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LOW COST POZZOLANA BASED CEMENT FROM INDUSTRIAL AND AGRICULTURAL WASTE MATERIALS

BY

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DECLARATION

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

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To Margaret Nyambaiyũ, Geoffrey Wachira and Joseph Kimarũ.

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ABSTRACT

This thesis reports the results of a study aimed at making low cost cement from some agricultural and industrial wastes. The utilization of these wastes would avail an economical and environmentally friendlier waste disposal methods and cheap cementing material. The cement made was based on the materials whose pozzolanic reaction was investigated.

The materials tested for pozzolanicity included rice husks ash (RHA) from wastes of rice milling factories, spent bleaching earth (SBE) from oil processing factories and broken bricks (BB) from clay products manufacturers. Natural pozzolana (Ptuff) used for making East African Portland pozzolana cement was tested for comparative purposes. Heat content of rice husks (RH) and spent bleaching earth (SBE) was found to be adequate for activation of silica and alumina in the pozzolanic materials. Only a little kerosene was necessary for ignition. Acetylene lime sludge (ALS) from acetylene manufacturing industry and commercial hydrated lime (CHL) were used for the pozzolana-hydrated lime reaction.

Pozzolanic activity of the materials with commercial hydrated lime (CHL) in different ratios was investigated on the pozzolanic materials separately. A blended calcined mix and a calcined blended raw mix of the materials was similarly tested. The results showed that the test materials were active pozzolanas. A 1: 2 ratio of the pozzolanic material: CHL gave the best results. The 1: 2 ratio now using ALS

was also investigated on the materials. ALS showed a superior performance than CHL with all the pozzolanic materials under test. Calcined blended raw mix exhibited a better performance than the blended calcined mix.

The test materials were then singly interground in different proportions with laboratory made ordinary Portland cement (OPC) as per the Kenya Standard (KS) 02 1263 of 1993 [1] for cement tests. The resulting mixtures were then assessed using the same standard. The results showed that up to 25 percent replacement of the cement with the pozzolanic materials under test met the standard requirements.

Calcined blended raw mix was interground with ALS and OPC from Bamburi Cement Factory in different percentages. The resulting products were subjected to the Kenya Standard [1]. Up to 45 percent replacement of the OPC with the material under test met the standard requirements, while higher percent replacements failed. A rough financial estimate suggested a running cost saving of up to 20 percent per tonne of PPC.

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EXPLANATORY NOTES

CEMENT CHEMICAL NOMENCLATURE AND SYMBOLS

C = CaO; S=SiO_2; A=Al_2O_3; F=Fe_2O_3; M=MgO; N=Na_2O; K=K_2O; $\overline{S}$ = SO_3; H= H_2O;

C_3S = Tricalcium Silicate ($3CaO.SiO_2$)

C_2S = Dicalcium Silicate ($2CaO.SiO_2$)

C_3A = Tricalcium Aluminate ($3CaO.Al_2O_3$)

C_4AF = Tetracalcium Aluminate Ferrite ($4CaO.Al_2O_3.Fe_2O_3$)

SOME COMMON AND OTHER ABBREVIATIONS USED IN THIS WORK.

OPC = Ordinary Portland Cement

PPC = Portland Pozzolana Cement

BS = British Standard

KS = Kenya Standard

ASTM = American Standard for Testing and Materials

W/C ratio = Water to Cement ratio

BB = Broken Bricks

C-W BB = Broken Bricks from Kenya Clay Products Limited – Ruiru (Nairobi).

G-45 BB = Broken Bricks from Clay Products Manufacturer - Githurai – 45 (Nairobi)

RH = Rice Husks

RHA = Rice Husks Ash

SBE = Spent Bleaching Earth

SBE^1 = Spent Bleaching Earth from Kasuku Packers (KAPA) Kenya Limited

SBE^2 = Spent Bleaching Earth from Unilever Kenya Limited

Ptuff = Pozzolana Used for Making the East Africa Portland Cement®

ALS = Acetylene Lime Sludge

CHL= Commercial Hydrated Lime

E.A.P.C.C = East Africa Portland Cement Company

E.D.T.A = Ethylenediaminetetraacetic Acid

IST = Initial Setting Time

FST = Final Setting Time

LOI = Loss on Ignition

r.p.m. = Rotations Per Minute

ISO = International standard for organization

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CHAPTER ONE

1.0 INTRODUCTION

Cement in most developing countries like Kenya is highly expensive. This is because its production, based on large-scale factories is modelled on those in industrialised nations. Problems associated with such industries are; the long time spent in their construction (which depends on the time a given country would take to budget for, plan and initialise their construction), dependency on imported machinery (which mainly are expensive to buy and may take time before importation if need be), difficulty in obtaining capital for new plants as well as limited number of locations, where raw materials are adequate [2]. Globally, energy contributes most to the Portland cement cost. Fuel cost in Kenya and other developing countries is about four times higher than the global average [3]. This makes the cement in these regions highly expensive. Transportation costs due to poor infrastructure and limited number of cement industries, also contribute to the increased cost of the cements.

Several initiatives have been made to help lower the cost of cement worldwide. The main ones involved the shift from wet to dry process of manufacturing cement. This basically helped lower the overall energy consumption [4]. Local cement factories have adopted this process. Other strategies involve partial replacement of cement by natural pozzolanas and establishment of cement factories near consumers to cut down on transportation cost. Examples include

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the establishment of Bamburi grinding plant in Athi River near Nairobi and implementation of low cost house construction building concrete panels [5]. Cement however remains expensive making housing and building projects expensive.

The expensive hydraulic cement has led to poor cement free housing construction for most people living in Kenya and in many other developing countries. Statistics show that 58 percent of household constructions in Kenya have walls either made of mud or wood, and 63 percent of the households have earth floors [6]. Cracks in poorly constructed houses, especially mud houses, provide dark vents and holes for breeding or entry of jiggers, rats, bedbugs and mosquitoes. These pose a health risk, with the malaria occurrence, for example, being related to poor household construction [7, 8].

Waste management is a problem of most industrial and agricultural concerns. Most methods of waste disposal adopted are environmentally unfriendly or costly. Spent bleaching earth (SBE), broken bricks (BB), rice husks (RH) and acetylene lime sludge (ALS) are locally produced agricultural and industrial waste materials. Their utilisation to produce pozzolana–hydrated lime or pozzolana based cementing material would help avail an economical and environmentally friendlier waste disposal method and a cheap cementing material.

This work has looked for low cost and alternative ways of making pozzolanic cements using the above-mentioned waste materials. Amorphous silica and/or alumina in pozzolanas react with calcium hydroxide at room temperature in presence of water to form similar compounds formed when Portland cements hydrate. Since pozzolanas can be activated at relatively low temperatures, their production cost is relatively low compared to Portland cements.

1.1 WASTE MANAGEMENT

Wastes are considered unnecessary materials, the by-products of most human activities, which are either in form of solids, liquids or gases. Most of the waste materials are agriculturally and industrially based.

Many methods of waste disposal have been used, for example, reallocation, burning, compaction, recycling and dumping in landfills or water bodies. These methods apart from recycling have environmental consequences. Reallocation simply transfers a problem from one site to another. Burning, another common waste disposal technique introduces carbon dioxide and other elemental particles into the atmosphere. Dumping on the land surface, in landfills and water bodies provide a temporary solution to waste management problems [9].

Attention is now shifting from mere safe waste disposal techniques to resource recovery techniques and recycling whereby, the by-products of processes can be

put into economically viable use. Materials and items having low utility due to depreciation resulting from use can similarly be recycled to produce either the original or new products. Explorations of ways of economically utilising waste materials continue to receive great attention in both developed and developing countries [10].

Rice husks are agricultural wastes from rice processing mills. BBs are wastes from under- or over-burnt materials or broken finished products from clay works products. Bleaching earths are clays, which in their natural state or after chemical or physical activation have the capacity of bleaching or adsorbing colouring matters from oils [11]. Colouring matters adsorbed by bleaching earth include chlorophyll and beta carotenoids. The bleaching earth that has been used for decolourising vegetable or lubricating oils forms a solid sludge called spent bleaching earth (SBE).

Acetylene lime sludge (ALS) is a by-product in the manufacture of acetylene gas, an organic compound of high commercial use. The sludge is a by-product according to the following equation [12]

$$CaC_{2\,(s)} + 2H_2O_{(l)} \longrightarrow C_2H_{2(g)} + Ca(OH)_{2(s)} \quad \text{.....(1.1)}$$

The products discussed above have been assessed for their potential as pozzolana and as hydrated lime for $Ca(OH)_2$ in this work.

1.2 STATEMENT OF THE PROBLEM

Portland cements are costly. They require a lot of energy for their production. In Kenya, cement is manufactured in two locations only, hence transportation of the cement to consumers, also contributes to the high cost. The cost of cement is a major contributor to the poor housing conditions. BB, ALS, SBE and RH are a waste problem. Production of some form of cementious material or cement at relatively low or no cost of fuel near the consumer where raw materials are available would be highly desirable. BB, SBE, and RHA have chemical composition similar to most natural pozzolanic materials. ALS is a potential hydrated lime for pozzolana-hydrated lime reaction. Utilization of these materials to make pozzolana-hydrated lime cement would not only avail a better and economical method of waste disposal but also an affordable and cheaper cementing product.

1.3 GENERAL OBJECTIVE

To investigate the possibility of making affordable pozzolanic cement from agricultural and industrial wastes.

1.4 OBJECTIVES OF THE PROJECT

1. To characterize SBE in terms of its calorific value, oil and ash content and ignition temperature.

2. To investigate the chemical composition of SBE and BB compared to RHA and Ptuff as well as ALS compared to CHL.
3. To investigate the suitability of SBE and BB as pozzolanic materials as compared to RH and Ptuff, separately and in blended form.
4. To investigate the effect of varying pozzolana: hydrated lime ratio on the performance of the pozzolanic cements.
5. To investigate the suitability of ALS as raw material for pozzolanic cement, compared to CHL.

1.5 JUSTIFICATION OF THE PROJECT

The area under settlement and industrial activities continue to increase due to rapid population growth and industrial expansion. This leads to decrease in land available for crop production. Apart from the effect of increasing population, poor waste management also contributes to the decrease in productive land.

Biodegradability of such agricultural and industrial wastes such as RH, and oil retained in SBE, is very slow, while others, for example, BB, ALS and SBE clay are non-biodegradable. This makes the increased agricultural and industrial activities to accumulate these materials on land surface. The profitable uses of these wastes are few and ineffective. Use of RHA, for example, as fertilizer is poor given that it's mainly composed of silica. The husks have low feed value and are hence unsuitable for use as fodder or in manufacturing of cattle feed.

Reactivated SBE has low bleaching capacity necessitating re-bleaching of the oils. Utilization of these waste materials as pozzolanic materials would effectively, safely and economically dispose of these wastes.

Several factors need to be boosted to help achieve industrialization of Kenya by the year 2020. Establishment of local production industries, availability of cheap, locally available raw materials and products are among the factors. RH, SBE, BB and ALS are potential locally available affordable materials. Establishment of small-scale pozzolana based cement plants where these raw materials are available or easily accessible would avail production industries and cheap products. This would also avail employment opportunities at reasonably low capital input. With the attainment of above aspects, these factors towards industrialization would be boosted.

Based on growing population and increasing poverty level in Kenya, slums development and mud houses construction are unavoidable. Based on the above-employment creation and availing of local affordable cementing material, socio-economic condition, housing and building will be boosted. Slums and mud houses construction will thus be slowly eradicated and replaced with better housing facilities.

Quarrying of naturally found pozzolanic materials or cement making raw materials leave pits that are neither utilizable nor coverable. Four million cubic meter of volcanic ash and two million cubic metre of limestone, for example, need to be quarried to obtain limestone, a cement making raw material, at Kabini by the E.A.P.C.C. [8]. This will and has already created pits that may not be filled in the near future. Ironically, potential pozzolanic industrial and agricultural waste materials accumulate on land surfaces. Utilization of these materials would thus decrease mining pits and land surfaces accumulation.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 CEMENT

The word cement, in a broad sense, denotes any kind of adhesive. In building and concrete engineering, it denotes substances that can be used to bind together sand and broken stones, or other forms of aggregates into a solid mass [13].

There are basically two types of cements, hydraulic and non-hydraulic. Hydraulic cements, the most common, will set and harden on addition of water. An example of hydraulic cements is Portland cement. Non-hydraulic cements do not set or harden in water, but set on exposure to substances other than water. An example of non-hydraulic cement is "fat lime" which hardens on exposure to carbon dioxide [14].

The most commonly used cements today are hydraulic, Portland cement being the most popular. Portland cement consists principally of four compounds; tricalcium-silicate (C_3S), β-dicalcium silicate (β-C_2S), tricalcium aluminate (C_3A) and a phase approximating to tetracalcium aluminate ferrite (C_4AF). These compounds are formed by a series of reactions at temperatures rising to the region of 1300 to 1500 °C, between lime on the one hand and silica, alumina and iron oxide on the other [15].

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 material, for example, clay or shale, provides alumina and silica [16].

2.1.1 CEMENT MANUFACTURING PROCESS

The manufacturing process of cement essentially consist of grinding the raw materials, mixing them intimately in certain proportions and burning in mainly a large rotary kiln where they sinter to form small grayish balls called clinker. The clinker is then cooled, mixed with a small amount of gypsum - to control setting time, ground in ball mills into required fineness and packed. The resulting product is commercial Portland cement. Raw materials composition used for manufacture of cement is strictly controlled within certain limits. Control is done by analysis of the oxides of chemical constituents. Table 2.1 gives the approximate limits of the oxides in raw materials used in manufacture of Portland cement [17].

Table 2.1: Composition of typical raw materials of Portland cement [17].

Oxide	**Symbol**	**Contents Percentage**
CaO	C	60-67
SiO_2	S	17-25
Al_2O_3	A	3-8
Fe_2O_3	F	0.5-6.0
MgO	M	0.1-4.0
Alkalis	-	0.4-1.3
SO_3	$\overline{S}$	1.3

Mixing and grinding of the raw materials can be done either in water or in a dry condition hence wet or dry processes [17] for cement manufacture.

2.1.1.1 Wet Process

This process basically involves raw materials being crushed and ground to form a slurry in wash mills. When chalk is used as the calcareous material, it is finely broken up and dispersed in water in a wash mill. The clay is broken up and mixed with water in a wash mill also. The two slurries are mixed in given proportions in a storage tank [14]. When limestone is used, it is blasted, crushed then fed into a ball mill with the clay dispersed in water. The slurry mix is also fed into a storage tank. The slurry has a water content of between 30-50 % and only a small fraction of the material, less than 2 % is larger than 90 μm. The slurry is then fed into a rotary kiln. This is a large refractory lined steel cylinder, up to 8 m in diameter and 250 m in length, slowly rotating about it's own axis which is slightly inclined to the horizontal. The slurry is fed from the upper end. The slurry, in its movement down the kiln, encounters progressively higher temperatures. As the materials move down the kiln, they sinter as the chemical components react to form the clinker [13]. Much energy is used in drying the slurry.

2.1.1.2 Dry Process

The raw materials are fed in correct proportions into a grinding mill, where they are crushed and reduced in size to a fine powder. The dry powder called raw

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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 raw meal is pre-heated to a temperature of about 800 °C before being fed into the rotary kiln [4]. Schematic representation of this process is given in figure 2.1.

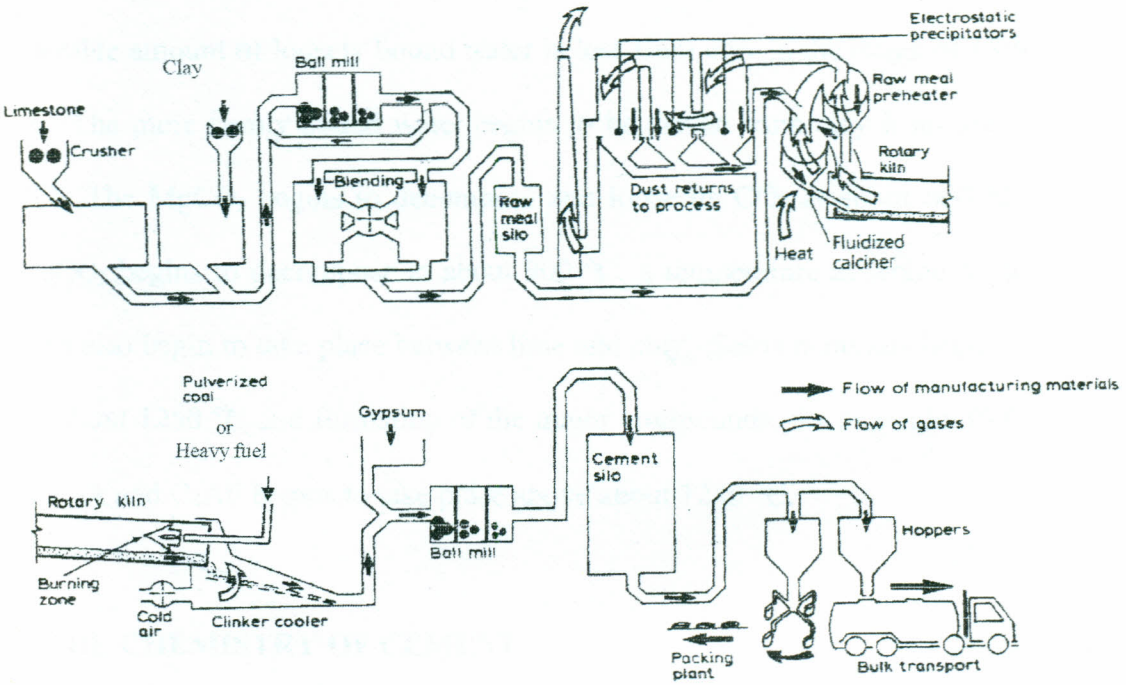


Figure 2.1: Schematic representation of the dry process [4]

Comparatively, less energy is used in grinding and blending of raw materials in the wet process than in dry process [17]. Kiln energy consumption in the dry

process is however much less than in the wet process due to kiln feed moisture content. Summing up the two energy consumptions, the dry process uses much less energy than the wet process [18]. This makes the dry process more economical and therefore more common. Locally, for example, the E.A.P.C.C. shifted from the wet to dry process due to the same reasons.

2.1.1.3 Reactions in the Kiln

Various reactions take place in succession with increasing temperature as the materials move through the kiln [18]. At 100 °C, free water is evaporated. A considerable amount of loosely bound water is lost from clay in the range of 150-350 °C. The more firmly bound water begins to be driven from clay from about 500 °C. The $MgCO_3$ begins to decompose and loose its CO_2 at about 600 °C. The $CaCO_3$ begins to decompose at about 900 °C, a temperature at which some reactions also begin to take place between lime and clay. Some materials begin to melt at about 1250 °C and formation of the major compounds, for example, C_3S, β-C_2S, C_3A and C_4AF begins to take place above about 1280 °C.

2.1.2. THE CHEMISTRY OF CEMENT

2.1.2.1. Portland Cement Phases Manufacture

The main phases with significant cementious properties in Portland cement with respect to strength are C_3S and β-C_2S. C_4AF and C_3A are of little significance in this respect as illustrated in figure 2.2 [19]. 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 that 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.

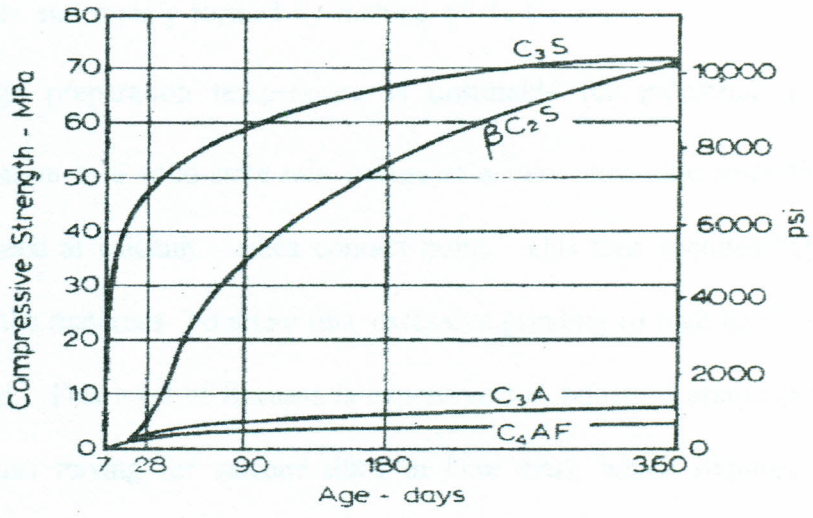


Figure 2.2: Compressive strength of the various component phases of Portland cement [19].

Under laboratory conditions, using 74 % CaO and 26 % SiO_2, C_3S is slowly formed at between 1250 °C – 2100 °C [20] according to equation (2.1)

$$3CaO + SiO_2 \xrightarrow{1250 - 2100\ ^\circ C} 3CaO.SiO_2 \quad \text{.....(2.1)}$$

Below 1250 °C, only a little of β-C_2S is formed. C_3S melts above 2100 °C and decompose to β-C_2S and CaO, hence its formation cannot be accelerated by melting the mixture. This thus causes an industrial problem. When other

compounds capable of forming a liquid phase in the stability range of C_3S are added to the mixture of CaO and SiO_2, the two components can dissolve in the liquid phase, react to give C_3S and crystallize out. Al_2O_3 and Fe_2O_3 form the liquid phase.

β-C_2S is exclusively and rapidly formed by melting 65 % CaO and 35 % SiO_2 at 2130 °C. Its high preparation temperature is unsuitable for industrial use. However its formation in a solid-state mix occurs at a very slow rate since the reaction only proceed at calcium – silica contact point. This thus requires high level of mixing of the materials. To attain this, extensive grinding to high levels of fineness is required. This level of fineness is expensive for industrial attainment. Nature provides this mixing for calcium-silica in lime marl, which requires a lower level of grinding [21].

2.1.2.2. Hydration of Portland Cement

When cement comes into contact with water its strength starts to develop. This is referred to as the hydration of cement. The process involves reaction between water and the main phases of cement to form hydrated compounds that build up the composite concrete [22].

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 [23].

When calcium silicates hydrate under a limited amount of water as in the case of cement paste, they undergo hydrolysis to produce calcium silicate hydrate ($C_3S_2H_3$) and calcium hydroxide (CH). The products of hydration of C_3S and β-C_2S are considered to be the same from consideration of their heat of hydration and surface area of the products of hydration [22]. Hydration of these phases is represented in equations (2.2), (2.3) and (2.4) [24,25]

$$2C_3S + 6H \longrightarrow C_3S_2H_3 + 3CH \quad \text{.....(2.2)}$$

$$2C_2S + 4H \longrightarrow C_3S_2H_3 + CH \quad \text{..... (2.3)}$$

The hydration product of C_3A is a prismatic dark interstitial material [26],

$$C_3A + 6H \longrightarrow C_3AH_6 \quad \text{.....(2.4)}$$

This reaction represented by equation (2.4) is exothermic. It leads to an immediate stiffening of the cement paste; commonly referred to as flash set. Gypsum, ($C\overline{S}H_2$) or anhydrous calcium sulphate ($C\overline{S}$) is added to cement to slow down this reaction. Gypsum reacts with C_3A to form a crystalline

impermeable layer called ettringite on unhydrated C_3A, which temporary prevents further hydration of C_3A for about 1-2 hours [35].

$$3C\overline{S}H_2 + C_3A + 26H \longrightarrow C_6A\overline{S}_3H_{32} \quad \text{.....(2.5)}$$

Ettringite

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, that is after about 24 hours when substantial degree of hardening of the cement paste has occurred. Gypsum is found to disappear from the mixing water into the paste, its role as a setting retarder is over. However, C_3A still present attacks the ettringite and calcium hydroxide as represented in equations (2.6) and (2.7) [27].

$$2C_3A + C_6A\overline{S}_3H_{32} + 4H \longrightarrow 3C_4A\overline{S}H_{12} \text{.....(2.6)}$$

$$C_3A + CH + 12H \longrightarrow C_4AH_{13} \text{.....(2.7)}$$

The hydration products of C_3A are of no binding significance [28] and in addition, its attack by sulphates (from acidic environment and excess gypsum) leads to formation of ettringite as in equation 2.5. This ettringite formed is expansive because it is formed on hardened paste.

C_4AF hydration reaction is much slower than that of C_3A. Its reaction proceeds as represented in equation (2.8) [29].

$$C_4AF + 4CH + 22H \longrightarrow C_4AH_{13} + C_4FH_{13} \quad \text{.....(2.8)}$$

2.1.3. MECHANICAL STRENGTH OF HYDRATED CEMENT PASTE.

Mechanical strength accounts for the binding ability of cement paste. It is related to the interactive forces, or bonds acting both within the individual products of cement hydration (intraparticle bonds) mainly chemical and forces between products of cement hydration and aggregates (interparticle bonds) primarily physical. The main bonding hydration product of cement is the $C_3S_2H_3$ resulting from hydration of β-C_2S and C_3S. $C_3S_2H_3$ is made up of a random arrangement of the particles bonded together by surface forces with occasional strong ionic-covalent bond linking adjacent particles. The cement-aggregate interparticle force growth develops through deposition of $Ca(OH)_2$ film on the aggregate surface. This is covered by a layer of elongated $C_3S_2H_3$ particle producing a hair-brush morphology. Secondary large $Ca(OH)_2$ crystals finally fill space near the $Ca(OH)_2$ – $C_3S_2H_3$ interfaces. Cement-aggregate bonds thus result from some combination of mechanical interlocking of the hydrated cement with the aggregate surface [30,31].

2.2. POZZOLANAS

A pozzolana is defined as a siliceous and/or aluminous materials which in itself, possesses little or no cementious 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 cementious properties [32]. The name pozzolana is derived from the village of Pozzuoli in Italy, where the Romans quarried volcanic ash. This was the first pozzolana that formed cement with hydraulic properties when mixed with lime putty [33]. Many other materials, both natural and artificial, have this pozzolanic property. Builders from Roman times to the present day have extensively used pozzolanas either in conjunction with lime, or more recently with Portland cement.

Pozzolanas occur either naturally or can be made artificially. The natural pozzolanas are mostly materials of volcanic origin, but include certain diatomaceous earths. The pozzolanas of volcanic origin consist of glassy materials or compacted tuffs arising from the deposit of volcanic dust and ash [33]. Artificial pozzolanas are mainly products obtained by heat treatment of natural materials, such as pulverized fired clay or BB (made by grinding up reject bricks and tiles from the brick tiles kiln), certain siliceous rocks, pulverized fuel ash (PFA) and ash from agricultural wastes such as RH [19, 34]. Ignorance of the potential for cements from pozzolanas in many countries, including Kenya, has often meant that these potentially, very cheap locally available materials are not

used. However other countries, for example, India and Egypt have progressed in their production technology and use.

2.2.1. NATURAL POZZOLANAS

Natural pozzolanas are formed from volcanic ash and dust that has undergone rapid cooling and in some cases has subsequently suffered considerable chemical alteration. The alteration is generally attributed to the action of superheated steam and carbon dioxide below the earth surface. The effect of this has been to convert much of the original materials into a more chemically reactive modification, whilst the basic constituents have been partially removed under the combined influence of the carbon dioxide and water.

Volcanic materials owe their pozzolanic properties to the volcanic glass. Volcanic ash with high content of crystalline minerals is much more stable and show low pozzolanic activity [35].

2.2.2. ARTIFICIAL POZZOLANAS

When pulverized coal is burnt in boilers, the resultant ash consists of roughly spherically shaped particles. This ash is called pulverized fuel ash (PFA) and has pozzolanic properties [36]. It is mainly composed of glassy siliceous materials whose components combine with hydrated lime during hydration of cement. The rate of reaction of PFA with hydrated lime is increased by fine pulverization of

the coal before firing. It can also be increased by grinding of the fly ash in a ball mill to a higher fineness [37] and effective moist curing at high temperature [38]. PFA use in concrete improves on workability of the concrete due to the spherical shape of glass particles, retardation of C_3A hydration due to its SO_3 content hence maintaining workability for long [39, 40]. PFA reactivity with hydrated lime to form cementious material is detected as early as a few hours after mixing and significantly after 28 days [41, 42].

Rice husks are solid waste materials obtained from rice processing factories. Their disposal methods include burning in open field or as source of fuel. RHA is applied in rice farms to increase productivity and as an anti-caking agent in fertilizers [43]. These methods do not utilize fully its high silica content due to its inert form [34]. When RH are burnt under controlled conditions, pozzolanic RHA is produced. The potential of RHA as a cement lies in its high silica content and high proportion of ash by weight in plant residue compared to other plant residues [34]. Table 2.2 shows percentage silica content and proportion of ash by weight in some plant residues.

RHA as a pozzolana is based on the nature of silica in the ash: Crystalline silica is less reactive than amorphous silica. The presence of amorphous silica depends on the combustion temperature of RH. Different researchers have reported different processing conditions of the RH which give amorphous silica rich RHA. Under

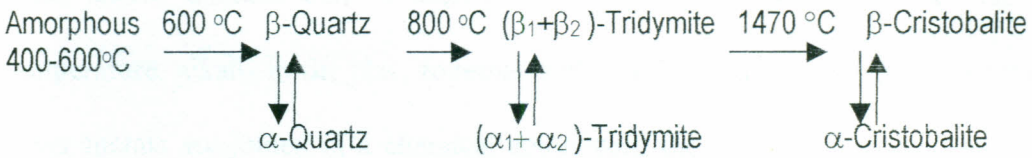
different conditions of incineration of the RH, amorphous silica dominates below a defined temperature over which quartz, crystabillite and tridymite silica in the ash are predominantly formed [44, 45].

Table 2.2: Percentage silica content and proportion of ash by weight in plant residues [34].

Plant	**Part of Plant**	**Ash %**	**Silica %**
Sorghum	Leaf sheath epidermis	12.55	88.70
Wheat	Leaf sheath	10.4	90.56
Corn	Leaf blade	12.15	64.32
Bamboo	Nodes (inner portion)	1.49	57.40
Sugar-cane	Baggasse	14.71	73.00
Lantana	Leaf & Stem	11.24	23.28
Sunflower	Leaf & stem	11.53	25.32
Rice	Husks	22.15	93.00
Rice	Straw	14.65	82.00
Breadfruit	Stem	8.65	81.80

Ochungo [46], reported that, when it is produced at temperatures in the range of 200-700 ^{0}C in a highly ventilated kiln, the ash consist predominantly of amorphous silica. A 12 hours incineration of RH at 800 °C produces a large proportion of the amorphous silica [47]. For prolonged periods, under oxidizing conditions, amorphous silica is produced at temperatures below 500 °C or up to 680 °C for less than one minute [44]. Yeoh *et. al* [48] observed that for less than one hour, amorphous silica could still be produced below 900 °C. Kapur [47] concluded that an increase in temperature for a given incineration period,

increases crystalline form. Austrheim [49] observed the following structural transformation of silica in RH as a function of incineration temperature



Specific surface area of RHA particles is influenced by both time and temperature of incineration [50]. Specific surface area influences RH chemical activity. Vigorous combustion leads to collapse of the pore structure and hence pyroprocessing in an oxidizing atmosphere reduces specific surface area. Under slow combustion rate, greater specific surface area is obtained [50].

RHA from rice mills and hydrated lime ground together in a small ball mill has given suitable cement for masonry mortar [51]. Alternatively, RH is mixed with clay (1:1) and water and shaped into cakes. These are then dried in the sun and fired in an open clamp. The product is ground to a fine powder in a ball mill to pass through a 200- mesh (75 micron) sieve. If the clay content of the soil is greater than 20 %, a highly reactive pozzolana is produced. Burning of rice husk and waste-lime sludge mixture produces hydraulic binder for making masonry mortar, plaster and concrete [52].

Burnt clays have been used as pozzolana for a long time. Romans used crushed pots and bricks in their mortars in Northern Europe. In India, grinding reject

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bricks and tiles in a ball mill or hammer mill has made pozzolana, and it has been sufficiently reactive to make masonry mortars [53]. In brick making, highly rich silica and/or alumina clay is heated up to a temperature of 900 °C. At this temperature, alkalis in the clay, together with small amounts of oxides of iron and other metals are joined in a chemical union with the alumina and/or silica in the clay to form a dense and durable mass. Between 600 - 900 °C, all common clay minerals make active pozzolanas depending on the nature of clay [53]. At this temperature the chemically bound water is driven off rendering silica and/or alumina free to react with hydrated lime at room temperature to form cementious material [53, 54].

SBE in most developing nations, for example Kenya, has no proper disposal method. The SBE from Nairobi, for example, is dumped on land surface in the designated dumping site at Dandora. Dumping leads to land degradation. The accumulation effects reduce land available for settlement or industrial activities. SBE contains a lot of oil, which is an organic biodegradable matter. When it is introduced to water bodies through runoff water, it notably and immediately increases the biological oxygen demand (BOD) and chemical oxygen demand (COD) just like oil spills into water [55]. This leads to death of aquatic life as well as deterioration of recreational and aesthetic value [56]. The oil and dust particles introduced in water bodies poses a threat to aquatic life as a result of

deoxygenating and clogging the lower water levels as well as clogging of fish gills [57].

No literature has been cited on the use of SBE as pozzolanic material. The potential of using SBE as pozzolanic material was investigated in this study. This was based on existing literature on the mineralogical composition and chemical constituent of the unspent bleaching earth.

2.2.3 POZZOLANIC ACTIVITY

The reaction between pozzolana, hydrated lime and water to form compact hard materials at ordinary temperature is called pozzolanic activity. Pozzolanas react with hydrated lime because of the presence of active amorphous silica and alumina, which react with calcium hydroxide at room temperature [58]. In the pozzolanic reaction, chemisorption of $Ca(OH)_2$ on the surface of silanol groups dissolves silica because of the high pH of the solution. Silica reacts with $Ca(OH)_2$ to form a hydrated layer on its surface [59]. The mechanism of the hydration reaction of pozzolana - calcium hydroxide has been described by Takemoto and Uchikawa [60].

On mixing pozzolana and calcium hydroxide with water, the liquid becomes saturated with calcium hydroxide within a very short time;

$$Ca(OH)_{2(S)} \xrightarrow{H_2O_{(l)}} Ca^{2+}_{(aq)} + 2OH^-_{(aq)} \quad \text{.....(2.9)}$$

Water attacks pozzolana grains protonically thereby dissociating the $Si(OH)_4$ groups on the grain surface to silicate (SiO_4^{4-}) and hydroxonium (H_3O^+) ions. This leaves the pozzolana grains being negatively charged;

$$Si(OH)_{4(S)} + 4H_2O_{(l)} \longrightarrow SiO_4^{4-}{}_{(aq)} + 4H_3O^+_{(aq)} \quad \text{.....(2.10)}$$

Electrostatic adsorption of calcium ions on the grain surface then takes place. Sodium and potassium ions in the pozzolana are then released into the liquid phase. The dissolving out of the two cations (K^+ and Na^+) leaves a thin amorphous silica-alumina rich layer on the surface of the pozzolana grains. Silicate and aluminate ions in the layer gradually begin to diffuse to the surface. At the surface, they react with calcium ions forming the respective silicate and aluminate hydrates thereby increasing the thickness of the layer. Calcium silicate hydrates precipitates out more easily than calcium aluminate hydrate due to the higher electrostatic charge on silicates than on aluminates [69].

$$SiO_{2(s)} + nCa^{2+}_{(aq)} + 2nOH^-_{(aq)} \longrightarrow nCaO.SiO_2.nH_2O_{(s)} \quad \text{...(2.11)}$$

The calcium silicate hydrate formed accounts for the compact hard material formed by the mixture of pozzolana, hydrated lime and water in the pozzolanic reaction.

2.2.4. FACTORS AFFECTING POZZOLANIC ACTIVITY

Chemical and mineralogical composition, morphology, the amount of glassy phase and fineness influence the pozzolanic activity [61]. Admixtures and thermal treatment of pozzolanas also influence the reactivity. Long-term strength development is influenced by the amorphous structure or glass phase and high silica-alumina content. Fineness influences the short-term reactivity [61]. Temperature accelerates the hydrated lime-pozzolana reaction just like other chemical reactions. Luke and Glasser [62] 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. At elevated temperatures, however, other dependent factors as solubility of cement compounds and stability of hydration products reduce pozzolanic activity. Above 75 °C, for example, ettringite is converted to monosulphate, which decomposes to hydrogarnet at even higher temperature [63]. This decreases the strength of pozzolana-hydrated lime cements.

2.2.5. ASSESSMENT OF POZZOLANIC ACTIVITY

An assessment of pozzolanic activity is essential before any material is used for making pozzolanic cement. The quality of pozzolana is assessed through chemical and/or physical means. The analysis are done on the sample which have been ground to a given fineness level. The ASTM C 593 [58] requires that the maximum percentage retention in a 600 μm sieve be 2.0 percent and for 75 μm

sieve be 30 percent when wet sieved. This is because fineness affects both pozzolanic activity and W/C ratio demand [37]. The chemical means include pozzolanicity test and chemical constituent analysis whereas physical methods include compressive strength of pozzolana-hydrated lime cement, setting time, pozzolanic activity index among others.

Pozzolanic activity index is a measure of the ratio of compressive strength for partial replacement of cement by pozzolana to that of a mix without replacement. The outcome of the test is influenced by the cement used, especially its fineness and alkali content [64]. This index may not give the actual contribution of the pozzolana in the observed ratio. In fact it only shows the extent of reduction of strength of replaced cement by the pozzolana addition.

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 molded 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 7^{th} and/or 28^{th} day of curing [58]. This is the ultimate method of assessing pozzolanic activity as it gives the actual strength of the pozzolana-hydrated lime cements.

Setting time has also been used for assessing both Portland and pozzolana-CHL cement. A penetration test is done on paste to determine the right W/C ratio for forming a workable paste. Initial setting time and final setting range gives the time span of cement paste between which it hardens to an unworkable paste. Setting time allows for placement and workability of cement. Blanks and Kennedy [19] stated that pozzolanic cement should set at between 50 and 100 hours. Kenya Standard (KS 02 1263 of 1993) [1] allows for between 45 and 600 minutes for PPC.

Chemical means employ a Pozzolanicity test [65] which compares the quantity of $Ca(OH)_2$ produced by hydration of neat cement (saturated medium) and pozzolanic cement in a solution with a W/C ratio of 5.0. If the concentration of $Ca(OH)_2$ in the solution is lower than that of the saturated medium, the cement satisfies the test of pozzolanicity. The underlying principle is that the pozzolanic activity consist of fixing calcium hydroxide by the pozzolana, so that the lower the resulting quantity of calcium hydroxide, the higher the pozzolanicity. International standard for organization (ISO) 863 1990 (E) standard pozzolanicity diagram (solubility curve) as given in figure 2.3 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 [65].

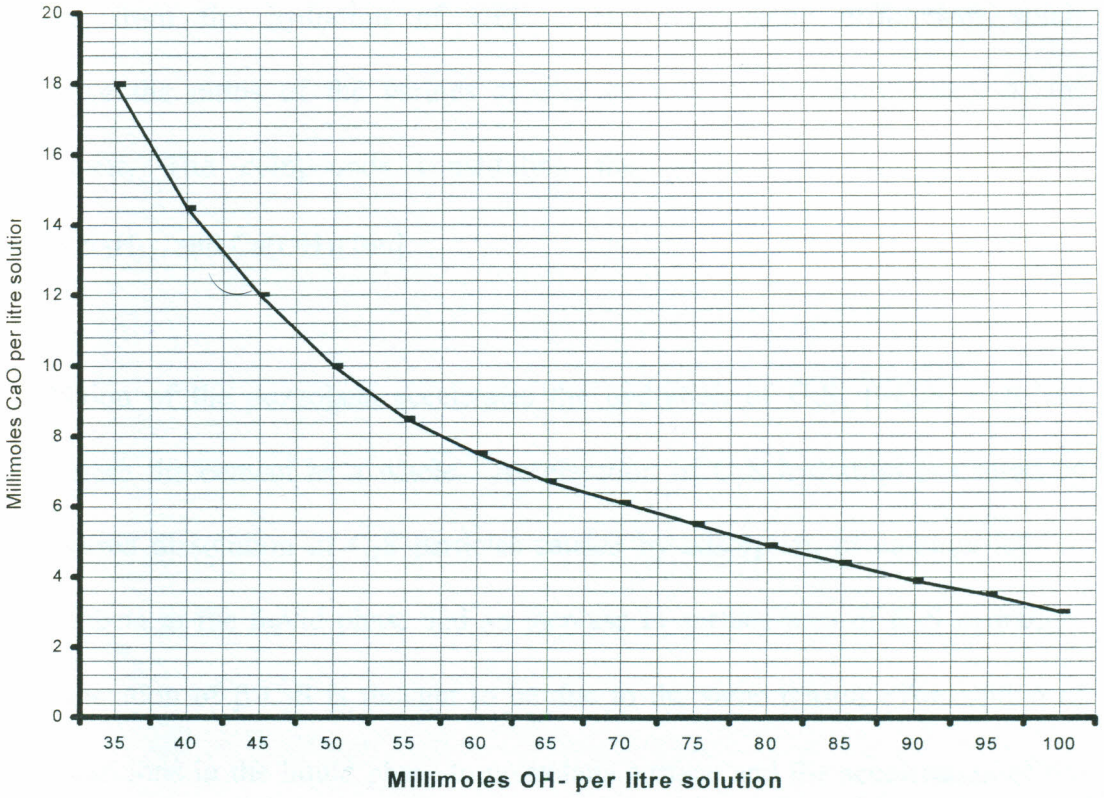

Figure 2.3; Pozzolanicity Test Diagram[65]

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.

2.3. HYDRATION OF POZZOLANA - CEMENT SYSTEM

The products formed on hydration of pozzolanic cement are generally the same as those from the hydration of OPC. However, some differences solely 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, $C_6A\overline{S}_3H_{32}$, and $Ca(OH)_2$ [66].

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 surface area of C_3S hydration. Acceleration of β-C_2S is thought to be due to the same reason. Adsorption of calcium ions in the liquid phase to pozzolana surface and the acceleration of the dissolution due to the precipitation of ettringite on the pozzolana surface also accelerate C_3A hydration. C-S-H and C-A-H from pozzolana-calcium hydroxide reaction are formed after one day and their physical properties develop in stages [67].

2.4. ADVANTAGES OF POZZOLANA ON MATURED CONCRETE

2.4.1. ACID AND SULPHATE ATTACKS

Liquids with a pH below 6.5 attack concretes [68, 69]. Acid rains, which consist of sulphuric acid and nitric acid with a pH of 4.0-4.5 cause surface weathering of exposed concrete [70]. Sulphuric acid attacks $Ca(OH)_2$ as in equation (2.12) [71]

$$Ca(OH)_2 + H_2SO_4 \longrightarrow CaSO_4 + 2H_2O \quad \text{.....(2.12)}$$

Use of pozzolanic cement is beneficial in reducing the ingress of aggressive substances. Pozzolana fixes $Ca(OH)_2$ which is usually the susceptible product of hydration of cement as far as acid attack is concerned. In addition, pozzolana prevents ingress of sulphates into concrete by making the concrete denser with low permeability. This is achieved by additional cementious material formed by the pozzolana - $Ca(OH)_2$ reaction. Blended cement with pozzolana is thus recommended for moderate and severe exposure to sulphates. A blend of sulphate resisting cement and pozzolana between 25 and 40 percent of total cementious materials is recommended [72, 73].

2.4.2. COMPRESSIVE STRENGTH OF PORTLAND POZZOLANA CEMENT

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. PPCs have a slow strength gain rate due to a low pozzolana-$Ca(OH)_2$ reaction hence require

curing over a comparatively long period [73]. This depends on the degree of replacement of the cement and the reactivity of the pozzolana as exemplified in figure 2.4 [4].

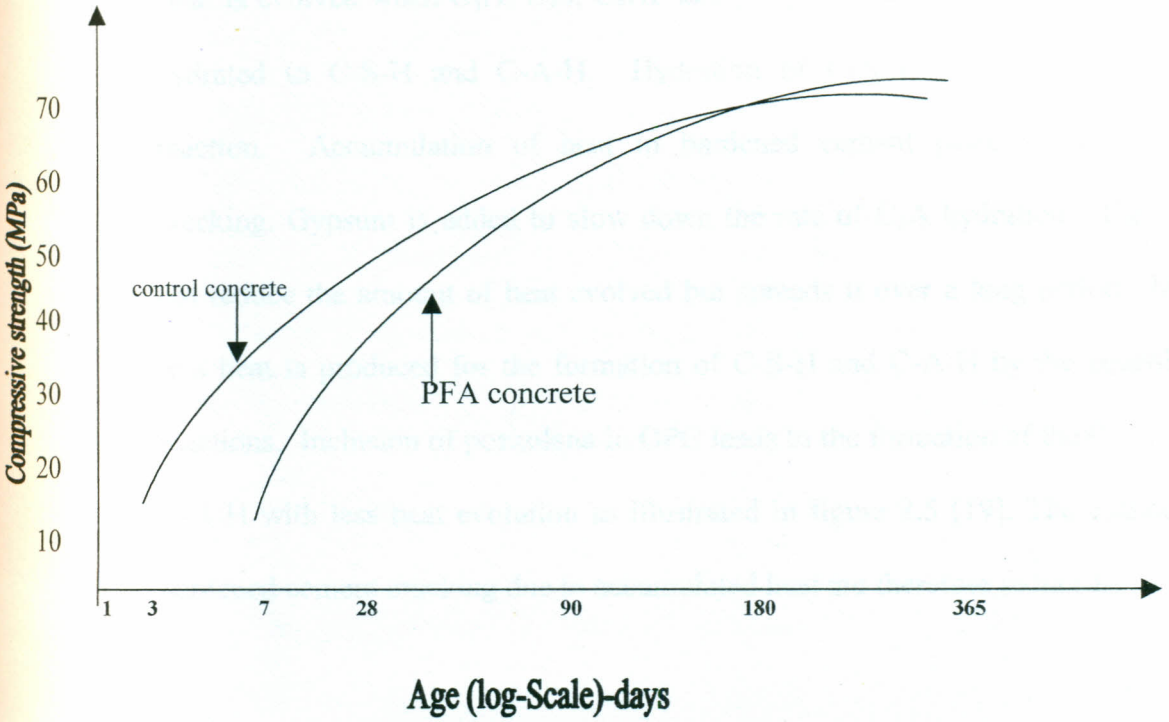

Figure 2.4: Relative rates of strength development of OPC (control) and concrete with fly ash replacement [4]

The early strength of PFA concrete is low from the figure above. This is so because initially less cement is available to hydrate and form cementious material. As it does so, it releases $Ca(OH)_2$, which reacts with the pozzolana to form additional cementious material. Control concrete have more cement initially which hydrates to form cementious material and $Ca(OH)_2$. Since no pozzolana is available to react with the $Ca(OH)_2$ released, no additional cementious material is formed. The control reaches its maximum hydration as the PFA concrete

continues to hydrate for a period of about five years and hence the observed long-term increase in strength [4].

2.4.3. HEAT OF HYDRATION

Heat is evolved when C_3A, C_3S, C_4AF and β-C_2S phases of Portland cement are hydrated to C-S-H and C-A-H. Hydration of C_3A is the most exothermic reaction. Accumulation of heat in hardened cement paste causes thermal cracking. Gypsum is added to slow down the rate of C_3A hydration. This does not reduce the amount of heat evolved but spreads it over a long period. Much less heat is produced for the formation of C-S-H and C-A-H by the pozzolanic reactions. Inclusion of pozzolana in OPC leads to the formation of the C-S-H and C-A-H with less heat evolution as illustrated in figure 2.5 [19]. The chances of hardened cement cracking due to accumulated heat are therefore reduced.

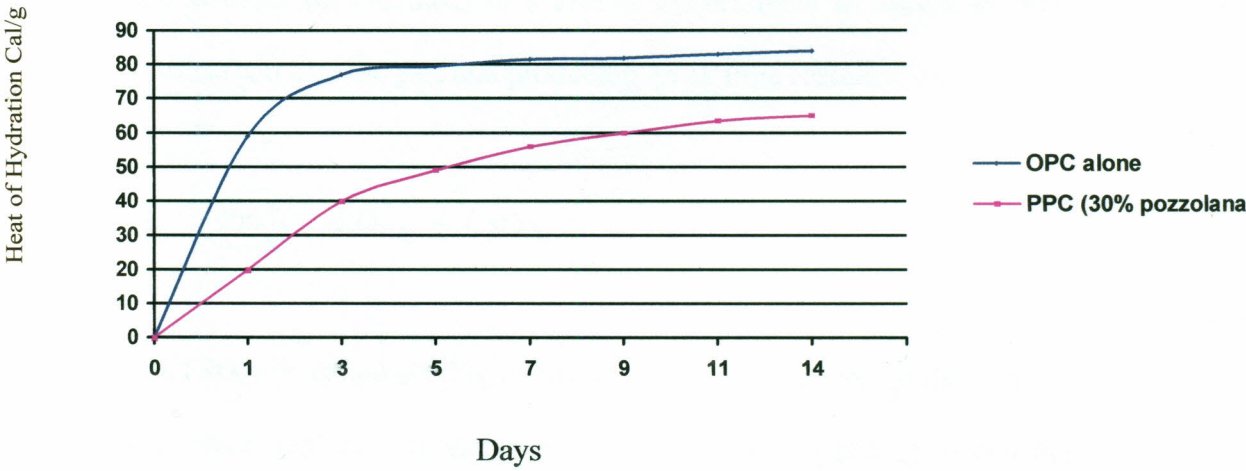

Figure 2.5; Relative heats of hydration of OPC and PPC [19]

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2.4.4. ALKALI-AGGREGATE REACTION

Some aggregates contain silica in a form, which reacts with Na_2O and K_2O present in Portland cement to form expansive alkali-silica-gel [74]. Pozzolana react with $Ca(OH)_2$ liberated by the hydration of Portland cement thereby lowering the pH of the pore solution and hence reduce alkali-silica reaction in the aggregate. Alternatively, reactive glass phase of silica in pozzolana consume the alkali to form non-expansive calcium-alkali-silica gel leaving no free alkalis. Pozzolana also reduces permeability of concrete due to formation of additional cementious material. This reduces moisture movement in the concrete. All these factors lower the possibility of the alkali aggregate reaction [75, 76].

2.5 LIME

Lime is made from calcium carbonate through a two-stage process. First, limestone is burnt (or calcined) in a kiln at temperatures in excess of 900 ^{0}C, driving off carbon dioxide gas, and producing quick lime (calcium oxide).

$$CaCO_{3(S)} \xrightarrow{\geq 900\ ^0C} CO_{2(g)} + CaO_{(S)} \quad \text{.....(2.13)}$$

The second stage is called slaking or hydration. Water is added to the quicklime. Quicklime reacts rapidly with water, evolving heat and expanding so that lumps of quicklime break down to a fine powder called slaked or hydrated lime (calcium hydroxide) [77]

$$CaO_{(S)} + H_2O_{(l)} \longrightarrow Ca(OH)_{2(S)} \quad \text{.....(2.14)}$$

Although slaking of lime generates heat, the overall process requires a lot of energy. The process is thus expensive making the product expensive [78]. This calls for cheap alternative source of $Ca(OH)_2$.

ALS has limited uses. Most legislation restricts the methods of storage and disposal of the ALS. It has become increasingly important to find consumers for the by-product [79]. The ALS is marketed for industrial wastewater treatment, neutralization of spent pickling acid, as a soil conditioner in road construction, and in the production of sand – lime bricks [79]. In Kenya, the ALS is cheaply sold to road constructors and white wash manufacturers. Since hydrated lime is a necessary component of pozzolanic cements, ALS could thus be a cheap raw material for making cementious materials. The ALS can be thermally dried to remove excess water and used in pozzolana-hydrated lime cements. This possibility has been assessed in this work.

2.6 BLEACHING EARTHS

These are clays with finely crystalline silicates of aluminium and/or magnesium with variable amounts of water of hydration. Bleaching clays are classified as Fuller's earth and bentonite according to their inherent properties [80].

Fuller's earth is clay that in its natural form has the capacity to decolorize oils, fats and grease. Most Fuller's earths have high silica and alumina content. The high silica content may have some bearing in its decolorizing power. It is made up of mainly attapulgite clays [81].

Bentonites are clays produced by devitrification of volcanic ash. The main types of these clays are Wyoming and sub-or meta-bentonite. The meta-or sub-bentonite type have high decolorizing ability after acid treatment and are identical to the Fullers earth in this respect, while the Wyoming type have no such property. Bentonite clays mainly consist of Montmorillonite, although some may consist of the rare clay minerals beidellite and nontronite with fragments of kaolinite, illite felspar, gypsum, unweathered volcanic ash, calcium carbonate, quartz and traces of other minerals [81].

Properties of clays, their classification and relation to one another are best understood when their lattice structure is known. Basically the clay minerals are built up from layer lattice structures stacked parallel to each other in sandwich fashion normal to the c-axis of the crystal. The structure of montmorillonite, for example, proposed to be as shown below in figure 2.6, shows that a gibbsite ($Al(OH)_3$ unit) layer is sandwiched between two silica sheets, to form the structural unit [82].

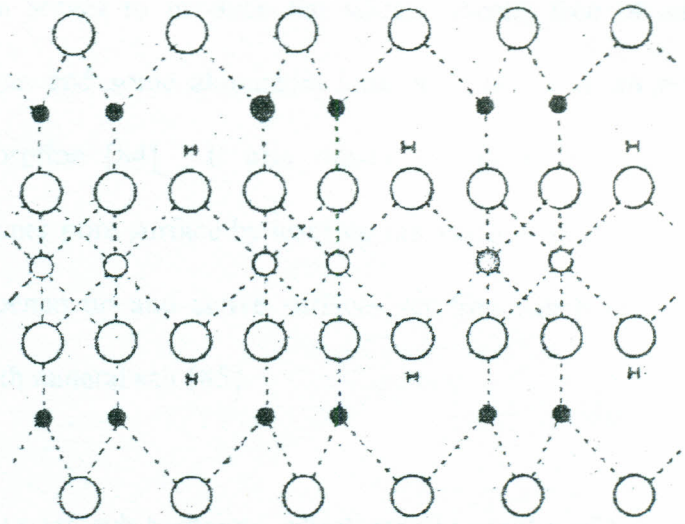

Figure 2.6; Schematic representation of montmorillonite clay [82].

Key; Big circles represent Oxygen atoms

Small circles represent Silica atoms

Small shaded circle represent Aluminium atoms.

Bleaching clays are often subjected to various physical and chemical treatments to enhance their adsorptive capacity. This gives them certain desirable properties with respect to their application. All such processes are called "activation". Acid and heat-activation are some of the examples. The mostly used activation method is the acid-activation [83].

2.6.1 ACID ACTIVATION OF BLEACHING EARTHS

Acid-activation serves to produce flat silicate sheets, free of adsorbed cations except hydrogen and some aluminium ions, and thus give an extended surface useful in adsorption [84]. It also causes enlarging of capillaries and hence increases the inner pore surface by leaching out various mineral constituents. The structure is opened up and active surfaces set free which in their natural form were sealed with mineral salt [85].

Activatable clays are sub-bentonite, which mostly consist of low swelling type of montmorillonite. Interstratified structure of illite and montmorillonite with appreciable base-exchange capacity are also activatable. Acid treatment in effect replaces exchangeable K^+, Na^+ and Ca^{2+} by H^+ in the interlamellar space and also leaches out a part of the Al^{3+}, Fe^{2+} and Mg^{2+} from the lattice structure. This renders the clay physically more porous and electro-chemically more active [86]. Hydrochloric and sulphuric acid are the frequently used activating agents. Since silicon-oxygen layers sandwich both sides of the basic lattice constituents and on account of relatively small openings in the silicon-oxygen network, the removal of Al^{3+} and others, can only be achieved through broken silicon-oxygen layer [86]. The changes taking place in an idealized montmorillonite may be expressed as in equation (2.15) and (2.16)

$$(Al_4)\,(Si)_8\,O_{20}\,(OH)_4 + 3H^+ \xrightarrow{\uparrow H^+} (Al_3)\,(Si_8)\,O_{20}\,(OH)_2 + Al^{3+} + 2H_2O \quad ..(2.15)$$

and

$$(Al_4)(Si)_8O_{20}(OH)_4 + 6H^+ \xrightarrow{2H^+} (Al_2)(Si_8)O_{20} + 2Al^{3+} + 4H_2O \quad \ldots(2.16)$$

At this stage, half the aluminium atoms have already been removed from the structure together with two hydroxyl groups. The remaining Al^{3+} ions are tetrahedrally coordinated with four remaining oxygen atoms. This change from octahedral to tetrahedral coordination leaves the crystal lattice with negative charge, which is balanced by a hydrogen ion. In other words the acid-activated clay becomes negatively charged on the crystal surface and is neutralized by hydrogen ions at the interface. This is considered to be the cause of acidity associated with the activity of bleaching [86]. As the acid treatment proceeds, greater dissolution of octahedral aluminium ions occurs and a silica-tetrahedral skeleton remains at the end.

$$\overset{2H^+}{(Al_2)}(Si_8)O_{20} + 3H^+ \xrightarrow{H^+} Al^{3+} + (Al)(Si_8H_4)O_{20} \quad \ldots\ldots(2.17)$$

$$\overset{2H^+}{(Al_2)}(Si_8)O_{20} + 6H^+ \longrightarrow 2Al^{3+} + (Si_8H_8)O_{20} \quad \ldots\ldots(2.18)$$

2.6.2. MECHANISM OF BLEACHING

The mechanism of bleaching is such that when a reagent attacks a surface, it leaves the acid and basic constituents out of balance on the surface. The open bonds thus created may be limited to the visible surface or of a lamella cleavage surface. The bleaching action of clays involves the union (or interaction) of acidoid particles (of clays) with the basic coloured ions in suspension [87].

King and Wherton [88] suggested that bleaching of vegetable oil with adsorbent materials involves adsorption, oxidation and other chemical reactions. They concluded that in decolorizing oils, four reactions control the mechanism, and that equilibrium exist between two favorable and two unfavorable reactions. Adsorption of colour and oxidative decrease in colour are favorable, oxidative increase in colour and stabilization against adsorption are unfavorable. Adsorbents are shown to catalyze the oxidation reaction.

Commercial bleaching is carried out by either percolation or contact process. Percolation process is for bleaching lubricating oils. In contact process, the clay used is mainly acid activated for bleaching vegetable oils. In this process, a required proportion of the oil and clay is mixed and heated to between 80 to 120 °C for 10-20 minutes. The slurry is then filter pressed to remove clay [11]. The sludge clay after filter pressing is the spent bleaching earth (SBE).

2.6.3 THERMAL ANALYSIS OF BLEACHING EARTHS AND POZZOLANIC ACTIVITY

Thermal analysis involves investigational methods on physical properties of a sample continuously subjected to a controlled temperature change. Such physical changes are in mass that forms the bases of thermogravimetry (TG) and in energy that forms the bases of differential thermal analysis (DTA). Derivative thermal gravimetry (DTG) curve represent the rate of mass change as a function of temperature or time [89]. Basically, acid activatable earths have been shown to be mainly montmorillonite. Pure montmorillonite clays show three main peaks in TG, DTG and DTA as shown in figure 2.7 [90, 91]. The three main peaks correspond to:

- 1-2- loss of adsorbed water
- 3 - loss of structure water
- 4 - Transformation - Recrystallisation peak.

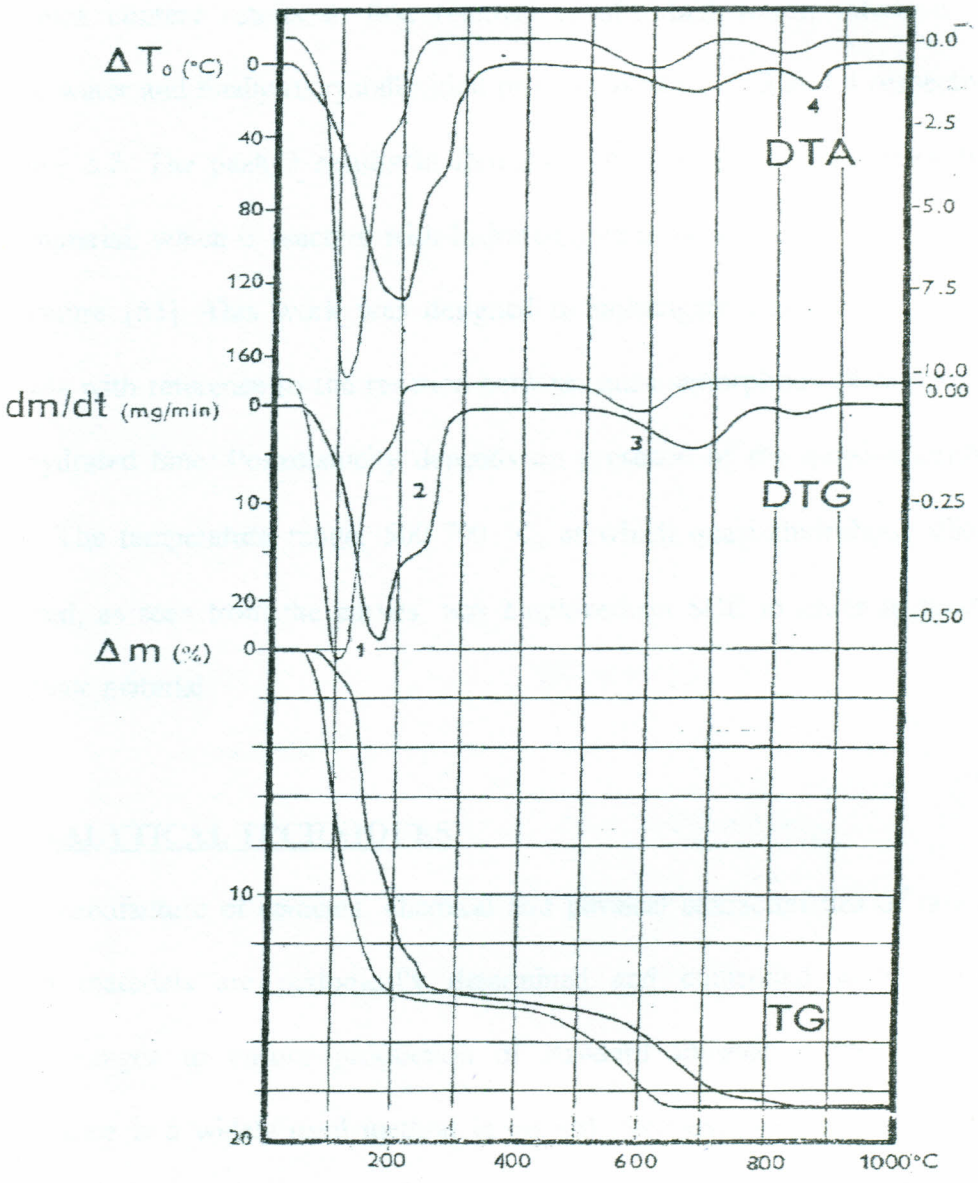

Figure 2. 7: Thermal analysis of Montmorillonite clay [90, 91]

Peak 3 is the most important peak as far as pozzolanic activity of clays is concerned. The peak occurs at 500 – 700 °C. This corresponds to the temperature at which the clay undergoes dehydroxylation.

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Thermal analysis helps to monitor heating effects on a sample. Heating clays with high silica content results in first removal of absorbed water, interlayer and hydrate water and finally recrystallization process, peaks 1-2, 3 and 4 respectively in figure 2.7. The peak 3 results in formation of a collapsed quasi-amorphous silica material, which is reactive with hydrated lime in presence of water at room temperature [53]. This work was designed to investigate pozzolanicity of test materials with reference to the reaction between quasi-amorphous silica materials with hydrated lime. Pozzolanicity depends on presence of the quasi-amorphous silica. The temperature range, 500-700 °C, at which quasi-amorphous silica is produced, as seen from the curves, was employed on SBE in order to produce pozzolanic material.

2.7. ANALYTICAL TECHNIQUES

In the manufacture of cements, chemical and physical characteristics of raw and finished materials are periodically determined and controlled within certain specific ranges to ensure production of standard finished product. X-ray fluorescence is a widely used method in cement chemical analysis for both raw and finished products. It is mainly used for analysis of Si^{4+}, Al^{3+}, Fe^{3+}, Mg^{2+} and Ca^{2+}. The method is widely used because it is quick, non-destructive and accurate especially for elements with large atomic number. Gravimetric analysis is used to compliment the technique. Due to rapid fall in accuracy of the X-ray technique for

elements with low atomic number, analysis of potassium and sodium in raw materials and finished products are carried out using flame photometry [92].

Physical analysis of raw materials and finished product mainly involves the particle size distribution in raw and finished materials, setting times and compressive strength of the finished product. Particle size distribution for pozzolana is mainly done through sieve analysis, setting time analysis by use of a Vicat apparatus while compressive strength analysis is carried out by a machine for cured cement cubes.

2.7.1. X-Ray FLUORESCENCE ANALYSIS (XRFA)

XRFA involves characteristic X-rays being emitted from transitions involving K and L electrons by excited sample atoms. The wavelengths and intensity of emission measurements are used for qualitative and quantitative analysis respectively [93]. Atoms in samples are excited by bombardment with primary X-rays. These are produced by bombardment of a target, mainly tungsten, with a stream of high-energy electrons or nuclear particles, at 20 to 50 KeV from a radioactive source such as Americium-241 (^{241}Am) [94]. The primary X-rays are directed onto a secondary target, the sample, where a proportion of the incident rays is absorbed. This absorption process leads to the ejection of inner K or L electrons from the atoms of the sample. Subsequently, the excited atoms relax to the ground state. During relaxation, many excited atoms will lose their excess

energy in the form of secondary X-ray photons as electrons from higher orbital drop into the "holes" in the K or L shell. The re-emission of X-rays in this way is known as X-ray fluorescence [92]. Not all excited atoms will relax by the re-emission of X-rays and the proportion that do so is known as the fluorescence yield factor ϕ. The amount of primary radiation absorbed I_a and the intensity of the fluorescence emission I_f are related through equation (2.21) [95]

$$I_f = \phi I_a \quad \text{.....(2.21)}$$

ϕ may be as high as 0.5 for heavy elements but falls off rapidly to about 0.01 for elements with atomic number less than 15 [95].

2.7.2 FLAME PHOTOMETRY

Flame photometry is based on the measure of the amount of radiation emitted by excited atoms in a flame. It is widely used in determination of sodium and potassium ions in samples. It involves introduction of a sample solution to a flame in form of aerosol, drying of the sample in the flame, dissociation of the sample to constituent atoms, followed by thermal excitation and finally transition to ground state from excited state. During transition to ground state, a characteristic detectable radiation of a given intensity is emitted by the excited atoms. The intensity of emission is proportional to the concentration of the atoms in the sample. The concentration of the analyte in the sample is obtained from a

calibration curve plotted from emissions of known concentration of samples [93, 95]. Schematic representation of flame emission spectrometer is as shown in figure 2.8 below [96].

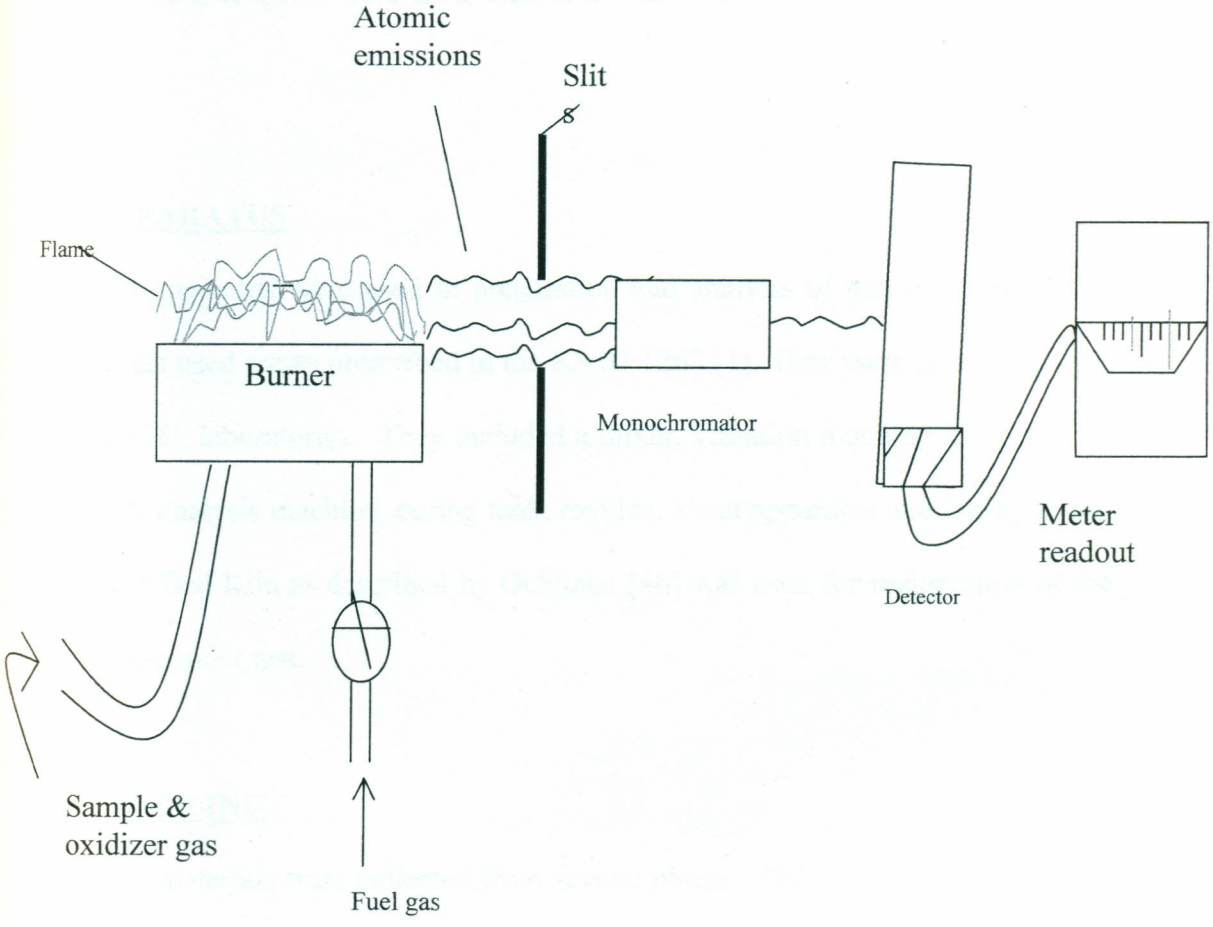

Figure 2.8; Schematic representation of flame emission spectrometer [96].

CHAPTER THREE

3.0 EXPERIMENTAL

3.1 REAGENTS

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

3.2 APPARATUS

Several apparatus were used in preparation and analysis of test materials. Most apparatus used are as prescribed in the KS 02 1263 [1]. They were provided in the E.A.P.C.C. laboratories. They included a mixer, vibration machine, compressive strength analysis machine, curing tank, moulds, Vicat apparatus and curing room. A Fixed Bed Kiln as described by Ochungo [46] was used for incineration of the materials under test.

3.3 SAMPLING

The test materials were collected from several places. SBE from Kasuku Packers (KAPA) and Unilever Kenya limited oil processing factories in Nairobi, RH from Mutithi rice milling station in Mwea, BB from Kenya Clay Products Limited and Clay Products Manufacturers in Nairobi, ALS from acetylene manufacturing company in Nairobi, Ptuff from E.A.P.C.C. in Athi River, laboratory made OPC and Bamburi OPC from E.A.P.C.C. Each of the samples as received from the

respective sources, was thoroughly mixed before being subjected to treatment. 200 g of the sample was taken for chemical analysis by spreading the material and taking 50 evenly spaced spoons in accordance with the ASTM C 593 [58]. The remaining samples were packed in plastic containers for further work as test materials.

3.4 CHARACTERIZATION OF RAW SBE

3.4.1 CALORIFIC VALUE

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 water to make 0.1M solutions. 0.1M 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 the 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 piece 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 pippeted into the bomb and the bomb assembled. The assembled bomb was tested

for circuit completeness by a firing circuit test plug. The bomb was finally filled with 30 bars of oxygen. Water was 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 in the calorimeter vessel and checked for any leakage (confirmed by absence of bubbling). Readjustment of 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 stabilise. The initial temperature of the calorimeter was taken after stabilising 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 to within 0.002 °C.

The following was done for correction purposes due to sulphates being converted to sulphuric acid and nitrogen dioxide to nitric acid. 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 CO_2.

The hot solution was titrated against the $Ba(OH)_2$ solution using phenolphthalein indicator to determine total acidity. 20 ml of the 0.1M 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 0.1M HCl solution using methyl orange as indicator.

3.4.2. OIL CONTENT OF SBE

Soxhlet apparatus were used. 100 g of the SBE was packed in the soxhlet thimble and fitted in to 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 sun dried 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.

3.4.3. IGNITION AND SELF COMBUSTION TEMPERATURES

1 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 still 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 desicator and weighed. The crucible and its content were reheated, cooled and weighed to a constant weight. The ash content was calculated as

$$\text{Ash content } \% = \frac{W_f \times 100}{W_o}$$

Where, W_o is original weight of sample

W_f is weight of sample after heating

3.5 TREATMENT OF TEST MATERIALS

5 kg of raw KAPA SBE as obtained from sampling site was calcined at 550 °C in an ordinary temperature monitored furnace model FSE-520-210P for four hours. The sample was labelled ''en- masse SBE''. 375 g of the raw SBE was thinly spread in a 20 cm by 40 cm container. It was subjected to the same treatment as

the en masse SBE. The resulting ashed SBE was finely ground using a laboratory ball mill KS 02 1263 of 1993 [1].

BB as obtained from the sampling site, was crushed using a laboratory crusher, then dried at 100 °C and ground using a laboratory ball mill.

500 g of the ground BB from Clay Works Manufacturers (C-W BB) was calcined at 600 °C for four hours in an ordinary temperature monitored furnace model FSE-520-210P. This sample was labelled ''activated C-W BB''.

RH as obtained from the sampling site, was fed into the fixed bed kiln (FBK) [46], a little paraffin put at the firing window and ignited. The temperature was controlled below 700 °C through the action of opening and closing the ventilation windows [46]. The resulting product was ground using a laboratory blender.

Ptuff as obtained from the sampling site, was first crushed using a laboratory crusher, then dried at 100 °C and finally ground using a laboratory ball mill.

8 kg of RHA, 5 kg of ashed SBE and 8 kg of ground BB were inter-ground using a laboratory ball mill. The sample was labelled ''ashed mixture''.

A blended raw mix of RH, SBE and ground BB was fed into the FBK [46]. This was done by thinly spreading 5 kg of RH at the base, then 8 kg of crushed and ground C-W BB followed by a thin spread of 5 kg of RH, then a spread of 8 kg of SBE and finally 30 kg of RH was spread over the whole mass. A little paraffin was put at the firing window and ignited. Temperature was controlled as for the RH above. This sample was labelled "Combined".

ALS as received, was first allowed to settle and the excess water decanted. 400 g of the decanted ALS was dried to a constant weight at 100 °C in an ordinary temperature monitored furnace. It was then ground using a laboratory blender and mixed thoroughly. 200 g of the resulting sample was sampled for chemical analysis and the rest parked in airtight plastic containers for the pozzolana–ALS cement investigations. CHL was used as received.

3.6 SIEVE ANALYSIS

50.00 g of treated pozzolanic samples were weighed into 90-μm and 212-μm [1] sieves. Water with sufficient pressure to push finer particles through the sieves but not to cause splash of the sample was applied. After 3 minutes of passage of water, the sieve and residue were put on a hot plate at 130 °C for 20 minutes. The dried residue was weighed and expressed as a percentage of wet sieved sample[1].

3.7 CHEMICAL CONSTITUENT ANALYSIS

3.7.1 CALCIUM HYDROXIDE CONTENT OF CHL AND ALS.

The calcium hydroxide content of CHL and ALS was determined in accordance with the ASTM C 593 [58] procedure as outlined below.

Sucrose solution was prepared by dissolving 100 g of table sugar in 200 ml of water. The solution was neutralized by dropwise addition of 0.1 M sodium hydroxide solution. 0.5 g of the sample was ground to pass through a 45-μm sieve [1]. The sample was digested with 50 ml of the sucrose solution for 15 minutes in a corked 250 ml conical flask. The solution was filtered immediately under vacuum through a Buchner funnel into a vacuum flask using a dry Whatman filter paper number 41. The conical flask and the residue were washed using cold water into the vacuum flask. To the filtrate, 5 drops of phenolphthalein indicator was added and the solution titrated against 0.1M HCl solution. The percentage concentration of calcium hydroxide, [$Ca(OH)_2$], in the sample was calculated as follows;

$$[Ca(OH)_2] = \frac{V \times 0.1 \times 74.09 \times 100}{1000 \times 2 \times M}$$

Where;

V is the volume of the 0.1M HCl used.

M is the mass of the sample taken.

74.09 is the mass of $Ca(OH)_2$.

3.7.2. X-RAY FLUORESCENCE ANALYSIS

10.0 g of the treated pozzolana sample was ground to pass through a 45-μm sieve. 1 g of flux (starch) was added and the mixture completely mixed by rolling and shaking in a plastic container. The resulting mixture was made into a pellet. The pellet was put into a sample cup of Sequential X-ray spectrophotometer (SRS) model 3000 for analysis of Si, Al, Fe, Mg, and Ca. The results were recorded in terms of oxides of the elements.

3.7.3 GRAVIMETRIC ANALYSIS AND FLAME PHOTOMETRY

3.7.3.1. Preparation of Sample for Gravimetric Analysis and Flame Photometry

British standard (BS) [69] procedure was adopted for gravimetric and flame photometric analysis. 100 g of 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 following were analyzed for:

3.7.3.2 Silicon Oxide

1.000 g of the pozzolana sample and 1.000 g of ammonium chloride were carefully mixed in a 250 ml beaker. The sample was then spread evenly over the bottom of the beaker and covered by a clock glass. 10 ml of hydrochloric acid was slowly added, down the side of the beaker using a graduated pipette. When the

reaction had subsided, the mixture was stirred with a glass rod to break any lumps, which had formed. The beaker with its cover was placed on a water bath for 30 minutes at 80 – 100 °C. Stirring was continued to avoid formation of lumps. 50 ml of hot water was used to dilute the syrupy residue at the bottom of the beaker, which was, then poured to Whatman filter paper number 41. The precipitate was thoroughly washed twice with hot hydrochloric acid and hot water until the washings were free of chloride ions. Cl^- ions absence was tested by means of silver nitrate solution. The filtrate was preserved for total R_20_3 (Al_2O_3 + Fe_2O_3) determination. The precipitate with its filter paper was placed in a preweighed platinum crucible and covered with a lid. It was heated gently to smoke off the filter paper without flaming, so that entrainment of silica did not take place. It was ignited at 1200 °C in an electric furnace for 45 minutes to a constant weight. It was then cooled in a desicator to room temperature and the crucible weighed. This gave the weight of impure silica. The contents of the crucible were moistened with a few drops of water, three drops of concentrated sulphuric acid and 5 ml of hydrofluoric acid. The resulting product was evaporated on a sand bath, ignited for 5 minutes at temperature of 1200 °C, then cooled in a desicator and weighed. The obtained weight was subtracted from the impure silica weight to obtain pure silica weight. The crucible and content were reserved for determination of R_2O_3 group.

3.7.3.3 R_2O_3 ($Al_2O_3 + Fe_2O_3$)

5 ml of Bromine water were added to the filtrate from the silica separation. The mixture was evaporated until all free bromine was driven off. The mixture was then adjusted to a volume of 150 ml. 3 drops of methyl red and 1.0 g of ammonium nitrate was added to the solution, and then boiled. Ammonium solution was added until just alkaline to the methyl orange indicator. The mixture was vigorously stirred during precipitation. It was covered with a cork glass to allow for precipitation for a few minutes. The solution was then decanted on to a Whatman filter paper number 41, which had thoroughly been rinsed with dilute solution of ammonium nitrate (20g of NH_4NO_3 per liter, made just alkaline to methyl red with ammonium solution). To the precipitate, a hot solution of ammonium nitrate was added, and the mixture re-filtered. The precipitate was washed with the same solution. The filtrates were preserved for CaO determination. The filter paper and its precipitate were placed in the beaker used for precipitation. 100 ml of NH_4NO_3 solution was added and redissolution done using HCl solution. A second precipitation was done using dilute solution of NH_4NO_3 and filtered as before. The filtrates were reserved for CaO determination. The filter paper and its contents were placed in crucible containing the residue from evaporation of the fluorosilic acid. After smoking off the paper, the precipitate was ignited at a temperature of 1200 °C for 30 minutes. It was allowed to cool in a dessicator then weighed to give the gross weight of R_2O_3.

3.7.3.4 Calcium Oxide

The combined filtrates from the R_2O_3 group were evaporated to a volume of about 300 ml. They were made just acidic with hydrochloric acid. 2 g of oxalic acid hydrate were added. The solution was boiled and neutralized while still boiling with dilute ammonia until just alkaline to the indicator. The solution was allowed to settle, while keeping the solution hot for about 15 minutes. After cooling for 45 minutes, it was filtered with a Whatman filter paper number 40. The residue was washed with a cold solution of ammonium oxalate (1g/l). The filtrates were reserved for magnesium oxide determination. The filter paper and its content were placed in the beaker in which the first precipitation had been carried out. It was digested with 50 ml of hydrochloric acid. After digestion, it was diluted to 20 ml with ammonium oxalate solution (50g/l). The temperature of the solution was raised to between 70 – 80 °C, calcium oxalate was precipitated by neutralizing the solution with 50 % ammonia. The solution was stirred throughout the precipitation and allowed to stand as before. It was filtered through Whatman filter paper number 40 and the residue washed with the ammonium oxalate solution (1g/l). The filtrate was reserved for magnesium oxide determination. The filter paper and its content were ignited in a weighed platinum crucible for 20 minutes at 1200 °C. It was finally cooled in a desicator. The weighing of the crucible was done after every 5 minutes then re-ignited until a constant weight was obtained.

3.7.3.5 Magnesium Oxide

The combined filtrates from the calcium determination were evaporated to dryness with 40 ml of nitric acid. The residues were dissolved in dilute hydrochloric acid and diluted to 200 ml using water. To the solution, 20 ml of saturated diammonium hydrogen phosphate solution and 50 ml of ammonia solution were added. The solution was cooled under a stream of cold water to room temperature and stirred using a stirring rod. It was allowed to settle for another 30 minutes and filtered on a Whatman filter paper number 40. The residue was washed with cold-water solution containing 25 ml of ammonia per liter. The filter paper and residue were moistened with two drops of concentrated nitric acid and placed in preweighed porcelain crucible, smoked off and ignited at 1000 °C for 20 minutes then reweighed. The weight obtained was for $Mg_2P_2O_7$. The results were multiplied by 36.23 to obtain MgO.

3.7.3.6 Iron Oxide

40 ml of cold water were added to 1.0 g of pozzolana sample in 250 ml beaker. 10 ml of hydrochloric acid was added while stirring the mixture. The solution was heated until the cement decomposed. The solution was boiled and treated with $SnCl_2$ solution until the solution turned colorless. The $SnCl_2$ was made by dissolving 5 g of $SnCl_2.H_2O$ in 10 ml of concentrated HCl and made to 100 ml by water. One excess drop was added and the solution cooled to room temperature. The interior of the beaker was rinsed with water. 10 ml of saturated $HgCl_2$

solution was added all at once. The resulting solution was vigorously stirred for 1 minute. 10 ml of 50 % phosphoric acid and two drops of barium diphenylamine sulphonate indicator were added to the solution. Sufficient amount of water was added such that the volume after titration with standard 0.1M $K_2Cr_2O_7$ solution was between 75 and 100 ml. The $K_2Cr_2O_7$ solution was standardized against pure Fe_2O_3. The end-point was taken where one drop caused a permanent intense purple color. Percentage of Fe_2O_3 was calculated as

$$\% Fe_2O_3 = 0.004V \times 100$$

Where V = ml of $K_2Cr_2O_7$ solution required by 1 g of cement sample

3.7.3.7 Aluminium Oxide

Al_2O_3 content was obtained from subtracting F_2O_3 content from the total R_2O_3.

3.7.3.8 Sulphate Content as $S0_3$

25 ml of cold water were added to 1.000 g of sample in 250 ml beaker. 5 ml of hydrochloric acid were added to the mixture while continuously stirring. The solution was heated to sample decomposition. The solution was 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 $BaCl_2$ solution (100g/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 then left to cool for 2 hours, ensuring the volume of solution remained 225 ml to 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 from chlorides. The filter paper and its content was placed in a weighed platinum crucible, smoked off and ignited at 900 °C for 15 minutes, cooled in a desicator and weighed. Verification of the constant weight obtained was done by a second ignition after 5 minutes of cooling. SO_3 content was obtained by;

SO_3 % content = W x 34.3

Where W = Weight of $BaSO_4$ in grammes.

3.7.3.9 Na_2O and K_2O.

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 H_3PO_4 and diluting the mixture to a liter with water. Different amounts of the stock solution were mixed with 50 % HCl and 50 % H_3PO_4 and diluted to 100 ml with water. These made the photometric standards for making calibration curve.

1.0 g 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 on a sand bath until the residue remained just moist.

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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 manner.

3.7.3.10 Loss on Ignition (LOI)

1.0 g of treated pozzolanic sample in a preweighed 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 LOI.

3.8 COMPRESSIVE STRENGTH EVALUATION

Compressive strength analysis was determined in accordance with the ASTM 593 part C [62] procedure but with slight modifications, due to unavailability of some resources. KS [1] 70.7 mm cubes were used instead of the ASTM 593 part C [62] 50 mm cubes. The mortar was therefore compacted into the cubes using KS [1] vibrating machine instead of the ASTM 593 part C [62] Jolting table. Other parts

of the procedure remained as outlined in the ASTM 593 part C [62] as explained below.

3.8.1 COMPRESSIVE STRENGTH EVALUATION OF POZZOLANA-HYDRATED LIME CEMENTS

Each of the treated pozzolana test material samples was inter-ground with CHL or ALS in a 2:1, 1:1 and 3:1 pozzolana: hydrated lime ratios using a laboratory ball mill. For SBE-, RHA- and combined-hydrated lime cements, 174 g of pozzolana cements and 122 ml of water were taken, but for Ptuff and BB-hydrated lime cements, 187 g of the pozzolana cements and 95 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 BS [100] (in case of SBE-, RHA- and combined-hydrated lime cements) or 513 g of standard graded sand BS [100] (in case of Ptuff and BB-hydrated lime cements) 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 for 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. The mortar was 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 of 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 vapour oven 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 then analysed 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 an 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 as

$$C_c = F/A$$

Where, C_c = Compressive strength in kN/m^2

F = Maximum applied force for failure in kN

A = Cross section area of the specimen in m^2

3.8.2. COMPRESSIVE STRENGTH EVALUATION OF PORTLAND POZZOLANIC CEMENTS (PPCS).

This was determined in accordance with the KS 02 1263 [1] as follows;

Each of the treated pozzolana material samples was inter-ground with laboratory made OPC. This was used to make PPCs with 0, 15, 20, 25, 30, 35 and 40 % by weight of pozzolana. 185 g of the resulting sample and an amount of water, which varied with the type of PPC taken as specified in table 3.1, were put into the bowl of the mechanical mixer and the machine set to run at low speed. After 30 seconds, 555 g of standard graded sand BS [100] was slowly added into the bowl for the next 30 seconds. Paste mixing and mortar cubes preparation was done as in section 3.8.1 above, but nine mortar cubes were made. The process was repeated three times. The cubes were kept in a curing room for 24 hours, after which they were de-molded, weighed, marked with crayon and transferred into the curing tank for a period of 3, 7 or 28 days. At the end of each curing period, 3 cubes were removed from water, wiped off and their compressive strength determined as above.

Table 3.1; Quantity of water used in making the cement-sand mortar cubes

Pozzolana Incorporated	% Pozzolana	Amount o f Water (ml)
All Pozzolana	0, 15 and 20	74
Ptuff or BB	25	74
	30, 35 and 40	79
RHA, SBE and Combined	25 and 30	80
	35 and 40	82

3.8.3 COMPRESSIVE STRENGTH EVALUATION OF BAMBURI-COMBINED-ALS PPCS

Bamburi factory OPC as received from the sampling site was inter-ground with the combined-ALS cement in a laboratory ball mill to make PPCs with 40, 45, 47, 50 and 60 % by weight of combined-ALS cements. The rest of the procedure was done as described in section 3.8.2 above. In this case 82 ml of water were used for the 40 and 45 % replacements whereas 85 ml were used for the other replacements.

3.9 SETTING TIME

This was determined in accordance with the KS 02 1263 [1] as outlined hereafter.

3.9.1 PENETRATION TEST

For penetration test, the following samples were prepared. 400 g of Ptuff or BB, 300 g of SBE or combined hydrated lime cements were mixed with 159 ml, 223 ml and 238 ml of water respectively. They were vigorously mixed by means of two trowels for 240 seconds on a flat stainless steel surface table. The paste was transferred immediately into the mould, which had been placed on a lightly greased plane metallic base–plate and filled to excess without undue compaction. The excess paste was removed by gentle sawing motion with a straight-edged trowel in such a way as to leave the paste filling the mould and having a smooth upper surface.

The Vicat apparatus was calibrated with plunger attached in advance of the test by lowering the plunger to rest on the base plate to be used and adjusting the pointer to read zero on scale. The plunger was raised to a standby position for 2 seconds in order to avoid initial velocity or forced acceleration of the moving parts. The moving parts were then quickly released and the plunger allowed to penetrate vertically into the center of the paste. The release of the plunger occurred 4 seconds after zero time. The scale was read when penetration had ceased. The scale reading, which indicated the distance between the bottom phase of the plunger and the base plate, together with the water content of the paste was recorded and expressed as a percentage by mass of the cement. The plunger was cleaned immediately after penetration. The test was repeated with pastes containing different water contents until one was found to produce a distance between plunger and base plate of 6 mm.

3.9.2 DETERMINATION OF INITIAL SETTING TIME

The Vicat apparatus was calibrated with the initial setting time needle attached in advance of the test, by lowering the needle to rest on the base plate to be used and adjusting the pointer to read zero on the scale. The needle was raised to a standby position. Vicat mould was filled with paste of standard consistency as above. The filled mould and base plate was placed into the curing room and after 45 minutes, was transferred and positioned under the needle. Initial setting time was determined as described in section 3.9.1 but penetrations were done after every 5

minutes on the same paste. Initial setting time recorded to the nearest 5 minutes, was the duration taken for the distance between the base plate and the needle on penetration, to be 10 mm. Interval time between penetration tests near the end point was reduced to one minute to ensure that successive results did not fluctuate excessively.

3.9.3 DETERMINATION OF FINAL SETTING TIME

After determining initial setting time, the final setting time needle was fixed into the Vicat apparatus. The filled mould and base plate were placed into the room after initial setting time was determined. After an additional 30 minutes, it was transferred and positioned under the needle. Final setting time was determined as above in section 3.9.2. The time recorded was also measured from zero up to when the needle circular ring could not make a mark on the paste. The time interval between testing was done as for the initial setting time above.

3.10 POZZOLANICITY TEST

Pozzolanicity test was determined in accordance with the International Standard for Organisations (ISO) [65] as outlined below.

3.10.1. PREPARATION OF REAGENTS

Requisite amount of Ethylenediaminetetraacetic acid disodium salt dihydrate (EDTA) was dissolved in water to make 0.025M EDTA solution. The solution

was standardized against calcium carbonate dried at 160 °C. Murexide indicator was prepared by inter-grinding 0.5 g of murexide and 100 g of potassium chloride dried at 110 °C.

3.10.2 STORAGE AND FILTRATION

100 ml of freshly boiled water was pippeted into the plastic container and the sealed container placed in the thermostatic enclosure at 40 ± 0.2 °C until equilibrium was reached (about I hour). The container was removed from the thermostatic enclosure. 20.00 g of the PPC under test were poured into the container using a wide stem funnel. The container was then sealed immediately 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 replaced immediately into the thermostatic enclosure to avoid any appreciable decrease in temperature. After a period of 8 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 Whatmann 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.

3.10.3 DETERMINATION OF HYDROXYL ION CONCENTRATION

The vacuum flask was shaken to homogenize the filtrate. 50 ml of the filtrate were pippeted 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, $[OH^-]$, in millimoles per liter was calculated as

$$[OH^-] = \frac{1000 \times 0.1 \times V}{50}$$

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

3.10.4 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 the 0.025M EDTA solution by means of the 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 as

$$[CaO] = \frac{1000 \times 0.025 \times V}{50}$$

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

CHAPTER 4

4.0 RESULTS AND DISCUSSION

A study has been conducted on making pozzolanic cement from waste materials on a laboratory scale. Performances of the pozzolana material have been studied when incorporated with acetylene lime sludge (ALS), commercial hydrated lime (CHL), laboratory made ordinary Portland cement (OPC) and Bamburi OPC. Performance of the pozzolana varied from one material to another, due to raw material differences. The materials studied shown in table 4.2, were based on their chemical constituent of silica and alumina content. They all produced active pozzolanas with hydrated lime.

4.1 RAW SPENT BLEACHING EARTH (SBE)

SBE as obtained from Unilever Kenya Limited and KAPA Oil Refineries Limited-Kenya was similar in their general appearance. The earths were dark grey in color, oily and finely pulverized. Characterization test results are given in table 4.1.

Table 4.1; Characterization of raw SBE

Property	**SBE[1]**	**SBE[2]**
Calorific value	15.825J/g	13.952J/g
Oil content	38.51wt %	32.13wt %
Ignition temperature	239 °C	237 °C
Maximum self Combustion temperature	475 °C	450 °C
Ash content	52.28 wt %	58.64 wt %

Oil content of the SBEs varied from one source to the other. SBE[1] had higher oil content than SBE[2]. This may be attributed to the difference in filter pressing process of the SBE by the different oil processing factories. SBE mainly consisted of bleaching clay and oil. A typical calculation of calorific value of the SBE is shown below.

Weight of crucible and sample	8.420	
Weight of crucible	5.901	
Fuel weight		2.519
Final temperature	25.880 °C	
Initial temperature	22.015 °C	
Temperature rise		3.865 °C
Total heat capacity		10.380 J/K

Total heat released from the sample was calculated by multiplying the total heat capacity by the temperature rise; $10.380 \times 3.865 = 40.119$ J

Constant heat gain was provided by the Gallenkamp manual as 0.126 J

Nitric acid correction was calculated as follows

Titration With $Ba(OH)_2$

ml of $Ba(OH)_2$ used	= 13.625
Solution molarity	= 0.096
ml of 0.1M Solution	= 13.080

Sodium carbonate added	=20.000 g
Solution molarity	= 0.100
ml of 0.1M Solution	=20.000

Titration With Hydrochloric Acid

ml of HCl used	= 13.050
Solution molarity	= 0.096
ml of 0.1M solution	= 12.5280

$$\text{Nitric acid correction} = \frac{6(20.000 - 12.528)\ \text{J}}{1000}$$

$$= 0.045$$

Subtraction of the nitric acid correction and the constant heat gain from the total heat release gave the corrected heat from fuel as;

$$40.119\ J - (0.126\ J + 0.045) = 39.948\ J$$

Heat from 1 g of fuel was calculated by dividing the corrected heat from fuel by the weight of fuel used as

$$\frac{39.948\ J}{2.519} = 15.859$$

Sulphuric acid correction was calculated as

$$= \frac{15.1\{13.080 - (20.000 - 12.528)\}}{1000 \times 2.519}$$

$$= 0.034\ J$$

Gross Calorific Value was calculated by subtracting the sulphuric acid correction from the heat from 1 gram of fuel as

$$15.859 - 0.034 = 15.825\ J/g$$

In light of the oil content, SBE has been blended with animal feed to act as a source of fatty acids [97]. It has also been applied to farms as fertilizer especially to cornfields [98].

When heated by a Bunsen burner in a silicon carbide crucible, the oil in SBE started to volatilise at a temperature of 150 °C. The volatiles ignited at 239 °C for SBE^1 and 237 °C for SBE^2 to a yellow flame. The flame continued to burn on its own to a temperature of 475 °C for SBE^1 and 450 °C for SBE^2. After self-combustion, the SBEs still had 14.94 % oil withheld. This oil was driven off to 4.12 % for SBE^1 and 6.72 % for SBE^2 on continued heating at 550 °C for four hours. At 1000 °C, the oil was driven off completely after 45 minutes of continuous heating. King and Wherton [88] observed that the phenomenon of bleaching oil using clay involved physical and chemical adsorption. This leads to chemically and physically adsorbed oil. The physically adsorbed oil must have

been the one volatilising off to ignite at 239 °C and 237 °C for SBE^1 and SBE^2 respectively, while the chemically adsorbed being the one removed from the SBE at 1000 °C.

SBE may be used as a source of some kiln energy with respect to the temperature at which the oil was driven off and its calorific value. Heavy fuel oil used by the local cement industries in the kiln has a calorific value of 43.2 J/g [99]. The calorific value of the SBE^1 and SBE^2 is 36.6 % and 32.3 % of the heavy fuel oil respectively. The SBE can therefore gainfully be used as a partial replacement of the heavy fuel oil in the kiln. The application may be adopted in such a way that the SBE is jetted into the kiln with the heavy fuel oil or using a separate line. One would have to determine the proportion of the supplemented compounds by the SBE ash so as to adjust the composition of the kiln feed.

The calorific value of the SBE may also be utilized in the preheaters. In this case, the SBE would be incorporated in the raw meal in a predetermined proportion so as to maintain the right overall raw mill material proportion. Some possibility may exist that the hot gases from the kiln may blow the volatile oils away but some of the chemically adsorbed oil could still be used to generate energy in the kiln. The SBE ash incorporated could act as a correction for low silica and alumina content of the raw materials.

The calorific value of the SBE can also be used for production of domestic energy. It can be bricketed or intermixed with RH or sawdust. A research is therefore necessary to be able to investigate on such possibilities. SBE energy in this study was used in partial activation of the SBE separately and with BB plus RH in a blended raw mix.

After complete combustion of the oil from SBE, the ash content was more than two times higher than the 22.15 % reported for RH [24]. SBE could therefore yield more of the pozzolanic material comparatively if it were active.

4.2 TREATED POZZOLANIC SAMPLES

4.2.1 SIEVE ANALYSIS

The percentage retention of the treated pozzolanic materials on specific sieves is shown in table 4.2.

Table 4.2; Percentage sieve retention

Sample	90 μm % retention	212 μm % retention
C-W BB	7.92	1.40
G-45 BB	7.31	1.42
RHA	7.19	1.40
SBE[1]	6.87	1.38
SBE[2]	6.86	1.34
Ptuff	7.01	1.40
Combined	7.18	1.42

Sieve analysis was done on treated pozzolanic materials to ensure that the material fineness does not vary appreciably. Fineness affects pozzolanic activity and W/C ratio demands.

The 90 and 212-μm sieves used are KS [1] sieves for PPC. They were used due to unavailability of the ASTM C 593 [58] 75 and 600-μm sieves. Although no standard exists for the 90 and 212-μm sieves on pozzolana – hydrated lime, comparing the approximately 7 % retention on the 90-μm sieve to the 30 % standard retention on the 75-μm sieve, it is reasonable to assume that the standard requirements are met. A similar conclusion can be drawn on the results of the 212-μm sieve on the standard 600-μm sieve. Therefore the materials were fine enough for the pozzolanic reactions.

4.2.2. CHEMICAL CONSTITUENTS

The results of the chemical analysis of the treated samples are given in table 4.3. The results shown are average of the XRFA and gravimetric analysis results apart from results for sodium and potassium where only flame photometry was used and LOI where only gravimetric analysis was used.

Table 4.3; Chemical Constituents of treated Pozzolanic Samples

Compound	En-masse SBE	SBE[1]	SBE[2]	C-W BB	G-45 BB	Ptuff	RHA
	% by weight	% by weight	% by weight	% by weight	% by weight	% by weight	% by Weight
CaO	2.01	3.12	3.02	0.44	4.08	2.07	1.38
SiO_2	65.88	69.15	67.70	65.71	63.31	57.86	80.61
Al_2O_3	11.10	12.15	12.37	20.47	17.66	12.23	0.53
Fe_2O_3	2.79	3.96	4.04	7.89	6.70	10.02	0.47
SO_3	1.83	2.84	2.99	0.22	0.39	0.11	0.01
MgO	3.02	4.18	4.05	1.95	2.32	1.45	2.39
K_2O	0.49	0.58	0.59	3.52	2.34	1.47	0.15
Na_2O	0.20	0.30	<0.01	1.55	1.02	2.27	0.20
LOI (Loss on Ignition)	12.95	4.12	6.72	0.90	0.57	14.62	3.49
SiO_2+ Al_2O_3+ Fe_2O_3	79.77	85.16	84.11	94.07	87.67	80.11	81.61

The individual results of XRFA, gravimetric analysis and flame photometry appear in appendix 2. A pozzolanic material must contain a minimum of 70 % of the sum of the oxides of aluminium, silicon and iron [1]. This avails the required glassy phase content to react with hydrated lime in presence of water at room temperature to produce the cementing materials [101].

The materials under test therefore surpassed the standard. The major oxide content of the en-masse SBE was comparatively lower and was thought to be due to a high LOI content which may be due to a low decarbonation of the en-masse SBE as there was insufficient ventilation during its calcination in the muffle furnaces.

As expected, SBE^1 and SBE^2 did not show appreciable difference in their chemical composition. The difference in BBs was attributed to different clay sources for the different clay manufacturers. The LOI for Ptuff was relatively high; this may be attributed to bound water.

4.2.3. POZZOLANA-CHL CEMENTS

The results for compressive strength and setting time tests for various ratios of pozzolana to hydrated lime cements are given in table 4.4.

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Table 4.4; Compressive strength and setting time for Pozzolana-CHL cements.

Pozzolana	Pozzolana: CHL	Initial setting time (IST)/ Minute	Final setting time (FST)/ Minute	7-day Compressive strength/MPa	28-days Compressive strength/MPa
En masse	2:1	Indeterminable	Indeterminable	0.00	0.00
SBE[1]	2:1	123	311	9.86	10.92
SBE[2]	2:1	127	320	9.94	10.07
SBE[1]	1:1	128	315	7.57	7.91
SBE[1]	3:1	110	268	6.67	6.82
C-W BB	2:1	850	1702	6.27	6.28
	1:1	1002	1351	4.74	5.01
	3:1	645	1226	4.46	4.34
G-45 BB	1:1	180	266	9.32	10.42
	3:1	175	253	9.64	10.73
	2: 1	160	239	12.97	13.20
Activated C-W BB	2: 1	284	549	9.20	9.98
Ptuff	2:1	283	541	8.94	8.99
	1:1	320	545	7.47	7.51
	3:1	290	527	8.12	8.00
RHA	2:1	351	482	5.48	5.60
	1:1	360	498	3.99	5.09
	3:1	323	445	3.75	3.83
Combined	2:1	290	471	8.37	8.90
Ashed mixture	2:1	301	552	7.73	7.80

The results suggested that en - masse SBE pozzolana-CHL had no pozzolanic activity due to high carbon content. High carbon content reduces compressive strength of pozzolanas as had been observed in the case of RHA [102]. Carbon content in RHA is directly controlled by LOI control [62]. Carbon content for the en - masse SBE as reflected in its LOI, was 12.95 % by mass compared to the 4.12 % and 6.72 % for SBE^1 and SBE^2 respectively. Calcination of large amount of SBE in the muffle furnace did not provide enough ventilation for its decarbonization. This led to the residual high carbon content.

Calcination of SBE in small amounts, reduced carbon content appreciably. SBE^1 LOI reduced to 4.12 % whereas for SBE^2 reduced to 6.72 % by mass. Although at 1000 °C the LOI could be driven to zero, at this temperature crystallization of the major oxides of the SBE would take place. This would produce a non-pozzolanic material. It is at 550 °C that pozzolanic SBEs are produced. With CHL, they showed a performance as tabulated in table 4.4. There is no appreciable difference between them in their compressive strength and setting time within experimental errors. Because of the similarity, SBE^1 was taken exclusively for further investigations.

The reaction of CHL with silica and alumina in all the other pozzolanas to form cementious materials was evident. The ASTM C 593 standard requires [62] a minimum of 4.1 MPa at the 7^{th} and/or 28^{th} day of curing of the pozzolana-hydrated cements. The compressive strength of the cements was well above the

standard requirements apart from en masse SBE and RHA cements. The en masse SBE cement failed in all curing periods, the 1: 1 ratio of RHA: CHL cement failed on the 7^{th} and 28^{th} day. The difference in 7 and 28-day compressive strengths of the cements is not significantly large. This is because pozzolana-CHL cements cured at 54 ± 2 °C for 7 days is an accelerated hydration [103].

Compressive strength of C-W BB though within the standard could be improved further through firing. The activated C-W BB had an improved performance. The level of amorphousness and reactive SiO_2, Al_2O_3 and Fe_2O_3 with CHL must have increased appreciably as observed by the improved performance. Compressive strength at 7-day improved from 6.27 to 9.20 MPa while the 28-day improved from 6.28 to 9.98 MPa.

Even after activation of the C-W BB, it still showed a lower compressive strength than that of G-45 BB. C-W BB with a higher major oxide content therefore had a lower pozzolanic activity in terms of compressive strength than G-45 BB. This could be attributed to a possibility of a lower glassy phase content of the major oxides of C-W BB than in G-45 BB. If this was so, these results would have concurred with Dhir [36] findings that high major oxide content does not necessarily correspond to higher pozzolanic activity. More research is required to determine the glassy content of the BBs.

Deviation from the 2:1 pozzolana: hydrated lime ratio affected the cement performance. This is due to either an increase in pozzolana or CHL, which behaves as inert material on its own. A reduction in compressive strength in C-W BB-CHL and ptuff-CHL cement at the 28^{th} day compared to the 7^{th} day was observed in the 3:1 ratio. This would be due to the leaching of the unbound pozzolana particles that were not involved in the pozzolana-CHL reaction. There were pores and voids that were physically visible to the naked eye on the cured mortar cubes. Vents and voids may create avenues for sulphates and acid attacks on the unreacted $Ca(OH)_2$, MgO and alkalis in the same manner as in Portland cement [70,71]. This weakens the cured cement mortar. In the 1:1 ratio cement, although CHL was in excess, due to its binding property [104] with itself in presence of water, it could not be leached out. Hence its 28^{th} day results did not show a reduction in compressive strength. Although $Ca(OH)_2$ forms cementious material it is subject to attack by acids and sulphates. This would therefore call for strict control of the pozzolana-hydrated lime ratio.

In all the ratios, the setting times of most of the pozzolana-CHL cements were well within Kenya standard [1] range of 45 and 600 minutes initial setting time and final setting time, C-W BB-CHL and en masse SBE-CHL cements however failed. The standard [1] setting time is sufficient to allow for workability and placement of the cement as well as hold building masses together. On activation of the C-W BB, initial setting time improved from 850 to 284 while the final

setting time improved from 1702 to 549 minutes. The improvement was consistence with that of the compressive strength above.

4.2.4 PORTLAND POZZOLANA CEMENTS (PPCs)

When the treated pozzolanas were inter-ground with the laboratory made OPC to form PPCs, they required W/C ratio given in table 4.5

Table 4.5; W/C ratio of PPCs

Pozzolana incorporated	% of pozzolana incorporated	W/C ratio
All pozzolana	0, 15, 20	0.40
Ptuff or BB	25	0.40
	30, 35 and 40	0.43
RHA, SBE and Combined	25 and 30	0.43
	35 and 40	0.44

The difference in the W/C ratio was due to difference in wetting ability of the pozzolanic materials used. It was observed that SBE, RHA and combined required a lot more water to wet, let alone to form a workable paste. BBs and Ptuff required little water to wet and form a workable paste. This case was more pronounced when the test materials were mixed with hydrated limes where they formed a larger proportion as indicated in section 3.8.1. The high W/C ratio increase in PPC is detrimental as it causes pores and voids development in cured concrete especially at early stages of cement hydration. This is due to loss of evaporable free water at early stages of cement hydration [105]. In the long term, however, it is beneficial as these voids create more space for cement to hydrate

and thereby increasing the strength of the cement. Superplastisizers may be used to reduce the high water demands in adverse conditions [106], because they improve the workability of the paste.

Figure 4.1 shows results of compressive strength of the PPCs made using the pozzolanic materials in different proportions with the OPC at the 3rd –day.

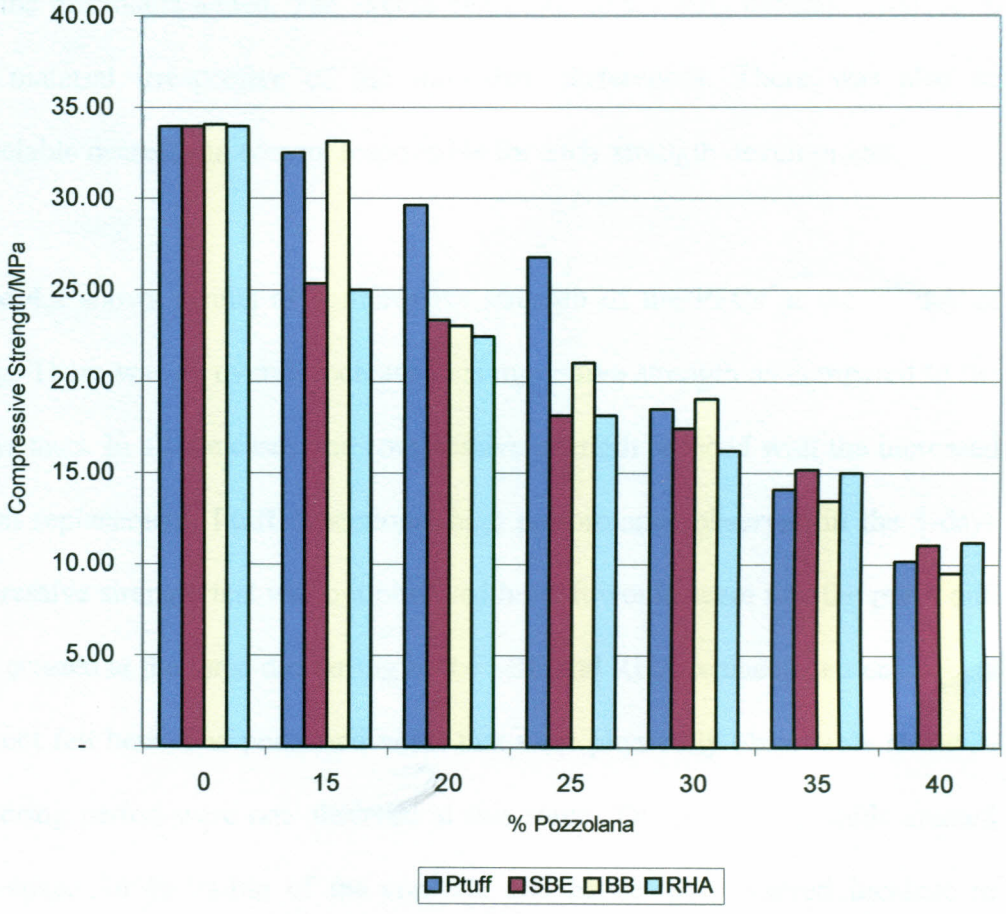


Figure 4.1: 3 – Days Compressive Strength Development of Portland Pozzolana Cements.

Ptuff replaced cement recorded the highest strength up to 25 % replacement after which it behaved like the others. The results therefore justified the use of Ptuff by the local cement factories to manufacture PPCs. Although Ptuff and C-W BB cements had the same W/C ratio, the results suggested that Ptuff had a higher pozzolanic activity and thus showed a higher compressive strength than C-W BB at the 3rd day. Beyond 30 % of replacement, all the cements behaved similarly. Most probably, the hydrating cement does not release enough $Ca(OH)_2$ to react with the pozzolana added. The excess pozzolana in the circumstance behaves as inert material irrespective of the individual differences. There was also an appreciable decrease in cement responsible for early strength development.

Figure 4.2 shows results of compressive strength of the PPCs at the 7th day of curing. There was an overall increase in compressive strength as compared to the 3–days tests. In all the cases, the compressive strength reduced with the increased cement replacement. Ptuff exceptional high performance observed in the 3-days compressive strength test was not observed here. It would seem that the pores and voids created at the three day curing of the SBE and RHA replaced cement effects were not felt here. The pores and voids that were physically observable at the 3-day curing period were not observed at this stage. The pores and voids created more space for hydration of the concrete and hence the observed increase in strength to equate the Ptuff replaced cement. In all cases, 15 % replacement had no significant drop while there was a sharp drop in performance above 20 %

replacement. This could be because less cement was available, hence $Ca(OH)_2$ was not enough to react with the added pozzolana.

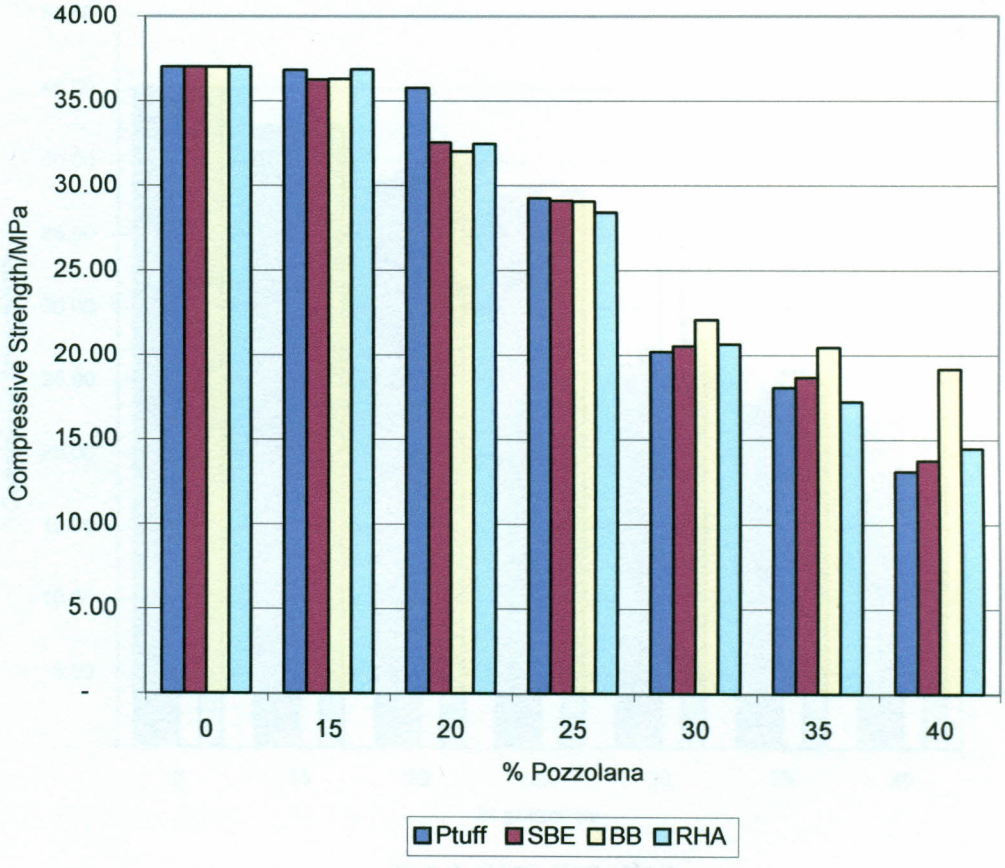


Figure 4.2: 7 – Days Compressive Strength of Portland Pozzolana Cements

Figure 4.3 shows the results of the PPCs at the 28th day of curing.

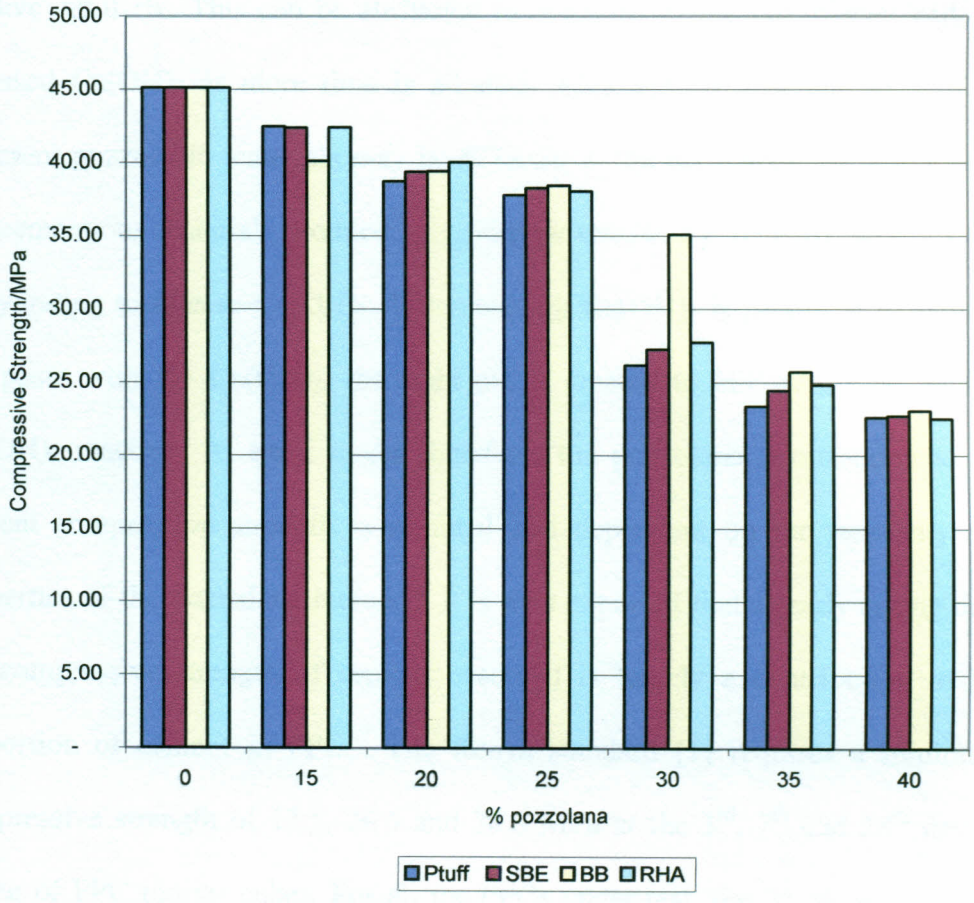


Figure 4.3: 28 – Days Compressive Strength of Portland Pozzolana Cements

As expected, there was a decrease in compressive strength with replacement, which was similar in all the cements. A sharp fall in compressive strength was

observed at 30 % replacement except for BB replaced cement, whose sharp fall was at 35 %. At the 3-days of curing, the 0, 15, 20 and 25 % replacements behave differently but as curing proceeds from the 7th to the 28th day, the materials tend to behave similarly. This can be attributed to reactions of the pozzolanas with the released $Ca(OH)_2$ as more time is allowed. Although the reaction rates of the different pozzolanic materials may be different at the early ages, as time passes, the cementious materials produced give similar results. At the early ages, cement is hydrating to release $Ca(OH)_2$. When enough $Ca(OH)_2$ is produced to saturate the paste with the $Ca(OH)_2$, the right pH is created to initiate the pozzolana-$Ca(OH)_2$ reaction. At early stages therefore, the pozzolana contribution to the cement compressive strength is minimal and dependent on the reactivity and properties of the pozzolana included. It is thus expected that at early curing days the compressive strength of cement observed is largely a contribution of the proportion of cement in PPC. The Kenya standard [1] requires a minimum compressive strength of 17.5, 26.5 and 38.0 MPa at the 3rd, 7th and 28th day of curing of PPC mortar cubes. For all the PPCs under test, the 25 % replacement passed the standard requirements at all curing periods.

Figure 4.4 – 4.7 shows a comparative assessment of the strength development of the cements replaced with the different pozzolanic material as a function of curing periods.

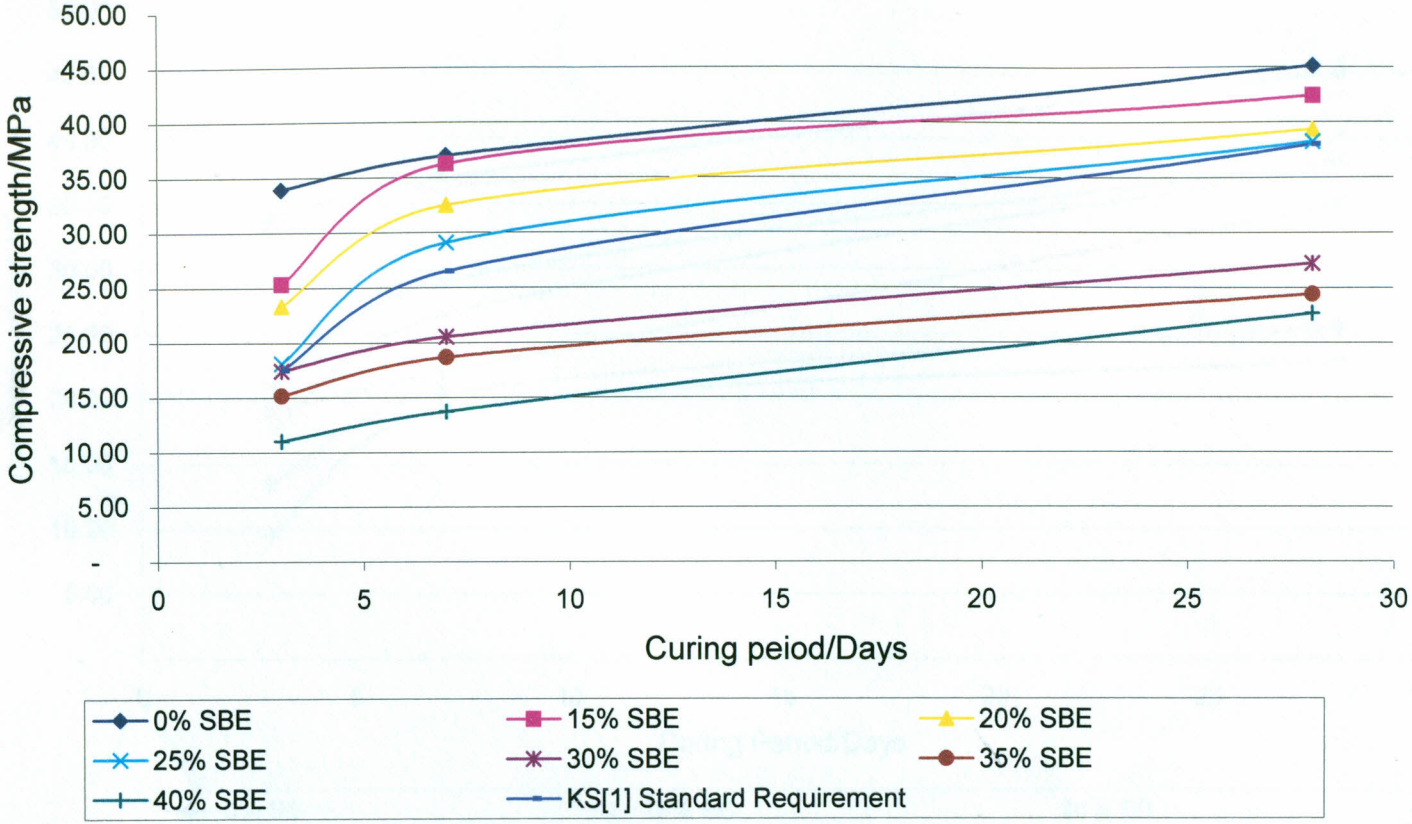
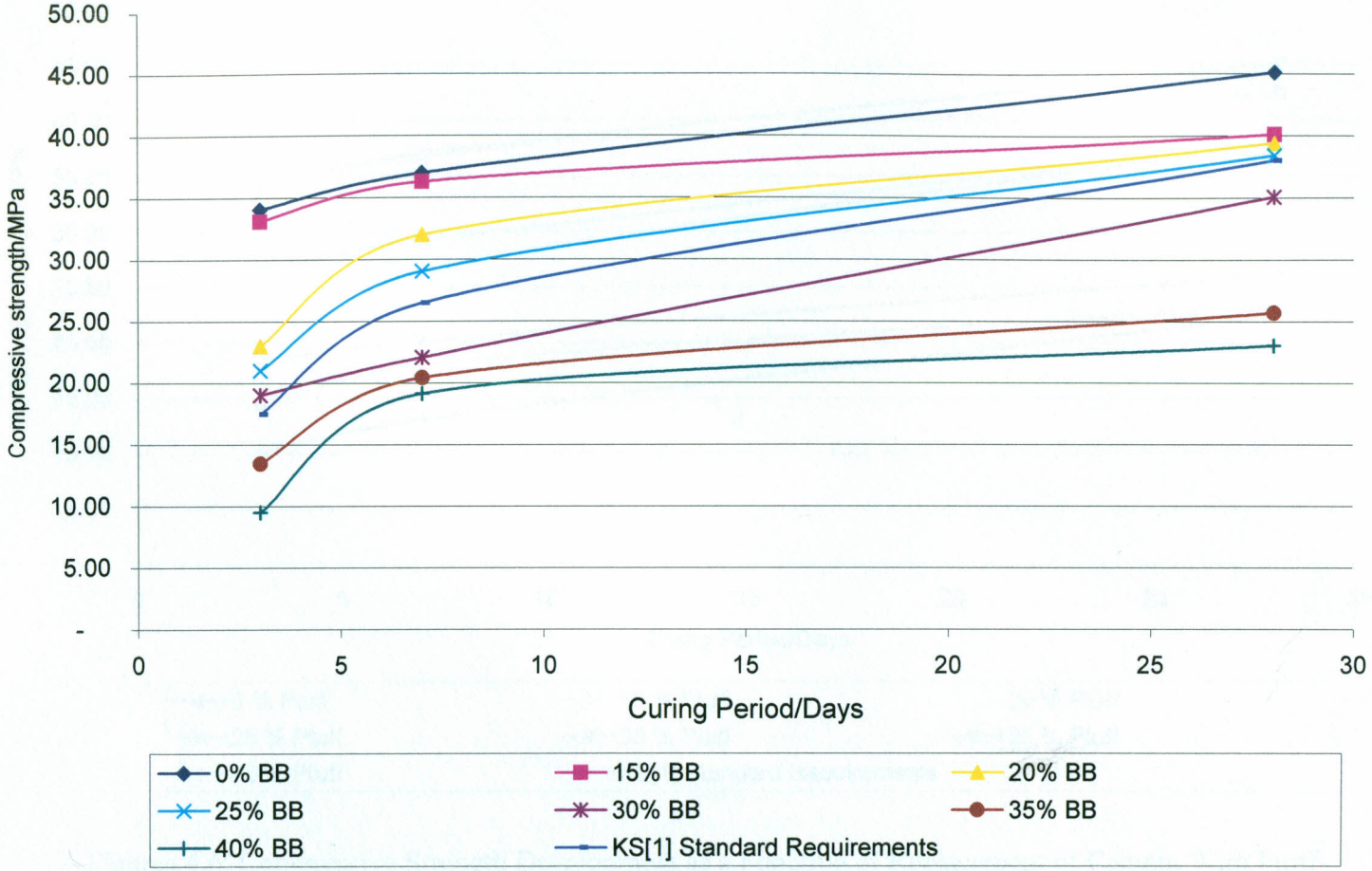
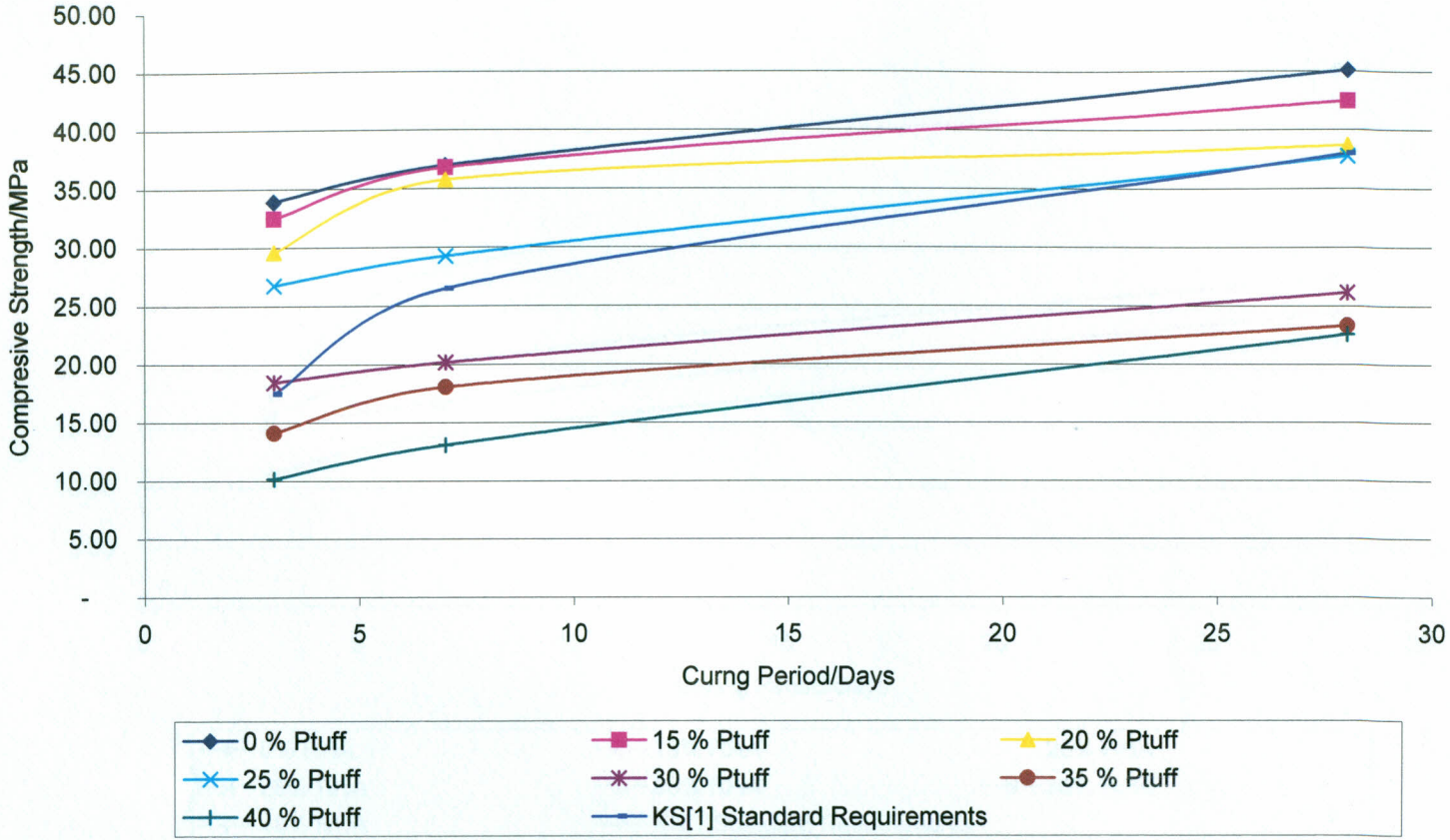


Figure 4.4: Compressive Strength Development as a Function of Replacement of Cement With SBE



Figures 4.5: Compressive Strength Development as a Function of Replacement of Cement With BB



Figures 4.6: Compressive Strength Development as a Function of Replacement of Cement With Ptuff

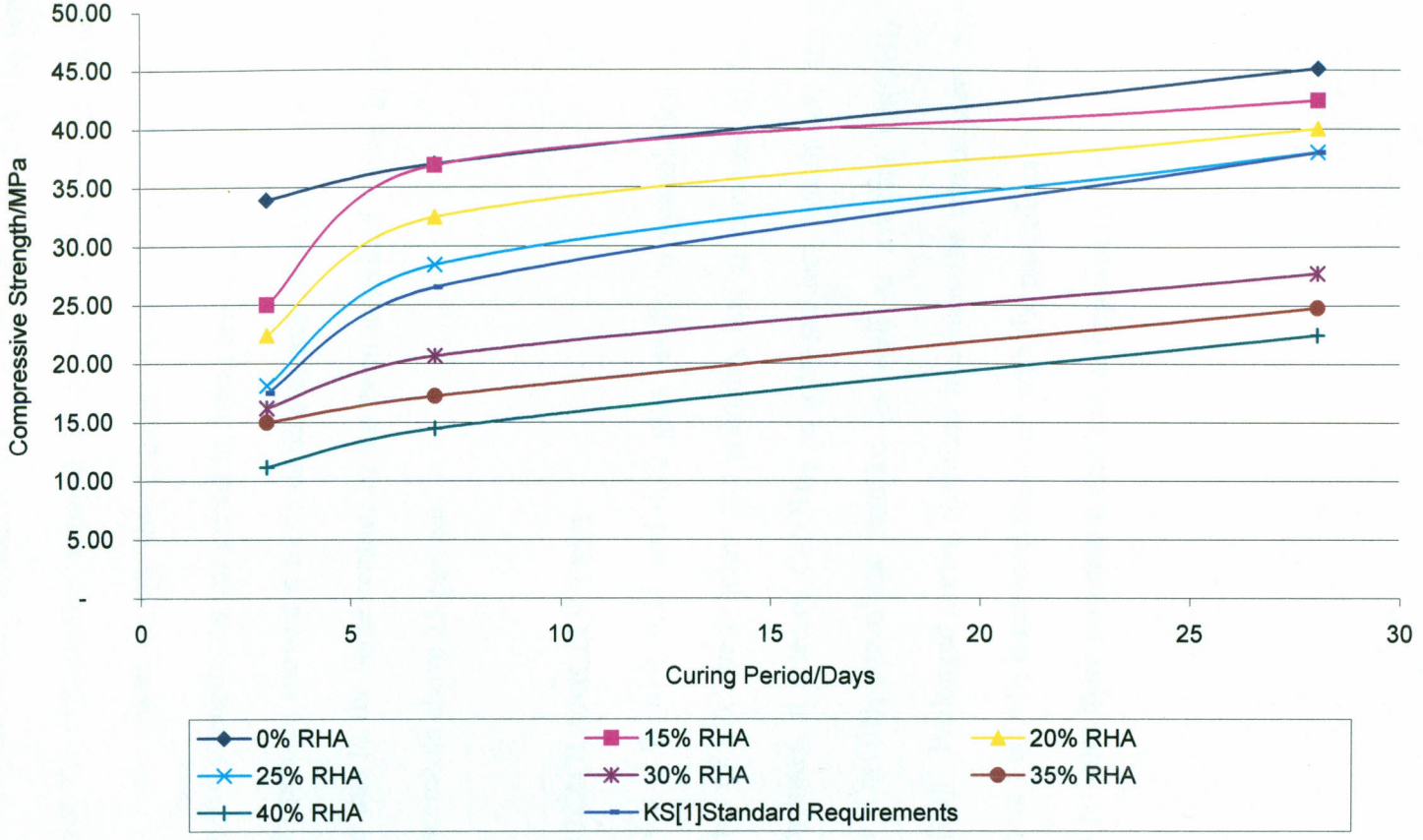
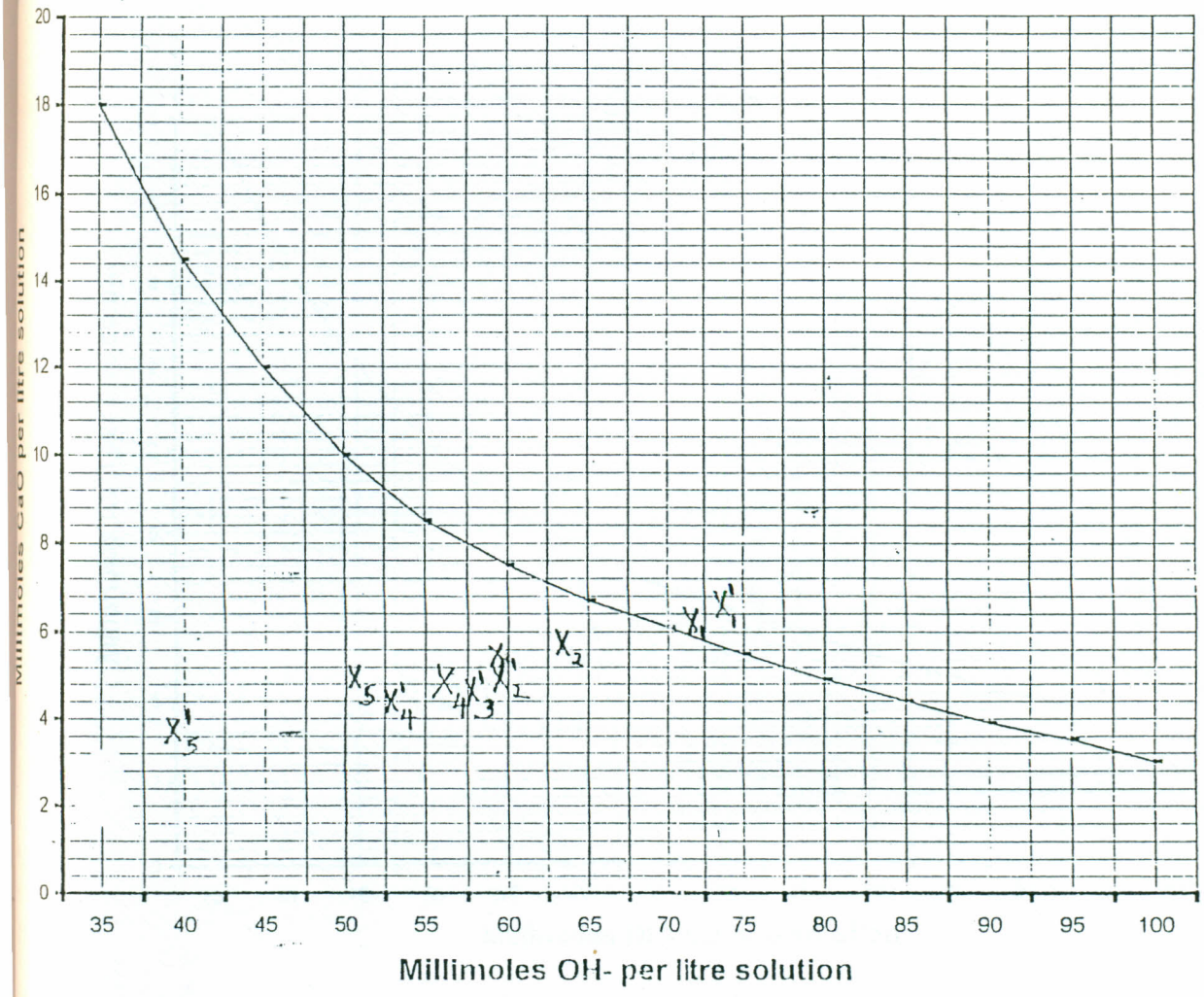


Figure 4.7: Compressive Strength Development as a Function of Replacement of Cement With RHA

In all the cases above, there was a substantial compressive strength development as the curing period proceeded. It was observed that the higher the replacement, the lower the compressive strength in all these curing periods. Above the 25 percent replacement in all the cement, there was a substantial decline in compressive strength. As compared to lower replacement levels, the replacement above 25 percent showed a more decline at and after the 7^{th} day of curing. This could be due to the same reasons as has been described earlier in this section on the replacements above 25 percent.

4.2.5. POZZOLANICITY TEST

Figures 4.8, 4.9, 4.10, 4.11 and 4.12 give results of pozzolanicity test. All the coordinates of PPC were below the solubility line as opposed to OPC. As the cement hydrates, it releases $Ca(OH)_2$ as a by-product, which sets the right pH value for $Ca(OH)_2$-pozzolana reaction as well as availing $Ca(OH)_2$ for the reaction [60]. Prolonged curing therefore increases the compressive strength of PPC as more $Ca(OH)_2$ is released that react with the pozzolana incorporated in the cement to produce more cementious material, as opposed to OPC [60].



0% SBE (8-days) X^1_1=0% SBE (15-days)
15% SBE (8-days) X^1_2=15% SBE (15-days)
20% SBE (8-days) X^1_3=20% SBE (15-days)
25% SBE (8-days) X^1_4=25% SBE (15-days)
30% SBE (8-days) X^1_5=30% SBE (15-days)

Figure 4.8; Pozzolanicity Diagram For Portland SBE Cement

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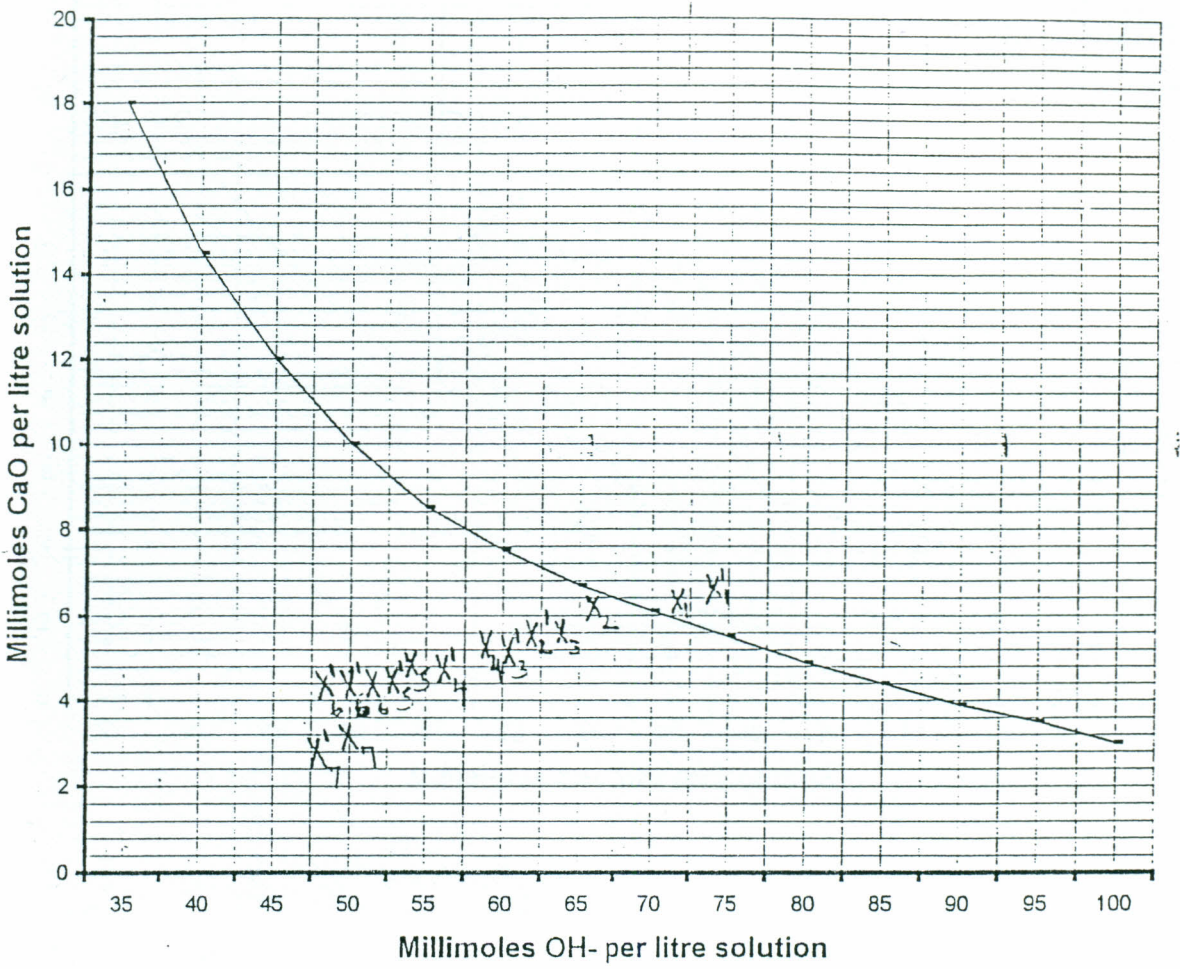
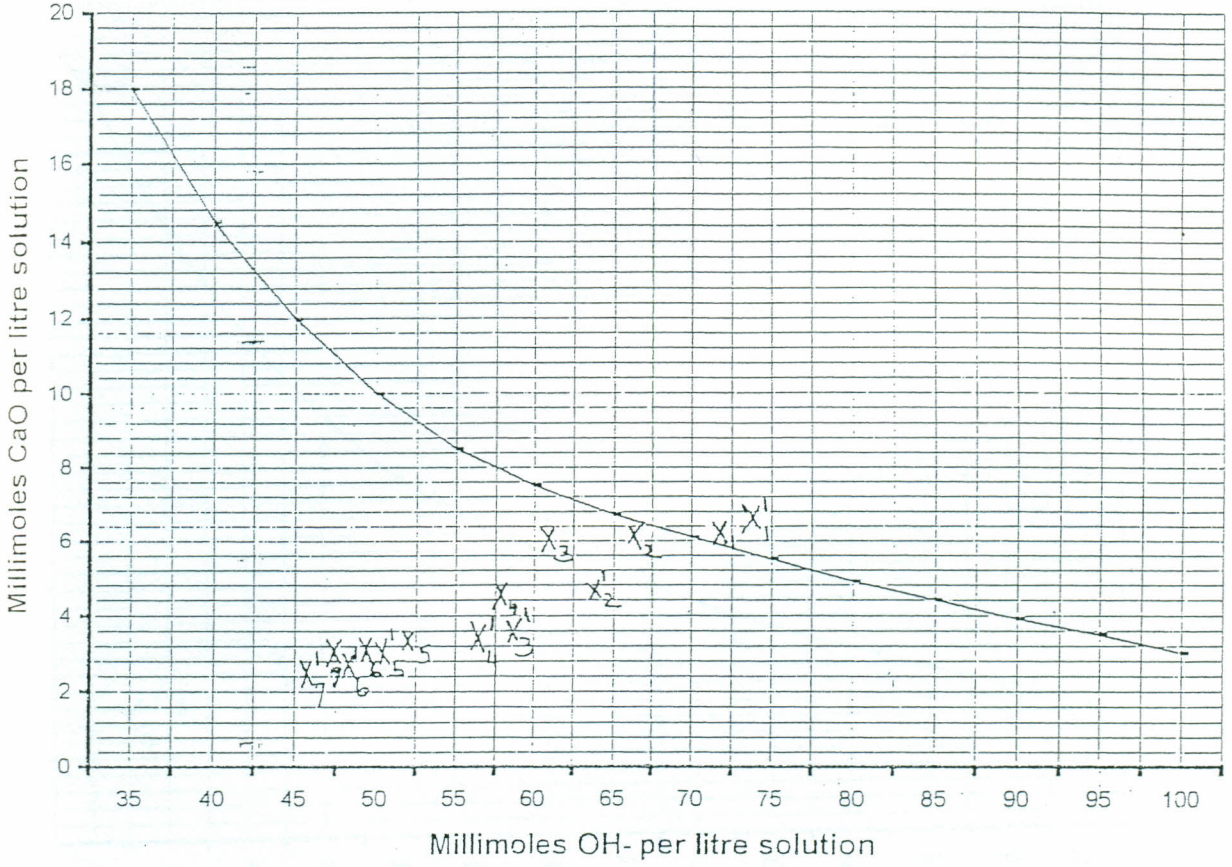


X_1=0% C-W BB (8-days)
X_2=15% C-W BB (8-days)
X_3=20% C-W BB (8-days)
X_4=25% C-W BB (8-days)
X_5=30% C-W BB (8-days)
X_6=35% C-W BB (8-days)
X^1_7=40% C-W BB (8-days)

X^1_1=0% C-W BB (15-days)
X^1_2=15% C-W BB (15-days)
X^1_3=20% C-W BB (15-days)
X^1_4=25% C-W BB (15-days)
X^1_5=30% C-W BB (15-days)
X^1_6=350% C-W BB (15-days)
X^1_7=40% C-W BB (15-days)

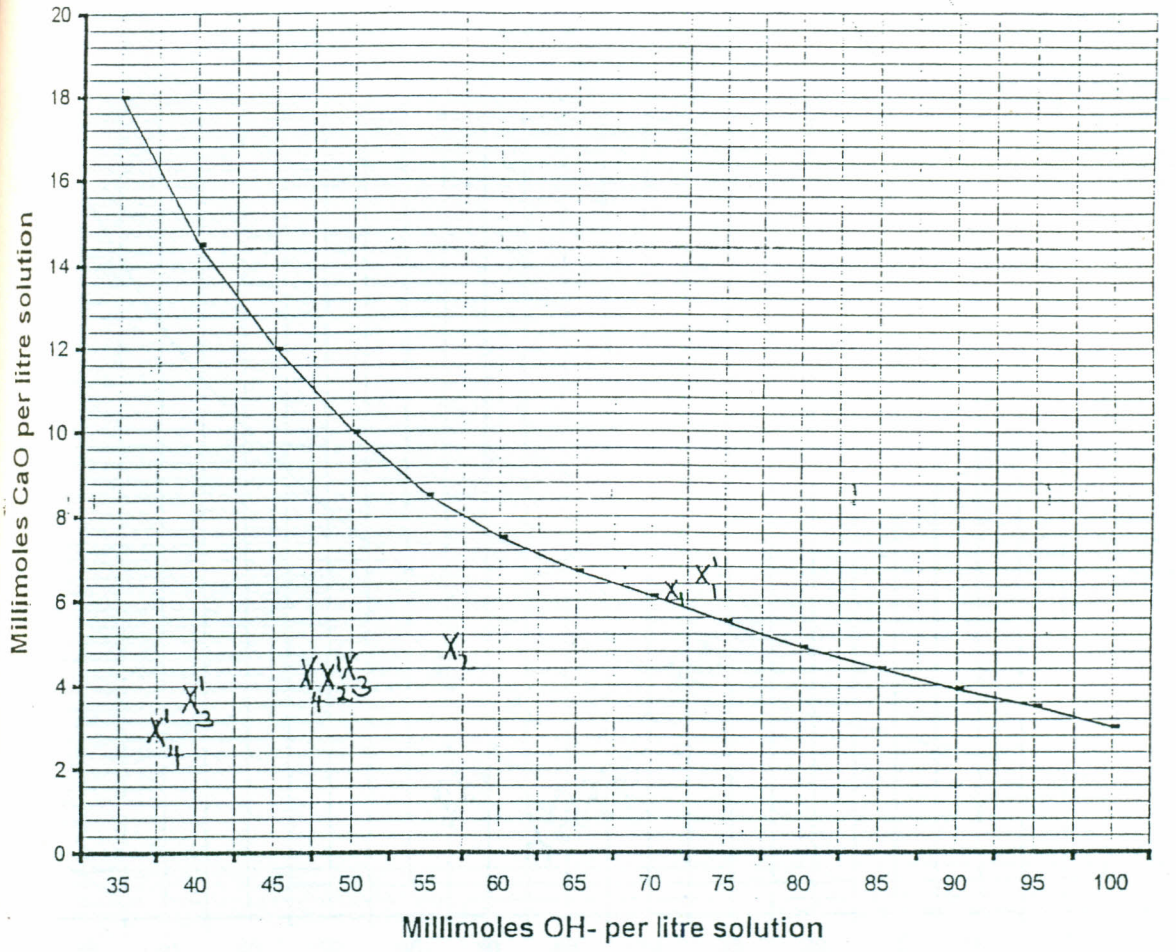
Figure 4.9; Pozzolanicity Diagram For Portland Activated C-W BB Cement



X_1=0% G-45 BB (8-days)
X_2=15% G-45 BB (8-days)
X_3=20% G-45 BB (8-days)
X_4=25% G-45 BB (8-days)
X_5=30% G-45 BB (8-days)
X_6=35% G-45 BB (8-days)
X^1_7=40% G-45 BB (8-days)

X^1_1=0% G-45 BB (15-days)
X^1_2=15% G-45 BB (15-days)
X^1_3=20% G-45 BB (15-days)
X^1_4=25% G-45 BB (15-days)
X^1_5=30% G-45 BB (15-days)
X^1_6=350% G-45 BB (15-days)
X^1_7=40% G-45 BB (15-days)

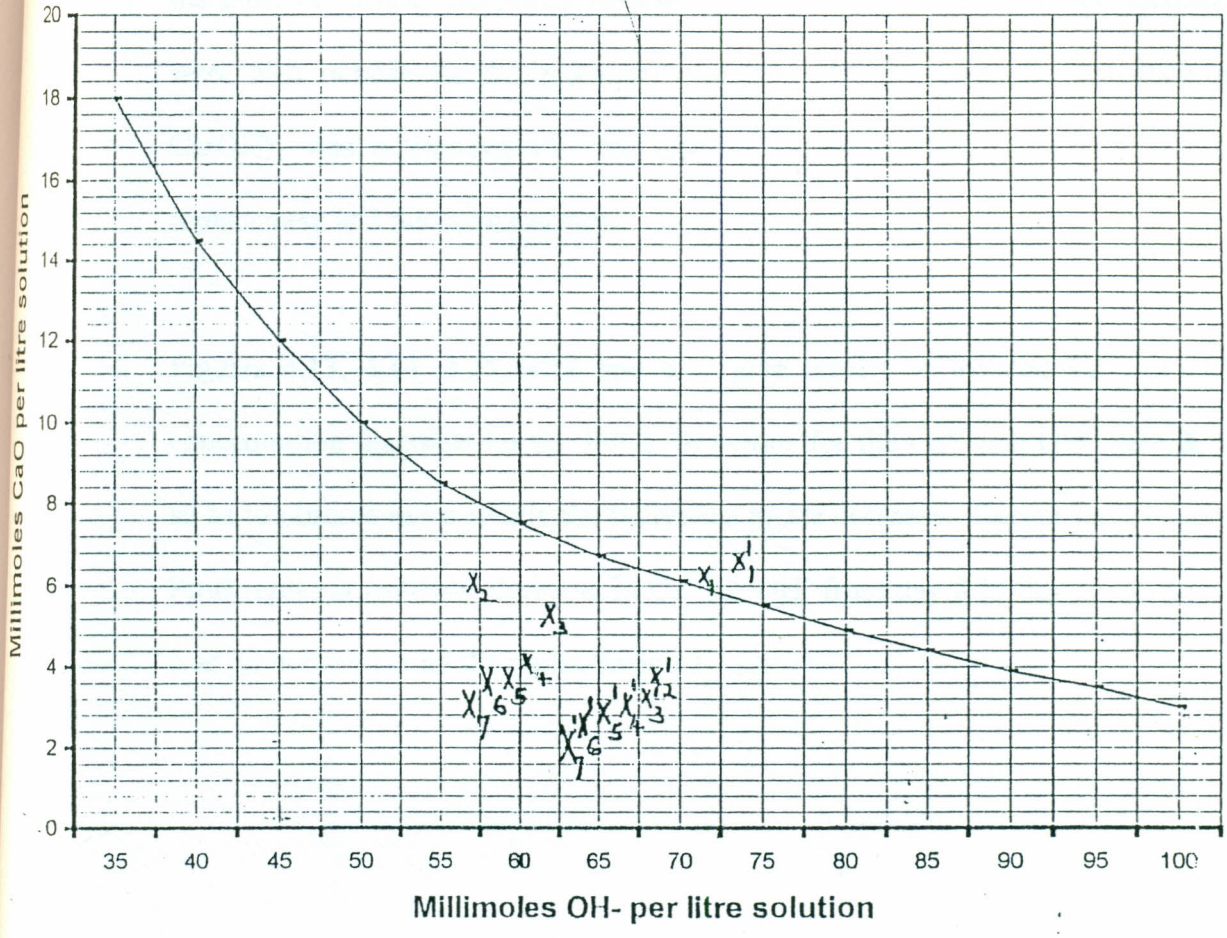
Figure 4.10; Pozzolanicity Diagram For Portland G-45 BB Cement



X_1=0% RHA (8-days)
X_2=15% RHA (8-days)
X_3=20% RHA (8-days)
X_4=25% RHA (8-days)

X^1_1=0% RHA (15-days)
X^1_2=15% RHA (15-days)
X^1_3=20% RHA (15-days)
X^1_4=25% RHA (15-days)

Figure 4.11; Pozzolanicity Diagram For Portland RHA Cement



X_1=0% Ptuff (8-days)
X_2=15% Ptuff (8-days)
X_3=20% Ptuff (8-days)
X_4=25% Ptuff (8-days)
X_5=30% Ptuff (8-days)
X_6=35% Ptuff (8-days)
X_7=40% Ptuff (8-days)

X^1_1=0% Ptuff (15-days)
X^1_2=15% Ptuff (15-days)
X^1_3=20% Ptuff (15-days)
X^1_4=25% Ptuff (15-days)
X^1_5=30% Ptuff (15-days)
X^1_6=350% Ptuff (15-days)
X^1_7=40% Ptuff (15-days)

Figure 4.12; Pozzolanicity Diagram For Portland Ptuff Cement

For SBEs, the reduction in Ca^{2+} and OH^- was so large that for 35 and 40 percent, the points were so low that they were outside the Pozzolanicity diagram's margins. For RHA, the points representing 30, 35 and 40 percent replacements were also outside the Pozzolanicity margins. In all cases, the reduction in $Ca(OH)_2$ was a function of the type of incorporated pozzolana, extent of replacement and the curing period.

Figures 4.13, 4.14, 4.15, 4.16 and 4.17 give results of isolated Ca^{2+} or OH^- concentration diagrams for the PPCs. Isolations for the Ca^{2+} and OH^- were done so as to observe more clearly the individual phase decrease. Except for OPC and Ptuff replaced cements, decrease in Ca^{2+} or OH^- from day 8 to day 15 of curing was pronounced in all the replacements.

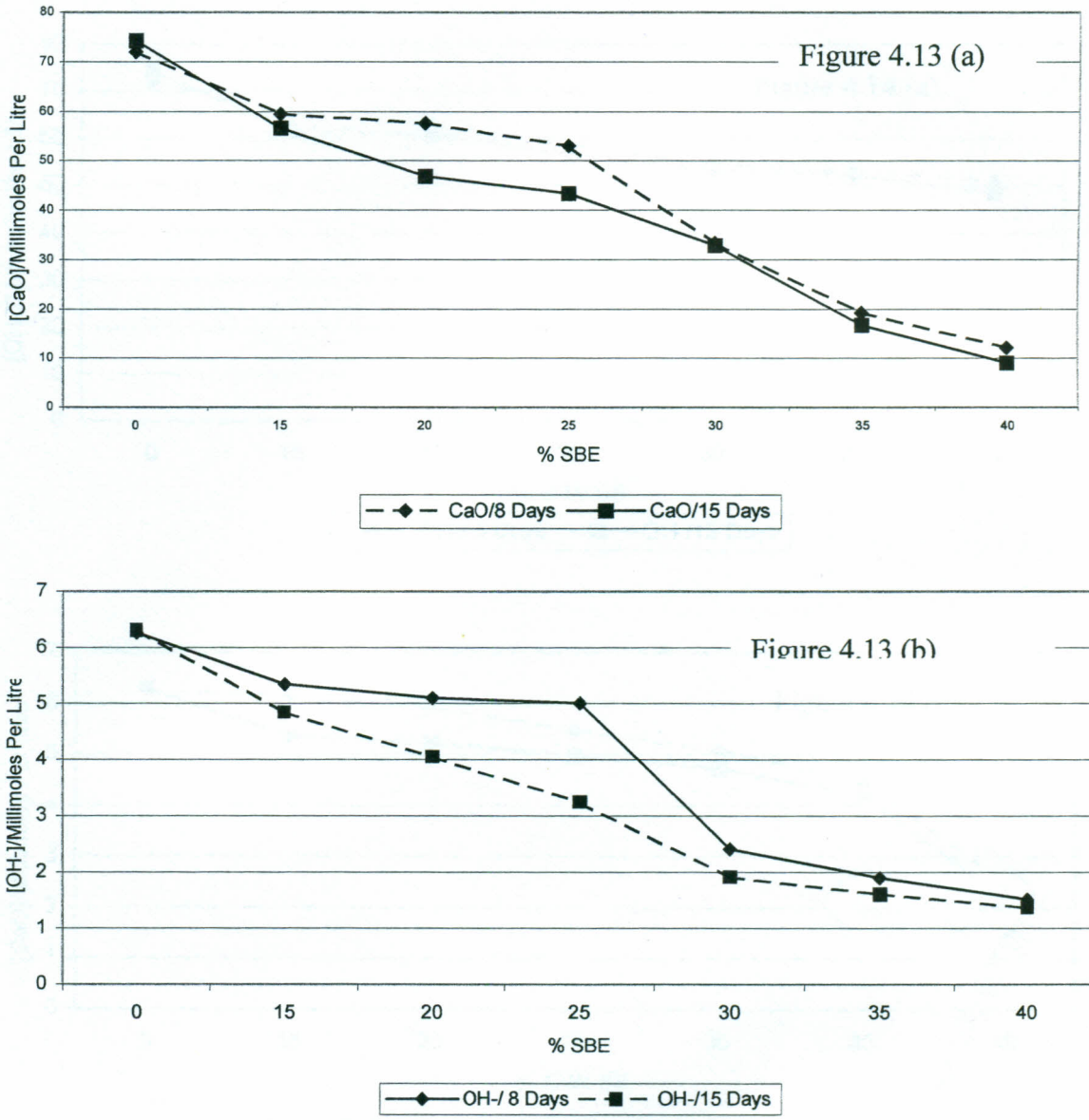
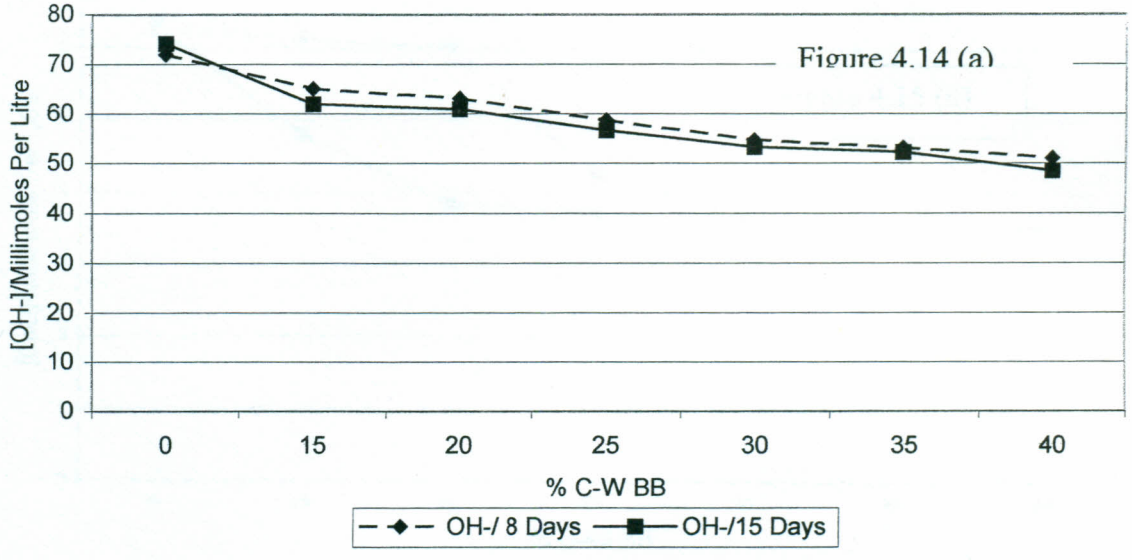


Figure 4.13 (a and b): Pozzolanicity Graph for Portland SBE Cement



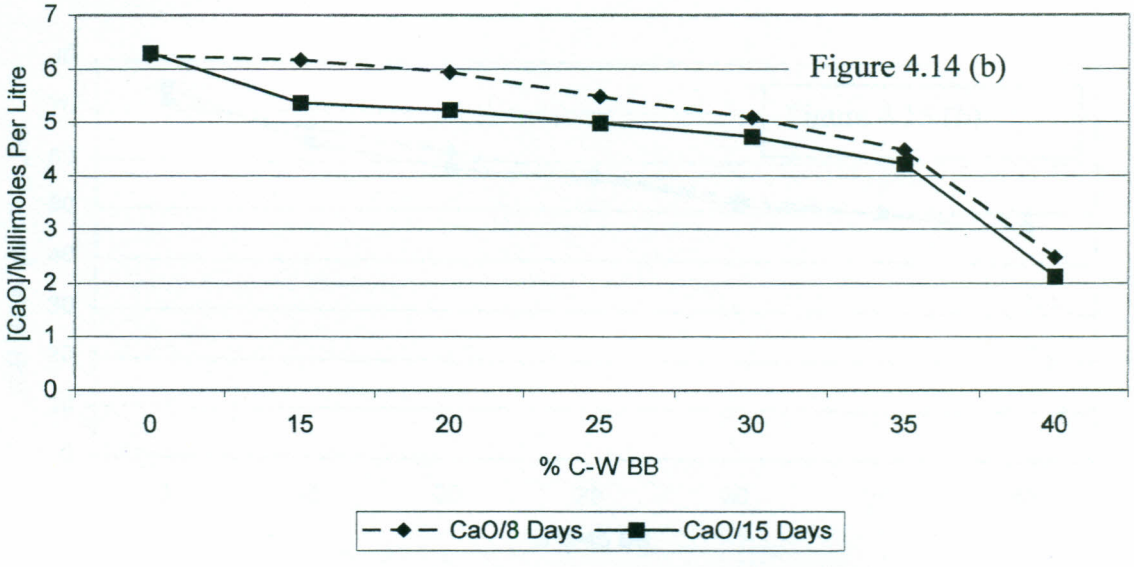
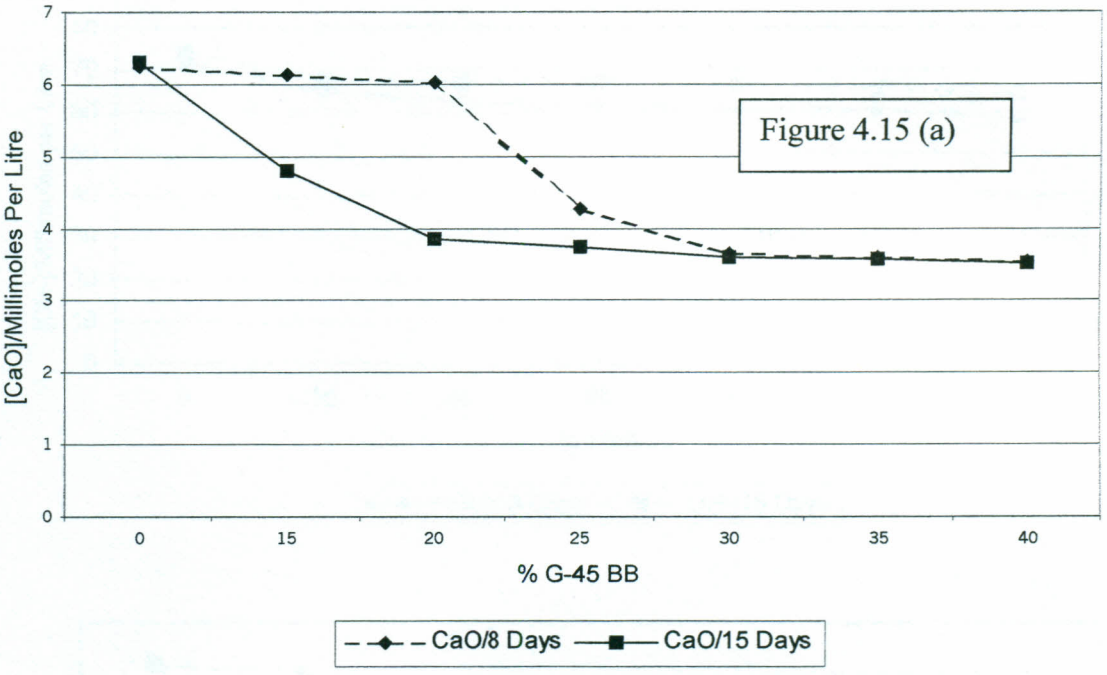


Figure 4.14 (a and b): Pozzolanicity Graph for Portland C-W BB Cement



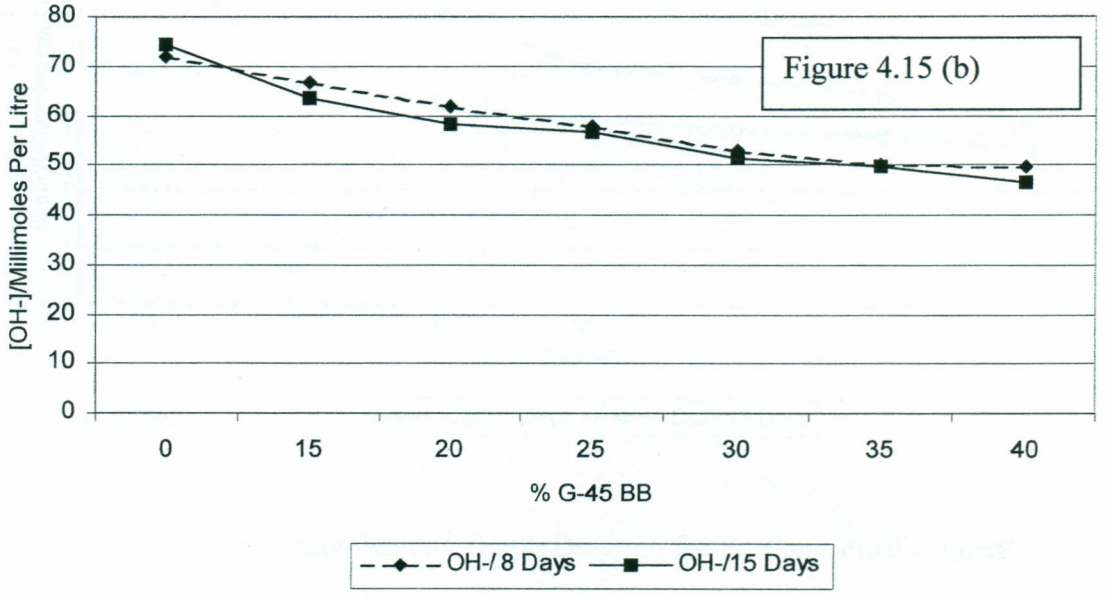
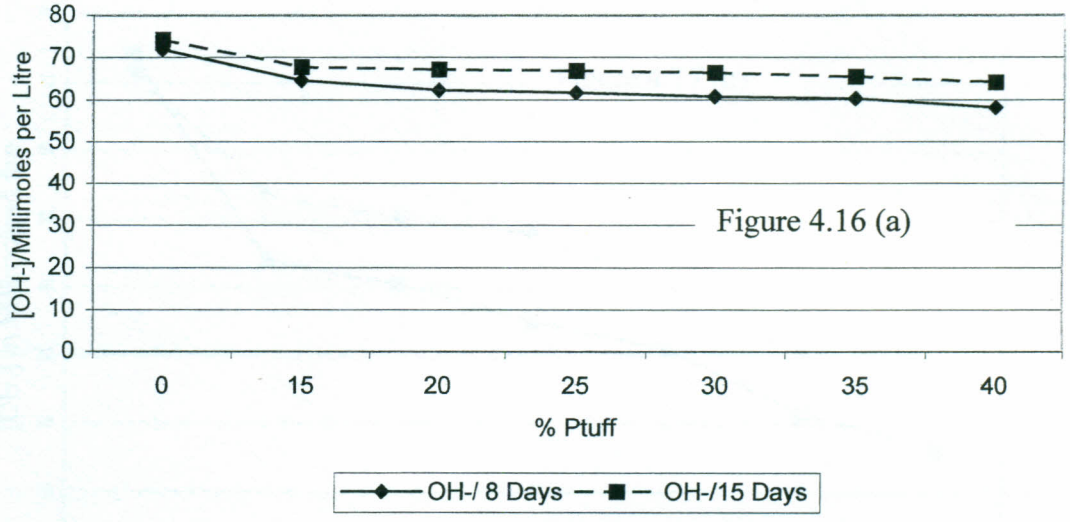


Figure 4.15 (a and b) Pozzolanicity Graph for Portland G-45 BB Cement



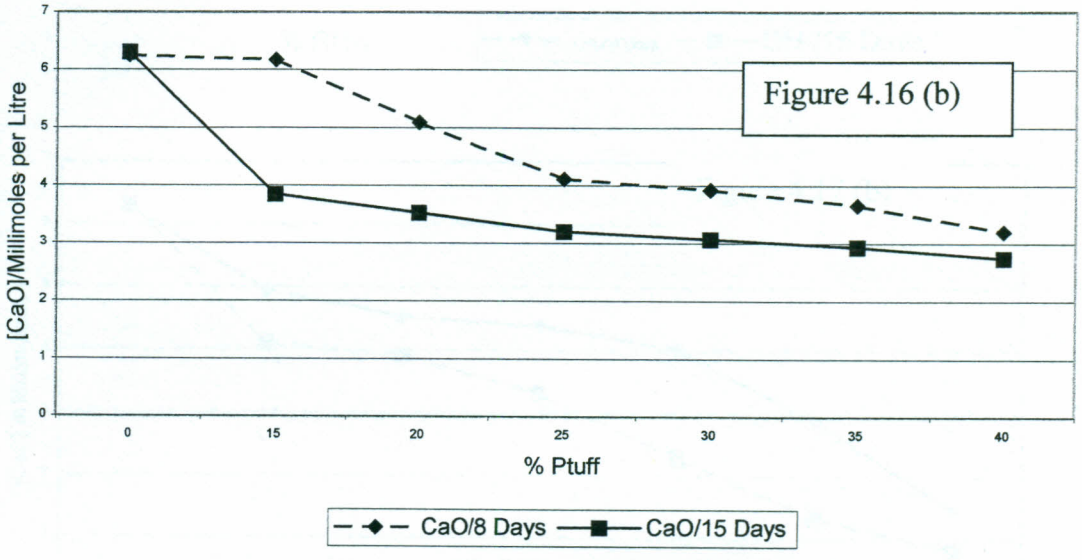


Figure 4.16 (a and b): Pozzolanicity Graph Diagram for Portland Ptuff Cement

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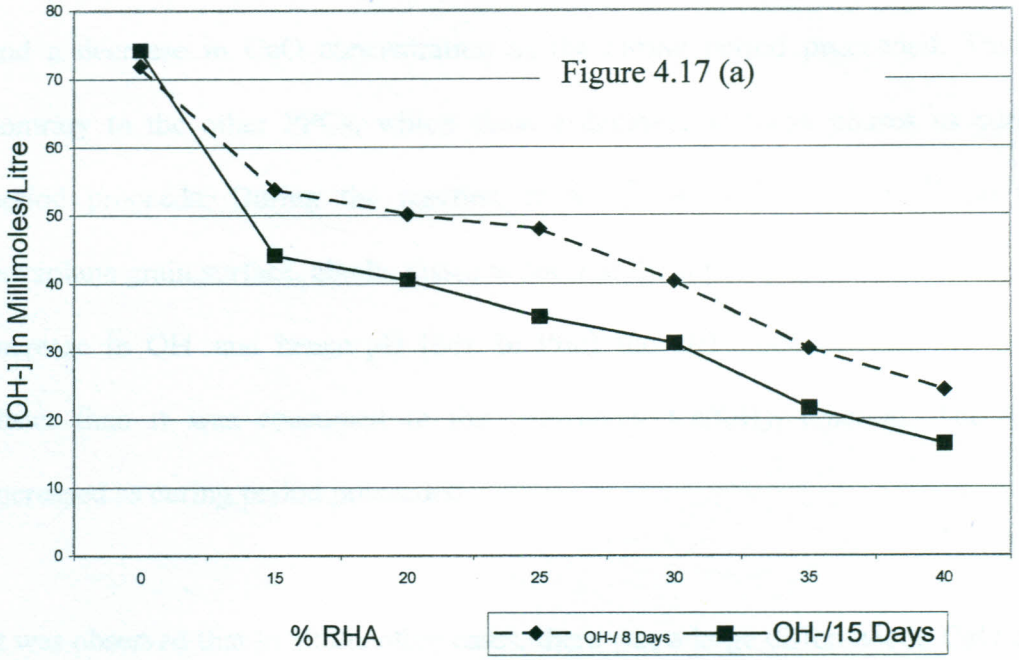


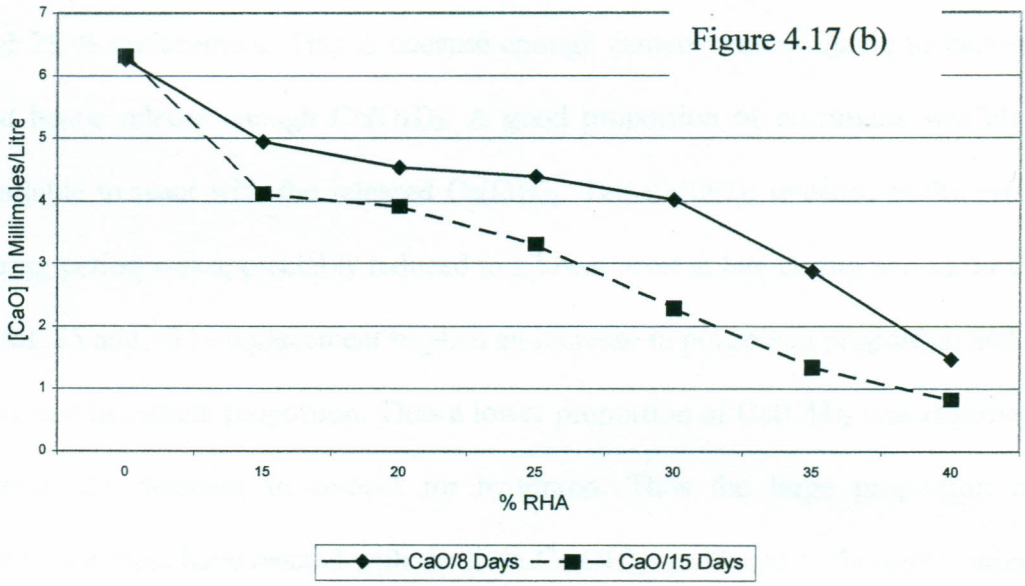


Figure 4.17 (a and b): Pozzolanicity Graph for Portland RHA Cement

The results show that for the Ptuff replaced cement there was an increase in OH^- and a decrease in CaO concentration as the curing period proceeded. This is contrary to the other PPCs, which show a decrease in these phases as curing period proceeds. During the reaction of SiO_4^{4-} and AlO_2^- with Ca^{2+} on the pozzolana grain surface, alkalis dissolve out into the liquid phase. This causes an increase in OH^- and hence pH [60]. In Ptuff the OH^- concentration increased faster than it was consumed in the pozzolana- $Ca(OH)_2$ reaction. The OH^- increased as curing period proceeded.

It was observed that in all the other cases, there was a large difference in CaO and OH^- concentration between the 8^{th} and 15^{th} day of curing and especially for the 20 and 25 % replacement. This is because enough cement was available to hydrate and hence release enough $Ca(OH)_2$. A good proportion of pozzolana was also available to react with the released $Ca(OH)_2$. The $Ca(OH)_2$ released at the early curing period was appreciably reduced to a lower level at late curing period. In all cases, 35 and 40 % replacement implied an increase in pozzolana proportion and a decrease in cement proportion. Thus a lower proportion of $Ca(OH)_2$ was expected due to the decrease in cement for hydration. Thus the large proportion of pozzolana must have reacted with the little $Ca(OH)_2$ produced at the early curing period. A low proportion of the $Ca(OH)_2$ is left to react with the unreacted pozzolana. This then implies that, for the prolonged period of curing the small amount of the $Ca(OH)_2$ reacts insignificantly. This gave a small difference in the

CaO or OH^- between the two curing periods. An optimum replacement in terms of $Ca(OH)_2$ released by the hydrating cement would thus be 25 %. The 25 % replacement of cement from this work concurs with the local PPC manufacture optimum replacement figure, although the compressive strength test is basically used to determine this figure.

SBE and RHA replaced cements are observed to reduce CaO and OH^- to the least amount as seen in their Pozzolanicity test diagrams. One would assume that they should have the best pozzolana-hydrated lime compressive strength and setting time performances. This was not the case. RHA had the poorest performance in these aspects. This was so, because pozzolanicity test does not show the contribution of pozzolana-hydrated lime reaction in producing cementious materials [107]. It shows the effect of pozzolana in reducing the $Ca(OH)_2$ phase in hydrated cement. The extent of reduction may not necessarily be related to additional cementious compounds properties [107]. This is because the interval of analysis may not be sufficient to allow for complete pozzolana lime-reaction to form the hard cementious material.

In respect to the compressive strength of the materials, setting times and reduction of CaO and OH^- in Portland pozzolana cement, all the materials are potential pozzolanic materials for use both in pozzolana-hydrated lime cements and in partial replacement of the Portland cement. Up to 25 % replacement, the cements

met the Kenya standard [1] requirements. These cements can therefore be used for any PPC recommended purpose.

4.3. COMBINED CEMENT

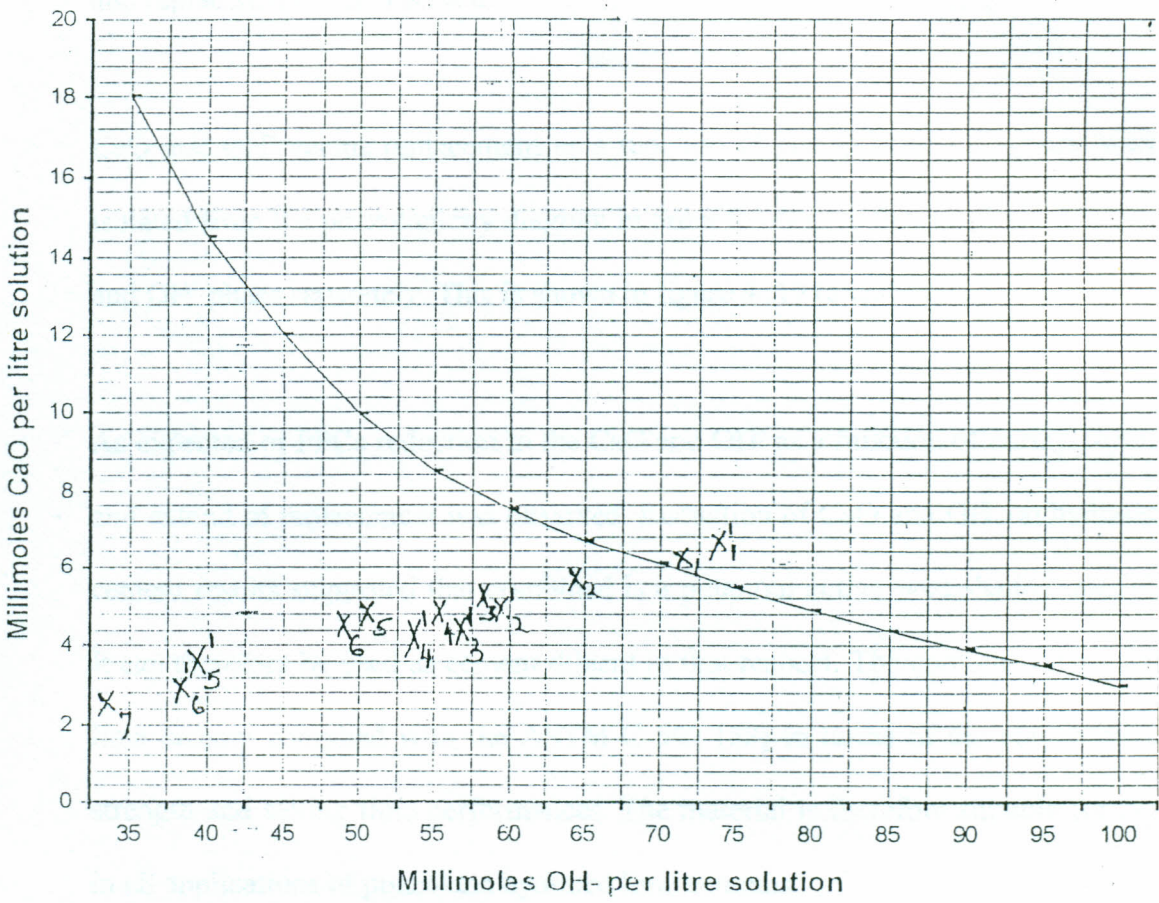
Although SBE showed a calorific value comparable to that of RH [108], the energy was not sufficient to fully activate the SBE. An external source of energy was thus required. Activated C-W BB showed improved performance in terms of compressive strength and setting time. This would imply increased energy cost for the higher quality pozzolana production. Incineration of RH alone however, generates about 15 J/g heat [108]. This energy is normally lost. It was important therefore to devize a way that the RH energy would be utilized to activate the SBE and BB.

The mix would be based on compressive strength performance and setting times of the SBE, RHA and BB. An ideal proportion would have been one with highest proportion of SBE, then BB and with least RH because of the pozzolanicity of these materials according to their compressive strengths as shown in table 4.4. When RH is compacted and ignited, its combustion temperatures increase to very high values [109]. This produces predominantly crystalline silica, which is not pozzolanic. A large proportion of SBE and BB would have compacted the RH. Bearing in mind the necessity of providing just enough activation energy and

avoidance of compaction, a workable mix was tried. The ratio of 1:1:5 of raw SBE: BB: RH respectively was chosen. The resulting ash was labelled Combined.

The performance of the combined was compared to that of the ashed blended mix 5: 8: 8 of SBE: BB: RHA. The results are given in table 4.4. The ratio of ashes in combined and ashed blended mix–CHL cement, calculated in terms of the ash content of SBE, RH and BB, were the same. Combined-CHL cement had a performance that was lower than activated C-W BB and SBE but higher than that of RHA-CHL cements. The performance, in terms of compressive strength and setting times of pozzolana-hydrated lime cement, of the combined was higher than the ashed blended mix-CHL cement. This shows that energy of the RH and SBE was used for activation of the BB, SBE and RH.

The pozzolanicity test of the Portland combined cement in various ratios was performed. The results are given in figure 4 .18.



X_1=0% Combined (8-days)
X_2=15% Combined (8-days)
X_3=20% Combined (8-days)
X_4=25% Combined (8-days)
X_5=30% Combined (8-days)
X_6=35% Combined (8-days)
X^1_7=40% Combined (8-days)

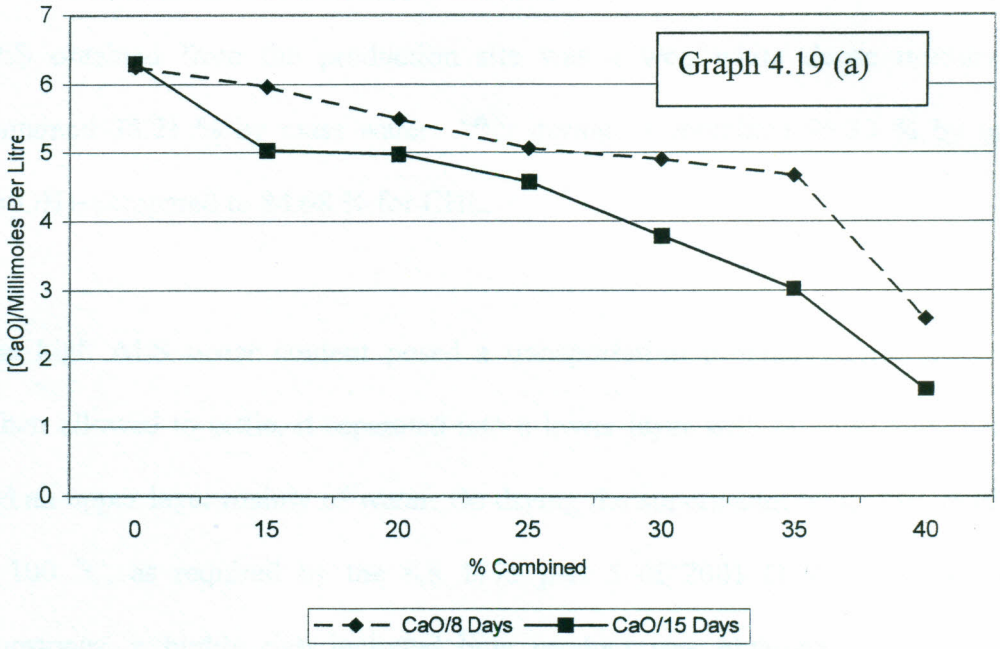
X^1_1=0% Combined (15-days)
X^1_2=15% Combined (15-days)
X^1_3=20% Combined (15-days)
X^1_4=25% Combined (15-days)
X^1_5=30% Combined (15-days)
X^1_6=35% Combined (15-days)

Figure 4.18; Pozzolanicity Diagram For Portland Combined Cement

As expected of PPCs, the reduction of CaO and OH^- as a function of curing period and replacement was observed.

CaO and OH^- versus replacement as a function of curing period diagrams were isolated from the pozzolanicity diagram in order to observe the change in the CaO and OH^- phase separately. This is shown in figure 4 .19 (a and b).

As expected of PPCs reduction in the CaO and OH^- as a function of curing period and extend of replacement was observed. Reduction of CaO and OH^- on hydrated cement results suggested that combined is a potential active pozzolanic material. It can therefore be used as cement diluent in that respect. The combined-hydrated lime cement complied with the ASTM C 593 [58] in terms of the compressive strength and setting time performances. The material is therefore suitable for use in all applications of pozzolana hydrated lime cements.



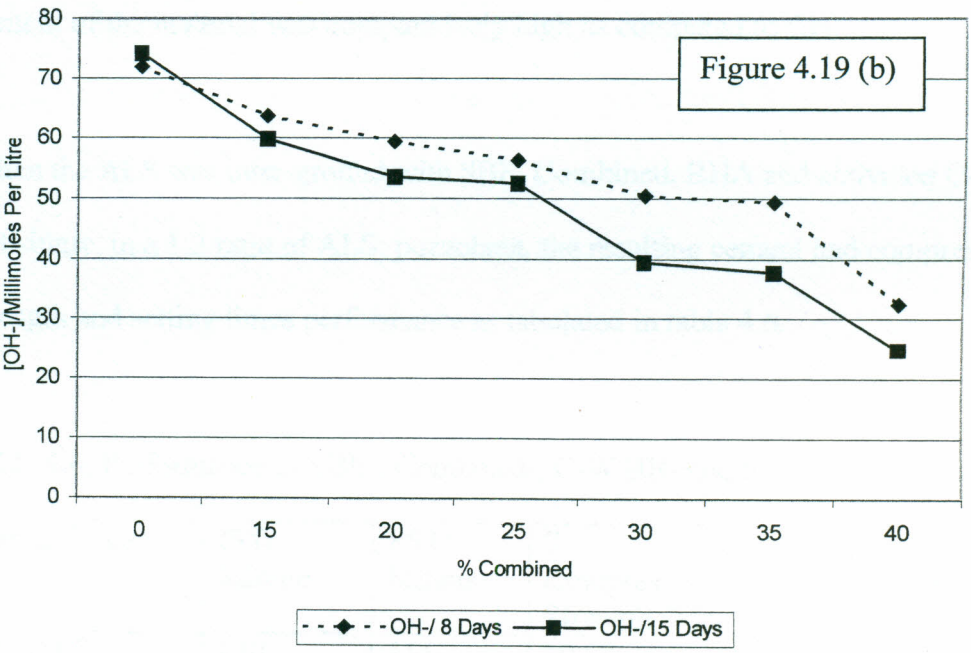


Figure 4.19 (a and b): Pozzolanicity Graph for Portland Combined Cement

4.4. ACETYLENE LIME SLUDGE (ALS)

ALS obtained from the production site was a wet, white dense mixture. It contained 38.21 % by mass water. After drying, it contained 96.33 % by mass $Ca(OH)_2$ compared to 84.08 % for CHL.

The high ALS water content posed a transportation problem of the material. When allowed to settle, it separated into a lower layer with less wet supernatant and an upper layer mainly of water. On drying the supernatant material overnight at 100 ^{0}C, as required by the KS 1775 part 5 of 2001 [104] for limes and limestones, a highly rich hydrated lime product was obtained. The $Ca(OH)_2$ content of the material was comparatively high as compared to CHL.

When the ALS was inter-ground with SBE, Combined, RHA and activated C-W BB singly, in a 1:2 ratio of ALS: pozzolana, the resulting cement had compressive strength and setting times performance as tabulated in table 4.6.

Table 4.6; Performance of SBE-, Combined-, C-W BB- and RHA- ALS Cement.

Cement Type	IST/ Minute	FST/ Minute	7 Days Compressive Strength (Mpa)	28 days Compressive Strength (Mpa)
SBE-ALS	120	314	10.58	11.41
Combined-ALS	266	463	10.52	11.17
Activated C-W BB-ALS	263	526	10.00	10.06
RHA-ALS	349	462	5.82	5.93

The pozzolana-ALS cements had an improved performance in terms of compressive strength and setting times as compared to the pozzolana-CHL cements shown in table 4.4. This must have been due to its high $Ca(OH)_2$ content. The cements are therefore suitable for use for all purposes of pozzolana-hydrated lime cements, for example in flooring, plastering, among other uses of pozzolana-hydrated lime cements.

Pozzolana-ALS cements were used to make mortar cubes some of which are shown in plate 4.1. The cements produced mortar cubes of different colors ranging from white, reddish white to red. The colors of the resulting cements were different because of the difference in the pozzolanic materials coloration. These cements can therefore be used in flooring or plastering where such colors are preferred without necessarily applying paints. This would thus reduce the cost of painting for aesthetic purposes

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Plate 4.1; Pozzolana-ALS Mortar cubes

From left to right the pozzolana incorporated is RHA, SBE, activated C-W BB and Combined respectively.

Comparing the cost of drying ALS and production of CHL from calcium carbonate, drying ALS has a lower energy requirement. This heat can be trapped from the released heat from 'combined' incineration. Incineration of Combined releases gases, for example SO_3, which cause pollution to the atmosphere. During the course of drying the ALS, the gases released from the combined can be directed to the ALS, which would absorb it with formation of $CaSO_4$. This would however reduce the percentage content of the $Ca(OH)_2$, although not to such a significant extent because the percentage is very low (table 4.3). This is as per the following equation;

$$Ca(OH)_{2\,(aq)} + SO_{3(g)} \longrightarrow CaSO_{4(s)} + H_2O_{(l)} \quad \text{..... 4.1}$$

4.5 PORTLAND-COMBINED-ALS CEMENT

There was a marked distinct change in performances in terms of pozzolanicity and compressive strengths at and above 25 % of replacement in the PPCs discussed earlier. This was mainly attributed to pozzolana and $Ca(OH)_2$ proportions in the PPCs. The presence of a less cement proportion subsequently yielded less $Ca(OH)_2$ on its hydration. This implies that a large proportion of pozzolana added finally did not produce cementious material. Early compressive strength of PPCs depends on the properties of Portland cement incorporated [61]. Due to these reasons, a proportion of combined and ALS in a 2:1 ratio were inter-ground with commercial OPC from Bamburi cement factory. The resulting product had performance as given in figure 4.20 and 4.21. Figure 4.20 shows comparative strength development between the cements as curing period proceeds whereas figure 4.21 shows strength development for a given cement as curing period proceeds.

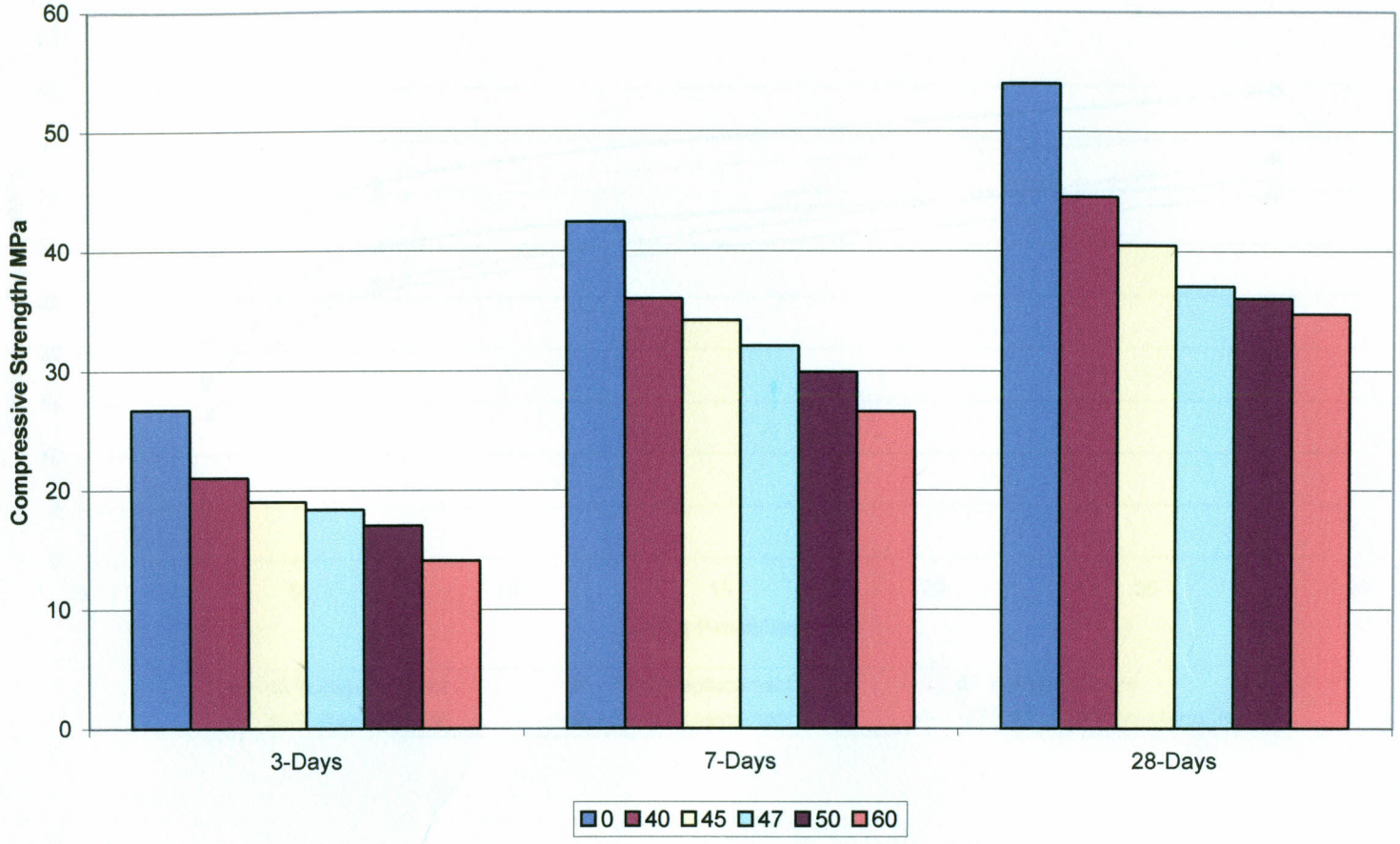

Figure 4.20: Compressive Strength Development of Portland-Combined-ALS Cement

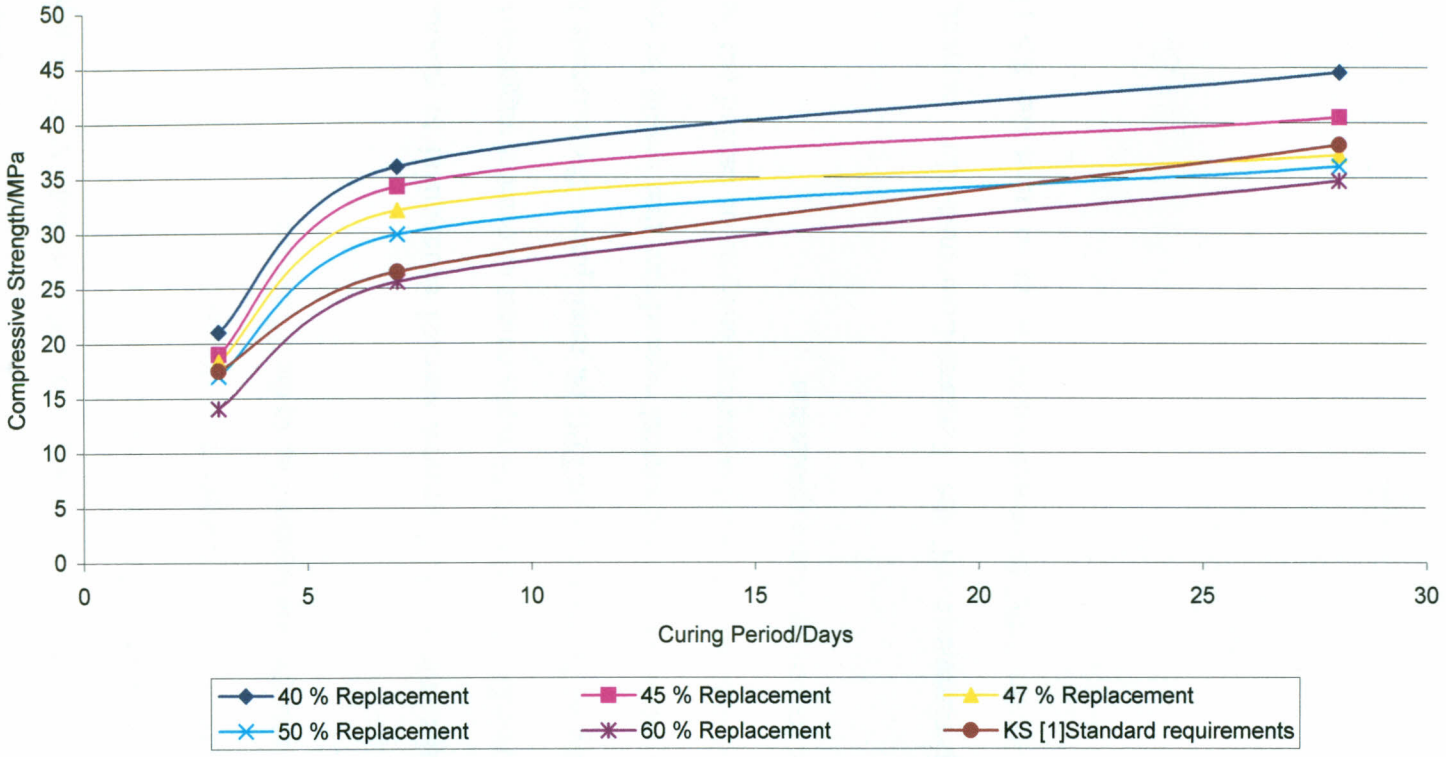

Figure 4.21; Compressive Strength Development of Portland-Combined-ALS Cement as a Function of Curing Period

It was observed that the compressive strength of the resulting product was still above all the other PPCs discussed earlier in terms of compressive strength development at a given replacement and curing period. At 45 % replacement as observed from figure 4.21, the cement satisfied the KS 02 1263 of 1993 [1] standard requirements on compressive strength at all curing periods. The 47 % replacement satisfies the standard up to the 7^{th} day but fails at the 28^{th} day.

The Portland-combined-ALS cement seemed economical to produce. A rough estimate (appendix 1) on the 45 % replacement of cement suggested a saving of approximately 20 % per tonne of PPC on retail price. The estimate however did not take into consideration the capital expenditure that would be required. It is recommended that more detailed economic analysis be carried out before further consideration for commercial exploitation.

From the performance of the Portland-Combined-ALS cement, a 45 % replacement of the OPC is recommended so as to meet the KS [1] standard requirements.

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATIONS

From the results of this work, the following conclusions and recommendations were made.

5.1 CONCLUSIONS

SBEs from the different oil processing factories had different calorific values and ash contents, which was due to the differences in oil contents. The major oxides percentage, SiO_2, Al_2O_3 and Fe_2O_3, of the SBEs ash was within the Kenya standard. Based on the ash and major oxides content, the SBEs are potential pozzolanic materials.

Activation of a large mass of SBEs to obtain pozzolanic materials was not economical. This is because it would require a higher amount of external source of activation energy and long activation periods.

BBs from the different sources are potential pozzolanic materials. The chemical constituent difference may be attributed to different clay sources for making the bricks by the different manufacturers. Pozzolanicity difference may also be attributed to difference in glassy phase content.

Further activation of poorly performing BB improves their pozzolanic activity. This is most probably due to improvement of their glassy phase content.

Utilization of the calorific value of SBEs and RH for activation of the SBEs, RH and BB is economically viable. This is possible because the RH completely burns on itself liberating heat that if untapped for use is lost. Although SBE has a calorific value comparable to RH, it cannot be self-activated. When the SBE, BB and RH were combined in a 1: 1: 5 ratio and ignited, the calorific value of RH and SBE activated the three and produced a pozzolanic material. This combination has been named ''Combined'' in this study.

ALS, a by-product of the acetylene gas manufacturing company, when dried, is a hydrated lime. The lime produced this way had a $Ca(OH)_2$ content of 96.33 %. This was comparatively higher than that of the commercial hydrated lime. The ALS is a potential $Ca(OH)_2$ material for use in the pozzolana-hydrated lime cements. Its use in pozzolana-hydrated lime cements resulted in superior performance compared to CHL.

A 45 % replacement of the Bamburi factory OPC with the combined-ALS cement made a product that complied with the Kenya standard PPC in all aspects. The PPC made this way was estimated to give an economic saving of 20 % per tonne

of PPC. The PPC can be used for any recommended KS 02 1263 of 1993 [1] PPC use.

5.2 RECOMMENDATIONS

A pilot plant should be constructed to assess the viability of a cement based on the combined pozzolanic materials produced from this work. The Portland-combined-ALS PPC made in this work can be used in such fields as in the making of concrete benches, for example, the ones all over Kenyatta University and concrete blocks.

Optimum RH: SBE: BB ratio should be further determined for production of the combined pozzolanic material. This should be based on an economic and quality stand.

Research should be carried out to assess the suitability of using the heat released during the calcination of the combined material in drying of the ALS. A design should be introduced for tapping of the heat from the kiln of the combined incineration. Such a design would perhaps have a pipe with running tap water through the burning materials and then to the ALS reservoir. The boiled water or steam, would then release its heat to the ALS, thus drying it.

Research should also be carried out to assess the possibility of using the heat content of the SBE for domestic purposes. This would include using it as brickets or intermixing it with RH or sawdust.

Kilns other than the FBK should be assessed for production of the combined pozzolanic material. FBK is highly affected by the materials compaction. Other kilns like the rotary kiln should be assessed.

A more detailed economic analysis should be carried out to assess on the 45 percent replacement of the cement by the 'combined'-ALS mixture. This should be done before setting up a pilot plant for its production.

An investigation should be carried out to determine savings of incorporating the SBE in the kiln during manufacture of cement. The investigation should assess direct injection of the material into the kiln vis a vis introduction with the raw mill through the preheaters.

REFERENCES

1. Kenya Standard, *Specification For Portland Pozzolana Cements,* KS 02 1263, Kenya Bureau of Standards, Nairobi, (1993).
2. Spence, R. J. S., Small Scale Production of Cementious Materials, Intermediate Technology Publication Ltd, London, 4, (1983).
3. East Africa Standard, Tuesday May, 8th 2001, Nairobi, Kenya, Tom Mogusu (ed.), 12, Col.1.
4. Naville, A. M. and Brooks, J. J., Concrete Technology, Longman, New York, 8-68, (1987).
5. Sunday Nation, Sunday September, 8th 2002, Nation Media Group, Nairobi, Kenya, 20 – 21.
6. Republic of Kenya, 1999 Population and Housing Census, Counting our People for Development, Vol. II, Government Printer, Nairobi, xiv-xv, (Jan. 2001).
7. Koram, K. A., Bennett, S., Adiamah, J. H. and Greenwood, B. M., Socioeconomic Risk – Factors for Malaria in a Peri-urban Area of the Gambia; *Transaction of the Royal Society of Tropical Medicine and Hygiene,* **89,** (2), 146-150, (1995).
8. Ghebreyesus, T. A., Haile, M., Witten, K. H., Getachew, A., Yahannes, M., Lindsay, S. W. and Byass, P., 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, (2000).

9. Pfafflin, J. R. and Tompeck, M. A., *Recycling Waste Materials,* Encyclopedia of Environmental Science and Engineering, 3rd edn, Pfafflin, J. R. and Ziegler, E. N. (Eds.), Vol. 2, Gordon and Breach Science Publishers, 776, (1993).
10. Spence, R. J. S. and Cook, D. J., Building Materials in Developing Countries, Wiley, London, 125-157, (1983).
11. Kimber, D. S. and McGregor, (Eds.), Brassica Oil Seeds Production and Utilisation, CAB international, , 285-286, (1995).
12. Meislich, E. K., Meislich, H. and Sharefkin, J., 3000 Solved Problems in Organic Chemisrty, McGraw Hill, New York, 208, (1994).
13. Czernin, W., Cement Chemistry and Physics For Engineers, 2nd Edn., Foreign Publication Inc., London, 23–153, (1980).
14. Lea, F. M., The Chemistry of Cement and Concrete, 3rd Edn., Edward Arnold (Publishers), London, 11-18, (1970).
15. Murdock, L. J., Brook, K. M. and Dewar, J. D., Concrete Materials and Practice, 6th edn., Edward Arnold, London, (1991).
16. Toxell, G. E., Davis, H. E., and Kelly, J. W., Composition and Properties of Concrete, 2nd edn., McGraw Hill Book Company, New York, (1968).
17. Kulkarni, P. D., Ghosh, R. K. and Phull, Y. R., Textbook of Concrete Technology, New Delhi, (1983),

KENYATTA UNIVERSITY LIBRARY

18. Neville, A. M. Properties of Concrete, 4th edn, Longman, New York, 84, (1986).

19. Blanks, F. R. and Kennedy, L. H., The Technology of Cement and Concrete, **1**, John Wiley and Sons, Inc., London, 100-190, (1983).

20. Glassers, F. P., Reaction Occurring During Clinker Making, *Structure and Performance of Cements*, Barness, P. (Ed.), Applied Science Publishers, London, 77, (1983).

21. Mackenzie, K. J. D. and Banerjea, R. K., *Trans. J. Brit. Ceram. Soc.* **77**, 88, (1978).

22. Odler, I. and Dorr, H., Early Hydration of Tricalcium Silicate and Kinetics of the Hydration Process and the Stoichiometry of the Hydration Products, *Cement and Concrete Research*, **9**,(2), 239-48, (March 1979).

23. Bogue, R.H and Lerch, W., Hydration of Portland Cement Compounds, *Industrial and Engineering Chemistry*, **26**, (8), Easton, Pa., 832-47, (1934).

24. Ramachandran, V. S. and Zhang, C.M., Influence of $CaCO_3$, *IL Cemento*, **3**, 129-52, (1986).

25. Diamond, S., C/S Mole Ratio of C-S-H Gel in a Mature C_3S Paste as Determined by EDXA, *Cement and Concrete Research*, **6**, (3), 413-16, (1976).

26. Cotton, B. The First Mix in Cement Hydration; *Hydration and Setting of Cements, 16th Proc. of The Int. Rilem Workshop*, Chapman and Hall, 96, (1992).

27. Jawed, T, Skalny, J. and Young, J. F, Hydration of Portland Cement; *Structure and Performance of Cements* Barness, p (Ed), Applied Science Publishers, London, 81, (1983).

28. Beaudoin, J. J. and Ramachandyan, V. C., A New Perspective on the Hydration Characteristic of Cement Phases, *Cement and Concrete Research*, **22**, (4), 689-94, (1992).

29. Negro, A, and Staffieri, L., *Zement-Kack-Gips* **32**, 83, (1979).

30. Struble, L., Skalny J. and Mindess, S., *Cement and Concrete Research,* **10,** (2), 277, (1980).

31. Maso, J.C., *7th International Congress on the Chemistry of Cement*, Paris, **1**, VII 1/3, (1980).

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

33. Sersale, R., Structure and Characterization of Pozzolanas and Fly Ash, *Proc. 7th Int. Congr. on the Chemistry of Cements*, Paris, Sub-Theme, IV –I, 1-18, (1980).

34. Cook, D. J., *Rice Husk Ash*; Concrete Technology and Design, Cement Replacement Materials, Vol. 3, Swamy, R. N. (Ed.), Surrey University Press, New Delhi, 171, (1986).

35. Sersare, R., Aspects of the Chemistry of Addition in Advances in Cement Technology, Ghosh, S. N. (Ed.), Pergamon, Oxford, 537-567, (1980).

36. Dhir, R. K., *Pulverised Fuel Ash*, Concrete Technology and Design Cement Replacement Materials, Vol. 3, Swamy, R. N. (Ed.), Surrey University Press, New Delhi, 197, (1986).

37. Dhir, R. K., Hubbard, R. H., Munday, J. G. L. and Jones, M. R., Characteristics of Low Lime Fly Ashes Significant to Use in Concrete; *Proc. 2nd Conf. on Fly Ash, Silica Fumes, Slag and Natural Pozzolans in Concrete*, Malhorta, V. M., (Ed.), Madrid, ACI Spec. Pub., SP –91, 693-722, (April 1986).

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

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

40. Lane, R. O. and Best, J. F., Properties and Use of PFA in Portland Cement Concrete; *Concrete International*, **4**, (7), 81-92, (1982).

41. Ghosh, A. and Pratt, P. L., Studies of Hydration Reactions and Microstructure of Cement – Fly Ash Paste; *Proc. Symp. on Fly Ash Incorporation in Hydrated Cement System*, Diamond, S. (Ed.), 82-91, (1981).

42. Owens, P. L. and Butter, F. G., The Reaction of Fly Ash and Portland Cement with Relation to the Strength of Concrete as a Function of Time and

Temperature; *Proc. 7th Int. Congr. on the Chemistry of Cement*, Paris, **3**, 4/60-4/65, (1980).

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

44. Mehta, P. K., the Chemistry and Technology of Cements Made from Rice Husk Ash, *Proc. UNIDO/ESCAP/RCTT Workshop on Rice Husk Ash Cement,* Peshawar, 113-122, (1979).

45. Boateng, A. A., and Skeete, D. A., Incineration of Rice Hull for Use as a Cementious Material: The Guyana Experience; *Cement and Concrete Research,* Pergmon Press, **20**, 795-805, (1990).

46. Ochungo, G. J., The Production of Rice Husk Ash Based Cementious Materials, MSc. Thesis, Department of Chemistry, Kenyatta University, Naiorbi, (1993).

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

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

49. Austrheim, I., Cristobalite and Tridymite Crystallization in Amorphous Silica collected from the Smoke from Silica Metal Furnace, *Trans. J. Br. Ceram. Soc.*, **76**, (6), 134-138, (1976).

50. Ankra, K., Studies of Black Silica Produced Under Varying Conditions, Ph.D. Thesis, University of California, Berkerley, (1976).

51. Chopra, S. K., Ahluwalia, S. C. and Laxmi, S., Technology and Manufacture of Rice Husk Ash Masonry (RHAM) Cement; *Proc. ESCAP/RCTT Third Workshop on Rice Husk Ash Cement*, New Delhi, (1981).

52. Ghosh, S. N., Advances in Cement Technology, Pergamon Press, New York, 649-673, (1983).

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

54. Spence, R. J. S., Lime and Surkhi Manufacture in India, Appropriate Technology, Vol. 1, 25-35, (1974).

55. WHO/UNEP-Europe, *Waste Discharge into the Marine Environment*; Principle Guidelines for the Mediterranean Action Plan, Pergamon Press, Sydney, 79, (1982).

56. Duedall, W. I., Kester, D. R., Park, P. K. and Ketchem, B. H., Wastes in the Ocean, Vol. 4, John Wiley and Sons, New York, 68-73, (1985).

57. Ellis, K. V., Surface Waste Pollution and its Control, Macmillan, London, 186, (1989).

58. Annual Book Of ASTM Standards, No. 593, Part C, *Standard Specification for Fly Ash and Other Pozzolanas for Use with Lime*, American Society of testing and Materials, Philadelphia, (1991).

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

60. Takemoto, K. and Uchikawa, H., Hydration of Pozzolanic Cement; *Proc. 7th Int. Congr. On the Chemistry of Cements*, Paris, Sub-Theme, IV- 2 –28, (1980).

61. Cook, D. J., Natural Pozzolans, Cement Technology and Design Vol 3; Cement Replacement Materials, Swamy, R. N (Ed.), 177-196, (1986).

62. Luke K. and Glasser, F.P., Internal Chemical Evolution of the Constitution of Blended Cements; *Cem. Conc. Res.* **18**, 495-502, (1988).

63. Huang, S., Hydration of Fly Ash Cement and Microstructure of Fly ash Cement Pastes; *CBI Res.* 2.8.1: *Swedish Cem. Res. Inst.*, Stockholm, (1981).

64. Sybertz, F., Comparison of different methods for testing the pozzolanic activity of fly ashes, *in fly ash silica fume slag and natural pozzolans in concrete*, Machotra, V.M. (Ed.), Detroit, Michigan, **1,** ACI SP-114, 477-97, (1989).

65. International Standard for Organization (ISO), *Cement – Test Methods – Pozzolanicity Test for Pozzolanic Cements, ISO 863: 1990 (E)*, Switzerland, (1990).

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

67. Takemoto, K. and Uchikawa, H., *Proc. 7th Int. Congr. Chem. of Cem.*, Paris, I, IV/2/1-IV/2/26, (1980).

68. Concrete 2000: Economic and durable Construction through Excellence, *Pro. Int. Conf. Held at Univ. Dundee, Scortland*, Dhir, R. K. and Jones, M.R. (Eds.), **2,** (7-9 Sept, 1993).

69. British Standard Part 2, *Methods of Testing Cement, Chemical Tests*, British Standard Institution, London, (1970).

70. Kong, H. L. and Orbison, J. G., Concrete Deterioration Due to Acid Precipitation, *ACI Materials Journal*, **84**, (3), 110-16, (1987).

71. Fattuhi, N. I. and Hughes, B. P., The Performance of Cement Paste and Concrete Subject to Sulphuric Acid Attack, *Cement and Concrete Research*, **18**, (4), 545-53, (1988).

72. Odler, I. and Glasser, M., Mechanism, of Sulfate Expansion in hydrated Portland Cement, *J. Amer. Ceramic SIC.*, **71**, (11), 1015 – 20, (1988).

73. ACI 201.2R-1992, Guide to Durable Concrete, *ACI Manual of Concrete practice part 1: Materials and General Properties of Concrete*, Michigan, 41, (1994).

74. Proc. One-Day Conf. On Alkali-Silica Reaction, The Concrete Society, London, 34, (October 1985).

75. Nixon, P. J. and Gaze, M. E., The Effectiveness of Fly Ashes and Granulated Blast Furnace Slags in Preventing AAR; *Proc. 6th Int. Conf. On Alkalis in Concrete*, Doran, G. M. and Rostam, S. (Eds.), Copenhagen, 61-68, (June 1983).

76. Building Research Establishment: Alkali Aggregate Reactions in Concrete; *BRE Digest*, 258, HMSO, London, 6, (1982).

77. Shriver, D. F., Alkins, P. W. and Langford, C. H., Inorganic Chemistry, 2nd edn. University Press, Oxford, 173, (1994).

78. Meislich, E. K., Meislich, H. and Sharefkin, J., 3000 Solved Problems in Organic Chemisrty, McGraw Hill, New York, 208, (1994).

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

80. Ross, C. S. and Hendricks, S. B., *Pof. Pap. U.S. Geol. Surv.*, **205B**, (1945).

81. Ross, C. S. and Shannon, E. V., *Jnl. Amer. Cer. Soc.*, **9**, (2), 77-96, (1926).

82. Levy, F., Crystalllography and Crystal Chemistry of Materials with Layered Structures, Reidel Publishing Company, Boston, 237, (1957).

83. Nutting, P. G., The Bleaching Clays; *U.S. Dept. of The Inter. Geol. Surv. Circ.*, **3**, (1933).

84. Mills, G. A., Holmes, J. and Cornelius, E. B., *Jnl. Phys. Colloid. Chem.*, **54**, 1170, (1950).

85. Puri, A. N., Balwant, R. and Ratti, T. R., *Jnl. Indian Chem. Soc. Industr. Edn.*, **9**, 22, (1947).

86. Richard, A. D., Industrial Minerals and Rocks, 2nd Edn., The American Institute of Mining and Metallurgical Engineering, New York, 127, (1949).

87. Patterson, H. W., *Jnl. Amer. Oil. Chem. Soc.*, **53,** 339, (1976).

88. King, R. R. and Wherton, F. W., *Jnl. Amer. Oil. Chem. Soc.*, **26,** 201-210, (1949).

89. Haines, P. J., Thermal Methods of Analysis, Principles, Applications and Problems, Chapman and Hall, London, 105, (1995).

90. Dodd, W. J. and Tonge, K. H., Thermal Methods; Analytical Chemistry by open Learning, John Wiley and Sons, New York, 1-22, (1987).

91. Mackenzie, R.C., Differential Thermal Investigation of Clays. London, Mineralogical Society, (1957).

92. Fifield, F. W. and Kealey, D., Principles and Practice of Analytical Chemistry, 4th Edn., New York, Chapman and Hall, 232-348, (1995).

93. Process Analytical Chemistry, McLennan, F. and Kowalski, B. R. (Eds.), Blackie Academic and Professional, London, 340, (1995).

94. Schenk, G. H., Hahn, B. R. and Hartkopf, A. V., Introduction to Analytical Chemistry, 2nd edn., Allyn and Bacon, Inc., Sydney, 349-358, (1981).

95. Skoog, D. A. and Leary, J. J., Principles of Instrumental Analysis, 4th edn., Saunders College Publishers, Fort Worth, (1992).

96. Khopkar, S. M., Basic Copncepts of Analytical Chemistry, Wiley Eastern Limited, New Delhi, 226-227, (1984).

97. Alzubaidy, S. N., 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**, (ISS), 13-19, (1992).

98. Barbar, Z. M., Bleaching Earth: Reuse as Animal Feed, Fertilizer; Case Number 4642, Indian Institute Of Recycling, Hammond, (2002).

99. Personal Communication with Gikonyo, S., Lubricants advisor, BP Kenya Limited, Nairobi, (2003).

100. Dhir, R. K., M. R. Munday, J. G. L. and Hubbard, F. H., Physical Characterization of U. K. Pulverized Fuel Ashes For Use in Concrete; *Mag. Concr. Res.*, **37**, (131), pp 75-87, (1985).

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

102. Cook, D. J. and Suwanvitaya, P., Rice Hush Ash Based Cements – A State of The Art Review, New Delhi, (1981).

103. Lea, F. M., The Testing of Pozzolanic Cements; *Cem. Technol.*, **4**, 21-25, (1973).

104. Kenya Standard, *Methods of Test for Limes and Limestone Chemical Compositions,* KS 1775 Part 5.1 2001, Kenya Bureau of Standards, Nairobi, (2001).

105. Mehta, P. K., Studies in Blended Cements Containing Santorin Earth; *Cem. Conc. Res.*, **11**, 507-518, (1981).

106. Mather, B., use of Concrete of Low Portland Cement Content in Combination With Pozzolanas and Other Admixtures in Construction of Concrete Dams; *Jnl. Amer. Conc. Inst.*, 71, 589-599, (1974).

107. Smith, A. and Halliwell, F., The Application of The BS 4550 Test For Pozzolanic Cement to Cements Containing Pulverized Fuel Ashes; *Mag. Conc. Res.*, **31**, 159-170, (1979).

108. Chopra, S. K., Utilization of Rice Husk For Making Cement and Cement Like Binders; *Rice Husk Ash Cement Proceed. UNIDO/ESACAP/RCTT/PCSIR Joint Workshop*, Peshwar, 135-149, (1979).

109. Chopra, S. K., Ahluwalia, S. C. and Laxmi, S., Technology andMAnufacture of Rice-Husk Ash Masonry (RHAM) Cement; Proc. ESCAP/RCTT Third Workshop on Rice-Husk Ash Cement, New Delhi, (1981).

APPENDIX 1

COST ANALYSIS FOR PORTLAND-COMBINED-ALS CEMENT

The following are expenses expected of materials.

Buying and Transport Cost

	Kshs.
RH buying, loading and transport 35-tonnes	= 50,000
BB buying and loading 7- tonnes	= 120
BB transport 7- tonnes	= 2,000
BB pre-grinding 7- tonnes	= 1,000
ALS 15- tonnes s buying	= 20,000
ALS 15- tonnes transport	= 6,000
SBE buying and loading 7- tonnes	= 0.00
SBE transport 7- tonnes	= 10,000
Bamburi cement 20- tonnes buying	= 400,000
Bamburi cement transport 20- tonnes	= 0.00

Preprocessing Cost of the Pozzolanic Materials

Ignition fuel	= 200.00
Two casual laborers	= 20,000.00
Kiln maintenance	= 500.00
Blending	= 10,000

Assumptions made

1. Raw materials were considered to be free of charge.
2. Analysis done for the cement containing 45% Combined-ALS and 55% OPC
3. Processing and processing factory assumed to be at Kenyatta University.
4. Costs have been estimated on a running firm and not to be established
5. ALS transported is decanted.
6. Estimates made on a 72 tonnes of cement production has been taken without any special consideration

Facts.

1. Capital cost was not included in the percentage saving estimate.
2. Transport costs have been considered from source of raw materials to Kenyatta University through private hire.
3. Paraffin cost was obtained from Paraffin dealers.

Savings Calculation

Total Cost of 72 tonnes of Portland Combined ALS cement	= 519,820
Miscellaneous	=20,180
Total Cost of 72 tonnes of PPC	= 676,800
Saving as a percentage of PPC Cost per tonne	= 20 %

APPENDIX 2

XRFA Results for Chemical Constituents of treated Pozzolanic Samples

Compound	En-masse SBE	SBE[1]	SBE[2]	C-W BB	G-45 BB	Ptuff	RHA
	% by weight	% by weight	% by weight	% by weight	% by weight	% by weight	% by Weight
CaO	2.01	3.10	3.00	0.44	4.08	2.07	1.38
SiO_2	65.90	69.15	67.65	65.71	63.30	57.85	80.60
Al_2O_3	11.10	12.17	12.44	20.49	17.65	12.24	0.53
Fe_2O_3	2.77	3.95	4.03	7.87	6.69	10.00	0.47
SO_3	1.83	2.84	2.99	0.22	0.38	0.10	0.01
MgO	3.00	4.18	4.05	1.95	2.31	1.45	2.40
K_2O	-	-	-	-	-	-	-
Na_2O	-	-	-	-	-	-	-
LOI (Loss on Ignition)	-	-	-	-	-	-	-

Gravimetric Analysis and Flame Photometry (Na_2O and K_2O) Results for Chemical Constituents of treated Pozzolanic Samples

Compound	En-masse SBE	SBE[1]	SBE[2]	C-W BB	G-45 BB	Ptuff	RHA
	% by weight	% by weight	% by weight	% by weight	% by weight	% by weight	% by Weight
CaO	2.01	3.14	3.04	0.43	4.08	2.06	1.37
SiO_2	65.87	69.14	67.75	65.70	63.31	57.86	80.62
Al_2O_3	11.10	12.16	12.30	20.45	17.66	12.22	0.54
Fe_2O_3	2.81	3.98	4.05	7.91	6.70	10.04	0.46
SO_3	1.83	2.84	2.99	0.22	0.39	0.11	0.01
MgO	3.05	4.19	4.05	1.95	2.32	1.44	2.38
K_2O	0.49	0.58	0.59	3.52	2.34	1.47	0.15
Na_2O	0.20	0.30	<0.01	1.55	1.02	2.27	0.20
LOI (Loss on Ignition)	12.95	4.12	6.72	0.90	0.57	14.62	3.49

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