AN ALTERNATIVE ROUTE FOR MANUFACTURE OF DIAMMONIUM PHOSPHATE

BY

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DECLARATION

I declare that this thesis is my original work and has not been presented for a degree or any other award in any other university

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DEDICATION

To my only sons, Francis Sifuna Wekesa, Victor Emmanuel Asika, Michael Omolo and Dennis Jacob Ochieng, whom I believe this work, will be a source of inspiration to their lives.

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LIST OF SYMBOLS

Symbol	Description	Units
M	Mass	kg
E	Energy	J
p	Power	Watts or J/s
q	Heat transfer rate	Watts
k	Thermal conductivity of material	W/mK
T	Temperature	^oC
A	Surface area	M^2
h	Convection heat transfer coefficient	W/m^2K
L	Length	M
t	Time	seconds
C	Calorific value	J/g
c	Specific heat capacity	J/g^oC
r	Radius	mm
σ	Stefan- Boltzman constant	5.67×10^{-8} W/m^2k^4
ρ	Density	kg/m^3

LIST OF ABBREVIATIONS

Abbreviation	Description
BOC(K)	British Oxygen Company (Kenya)
DAP	Diammonium phosphate
FAO	Food and Agricultural Organization
GDP	Gross Domestic Product
GJ	Gega Joules
KPLC	Kenya Power and Lighting Company
KNBS	Kenya National Bureau of Statistics
KWh	Kilo Watt hour
MPA	Molybdophosphoric acid
Mt	Metric tons
NPK	Nitrogen Phosphorus Potassium
PA	Phosphoric acid
PHU	Percentage Heat Utilized
PMB	Phosphomolybdenum blue
TSP	Triple Super Phosphate
USA	United States of America
USDA	United States Development agency

ABSTRACT

The present study was undertaken with the aim of producing Diammonium Phosphate (DAP) using air as a source of nitrogen and bones a source of phosphoric acid. Oxygen was removed from air by passing air over heated copper granules in the temperature range of 300^{o}C – 500^{o}C. Copper granules were heated using charcoal packed in a ceramic charcoal stove. The nitrogen was reacted with lithium to form lithium nitride which was hydrolysed to produce ammonia. The phosphoric acid extracted by boiling bones with concentrated hydrochloric acid or phosphoric acid was reacted with ammonia produced from hydrolysis of lithium nitride to form diammonium phosphate. The percentage concentration of phosphorus in the fertilizer was determined using U.V spectroscopy whereas that of nitrogen was determined by titration. The cost of energy for the production of one tone of DAP using this procedure was calculated and results show that the total energy required was 4.95 GJ. This is equivalent to 1375 kW. The cost of basic materials (operational costs and production costs) of producing one tone of DAP using this procedure was found to be $1070.88 while the estimated cost of regenerating lithium from lithium chloride was 1.26 GJ, which is equivalent to 350 kW.

CHAPTER ONE

INTRODUCTION

1.1 Background information

Agriculture is the most important sector in the Kenyan economy. It accounts for approximately three quarters of the gross domestic product (GDP), employs more than two thirds of the labour force and accounts for about 70% of the export earnings (Stewart, 2006). One of the main causes of poverty is a low agricultural yield, which in turn, is directly related to inadequate fertilizer inputs. Farmers are unable to put sufficient fertilizers because of the high costs. Therefore any contribution towards lessening the cost of farm inputs is highly desirable.

Fertilizer is defined as "any material that is organic or inorganic, natural or synthetic, which supplies one or more of the chemical elements required for the plant growth" (Jahn, 2004). Fertilizers are added to soils and plants for replenishment of chemical elements that have been reduced or exhausted by crops previously grown and customizing the nutrient content of soils to particular growing objectives (Considine, 1994), hence, their importance cannot be over-emphasized. Affordability of fertilizers by Kenyan farmers continues to decrease because of high cost attributed to the cost of importation and high fuel prices (Hadaad, 1999). As an example, we can note that during the year 2005, Kenya imported 450,000 tons of nitrogen fertilizers valued at Kshs. 2.1 billion which is approximately $30 million. During the following year, the same quantity was imported at Kshs. 3.5 billion which is approximately $50 million (K.N.B.S, 2006). USDA figures indicate that the costs of fertilizers have risen enormously from $300 per ton in 2007 to $792 per ton by 15th February 2008. Although the Kenya government does not tax fertilizers, the same impact was felt by Kenyan farmers because the prices increased from approximately Kshs.1800/= per 50 kg bag in 2007 to Kshs.4400/= in March 2008. The cost of importation also increased to 89,500 tons at Kshs. 2.6 billion in 2007 and 102,900 tons at Kshs. 6.1 billion in 2008.

A more recent report indicates that by June 2008, a ton of diammonium phosphate was going at \$1050 in the U.S.A (Spencer, 2008).

Plants require six major nutrients namely calcium, sulphur, magnesium, nitrogen, potassium and phosphorus. Most of the soils contain sufficient amounts of the first three. Synthetic fertilizers, therefore, concentrate in supplying one or more of the last three elements namely nitrogen, phosphorus and potassium indicated on a bag of fertilizers as (NPK) in which N = 17% nitrogen, P = 46% P_2O_5 and K = 0% K_2O (Lapedes, 1997). They are used in modern agriculture to correct known plant nutrient deficiencies and provide high levels of nutrition. This aids plants in withstanding stress conditions, maintains optimum soil fertility and improves crop quality. They are an increasingly important factor in prosperous agriculture, indispensable in the maintenance of soil fertility and reduction of crop unit cost of production through substantial increased yield per acre (Sauchelli, 1967). A fertilizer such as diammonium phosphate is widely used during planting since it contains high levels of both nitrogen and phosphorus. Diammonium phosphate has a high nutrient concentration, good storage and handling facilities, high water solubility and relative ease of production in large plants.

Nitrogen in the atmosphere is in its elemental form, hence, it must be fixed or combined with other elements either by chemical or biological nitrogen fixation. Owing to growing world population, the demand for food has increased, thus, putting pressure on natural nitrate sources such as Chilean nitrate and Peruvian quano from bird’s wastes (Tudge, 2003), hence, need for commercial fertilizers. Fritz Haber (1908) is credited with the first successful development of manufacturing ammonia from a combination of hydrogen and nitrogen. In this process, one mole of nitrogen combines with three moles of hydrogen under extremely high conditions of temperature and pressure to give two moles of ammonia.

The cost of electricity in Kenya is approximately Kshs. 10.45/KWh (K.P.L.C, 2008) which is high as compared to the U.S.A, which is Kshs. 6.70/KWh (Annual power industrial report, Form EIA – 861, 2003). The high cost of equipment required for production of ammonia and the cost of electricity in Kenya are some of the contributing factors that have led to our country importing nitrogen fertilizers. A comparison of the cost of electricity in the U.S.A and Kenya gives a clear indication that the energy needed to run an ammonium plant in Kenya using electricity as the source of energy would be very expensive.

1.2 Problem statement

Although diammonium phosphate is obtained by reacting concentrated phosphoric acid extracted from flouroapatite with ammonia, economic deposits in the country are not there. Bones, which are fairly rich in phosphates with 17-20% P_2O_5 (Considine, 1994) are a reasonable source. Nitrogen is in abundance in air, but the total energy required to convert it to one tone of ammonia is 9.21 GJ, which is high. This process also requires very high pressures which are very expensive to produce and maintain because of need to build extremely strong pipes and containment vessels to withstand the very high pressures. This increases the capital costs when the plant is built and running costs. This has lead to ammonia being imported. Although we can combine the lithium with nitrogen easily, the initial cost of lithium is very high. The lithium nitride formed once hydrolyzed has to be regenerated to lithium by electrolysis. The cost of energy required to electrolyze lithium is 35kWh/kg (Kipouros, 1998), hence, the total energy required to regenerate 10kg of lithium is 1.26 GJ. Practically all the nitrogen and phosphorus fertilizers are imported leading to very high costs. As a consequence of this, very few farmers are able to access fertilizers leading to poor crop production. Kenya being economically agriculturally based, this threatens the future economic stability and food security in the country.

1.3 Objectives of study

This research project was aimed at preparing diammonium phosphate fertilizer, $(NH_4)_2HPO_4$, using bones as a source of phosphorus and air as a source of nitrogen.

1.3.1 Specific objectives

This study was guided by the following specific objectives
To:

(a) Investigate a suitable range of temperatures at which copper granules can be heated to completely remove oxygen from a given volume of air.

(b) Estimate the volume of nitrogen produced by using the mass of copper oxide formed and converts it to lithium nitride.

(c) Investigate effectiveness of various reducing agents in reducing copper oxide formed.

(d) Extract phosphoric acid from bones.

(e) Hydrolyze the lithium nitride formed in (c) above to generate ammonia and react with phosphoric acid extracted from bones to prepare diammonium phosphate fertilizer.

(f) Determine the percentage concentration of phosphorus and nitrogen in the fertilizer prepared and compare the results with those for commercial fertilizers.

(g) Calculate the total energy for the production of a tone of DAP using this procedure and compare it with the total energy estimate for producing one tone of commercially available DAP to determine whether this new route is a feasible alternative.

1.4 Justification of the study

Availability of fertilizers locally will not only lead to higher agricultural yields but also to higher economic development as a whole. This method is useful because although the cost of lithium is high, the process is viable in that the lithium metal and copper granules are bought once and regenerated. In addition to ammonia, chlorine, which is a commercially important product, is also produced. This should offset the cost of this operation.

1.5 Scope and limitations

(a) Availability of bones in sufficient quantities at a particular place is a serious limiting factor.

(b) Once copper has reacted with oxygen to form copper oxide and thus leave only nitrogen, the copper must be regenerated by reducing the oxide.

(c) Once the lithium has been converted to lithium nitride and hydrolyzed to lithium hydroxide, the metal must be regenerated by electrolysis.

CHAPTER TWO

LITERATURE REVIEW

2.1 Minerals and their effects on plant growth

Essential minerals required for plant growth are divided into macronutrients and micro- nutrients. The macronutrients are those needed by plants in large quantities. These are nitrogen, phosphorus, potassium, sulphur, calcium and magnesium. Micronutrients are manganese, copper, zinc, boron, cobalt, iron, molybdenum and chlorine (Tisdale, 1985).

Nitrogen plays a very important role in protein formation. It is a constituent of protoplasm of all living cells, forms part of the chlorophyll, enhances vegetable growth especially in crops where leaves are harvested and increases the size of grain and protein content in cereals (Tisdale, 1985). In circumstances where nitrogen is missing, leaves suffer from chlorosis, that is, they lose chlorophyll and become yellow. Lack of it also results to stunted growth and short roots. In some crops such as tomatoes, there is production of pigments such as anthocyanin (Rusell, 1984).

Phosphorus on the other hand, enhances formation, development and establishment of roots particularly secondary roots (Cathcart, 1980). It plays several important roles such as respiration, fat and albumen formation, cell division, carbohydrates synthesis and degradation, seed germination, root development, flowering, seed and fruit formation and crop maturation, and hasten the ripening of fruits. Insufficient phosphorus results in retardation of the development of the actively metabolizing organisms of the plants hence stunted growth, poor yields, poor root and bark development, flowering and seed germination (Tisdale, 1985).

2.2 Nitrogen sources

Nitrogen element is all over the whole earth. The approximate distribution of N throughout the soil – plant / animal – atmosphere system include: Atmosphere, sea, soil, plants, microbial in soil, animals and people. The majority of nitrogen in the atmosphere with the form of nitrogen gas occupies 78 % of the total atmosphere and 99 % of total nitrogen in the earth. However, nitrogen gas cannot be absorbed directly by plants. Other forms of nitrogen in atmosphere include nitrous oxide N_2O, nitric oxides and ammonia. In soil, total nitrogen content of top 12 inches of most cultivated soils ranges from 0.03 to 0.4 %. 95 % of total nitrogen in soil is in organic forms (e.g. proteins, amino acids, amino sugars and other complex nitrogen compounds), which are not available directly to growing plants. The inorganic form of nitrogen in soil includes ammonium (NH_4^+), nitrite (NO_2^-), and nitrate (NO_3^-).

Except some plants like legume that can fix N_2 from atmosphere for nutrient, all other plants have to uptake nitrogen from soil water by root. There are two forms of soil nitrogen that plants can uptake: ammonium (NH_4^+) and nitrate (NO_3^-). NO_3^- is soluble in water and NH_4^+ can be attached to soil clay particles and organic matter. Ammonium can be converted into nitrate by bacteria.

The N sources include commercial fertilization (64 %), electrical and biological N_2 fixation (3 %), legume and crop residues (21 %) and animal manure (12 %). N_2 fixation is any natural or industrial process that causes free nitrogen, which is a relatively inert gas plentiful in air, to combine chemically with other elements to form more reactive nitrogen compounds such as ammonia, nitrates or nitrites.

N_2 fixation includes industrial N_2 fixation, electrical N_2 fixation and biological N_2 fixation. Industrial N_2 fixation is the conversion of relative inert gas N_2 to more reactive ammonia. The

Haber – Bosch process is the most economical for the fixation of nitrogen and is one of the basic processes of the chemical industry in the world. The biological N_2 fixation is biologically mediated conversion of atmospheric N_2 to N – containing organic compounds such as ammonia. The reduction reaction from N_2 to NH_4^+ is mediated by the enzyme nitrogenase, which contains Fe and Mo. The electrical N_2 fixation is implemented by lightning. Lightning causes nitrogen and oxygen gases in the air to combine as nitrate (NO_3^-). Nitrate is soluble in the rain and fall on to soil.

The decomposition of crop residue provides another source of nitrogen to plants. Mineralization and immobilization are two N processes in which crop residues are converted into reusable nitrogen. Mineralization is the conversion of organic forms of N (e.g. proteins, nucleic acids and amino sugars) to inorganic N (NH4+). With nitrification, ammonium can be continuously converted into nitrate, which is soluble and will be absorbed by plant through water. When the organic residues are rich in carbon and low in nitrogen, bacteria use inorganic forms of nitrogen to keep a right balance between nitrogen and carbon. This process is called immobilization, which makes the N temporarily unavailable to the plant.

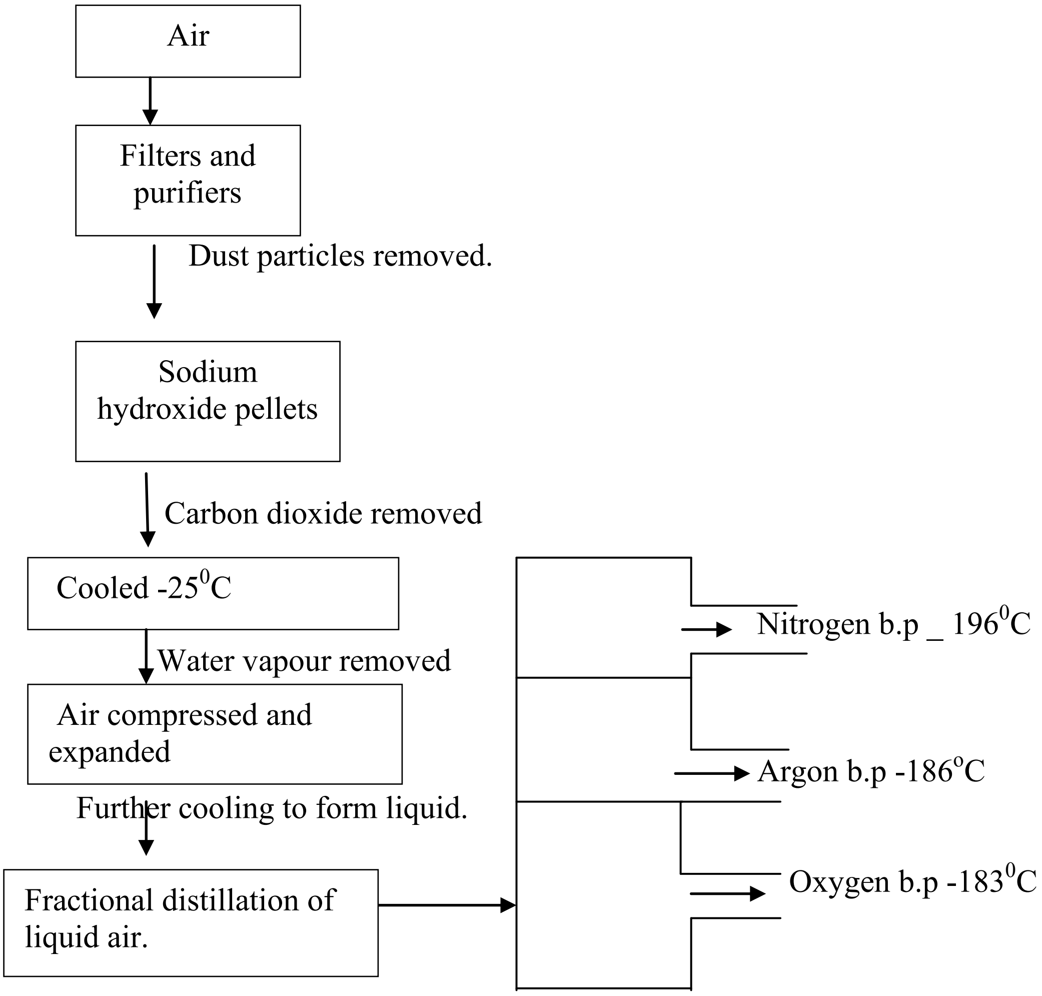
Animal manure contains a rich and wide range of nitrogen nutrient such as urea. Poultry manure has the highest N content (4 – 6 %), followed by swing manure (3.5 – 4.5 %), dairy manure (2.3 – 3.0 %) and beef manure (1.3 – 8 %). Other sources of N include wet decomposition such as rainfall and mist and dry deposition such as dust. Vehicles and power stations emit oxidized N (NO_x) to the air, and ammonia is volatized from agriculture. There are lots of N compounds suspend in the air. In these N compounds, nitrate (NO_3) can fall onto the soil in wet deposition such as rain and mist, while nitrogen dioxide (NO_2), ammonia (NH_4^+) and nitric acid (HNO_3) will fall onto soil in dry deposition.

2.3 Phosphate rich organic manure

Sekhar, D.M.R (2002) observed that farm yard manure (FYM) enriched with high grade (+ 34 %P_2O_5) rock phosphate in fine size (d80 at 23 microns) shows better agronomic efficiency than diammonium phosphate when applied on equal P_2O_5 basis. The advantage with phosphate rich organic manure is that it shows equal residual effect that is it works for two consequent crops. The dissolution of P from phosphate rich organic manure is low and due to the organic acids released by the plant roots and microorganism hosted (naturally present or advertently added) by the soil and the organic matter. Further organic matter (those matrixed rock phosphate rock phosphate particles) complexes soil cations thereby preventing fixation of P.

2.4 Processes in ammonium phosphate production

The main reagents involved in production of ammonium phosphate fertilizer are ammonia and phosphoric acid. Ammonia is manufactured in the Haber process. The nitrogen is obtained from fractional distillation of liquefied air and the hydrogen is obtained from catalytic cracking of natural gas, mainly methane. The air must be cleaned before cooling and liquefaction. The liquid air is filtered to remove solid carbon dioxide and hydrocarbons and then distilled. Liquid air enters the top of the column where nitrogen, the most volatile component (boiling point at -196^{o}C) passes off as a gas. In the middle of the column, gaseous argon is removed. Liquid oxygen, the least volatile component collects at the bottom. This process is summarized in Scheme (I);



Scheme I Fractional distillation of air (Ramsden, 1998)

In countries where electricity is cheaper, hydrogen may be obtained from electrolysis of water. Otherwise, the main source of hydrogen is catalytic cracking of natural gas, mainly methane or naphtha (a fraction of crude oil containing 5-9 carbon atoms) with steam or by partial oxidation with oxygen. The catalyst used in these processes is nickel, at temperatures of about 700-1000°C. Equations 2.1, 2.2, 2.3 and 2.4 give a summary of these processes;

$$C_6H_{4(g)} + 6H_2O_{(g)} \xrightarrow{\text{Nickel,}700\ ^oC} 6CO_{(g)} + 13H_{2(g)} \qquad 2.1$$

$$CH_{4(g)} + H_2O_{(g)} \xrightarrow{\text{Nickel, }700\ ^0C} CO_{(g)} + 3H_{2(g)} \qquad 2.2$$

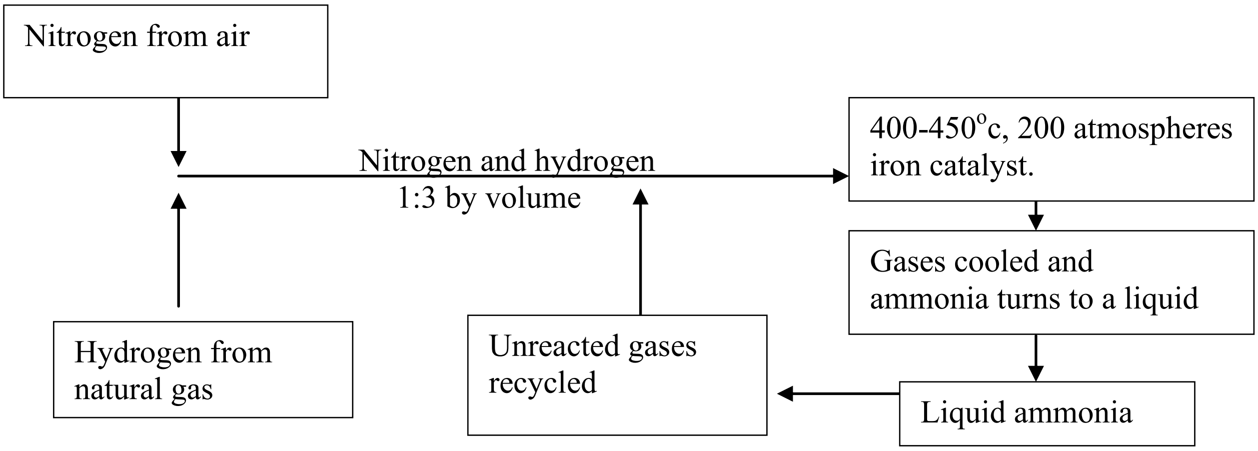
$$C_6H_{14\,(g)} + 3O_{2\,(g)} \xrightarrow{\text{Nickel, 700 }^0\text{C}} 6CO_{(g)} + 7H_{2\,(g)} \qquad 2.3$$

$$2CH_{4\,(g)} + O_{2\,(g)} \xrightarrow{\text{Nickel, 700 }^0\text{C}} 2CO_{(g)} + 4H_{2\,(g)} \qquad 2.4$$

Whereas nitrogen and hydrogen do not react under normal conditions, they react when heated under pressures in presence of an iron catalyst. This is supported on potassium hydroxide as a promoter. The reaction involved is given in equation 2.5;

$$N_2\,(g) + 3H_{2\,(g)} \overset{\text{Iron, 400-450 }^0\text{C}}{\rightleftharpoons} 2\,NH_{3\,(g)} = -\,92KJ\,/Mol \qquad 2.5$$

The Haber process can be summarized as presented in Scheme (II);



Scheme II The Haber Process (Ramsden, 1998)

2.5 Air separation in the presence of a magnetic field

A recent report by Stuzelwicz (2007), which does not appear to have been subjected to industrial testing, shows that oxygen which is paramagnetic can be separated from liquid air by a strong magnet. When membranes are filled with neodymium powder, magnetized and air is forced to pass through by applying a pressure difference on either side of the membrane, a potential gradient is created within the membrane. The membrane is made of a dense polymer. When an external field (electric, magnetic) acts on the system, permeation process takes place. Whereas oxygen is paramagnetic, nitrogen is diamagnetic. The substantial difference between the two in response to the magnetic field makes it possible to separate oxygen from nitrogen

2.6 Manufacture of diammonium phosphate fertilizer

Diammonium phosphate fertilizer is formed by reacting concentrated phosphoric acid with ammonia under controlled conditions. Concentrated phosphoric acid is produced using two main processes, namely, thermal and wet. In thermal processes, phosphorus is heated in a mixture of air and steam in a stainless steel combustion chamber.

$$P_{4(s)} + 5O_{2(g)} \longrightarrow P_4O_{10(s)} + 6H_2O_{(l)} \longrightarrow 4H_3PO_{4(aq)} \qquad 2.6$$

The wet process involves fluoroappatite, $Ca_3\,(PO_4)_2.CaF_2$, fed in a series of reactors and mixed with sulphuric acid (Marshall, 1979). The reaction equation is as shown in equation 2.7;

$$3Ca_3\,(PO4)_2.CaF_{2(s)}+9H_2SO_{4(l)}+18H_2O_{(l)} \longrightarrow 6H_3PO_{4\,(l)} + 9\ CaSO_4.2H_2O_{(s)} + HF_{(g)} \quad 2.7$$

Whereas common mineral acid can be used to digest phosphate rock, only sulphuric acid is employed on a commercial scale for wet phosphoric acid manufacture. This is not only for cost reasons, but also because the main products can be separated without difficulty by filtration under proper conditions. Under typical plant conditions, tri calcium phosphate in phosphate rock, sulphuric acid and water react to yield phosphoric acid and gypsum according to the overall reaction equation 2.8;

$$Ca_3\,(PO_4)_{2(s)} + 3H_2SO_{4\,(l)} + 6H_2O_{\,(l)} \longrightarrow 3CaSO_4.2H_2O_{(s)} + 2H_3PO_{4(aq)} \qquad 2.8$$

When a large excess of phosphoric acid is present the reaction takes place in several stages which include the decomposition of tri calcium phosphate by phosphoric acid at the rock and acid interface, to give mono calcium phosphate in solution as shown in equation 2.9;

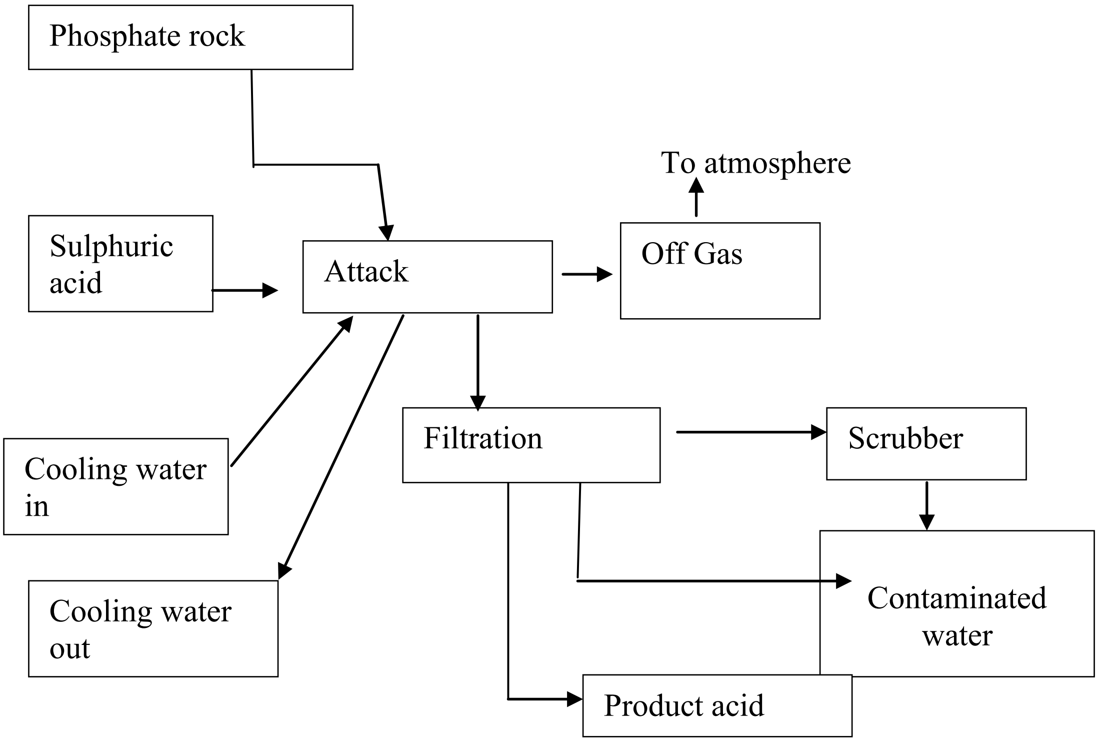
$$Ca_3\,(PO_4)_{2(s)} + 4H_3PO_{4\,(l)} \longrightarrow 3Ca\,(H_2PO_4)_{2\,(aq)} \qquad 2.9$$

Water, carbon dioxide (from any carbonate present), and some flourine are lost as gases during the reaction, but the calcium sulphate and other residual minerals remain in the dry product, which has a phosphorus pentoxide content of about 21% (Kirk Othmer, 2004). Triple super phosphate is made by reaction of phosphate rock with phosphoric acid to produce mono calcium phosphate as shown in equation 2.10;

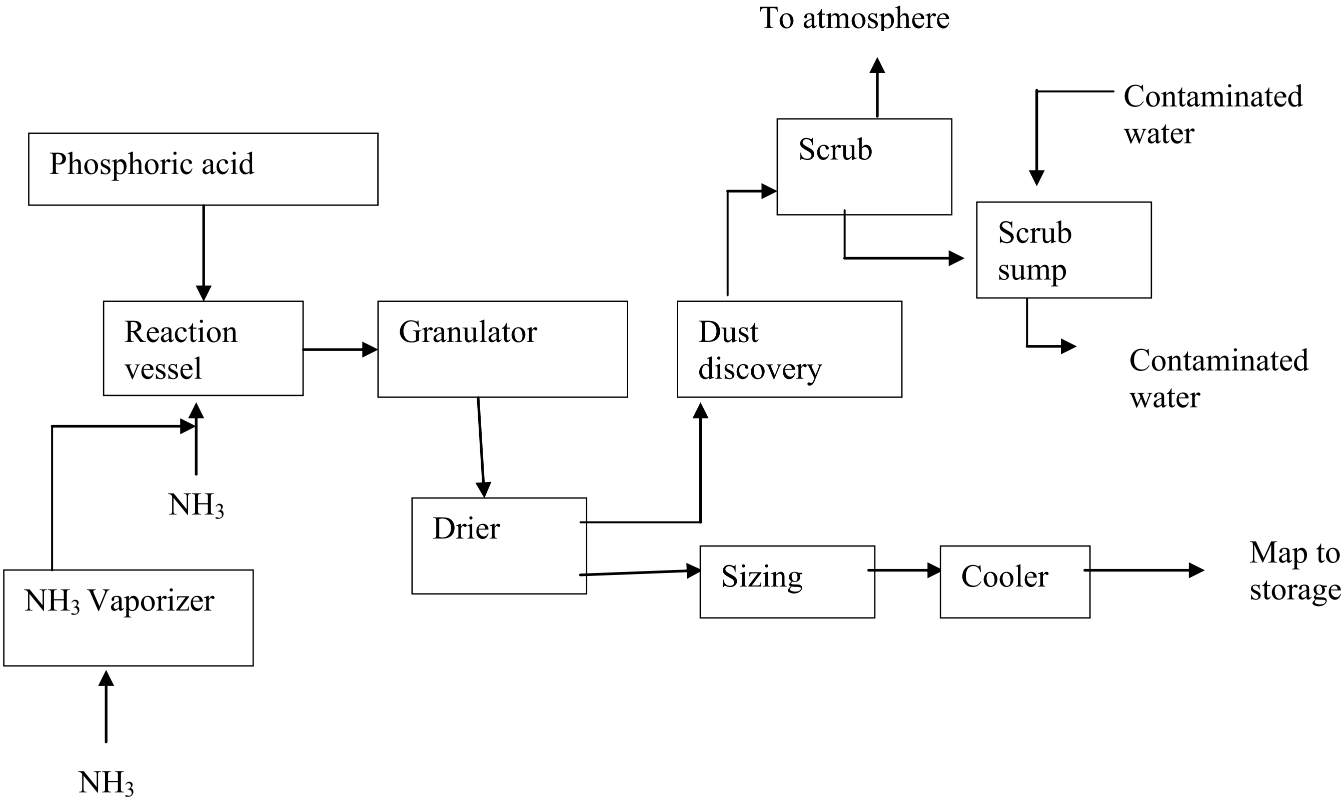
$$Ca_{10}(PO_{4)}(OH)_{2(s)} + 14\ H_3PO_{4(aq)} \xrightarrow{\qquad} 10\ Ca(H_2PO_4)_{2(s)} + 2H_2O(l) \qquad 2.10$$

This reaction is carried out for about eight hours in a digestion system. The reaction itself is essentially complete in a matter of a few minutes, but the additional time is needed to ensure the formation of gypsum crystals of a size adequate to permit rapid filtration (Nyes, 1979).

The phosphate rock contains some minor impurities such as fluorine, iron, aluminium, silica and uranium. Fluorine, which is the main problem, is evolved from the attack vessel and other plant equipment as either the gaseous compound silicon tetrafluoride (SiF_4) or hydrofluoric acid. SiF_4 hydrolyses very quickly in moist air to fluorisilic acid (H_2SiF_6) and SiO_2. Both SiF_4 and HF can be collected in a wet scrubble unit (Ando, 1987). The phosphoric acid plant also generates dust. Phosphogypsum generated in the process is often disposed off as slurry to storage/settling pond or waste heap (World Bank, 1996). This process is summarized as shown in Scheme (III);



Scheme III Industrial preparation of phosphoric acid (Saucheli, 1967)



Scheme IV Industrial manufacture of ammonium phosphate fertilizer (Saucheli, 1967)

2.7 Reactions of copper with oxygen/ air

Heated copper metal reacts with oxygen to form copper oxide. This oxide is readily reduced back to the metal by passing hydrogen gas over the heated metal oxide (Robert, 1974). The enthalpy of formation of copper oxide is -155.26KJ/mole (Hicks, 1992). Combustion reactions are always exothermic and hence the enthalpy change is always negative. This is shown clearly by the energy level diagram in figure 2.1;

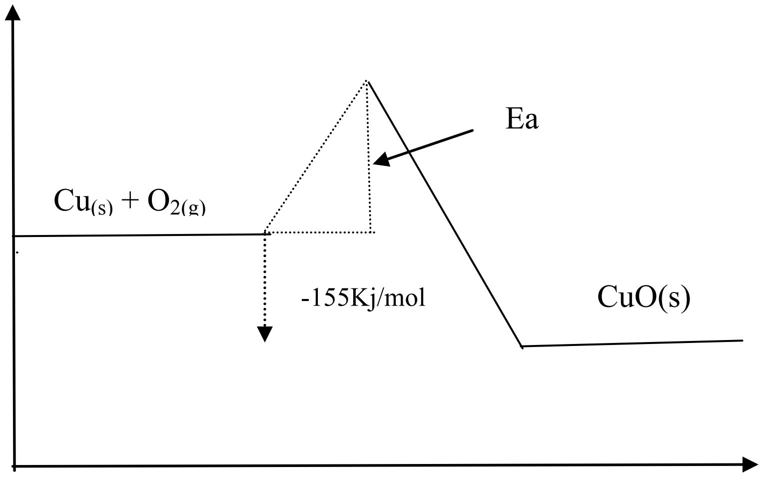


Fig.2.I Enthalpy diagram for the reaction of copper and oxygen (Hicks, 1992)

2.8 Properties and preparation of hydrogen

Hydrogen occurs chiefly in combination with oxygen in water, in organic matter such as plants, petroleum and coal. It is prepared by the action of steam on heated carbon, by thermo decomposition of certain hydrocarbons, by electrolysis of water or by displacement of acids by electropositive metals (Robert, 1974). Currently, there are two main uses of hydrogen. First, about half is used to prepare ammonia in the Haber process and the other half is used to convert heavy petroleum into lighter fractions suitable for use as fuels. This process is known as hydro cracking.

2.9 Electrolysis of lithium chloride

A typical electrolyte used in this cells is a LiCl-KCl eutectic mixture (58.2 mol % LiCl-41.8 mol % of KCl), which melts at 352°C. The density of this eutectic salt decreases slightly from 1.6741 g/cm^3 at 400°C to 1.6214 g/cm^3 at 500°C. The viscosity of this electrolyte is well known as a function of temperature and is 3.1 cp at 400°C. The surface tension is 130 dyne/cm at 450°c. The specific resistance is a function of temperature and is found to decrease slightly with increase in temperature, being 0.8 ohm.cm at 400°C and 0.55 ohm.cm at 500°C. The solubility data for Li_2S for this electrolyte is 800 ppm at 400°C. The eutectic electrolyte is generally prepared by mixing accurately weighed proportions of the reagent grade lithium chloride and potassium chloride and treating the mixture with concentrated hydrochloric acid. The lithium chloride content of the electrolyte is increased to approximately 67 mol % to improve the performance of LiAl/FeS cells. This increases the operating temperature to about 475°C. The negative electrodes are Li-Al and Li-Si systems. Positive electrodes are FeS or FeS_2 (Bach, 1985). During electrolysis, lithium metal is collected in liquid form at the cathode as shown in equation 2.11 while chlorine gas is collected as at the anode indicated in equation 2.13

$$Li_{(l)} \longrightarrow Li_{(g)} + e \qquad 2.11$$

$$Cl_{(l)} + e \longrightarrow Cl^- \qquad 2.12$$

$$Cl^- + Cl^- \longrightarrow Cl_{2\,(g)} \qquad 2.13$$

2.10 Preparation of calcium hydrogen phosphate ($CaHPO_4$) fertilizer from bones

When di-calcium phosphate is prepared from bones it is degreased by solvent extraction and then leached with a weak solution of hydrochloric acid to separate the tri-calcium phosphate component from the organic ossein. It passes into solution as mono calcium phosphate and calcium chloride as shown in equation 2.14;

$$Ca_3(PO_4)_{2(s)} + 4\,HCl_{(aq)} \longrightarrow 2\,CaCl_{2\,(l)} + Ca(H_2PO_4)_{2(l)} \qquad 2.14$$

Careful addition of calcium oxide precipitates di-calcium phosphate as shown in equation 2.15; Calcium oxide is obtained from heating calcium carbonate at approximately 900°C (Sauchelli, 1967).

$$Ca(H_2PO_4)_{2(l)} + CaO_{(s)} \longrightarrow 2CaHPO_{4(s)} + H_2O_{(l)} \qquad 2.15$$

2.11 Lithium nitride

It is prepared by passing dry nitrogen gas over heated lithium metal. The reaction is as shown in equation 2.16;

$$6\,Li_{(s)} + N_{2\,(g)} \longrightarrow 2\,Li_3N_{(s)} \qquad 2.16$$

Molecular nitrogen has a triple bond, hence, highly unreactive. Therefore, for nitrogen gas to react with lithium, the triple bond must be broken. The reaction between lithium and nitrogen is exothermic and occurs at ordinary temperatures although adjusting temperature and nitrogen flow rate may control it. It proceeds faster when the metal is heated in nitrogen (Consdine, 1994). This process can be carried out under a wide range of temperatures, for instance, from 25°C to 350°C, but desirable to operate between 180°C and 250°C. Lithium nitride ignites when exposed to air and reacts with water to form lithium hydroxide and ammonia.

$$Li_3N_{(s)} + 2H_2O_{(l)} \longrightarrow 3LiOH_{(aq)} + NH_{3\,(g)} \qquad 2.17$$

2.12 Methods of regenerating copper (II) oxide

Several fuels are used to regenerate copper (II) oxide to copper (Rooney, 2006). They include hydrogen, methane, carbon and carbon monoxide. These reduction processes all involve heating the copper before passing a reducing agent. The reaction equations 2.18, 2.19, 2.20 and 2.21 give a summary of the reduction processes;

a) $CuO_{(s)} + H_{2(g)} \longrightarrow Cu_{(s)} + H_2O_{(l)}$ 2.18

b) $4CuO_{(S)} + CH_{4(g)} \longrightarrow 4Cu_{(s)} + 2H_2O_{(l)} + CO_{2(g)}$ 2.19

c) $CuO_{(s)} + C_{(s)} \longrightarrow Cu_{(s)} + CO_{(g)}$ 2.20

d) $CuO_{(s)} + CO_{(g)} \longrightarrow Cu_{(s)} + CO_{2(g)}$ 2.21

2.13 Quantitative determination of phosphorus

Orthophosphate and molybdate ions condense in acidic solution to give molybdophosphoric acid (phosphomolybdic acid), which upon selective reduction with hydrazinium sulphate produces a blue color due to molybdenum blue of uncertain composition as shown in equation 2.22;

$$H_3PO_4 + 12\ MoO_4^{2-} + 24H^+ \longrightarrow (H_3PMo_{12}O_{40}) + 12H_2O \qquad 2.22$$

The 12-molybdophosphoric acid ($H_3PMo_{12}O_{40}$) usually abbreviated as 12MPA is then reduced to phosphomolybdenum blue, PMB, by hydrazinium sulphate.

$$\text{12-MPA + hydrazinium sulphate} \longrightarrow \text{PMB} \qquad 2.23$$

The intensity of the blue colour is proportional to the amount of phosphate initially incorporated in the heteropoly acid. The resulting blue complex exhibits maximum absorption at 820 – 830nm (Skoog, 2004).

2.14 Material and energy balance

This refers to complete accounting for all mass and energy in chemical processes. Material consumed means the quantity of material fed into the process. Material or product gotten out refers to the quantity of material turned into product plus that which was not changed into products assuming no accumulation in the process. Energy requirement (in the form of heat) of the process means the amount of heat utilized (supplied) or given out during the process assuming no heat loss due to radiation.

A material balance is an exact accounting of all the material that enters, leaves, accumulates or is depleted in an industrial process or a particular process equipment in a given time interval. It gives an estimate of all the material requirements and products formed during a process. All material balance calculations are based on the principle of conservation of mass, which states that matter can neither be created nor destroyed, but may undergo physical or chemical changes. An energy balance gives an idea of the energy requirements in a system undergoing a change. All chemical reactions are accompanied by either absorption or evolution of energy as a consequence of the forces involved in chemical bonding. The reaction is exothermic when heat is evolved and endothermic when heat is absorbed (Ghosal, 2004).

Material balance can be classified into two;

a) Material balance with chemical reactions which are dealt with under the unit processes such as oxidation, combustion, nitration, reduction and ammoniation.
b) Material balance without chemical reactions which are dealt under unit operations such as distillation, absorption, extraction, mixing, filtration and crystallization

The law of mass balance states that mass input = mass output + accumulation. In material balance involving chemical reactions, the following terms are used;

a) Excess reactant and limiting reactant
b) Theoretical yield and actual yield
c) Degree of completion
d) Percentage yield, percentage conversion and percentage selectivity
e) Tie component

Excess reactant is the reactant, which is present in excess than theoretically required to combine with another reactant (limiting reactant). Limiting reactant is the reactant which is present in its normal theoretically required quantity to combine with the other reactant (excess reactant). Theoretical yield is the amount of product that is obtained if all the limiting reactant is completely consumed during the reaction. Actual yield is the amount of product that is obtained in a reaction and is always less than the theoretical value due to not reacting completely of the limiting reactants. The reaction is said to be a 100% complete when all the limiting reactant is consumed to form the desired product. Percentage yield is the amount of product obtained divided by the expected amount if all materials react totally as per expectation. Percentage selectivity refers to the percentage conversion of the reactants to form the desired products, when the reactant is consumed partially to form another product through side reactions. Tie component refers to the component which does not undergo any chemical change during the reaction (Ghosal, 2004).

2.15 Heat transfer

This refers to the science that predicts the energy transfer which may take place between material bodies as a result of temperature difference. There are three modes of heat transfer namely; conduction, radiation and convection. When a temperature gradient exists in a body, there is an energy transfer from the high temperature region to the low temperature region. The energy is transferred by conduction and that the heat transfer rate per unit area is directly proportional to the temperature as shown in equation 2.24;

$$\frac{q}{-A} \alpha \frac{\delta T}{\delta x} hence\, q = -KA\frac{\delta T}{\delta x} \qquad 2.24,$$

where q = heat transfer rate,

$\frac{\delta T}{\delta x}$ = temperature gradient in the direction of heat flow

K (constant) = thermal conductivity of the material.

For the transfer of heat energy in a solid where the temperature is changing with time, the energy is calculated using the equation;

Energy conducted in the left face

\+ =change in internal energy + energy conducted in the right face

heat generated within the element

2.25

Thermal conductivity involves molecules in continuous random motion, colliding with one another and exchanging energy and momentum. If a molecule moves from a high temperature region to a region of lower temperature, it transports kinetic energy to the lower temperature part of the system and gives up this energy through collisions with lower energy molecules. Thermal energy in solids is conducted by two modes namely; lattice energy and transport by free electrons. When a current or macroscopic particle of fluid crosses a specific surface such as the boundary of a control volume, it carries with it a definite quantity of enthalpy. The overall effect of convection is expressed using Newton's law of cooling governed by the equation 2.26;

$$q = hA(T_w - T_\infty) \qquad 2.26,$$

where h is the convection heat transfer coefficient.

Thermal radiation refers to energy transfer through regions where a vacuum exists as a result of temperature difference. Thermodynamically, an ideal thermal radiator or black body will emit energy at the rate proportional to the fourth power of the absolute temperature of the body and directly proportional to its surface area as indicated in equation 2.27;

$$q_{\text{emmited}} = \sigma AT^4 \qquad 2.27,$$

where σ is the proportionality constant called the Stefan- Boltzmann constant with the value 5.669 X 10^{-8} W/M^2.K^4.

Equation 2.27 is called the Stefan- Boltzmann constant equation.

2.16 Energy consumption in manufacturing of diammonium phosphate fertilizer

Fertilizers are applied to plants to supply three primary nutrients; nitrogen, phosphorus and potassium. The type of manufacturing process, amount of raw materials, amount of energy consumed and the amount of primary nutrient contained in the final product vary widely among fertilizers (Mahader, 1994). Ammonia is used as a basic ingredient for most of the nitrogen fertilizers and also used directly as anhydrous or liquid ammonia. Natural gas is the major source of feedstock and fuel. Table 2.1 presents the energy use estimates for ammonia production from the two processes and their weighted average in 1987. The total energy required to produce a tone of ammonia is 42.02GJ (Mahader, 1994).

Table 2.1 Average energy consumption in the production of ammonia fertilizer in 1987

Processing type	Natural gas (GJ/Mt)	Electricity (GJ/Mt)	Steam (GJ/Mt)	Total (GJ/Mt)
A Reciprocating				
Feedstock	25.29	-	-	25.29
Reformer process	8.69	0.44	-	9.13
Other processing	5.33	3.81	0.42	9.56
Total	39.31	4.25	0.42	43.98
B Centrifugal				
Feedstock	25.14	-	-	25.14
Reformer process	13.31	-	-	13.31
Other processing	2.49	0.75	0.38	3.62
Total	40.94	0.75	0.38	42.07
C Weighted average	40.13	2.50	0.40	42.02

Phosphoric acid is a major intermediate product of phosphate fertilizers and mixed fertilizers. Phosphoric acid is processed into grades of different P_2O_5 concentration. The commercial grades are filter grade, merchant grade and TSP/DAP grade.

Table 2.2 Average energy consumption in the preparation of TSP/DAP grade phosphoric acid in 1987

	Natural gas(GJ/Mt)	Electricity (GJ/Mt)	Fuel oil (GJ/Mt)	Imported steam (GJ/Mt)	Exported steam (GJ/Mt)	Total
Rock preparation	0.92	2.5	0.37			3.78
Sulphuric acid	0.04	0.53	0.05	0.11	(6.74)	(6.01)
Filter grade PA		1.33		1.06		2.39
Concentration to TSP		0.71		4.51	(0.07)	5.16
Total	0.95	5.07	0.42	5.67	(6.80)	5.31
Dihydrate Wet-Rock Method						
Rock preparation	0.04	2.36	0.05			2.46
Sulphuric acid	0.04	0.53	0.05	0.11	(6.74)	(6.01)
Filter grade PA		1.21	0.03	0.22		1.46
Concentration to TSP		0.71		4.51	(0.07)	9.16
Total	0.08	4.82	0.13	4.83	(6.80)	3.06
Hemihydrate Wet- Rock Method						
Rock preparation	0.04	2.36	0.05			2.46
Sulphuric acid	0.04	0.53	0.05	0.11	(6.74)	(6.01)
Filter grade/TSP PA		1.21	0.03	0.22		1.46
Total	0.08	4.11	0.13	0.32	(6.74)	2.1
Weighted average for TSP grade	0.30	4.77	0.20	4.37		2.85

Table 2.3 The total energy estimate for production of diammonium phosphate (Mahadev, 1994).

	Natural gas(GJ/Mt)	Electricity (GJ/Mt)	Fuel oil (GJ/Mt)	Imported steam (GJ/Mt)	Exported steam (GJ/Mt)	Total(GJ/Mt)
Phosphoric acid	0.14	2.22	0.09	2.03	9.16	1.32
Ammonia	9.05	0.24			0.08	9.21
Processing	0.16	0.36	0.07	0.30		0.89
Total	9.35	2.83	0.17	2.32	3.24	11.43

TSP grade phosphoric acid input : 1.106 mt/mt of DAP (Muhadar and Hignett, 1987). For example, the total energy consumption of 1.32 GJ in the form of phosphoric acid for DAP is obtained by multiplying 1.106 mt of phosphoric acid times 0.42.

2.17 Water boiling test (WBT) for performance evaluation of the ceramic charcoal stove (Rani, C.S 1992)

Standard water boiling test is used to test the performance of the ceramic charcoal stove using charcoal as a fuel and aluminium pot. The WBT is chosen because of its simplicity and reliability indicator of stove performance (Smith and Edwards, 1993). The WBT measures the thermal efficiency of the stove, the specific fuel consumption (SFc) and both minimum and maximum firepower. The thermal efficiency combines both the efficiency of combustion as well as heat transfer to the cooking pot. The specific fuel consumption (SF_C) measures the fuel used to boil one liter of water under standard ambient temperature. The stove firepower measures the rate of fuel energy consumed over the full test duration but not the output power to the spot. The WBT simulates the cooking process and has been used to test various types of stoves throughout the world. (Smith and Edwards, 1993). Several parameters which are measured include the initial mass of charcoal, mass of the aluminium pot, initial mass of aluminium pot and water, capacity of the alumnium pot, initial temperature of water, room temperature, initial mass of water used and mass of tin.

2.18 Stove performance indicators.

Thermal efficiency (hc): This is a ratio of the work done by heating and evaporating water to the energy consumed by burning the fuel. It is calculated using the equation 2.28;

$$[4.186 \times W_i \times (T_f - T_i) + 2260 (W_i - W_f)] \div [M_c \times C_c] \qquad 2.28$$

Where,

W_i - the mass of water, T_i – initial temperature of water, T_f – final temperature of water, W_i – initial mass of water, W_f – final mass of water, M_c – mass of fuel consumed and C_c – calorific value of fuel used.

In this calculation, the work done by heating water is determined by adding two quantities: (1) the product of the mass of water in the pot, (W_i), the specific heat of water (4.186 J/g^oC) and the change in temperature and (2) the product of the amount of the water evaporated from the pot (M_c) and the latent heat of evaporation of water (2260 J/g). The denominator is determined by taking the product of the mass of fuel consumed (M_f) during this phase of the test and the calorific value of the fuel sample (C_v)

Burning Rate: This is a measure of the rate of fuel consumed (Mf) while bringing water to a boil. It is calculated by dividing the equivalent fuel consumed by the time of the test in minutes.

$$Rc = Mf \div t \qquad 2.29.$$

Fire Power (FP_c): This is the ratio of the fuel energy consumed by the stove per unit time. It shows the average power output of the stove in Watts during the test phase.

$$FP_c = [M_c \times C_c] \div [60I] \qquad 2.30$$

Evaporation Rate (W_c): This is a measure of the rate of water loss through evaporation during the test.

$$W_c = M_2 \div t \qquad 2.31$$

2.19 Determination of energy used in preparation of diammonium phosphate

The calculations for heat transfers during the reactions in the preparations for the sample diammonium phosphate are based on the equation

Energy conducted in the left face + heat generated within the element = change in internal energy + energy conducted in the right face (Holman, 1997) 2.32

Where,

Energy in the left side is expressed as

$$q_x = -KA\frac{\delta T}{\delta x}, \qquad 2.33$$

Energy generated within the element is expressed as

$$\dot{q}\,A\delta x \qquad 2.34$$

Change in internal energy is expressed as

$$\rho CA\frac{\delta T}{\delta \tau}dx \qquad 2.35$$

Energy out the right face is

$$q_{x+dx} = \left[-KA\frac{\delta T}{\delta x}\right]_{x+dx} \qquad 2.36$$

$$= -A\left[K\frac{\delta T}{\delta x} + \frac{\delta}{\delta x}\left(K\frac{\delta T}{\delta x}\right)dx\right] \qquad 2.37$$

A combination of this relation is given by the equation

$$\frac{\delta}{\delta x}\left(K\frac{\delta T}{\delta x}\right) + \dot{q} = \rho C\frac{\delta T}{\delta \tau} \qquad 2.38$$

Where,

q = heat transfer rate

δt/δx = temperature graduate in the direction of heat flow

k = thermal conductivity of the material

c = specific heat capacity of the material

ρ = density

A = area

CHAPTER THREE

MATERIALS AND METHODS

3.1 Introduction

This chapter describes and justifies the research methodology, procedures, materials, chemicals and instruments used in preparation of diammonium phosphate (DAP) fertilizer. It also describes the method of determining the percentage compositions of nitrogen and phosphorus in the fertilizer prepared. All the weights of solid samples were carried out on an electronic analytical balance (model, AAA, Adam Equipment Co. Ltd, Britain) while measurements of liquid samples were done using graduated cylinders. Airflow was measured using an air flow meter while temperature was measured using a pocket-sized thermocouple, Probe M (Portugal).

3.2 Collection of materials

a) Bones were collected from ‘meat roasting’ areas as municipal solid wastes in Mumias district, Kenya. They were washed with tap water, rinsed using de-ionized water and dried in an oven (WTC binder, 150533, Germany) at 110^oC (Smith, 1993). This was to make sure that all the water was removed.

b) Air and hydrogen were obtained commercially from B.O.C, Kenya (Industrial area, Nairobi).

c) Lithium and Copper were bought from Kobian Kenya Limited, Nairobi (Kenya).

d) Bunsen burner flame was used to determine the temperatures at which copper was to be heated to remove oxygen from air.

e) Charcoal was bought from local vendors at Githurai market, 25 km from Nairobi city center, Kenya, along Thika Road.

f) All glassware were washed thoroughly with soap, rinsed with distilled water and dried in the oven at temperatures of 110^oC.

3.3 Preparation of reagents

The reagents used in this experiment were analar and prepared using standard methods as highlighted in Vogel's text book of quantitative inorganic analysis (Vogel, 1980). They were prepared as follows;

a) Sodium molybdate (analar) was prepared by dissolving 12.5 g in 5 M H_2SO_4 and made up to 500 ml with 5 M H_2SO_4.

b) Hydrazinium sulphate was prepared by dissolving 1.5 g of the salt in 1000 ml of distilled water.

c) Potassium dihydrogen phosphate was prepared by dissolving 0.2198 g of the salt in 1000 ml of distilled water.

d) 5 M H_2SO_4 was prepared by dissolving 280 ml of 46 M sulphuric acid (specific gravity = 1.84 g/cm^3) in 1000 ml of distilled water.

e) 40% NaOH was prepared by dissolving 40 g of sodium hydroxide pellets in cold distilled water, cooled and made up to 100 ml.

f) 4% H_3BO_3 was prepared by dissolving 4 g of H_3BO_3 in 100 ml of distilled water.

g) 50% H_2O_2 was prepared by dissolving 60 ml of 100 v H_2O_2 in 100 ml of distilled water.

h) Oxygen absorbent was prepared mixing 1000 ml of concentrated ammonium hydroxide with 1000 ml of ammonium chloride solution. Ammonium chloride solution was prepared by dissolving 300 g of ammonium chloride in 1000 ml of distilled water. A 250 ml bottle, half filled with copper turnings was filled nearly full with NH_4Cl-NH_4OH solution (Considine, 1974).

i) 6 M H_3PO_4 was prepared by dissolving 300 ml of 32.23 M phosphoric acid in 1000 ml of distilled water.

j) Nessler's reagent was prepared by adding potassium iodide solution to a solution of mercury chloride in excess till the red precipitate dissolved. Then 100 ml sodium hydroxide solution was added and diluted to 1000 ml using distilled water (Srivastava, 1981).

k) 1 M KI solution was prepared by dissolving 5.135 g of potassium iodide in 31.25 ml of distilled water.

l) 1 M $HgCl_2$ was prepared by dissolving 4.25 g of mercury iodide in 31.25 ml of distilled water.

m) 50% NaOH was prepared by dissolving 50 g of sodium hydroxide in 100 ml of distilled water

n) Water was distilled using the Elgastal Micrimeg deionizer Catridge Model WSB/4, Britain.

3.4 Heating of copper granules at various temperatures

An empty combustion tube (43.5 cm long and 3.6 cm in diameter) was weighed and its mass recorded. It was packed with 856.28 g of copper granules and its mass taken. Asbestos was placed at each end to prevent the granules from being blown off when air is passed. The mass was taken once more. The gas inlet and outlet tubes were fitted on the glass column and placed on a retort stand as shown in Figure 3.1

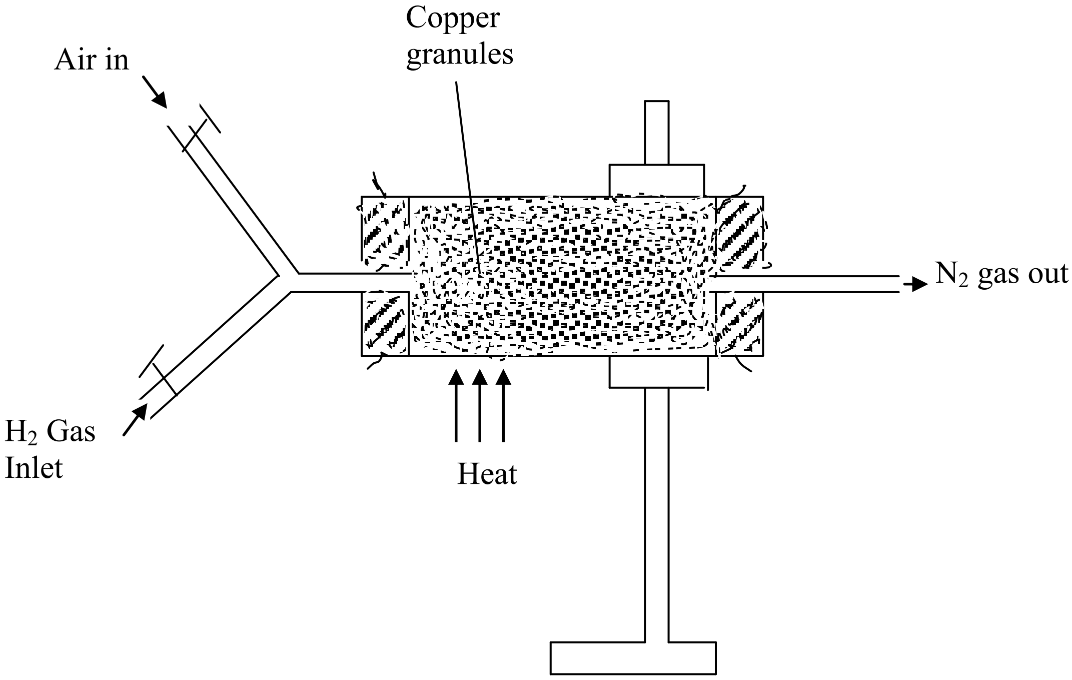


Fig. 3.1 Glass column packed with copper granules

The combustion tube was wound with a copper wire to ensure that the copper granules were uniformly heated as shown in Figure 3.2.

Fig. 3. 2 Glass column wound with copper wire

Copper granules were then heated to temperatures of 250°C, 300°C, 350°C, 400°C, 450°C and 500°C respectively for one hour. Compressed air was first passed through sodium hydroxide pellets to remove carbon dioxide and then through a bottle of 46 M sulphuric acid to remove moisture. It was also passed through a column (45.3 cm long) of phosphorus pentoxide to remove moisture (Muriithi, 1972).

It was then passed over heated copper granules at the rate of 200 ml/ sec as measured using an air flow meter (Appendix 9). This volume was arrived at after several experiments to determine the efficient rate at which air could be passed. A lower volume rate took a longer time for the reaction to be completed while a higher volume rate led to air passing without being oxidized. The volume of air coming out was equally maintained using an adjustable knob on the regulator. The temperatures were measured using a thermocouple (pocket sized thermocouple, Probe M) shown in Appendix 8, while the time taken for copper to be oxidized was measured using a stop clock. After the copper granules had been oxidized, the glass column was removed from the source of heat, left to cool and its mass recorded. The mass of copper oxide formed was used to tabulate the mass of oxygen that reacted and hence the mass of nitrogen separated from the air passed. The results are as shown in Table 4.1.

3.5 Investigating the effectiveness of various reducing agents in reducing the copper oxide formed

Reducing agents that included carbon monoxide, methane gas, kerosene and hydrogen were used (Rooney, 2006). An empty combustion tube was weighed and its mass recorded. 3.0 g of copper (II) oxide were placed along the base of the tube and spread out on the middle of the tube. This was to ensure that heating was not too close the rubber tubing and that there is no tendency for the granules to be blown out of the combustion tube when the reducing agent is turned on. It was reweighed and the mass of the tube plus copper (II) oxide noted. The combustion tube was clamped and rubber tubing connected as shown in Figure 3.3. Methane gas was turned on and adjusted to get a gentle flow.

Copper (II) oxide was heated using a Bunsen burner flame as the gas was continuously passed. It was observed that after a few seconds, the copper (II) oxide glowed and started turning reddish brown. Heating continued for 20 minutes to ensure that all the oxide had reacted. The Bunsen burner was removed to allow the combustion tube to cool with methane gas still passing over the copper while excess gas burning. This was to prevent air from coming into contact with the hot copper and converting back to the oxide. When the tube was cool, the gas was turned off and the tube plus copper weighed. Figure 3.3 shows the apparatus for reducing the copper oxide using methane gas while in Figure 3.4, the procedure was as described earlier but the apparatus were arranged such that nitrogen gas bubbled through kerosene in a conical flask before it reaches the reduction tube. A faint glow was observed as the oxide was reduced.

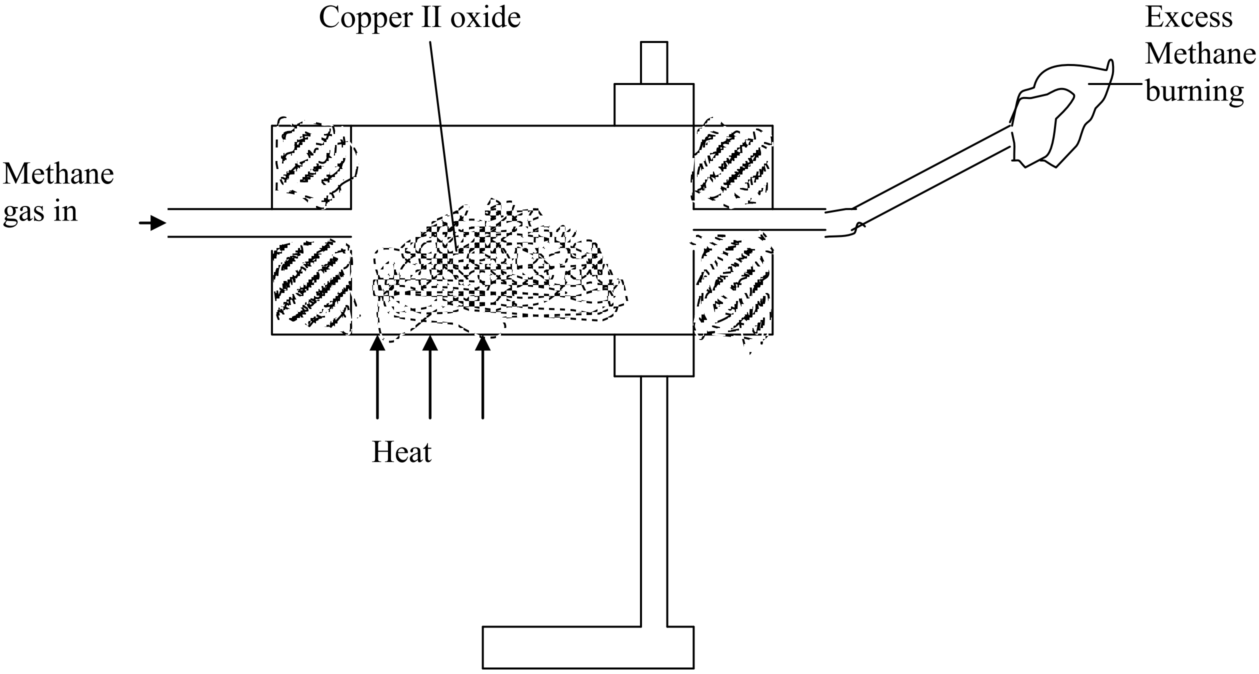


Fig. 3.3 Reduction of copper oxide using methane gas

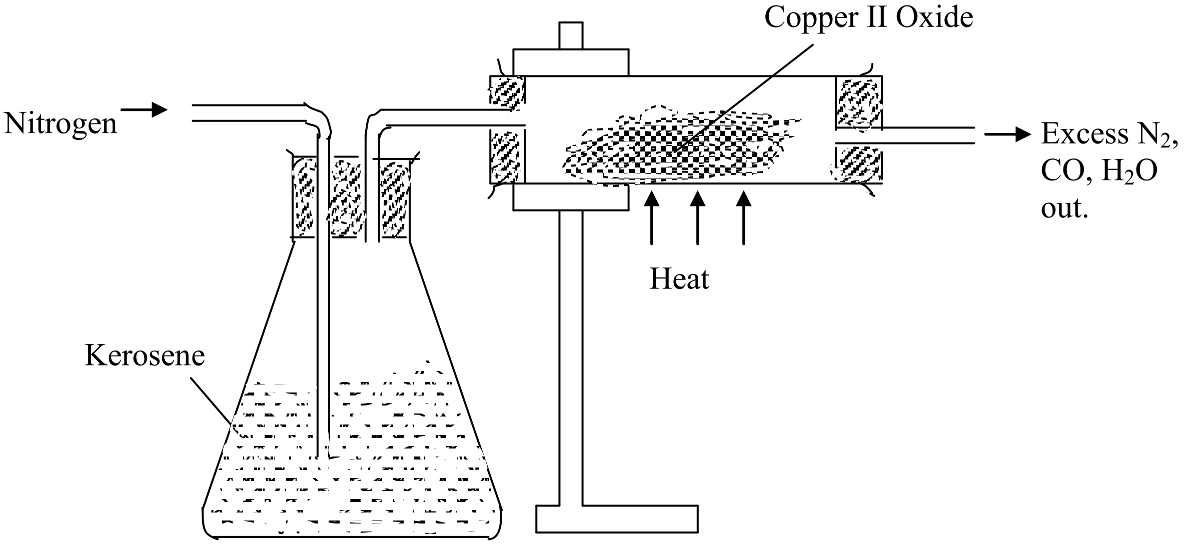


Fig. 3.4 Bubbling nitrogen through kerosene

Charcoal was crushed into powder and packed in a combustion tube, weighed and the apparatus arranged as shown in Figure 3.5. Both the charcoal and copper oxide were heated simultaneously before air was passed. A red glow was observed as the copper oxide was being reduced and the black granules changed to reddish brown.

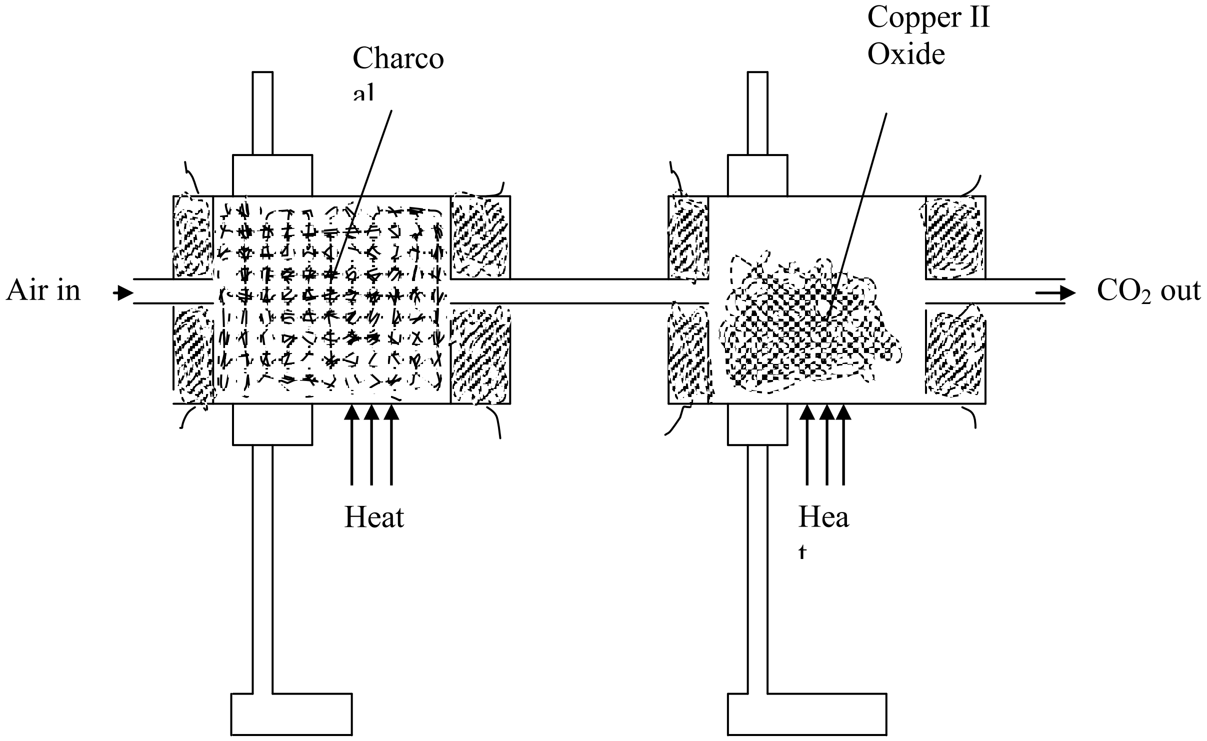


Fig. 3.5 Reduction of copper oxide using carbon monoxide

Figure 3.6 shows the apparatus used for reduction of copper oxide using hydrogen gas (Robert, 1974).

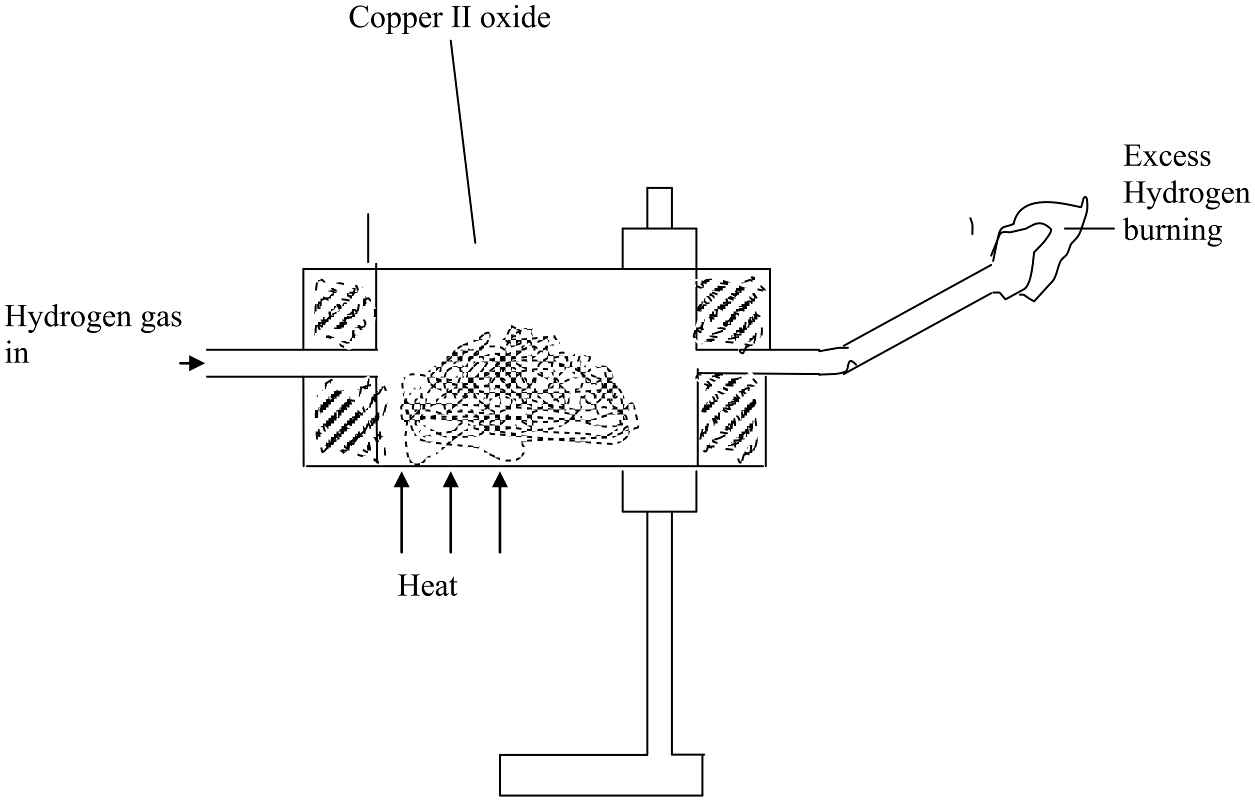


Fig. 3.6 Reduction of copper oxide using hydrogen

The results are recorded in Table 4.2.

3.6 Design of a ceramic stove

Besides the use of a Bunsen burner to heat copper granules, a ceramic charcoal stove made of clay was designed. The design shown in Figure 3.7 was arrived at after a personal interview with people who roast maize in Kahawa Wendani estate, Nairobi. The interview was based on the effectiveness of the stove used to roast maize in terms of amount of charcoal used and the time it takes for the charcoal to be consumed. The height of the combustion chamber was based on the amount of charcoal to be used in each experiment (1 kg) because 1 kg of charcoal would produce the same amount of energy required (14252.06 W) as was for the case of energy produced by the Bunsen burner. It was also made to have a greater heat transfer due to the closer proximity of the glass column to the radiant heat. The size of the gap was derived from the equation

$$[2.5 \times \text{diameter of the combustion chamber}] \div \text{Diameter of pot} = \text{gap} \qquad 3.1$$

Fig. 3.7 A ceramic charcoal stove made of clay

The diameter of the ceramic stove was dependent on the length of the combustion tube. The ceramic charcoal stove was modeled at Kenyatta University Fine Art workshop, placed under the shade for one week to dry and fired in the oven at 900°C for 24 hours. The performance of this ceramic charcoal stove was tested using the procedure highlighted in section 2.17. In this experiment, charcoal was weighed, placed in the stove and lit using 10 ml of kerosene. The fire was left simmering for 10 minutes for charcoal to light well. The stove was covered with a lid and apparatus set as shown in Figure 3.8. 900 ml of water was placed in the aluminium pot and placed on the ceramic stove as shown in Figure 3.8. The thermometer was inserted to measure the change in temperature during the experiment.

Fig. 3.8 Apparatus set for water boiling test

The change in temperature of water in °C was recorded at intervals of 10 minutes for two hours and results recorded in Table 4.3. The values were plotted in Figure 4.1. At the end of the experiment, the mass of the aluminium pot and the remaining water was recorded. The charcoal that remained was placed in a tin, closed tightly and left to cool. It was later weighed and the mass of charcoal that remained was tabulated by getting the difference between the mass of the charcoal that remained plus tin and the initial mass of tin plus lid. The mass of charcoal that was used was also calculated by getting the difference between the initial mass of charcoal weighed at the beginning of the experiment and what remained at the end of the experiment. The results are recorded in Table 4.4.

3.7 Separation of nitrogen from air

Compressed air was released from the gas cylinder at a very slow rate. The volume was measured using an air flow meter and controlled by an adjustable knob on the regulator. Air was passed through a cleaning system as highlighted in section 3.4. One Kg of charcoal was weighed, placed in the ceramic charcoal stove and lit using 10 ml of kerosene. It was left simmering for ten minutes. The ceramic charcoal stove was then covered using a lid and the glass column packed with 856.28 g of copper granules set up as shown in Figure 3.9. It was covered with asbestos to minimize heat loss (asbestos, k = 0.078, Mills, F.A 1995).

Fig. 3.9 Glass column covered with asbestos

The intensity of heat produced by the burning charcoal depended on the amount of air entering the stove through the air hole on the side of the ceramic stove. The air hole was left open to allow air to enter the stove. The temperatures just below the column and the side of the stove were measured using a Pocket size thermocouple, Probe M and results recorded in Table 4.4. Clean dry air was passed over heated copper granules at a rate of 292.68 ml/ sec. The time taken for the copper to be oxidized was measured using a stop clock and recorded. The charcoal that remained after the experiment was placed in a tin, covered with a lid and left to cool. The tin was covered tightly with a lid to prevent any further oxidation such that the little carbon dioxide formed inside extinguished the charcoal. The mass of the remaining charcoal was taken and the difference with the initial mass of charcoal used gave the amount of fuel used in the experiment. This procedure was repeated six times and results recorded in Table 4.4. The mass of oxygen that reacted with copper granules was tabulated by subtracting the initial mass of copper granules plus column from the mass of copper oxide formed plus column. The mass of oxygen obtained was converted to equivalent moles. Given that one mole of every gas occupies a volume of 22400 ml at s.t.p, the moles of oxygen were converted to volume by multiplying with 22400. The volume of nitrogen plus inert gases was obtained by subtracting the volume of oxygen that reacted with copper granules from the total volume of air passed. It was then converted to the number of moles and mass. The percentage volume of oxygen that was separated from air was calculated using the equation;

% oxygen = [volume of oxygen that reacted with copper granules × 100] ÷ total volume of oxygen passed 3.6.

3.8 Reaction of lithium with dry nitrogen gas

Lithium reacts with oxygen when exposed to air; hence it was cut while under paraffin. Its mass was first determined by measuring the mass of the beaker then the sum of mass of beaker and paraffin and finally the sum of mass of beaker, paraffin and lithium. The mass of lithium used was calculated by getting the difference between the mass of beaker and paraffin and the total mass of beaker, paraffin and lithium.

The nitrogen separated from air as highlighted in Section 3.7 was passed through a solution of ammonium chloride- ammonium hydroxide solution placed in a bottle half filled with copper granules. It was then passed through concentrated sulphuric acid for drying before passing over heated lithium metal at 250^{o}C using a block digester (KI 16, Britain) as shown in Figure 3.10.

6. 01 g of lithium metal was cut into very small pieces while under paraffin on a watch glass, transferred to a reaction flask and its mass taken. It was placed in a block digester and heated until it melted as nitrogen gas was passed over. The reaction of heated lithium with nitrogen was exothermic and fast. A continuous red glow was observed during this reaction. On completion, the reaction flask was removed from the hot plate and left to cool as nitrogen was continuously passed. The mass of the reaction flask with lithium nitride was recorded. The mass of lithium nitride formed was calculated by getting the difference of the mass of the reaction flask and lithium from the sum mass of the reaction flask and lithium nitride. The experiment was repeated three times using the same procedure and the mass of lithium nitride formed in each experiment was 9.47g ±0.2 (s.d).

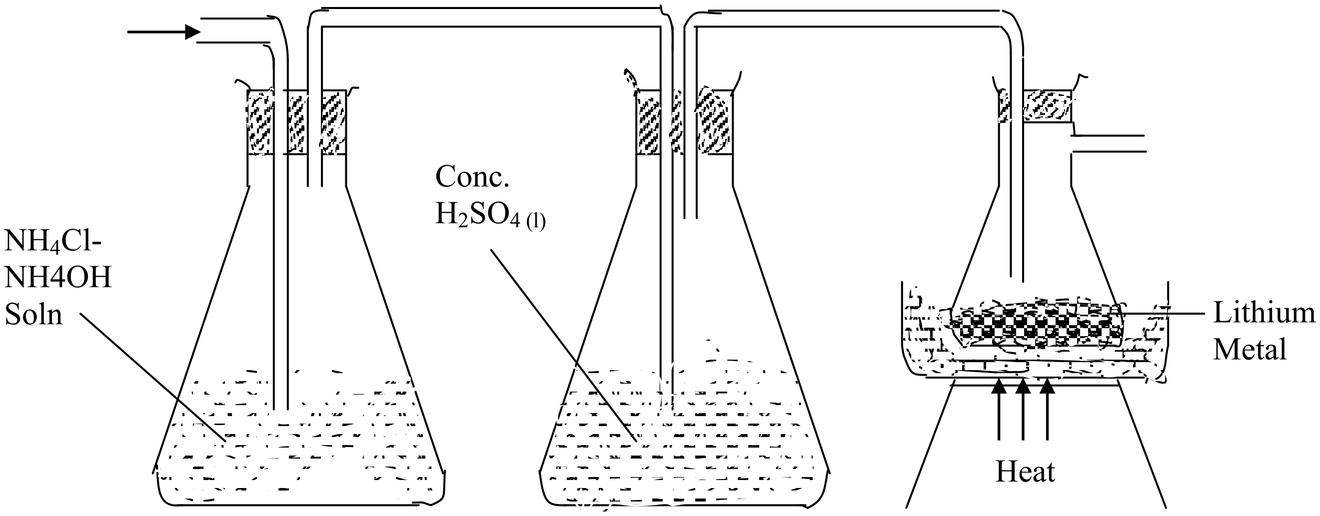


Fig. 3.10 Reaction of dry nitrogen with heated lithium metal

3.9 Extraction of phosphoric acid from bones

In order to prepare diammonium phosphate, it was necessary to determine the concentration of phosphorus in the bones. This was done by weighing 9.0 g of ground bones and digested using 50 ml of 12 M hydrochloric acid. The expected reaction equation is

$$Ca_3(PO_4)_2.Ca(OH)_2(s)+HCl(l) \longrightarrow CaCl_2(aq)+Ca(HPO_4)_2(s)+H_2O(l) \quad 3.7$$

200 ml of 5M H_2SO_4 was added to precipitate the calcium ions. The calcium sulphate formed was separated by filtration. 1 ml of the filtrate was diluted to 1000 ml using distilled water and tests for percentage composition of phosphorus was determined as highlighted in Section 3.13. The results were as recorded in Appendix 11.

A calibration curve of concentration against absorbance was constructed using the values in Appendix 11 as shown in Appendix 12. From the equation obtained in the calibration curve, the concentration of the sample was calculated by substituting the values of absorbance in the equation. The percentage concentration of phosphorus was calculated using equation 3.8 and results recorded in Table 4.6.

$$\% P = \{concentration \div mass\ taken\} \times dilution\ factor \times 100 \quad 3.8$$

The absorbance of the sample was 0.992 and using the equation obtained from the calibration curve (Appendix 11), the results show that bones contained 16.44% P_2O_5, hence, not enough to prepare a superphosphate that can compare with what is offered commercially to farmers. On this ground, 50.0 g of bones were digested using different concentrations of phosphoric acid. 2 M, 4 M, 6 M, 8 M and 10 M phosphoric acid were used. This was to determine the effect of change of concentration on the rate of reaction with bones. The results obtained and shown in Appendix 5 gave the basis on which 6 M phosphoric acid was used to digest the bones. 50.0 g of ground bones were digested using 300 ml of 6 M phosphoric acid. The mixture was heated in a Bunsen burner flame to increase the rate of digestion. The time taken for the bones to be completely digested was 36 minutes. The reaction equation involved is

$$3Ca_3\,(PO_4).Ca\,(OH)_{2}(s) + 14H_3PO_4\,(aq) \longrightarrow 10Ca\,(H_2PO_4)_2(s) + 2H_2O\,(l) \qquad 3.9$$

100 ml of distilled water was added to each beaker to make the extract more soluble. 200 ml of 5M sulphuric acid was added to each sample extract to separate the calcium ions from phosphoric acid. The calcium ions were precipitated as calcium sulphate and separated by filtration. The reaction equation involved is

$$Ca\,(H_2PO_4)_2(s) + H_2O + H_2SO_4\,(aq) \longrightarrow CaSO_4(s) + 2H_3PO_4\,(aq) + H_2O\,(l) \qquad 3.10$$

3.10 Hydrolysis of lithium nitride to generate ammonia

28.4 g of lithium nitride prepared in section 3.8 was hydrolyzed with 50 ml of distilled water. The ammonia gas produced was reacted with 30 ml of 9.8 M H_3PO_4 extracted from bones as highlighted in section 3.10 as shown in Figure 3.11.

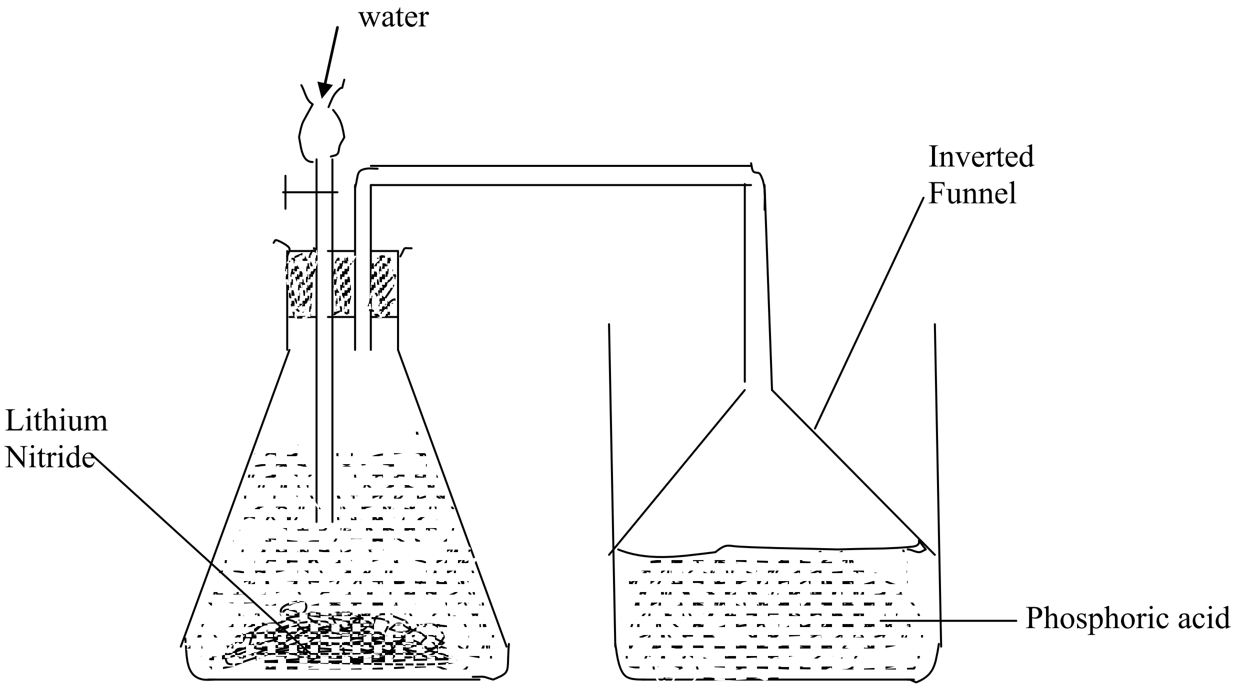


Fig. 3.11 Hydrolysis of lithium nitride

The beaker containing 30 ml of 9.8 M phosphoric acid was immersed in ice because the reaction was exothermic. The highest temperature recorded during the reaction was 95^{o}C but the crystals formed at 51^{o}C. The crystals formed were filtered through Whatman No 1 filter paper, air dried for seven days and weighed. The crystals formed were analyzed for concentration of phosphorus as highlighted in section 3.11. The standards were prepared and their absorbance and concentration recorded in Appendix 12. A curve of concentration against absorbance for the standards was calibrated as shown in Appendix 13 and the equation used to calculate the concentration of phosphorus in the sample. 20 more samples were prepared using the same procedure and results recorded in Appendix 3.

3.11 Quantitative determination of phosphorus

The spectrophotometric method was used to determine the concentration of phosphorus. The method depends on reduction of molybdophosphate with hydrazinium sulphate to form a blue complex which is stable at room temperature. In this process, a standard phosphate solution was prepared by measuring 0.2198 g of potassium di-hydrogen phosphate as highlighted by Vogel (1978), Skoog (2004), Thomas (1980), Kirk (1991) and Furman (1962) and dissolved in 1000 ml of distilled water. The volumes of 1 ml, 2 ml, 3 ml, 4 ml, 5 ml, 6 ml, 7 ml, and 8 ml were transferred from the standard phosphate solution prepared to 100ml volumetric flasks and diluted to the mark with distilled water. 25 ml of each was transferred to the 50 ml volumetric flask, 5 ml of the molybdate solution was added followed by 2.0 ml of hydrazinium sulphate and diluted to the mark with distilled water. The samples were prepared by weighing 0.5 g of diammonium phosphate crystals prepared and dissolving to 1000 ml of distilled water to form the stock solution. To obtain the working solutions for each of the samples, 100 ml of each of the stock solution was transferred to 1000 ml beakers and diluted to the mark. 25 ml of each working solution was transferred to the 50 ml volumetric flasks, reagents added and made to the mark with distilled water. The flasks were immersed in boiling water bath for thirty minutes, removed and immersed in ice for twenty minutes to cool rapidly. The volumes were adjusted to the mark and absorbance measured using a U.V spectrophotometer (CECIL CE 2041, England) at a wavelength of 830 nm against a blank.

3.12 Determination of the percentage composition of nitrogen

This was done by titration as highlighted by Skoog (2004), Vogel (1978), Furman (1962), Kirk (1991), Thomas (1980) and Archbald (1965). 1.0 g of a sample was weighed and transferred to a digestion flask. 25 ml of boric acid solution (4%) was transferred to a titration receiver flask and placed on the distillation unit. The sample in the digestion flask was attached to the distillation unit. 50 cm^3 of NaOH (40%) solution was added to initiate steam distillation. Distillation took 20 minutes after which the receiver flask was removed; 5 drops of screened methyl red indicator solution were added and titrated with 0.05 M sulphuric acid to a grey end point. A blank determination was carried out using the same procedure but in the absence of the sample. The percentage composition of nitrogen was calculated using equation 3.11 and results recorded in Appendix 4.

$$\% N = [(T-B) \times 14.007 \times N \times 100] \div \text{mass of sample (g)} \qquad 3.11$$

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Heating copper granules at various temperatures using a Bunsen burner flame

Table 4.1 Results for heating copper granules at various temperatures

Temperature (°C)	250	300	350	400	450	500
Time taken to heat copper granules (min)	60	60	60	60	60	60
Volume of dry air passed (ml)	200	200	200	200	200	200
Time taken for the reaction to stop (min)	31.00	38.07	39.12	40.00	40.00	40.00
Total volume of air passed (ml)	372000	456840	469440	480000	480000	480000
Mass of copper oxide formed + column (g)	1282.80	1316.76	1320.49	1323.67	1323.66	1323.77
Mass of oxygen removed(g)	103.00	136.96	140.69	143.87	143.86	143.97
Mass of nitrogen removed (g)	362.56	444.17	456.20	467.58	467.53	467.90
% volume of oxygen removed	92.29	99.93	99.89	99.91	99.90	99.98
Mass of natural gas used (g)	30.00	36.90	37.90	38.76	38.76	38.76

It is observed from this table that when 856.28 g of copper granules are heated using a Bunsen burner flame at temperatures as low as 250°C and as high as 500°C and equal volumes of air passed over, oxygen is effectively separated. The percentage volume of oxygen separated at temperatures of 300°C, 350°C, 400°C, 450°C and 500°C is 99.9 %. These results are in agreement with what was obtained by Muriithi, (1972).

4.2 Reduction of copper (II) oxide using different reducing agents

Table 4.2 Results for reduction of copper (II) oxide using different reducing agents

Fuel	Average mass of copper(II) oxide used(g)	Mass of copper obtained (g)	% efficiency
Methane	3.00	2.60	91.67
Kerosene	3.00	2.48	96.70
Carbon monoxide	3.00	2.61	92.50
Hydrogen	3.00	2.43	99.90

From the table, it is observed that copper oxide was reduced by hydrogen, kerosene, carbon monoxide and methane. This agrees with the observations made by Rooney (2006). The process of reduction was slower when natural gas was used as compared to when nitrogen gas was bubbled through kerosene. This is because kerosene contains paraffin, olefins and aromatics (Block, 1991). The aromatics have high energy contents per volume even though they tend to have low heating values per unit mass (calorific value of kerosene = 43.61 MJ/kg). The higher density more than compensates for the lower energy content on a weight basis (Van Gerpen, 2004).The observations also showed that heated copper oxide was readily reduced when hydrogen was used. This can be attributed to the fact that hydrogen has a high calorific value of 121 MJ/kg (Considine, 1994).

4.3 Performance evaluation of the ceramic charcoal stove

Table 4.3 Temperature profiles during simmering phase

Temperature of water (^{o}C)	23	38.5	47.6	53	57.3	60	62	63.6	65.2	66.2	66.7	67	67
Time (min)	0	10	20	30	40	50	60	70	80	90	100	110	120
Wall temperature (^{o}C)	23	50	94	149	176	198	205	220	252	269	283	287	292
Temperature inside the stove	23	104	210	256	289	321	367	388	400	407	408	406	403
Room temperature	23	23	23.50	25.00	25.50	26.00	27.00	27.50	33.00	33.50	34.00	34.00	34.00

Figure 4.1 Water temperature profiles using the VITA test experiment. It is noted from Table 4.5 and the Fig. 4.1 that there is a sharp increase in temperature for the first 50 minutes and then a gradual increase for another 60 minutes. There is minimal change from 110^{o}C regardless of how much steam is produced. The local boiling temperature is influenced by several factors including altitude, minor inaccuracies in the thermometer and weather conditions. For these reasons, the local boiling temperature cannot be assumed to be 100^{o}C.

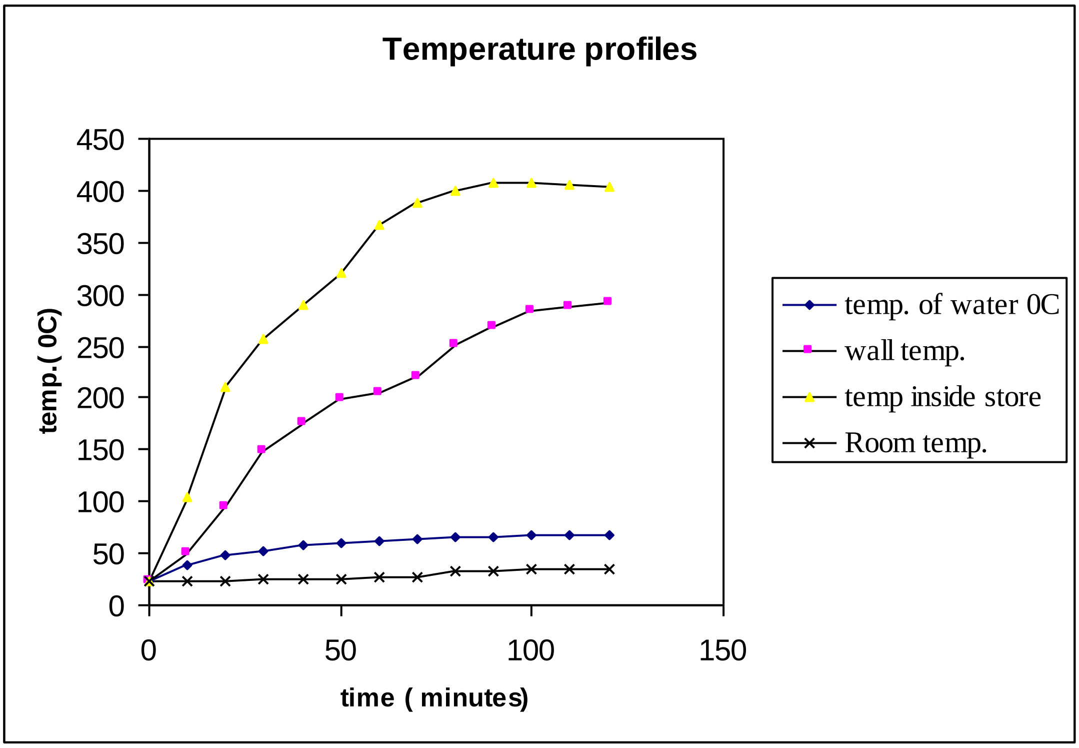


Fig. 4.1: Temperature profiles during simmering phase

Table 4.4 Test results for a ceramic charcoal stove using VITA test procedure

Measured parameter	N	Mean ± std error
Fuel consumed (g)	6	292.11 ± 51.79
Water vaporized (g)	6	130.35 ± 33.82
Time taken to ignite (min)	6	10.00 ± 00
Final temperature of water (^oC)	6	67.00 ± 3.03
Burning rate (g of fuel/min)	6	2.43 ± 0.43
SFC (g/ g H_2O)	6	0.41 ± 0.12
Fire Power (kW)	6	1.46 ± 0.15
Evaporation rate (g H_2O/min)	6	1.09 ± 0.28
Efficiency %	6	50.69 ± 9.44
Time taken to boil water (min)	6	120 .00 ± 00

The results obtained from the water boiling test using VITA test procedure (Rani, C.S 1992) show that the efficiency of the ceramic charcoal stove is relatively consistent and in good agreement with reported efficiencies (Smith, 1994 and Pruszko, 2004). This can be attributed to the provision of the thick wall (14.74 mm) that reduces the heat loss from the walls of the combustion chamber. The amount of heat lost through the ceramic charcoal stove could be minimized further by having a double wall with air space between the walls.

4.4 Separation of nitrogen from air

Table 4.5 Summarized results for separation of nitrogen from air

Measured parameters	N	Mean± Std. Error
Mass of charcoal used (g)	6	589.38 ± 3.93
Volume of air passed per second (ml)	6	292.68 ± 9.91
Time taken for reaction to stop (sec)	6	2406.62 ± 94.54
Total volume of air passed (ml)	6	704337.68 ± 165.98
Mass of nitrogen collected (g)	6	694.11 ± 3.33
Mass of copper + column (g)	6	1390.99 ± 0.04
Mass of oxygen deposited (g)	6	211.18 ± 1.04

When a volume of 704337.56 ml ± 165.98 (sd) of air was passed over 856.28 g of heated copper granules for 2406.62 sec, 211.18 g ± 1.04 (sd) of oxygen were removed. The mass of nitrogen collected was 694.11 ± 3.33 (sd). It is evident from this table that this process facilitated 99.9% separation of oxygen from air as calculated in section 3.7.

4.5 Reaction of lithium with nitrogen

Table 4.6 Results for the reaction of lithium with nitrogen

Parameter measured	N	Average ± std deviation
Mass of lithium used (g)	3	6.02 ± 0.01
Temp of block digester (^oC)	3	250 ± 0.00
Time taken for reaction to stop (sec	3	740 ± 34.64
Mass of lithium nitride formed (g)	3	9.47 ± 0.00
Temp inside the reaction flask (^oC)	3	240.67 ± 1.16

4.6 Quantitative determination of phosphorus in bones

Table 4.7 % concentration of phosphorus in bones

Sample code	absorbance	Concentration(PPM)	%concentration P_2O_5
bones	0.992	0.218	16.44

4.7 Quantitative determination of phosphorus and nitrogen in the samples prepared and commercial diammonium phosphate.

Table 4.8 Results for quantitative determination of phosphorus and nitrogen in the three samples.

Code	$\%P_2O_5$	%N
(1) Commercially obtained DAP	36.45 ±0.06	18.19 ±4.04
(2) DAP prepared using 6 M H_3PO_4	28.11 ±0.06	17.05 ±2.02
(3) DAP prepared from reacting bones with 6 M H_3PO_4	44.58 ±0.06	17.14 ±2.02

From this table, it is observed that the concentration of phosphorus in sample 3 is 44.58%, while that of sample 2 is 28.11%. Since concentration of phosphorus in bones was found to be 16.44% as shown in section 4.6, this indicates that all the phosphorus was extracted from the bones during the digestion. In comparison with sample 1, which was commercially obtained, the results indicate that the samples prepared in the laboratory contained a higher concentration of phosphorus by 18.24 %. This was calculated as shown;

$$44.58 - 36.45 = 8.13$$

$$[\{8.13/44.58\} \times 100] = 18.24\%$$

This value is in agreement with the values given in literature that the triple superphosphates prepared by digesting rock phosphate with phosphoric acid yields 38.93 – 54.96%P (Tisdale, 1993). The percentage concentration of nitrogen in the sample 3 was 17.14% as compared to what was commercially obtained that had 18.19%.

4.8 Heat energy used in separation of nitrogen from air

Table 4.9 Heat energy used in separation of nitrogen from air

Parameter measured	N	Average ± std deviation
Mass of charcoal used (g)	6	590.22 ± 3.90
Total amount of heat produced by charcoal (J/s)	6	8044.77 ± 53.94
Wall temp (^oC)	6	383.67 ± 11.83
Temp just below the glass column (^oC)	6	395.50 ± 10.63
Temp inside the glass column (^oC)	6	323.83 ± 11.03
Energy transferred to the copper granules (J/s)	6	2709.97 ± 179.20
Energy lost to the surrounding (J/s)	6	5334.84 ± 178.40
Room temperature (^oC)	6	33.67 ± 1.26

590.22 ± 3.90 g of charcoal was burnt to produce 8044.77 J/s ± 53.94 that separated 694.11g of nitrogen from 704337.56 ml of air. This demonstrated that the use of charcoal as a source of heat has a great potential to replace the use of electricity in separation of nitrogen from air.

4.9.1 Heat energy during digestion of bones

Given that the room temperature was 22^{o}C, the maximum temperature attained during digestion of bones was 108^{o}C, the mass of methane gas used was 147.24 g, and therefore, the energy produced was calculated using the equation;

$$q = [\{ \text{heating value} \times \text{mass}\} \div \text{time taken for digestion} \qquad 4.1$$

$$= [\{ 882402 \times 147.24\} \div 138.58]$$

$$= 937.55 \text{ J/s}$$

4.9.2 Heat energy used in separation of nitrogen from air

The ceramic stove used in the experiment was spherical in shape hence the equation applied was

$$q = \{4\pi k(T_1 - T_0)/[1/r_1 - 1/r_0]\} \qquad 4.2$$

For example in experiment 1 (Appendix 15);

The amount of heat lost to the environment though the ceramic stove

$$= [4 \times 3.14 \times 1.4\ (378 - 333)] \div 0.161$$

$$= 4914.78 \text{ J/s}$$

The heat transferred to the copper granules through the glass was calculated using the equation

$$q = k(2\pi L)[T_1 - T_0]/\mathrm{In}\{r_0/r_1\} \qquad 4.3$$

For example in experiment 1 (Appendix 15);

Amount of heat transferred to copper granules

$$= [-\ 1.09 \times 2 \times 3.14 \times 0.435\ (305 - 378)] \div 0.08066$$

$$= 2694.88 \text{ J/s}$$

The total amount of energy produced by charcoal used in each experiment was calculated using the formula

$$\{[\text{heat of combustion} \times \text{mass}] \div \text{time taken}\} \qquad 4.4$$

For example in experiment 1 (Appendix 15); the mass of charcoal used was 583.79 g and the time taken for the reaction to stop was 2387.69 seconds, hence,

The total amount of energy produced

$$= [583.79 \times 32802.56] \div 2387.69$$

$$= 8020.21 \text{ J/s}$$

4.9.3 Energy transfer during the reaction of lithium with nitrogen

The total amount of heat energy produced by the block digester was 250 W; the total heat energy transferred from the digester through the reaction flask to lithium was calculated using the

Fourier's equation

$$q = \{4\pi k\ [T_I - T_0]\}/\{1/r_1 - 1/r_0\} \qquad 4.5$$

Energy transferred to the lithium from the heated digester was

$$q = \{4\pi k\ [T_I - T_0]\}/\{1/r_1 - 1/r_0\}$$

$$= [4 \times 3.14 \times -1.09\ (240 - 250)] \div 1.12$$

$$= 122.24 \text{ J/s}$$

Total amount heat produced

= heating value × time taken

= 250 W × 720 s

= 0.18 MJ

4.10 Material balance

4.10.1 Separation of nitrogen from air

The reaction equation involved in this experiment is

$$2\ Cu_{(s)} + \text{air/ heat} \longrightarrow 2CuO_{(s)} + N_{2\ (g)} \ldots\ldots\ldots\ldots\ 4.6$$

The mass of copper granules used was 856.28g and 211.18 g ± 1.04 (s.d) of oxygen combined with the heated copper granules in each experiment as shown in Table 4.4. Volume of air passed was 704337.68ml ± 165.98 (s.d) as measured using an air flow meter and a yield of 694.11 g ± 3.33(s.d) of nitrogen was collected. This accounts for 99.9% separation.

Total volume of air passed = volume of oxygen removed + volume of nitrogen collected. An assumption is made that the 1218.41ml of air at s.t.p forms the volume that accumulated in the process and that which did not react.

4.10.2 Reaction of lithium with nitrogen

The reaction equation involved in this process is

$$6Li(s) + N_2(g) \longrightarrow 2Li_3N(s) \text{ .... } 4.7$$

Lithium nitride has a molecular weight of 34.83g while lithium has a molecular weight of 6.941g. 6.02g ± 0.02 of lithium reacted with nitrogen to form 9.47g ± 0.00 of lithium nitride. In this reaction lithium was the limiting reactant whereas nitrogen was the excess reactant. The number of moles of lithium that reacted was 0.864. From the reacting mole ratios, the number of moles of nitrogen that reacted with 6.02g of lithium was 0.144moles, which are equivalent to 4.034g of nitrogen gas. Therefore the theoretical mass of lithium nitride expected to have been formed was 10.054g. Therefore, the percentage yield was 94.19%.

4.10.3 Hydrolysis of lithium nitride

Lithium nitride is hydrolyzed with water as follows;

$$Li_3N(s) + 3H_2O(l) \longrightarrow 3LiOH(aq) + NH_3(g) \text{ .... } 4.8$$

The total mass of lithium nitride hydrolyzed was 28.4g, which was equivalent to 0.81moles. From the reaction equation, 0.81 moles of lithium nitride when hydrolyzed yielded 0.81 moles of ammonia gas, hence, the mass of ammonia liberated was 13.86g.

4.10.4 Digestion of bones with phosphoric acid

When bones were digested using 12M HCl as shown in section 3.9, concentration of phosphorus analyzed was 16.44%, but when 6M phosphoric acid was used to digest bones, the concentration of phosphorus was 28.11%. The phosphorus concentration in the sample prepared was 44.58%. Therefore the percentage recovery of phosphorus was 99.84% because the total percentage phosphorus in the 6M phosphoric acid used and what was in the bones was 44.63%.

4.10.5 Reaction of ammonia with phosphoric acid

The expected reaction equation is

$$2NH_3\,(g) + H_3PO_4\,(aq) \longrightarrow (NH_4)_2HPO_4(s) \ldots\ldots\ldots\ldots\ldots\ 4.9$$

13.86 g of ammonia gas liberated during hydrolysis of lithium nitride reacted with 30ml of 9.8 M phosphoric acid to yield 13.65g of diammonium phosphate. From the reaction mole ratios, 34g of ammonia gas react with 98g of phosphoric acid to yield 132g of diammonium phosphate. Therefore, 13.86g of ammonia gas that was formed from hydrolysis of 28.4g of lithium nitride were supposed to yield 41.46g of diammonium phosphate. Therefore the percentage yield of diammonium phosphate prepared in the laboratory was 33%.

4.11 Average energy consumption in the production of one tone of diammonium phosphate

Table 4.10 Average energy consumption in the production of one tone of diammonium phosphate

Process type	Natural gas (GJ)	Electricity (GJ)	Biomass (GJ)	Total energy (GJ)
Separation of nitrogen from air	-	-	0.004	0.004
Recycling of lithium	-	1.260	-	1.260
Formation of lithium nitride	-	0.299	-	0.299
Bones preparation	-	0.013	-	0.013
Phosphoric acid extraction	3.375	-	-	3.375
Total	3.375	1.572	0.004	4.951

The total energy estimate for production of one tone of diammonium phosphate using this procedure is 4.951 GJ.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

It was observed that when 856.28 kg of copper granules are heated to a temperature of 383.66^{o}C and 704337.68 ml ± 165.98 (s.d) of air passed over at a rate of 292.68 ml/sec ± 9.91 (s.d), 694.11 g ± 3.33 (sd) of nitrogen is separated from air. Further observations showed that when the nitrogen obtained reacted with 18.05 g of heated lithium metal to form 28.41 g of lithium nitride; a percentage conversion of 94.19 % was obtained.

Results for different methods of reducing copper (II) oxide back to copper indicated that hydrogen was the best reducing agent. This was concluded after comparing the mass of copper obtained and the percentage efficiency of the reducing agents.

It was also observed that when 6 M phosphoric acid was used to digest the bones, the percentage recovery of phosphorus was 99.84 %. When the extract was reacted with ammonia gas, the diammonium phosphate crystals were formed with the percentage phosphorus concentration of 44.58 % (P_2O_5). In comparison to what is offered commercially, it can actually be concluded that the fertilizer prepared is better.

It was also observed that the total energy estimate for the production of one tone of diammonium phosphate using this procedure was 4.95 GJ. This value was quite low in comparison with the total energy estimate for one tone of commercially available diammonium phosphate which is 11.43 GJ as cited in literature section 2.16. The cost of basic materials required in terms of capital costs, operational costs and production costs needed to prepare one tone of DAP using this procedure is $ 2201.86.

5.2 RECOMMENDATIONS

This study showed that digesting bones with a lower concentration of phosphoric acid and reacting with ammonia gas can prepare diammonium phosphate fertilizer that has approximately similar concentration of nitrogen and phosphorus like what is commercially offered to farmers. The results of this study indicate that substantial energy efficiency is achieved in the production of one tone of diammonium phosphate. In view of these, a pilot study on the economic cost of achieving such efficiency is highly recommended.

With necessary equipment, it would also be of interest to practically determine the energy consumption in regeneration of lithium from lithium hydroxide formed either by electrolysis of lithium hydroxide or lithium carbonate.

It was also found that hydrogen is the best reducing agent; therefore, investigations should be carried out to determine a cheaper and suitable method of producing hydrogen.

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Appendix 1

Heating of copper granules using a ceramic charcoal stove

Mass of charcoal used (g)	Volume of dry air passed/sec	Time taken for the reaction to stop (sec)	Total volume of air passed(ml)	Mass of copper oxide formed +collumn	Mass of oxygen removed
583.79	295.08	2387.69	704571.43	1391.11	211.31
584.90	291.27	2415.99	703712.67	1390.90	211.10
590.01	291.83	2413.40	704299.60	1391.08	211.28
590.44	291.76	2413.71	704083.60	1390.94	211.13
596.03	293.75	2398.19	704477.35	1390.95	211.15
591.12	292.39	2410.74	704881.43	1390.93	211.13

Appendix 2

Performance evaluation of the ceramic charcoal stove

Initial parameters measured during the water boiling test

Number	Initial mass of charcoal (g)	Mass of aluminium pot (g)	Initial mass of aluminium pot + water (g)	Room temperature (^oC)	Initial mass of water (g)	Initial mass of tin + lid (g)
1	1002.80	143.19	1093.60	24.00	950.41	427.00
2	1016.30	143.19	1079.30	23.00	936.11	426.60
3	1005.80	143.19	1074.10	24.00	930.91	304.50
4	1007.20	143.19	1092.80	24.00	941.61	428.00
5	1003.10	143.19	1098.20	23.00	955.01	428.30
6	1011.40	143.19	1072.60	24.00	929.41	426.40

Final parameters recorded during the water boiling test

Number	Final mass of charcoal + tin (g)	Final mass of charcoal (g)	Final mass of aluminium pot + water (g)	Mass of charcoal used (g)	Mass of water that remained (g)
1	1180.10	653.10	995.80	349.70	852.61
2	1152.90	726.30	904.53	290.00	761.34
3	1110.70	806.20	979.50	199.60	836.31
4	1117.80	689.80	952.20	318.00	809.01
5	1113.70	685.40	959.80	317.70	816.61
6	1160.13	733.73	918.66	277.67	775.47

Appendix 3

Data for average absorbance and percentage concentration of phosphorus in the 22 samples. Sample 21 was prepared by reacting ammonia gas with 6M phosphoric acid while sample 22 was bought from the market.

Sample code	Mass taken	Absorbance 1	Absorbance 2	Average absorbance	concentration	% composition of phosphorus
1	0.4969	0.1024	0.1024	0.1024	0.1929	19.41
2	0.4955	0.1037	0.1037	0.1037	0.1966	19.84
3	0.4969	0.1039	0.1035	0.1037	0.1966	19.78
4	0.5037	0.1007	0.1007	0.1007	0.1879	18.65
5	0.5064	0.1022	0.1022	0.1022	0.1922	18.98
6	0.5029	0.1006	0.1008	0.1007	0.1879	18.68
7	0.4994	0.1007	0.1007	0.1007	0.1879	18.81
8	0.4952	0.1062	0.1062	0.1062	0.2037	20.57
9	0.4996	0.1060	0.1064	0.102	0.2037	20.39
10	0.5037	0.1034	0.1040	0.1037	0.1966	19.52
11	0.5011	0.1032	0.1032	0.1032	0.1951	19.47
12	0.5106	0.1037	0.1027	0.1032	0.1951	19.10
13	0.5052	0.1052	0.1052	0.1052	0.2009	19.88
14	0.5004	0.1033	0.1041	0.1037	0.1966	19.64
15	0.5037	0.1057	0.1047	0.1052	0.2009	19.94
16	0.5006	0.0997	0.0997	0.0997	0.1851	18.49
17	0.5100	0.1027	0.1017	0.1022	0.1922	18.84
18	0.5185	0.1057	0.1057	0.1057	0.2023	19.51
19	0.4948	0.1061	0.1053	0.1057	0.2023	20.44
20	0.4994	0.1033	0.1031	0.1032	0.1951	19.53
21	0.5021	0.077	0.077	0.077	0.1198	11.93
22	0.4938	0.090	0.090	0.090	0.1572	15.91

Appendix 4

Results for determination of percentage composition of nitrogen in the fertilizers prepared.

Sample code	Mass of sample taken(g)	Titration 1	Titration 2	Titration 3	Average titre(ml)	Average titre for the blank	%N
1	1.0015	17.80	17.85	17.85	17.83	17.58	17.21
2	1.0011	17.80	17.80	17.75	17.78	17.53	17.17
3	0.9999	17.65	17.70	17.65	17.67	17.43	17.09
4	0.9998	17.70	17.70	17.65	17.68	17.44	17.11
5	1.0019	17.75	17.80	17.80	17.78	17.53	17.16
6	1.0003	17.75	17.75	17.70	17.73	17.49	17.01
7	0.9997	17.60	17.65	17.65	17.63	17.39	17.05
8	1.0007	17.95	17.95	17.95	17.95	17.71	17.10
9	1.001	17.90	17.90	17.95	17.92	17.68	17.11
10	1.0009	17.80	17.85	17.85	17.83	17.58	17.18
11	0.9999	17.70	17.60	17.60	17.63	17.36	16.03
12	0.9999	17.65	17.60	17.70	17.65	17.41	17.90
13	1.0021	20.90	21.15	2095	21.00	20.75	17.66
14	1.009	17.95	17.80	17.80	17.85	17.60	17.54
15	1.0017	18.85	19.00	18.85	18.83	18.58	17.24
16	0.9998	18.80	18.85	18.85	18.83	18.58	16.19
17	0.9999	19.05	19.10	19.05	19.07	18.83	17.83
18	0.9998	17.80	17.95	17.85	17.87	17.63	17.14
19	1.0001	17.95	18.00	18.10	18.02	17.77	17.18
20	1.0004	18.15	18.00	18.45	18.20	17.96	16.98
21	1.0024	17.85	17.85	17.95	17.88	17.63	17.20
22	1.0014	19.05	19.00	18.95	19.00	18.74	18.13

Appendix 5

Determination of the rate of reaction of different concentrations of phosphoric acid with 50.0g of bones.

samples	Concentration(M)	Mass of bones(g)	Volume of acid used(ml)	Time taken for digestion to be complete(minutes)	Mass of sample that remained(g)
1	2	50.02	300	30	7.99
2	4	50.13	300	30	3.61
3	6	50.03	300	30	1.66
4	8	50.01	300	30	0.75
5	10	50.02	300	30	0.11

Appendix 6

Effect of change of volume on the rate of reaction of 5.0g of bones.

Mass of sample(g)	Molarity(M)	Volume (ml)	Number of moles used	observations
5.01	6	40	0.24	All sample dissolved
4.99	6	60	0.36	All sample dissolved
5.01	6	80	0.48	All sample dissolved
5.02	6	100	0.60	All sample dissolved

Appendix 7

Effect of change of concentration of sulphuric acid on precipitation of Ca^{2+} (300ml of 6M H_3PO_4 used to digest 50g of bones completely).

Molarity of acid(M)	Volume of extract(ml)	Volume of acid used(ml)	observations
0.1	5	15	White ppt
0.5	5	15	White ppt
1.0	5	15	White ppt
1.5	5	15	White ppt
2.0	5	15	White ppt
2.5	5	15	White ppt
3.0	5	15	White ppt
3.5	5	15	White ppt
4.0	5	15	White ppt
4.5	5	15	White ppt
5.0	5	15	White ppt

Appendix 8

Pocket size thermocouple, probe M, Portugal

Appendix 9

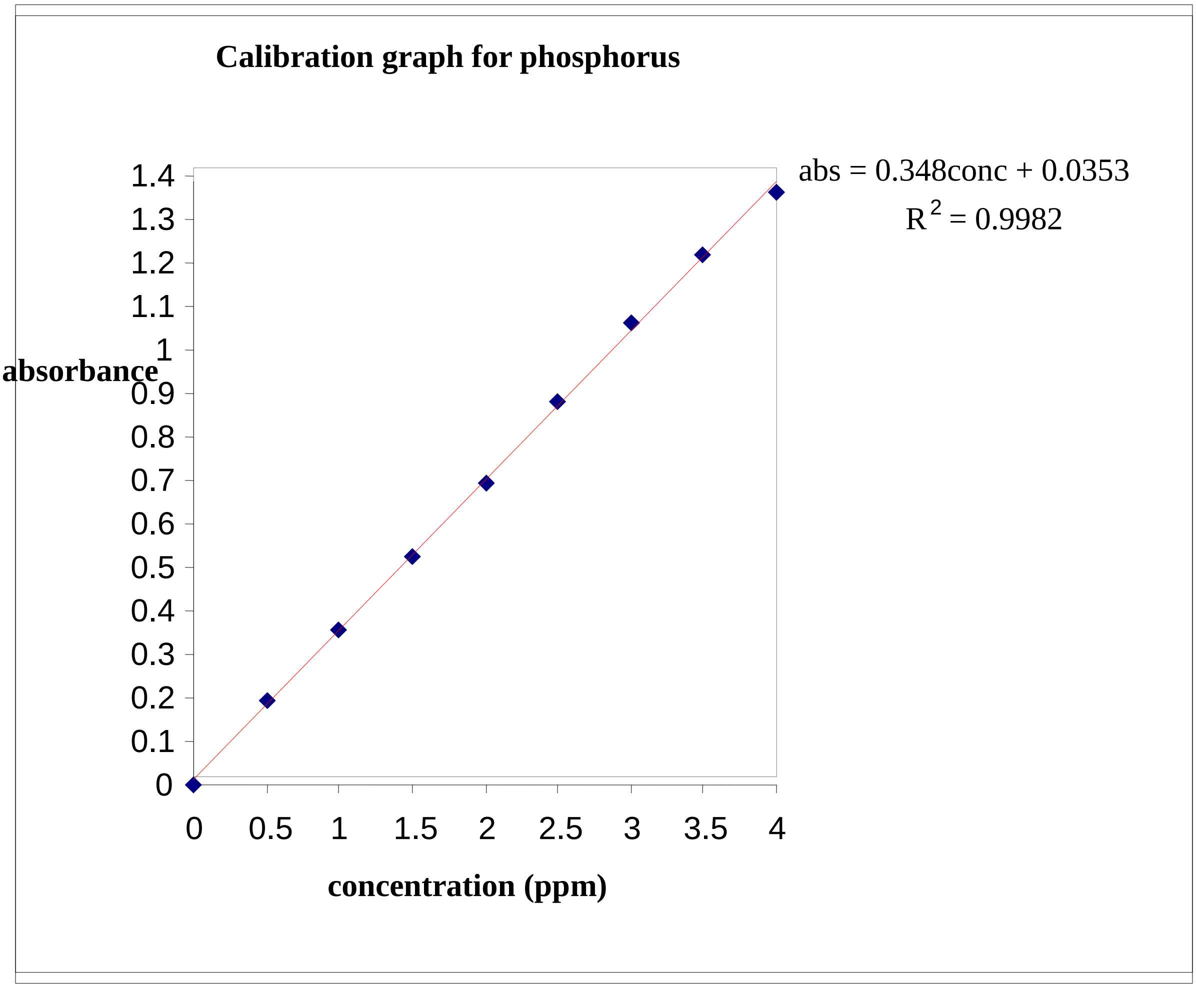
Air flow meter

Appendix 10

Table of concentration and absorbance for the standard phosphate solution

Concentration (ppm)	Absorbance
0	0
0.05	0.227
0.10	0.454
0.15	0.681
0.20	0.908
0.25	1.335
0.30	1.366

Appendix 11

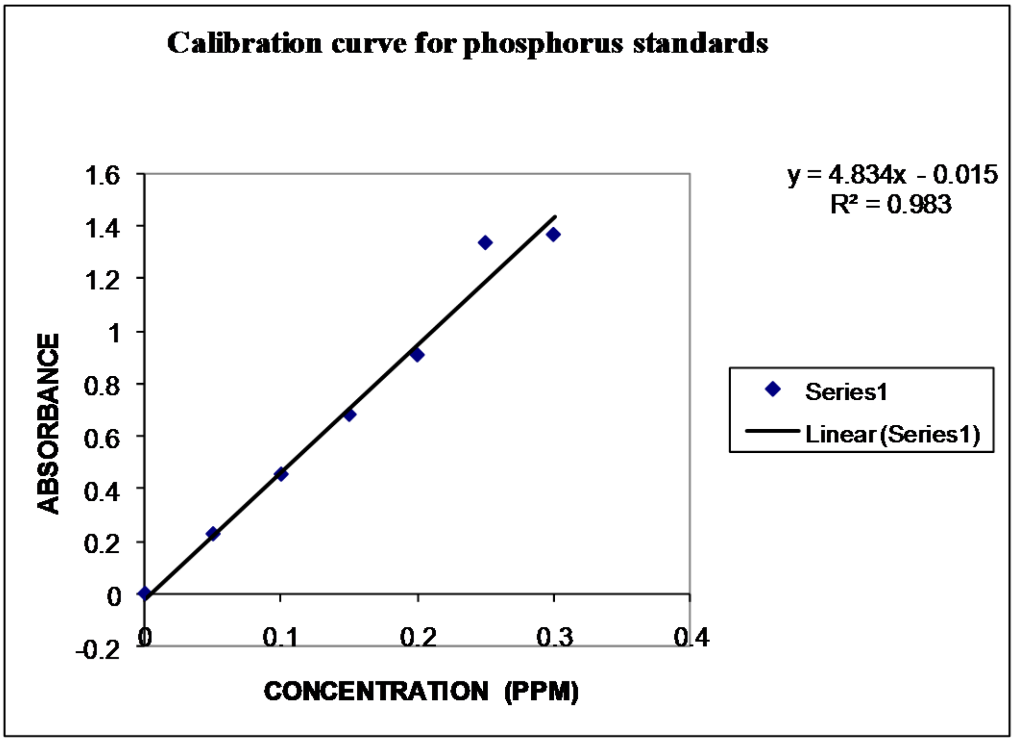

Calibration graph for phosphorus
abs = 0.348conc + 0.0353
R² = 0.9982
absorbance
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
0.5
1
1.5
2
2.5
3
3.5
4
concentration (ppm)

Appendix 12

Average absorbance and concentrations for the standard solutions

Volume of standards taken (ml)	Average absorbance	Concentration(ppm)
1	0.2295	0.5
2	0.3904	1.0
3	0.5605	1.5
4	0.7313	2.0
5	0.9185	2.5
6	1.0990	3.0
7	1 .2550	3.5
8	1.3970	4.0

Appendix 13


Calibration curve for phosphorus standards
y = 4.834x - 0.015
R² = 0.983
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
-0.2
ABSORBANCE
0
0.1
0.2
0.3
0.4
CONCENTRATION (PPM)
Series1
Linear (Series1)

Appendix 14

Sample calculations for average energy consumption in production of one tone of DAP

(i) Mass of charcoal required to separate nitrogen from air

= 13.5 kg.

Energy produced = {13.5 ×1000 ×32802.56} ÷ { 94.78 × 3600 }

=1297.84 J/s

= 0.00467 GJ

(ii) Amount of energy required to recycle 10 kg of lithium

35 kWh = 1 kg

10 kg = 350 kWh

1 kWh = 3.6 MJ

Therefore, 350 kWh = 1260 MJ

= 1.260 GJ

(iii)Amount of energy required to convert 10 kg of lithium to lithium nitride

6.01 g produces 9.47 g of lithium nitride

Therefore, 10000 g of lithium will produce 15757.07 g of lithium nitride

9.47 g is converted within a period of 0.2 hours

Block digester produces 250 W, that is, 250 J/s

15757.07 g will require a period of {15757.07g × 0.2} ÷ 9.47

= 332.77 hours

If 1sec = 250J

Therefore, 332.77 hours = 332.77 × 3600 × 250

= 0.299 GJ

(iv) Phosphoric acid extraction from bones

50 g of bones took 138.58 sec to be digested, hence, 1454544 g of bones will require 4031414.15 sec.

50 g of bones required 147.24 g of methane for complete digestion; hence, 1454544g will require 4283341.17 g of methane

Energy required = {882402 × 4283341.17}÷ 4031414.15

= 937544.16 J/s

= 937.5 KJ/s

= 3375.15 MJ

= 3.375 GJ

(v) Bones preparation

Oven – 320 W

Bones dried for 12 hours, hence.

Amount of energy used = 320 × 12 × 3600

= 13824000 J

= 0.013 GJ

Appendix 15

Heat energy used in separation of nitrogen from air

Experiment	1	2	3	4	5	6
Mass of charcoal used (g)	583.79	589.90	590.01	590.44	596.08	591.12
Total amount of heat produced by charcoal (W)	8020.21	8009.21	8019.32	8024.12	8152.50	8043.27
Wall temperature (^oC)	365.00	381.00	383.00	390.00	401.00	382.00
Temp just below the glass column (^oC)	378.00	393.00	396.00	399.00	411.00	396.00
Temp inside the glass column (^oC)	305.00	317.00	326.00	329.00	335.00	331.00
Energy transferred to the copper granules (^oC)	2694.88	2824.48	2601.49	2898.80	2824.47	2415.67
Energy lost to the surrounding (W)	5325.33	5184.73	5417.83	5125.32	5328.23	5627.60
Room temperature (^oC)	33.00	33.00	33.00	35.00	38.00	36.00