

**INVESTIGATION OF THE PYROPROCESSING AND THE OPTIMUM
MIX RATIO OF RICE HUSKS, BROKEN BRICKS AND SPENT
BLEACHING EARTH TO MAKE POZZOLANIC CEMENT**

BY
NALOBILE PROTUS (B.Ed, Sc)
Reg No: I56/10702/2006
DEPARTMENT OF CHEMISTRY

**A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE AWARD OF THE DEGREE OF MASTER OF SCIENCE IN THE
SCHOOL OF PURE AND APPLIED SCIENCES KENYATTA UNIVERSITY**

MAY 2014

DECLARATION

This thesis is my original work and has not been presented for a degree in any other university or for other award.

Sign..... Date.....

We confirm that the work reported in this thesis was carried out by the candidate under our supervision.

DR KARANJA WA THIONG'O

DEPARTMENT OF CHEMISTRY

Signature

Date.....

DR MUTHENGIA W. JACKSON

DEPARTMENT OF CHEMISTRY

Signature

Date.....

DEDICATION

To my beloved wife, Violet Nafula, Daughters Blessing , Chelsea and Son Keith, my Father Justus and mum Loice. You are the strength that keeps me going.

ACKNOWLEDGEMENT

I am grateful to my University supervisors Dr. Karanja wa Thiong'o and Dr. Jackson W. Muthengia for their supervision, advice and patience throughout the experimental and writing of this thesis. My gratitude is also owed to East African Portland Cement Company (E.A.P.C.C) and Kenyatta University for their provision of the facilities, funds and materials for this work.

My sincere gratitude goes to Kenyatta University technical staff in Chemistry department especially Mr. Elias Maina, Mr. Cornelius Waswa and Mr. Dennis Osoro for their technical support and assistance. I am also grateful to the Kenyatta University Chemistry department teaching staff and my colleagues during the master's program for their moral and academic support.

Special thanks go to Mr. Oloo of the Fine Arts Department, Mr. Njoka and Mr. Adagala of the Engineering department for allowing me to use the facilities in their respective departments. I am also very grateful to the teachers service commission (TSC) for a study leave that enabled me to have time for this work.

Last and most importantly, I give praise and honor to God for giving me Life, grace and courage to me in this study period.

TABLE OF CONTENTS

DECLARATION	ii
DEDICATION	iii
ACKNOWLEDGEMENT	iv
TABLE OF CONTENTS.....	v
LIST OF SYMBOLS AND ACRONYMS.....	ix
LIST OF TABLES	x
LIST OF FIGURES	xi
ABSTRACT.....	xii
CHAPTER ONE.....	1
INTRODUCTION	1
1.1 BACKGROUND	1
1.2 STATEMENT OF THE PROBLEM	2
1.3 GENERAL OBJECTIVES	2
1.3.1 SPECIFIC OBJECTIVES.....	3
1.4 JUSTIFICATION OF THE PROJECT.....	3
CHAPTER TWO	5
LITERATURE REVIEW	5
2.1 CEMENT	5
2.1.2 PORTLAND CEMENT PHASES MANUFACTURE	8
2.1.3 HYDRATION OF PORTLAND CEMENT	9
2.2 POZZOLONAS	11
2.2.1 POZZOLANIC ACTIVITY.....	12
2.3 LIME-POZZOLANA CEMENT	17

2.4	PORTLAND POZZOLANA CEMENT.....	18
2.5	ANALYTICAL TECHNIQUES.....	19
2.5.1	ATOMIC ABSORPTION SPECTROSCOPY (AAS).....	20
2.5.2	FLAME PHOTOMETRY.....	21
2.5.3	COMPRESSIVE STRENGTH ANALYSIS.....	22
	CHAPTER THREE.....	23
	METHODOLOGY.....	23
3.1	REAGENTS.....	23
3.2	APPARATUS.....	23
3.3	SAMPLING.....	23
3.4	CHARACTERIZATION OF RAW SBE.....	23
3.4.1	CALORIFIC VALUE.....	23
3.4.2	OIL CONTENT OF SBE.....	25
3.4.3	IGNITION AND SELF COMBUSTION TEMPERATURES.....	25
3.4.4	OIL CONTENT AFTER SELF-COMBUSTION.....	26
3.4.5	ASH CONTENT.....	26
3.5	INCINERATION OF THE POZZOLANA.....	26
3.6	CHEMICAL CONSTITUENT ANALYSIS OF POZZOLANA SAMPLES	28
3.6.1	ATOMIC ABSORPTION SPECTROSCOPY ANALYSIS.....	28
3.6.2	GRAVIMETRIC ANALYSIS AND FLAME PHOTOMETRY.....	28
3.6.2.1	SULPHATE CONTENT AS SO ₃	28
3.6.2.2	SODIUM OXIDE (Na ₂ O) AND POTASSIUM OXIDE (K ₂ O).....	29
3.6.2.3	LOSS ON IGNITION (LOI).....	30

3.7	POZZOLANICITY TESTS	30
3.7.1	CHANGE IN ELECTRICAL CONDUCTIVITY OF SATURATED Ca(OH) ₂ SOLUTION.....	30
3.7.2	POZZOLANICITY BY USE OF THE STANDARD POZZOLANICITY CURVE.....	31
3.7.2.1	DETERMINATION OF HYDROXYL ION CONCENTRATION.....	31
3.7.2.2	DETERMINATION OF CALCIUM OXIDE CONCENTRATION.....	32
3.8	COMPRESSIVE STRENGTH ANALYSIS	32
3.8.1	COMPRESSIVE STRENGTH EVALUATION OF POZZOLANA- ALS CEMENT	33
3.8.2	COMPRESSIVE STRENGTH EVALUATION OF POZZOLANA-ALS- OPC CEMENT	34
3.9	DATA ANALYSIS.....	35
CHAPTER FOUR.....		36
RESULTS AND DISCUSSION.....		36
4.1	INTRODUCTION	36
4.2	RAW SPENT BLEACHING EARTH (SBE).....	36
4.3	CHEMICAL CONSTITUENTS	39
4.3	POZZOLANICITY TESTS	42
4.3.1	CHANGE IN ELECTRICAL CONDUCTIVITY OF SATURATED Ca(OH) ₂ SOLUTION.....	42
4.3.2	POZZOLANICITY BY USE OF THE STANDARD POZZOLANICITY CURVE	44
4.4	COMPRESSIVE STRENGTH EVALUATION	46

4.4.1	COMPRESSIVE STRENGTH OF POZZOLANA-ALS CEMENTS.....	46
4.4.2	COMPRESSIVE STRENGTH OF POZZOLANA-ALS-OPC CEMENTS	47
CHAPTER FIVE		51
CONCLUSIONS AND RECOMMENDATIONS		51
5.1	CONCLUSIONS.....	51
5.2	RECOMMENDATIONS	52
REFERENCES		55
APPENDIX I		65
RAW DATA FOR ELECTRICAL CONDUCTIVITY AND CHEMICAL CONSTITUENT ANALYSIS		65
APPENDIX II.....		67
COST ANALYSIS FOR THE POZZOLANA-ALS-OPC CEMENT.....		67

LIST OF SYMBOLS AND ACRONYMS

ALS	Acetylene Lime Sludge
BB	Broken Bricks
C	CaO
C ₂ S	Dicalcium silicate (2CaO.SiO ₂)
C ₃ A	Tricalcium Aluminate (3CaO.Al ₂ O ₃)
C ₃ S	Tricalcium silicate (3CaO.SiO ₂)
C ₄ AF	Tetra calcium Aluminate Ferrite (4CaO.Al ₂ O ₃)
F	Fe ₂ O ₃
FBK	Fixed Bed Kiln
H	Water (H ₂ O)
KS	Kenyan Standard
OPC	Ordinary Portland cement
PLC	Pozzolana Lime Cement
PPC	Portland Pozzolana Cement
RH	Rice Husks
RHA	Rice Husks Ash
S	SiO ₂
SBE	Spent Bleaching Earth

LIST OF TABLES

Table 2.1	Major mineral constituents of Portland cement.....	8
Table 4.1	Characterization of raw SBE.....	39
Table 4.2	Chemical constituents of BB, SBE and the pozzolana samples.....	42
Table I-1	Results of change in electrical conductivity of a saturated solution of Ca(OH) ₂	67
Table I-2	Results of change in electrical conductivity of saturated of Ca(OH) ₂ for pozzolana with equal amounts of BB.....	67
Table I-3	Change constituent Analysis (AAS, Gravimetric analysis and flame photometry.....	69

LIST OF FIGURES

Figure 2.1	Compressive strength of the various component phases of Portland cement.....	9
Figure 2.2	Pozzolanicity Test diagram.....	17
Figure 2.4	Relative rates of strength development of OPC (control) and concrete with fly ash replacement.....	20
Figure 4.1	Change in conductivity with increase in amount of BB.....	44
Figure 4.2	Change in conductivity of the pozzolana samples with equal masses of BB.....	46
Figure 4.3	Pozzolanicity Diagram for pozzolana- ALS cements on the 8 th day.....	47
Figure 4.4	Pozzolanicity Diagram for pozzolana-ALS cements on the 15 th day.....	47
Figure 4.5	Compressive Strength development of the Pozzolana-ALS cements...	48
Figure 4.6	Compressive Strength development of OPC-ALS as a function of curing Period.....	50
Figure 5.2	the complete Kiln Design.....	54

ABSTRACT

This thesis reports the results of a study aimed at optimizing pozzolanic activity of a blend of Rice Husks (RH), Spent Bleaching Earth (SBE) and Broken Bricks (BB) to form pozzolana that would have pozzolanic activity comparable to natural pozzolanas. Four ratios of RH, BB, and SBE were burnt in the Fixed Bed Kiln (FBK). The starting ratio had 20 kg of RH, 0 kg of BB and 4 kg of SBE. The amount of BB was increased by 2 kg each to a maximum of 6 kg as the mass of SBE was kept constant. The effect of varying the particle size of BB in the blended mix was also examined in two samples with equal amounts of RH, BB, and SBE. The resultant ashes were subjected to various pozzolanic tests. This included; change in conductivity by use of a saturated solution of calcium hydroxide, the standard pozzolanicity curve (ISO, 1990) and compressive strength using the ASTM C 593. The samples with variable fineness of BB before calcinations had no effect on the pozzolanicity of the whole calcined blended pozzolana. The calcined blend with 10: 1: 2 mix of RH: BB: SBE exhibited the highest pozzolanic activity. This sample was mixed with acetylene lime sludge (ALS) in the ratio of 2:1 pozzolana: ALS. The resultant mixture was then blended with OPC in various ratios at percent weights of 46 %, 48%, 50% and 52% to make Portland pozzolana cements. These cements were tested for their compressive strength tests in accordance to the KS EAS 18 part 1 equivalent to EN 197-1 standard. Up to 50 % replacement of OPC met the standard requirements.

CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND

Conventional building materials in most developing countries, like Kenya are beyond reach to a majority of the population. This is due to their high cost (UNCHS, 2006). In addition to the escalation in the cost of building materials, there are rising environmental concerns due to the extensive exploitation of natural resources related to general construction and other housing development activities. These urge the search for alternative technological options.

The most commonly used type of cement in Kenya is Portland cement. This is made by heating calcareous and argillaceous materials in a rotary kiln at temperatures in excess of 1300 ° C (Taylor, 1997). In Kenya, Portland cement is expensive to a majority of the population. This is due to the rising cost of production especially the high energy demands associated with the making of clinker, where the temperatures are in excess of 1300 ° C (Bogue, 1955).

Cement manufacturers have been innovating new strategies to reduce the cost of cement worldwide. This has been done by mainly shifting from the wet process of manufacturing cement to the dry process (Neville and Brooks, 1987). Other strategies involve partial replacement of cement by natural pozzolanas and making of pozzolana-lime binders blended with a small amount of OPC (Mindendorf, *et al.*, 2005). There are now a wide variety of blended cements available (Swamy, 1986). The inorganic materials that are used to reduce cement quantities can be blended and/or ground intimately with clinker and/or cement during manufacture, or blended while preparing the concrete or mortar. The most commonly used minerals are fly ash, granulated slag, micro silica (silica fume) and various natural and calcined

pozzolanas (Robert, 1992). In Kenya, natural pozzolanas for use in blended cements are plenty. They have been investigated by (Waswa-Sabuni *et al.*, 2002; Muthengia, 2003) among many others.

Muthengia (2003) investigated the possibility of using a calcined blended mix of rice husks (RH), broken bricks (BB) and spent bleaching earth (SBE) as a pozzolana. A blend of the materials in the ratio of 5:1:1 was tried and it gave very promising results. However the optimization of the ratios especially the amount of BB in the blend, and the variation of the pyroprocessing parameters to determine its maximum pozzolanicity were not done. If a workable calcined blended raw mix is obtained, it will help lower the cost of cement when replacement of OPC is done at higher proportions than before (Muthengia, 2003).

1.2 STATEMENT OF THE PROBLEM

Replacement of OPC with blended mix pozzolana of BB, SBE and RH with lime has been successful up to 45 percent. Higher replacements of 50 percent or more have failed to meet the required standards (Muthengia, 2003). Blending of OPC with 50 percent or higher of a blend of BB, SBE, and RH may lower the cost of cement. There is need therefore to determine the optimum mix ratio of these pozzolanas and varying the pyroprocessing parameters of these materials to improve on their pozzolanicity.

1.3 GENERAL OBJECTIVES

- i. To determine the optimum mix ratio of rice husks (RH), broken bricks (BB) and spent bleaching earth (SBE), for their improved pozzolanicity.

- ii. To increase the percentage blend of the calcined raw mix pozzolana RH, BB and SBE in OPC.

1.3.1 SPECIFIC OBJECTIVES

- i. To determine the effect of varying the mass of BB in the RH: BB: SBE ratio on the pozzolanic activity of the resultant ash.
- ii. To determine the chemical composition of the resultant ash of the various blended calcined mix ratios of RH: BB: SBE.
- iii. To determine the strength development of the RH, BB and SBE pozzolana in blend with Acetylene lime sludge (ALS).
- iv. To determine the compressive strength of OPC in blend with more than 45 % of the pozzolana-ALS cement.

1.4 JUSTIFICATION OF THE PROJECT

Portland cement is expensive. This is because of the energy utilized during its production (Garcia and Fernandez, 2007). A majority of the Kenyan population therefore cannot afford the cement, which is a major building material for housing and general construction. There is need therefore for alternative pozzolana cement that requires less energy for its production. Such a possibility has been investigated in Kenya using RHA as an artificial pozzolana in blend with OPC (Waswa-Sabuni *et al*, 2002). Pozzolana for production for low cost cement using locally available agricultural and industrial wastes has also been investigated by Muthengia (2003).

RHA, BB and SBE have been investigated as suitable for use as artificial pozzolana. The pozzolanicity of these materials varied as BB > ashed SBE > RHA. Use of a blend of RHA, BB

and SBE was found to have lower pozzolanic activity than blended calcined mix of RH, BB and SBE (Muthengia, 2003). The optimum mix of these pozzolanic materials, have not been investigated for their effective use as alternative artificial pozzolana to make pozzolanic cement.

Establishment of local production industries, availability of cheap, local raw materials and products are among the factors that would help achieve Kenya vision 2030. RH, SBE, BB and ALS are potential locally available raw materials. Establishment of small-scale pozzolana based cement plants where these raw materials are available or easily accessible would avail affordable cementitious material. This would also create employment opportunities at reasonably low per capital input.

Replacing of OPC with calcined raw mix of BB, SBE and RH in blend with ALS, has successfully met the required standards up to 45 %. Replacement of 46 % and above failed to meet the required standards. Blending of OPC with this percentage or higher of this blended pozzolana would help lower the cost of PPC. This would also help in effective utilization of these wastes by economically disposing them off (Muthengia, 2003). Agricultural wastes have been utilized as pozzolanic materials in other developing countries. RH, rice straw ash, peanut shell ash and sugarcane straw ash have been investigated for use as pozzolana in Cambodia using labor based technology (Gleeson, 2002). Research is therefore necessary to establish the optimum way and practicability of producing pozzolana from RH, BB, SBE and ALS for making pozzolana on a small scale.

CHAPTER TWO

LITERATURE REVIEW

2.1 CEMENT

Cement is any material capable of developing adhesive and cohesive properties that help to bind together mineral fragments to produce compact mass (Toxell, *et al.*, 1968). In building and concrete engineering, it denotes substances that can be used to bind together sand and other forms of coarse or fine aggregates into a solid mass (Czernin, 1980). The term is confined mostly to inorganic binders.

There are basically two types of cements namely hydraulic and non-hydraulic. The most commonly used cements today are hydraulic, Portland cement being the most popular. Portland cement consists principally of four compounds namely tricalcium-silicate (C_3S), beta-dicalcium silicate ($\beta-C_2S$), tricalcium aluminate (C_3A) and a phase approximating to tetracalcium aluminate ferrite (C_4AF) (Blanks and Kennedy, 1983). These compounds are formed by a series of reactions at temperatures ranging from 1300 °C to 1500 °C, between lime on one hand and silica, alumina and iron oxide on the other (Murdock, *et al.*, 1991). The basic raw materials for manufacture of Portland cement are usually calcareous and argillaceous materials. Calcareous materials, for example, chalk and marl provide calcium carbonate while argillaceous materials, for example, clay or shale, provide alumina and silica (Toxell *et al.*, 1968).

The three main types of cement produced are Ordinary Portland, Rapid Hardening and Moderate-Heat. Rapid-Hardening Cement is used in precast concrete, pipes and tiles. It is finely ground so that it hydrates more quickly. It has more gypsum than other cements

(American Concrete Pipe Association, 1988). Moderate-Heat Cement is used for the construction of hydro-electric dams. This is because heat of hydration by Ordinary Portland Cement is quite high. The heat results in expansion and cracking. In addition a few cements are manufactured for special use. An example is Sulphate Resisting Cement which is used in environments rich in sulphates (Lea, 1970).

2.1.1 PORTLAND CEMENT MANUFACTURE

Portland cement is made by heating raw materials rich in oxides of silicon, calcium, aluminium and iron to temperatures of around 1200 °C - 1450 °C. The chemical reactions occurring within the partially molten mass during heating result in the formation of the four main cement materials. Table 2.1 gives the approximate limits of the major mineral constituents of Portland cement (Bogue, 1955). Raw materials composition used for manufacture of cement is strictly controlled within certain limits. Control is done chemical constituents analysis (Kulkarni *et al.*, 1983). Mixing and grinding of the raw materials can be done either in wet or in a dry condition hence wet or dry processes for cement manufacture (Kulkarni *et al.*, 1983).

Table 2.1: Major Mineral Constituents of Portland cement

Compound	Abbreviation	Chemical formula	Typical concentration (%)
Tri-calcium silicate	C ₃ S	3CaO.SiO ₂	60-70
Di-calcium silicate	C ₂ S	2CaO.SiO ₂	10-20
Tri-calcium aluminate	C ₃ A	3CaO.Al ₂ O ₃	5-10
Tetra-calcium aluminoferrite	C ₄ AF	4CaO.Al ₂ O ₃ .Fe ₂ O ₃	3-8

The Wet process involves raw materials being crushed and ground to form slurry in wash mills (Lea, 1970). The slurry mix is fed into a storage tank. The slurry has water content of between 30 – 50 percent and only a small fraction of the material, less than 2 percent is larger than 90 μm . The slurry is then fed from the upper end of the rotary kiln. As the slurry moves down the kiln, it encounters progressively higher temperatures (Czernin, 1980). This process has been abandoned by many Cement manufacturing companies, since it uses a lot of energy in drying the slurry.

In the dry process raw materials are fed in correct proportions into a grinding mill, where they are crushed and reduced in size until more than 85 percent of the material is less than 90 μm (Neville, 1987). The dry powder, called raw meal, is then pumped into a blending silo. At this stage, final adjustment is made to the proportioning of the materials required for the manufacture of cement. Upward movement induced by compressed air usually does blending in the silos. The raw meal, usually with a moisture content of about 0.2 %, is passed through a pre-heater, where the particles are suspended in the rising gases from the kiln (The Cement and Concrete Association, 1989).

2.1.2 PORTLAND CEMENT PHASES MANUFACTURE

The main phases with significant cementitious properties in Portland cement with respect to strength are C_3S phase and/or with little β - C_2S . C_4AF and C_3A are of little significance in this respect as illustrated in figure 2.1 (Blanks and Kennedy, 1983). An ideal Portland cement would thus contain only C_3S phase and/or with little β - C_2S phase. Energy demand for production of only C_3S and β - C_2S phases is however very high and hence the process is industrially uneconomical. Fe_2O_3 and Al_2O_3 , which lead to formation of C_4AF and C_3A , provide a liquid phase in which C_3S and β - C_2S are formed at a lower energy demand. Compressive strength of cement is chiefly contributed by C_3S and β - C_2S as illustrated in figure 2.1 (Blanks and Kennedy, 1983).

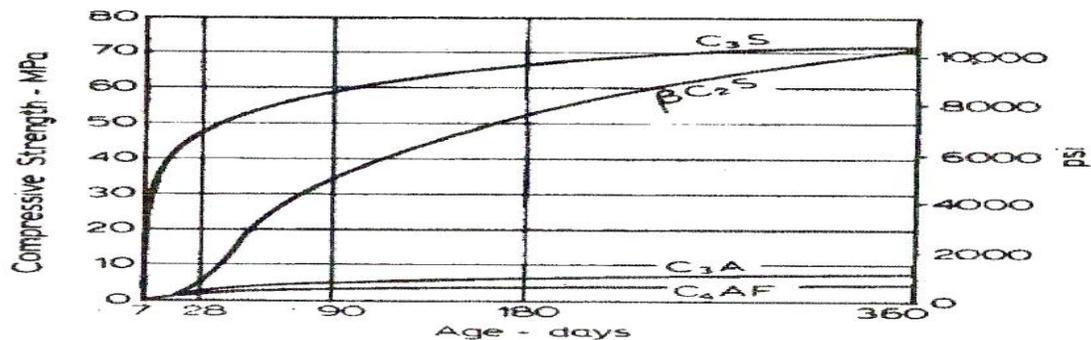
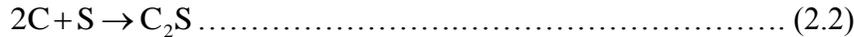


Figure 2.1 compressive strength of the various component phases of Portland cement

The formation of C_3S occurs when CaO and SiO_2 react. When 74 % of CaO is mixed with 26 % of SiO_2 and heated between 1250 °C-2100 °C, C_3S is formed as shown in equation 2.1 (Glassers, 1983).



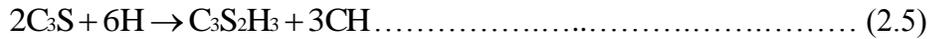
Above 2100 °C, C₃S melts and decomposes to give β-C₂S and C. Thus β-C₂S is exclusively and rapidly formed by reacting 65 % of CaO and 35 % of SiO₂ at 2130 °C (Blanks, 1983). The other phases of Portland cement are formed according to equations 2.2, 2.3 and 2.4 (Glassers, 1983).



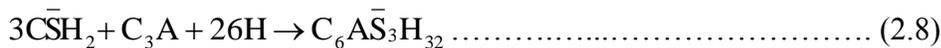
2.1.3 HYDRATION OF PORTLAND CEMENT

When cement comes into contact with water its strength starts to develop, heat is also liberated. This is referred to as the hydration of cement and the heat produced is called heat of hydration. The process involves reaction between water and the main phases of cement to form hydrated compounds that build up the composite mortar (Odler and Dorr, 1979). This results in hardening of cement. The products of cement hydration have been studied by taking them to be chemically the same as the products of hydration of individual compounds under similar conditions. Minimal chances exist that the product of the reaction may influence one another or themselves may interact with other compounds in the system (Bogue, 1955).

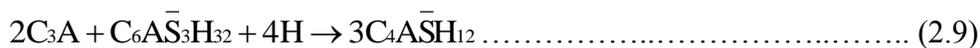
When calcium silicates hydrate under limited amount of water as in the case of cement paste, they undergo hydrolysis to produce calcium silicate hydrate (C₃S₂H₃) and calcium hydroxide (CH). The products of hydration of C₃S and β-C₂S are considered to be the same from consideration of their heat of hydration and surface area of the products of hydration (Odler and Dorr, 1979). Hydration of C₃S, C₂S and C₃A is represented in equations 2.5-2.7 (Czernin, 1962; Taylor, 1997).



The hydration product of C_3A is a prismatic dark interstitial material (Negro, 1979). This reaction represented by equation 2.7, is exothermic. It leads to an immediate stiffening of the cement paste. This is commonly referred to as flash set. Gypsum, ($\bar{C}\bar{S}\bar{H}_2$) or anhydrous calcium sulphate is added to cement to slow down this reaction. Gypsum reacts with C_3A to form a crystalline impermeable layer called ettringite ($C_6\bar{A}\bar{S}_3\bar{H}_{32}$) on unhydrated C_3A , which temporarily prevents further hydration of C_3A for about 1-2 hours (Sersare, 1980). The reaction is represented in equation 2.8.



Crystallization of ettringite builds pressure, due to expansion, causing the layer to crack. The crack opens up exposing more C_3A for further hydration and reaction with more gypsum. The crystallization and cracking process continues until no more gypsum is available or is inaccessible. This is after about 24 hours when substantial degree of hardening of the cement paste has occurred. The C_3A that remains may react with the ettringite and calcium hydroxide as represented in equations 2.9 and 2.10 (Rasheeduzzafar, 1990).



The hydration products of C_3A are of no binding significance. It may also be attacked by sulphates leading to formation of ettringite. This ettringite formed after cement has hardened is expansive and may cause cracking of mortar or concrete (Beaudoin and Ramachandyan, 1992).

C_4AF hydration reaction is much slower than that of C_3A . Its reaction proceeds as represented in equation 2.8 (Taylor, 1997).



2.2 POZZOLONAS

According to ASTM Standard C 618, a pozzolanas is defined as a siliceous and/or aluminous material which in itself possess little or no cementitious value but which will, in finely divided form and in presence of moisture, react chemically with calcium hydroxide at ordinary temperature to form compounds possessing cementitious properties (Ropke, 1982). Within the building industry, the term pozzolana covers all materials which react with lime and water to give calcium silicate hydrate and calcium aluminate hydrate. According to this Standard, the requirements for the chemical composition of natural pozzolana are approximately 70 % by content in silicon dioxide (SiO_2), aluminium oxide (Al_2O_3) and iron oxide (Fe_2O_3). The loss on ignition should not exceed 10 % by weight. The acidic and amphoteric oxides (silica, alumina and ferric oxide) content vary widely from one pozzolana to another (Bensted and Barnes, 2002).

Pozzolanas are classified into two classes: natural and artificial. Artificial pozzolanas are those materials in which the pozzolanic property is not well developed and usually have to undergo pyro-processing before they become pozzolanic. Examples of such material are fly ash, burnt clay, spent oil clays, calcined bauxite waste and suitably burnt fibrous agricultural residues such as rice husk ash (Hammond, 1983). Fly ash, collected from the flue gases of thermal plants and boilers that use powdered coal as fuel, is the most widely used artificial pozzolana in the world (Lea, 1970 and Chopra *et al.*, 1981).

Natural pozzolanas are formed from volcanic ash and dust. These ashes result from explosive eruptive volcanoes and are forced to solidify as a pyroclastic glass (glass fragments formed by rapid quenching of magma produced by volcanic explosions) (Malquori, 1960). Examples of natural pozzolana include volcanic tuff, diatomaceous earth and bauxite (Muller, 2005). On account of the high surface area, resulting from the forced expulsion of gases due to rapid quenching of magma, natural pozzolanas can be used in their natural state without further processing and are highly reactive towards lime (Malquori, 1964; Lea 1970.).

Research has been done on various artificial pozzolanas such as RHA, BB, SBE and burnt clay in Kenya (Waswa-Sabuni *et al.*, 2002; Muthengia, 2003). Waswa-sabuni (2002) showed that the engineering properties of the cement resulting from a mixture of OPC plus RHA and lime plus RHA were satisfactory with addition of up to 50 % RHA. The RHA improved greatly the compressive strength of lime. The cost of producing RHA was considered in pricing the resulting binder and it showed that the use of RHA to supplement OPC and lime reduced the overall cost of the binder. Muthengia (2003) investigated the pozzolanicity of RHA, BB and SBE. The results showed that BB was more reactive than RHA and SBE in that order. However the pozzolanicity of a combined raw calcined blend of RH, BB and SBE showed superior reaction than the blended mix of RHA, BB and SBE

2.2.1 POZZOLANIC ACTIVITY

Pozzolanic activity is the reaction between pozzolana, hydrated lime and water to form compact materials of cementious properties at ordinary temperatures. The activity of pozzolana, which is essentially determined by the reactive silica content, is also closely controlled by its specific surface area, chemical and mineralogical composition (Massazza,

1993; Tereibasoglu, 1995; Rodriguez *et al.*, 2002.). Reactive silica is readily dissolved in the matrix as $\text{Ca}(\text{OH})_2$ becomes available during the hydration process. These pozzolanic reactions lead to the formation of additional cementitious calcium silicate hydrates (Antiohos and Tsimas, 2005).

Pozzolanas with a high content of Silica and alumina but a low content of MgO and SO_3 generally exhibit a high pozzolanic activity (Treibasoglu, 1995; Erdogdu *et al.*, 1999). However, every pozzolana with a strong acidic character does not show pozzolanic activity (Rodriguez *et al.*, 2002), and hence the assessment of pozzolanic activity of a given natural pozzolana is a prerequisite for its use in the cement industry.

In the pozzolanic reaction, pozzolanic particles are protonically attacked by water in the highly alkaline lime solution. This dissociates the Si-OH group on the surface of the particles to silicate (SiO_4^{4-}) and hydroxonium (H_3O^+) ions. As a result, the surface of the particle is left negatively charged and therefore absorbs Ca^{2+} from $\text{Ca}(\text{OH})_2$. This initiates the dissolution of alkalis in the pozzolana in liquid phase. Further, the Ca^{2+} at the particle surface react with silica and alumina to form a film or a layer which thickens with time. The general pozzolana-lime reaction is given by equation 2.12 (Takemoto and Uchikawa, 1980).



Pozzolanic activity is influenced by many factors. These include the fineness of the pozzolana, the presence of accelerating additives, temperature as well as optimum pozzolana-lime ratio (Cook, 1986). Admixtures and thermal treatment of pozzolanas also influence the reactivity. Long-term strength development is influenced by the amorphous structure of the pozzolana and high silica-alumina content with fineness contributing to short-term reactivity (Glassers, 1983).

Temperature accelerates the hydrated lime-pozzolana reaction just like other chemical reactions. Luke and Glasser (1988) observed that, the reactivity of British fly ash with hydrated lime at 25 °C in two years, was about equivalent to that obtained in 3 months at 40 °C or about one month at 55 °C. The amount of lime available for the reaction also influences the pozzolanic reaction. This has been found to affect the strength development of the pozzolana-lime cements (Costa and Massazza, 1981). For an optimum reaction, many researchers have reported a ratio of between 2:1 and 3:1 pozzolana-lime ratio (Colleparidi *et al.*, 2004).

An assessment of pozzolanic activity is done before a material is used for making pozzolanic cement. The quality of pozzolana is assessed through chemical and/or physical means. The analyses are done on the sample which has been ground to a given fineness level. The ASTM C 593-76a (Annual Book of ASTM Standards, 1991) requires that the maximum percentage retention in a 45 µm sieve to lie between 12 and 34 percent, when wet sieved. This is because fineness affects both pozzolanic activity and Water-Cement (W/C) ratio demand. Increase in particle fineness increases the rate of the pozzolanic reaction of the cement (Dhir *et al.*, 1986, Cavdar and Yetgin, 2007).

Another method used for assessment of pozzolanic activity is the determination of the compressive strength of the pozzolana incorporated with lime (Annual book of ASTM Standards, 1991). Compressive strength of pozzolana-hydrated lime cement involves compacting a mixture of standard graded sand, pozzolana, hydrated lime and water in certain proportions to obtain a paste of normal consistency and workability. The paste is then molded into cubes. The moulded cement cubes are cured in a highly humid ventilated thermostatic incubator at 54 ± 2 °C for a period of 7 days. They are then cured for an additional 21 days in a

highly humid curing room at 23 ± 2 °C. Active pozzolanas will develop better than 4.1 Mpa at the 7th and/or 28th day of curing (Annual Book of ASTM Standards, 1991). This is the ultimate method of assessing pozzolanic activity as it gives the actual strength of the pozzolana-hydrated lime cements.

Chemical means employ a Pozzolanicity test (International Standard for Organization, 1990) which compares the quantity of calcium hydroxide produced by hydration of neat cement (saturated medium) and pozzolanic cement in a solution with a water cement ratio (W/C) of 5.0. If the concentration of calcium hydroxide in the solution is lower than that of the saturated medium, the cement satisfies the test for pozzolanicity. The underlying principle is that the pozzolanic activity fixes calcium hydroxide through the pozzolana-lime reaction, so that the lower the resulting quantity of calcium hydroxide, the higher the pozzolanicity. International standard for organization (ISO) 863 1990 (E) standard pozzolanicity curve, as given in figure 2.2 is used to represent the position of cement under test in terms of its CaO and OH⁻ concentration. It involves taking the concentration of CaO and OH⁻ of hydrated cement paste after a period of eight and /or fifteen days as coordinates of the figure 2.3 (International Standard for Organization,1990). If the coordinates representing the cement lie below the solubility curve in the figure, the cement is considered pozzolanic, otherwise it fails the test. The lower the point representing the cement below the solubility line, the higher the reactivity of the pozzolana.

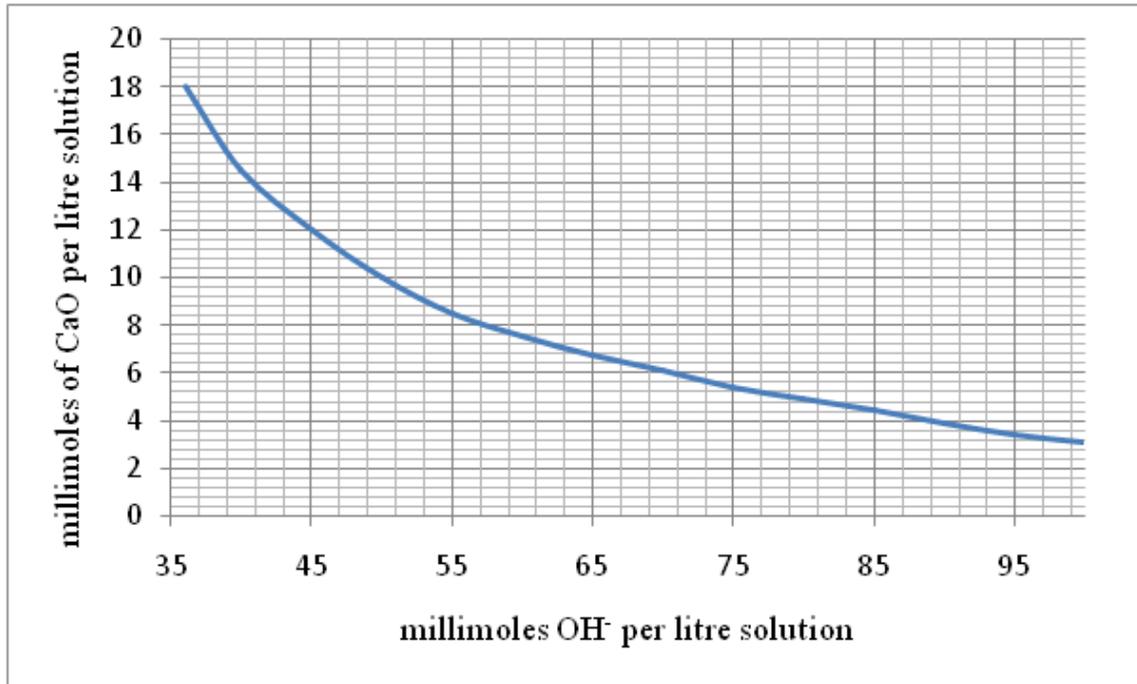


Figure 2.2: Pozzolanicity Test diagram

Another way of evaluating the pozzolanic reaction involves the determination of the drop in electrical conductivity caused by a pozzolana to a saturated solution of calcium hydroxide (Luxan *et al.*, 1989). This is a rapid method. The drop is caused by the reduction of the dissolved calcium hydroxide upon reaction with the amorphous silica in the pozzolana according to equation 2.9. The test involves an initial measurement of the conductivity of a saturated calcium hydroxide (200 ml at 40 °C). To this solution, 5 g of the pozzolana under test is added and the solution stirred continuously for two minutes using a magnetic stirrer. Electrical conductivity of the resulting solution is measured. The difference between the initial and final conductivities is calculated as a measure of the pozzolanic activity (Goni *et al.*, 2003).

Chemical composition analysis is also used in determining the pozzolanic activity of a material. According to the ASTM C 618 Standard (1994), a material would be considered

pozzolanic if it has a content of SiO_2 , Al_2O_3 and Fe_2O_3 in excess of 70 %. These are considered as the major oxide content of pozzolana. They avail the required glassy content to react with added lime, and excess lime in case the pozzolana is blended with OPC. This reaction takes place in the presence of water at room temperature to produce the cementing materials (Cook, 1983; Igor *et al.*, 2010).

2.3 LIME-POZZOLANA CEMENT

Lime-pozzolana cements (LPC) are produced by blending pozzolana with lime. Lime-pozzolana cements have been used by numerous ancient civilizations of builders, and are now gaining popularity as environmental sustainable alternatives to Portland cement for masonry and concrete applications (Walker and Pavia, 2010). Their strength develops relatively slowly compared to Portland cement but their ultimate strength can be very high (Swamy, 1983). The hydration products of lime-pozzolana cements are similar to those found in hydraulic lime mortars and cements (Massazza, 2002), although their formation is considerably slower than cement pastes. Lime with hydraulic properties has faster setting times, higher mechanical strength and lower permeability and flexibility along with improved resistance to salt, frost and moisture damage (Pavia and Regan, 2010).

The quality of the lime used to make LPC is as important as the quality of the pozzolana. ASTM C 141 (1989) requires a hydraulic lime to have between 65 % and 75 % $\text{CaO} + \text{MgO}$, 16 % to 26 % SiO_2 , a maximum of 12 % Fe_2O_3 , and a minimum of 8 % CO_2 . Compressive strength of lime-Pozzolana cement is low. Recommended compressive strength for a 7th and/or 28th day of curing is 4.1 MPa (ASTM 593 C, 1991).

2.4 PORTLAND POZZOLANA CEMENT

Portland pozzolana cement (PPC) is produced by grinding together Portland cement clinker and pozzolana with addition of gypsum or calcium sulphate. It can also be produced by uniformly blending Portland cement and fine Pozzolana (KEBS, 2001). PPC produces less heat of hydration and offers greater resistance to attack by aggressive media than OPC (Blanks and Kennedy, 1983). In the manufacture of PPC, the Kenya standard recommends a maximum of 35 % pozzolana material added to the clinker (KEBS, 2001). With this percentage, the available silica and alumina react with the lime produced during hydration of cement to produce additional cementitious products.

The products formed on hydration of pozzolanic cement are generally the same as those from the hydration of OPC. However, some differences may involve the ratios of the various species as well as the morphology of the products. The compounds constituting the products are C-S-H, C-A-H, $C_6\bar{A}\bar{S}_3H_{32}$ and $Ca(OH)_2$ (Uchikawa *et al.*,1986). Addition of the pozzolana accelerates the hydration of C_3S , β - C_2S , C_3A and therefore the cement as a whole. Acceleration of C_3S hydration is caused by increased dissolution of C_3S particles caused by adsorption of calcium ions to pozzolana in the liquid phase and an increase in the surface area of C_3S hydration. Accelerated hydration of β - C_2S is thought to be due to the same reason (Takemoto and Uchikawa, 1980).

In presence of pozzolana and water, the $Ca(OH)_2$ formed on hydration of Portland cement, react to form additional cementing material as opposed to OPC. The long-term strength of PPC is hence higher compared to that of OPC. PPC have a slow strength gain rate due to a low pozzolana-lime reaction hence require curing over a comparatively long period (The Concrete

Society, 1985). Compressive strength development of PPC as a function of time is shown in figure 2.3 (Neville and Brooks, 1987).

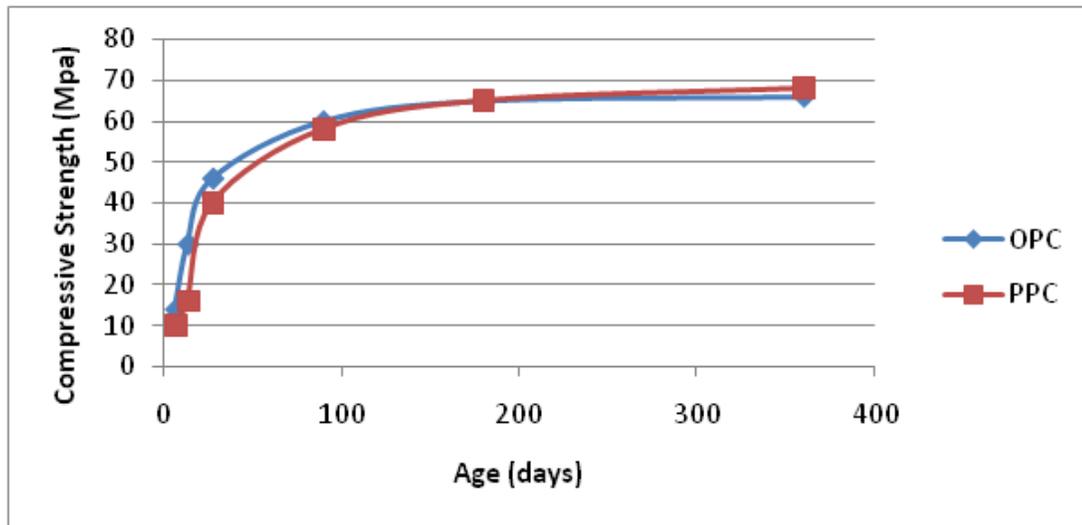


Figure 2.3: Relative rates of Strength development of OPC and PPC with fly ash pozzolana.

The early strength of PPC mortar is low from the figure 2.3. This is so because initially less cement is available to hydrate and form cement material. As it does so, it releases Ca(OH)_2 , which reacts with pozzolana to form additional cementitious material. Control concrete has more cement initially which hydrates to form cementitious material and Ca(OH)_2 . Since no pozzolana is available to react with the Ca(OH)_2 released, no additional cementitious material is formed. The control reaches its maximum hydration as the PPC mortar continues to hydrate for a period of about five years and hence the observed long-term increase in strength (Neville and Brooks, 1987).

2.5 ANALYTICAL TECHNIQUES

Chemical and physical analysis is carried out on both raw materials and finished products of cement. In this work chemical constituent analysis was done using various methods. These include atomic absorption spectroscopy (AAS), Flame photometry and gravimetric analysis.

2.5.1 ATOMIC ABSORPTION SPECTROSCOPY (AAS)

This is a spectral-analytical procedure for the quantitative determination of chemical elements employing the absorption of light by free atoms in the gaseous state (McCarthy, 2012). The technique is used for determining the concentration of a particular element in a sample. Elements absorb light at specific wavelengths characteristic to them. This absorption of light is associated with the transition of atoms from one steady state to another (Van Loon, 1980).

The quantity of interest in atomic absorption measurements is the amount of light at the resonant wavelength which is absorbed as the light passes through a cloud of atoms. As the number of atoms in the light path increases, the amount of light absorbed increases in a predictable way. By measuring the amount of light absorbed, a quantitative determination of the amount of analyte element present can be made. The use of special light sources and careful selection of wavelength allow the specific quantitative determination of individual elements in the presence of others (Richard and Kerber, 1993). To calculate the amount of light absorbed by a cloud of atoms, parallel beams of light at the resonance wavelength for the atoms concerned are considered when striking a cell containing atoms. If a light intensity I_0 is irradiated through a cell containing atomic species of an element, the intensity of the transmitted radiation, I , after absorption is given by the equation 2.13 (Skoog and Leavy, 1992).

$$I = I_0 \exp(-c\epsilon l) \dots\dots\dots (2.13)$$

Where I is the intensity of final transmittance I_0 is the intensity of initial transmittance, c is the concentration of the analyte, ϵ is the molar absorption coefficient, l is the path length

Taking logarithms on both sides of equation 2.13, yields equation 2.14.

$$\log (I_0/I) = c\epsilon l \dots\dots\dots (2.14)$$

By defining $\log (I_0/I) = A$, where A is the absorbance, then equation 2.14 can relate the absorbance to the concentration of the analyte as shown in equation 2.15.

$$A = c\epsilon l \dots\dots\dots (2.15)$$

Where, ϵ is the molar absorption coefficient of the sample (Welz and Sperling, 1999).

Basically, the method involves nebulisation of a sample into an atomizing chamber where it is volatilized, decomposed, atomized and absorption of the incidence radiation I_0 , occurs. The final stage then involves the measurement of the absorbance which is proportional to the concentration. This is done using equation 2.15.

2.5.2 FLAME PHOTOMETRY

Flame photometry is a branch of atomic spectroscopy in which the species examined in the spectrometer are in the form of atoms. This technique uses a flame that evaporates the solvent and also sublimates and atomizes the metal and then excites a valence electron to an upper energy state. Light is emitted at characteristic wavelengths for each metal as the electron returns to the ground state that makes qualitative determination possible (Skoog, 1992).

The intensity of emission is proportional to the concentration of the atoms on the sample. This is described by the Scheibe-Lomakin equation 2.16.

$$I = k.C^n \dots\dots\dots (2.16)$$

Where C, is the concentration of the element, k is constant of proportionality and n is

approximately equal to 1 at the linear part of the calibration curve. Therefore the intensity of emitted light is directly proportional to the concentration of the sample (McLennan and Kowalski, 1995).

2.5.3 COMPRESSIVE STRENGTH ANALYSIS

Compressive strength is the capacity of cement to withstand loads tending to break it (Groover, 2002). This is the ultimate test with which the strength of cements engineering property is determined. Measurement of compressive strength is affected by the specific test method and conditions of measurements.

In determination of compressive strength test, mortar cubes or prisms are compacted using a standard vibrating machine. These are made with specific standard sand in varying ratios depending on standard. In the European Norm (EN) standard, mortar prisms measuring $40 \times 40 \times 160$ mm are made (KEBS, 2001) are made. This is done by dry mixing 450g of the cement with 1350 of standard graded European Norm sand. Requisite amount of water is added and mixture compacted in a mechanical mixer for one minute. The compressive strength is determined after a period of curing for 1, 7 and 28 days at $20 \pm 1^\circ\text{C}$.

CHAPTER THREE

METHODOLOGY

3.1 REAGENTS

Analar grade reagents were used. Distilled water was used in all preparations of the reagents.

3.2 APPARATUS

Several apparatus were used in the preparation and analysis of test materials. Most apparatus were used as prescribed in the KS EAS 18 Part 1 (KEBS, 2001) and KS 02 1263 (KEBS, 1993). They were provided at the East African Portland Cement Company (E.A.P.C.C) laboratories. They included a mixer, vibration machine, compressive strength analysis machine, curing tank, moulds, and curing room. Chemical tests were performed at Kenyatta University Chemistry Laboratory and Mines and Geology laboratory at Industrial Area-Nairobi. A Fixed Bed Kiln (FBK) (Ochungo, 1993) was used for incineration of the test materials.

3.3 SAMPLING

The test materials were sampled from several places. SBE from BIDCO Oil Refineries in Thika-Kenya, RH from Mwea Rice Mills Limited in Mwea, BB from Clay Works Manufacturers Limited in Ruiru, ALS from Welding Alloys Limited (WAL) in Nairobi, OPC from East African Portland Cement Company (E.A.P.C.C) at Athi River. Each of the samples as received from the respective sources was thoroughly mixed before being subjected to treatment and/or analysis.

3.4 CHARACTERIZATION OF RAW SBE

3.4.1 CALORIFIC VALUE

This was done in accordance to European Norm (EN) 14213 standard (2003). A bomb calorimeter model CAB101.AB1.C was used. Reagents were prepared by taking requisite

amounts of barium hydroxide, sodium carbonate and concentrated hydrochloric acid then dissolving them in separately water to make 0.1 M solutions. 0.1 M HCl was standardized against dried sodium carbonate using methyl orange as indicator. Barium hydroxide and sodium carbonate solutions were standardized against the standardized hydrochloric acid using methyl orange as indicator.

Approximately 3.000 g of the sample was briquetted using a bomb briquette press embedding one end of a 90 mm firing cotton thread in it. The pellet was placed in the bomb crucible. The bomb cap was placed on its stand provided with the outfit. Firing nickel wire was stretched between the electrodes of the bomb. The un-embedded end of the firing cotton thread was tied to the stretched firing wire. The crucible was then placed into position. 1 ml of water was pipetted into the bomb and the bomb assembled. The assembled bomb was tested for circuit completeness by a firing the circuit test plug. The bomb was finally filled with 30 bars of oxygen. Water was then added into the calorimeter can until a weight of 3 kg was attained to submerge the bomb completely. The bomb was then placed on the three supports into the calorimeter vessel and checked for any leakage (confirmed by absence of bubbling). Re-adjustment of the calorimeter temperature was done by the use of the balance control knob. The cooling water was adjusted to flow at a rate of 300 ml per minute. The cover of the water jacket with thermometers and thermistors was lowered. Completeness of the circuit was re-confirmed. The temperature of the jacket and calorimeter vessel was allowed to stabilize. The initial temperature of the calorimeter was taken after stabilizing to 0.001° C and fire switch pressed for 2 seconds to ignite the sample. Satisfactory firing was confirmed by the failure of the test switch. The final temperature of the apparatus was taken after 10 minutes to 0.001 °C. A second reading was taken after sequential three minutes until the readings agreed within 0.002

°C.

After final temperature reading, a period of 30 minutes was allowed before releasing the pressure by a milled pressure release cap so that no acid mist was lost. The contents of the bomb were washed into borosilicate glass beaker using water. The interior of the bomb and the bomb cap were washed and their washings transferred into the beaker. The washings were diluted to 100 ml, filtered and boiled to expel carbon dioxide. The hot solution was titrated against the $\text{Ba}(\text{OH})_2$ solution using phenolphthalein indicator to determine total acidity. 20 ml of the 0.1 M sodium carbonate solution was added to the same solution, and then warmed, filtered and the precipitate washed with water. After cooling, the filtrate was titrated against the 0.1 M HCl solution using methyl orange as indicator. Calorific value was determined in the usual way and expressed in grams per joule.

3.4.2 OIL CONTENT OF SBE

Determination of oil content was done in accordance to the BS EN ISO 659 standard (1999). Soxhlet apparatus were used. 100 g of the SBE was packed in the Soxhlet thimble and fitted into the Soxhlet apparatus. Hexane was used for oil extraction by continued boiling for a period of four hours. Hexane was separated from the oil by use of rotor vapor apparatus. The oil free SBE and extracted oil were sundried to a constant weight. The extracted oil was expressed as a percentage of the original SBE weight. Verification of full oil extraction was done by re-extraction of the oil from the SBE to a constant weight. A total of three samples were done.

3.4.3 IGNITION AND SELF COMBUSTION TEMPERATURES

1.000 g of SBE in a silicon carbide crucible was slowly heated by use of a Bunsen burner flame until it ignited. Temperature measurement was done by use of two digital thermometers

number GTH 1160 fitted with heat sensors probe model RS Number 610-067. After ignition, temperature was then monitored to determine the maximum self-combustion temperature. The resulting product was preserved for determination of oil content after self-combustion.

3.4.4 OIL CONTENT AFTER SELF-COMBUSTION

The product from section 3.4.3 was weighed and heated at 1000 °C to a constant weight in a furnace model FSE-520-210P. The difference in weight before heating and after heating at 1000 °C was expressed as a percentage of the original weight of the sample. This was done to determine the amount of oil withheld after self-combustion.

3.4.5 ASH CONTENT

1.000 g of SBE was heated at temperature of 1000 °C in a pre-weighed platinum crucible in a furnace model FSE-520-210P. It was then cooled in a desiccator and weighed. The crucible and its content were reheated, cooled and weighed to a constant weight. The ash content was calculated using equation 3.1.

$$A = \frac{W_f}{W_o} \times 100 \dots\dots\dots (3.1)$$

Where, A is the ash content as a percent, W_o is original weight of sample; and W_f is weight of sample after heating.

3.5 INCINERATION OF THE POZZOLANA

RH and SBE as obtained from their respective sources were incinerated in the form they were sampled. Some of the BB was first crushed using a laboratory crusher, and then finely ground to pass through 90 µm sieve (KEBS, 2001), using a laboratory ball mill. Other broken bricks were not finely milled after crushing. It was used in the crushed form where some particles

were as large as 3 mm in diameter.

The RH, ground BB and SBE were then fed into the FBK (Ochung'o, 1993). This was done in accordance to Muthengia (2003) but with variation in the feed ratios. 5 kg of RH was spread on the floor of the FBK, followed by 2 kg of BB, then 5 kg of RH, then 4 kg of SBE and finally 10 kg of RH was spread over the whole mass. A little paraffin was put at the window of the kiln and the whole mass ignited. The window was closed. The temperature of the kiln was controlled below 700 °C through the action of opening and closing the ventilation windows. The temperature of the kiln was monitored using a thermocouple with a long probe. The resulting ash was collected after cooling for a period of 3 hours. It was then ground to pass through 90 µm sieve using a laboratory ball mill and taken for other tests.

The procedure above was repeated for making other samples but in each successive arrangement more BB was added. These gave test ashes with the ratios of RH: BB: SBE of 20: 0: 4, 20:1:4, 20:2:4, 20:4:4, 20:6:4. These were labeled as sample 1, 1.5, 2, 3 and 4 respectively. The procedure was repeated but this time using 2 and 4 kg of BB. The BB in these two samples had particles as of about 3 mm in diameter. The resulting ashes were labeled sample 5 and 6 respectively. The resulting labeled ashes were preserved in airtight plastic containers for further tests. A test sample in which all the pozzolanas were mixed with no specific order was followed was fed into the FBK for incineration.

3.6 CHEMICAL CONSTITUENT ANALYSIS OF POZZOLANA SAMPLES

3.6.1 ATOMIC ABSORPTION SPECTROSCOPY ANALYSIS

1.0 g of ground sample was placed in a 50 ml plastic bottle. 2 ml of 1: 1 concentrated HCl and HNO₃ were added and the bottle stoppered loosely and left to stand overnight. 3 ml of HF was added and the bottle immediately stoppered to avoid loss of silicon and the sample left to stand for six hours. Heating was then done in a water bath to facilitate the dissolution of the sample. 50 ml of boric acid was then added and the solution left to stand for one hour. 46 ml of distilled water was then added. Samples containing 1 part per million concentrations of the elements under test were also prepared in the same manner as the sample and used as standards during the analysis. For the standards, dilutions of two, four and eight were made. The samples were then analyzed using the atomic absorption spectrometer.

3.6.2 GRAVIMETRIC ANALYSIS AND FLAME PHOTOMETRY

This was done on accordance to the British Standard procedure (British Standard, 1970). 100 g of the pozzolana sample was ground to pass through 150 µm sieve and transferred to a clean dry 200 ml bottle with an airtight closure. The sample was thoroughly mixed by tumbling, rolling and shaking for at least 2 minutes. The resultant sample was used for analysis of sulphates, sodium oxide and potassium oxide.

3.6.2.1 SULPHATE CONTENT AS SO₃

25 ml of cold water were added to 1.000 g of sample in 250 ml beaker. 5 ml of hydrochloric acid was added to the mixture while continuously stirring. The resultant solution was heated to sample decomposition. The solution was then diluted to 150 ml and heated to between 90 and 100 °C for 15 minutes. It was then filtered on Whatman filter paper number 40. The residue

was washed with hot water. The filtrate was diluted to 250 ml and boiled. 10 ml of BaCl₂ solution (100 g/l) was added from a pipette. The solution was boiled for 15 minutes and allowed to stand for about 30 minutes at between 90 and 100 °C. It was left to cool for 2 hours, ensuring the volume of solution remained at between 225 ml and 260 ml. The volume was maintained by addition of water when necessary. The precipitate was filtered on a Whatman filter paper number 42 and washed free of chlorides. The filter paper and its content was placed in a weighed platinum crucible, smoked off and ignited at 900 °C for 15 minutes. It was then cooled and weighed. Verification of the constant weight obtained was done by a subsequent ignition after 5 minutes of cooling to a constant weight. The SO₃ content was obtained by equation 3.2.

$$\text{SO}_3 \text{ \% content} = W \times 34.8 \dots\dots\dots (3.2)$$

Where W is weight of BaSO₄ in grams.

3.6.2.2 SODIUM OXIDE (Na₂O) AND POTASSIUM OXIDE (K₂O)

1.0 M mixed stock solution of NaCl and KCl was prepared by dissolving requisite amounts of NaCl and KCl in 50 % solutions of HCl and H₃PO₄ and diluting the mixture to one litre with water. Different amounts of the stock solution were mixed with 50 % H₃PO₄ and diluted to 100 ml with water. These made the photometric standards of 1000 parts per million for making calibration curve.

1.0g of sample was weighed in a platinum dish. 5 ml of water, 40 drops of 12 M perchloric acid and 10 ml of 12 M hydrofluoric acid were consecutively added. The mixture was evaporated in a sand bath until the residue remained just moist. The residue was dissolved in 40 ml of water and 20 ml of 50 % HCl. The resulting solution was transferred to 100 ml beaker. The solution

was boiled and filtered into a 200 ml volumetric flask. Hot water was used for diluting to a final volume of about 150 ml. 20 ml of 50 % H_3PO_4 was added and made up to the mark. Requisite amounts of this solution were mixed with 50 % HCl and 50 % H_3PO_4 and diluted to 100 ml with water. This made the sample solution for flame photometric measurement. The standard photometric solutions and sample solution were then analyzed using a flame photometer in the usual way.

3.6.2.3 LOSS ON IGNITION (LOI)

1.0 g of pozzolanic sample in a pre-weighed porcelain crucible was heated at 1000 °C to a constant mass in a furnace model FSE-520-210P. The difference in mass between the original mass of the sample and the final mass was expressed as a percentage of the original mass to obtain loss on ignition (LOI).

3.7 POZZOLANICITY TESTS

3.7.1 CHANGE IN ELECTRICAL CONDUCTIVITY OF SATURATED $\text{Ca}(\text{OH})_2$ SOLUTION

This was done in accordance to Luxan *et al.*, (1989) and Bui (2001). 200 ml of distilled water was placed in a glass beaker on a hot magnet plate and heated to 40 ± 1 °C. A magnetic stirrer was placed into the water. Calcium hydroxide powder was added to the distilled water to make a saturated solution. Electrical conductivity of this solution was determined using a conductivity meter. 5.0 g of the pozzolana sample was added to the saturated solution maintained at 40 ± 1 °C. The contents of the beaker were continuously stirred for two minutes. The electrical conductivity of the resulting solution was then measured. The difference between the conductivity of the saturated solution of calcium hydroxide and the pozzolana solution was calculated as a measure of the pozzolanic activity of the sample. This

procedure was done in triplicate for each of the pozzolana samples and the average recorded.

3.7.2 POZZOLANICITY BY USE OF THE STANDARD POZZOLANICITY CURVE

This was done in accordance with the International Standard for Organizations (ISO) (1990).

The pozzolana samples were blended with OPC in the ratio of 2:3 by weight. This was done by mixing the blend thoroughly in a laboratory ball mill for one hour to make the resulting PPC.

100 ml of freshly boiled water was pipetted into a 250 ml plastic container. The container was sealed and placed in the thermostatic enclosure at 40 ± 2 °C until equilibrium was reached (about 1 hour). The container was removed from the thermostatic enclosure. 20.00 g of the blended cement under the test was added to the water in the plastic container and shaken vigorously for 20 seconds to avoid formation of lumps. A horizontal rotary motion was used which prevented any part of the sample or liquid from being thrown up and remaining separated from the rest of the solution. The container was placed immediately into the thermostatic enclosure to avoid any appreciable decrease in temperature. After a period of 8 and/ or 15 days in the thermostatic enclosure, the container was removed from the thermostatic enclosure. The solution was then filtered immediately under vacuum through the butchner funnel into the vacuum flask using a dry Whatman filter paper number 41. The flask was sealed immediately to avoid any appreciable carbonation by atmospheric carbon dioxide and allowed to cool to room temperature.

3.7.2.1 DETERMINATION OF HYDROXYL ION CONCENTRATION

The vacuum flask was shaken to homogenize the filtrate. 50 ml of the filtrate were pipetted into a 250 ml conical flask. Five drops of methyl orange indicator were added. The resulting

solution was titrated against the 0.1M HCl to determine total alkalinity. The hydroxyl concentration in millimoles per liter was calculated according to equation 3.3.

$$[\text{OH}^-] = \frac{1000 \times 0.1 \times V}{50} \dots\dots\dots (3.3)$$

Where, V the volume of the 0.1 M HCl solution used for the titration.

3.7.2.2 DETERMINATION OF CALCIUM OXIDE CONCENTRATION

To the solution that remained after completing [OH⁻] determination, 5 ml of the sodium hydroxide solution and 50 mg of the murexide indicator were added. The resulting solution was titrated against 0.025M EDTA solution by means of burette until the color changed from purple to Violet. Before and during titration, the pH value of the solution was always confirmed to be 13 by means of a pH meter. If the pH deviated from this, it was adjusted by addition of a requisite amount of the sodium hydroxide solution. To facilitate this, the EDTA was slowly added. Calcium oxide concentration, [CaO], in millimoles per liter was calculated using equation 3.3.

$$[\text{CaO}] = \frac{1000 \times 0.025 \times V}{25} \dots\dots\dots (3.4)$$

Where V , is the volume of the 0.025M EDTA solution used for the titration.

3.8 COMPRESSIVE STRENGTH ANALYSIS

Compressive strength analysis of Pozzolana-ALS-OPC cement was determined in accordance with the EN 196-1 (KEBS, 2001). In this case, 40×40×160mm mortar prisms were used. The ASTM 593 part C (ASTM, 1991) was adopted for analysis of compressive strength for the Pozzolana-ALS cements. However this was done with slight modifications. 70.7 mm mortar cubes were used instead of the 50 mm mortar cubes prescribed in the standard due to their

availability.

3.8.1 COMPRESSIVE STRENGTH EVALUATION OF POZZOLANA- ALS CEMENT

Each of the test pozzolana material was inter-ground with ALS in a 2:1 pozzolana: ALS ratios using a laboratory ball mill. 174 g of pozzolana cements and 122 ml of water were taken and put in the bowl of the mechanical mixer. The machine was set to run at low speed (140 r.p.m). After 30 seconds, 476 g of standard graded sand (ASTM, 1991), was slowly added into the bowl for the next 30 seconds. The machine was set to run at high speed (285 r.p.m) for the next 30 seconds and stopped at 90 seconds. For the first 15 seconds of the stoppage, the mortar on the surface of the bowl was scrapped off with a plastic scoop and the whole mortar scrapped to one side of the bowl. The mixer was then started at high speed for a further 60 seconds which stopped automatically. The mortar was then transferred into the hopper of the mould and immediately compacted for 120 seconds by a vibrating machine model 7115/A31648 capacity 2000 kN. The mortar that was on the surface of the mould as a result of striking off the mortar during compacting was wiped off. The mould was then covered with 100 x 100 mm plate glass sheet. The above process was done in sextuplet.

The cubes were transferred to a closed vapor above water at 54 ± 2 °C for a period of 7 days, after which they were removed from the oven and cooled to 23 ± 2 °C. The cubes were de-moulded by unscrewing the mould screws. The cubes were weighed and marked with crayon. Three cubes were analyzed for compressive strength using the compressive strength machine. The remaining cubes were transferred to the curing tank and submerged at least 5 mm below water for additional 21 days at 20 ± 2 °C. The cubes were then removed from water and allowed to drain in a non-absorbent surface. They were then tested for compressive strength

using the compressive strength machine within one hour of removal from water. Compressive strength was calculated using equation 3.5.

$$C_c = \frac{F}{A} \dots\dots\dots (3.5)$$

Where C_c , is the compressive strength in kN/mm^2 , F is the maximum applied force for failure in kilo Newtons (kN) and A , is the cross section area of the specimen The compressive strengths were later converted from kN/mm^2 to Mega Pascals (Mpa) by multiplying with 10^3 .

3.8.2 COMPRESSIVE STRENGTH EVALUATION OF POZZOLANA-ALS-OPC CEMENT

This was determined in accordance with the EN 196-1 (KEBS, 2001). Mortar prisms were made by dry mixing 300g of the pozzolana sample with 150 g of ALS. This was a pozzolana-Lime ratio of 2:1. The Pozzolana-ALS cement made was used to replace OPC at percent weights of 45 %, 46%, 48%, 50% and 52%. This was achieved by mixing requisite amounts of pozzolana-ALS cement with OPC. 82 ml of water was added to the cement sample in the stainless steel bowl for the 45 % replacement. 85 % of water was used for other replacements. The mixer was started to run for 30 seconds after which 1350 g of standard graded European Norm (EN) sand was added. Mixing was continued for an additional 30 seconds. Manual mixing was done with a wooden stick after which the mixer was left to run for an additional minute. The mixture was then put into a grease lubricated $40 \times 40 \times 160$ mm three-pong mould. The mortar was compacted using standard jolting apparatus. The mortar and the mould were stored in a moist room of relative humidity greater than 90 percent and a temperature of 20 ± 2 ° C. A total of 9 prisms were prepared for each sample. After 24 hours, the mortar was de-moulded and three prisms were taken and broken into two halves each using the compressive

strength machine. Each half was tested for compressive strength using the compressive strength machine. The average compressive strength for the three prisms per sample was recorded. The rest of the prisms were de-moulded and transferred to the curing tank at 20 ± 2 ° C. These were cured for 28 days. Compressive strength evaluation for the other prisms was done on the 7th and 28th days.

3.9 DATA ANALYSIS

The data collected was analyzed in two main ways. It was primarily presented using graphical techniques by the scatter plots (Blair and Higgins, 1980) and cross tabulations which considered the standard deviation (Gunnick and David, 1997). The other way was by use of the t-test and analysis of variance (ANOVA). This was the general linear model .This was used in cases where three or more tests were done for statistical significance. A computer software program called statistical program for social sciences (SPSS), was applied in the case of the t-tests and ANOVA tests.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 INTRODUCTION

This chapter outlines the results obtained from this study. Characterization results of SBE are reported. The chemical constituents of SBE, BB and the various pozzolana samples constituting a calcined blend mix of RH, BB and SBE in various ratios have been reported. The corresponding pozzolanicity of the pozzolana samples are reported. These include; use of the Standard pozzolanicity curve, decrease in electrical conductivity of saturated Ca(OH)_2 , and chemical constituent analysis. The compressive strength of pozzolana-ALS and those in blend with OPC are also presented.

4.2 RAW SPENT BLEACHING EARTH (SBE)

SBE as obtained from Bidco Oil Refineries at Thika-Kenya was light grey in color, oily and finely pulverized. Characterization test results are given in the table 4.1.

Oil content of the SBE used in this study was slightly lower than those used in the study by Muthengia (2003). This may be attributed to the differences in the filtering processes of the different oil manufacturing industries. For this reason, most oil processing companies will prefer processes that would withhold as little oil as possible (Hayder *et al.*, 2011). In the oil manufacturing industry, the lower the oil content in the SBE the more the profit for the manufacturer as less oil is wasted in the filtering process. The amount of oil withheld content was comparable to other SBE studied elsewhere (Huang, 2010).

Table 4.1: Characterization of raw SBE

Property	Character
Calorific value	13.23 ± 0.0259 J/g
Oil content	29.52 ± 0.5022 wt %
Ignition temperature	235.0 ± 0.8165 °C
Maximum self-combustion temperature	438.0 ± 1.633 °C
Ash content	61.25 ± 0.0867 wt %

The oil present in SBE has led to research in best ways of recycling it. Such oil has been found to be of low quality, but can be used for biodiesel production (Park *et al.*, 2007). It has also been investigated as a possible component in making lubricating grease (Hayder *et al.*, 2011). However due to economic, ecological and/or logistical issues, these methods have not been widely used by the industry. Incineration of SBE remains the main disposal method (Shanks, 2007).

The high oil content and its spontaneous auto ignition is the main cause of fire hazards associated with handling of SBE especially when dumped in open sites (Pollard, 1990). Therefore SBE is classified as a hazardous waste, since the oil in the SBE contributes to its pollution aspect. Untreated SBE cannot be used as land fill material. This is due to its high organic content which exceeds the limit of waste acceptance criteria (WAC) for hazardous waste landfills under the EU land fill Directive (EA, 2006).

The calorific value of the Bidco Oil refineries SBE was also found to be lower than those obtained by Muthengia (2003). These calorific values can be attributed to the amount of oil content present in the SBE samples. In line with the high calorific value, SBE has been investigated as a source of energy in the activation of RH and BB in the production of combined pozzolanic materials (Muthengia, 2003). It has also been investigated as a possible source of making SBE fuel briquettes. Other options include using SBE as an alternative fuel in cement kilns or as a feedstock for the production of clay bricks (Srihartini *et al.*, 2007).

When heated with a Bunsen burner in a silicon crucible, the oil in the SBE started to volatilize at a temperature of 160 °C. The volatiles ignited at 235 °C to a pale yellow flame. The flame continued to burn on its own to a temperature of 438 °C. These self-ignition temperatures are important in the production of artificial pozzolana. Reactive silica in the pozzolana is formed in the temperature range of 550 °C to 700 °C (Chandaresekhar *et al.*, 2006). A maximum ignition temperature of 438 °C, would therefore not affect the pozzolanicity of the resulting pozzolanic material when the SBE is used to make pozzolana.

After complete combustion of the oil from the SBE, the ash content was quite high in comparison with what other authors have investigated (Srihartini, *et al.*, 2009; Muthengia, 2003). High ash content would be due to low amount of volatiles. It is also important in that it would increase the amount of pozzolana after incineration.

4.3 CHEMICAL CONSTITUENTS

The results of the chemical constituent analysis of the pozzolana samples are given in table 4.2. The results shown are those for AAS, gravimetric analysis and Flame Photometry was used. For sodium and potassium, Flame photometry was used, for LOI, gravimetric analysis was used. For all the others, AAS was used.

From table 4.2, the results show that all the pozzolana samples except SBE, had the sum of SiO_2 , Al_2O_3 and Fe_2O_3 above the Kenya Standard KS 02 1263 (KEBS, 1993) as well as the ASTM C 618 (1994). These oxides are considered as the major components of pozzolanas. A pozzolanic material must contain a minimum of 70 percent of the sum of the oxides of aluminium, silicon and iron (KEBS, 1993). This avails the required glassy content to react with added lime in the presence of water at room temperature to produce the cementing materials according to equation 4.1 and 4.2 respectively (Cook, 1983 and Igor *et al.*, 2010).

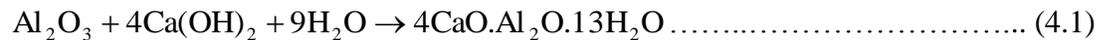


Table 4.2 Chemical Constituent of BB, SBE and the pozzolana samples

Oxide	% by weight							
	BB	SBE	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6
CaO	0.46	2.30	0.87	0.65	0.55	0.45	3.03	2.01
SiO ₂	64.84	66.60	74.3	80.5	81.20	82.50	76.90	75.92
Al ₂ O ₃	21.54	6.20	7.68	7.80	7.92	8.00	6.73	6.04
Fe ₂ O ₃	7.87	3.40	6.80	6.90	7.90	3.67	4.50	3.98
SO ₃	0.23	-	0.31	0.13	0.12	0.30	0.12	0.52
MgO	1.94	3.20	1.70	1.90	1.74	1.70	1.72	2.24
K ₂ O	3.62	1.90	1.99	1.59	1.70	2.20	1.80	3.20
Na ₂ O	1.47	2.80	1.44	0.45	0.55	0.54	0.55	0.55
LOI	0.88	14.00	3.99	2.99	4.01	4.70	4.20	5.54
SiO ₂ + Al ₂ O ₃ +Fe ₂ O ₃	94.07	71.6	88.78	91.00	89.82	88.27	88.33	85.94

In case the pozzolana is blended with OPC, the silica and alumina reacts with the lime liberated during hydration of cement. This results in the formation of more cementitious material. This is responsible for the development of long term strength in PPC. Reduction in lime from the OPC makes cement denser. This increases resistance to acid and sulphate attack (Mehta, 1977).

The alkali content (Na₂O) varied from 1.47 % in BB to 0.45 % in sample 6. These values are lower than the maximum alkali content of 1.5% required for pozzolana (KEBS, 2001). Higher levels of the alkalis may result to expansion of cured mortar through alkali aggregate reactions (Garcia and Fernandez, 2007). The alkali levels are responsible for the pore water in cured cement paste for maintaining a pH of above 12. This is important in passivating the rebar if

embedded and also availing the medium for cement hydration (Diamond, 1981).

The MgO levels of the pozzolana samples were below the maximum limits of 5 percent as per ASTM standard (ASTM C, 1991). For commercial cements the ISO standard recommends a maximum of 2.8 percent (ASTM C, 1991). The MgO is limited because of it being associated with destructive expansion of concrete. This is because in cured mortar and concrete, MgO forms expansive $Mg(OH)_2$ on reaction with water. This may further react with the silica in the pozzolana to form non cementitious magnesium silicate hydrates. This is shown by equations 4.3 and 4.4 (Mather, 1968).



The LOI of the samples increased with the increase in the amount of total clay available in the sample. This was due to increased compaction of BB and SBE. This might have caused reduction of air spaces for complete incineration of the RH and activation of the SBE (Muthengia, 2003). It was noted that LOI was highest with the samples that had crushed BB. However all the samples tested were within the limits of the standard of pozzolanas (KEBS, 2001). High LOI decreases pozzolanicity (Shihembetsa, 2002; Sensale, 2006.). LOI signifies the amount of carbon content in the samples. High carbon content in pozzolana may affect the workability of concrete (Payaa *et al.*, 2002).

4.3 POZZOLANICITY TESTS

4.3.1 CHANGE IN ELECTRICAL CONDUCTIVITY OF SATURATED $\text{Ca}(\text{OH})_2$ SOLUTION

The results of the change in electrical conductivity of the pozzolana samples in saturated calcium hydroxide are shown in the figure 4.1.

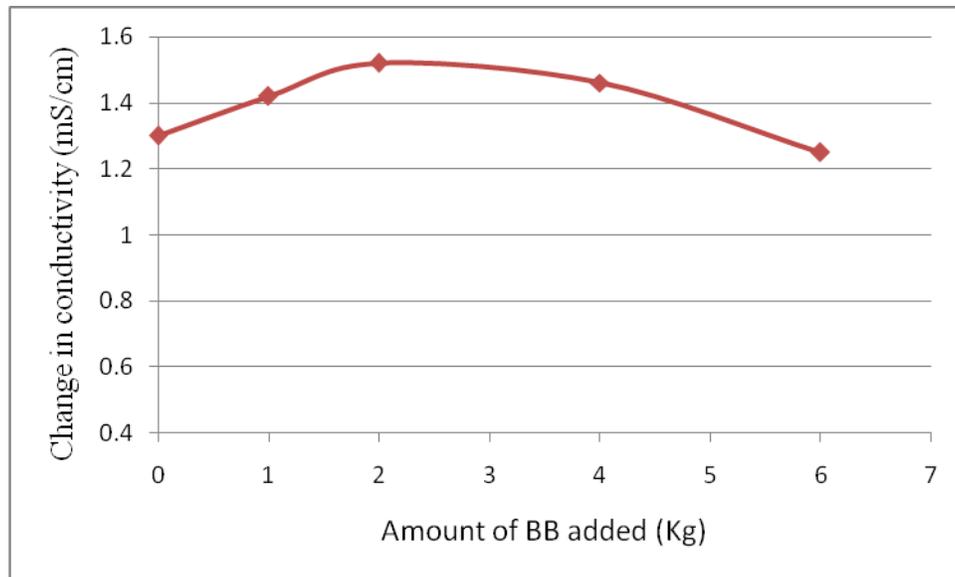


Figure 4.1 Change in conductivity with increase in amount of BB in RH: BB: SBE

From figure 4.1 it is observed that the sample with the RH: BB: SBE ratio of 20:2:4 by weight, showed the highest change in conductivity. According to Luxan (1989) the sample which shows the highest change in conductivity has the highest value of pozzolanicity. Luxan (1989) further noted that sample which give a conductivity change of above 1.4, are potentially very good pozzolanic materials. In this case, the pozzolanicity increased as the amount of BB was increased in the RH: BB: SBE ratio. Muthengia (2003) observed that the pozzolanic activity of BB, ashed SBE and RHA increased in the order where BB greater than ashed SBE, greater than RHA. It was therefore expected that increase in the amount of BB in the pozzolana mixes would increase the pozzolanicity of the samples. However from the above conductivity tests

this was not the case. When the amount of BB added was beyond 2 kg in the 20 kg RHA and 4 kg SBE mix, pozzolanic activity of the resultant ash decreased. This implied a decrease in the available reactive silica in the samples. This could have been due to compaction of the whole mix mass. Compaction of the samples by an increased amount of BB may have reduced effective burning of the materials being incinerated (Muthengia, 2003). This must have resulted in less pozzolanic material being formed. Compared to the chemical constituents of the samples in table 4.1, it can also be seen that the LOI of the samples increased with an increase in the amount of BB in the samples. This confirms the reduction in the burning as more organic materials in the pozzolanas show less burning.

Figure 4.2 shows the change in conductivity of the pozzolana samples 3 and 4 compared to those of sample 5 and 6 respectively. Comparing t values for samples 5 and 3, t calculated is 4.648, while t critical at 95 % confidence level is 2.776. The change in fineness of the BB with amount of added BB as 4 kg does not have a significant effect on pozzolanicity at this stage. However when amount of BB added was 6 kg as in sample 6, t calculated was 0.775 compared to t critical of 2.776. This meant that there was a significant change in pozzolanicity when less fine BB was used. This could be attributed to the uniformity of the amount of milled BB and that not milled. Since the actual amounts of the different sizes of BB were not considered during incineration, sample 6 could have had finer particles of BB (90 μm) than the larger ones of about 3 mm.

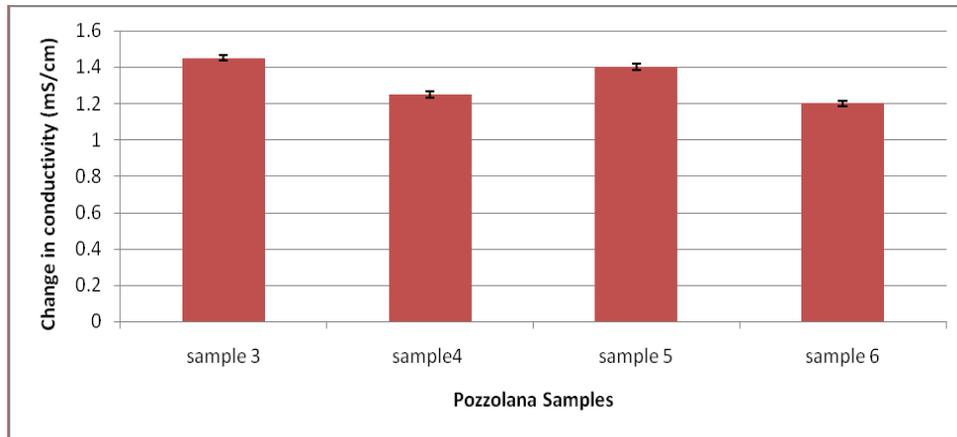


Figure 4.2 Change in Conductivity of pozzolana samples equal masses of BB

4.3.2 POZZOLANICITY BY USE OF THE STANDARD POZZOLANICITY CURVE

Figures 4.3 and 4.4 give the results of CaO and OH⁻ concentrations of the various pozzolana samples at the 8th and 15th day of curing (ISO, 1990). All the coordinates of the pozzolana samples were below the solubility isotherm. This is because as the cement hydrates, it releases calcium hydroxide as a by-product. This sets the right pH value for Ca(OH)₂ to react with the pozzolana as well as availing the Ca(OH)₂ for the reaction (Takemoto, 1980). In PPC, the released Ca(OH)₂ react with the pozzolana incorporated in the cement to produce more cementitious material. This lowers the concentration of CaO in the pore solution. For all the samples, the OH⁻ remains fairly constant at the 8th day of curing. This is because the pozzolanic reaction involves only the Ca(OH)₂ and not the K₂O and Na₂O (Takemoto and Uchikawa, 1980).

The alkali oxides are responsible for the pore solution pH with Ca(OH)₂ acting as a buffer store for OH⁻ (Diamond, 1981).

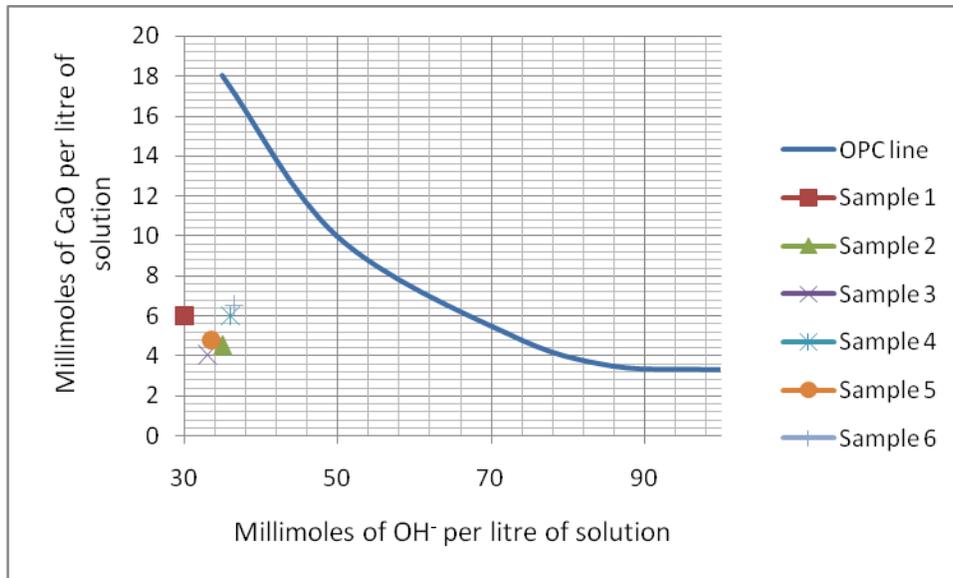


Figure 4.3 Pozzolanicity diagram for pozzolan-ALS cements on the 8th day of curing.

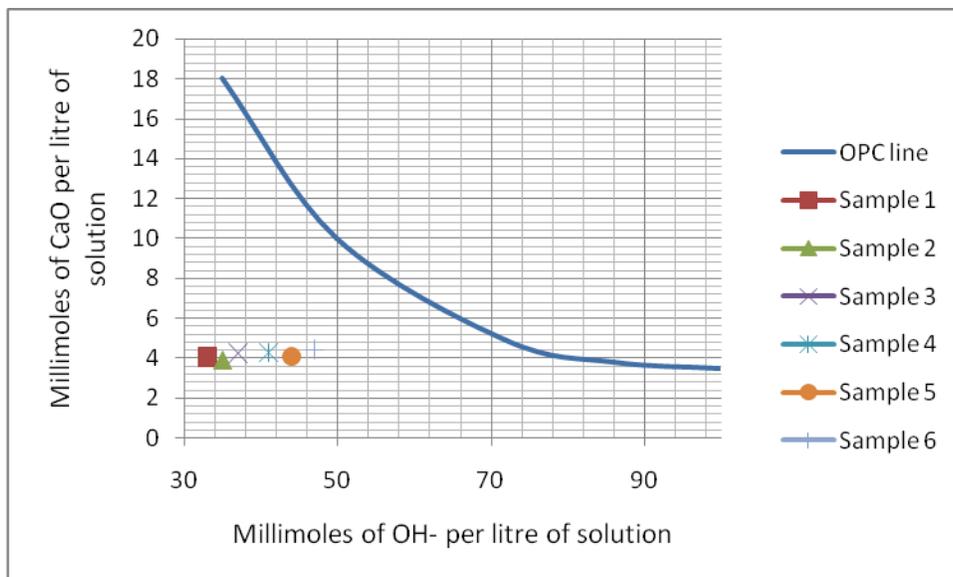


Figure 4.4 Pozzolanicity diagram for pozzolana-ALS cements on the 15th day of curing.

All the samples had a 40 percent replacement of the pozzolana containing RH: BB: SBE. The reduction in the Ca^{2+} and OH^- was more pronounced compared to the same replacements for the individual pozzolana of RHA, BB and SBE as observed by Muthengia (2003). This indicated that the incineration of the three pozzolanas results in a more reactive sample. The

15th day pozzolanicity diagram indicates even lower coordinates for all the PPC samples made. The coordinates are low because the pozzolana samples in solution release reactive silica that reacts with the released Ca(OH)_2 . The sample number 2 showed the lowest coordinates. This may be attributed to the fact that it had the highest amount of amorphous silica that readily reacts at room temperature, than all the other samples.

4.4 COMPRESSIVE STRENGTH EVALUATION

4.4.1 COMPRESSIVE STRENGTH OF POZZOLANA-ALS CEMENTS

Results of the 7th day and 28th day compressive strengths of pozzolana-ALS cements are shown in figure 4.5.

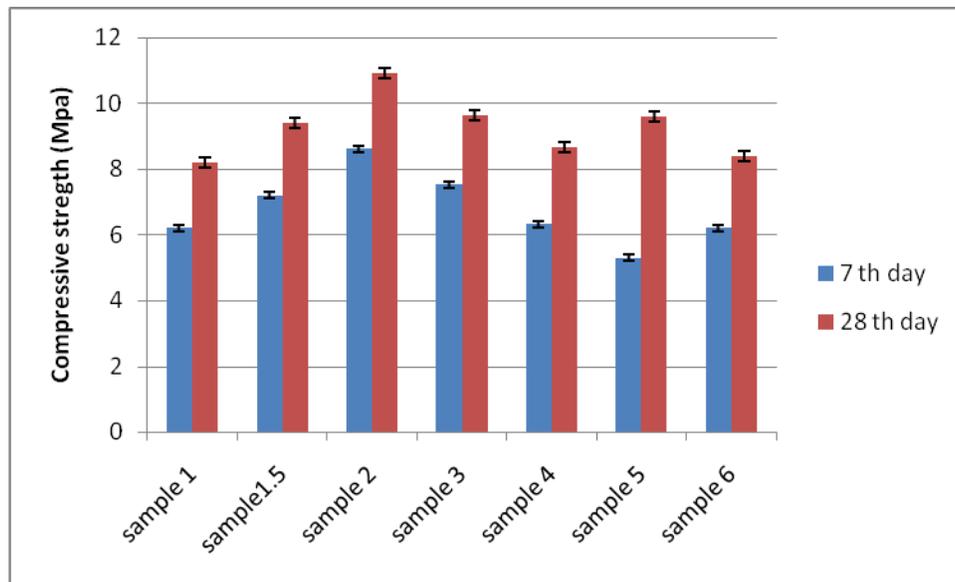


Figure 4.5 Compressive Strength of the Pozzolana-ALS cements

The pozzolanic activity increased with an increase in the amount of BB up to 2 kg. There after the activity reduced. Studies had shown that the pozzolanic activity of the pozzolanas in this study varied in the order BB greater than ashed SBE, greater than RHA (Muthengia, 2003). It

was therefore expected that the compressive strength would increase with the increase in the amount of BB added. However this was not the case. A similar trend as the variation of compressive strength with amount of BB added was observed in pozzolanicity tests (figure 4.2). This could be attributed to pozzolanic activity changes with amount of amorphous or crystalline silica. This could perhaps be attributed to the increase in compaction of pozzolana samples as a result of addition of more BB. Compaction of the whole mass of the pozzolana being incinerated would increase the possibility of production of crystalline phases of silica in the sample. The pozzolanic activity is enhanced by the presence of non-crystalline silica in a pozzolana (Mehta, 1979, Boeteng and Skeete, 1990). More so LOI was high in samples 3, 4 and 5 which lower pozzolanic activity. The $(\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3)$ was also low in these samples. These constituents are important in pozzolana-lime strength development (Muller, 2005).

From figure 4.5, it is clear that both the 7th and 28th day compressive strength of all the pozzolana samples was higher than the minimum standard requirements. ASTM C 593 standard prescribes a minimum of 4.1 Mpa at the 7th and/ 28th day curing. The difference between the 7th and 28th day compressive strengths is small. This is because the pozzolana-ALS cements were cured at 54 ± 2 °C. This is an accelerated hydration (Lea, 1973). The test samples would therefore be ideal for the making pozzolana-lime cement. Sample 2, with the optimum activity, was used to make pozzolana-ALS-OPC blends for further investigation.

4.4.2 COMPRESSIVE STRENGTH OF POZZOLANA-ALS-OPC CEMENTS

Figure 4.6 shows the compressive strengths of the various PPC at 1st , 7th , and 28th day of curing.

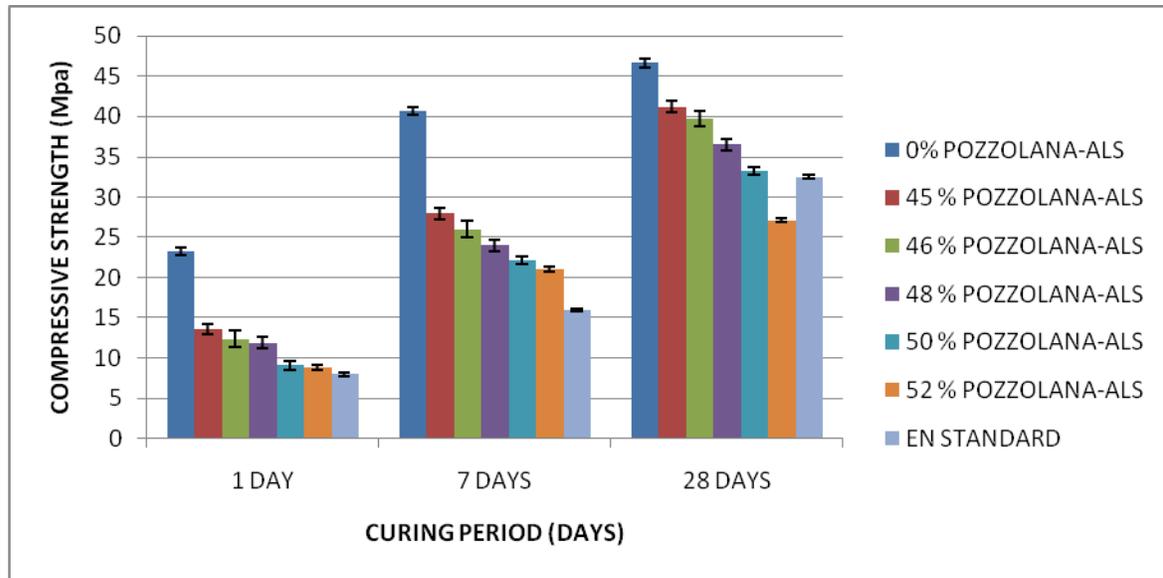


Figure 4.6 Compressive Strength Development of Pozzolana-ALS-OPC Cement as a function of curing period

From these results, it was observed that up to 50 % replacements of OPC with the pozzolana-ALS blend, met the standard requirement for Portland pozzolana cement (KEBS, 2001). The highest replacement that met standard requirements for PPC was the 50 % replacement. This would mean a 1:1 ratio mixture in the blend. Muthengia (2003) observed that a 5:1:1 RH: BB: SBE blended raw mix ratio pozzolana was able to meet the minimum requirements up to 45 % of OPC. The results in this study therefore show an improvement on this. This could be attributed to the improved pozzolanic activity of materials in this study.

As noted from pozzolanic reactions of the pozzolana samples (figure 4.1 and 4.2), pozzolanicity of the samples increased with an increase of the amount of BB added up to 2 kg, and there after a decrease. Therefore the optimum ratio used in the making of pozzolana-ALS-OPC cement had a ratio of 10: 1: 2 of RH: BB: SBE. Given that pozzolana-lime ratio was 2:1;

therefore the pozzolana-ALS cement alone had a 66.7 % of the pozzolana. The highest replacement possible that still met the KS EAS standards for PPC was the 50 % replacement. This therefore implied that the optimum replaced cement had pozzolana content of 33.3 %. Kenyan standards (KEBS, 2001), requires a maximum amount of pozzolana additives in PPC to be 35 %. Therefore in terms of these requirements, the cement made at 50 % replacement of OPC met the requirements. This is the commonly used PPC in Kenya, known as cement IV/B (P) 32.5 N. It is used for a wide range of applications from domestic to large building projects (KEBS, 2001).

The results show a general decrease in strength with an extra addition of the pozzolana-ALS cement. PPC show low early strengths compared to OPC, but their compressive strengths increase at late age of curing. This could be attributed to the fact that early strength decreases with increasing pozzolana content (Swamy, 1986). At this stage there is more pozzolana available in the cement than lime. Strength increases as the amount of combined lime increases in the PPC (Turrizian *et al.*, 1954). At 1st day of curing, most of the lime in the OPC would not be available for reaction with the pozzolana. As curing continues, compressive strength increases as the amount of free lime increases from both the ALS and the leached lime from the OPC (Gleeson, 2002). More cementitious products are therefore formed from this reaction at later age of curing.

The pozzolanicity of the raw blended mix of RH, BB and SBE used in this work has shown that a raw mix in the ratio of 10: 1: 4. It was expected that more BB could have increased the pozzolanicity. However this was not the case. This has been attributed to the compaction of the whole pozzolanic blend under incineration if more BB used. The pozzolanic materials could

not therefore be incinerated properly if more BB is used in the mix. More material can be used for making the pozzolana using this ratio. Higher pozzolanic activity was evident when this optimum ratio was used in blend with OPC. 50 % successful replacement of OPC is an attractive adventure. This means more cementitious material was formed when the optimum ratio of the pozzolanic material was used. Since they are regarded as waste, this would therefore bring the cost of OPC down and hence affordable to a majority of the population.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

In view of the results and analysis, the following conclusions were drawn

1. When RH, BB and SBE incinerated in the FBK in varying proportions by mass, resulting ash varied in its pozzolanic reaction. Pozzolanic activity increased with increase in the amount of BB in the raw blended mix up to 2 kg. The optimum mix ratio for RH: BB: SBE was 10:1:2.
2. The chemical composition of the resulting blends of the pozzolanas, varied with increased amount of BB in it. More BB increased the amount of total silica in the blends. However this did not necessarily increase the pozzolanic reactions of the resulting ash. This amount of the silica, alumina and iron which directly influence the reactivity of the pozzolana were found to be in optimum proportion when the ratio of RH: BB: SBE was 10:1:2.
3. Pozzolanic activity of the raw calcined blended mix of RH, BB and SBE did not considerably change with a variation in fineness of the BB used. This means that BB fineness varying from 90 μm to 3 mm in diameter would be suitable for use in making calcined raw blended mix pozzolana of RH, BB and SBE.
4. Strength development of the pozzolana-ALS cement increased with increase in the amount of BB in the pozzolana blends up to the ratio 10: 1:2, when it started reducing with each extra addition of the BB. However in all samples both the 7th day and 28th day compressive strengths were above the minimum standard requirements of 4.1 Mpa.
5. Blending of OPC with 50 % of the pozzolana-ALS cement met the required EN 196-1 standard currently being used in Kenya and East Africa. If investigated further on large

scale, this would mean that this pozzolanic materials and the ALS would be suitable in making PPC equivalent cement that can be used locally.

5.2 RECOMMENDATIONS

The following are the recommendations for further work.

- 1 A kiln design has been recommended for further investigation. Figure 5.2 shows the complete Kiln design.

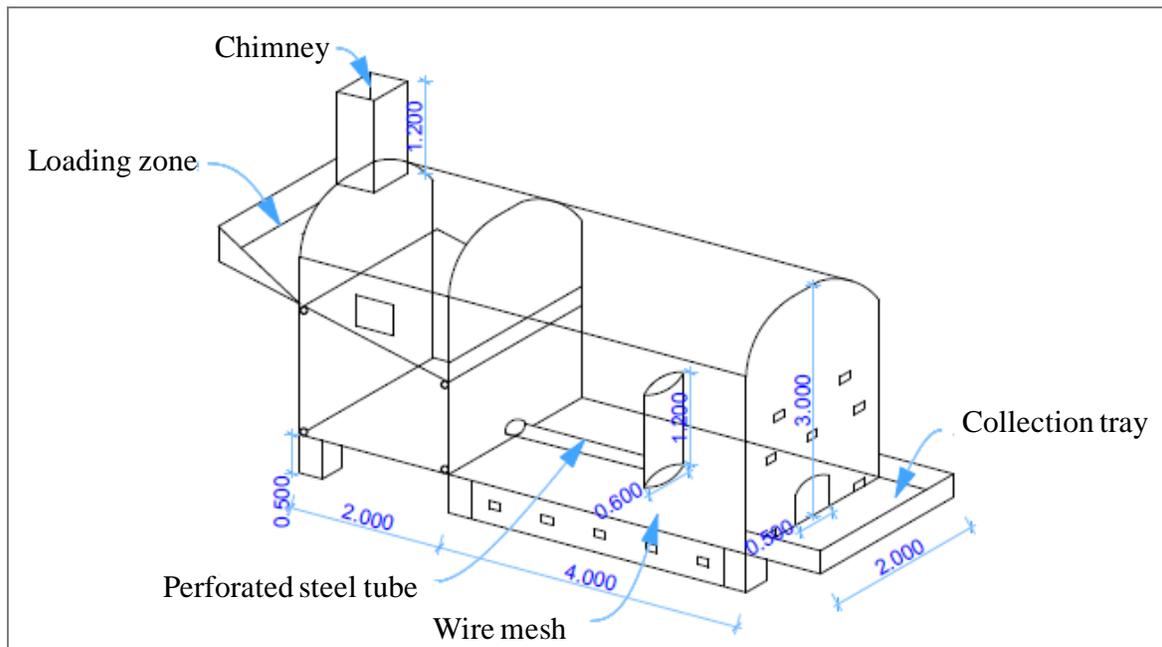


Figure 5.2: Complete Kiln design

The Kiln will have two compartments. The first compartment will be for the incineration of the blended mix pozzolana. This is a $4 \times 2 \times 3$ meter dome shaped compartment with a floor made of movable wire mesh. The middle consists of a cylindrical wire mesh which is in contact with a horizontal perforated steel pipe leading to the second compartment. The compartments are raised to 0.8 meters from the ground. The longer sides have four rectangular openings equidistant from each other, placed just below the main chamber.

Other similar holes are at the base of the chamber one on either side of the door. The door is dome shaped with base and maximum height being 0.5 m each. The front part will also consist of rectangular holes placed about the same height of the cylindrical wire mesh.

The second chamber is basically for drying of the raw materials and translating them en route from the loading zone. This is made possible by the inclusion of a slanting rolling steel sheet in the 2 m by 2 m chamber. This is made possible by use of the rollers shown. It has been proposed that, at this level the rollers be made of bicycle pedals. The movement to the first chamber is made possible by the opening door which has been designed to be at 1.2 m above the floor. This is to help in the slowdown of the movement of the material once the first chamber is full. Figure 4.12 shows the wall at the end of the second compartment.

The loading zone will consist of a 1 m by 2 m steel casing open on the upper part. The window is 1.7 m above the ground. This height would be within limits of an average height of a man. It could be made easier by the use of a mounted ladder. The raw materials are to be loaded in layers of RH, BB, and SBE in an alternating manner (Muthengia, 2003).

From the ash content of the RH and SBE from this study and studies done before (Ochung'o, 1993), a load of 800 kg of RH, 80 kg of BB and 160 kg of SBE, the resulting pozzolanic ash would weigh about 330 kg. Pozzolana ash in this work was produced after 8 hours. If the efficiency of the designed improves as projected, then this would result in producing two loads of pozzolana ash per day. This would be a total of 660 kg of

pozzolana per day. When combined with ALS in the ratio 2: 1, then 990 kg of pozzolana-ALS cement would be produced per day. These amounts are economic enough at a small scale plant.

- 2 A feasibility study should be carried out to look into the possibility of producing pozzolana and pozzolana-Lime cement on a larger scale in rice growing areas in the country. The regions to be studied include, Mwea, Ahero among others. Such a study should consider the actual amounts of RH produced in the regions, transportation costs of the ALS and availability of BB and SBE in these regions
- 3 .A study in which larger particles of BB than those used in this study be done.
- 4 An investigation to look into the possibility of using other locally available waste products should be investigated. Such materials that can be used in blend are Banana leaves, burnt clay, and sugarcane bagasse among others.
- 5 The kiln designed in this work should be built and investigated on its practicability. Economic aspects for bulk production of the pozzolana and pozzolana-lime cement using this kiln and the optimum mix of RH, BB and SBE should be investigated.

REFERENCES

- Adepegba, D. (1990), Nigeria pozzolana; the cheap alternative to Portland cement, UNESCO.
- Albuzaidy, S.N. (1992), Evaluation of SBE and Filtering Clay-A Bentonite Product from Palm Oil Refining as a potential Feed ingredient in Layer Diets; *Journal of Animal Feed science Technology*, **40**;13-19.
- American Concrete Pipe Association, (1988), Concrete Pipe Handbook.
- American Society for Testing & Materials (1989), Annual Book of ASTM Standards, Vol 04.01, Cement; Lime; Gypsum, Philadelphia.
- American Society for Testing and Materials (2006), ASTM C 618, Standard Specification for Coal, Fly Ash and Raw or calcined Natural pozzolan for use in concrete Section 4, volume 04.02
- Ankra, K. (1976), Studies of Black Silica Produced Under Varying Conditions, Ph.D Thesis, University of California, Berkeley.
- Annual Book of ASTM Standards, No. 593, Part C (1991), Standard Specification for Fly Ash and Other Pozzolanas for use with Lime, American Testing Materials, Philadelphia,
- Antiohos, S. and Tsimas, S. (2005), investigating the role of reactive silica in the hydration mechanism of high calcium fly ash/cement systems, *Cement and Concrete Composites*, **27**; 171-181.
- Austrheim, I. (1979), Cristobalite and Tridymite Crystallization in amorphous Silica Collected from the Smoke from Silica Metal Furnace, *Ceramic Society*, **76** (6); 134-138.
- Bakker, R. (1999), Application and advantages of blended cement concretes, QCL Group Technical Note.
- Beaudoin, J. J. and Ramachandyan, V. C. (1992), A new perspective on Hydration Characteristics of Cement Phases, *Cement and Concrete Research*, **22** (4); 689-694.
- Bensted, J and Barnes,P. (2001), structure and performance of concrete, London and New York, spon press.
- Bernard, H.L (1948), a Porters Book, New York Transatlantic Arts, 190-191.
- Beshara, A and Cheeseman, C. R. (2007), Stabilization and Solidification of spent Bleaching Earth Using cement Kiln Dust, London.

- Blair, R. C. and Higgins, J. J. (1980), a comparison of power of Wilcoxon's rank-sum statistic to that of student's t-Test under various non-normal distributions, *Journal of Education Statistics*, **5** (4).
- Blanks, F. R and Kennedy, L.H. (1983), the Technology of Cement and Concrete, **1**, John Wiley and Sons, Inc., London 100-190.
- Blanks, F.R. and Kennedy, L.H (1955), the technology of cement and concrete, John Wiley and Sons Inc, London, 100-190.
- Boateng, A. A. and Skeete, D. A. (1990), Incineration of Rice Hull for Use as a Cementious Material: The Guyana Experience; *Cement and Concrete Research*, **20**, Pergmon Press, 795-905.
- Bogue, R.H and Lerch, W. (1934), Hydration of Portland Cement compounds, *Industrial and Engineering chemistry*, **26**, (8); Easton, Pa., 832-847.
- Bogue, R.H. (1955), The Chemistry of Portland Cement, 2nd edition. *Soil Science*, **9** (4); 322.
- British Standard Institution, (1999), Oil content using Soxhlet apparatus, BS EN ISO 659, London.
- British Standard Institution, (2005), Testing methods of cement, Chemical analysis of cement BS EN 196 part 2, London.
- British Standard Part 2 (1970), Methods of Testing Cement, Chemical Tests, British Standard Institution, London.
- Bui, D.D. (2001), Rice husks Ash as a mineral Admixture for High performance Concrete, Delft University of Technology.
- Building Research Establishment (1982): Alkali Aggregate Reaction in Concrete; *BRE Digest*, 258, HMSO, London, (6).
- Cavdar, A and Yetgin, S. (2007), Availability of tuffs from northeast of Turkey as natural pozzolana on cement, some chemical and mechanical relationships, *Construction and Building Materials*, **21** (12); 2023-2082.
- Chandaresekha, S, Pramanda, P. N and Majeed, J (2006), effect of cacination temperature and heating rate on optimal properties and reactivity of rice husks ash, *Journal of Material Science*, **41**; 7926-7933.
- Chopra, S. K., Ahluwalia, S. C. and Laxmi, S. (1981), Technology and Manufacture of Rice husk Ash Masonry (RHAM) Cement; *Proceedings of ESCAP/RCTT Third Workshop on Rice Husk Ash Cement*, New Delhi.

Colleparidi, M, Colleparidi, S, Skarp, U and Troli, R. (2004), Optimization of silica Fume, Fly Ash and Amorphous nano-silica in superplasticized High-performance Concretes, Proceedings of 8th CANMET/ACI International conference on Fly Ash, Silica Fume, Slag and Natural pozzolanas in concrete, Las Vegas, USA, 23rd-29th may, 495-506.

Cook D.J. (1986), Rice husks; *concrete technology and design*, **3**, Cement replacement materials, Swamy R.N (Ed) Surrey University Press, 171-196.

Cook, D. J. (1986), *Calcined Clay, Shale and Other Soils*; Concrete Technology and Design Cement Replacement Materials, **3**, Swamy. R. N (Ed.), Surrey University Press, New Delhi, 40.

Cook, D.J (1983), Fly Ash in concrete technical Considerations; *Concrete International*, **5**; 51-59.

Cook, D.J, Pama, P.P and Paul, R.K (1986), Rice husks ash-lime cement mixes for use in masonry units, *Building Environment*, **12**; 281-288.

Czernin, W. (1962), Cement chemistry and physics for civil Engineers, London, Crosby Lockwood and Sons ltd.

Czernin, W. (1980), Cement Chemistry and Physics for Engineers, 2nd edition, Foreign Publication Inc., London, 11-18.

Daniel, R (1968), Kiln Design, construction and operation, Pitman publishing, London, 80-88.

Day, R. L (1992), pozzolans for use in low cost housing, state of the art report, universdad de Calgary, report no CE 92-1.

Deepa, G.N, Jagadish, K.S and Fraaij, A (2006), Reactive pozzolanas from rice husks ash: An alternative to cement for rural housing, *Cement and Concrete Research*, **36**; 1062-1071.

Deka, S. and Yasmin, S (2006), Utilization of lime sludge waste from paper mills for fish culture, *Current Science*, **90**; 18.

Dhir, R. K., Ho, N. Y. and Munday, J. G. L. (1986), PFA in Structural Precast Concrete; Full Scale Factory Trials; *Concrete*, **20** (1); 40-41.

Dhir, R. K., Munday, J. G. L., Hubbard, F. H., Jones, M. R and Duerden, S. M. (1985), The Use of PFA in Concrete, Report DM/10, Dundee University, 59.

Dhir, R.K, Munday, J.G.L and Ongi, L.T (1986), Characteristics of low lime fly ashes significant to use in concrete: *Proceedings of the 2nd conference on Fly ash, silica fumes slag and natural pozzolanas in concrete*, Malhotra, V.M (Ed), Madrid, ACI special publication, SP-91, 693-722.

Diamond, S. (1981), Effects of Two Danish Fly Ashes on Alkali Contents of Pore solutions of

- Cement-Fly Ash Pastes: *Cement and Concrete Research*, **11**; 383-394.
- Duedall, W. I., Kester, D. R., Park, P. K. and Ketchem, B.H. (1985), *Wastes in the Ocean*, **4**, John Wiley and Sons, New York, 68-73.
- Ephraim, E. M, Akeke, G. A and Ukpata, J. O (2012), Compressive strength of concrete with RHA as partial replacement of OPC, *Journal of Engineering Research*, **12**, 32-36.
- Erdogdu, K., Tokyay, M and Turker, P. (1999), trass and trass Cements, *Cement and Concrete World*, **3** (21), 52-59.
- European Norm standards 14213, (2003), Heating fuels- fatty acid and methyl esters (FAME); requirements and test standards.
- Fifield, F.W and Kealey, D. (1995), Principles and practice of analytical chemistry, 4th edition, New York, Chapman and Hall, 232-348.
- Gallius, W. A., Hansen, H., Pederson, L and Szwabowski, J. (1997), Pozzolanic properties of a variety of European Clay Bricks: *Building Research Information*, **25**, 170-175.
- Garcia, L.I, Palomo, A and Fernandez, J.A. (2007), Alkali Aggregate reaction in Activated fly Ash Systems, *Cement and concrete Research*, **37**, 175-183.
- Garcia, L.I., Palomo, A. and Farnandez, J.A. (2003), Alkali Aggregate Reaction in Activated Fly Ash Systems: *Cement and Concrete Research* **37**; 175-183.
- Gerardi, V., Minelli, F. and Viggiano, D (1998), Steam treated rice industry residues as an alternative feedstock for the wood based particle board industry in Italy, *Biomass Bioenergy* **14**; 295-299.
- Ghebreyesus, T.A., Haile, M., Witten, K.H., Getachew, A., Yahannes, M., Lindsay, S.W and Byass, P. (2000), Household Risk Factors for Malaria Among children in the Ethiopian Highlands; *Transaction of the Royal Society of Tropical Medicine and Hygiene* **94** (1);, 17-21.
- Ghosh, A. and Pratt, P. L. (1981), Studies of Hydration Reactions and Microstructure of Cement- Fly Ash Paste; *Proceedings of the Symposium on Fly Ash Incorporation in Hydrated Cement System*, Diamond, S. (Ed), 82-91.
- Ghosh, S. N. (1983), *Advances in Cement Technology*, Pergamon Press, New York, 649-673.
- Glasser, M and Order, L. (1998), Mechanics of sulphate expansion in hydrated Portland cement- *Journal of American Ceramics Society* **71**; 1015-1020.
- Glassers, F. P. (1983), Reaction Occurring During Clinker Making, *Structure and Performance of Cements*, Barness, P. (Ed.), Applied Science Publishers, London, 77.
- Gleeson, F. (2002), appropriate use of Pozzolana derived from Agro-Wastes in Cambodia using labor based appropriate technology, ILO.

Goni, S guerrero,A, Luxan, M.P and Macias, A. (2003), Activation of the Fly Ash pozzolan reaction by Hydrothermal conditions, *Cement and Concrete Research*, **33**, 1399-1405.

Groover, P.M. (2002), Fundamentals of modern manufacturing, John Wiley and sons, USA.

Gunnick, J. L. and David, H. A. (1997), the paired t-Test under artificial pairing, *the American statistician*, 51 (1), 912.

Hammond, A.A. (1983), pozzolana cements for low cost housing, proceedings of symposium on appropriate building materials for low cost housing, 73-83, Nairobi.

Hayder, A. A.,Rosli, M.Y., Abdurrahman, H.N., and Nizam, M.K (2011), Lubricating grease from spent bleaching earth and waste cooking oil: Tribology properties in *Journal of the Physical Sciences* **16**; 4695-4699.

Huang, S. (1981), Hydration of Fly Ash Cement and Microstructure of Fly Ash Cement Pastes; CBI Research 2.8.1: Swedish Cement Research Institution, Stockholm.

Huang, Yi-Pin and Chang, J.I (2010), Biodiesel production from residual oils recovered from spent bleaching earth: *Renewable Energy* **35** (1); 269-274.

Igor, S. P.,Montenegro, C. L. and Gunieri, G. A. (2010), Pozzolanic activity of Recycled Red Ceramic Bricks: *Construction Materials and Technologies- Second international conference on sustainable Construction Materials and Techonologies*, Zachai, J., Claisse, P., Naik, T. R., and Ganjjian, (Ed). Ancona, Italy.

International Standard for Organisation (ISO), (1990), Cement-Test Methods: Pozzolanicity Test for Pozzolanic Cements, ISO 863: 1990 (E), Switzerland.

Kapur, P. C. (1981), Tube in-Basket Rice Husk Burner for producing Energy and Reactive Rice Husk Ash, *Proceedings of ESCAP/RC77 Workshop on Rice Husk Ash Cement*, New Delhi.

Kenya bureau of standards (1991), Annual book of ASTM standards, No. 593 part C, Nairobi.

Kenya bureau of standards (1993), Specifications for Portland Pozzolana cements, KS 02 1263, Nairobi.

Kenya Bureau of Standards (2001), Kenya Standard specification For Portland pozzolana Cements KS EAS 18-1, Nairobi.

King, R.R and Wherton, F.W. (1949), *Journal of American Chemical Society* **26**;201-210.

Kirk-Othmer, (1979), Encyclopedia of Chemical Technology, John Wiley and Sons, 3rd Edition, 201.

Koram, K.A., Bennett, S., Adiamah, J.H and Greenwood, B.M. (1995), Socio-economic Risk-Factors for Malaria in Peri-urban Area of the Gambia; *Transaction of the Royal society of Tropical Medicine and Hygiene* **89**; (2), 146-150.

Kremser, H (1964), the use of pozzolana in Germany, Proceedings of Symposium on pozzolanas, their survey, manufacture and utilization, 102-106, New Delhi.

Kulkarni, P. D., Ghosh, R.K and Phull, Y. R. (1983), Textbook of Concrete Technology, New Delhi.

Lane, R. O. and Best, J. K. (1982), Properties and use of PFA in Portland cement Concrete; *Concrete International* **4**; (7), 81-92.

Lea, F.M. (1970), The Chemistry of Cement and Concrete, 3rd edition, Edward Arnold Publishers, London.

Lea, F.M. (1973), the Testing of Pozzolan cements: *Cement technology*, **4**, 21-25.

Leiva, P., Ciannamea, E.M., Ruseckaite, R.A. and Stefani, P.M (2007), Medium density particleboards from rice husks and Soy bean protein concentrate, *Journal of Application Polymer Science* **106**; 1301-1306.

Luke, K and Glasser, F. P. (1988), Internal Chemical Evolution of the Constitution of Blended Cements; *Cement and Concrete Research* **18**; 495-502.

Luxan, M.P, Madruga, F. and Saaveda, J. (1989), Rapid evaluation of pozzolanic activity of natural products by conductivity measurements, *Cement and Concrete Research* **19**; 61-68.

Malquori, G. (1964), Natural Italian pozzolanas, Proceedings of symposium on pozzolanas, their survey, manufacture and utilization, 11-12, CRRRI publication, New-Delhi.

Marther, M. C (1968), Field and laboratory studies of the sulphate resistance of concrete, *Performance of concrete* **1**; 66-76.

Martrena, F. J, Day, R.L., Mindendorf, B and Scrivener, K. (2005), Mixtures of Lime and Clay Pozzolan for High Volume Portland Cement replacement in Concrete.

Maso, J. C. (1980), *International Congress on the Chemistry of Cement*, **1**, (VII) 1/3, Paris.

Massaza, F. (1974), Chemistry of pozzolanic additions and mixed cements- principal paper, proceedings of the 6th international congress on the chemistry of cements, Moscow.

Massazza, F. (1993), pozzolanic cements, *Cement and Concrete Composites* **15**; 185-214, Bergamo, Italy.

- Massazza, F. (2002), properties and applications of natural pozzolans, structure and performance of cements, Benstead, J and Barnes, P (Editors), Spon press. London and New York.
- Mc Lennan, F and Kowalski, B. R (1995), Process Analytical Chemistry, Chapman and Hall.
- McCarthy, G. J and Walsh, A. (2012), Encyclopedia of Australian Science.
- Mehta, P. K. (1979), The Chemistry and Technology of Cements Made from Rice Husk Ash, *Proceedings of INIDO/ESCAP/RCTT Workshop on Rice Husk Ash Cement*, Peshawar, 113-122.
- Mehta, P.K (1975), Properties of Blended Cements, Cements Made from Rice Husks Ash, *Journal of American Concrete Institute*, **1**; 235-236.
- Middendorf, J., Mickley, J. K., Martirena, R.L (2005), Masonry Wall Materials prepared by using Agricultural Wastes, Lime and Burnt Clay in: Opportunities for the 21st Century, ASTM STP 1432, edited by Throop, D and Klinger, R.E., West Conshohocken, PA, 203.
- Mohatra V. M, Mehta, P. K (1996), pozzolanic and cementitious materials, Gordon and Breach publishers, London.
- Montes de Oca J. J. D (2009), Effect of lime-zeolite binder on compressive strength and durability properties of concrete, *Journal Revista Ingenieria de Construccion*, **24**, (2); 181-194.
- Moore, A.E. (1989), *Cement technology*. **8**; 33-34.
- Muller, J. C. (2005), Pozzolanic Activity of Natural Clays with Respect to Environmental Geotechnics, Zurich.
- Murdock, L.J. (1991), Concrete materials and practice-6th edition. Edward Arnold, London, 36-43.
- Murdock, L.J., Brook, K.M. and Dewar, J.D. (1986), Concrete Materials and Practice, 6th edition, McGraw Hill Book Company, New York.
- Muthengia, J.W (2009), Effect of selected Media on novel Portland Pozzolana Cement, Kenyatta University, Nairobi.
- Muthengia, J.W. (2003), Low cost pozzolana based cement from industrial and agricultural waste materials, Kenyatta University, Nairobi.
- Neville, A.M. (1986), Properties of Concrete, 4th edition, Longman, New York, 84.
- Neville, A.M. and Brooks, J.J. (1987), Concrete technology, John Wiley and Sons Inc, New York, 8-39.

Nixon, P. J and Gaze, M. E. (1983), The Effectiveness of Fly Ashes and Granulated Blast Furnace Slags in Preventing AAR; *Proceedings of the 6th Conference on Alkalis in Concrete*, Doran, G. M and Rostam, S. (Eds), Copenhagen, 61-68.

Nutting, P.G. (1987), The bleaching clays, *U.S department of international geology society*: **3**.

Ochung'o, G.J (1993), The production of rice husk cementitious materials, Msc thesis, Nairobi.

Odler, I. and Dorr, H. (1979), Early Hydration of Tricalcium Silicate and Kinetics of the Hydration process and Stoichiometry of Hydration Products, *Cement and Concrete Research* **9**; (2), 239-248.

Owens, P. L. and Butter, F. G. (1980), The Reaction of Fly Ash and Portland Cement with Relation to the Strength of Concrete as a Function of Time and Temperature; *Proceedings of the International Congress on the Chemistry of Cement*, **3**, (4/60-4/65), Paris.

PaayÂ, J., Monzo, J., Barrachero, M.V. and Mellado, A. (2001), Determination of amorphous silica in rice husks by rapid analytical method-*Cement and Concrete Research*, **31**; 227-231.

Park, E. Y, Sato, M and Kojima S. (2007), Lipase-catalyzed biodiesel production from waste activated bleaching earth as raw material in a pilot plant, *Bioresource Technology*, Article in press.

Pavian, S and Regan, D. (2010), Influence of Cement lime mortars, *Materials and Structures*, **43**; (3), 381-392.

Pollard, S.J.T., Scollars, .C.J., and Roger, P. (2003), Reuse of spent bleaching earth: a feasibility study in waste minimization for the edible oil industry: *Bioresource Technology*, **45**, (1), 53-58.

Price, W.H (1975), Pozzolanas, A review, *Journal of American concrete institute*, 225-232, New York.

Raask, E and Baskar, M.C. (1975), Pozzolanic activity of pulverized fuel ash, *Cement and concrete research*, **5**, 363-375.

Ray, S.M (1985), Elements of engineering design, Hall International, U.K limited.

Richard, D.B and Kerber J. D (1993), Concepts, Instrumentation and Techniques in Atomic Absorption Spectrophotometry.

Rodriquez-camacho, E. and Uribe-Afif, R. (2002), importance of using the natural pozzolanas on concrete durability, *Cement and concrete research*, **32**, 1851-1858.

Ropke, J. C. (1982), Concrete Problems, Causes and Cure, McGraw Hill book Company, New York, 27.

Sensale, R.G (2006), strength development of concrete with rice husk ash, *Cement and Concrete Composites*, **28**, 156-160.

Sersale, R. (1980), Structure and Characterization of Pozzolanas and Fly Ash, *Proceedings of the 7th International Congress on the Chemistry of Cements*, Sub-theme, IV-I, Paris, 1-18.

Sersare, R (1991), Blended cements; *Progress in Cement and Concrete Science Technology*, **1**; 314-343, Ghosh, S.N (editor), 314-343.

Shanks, P. (2007), Spent Bleaching Earth, AMC UK ltd.

Shihembetsa, L and Waswa-Sabuni, B. (2002), Burnt clay wastes as a Pozzolanic Material in Kenya: *Journal of Civil Engineering J.K.U.A.T*, **7**, 21-28, Nairobi.

Sihartini, N.H, Sieni, W. (2011), Physical properties and Characterization of Fuel Briquette made from spent Bleaching Earths: *Biomass and Bioenergy*, **35**, (10); 4209-4214.

Skoog, D.A and Leary, J.J. (1992), Principals of instrumental analysis - 4th edition, Saunders college publishers, Port Worth, 286-293.

Spence, R.J.B (1975), Lime and Surkhi manufacture in India-proceedings of the meeting on small scale manufacture of cement materials, technology publication, London, 137-146.

Strible, L., Skalny, J. and Mindness, S. (1980), *Cement and Concrete Research*, **10**, (2), 277.

Surana, M.S., and Joshi, S.N. (1988), Spectrophotometric method of estimating the reactivity of pozzolanic materials, *Advances in Cement Research*, **1** (4); 1841-1852.

Swamy, R. N. (1983), *New Concrete Materials*, **1**, Surrey University Press, New Delhi.

Sybertz, F. (1989), Comparison of different methods for testing the pozzolanic activity of fly ashes; *Fly Ash Silica Fume, Slag and Natural Pozzolans in Concrete*, **1**, V. M. (Ed), Detroit, Michigan, , ACI SP-114,477-497.

Takemoto, K and Uchikawa, H. (1980), Hydration of Pozzolanic Cement; *Proceeding of the 7th International Congress on the Chemistry of Cements*, Paris, Sub-Theme, IV-2-28.

Taylor H. F. W (1993), *Cement Chemistry*, academic press, London.

Taylor, H. F .W (1997), *Cement chemistry*, Taylor and Thomas Telgord Services ltd, London

Terzbasioglu, N. (1995), usability of andesite in production of trass cements, *Proceedings of Industrial Minerals Symposium*, Izmir.1-7.

The Cement and Concrete Association of New Zealand, (1989), *The Manufacture of Portland Cement*.

The Concrete Society, (1985), Proceedings on One-day Conference on Alkali-Silica Reaction, 34.

Toxell, G. E., Davis, H.E. and Kelly, J.W. (1968), Composition and Properties of Concrete, 2nd edition, McGraw Hill Book Company, New York.

Turriziani, R and Schippa, G (1954), Malte de pozzolana, calcee safato di calcio 1, *La Ricerca Scientifica*, **9**, 895-903

Uchikawa, H., Uchida, S. and Hanehara, S. (1986), 8th *International Congress on the Chemistry of Cement*, Rio de Janeiro, Sept 22-27, **IV**, 245-251.

UNHCS, (2006), The state of urban housing report, Nairobi.

Urhan, S. (1987), Alkali Silica and Pozzolanic Reactions in Concrete; *Cement and Concrete Research*, **17**; 141-143.

Van Loon, J. C. (1980), Analytical atomic absorption spectroscopy: Selected methods, Academic press, University of Carlifornia.

Walker, R and Pavia, S (2010), Behaviour and properties of lime-pozzolana pastes, 8th international masonry conference, edited by Jager, W.D, Haseltine, B and Fried, A., international Masonry society.

Waswa-Sabuni, B, Syagga, P. M, Dulo, S.O and Kamau, G.N (2002), RHA cement- An alternative cement for Kenya building industry, *Journal of civil Engineering*, JKUAT, 8, 13-26.

Welz, B. and Sperling, M. (1999), Atomic absorption Spectrometry, 3rd edition, Weinheim.

Yeoh, A. K., Bidin, R., Chong, C. N., and Tay, C. Y. (1979), the Relationship between Temperature and Duration of Burning of Rice Husk in the Development of Amorphous Rice Husk Ash Silica, Proceedings of UNIDO/ESCAP/RCTT Follow-up meeting on, Rice Husk Cement, Alor Setar, Malaysia.

APPENDIX I
RAW DATA FOR ELECTRICAL CONDUCTIVITY AND CHEMICAL
CONSTITUENT ANALYSIS

Table I-1: Results of Change in electrical conductivity of a saturated solution of $\text{Ca}(\text{OH})_2$

Sample	Amount of BB (kg)	Change in conductivity (mS/cm)			Standard deviation
1	0	1.25	1.25	1.40	± 0.0707
1.5	1	1.42	1.40	1.44	± 0.0094
2	2	1.48	1.54	1.54	± 0.0283
3	4	1.44	1.46	1.48	± 0.0163
4	6	1.30	1.25	1.20	± 0.0408

Table I-2: Results of Change in electrical Conductivity of a saturated solution of $\text{Ca}(\text{OH})_2$ for pozzolana samples with equal amounts of BB

Sample	Change in conductivity (mS/cm)				
	Test 1	Test 2	Test 3	mean	Standard deviation
3	1.44	1.46	1.48	1.46	± 0.0163
4	1.30	1.25	1.20	1.25	± 0.0408
5	1.39	1.40	1.41	1.40	± 0.0058
6	1.20	1.30	1.10	1.20	± 0.0817

Table I-3 Chemical Constituent Analysis (AAS, Gravimetric analysis and Flame photometry)

	BB			SBE			SAMPLE1			SAMPLE 2			SAMPLE3			SAMPLE 4			SAMPLE5			SAMPLE 6		
CaO	0.45	0.46	0.47	2.2	2.4	2.3	0.67	0.68	0.60	0.67	0.67	0.61	0.65	0.5	0.5	0.45	0.47	0.43	3.1	3.0	2.99	2.0	2.0	2.03
SiO ₂	64.8	64.9	64.82	66.5	66.7	66.6	74.5	75	73.4	81.1	80.9	79.2	81	82	80.6	82.55	81.9	83	77	76.9	76.8	75.9	75.8	76
Al ₂ O ₃	21.63	21.54	21.45	6.2	6.4	6	7.7	7.65	7.69	7.9	7.8	7.7	7.9	8	7.86	8	7.95	8.05	6.75	6.5	6.94	6.05	6.03	6.04
Fe ₂ O ₃	7.88	7.87	7.86	3.5	3.47	3.23	6.8	6.8	6.8	6.9	6.7	7.1	7.8	7.9	8	3.7	3.8	3.51	4.6	4.5	4.4	3.96	3.98	4
SO ₃	0.23	0.25	0.24	-	-	-	0.32	0.3	0.31	0.13	0.15	0.11	0.11	0.13	0.12	0.3	0.4	0.2	0.14	0.12	0.1	0.52	0.6	0.44
MgO	1.8	2.1	1.5	3.25	3.15	3.2	1.69	1.7	1.71	1.9	1.9	1.9	1.75	1.8	1.67	1.6	1.7	1.8	1.7	1.68	1.78	2.24	2.26	2.22
K ₂ O	3.6	3.62	3.64	1.89	1.91	1.9	2	2	1.97	1.55	1.6	1.62	1.7	1.7	1.7	2.3	2.3	2	1.75	1.85	1.8	3.2	3.2	3.2
Na ₂ O	1.4	1.6	1.41	2.7	2.9	2.8	1.46	1.44	1.42	0.45	0.5	0.4	0.5	0.6	0.55	0.5	0.56	0.56	0.55	0.57	0.53	0.54	0.56	0.55
LOI	0.9	0.92	0.82	14	13.9	14.1	4.02	4	3.95	2.9	3	3.07	4.2	4	3.83	4.7	4.8	4.6	4.1	4.4	4.1	5.54	5.6	5.48

APPENDIX II
COST ANALYSIS FOR THE POZZOLANA-ALS-OPC CEMENT

The following are expenses expected of materials to produce 1 ton of pozzolana-ALS cement

Buying and Transport cost	Ksh
RH transportation (2.4 tons)	=10,000
BB buying and transportation (240 kg)	= 500
BB pre-grinding	= 1000
ALS transportation (1.6 tons)	= 500
SBE transportation (160 kg)	= 200
Bamburi OPC buying (330 kg)	= 7000

Assumptions made

1. Raw materials were considered to be free of charge
2. Labor costs as done by the researcher was considered at the lowest rates
3. Analysis done is for the cost of producing 2 tons of pozzolana-ALS-OPC cement in the ratio 1:1 as determined by the research results.
4. All the processing done at Kenyatta university, and raw materials from nearby factories that is, Thika, Mwea, Ruiru and Nairobi's Industrial area.

Savings Calculations

Total cost of producing 2 tons of Pozzolana-ALS-OPC cement = 19200

Total cost of 2 tons of PPC= 32000

Savings as a percentage of PPC cost per ton= 40%