"UTILIZATION OF HARZADOUS INDUSTRIAL ALUMINA AND IRON WASTES IN THE CEMENT MANUFACTURING PROCESS"

By

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DECLARATION:

This Research Project paper for the Master of Art (Environmental Planning and Management) is my original work and has not been presented for a degree or diploma in any other University.

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ABSTRACT

This research was conducted with a major aim of improving cement raw material mineralogical composition; hence produce affordable and better quality cement.

Limestone is a major component in the cement manufacturing process. E.A.P.C.C hauls high purity limestone from Sultan Hamud and low purity limestone (Kunkur) from Athi River town. The research looked into possible ways of utilizing alternative raw materials which could promote the use of a higher proportion of the near by available kunkur so as to reduce material haulage costs; hence overall lowering of product unit cost.

The raw materials available were deficient in alumina and iron for optimum production of cement hence the focus was to explore the possibility of other secondary materials which could enrich these components in the raw materials.

This research was conducted by testing several materials containing alumina. The product which comformed with optimum quality specifications of cement was found to be the final waste product from aluminium rolling mills which was termed as **alumina dust**. This highly hazardous material solved a major operation problem in the plant and solved the aluminium plants major waste disposal problem. Thus; this waste product resulted in

- Cleaner production in the aluminium rolling plant and steel mills by the recycling of the wastes in the cement industry.
- Cost effective cement, which gives a costing of Ksh 916/t raw meal with very low limestone requirements of 65.5% and a kunkur ratio of 32%. As compared to the previous costing of Ksh. 950/t raw meal and a high limestone requirement of 70% and a kunkur ratio of 26%.
- Easier burning operation – appendix 6 figure 2. Which has better burnability giving higher throughput averaging at 103 tph as compared to 91 tph.
- Lower fuel consumption – appendix 6 figure 4. Where we achieved an efficiency of 921 kcal/kg as compared to 1131 kcal/kg on the previous mix.
- Profitable waste disposal where the Aluminium industry sells this waste at Ksh 1000/t.

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CHAPTER ONE

1.0 INTRODUCTION

Cements are binding agents consisting essentially of compounds of calcium oxide with hydraulic properties (i.e. ability to harden in air and water), which satisfy standard specifications on strengths and volume.

The main raw materials in the manufacture of cement are limestone (the source of lime (CaO)) and clays the sources of silica, alumina and iron ore. Owing to ever increasing competition in the market and depletion of natural resources, a research was conducted based on environmental protection issues, which successfully resulted in the innovation of partially substituting the clay component with hazardous industrial wastes from the aluminium and steel mills to produce quality cement.

In this research the raw materials used were high grade limestone from Kabini quarry in Sultan Hamud with an average total carbonate content of 87% and kunkur (chalk) which is a low grade limestone with an average total carbonate content of 65%.

Mill scale from steel mills and alumina dust from the aluminium rolling mills are the hazardous waste products utilized in this study. Other works have experimented on the substitution of natural iron ore with industrial waste iron ore (mill scale) from steel rolling mills hence there was confidence in the use of this waste in cement manufacture. However for the high alumina content alumina dust from aluminium rolling mills the confidence in its utilization was low because it had never been used in any other works neither was there any kind of information regarding the utilization of this waste.

People that work in aluminium smelting plants for long periods have been known to experience dizziness, impaired coordination, loss of energy. There is evidence to suggest that long-term accumulation of aluminium in the brain may result in Alzheimer's disease. Acid rain leaches out the aluminium in the soil and goes into our drinking water.

In Kenya the major concern is not on health but on agriculture, thus industries dealing in aluminium have to handle their waste with caution. This is because when the level of aluminium in water increases plants die due to lack of nutrients.

Although aluminium is the most abandoned metal in the earth's crust and is ubiquitous in its distribution, it has no known useful biological function.

Salient rationale for undertaking the study is the reduction of hazardous material in our environment. The human body has zero nutritional requirements for aluminium and it collects in the tissues. Aluminium absorption rates are relatively low, but they are cumulative.

The toxicity of iron ore is not as profound as for Alumina. However, in general high levels of iron ore generate toxicity in animals resulting in reduced water intake, reduced feed intake, nervous system disorders, sweating, lethargy and abdominal swelling which can lead to death.

1.1 DEFINITIONS

1.1.1 **Limestones** - Are sedimentary rocks composed of calcium carbonate. These form the main constituents of cement about 70% composition.

1.1.2 **Kunkur** – This is a low grade limestone with an average lime content of 65%. This also known as chalk.

1.1.3 **Clay** – Are clastic sediments i.e. they consist mainly of the remains of pre existing rocks which have been broken down by weathering or erosion.

1.1.4 **Mill scale** – Fine dust iron wastes from the steel mills.

1.1.5 **Gypsum** – Is a raw ore of calcium sulphate, which is used as a retarding agent in cement application.

1.1.6 **Clinker** – is the product attained when a finely ground homogenized mixture at specific ratio of limestone and clays (raw mix) is heated at 1500°C to form nodules.

1.1.7 **Alumina dust** – this is a waste product from the Alumina rolling mills. This is the main subject of this research.

1.1.8 **Fluxes** – These are compounds which lowers the temperature at which the liquid phase is formed and thus reduces the clinkering temperature e.g. iron ore, Alumina, Calcium fluoride,

1.1.9 **Volcanic Ash** – This is a siliceous clay based compound formed during volcanic action, in our context, it is found as an overburden on top of our limestone reserves at the Kabini Quarry.

1.1.10 **Pozzolana** – This is a material, which is capable of reacting with lime in the presence of water at ordinary temperature to produce cementitious compounds. Most pozzolanas are volcanic materials especially those known as tuffs. The term pozzolana is derived from Pozzuoli near mount Vesuviuos on the gulf of Naples.

1.1.11 **Lime Saturation Factor (LSF)** – This is a formula for calculating the optimum lime content in the mix.

1.1.12 **Silica Modulus (SM)** – or Silica ratio is the ratio of Silica (SiO_2) to the sum of Alumina (Al_2O_3) and Ferric oxide (Fe_2O_3).

1.1.13 **Iron Modulus (IM)** - also known as Alumina ratio (AR) is the ratio of Alumina to Ferric oxide.

1.2 ABBREVIATIONS

C - CaO (Lime)
S - SiO_2 (Silica)
A - Al_2O_3 (Alumina)
F - Fe_2O_3 (Iron oxide)
C_3S - $3CaO.SiO_2$ (Tricalcium silicate)
C_2S - $2CaO.SiO_2$ (Dicalcium silicate)
C_3A - $3CaO.Al_2O_3$ (Tricalcium Aluminate)
C_4AF - $4CaO.Al_2O_3.\ Fe_2O_3$ (Tetracalcium Aluminoferrite)
LSF - Lime saturation factor

SR - Silica ratio

AR - Alumina ratio

HM - Hydraulic modulus

LOI - Loss on Ignition

TCO_3 - Total carbonate

1.3 STATEMENT OF RESEARCH PROBLEM

The problem which led to the research was mainly due to the fact that the factory was unable to obtain average standard performance targets set in the production of cement as compared to other cement plants of similar design and capacity.

The key factors considered in the comparison were

- Kiln output
- Fuel consumption
- Run factor
- Product unit cost

It was observed that despite the plant having state of the art equipment and technology, it had the worst record among seven other plants including Bamburi Portland cement.

The major difference on the process as compared to other plants was clearly identified as the raw material chemical composition.

The raw materials were responsible for the following problems:-

- High fuel consumption averaging at 950 Kcal/kg clinker as compared to the designed fuel consumption of 800 Kcal/kg clinker.

- High raw mix cost mainly due to transportation costs. The plant was utilizing 70% of its materials (Limestone) from Sultan Hamud town, which is 100 kms away from the factory, and 25% of its material (kunkur), which is 10 km from the factory. Hence, there was need to come up with a method which could reduce the quantities from Sultan Hamud area and increase the use of materials from the kunkur quarry.
- Low productivity was experienced due to the poor raw material composition resulting in inconsistent plant operation.

In the research, It was clear that there was need to enrich the raw mix to the required levels by looking into alternative materials with higher iron ore and aluminium content. Initially the focus was on waste materials, which would be of minimum cost. This mode of utility would thus promote ***industrial waste sharing strategy.***

Thus whenever the waste additives were availed, it would also solve a waste disposal problem for those industries.

1.4 JUSTIFICATION OF THE STUDY

The computer models showed great potential and promise in solving all the above problems; hence it justified the need to spend more time and resources in the research. Environmental Protection Agencies have been particularly concerned globally on the manner of disposal of alumina wastes. This is because of their high toxicity. When exposed to the environment they affect the roots of plants due to increase in the level of alumina content in the soil hence eventually kill the plants.

In Kenya the Ministry of Environment and Natural Resources along with the Ministry of Health have restricted the disposal of alumina dust to the environment. Factories handling aluminium products are required to innhiliate the waste or at least put it in a closed area where rainwater cannot wash it away to the environment.

In this case the main problem was to solve the high cost of raw mix, low kiln output, high fuel consumption, low run factor and general poor plant operations.

In the design for solution, it was identified that the poor raw material mineralogical composition was the bottleneck. The major component to be tackled was clearly the Alumina content of the raw materials.

1.5 OBJECTIVES

1.5.1 The general objective was to enhance cleaner production through recycling of hazardous waste from Alumina and steel industries.

1.5.2 The objective of the research was to increase the company's profitability by stabilizing the process operation through the introduction of industrial wastes from the aluminium and steel rolling mills, hence improve plant efficiency.

1.5.3 Utilize alternative cheap waste materials in order to conserve raw materials.

1.5.4 Improve the clinker quality hence increase the addition of pozzolana in cement, which is the main profit-determining additive in the cement manufacturing process.

1.5.5 Increase the uptime of the plant by improving Raw material flowability during the wet season.

CHAPTER TWO

2.0 LITERATURE REVIEW

The development of hydraulic cements owes their name to Joseph Aspidin - a bricklayer from Leeds - England who in 1824 patented the product. It was termed Portland cement because when set with water and sand, it resembled a natural stone quarried on the isle of Portland in England.

Most hydraulic cements are specific combinations of silicates and aluminates of lime used in the form of concrete, which consists of cement, water, sand and gravel. (Helmer and Hespanhol 1977)

The raw material of Portland cement consists principally of a lime containing material (calcareous) such as limestone, marl, chalk or shells and an argillaceous material such as clay, shale or slag.

When a specific proportion of the calcareous and argillaceous materials are intimately mixed together with other silica, Alumina and iron oxide bearing materials and burnt at a clinkering temperature of 1450°C and grinding the resulting clinker, Portland cement is produced. A typical Portland cement is constituted as follows;

CaO – 64.1%
Fe_2O_3 – 3.0%
MgO – 1.4%
Al_2O_3 – 5.5%
SiO_2 – 22.0%
SO_3 – 2.1%
K_2O / Na_2O – 2.0%

The raw materials needed for cement manufacture are seldom found in their ideal chemical composition in the natural state hence the need to perform mix proportioning calculations in order to ascertain the content of alkalis, sulphate, chlorides and MgO introduced into the raw mix. The permissible limit values for these constituents must be conformed to.

The word ‘cement ‘ is of ancient Roman origin. The Romans made a kind of structural concrete composed of broken stone or similar material with burned lime as the binding medium. This form of construction was called "opus caementitium" later on the term ‘cementum’ was used to denote those admixtures which on being added to the lime, imparted “hydraulic” properties to it, i.e. gave it the power to set and harden under moist conditions or under water. (Lea 1971)

The present definition of cement as given in German standard DIN 1164 is as follows; “Cement is a finely ground nydraulic binding medium for mortar and concrete, consisting substantially of compounds of calcium oxide with silicon dioxide, aluminium oxide and ferric oxide which have been formed by sintering or fusion. When mixed with water, cement hardens both in air and under water and retains its strength under water. It has to possess consistency of volume (soundness) and attain a compressive strength of at least 25 N/mm2 at 28 days. The ideal raw material of cement manufacture is a rock, which already in its natural state contains the correct proportions of the consistencies to produce a cement clinker of the desired composition. Beside it should be available in abundance easy to quarry and of homogeneous character. (Kohlhaas 1983)

The calcium carbonate $CaCO_3$, which con[illegible]out 74 – 79% of the cement raw meal, is decomposed (dissociated, de[illegible]d, calcined) at temperatures theoretically from 896°C upwards in accor[illegible] the equation:

$$CaCO_3 \xrightarrow{heat} CaO + CO_2$$

The calcined products of $CaCO_3$ react with[illegible]the clays at first resulting in the formation of compounds with lower co[illegible]ne. Reaction phases begin at around 800°C. the solid reactions proceed[illegible]ly. The first formation of liquid phase, marking the start of what is k[illegible]sintering” or “clinkering” occurs at a temperature of between 1260°[illegible]10°C with further rise in temperature the proportion of liquid phase[illegible]s to around 20-30% (by weight). At 1450°C the main component o[illegible] cement is formed namely tricalcium silicate (C3S) known as Alite.

The process takes place in the rotary kiln, [illegible]a long cylinder rotating on its axis and inclined so that materials fed in a[illegible]r end travel slowly to the lower end.

Fuel is administered i.e. pulverized coal, o[illegible]al gas, is blown in by air blast and ignited. In the preheater moisture is d[illegible]nd at the lower end of the kiln the clinker passes into coolers. The comp[illegible]cool clinker then falls into conveyors and is transferred to storage hoppers or passed directly to the cement grinding mills. A small quantity of gypsum 4-5% is added during grinding to control the setting time and the finely ground cement passes to silos ready for dispatch. (Duda 1985)

2.1 TYPES OF PORTLAND CEMENNT

There are five types of Portland cement, which are included in the standard specifications of the American Society of Testing Materials and federal specifications board (ASTM).

The distinction in the various types is as shown in the given table 1.

Constituents of various types of cements

Compound	Type I	Type II	Type III	Type IV	Type V
$3CaO.SiO_2$ (C3S)	45	44	53	28	38
$2CaO.SiO_2$ (C2S)	27	31	19	49	43
$3CaO.Al_2O_3$ (C3A)	11	5	11	4	4
$4CaO.Al_2O_3.\ Fe_2O_3$ (C4AF)	8	13	9	12	9
$CaSO_4$	3.1	2.8	4.0	3.2	2.7
MgO	2.9	2.5	2.0	1.8	1.9
Free CaO	0.5	0.4	0.7	0.2	0.5

Type 1: This is used for general concrete construction where the special properties specified for types II, IV, and V are not required.

Type II: Used in general concrete construction exposed to moderate sulphate action or where moderate heat of hydration is required. (Lea 1971)

In addition to the standard types of Portland cement many modified cements have been manufactured e.g.

- Quick setting Portland Cement – which differs only from normal Portland cement in that its setting time is less i.e. < 45 minutes. Its rate of hardening may be similar to that of ordinary or rapid – hardening Portland cement.
- White Portland cement – is an ordinary Portland cement containing only a low proportion of iron oxide, so that its colour is white instead of grey.
- Water proofed Portland cement – are ordinary Portland cements to which has been added in grinding a small proportion of calcium stearate or a non-saponifiable oil.
- Hydrophobic cement – is a material obtained by grinding Portland cement clinker with water-repellant film forming substance such as a fatty acid in order to reduce the rate of deterioration under unfavorable storage or transport conditions.
- Low heat Portland cement – is one, which the chemical composition has been so adjusted so as to reduce the heat of hydration. Its rate of strength development, though not its ultimate strength, is lower than that of ordinary Portland cement. In the USA it is termed as Type IV cement.
- Sulphate resisting Portland cement – is a material with a composition so adjusted as to give it an increased resistance to sulphate bearing waters. In the U.S.A it is termed as Type V cement.

- Kiihl cement – is a Portland cement of low silica and high Alumina and iron oxide content that has been made in a number of European countries and Japan. In strength it corresponds to rapid hardening Portland cement.
- Iron ore cement – or erz cement was a type of Portland cement at one time manufactured near Hamburg in German with iron ore replacing the normal clay. It originally had a high iron oxide (about 8%) and low alumina (about 2%) content and was light to chocolate brown in colour with a higher specific gravity about 3.3 than Portland cement. Later the Al_2O_3: Fe2O3 ratio was some what increased and now its place has been taken by Ferrari cement.
- Ferrari cement – is a Portland cement originally with a ratio of alumina to iron oxide of 0.64 but now often approaching unity and having improved resistance to chemical attack. It falls in the class of sulphate resisting Portland cements.
- Expanding or non-shrinking cements - are cements, which expand slightly on hardening or have no net shrinkage or subsequent air-drying. They are manufactured in the USA and Russia.
- Air-entraining cements – are Portland or Portland blast furnace cements to which a small amount of an air–entraining agent has been added during grinding.

Other types of cements include;

- High Alumina cement – this kind of cement is manufactured by heating until molten or by sintering a mixture of limestone and bauxite. High-alumina cement is characterized by a very rapid rate of development of strength and approaches closely to its final strength in 24hrs after gauging. It's black in colour and has same setting time as that of Portland cement.

- Cements containing granulated blast furnace.
- Pozzolanic cements – these are produced by grinding together Portland cement clinker and a pozzolana or by mixing together a hydrated lime and pozzolana.
- Oil well cements – these are cements specially produced for cementing the steel casing of gas and oil wells to the walls of the borehole and to seal porous formations.
- Masonry cements – this group of cements consists of materials intended for use in mortar, they are often produced by grinding more finely than usual a mixture of Portland cement and limestone together with a plasticizer that entrains air.
- Magnesium Oxychloride or Sorel cement – Magnesium Oxychloride cement is the product obtained when magnesia and a solution of magnesium chloride react together. (Lea 1971)

As mentioned earlier on the section on problem background, the main parameter, which inhibited the achievement of plant efficiency, was raw material chemical composition. From laboratory analysis and computer model designs, it was very clear that there was need for a high Alumina content carrier so as to sweeten the raw mix.

Laboratory analysis revealed the following chemical composition of the waste samples from aluminium rolling mills.

The final raw mix design, which conformed to all cement parameters was attained as per the attached appendix 3. (Table 12.)

Reference from Kenya Industry properties office (KIPO) revealed that the closes related patents were only two, which were different from this one.

1. Use of cement kiln dust and red mud to produce hydraulic cement applied by the regents of the university of California in April 1986.
2. Use of Alumina clay with cement fly ash mixtures applied by JTM Industries Incorporation USA in October 1994.

The differences between this research and the above studies reviewed is that both projects dealt with materials which are non-toxic. The levels of alumina in red mud was 15% and iron contents was 46% as compared to alumina dusts whose alumina content ranges from 60 – 90% and mill scale iron content level 90%. These purities were high hence once exposed to the environment throug rainwater turned to be toxic particularly to vegetation.

The other major difference between the mentioned projects and this is that thei projects dealt with products ex cement works while in this project the additives were industrial wastes from aluminium and steel industries.

The literature for the use of mill scale from steel industries is mentioned in websites and texts but to a very scanty level. However, there is no literature on the use of alumina dust from the aluminium industry in the manufacture of cement or industrial disposal recycling mechanisms.

2.2 COMPOSITION OF THE EARTH'S CRUST

The most abundant elements in the earth's crust and atmosphere are: (Tolba & El-Icholy 1972)

Table 2.

Composition of Earth's minerals

ELEMENT	CHEMICAL SYMBOL	% BY WEIGHT
Oxygen	O	49.2
Silicon	Si	25.7
Aluminium	Al	7.5
Iron	Fe	4.7
Calcium	Ca	3.4
Sodium	Na	2.6
Potassium	K	2.4

Table 3.

Cement Oxides composition

OXIDES	CHEMICAL SYMBOL	CEMENT CHEMISTRY	% BY W
Silica	SiO_2	S	55.2
Alumina	Al_2O_3	A	14.2
Iron	Fe_2O_3	F	6.7
Lime	CaO	C	4.8

These four oxides typically constitute for 95% of the chemical composition of Portland cement clinker.

A typical chemical composition of the Alumina dust and mill scale utilized in this research is as attached in appendix 1 and 2.

2.3 NATURE OF PORTLAND CEMENT

Portland cement clinker is manufactured by heating a finely ground homogenized mixture of limestone and clays at a very high temperature of 1500°C, the clinker is then cooled and interground with about 6% gypsum to form Portland cement.

Portland cement clinker consists mainly of four oxides, CaO (lime), SiO_2 (silica) Al_2O_3 (alumina) and Fe_2O_3 (iron oxide).

In cement chemistry these oxides are denoted as

C – CaO

S – SiO_2

A – Al_2O_3

F – Fe_2O_3

M – MgO

Cs – $CaSO_4$

H – H_2O

N – Na_2O.

These oxides, which occur in Portland cement raw mix chemically, combine in the kiln to form four main compounds or minerals. These are;

Tricalcium silicate - 3 CaO. SiO_2 (C3S)

Dicalcium silicate - $2\ CaO.\ SiO_2$ (C2S)

Tricalcium Aluminate $3\ CaO.\ Al_2O_3$ (C3A)

Tetracalcium Aluminoferrite $4\ CaO.\ Al_2O_3\ (Fe_2O_3)$ (C_4AF)

The major influencing factor in cement manufacture is the raw material proportioning so as to produce the desired raw meal. The raw materials are proportioned so as to meet specific control ratios as follows:

1. The lime saturation factor (LSF)

$$LSF = \frac{C}{2.8S + 1.2A + 0.65F}$$

Normal target range = 0.93 – 0.98

2. Silica Ratio, SR $= \frac{S}{A + F}$

Normal target range = 2.2 – 3.0

Increasing silica – decreases the burnability of the clinker

3. Alumina ratio, AR $= \frac{A}{F}$

Normal target range = 1.4 – 1.8

Alumina ratio determines the composition of the liquid phase in the clinker changes in alumina ratio can affect the kiln coating, cement colour and cement properties such as setting time and heat of hydration.

The chemical composition of Portland cement clinker is described through its several oxide components.

- Calcium and silica oxides, which form calcium silicates responsible for strength development.

- Alumina and iron oxides – improve burnability and act as fluxes to bring down the temperature of formation of silicate phases. (Peray 1986)

The raw mix design is set to optimize these proportions of the desired oxides so that one attains:

- Smooth and trouble free operations
- Production efficiency and fuel economy
- Quality of products which satisfies specifications
- Cost of production is minimized.

Kiln chemistry is the most critical stage in cement manufacture. Any deficiencies here will ultimately lead to a poorer quality product, potential higher grinding costs, higher refractory wear and failure.

2.6 DESIGN PROCEDURES

For the production of cement, it is necessary to have or make raw material mixtures whose chemical composition is within certain limits. The continuous production of high quality cement is possible only if the raw mix possesses optimum composition and further more if variations in this composition remain within the narrowest possible range.

The raw material composition specific ratios are called 'Moduli'. These are infact proportioning formulas into which the percentages of the various oxides as determined by chemical analysis should be substituted as earlier mentioned i.e. LSF, SM, IM.

Table showing limiting values of chemical composition of cement raw materials after ignition;

Table 4.

Cement raw materials composition

Oxide	**Limiting value m %**	**Content m %**
CaO	60 - 69	65
SiO_2	18 - 24	21
Al_2O_3	4 - 8	6
Fe_2O_3	1 - 8	3
MgO	< 5	2
K_2O, Na_2O	< 2	1
SO_3	< 3	1

In the manufacture of Portland cement Aluminium oxide plays a very important role thus a research on alternate sources of alumina formed the core of this project.

Aluminium oxide or alumina Al_2O_3 occurs in nature as corundum ($2Al_2O_3$). Its melting point is 2045°C.

Alumina in a combined state is an important constituent of cements in which it behaves as an acid. Cements with a high total alumina and ferric oxide content are easily clinkered and unless carefully burnt, tend to cause ring formation in the kiln. Thus the ratio is termed as iron modulus (IM) also known as alumina ratio (AR) i.e. $I.M = Al_2O_3/Fe_2O_3$

Since the oxides both occur almost entirely in the liquid phase at clinkering temperature this modulus characterizes the composition of that phase. If the ferric oxide content is higher, so that the iron modulus is lower, the viscosity of the melt decreases. The average IM level is between 1.8 – 2.8. Increase of alumina with no change or with a reduction in ferric oxide content, hastens the setting of cement.

2.5 CALCULATION OF THE RAW MIX PROPORTIONS

2.5.1 TWO COMPONENT MIX

For the approximate calculation of the mix proportions for two raw materials components it is convenient to set down the relevant values in an "X" pattern, at the center of which is written the desired $CaCO_3$ content of the raw mix. The $CaCO_3$ content of the limestone is written in the upper left hand corner and the $CaCO_3$ content of the clay is written in the lower left-hand corner.
The differences between the last mentioned values and the desired $CaCO_3$ content of the raw mix at the center of the "X" are now written in the diagonally opposite corners.

The values thus finally obtained represent the proportions of the raw materials, which will form the desired mix.

Suppose the following raw materials are available;

Table 5.

Composition of a typical mix design

%	SiO2	Al2O3	Fe2O3	CaO	MgO	Loss on Ignition
Limestone	3.8	0.9	0.6	52.9	0.3	41.5
Clay	53.4	20.2	7.5	4.3	2.1	12.5

From the calcinations equation,

$Ca \quad C \quad O_3 \qquad = \quad Ca \quad O \quad + \quad C \quad O_2$

$(40 + 12 + 48) \qquad = \quad (40 + 16) \quad + (12 + 32)$

100 parts of $CaCO_3$ = 56 parts CaO + 44 parts CO_2

The limestone contains 52.9 x 100 /56 = 94.5% $CaCO_3$

The clay contains 4.3 x 100 /56 = 7.7% $CaCO_3$

(It's is assumed that all the CaO is present as $CaCO_3$)

For 77% $CaCO_3$ in the raw meal the above mentioned "X" pattern for computation gives;

94.5 \ / 69.3 (Parts of CaCO3 deficient in the clay)

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7.7 / \ 17.5 (Parts of CaCO3 in excess in the limestone)

The raw mix should therefore be proportioned as follows: (Kohlhaas 1983)

$$\frac{\text{Limestone}}{\text{Clay}} = \frac{69.3}{17.5} = \frac{3.96}{1}$$

The following analysis values are calculated;

Table 6.

Mix design composition calculations

%	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Loss on ignition
Limestone 3.96 parts	15.1	3.6	2.4	209.5	1.2	164.3
Clay 1 part	53.4	20.2	7.5	4.2	2.1	12.5
	68.5	***23.8***	***9.9***	***213.8***	***3.3***	***176.8***
Raw mix (%)	13.8	4.8	2.0	43.1	0.7	35.6
Raw mix (%) ignited	21.4	7.5	3.1	66.9	1.1	

2.5.2 FOUR COMPONENT RAW MIX DESIGN

Raw mix design is a theoretical model of an actual raw meal mix based on raw materials chemistry calculations. It proposes potential raw meal chemistry and clinker factors. It's a reliable guide and helps in simulating the practical mix, and is fairly accurate and faster to design. It is programmable in spreadsheet computer software.

Initially, the design is fed with the chemistry of the primary raw materials to be ground to make raw meal e.g.

Table 7.

Composition of primary raw materials

%	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K2O	Na2O	LOI	TCO3
Limestone	9.26	1.35	0.63	47.39	2.29	0.45	0.41	38.20	86.41
Kunkur	22.50	4.46	1.88	35.76	2.18	0.47	0.46	31.35	65.51
Alumina dust	23.75	58.72	1.84	1.19	1.18	0.11	0.78	12.00	
Iron ore	13.79	18.13	61.42	0.15	5.38	0.29	0.33		

A mix ratio is then formulated in the design to obtain target quality parameters for the potential raw meal chemistry.

A typical mix ratio is as shown below.

Table 8.

Typical raw mix composition

Limestone	67.0%
Kunkur	30.0%
Iron ore	0.5%
Alumina dust	2.5%

A potential raw meal chemistry is as shown below.

Table 9.

Potential raw meal chemistry

%	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K2O	Na2O	LOI	TCO3
Min	14.00	3.00	1.90	42.00	2.10	0.20	0.20	35.00	76.80
Max	14.50	3.30	2.00	42.50	2.50	0.50	0.50	35.50	77.30

As mentioned earlier, the mix ratio above is manipulated to achieve the potential raw meal chemistry.

An example of how the design calculates net compounds from the above 4 major compounds is as shown below:

(I) For (SiO_2 - Silica):

67.0/100 x silica in limestone

\+ 30.0/100 x silica in kunkur

\+ 2.5/100 x silica in alumina dust

\+ 0.5/100 x silica in iron ore

= x % SiO2 in resultant raw meal chemistry

When X % SiO2 value falls below 14.00 % target value, the mix ratio for kunkur is adjusted upwards to improve the levels of Silica - and vice versa.

(2) For (CaO - lime):

67.0/100 x Lime in limestone

\+ 30.0/100 x Lime in kunkur

\+ 2.5/100 x Lime in alumina dust

\+ 0.5/100 x Lime in iron ore

= y % CaO in resultant raw meal chemistry

When y % CaO value falls above 42.50 % target value, the mix ratio for limestone is adjusted downwards in order to lower the levels of Lime - and vice versa.

(3) For (Al_2O_3 - alumina):

67.0/100 x Alumina in Limestone

\+ 30.0/100 x Alumina in kunkur

\+ 2.5/100 x Alumina in alumina dust

\+ 0.5/100 x Alumina in iron ore

= z % Al_2O_3 in resultant raw meal chemistry

When z % Al2O3 value falls below 3.00 % target value, the mix ratio for alumina dust is adjusted upwards in order to increase the levels of Alumina - and vice versa.

(4) For (Fe_2O_3 – Iron oxide):

67.0/100 x Iron oxide in Limestone

\+ 30.0/100 x Iron oxide in kunkur

\+ 2.5/100 x Iron oxide in Alumina dust

\+ 0.5/100 x Iron oxide in iron ore

= w % Fe_2O_3 in resultant raw meal chemistry

When w % Fe_2O_3 value falls above 2.00 % target value, the mix ratio for Iron ore is adjusted downwards in order to lower the levels of iron oxide - and vice versa.

After the task for searching an appropriate mix ratio that can deliver target raw meal chemistry is accomplished, the design will simultaneously and automatically calculates raw meal and clinker factors based on the raw meal chemistry achieved. Some of the factors are listed below.

LSF, MS, MA, C3S, C2S, C4AF, C3A, LPH e.t.c – which have been explained in details earlier. (Duda 1985)

CHAPTER THREE

3.0 METHODOLOGY

The methodology involved sampling from the aluminium and iron rolling mills and conducting experimental analysis of the wastes in the laboratory.

3.1 SAMPLING

The sampling was done by taking five representative samples of wastes from the following industries;

(i) Crystal industries in Kikuyu – Dealing in aluminium rolling.

(ii) Kusco in Kikuyu – Manufacturers of Iron ore ingots

(iii) Aluminium Enterprises in Kikuyu – Manufacturers of aluminum sheets and pots.

(iv) Booth Manufacturing Thika – Manufacturers of aluminium windowpanes.

(v) Emco metals Nairobi – Producers of iron bars.

(vi) NARCOL Mombasa – Manufacturers of aluminium sheets.

(vii) Kalu works Mombasa – manufacturers of aluminium sheets.

3.2 SAMPLE TREATMENT

1kg of sample was taken and quartered out of which 200g sample was dried and moisture determined. 50g was pulverized to a fineness of 63 microns. The sample was then coded and analyzed for SiO_2, Al_2O_3, Fe_2O_3, K_2O, Na_2O, CaO, MnO, MgO, and L.O.I. P_2O_5, Cl, SO3.

3.3 INSTRUMENTS	MODEL
UV/VIS Spectrophotometer	Cary 50 (Varian)
X-Ray Spectrometer	SRS 3000 using Spectraplus (Bruker)
Weigh balance	
Grinding mill	Herzog

3.5 REAGENTS	SOURCE
Hydrochloric Acid (A.R.)	Mannigate chemicals / Kenya Schools Laboratory Supplies / Laborama Chemicals.
Silver nitrate	
Nitric Acid solution (A.R)	
Sulphuric Acid: (A.R.)	
Hydrofluoric Acid (A.R.)	
Ammonium chloride (A.R.)	
Bromine:	
Ammonia (approx. 25%)	
Methyl red:	
Ammonium nitrate (A.R.)	
Ammonium moxalate:	
Potassium sodium carbonate (A.R.)	

METHODS OF DATA ANALYSIS

A) WET METHOD (GRAVIMETRIC)

3.5 DETERMINATION OF $SI0_2$

3.5.1 Reagent preparation:

Nitric Acid solution: 10g.AgN03 + 30 ml HN03 conc. (A.R.)
+ dist. Water to 100 ml

3.5.2 Procedure:

0.5g. sample is transferred to an evaporation dish and stirred with a few drops of water

and 50 drops HCl. When everything is dissolved evaporate to dryness on sand bath (120°c) until the material becomes completely dry and does not smell of acid. After cooling humidify the yellow-green mass with 20 drops of HCl and cover with watch glass for 10 minutes. Add boiling water and heat to boiling. Filter through a No. 41 (11.0 cm) filter to a 400 ml beaker and wash the filter with boiling water until Cl no longer can be identified.

Place the wet filter in a pt crucible (weight c) and dry, carbonize and calcinate the $SI0_2$ + (R_2O_3) (1/2 hour at 1200° c or Suhr's Burner for 2 minutes). Cool 10 minutes in desiccator and weigh (b).

Humidify the $Si0_2$ with 2 drops of water and fill the crucible 3/4 full with HF and add 1 drop of H_2SO_4. After evaporation to dryness in incinerator, ignite the crucible (Meker burner) first carefully and then strongly for 5 minutes. Finally 1/2 hour in el. Furnace at 120^0c, cool and weigh (a). The crucible should always be covered with a lid.

3.5.3 Calculation See (3.6.3).

3.5.4 Comments

The temperature at which the sample is dried after treatment with HCl must not exceed 130°c as $FeCl_3$ is volatile above this temperature. Do not use more humidifying the dried $SI0_2$ than absolutely – necessary as this will require too much NH_3 for neutralizing.

To test for Cl take out one ml. Of the filtrate in a test tube and add 1 ml. $AgN0_3$ solution. If the sample is still clear there is no Cl present. The sample is thrown away.

3.6 DETERMINATION OF $R_2 0_3$

R_2O_3 is the sum of Alumina and Iron, calculated as oxides. Al and Fe is precipitated by Ammonia as hydroxide (eventually as phosphates in samples which contain phosphorus). Before the precipitation Fe++ is oxidized to Fe +++ by Br_2.

$Al^{+++} \quad + 30H \rightarrow \quad Al\,(OH_3)$:

$Fe^{+++} \quad + 30H \rightarrow \quad Fe\,(OH_3)$

38.

Very strong precautions must be taken to avoid too much NH_4OH when precipitating If the pH exceeds 6 -6.3 the following process will take place.

$Al\,(OH_3) \quad + \quad 30H \rightarrow \quad Al03^{-} \quad + \quad 3H_2O$

Precipitate Soluble

Note:

Eventually phosphate and Titanium present in the sample will also be calculated as R_2O_3.

3.6.1 Reagents preparation:

Bromine	excess of Br_2 in distilled water
Ammonia	NH_3 conc. A.R. (approx. 25%)
Methyl red	0.2 methyl red in 60% C_2H_5OH
Wash liquid (1 % solution)	10g NH_4N0_3 + conc. NH_3 water until reaction (methyl red) (pH.7) + dist. Water to 1000 cc

3.6.2 Procedure:

Evaporate the filtrate from $Si0_2$ to approximately 150 cc and add 2g NH_4Cl + 5 drops of Bromine water. Excess of Bromine is removed by boiling (2-3 minutes). Add NH_3 gradually with constant stirring until the solution is pH6. Add an excess of NH_3 (2 drops) and continue boiling for 2 minutes.

Filter through a 11.0 cm No. 40 filter paper in a fluted funnel into a 600 cc beaker. Rinse the 400 ml beaker once with boiling NH_4N0_3 solution and wash the precipitate twice with the same liquid.

Transfer the filter and the precipitate to the same beaker, which was used for the precipitation. Pulp the filter paper and rinse the funnel. Add 2g NH_4N0_3 and 100 cc water, heat to boiling and add HN03 drop by drop until the precipitate is dissolved.

In the boiling liquid R_2O_3 is again precipitated by adding NH_3 until pH6 and a slight smell of NH_3. Continue boiling for 2 minutes-and filter the mixture quickly through an 11 cm No. 41 paper into the same 600 cc. Beaker. Loosen adhering material from the sides of the beaker with a rod and push the mass out into the filter. Rinse out the beaker and wash the filter with the same boiling wash liquid churning up the contents of the filer thoroughly. Continue washing until the filtrate is free from Chloride (see 3.4.4.). (The filtrate is used later for Ca0 and MgO determination). Filter and precipitate is transferred to the ignited crucible from the determination of $S10_2$. (If this crucible is not yet ready in this stage of the procedure go on with determination of Ca0 and MgO until it is ready). The content of the crucible is dried and carbonized in the incinerator and ignited for 1/2 hour over a Merker Burner. Then ignite for an hour at 1200°c in the furnace. Allow 10 minutes (stopwatch) cooling in desiccator and weigh (c). Evaporate eventually $Si0_2$ by humidifying with water and cover the precipitate completely with HF + 1 drop of H_2SO_4. Evaporate to dryness in incinerator ignite over Merker Burner at first carefully and then strongly for 30 minutes. Finally place the crucible for an hour at 1200oc in the furnace, cool 10 minutes. (stopwatch) and weigh (d).

3.6.3 Calculation:

$$\% \text{ Si02} = \frac{(b-a)+(e-d).100}{G}$$

$$R_20_3 = \frac{(d-c).1\ 00}{G}$$

a, b, c, d, e, =

Si02 Crucible after HF evaporation = a

" + Si02 (before HF) = b

Crucible empty = c

R_2O_3 crucible after HF evaporation = d

Crucible after R_2O_3 (Before HF) = e

Crucible empty = c

3.6.4 Comments:

If TiO_2 or P_2O_5 is present in considerable amounts this must be determined separately.

It is necessary to precipitate twice because eventually precipitated Ca $(OH)_2$ will be dissolved with NH_3 + NH_4 01.$M_2(OH)_2$ is not completely soluble in NH_3 why NH_4Cl is added in great excess.

$$Mg(OH)_2 \rightleftharpoons Mg^{++} + 20H^-$$

$$NH_3 + H_2O \rightleftharpoons NH_4OH \rightleftharpoons (NH_4^+) + (OH^-)$$

$$NH_4Cl \rightarrow NH4^+ + Cl^-$$

It is seen that OH^- is suppressed; that is also why Al is not dissolved again. Al $(OH)_3 + 30H - Al0_3^{---} + 3H_2O$

It is now seen why it is very important that NH_3 is only added in small excess.

It is important to filter quickly because the alkaline liquid takes up CO_2 from the atmosphere to precipitate.

$CaCO_3$ -$Ca(OH)_2 + CO_2\ CaCO_3 + H_2O$

The crucible from SiO_2 is used again for R_2O_3 in order to reduce fault due to weighing inaccuracy.

3.7 DETERMINATION OF Ca0

In the R_2O_3 filtrate Ca is precipitated as heavy soluble

$Ca(Coo)_2$: $Ca^{++} \quad + \quad (COO^-)_2 \longrightarrow \quad Ca(COO)_2$

The oxalate precipitate is ignited

$Ca(COO)_2 \longrightarrow \quad Ca0 \quad + \quad Co_2 + Co$

3.7.1 Reagents preparation .

Silver nitrate	10g. $AgN0_3$ + 30 cc,HNO_3 conc. A.R. + Dist. Water to 100 cc

3.7.2 Procedure

Evaporate the total filtrate from R_20_3 to approximately 300 cc and add NH3 during boiling to alkaline reaction (methyl red) and 2g $(Coo\ NH_4)_2\ H_2O$.

After boiling in 2 minutes place the beaker, covered by watch glass, 2 hours at 90 c. (Water bath or cold plate).

Filter through No. 40 (11.0 cm) filter to a 600 mi. Beaker and wash free for chloride (as previously) with the boiling wash liquid.

Transfer filters and precipitate to an ignited and weighed pt crucible and carbonize in incinerator. Heat over Merker Burner and ignite in furnace at 1200°c for 45 minutes. Cool 10 minutes (stop watch very important) in desiccator and weigh. Continue igniting 1/2 hour at a time until constant weight is found (at least 3 ignitions).

3.8 DETERMINATION OF Fe_20_3.

The dichromate principle in the titration is:

$6\ Fe^{++} + Cr_20_7^{--} + 14H^{+} \quad 6Fe^{+++} + 2\ Cr^{+++} + 7H_2O$

Sodium diphenylamine -p -sulphonate, used as an indicator

Before the titration Fe +++ is reduced to Fe ++ with stannous chloride:

$2Fe^{+++} + Sn^{++} \quad 2Fe^{++} + Sn^{++++}$

Excess of stannous ions are removed by adding Hg ++ ions'

$Sn^{++} \quad 2Hg^{++} \quad Sn^{++++} + 2Hg$

Hg + ions are precipitated as the very heavy soluble Hg2C12:

$2Hg^{+} + 2Cl^{-} - Hg_2Cl_2$

3.8.1 Reagents preparation

Stannous Chloride:	5g SnCl2, 2H2O is dissolved in 5 mi. HCl,
Dilute with 95 cc.	Dist. Water and add a small Quantity of metallic Sn.
Mercuric Chloride:	5g HgCl2 + dist. Water to 100 ml
Acid mixture: 350	ml.Dist. Water + 150 ml 85 H_3PO_7 is mixed (after cooling) with a cold mixture of 350 ml. Dist. Water + 100 ml 96 H_2SO_4
Indicator:	0.2 solution of sodium diphenylamina -p - sulphonate in water
Potassium dichromate Solution:	0.9800 9 $K_2(Cr_20_7$ A.R. dried 1 hour at 200°c + dist. Water to 1000 mi. (0.02N)

3.8.2 Procedure:

Dry the sample for 3/4 hour at 110°c before weighing in a pt crucible. Ignite over Meker Burner carefully for 15 minutes. Only the bottom of the crucible should be red. Cool and add Potassium sodium carbonate + 2 $KN0_3$ (4 times the weight of the sample). Heat slowly over meker burner (lid) so that only the bottom becomes red (16 minutes) and then strongly until the molten sample does gush. The crucible is then dipped in cold water without previous cooling and the mass is treated in a crystallizing dish with 10 ml water and 15 ml conc. H.Cl.

Test the crucible for iron: ignite the crucible for 10 minutes in the furnace at 1200°c and add 3 -4 drops of conc. H.Cl. after cooling if the acid is coloured yellow transfer it to the dish and repeat the treatment until the acid is colourless.

B) FUSION METHOD

3.9 QUANTITATIVE CHEMICAL ANALYSIS OF ALUMINA DUST BY FUSION METHOD USING UV/VIS - SPECTROPHOTOMETER.

3.9.1 Introduction

UV/VIS Spectrophotometric method is used to analyse full chemistry of cement and its raw materials. The spectrophotometer machine is used in the determination of SiO_2, Al_2O_3 and Fe_2O_3 compounds.

Principle of operation
When a polychromatic radiation is passed into these compounds in a cuvette, some of the radiation may be absorbed and the rest is either transmitted or scattered. The fraction transmitted may be determined as a function of frequency by the spectrophotometer machine.

3.9.2 Analysis

Chemical reagents and apparatus	***Source***
☐ NaOH pellets,	
☐ Gold crucible with a lid (95% gold & 5% palladium).	Mannigate agencies/ Laborama chemicals.
☐ Beakers	
☐ HCl (1:1)	
☐ Whatman no. 41 filter paper	
☐ Volumetric flasks	
☐ Pipettes	
☐ Molybdic acid	
☐ Ferron solution	
☐ Distilled water	

3.9.3 Procedure

Weigh 0.16g of alumina dust sample & 5g of NaOH into the gold crucible with a lid. Heat on a Bunsen burner with flame of low heat for 5 min, increase the flame and heat for 20 min. swirl your crucible to cool. Insert the crucible with contents into a P.T.F.E type plastic beaker containing little H_20 then add 60 mils of HCl

(1:1) and boiling H_20 to the 200 ml. Level mark of the beaker. Using tongs, mix the contents carefully to achieve a yellowish colour. [The reaction is explosive!] Filter through filter paper no. 41 up to the mark of a 250 ml. volumetric flask. Cool the solution for about 15-min (So as to bring the temp of the solution to room temperature).

SiO_2 determination

Pipette 10 ml. of prepared sample into a 100 ml. volumetric flask. Add 10 ml. of Molybdic acid and top up with distilled water to the level mark. Shake well.

Fe_2O_3 & Al_2O_3 determination

Pipette 5 ml. of prepared sample into a 100 ml. volumetric flask. Add 20 ml. of Ferron solution and top up with distilled water to the level mark. Shake well.

Blank preparation

For SiO_2 determination: Into a 100 ml. volumetric flask add 10 ml. of Molybdic acid and top up with distilled water to the level mark. Shake well.

For Fe_2O3 & Al_2O_3 determination: Into a 100 ml. volumetric flask, add 20 ml. of Ferron solution and top up with distilled water to the level mark. Shake well.

Reading the U.V spectrophotometer

SiO_2:

Rinse cuvette cell about 6x with SiO_2 blank, before picking the one to be used for the reading. Wipe with Kleenex medical wipes (or tissue paper), Read at 410 nm. Repeat the above steps to read Absorbance for the prepared alumina dust sample. The machine has been programmed to give out % composition immediately you read out.

Fe_2O_3 & Al_2O_3:

Rinse cuvette cell about 6x with blank, before picking the one to be used for the reading. Wipe with Kleenex medical wipes (or tissue paper), Read Fe_2O_3 O.D at 600 nm. And Al_2O_3 O.D at 365 nm. Repeat the above steps to read Absorbance for the prepared alumina dust sample. The machine has been programmed to give out % composition immediately you read out.

C) X-RAY ANALYSIS

3.6 QUANTITATIVE CHEMICAL ANALYSIS OF ALUMINA DUST USING SRS 3000 X-RAY SPECTROMETER

3.10.1 Preparation of Pellet

Grind twice a small amount of your sample in the "*HERZOG*" grinding machine, to flash out the system. Weigh 12g of sample and mix with 1.2g of binder. Shake well in a small plastic container and press program 1 to initiate grinding. Re-shake well your ground sample.

Using the Pressing machine; Press button 1 for the machine to create an empty filling space. Pour your sample in and cover with the metallic cover top. Screw tight. Re-press the button to compress your sample material. When finished, unscrew and while holding the top cover, press button 1 to lift up the formed pellet. When the sound stops press button 0 to complete the program.

3.10.2 Sample analysis using SRS 3000 X-ray Spectrometer

Clip tight your pellet into sample cup. Position the cup appropriately inside the x-ray magazine. In the computer software, at the "Default Sample Set file", type in the sample identification, position, and analytical program to use. Press "F10" to begin the testing.

After about 3 minutes, the X-ray will display full chemical analysis results of the sample analyzed.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

Table 10 (appendix 1) – is a typical analysis results of alumina dust.

Table 11(appendix 2) – is a typical analysis results of mill scale (industrial iron oxide).

Table 12 (appendix 3) – Gives a raw mix design with alumina dust and alumina clay.

Table 13 (appendix 4) – Gives a raw mix design of volcanic ash and alumina dust.

Table 14 (appendix 5) – Gives a summary of the kiln performances indicators while using Salama clay alone, Salama clay + volcanic ash, Salama clay + a/dust between may and July 2003.

Table 15 (appendix 6 : figures 1- 8) – Gives individual performances of the three clay mixes on specific process parameters i.e. cost, density, fuel efficiency, cement strength, raw meal proportions, kiln feed rate, clinker soundness and clinker grindability.

4.1 Typical raw mix designs utilized in this experiments are as outlined in appendix 3. where a favorable kunkur ratio averaging 30% is attained with a silica modulus averaging 2.7 giving good raw meal chemistry, factors and ratios.

Appendix 4 – depicts raw mix ratios utilizing alumina dust and alumina clay at ratios of 1:1. It is observed that the most economical theoretical mix is that of a ratio 1:1 volcanic ash: alumina dust which gives a costing of Kshs. 916 per tonne raw meal with very low limestone requirements of 65.5% and a favourable high kunkur ratio of 32.07%

4.2 It is noted that alumina dust mix increases the kunkur addition by about 10% as compared with the normal standard mix using Salama Clay alone while attaining the target raw material and product chemistry.

Appendix 5 shows the results on various mixes utilizing alumina dust, volcanic ash and Salama clay alone.

The purpose of this exercise was to compare in actual plant running condition the effects of these mixes on key process parameters such as the feed rate, bulk density, free lime, specific fuel consumption, product grindability and product compressive strengths.

4.3 It is observed in appendix 6 (figure 1.) that the Salama clay and alumina dust mix have the lowest product unit cost of Kshs 958 per tonne raw meal.

Appendix 6 (figure 2.) depicts better burnability giving higher throughput averaging at 103 tonne/hr as compared to 91 tonne/hr and 92 tonne/hr for salama clay and salama clay: volcanic ash mixes respectively. The optimum kiln feed rate at 110 t/hr.

4.4 In appendix 6 (figure 3.) the alumina dust mix produces the best bulk density as per target requirements.

4.5 In appendix 6 (figure 4.) the fuel requirements for the alumina dust mix were higher than that of the volcanic ash i.e. 929 Kcal/kg compared to 921 Kcal/kg, however, it was lower than the current existing fuel efficiencies of the salama clay mix of 1131 Kcal/kg. The target is 900 Kcal /kg.

4.6 Appendix 6 (figure 5.) shows that alumina dust mix produced a free lime averaging at 1.23% versus a target of 1.5%. The salama clay mix gave a better result at 1.65% while the volcanic ash mix was lower at 1.1%.

4.7 Appendix 6 (figure 6.) shows that the alumina dust mix produced clinker of better grindability as shown by the higher cement production rate of 54.5 t/hr as compared to the others.

4.8 Appendix 6 (figure 7.) shows that the overall cement strengths development was above the set required targets; however, the salama clay mix showed better strengths on the two days, 7 days and 28 days compressive strengths.

4.9 Appendix 6 (figure 8.) shows that the alumina dust mix has overall consistent and better performing cement as depicted by score points where for a total point aggregate of 24 the alumina dust mix scored 21 points giving a percent % score of 88%. This was followed by the salama clay mix with 15 points equivalent to 63% and the volcanic ash mix which scored 12 points equivalent to 50%.

4.10 Another set of trial tests was conducted in March, April, May, June and July 2003. These gave similar results as shown in Table 16 (appendix which gave a positive performance result in favour of the alumina dust mix in terms of cost, product quality and effeciency.

This confirmed the effectiveness of utilizing the industrial wastes in the manufacture of Portland cement.

It is observed that;

- The ability of the alumina dust in raising the kunkur ratio is beneficial because it drastically reduces the overall transport costs because the kunkur quarry is a mere stone throw away from the processing plant (10 km) as compared to the Kabini limestone quarry which is 100 km away.
- Increased kunkur ratio results in an easy burning mix because the burnability of kunkur is higher than that of limestone and will increase the life of our quarries.
- Pozzolana addition increases at the cement mills probably due to better clinker formation hence reactivity.
- Alumina dust raw mix gives a more stable and consistent chemistry hence higher plant run time.
- The fuel consumption was expected to improve due to the stable chemistry and run time but this was not achieved in the trial tests.
- The higher run time attained with alumina dust mix translates to a better equipment effectiveness and higher savings on refractory.
- With the successful completion of the project Kenya Industrial properties office (KIPO) allowed a formal application for grant of patent for this mode of cement manufacture. A filing date was registered and the format for writing the patent application given.

CHAPTER FIVE

CONCLUSION

The salient feature of the research was that it was possible to utilize the two hazardous wastes from the aluminium and steel industries in producing high quality cement thus simultaneously rid the environment of these harmful by products.

Alumina dust, a harmful waste product from the aluminium industries and mill scale a waste from the Steel Industries has successfully been removed from the environment through the cement manufacturing process with beneficial results.

This mode of waste recycling has a high potential in reducing product unit cost hence increased profitability in East African Portland Cement Co. Ltd. At the same time make the environment clean, friendlier thus a better place to live in.

RECOMMENDATIONS

- This mode of hazardous waste disposal through *industrial waste sharing strategy* should be promoted by the company to all similar industries having this waste disposal problem worldwide.
- Incentives should be put in place by the government to encourage the cement plants to incinerate these hazardous wastes in the cement kilns through waiver of taxes.

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Appendix 1

Table 10
Typical analysis results of Alumina dust

Parameters	**Test Results** **(%)**
Lime (CaO)	1.75
Silica (SiO2)	8.50
Iron Oxide (Fe2O3)	2.54
Alumina (Al2O3)	70.04
Magnesia (MgO)	2.60
Potassium Oxide (K_2O)	0.39
Sodium Oxide (Na2O)	1.20

Appendix 2

Table 11
Typical analysis results of Mill scale

Parameters	**Test Results (%)**
Lime (CaO)	0.14
Silica (SiO2)	3.40
Iron Oxide (Fe2O3)	88.38
Alumina (Al2O3)	1.38
Magnesia (MgO)	0.53
Potassium Oxide (K_2O)	1.23
Sodium Oxide (Na2O)	0.36

Appendix 3 Table 12

MIX 1 - CURRENT

EAST AFRICAN PORTLAND CEMENT CO LTD.

RAW MIX DESIGN WITH ALUMINIUM DUST & ALUMINA CLAY
MIX RATIO = 1:1

L/STONE	MILL FEEDS
KUNKUR	MILL FEEDS
IRON ORE	MILL FEEDS
ALUMINA CLAY/ ALUMINA DUST MIX	MILL FEEDS

MATERIAL ANALYSIS.

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	LOI	"TCO3"
LIMESTONE	10.44	1.69	0.72	47.63	2.32	38.97	86.28
KUNKUR	21.17	4.47	2.17	35.20	2.12	32.63	67.30
IRON ORE	15.39	16.96	65.39	0.11	1.52		
ALUMINA CLAY/ → / ALUMINA DUST MIX	35.50	41.01	8.38	2.73	1.84		

RATIOS

LIMESTONE	63.74	64.74	65.74	66.74	67.74
KUNKUR	33.76	32.76	31.76	30.76	29.76
I/ORE	0.90	0.90	0.90	0.90	0.90
ALUMINA CLAY/ →	1.60	1.60	1.60	1.60	1.60
/ ALUMINA DUST MIX	100.00	100.00	100.00	100.00	100.00

RAW MEAL CHEMISTRY						**TARGET**
SiO_2	14.51	14.40	14.29	14.19	14.08	14.00 -14.50
Al_2O_3	3.40	3.37	3.34	3.31	3.28	3.10 - 3.30
Fe_2O_3	1.91	1.90	1.89	1.87	1.86	1.95 -2.00
CaO	42.29	42.41	42.54	42.66	42.78	42.00 - 42.50
MgO	2.24	2.24	2.24	2.24	2.25	Less than 2.5
LOI	35.86	35.92	35.98	36.05	36.11	
TOTAL	100.20	100.24	100.28	100.32	100.36	
TOTAL CO3"	77.72	77.91	78.09	78.28	78.47	76.50 -77.00

FACTORS						**TARGET**
LSF	0.920	0.930	0.940	0.950	0.960	0.920 -0.940
HM	2.13	2.16	2.18	2.20	2.23	
SM	2.73	2.73	2.74	2.74	2.74	2.60 - 2.80
IM	1.77	1.77	1.77	1.77	1.77	1.50 -1.80
% LIQUID	27.08	26.93	26.78	26.62	26.47	25.50 -27.00
C_3S	55.85	58.21	60.56	62.92	65.27	
C_2S	21.91	19.66	17.41	15.16	12.91	
C_3A	8.87	8.80	8.72	8.65	8.57	
C_4AF	8.96	8.89	8.83	8.76	8.69	

Appendix 4. Table 13

EAST AFRICAN PORTLAND CEMENT CO LTD.

MIX DESIGN

[USING VOLCANIC ASH & ALUMINIUM DUST]

RAW MATERIALS

LIMESTONE
KUNKUR
SALAMA CLAY
ALUMINIUM DUST
IRON ORE
VOLCANIC ASH (Kabini H. Quarry)

MATERIAL ANALYSIS.

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	LOI	TCO_3	Ksh/T
LIMESTONE	9.56	2.09	0.51	47.38	2.20	0.15	0.31	37.58	86.00	1,100
KUNKUR	23.00	4.64	1.89	35.89	2.01	0.38	0.24	31.56	65.20	400
SALAMA CLAY	55.60	23.02	10.16	0.13	0.38	0.60	0.71	9.00		1,250
VOLCANIC ASH (Kabini H. Quarry)	44.73	11.93	15.72	6.66	8.97	0.80	2.10	8.80		600
4/1 - V/ASH : ADUST	41.03	21.33	12.93	5.58	7.39	0.66	1.75	9.04		1,140
3/1 - V/ASH : ADUST	40.10	23.68	12.23	5.31	7.00	0.63	1.67	9.10		1,275
2/1 - V/ASH : ADUST	38.56	27.59	11.07	4.85	6.34	0.57	1.52	9.20		1,500
1/1 - V/ASH : ADUST	35.48	35.43	8.75	3.95	5.03	0.46	1.23	9.40		1,950
IRON ORE	25.14	5.35	64.44	0.10	1.43	0.55	0.01	2.00		3,345
ALUMINIUM DUST	26.22	58.92	1.77	1.24	1.08	0.12	0.36	10.00		3,300
7/1 - V/ASH : ADUST	42.42	17.80	13.98	5.98	7.98	0.72	1.88	8.95		938
9/1 - V/ASH : ADUST	42.88	16.63	14.33	6.12	8.18	0.73	1.93	8.92		870

		VASH:ADUST	VASH:ADUST	VASH:ADUST	VASH:ADUST	VASH:ADUST	VASH:ADUST	VASH:ADUST	VASH:ADUST
	CURRENT	4:1	3:1	2:1	1:1	1:0	0:1	7:1	9:1
RATIOS	MIX 1	MIX 2	MIX 3	MIX 4	MIX 5	MIX 6	MIX 7	MIX 8	MIX 9
LIMESTONE	70.20	67.50	67.05	66.40	65.50	78.40	64.70	69.00	69.80
KUNKUR	**26.10**	**29.14**	**29.79**	**30.76**	**32.07**	**13.10**	**33.23**	**26.92**	**25.75**
SALAMA CLAY	2.40								
VOLCANIC ASH (Kabini H. Quarry)						8.50			
4/1 - V/ASH : ADUST		2.20							
3/1 - V/ASH : ADUST			1.93						
2/1 - V/ASH : ADUST				1.53					
1/1 - V/ASH : ADUST					1.03				
IRON ORE	1.30	1.16	1.23	1.31	1.40	0.00	1.50	0.98	0.90
ALUMINIUM DUST							0.57		
7/1 - V/ASH : ADUST								3.10	
9/1 - V/ASH : ADUST									3.55
TOTAL	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
COST (Ksh/tonne)	**950**	**923**	**922**	**920**	**916**	**966**	**914**	**929**	**932**
RAW MEAL CHEMISTRY									
SiO_2	14.33	14.31	14.30	14.30	14.32	14.26	14.32	14.31	14.30
Al_2O_3	3.30	3.29	3.31	3.31	3.30	3.26	3.31	3.30	3.29
Fe_2O_3	1.93	1.93	1.93	1.93	1.93	1.98	1.93	1.93	1.93
CaO	42.63	42.56	42.56	42.58	42.59	42.41	42.59	42.54	42.53
MgO	2.10	2.25	2.23	2.19	2.16	2.75	2.12	2.32	2.36
K_2O	0.23	0.23	0.23	0.23	0.23	0.24	0.23	0.23	0.23
Na_2O	0.30	0.32	0.31	0.30	0.29	0.45	0.28	0.34	0.35
LOI	34.86	34.79	34.80	34.83	34.86	34.35	34.89	34.72	34.69
TOTAL	99.68	99.68	99.68	99.68	99.67	99.70	99.67	99.68	99.69
TOTAL CO_3''	77.39	77.05	77.09	77.16	77.24	75.97	77.31	76.89	76.82
FACTORS									
LSF	0.940	0.940	0.940	0.940	0.940	0.940	0.940	0.940	0.940
HM	2.18	2.18	2.18	2.18	2.18	2.17	2.18	2.18	2.18
SM	2.74	2.74	2.73	2.73	2.74	2.72	2.73	2.74	2.74
IM	1.71	1.71	1.71	1.71	1.71	1.64	1.71	1.71	1.70
% LIQUID	26.09	26.25	26.30	26.27	26.17	26.89	26.19	26.34	26.38
C3S	60.80	60.66	60.58	60.71	60.75	60.08	60.66	60.46	60.47
C2S	17.20	17.13	17.18	17.10	17.16	16.95	17.26	17.21	17.15
C3A	8.41	8.39	8.43	8.43	8.40	8.05	8.45	8.39	8.36
C4AF	9.02	8.98	9.02	9.02	9.02	9.18	9.03	8.97	8.99

Appendix 5 Table 14

EAST AFRICAN PORTLAND CEMENT CO. LTD

PERFORMANCE OF VARIOUS CLAY MIXES

Clay Mix Used	COST KSH / T	POINTS SCORED
S/ CLAY : A/ DUST	958	3
S/ CLAY : V/ ASH	965	2
SALAMA CLAY	968	1

KEY
3 POINTS - BEST
2 POINTS - GOOD
1 POINT - FAIR
TOTAL POINTS = 24

Clay Mix Used	CLINKER Lt. Wt g/l *1300*	POINTS SCORED
S/ CLAY : A/ DUST	1309	3
SALAMA CLAY	1222	2
S/ CLAY : V/ ASH	1122	1

Clay Mix Used	K / FEED Feed Rate tph *103*	POINTS SCORED
S/ CLAY : A/ DUST	103	3
S/ CLAY : V/ ASH	92	2
SALAMA CLAY	91	1

Clay Mix Used	CLINKER Efficiency Kcal / kg *905*	POINTS SCORED
S/ CLAY : V/ ASH	921	3
S/ CLAY : A/ DUST	979	2
SALAMA CLAY	1131	1

Clay Mix Used	CLINKER FCaO % *1-1.5*	POINTS SCORED
SALAMA CLAY	1.65	3
S/ CLAY : A/ DUST	1.23	2
S/ CLAY : V/ ASH	1 10	1

Clay Mix Used	Min. Mortar Prisms C/ Strength			POINTS SCORED
	2 dys N/mm² *13*	7 dys N/mm² *27*	28 dys N/mm² *35*	
SALAMA CLAY	18.2	31.2	38.4	3
S/ CLAY : A/ DUST	16.5	30.0		2
S/ CLAY : V/ ASH	15.1	26.6	36.5	1

Clay Mix Used	CEMENT MILL 4 tph *55*	POINTS SCORED
S/ CLAY : A/ DUST	54.45	3
SALAMA CLAY	53.69	2
S/ CLAY : V/ ASH	49.16	1

Clay Mix Used	RAW MEAL RATIOS				POINTS SCORED
	LST % *68*	KK % *27*	IO / MS % *1*	ACLY % *4*	
S/ CLAY : A/ DUST	70.96	25.76	0.79	2.50	3
SALAMA CLAY	71.73	23.22	1.10	3.95	2
S/ CLAY : V/ ASH	73.77	18.25	0.26	7.80	1

SUMMARY OF SCORES

Clay Mix Used	TOTAL POINTS SCORED	% SCORE
S/ CLAY : A/ DUST	21	88%
SALAMA CLAY	15	63%
S/ CLAY : V/ ASH	12	50%

Appendix 6 **Table 15**

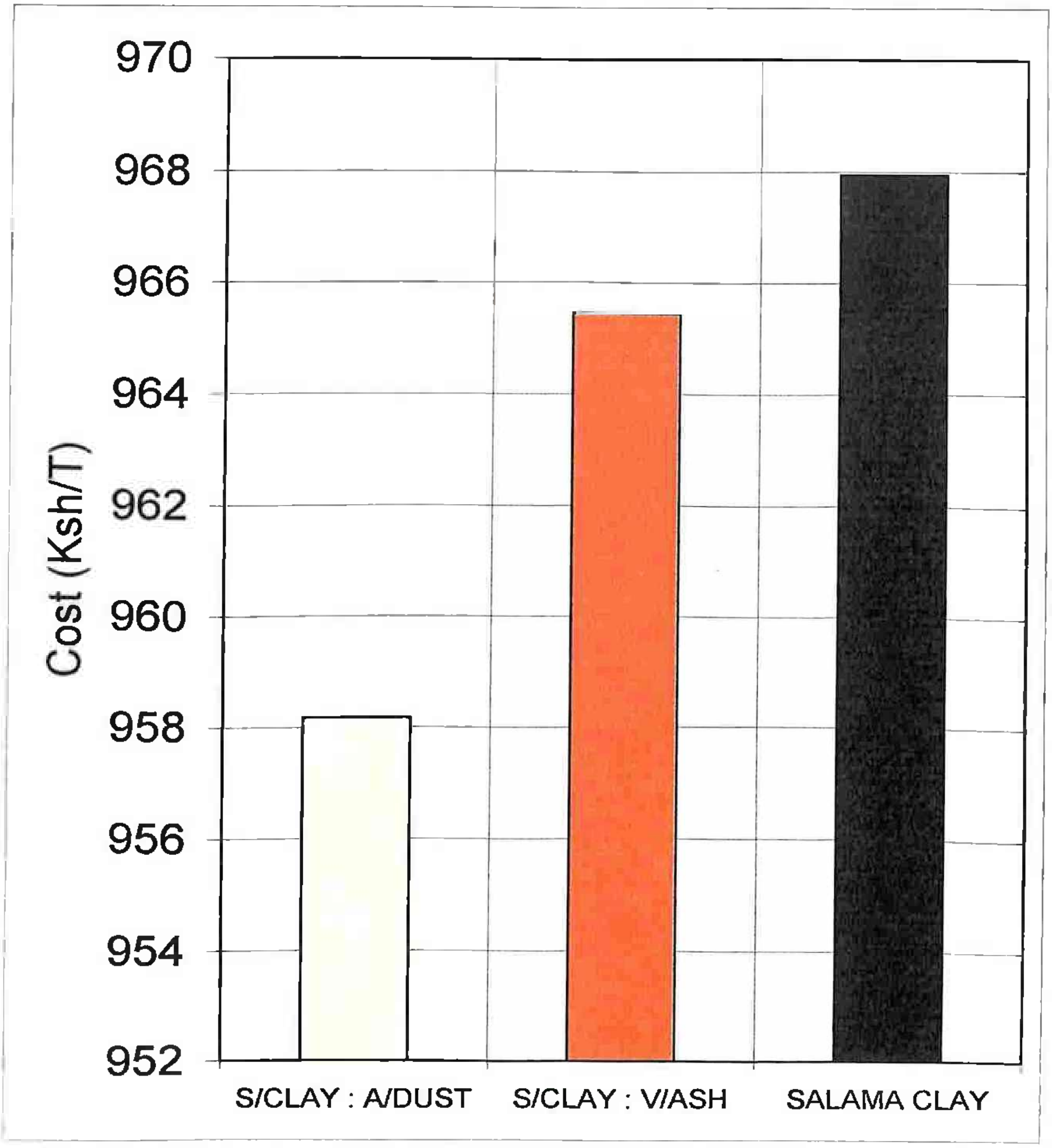
EAST AFRICAN PORTLAND CEMENT CO. LTD

PERFORMANCE OF VARIOUS CLAY MIXES

												DESPATCH CEMENT QUALITY		
Clay		RAWMEAL RATIOS					K/FEED	CLINKER			CEMENT	Mn. Mortar Prisms C/ Strength		
Mix Used	Date Used	LST %	KK %	IO/ MS %	ACLY %	COST KSH/ T	Feed Rate tph	Lt. Wt g/l	FCaO %	Efficiency Kcal / kg	MILL 4 tph	2 dys N/mm²	7 dys N/mm²	28 dys N/mm²
	Target	*68*	*27*	*1*	*4*		*103*	*1300*	*1-1.5*	*905*	*55*	*13*	*27*	*35*
SALAMA CLAY BEFORE VOL ASH USAG	15/06/03	74.88	19.92	0.87	4.33		58	1216	1.57	1813	49.96			
	16/06/03	77.05	17.64	1.03	4.28		103	1236	2.69	889	52.57	17.9	30.3	37.6
	17/06/03	75.30	19.76	0.89	4.05		98	1278	2.20	913	58.08	20.0	32.9	38.7
	18/06/03	71.27	24.13	0.97	3.64		102	1274	1.52	890	58.45			
	19/06/03	67.72	27.43	1.02	3.84		102	1242	1.36	898	58.28	18.7	32.7	39.8
	20/06/03	68.46	26.24	1.52	3.77		76	1219	0.96	1586	48.20	17.8	29.7	38.0
	21/06/03	67.45	27.44	1.38	3.73		101	1090	1.29	930	50.29	16.4	30.3	38.2
AVG		**71.73**	**23.22**	**1.10**	**3.95**	**966**	**91**	**1222**	**1.65**	**1131**	**53.69**	**18.2**	**31.2**	**38.4**
S/CLAY : V/ASH (1 : 1)	29/05/03	70.77	21.02	0.42	7.79		107	1096	1.64	900	44.12			
	30/05/03										43.75			
	31/05/03	71.69	19.73	0.49	8.09		48				46.41	13.7		36.7
	01/06/03	74.42	17.89	0.08	7.61		96	1136	0.65	909	49.36			
	02/06/03	75.35	17.11	0.06	7.48		94	1101	1.94	992	50.64	13.0	24.9	34.6
	03/06/03	75.38	17.05		7.57		106	1157	0.66	902	54.80	18.3	25.6	36.5
	04/06/03	75.03	16.70		8.28		104	1169	0.59	902	55.07	15.4	29.4	38.3
AVG		**73.77**	**18.25**	**0.26**	**7.80**	**965**	**92**	**1122**	**1.10**	**921**	**49.16**	**15.1**	**25.6**	**36.5**
S/CLAY : A/DUST (2 : 1)	22/07/03	72.26	24.53	0.78	2.43		102	1303	0.70	932	52.10	17.0	30.2	38.0
	23/07/03	71.98	24.83	0.80	2.40		100	1272	1.40	1020	55.57	17.1	30.7	36.0
	24/07/03	70.84	25.99	0.82	2.36		107	1354	1.31	911	54.28			
	25/07/03	70.53	26.17	0.77	2.53		106	1304	1.82	909	55.16	15.4	28.5	35.7
	26/07/03	70.88	25.76	0.77	2.58		108	1236	2.00	905	55.12	16.4	30.6	37.1
	27/07/03	70.11	26.45	0.79	2.65		92	1377	0.54	1279	54.01			
	28/07/03	70.10	26.59	0.79	2.52		107	1316	0.86	898	54.91	16.7	29.5	38.5
AVG		**70.96**	**25.76**	**0.79**	**2.50**	**958**	**103**	**1309**	**1.23**	**979**	**54.45**	**16.5**	**29.9**	**37.1**

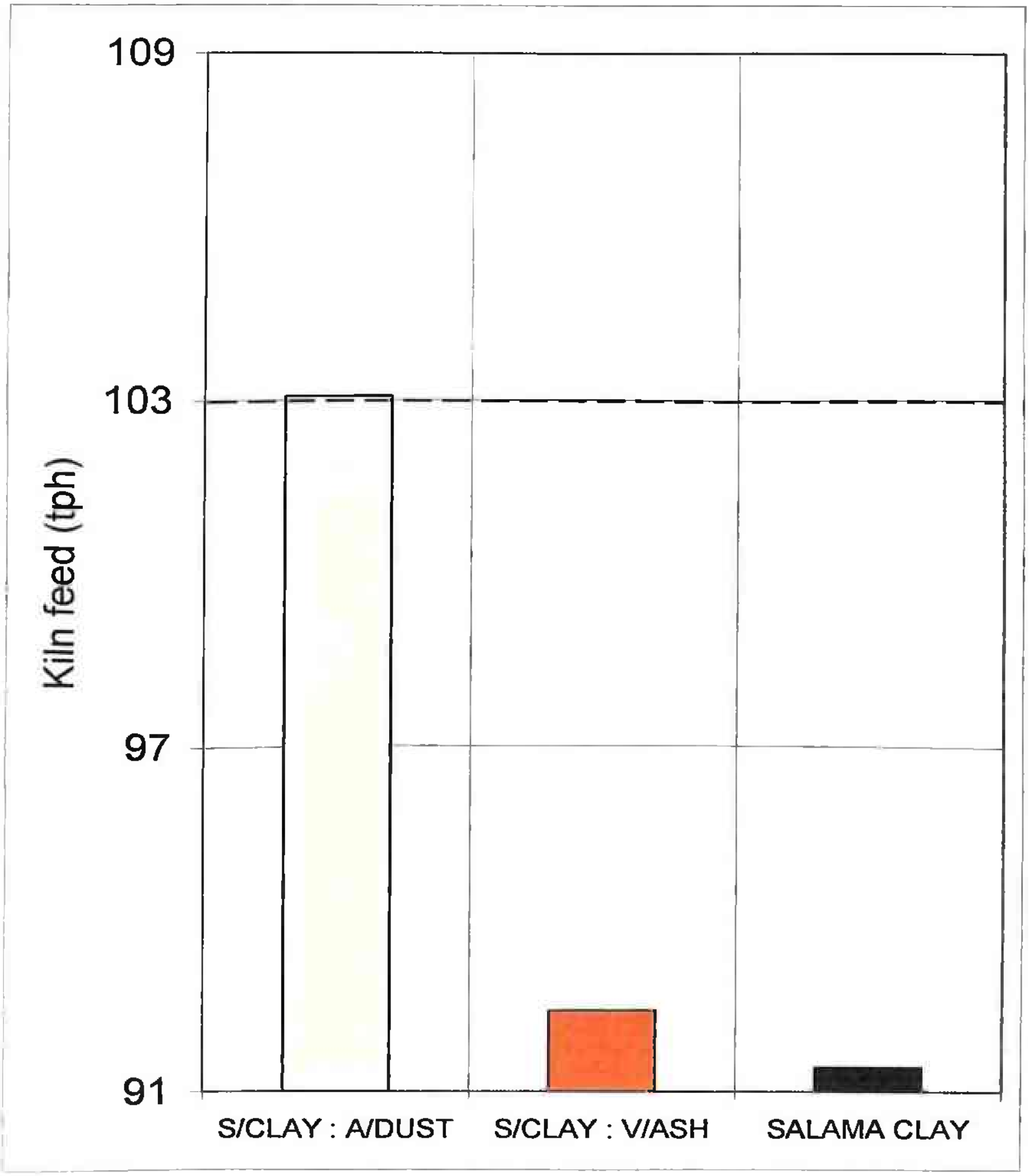
Appendix 6 **Figure 1.**

Cost of various mixes



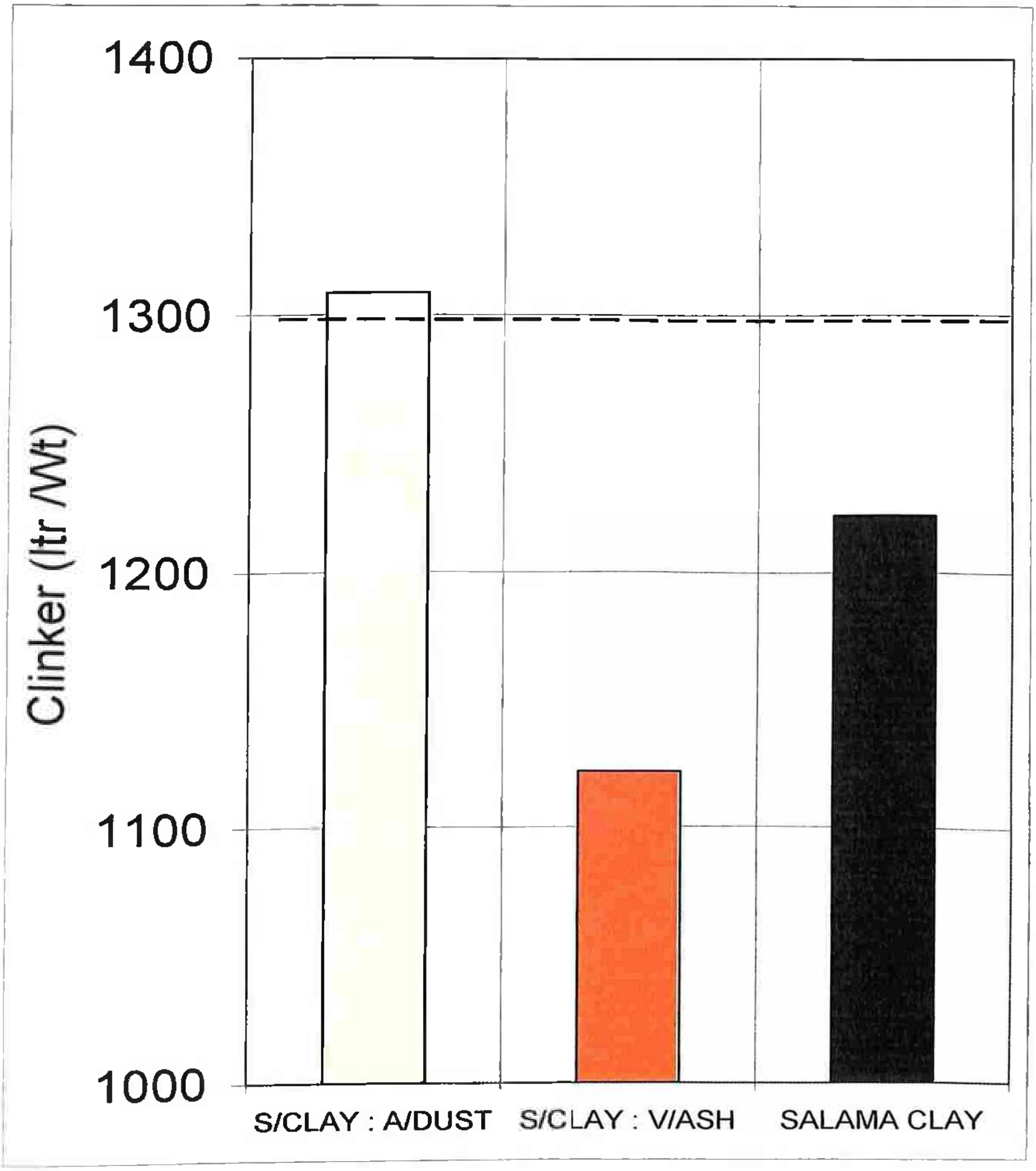
Appendix 6 **Figure 2**

Effect on various mixes on kiln feed rate



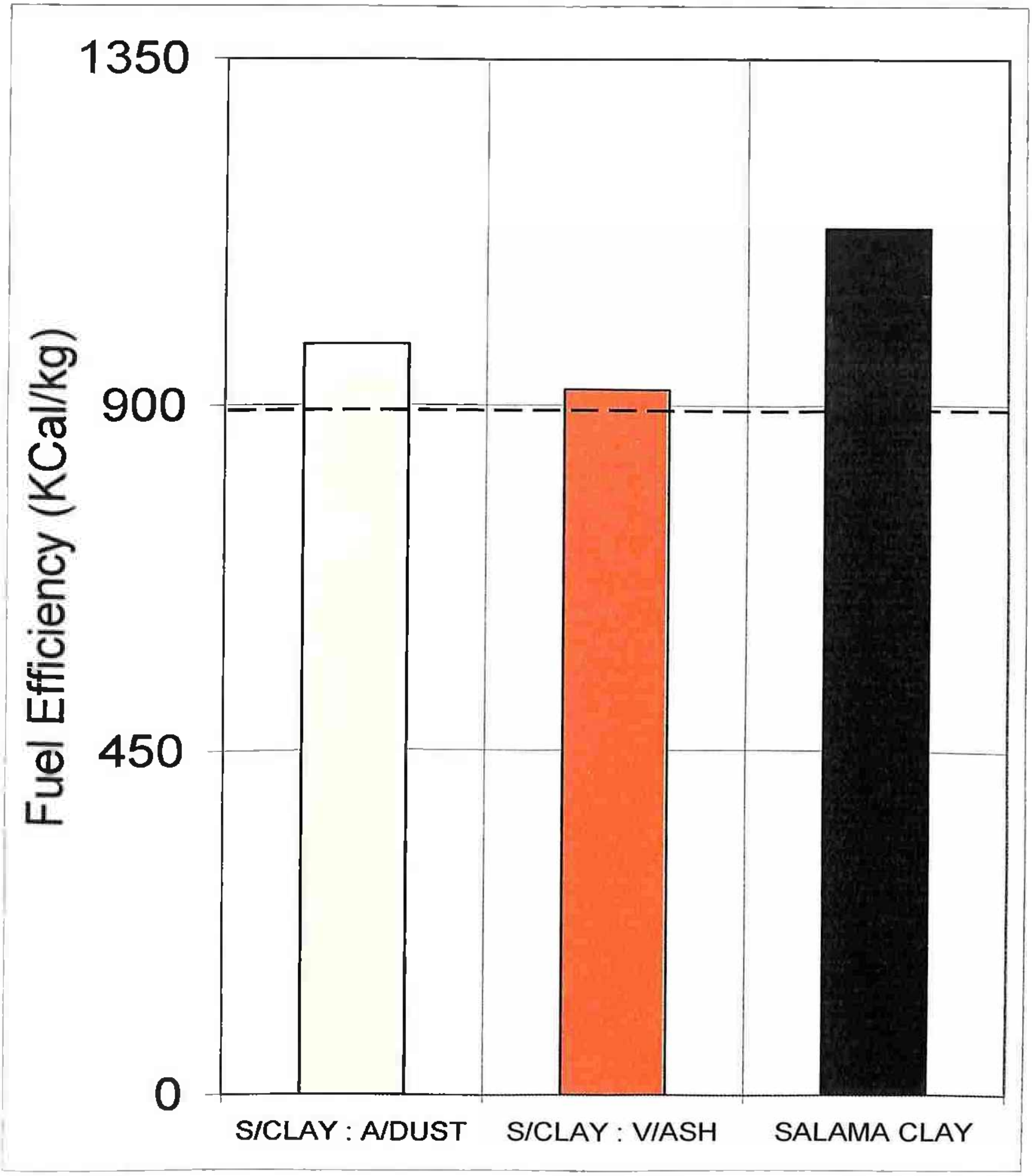
Appendix 6 **Figure 3.**

Clinker bulk density of various mixes



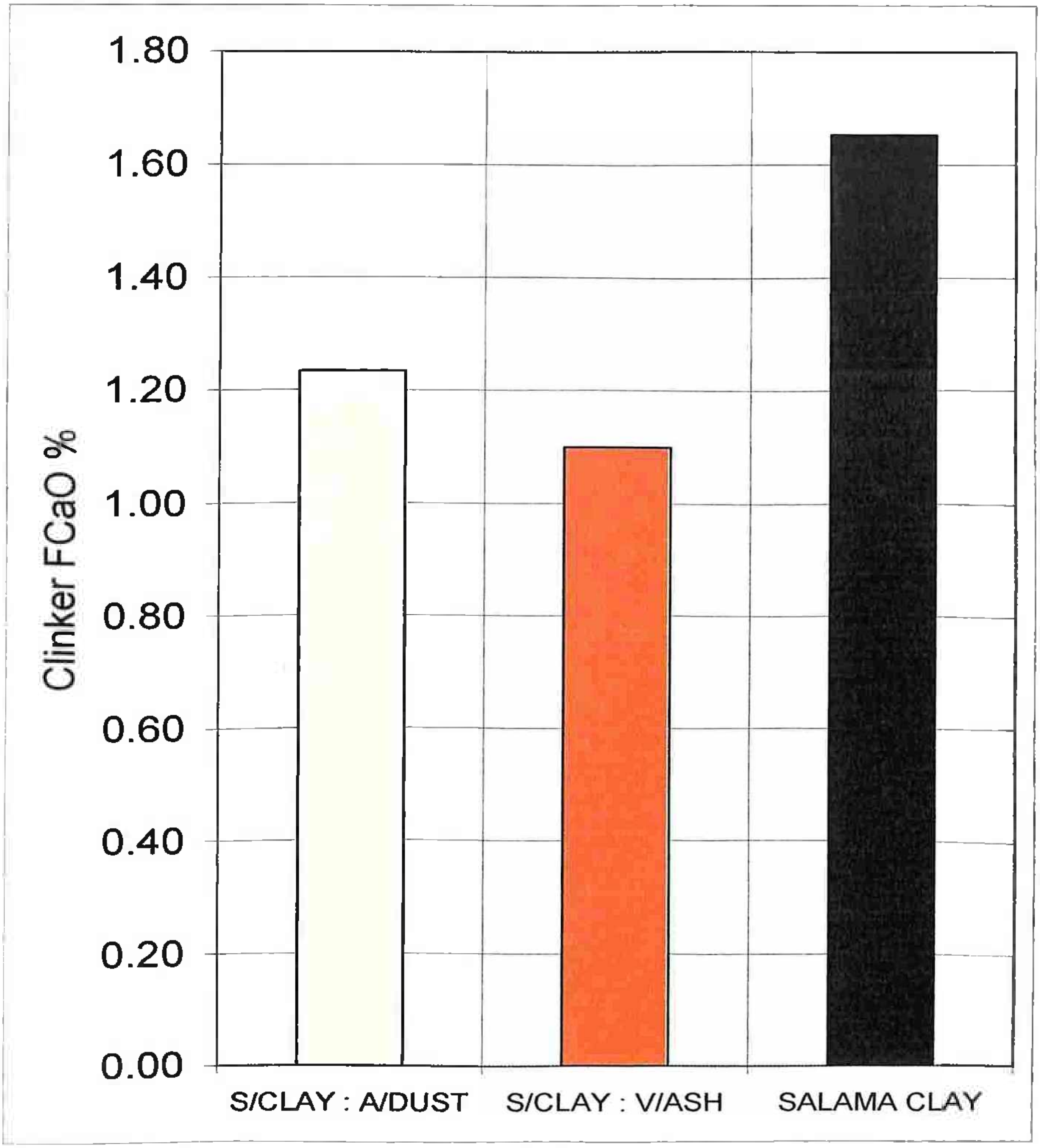
Appendix 6 **Figure 4.**

Specific fuel consumption of various mixes



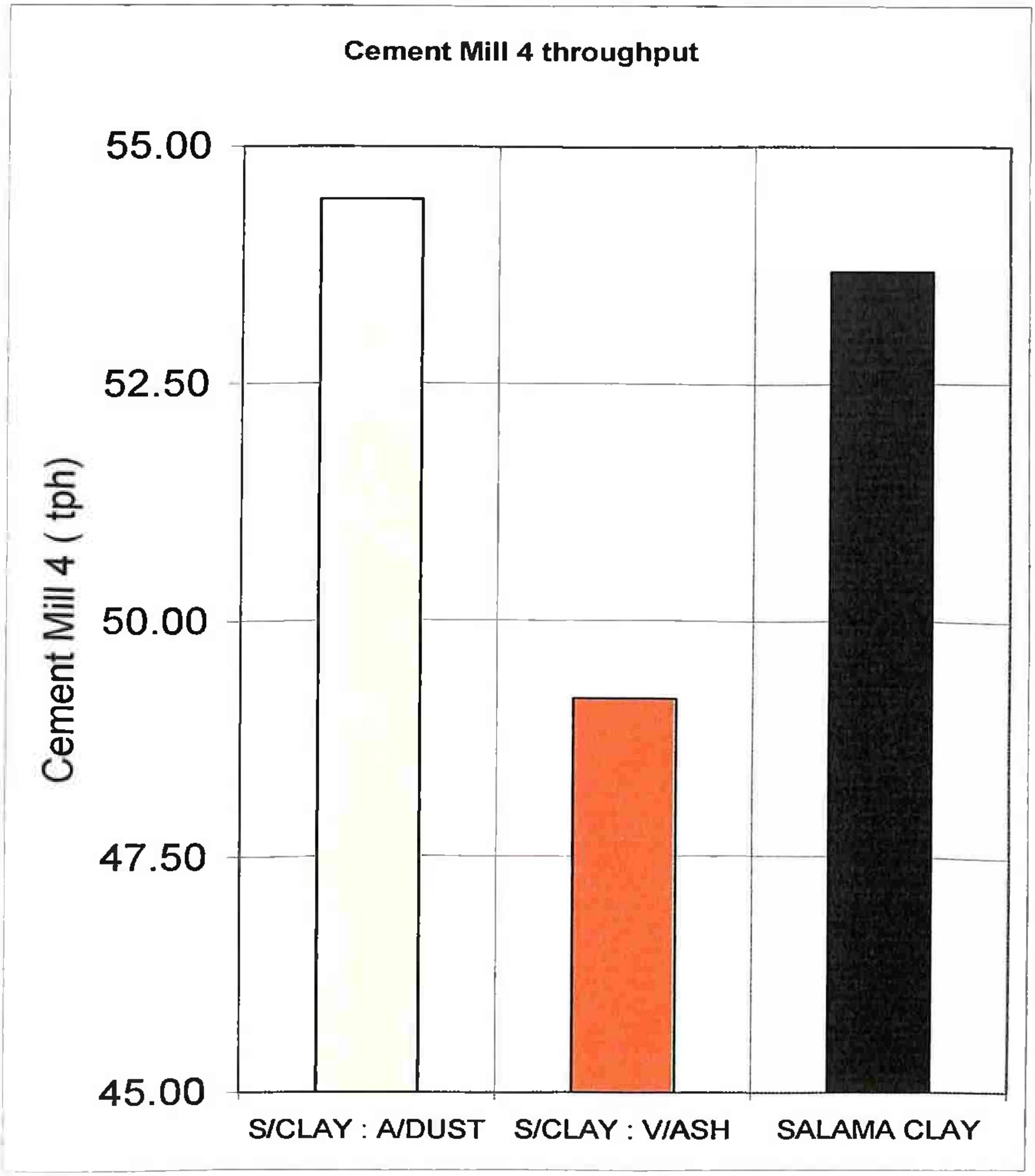
Appendix 6 **Figure 5.**

The impact of various clay mixes on clinker free lime



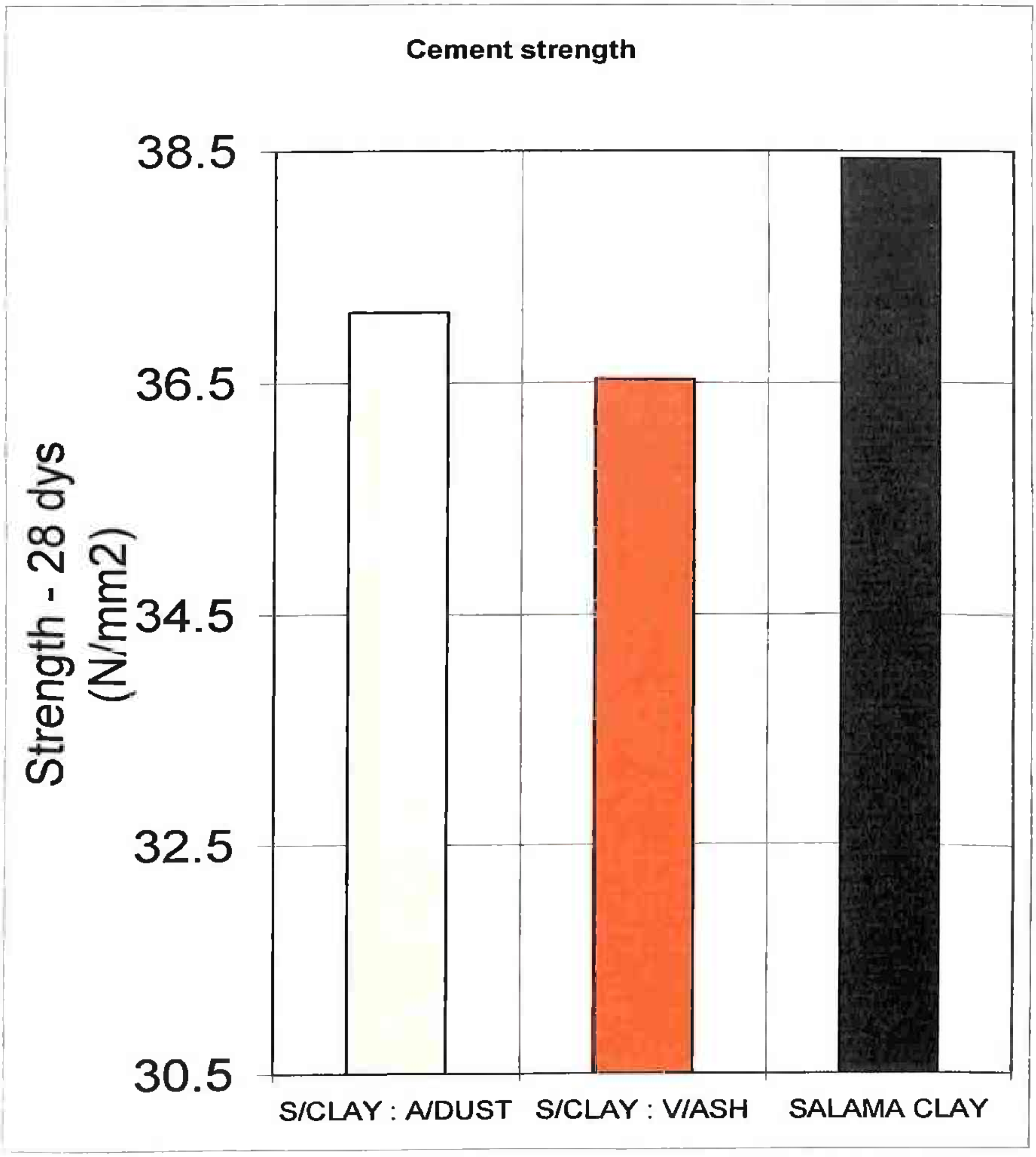
Appendix 6 **Figure 6.**

The impact of clinker from various mixes on mill feed rates

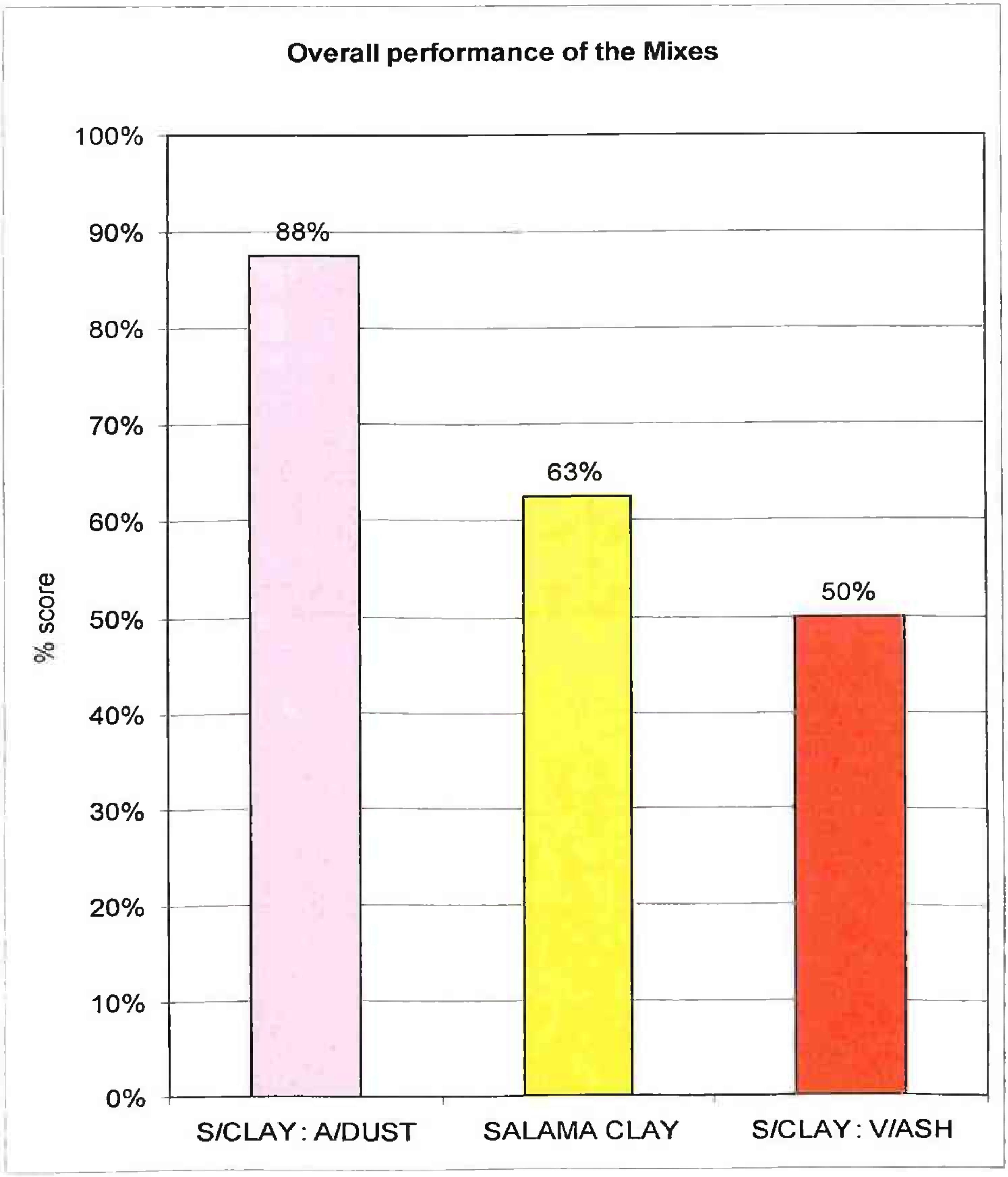


Appendix 6 **Figure 7.**

Cement strength development on various mixes



Appendix 6 **Figure 8.**



Appendix 7 **Table 16.**

Confirmatory results on the performance of various clay mixes

EAST AFRICAN PORTLAND CEMENT CO. LTD

PERFORMANCE OF VARIOUS CLAY MIXES

												DESPATCH CEMENT QUALITY		
		RAW MEAL RATIOS					KILN	CLINKER			CEMENT	Min. Mortar Prisms C/Strength		
CLAY MIX USED	DATE USED	LST %	KK %	IORE %	ACLY %	COST Ksh / Ton	FEED tph	Lt. Wt g/l	FCaO %	Efficiency Kcal / kg	MILL 4 tph	2 dys N/mm^2	7 dys N/mm^2	28 dys N/mm^2
Targets		*68*	*27*	*1*	*4*		*103*	*1300*	*1-1.5*	*905*	*55*	*13*	*27*	*35*
Salama clay	1-10/3/03	71.59	23.16	0.50	4.75	956	106	1247	1.65	876	55.92	16.42	32.23	41.90
S/clay : V/ash (1:1)	23/5-4/6/03	70.08	21.49	0.28	8.22	942	96	1142	1.12	941	51.05	15.33	28.08	37.11
S/clay : A/dust (2:1)	15/7-1/8/03	69.92	26.51	0.76	2.81	955	102	1306	1.36	989	54.12	16.35	30.47	

N.B:

RAW MATERIALS COST PER TON

LIMESTONE = KSH 1,100
KUNKUR = KSH 400
IRON ORE = KSH 3,345
SALAMA CLAY = KSH 1,250
BAUXITE = KSH 4,000
VOLCANIC ASH = KSH 600
ALLUMINA DUST = KSH 3,300