ADDIS ABABA UNIVERSITY
ADDIS ABABA INSTITUTE OF TECHNOLOGY
SCHOOL OF CHEMICAL AND BIO ENGINEERING

Characterization and Optimization of Volcanic Ash and Portland Cement blend for Property Enhancement of Concrete

A Thesis Submitted to the School of Chemical and Bio-Engineering Addis Ababa Institute of Technology in Partial Fulfillment of the Requirement for Degree of Master of Science in Chemical Engineering under Environmental stream.

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This is to certify that the thesis prepared by Solomon Zeleke, entitled: Characterization and Optimization of Volcanic Ash blending to Portland Cement for property Enhancement of Concrete submitted in partial fulfillment of the requirement for the degree of Master of Science (Chemical and Bio Engineering) compiles with the regulation of the University and meets the accepted standards with respect to originality and quality.

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DECLARATION

I declare that this thesis entitled “Characterization and Optimization of Volcanic Ash blending to Portland Cement for property Enhancement of Concrete” has not been submitted in any form for another degree, diploma or award at any university or other institution of the ternary education. Whenever contributions of others are involved, every effort is made to indicate this clearly, with the due reference to the literature and discussions. Information taken from published and unpublished work of others has been acknowledged in the text and list of references is given. The work was under guidance of Dr.Eng.Hundessa Dessalegn (Assistant professor) instructor in Addis Ababa University, School of Chemical and Bio Engineering

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ABSTRACT

Volcanic Ash is one of naturally occurring Pozzolanaic material that was tested in this research work for partial replacement of cement for production of concrete. With respect to reduction of cement consumption for sustainable construction (i.e. reducing GHG emission) evaluation of the strength reduction is crucial as it has a severe impact on the structure under construction. This paper examines the effects of replacing cement by using Lege-Dadi Volcanic Ash on the strength and certain durability characteristics of concrete. The research aims to determine the optimal amount of Volcanic Ash for production of high-grade concrete. Preliminary tests of the different properties of materials used for this research were carried out. The Lege Dadi Volcanic Ash satisfied the requirement of ASTM C618-00.The samples of Volcanic Ash were prepared in five different proportions (0, 5, 10, 15 & 20 wt %) and design mix ratio of 1: 2.9: 3.9 with a 0.61 w/c ratio to make 45 cubic and 27 cylindrical concrete samples. The cubic samples were used to assess compressive strength tests where as the cylindrical samples were used to determine abrasion resistance, water absorbency and acid attack tests. Uniaxial compressive tests were used to examine the strength of concrete achieved after 3, 7 and 28 days of curing. Result of compressive strength show that early strength of concrete samples were low, but as the curing period increases their compressive strength increases.15 % replacement of Volcanic ash was an optimum replacement in this research with compressive strength of 21.3 MPa less than by 4 % with the control (i.e. 0% of Volcanic Ash)and expected to increase in subsequent curing days. The permeability of cylindrical concrete samples decreases as the percentage of volcanic ash in the mix increases, the weight loss due to abrasive force of samples containing volcanic ash were not considered as significant. Acid significantly attacks the surface texture of both control and Volcanic Ash sample concrete cylinders. However, after 28 days of immersion samples contain Volcanic Ash powder reduces the mass loss, compared to the reference control concrete samples.

Keywords: *Pozzolanic materials, Compressive strength, Concrete mix ratio, water to Cement ratio,*

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LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectrometer
ACI	American Concrete Institute
ASTM	American Society for Testing and Material
AASHTO	American Association of State Highway and Transportation Officials
BS	British Standard
C-S-H	Calcium Silicate Hydrates
EDXRF	Energy Dispersive X-ray fluorescence
ES	Ethiopian Standards
GHG	Green House gas
GGBF	Ground Granulated Blast Furnace Slag
LoI	Loss on Ignition
MPa	Mega Pascal
PPC	Portland pozzolana Cement
RHC	Rapid Hardening Cement
SCMs	Supplementary Cementitious Materials
W/C	Water Cement ratio
OPC	Ordinary Portland cement
VA	Volcanic Ash

CHAPTER ONE

INTRODUCTION

1.1 Background of the study

Concrete has been proved to be a leading construction material nowadays; it's the most consumed material and is an essential component of infrastructure and housing programs, which are necessary for socioeconomic growth and development. It is a mixture of portland cement or any other hydraulic cement, fine aggregate, coarse aggregate and water, with or without admixtures. It has become most widely used construction material due to the availability of its constituents, flexibility, strength, durability, impermeability etc.

Cement is one of the essential ingredients of concrete which is a finely ground powder that binds two or more non adhesive substances together. When mixed with water it sets and hardens in to a solid mass up on hydration. Its production process contributes to environmental problem; it is expensive to buy when compared to other concrete materials such as gravel, sand, water etc. The problems of pollution and cost have led to researches on cement alternatives or substitutes that will fully or partially replace cement in the construction industry (Ogunbode, 2011)

Nowadays, many countries have adopted a sustainable development program based on the use of supplementary cementitious materials (SCMs), namely pozzolanic materials in partial replacement of cement. In order to overcome the economic and environmental impacts of cement industry, many researches has been carried out by scientific community in the world on using SCMs as partial replacement of cement in concrete with an objective to decrease the greenhouse gas emissions, minimize the harmful environmental impacts, and reduce the consumption of natural resources and the energy.

The American Society for Testing and Material (ASTM C125-06) defined pozzolan as a siliceous or siliceous and aluminous material, which in itself possesses little or no cementitious value but which will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties.

Many research Results on pozzolans showed that it can be used to partially replace Ordinary Portland Cement (OPC). This can lead to reactions between major constituents of OPC and that of the pozolans known as pozzolanic reaction. Pozzolanic reactions are silica reactions that take place in the presence of calcium hydroxide and water to produce calcium silicate hydrates(C-S-H).

Volcanic ash is a naturally available supplementary cementacious material formed during volcanic eruption. It has a particle size of less than 2mm diameter of fragmented magma or pulverized rock. It is hard, does not dissolve in water and is extremely abrasive, mildy corrosive and conducts electricity when wet. It's used in various countries in the world because it reduces cost and improves quality and durability of concrete.

Volcanic ash soils are distributed exclusively in regions where active and recently extinct volcanoes are located. It covers approximately 124 million hectares or 0.84% of the world land surface (Leamy 1984). Approximately 60% of volcanic ash soils occur in tropical countries. Some of African countries rich in volcanic ash deposit are Rwanda, Uganda, Cameroon, Ethiopia, Algeria and Sudan can be counted (Samizi, 2017) and (Akahashi & Hoji, 1998) Volcanic ashes normally require no heating to enhance pozzolanic reactivity and, if they are already in a powdered state, may need little or no grinding. Volcanic ash pozzolanas are commercially exploited in many countries in the world.

Ethiopia is one of the volcanic tuff rich countries in Africa (Akahashi & Hoji, 1998). A huge volcanic tuff deposit is found in the Main Rift valley of Ethiopia, almost there were no researches conducted in the area of using volcanic ash in replacement of cement for construction purposes. This research work therefore is done to characterize and optimize volcanic ash blending to OPC for production of strong and durable concrete .The research is conducted on the Volcanic ash deposits found in the area of 'Lege Dadi' in Oromia Regional State, Oromia special zone around finfinne.

1.2 Statement of Research Problem

Cement as an important constituent of concrete is becoming gradually expensive compared to other ingredients of concrete. The mining of its raw materials leads to depletion of natural resources and degradation of environment. Its production process is characterized by

consumption of huge amount of energy and emission of CO_2 to the environment. Each tone of cement produced requires approximately 105kwh of electricity and 60-130kg of fuel oil and it causes approximately 5% of global man made CO_2 emission, about 50% emissions are process emissions that happened during clinker production 40% come from burning of fuels to heat the cement kiln and about 10% come from electricity use and transportation.(Ministry of Industry, 2015)

In view of this and other problems associated with production and use of cement, a lot of research efforts were made around the world to find an alternative material that will partially or fully replace cement in concrete production. The results showed that using supplementary cementing materials (SCM), such as blast furnace slag, fly ash, silica fume, burnt shale, limestone powder and natural pozzolan can be used to partially replace cement in concrete. Volcanic ash is one of the class of natural pozzolans is the focus of this research work in partially replacing ordinary Portland cement.

1.3 Significance of the Study

The development of supplementary cementitious materials (SCMs) such as volcanic ash is said to be fundamental to advancing low-cost construction materials by reducing the use of cement in concrete for the production of self-sufficient means of shelter especially in developing countries like Ethiopia. Apart from improving concrete properties, the main benefits of SCMs include saving natural resources and energy as well as protecting the environment.(Olusola, 2010).Besides, reduction of the concrete manufacturing costs, the partial replacement of cement will make it possible substantially to decrease the gas emissions (0.89t CO2/t clinker). The choice of this kind of materials has been recommended by their interesting mechanical properties, abundance and economic exploitation with lower environmental impact. Indeed, from an energy performance standpoint, the total energy required to produce cement was evaluated to be in the range 800–1200 kWh per ton of cement, including around 50 kWh/t for the finish grinding of the clinker. In the case of volcanic powder, the energy needed for the grinding of this material was evaluated at 75 kWh/t. This process energy was assumed to be zero kWh/t if the volcanic powder is a by-product.(Labbaci et al, 2017)

1.4 Objectives

1.4.1 General Objective

The aim of this research work is to characterize and optimize Volcanic Ash blending to Portland cement to produce strong and durable concrete.

1.4.2 Specific Objectives

- To analyze the chemical compositions and the physical properties of volcanic ash.
- To assess the property of concrete mixture that contains volcanic ash at fresh stage.
- To assess the physical properties of fine and coarse aggregates
- To evaluate the compressive strength and density of concrete that contains volcanic ash.
- To evaluate the durability properties of concrete that contains volcanic ash.
- To determine the optimum volcanic ash content blended with Portland cement in producing standard concrete.

CHAPTER TWO

LITERATURE REVIEW

2.1. Introduction

Concrete - most widely used construction material in the world over, it is the material, which is used more than any other man made material on the earth for construction works mainly due to its low cost, availability, its long durability, and ability to sustain extreme weather environments. In the concrete, cement chemically reacts with water and produces binding gel that binds other component together and creates stone type of material. The reaction process is called 'hydration' in which water is absorbed by the cement.(IndiaNTPC, 2007)

The primary product of cement hydration is a complex and poorly crystalline calcium-silicate hydroxide gel (or CSH). A secondary product of hydration is calcium hydroxide, a highly crystalline material. A category of siliceous materials known as pozzolans have little or no cementitious value, but in finely divided form and in the presence of moisture will react chemically with calcium hydroxide to form additional CSH. This secondary hydration process has a generally beneficial effect on the final concrete properties. Examples of pozzolans are fly ash, ground granulated blast-furnace slag, and microsilica, silica fume, volcanic ashes etc. (Material, n.d.)

2.2. Concrete

2.2.1. Fundamentals of concrete

Concrete is basically a mixture of two components: aggregates and paste. The paste, comprised of Portland cement and water, binds the aggregates (usually sand and gravel or crushed stone) in to a rock like mass as the paste hardens because of chemical reaction of cement and water. Supplementary cementitious materials and chemical admixtures may also be included in the paste.

Aggregates are generally divided in to two groups: fine and coarse. Fine aggregates consists of natural or manufactured sand with particle sizes ranging up to 9.5mm;coarse aggregates are particle retained on the 1.18mm(No.16) sieve and ranging up to 150mm in size.

The paste is composed of cementitious materials, water and entrapped air or purposely entrained air. The paste constitutes about 25% to 40% of total volume of concrete. Since aggregates make up about 60% to 75% of the total volume of concrete, their selection is important. Aggregates should consist of particles with adequate strength and resistance to exposure conditions and should not contain materials that will cause deterioration of the concrete. A continuous gradation of aggregate particle sizes is desirable for efficient use of paste.

The quality of the concrete depends up on the quality of paste and aggregate, and the bond between the two. In properly made concrete, each and every particle of aggregate is completely coated with paste and all of the spaces between aggregate particles are completely filled with paste.

For any particular set of materials and conditions of curing, the quality of hardened concrete is strongly influenced by the amount of water used in relation to the amount of cement. Unnecessary high water contents dilute the cement paste (the glue of concrete).the less water used the better the quality of concrete-provided the mixture can be consolidated properly. Smaller amounts of mixing water result in stiffer mixtures; but with vibration, stiffer mixtures can be easily placed. Thus, consolidation by vibration permits improvement in quality of concrete.

The freshly mixed(plastic) and hardened properties of concrete may be changed by adding chemical admixtures to the concrete, usually in liquid form, during batching chemical admixtures are commonly used to: adjust setting time or hardening, reduce water demand, increase workability, intentionally entrain air and to adjust other fresh or hardened concrete properties.

After completion of proper proportioning, batching, mixing, placing, consolidating, finishing and curing, concrete hardens into a strong, noncombustible, durable, abrasion resistant, and water tight building material that requires little or no maintenance. Furthermore, concrete is an excellent building material because it can be formed in to a wide variety of shapes, color and textures for use in an unlimited number of applications.(Steven H.et al,1988)

2.2.1. Freshly mixed concrete

Freshly mixed concrete should be plastic or semi fluid and generally capable of being molded by hand. In plastic concrete mixture all grains of sand and piece of gravel or stone are encased and held in suspension. The ingredients are not apt to segregate during transport; and when the concrete hardens, it becomes a homogenous mixture of all the components. During placing, concrete of plastic consistency does not crumble but flows sluggishly without segregation.(Beatrix Kerkhoff, 1988)

2.2.1.1. Mixing

The sequence of charging ingredients in to a concrete mixer can play an important part in uniformity of the finished product. The sequence, however, can be varied and still produce quality concrete. Different sequence requires adjustments in time of water addition, the total number of revolutions of the mixer drum, and the speed of revolution. Other important factor in mixing are the size of the batch in relation to the size of the mixer drum, the elapsed time between batching and mixing, and the design, configuration, and condition of mixer drum and blades.(Steven H.Kosmatka, Beatrix Kerkhoff, 1988)

2.2.1.2. Workability

The ease of placing, consolidating, and finishing freshly mixed concrete and the degree to which it resists segregation is called workability. Concrete should be workable but the ingredients should not separate during transport and handling. Factors that influence the workability of concrete are:

1.The method and duration of transportation
2.Quantity and characteristics of cementatious materials
3.Concrete consistency
4.Grading, shape and surface texture of fine and coarse aggregates
5.Entrained air
6.Water content
7.Concrete and ambient air temperatures
8.Admixtures

A uniform distribution of aggregate particles and the presence of entrained air significantly help control segregation and improve workability. Properties related to workability include consistency, segregation, mobility, pumpability, bleeding and finishability. Consistency is considered a close indication of workability. Slump is used as a measure of the consistency or wetness of concrete. A low slump concrete has a stiff consistency. If the mix is too wet, segregation and honey combing can occur, the consistency should be the driest practicable for placement using available consolidation equipment.(Steven H.Kosmatka, 1988)

2.2.1.3. Slump test

This is a test used extensively in site work all over the world. The slump test does not measure the workability of concrete but is very useful in detecting variations in the uniformity of a mix of given nominal proportions. Mixes of stiff consistence have a zero slump, so that in the rather dry range no variation can be detected between mixes of different workability. Rich mixes behave satisfactorily, their slump being sensitive to variations in workability. However in a lean mix with a tendency to harshness a true slump can easily change to the shear type or even to collapse, and widely different values of slump can be obtained in different samples from the same mix. (Eren, 2015)

Table2. 1 Degree of workability and slump of concretes with 19 or 38 mm maximum size of aggregate

Degree of workability	**Slump (mm)**	**Use for which concrete is suitable**
Very low	0-25	Roads vibrated by power operated machines. At the more workable end of this group, concrete may be compacted in certain cases with hand operated machines
Low	25-50	Roads vibrated by hand operated machines. At the more workable end of this group, concrete may be manually compacted in roads using aggregate of rounded or irregular shaped. Mass concrete foundations without vibration or lightly reinforced sections with vibration.
Medium	50-100	At the less workable end of this group, manually compacted flat slabs using crushed aggregates.

		Normal reinforced concrete manually compacted and heavily reinforced sections with vibration.
High	100-175	For sections with congested reinforcement, not normally suitable for vibration.

2.2.1.4. Consolidation

Vibration sets in to motion the particles in freshly mixed concrete, reducing friction between them, and giving the mixture the mobile qualities of thick fluid. The vibratory action permits use of a stiffer mixture containing larger proportion of coarse and a smaller proportion of fine aggregate. The larger the maximum size aggregate in concrete with a well-graded aggregate the less volume there is to fill with paste and the less aggregate surface area there is to coat with paste; thus less water and cement are needed. Concrete with an optimally graded aggregate will be easier to consolidate and place. Consolidation of coarser as well as stiffer mixtures results in improved quality and economy. On the other hand, poor consolidation can result in porous, weak concrete with poor durability.(Beatrix Kerkhoff et al, 1988)

2.2.1.5. Hydration, setting time and hardening

The binding quality of Portland cement paste is due to the chemical reaction between the cement and water called hydration.

Portland cement is not simple chemical compound; it is a mixture of many compounds. Four of these make up 90% or more of the weight of Portland cement: tricalcium silicate,dicalcium silicate,tricalcium aluminate,and tetra-calcium aluminoferrite. In addition to these major compounds, several others play important roles in the hydration process. Each type of Portland cement contains the same four major compounds, but different proportions.

The two calcium silicates, which constitute about 75% of the weight of Portland cement, react with water to form two new compounds: calcium hydroxide and calcium silicate hydrate. The latter is by far the most important cementing component in concrete. The engineering properties of concrete-setting and hardening, strength, and dimensional stability-depends primarily on calcium silicate hydrate. It is the heart of concrete.(Beatrix Kerkhoff et al, 1988)

The chemical composition of calcium silicate hydrate is somewhat variable, but it contains lime (CaO) and silicate (SiO_2) in ratio on the order of 3 to 2.the surface area of calcium silicate hydrate is some 300 square meters per gram. In hardened cement paste, the calcium silicate hydrate forms dense, bonded aggregations between the other crystalline phase and the remaining unhydrated cement grains; they also adhere to grains of sand and to pieces of coarse aggregate, cementing everything together.(Diamond & White, 1963)

As concrete hardens, its gross volume remains almost unchanged, but hardened concrete contains pores filled with water and air that have no strength. The strength is in the solid part of the paste, mostly in calcium silicate hydrate and crystalline compounds.

The less porous the cement paste, the stronger the concrete. When mixing concrete, therefore, no more water than is absolutely necessary to make the concrete plastic and workable should be used. Even then, the water used is required for complete hydration of the cement. About 0.4 gram of water per gram of cement are needed to completely hydrate cement(power 1948 and 1942).However, complete hydration is rare in field concrete due to lack of moisture and the long period of time(decades)required to achieve complete hydration.

Knowledge of rate of reaction between cement and water is important because it determines the rate of hardening. The initial reaction must be slow enough to allow time for the concrete to be transported and placed. Once the concrete has been placed and finished, however, rapid hardening is desirable. Gypsum, added at the cement mill when clinker is ground, act as regulator of the initial rate of setting of Portland cement. Other factors that influence the rate of hydration include cement fineness, admixtures, amount of water added, and temperature of the materials at the time of mixing.fig illustrates the setting properties of concrete mixtures at different temperatures.

2.2.2Hardened concrete

2.2.2.1. Curing

Increase in strength with age continues provided:

1.Unhydrated cement is still present

2.The concrete remains moist or has relative humidity above 80% (Aldea et al, 2000)

3.The concrete temperature remains favorable and

4.Sufficient space is available for hydration products to form

When the relative humidity within the concrete drops to about 80%, or the temperature of the concrete drops below freezing, hydration and strength virtually stop.

2.2.2.2. Drying rate of concrete

Concrete does not harden or cure by drying. (Or more precisely, the cement in it) needs moisture to hydrate and harden. When concrete dries out, it ceases to gain strength; the fact that it is dry is no indication that it has undergone sufficient hydration to achieve the desired physical properties. Knowledge of the rate of drying is helpful in understanding the properties or physical condition of concrete. Freshly cast concrete usually has an abundance of water, but as drying progresses from the surface in ward, strength gain will continue at each depth only as long as the relative humidity at that point remains 80%. A common illustration of this is the surface of the concrete floor that has not had sufficient moist curing. Because it has dried quickly, concrete at the surface is weak and traffic on it creates dusting. Also, when concrete dries, it shrinks as it loses water, just as wood and clay do(though not as much).Drying shrinkage is a primary cause of cracking, and the width of crack is a function of the degree of drying, spacing or frequently of cracks, and age at which the cracks occur.

2.2.2.3. Compressive Strength

Compressive strength may be defined as the measured maximum resistance of a concrete specimen to axial loading. It is generally expressed in Mega Pascal (MPa) or pounds per square inch (Psi) at an age of 28 days. Other test ages are also used; however, it is important to realize the relationship between the 28-day strength and other test ages. Seven-day strength is often estimated to be about 75%of the 28-day strength and 56-day and 90-day strengths are 10% to 15% greater than 28-day strengths. (Steven H et al, 1988)

The compressive strength is the most important property of hardened concrete and is generally considered in the design of concrete mixtures. It is customary to estimate the properties of concrete in the structure from compression tests on specimens made from fresh concrete as it is placed and cured in the standard manner. Dimensions of the concrete specimens usually have the following sizes: Cylindrical specimens of diameters 7.5, 10, 15 cm and Cube specimens of dimension 5, 10, 15 cm. (Eren, 2015)

Compressive strength is affected by many factors the water-cement ratio (or water-cementitious material ratio), the extent to which hydration has progressed, the curing and environmental conditions, and the age of concrete. Therefore, the actual strength of concrete will not be the same as the strength of specimen.(Eren, 2015)

2.2.2.3. Testing for Compressive Strength

The compressive strength of concrete is determined from compressive test on cylindrical / cube specimens. Empty moulds are filled with fresh concrete using a standard procedure. After 24 hours the specimens are taken out of the moulds and moist cured for 28 days at the end of the curing period they are tested.

$$fc = \frac{failure\ load}{Cross\ sectional\ area} \qquad \textbf{2.1}$$

Moisture content of specimens affects the compressive strength. Air-dried specimens (at the time of testing) are shown to possess more compressive strength than that of saturated specimens, on the order of 20 to 25 %. Speed of testing: a slower rate will show a lower strength. In laboratory: (2-3 minutes) to reach failure.(Eren, 2015)

Durability

Besides its ability to sustain loads, concrete is also required to be durable. The durability of concrete can be defined as its resistance to deterioration resulting from external and internal causes. The external causes include the effects of environmental and service conditions to which concrete is subjected such as weathering, chemical actions and wear. The internal causes are the effects of interaction between the constituent material such as alkali-aggregate reaction, volume changes, absorption and permeability.

In order to produce a durable concrete care should be taken to select suitable constituent materials. It is also important that the mix contains adequate quantities of materials in proportions suitable for producing a homogeneous and fully compacted concrete mass.(Eren, 2015)

2.2.4.1. Factors Affecting Durability

The durability of concrete is its resistance to deterioration resulting from external or internal causes.

2.2.4.1.1. External Causes

Physical, chemical or mechanical:

a) Leaching out of cement

b) Actions of sulphates, seawater and natural slightly acidic water. The resistance to these attacks varies with the type of cement used and increases in the order; OPC and RHC (Rapid Hardening Cement) Environmental such as occurrence of extreme temperatures, abrasion and electrostatic action.

2.2.4.1.2. Internal Causes:

a) Alkali-aggregate reactions

b) Volume change due to difference in thermal properties of the aggregate and cement paste.

c) Permeability of concrete.

2.2.4.2. Density

Conventional concrete, normally used in pavements, buildings, and other structures, has density (unit weight) in range of 2200 to 2400kg/m3.the density of concrete varies, depending on the amount and density of the aggregate, the amount of air that is entrapped or purposely entrained, and the water and cement contents, which in turn are influenced by the maximum size of aggregate. Reducing the cement paste content (increasing aggregate volume) increases density values of density of fresh concrete are given in table below(Steven H.et al, 1988)

Table2. 2 Average density of fresh concrete

Maximum size of agg in mm	Air content %	Water kg/m^3	Cement kg/m^3	density				
				Relative density of aggregates				
				2.55	2.60	2.65	2.70	2.75
19	6	166	336	2149	2227	2259	2291	2323
37.5	4.5	145	291	2259	2291	2339	2371	2403
75	3.5	121	242	2307	2355	2387	2435	2467

2.2.4.3. Permeability and water tightness

Concrete used in water-retaining structures or exposed to weather or other sever exposure conditions must be virtually impermeable or watertight. Water tightness is often referred to as the ability of concrete to hold back or retain water without visible leakage. Permeability refers to the amount of water migration through concrete when the water is under pressure or to the ability of concrete to resist penetration by water or other substances (liquid, gas, or ions).Generally, the same properties of concrete that make it less permeable also make it more watertight.(Steven H.et al, 1988)

2.4.4.4. Abrasion resistance

Floors, pavements, and hydraulic structure are subjected to abrasion; therefore, in these applications concrete must have a high abrasion resistance. Test results indicate that abrasion resistance is closely related to the compressive strength of concrete. Strong concrete has more resistance to abrasion than does weak concrete. Since compressive strength depends on water-cement ratio and curing, a low water-cement ratio and adequate curing are necessary for abrasion resistance. The type of aggregate and surface finish or treatment used also have a strong influence on abrasion resistant than soft aggregate and a steel-troweled surface resists abrasion better than a surface that had not been troweled. Abrasion tests can be conducted by rotating steel balls, dressing wheels, or disks under pressure over the surface(ASTM C 779),other types of abrasion tests are also available (ASTM C 418 ASTM C 944)

2.4.4.5. Chemical resistance

Portland cement concrete is resistant to most natural environments; however, concrete is sometimes exposed to substances that can attack and cause deterioration. Concrete in chemical manufacturing and storage facilities is especially prone to chemical attack. Acids attack concrete by dissolving cement paste and calcareous aggregates.

2.2.4.5.1. Sulfate attack

Excessive amount of sulfates in soil or water can attack and destroy a concrete that is not properly designed. Sulfates (for example calcium sulfate, sodium sulfate, and magnesium sulfate) can attack concrete by reacting with hydrated compounds in hardened cement paste. These reactions can induce sufficient pressure to disrupt the cement paste, resulting in disintegration of concrete (loss of paste cohesion and strength).calcium sulfate attacks calcium aluminate hydrate and forms ettringite. Sodium sulfate reacts with calcium hydroxide and calcium aluminate hydrate forming ettringite and gypsum. Magnesium sulfate attacks in a manner similar to sodium sulfate and forms ettringite, gypsum, and also bruicite (magnesium hydroxide).brucite forms primarily on concrete surface; it consumes calcium hydroxide, lowers the PH of the pore solution, and then decomposes the calcium silicates (santhanman and others 2001).

2.3. Cement

2.3.1. Introduction

Cement in general termed as Ordinary Portland Cement (OPC), and is used as a perfect binding material across the world. It will also commonly available for material for general use around the globe, an ingredient to mortar, stucco and grout. Cements are finely ground powders and all have the important property that when mixed with water a chemical reaction (hydration) takes place. This reaction produces a very hard and strong binding medium for the aggregate particles. In its plastic stage, cement mortar gives to the fresh concrete a cohesive property. The cements have many differing properties, in terms of setting and hardening characteristics, and their resistance to chemical, temperature and other effects. These are obtained by differences in the fineness of

grinding and the properties of raw materials. The cement to be used in a particular concrete or mortar will be selected on the basis of the particular properties required.

Cement is produced from limestone by grinding, calcining then grinding to produce a fine powder, which intern is mixed with gypsum to retard setting time.(Eren, 2015)

2.3.2. Manufacturing of Portland cement

The details of the cement making process vary widely. However, the fundamental stages in cement production are all the same and as follow. (Eren, 2015)

1. The raw materials are reduced to fine particle size to be mixed intimately.
2. Raw materials are blended and mixed to produce uniform chemical composition containing calcium carbonate, silica, alumina, iron oxide etc.
3. The blended raw mix is heated to the point where all the moisture is driven off as steam or water vapor.
4. The dried mix is heated to decarbonation or calcination temperature, about 800^0C. At this temperature, the calcium carbonate in the mix is dissociated into calcium oxide (free lime), which remains in the mix, and carbondioxide which driven off as gas.
5. The mixture is further heated and as the temperature rises, the oxides of calcium, silicon, aluminium and iron react to form calcium silicates, calcium aluminate and calcium aluminoferrite. These are principal active compounds of Portland cement. This process is completed at a temperature of around 1400^oC and the resulting product is Portland cement clinker (1.8 tons of raw material produces 1 ton of clinker).
6. The clinker is cooled to a temperature at which it can be handled of about 60-150^0C. Clinker may be sent directly to the finish grinding mills, but is usually stockpiled. Clinker may be stored for long periods without deterioration. When the cement is to be transported for a very far place, it may be easy to ship the clinker rather than finished cement. Of course, the grinding operation should be performed somewhere near to the point of use.
7. Clinker is ground to the specified fineness with the addition of a small proportion of gypsum to control the setting time of the finished cement. When it is required, the slag is also added during the grinding.

8. The finished cement is stored in silos for a relatively short time before being sent to the customer in bags or in bulks.

2.3.3. Physical properties of cement

Specification for cement place limits on both its physical properties and often chemical composition. An understanding of significance of some of physical properties is helpful in interpreting results of cement tests. Tests of physical properties of cements should be used to evaluate the properties of cement, rather than concrete. Cement specifications limit the properties with respect to the type of cement. Cement should be sampled in accordance with ASTM C 183 (AASHTO T 127). During manufacture; cement is continuously monitored for its chemistry and following properties.

2.3.3.1. Particle size and Fineness

Portland cement consists of individual angular particles with a range of sizes. Approximately 95% of cement particles are smaller than 45 micrometer, with average particle around 15 micrometers. The overall particle size distribution of cement is called "fineness." The fineness of cement affects heat released and rate of hydration. Greater cement fineness (smaller particle size) increases the rate at which cement hydrates and thus accelerates strength development. The effects of greater fineness on paste strength are manifested principally during the first seven days.

In early 1900s,cement fineness was expressed as the mass of cement per fractional size (percent weight retained on specific sieve size).Today, fineness is usually measured by the blaine air permeability test (ASTM C 204 or AASHTO T 153) that indirectly measures the surface area of cement particles per unit mass. Cements with finer particles have more surface areas per kilogram of cement**.**(Steven H.et al, 1988)

The measurement of fineness is defined as specific surface and is expressed as surface area of the grains in a sample per mass of that sample. For example, British Standard (BS12-1991) specifies the max cement fineness as 325m^2/kg, though in practice it is usually in the range 350-380 m^2/kg. (Eren, 2015)

2.3.3.2. Soundness

Soundness refers to the ability of a hardened paste to retain its volume. Lack of soundness or delayed destructive expansion can be caused by excessive amounts of hard burned free lime or magnesia (periclase) content and the maximum expansion as measured by the autoclave-expansion test.since the adoption of the autoclave-expansion test (ASTM C 151 or AASHTO T 107) in 1943,there have been exceedingly few cases of abnormal expansion attributed to unsound cement

2.3.3.3. Consistency

Consistency refers to the relative mobility of freshly mixed cement paste or mortar or to its ability to flow. During cement testing, pastes are mixed to normal consistency defined by a penetration of 10±1mm of the vicat plunger (see ASTM C 187 or AASHTO T 129).mortars are mixed to obtain either a fixed water-cement ratio or to yield a flow within a prescribed range. The flow is determined on flow table as described in ASTM C 230 (AASHTO M 152) and ASTM C 1437.Both the normal consistency method and the flow test are used to regulate water contents of pastes and mortars, respectively, to be used in subsequent tests; both allow comparing dissimilar ingredients with same penetrability or flow.

2.3.3.4. Setting time

The object of setting time test is to determine: the time elapses from moment water is added until the paste ceases to be fluid and plastic(called initial set) and the time required for paste to acquire a certain degree of hardness (called final set).

To determine if cement sets according to the time limits specified in cement specifications, tests are performed using either the vicat apparatus (ASTM C 191 or AASHTO T 131) or Gilmore needle (ASTM C 266 or AASHTO T 154)

Initial set of cement paste must not occur too early and final set must not occur too late. The setting times indicate that a paste is or is not undergoing normal hydration reaction. Sulfate (from gypsum or other sources) in cement regulates setting time, but setting time is also affected by cement fineness, water- cement ratio, and any admixtures that may be used. Setting times of concretes do not correlate directly with setting time of paste because of temperature differences in the field (as contrasted with the controlled temperature in testing lab)

2.3.3.5. Loss on ignition

Loss on Ignition (LOI) of Portland cement is determined by heating a cement sample of known weight to between 900^{o}C and 1000 ^{o}C until a constant weight is obtained. The weight loss of the sample is then determined. Normally, a high loss on ignition is an indication of prehydration and carbonation, which may cause by improper or prolonged storage or adulteration during transport. The test for loss on ignition is performed in accordance with ASTM C 114 (AASHTO 105).LOI range from 0 to 3%.

2.3.3.6 Density and relative density

The density of cement is defined as the mass of a unit volume of the solids or particles, excluding air between particles. It is reported as mega gram per cubic meter or gram per cubic centimeter (the numeric value is the same for both unit).the particle density of Portland cement ranges from 3.10 to 3.25,average 3.15 Mg/m^3.portland-blast-furnace-slag and Portland pozolan cements have densities ranging from 2.90 to 3.15,averageing 3.05 Mg/m^3.The density of a cement, determined by ASTM C 188 (AASHTO T 133),is not an indication of the cement's quality; its principal use is in mixture proportioning calculations.

For mixture proportioning, it may be more useful to express the density as relative density(also called specific gravity).the relative density is a dimensionless number determined by dividing the cement density of water at 4 ^{o}C. The density of water at 4 ^{o}C is 1.0Mg/m^3 (1.0g/cm^3 or 1000kg/m^3).

The relative density of 3.15 is assumed for Portland cement in volumetric computations of concrete mix proportioning. However, as mix proportions list quantities of concrete ingredients in kilograms or pounds, the relative density must be multiplied by density of water at 4 ^{O}C stated as 1000kg/m$^{3.}$ To determine the particle density in kg/m ^{3} this product is then divided in to mass or weight of cement to determine the absolute volume of cement in cubic meters.

2.3.3.6.1. Bulk density

The bulk density of cement is defined as the mass of cement particles plus air between particles per unit volume. The bulk density of cement can vary considerably depending on how it is handled and stored. Portland cement that is fluffed up may weigh only 830kg/m^3,where as when consolidated by vibration, the same cement can weigh as much as 1650kg/m^3.for this reason,

good practice dictates that cement must be weighted for each batch of concrete produced, as opposed to use of volumetric measure.

2.3.4. Types of Cement

Different types of Portland cement are manufactured to meet various normal physical and chemical requirements for specific purpose. Portland cements are manufactured to meet the specifications of ASTM C 150, AASHTO M 85, or ASTM C 1157

ASTM C 150, standard specification for Portland cement, provides for eight types of Portland cement using Roman number designation as follows:

2.3.4.1. ASTM (American Society for Testing and Materials) Types

Type I Normal (ordinary) Portland cement

Type I-A Air-entrained type-I Cement

Type II Modified Portland cement

Type II-A Air-entrained type-II Cement

Type III High Early strength Portland cement

Type III-A Air-entrained type-III Cement

Type IV Low heat Portland cement

Type V Sulfate Resistant Portland cement

Table2. 3 Chemical composition and fineness of cements

Type of Portland cement	Chemical composition %							Blain fineness m^2/kg
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O_{eq}	
I	20.5	5.4	2.6	63.9	2.1	3.0	0.61	369
II	21.2	4.6	3.5	63.8	2.1	2.7	0.51	377
III	20.6	4.9	2.8	63.4	2.2	3.5	0.56	548
IV	22.2	4.6	5.0	62.5	1.9	2.2	0.36	340
V	21.9	3.9	4.2	63.8	2.2	2.3	0.48	373

ASTM C 150 (AASHTO M 85) standards of chemical composition of cement, Adapted from PCA (1996) and Gebhardt (1995)

Table2. 4 Constituents of Ordinary Portland Cement

No	Name of compound	Chemical composition	Abbreviation	Percentage
1	Tricalcium silicate	$(CaO)_3.SiO_2$	C_3S	45-75
2	Dialcium silicate	$(CaO)_2.SiO_2$	C_2S	7-32
3	Tricalcium aluminate	$(CaO)_3.Al_2O_3$	C_3A	0-13
4	Tetracalcium alumino ferrite	$(CaO)_4Al_2O_3.Fe_2O_3$	C_4AF	0-18
5	Gupsum	$CaSO_4.2H_2O$		2-10

2.4. Blended cement

Blended cements are produced by intimately and uniformly inter grinding Ordinary Portland Cement (OPC) with one or more supplementary Cementing Materials(SCMs).Most of SCMs are generally not used as cements by themselves, but when blended with OPC, they make a significant cementing contribution to the properties of hardened concrete through hydraulic or pozolanic activity. Blended cements are used in all aspects of concrete construction in the same manner as Portland cements and can be the only cementatious material in concrete or they can be used in combination with SCMs added at the concrete plant.(Roosyanto, n.d.)

2.5. Supplementary Cementing materials (SCMs)

Supplementary cementing materials are materials when used in conjunction with Portland cement, and must never be used on their own, contributes to the properties of the hardened concrete through hydraulic or pozzolanic activity, or both. These materials make considerable contribution to reduction of the CO_2 emissions from cement works and enhance the quality as well.

Supplementary cementing materials represent a broad class of predominantly glassy materials that have been found to provide beneficial properties to Portland cement concrete. The material may be inter ground with cement clinker to create a blend cement or they may be added directly to the concrete mixer during batching process.(Roosyanto, n.d.)

2.5.1. Reaction of supplementary cementing materials

Hydraulic cement is a material that sets and hardens when it comes in contact with water through a chemical reaction called hydration. After being mixed with water, Portland cement in the

blended cement starts to hydrate immediately and then follow the supplementary cementing materials:

The reaction of pozzolans materials (natural, fly ash and silica fume) with calcium hydroxide,$Ca(OH)_2$, released by the hydration of Portland cement. These materials are known as pozzolanic property. In very broad terms, the primary reaction in hydrating cement is the following:

Cement + water =calcium silicate hydrate (C-S-H) + calcium hydroxide, $Ca(OH)_2$.calcium silicate hydrate (C-S-H) is the primary compound that contributes to the strength and impermeability of hydrated cement paste. Calcium hydroxide is not as strong and is more soluble, so it is somewhat less desirable. Adding pozzolans, in the presence of water, results in conversion of calcium hydroxide to more Supplementary cementing materials have the different characteristics from each other but are all less reactive than Portland cement. Because do not dissolve rapidly, extremely fine supplementary cementing materials particles act as nuclei for the formation of calcium silicate hydrate which would otherwise form only on cement grains. This "fine SCMs" effect brings about a denser and more homogenous microstructure of the hardened cement paste and aggregate paste interfacial zones, resulting in improved workability, strength and impermeability. The extent of the fine-SCMs effect depends on the content of extremely fine particle in the cementing materials. This property affects the rate of early- age strength gain and affects the rate of heat development, the lower the temperature rise and therefore the smaller the likelihood of thermal cracking.(Roosyanto, n.d.)

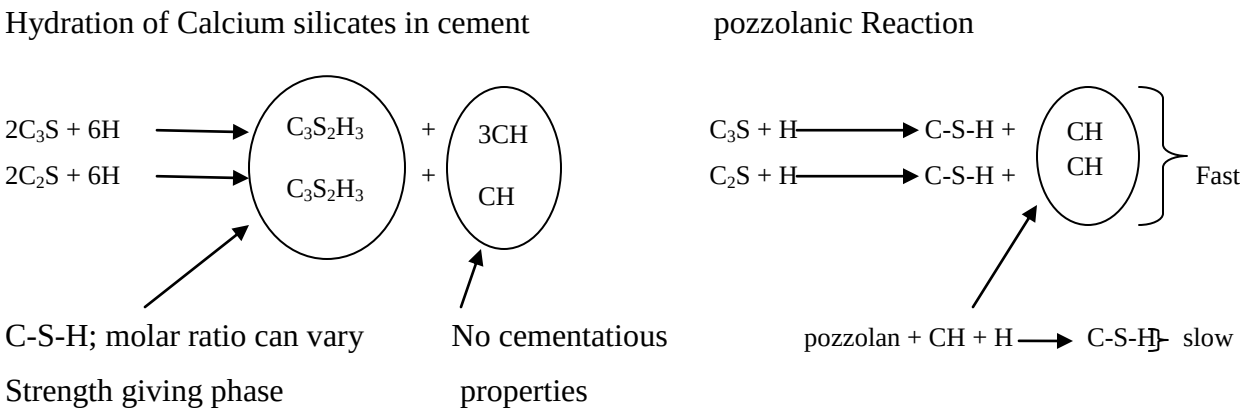

Figure 2.1 shows hydration and pozzolanic reactions (Main reaction in blended cement)

2.5.2. Effect of SCMs in concrete applications

SCMs in concrete affect a wide range of fresh and hardened concrete properties. Some of the effects may be considered desirable and the reason why the materials used. Other side effects may be less desirable and have to accommodate. An understanding of all the potential effects is essential to prevent surprises (Roosyanto, n.d.)

2.5.2.1. Fresh concrete:

In general, SCMs improve the consistency and workability of fresh concrete because an additional volume of fines to the mixture. Concrete with silica fumes is typically used at low water content with high range water reducing admixtures and these mixtures tend to be cohesive and sticker than plain concrete.fly ash and slag generally reduce the water demand for required concrete slump. Concrete setting time may be retarded with some SCMs used at higher percentages. This can be beneficial in hot weather. The retardation is offset in winter by reducing the percentage of SCMs material in concrete. Because of the additional fines, the amount and rate of bleeding of these concrete is often reduce. This is especially significant when silica fume is used. Reducing bleeding in conjunction with retarded setting can cause plastic shrinkage cracking and may warrant special precaution during placing and finishing

2.5.2.2. Strength

Concrete mixtures can be proportioned to produce the required strength and rate of strength gain as required for application. With SCMs other silica fume, the rate of strength gain might be lower initially, but strength gain continues for a longer period compare to mixtures with only Portland cement, frequently resulting in higher ultimate strengths. Silica fume is often used to reduce concrete compressive strength in excess of 70 MPa. Concrete containing SCMs generally need additional consideration for curing of both the test specimens and the structure to ensure that potential properties are attained

2.5.2.3. Durability:

SCMs can be used to reduce the heat generation associated with cement hydration and reduce the potential for thermal cracking in mass structural elements. These materials modify the microstructure of concrete and reduce its permeability there by reducing the penetration of water

and water-born salt in to concrete. Watertight concrete will reduce various forms of concrete deterioration, such corrosion of reinforce steel and chemical attack. Most SCMs can reduce initial expansion of concrete due to chemical reaction such as alkali aggregate reaction and sulfate attack. Resistance of freezing and thawing cycles required the use of air entrained concrete. Concrete with a proper air void system and strength will perform well in this condition

2.5.2.4 Permeability

SCMs generally improve potential concrete durability by reducing permeability. Almost all durability-related failure mechanisms involve the movement of fluids through the concrete. Tests show that the permeability of concrete decreases as the quantity of hydrated cementitious materials increases and water-cementatious materials ratio decreases. With adequate curing, fly ash, GGBF slag, and natural pozzolans generally reduce the permeability and absorption of concrete. GGBF slag and fly ash can result in very low chloride. Penetration test results at later age. Silica fume and metakaoline are especially effective and can provide concrete with very low chloride penetration (Berger et al.1997)

2.6. Pozzolanas

A pozzolan is defined in ASTM C 618 as "a siliceous or asiliceous and aluminous material, which in itself possesses little or no cementatious value but which will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperature to form compounds possessing cementitious properties.'' These characteristics make pozzolans ideal addition to Portland cement concrete mixtures.

ASTM C 618 outlines the physical and chemical requirements of pozzolanic materials. Pozzolanic materials include natural pozzolans (class N) and by product materials. Natural pozzolans are notably volcanic ashes, diatomaceous earth, calcined clay, metakaoline clay, and rice hull ash. By product material is most typically fly ash, classified as either class F or class C, reflecting a difference in chemical composition and origin.

The chemical composition of pozzolanas is not significant for showing their behavior. More important is their mineralogy, and its proportion between the crystalline and glassy phase. The crystalline phases are chemically in active and the glassy structures are chemically active. Both of these structures will influence the characteristic of pozzolanic activities. In general, pozzolanic

activities can be affected by different mineorological component, such as amorphous material present in a glassy form, amorphous material containing considerable quantity of strongly bound water, eg monomorillonite, poorly crystalline clay minerals, eg fire clay etc.

2.6.1. Classification of pozzolanas

Ramezanianpour (2014) classified pozzolan based on their origin:

1. Artificial pozzolan
2. Natural pozzolan

2.6.1.1. Artificial pozzolan

Artificial pozzolans are the materials with low pozzolanic activity and need further treatments to achieve pozzolanic activity; it results from chemical or structural modifications of materials originally having no or only weak pozzolanic properties (Ramezanianpour, 2014). Examples of artificial pozzolans as stated by (Shetty, 2009) are;

i. Fly ash
ii. Blast furnace slag
iii. Silica Fume
iv. Rice Husk ash
v. Matakaoline
vi. Surkhi

2.6.1.2. Natural Pozzolans

Naturally occurring pozzolan deposits are mainly of volcanic origin. They occur as tuffs, volcanic ash and pumicite and are found abundantly in areas with a geological history of volcanic activity. The meaningful use of such volcanic debris can transform them in to natural resources, and does not only provide a lower cost of cement and concrete but can also help to decrease CO_2 emissions related to Portland cement production by replacing clinker.

In general, a good natural pozzolan contains low quantities of unreactive minerals, alkali fieldspar and quartz and high quantities of reactive components such as zeolite minerals and volcanic glass. The dissolution of the silicates in the alkaline cement pore solution enables them

to react readily as the cement hydrates. Chemically natural pozzolans are comprised principally of silicon and aluminum oxides.

The materials that have been investigated or even commercially applied as natural pozzolans the recent years are classified as follows:(Christos Dedeloudis1 et al, 2018)

i) Volcanic ash (VA) and pumice
ii) Scorias
iii) Tuffs
iv) Diatomite
v) Hydrothermal siliceous sinters
vi) Bentonite
vii) Perlite

2.7. Volcanic ash and pumice

Volcanic ash and pumice are non consolidated material consisting of a mixture of minerals and glassy phases ejected during volcanic eruption. Volcanic ash is the fine counterpart, pumice the coarser counterpart. Often they are found mixed or interstratified as during volcanic eruptions first the coarse material is deposited while the latter the finer material settles. In areas that experienced past volcanic activity, volcanic ashes and pumices have been widely used with Portland cement and other components to make blended cements. The pozzolanic activity of this material is related to siliceous components. Comprehensive has been conducted over the last few years on the use of volcanic ash and pumice in cement and concrete production (Christos Dedeloudis1 et al , 2018)

Table 2.5 Standard Specification of Class N Pozzolans according to ASTM C 618

Test /property	Requirement
$SiO_2 + Al_2O_3 + Fe_2O_3$, %	≥ 70
SO_3, %	≤ 4.0
Moisture content, %	≤ 3.0
Loss on Ignition,%	≤ 5.0
Amt retained when wet-sieved on 45 µm(No.325) sieve,%	≤34
Strength activity index,7-day,% of control	≥75
Strength activity index,28-day,% of control	≥75
Water requirement,% of control	≤115
Soundness: autoclave expansion or contraction,%	≤0.8
Density, variation from average,%	≤ 5.0
Percentage retained on 45 µm sieve, variation (percentage points from average)	≤ 5.0
Available alkalis,%	≤ 1.5

CHAPTER THREE

MATERIALS AND METHODS

3.1 Materials

The materials used for this research work are; volcanic ash, Ordinary Portland cement, sharp river sand, crushed granite stone and curing media. Materials preparation and testing of concrete samples will be done in adherence to appropriate Ethiopian, ASTM and BS standards. The chemical composition and physical tests of volcanic ash were conducted at Geological Survey of Ethiopia and Mugher Cement Enterprise, Addis Ababa. The Milling and sieving of Volcanic ash was carried out in mechanical unit operation lab of School of Chemical and Bio Engineering, Addis Ababa University Institute of Technology, while all other experimental works were conducted in Material test laboratory of School of Civil and Environmental Engineering, Addis Ababa University Institute of Technology.

3.1.1 Lege Dadi Plateau Volcanic Ash

The Lege Dadi Plateau volcanic ash used in this research is obtained from Ethiopia, Oromia Regional State, Oromia special Zone. The place is situated in North West Shewa, Oromiya, its geographical coordinates are 9° 5' 0" North, 38° 55' 0" East and its original name (with diacritics) is Lege Dadi.

The material was first ground using rubber mortar to reduce its size at the site for ease off transportation. The extracted volcanic ash materials was then packed in a bag of about 100kg and transported by truck to Addis Ababa Institute of Technology School of Chemical and bio engineering laboratory for investigations. The material taken to the lab contained high moisture because sample had been taken during rainy season. The material was spread on floor in mechanical unit operation lab for a week to reduce the moisture content naturally; it was then dried in oven at 105 ^{0}c for 24 hours using trays. After drying it was carried to for milling using jaw crusher and electronic balls milling machine and sieved through 75μm sieve aperture.

Figure 3. 1 Volcanic Ash at plateau of Lege Dadi, Oromia Special zone, where sample was taken for the research work

Figure 3. 2 Volcanic ash ground and sieved to 75µm

Figure 3. 3 Blaine permeameter

3.1.2. Cement

Ordinary Portland Cement of Mugher Cement Enterprise obtained from Addis Ababa Market was used for this research.

3.1.3. Fine aggregates

The fine aggregates used in this research was clean and saturated surface dried sharp river sand obtained from Mojo area. It will be sieved through 5mm sieve to take away any impurities and larger size aggregates in accordance to ES.

3.1.4. Coarse aggregates

Totally crushed granite stone that conformed to ES was used for this research and it is obtained from quarrying area of Goro, Addis Ababa. It was also sieved passing through 20mm sieve and retained on 10mm sieve.

Figure 3. 4 Coarse and Fine aggregates

3.2. Concrete mix details

The Volcanic Ash, sand, coarse aggregate and Ordinary Portland Cement were mixed together to make concrete. M25 was used as a benchmark based on ACI-211.1-91 guidelines for research. The proportions of materials for concrete were 1: 2.9: 3.9 of cement, sand and coarse aggregate respectively with water to cement ratio of 0.61. Experiments were conducted to replace cement by changing the composition of concrete mixture in the series of 5, 10, 15 and 20% of Volcanic Ash (i.e. percentage of Volcanic Ash added in the mixture). After mixing, the paste (i.e. concrete) was casted into 100mm cubic mica molds that were properly fixed and smeared with oil. For efficacy compaction, vibration was introduced to the cubes through vibrator. The concrete cubes were then left in the mold overnight. The following morning concrete cubes were removed from the mold and their weight was recorded. They were then deepened into curing sink for 3, 7 and 28days. After curing; the concrete cubes were tested to identify the achieved quality of mechanical properties of the concrete based on percentage changes of Volcanic Ash in the mixture of concrete.

Lab trial mix-type prepared according to procedure of ACI-211.1-91 guidelines, details of mix preparation of cubes was described in (Day et al., 2002)

Table 3. 1 Mix proportion for cubes

Volcanic Ash contents (%)	No of cubes	Cement (gm)	Volcanic Ash (gm)	Fine aggregate (gm)	Coarse aggregate(gm)	Water (gm)
0%	9	2673	0	7785	10431	4005
5%	9	2539	134	7785	10431	4005
10%	9	2406	267	7785	10431	4005
15%	9	2272	401	7785	10431	4005
20%	9	2138	535	7785	10431	4005

With same procedure, proportional mix and technique to prepare concrete cubes, cylindrical shape concretes with diameter 100mm and height 200mm were prepared for durability tests. Acid attack, water absorption and abrasion resistance tests were conducted with these concrete cylinders

Table 3. 2 Mix proportion for cylinders

Volcanic Ash contents (%)	No of cylinders	Cement (gm)	Volcanic Ash (gm)	Fine aggregate (gm)	Coarse aggregate(gm)	Water (gm)
0%	9	4197	0	12222	16377	883
10%	9	3777	418	12222	16377	883
20%	9	3358	839	12222	16377	883

Figure 3. 6 Samples weighted and proportioned for mixing

Figure 3. 5 Concrete casted to 100mm cubic micas

3.2.1. Mixing and curing water

Clean tap water fit for drinking supplied for public will be used for the production and curing of concrete samples. The water conforms to ES

3.2.2. Curing of specimens

After mixing the concrete, it was cast into moulds. The moulds and specimens stored under laboratory conditions for 24 hours and then specimens were transferred to the curing basin. They were then tested after 3, 7, and 28 days of curing .The Portland cement volcanic ash concrete

samples were cured by completely immersing into the curing media. Bowl baths that had the capacity of 50 liters of water were used to cure concrete samples, this was done to allow the specimens to be placed and cured properly without overflow.

Figure 3. 8 Concrete samples in curing baths

Figure 3. 7 concrete surfaces drying and ready for crushing

3.2 Methods

3.2.1 Preliminary tests of materials

The preliminary tests of materials carried out were: Chemical composition of volcanic ash, specific gravity and bulk density of volcanic ash, OPC, fine and coarse aggregates were determined. Also sieve analysis and moisture content for fine and coarse aggregates, consistency, setting time and soundness test for volcanic ash and cement blend were carried out.

3.2.1.1. Chemical composition of volcanic ash

The chemical composition test of Lege Dadi Volcanic Ash was carried out at Geological Survey of Ethiopia using Atomic Absorption Spectrometer (AAS), HF attack, and gravimetric methods. The compositions Al_2O_3, Fe $_2O_3$, Na_2O, K_2O, MgO, CaO, and MnO were determined by Atomic Absorption Spectrometer.

Weigh 0.5 g sample of volcanic ash (previously finely ground and air dried at 105 ^{0}C for 2 hours) in a platinum crucible and mixed with about 10 g of sodium carbonate, kept the crucible with lid in a muffle furnace, heated slowly and finally ignited at 1050 ± 25^{0}C to complete the fusion, cooled the crucible then placed in 100 ml water in a 500 ml beaker, added slowly 30ml 5% HCl, warmed until the fused mass was completely disintegrated and removed from the crucible and lid, washed the crucible with hot water, crushed any lumps remaining in the solution by glass rod, then 5ml 5 % hydrochloric acid was also added in excess.

Evaporated the solution, obtained from the fusion to completely dryness/baked, added 20 ml 5% HCl shaken, then added 100ml hot water, heated on hot plate for boiling for 2 minutes with continuous stirring with glass rod. Filtered the solution through ashless filter paper No.40 (whatman) or pulp and washed the residue with 5 times of hot water.(Akbar et al., 2016)

The precipitate was used for SiO_2 analysis, while the filtrate was used for Al_2O_3, Fe_2O_3, Na_2O, K_2O, MgO, CaO, and MnO analysis through Atomic Absorption Spectrometer. Gravimetric method is used to analyze the composition of sulfate (SO_3) in the volcanic ash sample.

In order to determine the loss on ignition (LOI) Weigh 1 g of material into a tarred platinum crucible and ignite in a muffle furnace at a temperature of 750 ± 50 ^{0}C for 15 min. Cool to room temperature in desiccators and weigh base on ASTM C114-15 2015 procedure. (Bernal et al., 2017)

$$\% \text{ LOI} = \frac{A-B}{A} * 100 \qquad \textbf{3.1}$$

where A is the mass of the crucible and sample before ignition and B is the mass of the crucible and sample after ignition.

Figure 3. 9 Atomic Absorption Spectroscopy

3.2.1.2. Specific gravity of volcanic ash

Specific gravity of the volcanic ash was determined at inorganic lab school of Chemical and bio engineering using Le Chatelier's flask.50gm weigh volcanic ash passed through 75 micron mesh was introduced in to the flask that already contain kerosene free of water at 20^0C. (ASTM C 311-05, 2008) standard had been used for the test.

Figure 3. 10 Lechatelier's flask with volcanic ash sample

3.2.1.3. Bulk and specific density of coarse aggregate

Bulk density of coarse aggregate was determined in accordance to ES (Dinku, 2002), 5kg of aggregate was taken as a sample by quartering 20kg of specimen and all materials passing sieve no.4 (4.75mm) was rejected from the sample taken. The apparatus used were weighing balance, sample container, oven etc.

Figure 3. 11 wash off coarse aggregate to determine specific gravity

3.2.1.4 Bulk and Specific gravity of fine aggregate

Specific gravity of the fine aggregates was determined using pyknometre flask; the procedure used was in accordance with ES (Dinku, 2002). The apparatus used during the test include pyknometer bottle, funnel, spatula and weighing balance.

Figure 3. 12 100ml pycnometer bottle with fine aggregate sample

3.2.1.5. Sieve analysis of coarse and fine aggregates

In accordance to ES (Dinku, 2002), 2kg of coarse aggregates was weighed and then poured on different sizes of sieves passing through 37.5mm, 19mm, 9.50mm and 4.75mm. Weight of aggregates retained and passing on each sieve was taken down and percentage passing would be calculated. Also the same procedure was used for fine aggregates of 500gm passing through sieve sizes 9.5mm, 4.75mm, 2.36mm, 1.18mm, 600μm, 300μm, 150μm and pan. Fineness modulus of fine and coarse aggregates were determined as sum of cumulative percentage of aggregates retained on each of a series of sieves (each sieve having a clear opening that is half of the preceding one) and the total divided by 100.

3.2.1.6. Moisture content of coarse and fine aggregates

1kg of coarse aggregates is weighed as (A) using weighing balance, the material is then poured on wide metal container, spread and put inside an electric oven for 24hours at 105 ^{0}C. After 24hours the aggregates was removed from the oven and allowed to cool down at room

temperature, and then the aggregates is weighed again as (B). The same procedure was applied for 0.5kg of fine aggregates and finally the moisture content were determined in accordance to ES.

$$\text{Moisture content} = \frac{A-B}{B} * 100 \qquad \textbf{3.2}$$

3.2.1.7. Setting time and soundness of materials

Setting time and soundness tests were conducted with cement paste of normal consistency; initial setting time and final setting time were carried out using Vicat apparatus, and le chartelier apparatus according to ES (Dinku, 2002). Three different mixes; 0%, 10% and 20% replacement paste were prepared for both setting time and soundness tests.

Consistency

$$\text{Consistency} = \frac{water\ consumed}{weight\ of\ cement\ sample} * 100 \qquad \textbf{3.3}$$

Figure 3. 13 Viccat apparatus for testing consistency and setting time

3.2.2 Testing of fresh Portland cement /volcanic ash concrete

Fresh property of Portland cement volcanic ash concrete is assessed to test its level of fluidity and mobility using slump test method.

3.2.2.1. Slump test

Slump test method is used to test the workability of the fresh Portland Cement Volcanic Ash concrete as provided in ES (Dinku, 2002). The apparatus used to carrying out this test consist of mould, scoop, sampling tray, trowel, tamping rod, and ruler. The internal surface of the mould is clean and damp free from unneeded moisture then placed on sampling tray and hold firmly against the surface below. The fresh concrete is poured into the mould in three layers, approximately one third of the height of the mould where each layer was tamped 25 strokes and the mould is removed gently vertically upward. The slump is measured (nearest 5mm) to determine the difference between the height of the mould and the height of slump concrete.

Figure 3. 14 Slump cone and slump measurement of fresh concrete mix

3.2.3 Testing of hardened concrete samples

Water was used as a curing media for concrete samples produced .The concrete specimens were crushed after 3, 7, and 28 days. The tests carried out were:

3.2.3.1. Density test

The concrete specimens are removed from the curing container and placed outside to surface dried, then weighed using weighing balance to determine the mass of the samples in accordance to ES.

3.2.3.2. Compressive strength test

The concrete samples (cubes) were removed from the curing basin and placed outside to surface dried, weighed and positioned at the centre of hydraulic automatic compression machine for crushing.

Figure 3. 15 Compressive strength measuring machine and some of the crushed samples

3.2.3.3. Water absorption test

The concrete samples (cubes) were removed from the curing tank and allowed to dried, then placed in the electronic oven to oven dried at 105 ^{0}C for 72 hours. The samples were removed from the oven and allowed to cool at room temperature then weighed to determine the initial weights. The final weights were determine after immersing the concrete samples in the curing medium for 30 minutes then removed to cloth dried and re-weighed again.

$$\text{Absorption\%} = \frac{M2-M1}{M1} * 100 \qquad \textbf{3.4}$$

Where M1 is dry mass of the test piece and M2 is the mass of saturated specimen

Figure 3. 17 Oven to dry sample for water absorption test

Figure 3. 16 Dried and weighted samples

3.2.3.4. Abrasion resistance test

The concrete samples (cubes) were removed from the container and allowed to surface dried, weighed and the values were recorded as W1. A weight of 3.5kg was mounted and tightly fixed to the wire brush and stroke the specimen surface for 60 times at equal speed, then the specimen was re-weighed and the value was recorded as W2. Final weight was deducted from the initial weight to determine the lost in weight of each sample as stated by Gambo (2014) using equation

$$\text{Abrasion resistance} = \frac{W1-W2}{M2} * 100 \qquad \textbf{3.5}$$

3.3 Experimental Design and Data Analysis

The experiment was conducted in a completely randomized design .Samples were analyzed in triplicate. The results obtained for different tests carried out in this research work were analyzed using simple statistical tools (mean and percentage). Mean, represented by X or μ is the most commonly used measure of central tendency which is the sum of scores divided by the total number of scores, often represented by equation

$$\bar{X} = \frac{\sum Xi}{N} \qquad \textbf{3.6}$$

Ms Excel has used as a software for analysis and interpretation of data.

CHAPTER FOUR

DATA PRESENTATION, ANALYSIS AND DISCUSSIONS

4.1. Presentation of Results of Preliminary Test

The results of preliminary tests conducted for this research work were; chemical composition of Lege Dadi Plateau volcanic ash, specific gravity and bulk density, moisture content, sieve analysis of the aggregates, setting time and soundness test and slump test of fresh OPC Volcanic ash blend concrete.

Table 4. 1 Shows Chemical composition analysis results of volcanic ash sample and ASTM C618-05 Requirements

Material content	Percentage composition (%)	Result	Requirement according to ASTM C618-05
Silcon Oxide ($SiO_{2)}$	72.24	(SiO_2) + (Al_2O_3) + (Fe_2O_3)=89.31%	(SiO_2) + (Al_2O_3) + (Fe_2O_3) =70% minimum
Aluminium Oxide ($Al_2O_{3)}$	14.39		
Iron Oxide ($Fe_2O_{3)}$	2.68		
Calcium Oxide (CaO)	0.40		
Magnesium Oxide (MgO)	0.34		
Sodium Oxide (Na_2O)	1.72		
Potassium Oxide (K_2O)	2.48		
Manganese Oxide (MnO)	<0.01		
Phosphorus Oxide ($P_2O_{5)}$	0.02		
Sulphur Oxide (SO_3)	0.003%	0.003%	Maximum,4%
Titanium Oxide ($TiO_{2)}$	0.13		
Moisture content (H_2O)	0.39	0.39%	Maximum,3%
Loss on Ignition (LOI)	3.86	3.86%	Maximum,10%

ASTM C 618-5 states that for a material to be a pozzolan the summation of composition of Silicon Oxide ($SiO_{2)}$, Aluminum Oxide ($Al_2O_{3),}$ Iron Oxide ($Fe_2O_{3)}$ must be minimum of 70%. From the results of Atomic Absorption spectrometer and HF attack test the major oxides of

Volcanic Ash sample used in this research were summed up to 89.31%. The result fulfilled ASTM 618-5 requirements.

The moisture content of the Volcanic Ash sample was approximate of 0.39 %,the surface area of the sample was 4972 cm^2/gm and Loss on ignition (LOI) showed 3.8 % which was in the range of requirement stated by ASTM C 618-5(ASTM C618C–00, 2000). LOI of naturally found supplementary cementacious materials should not be more than 10% this is because the Volcanic Ash shouldn't contain excess quantity of moisture and/or undesirable impurities, such as carbon that have significant impact on the concrete produced using Volcanic Ash as an additive to cement

The result of gravimetric analysis showed the composition of sulfate in the Volcanic Ash sample was 0.003% which was in the range stated by ASTM standard that states for pozzolanic materials the maximum sulfate content should not more than 4%.This is to mean that concrete produced by blending Volcanic Ash with OPC would not exposed to sulfate attack from its own source.

4.1.1. Specific gravity and bulk density of Materials

Table 4. 2 Specific gravity and Bulk density of materials used for research

No	Material	Specific Gravity	Bulk Density(Kg/m^3)
1	Coarse aggregates	2.59	1350
2	Fine aggregates	2.45	1550
3	Ordinary Portland Cement (Mugher)	3.15	3150
4	Lege-Dadi Volcanic ash	2.32	2320

The results of specific gravity obtained satisfied the requirements of ACI E1-99 which states specific gravity for normal weight aggregates should be in the range 2.30 to 2.90

4.1.2. Consistency, Setting time and Soundness

Table 4. 3 Results of consistency, setting time and soundness of OPC and volcanic ash blend

Cement and Volcanic Ash blend paste		0%	10%	20%
Consistency		34%	32%	31.5%
Setting time	Initial setting time	140min	150min	180min
	Final setting time	205min	210min	230min
Soundness		0.40%	0.25%	0.21%

Variation in normal consistency, setting times and soundness with different percentages of VA are presented in the table 4.3. Normal consistency of the paste decreased by 7.94% when the VA content was varied from 0 to 20%. The decrease in normal consistency was due to the reduction of cementitious binder in the fresh mixture with the increase of VA content. On the other hand, Specific gravity of VA was less than that of cement, which resulted in the larger volume of VA compared to the volume of cement replaced as the replacement was made by mass. As a result, the overall volume was increased needing more water to form a paste of same consistency for different % of VA in the mixture.

Setting times results showed an increase in both setting times with the increase in VA content. Initial setting time increased by 28.6% whereas increase in final setting time was 12.2% with the increase in VA content from 0 to 20%. This was reasonable as the increase of VA or VP content reduced the cement content in the mixture and also decreased the surface area of the cement. As a result, the hydration process slowed down causing setting time to increase. The slow hydration means low rate of heat development. This is of great importance in mass concrete construction, for which Portland volcanic ash cement (PVAC) can be mostly used, besides other general uses.(Siddique, 2011)

The results of initial and final setting times for both replacements (10% and 20% VA) were as per recommendation of Ethiopian standard. That is the initial setting time for cement should not less than 45 minutes and final setting time not to exceed 10 hours. 20% replacement has significant delay of setting time in comparison with the plain ordinary Portland Cement paste obtained.

The autoclave expansion of the paste mixes decreased with the increase in VA content. All mixes containing 0%, 10% and 20% VA, satisfied the ASTM C 618 requirement of 0.8% maximum.

The blended cement showed a very low expansion due to the increase in calcium-silicate hydrate (C-S-H) content and changes to the C/S ratio of the C-S-H gel.(Nigri et al., 2017)

4.1.3. Moisture Content of materials

Table 4. 4 Moisture contents of materials

No	Materials	Weight of material before oven dry (kg)	Weight of material after oven dry (kg)	Mc Percentage (%)
1	Coarse aggregates	2	1.96	2
2	Fine aggregates	0.5	0.460	8.6
3	Portland cement	0.5	0.499	0.2
4	Volcanic ash	0.5	0.498	0.39

According to ACI E1-99 moisture content for coarse aggregates should be within 0 to 2% and for fine aggregates should be within 0 to 10% which denote that the test on the aggregates has conformed to the standard.

4.1.4. Water absorption of materials

Table 4. 5 Results of water absorption test

No	Materials	Weight of saturated-surface-dry sample in air (g)	Weight of material after oven dry (g)	Mc Percentage (%)
1	Coarse aggregates	4900	4830	1.45
2	Fine aggregates	50	44	13.6

4.1.5. Sieve Analysis of Fine Aggregates

Table 4. 6 Result of Sieve Analysis of Fine Aggregates

Sieve size	Weight of sieve	Weight of sieve and retained	Weight retained	Percentage retained (%)	Cumulative coarser (%)	Cumulative passing (%)	ES Requirement
9.5mm	0.585	0.590	0.005	1	1	99	100
4.75mm	0.430	0.440	0.01	2	3	97	95-100
2.36mm	0.390	0.410	0.02	4	7	93	80-100
1.18mm	0.355	0.410	0.055	11	18	82	50-85
600 µ	0.325	0.545	0.22	44	62	38	25-60
300 µ	0.300	0.425	0.125	25	87	13	10-30
150 µ	0.285	0.335	0.05	10	97	3	2-10

pan	0.260	0.275	0.015	3	100		

$$FM=\sum \frac{cumulative\ coarser}{100}=\frac{275}{100}=2.75 \qquad 4.1$$

The fineness modulus was calculated as 2.75 Ethiopian standard requirements of the fineness modules of medium size fine aggregate is in range 2.6 and 2.9 and the result fulfills the requirement. In addition the table showed us the size distribution /gradation/ of the fine aggregates satisfies Ethiopian requirements (Addissie, 2005)

4.1.6. Coarse Aggregates

Table 4. 7 Result of Sieve Analysis of coarse aggregate

Sieve size	Weight of sieve	Weight of sieve and retained	Weight retained	Percentage retained (%)	Cumulative coarser (%)	ES requirements
75mm			0		100	--
63mm			0		100	--
37.5mm	1.085	1.085	0		100	100
19mm	1.190	2.235	1.045		52.2	95-100
13.2mm	1.155	2.190	---	--	--	--
9.5mm	1.165	2.040	0.875		96	25-55
4.75mm	1.265	1.325	0.06		99	0-10

Ethiopian standard has not set requirements concerning the fineness modules of coarse aggregate samples. According to CRD (corps of engineers CRD-C 104) fineness modulus calculation coarse aggregates for concrete preparation is in range 5.5 and 8.5. The calculated value of fineness modulus of coarse aggregate of the sample is 5.5 which fulfilled the stated requirements.

4.2. Workability of fresh concrete

Table 4. 8 Slump Test Results

No	Percent replacement VA with OPC	Slump (mm)
1	0%	55
2	5%	53
3	10%	51
4	15%	48
5	20%	46.5
6	25%	44

Same volume of water was used for all mixes. It was observed from the test result that there was 20% reduction in slump as the VA content varies from 0% to 25%.In general, some reduction in slump by natural pozzolan addition was because the cement was partially replaced with natural pozzolan by weight and therefore, according to lower specific gravity of natural pozzolan in comparison with that of cement, the volume of solids in the paste was higher than that of the control mixture. Then more mixing water is necessary for lubricating particles.(Christos Dedeloudis1 et al., 2018)

The increase in volume may require more mixing water but this is not necessary a disadvantage. As indicated in Ramezanianpour et al (2013), this increase in volume allows for a more stable mix, and better conditions for the design of fluid mixes such as self-consolidating concrete might be obtained

Particle size, shape and internal structure are very important characteristics that define the impact of the pozzolan on water demand. In general, pozzolanic cements require higher fineness than ordinary Portland cement to achieve similar strength level, due to its slower reaction rate. Therefore, the increase in water demand can initially be linked to this technological aspect that is a consequence of cement design rather than the properties of the natural pozzolan itself. (Christos Dedeloudis1 et al., 2018)

The trial sample slump was designed to be in the range between 25mm and 100mm. This slump has selected to concrete work like beams, reinforced walls and columns according to ACI 211-1-91.

4.3. Test results of hardened concrete

4.3.1. Visual observation

There was no wear and tear observed on results of concrete cylinders used as control cured in water for 28 days. However there was significant change in appearance of concrete cylinders cured in 3% diluted sulfuric acid solution. The acid attacked the surface texture of cylinders and change the color of concrete to a white appearance in addition there was an observed weight loss on concrete cylinders of both control and VA samples.

Trial test samples immersed in 3% diluted sulfuric acid; white milky color was observed during the seven days of curing on both the control and VA samples. This was due to the formation of calcium sulfate following the reaction of the calcium hydroxide with the sulfuric acid.(Labbaci et al., 2017)

$Ca(OH)_2 + H_2SO4 \longrightarrow CaSO4 + 2H_2O.$

Deposited gypsum forms a thick white layer on the surface of the concrete molds. After 28days of curing there was a considerable loss of mass of the samples due to the formation of pulpy, crispy or water soluble materials created and settled at the bottom of curing bath. This may be due to the acid attacked the gypsum layer (calcium sulfate) that lead formation of precipitate which easily leached out. In addition, the calcium sulfate formed in the initial operation reacts with the calcium aluminate phase in cement to form the hydrated sulfoaluminate calcium ($Ca_6Al_2(SO4)_3(OH)_{12}26H2O$) ‘‘ettringite”. The hydrated sulfoaluminate calcium is an expansive element which creates cracks, loss of cohesion and strength and changes in porosity.(Labbaci et al., 2017)

It was noted, mainly, that after 28 days of immersion, that the samples contain VA powder reduced mass loss, compared to the reference control concrete sample

4.3.2. Density of hardened concrete samples

Table 4. 9 Average density of concrete cylindrical samples cured in water (Kg/m^3)

No	Replacement percentage	Day 7 Average density in (Kg/m^3)	Day 28 average density in (Kg/m^3)
1	0%	2078	2093
2	10%	2097	2103
3	20%	2018	2042

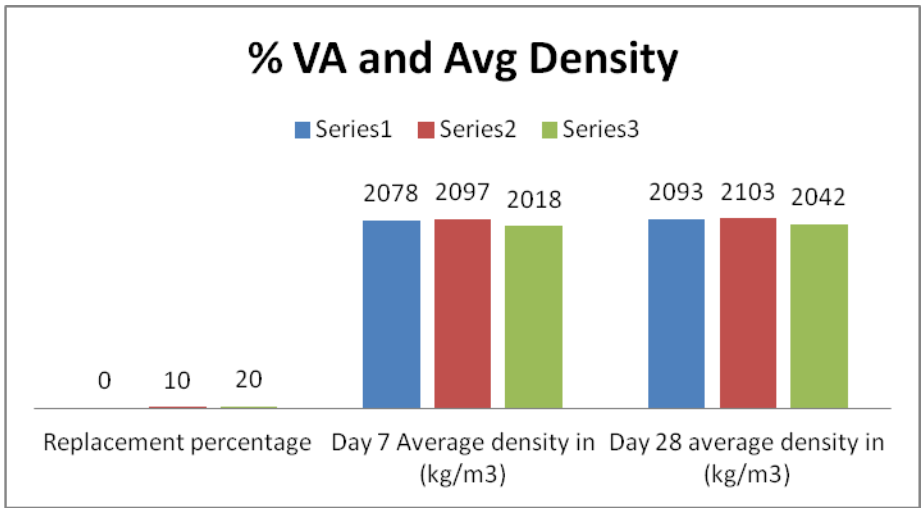

Figure 4. 1 Comparison of average density at different curing days with vary % Volcanic Ash.

The average density ranged from 2056-2199 Kg/m^3 for cylindrical samples. The control sample and 10% VA samples have not significant difference in their average densities whereas 20% VA sample shown 3% decrease during 7 day curing periods and 2.5% decrease during 28day curing periods. This was caused by the lower specific gravity of the volcanic ash in comparison with the OPC. We can also see from the figure as curing period increases from 7days to 28days the average unit weight has shown an increase for both the control and VA concrete samples.

4.3.3. Compressive strength test of hardened concrete samples

Table 4. 10 Average compressive strength of cubic samples

% Replacement of VA	Average Compressive Strengths of concrete cubes in MPa		
	Day 3	Day 7	Day 28
0%	11.83	10.93	22.2
5%	10.75	10.28	20
10%	8.15	8.65	19.98
15%	8.3	7.9	21.3
20%	8.03	8.2	16.9

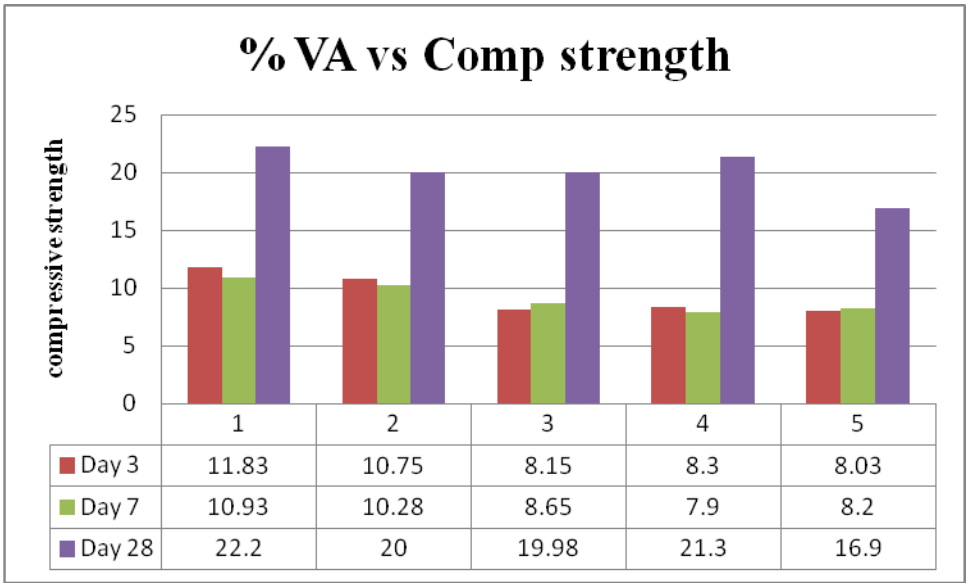

Figure 4. 2 Comparison of strength at different curing days with % volcanic Ash

The table and graph showed average compressive strength of OPC and Volcanic ash blend concrete cubic samples cured for 3, 7, and 28 days. The results of compressive strength at 28th day showed 5%, 10%, 15%, 20% replacement of Volcanic Ash had 20, 19.98, 21.3, 16.9 MPa respectively.

The pozzolanic reaction between natural pozzolans and calcium hydroxide usually occurs after the C_3S in the cement has started hydrating and portlandite is formed as a result.

Usually pozzolanic effects of strength improvement are more pronounced at late ages (i.e. beyond 28 days) than at early age. It was reported by several researchers that most oblivious

disadvantage of the natural pozzolan used as a substitute for Portland cement is that early strength is normally decreased(Ozvana,et al.,2012 and Itim,et al.,2011).The strength of the pozzolanic cement is directly affected by the mineralogical features (micro-meso porosity, particle size, surface areas)of pozzolanic material. (Christos Dedeloudis1 et al., 2018)

In general, at the early age of curing (up to 7 days), 30% natural pozzolan substituting Portland cement mixture was slightly lower than reference OPC in regard to compressive strength. As time goes by natural pozzolan continue to react with the calcium hydroxide produced by cement hydration and increase the compressive strength by producing additional C-S-H. After 21 curing days, the 30% natural pozzolan/70% Portland cement mixture begun to exceed the reference OPC by about 15 %.The pozzolanic reaction continues until there would no free calcium hydroxide available in mass and the compressive strength exceeds the reference OPC by 30-40%.(Christos Dedeloudis1et al, 2018)

As it had been described about 80-100% of compressive strength of concrete would be attained after 28 days of curing. As we saw from the results of sample tests taken on 28th day of curing 15 % replacement had 21.3MPa strength which is less than by 4 % with the control but expected to increase more than the control in the subsequent curing periods with further pozzolanic reactions.

Figure 4. 3 Variation of compressive strength with composition variation of volcanic ash

% Replacement of VA	Compressive strength in Mpa at 28 day curing	Deviation of compressive strength in Mpa	Deviation of compressive strength in %	Remark
0%	22.2			Reference mix
5%	20	2.2	9.9%	
10%	19.98	2.22	10%	
15%	21.3	0.9	4.06%	Optimal mix
20%	16.9	5.3	24%	

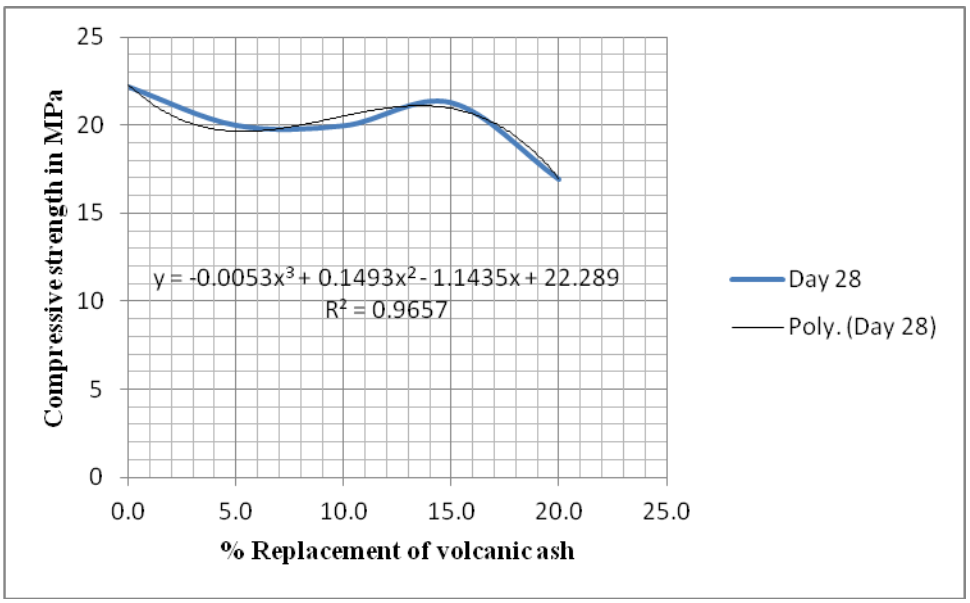

Figure 4. 4 Graph with polynomial equation that show optimum replacement of volcanic ash

Graph show 15% volcanic ash replacement resulted optimal compressive strength of the concrete specimen. Lower strength was obtained for blends of higher substitution 20%. 5% and 10% replacements show they are 10% less than the control mix.

4.3.4. Water absorption of hardened concrete

Table 4. 11 Result of Water Absorption Tests

No	Replacement percentage	Absorption percentage (%)			Absorption of Average of 3 cylinders (%) 28 curing days
		CA1	CA2	CA3	
1	0%	3.6	3.7	3.9	3.73
2	10%	1.75	1.6	1.6	1.65
3	20%	0.8	0.8	1	0.87

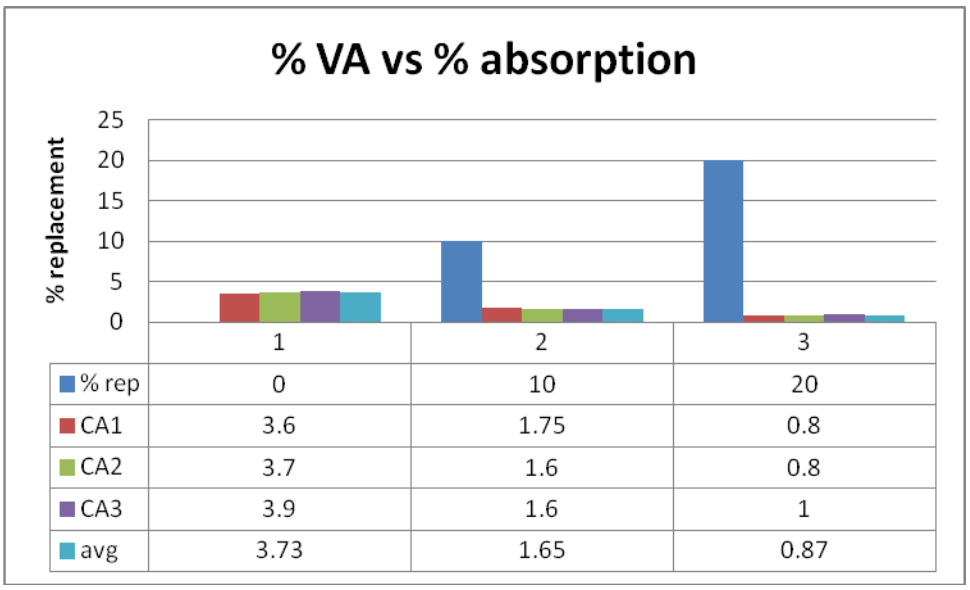

Figure 4. 5 Graph show percentage of volcanic ash vs water absorption

As the percentage of VA increases from 0% to 20% the average water absorption reduced from 3.73% to 0.87%.This indicates as the contents of volcanic ash in the mix increases the concrete become more dense and impermeable to water molecules.

SCMs generally improve potential concrete durability by reducing permeability. Almost all durability-related failure mechanisms involve the movement of fluids through the concrete. With adequate curing natural pozzolans generally reduce the permeability and absorption of concrete. (Aldea et al., 2000)

4.3.5. Abrasion Resistance of hardened concrete

Table 4. 12 Results of Abrasion Resistance

No	Replacement percentage	Abrasion resistance percentage (%)			Abrasion resistance of Average of 3 cylinders (%)
		CB1	CB2	CB3	
1	0%	1.2	1.55	0.4	1.05
2	10%	0.5	0.48	0.32	0.43
3	20%	0.12	0.28	0.24	0.21

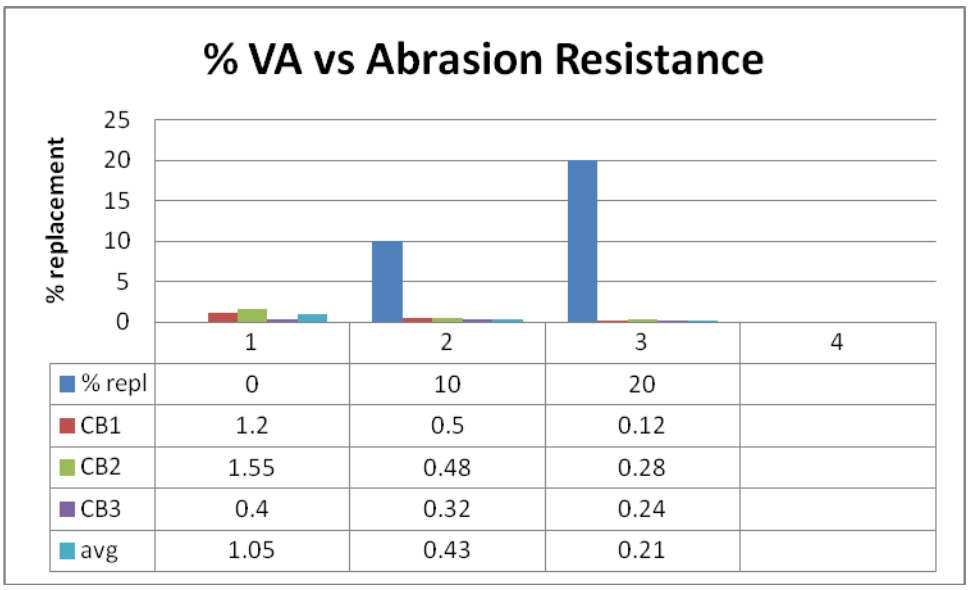

Figure 4. 6 Graph shows percentage of volcanic ash vs Abrasion Resistance

As the percentage of replacement of VA increases from 0% to 20% there was a decrease in mass loss from 1.05 % (control) to 0.21 % due to an impact force. The decrease in mass was not considered as significant. The slight difference may indicate that the more volcanic ash content in the mix, the denser and the stronger the concrete specimen and as the ash content increases the concrete structures resists wear, tear and fatigue forces. It becomes more abrasive resistant structure.

The impact resistance and abrasion resistance of concrete are related to compressive strength and aggregate type. Supplementary cementing materials generally do not affect these properties beyond their influence on strength.(Steven H.Kosmatka, Beatrix Kerkhoff, 1988)

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

- The conformity of the chemical composition of the Lege-Dadi plateau volcanic powder tested with the regulations required by standard ASTM C618-00. It was found that the total silicon, aluminium and iron oxide content is higher than the minimum requirement. Sulfur trioxide and loss on ignition are much lower than the upper limit of the ASTM C618-00. Physical properties of the Volcanic Ash such as bulk density, moisture content, and autoclave expansion comply requirements of ASTM C618-00, where as initial and final setting times of blends of OPC and Volcanic Ash are in limits of Ethiopian Standards and increased with increasing VA content. Therefore, Volcanic Ash used in this research work could be suitably used as replacement of cement in concrete production as pozolanic material.
- As percentage replacement of Volcanic Ash increased, it led to an increase of water demand and setting time
- The test results showed that the compressive strength of samples containing various proportion of Volcanic Ash at the early age of curing (up to 7 days) lower than the average reference control sample. At 28 days of curing period sample containing 15% replacement of Volcanic Ash had strength of 21.3 MPa where as the control sample strength was 22.2 MPa. This indicates as curing period increased, concrete samples containing volcanic ash become stronger.
- Concrete samples with Volcanic Ash replacements show low permeability to water and resist abrasive forces; this is because natural pozzolans increases the long term compressive strength of concrete and makes the concrete matrix stronger and denser. Acid significantly attack concrete structures but the attack is reduced with VA replacements.

According to the results of this research, it can be concluded that Volcanic Ash can be used as effective pozzolanic materials to replace portion of Portland cement. They allow a high compressive strength and good resistance to abrasion forces and chemical attacks. Moreover,

the use of this material in its natural state, without calcinations, will allow an economic exploitation with lower environmental impact.

5.2. Recommendations

- Lege-Dadi plateau Volcanic Ash can be use to partially replace Portland Cement in concrete production
- The optimum replacement of this naturally existing volcanic powder is 15% of Portland cement as per discovery of this research work.
- The workability of concrete mix containing Volcanic Ash can be improved by careful addition of water by controlling water to cement and pozzolan ratio w/(c+p).
- Detail Cost Benefit Analysis to determine the economic feasibility of using Lege-Dadi Volcanic Ash has to be studied.
- Chemical durability properties such as resistance to chloride attack, resistance to sulfate attack, alkali-silica reaction etc has to be studied.

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APPENDICES

A: Specific gravity of volcanic ash

Mass of volcanic ash used=50gm

Initial readings of the lechateler's flask=1ml

Final reading=22.55ml

Difference in readings=21.55 ml

Specific gravity=50/21.55=2.32

B: Moisture content of fine and coarse aggregates

A) Fine Aggregate

Weight of Original sample (A) =500gm

Weight of dry sample (B) @ 105^0 C=460gm

$$(W\ \%) = \frac{500-460}{460} \times 100\% = 8.6\%$$

B) Coarse aggregate

Weight of original sample (A) =2000gm

Weight of dry sample (B) @ 105^0 C=1960gm

$$(W\ \%) = \frac{2000-1960}{1960} = 2.0\%$$

C: Specific gravity and absorption capacity of coarse aggregate

A= Weight of oven-dry sample in air (g) =4830

B= Weight of saturated-surface-dry sample in air (g) = 4900

C= weight of saturated sample in water (g) = 3036

$$\text{Bulk specific gravity} = \frac{A}{B-C} = \frac{4830}{4900-3036} = 2.59$$

$$\text{Apparent specific gravity} = \frac{A}{A-C} = \frac{4830}{4830-3036} = 2.69$$

Bulk specific gravity (saturated surface dry basis) = $\frac{B}{B-C} = \frac{4900}{4900-3036} = 2.63$

Absorption capacity= $\frac{B-A}{A} \times 100\% = \frac{4900-4830}{4830} \times 100 = 1.5\%$

D: Specific gravity and absorption capacity of fine aggregate

Bulk specific gravity

Bulk sp gr = A / (B+500-C) where

A=weight of oven dry sample in air (g)

B=weight of pycnometer filled with water (g)

C=weight of pycnometer with sample and water to calibration mark (g)

Bulk specific gravity (saturated-surface-dry basis)

Bulk sp gr (saturated-surface-dry basis) =500 / (B+500-C)

Apparent specific gravity

Apparent sp gr =A / (B+A-C)

Absorption

Absorption (%) = (500-A) / A X 100%

C=0.9976Va + 500 + W, Where;

C= weight of picnometer filled with sample plus water (g)

Va=volume of water added to pycnometer (cm^3)

W=Weight of pycnometer empty (g)

B=0.9976V + W

B= weight of flask filled with water (g)

V= volume of flask (cm^3)

W= weigh of the flask empty (g)

Results of Specific gravity and absorption capacity of sample fine aggregate

A = 44gm

B = 0.9976 (100) + 45 = 99.76 + 45 = 144.76

C= 0.9976 (82) + 50 + 45 = 176.8

Bulk specific gravity = 44 / (144.76 + 50 – 176.8) = 44 / 17.96= 2.45

Bulk specific gravity (SSD) = 50 / (144.76 + 50 -176.8) = 2.78

Apparent specific gravity = 44 / (44 + 144.76 – 176.8) = 3.67

E: Procedure for selection of mix proportions (ACI-211.1-91)

Step1. Choice of slump -- See Table A1.5.3.1.

- Concrete for beams, reinforced walls and columns recommended slump is maximum 100mm and minimum 25mm

Step 2. Choice of nominal maximum size of aggregate.

- Maximum size of aggregate: 38.1mm

Step 3. Estimation of mixing water and air content -- See Table A1.5.3.3.

- Mixing water is function of slump and size of aggregates: 181kg/m^3

Step 4. Selection of water-cement ratio --See Table A1.5.3.4.

- For 25 MPa target strength and for non air entrained concrete w/c ratio: 0.61

Step 5. Calculation of cement content.

- W/C ratio=0.61 ⇨ C=W/0.61=181/0.61=296.72kg/m^3

Step 6. Estimation of coarse aggregate content

- The dry mass of coarse aggregate required for a cubic meter of concrete is equal to the value from Table A1.5.3.6 multiplied by the dry-rodded unit mass of the aggregate in kilograms per cubic meter: 0.71*1600= 1136kg

Step 7. Estimation of fine aggregates based on mass basis

- From Table A1.5.3.7.1, the mass of a cubic meter of non-air-entrained concrete made with aggregate having a nominal maximum size of 37.5 mm is estimated to be 2410 kg.

Water (net mixing) = 181kg

Cement= 296.72kg

Coarse aggregate= 1136kg

Total = 1613.72kg

Mass of fine aggregate will be (2410-1613) = 797kg

Step 8. Moisture content 2% in coarse aggregates and 8.6% in fine aggregates

Coarse aggregates (wet) = 1136*1.02=1159kg

Fine aggregates (wet) = 796*1.086=865.5kg

Absorbed water is not part of mixing water, must be excluded

181-1159*0.015-865*0.14=42.5kg

<u>After adjustment</u>

Water (to be added) = 42.5kg

Cement = 297 kg

Coarse aggregate = 1159kg

Fine aggregate = 865 kg

Total = 2363kg/m^3

Step 9.For lab trial batch (1000cm^3)

Water = 42.5 + 20 gm = 62.5gm

Cement = 297 gm

Coarse aggregate = 1159 gm

Fine aggregate = 865 gm

Total = 2386 gm/1000cm^3

F: Compressive strength test results of concrete cubes

% Replacement	Strength of cubes in MPa								
	Day 3			Day 7			Day 28		
	Cube specimen strengths			Cube specimen strengths			Cube specimen strengths		
0%	13.25	14.4	--	12.6	13.25	--	22.15	22.25	--
5%	12.3	13.2	10.9	12.6	11.95	--			20
10%	9	10.25	10.05	10.65	--	9.15	20.65	18.45	19.3
15%	10.85	9.25	9.75	9.55	10.25	6.85	22.1	20.5	17.55
20%	9.6	10.45	9.55	10.45	9.85	9.95	14.65	16.95	16.7 & 16.85

G: Water absorption results of concrete cylindrical samples cured for 28 days

No	Replacement percentage	Dry mass of concrete specimen(M1)			Mass of saturated concrete specimen(M2)		
		CA1	CA2	CA3	CA1	CA2	CA3
1	0%	2858.4	2750.9	2885	2961.9	2853.6	2998.5
2	10%	3001.3	3122.4	3047.9	3054	3172.6	3097.4
3	20%	3150.2	3175.6	3152.9	3175.9	3202.1	3185.9

H: Abrasion resistance test results of concrete cylindrical samples cured for 28 days

No	Replacement percentage	SSD mass of concrete specimen W1			Mass of concrete specimen after test W2		
		CB1	CB2	CB3	CB1	CB2	CB3
1	0%	3238.7	3295.3	3111.9	3201.1	3245	3100
2	10%	3310.8	3261	3297.3	3295.5	3245.3	3286.8
3	20%	3332.7	3312.6	3298.3	3328.7	3303.3	3290.5