobel JP7	Vwang JP8	Kwi JP9	Danwal JP10
Mg (ppm)	53410 7	3622	3656	16840	3591	BDL	4580	BDL	BDL	5898
Al (ppm)	376100	52860	33360	26610	22400	132800	113300	81300	83070	130000
Ca (ppm)	69940	BDL	BDL	22270	BDL	BDL	BDL	BDL	BDL	BDL
Ti (ppm)	28710	2856	8978	4495	4505	9801	8075	11610	12730	2761
V (ppm)	388	364.6	153	42	318	326	155.5	108	591	119
Mn (ppm)	1341	240.3	166.5	607	449	208	304	531	150	159.5
Dy (ppm)	4.9	3.4	2.3	3.14	2.73	5.9	10.6	9.2	2.9	7.7
Na (ppm)	208.9	74.0	597	294	97.2	230	389	253	46.	144.5
K (ppm)	1368	BDL	1916	2408	BDL	BDL	BDL	1831	BDL	4572
As (ppm)	3.8	2.3	2.5	10.04	3.1	10	6.6	2.0	9.8	1.56
La (ppm)	36.8	8.8	57.7	43.4	36.2	328	298.6	103.0	13.2	80.85
Sm (ppm)	5.9	2.3	12.9	8.8	6.2	25	34.8	14.0	2.9	11.7
U (ppm)	4.9	1.8	1.9	12.5	7.6	5.5	8.0	4.3	4.2	3.7
Sc (ppm)	28.74	29.8	30.6	12.55	8.28	28.6	218.3	13.42	45.6	11.04
Cr (ppm)	186.4	764.3	208. 5	60.55	51.6	665	129	74	805	67.2 7
Fe (ppm)	105800	304100	142400	94410	42590	179500	106200	61580	393200	50260
Co (ppm)	11.12	52	70.9	7.1	2.9	6.8	6.3	7.2	8.7	7.7
Zn (ppm)	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Br (ppm)	BDL	3.9	1.6	4.4	0.5	2.4	604	2.0	1.8	0.7
Rb (ppm)	BDL	BDL	BDL	32	BDL	BDL	BDL	BDL	BDL	53.3
Sb (ppm)	BDL	BDL	BDL	0.85	BDL	0.6	BDL	BDL	BDL	BDL
Cs (ppm)	BDL	BDL	1.5	2.5	BDL	BDL	BDL	1.6	BDL	BDL
Ba (ppm)	BDL	900	559	BDL	BDL	BDL	BDL	147	BDL	233
Eu (ppm)	BDL	0.8	3.5	1.2	0.9	4.2	3.4	2.2	0.7	2.33
Yb (ppm)	2.93	BDL	2.9	7.1	6.4	3.9	5.2	5.3	1.3	3.7
Lu (ppm)	0.46	0.26	0.44	0.92	0.92	0.43	0.52	0.71	0.50	0.37
Hf (ppm)	17.4	5.0	13.5	31.5	161	194	29.2	63.5	2.6	10.4
Ta (ppm)	4.2	0.9	7.4	10.3	12.8	5.1	11.9	5.7	13.5	2.2
Th (ppm)	15.5	2.9	12.8	62.4	43.4	20.6	64.7	42.7		30.9

BDL: - Below Detection Limit NA: - Not Analysed

ppm: - part per million

The values of the oxides in terms of percentage by weight are obtained by dividing the corresponding ppm by 10,000.

Table 4.4(b): Oxides Composition of the Jos Plateau volcanic materials; NAA Method

Element	Bang JP11	Kwok JP12	Wunat JP13	JP14 Kuba	J 15 Kerang	J 16 Ampang	JP17 Kuben	JP 18 Niyes	JP 19 Larpia	JP 20 Kombun
Mg (ppm)	BDL	4172	7749	BDL	55500	5734	BDL	52660	5327	BDL
Al (ppm)	84660	133500	128200		91380	147600	90120	69430	120200	95480
Ca (ppm)	BDL	BDL	BDL	BDL	45800	BDL	BDL	40700	BDL	BDL
Ti (ppm)	3627	7244	10960	5635	BDL	11740	6401	11690	13370	3127
V (ppm)	58	283	316	392	196	229	646	143	322	534
Mn (ppm)	188	168	235	192	1322	152	429	1466	220	318
Dy (ppm)	13	3.8	3.3	2.02	4.78	3.32	3.19	4.6	3.66	3.58
Na (ppm)	142	169	131	127	2613	127	67.8	10440	191	119
K (ppm)	1528	1551	BDL	3029	2125	1086	1188	3.34	662	1951
As (ppm)	4.10	9.9	12.3	27.2	BDL	5.94	14.6	BDL	10.9	10.9
La (ppm)	0.5	32.7	59.2	20.8	26.5	94.2	21.9	47.2	42.3	52.7
Sm (ppm)	64.8	5.6	6.9	BDL	BDL	BDL	BDL	BDL	BDL	BDL
U (ppm)	15.1	6.3	5.1	1.90	BDL	3.42	10.3	BDL	7.59	8.12
Sc (ppm)	15.7	15.16	17.7	17.4	31.6	20.5	49.8	2.51	28.9	31.1
Cr (ppm)	8.8	273	248	579	596	290	713	700	803	845
Fe (ppm)	43	119100	166100	245600	108400	144700	417600	106600	231300	269300
Co (ppm)	43510	5.1	11.05	11.1	7708	10.6	21.4	81.4	11.4	10.4
Zn (ppm)	4.8	BDL	99	BDL	BDL	86	BDL	203	BDL	BDL
Br (ppm)	BDL	1.20	2.0	4.97	BDL	BDL	BDL	BDL	BDL	BDL
Rb (ppm)	38	BDL	BDL	BDL	BDL	BDL	BDL	64	BDL	BDL
Sb (ppm)	BDL	0.56	NA	1.35	BDL	BDL	0.79	BDL	BDL	BDL
Cs (ppm)	3.5	1.03	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Ba (ppm)	BDL	BDL	BDL	BDL	799	156	BDL	755	BDL	BDL
Eu (ppm)	0.9	BDL	0.9	BDL	3.10	1.99	1.27	3.26	1.02	1.50
Yb (ppm)	9.1	2.6	2.3	2.86	2.19	3.65	BDL	2.34	2.99	4.78
Lu (ppm)	1.24	0.35	0.36	0.44	0.68	0.45	0.40	0.35	0.39	0.04
Hf (ppm)	19.7	14.88	11.3	15.4	6.24	12.6	7.10	7.07	8.66	12.9
Ta (ppm)	16.6	10.4	4.1	2.13	4.39	BDL	1.85	5.26	3.25	1.82
Th (ppm)	48.6	26.4	28.3	24.8	7.11	13	45.02	8.30	14.3	30.1

BDL: - Below Detection Limit NA: - Not Analysed

ppm: - part per million

The values of the oxides in terms of percentage by weight are obtained by dividing the corresponding ppm by 10,000.

4.1.2.2 Lost on ignition of Jos Plateau volcanic materials

The Loss on ignition of the samples of the volcanic deposits results is presented in Figure 4.1.

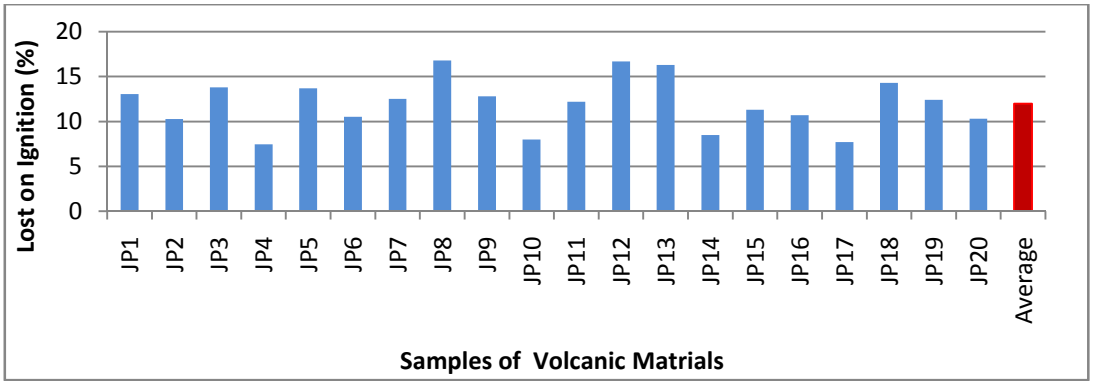


Figure 4. 1: The values of the LOI of Jos Plateau volcanic materials

4.1.2.3 Moisture contents of the Jos Plateau volcanic materials

The result of the moisture contents determination is presented in Figure 4.2.

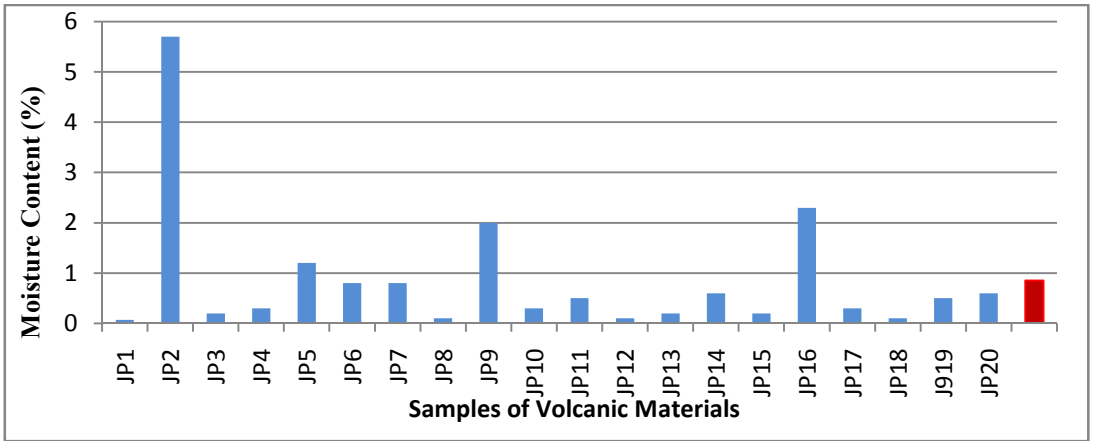


Figure 4.2: The values of the Moisture Contents of Jos Plateau volcanic materials.

4.1.3 Dangote Cement Characteristics

4.1.3.1 Chemical characteristics

(a)The results oxides composition of *Dangote* cement is presented in Table 4.5.

Table 4.5: Chemical Composition of *Dangote* Cement with ASTM Requirement

Component	Dangote Content %	ASTM C 150 (2004) limits
CaO	79.46	60-67
SiO_2	8.56	17-25
Al_2O_3,	1.7	3-8
Fe_2O_3	3.95	0.5-6.0
MgO	0.03	0.1-4.0
SO_3	1.62	1-3
MnO	0.02	-
SrO	0.74	-
Alkalis	0.21	0.2-1.3

(b) Loss on ignition and the moisture content of *Dangote* Cement

The results of the chemical analysis showed that the loss on ignition and the moisture contents of the *Dangote cement were* 8.8 % and 0.3% by weight respectively of the materials tested.

4.1.4 Aggregates

(a) Sieve analysis of aggregates

The results of the sieve analysis of the fine and coarse aggregate are presented in Table 4.2

Table 4.6 Sieve analysis of aggregates

Sieve no.	Sand retained (g)	Crushed stone retained (g)
20	-	66
10	-	638
5	18	266
2.36	34	19
1.18	86	2
600	195	5
300	124	1
150	28	0.5
Pan	15	0.5
Total	500g	1000g

4.1.4 Physical Characteristics of concrete containing Jos Plateau volcanic materials

4.1.4.1 Pozzolanic activity index of Jos Plateau volcanic materials with lime

Figure 4.5 is the Pozzolanic Activity Index with Lime (PAIL) determines.

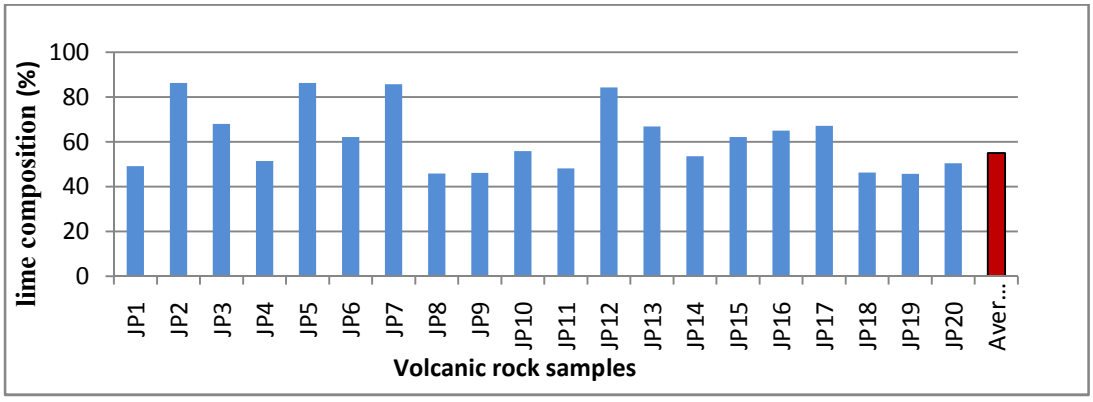


Figure 4.3: Pozzolanic Activity Index Jos Plateau volcanic materials with Lime

4.1.4.2 Specific gravity of Jos Plateau volcanic materials

The volcanic materials SG (Table 4.7).

Table 4.7: Specific gravity of Jos Plateau volcanic deposits

SAMPLE	WT USED	INITIAL VOL (V_1)	FINAL VOL. (V_2)	$V_2 - V_1$	SG = ($^{g}/_{v2} - v_1$)
JP1	20.00	20.00	28.50	8.50	2.35
JP2	20.00	20.00	29.00	9.00	2.22
JP3	20.00	20.50	29.50	9.00	2.22
JP4	20.00	20.00	28.00	8.00	2.25
JP5	20.00	20.00	28.00	8.00	2.50
JP6	20.00	20.00	28.00	8.00	2.50
JP7	20.00	20.50	29.00	8.50	3.35
JP8	20.00	20.00	28.00	8.00	2.50
JP9	20.00	20.00	27.50	7.50	2.67
JP10	20.00	20.00	28.00	8.00	2.50
JP11	20.00	19.00	28.50	9.50	2.11
JP12	20.00	20.00	28.00	8.00	2.50
JP13	20.00	21.00	28.00	7.00	2.86
JP14	20.00	20.00	28.00	8.00	2.50
JP15	20.00	19.50	29.00	9.50	2.11
JP16	20.00	21.50	30.00	8.50	2.50
JP17	20.00	20.00	27.50	7.50	2.67
JP18	20.00	19.50	28.00	8.50	2.35
JP19	20.00	20.00	27.00	7.00	2.86
JP20	20.00	20.00	28.50	8.00	2.5
Average					**2.41**

4.1.4.3. Setting time of concrete containing Jos Plateau volcanic materials

The results of Setting Times of the Portland pozzolan cement mortar at 15 % partial replacement of the Portland cement in the mixes are presented in table 4.8.

Table 4.8 Setting Time of Cement Mortar containing Jos Plateau volcanic materials

Sample	IST-Minutes	FST-Minute	Sample	IST-Minutes	FST-Minutes
JP1	**156**	**212**	**JP11**	**155**	**209**
JP2	**157**	**212**	**JP12**	**156**	**211**
JP3	**159**	**213**	**JP13**	**162**	**216**
JP4	**155**	**211**	**JP14**	**159**	**208**
JP5	**160**	**216**	**JP15**	**156**	**210**
JP6	**155**	**210**	**JP16**	**155**	**205**
JP7	**160**	**215**	**JP17**	**158**	**213**
JP8	**159**	**214**	**JP18**	**155**	**212**
JP9	**158**	**213**	**JP19**	**157**	**210**
JP10	**158**	**212**	**JP20**	**157**	**210**
Average				**158**	**212**

4.1.4.4 Soundness of cement paste containing Jos Plateau volcanic materials

The result of soundness test (Table4.9).

Table 4.9: Soundness Test of cement paste containing Jos Plateau volcanic materials.

Sample	L1 (mm)	L2 mm)	Δ(mm)	Sample	L1(mm)	L2(mm)	Δ(mm)
Control	2	3	0.20	Control	2	3	0.2
JP1	3	5	0.40	JP11	3	5	0.4
JP2	4	4	0.0	JP12	4	4	0.0
JP3	3	3	0.0	JP13	3	4	0.2
JP4	4	5	0.20	JP14	4	5	0.2
JP5	4	4	0.0	JP15	3	4	0.2
JP6	4	5	0.20	JP16	3	4	0.2
JP7	3	4	0.20	JP17	3	3	0.0
JP8	3	4	0.20	JP18	4	5	0.2
JP9	3	5	0.40	JP19	3	5	0.4
JP10	3	4	0.20	JP20	3	3	0.0
Average							0.17

Note;L1- Distance between pointers before heating (mm);L2 -Distance between pointers after heating (mm); Δ – Percentage change in length (mm).

4.1.5 Mechanical characteristics

4.1.5.1 Compressive strengths of concrete cubes with no replacement of OPC

Nine concrete cubes were prepared in 150mmx150mmx150mm steel moulds and tested in accordance with ASTM C 109/C 109M (2001); three cubes were crushed at 7, 14 and 28 days with the resulting compressive are presented in Table 4.0.

Table 4.10: Compressive Strengths of *Dangote* Cement Concrete Cubes

Crushing regime	Compressive strengths
7 Days	20.18 N/mm^2
14 Days	23.93N/mm^2
28 Days	26.0N/mm^2

4.1.5.2 Compressive strength of concrete containing Jos Plateau volcanic materials

The Compressive Strengths of concrete containing Jos Plateau volcanic materials the in partial replacements were evaluated at 7, 14 and 28 days curing. The Concrete cubes were cast utilising volcanic samples at 5, 10, 15, 20, 30 and 40% in partial replacements of the PC for each of the samples.

(a) Concrete Containing Volcanic Materials-Sample JP1

The Compressive Strengths of concrete containing sample JP1 volcanic materials are shown in Figure 4.4(a).

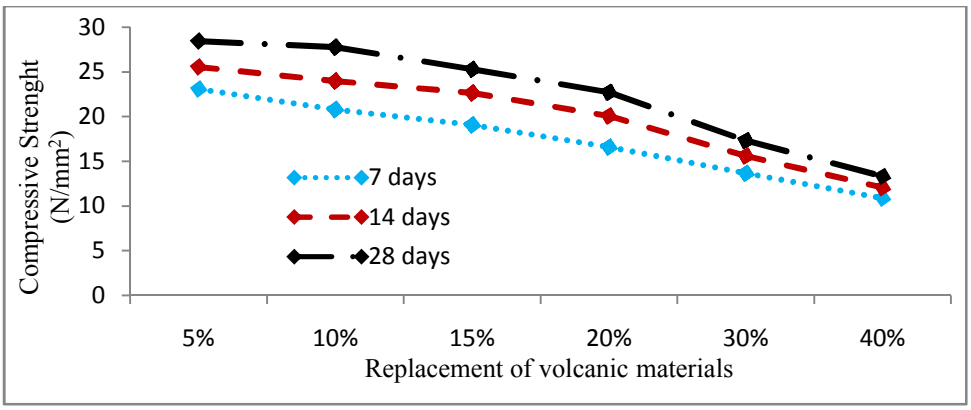


Figure 4.4(a): Compressive Strength (N/mm^2) of concrete containing JP1 **volcanic materials evaluated at 7, 14, and 28 days curing.**

(b) Concrete Containing Volcanic Materials-Sample JP2

The Compressive Strengths of concrete containing sample JP2 volcanic materials are shown in Figure 4.4(b).

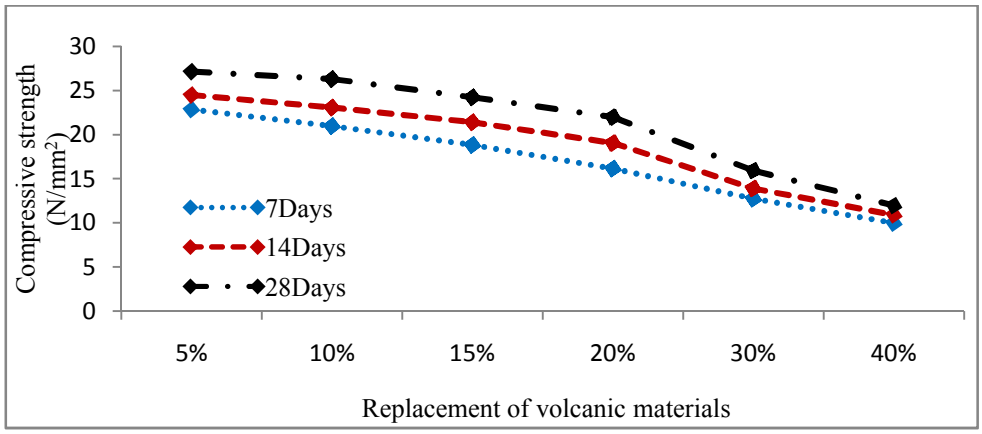


Figure 4.4b: Compressive Strength (N/mm^2) of concrete containing JP2 **volcanic materials evaluated at 7, 14, and 28 days curing.**

(c) Concrete Containing Volcanic Materials-Sample JP3

The Compressive Strengths of concrete containing sample JP3 volcanic materials are shown in Figure 4.4(c).

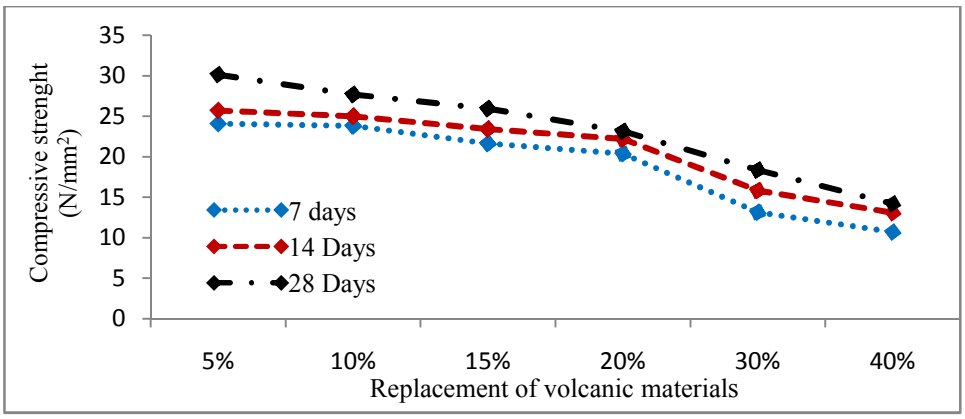


Figure 4.4(c): Compressive Strength (N/mm^2) of concrete containing JP3 **volcanic materials evaluated at 7, 14, and 28 days curing.**

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(d) Concrete Containing Volcanic Materials-Sample JP4

The Compressive Strengths of concrete containing sample JP1 volcanic materials are shown in Figure 4.4(d).

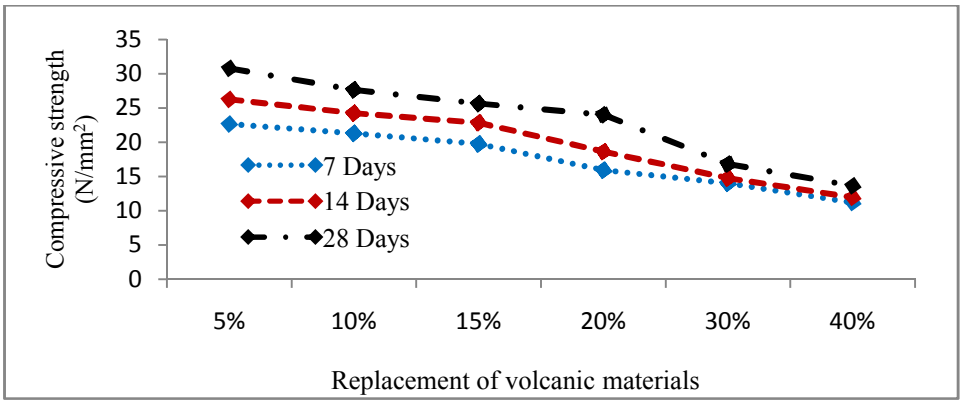


Figure 4.4(d): Compressive Strength (N/mm^2) of concrete containing JP4 **volcanic materials evaluated at 7, 14, and 28 days curing.**

(e) Concrete Containing Volcanic Materials-Sample JP5

The Compressive Strengths of concrete containing sample JP5 volcanic materials are shown in Figure 4.4(e).

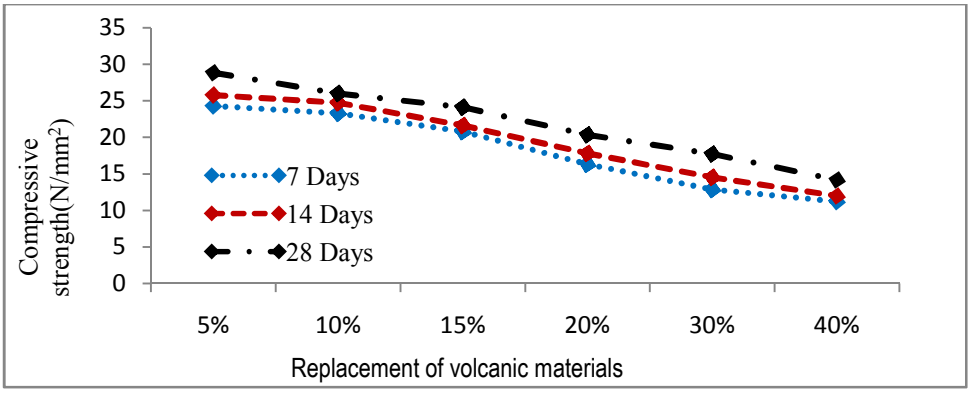


Figure 4.4(e): Compressive Strength (N/mm^2) of concrete containing JP5 **volcanic materials evaluated at 7, 14, and 28 days curing.**

(f) Concrete Containing Volcanic Materials-Sample JP6

The Compressive Strengths of concrete containing sample JP6 volcanic materials are shown in Figure 4.4(f).

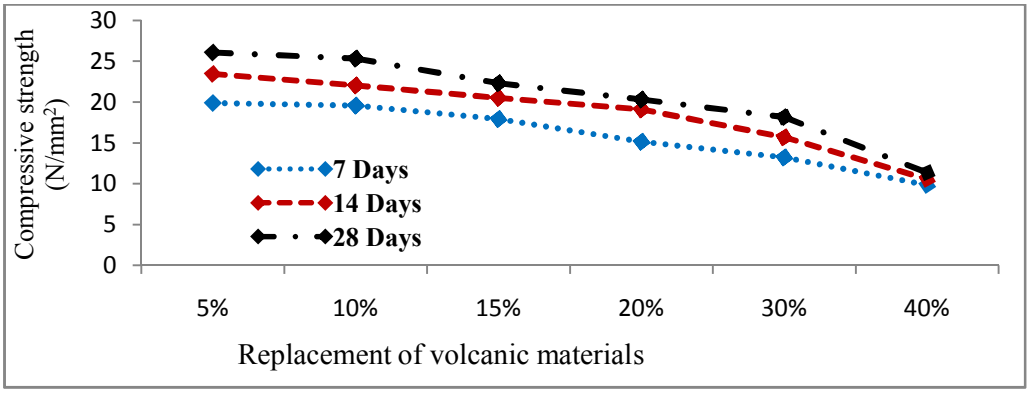


Figure 4.4(f): Compressive Strength (N/mm^2) of concrete containing JP6 **volcanic materials evaluated at 7, 14, and 28 days curing.**

(g) Concrete Containing Volcanic Materials-Sample JP7

The Compressive Strengths of concrete containing sample JP7 volcanic materials are shown in Figure 4.4(g).

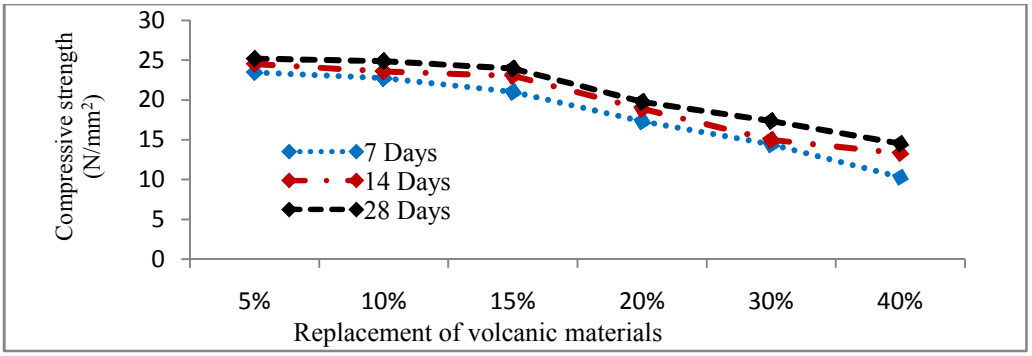


Figure 4.4(g): Compressive Strength (N/mm^2) of concrete containing JP7 **volcanic materials evaluated at 7, 14, and 28 days curing.**

(h) Concrete Containing Volcanic Materials-Sample JP8

The Compressive Strengths of concrete containing sample JP8 volcanic materials are shown in Figure 4.4(h).

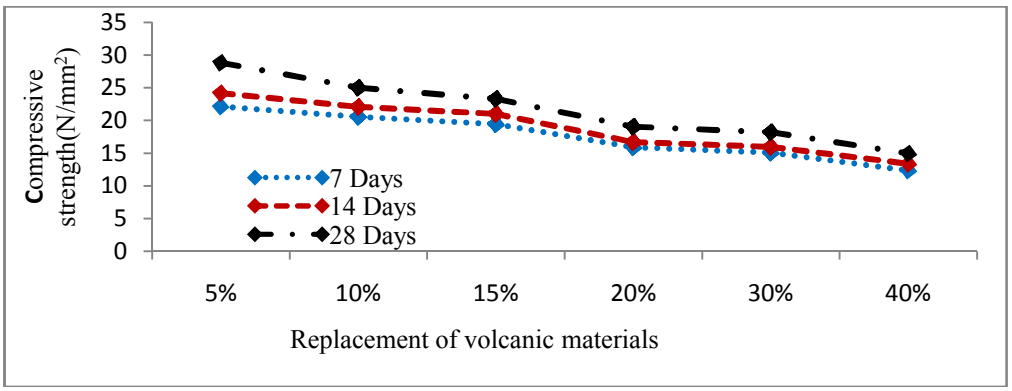


Figure 4.4 (h): Compressive Strength (N/mm^2) of concrete containing JP8 volcanic materials evaluated at 7, 14, and 28 days curing.

(i) Concrete Containing Volcanic Materials-Sample JP9

The Compressive Strengths of concrete containing sample JP9 volcanic materials are shown in Figure 4.4(i).

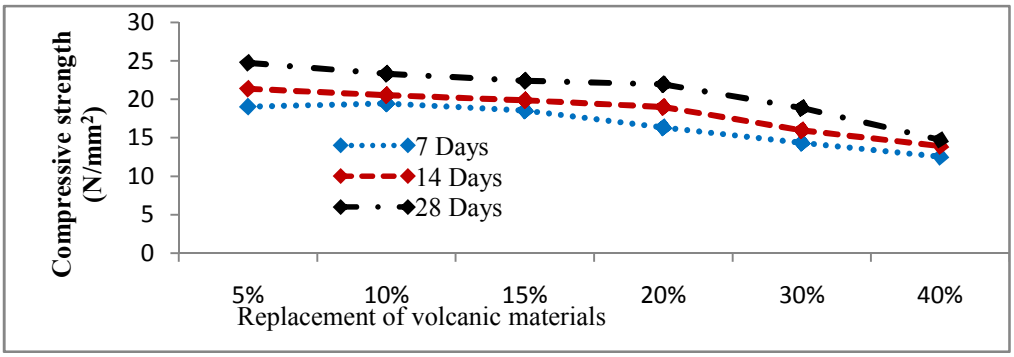


Figure 4.4(i): Compressive Strength (N/mm^2) of concrete containing JP9 **volcanic materials evaluated at 7, 14, and 28 days curing.**

(j) Concrete Containing Volcanic Materials-Sample JP10

The Compressive Strengths of concrete containing sample JP10 volcanic materials are shown in Figure 4.4(j).

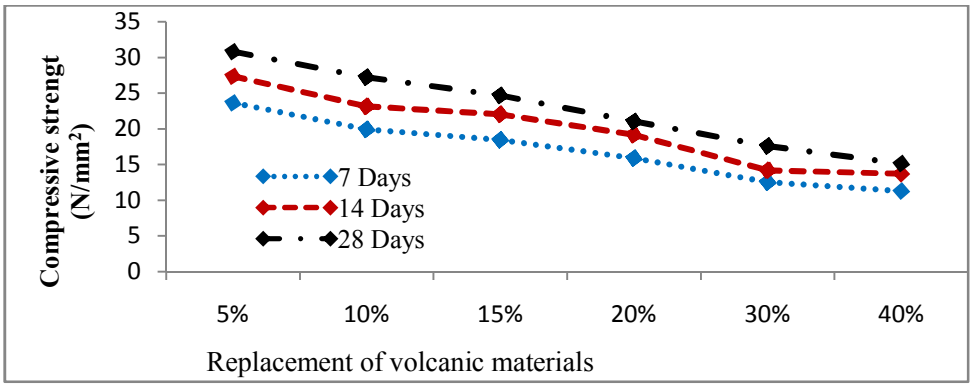


Figure 4.4(j): Compressive Strength (N/mm^2) of concrete containing JP10 **volcanic materials evaluated at 7, 14, and 28 days curing.**

(k) Concrete Containing Volcanic Materials-Sample JP11

The Compressive Strengths of concrete containing sample JP11 volcanic materials are shown in Figure 4.4(k).

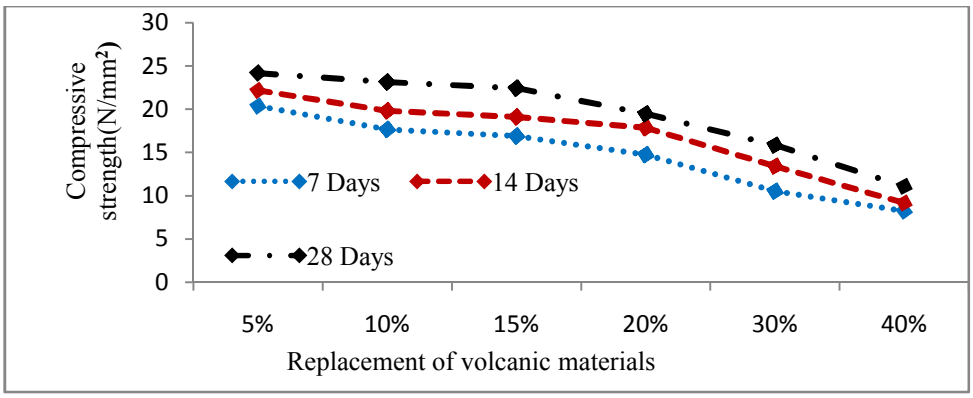


Figure 4.4(k): Compressive Strength (N/mm^2) of concrete containing JP11 **volcanic materials evaluated at 7, 14, and 28 days curing.**

(l) Concrete Containing Volcanic Materials-Sample JP12

The Compressive Strengths of concrete containing sample JP12 volcanic materials are shown in Figure 4.4(l).

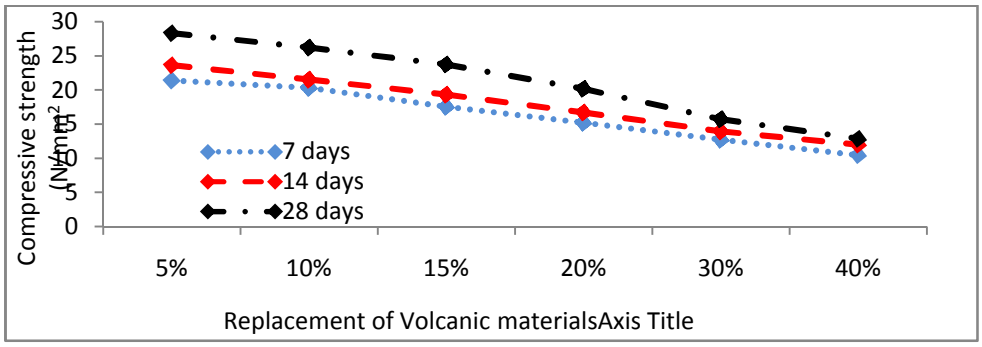


Figure 4.4(l): Compressive Strength (N/mm^2) of concrete containing JP12 **volcanic materials evaluated at 7, 14, and 28 days curing.**

(m) Concrete Containing Volcanic Materials-Sample JP13

The Compressive Strengths of concrete containing sample JP13 volcanic materials are shown in Figure 4.4(m).

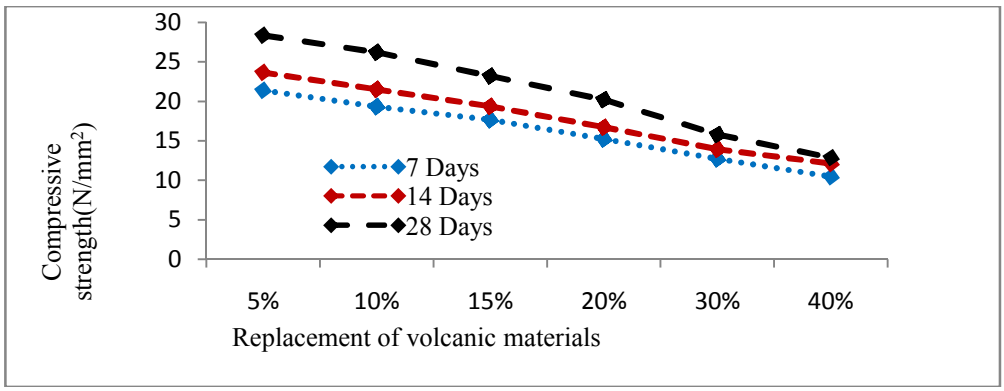


Figure 4.4(m): Compressive Strength (N/mm^2) of concrete containing JP13 **volcanic materials evaluated at 7, 14, and 28 days curing.**

(n) Concrete Containing Volcanic Materials-Sample JP14

The Compressive Strengths of concrete containing sample JP14 volcanic materials are shown in Figure 4.4(n).

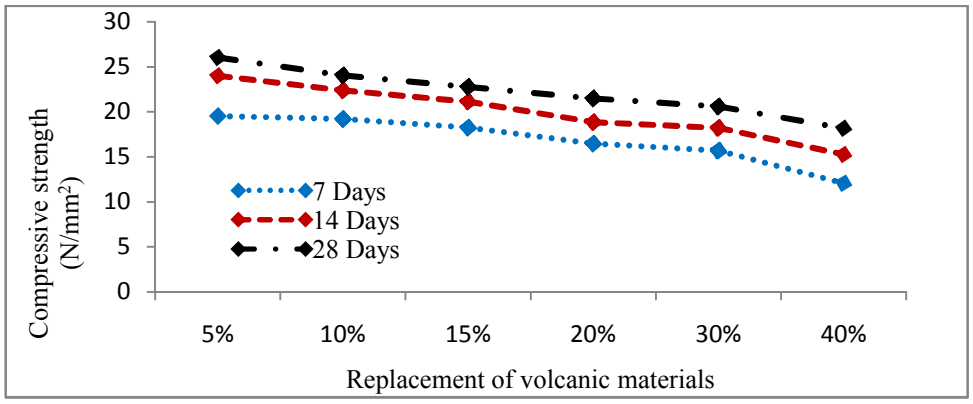


Figure 4.4(n): Compressive Strength (N/mm^2) of concrete containing JP14 **volcanic materials evaluated at 7, 14, and 28 days curing.**

(p) Concrete Containing Volcanic Materials-Sample JP15

The Compressive Strengths of concrete containing sample JP15 volcanic materials are shown in Figure 4.4(p).

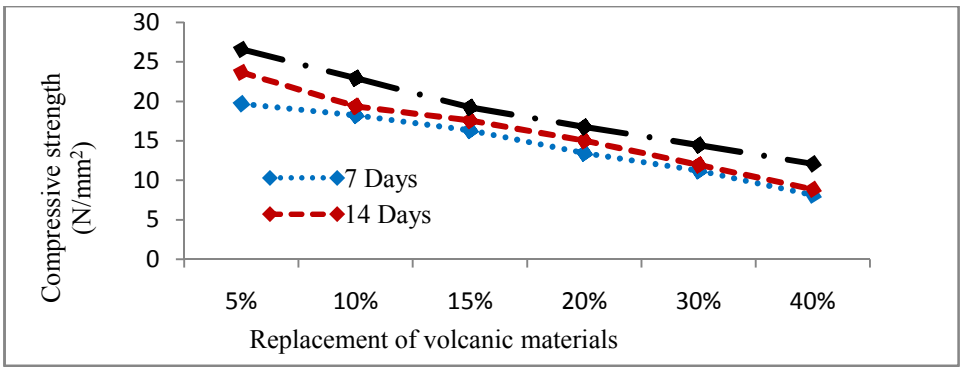


Figure 4.4(p): Compressive Strength (N/mm^2) of concrete containing JP15 **volcanic materials evaluated at 7, 14, and 28 days curing.**

(q) Concrete Containing Volcanic Materials-Sample JP16

The Compressive Strengths of concrete containing sample JP16 volcanic materials are shown in Figure 4.4(q).

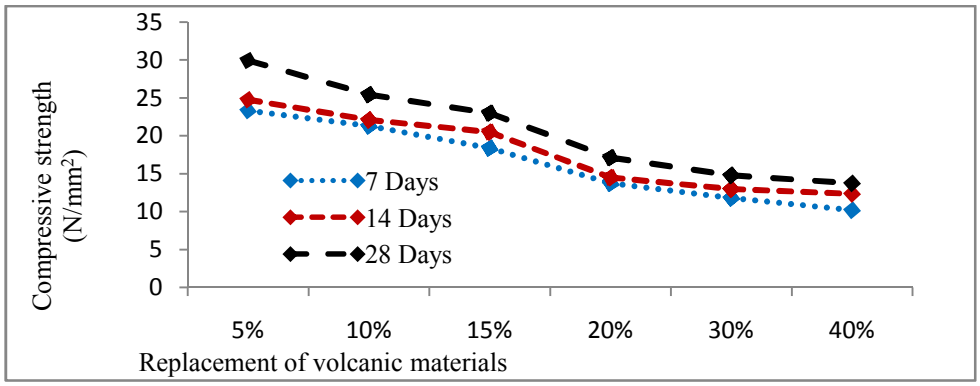


Figure 4.4(q): Compressive Strength (N/mm^2) of concrete containing JP16 **volcanic materials evaluated at 7, 14, and 28 days curing.**

(r) Concrete Containing Volcanic Materials-Sample JP17

The Compressive Strengths of concrete containing sample JP17 volcanic materials are shown in Figure 4.4(r).

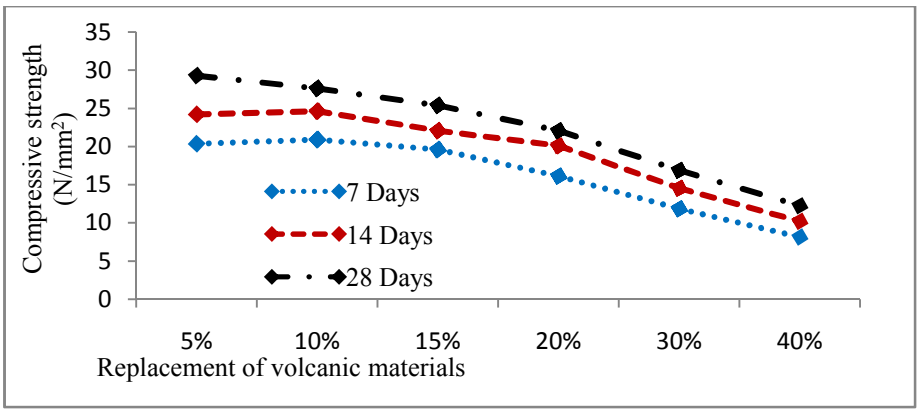


Figure 4.4(r); Compressive Strength (N/mm^2) of concrete containing JP17 **volcanic materials evaluated at 7, 14, and 28 days curing.**

(s) Concrete Containing Volcanic Materials-Sample JP18

The Compressive Strengths of concrete containing sample JP18 volcanic materials are shown in Figure 4.4(s).

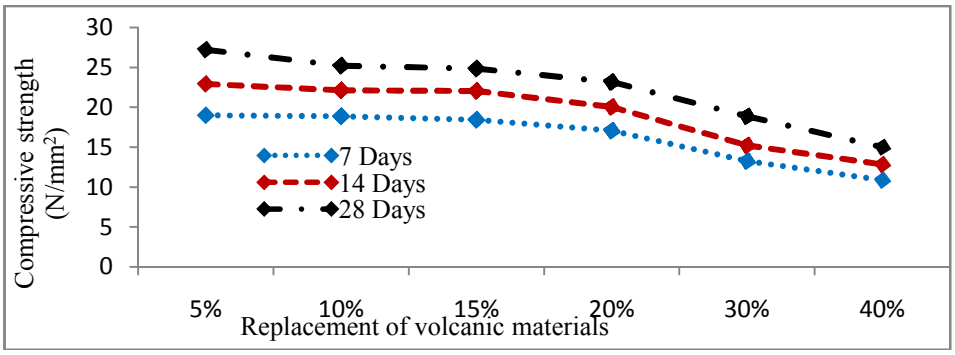


Figure 4.4(s): Compressive Strength (N/mm^2) of concrete containing JP18 **volcanic materials evaluated at 7, 14, and 28 days curing.**

(t) Concrete Containing Volcanic Materials-Sample JP19

The Compressive Strengths of concrete containing sample JP19 volcanic materials are shown in Figure 4.4(t).

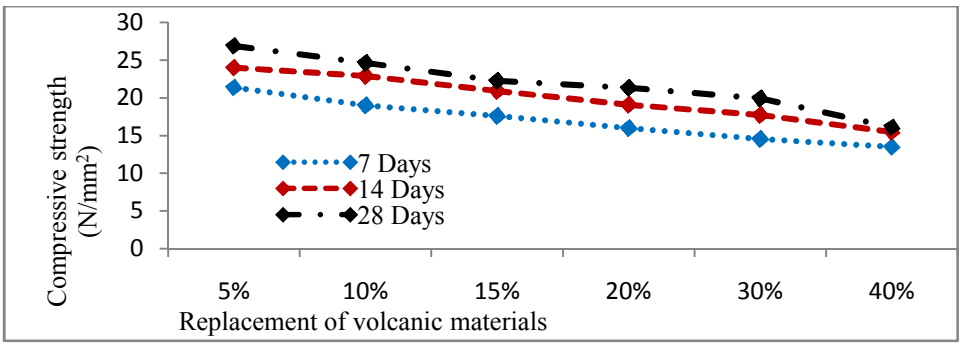


Figure 4.4(t): Compressive Strength (N/mm^2) of concrete containing JP19 **volcanic materials evaluated at 7, 14, and 28 days curing.**

(u) Concrete Containing Volcanic Materials-Sample JP20

The Compressive Strengths of concrete containing sample JP20 volcanic materials are shown in Figure 4.4(u).

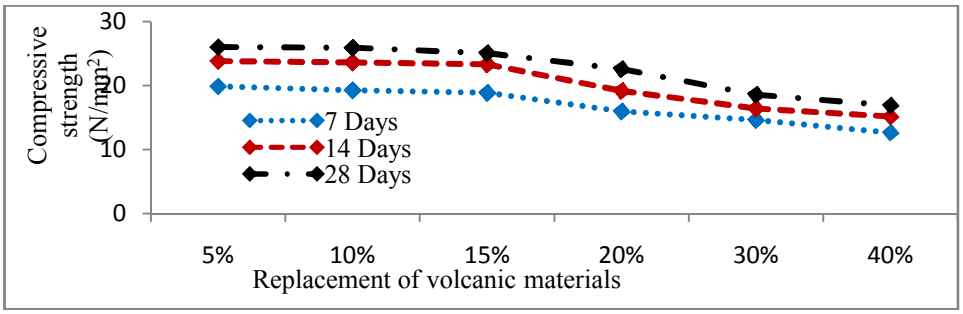


Figure 4.4(u): Compressive Strength (N/mm^2) of concrete containing JP20 **volcanic materials evaluated at 7, 14, and 28 days curing.**

4.1.5.3 Pozzolanic activity index of the Jos Plateau volcanic materials with OPC

(a) PAI with Concrete Containing 5% of Jos Plateau volcanic materials

Figure 4.5 shows the % of the PAI of the Jos Plateau volcanic materials with OPC in concrete containing 5% of the volcanic materials evaluated at 28 days curing.

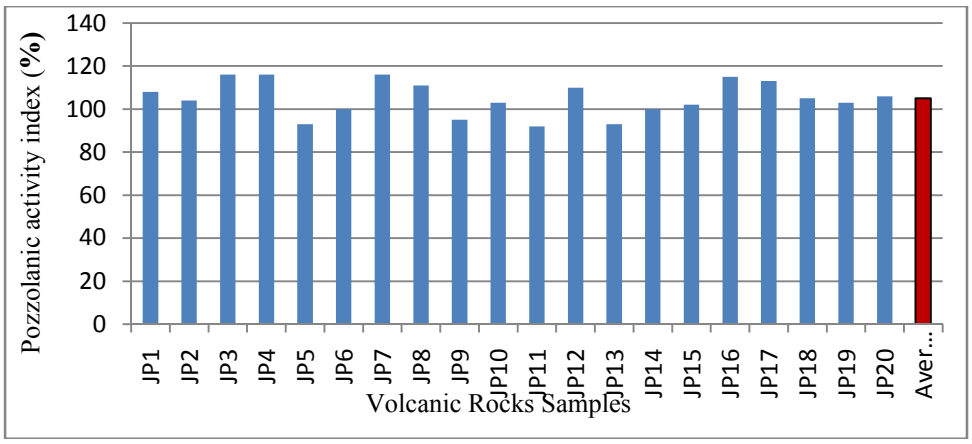


Figure 4.5: Pozzolanic Activity Index of concrete containing 5% volcanic materials.

(b) PAI with Concrete Containing 10 % of Jos Plateau volcanic materials.

Figure 4.6 shows the % of the PAI of the Jos Plateau volcanic materials with OPC in concrete containing 10% of the volcanic materials evaluated at 28 days curing.

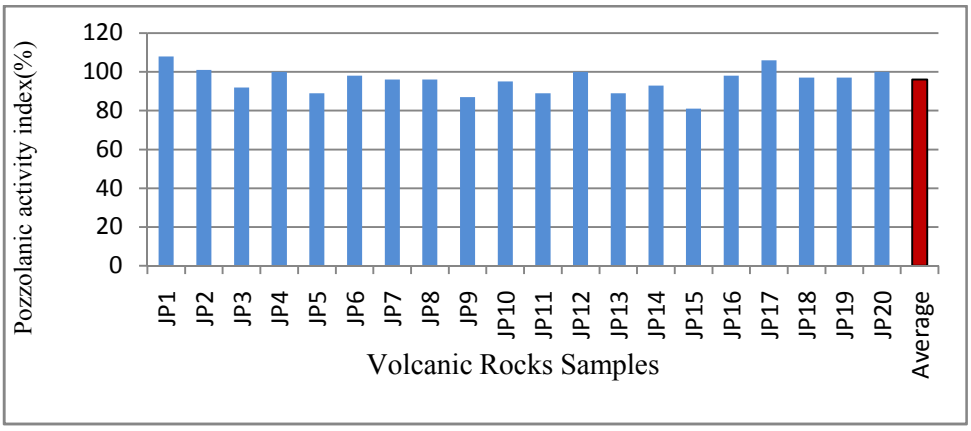


Figure 4.6: Pozzolanic Activity Index of concrete containing 10% volcanic materials.

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(c) PAI with Concrete Containing 15% of Jos Plateau volcanic materials.

Figure 4.7 shows the % of the PAI of the Jos Plateau volcanic materials with OPC in concrete containing 15% of the volcanic materials evaluated at 28 days curing.

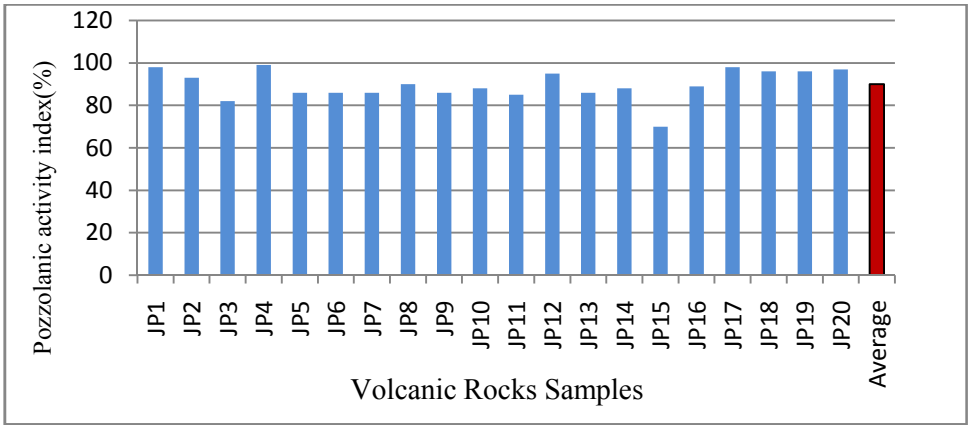


Figure 4.7: Pozzolanic Activity Index of concrete containing 15% volcanic materials.

(d) PAI with Concrete Containing 20% of Jos Plateau volcanic materials.

Figure 4.8 shows the % of the PAI of the Jos Plateau volcanic materials with OPC in concrete containing 20% of the volcanic materials evaluated at 28 days curing.

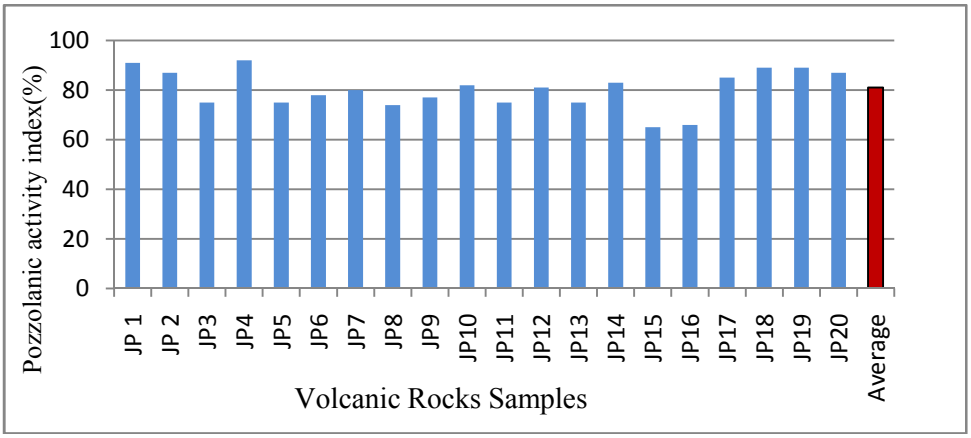


Figure 4.8: Pozzolanic Activity Index of concrete containing 20 % volcanic materials.

(e) PAI with Concrete Containing 30% of Jos Plateau volcanic materials.

Figure 4.5 shows the % of the PAI of the Jos Plateau volcanic materials with OPC in concrete containing 30% of the volcanic materials evaluated at 28 days curing.

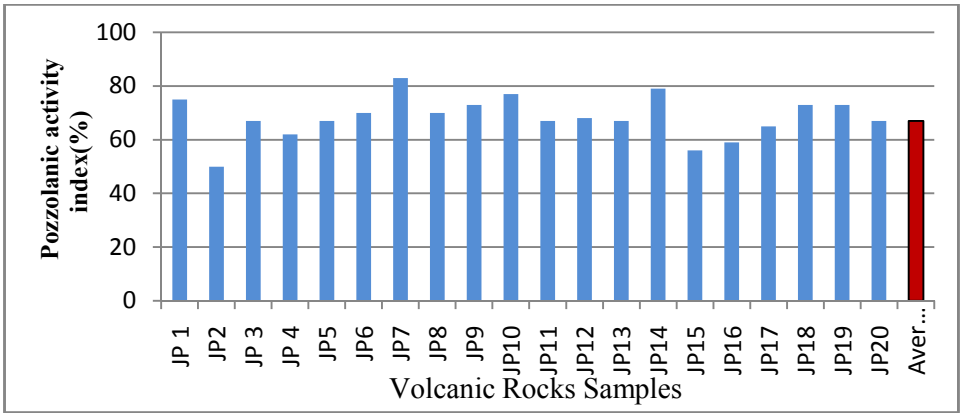
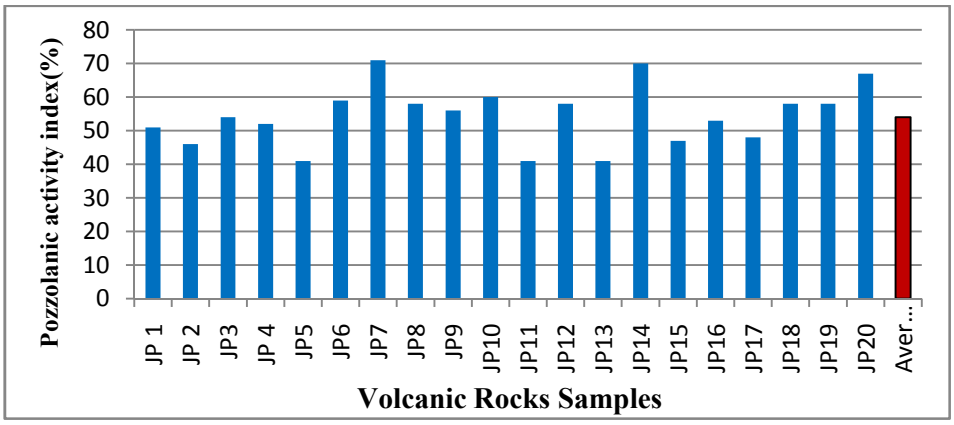


Figure 4.9: Pozzolanic Activity Index of concrete containing 30% volcanic materials.

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(f) PAI with Concrete Containing 40% of Jos Plateau volcanic materials.

Figure 4.10 shows the % of the PAI of the Jos Plateau volcanic materials with OPC in concrete containing 40% of the volcanic materials evaluated at 28 days curing.



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Figure 4.10: Pozzolanic Activity Index of concrete containing 40% volcanic materials.

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4.2 ANALYSIS

4.2.1 Jos Plateau Volcanic landscape

The field and literature studies showed that the Jos Plateau comprises of innumerable Land Marks of volcanic hills of fluvio-volcanic origin of historic volcanism. These pyroclastic falls volcanic deposits cover approximately nine Local Government Areas of the state.

4.2.2 Chemical Characteristics of Jos Volcanic Materials

4.2.2.1 Oxides composition of the Jos Plateau volcanic materials

The EDXRF techniques results (Table 4.4) indicated the presence of 5 trace elements namely Mn_2O_3, CO_2, NiO, TiO_2 and Cr_2O_3. While Table 4.3, the results of the oxides analysis by the NAA showed that the Jos Plateau Volcanic materials consist of 30 mineral oxides in varying degrees ; major, minor and trace (including rear elements) elements with as low as 0.5 ppm.-The comparisons of the elements of SiO_2, Al_2O_3 and Fe_2O_3 CaO, MgO and SO_3 by the three analysis techniques evaluated are presented in Table 4.11.

Table 4.11 (a): Mista-Ali Sample (JP1) Oxides composition

Item	EDXRF Method	Wet Method	NAA Method
$SiO_2 + AI_2O_3 + Fe_2O_3$ (%)	91.25	76.46	
Sum of minor oxides (%)	5.40	4.16	
SO_3 (%)	ND	0.45	NA
MgO (%)	3.43	3.43	5.34
Alkalis as Na_2O (%)	ND	NA	0.021
SiO_2 (%)	29.80	29.30	NA
AI_2O_3 (%)	25.70	25.82	37.60
Fe_2O_3 (%)	35.75	21.36	10.80
CaO (%)	0.18	0.28	6.99

ND- Noting Dictated NA – Not Analysed

Table 4. 11 (b): Kaskadi Sample (JP2) Oxides composition

Item	EDXRF Method	Wet Method	NAA Method
$SiO_2 + AI_2O_3 + Fe_2O_3$ (%)	91.63	74.95	-
SO_3 (%)	ND	0.07	-
MgO (%)	ND	3.43	0.362
Sum of minor oxides (%)	7.54	3.78	-
Alkalis as Na_2O (%)	ND	NA	0.01
SiO_2 (%)	29.40	31.90	NA
AI_2O_3 (%)	25.70	24.07	5.29
Fe_2O_3 (%)	35.75	18.98	30.41
CaO (%)	0.35	0.28	BDL

Table 4. 11 (c): Miango Sample (JP3) Oxides composition

Item	EDXRF Method	Wet Method	NAA Method
$SiO_2 + AI_2O_3 + Fe_2O$ (%)	90.16	95.31	-
Sum of minor oxides (%)	5.91	2.47	-
SO_3 (%)	ND	0.48	-
MgO (%)	0.05	1.71	0.37
Alkalis as Na_2O (%)	ND	NA	0.06
SiO_2 (%)	41.1	65.20	NA
AI_2O_3 (%)	35.5	26.13	3.34
Fe_2O_3 (%)	13.56	8.98	14.24
CaO (%)	0.16	0.28	-

Table 4. 11 (d): Gwafan Sample (JP4) Oxides composition

Item	EDXRF Method	Wet Method	NAA Method
$SiO_2 + AI_2O_3 + Fe_2O_3$ (%)	93.04	90.84	-
Sum of minor oxides (%)	1.16	2.06	-
SO_3 (%)	ND	0.07	-
MgO (%)	0.03	1.71	1.68
Alkalis as Na_2O (%)	ND	NA	0.029
SiO_2 (%)	27.40	52.50	NA
AI_2O_3 (%)	20.00	13.19	2.66
Fe_2O_3 (%)	45.60	25.15	9.44
CaO (%)	1.18	0.28	2.23

Table 4. 11 (e): Furaka Sample (JP5) Oxides composition

Item		EDXRF Method	Wet Method	NAA Method
$SiO_2 + AI_2O_3 + Fe_2O_3$	(%)	90.16	95.31	-
Sum of minor oxides	(%)	5.91	2.47	-
SO_3	(%)	ND	0.48	-
MgO	(%)	0.05	1.71	0.37
Alkalis as Na_2O	(%)	ND	NA	0.06
SiO_2	(%)	41.1	65.20	NA
AI_2O_3	(%)	35.5	26.13	3.34
Fe_2O_3	(%)	13.56	8.98	14.24
CaO	(%)	0.16	0.28	-

Table 4. 11 (f): Lobel Sample (JP6) Oxides composition

Item		EDXRF Method	Wet Method	NAA Method
$SiO_2 + AI_2O_3 + Fe_2O_3$	(%)	93.04	83.45	-
Sum of minor oxides	(%)	3.10	1.04	-
SO_3	(%)	ND	0.76	NA
MgO	(%)	0.06	ND	1.68
Alkalis as Na_2O	(%)	ND	NA	0.029
SiO_2	(%)	27.40	32.40	NA
AI_2O_3	(%)	20.00	20.51	11.33
Fe_2O_3	(%)	45.60	30.54	10.62
CaO	(%)	1.18	0.28	-

Table 4. 11 (g): Fobour Sample (JP7) Oxides composition

Item		EDXRF Method	Wet Method	NAA Method
$SiO_2 + AI_2O_3 + Fe_2O_3$	(%)	94.37	74.45	-
Sum of minor oxides	(%)	4.37	0.68	-
SO_3	(%)	ND	ND	NA
MgO	(%)	0.15	0.40	0.36
Alkalis as Na_2O	(%)	ND	NA	0.10
SiO_2	(%)	31.60	32.80	NA
AI_2O_3	(%)	24.80	20.69	2.24
Fe_2O_3	(%)	35.23	20.96	4.26
CaO	(%)			

Table 4. 11 (h): Vwang Sample (JP8) Oxides composition

Item		EDXRF Method	Wet Method	NAA Method
$SiO_2 + AI_2O_3 + Fe_2O_3$	(%)	96.19	76.53	-
Sum of minor oxides	(%)	2.66	0.65	-
SO_3	(%)	ND	0.07	NA
MgO	(%)	0.06	0.20	-
Alkalis as Na_2O	(%)		NA	0.03
SiO_2	(%)	31.40	37.0	NA
AI_2O_3	(%)	40.60	29.75	8.13
Ferrite oxide (Fe_2O_3)	(%)	24.19	9.78	6.16
CaO	(%)	0.19	0.28	

Table 4. 11 (i): Kwi Sample (JP 9) Oxides composition

Item		EDXRF Method	Wet Method	NAA Method
$SiO_2 + AI_2O_3 + Fe_2O_3$	(%)	91.35	84.05	-
Sum of minor oxides	(%)	5.64	0.28	-
SO_3	(%)	ND	ND	NA
MgO	(%)	0.05	ND	-
Alkalis as Na_2O	(%)	ND	NA	BDL
SiO_2	(%)	44.50	16.80	NA
AI_2O_3	(%)	25.98	19.13	8.31
Fe_2O_3	(%)	19.83	48.12	39.32
CaO	(%)	0.11	0.28	

Table 4. 11 (j): Kombun Sample (JP16) Oxides composition

Item		EDXRF Method	Wet Method	NAA Method
$SiO_2 + AI_2O_3 + Fe_2O_3$	(%)	90.96	78.05	-
Sum of minor oxides	(%)	3.73	1.93	-
SO_3	(%)	ND	0.34	NA
MgO	(%)	0.11	1.31	BDL
Alkalis as Na_2O	(%)	NA	NA	0.01
SiO_2	(%)	31.80	33.80	NA
AI_2O_3	(%)	24.00	21.88	9.55
Fe_2O_3	(%)	35.16	22.37	26.93
CaO	(%)	0.17	0.28	BDL

Table 4. 11 (k): Kwok Sample (JP11) Oxides composition

Item		EDXRF Method	Wet Method	NAA Method
$SiO_2 + AI_2O_3 + Fe_2O_3$	(%)	92.86	76.70	-
Sum of minor oxides	(%)	2.12	2.48	-
SO_3	(%)	ND	ND	NA
MgO	(%)	0.05		0.42
Alkalis as Na_2O	(%)	NA	NA	0.02
SiO_2	(%)	32.30	38.90	NA
AI_2O_3	(%)	40.10	29.63	13.35
Fe_2O_3	(%)	19.66	8.17	11.91
CaO	(%)	0.26	0.28	BDL

Table 4. 11 (l): Kuben Sample (JP12) Oxides composition

Item		EDXRF Method	Wet Method	NAA Method
$SiO_2 + AI_2O_3 + Fe_2O_3$	(%)	90.97	82.60	-
Sum of minor oxides	(%)	1.67	4.01	-
SO_3	(%)	0.10	1.90	NA
MgO	(%)	ND	2.20	BDL
Alkalis as Na_2O	(%)	NA	NA	0.01
SiO_2	(%)	17.00	20.60	NA
AI_2O_3	(%)	14.60	16.88	9.01
Fe_2O_3	(%)	59.37	48.12	41.76
CaO	(%)	0.12	ND	BDL

Table 4. 11 (m): Danwal Sample (JP13) Oxides composition

Item		EDXRF	Wet Method	NAA Method
$SiO_2 + AI_2O_3 + Fe_2O_3$	(%)	91.07	83.23	-
Sum of minor oxides	(%)	3.93	1.60	-
SO_3	(%)	ND	0.21	NA
MgO	(%)	0.09	0.28	0.59
Alkalis as Na_2O	(%)	ND	NA	0.01
SiO_2	(%)	44.60	51.80	NA
AI_2O_3	(%)	30.10	23.25	13.00
Fe_2O_3	(%)	16.37	8.18	5.00
CaO	(%)	0.17	0.28	BDL

Table 4. 11 (n): Bang Sample (JP14) Oxides composition

Item		EDXRF Method	Wet Method	NAA Method
$SiO_2 + AI_2O_3 + Fe_2O_3$	(%)		83.19	-
Sum of minor oxides	(%)	2.99	1.99	-
SO_3	(%)	ND	ND	NA
MgO	(%)	0.06	1.71	BDL
Alkalis as Na_2O	(%)	ND	NA	0.01
SiO_2	(%)	19.50	23.30	NA
AI_2O_3	(%)	17.7	21.75	8.40
Fe_2O_3	(%)	53.11	38.14	-
CaO	(%)	0.15	0.28	BDL

Table4. 11 (o): Kuba Sample (JP15) Oxides composition

Item		EDXRF Method	Wet Method	NAA Method
Sum of minor oxides	(%)	95.68	81.63	-
Sum of minor oxides	(%)	3.17	1.88	-
SO_3	(%)	ND	0.41	NA
MgO	(%)	0.07	0.91	BDL
Alkalis as Na_2O	(%)	ND	NA	0.01
SiO_2	(%)	19.00	19.20	NA
AI_2O_3	(%)	18.60	20.50	-
Fe_2O_3	(%)	58.08	41.93	24.56
CaO	(%)	0.11	0.56	BDL

Table 4. 11 (p): Niyes Sample (JP17) Oxides composition

Item		EDXRF	Wet Method	NAA Method
$SiO_2 + AI_2O_3 + Fe_2O_3$	(%)	90.20	62.68	-
Sum of minor oxides	(%)		7.70	-
SO_3	(%)	ND	ND	NA
MgO	(%)	0,40	9.88	5.23
Alkalis as Na_2O	(%)	NA	NA	1.04
SiO_2	(%)	36.06	32.90	NA
AI_2O_3	(%)	16.00	18.00	6.90
Fe_2O_3	(%)	28.14	11.78	10.66
CaO	(%)	8.21	0.28	4.07

Table 4. 11 (q): Wunat Sample (JP14) Oxides composition

Item		EDXRF Method	Wet Method	NAA Method
$SiO_2 + AI_2O_3 + Fe_2O_3$	(%)	91.94	71.45	-
Sum of minor oxides	(%)		5.64	-
SO_3	(%)	ND	4.05	NA
MgO	(%)		1.31	0.74
Alkalis as Na_2O	(%)		NA	0.01
SiO_2	(%)	35.00	36.00	NA
AI_2O_3	(%)	27.60	20.88	12.80
Fe_2O_3	(%)	29.34	14.57	16.61
CaO	(%)	0,20	0.28	BDL

Table 4. 11 (r): Kerang Sample (JP18) Oxides composition

Item		EDXRF Method	Wet Method	NAA Method
$SiO_2 + AI_2O_3 + Fe_2O_3$	(%)	83.32	64.01	-
Sum of minor oxides	(%)		13.95	-
SO_3	(%)	ND	0.21	NA
MgO	(%)	0.35	12.90	3.60
Alkalis as Na_2O	(%)		NA	0.37
SiO_2	(%)	32.80	36.20	NA
AI_2O_3	(%)	18.00	14.63	8.26
Fe_2O_3	(%)	32.40	13.18	12.32
CaO	(%)	7.2	0.84	4.8

Table 4. 11 (s): Larpia Sample (JP19) Oxides composition

Item		EDXRF Method	Wet Method	NAA Method
$SiO_2 + AI_2O_3 + Fe_2O_3$	(%)	91.26	82.53	-
Sum of minor oxides	(%)	3.72	2.13	-
SO_3	(%)	ND	0.21	NA
MgO	(%)	0.06	1.92	5.30
Alkalis as Na_2O	(%)	NA	NA	0.02
SiO_2	(%)	29.20	48.80	NA
AI_2O_3	(%)	24.10	25.38	12.02
Fe_2O_3	(%)	37.96	25.35	23.13
CaO	(%)	0.14	ND	BDL

Table 4. 11 (t): Ampang West Sample (JP20) Oxides composition

Item		EDXRF Method	Wet Method	NAA Method
$SiO_2 + AI_2O_3 + Fe_2O_3$	(%)	92.19	79.71	
Sum of minor oxides	(%)	4.22	1.39	-
SO_3	(%)	ND	0.48	NA
MgO	(%)	NA	0.91	0.57
Alkalis as Na_2O	(%)	ND	NA	0.01
SiO_2	(%)	24.60	26.50	NA
AI_2O_3	(%)	20.70	23.25	14.76
Fe_2O_3	(%)	46.89	29.96	14.47
CaO	(%)	0.13	ND	BDL

4.2. 2.2 Major Oxides of the Jos Plateau volcanic materials

(a) The Major Oxides are SiO_2, AI_2O_3 and Fe_2O_3.

The analysis of the results (Table 4.1) of major elements showed that SiO_2 varied

from 16.80 (JP9) to 63.8 (JP18) with an average of 36.41 % of the samples tested. Al_2O_3 values ranged from 13.19 % (JP4) to 29.63 % (JP12) with an average of 21.20 %; and Fe_2O_3 was found to range from 8.17% (JP12) to 48.12 % (JP9 and JP16) with an average of 22.99 % of the samples studied.

(b) The sum of the major oxides of the Jos Plateau volcanic materials

The results (Figure 4.11) showed that the average of the sum oxides of SiO_2 + AI_2O_3+ Fe_2O_3 of 90 % (18) of the samples tested vary from 71.45 (JP14) to 95.31% (JP3); and 2 samples results were 62.94% (JP17) and 65.26% (JP18) with an average of 82.13%.

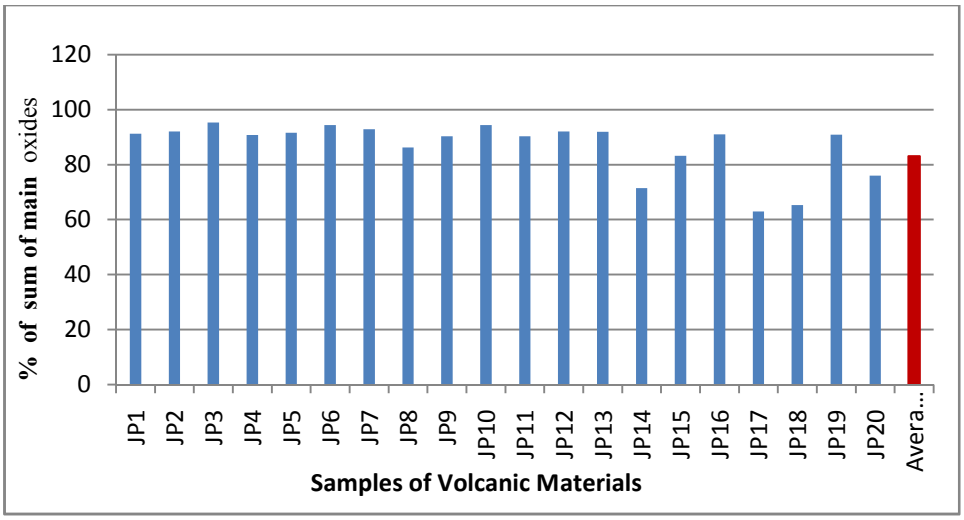


Figure 4. 11: The sum of the oxides of SiO_2 , AI_2O_3 and Fe_2O_3 the Jos Plateau volcanic deposits.

4.2.2.3 Minor Oxides of the Jos Plateau volcanic materials

(a) Oxides of minor elements of the Jos Plateau volcanic materials

The analysis of the minor oxides: The results (Table 4.1) of oxides composition of the volcanic samples indicated as follows;

i. CaO varied from zero% by weight (JP16) to 0.84 % (JP15) with an average of 0.29% by weight.

i. MgO presence in the materials had values between zero and 3.43% by weight in 95% (19) of the samples of the materials tested. Sample JP17 had its value as 9.88% by weight of the materials tested. However the average % of the 20 samples tested stood at 1.81 %.

iii. SO_3 had its values from zero to 4.05 % with an average of 0.53 % the 20 samples of the volcanic materials tested.

iv. The alkalis (Na_2O and K_2O) were not dictated in 40 % (8) of the samples tested; while the alkalis in the remaining of the samples varied from 0.04 % (JP5) to 1.55 % (JP17) with an average of 0.25 % by weight of the samples tested.

v. Trace elements were dictated mostly through NAA technique of oxides analysis: Titanium (TiO_2) showed significant presence in 95% of the samples investigated, varying from 2,761 ppm (0.28 %) (JP10) to 2, 8710 ppm (2.87%) (JP1) with an average of 7,693 (0.77%) ppm by weight in all the samples analysed; Mn_2O_3 was traced in all the samples tested varying from 150 ppm (JP9) to1446 ppm (JP18); Cobalt (Co) also traced , ranging from 5.1 ppm (JP12) to 818 ppm (0.08%) (JP18) ; and except JP11 and JP15 with presented higher values of 43510 ppm(4.35%) and 7708 ppm (0.77%)

respectively; Chromium (Cr) as well was found between 8.8 ppm (JP11) and 845 ppm (0.085%)(JP20).

(b) Sum of Minor Oxides of the Jos Plateau volcanic materials

The results (Figure 4.2) of the test carried out showed that the sum of the minor oxides of 85 % of the samples of the volcanic materials investigated varied from 0.55 % (JP5) to 4.69 % (JP18). Samples JP1 (5.556 %), JP2 (6.7 %) and JP15 (7.66 %) showed higher values. The average sum of the minor oxides obtained was 3.16 %.

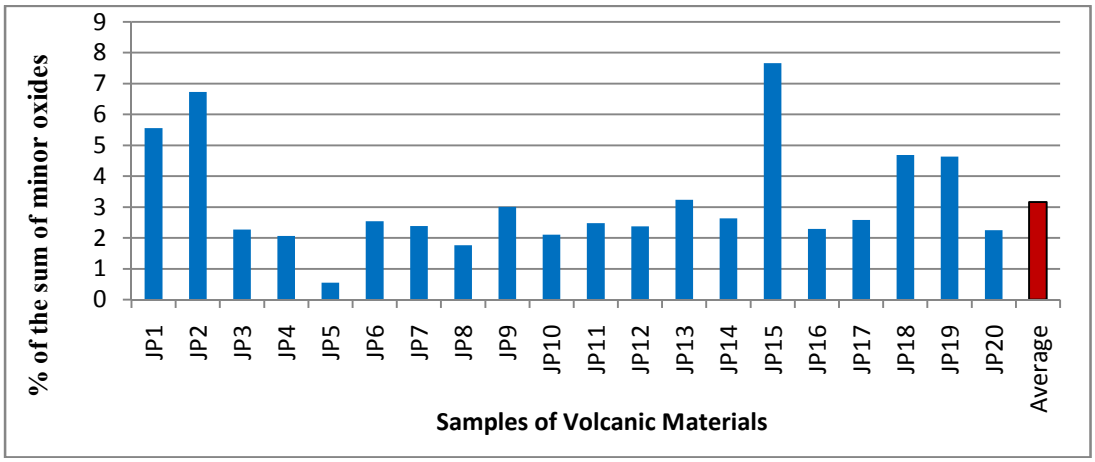


Figure 4. 12: The sum of the minor oxides of Jos Plateau volcanic deposits

4.2.1.4 Loss on Ignition of the Jos Plateau volcanic materials

The LOI (Figure 4.3) for samples are between 7.7% and 19.25% with an average of 12.33% of the materials by weight. The results of the tests indicated that the LOI of 30 % (6) samples were within the ASTM C 109/C 109M (2001) maximum recommendations of 10% for a material to be used as a pozzolana.

4.2.1.5 Moisture Contents of the Jos Plateau volcanic materials

The result of the tests (Figure 4.4) conducted showed that the MC of 95 % (19) of the samples tested are 0.10 to 2.30% by weight with an average of 1.09% by weight of the materials. This is within the value of 3% recommendation of ASTM C 618 (2005). The result of the tests (Figure 4.4) conducted showed that the MC of 95 %(19) of the samples tested are 0.10 to 2.30% by weight.

4.2.1.6 Comparison of Jos Plateau Natural Pozzolan with Class N of ASTM C 618

Table 4.12 is the comparison of Jos Plateau Natural Pozzolan with Class N of ASTM C 618. The standard specification is categories into chemical and physical requirements which the material ought to certified prior to its utilization in concrete mixtures.

Table 4.12: Conformance of Jos Plateau volcanic materials with ASTM C 618 (2005)

Description	Compound (%) Jos Plateau natural pozzolan	ASTM C 618(2005)
$\sum SiO_2), Al_2O_3$ and Fe_2O_3	71.45 - 95.31%	70 % min
SO_3	0 to 4.05 %	4.0 % max
MgO	0 to 3.43	6.0 % max
∑ minor oxides	0.55 % - 4.69 %	5 %
Available alkalis, as equivalent as Na_2O	0 - 1.55 %	1.5 % max
Loss on ignition	7.7% and 19.25%	10 % max
Moisture content	0.10 to 2.30%	3 % max

4.2.3 Chemical Characteristics Dangote Cement

4.2.3.1 Oxides composition of Dangote Cement

The results oxides composition of *Dangote* cement in Table 4.1 showed that that SiO_2, AI_2O_3, CaO , MgO and the alkalis are 8.56,1.7, 79.46, 0.03 and 0.21% by

weight respectively as against ASTM C150 limits of 17-25, 3-8, 60-67 and 0.2-1.3 % by weight in same order.

4.2.3.2 Loss on ignition and the moisture content of Dangote Cement

The results of the chemical analysis showed that the loss on ignition and the moisture contents of the *Dangote cement were* 8.8 % [ASTM C 150 (2004) limits] and 0.3% by weight respectively of the materials tested.

4.2.4 Physical characteristics of the Jos Plateau volcanic materials

(a) Specific gravity of the Jos Plateau volcanic materials

From the result of the study in Table 4.5, the materials exhibited specific gravity of 2.11 to 2.86 with an average of 2.36. From the result of the study, two samples (JP11 and JP12) representing 10% has its value (2.11) slightly below the stated low range of the Specific Gravity (SG) for a pozzolan with an average of 2.41 (Table 4).

4.2.5 Physical Characteristics of Concrete and Mortar containing Jos Plateau Volcanic materials

4.2.5.1 Pozzolanic Activity Index Jos Plateau volcanic materials with Lime

The Pozzolanic Activity Index (PAIL) with Lime test results (Figure 4.3) indicated that the % of lime total activity of samples JP2 (86.28), JP5 (86.28), JP7 (85.76), and JP12 (84.3) were high. While six samples (30%) [JP1 (49.08), JP8 (45.9), JP9 (46.1), JP11 (48.1), JP18 (46.33) and JP19 (45.7)] had their lime activity lower than 50%.

4.2.5.2 Setting time of concrete containing Jos Plateau volcanic materials

The results of the Initial Setting and Final Setting Times (Table 4.10) indicated that the Initial Setting Time (IST) for the samples evaluated varied from 155 to 162 minutes with an average of 158 minutes. The result also indicated that the Final Setting Times of the samples varied from 205 to 216 minutes with an average Final Setting Time of 212 minutes.

4.2.5.3 Soundness of concrete containing Jos Plateau volcanic materials

The result (Table 4.11) of soundness test showed the changes in volume varied from zero (samples JP2, JP3, JP5, JP12, JP17 and JP20) to 0.40% with an average of 0.17 for all the samples studied.

4.2.6 Mechanic characteristics

4.2.6.1 Compressive strength of portland cement concrete (control) cubes.

The results(Table 4.13) of the compressive strength of concretes with zero replacements of the OPC in the concrete mixtures produced under the condition were obtained as 20.18 N/mm^2, 23.93N/mm^2 and 26.86N/mm^2 at 7, 14 and 28 days of respectively.

4.2.6.2 Compressive strengths of concrete containing Jos Plateau volcanic materials

The results in Figure 4.4(a-u) showed that partial replacement of OPC in concrete mix gave varied compressive strengths in relation to the concrete cubes with zero replacement of the PC as follows;

i. The evaluation showed that 75% (15 samples) of the samples with 5% replacement of the PC had their compressive strength above the control cube compressive strengths at 28 days crushing; samples JP9, JP11, JP12, JP14, JP15 compressive strength were less than the control specimens. Four samples; JP3, JP4, JP10 and JP17 with 105 replacements showed compressive strengths of the cubes tested above the control cube concrete mixtures. Only sample JP14 with 30 % replacement tested at 28 days gave compressive strength above the control.

ii. 75% (15 samples) of the samples evaluated with 5 to 20 % partial replacement of the Portland cement in the concrete mixtures gained above 75 % compressive strengths of the control cubes tested. Samples JP7, JP8, and JP11 and JP16; 5 to 15% only partial replacement had the compressive strengths above 75 % of the control. For JP15, 5 and 10% replacement its compressive strengths above 75 % of the control.

iii. Increased in the volcanic materials replacements of the PC beyond 20% showed a decrease in the compressive of the concrete cubes mixes tested at 7, 14 and 28 days.

iv. The results (Figure 4.13) of analysis of the average Compressive strength ($N/mm^{2)}$ of the Jos Plateau volcanic deposits showed that only 5% partial

replacement of the PC with the volcanic materials gave compressive strengths of 27.92 N/mm^2 about 7.4% above the control cube strengths of 26.05 N/mm^2 at 28 days.

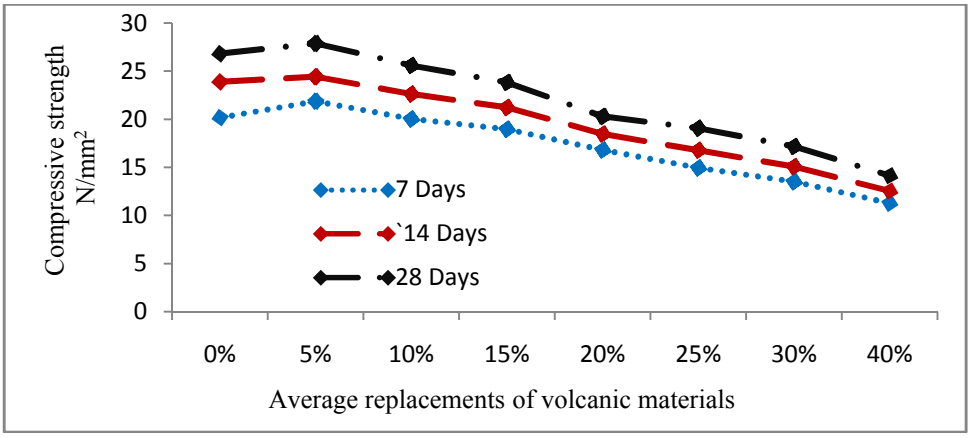


Figure 4.13: Average Compressive Strength (N/mm$^{2)}$ of Concrete Containing Jos Plateau Volcanic Materials

The analysis in Table 4.11 indicated that concrete containing 5 to 20 % of the volcanic pozzolans tested at 7, 14 and 28 days gave compressive strengths above 75 % of concrete with zero % volcanic materials. But concrete cubes with 30 and 40% Portland cement replacements failed below 75% of the control cubes.

Table 4.13: compressive strength of portland volcanic cement concrete

% replacement of OPC	Compressive strengths (N/mm^2) 7 day crushing	14 day crushing	28 day crushing
0	20.18 (15.12*)	23.93 (17.95*)	26.00(19.54*)
5	21.88	24.45	27.92
10	20.05	22.67	25.61
15	19.00	21.27	23.86
20	16.83	18.51	20.34
30	13.54	15.10	17.19
40	11.29	12.56	14.16

*75% of the compressive strengths of the control cubes

4.2.7 The Pozzolanic Activity Index of Jos Plateau volcanic materials with OPC

The Pozzolanic activity index of the volcanic materials with Portland cement in various replacements is as follows;

i. 5% replacement of the OPC: The results (Figure 4.5) of the pozzolanic activity index with Cement (PAIC) of the pozzolan showed that with 5% replacement of the PC, it varied from 92% (JP11) to 116% (JP3, JP4 and JP7) with an average index of 105.

ii. 10% replacement of the OPC: 10% replacements (Figures 4.6); the PAIC ranged from 81(JP15) to 108 (JP1) with an average of 96%.

iii. 15% replacement of the OPC: PAIC with 15% replacement of the OPC with Volcanic materials and the compressive strengths measured at 28 days. The activity index (Figure 4.7) varied from 70 (JP15) to 98(Samples JP1 and JP17) with an

average of 90.

iv. 20% replacement of the OPC: PAIC with 20% replacement of the PC with volcanic materials and the compressive strengths measured at 28 days (Figure 4.8); The activity index vary from 65 (JP5) to 91(JP1) with an average index 81.

v. 30% replacement of the PC: With 30% replacement of PC (Figure 4.9), an activity index varied between 56 (JP15) and 83 (JP7) with average of 67.

vi. 40 % replacement of the OPC: PAIC with 40 % Figure 4.10 is the PAIC the PC. The activity index at 28 days varied from 41(JP5, JP11, JP13) to 70 (JP14). The average index is 54 for the 40% replacements.

4.3 DISCUSSION

4.3.1 Jos Plateau Volcanic landscape

The Jos Plateau Volcanic landscape is made up of volcanic features and formations made up of variety of volcanic hills, eroded but traceable outstanding cones, features and materials with eroded visible volcanic deposits spread all across the volcanic region. These relics are typical of historic volcanism (Wright, 1989).

4.3.3 Chemical Characteristics of Jos Volcanic Materials

4.3.3.1 Oxides composition

The results of the oxides composition of the volcanic materials indicated that the

NAA techniques identified 30 elements. These include trace and rear elements with as low value as 0.5ppm such Br (Sample JP5) (Br). The EDXRF method, detected 13 elements as well as minor elements of CaO, Na_2, MgO and SO_3 and trace elements of TiO_2, Cr_2O_3 Mn_3O and NiO).The Wet Chemistry analysed the main elements SiO_2, AI_2O_3 and Fe_2O_3 and four minor element (CaO Mg and SO_3).The uniqueness these methods of oxides evaluation enables the assessment of element of choice from the volcanic samples.

4.3. 3.2 Major Oxides of Jos Plateau volcanic deposits

The results of the chemical analysis showed that the volcanic deposits from Jos Plateau are Natural Pozzolans consisting substantially of oxides of Silica, Aluminium and Iron. This gives the pozzolan, the acidic character and great affinity to the lime and alkalis. Besides its finely subdivided form, it carries bubbling particles with large internal surface area owing to the gasses that accompany the magma during the volcanic the eruptions (Neville, 1996, ACI, 2000).

The chemical analysis showed that the average sums of the main oxides (SiO_2, AI_2O_3 and Fe_2O_3) were 82.13 %.This satisfied the recommendation of the ASTM C 618 (2008) of a minimum of 70% by weight for a materials to be used as a pozzolan in concrete mixtures. This is an indication of the pozzolanicity of the pozzolan (Buen and Selst, 1992*)*. However two samples (JP17 and JP18) had their sum of the main oxides as 62.68% and 64.01% respectively below the ASTM recommendation.

Thus the results of the chemical analysis (Table 4.1) showed that the SiO_2 varied from 16.80 to 63.8 with an average of 33.35%. The values of 80% were below 50% by weight of the material tested. But other chemical and mineralogical analysis of some notable global natural pozzolanas (Table 2.2) showed that the values of the SiO_2 are as high as 86 % by weight of most volcanic materials. The corresponding values of aluminum iron present in the volcanic rocks are high; aluminum varied from 13.19 % to 29.63 % with an average of 21.20 % by weight. The oxides of iron vary from 8.17% to 48.12 % with an average of 22.99 % of the 20 sample studied (Table4.1).The silica to aluminum + iron ratio is calculated to be between 56 to 95 % for most natural pozzolan worldwide. But result of the investigation indicated that the silica ratio is between 20 to 56% Silica impacts strength and give acidic character and great affinity to lime and the alkalis that it is considered to be the most important element in a pozzolan; AI_2O_3 controls the quick settings of cements and like silica gives the pozzolana an acidic character and great affinity to lime and the alkalis (Detwiler et al, 1996). Iron also impacts strength, hardness and colour to cement (Practical Action, 2005).

4.3.3.3 Minor Oxides of Jos Plateau volcanic deposits

The average sum of the minor oxides obtained was 3.16 %. ASTM C 618 (2005) recommends that sum of the minor oxides should not be more than 5% by weight. The existences of the minor compounds in the cementitious materials are important

to the strength and durability of concretes. The low values of the minor elements indicated the materials are sound (Neville and Brooks, 2008).

All the materials samples studied have no trace of carbon. Detwiler et al (1996) reported that carbon in cement absorbed air entraining admixtures in concretes and dark colour effects on concretes. The magnesium oxide presence in the materials under investigation had values between zeros to 3.43% by weight 1.81 %. These values are within the specifications of ASTM C 618 (2005) which recommend 5%. Neville and Brooks (2008) reported that the excess of these oxides do cause unsoundness in cement; this is as a result of expansion of concrete from hydration of crystalline MgO. ASTM C 150 limits oxide of MgO to 6% by weight. The average sulphur contents for the volcanic materials tested are 0.69% with only one sample containing 4.05%. Excess of sulphur makes cement unsound and leads to deterioration of concrete Small amount of sulphur contributes to the soundness of cement, while excess of it makes the cement unsound (Neville, 1996).

Alkalis- NA_2O and K_2O_3; the materials tested are showed that the average value alkalis (Na_2O and K_2O) values were 0.25 % by weight of the samples tested.
ASTM C 618 (2005) recommends 1.5%. These alkalis react with some aggregates in the surrounding cement paste with cause's expansion of cement and slowing down the rate of gain of strength in concrete production (Neville, 1998). Cement having Na_2O not less than 0.6% is considered to below in alkali and thus sound cement; high amount of alkalis presents the lower the gain in strength of the concrete (Gupta

and Gupta, 2004) reported that the. Furthermore alkalis react with some aggregates in the surrounding cement paste with cause's expansion of cement and expand the concrete. According to Neville, 1996), this expansion not only causes cracks but slows down the rate of gain of strength in concrete production.

4.3.3.4 Trace elements of Jos Plateau volcanic deposits.

The results of the investigations showed the presence of trace elements; of significant to the concrete are the oxides of Mn_2O_3, NiO, Co, TiO_2 and Cr_2O_3. These elements are extremely small in concentration levels. But Bhatty (1995) reported that their effects on cement can be significant if their concentrations are beyond certain levels; high levels of TiO_2 did improve the compressive strengths of cement clinkers; furthermore Mn_2O_3 are found marginally to increase free lime, thus reducing the early compressive strength of cement pastes; cobalt (Co) somewhat reduces the hydraulic activity of alite and increases the water demand and marginally reduces the late strength of cement paste. Among the trace element detected in the volcanic deposits is Chromium (Cr); it is known to accelerate the hydration of paste and improve the early strength of concretes, and has thus been used to develop high strength cements. 0.7570 addition of chromium as chromium chloride and nitrate accelerate paste hydration and result in high initial hydration peaks; the workability and the initial setting times are reduced.

4.3.3.5 Loss on ignition of Jos Plateau volcanic deposits volcanic materials

The results of the tests indicated that the LOI of 30 % (6) samples were within the ASTM C 109/C 109M (2002) maximum recommendations of 10% for a material to be used as a pozzolana. High values LOI do indicate the extent of hydration and carbonation of free lime and magnesia in the materials which are harmful to concretes.

4.3.3.6 Moisture contents of Jos Plateau volcanic deposits volcanic materials

The result of the tests conducted showed that the MC of the samples tested was in an average of 1.09% by weight of the materials. This is within the value of 3% recommendation of ASTM C 618 (2005). This, according to (Anonymous, 2002), indicated low presence of deleterious organic solvent, decomposable and combustible materials.

4.3.4 Physical Characteristics

4.3.4.1 Physical characteristics of Jos Plateau volcanic deposits volcanic materials

(a) Specific gravity of the Jos Plateau volcanic materials

The SG of the Portland cement is taken as 3.15 % (Gupta, 2004, Meral, 2004, Neville and Brook, 2005). From the result of the study (Table4.5), the materials exhibited specific gravity of 2.11 to 2.86 with an average of 2.36. Thus, in preparing the Portland Pozzolana Cement (PPC) combination mixes, the mixes were proportion and batched separately by volume (Neville, 1998).Replacement by

weight would result into considerable greater volume of the volcanic materials in the concrete mixtures.

4.3. Physical Characteristics of concrete containing Jos Plateau volcanic materials

4.3.5.1 Pozzolanic Activity Index of Jos Plateau volcanic deposits with Lime

The Pozzolanic Activity Index with lime varied of from 45.7 to 86.2%. 75% of the samples tested had the possibility of higher affinity to $Ca(HO)_{2;}$ Neville (1998) thus, asserted that the lower the resulting quantity of the $Ca(OH)_2$ in the medium, the higher the pozzolanic activity.

4.3.5.2 Setting time of concrete containing Jos Plateau volcanic materials

The average Initial setting and Final setting time of the samples investigated were 155 and 212 minutes respectively. This satisfied ASTM C 595 (2006)(Standard Specification for Blended Hydraulic Cements) and BSEN197-1(2000)(Cement, Composition, Specifications and Conformity Criteria for Common Cements); requirements of the minimum of 45 minutes and a maximum of 7 hours for the initial and final setting respectively. According to ACI (2000) and extended setting time characteristics of concrete containing a natural pozzolan would put more pressure on formworks. The final setting time indicated that less pressure would be exerted on formwork while the initial setting time of about two and half hours is good enough for concrete production and placement.

4.3.5.3 Soundness of concrete containing Jos Plateau volcanic materials

The tests results showed that the changes in volume varied from 0 to a maximum of 0.40%. ASTM C 618 (2005) recommended a maximum of 0.80% beyond which the materials is said to be unsound due to free lime and MgO which are deleterious concrete and cause its deterioration. The test results showed the sulfate resistance of the material is excellent as indicated by the low expansion values in the ASTM C 1012 sulfate resistance test (Neville, 1996).

4.3.6 Mechanic characteristics

4.3.6.1 Compressive strength of portland cement concrete (control) cubes.

The Compressive strength of portland cement concrete (control) cubes achieved were 20.18 N/mm^2, 23.93N/mm^2 and 26.86N/mm^2 at 7, 14 and 28 days of respectively. BS 12(1991): Specification for concrete stated the compressive strength requirements for this class of concrete as 16 and 32.5 N/mm^2 for 7 and 28 days respectively. The results of chemical analysis of *Dangote* cement showed that the oxides of CaO and were at variance with ASTM Standard Specification for Portland cement. ASTM C 150 (2005) the limits of CaO and SiO_2 as 60 - 67 % and 17-25 % respectively. However the values obtained for CaO and SiO_2 were 79.46% and 1.7 % respectively. The LOI of this cement was found to 8.8 % as against 1-3 % by weight. Magnesium oxide presence in the materials was very low; too low values of MgO slow down the rate of strength gains.

4.3.6.2 Compressive strengths of concrete containing Jos Plateau volcanic materials

There were increases in the compressive strength concrete containing the volcanic later ages above those of control cubes. For instance the concrete containing 5% volcanic materials achieved compressive strength of about 7 % above the control cubes at 28 days. According to South (2009), this is an indicator of the pozzolanic activity of the volcanic materials. The results of the tests also showed that the Compressive strengths of concretes with partial replacement of 5 to 20% of the materials tested at 28 days with were above 75 % of the control cubes' Compressive strengths. These values satisfied ASTM C 618 (2005) for the materials to be used in concrete.

4.3.7 The Pozzolanic Activity Index of concrete containing Jos Plateau volcanic materials with Portland cement

The results (Figures 4.7) showed that Pozzolanic Activity Index with the *Dangote* Cement at 5 to 20 % had an average of 81%. These are within the ASTM C 595(2006) minimum specification for a pozzolan to be utilised for pozzolan to use Portland Pozzolana Cement in concrete production. Thus these results are indicators of the reactivity of the pozzolan with Portland cement (ACI, 2000).

American Society for Testing and Material C 311(2000) recommended that Pozzolanic Activity Index (referred to the Strength Activity Index) be used to determine the mineral admixture level of strength development when in addition

with hydraulic cement. 30% and 40% replacements had an average index of 67 and 54 respectively. This level of the material replace should not be used in concrete (ASTM C 618, 2005)

CHAPTER 5

SUMMARY, CONCLUSION AND RECOMMENDATIONS

5.1 SUMMARY OF FINDINGS

(a) Chemical Analysis of Volcanic materials

(i) The results of the chemical analysis indicated that the principal oxides; Silica (SiO_2), Alumina (AI_2O_3) and Iron (Fe_2O_3) were substantially present in all the

samples investigated. Si_{O2} varied from 16.80 to 63.8 % with an average of 36.41 %; Al_2O_3 ranged from 13.19 % to 29.63 % with an average of 21.20 %; and Fe_2O_3 varied from 8.17% to 48.12 % with an average of 22.99 % by weight of the samples studied.

(ii) The average sum of the main oxides (SiO_2 + AI_2O_3 + Fe_2O_3) was 82.13%. This satisfied the 70% minimum recommendation of ASTM C 618(2005) as a minimum value by weight of the sum of these oxides for a material to be utilised as a pozzolan.

(iii) There also exist minor compounds in the materials studied which are important to the strength and durability of concrete; some of these compounds are SO_3, MgO, CaO and alkalis (Na_2O, K_2O). CaO varied from zero % to 0.84 % with an average Of 0.29% and MgO varied from zeros to 3.43% in 95 % (19) of the samples of the materials tested with average % of 1.81 %. SO_3 had its values were zero to 4.05 % with an average of 0.53 % the 20 samples of the volcanic materials tested. Alkalis (Na_2O and K_2O) values were not dictated in 40 % (8) of the samples tested. For the 60 % of the samples, the alkalis varied from 0.04 % to 1.55 % with bringing the average to 0.25 % by weight of the samples tested. ASTM C 618 (2005) recommends 1.5 %. The MgO presence varied from zeros to 3.43% by weight in all the materials studied. These were within the limits of 5% recommended by ASTM C 618 (2005).

(iv) The results of the tests carried out showed that the average sum of the minor was 3.16 %. ASTM C (2001) recommends that sum of the minor oxides should not

be more than 5% by weight.

(v) The investigations of the volcanic materials indicated the presence of 12 trace elements including Titanium (TiO_2), Manganese (Mn_2O_3), Cobalt (Co) and Chromium (Cr) with showed significant presence in the materials studied.TiO_2 for instance, was detected 'considerably' present in 95% of the samples investigated; varying from 0.28 to 2.87% by weight with an average of 0.77% in all the sample analysed.

(vi) The results of investigation indicated all the materials studied there was no trace of carbon.

(vii) The evaluations of the loss on ignitions the moisture contents of the volcanic deposits showed that there are likely presence of deleterious substances and existence of free lime and magnesia in some of samples. The results of test indicated that the LOI of only 30 % (6) samples were within the ASTM C 109/C 109M (2001) maximum recommendations of 10% for a material to be used as a pozzolana.

(viii) The result of the tests conducted showed that the MC of 95 % of the samples tested was within 0.10 to 2.30% by weight with an average of 1.09% by weight of the materials. This is within the value of 3% recommendation of ASTM C 618 (2005).This, according to (Anonymous, 2002), indicated low presence of deleterious organic solvent, decomposable and combustible materials. Sample JP2 was slightly higher (5.82%) than the recommended value, indicating the likely presence of these

deleterious substances the sample such as water, organic solvents, decomposable and combustible products that evaporated on heating, leading to weight loss of the materials.

(ix) Chemical evaluation of *Dangote* cement showed that SiO_2 and AI_2O_3 were 49.6 and 43.3 % respectively by weight below the recommended values of ASTM C 150 (2004). CaO were also found in excess 18.6% above the upper limits and the LOI was 8.8 % as against the recommendations of 0.3 % of the ASTM.

(b) Physical characteristics Portland Pozzolana Cement Concrete

(i) The result of the studies indicated that the average Initial Setting and Final Setting Times were 2 hours 36 minutes and 3 hours 32 minutes respectively. These were found to be within ASTM C 595 (2006) requirement a minimum of 45 minutes and a maximum of 7 hours for the Initial and Final Setting Times respectively.

(ii) The result of soundness test tests of the Portland pozzolan of paste of 85:15 showed an average change of 0.17 % for all the materials evaluated. ASTM C 618 (2005) recommends a maximum of 0.80%. This indicate absence of free lime and MgO in the materials. The sulfate resistance of the material is also excellent as indicated by the low expansion of the samples tested (Neville, 1996).

(iii) Though *Dangote* cement showed low values of SiO_2 and AI_2O_3; excess of CaO and very high LOI, the replacement of the 15% OPC with the pozzolan reduced the tendency of the paste to excessively change in length. This signified that the pozzolanic reactions had blocked the capillary pores which improved the soundness

of the paste (Neville, 1996, Shetty, 2006, Day, 1990).

(c) Compressive strength of Portland pozzolan cement concrete

The results of the compressive strengths of concrete containing volcanic materials as natural pozzolan in six partial replacements provided a pattern of strength development when tested at 7, 14 and 28 days curing;

(i) Addition of 5% volcanic materials increased the compressive strengths of the concrete mixtures by 7% above those of control concrete cubes.

(ii) 10 % replacement gave 1.50 % less of the control cubes (98.5 % of control).

(iii) 15 % replacement gave 8.20 % less of the control cubes (91.8 % of control).

(iv) 20 % replacement gave 21.80 % less of the control cubes (78.2 % of control).

(v) 30 % replacement gave 33.90 % less of the control cubes (66.1 % of control).

(vi) 40 % replacement gave 45.00 % less of the control cubes (55.0 % of control).

(vii)The analysis indicated that the replacement of 5 to 20 % of the OPC in the concrete samples met the requirement of the ASTM C 618(2005).

From ASTM C 595 (2005) cement designation for Blended Cements, the materials can be used in concrete for both Type IPM (% replacement is 0 -15 %). and Type IP (15-40 %).

(d) Pozzolanic activity index

The investigation showed that Pozzolanic Activity Index with *Dangote* brand of Portland cement at 28 days for 5, 10, 15 and 20 % replacements were 105. 96, 90 and 81% respectively; while those of 30 and 40% were 67 and 54% respectively. Accordingly, 5 to 20% partial replacements of the OPC are within the ASTM C 618

(2005) specification of minimum of 75% at 28 days for a pozzolan to be utilised in Portland Pozzolana Cement in concrete production (ASTM C 618, 2005).

(e) The results of the investigations showed that the Chemical and physical Characterisations of the volcanic deposits can be used to predict pozzolanic activity of a pozzolan. Concrete containing volcanic materials samples which met the chemical and physical requirements of ASTM C 618 (2005) all exhibited pozzolanic characteristic in partial replacement of the OPC in the concrete mixtures.

(f) The chemical characteristics of the volcanic materials investigated did not clearly Relate to values of the respective compressive strengths and the pozzolanic activity index of the pozzolans. For instance in 5% replacements of the OPC at 28 days curing, JP17 which had its sum of main oxides as 62.94% exhibited compressive strength of 29.32 $N/mm^{2;\ while}$ JP9 with a sum main oxides of 90.31% had a compressive strength of 24.71 N/mm^2.

(g) The Jos Plateau materials can be used for cement Type IP and P 0-15, and 15-40.

(h) The results of the investigations into the pozzolanic characteristics of the Jos Plateau volcanic deposits ascertained that the materials possesses chemical and pozzolanic characteristics both in fresh and hardened concretes made in partial replacement of Portland Cement in the concrete mixes. The study showed that the oxides of SiO_2, AI_2O_3 and Fe2O3 are substantially present in all the samples tested. The sum of the main oxides of $SiO_2 + AI_2O_3 + Fe_2O_3$ oxides 80.01 % with 90 % vary from 71.45 to 95.31%. The investigation showed further that the Strength Activity

of the portland pozzolan cement concrete (PAI with Portland cement) at 28 days for 5 to 20 % partial replacements of the OPC were within the performance requirements of ASTM C 618 (2005) of a minimum of 75% at 28 days for a pozzolan to be utilised in concretes. The result of soundness test tests of the Portland pozzolan of paste of 85:15 showed the changes in volume varied from 0 to 0.40 indicating the absence of free lime and MgO in the materials.

5.2 CONCLUSION

From the results of the assessment of the chemical, physical and mechanical characteristics of the Jos Plateau volcanic deposits; and concrete containing the volcanic materials; it is conclusive that the volcanic deposits possess pozzolanic characteristics as natural pozzolans for use in concrete. It is thus concluded, that the Jos Plateau Volcanic Deposits are potential pozzolanic materials for use in Ordinary Portland cements Blending.

5.3 RECOMMENDATIONS

(a) Use of Volcanic Materials for Cement Blending

In view of the results of the tests and the evaluation of the Jos Plateau volcanic deposits and its potential pozzolanicity and suitability for use as a partial replacement in concrete mixtures it is recommended as follows;

i. The production of Portland cement alone may not be enough to meet domestic cement demands in Nigeria consequently the pozzolan found on the Jos Plateau

may be considered to be a convenient substitute for the manufacturing blended cement. Thus the establishment of Blending Plant for the production of Portland Pozzolan Cements is recommended moreover there is no record on commercial Blending or Alternative Cement production or utilisation of volcanic materials in Nigeria. The quality of the pozzolan is similar to other natural pozzolans used as a supplementary cementitious material in countries such as China, the Philippines, Taiwan, Japan, India and other Pacific Rim countries.

ii. Partial replacement of Portland cement with the Jos Plateau volcanic deposits in concrete mixtures masonry works, pavements and blocks productions be restricted to a maximum replacement of 20 % of the OPC by volume to be precise in the ratio 80 (OPC): 20 (volcanic materials).

iii.The existing cement manufacturing firms should look at its existing investments in the cement industry and utilised the clinker substitution by partial replacement of the their cement clinkers with the natural pozzolans which will not only decipher the GHG emissions but equally earned carbon credit under the Carbon Finance Assistant initiative.

(b)Recommendations for Further Studies

i. The volcanic materials found on the Jos Plateau require grinding to certain fineness before use. It is recommended for further studies for pilot tests to determine the fines required to satisfy the strength activity requirements of the pozzolan; and to

also produce local grinding mill to meet the fineness the minimal requires pozzolanic activity index for the volcanic deposits.

ii.The minor and trace minerals such as Manganese (Mn_2O_3), Cobalt (Co) and Chromium (Cr) *et cetera* showed 'significant' presence in the materials studied.

iii. The results of chemical analysis of *Dangote* cement showed that the oxides of CaO and SiO_2 were at variance with ASTM Standard Specification for Portland cement. While ASTM C 150 (2005) the limits of CaO and SiO_2 as 60-67 % and 17-25 % respectively. The values obtained for CaO and SiO_2 were 79.46% and 1.7 % respectively; the LOI of this cement was also found to be 8.8 % by weight as against 1-3 % by weight standard specifications of the ASTM. It is recommended that the pozzolanic activity of the Jos Plateau volcanic deposits in partial replacements of other brands of Portland cement in use in Nigeria are studied to evaluate the effects of the compounds of CaO and SiO_2 (presence in the Portland cement brand) on strength activity of the natural pozzolans.

iv. It is recommended the volcanic deposits be investigated on strata to strata bases to ascertain further insight into the volcanic characteristics of each volcanic deposit.

v. An economic modeling on the suitability of the volcanic materials for low cost housing be investigated the results of this study.

vi. In the today's world of Carbon Trading, the value of GHG emission reductions for specific existing cement manufacturing companies be studied through substitution of the cement clinkers with the Jos volcanic materials for Carbon Finance Initiative (CFI) benefits.

vii.The use of Natural Pozzolan in concretes is known to improve resistant to chemical attacks; thus it is recommended that durability of concrete made with the Jos Plateau volcanic deposits in specific chemical environments are investigated.

v. Specific land maps depicting the boundaries of the volcanic deposits; and drilling in each location to ascertain the dept and the strata of the deposits.

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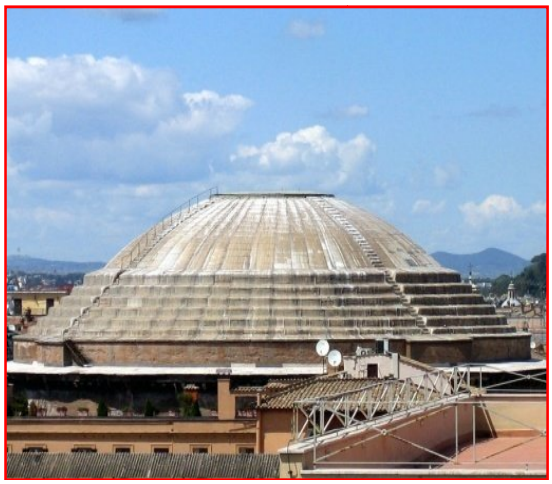
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Appendix: 'A'; Ancient Outstanding Structures



Dome of Pantheon exterior in 2011



Dome of Pantheon interior




Pantheon in Rome- its hemispheric dome (43m in diameter); its 2 millennia, Pumice was used.

Plate I: The Dome of Pantheon in Rome by 125- Source; Jackson (2003)






The Colosseum is 2 millennia old

Colosseum interior in 2011

Plate II: The Colosseum in Rome





Aqueducts (Rome) built between 38 and 52 AD-Source; Jackson (2003)

Plate III: Aqueducts (Rome) built between 38 and 52 AD

Appendix: 'B' Modern times used of pozzolans





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a) New shearwalls with forms been removed

(b) Workers placing High Volume Fly Ash concrete into the foundation

Plate IV: Barker Hall Project University of California-SOURCE; Shetty (2005)

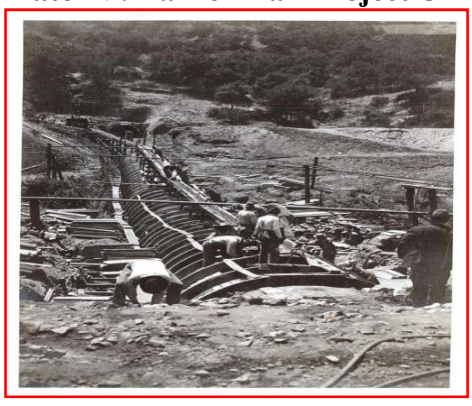


Plate V: Los Angeles Aqueduct (1912)

Aqueduct (1912)-Source; Azmar International (2000)



Plate VI: California Aqueduct- Source; Azmar International (2000)



Plate VII: Golden Gate Bridge SOURCE; Azmar International (2000)



Plate VIII: Bhakra Nangal Dam, India.

Source; Shetty (2005)

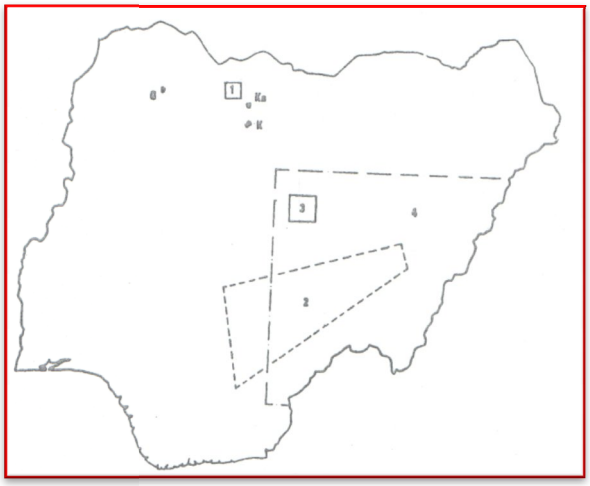
Appendix: 'C' Volcanic Deposit of Africa



▓ Approximate volcanic Areas

Plate IX: Volcanic deposits of Africa
Source; Day (1996)

Appendix: 'D' Areas of Volcanic Rocks are presented in Nigeria



Notes; 1 Runka and Gazamna (G) basaltic lavas, kimberite of Kafur (K) and clays of Kankara.

2 This area is made up of basic volcanic lavas, pyroclastic and minor intrusive rocks of the Benue Trough.

3 This is the fluvio-volcanic series of Jos Plateau Region.

4 This area covers the Jos Plateau, Benue Valley, and Adamawa High Lands (Mambilla Plateau) including the Cameroun Volcanic Line.

Plate X: Approximate areas of volcanic rocks are presented in Nigeria

Source; Wright (1996).

Appendix: 'E' Benue Trough

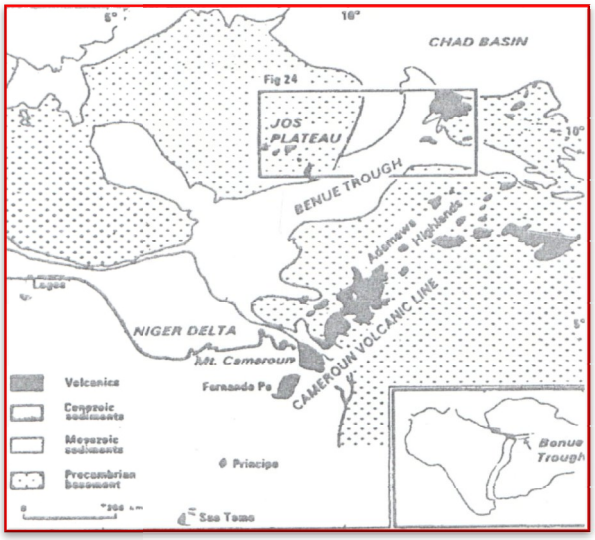


Plate XI: Benue Trough

Source; Wright (1996).

Appendix: 'F' Map of Nigeria

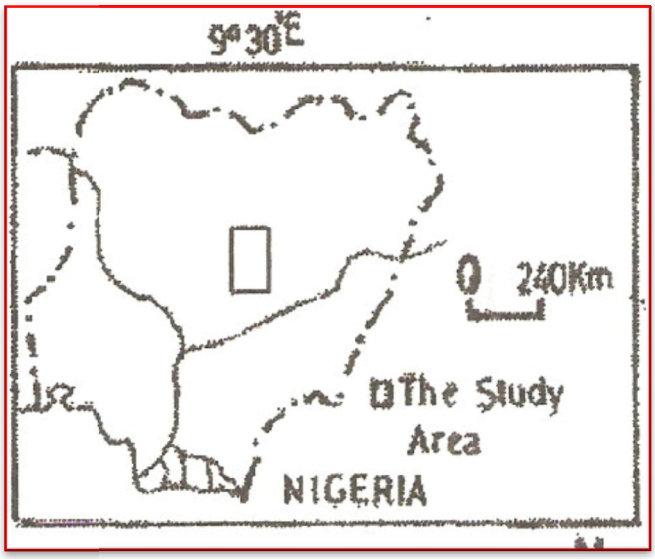


Plate XII: Map of Nigeria

Source; (Olowolafe, 2000)

Appendix: 'G' Administrative Map of Plateau State



Plate XIII: Administrative Map of Plateau
Source: Ministry of Information Jos (2005)

Appendix: 'H': Outstanding Volcanic Conical Hills

Plates ‘XII ’to ‘VIII’ present outstanding volcanic hills, complexes and features of the Jos Plateau



Plate XIV; Keran Volcanic Hills Complex
Field Survey (2008)



Plate XV; Kerang II Volcanic Hill
Field Survey (2008)



Plate XVI: Kerang Volcanic Complex
Field Survey (2008)



Plate XVII: Miango (Giwu) Twin Hills
Field Survey (2008)



Plate VIII: Foot Giwu Hill
Field Survey (2008)



Plate IXX: Niyes Volcanic Hill Plate
Field Survey (2008)





Plate XX: Kwi Conical Hill **Plate XXI: Purdong Volcanic**
Source; Ministry of Information Jos (2005)

Appendix: 'J': Volcanic Materials Exposed Soil Erosion

Volcanic Materials exposed by mining activities (Plate IXX and Plate XX)



Plate XXII: Exposal due to Soil Erosion

Field Survey (2008)

Appendix: 'K' Volcanic Materials Exposed by Mining Activities

Volcanic Materials exposed by mining activities (Plate XXI)



Plate X X III: Exposal Due to Mining Activities

Field Survey (2008)

Appendix: 'L' Volcanic Materials Exposed by Road Construction Activities

Volcanic Materials exposed by mining activities (Plate XIII and Plate XIV)





Plate XXIV: Exposed materials due construction activities (Jos South)
Field Survey (2008)

Appendix: ‘M’ Materials Presented in Forms of Pumice ‘Breads’

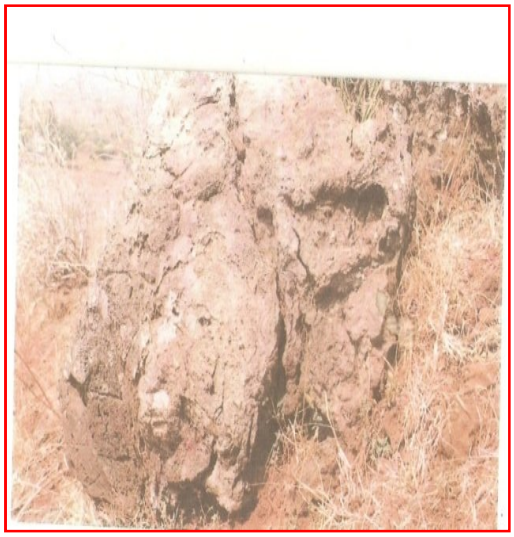


Plate XXV: ‘Bread Bomb’ Danwal



Plate XXVI: Pumice

Field Survey (2008)

Appendix 'N': Materials, Chemicals Equipment and Glassware

1. Wet chemistry technique

(a) Materials

(i) Chemicals

Sodium Carbonate, Potassium Carbonate, Hydrogen Chloride, distilled Water, Sulphuric Acid, hafnium(HF), sodium peroxide, methyl, methyl red, Barium Chloride, Barium Sulphate , Bauxite, sodium hydroxide, sodium carbonate, Ethylene Diamine Tetra Acetic Acid (EDTA) solution, zinc acetate, hydrochloric acid, ammonium hydroxide, acetic acid acetic acid – ammonium acetate buffer solution, xylenol orange indicator, standard zinc acetate solution, Magnesium Chloride, Potassium Hydroxide ,magnesium hydroxide, potassium cyanide, Hydroxylamine hydrochloride, Erichrome Black T indicator, Zinc Chloride potassium, mercuric chloride

(ii) Equipment

Muffle furnace capable of reaching a temperature of 1500^{o}C, weighing sets, desiccators, platinum crucible, filter paper, gauze wire, retort stand, pipette stand, hot plate, nickel crucible, No. 42 Whitman filter paper, No. 40 filter paper, filter paper 541, glass rods, pH indicator paper, a watch glass and a timer.

(iii) Glassware

Funnels, beakers, 500ml beaker, 25mls conical flask, measuring cylinder, burettes,

test tubes, 250ml beaker, 250ml conical flask and 250ml volumetric flask.

2. Energy Dispersive X- Ray Fluoresce method

(a) Materials

(i) **Chemicals**

K_2CO_3, $CaCO_3$, Ce_2O_3, WO_3, ThO_2, U_3O_8.

(ii) Equipment

A hydraulic press, agate mortar and pestle, an excitation source (that emits Ag - K X- rays- 22.1keV) , a Computer, and thick Pure Metal foils (Ti, Fe, Co, Ni, Cu, Zn, Zr, Nb, Mo, Sn, Ta, Pb).

3. Neutron Activation Analysis

The facility in Zaria is made up of a Miniature Neutron Source Reactor (MNSR) (Nuclear Reactor) with a tank-in pool structural configuration with a nominal thermal power rating of 31 kW, a gamma-ray spectrum analysis Wingspan 2004 (computer software developed for the analysis).

4. Loss on Ignition

Equipment

A furnace capable of reaching a temperature of 1500^{o}C (Plate XIV); flat bottom crucible of 50mm in diameter made of porcelain and silica gel as desiccators.

5. Moisture Content

Equipment

An Oven capable of reaching a temperature of 120^{o}C

Appendix 'P': Experimental Procedures of Chemical Analysis

1. Wet chemistry technique

The Wet Chemistry or the old chemistry Technique of chemical analysis was used as the first line of methods in evaluating the oxides composition of the volcanic materials. According to The National Metallurgical Development Centre Laboratory Manual was utilised in analysis of major elements in samples which percentages of the oxides by weight is 0.5% and above.

(a) Oxides of Silica (SiO_2)

The SiO_2 is determined by Gravimetric analysis. In this technique the chemical reaction separates the Silica from a sample solution.

Step 1; 1 gm of the sample was weighed in a Platinum crucible.

Step 2; the sample was then mixed thoroughly with a mixture of Na_2CO_3 $+K_2CO_3$ in a ratio 1:1.

Step 3; the crucible and the contents were placed in the furnace (Plate XI) and heated at a temperature of 950 ^oC in the Furnace for 20 minutes.

Step 4; It was allowed to Cool and the fused was extracted into a 400 ml beaker with 1:1 HCL 50ml. It was then Dehydrated and baked.

Step 5; It was allowed to cool again and 10ml of Concentrated HCl and hot distilled water added up to 150ml in a beaker. It allowed boiling further.

Step 6; The content was filtered through No. 41 filter paper and Washed with (1:4) HCL 3 times, and with hot water several times until the residue(filtrate) was free form HCl.

Step 7; the residue (filtrate) was then ignited in the Platinum Crucible at 950^{o}C to constant weight, cooled in the desicator and weighed= (w_1).

Step 8; 6 drops of 1:1 H_2SO_4 added to the residue and then 10 ml Hafnium HF and then evaporated slowly over a low heat.

Step 9; the residue was ignited again in the muffle furnace to a constant weight, cooled in a desiccators and weighed the crucible = (W_2).

Step 10; Calculations.

% of SiO_2 $\frac{(\quad -}{\qquad\qquad}$

Where; W1 = Weight of the Platinum Crucible with the material before Hydroflurisation.

W2 = Weight of the Platinum Crucible after Hydroflurisation.

Ws = Weight of the sample

(b) Oxides of sulphur (SO_3)

The SO_3 is determined by Gravimetric analysis. This carried out by the fusion method; the chemical reaction separates the Sulphur from a sample solution.

Step1; 0.2gm of sample weighed in a nickel crucible and 2gm of sodium peroxide was added and mixed with a thin dry glass rod. The mixture was covered with a thin

layer of the peroxide and then heated gently over a low flame at a temperature (dull red) just sufficient to produce complete fusion.

Step 2; to obtain the liquid condition, the mixture was heated up to 15 minutes. The melt was kept over the flame for 5 minutes. It was then removed from the heat and allowed to cool in air slowly.

Step 3; the crucible was then placed in a 500ml beaker and 100ml water poured on it. It was then covered quickly with a watch glass. The crucible was removed and washed with water, and watching it carefully out the boil for a few minutes with constant stirring. The liquid became greenish. 5mls of methyl was then added and boiled and it precipitated. When it was allowed to settle, the solution became clear.

Step 4; the solution was filtered hot through Whitman No. 40 filter paper in a 500ml beaker using a large size funnel. The residue was then washed with hot water 6 times. The precipitation was then discarded. A few drops of methyl red were added and made slightly acidic with HCl (about 3mls). 10mls of 10% $BaCl_2$ solution was added slowly and constantly stirred and kept hot for a few minute and then removed from the flame and kept overnight to allow the precipitate to settle.

Step 5; The precipitate was then filtered through No. 42 Whitman filter paper and washed ten times with hot water.

Step 6; the residue was then Transferred along with the filter paper in a weighed platinum crucible and ignited carefully at a temperature of 1000^{o}C. Cooled in desiccators and weighed again. From the weight of the $BaSO_4$ the percentage of S in the sample calculated as follows:

$$S\% = \frac{(\quad - \quad)}{(\quad)} .$$

Where, G1 = Weight of $BaSO_4$ formed from sample

G2 = Weight of $BaSO_4$ formed from blank

G3 = Weight of the sample taken

(c) Oxides of alumina (Al_2O_3)

The Al_2O_3 is determined by titrimetric analysis. The method measure the volume occupied by the compound using a solution of known reagent that reacts in certain way with the component under analysis.

Ethylene Diamine Tetra Acetic Acid (EDTA) Complexometry Method

Al_2O_3 is determined by the Complexometry method. The bauxite sample is fused with sodium hydroxide and a pine of sodium carbonate and the resultant sodium aluminate is extracted with water. The pH of the solution is adjusted to suitable range. An excess of Ethylene Diamine Tetra Acetic Acid (EDTA) solution is added and boiled to form a stable complex. After cooling, the excess of EDTA is determined by titrating (Plate XIII) with a solution of zinc acetate and the percentage of Al_2O_3 is calculated from the amount of actual EDTA used up.

Step1; 0.2gm of finely dried (powdered) sample of the material were placed in a nickel crucible and10 pellets of sodium hydroxide and a pinch of sodium carbonate added to the crucible.

Step 2; It was then kept over a hot plate (Plate XIV) for digesting-to melt and there after fused over a 10m flame. The crucible was kept to it cool in the air.

Step 3; the crucible along with its content were cooled and kept in a 250ml beaker and about 100ml of hot water was added and boiled for 10 minutes. It was removed from the flame and the crucible taken out with a glass rod, washed thoroughly with water and then transferred the washing into the beaker. The hot solution is then filtered through No. 40 Whitman filter paper into a 500ml conical flask. The precipitation was washed with hot water 6 times to ensure that no sodium aluminate remains entrapped in the precipitate.

Step 4; the filtrate is then acidified with hydrochloric acid. 25ml standard EDTA solution is then added. The pH was then adjusted to 5.0 - 5.5 with ammonium hydroxide and hydrochloric acid using pH indicator paper and then boiled for 15 minutes. It was allowed to cool, and 25ml acetic acid - ammonium acetate buffer solution was added. The pH is checked again and adjusted to 5.0 – 5.5. Two drops of xylenol orange indicator. A lemon yellow colour developed. It was titrated with standard zinc acetate solution. The colour changed at end point form lemon yellow to purple. From the titrated value, the Al_2O_3 % was calculated.

(d) Oxides of calcium (CaO)

The CaO is determined by titrimetric analysis. The method measure the volume occupied by the compound using a solution of known reagent, which reacts in certain way with the component under analysis.

Procedure for determination

Step 1; 0.2g of sample was weighed and placed into a 250ml beaker.

Step 2; hanged on to a hot plate with 20ml 1:1 HCl,

Step 3; It was filtered into a 250ml volumetric flask through filter paper 541.

Step 4; the filter paper was washed several times with hot water allowed to cool, made up, and shaken.

Step 5; 0.25ml of the aliquot and 100ml of distilled water were placed into a 250ml conical flask. 30mg $MgCl_2$ and 4ml 8m KOH added to precipitate magnesium hydroxide, after two minutes about 30mg each of potassium cyanide and Hydroxylamine hydrochloride were also added and allowed to dissolve by constant spinning.

Step 6; the solution was then titrated (Plate 3) with 0.01m EDTA using Erichrome Black T indicator until the colour changed from wine red to blue.

1ml 0.0m EDTA = 0.4008MG = 0.5608CaO

$$\% \text{ CaO} = \frac{\qquad\qquad}{\qquad\qquad}$$

(e) Oxides of Magnesium (MgO)

Calcium + Magnesium

Step 1; 0.2g of sample was weighed and placed into a 250ml beaker.

Step 2; hanged on to a hot plate with 20ml 1:1 HCl,

Step 3; it was filtered into a 250ml volumetric flask through filter paper 541.

Step 4; the filter paper was washed several times with hot water allowed to cool, made up, and shaken.

Step 5; 25ml of the aliquot was placed into a 250ml conical flask. 100ml of distilled water and 5ml buffer solution (by adding 55ml conc. HCl to 400ml distilled water). 30mg each of potassium cyanide and hydroxylamine hydrochloride. Allowed to cool by constant swirling.

Step 6; the solution was then titrated with 0.01m EDTA using Erchome Black T indicator until the colour changed from wine red blue.

Vol. Consumed by Ca^{++} + Mg^{++} + Mg^{++} - Vol. Consumed by Ca^{++} EDTA = 0.2432Mg = 0.4032MgO.

$$\text{Therefore \% MgO} = \frac{\qquad\qquad}{\qquad\qquad}$$

(f) Iron Fe_2O_3

The Fe_2O_3 is determined by Gravimetric analysis. The chemical reaction separates

the Iron from a sample solution.

Step 1; 0.2g of the samples were weighed and placed into a dry 25mls conical flask.

Step 2; 2mls of water, 25mls of concentrated HCl mix and cover.

Step 3; two drops of HF thereafter was added into the flask.

Step 4; It was then placed on a Hot Plate (Plate 4) and 5% $SnCl_2$ was added until the solution became colourless.

Step 5; It was Covered with silica crucibles and continued to boil hot plate until dissolution was completed.

Step 6; the solution removed from the hot plate, rinsed; the wall of the conical flask was covered and 5% potassium was added permeated until the yellow colour of fermions appeared.

Step 9; the solution was heated to boiling and 15% stannous chloride solution was added until the yellow colour was no longer evident.

Step 10; 15mls (1:3) H_2SO_4 mix was added and the wall of the conical flask was rinsed with water until total volume was equal to 100mls.

Step 11; the solution was cooled to 25^oC.

Step 12; 10mls of 2% mercuric chloride solution was added and mixed and allowed to stand for five minutes.

Step 13; 10mls of 0.02% Fe-indicator was added in $\underline{H_2\ P_3H_3PO_4(1:4)}$ titrate with 0.1N potassium dichromate.

1mls 0.1N $K_2CR_20_7$ – 0.005585g Fe.

$$\%Fe = \frac{\qquad\qquad\qquad\qquad\qquad\qquad}{}$$

2. Energy dispersive x-ray fluorescence (EDXRF) method

The samples are ground manually to powder with an agate mortar and pestle to grain size of less than 125µm. Pellets of 19mm diameter are then prepared from 0.3-0.5g powder with three drops of organic liquid binder and pressed afterwards at 10 tons with a hydraulic press. The measurement of the elements were performed using the Excitation Source by introducing the pellets of each of the samples into the x-ray fluorescence generator detector source emitting Silver (Ag)-Potassium(K) X-ray (22.1keV) in which all elements with lower characteristic excitation energies were accessible for detection in the samples for the analysis. The measurements of the elements are performed using the Excitation Source. The elements with the characteristic excitation energies are then accessible for detection in the samples.

The quantification of the elements was then carried out using the Emission-Transmission Method. This method involved the use of Molybdenum (Mo) as a target material as the source of monochromatic X-rays, which was excited through the sample by primary radiation and then penetrated on the way to the detector. The spectra for the samples were collected with the Cadmium 109 source and evaluated using the analysis of X- ray Spectra by Iterative Least Squares Fitting (AXIL) - a

soft ware program used for the analysis of the oxides of SiO_2, Fe_2O_3, Al_2O_3, MgO, CaO, SO_3, TiO_2, Na_2O, Mn_2O_3, CrO, Y_2O_3, and SrO).

(c) The Neutron Activation Analysis method

The volcanic materials samples were placed the reactor. The reactor's flux of neutrons from uranium fission interacts with the target nucleus of the element and when neutron energy bombards the sample it promotes radioactive nuclei of the target element. The radioactive nuclei then emit characteristic gamma rays; the detection of these rays indicates the presence of a particular element. The elements are then measured with a specifically design soft ware; the gamma-ray spectrum analysis Wingspan 2004 computer software for neutron activation analysis measurement of elements.

(b) The oxides composition

Sensitivity calibration of the system was performed using thick pure metal foils (Ti, Co, Ni, Cu, Zn, Zr, Nb, Mo, Sn, Ta, Pb) and stable chemical compounds (K_2CO $CaCO_3$, Ce_2O_3, WO_3, ThO_2, U_3O_8.The measurement of the elements was performed using the Excitation Source by introducing the pellets of each of the samples into the X-ray fluorescence generator detector source emitting Silver (Ag)-Potassium (K) X-ray (22.1keV) in which all elements with lower characteristic excitation energies were accessible for detection in the samples for the analysis. The measurement of the elements was performed using the Excitation Source; the measurement of x-rays intensities emitted by components of a target sample when excited by Silver-Potassium (Ag-K) X-rays (22.1 keV) from an annular excitation source of 25 milicurie (mC_i) Cadmium 109 (^{109}Cd).The system consists of the excitation source and a Silicon (Si) - Lithium (Li) semiconductor detector coupled to a computer controlled Analog to Digital Control Card (ADC).

The quantification of the elements was then carried out using the Emission-Transmission Method. This method involved the use of Molybdenum (Mo) as a

target material as the source of monochromatic X-rays, which is excited through the sample by primary radiation and then penetrate on the way to the detector. The spectra for the samples were collected with the Cadmium 109 source and evaluated using the analysis of X-ray Spectra by Iterative Least Squares Fitting (AXIL-QXAS) program source -a soft ware program used for the analysis of the oxides of SiO_2, Fe_2O_3, Al_2O_3, MgO, CaO, SO_3, TiO_2, Na_2O, and Mn_2O_3.

3. Neutron Activation Analysis method

(a) Samples preparation

Volcanic materials were collected from the selected sites from the Jos Plateau Volcanic sub Region. The samples were ground manually into powdered form of 125µm grain size with an agate mortar and pestle. 250mg-300mg of the powdered samples were weighed on a balance that was properly adjusted with the level indicator at the middle.

(c) Oxides determination

The sample of the materials are placed the reactor. The reactor's flux of neutrons from uranium fission interacts with the target nucleus of the element and when neutron energy bombards the sample it promotes radioactive nuclei of the target element. The radioactive nuclei then emit characteristic gamma rays; the detection of these rays indicates the presence of a particular element. The elements are then measured with a specifically design soft ware; the gamma-ray spectrum analysis Wingspan 2004 computer software for neutron activation analysis measurement of elements.

4. Determination of Loss on Ignition

The determinations of Loss on Ignition of the samples were undertaken by the

gravimetric method of analysis at the National Metallurgical Development Centre (NMDC) Jos. The determinations of the LOI of the samples were carried out according to ASTM C 25 (1999) Specifications.

Empty porcelain crucibles were fired at 950^{o}C for 1 hr, after which they are cooled in a desicator. 1g of sample was weighed into the crucibles as m_c and fired at same temperature and period. The crucibles with samples were then cooled in the desiccators and weighed again as m_a.

The difference in weight is taken and % loss on ignition calculated for all the samples thus;

$$w_l = \frac{\quad}{\quad} \times 100$$

Where wl is the lost on ignition of the dry mass of the sample in % (to the nearest 0.1%)

m_c is the weight of crucible + sample at ambient temperature after heating of crucible

m_b is the mass of crucible + sample before heating.

m_a weight of crucible+ sample after heating.

The materials were placed in a porcelain crucible and were fired at 950^{o}C for a period of 1 hour after which they were cooled in a silica gel desicator and the weight losses of the samples were subsequently measured and calculated. In this method a furnace capable of reaching a temperature of 1500^{o}C was used.

5. Determination of Moisture Content

The Gravimetric method of analysis is to be used. In this method, the sample is dried in an oven at various temperatures and weight loss at each temperature is subsequently measured until constant weight is obtained. The Moisture Content MC test is similar to that of the LOI heating of the sample of the material are carried out only at a temperature of 105^{o}C. The samples (1gram each) were carefully placed and dried in an Oven (Pate XVI) at a temperature of 105^{o}C in accordance with Nawy *et al* (2008) report on moisture content determination. The difference in weight before and after the drying is the MCs of the material which were subsequently calculated. This weight is referred to as the Moisture Content of the materials.