CHARACTERISTICS OF KENYAN

RICE HUSK ASH AND ITS

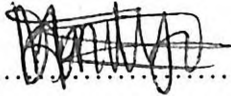# APPLICATIONS

BY

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B. Ed.(Sc.) (HONS.)

A thesis submitted in partial fulfilment for the Degree of Master of Science in Chemistry, University of Nairobi.

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DECLARATION

This thesis is my own original work and has not been submitted for examination to any other University.

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Dedication

This thesis is dedicated to my parents, Mr. Jackson Mbindyo Mbwika and Mrs. Monicah Syonguthi Mbwika.

ABSTRACT

The chemical composition of rice husk ash (RHA) from Mwea and Ahero was determined using various analytical techniques: atomic absorption spectrometry (AAS), X-ray fluorescence (XRF), X-ray diffraction (XRD), colorimetry and gravimetry.

Silica was found to be the major constituent (82.3-89.9%). The ash also contains the oxides of sodium (Na), manganese (Mn), iron (Fe), aluminium (Al), magnesium (Mg), calcium (Ca), phosphorous (P) and potassium (K) (0.07-2.1%). X-ray diffraction analysis indicated that the silica in field burned RHA was mainly amorphous. Igniting the RHA to about 1000°C was found to induce crystallinity in the amorphous silica. The amount of silica in RHA was found to vary with the loss on ignition (LOI), with a regression equation given by $Y = 92.4 - 1.00x$, where Y is the amount of silica and X is the LOI.

The ash obtained from the controlled burning of rice husks was ball-milled and used to replace 15, 20, 25 and 30% of ordinary portland cement (OPC). The compressive strength of mortar cubes cast using these RHA/cement blends was determined after 7, 28, 60 and 90 days of curing in water, and compared to that of control mortar cubes cast similarly using OPC alone. Results of the compressive strength of RHA cement mortar suggest that, RHA may be used to replace upto 23.4% cement without losing the short-term

strength of cement mortar. Slightly higher amounts ($\leq$ 30%) of RHA may also replace cement without losing the long-term mortar strength.

Cow pea plants (*Vigna unguiculata*), grown on similar plots, were treated with RHA, RHA enriched with KNO_3, and, a commercial fertiliser. The rate of growth was then compared to that of control plants, grown under similar conditions with no additives. Plants subjected to the additives showed increased vigour of growth in plant height and leaf size relative to the control plants.

Overall, the results obtained indicate the possibility of utilising RHA as a cement replacement material, and as a fertiliser. Moreover, rice husks burned in open fields in the areas sampled (which is usually the case), yield ash, whose silica is mainly amorphous, and is the most suitable form needed for cement replacement. This ash is also rich in K (1.24 - 2.1%) which is of nutritional importance to plants.

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CHAPTER 1

INTRODUCTION

1.1 GENERAL INTRODUCTION

The disposal of rice husks and other agro-wastes has for a long time posed a major challenge to farmers, millers, owners of food processing plants and environmental health managers. Such agricultural wastes, not only constitute an unmanageable burden on productive land, but their continued accumulation can also be a health hazard.

Although several methods of agro-waste disposal have been used, most of them involve either a re-location of wastes from their point of generation to suitable non-detrimental site, or end of pipe treatment processes [1]. Burning of wastes, an often used waste disposal technique, re-locates wastes from the terrestrial environment to the atmospheric environment. Landfills and dumping in water bodies are also common short-term solutions to the problem of waste disposal through re-location. However, in the long run, the materials thus disposed are still an environmental hazard [1].

During recent years however, there has been a re-awakening of interest in the area of resource recovery from waste. There is an increasing recognition that

wastes can usefully be recycled in economically viable processes [2,3]. Rice husks in particular, have caught the attention of researchers as a hidden resource of great potential. They constitute upto 25% of the weight of paddy and when burned, they yield 20-25% of their own weight as a silica rich ash [4]. This ash has been investigated for use as a filler, filter and absorbent material. It has also been investigated for use as a source of silica and carbon, and in a variety of construction applications such as production of cementitious binders for low cost housing. In the fertiliser industry, RHA has been investigated for use as an anti-caking agent and a coating for prills [5,6].

Currently, Kenya produces about 41,000 tonnes of rice annually [7]. By 1993, the production is projected to be 69,000 tonnes. Long term expansion programmes for rice production aim at producing 169,000 tonnes of rice annually. The amount of rice husks produced annually in Kenya has been estimated to be 8,500 tonnes [8]. Long term projections indicate that this amount will increase to 30,000 tonnes by the turn of the century. There has, however, been very little research done in Kenya on the utilisation of this abundant agro-waste. The focus of this research was, therefore, to examine the possible utilisation of RHA in Kenya.

Useful qualities in RHA relate to its chemical composition. This may, however, vary greatly depending on the source region of the husks and the pyroprocessing conditions. It was therefore necessary to establish the chemical composition of Kenyan RHA first, and compare it to that obtained from other

parts of the world. The utility of the ash as a cement replacement material and as fertiliser was then investigated.

1.1.1 AIMS OF THE PROJECT

The aims of this project were:

1. To determine the chemical composition of Kenyan rice husk ash and compare it to that reported in other parts of the world mainly Malawi, Egypt and India.

2. To investigate the technical feasibility of using RHA as a cement replacement material in Kenya.

3. To investigate the practical utility of Kenyan rice husk ash as a fertiliser.

1.1.2 JUSTIFICATION

The problem of accumulation of rice husks in Kenya is steadily on the rise due to the rapidly increasing production of rice. The husks have very low nutritional value hence are not useful as fodder. They also take a very long time to decay hence they are not suitable for re-cycling as compost manure. Although they can be used as fuel, the husks are bulky and difficult to transport for use in areas away from the milling centres where the need exists.

The most common means of disposal by the millers is to dump the rice husks in farmlands around the factory and set them on fire. Another common practice is to dump the husks into a river. Alternatively, the husks are burned within the factory premises. All these practices are however deleterious to the environment and hazardous to health.

There is, therefore, an urgent need for environmentally friendly means of disposing the husks.. This will curb any further damage to the environment through unsound disposal practices. Since this research dwelt on economically viable alternatives that can yield benefits to both the farmer and the miller, it is not only timely, but also highly relevant.

The cost of construction materials, especially cement, has increased drastically in recent years. Since cement is a major component in all construction works, the concept of cement replacement material is unique and can be of great benefit to our economy. The United Nations declaration on adequate shelter for all as a basic human right has received alot of emphasis in this country. The search for low-cost building inputs like RHA cement can greatly enhance existing efforts to realise this universal objective.

By examining the utility of RHA in recycling plant nutrients, the research is a pointer in an area which could see our dependence on imported fertilizer decrease.

The effect of ashing conditions on the physical nature of the silica in the RHA was studied. Included also were studies on the chemical composition of RHA from different areas in Kenya. This gave further insight into the chemical nature of RHA and is useful in exploring other areas of its utilisation.

CHAPTER 2

LITERATURE REVIEW

2.1 COMPOSITION, PHYSICAL AND CHEMICAL PROPERTIES OF RHA

Although literature reports on the study of the binding properties of RHA date as far back as 1924 [9], very little information on its properties, composition and uses, exists in current literature.

Chemical analysis of the RHA from different parts of the world has been reported and a composition range of the major components suggested [10]. Silica is the major constituent (86.9-97.3%). RHA also contains the oxides of sodium (Na), magnesium (Mg), phosphorous (P), calcium (Ca), iron (Fe), aluminium (Al) and manganese (Mn), which together can constitute upto 10%. Sulphates and phosphates also occur depending on cultivation practices and soil conditions. Trace quantities of the oxides of titanium (Ti), boron (B) and zinc (Zn) have also been reported in RHA.

When rice husk ash is heated, its mass decreases. This has been attributed to loss of carbon, carbonates and carbonaceous matter [11]. It is reported as loss on ignition (LOI) during analysis. The loss on ignition will depend on the

method of processing the husks and can vary from less than 1% to about 15%. The overall composition of RHA can vary depending on the strain of the rice, conditions of growth and the type of soil.

The changes in composition of RHA after extraction with acid and boiling water have been studied [12]. Leaching RHA with boiling water at 100°C for 5 minutes extracted 72% of the potassium oxide content and 50% of the magnesium oxide content. Only 13% of the sodium oxide and 8% of the calcium oxide content was extracted. This suggested that whereas most of the K and Mg in the RHA were in a soluble form, the Ca could be in insoluble forms like calcite and the Na bound in non available forms within the crystal lattice.

Similarly RHA containing 91.3% silica was enriched to 95.5% silica by soaking overnight in 0.5N hydrochloric acid (HCl) [13]. This could be attributed to the leaching of the alkali and basic constituents of the ash by acid.

Compared to other plant residues rice husks produce a considerably higher amount of ash on combustion [14]. The silica content of RHA is also higher compared to ash from the residues of other cereal plants like maize, wheat and barley.

The uniqueness of rice in absorbing large quantities of silica from the soil has been discussed [14]. It has been suggested that silica enters the plant through its roots in soluble forms, probably silicate or monosilicic acid and moves to the outer plant surfaces. It is then concentrated by evaporation and polymerises to form a cellulose silica membrane.

Silica increases the mechanical strength of the rice plants [15]. This safeguards the plant against disease and insect attack. It also promotes erect growth, favourably influences growth nutrient uptake and reduces transpiration.

The chemical processes taking place when rice husks are heated have been studied [16]. At temperatures below 100°C evaporation takes place and adsorbed water is lost. At about 350°C, volatile matter ignites and burning commences. Carbon is oxidised at temperatures between 400-500°C.

Above 600°C, silica is converted to quartz and at higher temperatures crystobalite, then tridymite, both crystalline forms of silica are formed. Prolonged heating above 800°C results in essentially crystalline silica being formed. The temperature at which the amorphous form of silica changes to crystalline forms is however a function of the rate of combustion and oxidising conditions.

X-ray diffraction has been used to study the occurrence of crystalline phases in RHA [17]. As the rice husk combustion temperature increases, the number of X-ray diffraction peaks observed in the X-ray diffractogram of the RHA increases. This suggests existence of a high proportion of crystalline forms of silica at high combustion temperatures.

2.2 THE CHEMISTRY OF CEMENT AND POZZOLANA

2.2.1 CEMENT

Cements are adhesive materials used to unite solids into a compact mass [18]. Cement is made by firing a mixture of lime and chalk with siliceous matter, at a temperature exceeding 1400°C, to form partially melted nodules called clinker. Additives are then added and the clinker ground to powder [19]. Gypsum, for instance, is added to control the setting of cement mortar. Calcium hydroxide is added as an activator. Napthalene derivatives may also be added as plasticisers, while calcium nitrite can be added to limit the corrosion of concrete steel reinforcement bars.

The properties of cement can be changed by using raw materials like bauxite and slag for special applications. Slag cements for instance, are resistant to sea and sulphate attack. Aluminous cements develop high strength rapidly. They can also be cast and are resistant to chemical attack [19]. The quality and quantity of cement can be increased by adding extender materials known as

pozzolana. These are silica rich materials which are known to confer desirable qualities to cement on blending. Fly ash, rice husk ash, diatomite and some volcanic tuffs are examples of pozzolanic materials.

Cements react with water to form hard materials. The chemical reactions taking place during this hardening process are not thoroughly understood. However it has been suggested that hydrolysis and hydration reactions are responsible for the hardening proccess [20, 21].

The hardening of cement is a function of the compound composition rather than bulk analysis composition. The major compounds found in clinker are:

1) Tri-calcium silicate $(3CaO.SiO_2)$

2) Di-calcium silicate $(2CaO.SiO_2)$

3) Tri-calcium aluminate $(3CaO.Al_2O_3)$

4) Tetra-calcium aluminoferrite $(4CaO.Al_2O_3.Fe_2O_3)$

The percentage composition of these compounds varies for different types of cement [19].

The calcium silicates in cement react with water to form a compound which has a colloidal structure and poor crystallinity known as toberomite gel (equations 1 & 2). It is this material which binds the two solids [20].

$$2(3CaO.SiO_2) + 6H_2O \ ----\rightarrow \ 3CaO.2SiO_2 + 3Ca(OH_2) \quad \textbf{(1)}$$

$$2(2CaO.SiO_2) + 6H_2O \longrightarrow 3CaO.SiO_2.3H_2O + Ca(OH)_2 \quad \cdots \cdots \quad (2)$$
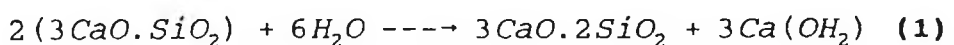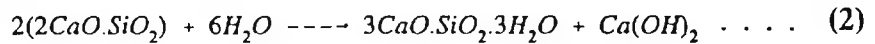
The tri-calcium aluminate phase, in the presence of soluble sulphates, reacts to form "ettringite". (equation 3). This is a hard substance whose expansion leads to the cracking of cement.

$$3CaO.Al_2O_3 + 3H_2O + 3CaSO_4 \longrightarrow 3CaO.Al_2O_3.3CaSO_4.H_2O \quad \cdots \cdots \quad (3)$$
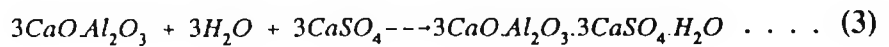
"Ettringite"

The ferrite phase takes a long time to be hydrated and also favours the formation of "ettringite".

The cementing properties of the various phases are favoured by poor crystallinity [21]. This has been attributed to imbalance in surface charges within the reacting phases. These imbalances are caused by deviations from stoichiometry, and irregularities in outline and internal structure. Such conditions favour mechanical interlocking and formation of intercrystalline links through ionic or covalent chemical bonds.

Most of the $Ca(OH)_2$ formed during the hydration of cement is crystalline and can be leached. This leads to weakening of the structure of cement, but may be prevented by adding pozzolana to cement.

2.2.2 POZZOLANA

Pozzolana are materials that react with lime, in the presence of water, under ordinary conditions to form cement like materials [22]. These materials are artificial or naturally occurring silica rich matter, and on their own they do not show cementing properties.

Fly ash, granulated blast furnace slag, calcined clay shells, bamboo ash, coconut husks, bagasse and RHA are known to be pozzolanic [22]. When added to cement they react with the calcium hydroxide set free during the hardening and setting of cement to form silicates of calcium.

Pozzolanic materials are usually easier to procure than cement. They also need little or no processing prior to blending with cement. They are, therefore, useful extenders in cement which can lower its overall cost.

The advantages of adding pozzolana to cement have been discussed [23, 24]. These include:

1) Lowering the heat of hydration of cement,

2) Increasing water tightness in mortar,

3) Reduction in the alkali aggregate reaction,

4) Improved resistance to attack by sulphates, soil and sea water,

5) Possible lowering of the cost of cement,

6) Possible improvement on the long-term strength of cement.

2.2.3 RICE HUSK ASH AS A POZZOLANA

The pozzolanic properties of RHA are based on its reactivity with lime. The lime is present either as a primary constituent in the RHA cement mix, or as a secondary product formed during the hardening of cement [25]. Since the RHA consists essentially of silica, calcium silicates are formed in these reactions.

The factors influencing the quality of the product formed include the crystalline or amorphous nature of the silica, the fineness of the ash, and, the presence of other materials like carbon.

When most of the silica in RHA is amorphous, the ash is well suited for use as a pozzolana. However, RHA composed of mainly crystalline silica shows poor pozzolanic properties [26]. Thus the RHA obtained from furnaces fired using rice husks shows poor pozzolanic properties. This has been attributed to the presence of mainly crystalline silica in the RHA.

A high proportion of carbon in RHA has been shown to lower the strength of cement mortar. However this effect is only significant when the percentage of carbon exceeds 20% [26]. This reduction in strength is primarily attributed to a reduction in the amount of silica.

The strength development potential of RHA cement cannot be directly correlated to the chemical composition of RHA [26]. Compressive strength

development tests are therefore, widely used in determining the overall quality of RHA cement mortar [27]. The force needed to crush mortar cubes cast in a standard way after 3, 7, and 28 days curing in water is an indication of the short-term strength of the cement mortar. Long term strength is similarly determined at 60, 90 and 180 days.

The strength properties, resistance to erosion and conductivity of RHA cement mortar have been reported [28 - 31]. RHA cement concrete showed superior long term strength compared to ordinary portland cement (OPC) when replacing upto 50% of OPC. However the water:cement ratio, the fineness of the ash, and the pyroprocessing conditions are factors that also influence the strength of the properties of the cement mortar.

RHA cement mortar has been found to have a low heat of hydration, a low coefficient of thermal expansion and low thermal conductivity [28 - 30]. The concrete thus has better insulation properties compared to OPC concrete. It has therefore been suggested to be suitable for use in mass concrete structure. Its slow rate of hydration reduces the problem of structural weaknesses associated with thermal gradients, heating and cooling effects in concrete.

Concrete blocks made from RHA cement were tested for corrosion when dipped in acetic acid, hydrochloric acid and sulphuric acid [31]. They were found to have superior resistance to acid and sulphate attack compared to OPC mortar blocks. RHA cement has thus found application in acidic environments like battery and acid manufacturing plants. It is also used in underwater or sea

concrete structures. Other applications of RHA cement include use in ordinary mortar, plasters, renderings, mass concrete and non-reinforced concrete structures.

Three main methods are used in the processing of rice husks for use in cement replacement [32, 33]. The husks can be burned in a heap, or under controlled conditions in a special type of incinerator. They can also be used as fuel then the ash formed is used to replace cement. Boiler ash is however crystalline and hard to grind. It also has poor binding properties. The ash obtained after burning the husks is ground to fine powder and used to replace upto 50% OPC or mixed with 20-50% lime for use in ordinary masonry work.

In a slightly different process [34, 35], the ash is intimately mixed with clay and lime, sun dried and burned. The powder obtained is then ball-milled and used as mortar or for cement replacement. Finely ground ash reacts faster with lime, showing early setting time and higher short-term strength. There is however a corresponding increase in the water requirements. This leads to a decrease in the compressive strength of the cement application.

The technical and commercial viability of producing RHA cement in Kenya has been discussed [8,36,37]. The relative cost of producing the cement is shown to vary depending on the location of the plant, the production process used, and the cost of fixed and variable plant inputs. For the process

considered in this work, the relative costs of producing the RHA cement at Mwea, Ahero and Tana delta are shown to be 73-89% relative to the cost of OPC [8]. The recent decontrolling of the price of cement and the implementation of the Tana delta project have been cited as factors that will greatly favour the production of RHA cement in Kenya.

Previous attempts to utilise rice husks in Kenya for commercial purpose include extraction of furfural, briquetting for fuel and as an admixture in feeders marsh [8]. None of these uses is however being exploited commercially.

2.3 ROLE OF POTASSIUM IN PLANTS

Potassium is one of the major nutrients required by plants for normal growth. The other nutrients include nitrogen, phosphorous, calcium, magnesium and sulphur. Plants also require trace quantities of copper, iron and manganese [38]. Potassium is the most important cation in terms of quantities taken up by the plant and amounts present in the soil. It is mainly taken up by plants as K^+ ions, and remains in ionic form within the plant cells and tissue.

The role of potassium in plant growth is not thoroughly understood [39-42]. However, potassium is known to be needed in the closing and opening of the stomata by guard cells. It encourages root growth, and increases resistance to plant diseases. This primary plant nutrient also influences growth and

distribution of xylem and phloem, and increases the size and quality of fruit and grain. Potassium ions have been linked to the stabilisation of intermediates in enzymatic processes, and the activation of enzymes and co-factors. They are also involved in the transport of photosynthate through the phloem. Potassium deficiency in plants has been associated with yellowing of leaves, necrosis, weakening of stalks, slowed growth and reduced fruit size.

Soils usually contain 0-1% potassium [43,44]. However, not all the potassium is readily available to plants. A large proportion, (90-98%) of the potassium in soils is trapped deep within the crystal lattices of minerals. It is unavailable to plants. The other proportion comprises of either of the following three categories:

1)   Non-exchangeable potassium in the outer lattice of minerals,

2)   Exchangeable potassium held against negative charges in colloids, and,

3)   Readily available potassium in solution.

Potassium in soils is susceptible to leaching and removal through plant harvest [45]. It is therefore necessary to replenish it by applying potassium fertiliser to deficient soil.

Although mineral fertilisers are commercially available sources of potassium, the ashes of certain plant residues have been shown to contain significant quantities of this important plant nutrient. The ash can therefore be applied to soils thus recycling nutrients and supporting plant growth.

CHAPTER 3

ANALYTICAL TECHNIQUES

3.1 PRINCIPLES OF THE INSTRUMENTAL TECHNIQUES

The major instrumental techniques used in this work were:

1) Atomic absorption spectometry (AAS).

2) X-ray fluorescence spectroscopy (XRF).

3) X-ray diffraction spectroscopy (XRD).

3.1.1 ATOMIC ABSORPTION SPECTROPHOTOMETRY (AAS)

Atomic absorption spectrophotometry (AAS) is a technique widely used in elemental analysis. The principles of the technique are based on the absorption of radiation by free atoms of elements [46]. Locally and elsewhere, A.A.S. has been used to analyse matrices ranging from chemical salts, sludges and biological samples, to geological samples. Its applications have therefore been amply discussed [47-50]. An atom at ground state has electrons in the lowest energy level. However, if two energy states m and n with energy E_m and E_n respectively, such that $E_n > E_m$ exist within the atom, electron transition can take place in response to absorption of radiation (fig. 1). Electrons in the m state can be excited to the n state by absorbing radiation of frequency V_{mn}.

Electrons in the n state can also undergo transitions to m state, emitting radiation of energy V_{nm}. The frequency of the radiation needed for the absorption process can be shown by the Einstein relation [46] (equation 4) to be:

$$v_{mn} = \frac{E_n - E_m}{h} \quad \ldots\ldots\ldots\ldots\ldots \quad (4)$$

where

E_m = Energy of lower state,

E_n = Energy of excited state,

h = Planck's constant (6.626×10^{-34} Js)

A = absorption   B = emission
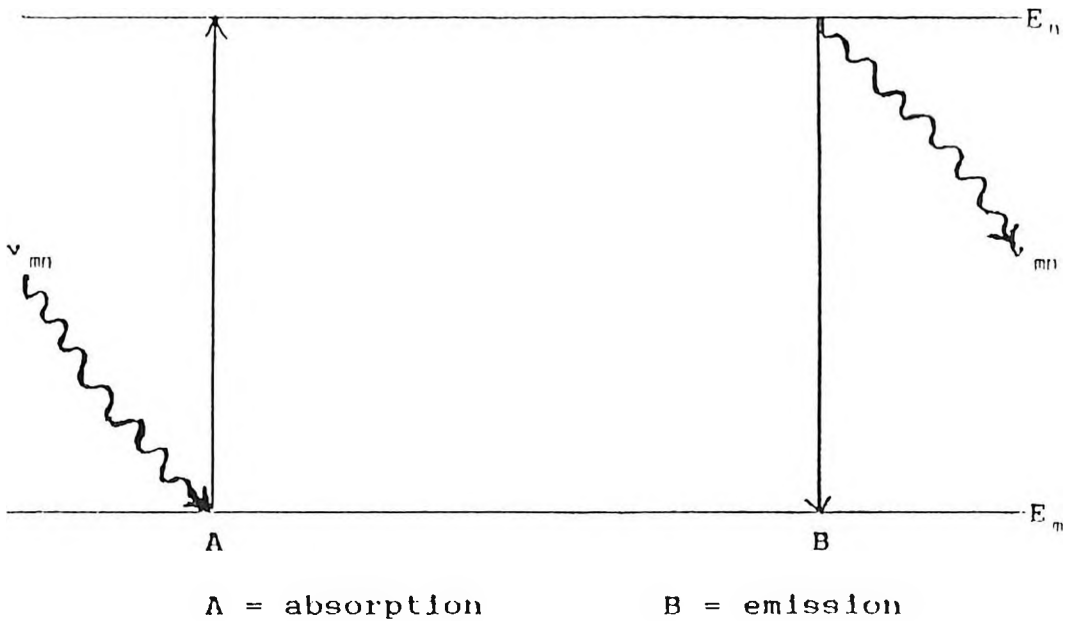
Fig. 1   The absorption and emission process in AAS

For a particular element this absorption takes place within a very narrow spectral range of about 0.01Å. Furthermore, absorption other than that originating from the ground state is very limited. This very specific nature of absorption and emission transitions forms the basis of qualitative and quantitative determinations of elements using A.A.S. The resonance radiation is the characteristic radiation of an element, that corresponds to the transfer of electrons from the ground state to higher energy levels.

The proportion of atoms in the excited state to the ground state can be found from the Boltzmann distribution [46] (equation 5).

$$\frac{N_n}{N_m} = \frac{G_n}{G_m} \exp \frac{(E_m - E_n)}{kT} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots (5)$$

where

N_n = the number of atoms in the excited state,

N_m = the number of atoms in the ground state,

G_n = statistical weight parameter for the excited state,

G_m = statistical weight parameter for the m state,

k = Boltzmann constant,

T = Absolute temperature,

The intensity of absorption varies exponentially to the incident radiation. It can be described by an equation analogous to the Beer-Lamberts' law [51] (equation 6):

$$P_v = P_o \exp(-K_v CL) \quad \cdots \cdots \cdots \cdots \quad (6)$$

where

P_0 = intensity of incident radiation,

P_ν = intensity of transmitted radiation,

L = path length of the absorbing medium,

C = concentration of the absorbing atoms,

k_ν = Absorption coefficient of the particular medium for the light of frequency ν.

K_ν is used to characterise absorption lines just as intensity characterises emission. Since the integrated absorption coefficient is proportional to the number of absorbing atoms (equation 7), atomic absorption spectra is useful quantitatively.

$$\int K_v \, dv = KN \quad \cdots \cdots \cdots \cdots \quad (7)$$

where

k_v = absorption coefficient at frequency v,

v = frequency,

K = constant,

N = number of absorbing atoms.

3.1.2 X-RAY FLUORESCENCE SPECTROMETRY

X-ray fluorescence spectrometry (XRF) is a non-destructive method of analysis, based on the production of secondary fluorescence radiation when X-rays interact with matter. The technique dates as far back as 1910 when the first characteristic spectra were observed by Barkla [52, 53]. Locally and elsewhere, the technique has been used in the analysis of elements in solid, air, water and sludge samples [54-57].

The transitions that take place within an atom when X-rays interact with matter give rise to spectral series labelled K, L, M, and N (fig.2).
For a particular element, the frequency of the radiation emitted is directly proportional to the square of its atomic number (equation 8).

$$v \quad = \quad k[z-\delta]^2 \cdots \cdots \cdots \cdots \cdots \cdots \cdots (8)$$

where

k and δ are constants which vary with the spectral series,

z = atomic number of emitting element,

ν = frequency of emitted radiation.

To a limited extent, the intensity of a selected emission line also varies

linearly with the concentration of the emitting species. Therefore, emission

lines can be used for the qualitative and quantitative analysis of elements using

XRF.

Ionisation level

N Levels

M Levels

M absorption edge

LΒ Lγ

Lα

L III
L II
L I
L absorption edge

L - series

KΒ   Kα

K - series

K Level
K absorption edge
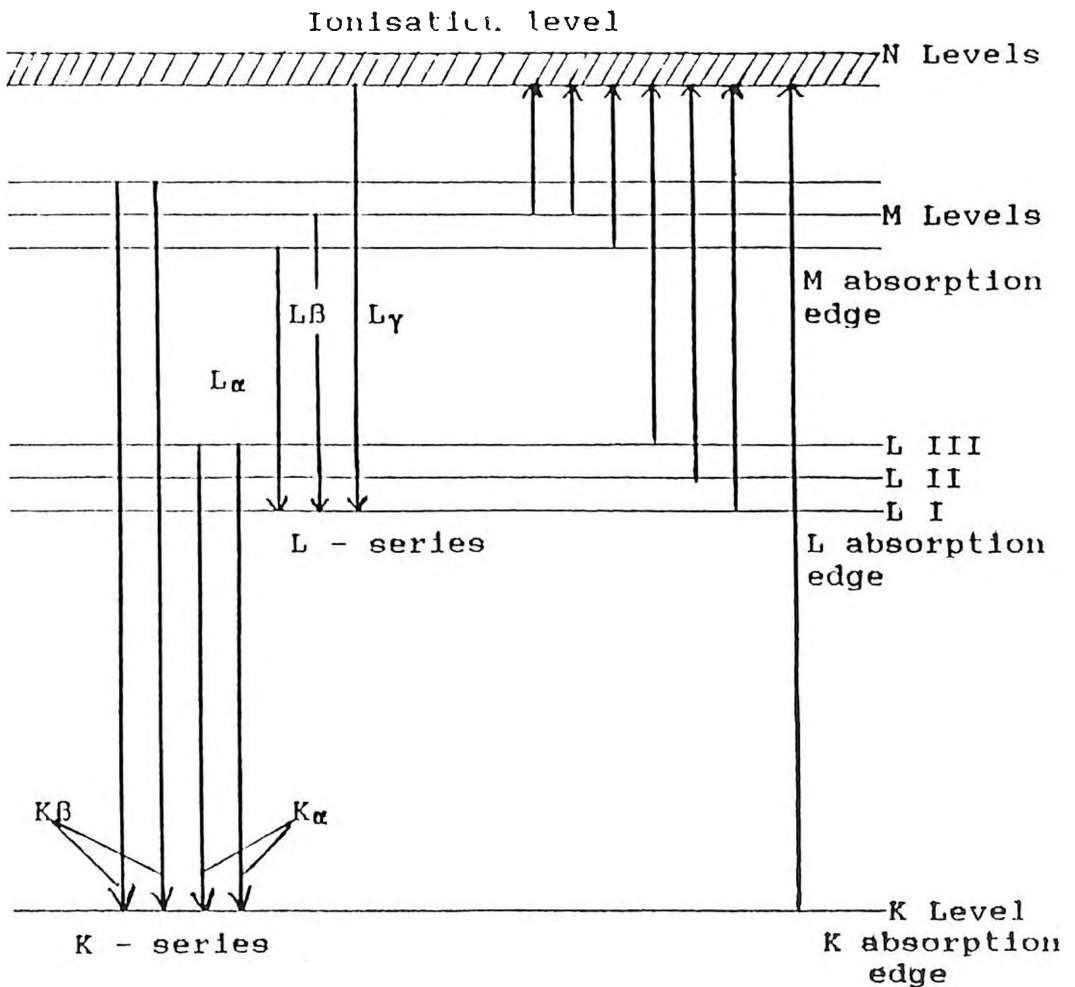
Fig. 2 The spectral series in X-ray fluorescence

The K-line spectral series is commonly used in the identification of elements. This consists of the K_α lines which are produced when electrons fall from the L shell to the K shell, and the K_β lines produced when electrons fall from the M shell to the K shell. K_α lines are much more intense than K_β lines.

Quantitative analysis in XRF is based on the fundamental parameter equation (Equation 9).

$$I_i = G_o K_i (\rho_i d) \ \frac{1 - e^{-a\rho d}}{a\rho d} \quad \cdots \cdots \cdots \quad (9)$$

where

I_i = fluorescent intensity (X-ray counts per second)

K_i = Relative excitation efficiency

$(cm^2 g^{-1})$,

G_o = Activity of excitation source (Geometrical constant)

a = combined absorption coefficient for primary and flourescent X-rays in the sample,

ρ and ρ_i are the density of the sample and the partial density of the element within the sample respectively (g cm^{-2}),

d = thickness of the sample.

The factor $\frac{1 - e^{-a\rho d}}{a\rho d}$ is the absorption correction factor. It is responsible for the attenuation of measured fluorescence within the sample. This factor strongly depends on the value of the product $a\rho d$. For thin samples, $a\rho d$ is

much smaller than 1. Equation 9 therefore transforms to:

$$I_i = G_o.K_i.\rho_i d \quad \cdots \cdots \cdots \cdots \cdots \cdots (10)$$

For thick samples, $a\rho d$ is much greater than 1 hence equation 9 transforms to:

$$I_i = G_o.K_i.\alpha_i.\frac{1}{a} \quad \cdots \cdots \cdots \cdots \cdots \cdots (11)$$

Where I_i, G_o, K_i and a, have the same meaning as in equation 10 above, and α_i is the concentration of the element in the sample. The absorption correction factor therefore has to be taken into account for thick samples.

3.1.3   X-RAY DIFFRACTION

Crystals can diffract X-rays. Planes of atoms or ions act as diffraction planes on which X-rays can be scattered. X-ray diffraction spectrometry is based on the coherent, unmodified, scattering of X-rays by diffraction planes within a crystal solid [58]. The scattered X-rays are in a definite phase relationship with one another and therefore can reinforce or interfere (fig. 3).

The conditions necessary for reinforcement to occur are set out in the Bragg equation [58].

$$n\lambda = 2d \sin\theta \quad \cdots \cdots \cdots \cdots \cdots \cdots (12)$$

where

> n   = small whole number corresponding to the order of the
>
>   diffracting plane,
>
> λ   = wavelength of scattered radiation,
>
> O   = glancing angle of incident radiation,
>
> d   = interplanar distance separating the planes in the crystal.
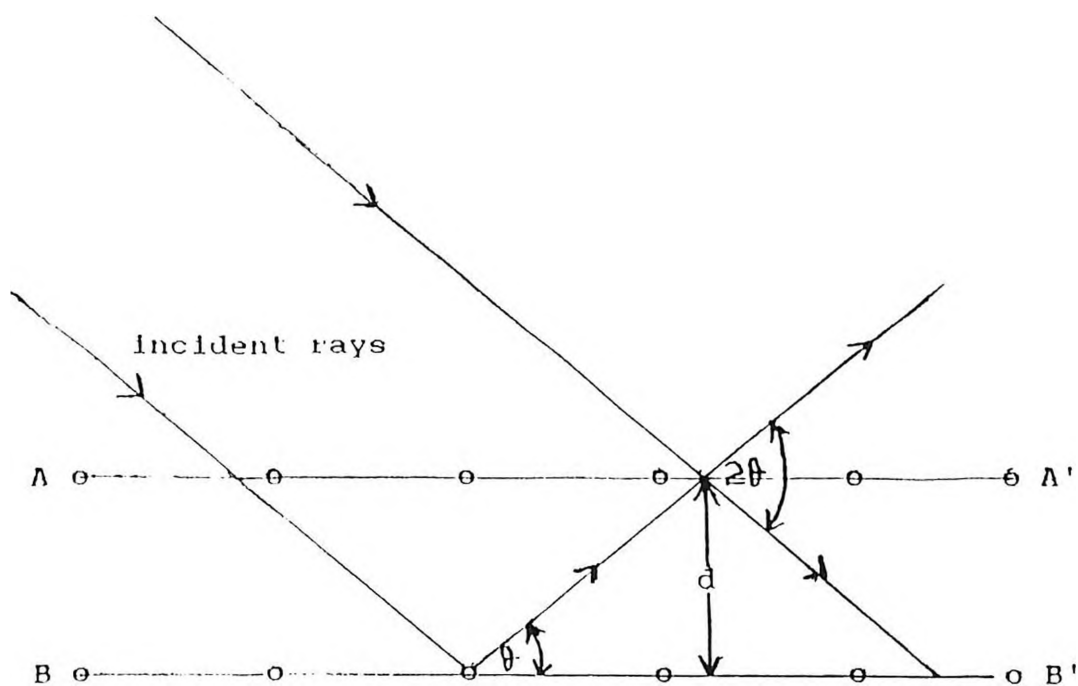
Fig. 3 Diffraction of X-rays by crystal layers AA'and BB'

This relationship is very precise, hence it is used in determining the inter-planar spacing d. Since d is remarkably constant for crystals of the same compound that are properly grown, it can be used for the identification of crystals through fingerprinting.

Qualitative X-ray diffraction analysis is based on the observation that "the same substance always gives the same diffraction pattern, and, in a mixture of substances, each produces its patterns independent of others hence the patterns are superimposed patterns of the separate components" [59].

X-ray diffraction (XRD) intensities can also be correlated to electron distribution, hence to the structure of the unit cell. By fingerprinting X-ray patterns against carefully selected standards, unknown crystalline compounds can be identified. Nevertheless the use of XRD in identifying unknown crystalline substances is still limited. However, detailed analytical schemes and tables have been developed [60 - 62] and, as they increase, the utility of the technique in crystal identification is bound improve.

3.2 INSTRUMENTATION

3.2.1 ATOMIC ABSORPTION SPECTROPHOTOMETRY

The atomic absorption spectrophotometer (fig. 4) has the following major components;

    1) Source of radiation,

    2) Nebuliser,

    3) Burner,

    4) Monochromator,

    5) Detector,

6) Amplifier,

7) Read out device.

The radiation source produces a sharp resonance line spectrum which falls on atomised sample vapour. Hollow cathode lamps are the most common radiation sources though vapour discharge tubes and electrodeless discharge systems are also used [46-48].

The atomisation apparatus consists of the nebuliser and the burner. The nebuliser functions to produce a fine mist or aerosol atomic vapour from which measurements are made. The burner produces atoms from the vapour. Although electrothermal atomisation systems have been investigated, oxidised fuel burners are commonly applied. Flameless and cold vapour atomisation techniques have also been used particularly with mercury. The fuel gases used include propane, hydrogen and acetylene.

An oxidising gas, usually air, nitrous oxide or oxygen mixed with an inert carrier gas like argon or nitrogen is mixed with the fuel. Air/acetylene and nitrous oxide/acetylene mixtures combine a high flame temperature with a slow propagation. They also do not produce radicals which affect atomisation and are therefore preferred .

```
┌──────────────┐      ┌──────────────┐      ┌──────────────┐      ┌──────────────┐
│  RADIATION   │ ──▶  │   ATOMISER   │ ──▶  │ MONOCHROMATOR│ ──▶  │   DETECTOR   │
│   SOURCE     │      │  (BURNER)    │      │              │      │              │
└──────────────┘      └──────┬───────┘      └──────────────┘      └──────┬───────┘
                             ▲                                           ┆
                             │                                           ▼
                      ┌──────┴───────┐      ┌──────────────┐      ┌──────────────┐      ┌──────────────┐
                      │              │      │   DIGITAL    │ ◀──  │  AMPLIFIER   │ ──▶  │    METER     │
                      │  NEBULISER   │      │   DISPLAY    │      │              │      │  READ-OUT    │
                      │              │      └──────────────┘      └──────────────┘      │   DISPLAY    │
                      └──────┬───────┘                                                  └──────────────┘
                             ▲
                             │
                      ┌──────┴───────┐
                      │    SAMPLE    │
                      └──────────────┘
```
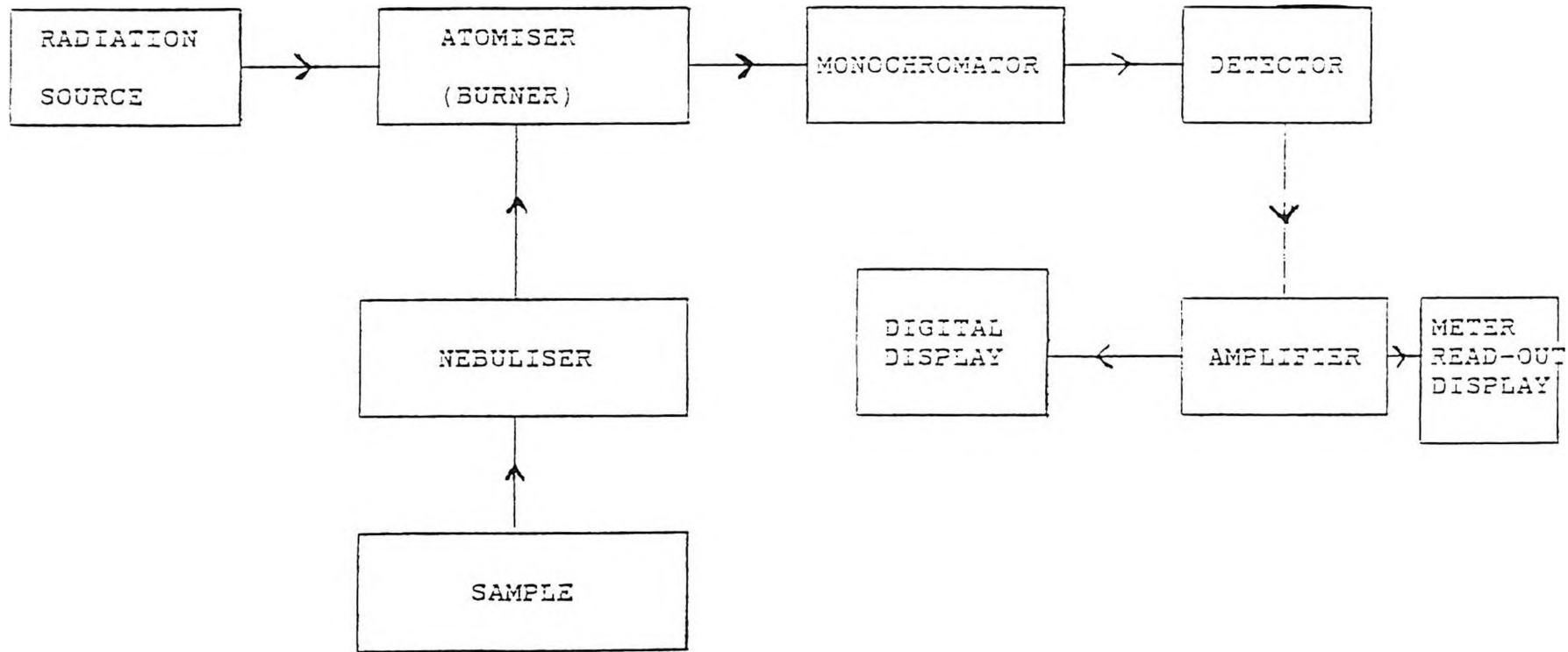
Fig. 4   Schematic diagram of the atomic absorption spectrometer.

The resonant line is isolated from non-absorbing lines falling within the same band width by a monochromator. This is either an interference filter, glass prism or diffraction crystals. A photomultiplier tube or a solid state detector receives the transmitted radiation, shapes it and passes it onto an amplifier. The amplifier is tuned to a modulated frequency, usually 50Hz or 400Hz, to which the lamp is also modulated. This eliminates the measurement of the component of the radiation signal originating from the flame, lamp or other emission process. The amplified signal is then presented in either a digital, display meter or print out format.

3.2.2 X-RAY FLUORESCENCE ANALYSIS

The X-ray fluorescence spectrometer (fig. 5) consists of:

1) primary radiation source,

2) sample presentation apparatus,

3) detector,

4) pre-amplifier,

5) amplifier,

6) multi-channel analyser

7) mini-computer.

The primary radiation source produces the exciting radiation which falls on the sample, producing secondary radiation. Radioisotope sources like ^{55}Fe, ^{109}Cd and ^{241}Am are conveniently used. X-ray tubes are also used, with the

advantage of controlling the energy of primary radiation, but the disadvantage of producing unsteady signals [52, 53].

Samples for analysis are in the form of solid pellets or thin substrates. The sample is presented above the detector in a sample holder of precise geometry, that ensures repeatability in an environment that is free from dust. The sample is wrapped in a mylar foil and in some instruments, vacuum or helium filled systems are used. Most commercial instruments however have an air path. A beryllium window placed before the detector filters long wavelength radiation and serves as an entrance for the X-rays. The radiation then falls on a solid state detector. This is usually a Si(Li) or Ge(Li) drifted system.

The detector is housed in a vacuum cryostat cooled by liquid nitrogen at 77K along with a field effect transistor pre-amplifier. The low temperature minimises background noise signals. X-ray photons falling on the detector lead to hole electron pair formation and, due to an applied negative potential bias, charge transfer occurs and a signal is generated.

The detector output is then amplified between 0-10V pulses. Very low or very high wavelength pulses are filtered off by the amplifier. Pulse height analysis is done in the multi-channel analyser and the signal presented in a monitor or cathode-ray tube.
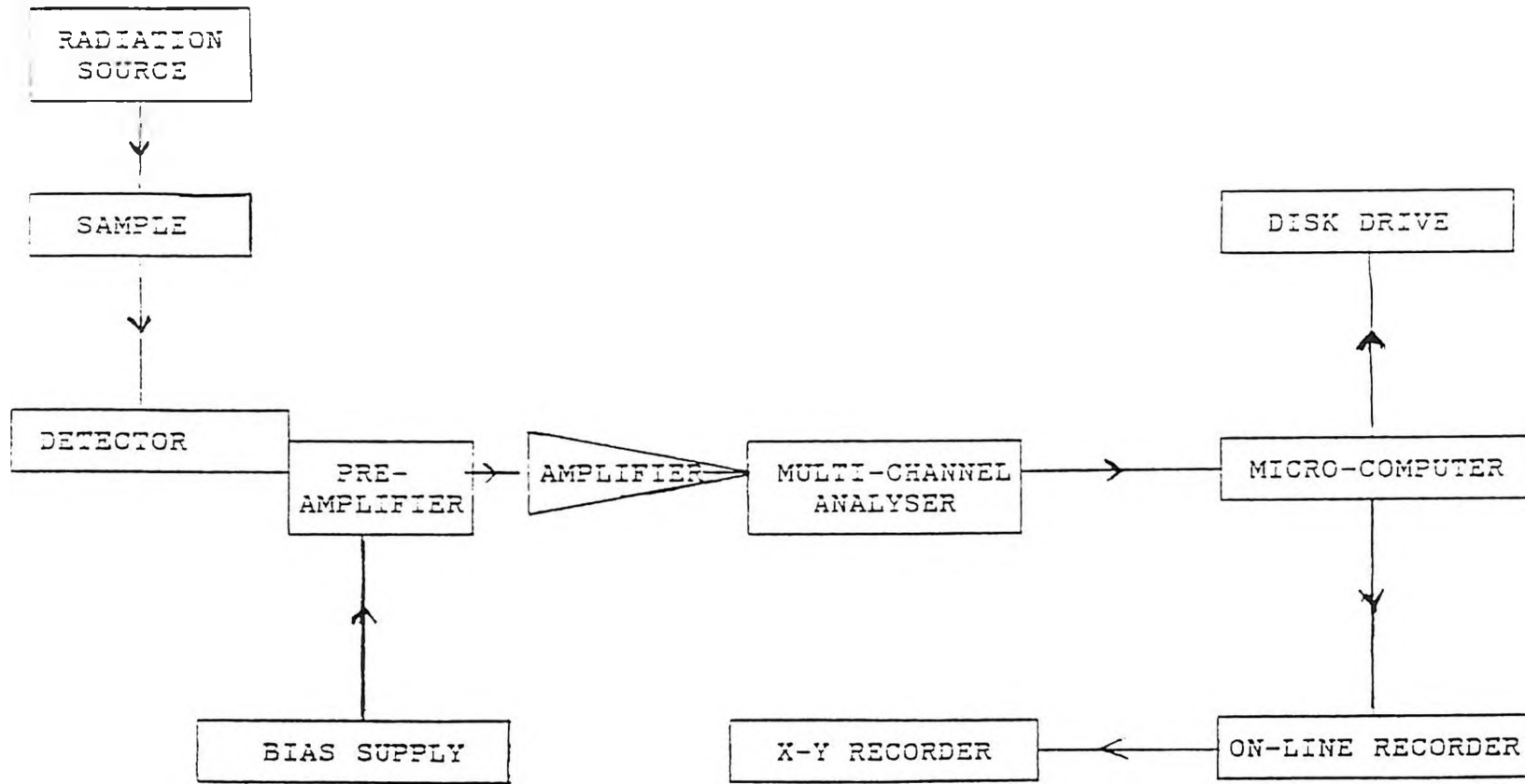
Fig. 5 Schematic diagram of the X-ray spectrometer.

Many spectrometers also have a printer which can make a permanent record of the spectra. A mini-computer is used to acquire the data, analyse peaks, compute intensity, correct for enhancement and other effects, and to give the concentration of the element of interest.

3.2.3 X-RAY DIFFRACTION

The X-ray diffractometer measures the intensity of diffracted X-rays as a function of wavelength. The major components of the X-ray spectrometer (Fig. 6) are;

     1) X-ray radiation source,

     2) Collimator,

     3) Goniometer,

     4) Monochromator,

     5) Detector,

The radiation source is an X-ray tube. It produces X-rays of desired wavelength which fall on the sample and are diffracted. The target anode could be made of copper, zinc or other suitable elements.

The radiation is collimated to give a narrow beam. The X-rays then fall on the sample which is mounted in a goniometer. The goniometer can rotate, thus changing the orientation of the sample hence varying the angle of incident radiation, θ. The diffracted beam passes through a filter system and falls on a detector. The speed of rotation of the detector and goniometer is
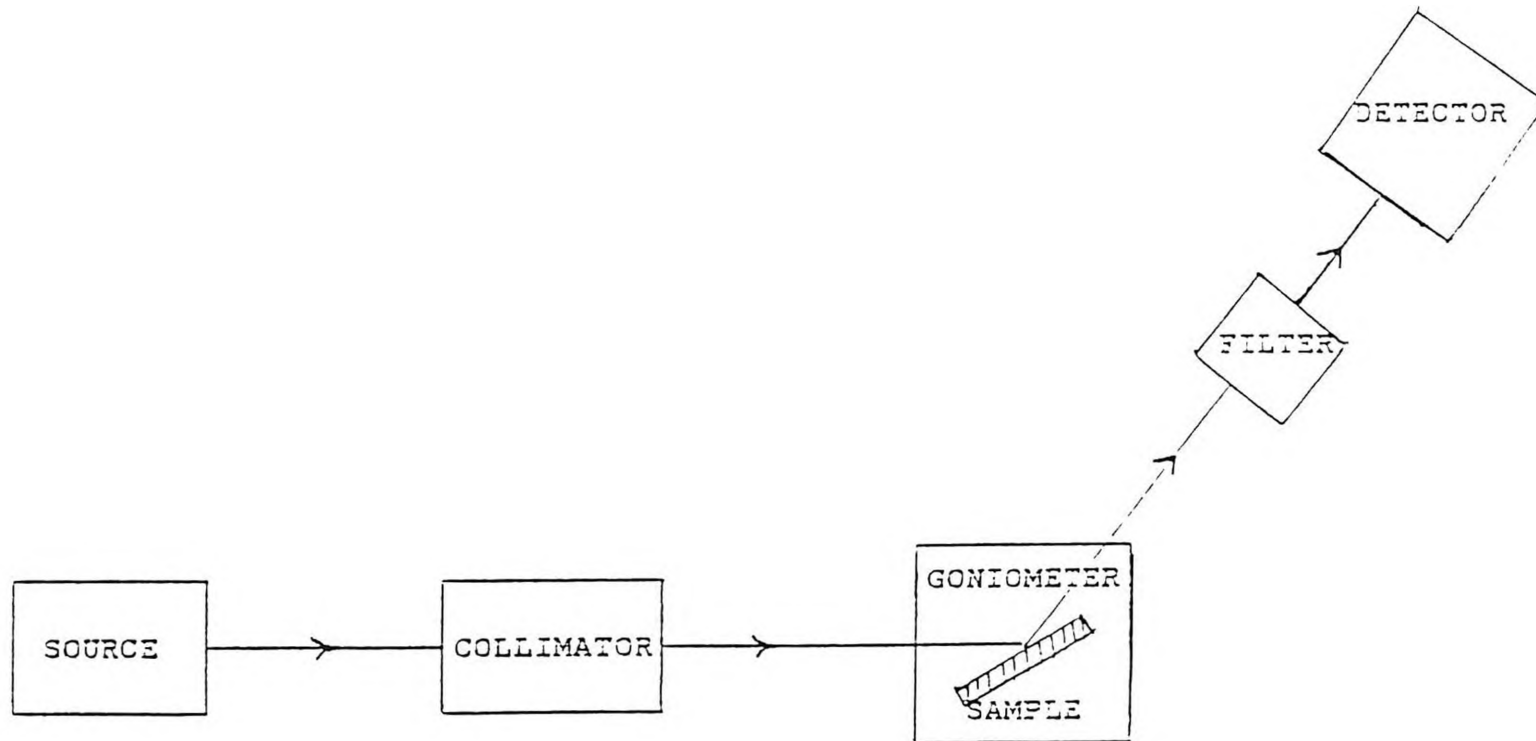
Fig. 6 Schematic diagram of the X-ray diffractometer.

synchronised through coupled drives. The detector rotates through an angle $2\theta°$ when the goniometer rotates $\theta°$. This allows the scanning of diffraction angles over a wide range of wavelengths in a polychromatic beam.

The detector is a scintillator or Geiger-Muller counter and the signal is presented graphically using an X-Y plotter. An on-line recorder produces a chart showing peak intensity (counts per second) as a function of the angle of incidence (0-90°).

Since high energy X-rays are involved, the goniometer and other devices in the instrument have lead shielding. A water cooling mechanism, a high voltage generator and a steady current regulator are also important devices in the X-ray diffractometer.

CHAPTER 4

MATERIALS AND METHODS

4.1   MATERIALS

4.1.1 REAGENTS AND CHEMICALS

All the chemicals used during the analytical and digestion procedure were of analytical grade. These included sulphuric, nitric and perchloric acids (all from Rie De Haen), hydrofluoric acid (Hopkins and Williams), sodium carbonate, sodium borate (British Drug House) and sodium di-hydrogen phosphate (Baker Analyser).

General purpose reagent, potassium nitrate, was used to enrich RHA for use as a fertiliser. A commercial fertiliser (N:P:K-20:10:10), supplied by Pharm Africa (K) Ltd., was used in the experimental plots.

Certified reference materials Soil-7 (International Atomic Energy Agency) and SY2 and SY3 (Canadian Geology and Survey) were analysed to determine the accuracy of the analytical procedures used.

Cement from the Bamburi Portland Cement Factory in Mombasa was used for blending with RHA.

4.1.2 **INSTRUMENTS**

A Varian Techtron Spectra AA6 atomic absorption spectrophotometer was used for the analysis of Na, K, Mn, Ca, Mg, Al, Fe and Si, while a Bausch and Lomb Spectronic 20 colorimeter was used for the determination of P.

X-ray diffraction studies were done with a Phillips X-ray diffractometer with the following components:

1) PW 1710 diffractometer control,

2) 1050/81 goniometer,

3) Zephyr ZEM 2500°C power generator,

4) PM 8203A Online recorder,

These three instruments are located at the Department of Mines and Geology, Ministry of Environment and Natural Resources (Madini House), Nairobi.

An X-ray fluorescence spectrometer located at the Centre for Nuclear Science Techniques, University of Nairobi was used for XRF analysis. The instrument consists of the following components:

1) Canberra Series 40 Multi-channel Analyser,

2) Ortec 571 Spectroscopy Amplifier,

3) Ortec 729 high Voltage Bias Supply,

4) Ortec 729 a Liquid Nitrogen Level Monitor,

5) DEC Professional 350 Series Mini-computer,

6) ^{55}Fe and ^{109}Cd annular excitation sources,

7) Si(Li) Ortec detector of active diameter 6mm, sensitive depth of 5.32mm and nominal Be window thickness of 23 μm.

A Denison T.I.B. compression testing machine located at the Department of Civil Engineering, University of Nairobi was used for compressibility tests.

Ball milling was done using a steel rolling ball-mill fabricated by Pamba Industries and located at the Housing Research and Development Unit (HRDU).

4.1.3 RICE HUSK INCINERATOR

Rice husks were burned in a mini kiln constructed at the HRDU. The design was similar to the one constructed earlier [37], which was a modification of the Pakistan Council for Scientific and Industrial Research (PCSIR) kiln design. It was 1.0m high, with a cross-sectional area of $0.81m^2$. Its total surface area was $4m^2$ and each side had four air inlets, each with a cross-sectional area of 25 cm^2. The holes could be closed with a tightly fitting brick.

4.2   PROCEDURES

4.2.1 SAMPLING

Mwea rice husks were collected from heaps inside the Mwea Rice Millers
Factory. They were packed into nylon gunny bags and transported to Nairobi
for analysis. Some RHA was also sampled from various heaps within about
5 Km radius of the Mwea Rice Millers Factory. The upper layer containing
charred husks was discarded and the ash below scooped with a spatula into a
polythene bag. The bottom layer in contact with soil was carefully avoided.
The samples were then transported to Nairobi for analysis.

Rice husks and RHA from Ahero were similarly sampled.   The sampling
points were located within the Municipal Council of Kisumu dumping grounds
near the Kisumu Technical Institute.

4.2.2 CHEMICAL ANALYSIS

4.2.2.1 DIGESTION PROCEDURE

For the determination of Na, K, Ca, Mg, Al, Fe, Mn and P, the RHA sample
was digested with a 3:1:1 vol/vol mixture of nitric, perchloric and sulphuric
acids [64]. The acid mixture (9mls) was added to 0.50 g of the sample and
heated gently in a covered beaker to allow maximum contact with the acid,

then more vigorously to near dryness. Concentrated hydrochloric acid (2mls), and de-ionised water (20mls) were then added. The solution was then filtered on ashless filter paper into a 100ml flask.

The paper and residue were then charred in a crucible and ignited at about 1000°C in a muffle furnace for 5 minutes [65]. The ash obtained was moistened with 3 drops of distilled water, then treated with 5 drops of concentrated sulphuric acid and 3 mls of hydrofluoric acid (HF), in polytetrafluoroethylene (PTFE) beaker. The treatment of the ashed residue with HF was neccesary in order to expel the silica in the residue and to release all the other elements into solution.

About 3 drops of concentrated HCl, followed by some dilute HCl (1:20) (5 mls) and finally de-ionised water (5 mls), were then added. The solution was then filtered onto the filtrate obtained earlier and brought to the mark. The samples were digested in triplicate. A blank consisting of the acid mixture without the sample was also similarly prepared.

For the determination of Silica (Si), 0.25 g of RHA were fused with 4.0 g of sodium carbonate and 3 g of borax in a platinum crucible to a fine melt [65]. On cooling, the fuse was dissolved in 50% hydrochloric acid then topped to 250 mls. A reagent blank was also similarly prepared, using the fusion mixture without the sample.

4.2.2.2 ATOMIC ABSORPTION SPECTROPHOTOMETRY

Sodium (Na) and potassium (K) were determined using the flame emission mode, while all the other elements except P were determined using the absorption mode [46]. Optimum analytical conditions as recommended by the instrument manufacturer were used [48].

4.2.2.3 COLORIMETRY

Phosphorous (P) was determined as the phosphovanadomolybdate complex using the acid digested solution [66, 67]. To 10 mls of the solution, 10mls of vanado-molybdate solution, (a 50:50 mixture of 0.25% ammonium metavanadate in 33% HNO_3 and 5% w/v aqueous ammonium molybdate) and 25 mls of distilled water were added. The solution was then allowed to stand for five minutes and its absorbance at 430 nm determined photometrically against a blank. The blank was prepared in a similar manner, using 10 mls of distilled water instead of the sample. The amount of P was then calculated by comparing the absorbance of the sample solution complexes to that of a standard similarly prepared using 10 mls of 0.05 mg/ml P.

4.2.2.4 GRAVIMETRY

Loss on ignition (LOI) was determined gravimetrically. 0.50 g of RHA were ignited at about 1000°C in a furnace for 15 minutes or till constant weight

was registered [68]. The percentage loss in weight after cooling the crucible and its contents in a dessicator was determined and reported as LOI.

4.2.2.5 X-RAY DIFFRACTION

X-ray diffraction analysis was done using the powder technique [63]. About 0.50g of the ash was ground to a fine powder using pestle and mortar, and a small amount on a glass slide mounted in the goniometer. The sample was then scanned for $2\theta = 2°-70°$ degrees using Cu anode radiation ($\lambda = 1.5418$) at 30 mA, 30kV, and a chart drive speed of $2°$ per minute.

4.2.2.6 X-RAY FLUORESCENCE ANALYSIS

About 0.50g of the finely ground sample was diluted with about 5.0 g of analar grade cellulose. The sample and diluent were then homogenised thoroughly with pestle and mortar [53]. About 2.0 g of the mixture was pressed into a pellet of diameter 2.5cm. For each RHA sample three such pellets were prepared. The pellets were then analysed using an ^{55}Fe and ^{109}Cd source at a counting time of 500s.

4.2.2.7 CASTING MORTAR CUBES

Casting of mortar cubes was done according to the British Standards Institution BS : 12 - 1971 procedure [68]. Four RHA cement blends were

obtained by mixing ball-milled RHA with OPC. These blends had 15, 20, 25 and 30% RHA in cement. 185g of this RHA cement was mixed with 555g of sand, 74ml of water were then added, and, a uniform mixture obtained.

This mixture was then compacted into a casting mould (70.7mm cube). Due to lack of a vibrating table, the mixture was compacted manually with a wooden compacting rod until all the mortar fitted into the cube.

The cubes were then left on the bench for 24 hrs then cured in water. For each RHA cement blend, a total of 15 cubes were cast. The mean compressive strength of three cubes for each blend was then determined after 7, 28, 60 and 90 days.

4.2.3 EXPERIMENTAL PLOT

A 4m x 4m experimental plot was tilled and properly levelled. It was then subdivided into 16 sub plots each 1m x 1m. These plots were then systematically grouped into four groups, (fig. 7) and cow pea seeds *(Vigna unguiculata)* planted. The planting was done with a spacing of 30 cm, 1 seed per hole and a planting depth of about 2cm.

The first group of plots (A), were treated with 1g of RHA per seed before planting. The RHA contained 2.1% K as determined using XRF. In the second group of plots (B), each seed was similarly subjected to 1g of RHA enriched with KNO_3. The enriched ash contained 10% K. Plots in the third
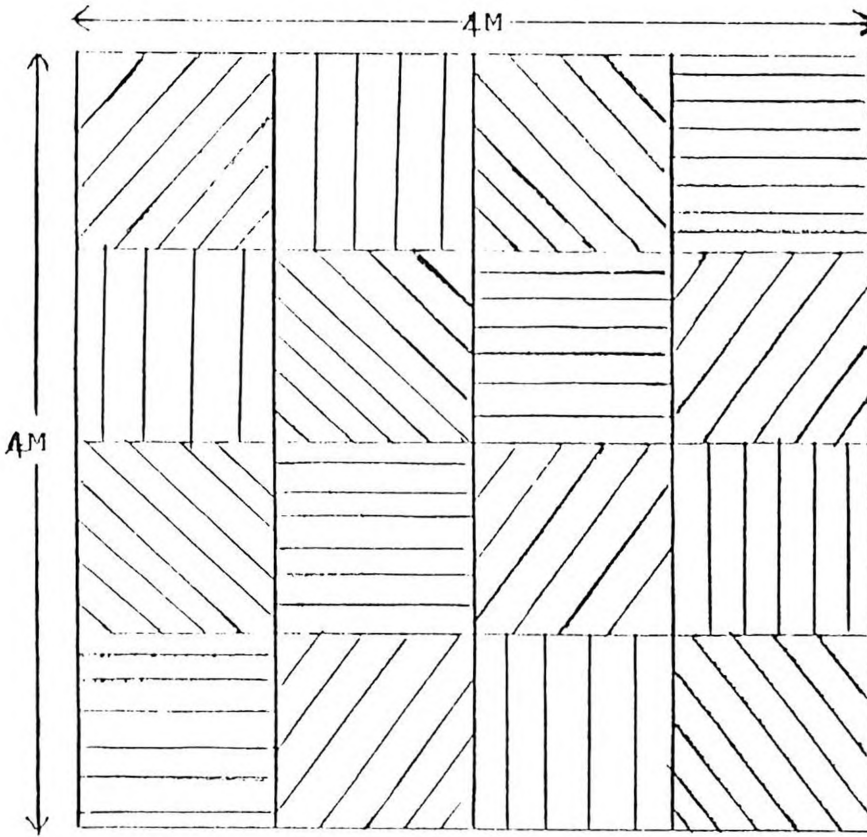
Subplots	Treatment
– A	RHA
– B	RHA + KNO_3
– C	Commercial fertiliser
– D	No additive

Fig. 7 Layout of the experimental plot.

group (C), were treated with 1g of commercial fertiliser (N:P:K-20:10:10) per seed before planting. No fertiliser was added to the control group of plots (D). The soil in the experimental plot had 1.26% $\pm$ 0.01 K (as determined using XRF). This application rate corresponds to 900 kg of the additives per hectare.

For each plant, the height was determined weekly for 8 weeks. The width of one leaf from among the first pair of leaves, for each plant, was measured at the widest point after every 2 days for 24 days.

CHAPTER 5

RESULTS AND DISCUSSION

5.1 ANALYSIS OF REFERENCE STANDARDS

In order to determine the accuracy and the sensitivity of XRF and AAS instruments, certified reference materials (CRM) were analysed. The results of the AAS analysis of CRM SY2 are shown in Table 1. The experimental values compare very well with the certified values (mean error $\pm 1.8\%$). On the basis of these results, the AAS analytical procedures adopted in this work were therefore verified as accurate and reliable.

Certified reference materials SY3 and Soil-7 were also analysed for potassium (K) using XRF in order to ascertain the validity of the technique in the analysis of RHA for K (Table 2). These results also compare well with the certified values (mean error ± 5.53 %).

The reliability of the XRF technique was also verified by analysing CRM SY 3 for other elements. The results (Table 3), further indicate that the technique is reliable and applicable for the analysis of these elements (mean error, $\pm 3.06\%$). The combined mean error for all the XRF analyses of CRM was $\pm 1.24\%$, which indicates that the technique can be a reliable and accurate tool for chemical analysis.

TABLE 1. ANALYSIS OF CERTIFIED REFERENCE MATERIAL SY2*.

CONSTITUENT (%)	EXPERIMENTAL VALUE A (%)	CERTIFIED VALUE B (%)	RELATIVE ERROR (%) $\frac{A-B}{B} \times 100$
SiO_2	59.90	58.90	+1.7
Fe_2O_3	6.00	6.47	-7.3
Mn_2O_3	0.30	0.30	0.0
MgO	2.72	2.64	+3.0
P_2O_5	0.58	0.54	-7.4
CaO	8.26	8.38	+1.4
Al_2O_3	10.62	11.80	-10.0
Na_2O	4.00	4.15	-3.6
K_2O	3.91	4.24	-8.4

* All constituents except P_2O_5 were analysed using AAS.

P_2O_5 determined colorimetrically.

TABLE 2. ANALYSIS OF CERTIFIED REFERENCE MATERIALS

FOR K_2O USING XRF.

CRM[*] (%)	EXPERIMENTAL VALUE A (%)	CERTIFIED VALUE B (%)	RELATIVE ERROR $\frac{B-A}{A} \times 100$ (%)
SY3	4.69	4.56	+2.85
S7	1.58	1.46	+8.20

[*] Certified reference material.

TABLE 3. XRF ANALYSIS OF CERTIFIED REFERENCE MATERIAL SY3.

CONSTITUENT (%)	EXPERIMENTAL VALUE A (%)	CERTIFIED VALUE B (%)	RELATIVE ERROR $\frac{B-A}{A} \times 100$ (%)
CaO	8.54	8.00	+6.75
Mn_2O_3	0.26	0.29	-10.34
Fe_2O_3	5.94	6.29	-5.59

5.2 PHYSICAL AND CHEMICAL CHARACTERISTICS OF RHA

5.2.1 COMPOSITION OF RICE HUSK ASH

Physically, the RHA samples from Mwea and Ahero appeared the same. Chemical analysis also revealed major similarities in composition. Results of the analyses (Table 4) showed that silica is the major constituent in RHA from both areas. In addition, the RHA also contains the oxides of Fe, Mn, K, Ca,

TABLE 4. COMPOSITION OF FIELD BURNED RHA FROM MWEA AND AHERO (%).

AREA	SiO_2	Fe_2O_3	Mn_2O_3	MgO	CaO	Na_2O	Al_2O_3	K_2O	P_2O_5	LOI[*]	TOTAL
MWEA	85.00	0.23	0.12	0.43	0.67	0.07	0.32	1.24	0.71	6.93	95.72
		±0.06									
n=10	±1.47		±0.01	±0.12	±0.30	±0.02	±0.08	±0.29	±0.42	±1.33	±1.25
AHERO n=6	89.44	0.41	0.14	0.42	0.58	0.47	0.46	1.35	1.55	3.66	98.48
	±0.52	±0.02	±0.01	±0.31	±0.05	±0.08	±0.11	±0.08	±0.25	±0.06	±0.41

[*] Loss on ignition

n = number of samples analysed in triplicate

± = standard deviation

Na, Al, Mg and P. The loss on ignition (LOI) reported could be attributed to carbon, carbonaceous materials and volatile matter in RHA [11].

There are six significant findings in the analysis of RHA from both regions. First, the major component in RHA from both areas was silica (Mwea 85.00%, Ahero 89.44%). However, Mwea samples showed a higher relative standard deviation (RSD) of the silica content ($\pm$1.73%) than Ahero samples ($\pm$0.58%). The very low values of the RSD for the analyses from both areas show that the silica content of the RHA does not vary widely within the rice production zones. Factors which could account for the slight variations observed include the strain of the rice, variations in soil conditions, sampling and homogeneity of the samples.

The oxides of K and P occur in considerably higher proportions, compared to the other oxides in both areas. This relatively high abundance of these two constituents is expected, since K and P are essential nutrients necessary for plant growth. Therefore, the continued growth and harvest of the rice crop could deplete the soil of these nutrients, leading to a decline in yields. The addition of commercial fertiliser to rice fields is however, considered an essential agricultural practise. The supply of these nutrients is thus constantly replenished.

The level of P_2O_5 was however higher by a factor of two for samples from Ahero. This could be due to variations in the amount of phosphate fertilisers

applied to rice fields in the regions. The low amount of P_2O_5 for Mwea could also suggest declining soil P status possibly linked to extensive monocultural practise.

No major differences were noted in the amount of manganese and magnesium oxides in RHA from both regions. However, RHA from Mwea was low in Na_2O, Al_2O_3 and Fe_2O_3 and slightly high in CaO. These differences could be due to variations in the composition of soil in these regions.

The loss on ignition (LOI) for both areas (Mwea 6.93%, Ahero 3.0%) is well below the 20% level considered to significantly influence strength properties of RHA cement mortar [26]. This suggests that the ash sampled could be suitable for use in cement replacement.

The amount of SiO_2 + Fe_2O_3 + Al_2O_3 for both areas is of interest. The amount of these components in any material has been suggested to be a useful indicator of its potential utility as a pozzolana. These are materials rich in silica that could be used as a mixture with cement. They are useful extenders which can also enhance the properties of ordinary portland cement. The American Society for Testing of Materials (ASTM) standards on pozzolana and fly ash [69], suggest that materials with a mean amount of SiO_2 + Fe_2O_3 + Al_2O_3 exceeding 70.0% could be considered to be suitable for use as pozzolana.

The values reported in this work (Mwea 85.6%, Ahero 90.3%) show that Kenyan RHA meets the ASTM criterion for chemical composition of pozzolana. Since currently RH in Kenya is an environmental burden with no major economic use, its utilisation for cement replacement is particularly attractive.

The total composition of the constituents analysed is less than 100%. The results show that the contribution for the 9 constituents analysed in RHA was 96% - 98% of the total weight. The 2% - 4% composition unaccounted for could be the contribution of other elements that were not considered, and the cumulative errors of individual analyses. Such errors are expected due to difficulties inherent in the analysis of samples [70].

The chemical composition of Kenyan RHA compares very well with that of RHA from other parts of the world (Table 5) [8,12]. The data indicates similar amounts of silica in RHA from Kenya, India, Malawi and Egypt, and minor variations in the amount of the other elements.

TABLE 5 COMPARISON BETWEEN THE COMPOSITION OF
KENYAN RHA AND THAT FROM OTHER PARTS OF THE
WORLD.

CONSTITUENT	COUNTRY			
	INDIA	MALAWI	EGYPT	KENYA
SiO_2	92.15	88.30	91.28	87.22
Fe_2O_3	0.21	-	0.48	0.32
Mn_2O_3	-	-	-	0.13
MgO	0.45	-	0.47	0.43
CaO	0.41	0.50	1.11	0.63
Na_2O	0.08	-	-	0.27
Al_2O_3	0.41	-	2.83	0.39
K_2O	2.31	3.40	1.79	1.30
P_2O_5	-	2.90	-	1.13
LOI[*]	2.77	2.90	0.23	5.30
TOTAL	98.79	98.00	98.19	97.12

[*] Loss on ignition

- not indicated.

The analysis of silica using AAS is tedious, and expensive platinum crucibles are required for fusion. Incomplete fusion and possible losses during the process could also lead to inaccurate results.

However, silica is the major reactive component in RHA which makes it suitable for use in cement replacement. It is, therefore, important that the amount of silica in RHA be known prior to blending. An indirect method for silica determination was attempted in this work and is suggested to be suitable for rapid routine analysis of RHA for silica prior to blending with cement. The method is based on regression analysis of the amount of silica and the LOI in selected RHA samples from Mwea. These samples were selected on the basis of their appearence, which can vary depending on the conditions under which the rice husks are burned. It was generally found that the more dark the ash, the higher the LOI. The LOI and the amount of silica were also found to show a linear correlation (fig. 8).

The regression line is accurately described by the equation below (r = 0.94):

$$Y = 92.4 - 1.00X \cdots \cdots \cdots \cdots \quad (13)$$

where Y and X are the amount of silica and LOI respectively. The equation above can be used to calculate the amount of silica if the LOI is known since this relationship seems to hold for all the combustion conditions investigated.
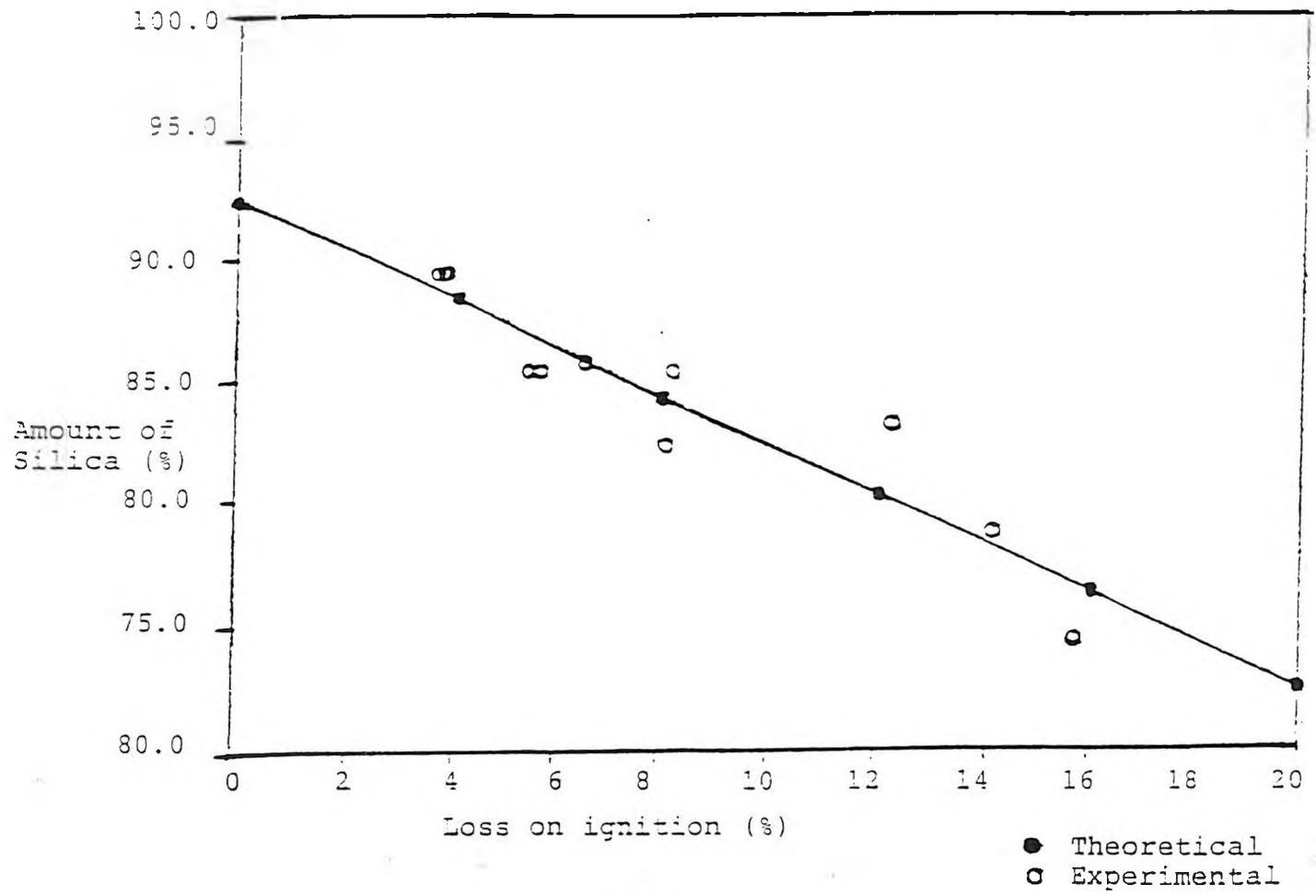
Fig. 8   Variation of the amount of silica with loss on ignition (LOI).

5.2.2 COMPARISON OF AAS AND XRF ANALYSIS

Three samples of RHA were analysed for K using both XRF and AAS analytical techniques (Table 6). K was singled out for its usefulness in plant growth. The rapid analysis of numerous RHA samples would be necessary if RHA which is rich in K is to be used as a fertiliser.

TABLE 6. COMPARISON BETWEEN AND AAS XRF ANALYSIS FOR K_2O IN RHA.

A.A.S.[*]	X.R.F.[*]
0.92 +0.03	1.04 +0.12
0.98 +0.07	1.11 +0.09
1.29 +0.05	1.69 +0.10

[*] n = 4

The results show a high correlation between the two techniques (r = 0.9986). The equation for the regression line is Y = 1.7942 - 0.6278 where Y is the result for the XRF analysis and X the corresponding value for AAS analysis.

The slight variations in the values obtained indicate slightly higher values for the XRF analyses. This is consistent with previous observations [48,70], and could be attributed to possible losses during the AAS digestion and matrix based enhancement effects during XRF analysis.

5.2.3 EFFECT OF AERATION ON COMPOSITION OF RHA

Among the factors that can influence the amount of carbon in RHA are combustion rate, aeration and temperature. The influence of varying aeration conditions during the pyroprocessing of RH was therefore investigated (fig. 9).

The LOI varies inversely with the area of ventilation of the kiln. When RH is burned in the open however, the LOI for the ash obtained is higher than that obtained when the kiln is fully ventilated. This dependence of LOI on the aeration during pyroprocessing is possibly due to changes in oxidation processes within the burning heap of husks.

The burning of rice husks under conditions of abundant supply of air such as when the kiln is fully ventilated favours an almost complete oxidation of carbon and carbonaceous matter. This explains the decrease in the LOI with increasing ventilation. When the supply of air is reduced, oxidation is incomplete and a high amount of carbon remains which explains the high LOI observed. However, when RH is burned in conditions of unlimited supply of
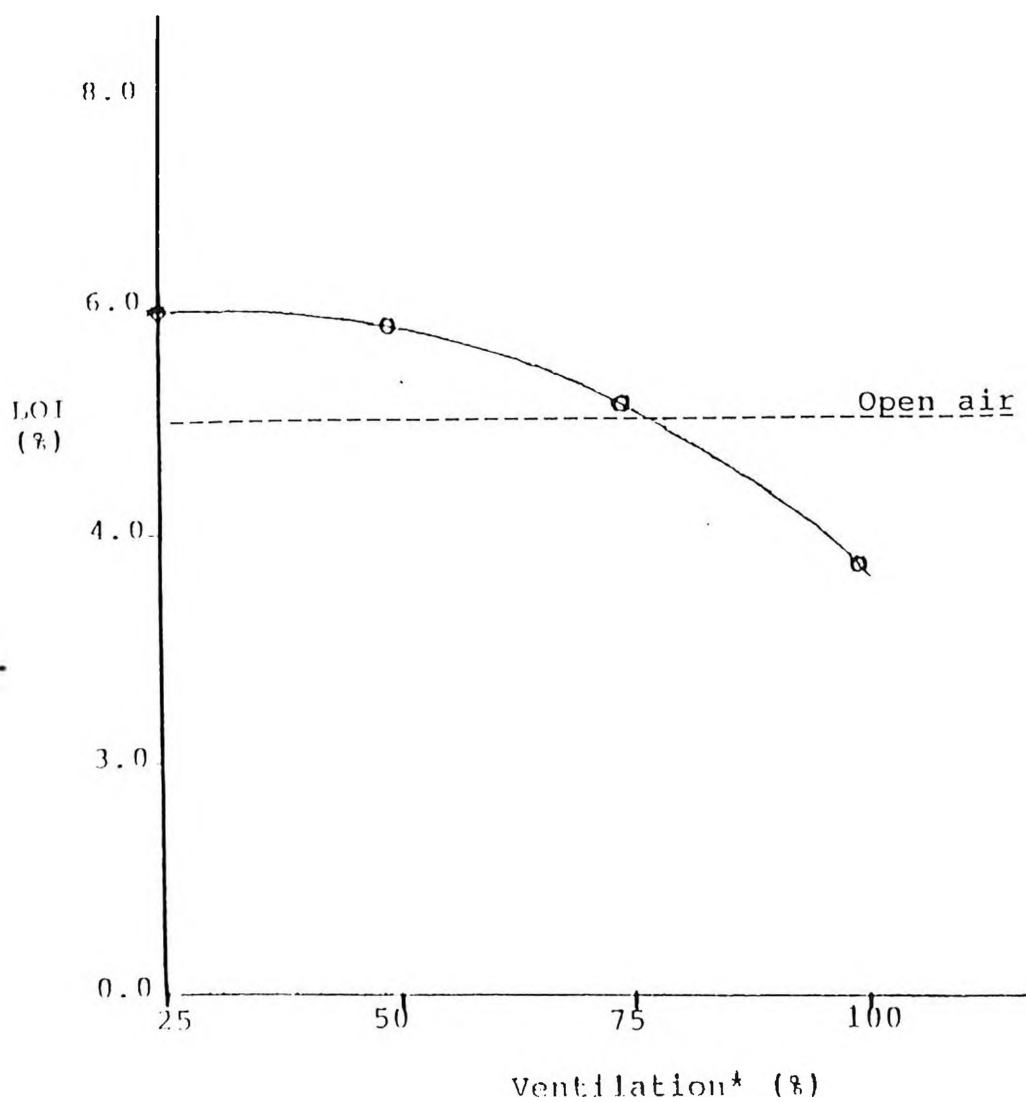
Fig. 9.   Effect of aeration on ignition loss

*Ventilation = $\dfrac{\text{No. of holes open}}{\text{Total no. of holes}}$ x 100

air such as in the open, the rate of combustion is probably very rapid, which may leave a high amount of unburned carbon. This could account for the higher LOI in RHA, when rice husks are burned in the open, compared to RHA obtained when the kiln is fully ventilated.

The practical implication of this dependence of LOI on conditions of aeration during pyroprocessing of rice husks is apparent. Pyroprocessing conditions can be varied to control the overall composition of RHA. This is based on the strong correlation between the amount of silica and the LOI, which are the major constituents of RHA. The quality of RHA can therefore be made more appropriate for cement replacement.

5.2.4 X-RAY DIFFRACTION ANALYSIS OF RHA

X-ray diffractometry showed no major peaks in the X-ray diffractogram of field burned RHA samples (fig. 10a). This suggests that the samples were composed of mainly amorphous silica and could be suitable for use in cement replacement. However, the XRD pattern of RHA ignited at about 1000°C showed major characteristic peaks in the XRD pattern (fig. 10b). These peaks indicate the presence of crystalline silica in the ignited RHA.

The occurrence of crystalline silica could be as a result of temperature induced polymorphic phase transitions, which transform amorphous forms of silica to crystalline states. Therefore, conditions of uncontrolled combustion that are
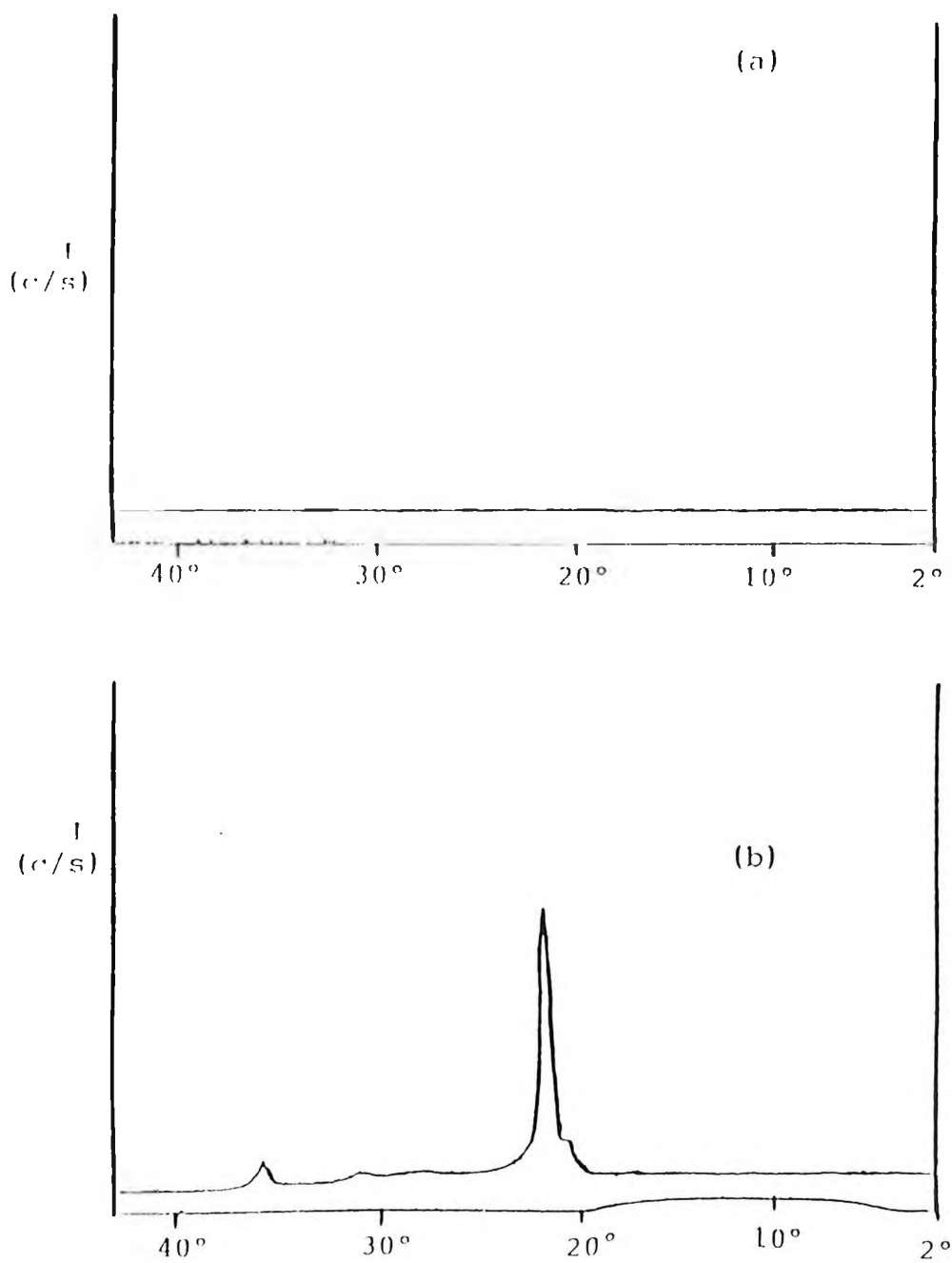
Fig. 10. X-ray diffractograms of:

a) Field burned RHA
b) RHA ignited at about 1000°C
for 20 minutes

c/s = counts per second

likely to achieve very high temperatures, can potentially yield RHA with mainly crystalline silica. Temperatures exceeding 1400°C have been reported in the interior of heaps of RH during the burning process. The RHA obtained from such heaps may show poor binding properties [26].

5.2 COMPRESSIBILITY TESTS

The use of RHA as a pozzolana has been attempted in several rice growing areas of the world [32-35]. The methods used involve replacement of some cement with a certain percentage of RHA, then using the formulation thus obtained in ordinary cement applications.

Although various standards have been set in order to compare the mortar strength properties of cementitious materials [68, 69], they are difficult to use. This is due to problems related to the availability of standard sand and cement. However, the use of control cement mortar, made from OPC, can give an indication of the relative mortar strength.

Most of the standards used compare the compressive strength of the experimental mortar to that of the control mortar after 3, 7, 28, 60 and 90 days curing in water. However, the 28 day compressive strength (28 d strength) of mortar is widely considered a reliable indicator of the short-term strength properties of cementitious materials [27]. The 60 d and 90 d compressive strength give the long-term strength properties.

The variation of mortar strength with time for the various RHA cement blends and the control (OPC) cement is shown in Table 7. The mortar strength of all the formulations increased with time. The observed increase in strength could be attributed to two types of reactions. These are hydration and hydrolysis reactions between cement and water, and reactions between free lime and RHA. These reactions result in the formation of silicates of lime, which are responsible for the hardening of cement.

In order to compare the short-term mortar strength of the RHA cement to that of the control (OPC) mortar, t-test statistics values [71] were calculated based on the 28 d strength. The results indicate significant differences at the 90% confidence level between the strength of the control (OPC) mortar, and that of the formulations containing 15% and 30% RHA. However, no significant differences were noted for the blends containing 20% and 25% RHA.

It was further noted that the 28 d mortar strength of the formulation containing 15% RHA was higher (113.6%), while that of the blend containing 30% RHA was lower (87.2%), relative to the control (OPC) mortar (100%). Therefore, these results suggest that the optimum formulation would contain between 15% and 30% RHA.

TABLE 7. COMPRESSIVE STRENGTH OF RHA CEMENT MORTAR[*].

AMOUNT OF RHA (%)	STRENGTH Nmm^{-2}			
	7 DAYS	28 DAYS	60 DAYS	90 DAYS
OPC ONLY (0%)	14.9 ±1.0	25.7 ±2.0	27.6 ±2.2	27.9 ±2.5
15	15.7 ±1.9	29.2 ±2.0	29.7 ±2.1	30.9 ±2.2
20	15.1 ±1.0	25.9 ±1.9	29.1 ±2.2	30.1 ±2.5
25	14.8 ±1.3	24.7 ±1.4	28.9 ±1.6	29.1 ±2.2
30	15.2 ±1.0	22.4 ±1.1	27.6 ±1.4	27.8 ±2.7

* Reported values are means of 3 replicates

± = Standard deviation

The optimum formulation was further investigated by linear extrapolation of the 28 d strength of the RHA cement formulations (fig. 11) and found to consist of 23.6% RHA and 76.4% OPC.
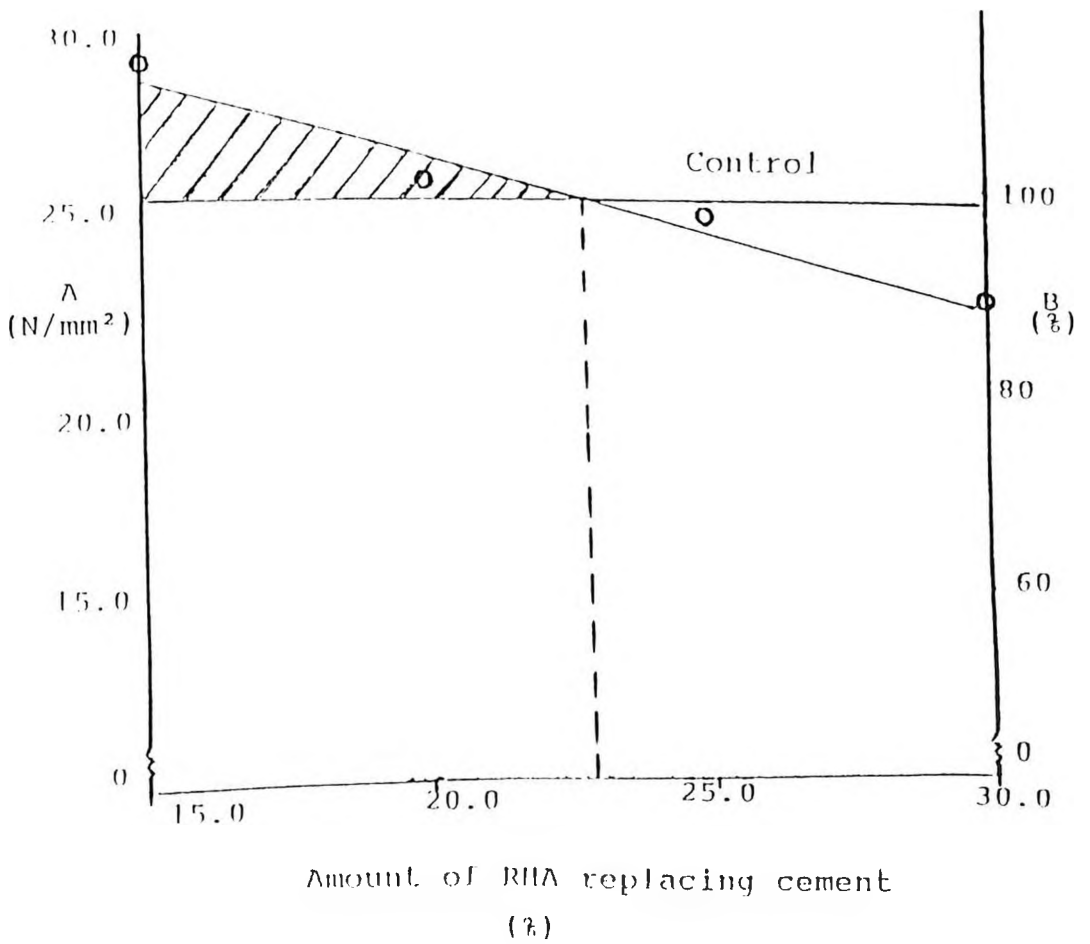
Fig. II. Variation of 28 day mortar strength with increasing amount of RHA in cement.

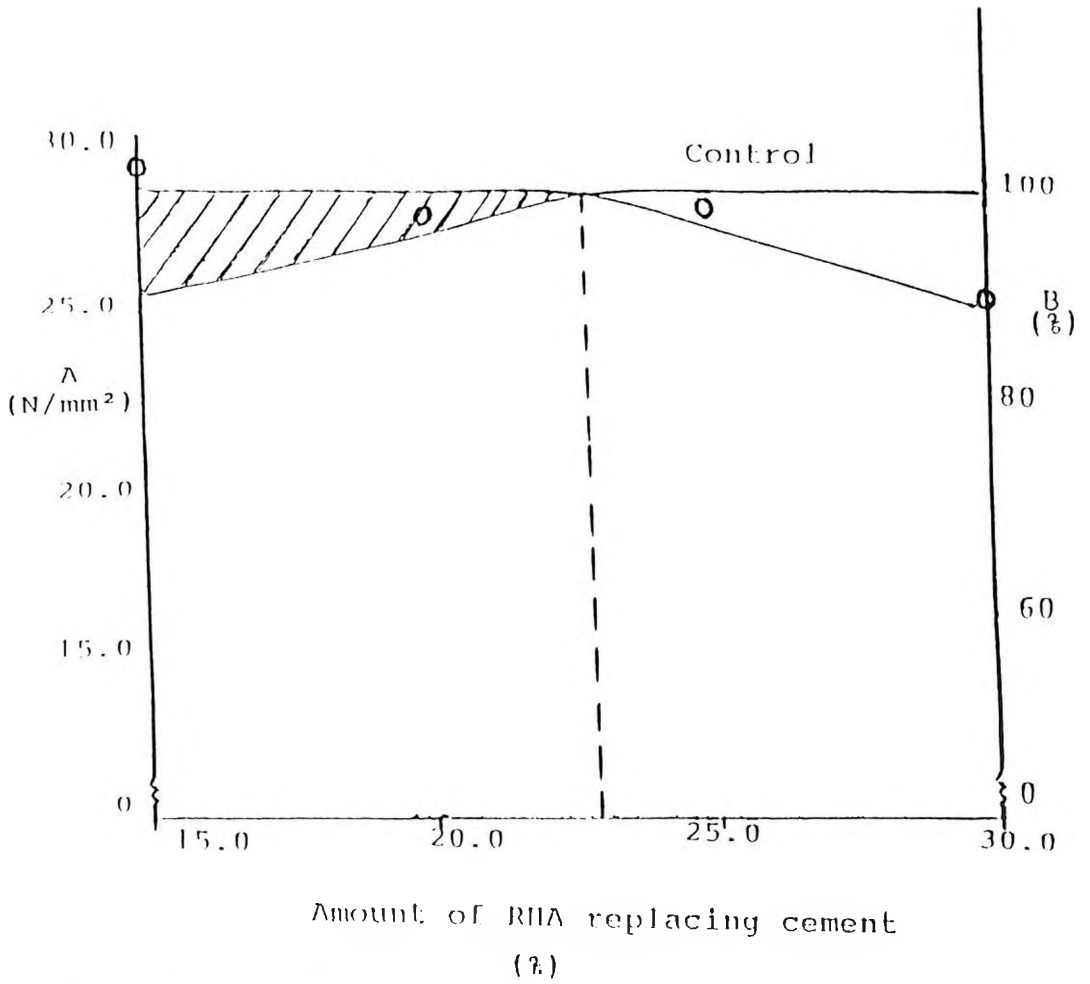A - Mortar strength
B - Mortar strength relative to control

Fig. 11. Variation of 28 day mortar strength with increasing amount of RHA in cement.

A - Mortar strength
B - Mortar strength relative to control

This composition falls within the range suggested by the t-test results and compares very well with that reported elsewhere [37]. Since the relative cost of RHA may be as low as 24% compared to OPC [8,36], such a blend would give mortar similar in quality to that of OPC but at a lower cost.

The long-term mortar strength (Table 7) of RHA cement was also compared to that of the control OPC mortar by calculating the t-test values for the 90 d strength. There was no significant difference at the 90% confidence level, between the 90 d mortar strength of all the RHA cement formulations and that of the control (OPC) mortar.

It is also significant that the formulation containing 25% RHA, which had lower 28 d strength (96.1%) relative to the control (OPC) mortar (100%), showed a higher 90 d strength (104.3%) than the control. Also, the formulation containing 30% RHA, whose 28 d mortar strength was lower (87.2%) than the control, showed a 90 d mortar strength (99.6%) comparable to that of the control (100%). These results suggest that the RHA cement blends showed a higher increase in the long term mortar strength compared to OPC. The increase in the strength of mortar between 28 d and 90 d was therefore investigated (Table 8).

TABLE 8. INCREASE IN THE COMPRESSIVE STRENGTH OF
MORTAR BETWEEN 28 AND 90 DAYS CURING IN WATER.

AMOUNT OF RHA (%)	STRENGTH (Nmm^{-2})			
	28 DAYS A	90 DAYS B	B-A (Nmm^{-2})	$\frac{B-A}{A} \times 100$ (%)
0	25.7	27.9	2.2	8.6
15	29.2	30.9	1.7	5.8
20	25.9	30.1	4.2	16.2
25	24.7	29.1	4.4	17.8
30	22.4	27.8	5.4	24.1

The mean increase in the compressive strength of RHA cement mortar between 28 and 90 days curing in water varies from 5.8% to 24.1% (mean, 16.0%). The corresponding increase for the control (OPC) mortar was 8.6%. This difference in the increase in strength shows the pozzolanic effects of

RHA. Pozzolana react primarily with the free lime produced during the hydration of cement. Pozzolanic cements therefore exhibit a slow gain in early strength compared to OPC but may develop superior long-term strength [31]. This characteristic has been cited as an advantage in the construction of mass concrete structures, and a disadvantage in rapid construction work [31].

The results obtained in this work compare very well with those reported elsewhere [23,31,37]. The findings indicate that about 20% of OPC can be replaced with RHA without losing the short-term strength of properties of mortar. In addition, upto 30% OPC could be replaced with RHA with no significant difference (P < 0.1) in the long-term strength of cement mortar. Since some cement applications like plasters and renderings do not necessarily require high binder strength [37], RHA cements with more than 30% RHA may possibly be suitable for such use.

Apart from mortar strength, other characteristics like flexion, shrinkage, water requirements, and ease of workability are also important qualities of cement. The blending of RHA cement should therefore strike an appropriate balance between the essential characteristics of the binder and the accruing cost savings.

5.3 RHA AS A FERTILISER

Table 9 shows the mean height of cow pea plants (*Vigna unguiculata*) treated with RHA (2.1% K), enriched RHA (10% K), a commercial fertiliser (10% K), and control plants grown on soil with no additive (1.3% K). Since the plots had been tilled and levelled to make the soil uniform, the only variable between different plots was the additive. For each group, a total population of 36 plants were planted. However, due to predation and other environmental limitations, the total population declined with time.

During the first 2 weeks of growth, there were significant differences (at the 90% confidence level) between the mean height of the control plants and that of the treated plants. The same trend was noted for week 7 and 8, for the plants treated with RHA enriched with KNO_3 but not for those treated with RHA alone. However, plants treated with RHA showed 84.4% increase in mean height between week 2 and week 6 while the corresponding increase for the control plants was 79.2%. Plants treated with RHA enriched in K, and those treated with a commercial fertiliser showed 100% increase in mean plant height during the same period. Since increase in plant height is indicative of the vigour of plant growth, it is apparent that the addition of RHA to soil was beneficial for the growth of the plants.

The standard deviation for the mean plant height generally increased with time. This could be due to the influence of increasing environmental stress

TABLE 9. MEAN HEIGHT (CM) OF COW PEA PLANTS (*VIGNA UNGUICULATA*) UNDER DIFFERENT FERTILISER[*] CONDITIONS.

PLOT	WEEK							
	1	2	3	4	5	6	7	8
C	3.3 ± 0.35	4.8 ± 0.20	5.6 ± 0.29	6.2 ± 0.69	8.0 ± 0.74	8.6 ± 0.74	9.1 ± 0.80	9.5 ± 0.82
R	3.3 ± 0.30	4.5 ± 0.12	5.3 ± 0.14	6.3 ± 0.15	7.6 ± 0.59	8.5 ± 0.68	9.2 ± 0.78	9.6 ± 0.82
E	3.3 ± 0.81	4.5 ± 0.31	5.3 ± 0.54	7.0 ± 0.87	8.6 ± 0.97	9.0 ± 1.01	9.6 ± 1.21	10.2 ± 1.69
F	3.8 ± 0.59	4.5 ± 0.34	5.5 ± 0.58	6.6 ± 0.90	8.2 ± 0.98	9.2 ± 1.12	9.8 ± 1.38	10.3 ± 1.77

[*]C - Control plants grown on untreated soil (1.26% K)
E - Soil treated with RHA (10% K)
R - Soil treated with RHA (2.1% K)
F - soil treated with commercial fertiliser (N:P:K-20:10:10)

factors on the plants. By week 8, the rains had subsided and a dry spell ensued. The experiment was therefore discontinued. The width of one of the first pair of leaves for each plant was measured for three and a half weeks (Table 10).

TABLE 10. **MEAN LEAF WIDTH OF COW PEA PLANTS (cm).**

PLOT*	AGE OF PLANT (DAYS)					
	9	12	15	18	21	24
C	1.9	2.1	2.3	2.4	2.5	2.6
R	2.0	2.1	2.4	2.5	2.6	2.8
E	1.7	1.9	2.2	2.4	2.7	3.0
F	2.2	2.3	2.5	2.6	2.9	3.0

*C - Control plants, no fertiliser.

R - RHA (2.1% K) added as a fertiliser.

E - RHA enriched to 10% K added.

F - Commercial fertiliser (N:P:K-20:10:10) added.

Plants treated with the commercial fertiliser, and those treated with enriched RHA had wider leaves compared to the control plants. Plants treated with RHA also had broader leaves than the control plants. This could be attributed to the fertiliser effect of the additives.

These results therefore indicate that the addition of RHA and RHA enriched with KNO_3 to cow pea plants had beneficial effects on their growth. This would also suggest that the widespread practise of burning rice husks on farmlands around the rice fields is useful in improving soil quality. Since RHA has been used in the fertiliser industry as a coating for prills [26], these results further assert its utility for such application. However, the application of RHA as a fertiliser should be supported further by other materials rich in the other essential plant nutrients like nitrogen and phosphorous.

It must however be noted that, there are other elements like N, P, Ca and Mg which contribute to plant growth, but are not readily and substantially available from RHA. Trace amounts of Cu, Fe and Mn also enhance photosynthetic activity in plants, but RHA may not be an adequate source of these nutrients. Therefore, RHA can only supplement but not replace other fertilisers. However, the burning of rice husks in the farms no doubt enhances soil aeration and percolation, with consequent beneficial effects on plant growth.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1   CONCLUSIONS

Results presented show that RHA from Mwea and Ahero is essentially similar in composition but the amount of Na and P differ significantly. This is probably due to differences in soil composition and the application of fertilisers rich in phosphorous to the soil in both regions.

The silica obtained from field burning of rice husks was found to be mainly amorphous, hence it could possibly be suitable for use as cement replacement material. Heating the RHA to temperatures around 1000°C transformed the silica to crystalline forms. This underscores the need for controlled pyroprocessing of rice husks if the RHA formed is to be used for cement replacement.

It was shown that a working curve based on the amount of silica and the LOI in RHA can be used for the rapid determination of silica. Also, the LOI, which is invariably linked to the amount of carbon in RHA, could be varied by closely controlling the air flow into the combustion kiln.

The analysis of RHA for K using XRF and AAS showed a correlation of 0.996. Since sample preparation procedure for XRF is less demanding than for AAS, the technique is preferred when analysing RHA for K in order to asses its utility as a fertiliser.

Results based on the 28 day strength of RHA cement mortar indicated that formulations with upto 23.4% RHA and 76.6% OPC could be used without losing the mortar strength properties of OPC. Formulations with higher replacements of upto 30% RHA may still be used with no significant difference (at 90% confidence level) in the 90 day strength of the mortar relative to OPC.

The results obtained also showed that the addition of RHA to soils could be beneficial to plant growth. Cow pea (*Vigna unguiculata*) plants treated with RHA (2.1% K) RHA enriched with KNO_3 (10% K) and a commercial fertiliser (N:P:K - 20:10:10) showed more rapid growth and had broader leaves than control plants grown on soil with no additives. The widespread practise of burning rice husks on farmland, then spreading the ash before planting, could therefore be a sound agricultural practise.

6.2 RECOMMENDATIONS

There is need, to analyse the composition of RHA from other rice growing areas like the Tana delta region in order to be wholly conclusive on the

composition of Kenyan RHA. There is also need to analyse soils from the rice growing regions in order to relate it to the composition of RHA.

Further research should be done on the characteristics of Kenyan RHA cement when different methods of processing the ash are used. Some of the areas that could be investigated include, the optimum ball-milling time for RHA, water requirements of RHA cement blends and methods of blending RHA with cement.

There is also need to do more extensive field trials on the utilisation of RHA cement. This will show the qualities of RHA cement under natural environmental conditions, in large scale applications.

Although detailed studies on the economic considerations for starting RHA production plants in Kenya have been done [8], they need to be appraised in view of the changing economic conditions.

Several rice millers approached were very excited on the possibility of finding a lasting solution to the accumulation of rice husks around their mills. Perhaps, they could be considered as a possible source of partial funding for further research on RHA. They could also be willing entreprenuers in the setting up of a RHA cement plant. There is need therefore, to approach them for discussions in order to create awareness and capture their interest.

Planning for further expansion in rice production should take into account the possibility of utilising the rice husks. This agro-waste material is suggested to be suitable for use in cement replacement and as a fertiliser.

The small scale application of RHA cement technology, blending with traditional technologies like wall plastering should be encouraged. At Ahero, it was found that the local people blend RHA with earth to plaster walls. When interviewed, they said that the blended plasters do not crack easily. This could be due to the filler effect of the RHA, which can fill the voids formed by moisture evaporating as the mud dries. This technology may form a suitable starting point towards consumer acceptability of RHA cement as a low cost substitute to cement.

The current practice of burning rice husks in the field is certainly beneficial for plant growth. The methods of application should however be improved, in order to avoid the hazard the ash poses to farmers during field preparation. There is also a danger of long-term changes in soil structure in the farms around the rice fields, due to continued application of the highly siliceous RHA. There is need therefore for continuous monitoring of soil conditions in these areas so as to identify any changes related the application of RHA.

Finally, there is need to involve rice farmers, millers and the local community, in the search for cost effective, environmentally friendly, and lasting methods of disposing rice husks. The strategies adopted should also

aim at improving the existing technologies to make them more appropriate and cost effective. Such an approach will ensure the co-operation of the local community, who are the consumers and ultimate beneficiaries, during the subsequent implementation process.

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