Diammonium Phosphate Fertilizer from Bone–Phosphate Enriched Phosphoric Acid and Ammonia from Lithium Nitride and its Efficacy in Tomato Growing

Makhanu Mutenyo Maxmilla (MSc. Chemistry
REG. NO. I84/13676/09

A Thesis Submitted in Fulfilment of the Requirements for the award of the Degree of Doctor of Philosophy (Chemistry) in the School of Pure and Applied Sciences, Kenyatta University

February, 2021

Declaration

I declare that this thesis is my original work and has not been presented in any other university/institution for certification. The thesis has been complemented by referenced works duly acknowledged. Where text, data, graphics, pictures or tables have been borrowed from other works including the internet, the sources are specifically accredited through referencing in accordance with anti-plagiarism regulations.

Signed.. Date..
Makhanu Mutenyo Maximilla

Supervisors' Declaration

The work described in this thesis was conducted by the candidate under our supervision.

Signed.. Date.................................
Dr Evans Changamu Ogwagwa
Chemistry Department
Kenyatta University

Signed.. Date......................................
Prof. Dickson Andala
Chemistry Department
Multimedia University of Kenya

Dedication

To my son Louis Naftali Makokha

Acknowledgements

This work could not have been accomplished without the goodwill and valuable contribution from other people. In view of this, I would like to gratefully acknowledge posthumously Prof. Naftali Muriithi for his guidance and advice during the early stages of my work. Having been the brain child behind this work, I would have wished that he be there to see this work completed. May God rest his soul in eternal peace. I would also like to acknowledge with gratefulness my other supervisors Dr. Evans Changamu and Prof. Dickson Andala for their encouragement and contribution towards the completion of this work. Their corrections and suggestions contributed to the present shape of my work. Many thanks go to the technical staff of the Appropriate Technology Centre and Chemistry Department. In particular, I would like to acknowledge Mr. Patrick Njoka, the chief technician (Appropriate Technology Centre) for ensuring that I had all the technical assistance I needed when I was doing my research. Many thanks also go to my late father Felix Makhanu Nabiswa who passed away on 30th July 2009 in the course of my studies, my brothers Francis Xaviour Makhanu, Ferdinand Nabiswa Makhanu, Simon Wafula Makhanu, and my only sister Inviolata Nafula Makhanu for their continuous financial assistance, prayers and encouragement throughout the period of this work. Lastly, am so humbled to sincerely appreciate the role played by Abel Makokha Kweyu towards the completion of this work. He is one among the few and no better words can be used to thank him except to ask our Almighty God to bless him. Above all, I give God all the glory and honour for giving me life and seeing me through the course.

Table of Contents

List of figures

List of Tables

Abstract

Phosphorus obtained from finite rock phosphate is one of the essential elements for food production and modern agriculture. Therefore, for sustainability of food supply and development in agriculture, management of phosphorus is key. The estimated periods within which the finite rocks might be depleted range from 30 to 300 years. There is a general agreement that there is a decrease in accessible reserves of phosphorus. Among the alternatives to rock phosphorus are animal bones disposed as waste from abattoirs in large cities and towns. Animal bones have a high concentration of phosphate that can be harvested and used in fertilizer production but they take many years to decompose and release the phosphate. The objective of this was to prepare bone-phosphate enriched phosphoric acid from discarded animal bones and use it to prepare DAP fertilizer and determine its efficacy in tomato growing in a greenhouse. Animal bones (predominantly cattle bones) were collected from Kachok Municipal dump site, Kisumu West District, Kenya. They were washed, dried and crashed to smaller particles using a hammer after which they were ground in a mill. The ground bones were extracted with 0.275M H_3PO_4 to give a 4.58 M bone phosphate-enriched phosphoric acid solution. Nitrogen was extracted from air by passing the air over heated copper filings and reacted with lithium to form lithium nitride. The lithium nitride was later hydrolysed to form ammonia which was reacted with the bone-phosphate enriched phosphoric acid to generate the diammonium phosphate $(NH_4)_2HPO_4$) fertilizer. Lithum metal was recycled by electrolysis of LiCl using electricity generated by a hybrid solar – wind system in a cell fabricated at Kenyatta University's Engineering Workshop. The percent composition of nitrogen (Kjeldahl) in the diammonium phosphate was found to be 17.14 % N while that of the phosphate was found to be 44.58 % P_2O_5. The process realized 98.87 % N_2 separation from air, 94.74 % lithium conversion to lithium nitride and 94.75% lithium nitride conversion to ammonia. The percentage yield of $(NH_4)_2HPO_4$) obtained from the reaction of ammonia with 4.58 M H_3PO_4 was 48.06 %. The efficacy of diammonium phosphate in the growing of tomatoes in a greenhouse was determined with the commercially obtained diammonium phosphate as the positive control and no fertilizer as the negative control. Growth parameters of the tomatoes including plant heights, leaf length, leaf width and root length were obtained over a period of twelve weeks. The results showed that the growth parameters recorded for tomato plants grown with synthesized fertilizer were not significantly different from those recorded for tomato plants grown with commercial fertilizer (p-values = 0.000 <0.05). However, growth parameters of tomato plants grown without any fertilizer were significantly different (lower in value) from those grown with fertilizer. Based on the results obtained, it can be concluded that the bone phosphate based fertilizer prepared in this study was as efficacious as the commercial fertilizer.this is a significant finding in that it shows that it shows that animal bones can be converted into readily available phosphatic fertilizer. A pilot study on production of the same is recommended.

CHAPTER 1

1 Introduction

1.1 Background information

Zero hunger is the United Nations' sustainable development goal number two whose main objective is to eliminate all forms of hunger and malnutrition by 2030 (UN DESA, 2015). This is achieved by making sure that all people (especially children) have sufficient and nutritious food throughout the year (UN DESA, 2015). It includes promotion of agriculture that is sustainable, small-scale farmer support, equal accessibility to land, improved technologies, accessible to ready markets and development of infrastructure (FAO, 2006). Phosphorus availability is one factor that is likely to stand in the way of attaining this sustainable development goal as well as its successor(s) for phosphate fertilizers. A recent review article in Contemporary Agriculture summarized the issues related phosphorus thus,

> " Phosphorus is an essential nutrient for all forms of life, which means that food cannot be produced without it. As the phosphate rock (concentrated source of phosphorus) is a non-renewable and finite resource, with no substitute, without more sustainable management of phosphorus its deposits could be depleted in a rather short period. In addition, much of phosphorus eventually ends up in environment, where it causes pollution. Hence, one could say that the lack of phosphorus and its inappropriate management could be a bottleneck for a sustainable food supply and agricultural development in general. Nevertheless, unlike some other challenges that modern agriculture has to face (for example, water and energy scarcity, climate changes etc.) the problem of phosphorus limited availability and accessibility has been largely neglected until recently."
>
> (Christopher *et al.*, 2018).

Phosphorus is currently supplied through phosphate fertilizers made from finite phosphate rock and therefore it has to be managed for sustainability of adequate supply of food and development of agriculture. There is however a lot of uncertainity because high quality reserves could be depleted in the next 30 – 40 years. Deposits that are of low grades as a result of contamination by heavy metals such as cadmium or uranium are likely to remain.(Marald *et al.*, 1998 and Emsley, 2000). Additionally, extraction and purification of these low grade deposits also result in environmental problems that result from huge amount of waste phosphogypsum contaminated by radionuclides (Marald *et al.*, 1998 and Emsley, 2000).

The process of producing phosphate fertilizers from rock phosphate has continued since 1867, and an increasing number of studies suggest that global phosphate rock extraction will reach its peak in the coming decades. The remaining potential reserves are characterized by poor quality that is costly to extract (Runge-Metzger, 1995; Steen, 1998; EconSanRes, 2003; Dery and Anderson, 2007 and Cordell and White, (2011). There is, however, no clear consensus on when extraction is likely to reach peak. Cordell *et al.*, 2009 and Cordell, 2010 estimates phosphorus to reach its peak between 50 – 100 years while Steen, 1998; Driver *et al.*, 1999 and Stewart *et al.*, 2005 reiterate that tis estimates exclude reserve bases that are not economical to mine. Cordell *et al.*, 2009 estimates the peak to be 350 years based on current production capacity excluding increased demand for phosphorus. The scarcity of natural rock phosphates is as a result of losses during agricultural runoff, erosion, animal wastes, hence, need for a more effective approach that addresses the future of phosphorus scarcity. This includes and not limited to exploring mechanisms that minimize leakage, recovery and recucling of phosphorus from various processing chains (Cordell *et al.*, 2009).

Larsen and coworkers suggested that extraction of phosphorus from waste water is a possible solution to large dependence on fossil deposits. So far the importance of nutrient recovery from wastewater has been underestimated, but it is clear that it could significantly contribute to overcome the looming phosphorous crisis (Larsen *et al.*, 2007). As more and more people move from rural to live in cities, food is moved from production zones to the cities and with it incorporated phosphorous which eventually ends up in municipal waste waters, slaughterhouse wastes and landfills. Recovery of phosphorus from such sources for food production should be priority going forward. Manufacture of phosphorus fertilizers from locally available organic waste products, such as human excreta, industrial organic waste by-products, animal dung, fish, ash, bones, and other slaughterhouse by-products was practiced before the discovery of chemical production (Cordell *et al.*, 2009). In early 17 and 18th centuries, England imported bones from its neighbors and used them to supplement animal and human excreta which were being used as sources of phosphorus (Cordell *et al.*, 2009).

Animal bones which contain carbonate – hydroxyl – apatite structure are always disposed off as wastes by abattoirs in large cities and towns yet they are sources of high concentration of phosphate that can be harvested and used in fertilizer production. Bones are the most concentrated forms of organic phosphates derived from feed and feed supliments and they are used for crop production. They have the highest phosphorus concentration in water soluble fraction (505mg/kg) as compared to processed phosphate which has 307mg/kg (Knox *et al.*, 2006). The calcium and phosphorus contents (25 – 29% Ca and 15 -19 % P) compares well the natural rocks (35 ± 2 % Ca and 15 ± 1 % P) (Coutand *et al*., 2008). Experimental results by Caynela (Caynela etal., 2009) indicate that when the soils are treated with bone meal there is an increase in carbon minerals, nitrogen, microbial biomass size and activity. Therefore, using bones in this study presents a recycling process of organic phosphorus.

Diammonium phosphate (DAP) fertilizer is a widely used phosphorus fertilizer applied to soils to address low levels of phosphorus as a result of intense agriculture (IPNI, 2015). It contains nitrogen which is important in promoting rapid vegetative growth and phosphorus which is a component of ATP and chlorophyll that is essential for food production. DAP is known to have good physical properties such as high solubility that makes it a popular choice in farming and use in other industries. It has other uses that include being used as a fire retardant and metal finishing (IPNI, 2015). It is produced from two common constituents, ammonia (from the Haber process) and phosphoric acid from phosphate rock. Industrial manufacture of phosphoric acid is done mainly by thermal and wet processes.

1.2 Statement of the problem

The major source of phosphorus used for the production of phosphate fertilizers is phosphate rock. Some of the disadvantages of phosphate rock is its scarcity, it is non-renewable and the process of extracting is expensive. Thus, alternative sources of phosphate are desirable. Animal bones form a rich source of phosphate but they release the phosphate slowly when crushed and used as fertilizers directly. The objective of this study, was to extract bone phosphate into commercial phosphoric acid and to react the phosphate-rich acid with ammonia to generate the diammonium phosphate, a much sought after fertilizer in crop production. To mitigate against the high cost of production of ammonia, alternative synthesis of ammonia was done through hydrolysis Li_3N obtained by reacting metallic Li with dinitrogen extracted from air on site. To ensure sustainability of the process power for electrolysis and heating of LiCl in a prefabricated electrolytic cell was generated on site using solar-wind hybrid system. The diammonium phosphate fertilizer prepared in the laboratory was evaluated by growing tomatoes in the greenhouse against the commercially obtained fertilizer. The data collected was analysed by the one way ANOVA.

1.3 Hypothesis

The efficacy of diammonium phosphate fertilizer prepared from bone-phosphate enriched phosphoric acid in the growing of tomatoes is not significantly different from that of commercial diammonium phosphate fertilizer.

1.4 Objective of study

1.4.1 General objective

To evaluate the efficacy of diammonium phosphate fertilizer prepared from bone phosphate-enriched phosphoric acid and ammonia generated from hydrolysis of lithium nitride in the growing of tomatoes in a greenhouse.

1.4.2 Specific objectives

i) To prepare lithium nitride from lithum metal and nitrogen extracted from air.

ii) To fabricate the electrolysis cell to run on solar-wind hybrid power source for the recovery of used lithium.

iii) To extract bone phosphate by acid hydrolysis for production of diammonium phosphate fertilizer.

iv) To synthesize and characterize diammonium phosphate fertilizers.

v) To evaluate the efficacy of the diammonium phosphate fertilizer prepared in growing tomatoes in a greenhouse.

1.5 Justification of study

Animal bones that are generally disposed of as waste by abattoirs in large cities and towns and take many years to decompose have a high concentration of phosphate that if harvested they can be used in fertilizer production. Recovering phosphate from the bones and using it to produce DAP helps in the recycling of the same to the environment and supports food production.

1.6 Significance of study

Animal bones which have the highest phosphorus concentration in water soluble fraction have been converted into readily available phosphates for crop production.

CHAPTER 2

2 Literature Review

2.1 Introduction

Phosphorus is a highly reactive element due to its position in occurrence in the earths crust, hence, it is found combined in nature in phosphates in organic rocks (White and Hammond, 2008). It is generally associated with Calcium, Sodium, Fluorine, Chlorine, Iron, Aluminium, Magnesium, Cadmium, and Uranium among others. In the biosphere, it exists almost exclusively as phosphate (PO_4^{3-}) in the form of orthophosphate esters. In lithosphere, it occurs mostly as apatite [$3Ca_3(PO_4)_2$ X $Ca.Fe(Cl)_2$]and fluorapatite [$Ca_5(PO_4)_3F$, hydroxyapatite [Ca_3 (OH) $(PO_4)_3$ which has P_2O_5 and CaO in the mole ratio 3:3 (Jogi, 2002).

The genetic memory unit (DNA) found in all living things contain phosphorus. RNA, a compound that initiates the process of reading the DNA genetic code to build proteins and other compounds that are important for plant structure and high yields of seeds is a component of phosphorus. Phosphorus is an important component of ATP, the "energy unit" in plants. Plant processes such as photosynthesis, growth of seedings, grain formation and maturity results to formation of ATP. ATP takes its role of capturing and converting the suns energy into useful plant compounds. Phosphorus is one of the three major constituents of inorganic chemical fertilizers (NPK) that is useful in production of food. It is important in stimulation of development of roots, increase in the strength of stalks and stems of plants, improvement in formation of flowers and production of seeds and aides crops to mature early and uniformly. The phosphorus contained in NPK fertilizers aides plants to increase their capacity in nitrogen fixation, enhanced disease resistance and its low levels results in stunded growth in plants.

Excess phosphates from fertilizers, detergents and soda enters rivers, lakes and oceans resulting in eutrophication causing water pollution. Sewage sludge is one of the methods used for returning nutrients to agriculture (Kirchmann *et al*., 2017). Other methods include, composting toilets, urine direction, more efficient application of fertilizers and technological innovations. Increase in growth of the world's population results to increased food requirements that directly impacts on development of agriculture, which is directly related related to increased production and consumption of phosphates. The inorganic fertilizers containing nitrogen, phosphorus and potassium plays a major role in imposing the amounts and quality of agricultural products. Hence, inorganic fertilizers are instrumental in provision of enough food required for the increasing world population (Kirchmann *et al*., 2017).

The most widely used inorganic phosphorus fertilizers in growing of crops globally is DAP. It contains nitrogen which is important in promoting rapid vegetative growth and phosphorus which is the main constituent of DNA and RNA (essential building blocks of life) (IPNI, 2015). DAP has excellent physical properties including its relatively high nutrient content and high solubility that makes it a popular choice in farming. It has other uses that include being used as a fire retardant, metal finishing, it's added to wine to support yeast (IPNI, 2015). DAP is made from two common constituents, ammonia (from the Haber process) and phosphoric acid. Industrially, concentrated phosphoric acid is produced from phosphate rock mainly by thermal and wet processes (Marshall, 1979).

This chapter looks at the role of phosphorus in attaining global food security, sources of phosphorus, processes of extraction of P from phosphate sources and their conversion to ammonium phosphate fertilizers.

2.2 The role of agrulture in providing the world's food security

The role of agriculture in development of kenya's economy cannot be undersestimated. Processes of production, processing and distribution of agricultural products directly provides employment and increases the percentage levels of the county's GDP. All industries (manufacturing, distribution and service) have a direct link to agriculture. Several factors such as unpredictable climatic change, unskilled farm management of farms, failure to adopt modern farming technologies, application of agro – inputs, have greatly affected productivity in agricultural sector (IFFRI, 2013).

A number of stakeholders agree that use of inorganic fertilizers is central to raising agricultural production. The world population is increasing year by year, for example, the world population as of October, 2011 was 7 billion and by March 2020, it was 7.8 billion (World Development Prospects, 2020). In Kenya, the total population as at 2014 was 44 million, in 2015 was 45 million and in 2016, the population rose to 46 million people (Population and Housing Census, 2017). Out of this total population, two to four million people in Kenya receive food aid annually (World Development Prospects, 2016) and this poses a serious challenge to food security.

It is estimated that from the year 2010 to 2030, the impct of malnutrition in the country as a result of a decrease in population work force will cost kenya $ 38.3 billion in GDP (Feed the Future Profile, USAID. 2019). Low agricultural yield which is directly related to inadequate fertilizer inputs is among the main causes of poverty (Feed the Future Profile, USAID. 2019). Farmers are unable to put sufficient fertilizers because of the high costs (Feed the Future Profile, USAID. 2019) and therefore, any contribution towards lessening the cost of farm inputs is highly desirable.

FAO 2018 defines food security as physically and economically accessing sufficient, safe and nutritious food by every person and if this is not available then the population is said to beinsecure in food availability. Lack of purchasing power and inappropriate utilization of food at household level is also refered to as food insecurity. Increase in agricultural input, therefore, is required to increase food production to cater for the rise in growing population. The upsurge in agricultural output is depended on increase in production on available farms by improved nutrient management practises and fertilizer technologies (FAO, 2018). Statistics shows that the average percentage yields as a result of applying fertilizer inputs ranges from about 40 – 60 % in USA and England and increases in the tropical countries (FAO, 2018).

Applications of chemical fertilizers has resulted to increased crop yields capable of providing food for a surging world population in the last fifty years (IFFRI, 2013), yet the mineral rock phosphate is scarce, expensive to extract and non – renewable (Cordell and White, 2009). The demand for nitrogen, phosphorus and potassium which are the main nutrients in inorganic fertilizers is estimated to increase from 1.8 % per annum from 2014 – 2018 with annual growth of 1.4, 2.2 and 2.6 % for nitrogen, phosphorus and potassium respectively during the period (FAO, 2018). Similarly, a breakdown of the percentage of nitrogen potential, phosphorus and potassium in the years 2014, 2015, 2016, 2017 and 2018 are as shown in Figure 2.1.

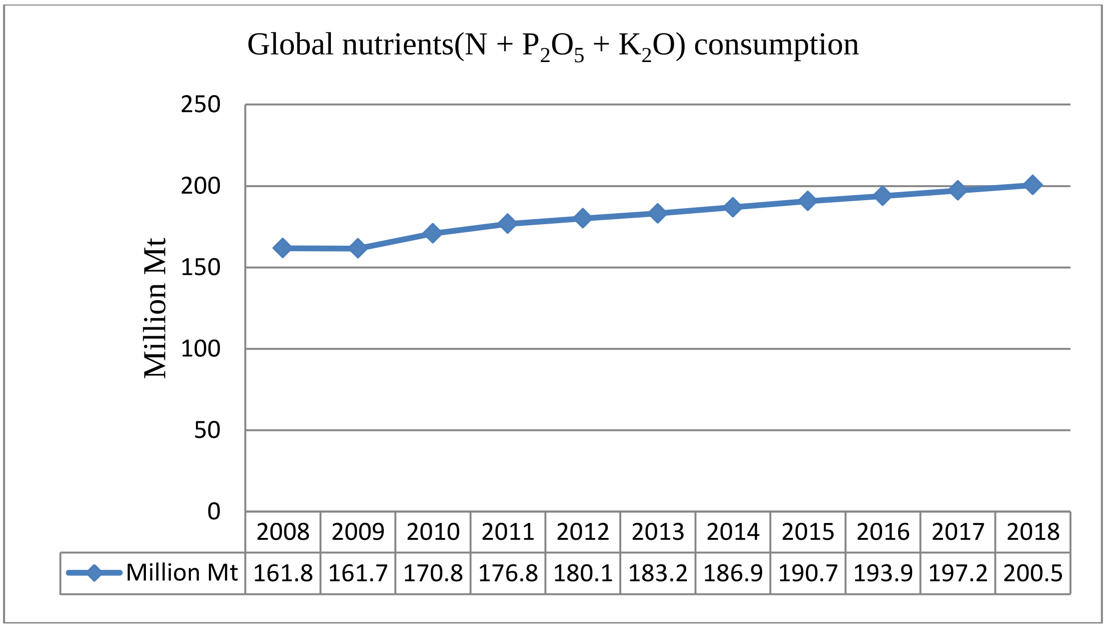


Figure 2.1: Global nutrients consumption (FAO, 2017)

The data in Tables 2.1 and 2.2 show that NPK's, DAP and CAN accounted for 71 % of the total fertilizers officially imported into Kenya (Kenya National Bureau of Statistics, 2016).

Table 2.1 Fertilizer imports in Kenya 2012 – 2015 (KNBS, 2016)

HS code	Fertilizer name	2012(volumes, MT)	2013(volumes, MT)	2014(volumes, MT)	2015(volumes, MT)
3105200000	NPK's	139578	129540	136880	166348
3105300000	DAP	126470	273939	144450	127672
3102400000	CAN	53616	101201	87900	99120
3105510000	NP	12058	20853	35594	65295
3102100000	UREA	46684	49983	64779	54419
Total fertilizer (Mt)		445180	690032	494720	556432

Table 2.2 Projected prices of fertilizer imports in 2015 (1/1/2015 – 31/12/2018) (KNBS, 2017)

HS code	Fertilizer name	Volumes (Mt)	Values (USD)	USD/Ton
3105300000	DAP	127672	65,628,853	514
3102400000	CAN	99120	35,551,865	328
3105513705	NP 23,23,0	64672	29,977,883	464
3105203104	NPK 25,5,5	46574	17,134,328	368
3102100000	UREA	43584	14,506,355	333
3105203120	NPK 26,22,0	38374	14,262,557	372
3105202522	NPK 17,17,17	31339	13,873,696	443

2.3 The role of fertilizer

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 replace the essesntial elements used or exhausted by crops previously grown and to modify soil nutrient contents as reguired by the set objectives (Considine, 1994), hence, their importance cannot be over-emphasized. 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 elemnts namely nitrogen, phosphorus and potassium indicated on a bag of fertilizers as (NPK) in which N = 17% nitrogen, P = 46 % P_2O5 and K = 0 % K_2O (Lapedes, 1997).

The first three essential plant nutrients (N, P, K) are required for plant growth (Dery and Anderson, 2007). Nitrogen and potassium are abundant and seemingly infinite, but phosphorus is finite and therefore low in proportion. Moreover, there is no alternative to phosphorus in the growth of all living organisms (Steen, 1998; Johnson, 2000), therefore, it is important to ensure there is continuous availability and accessibility to the phosphate sources. Nitrogen is important in promoting rapid vegetative growth, synthesis of amino acids, regulation of uptake of other nutrients, formation and function of chlorophyll (Ball, 2007).

Phosphorus on the other hand stimulates early root formation and growth, hastens maturity, development of seeds, changes in energy and processes of conversion of sugars to hormones transformation and conversion processes in which sugars are converted to hormones, protein and energy (Ball, 2007). Potassium is important for strengthening of cell walls (Ball, 2007). Chemical and composite and residue fertilizers are applied to obtain a balance in plant nutrients and growth because organic fertilizers tend to vary in composition (Ball, 2007). A fertilizer such as diammonium phosphate is widely used during planting since it consists of nitrogen and phosphorus which are in high concentration levels. Diammonium phosphate has a high nutrient concentration, good storage and handling facilities, its solubility in water is relatively high and relative ease of production in large plants (Ball, 2007). These has elevated the global urge for nitrogenous ingredients with world end user market producing over $98.6 billion and expected to hit $114 billion by 2018 (FAO, 2017).

2.4 Phosphorus fertilizer sources

The element phosphorus was discovered by the German alchemist Henning Brandt over 300 years ago. He carried out distillation of fifty gallons of urine to produce the ‘Philosopher’s Stone’ that was expected to yield gold (Emsley, 2000). From these experiments he discovered pure phosphorus that glowed in the dark and highly flammable. In 1840, the German chemist Liebig discovered phosphorus in low proportions that was used in plant growth. It was also used in chemical fertilizers. Before this discovery, compost and residue fertilizers were appled to crops to raise the levels of phosphorus in the soils (Marald, 1998).

The movement and exchange of phosphorus between the living and non living organisms in the earth’s crust that ranges from days to years makes phosphorus renewable. Hence, composite and residue materials that include residues from crops, wastes from food and animal wastes are also termed as renewable sources of phosphorus. Non renewable sources of phosphorus include the phosphate rock and it cycles between the earth and the hydrosphere. Phosphorus is found in combined form and therefore the mining industries measures phosphorus phosphorus pentoxide (P_2O_5), which contains 44% P.

Rock phosphate contains around 5–13% P (Brink, 1977; Gilbert, 2009 and Jasinski, 2009) and its usually concentrated to increased levels of 11–15% P during the manufacturing process. These levels are in comparison to 0.1% P, concentrations of phosphorus in the earth's upper crust. Rock phosphate is the source of all chemical phosphorus fertilizers like single superphosphates, diammonium phosphate and nitrophosphates.

There are four types of naturally occurring deposits of rock phosphate (Sayma and Sharba, 2019). Their structures contain quartz, silicates, carbonates, sulphates and sesquioxides. The igneous and metaphoric apatites are termed as less reactive as a result of their well developed crystalline structure that contains 30 – 45 % P_2O_5 (Schorr and Lin, 1997). Rock phosphates contain elements such as cadmium, uranium, lead, mercury and arsenic which are hazardous to the environment. Superphosphate fertilizers produced from rock phosphate contain those elements which when applied to soils they contaminate the agricultural land. The process of producing chemical phosphate fertilizers is by reacting the phosphate with dilute sulphuric acid as summarized by the equations 2.10, 2.11 and 2.12 below.

$$\mathrm{Ca_5(PO_4)_3\,X + 5H_2SO_4 + 10H_2O \rightarrow 3H_3PO_4 + 5CaSO_4.2H_2O + HX} \qquad 2.10$$

Where X may include OH, F, Cl, and Br.

$$\mathrm{Ca_3(PO_4)_{2\,(\mathit{s})} + 4H_3PO_{4(aq)} \rightarrow 3Ca(H_2PO_4)_{2\,(\mathit{s})}} \qquad 2.11$$

$$\mathrm{Ca(H_2PO_4)_{2\,(\mathit{s})} + 3H_2SO_{4(aq)} \rightarrow 3CaSO_{4(s)} + 6H_3PO_{4(aq)}} \qquad 2.12$$

Figure 2.2 summarizes the processes of industrial manufacture of phosphoric acid.

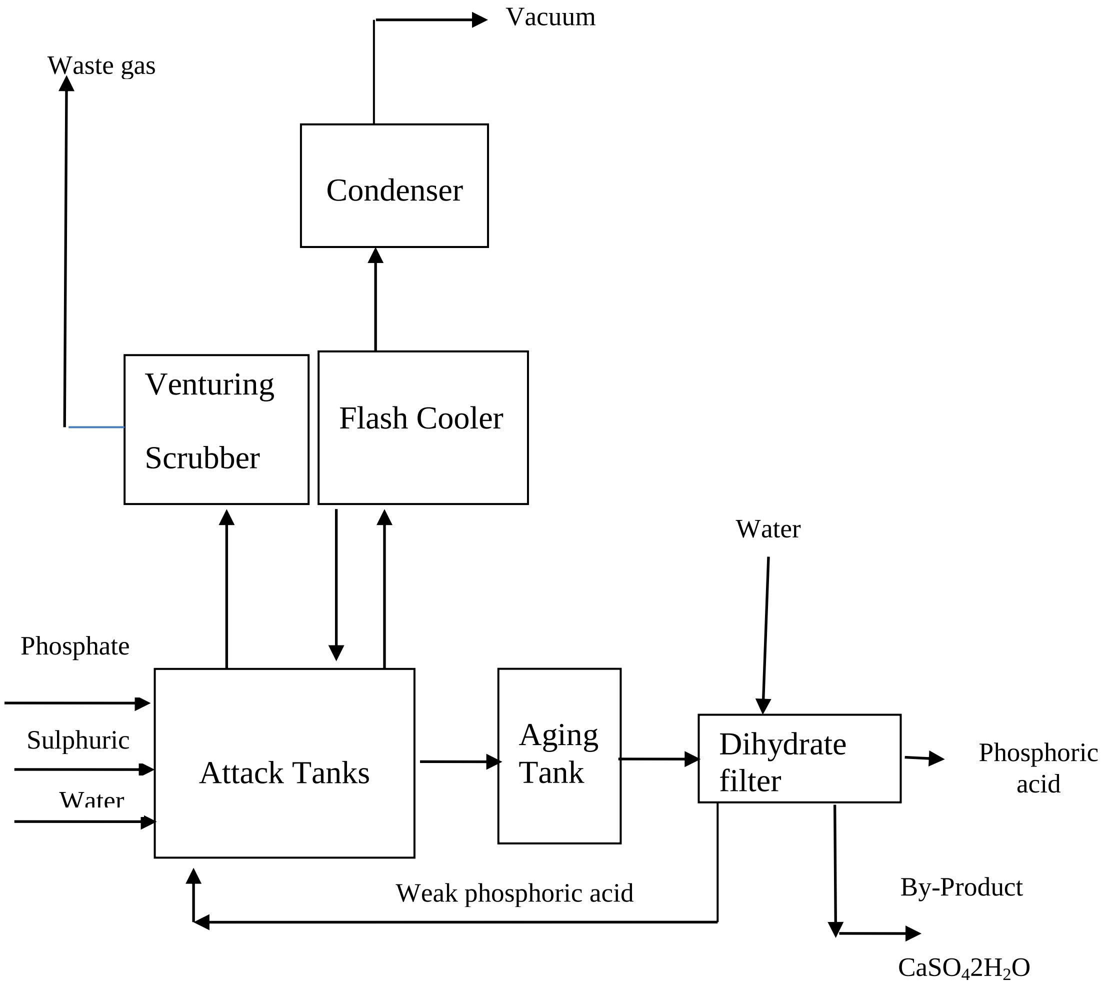


Figure 2.2: Processes of Phosphoric Acid Manufacture (David, 2016)

Orthophosphoric acid is extracted, reacted with ammonia gas to produce the N –P inorganic fertilizers that are DAP, MAP and APP (David, 2016).

Common phosphate-bearing rocks include limestone and mudstones shown in Fig. 2.3 and 2.4;

Figure 2.3: Phosphate Rocks (Leyshon, 1999)

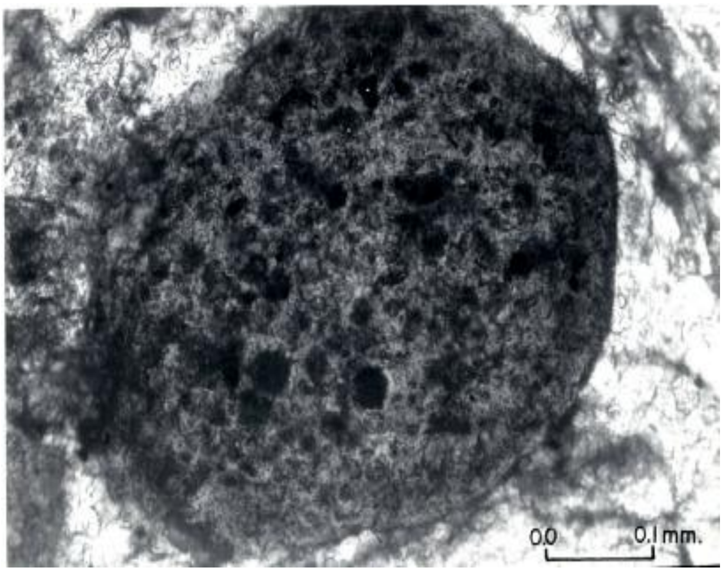


Figure 2.4: Black beds of Phosphate rich sedimentary rocks (Prothero *et al*., 2003)

2.5 Calcium orthophosphates

Various science studybinterests on calcium apatite and calcium orthophosphate cuts across the fields of geology, chemistry, biology and medicine (Lide, 2005). The orthophosphate anoin present in calcium orthophosphate contains calcium, phosphorus and oxygen as three major chemical elements. Their abundance in the lithosphere ranges among the first twenty elements: oxygen (~47 mass %), calcium (~3.3–3.4 mass %) and phosphorus (~0.08–0.12 %) by mass.

The calcium orthophosphates contain hydrogen as an acidic orthophosphate anion (HPO_4^{2-} or H_2PO^{4-}); hydroxide [$Ca_{10}(PO_4)_6(OH)_2$] with water of crystallization as $CaHPO_4{\cdot}2H_2O$) (Legerog, 1991). The combined forms of CaO and P_2O_5 results in various of calcium phosphates distinguished only by the presence of (PO_4^{3-}), (PO^{3-}), ($P_2O_7^{4-}$) and [(PO_3)n^{n-}](Legerog, 1991). In the presence of severally charged anions, calcium phosphates are identified by hydrogen ions attached to the anion for example,[Ca (H_2PO_4)$_2$], ($CaHPO_4$), [$Ca_3(PO_4)_2$] and ($Ca_2P_2O_7$). Eggshells, cockles, seashells, snail shells, oyster shells, cuttlefish shells and coral contain structures that have calcium phosphates and carbonates (Gergely *et al*., 2010). They are used to prepare pure CaO which is used to synthesize calcium phosphates. Animal bones, teeth and fish scales are sources of natural calcium phosphates which are directly extracted by calcination. Natural calcium orthophosphates are majorly used to produce white ane red phosphorus, phosphoric acid and chemical fertilizers like superphosphates and ammonium phosphates (Gergely *et al*., 2010).

2.6 Bones composition

Collagen fibres and inorganic bone mineral majorly comprise the crystal strucrures of the bone.bones found inside a living contains between 10 % and 20 % water, 60-70 % of the dry mass is bone mineral and small amounts of proteins and inorganic salts. Rock phosphate at different ages have different chemical activities, that is, hard or soft (Filippelli, 2011). Bone phosphate is more reactive than the rock phosphates because bone phosphate has a more reactive type of phosphorus. Rock phosphates naturally contain high levels of hazardous chemical elements and other impurities (contaminants) that could be of environmental concern when used (Knox *et al*., 2006) and (Sneddon *et al*., 2006).

One advantage of the bone phosphate over the rock phosphate is that bone phosphate has low levels of hazadours chemical impurities because bones take a shorter time to maturity. Bones also lack fluorine which plays a major role in the formation of sedimentary apatite in rock phosphate. Additionally bones have higher solubility index of log (ksp) of 45.2 compared with 57.0 for rock phosphate and 48.0 for the beneficiated rock phosphate(Coutand *et al.,* 2008). Bones have high phosphorus concentrations in water soluble fraction (505 mg/kg compared with 307 mg/kg for processed phosphate and 22 mk/kg for mineral phosphate (Knox *et al*., 2006).

Slaughter house waste is processed into bone meal and therefore acts as a raw material for production of phosphorus (Mondini *et al*., 2008). Caynela *et al*., 2009 reported that when agricultural soils are treated with bone meal there is an increase of carbon mineralization, nitrogen availability, microbial biomass size and activity in the soil**.**

2.7 Industrial uses of bones

Every constituent of bone has an application, for example, making of buttons, knife-handles, phosphates and lime are components of porcelain, the fat is worked up by the soap maker and chandler, and the gelatin is a source of glue (Mondini *et al*., 2008). Further, by dry distillation, not only bone charcoal, a valuable purifying medium, but ammonia and bone-tar are obtained (Mondini *et al*., 2008).

The fat is pale in color and is used in pharmacy for the manufacture of pomades, and by the soap-maker. The shavings and scrapings from the bone-carvers are treated for high-grade gelatin, while the fine meal from the drills, finds use in poultry and dog foods. The feet of sheep, horses and cattle (the hoofs having been removed) are also treated separately by the simple boiling process (Mondini *et al*., 2008). These bones yield oils which are largely consumed in the preparation of leather. Neat's foot oil (strictly the oil from the feet of cattle only), when separated from any deposited solid stearine, is used as a lubricant in clocks and guns being valued on account of its low solidifying temperature (Mondini *et al*., 2008).

Liquid glues, treated with acids, such as phosphoric, acetic or nitric acid remains liquid when cold, but the adhesiveness is unimpaired. Gelatin treated with hydrochloric acid to remove the phosphate of lime (Mondini *et al*., 2008). Carefully picked, spongy-bones are chosen and well cleansed (Mondini *et al*., 2008). The decalcified hones are treated with hot water and steam; the fat being skimmed off, the gelatin is obtained by evaporation of the aqueous liquors. Other applications of gelatin include being used for photographic emulsions, culture medium in bacteriology and employed as a dressing for white fabrics, silks and straw hats (Mondini *et al*., 2008).

The residual degreased and degelatinized bones are ground to a meal and used as fertilizer, being valuable on account of the phosphate of lime content. Raw bones are rarely used by the farmer. More often the bone-meals are converted into super phosphates. To effect this the ground bone-residues are treated with sufficient sulphuric acid to convert the insoluble tri-calcium phosphate of the bones into the more soluble mono calcium phosphate which is more readily assimilated by the plants (Mondini *et al*., 2008).

Dissolved bones furnish nitrogen to the soil without the necessity for compounding with additional ammoniacal salts. The expression is loosely used for superphosphate fertilizers made chiefly from bones. Animal charcoal, which is obtained as a residue from the carbonization of degreased bones comprise a gas suitable for illumination and heating, tar, and aqueous ammoniacal liquors (Mondini *et al*., 2008). The tar is redistilled, giving a volatile product condensing to bone oil. There is no practical use for this bone oil, which is a mixture of pyridine and fatty amine derivatives with a most offensive odour, except as a fuel for the factory boilers. Black varnishes such as Brunswick black are produced from the remains of tar (Mondini *et al*., 2008). The ammonia is recovered through steam distillation as sulphate from sulphuric acid collectors; the product is impure but suitable for fertilizer (Mondini *et al*., 2008).

The residual charcoal, which is the most valuable product of the carbonization, is removed from the retorts into closed iron coolers, dried, crushed and graded (Sayma and Sharba, 2019). Bone charcoal is used as a decolorizing and refining medium in sugar industry. The fine dust charcoal is sifted out and used in the preparation of blackings and ivory black. In sugar-refining the char is required from lentil to nut-size; about one ton is needed to decolorize one ton of sugar, but the char can be revivified by washing and reburning for a life of about two years (Sayma and Sharba, 2019). When the decolorizing power is exhausted the spent char is discarded by the sugar manufacturer, but finds a ready market as a source of superphosphate; or it may be calcined in air to bone ash.

Bone ash, also obtained by burning fresh bones, is composed of calcium phosphate; is used to make cupels for assaying, and is an important constituent of the paste used for English soft porcelain. Bone ash is treated with sulphuric acid and phosphoric acid to produce an alternative to cream of tartar in baking powders (Sayma and Sharba, 2019). The process of using bones as fertilizers was discovered by Justus Von Liebig in 1840. Up to 80% of the phosphorus is lost in thephosphorus cycle that involves food consumption, phosphate application on fields, food processing and final consumption (Sayma and Sharba, 2019). Composite crop residues, waste food items in dumpsites, manure, human excreta, struvite and other sources such as bone meal, ash and algae, are now being used as a source of phosphorus fertilizers (Sayma and Sharba, 2019).

2.8 Phosphoric acid manufacture by solvent extraction

Production of chemicals such as fertilizer, soap, detergent, food and beverages involves the use of phosphoric acid (Qureshi *et al.*, 2012). Rock phosphate is the major raw material in production of phosphoric acid, whereby, it is reacted with different mineral acids such as sulfuric, hydrochloric or nitric acid, or by burning of phosphorus produced through electro-thermal process (Muhammad *et al.*, 2012). The reaction with sulfuric acid is the most preferred. Reacting rock phosphate with hydrochloric acid yields a mixture of phosphoric acid and impurities like $CaCl_2$, $FeCl_3$, $FeCl_2$, $AlCl_3$ and $MgCl_2$ (Muhammad *et al.*, 2012).

Separation of phosphoric acid by decantation or filtration from salts is difficult because they are highly soluble making application of solvent extraction efficient (Muhammad *et al.*, 2012). When rock phosphate is reacted with hydrochloric acid, it is decomposed to give phosphoric acid and chlorides of calcium, iron, magnesium, aluminum as impurities (Muhammad *et al.*, 2012).

Efficient extraction of crude phosphoric acid (between 41% - 65%) is achieved with the use of amyl alcohol at varying ratios plus little amounts (Muhammad *et al*., 2012). During this process, a raffinate phase is formed which is recycled to fresh extract. Distilled water is added which enables separation of the organic phase and then phosphoric acid. Phosphoric acid obtained having 4.80 % P_2O_5 is concentrated up to 50 % P_2O_5 by estimating the level of impurities which are separated by post-precipitation (Muhammad, *et al*., 2012). This process is as shown in Figure 2.5;

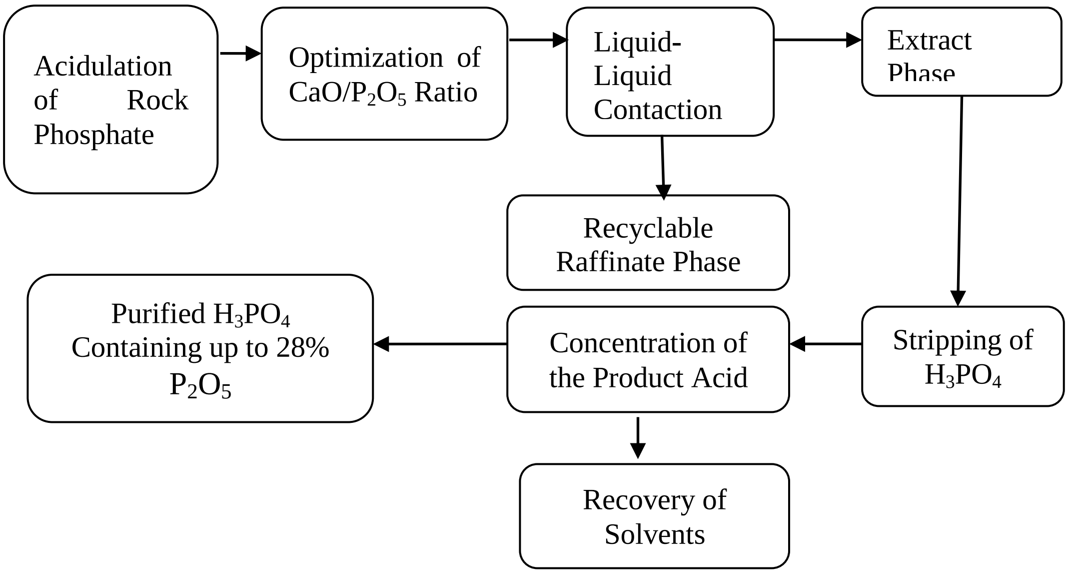


Figure 2.5: Solvent extraction of phosphoric acid (Muhammad *et al*., 2012)

2.9 Nitrogen sources

The N sources include commercial fertilization (64 %), electrical and biological N_2 fixation (3 %), legume and crop residues (21 %) and animal manure (12 %). The process of fixing nitrogen can either be done industrially or biologically. The industrial process converts the chemically inert nitrogen to a more reactive nitrogen that can combine with other elements to form compounds such as ammonia, nitrates or nitrites (Considine, 1994).

The biological N_2 fixation is biologically mediated conversion of atmospheric N_2 to N – containing organic compounds such as ammonia (Ball, 2007). 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 (Ball, 2007).

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” (Ball, 2007). With nitrification, ammonium can be continuously converted into nitrate, which is soluble and will be absorbed by plant through water. 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 (Ball, 2007).

Vehicles and power stations emit oxidized N (NO_x) to the air, and ammonia is volatized from agriculture (Ball, 2007). 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 (Ball, 2007).

Biological nitrogen fixation involves sixteen equivalents of MgATP as shown in the equation.

$$\mathrm{N_2} + 8\mathrm{H^+} + 8\mathrm{e^-} + 16\,\mathrm{MgATP} \rightarrow 2\mathrm{NH_3} + \mathrm{H_2} + 16\mathrm{MgADP} + 16\mathrm{PO_4^{3-}}$$

2.10 Processes in ammonia production

Nitrogen is one of the first three essential elements required by living organisms (Fryzuk and Samuel, 2000). However, this ubiquitous molecule is not easily taken up by all living organisms the way oxygen is taken up by living organisms. N_2 is incorporated into biological systems by the process of nitrogen fixation. In 2003 Schrock and co-workers reported the first process of producing ammonia through the reaction of a transition metal and nitrogen. The use of molybdenum – dinitrogen complex containing a triamide – monoamide tetradentate ligand produced ammonia at room temperature and at atmospheric pressure. The catalytic reaction was not efficient but realized the long-term goal of developing catalytic ammonia – producing reaction (Nishibayashi Yoshiaki, 2018).

Three processes were developed that utilize the highly abundant feedstock, dinitrogen gas (N_2); the Birkeland–Eyde arc process (Greenwood and Earnshaw, 1984) as shown in equation 2.3, the Frank–Caro cyanamide process (equation 2.4)

$$2N_{2(g)} + 5O_{2(g)} + 2H_2O_{(l)} \xrightarrow{\text{electric arc furnace}} 4HNO_{3(l)} \qquad 2.3$$

$$CaC_{2(s)} + N_{2(g)} \xrightarrow{1000℃} CaNCN_{(s)} + C_{(s)} \qquad 2.4$$

$$N_{2g} + 3H_{2(g)} \xrightarrow{Fe\ catalyst,\ 400℃,\ \sim 200℃} 2NH_{3(g)} \qquad 2.5$$

And the Haber–Bosch process (equation 2.5), where the two raw materials (hydrogen and nitrogen) for the reaction undergo a process of purification where all impurities are removed, then passed through the compressor at a pressure of 200 atm (ApplMax, 2005). This process results in increase in temperature of the mixture to about 300°C, increase in kinetic energy of particles hence, and a split in nitrogen and hydrogen molecules.

This mixture is then led to a converter whose temperature is 450°C and pressure of 200 atm (ApplMax, 2005). The convertor contains hot iron beds that acts as catalysts (ApplMax, 2005). The two gases react on the surface of the catalyst to form ammonia. The process only results into 15% conversion of the constituent gases to ammonia (ApplMax, 2005). Nitrogen, hydrogen and ammonia as a mixture are discharged from the converter, cooled, liquefied and ammonia collected. The melting points of nitrogen and hydrogen are lower than that of ammonia hence remains as gases and redirected back to the converter (ApplMax, 2005). The reaction equation is as shown in equation 2.6:

$$\mathrm{N_2} + 3\mathrm{H_2} \rightarrow 2\mathrm{NH_3} \quad \Delta\mathrm{H^o} = -92.0\ Kjmol^{-1} \qquad 2.6$$

This process of chemical nitrogen fixation requires very high pressures and temperatures hence require specialized equipment, making the process very expensive. This increases the capital and running costs when the plant is built. Efforts by scientists to come up with processes that are more efficient to replace the Haber-Bosch process are underway with the major objective of lowering the energy input in producing ammonia (ApplMax, 2005). The Haber process (ApplMax, 2005) can be summarized as shown in Figure 2.6;

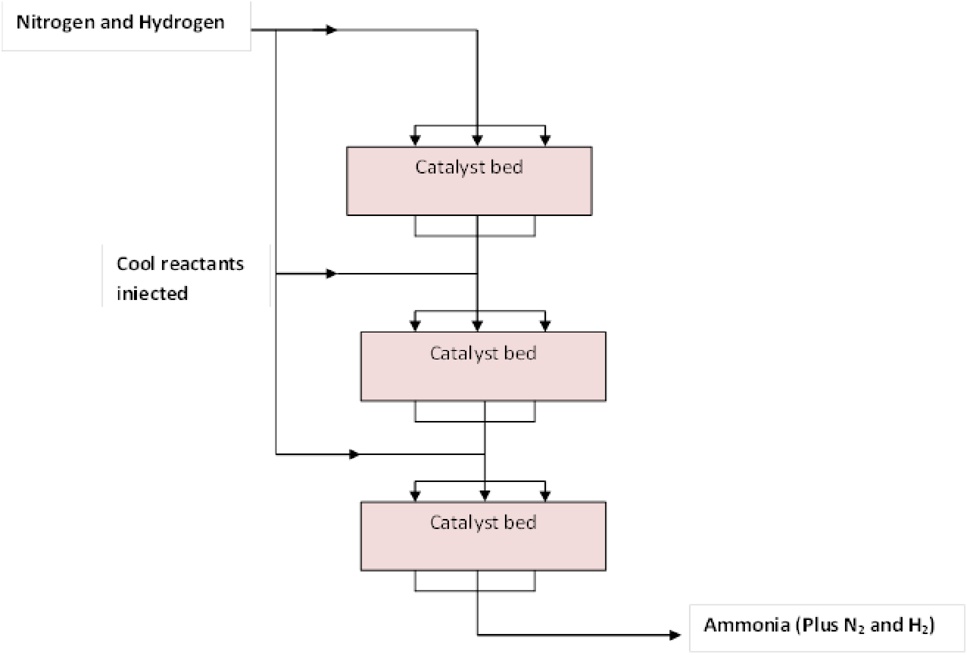


Figure 2.6: The Haber process (ApplMax, 2005)

Natural gas mainly methane is the major source of hydrogen. Methane is converted to hydrogen in the presence of steam and nickel catalyst, in which carbon and hydrogen molecules are separated (ApplMax, 2005). Equations 2.7, 2.8 and 2.9 give a summary of these processes:

$$C_6\,H_{4(g)} + 6\,H_2O_{(l)} \xrightarrow{\text{Nickel,700℃}} 6CO_{(g)} + 13H_{2(g)} \qquad 2.7$$

$$CH_{4(g)} + H_2O_{(l)} \xrightarrow{\text{Nickel,700℃}} CO_{(g)} + 3H_{2(g)} \qquad 2.8$$

$$C_6\,H_{14(g)} + 3\,O_{2(g)} \xrightarrow{\text{Nickel,700℃}} 6CO_{(g)} + 7H_{2(g)} \qquad 2.9$$

CHAPTER 3

3 Materials and Methods

3.1 Introduction

This chapter describes the research methods, procedures, materials, chemicals as well as the procedures and instruments used in the preparation of diammonium phosphate (DAP) fertilizer. It also describes the characterization of the diammonium phosphate synthesized in terms of percent composition of nitrogen and phosphorus as well as the efficacy studies in growing of tomatoes in a greenhouse.

3.2 Research design

The study was conducted in a six step process, (a) extraction of nitrogen from air, (b) use of the extracted nitrogen in the preparation of lithium nitride which was hydrolysed to obtain ammonia and LiOH, (c) fabrication and optimization of the LiCl electrolytic cell, (d) extraction of phosphate from animal bones into phosphoric acid to produce bone phosphate enriched acid for the production of diammonium phosphate fertilizer, (e) reaction of bone phosphate-enriched phosphoric acid with ammonia to form DAP and (f) evaluation of the efficacy of the DAP in tomato growing in a greenhouse.

3.3 Chemicals and reagents

All the chemicals and reagents used were of analytical reagent grade unless otherwise stated. All solutions were prepared in volumetric flasks using deionized water. All chemicals and reagents were bought from Kobian Kenya Limited, Nairobi and used as received. Compressed air in 34 kg cylinders were bought from BOC Kenya, Nairobi. The quality of the compressed air was in reference to ISO 8573.1:2010 Class 2. (ISO 8573.1:2010 provides general information about contaminants in compressed-air systems as well as links to the other parts of ISO 8573, either for the measurement of compressed air purity or the specification of compressed-air purity requirements).

3.4 Instrumentation

All the weighing of solids was done on an electronic analytical balance (model, AAA, Adam Equipment Co. Ltd, Britain) while measurements of liquid samples were done using graduated measuring cylinders. Airflow during the extraction of nitrogen from air was measured using an air flow meter while temperature was measured using a pocket-sized thermocouple, Probe M (Portugal). The extraction of phosphorus from bones was done in a glass reactor. Soapy water was used to wash all glassware, rinsed with deionized water and placed in the oven at 110 ^{o}C for drying. Ultraviolet – Visible spectra were recorded on CECIL CE 2041, England UV – Visible spectrophotometer. Water was deionized using the Elgastal Micrimeg deionizer Cartridge Model WSB/4, Britain.

3.5 Collection and pre- treatment of bones

Bones were collected from Kachok Municipal dump site, Kisumu West District, Kenya. They were washed with running tap water, rinsed with de-ionized water and dried in a temperature-controlled oven (WTC binder, 150533, Germany) at 110 ^{o} C for twelve hours. They were reduced in size using a hammer at Kenyatta University Physical Chemistry Research Laboratory and ground using a grinding machine at the Geology and Mines laboratories, Kenya, to enhance the rate of digestion in phosphoric acid.

Figure 3.1: Bones reduced into small size

3.6 Separation of N_2 from air and its reaction with lithium

Nitrogen was obtained from commercial compressed air through the set-up presented in Figure 3.2. The compressed air was bubbled through a concentrated NaOH solution to scrub CO_2. The CO_2 - free air was passed through a column of P_2O_5 on pumice stones to remove any moisture in the air.

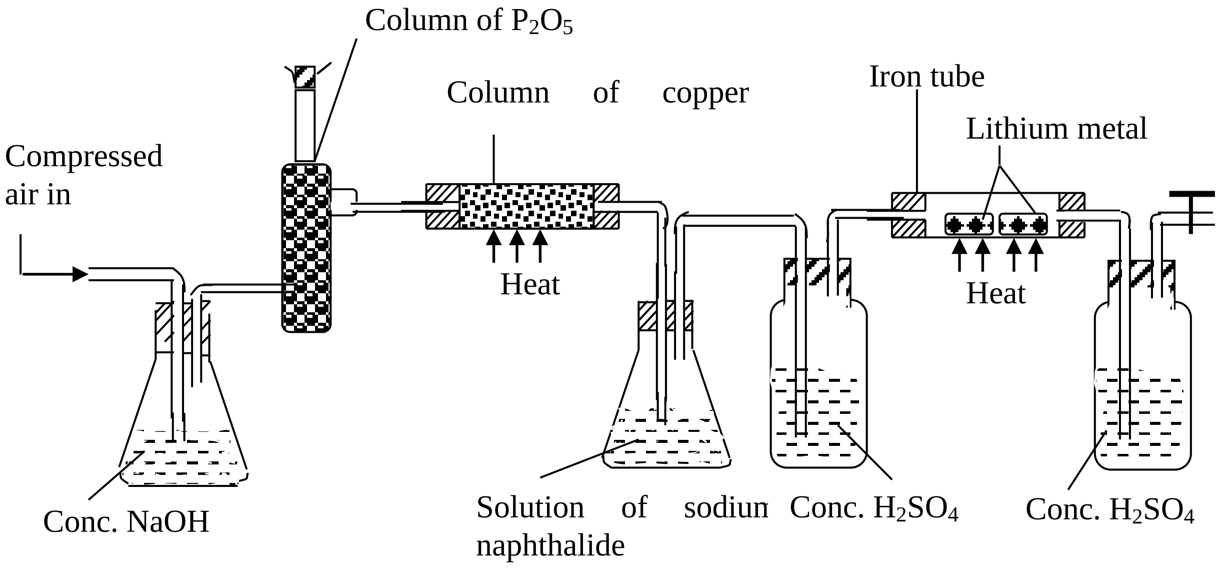


Figure 3.2: Extraction of nitrogen from compressed air and preparation of lithium nitride

The dry, CO_2 – free air was passed through a heated column of copper filings to remove oxygen. The hot, dry CO_2 - free, O_2 - free air exiting from the copper fillings column was bubbled through a solution of sodium naphthalide and then dried by bubbling through a conc. H_2SO_4 solution before being allowed into the vessel containing the metallic lithium for the production of lithium nitride. The set-up of apparatus for the heating of the copper filings column consisted of a clay-lined *Jiko* with a capacity to hold about 5.0 kg charcoal, a 36 mm diameter and 43.5 cm long glass column filled with about 850 g of copper fillings and closed at each end with a vermiculite clay cork. The *Jiko* was filled with about 1 kg of charcoal and lit. The temperature was raised by blowing air through the air hole. The set-up was flushed with a slow current of hydrogen gas to reduce any copper oxides in the heated copper filings until the temperature of the vessel reached 400^{o}C.

When the temperature was about 400 ^{o} C (measured using a pocket-sized thermocouple, Probe M), the hydrogen gas was closed and replaced with compressed air from a cylinder at a rate of 290 ml/sec as measured using an airflow metre and controlled by the regulator for five minutes. The dry nitrogen from the air was then allowed to enter the reaction chamber containing lithium metal in two stainless steel boats. The external temperature of the reaction tube was obtained using a thermocouple placed between the tube and the source of heat. The vessel nearer the entry point of nitrogen gas held 3.0 g of lithium and served as a final protection against oxygen and water vapour while the second vessel contained the 20.0 g of lithium required for the preparation of lithium nitride. The temperatures of heated lithium in the two stainless steel boats were maintained at 250 ^{o} C (using a hot plate) and each experiment lasted on average five minutes. After the experiment, the hot plate was withdrawn and nitrogen gas continuously passed to allow the lithium nitride formed to cool under the inert atmosphere. The boat containing the reddish – brown solid formed was removed and the sample transferred to a flat bottomed flask where the hydrolysis was to take place. This procedure was replicated till all the lithium prepared was used.

The mass of nitrogen separated was estimated from the known volume of air passed over the heated copper granules and the mass of copper oxide formed. The amount of oxygen removed by heated copper was calculated as the difference between mass of the cooled copper oxide formed and the initial mass of copper granules. Air was allowed to flow for five minutes then was stopped and a reducing agent (hydrogen) passed over the hot copper oxide/ copper mixture to regenerate the copper which had been oxidized. The amount of heat energy used in separation of air was calculated using the following *Fourier* series equation (Mills, 1995)

$$q = \left\{ \frac{4\pi k(T_1 - T_0}{\left[\frac{1}{r_1} - \frac{1}{r_0}\right]} \right\}$$

Where,

q = amount of heat transferred
T_1 = temperature inside the column
T_0 = temperature outside the column = constant (thermal conductivity of the column)
r_1 = inner radius of the column
r_0 = outer radius of the column
k = thermal conductivity

3.7 The electrolysis set up and pre- electrolysis

The electrolysis cell comprised of a three chamber arrangement that is the electrolytic cell (4595 cm^3 in volume), a separator compartment (2486 cm^3) and a buffer compartment (994.78 cm^3) fabricated at Kenyatta University engineering workshop out of stainless-steel sheets as described by Jean – Michel Verdier *et al.*, (1986). The details of the fabrication are given in *Appendix 8*. The electrolytic cell comprised of a stainless steel housing equipped with a single anode/cathode pair. The cathode was a perforated cylindrical stainless sheet welded to the bottom of the cell. The perforations permitted the circulation of the electrolytic medium within the electrolyser. The height was such that the upper end electrode would continuously remain under the surface of the electrolyte (when the cell is in operation). The anode was a cylindrical graphite rod positioned within the cathode but not touching the bottom of the cell. It was protected from Cl_2 attack by alumina sheathing over the surface area extending above the electrolytic medium and slightly below the surface of the medium (when the cell is in operation). The graphite electrode was held onto the cell head cylinder using high temperature aluminium oxide/ cement/ clay paste.

The temperature of the cell was monitored by a temperature probe thermocouple in a stainless-steel sheath located 2 cm above the bottom of the electrochemical cell. Scotch tape was wound round the electrolytic cell housing before the heating nichrome wire was wound round to avoid possible short circuiting. A layer of flexible insulation made of clay and aluminium oxide was also wrapped around the cell. The temperature of the cell was raised from room temperature to 450 ^{o} C at the rate of 10^{o} C/ min and recorded by the thermocouple. The gas outlet was dipped into a solution of concentrated sodium hydroxide to remove the resultant gas during electrolysis.

The electrolyte concentration was kept at 58 mol % LiCl- 42 mol % KCl mixture by addition of lithium chloride depleted through the buffer vessel. The graphite electrode was held into the cell head cylinder using high temperature aluminium oxide/ cement/ clay paste. Electrical connections were supplied by use of crocodile clips crimped to the electrodes and connected to the battery that was charged using a solar/ wind power system described below. Pre – electrolysis was first performed to test the influence of applied voltage on current efficiency of the cell. Predetermined amounts of lithium chloride and potassium chloride were weighed and placed into the cell and sealed. The cell was maintained under a continuous flow of argon during the pre - electrolysis period. The cell was connected to the battery power source where voltage was programmed to vary from 1.2 V – 2.7 V. Then the melting began by raising the temperature to 456^{o}C. The applied voltage that was used in the main electrolysis process was determined and recorded.

3.7.1 The pump

This was used to circulate the molten electrolyte during electrolysis. Its motor was equipped with a gearing system to reduce the speed from 1500 revolutions to 750 revolutions per minute and had a reverse interlocking system.

3.7.2 The separator

This was a cylindrical decantation compartment equipped with an outlet for discharging the upper light phase (the lithium metal) by overflow and an outlet for discharging the dense bottom phase that is the mixture of molten salts for recycling, to the buffer. It was made of stainless steel cylinder measuring 50 cm (height) x 25 cm (diameter) and a 0.75 cm pipe that would act as an inlet for withdrawal of lithium from the main cell during electrolysis. Inside the cylinder was a thin circular sheet then inserted which would act as a separator for the light and denser phase of the electrolyte.

3.7.3 The buffer

This cylindrical compartment was used to replace the amount of LiCl in the electrolyte that was consumed as a result of electrolysis. The buffer vessel was made from a cylindrical stainless steel sheet measuring 25 cm (height) x 20 cm (diameter) and 0.75” diameter pipe from the separator and another pipe that would be used to feed the depleted electrolyte.

3.7.4 The battery

A wind-solar hybrid system was connected to a storage battery type N100 manufactured by Associated Battery Manufacturers (ABM), Kenya. The voltage outputs from solar PV, wind and battery storage passed through individual DC/AC and AC/DC units, were integrated on the DC side and diverged to a single DC/AC inverter that acted as an interface between the power sources and the grid to provide the desired power. It had a storage capacity of 200 Ah which was used as storage medium and a voltage stabilizer. The battery rating was voltage of 12V with a current of 3.54A.

3.8 Electrolysis of molten KCl – LiCl mixture

Energy for electrolysis was drawn from a storage battery, type N100 (Associated Battery Manufacturers, Kenya) continuously charged by a wind-solar hybrid system. It had a storage capacity of 200 Ah, output 12V and 3.54A current.

Lithium chloride, LiCl (3859 g) and KCl (3150 g) were dried separately at 480 ^{o}C in an oven to a constant weight. They were mixed while in the oven and transferred to the electrolyte cell. The temperature of the cell was raised to 450 ^{o}C, at which electrolysis of the molten mixture takes place. Measurement of the molten salt temperatures was done using an R – type thermocouple that was placed in an alumina sheath imerced in the molten salt

The electrolysis was carried out continuously for five days and the mass of lithium collected by overflow method from the separator at an average of 23.02 g into the receiver flask that was maintained under a continuous flow of argon gas. The separator was heated through two points to maintain the same temperature as that of the electrolyte. The depleted LiCl was added through a provision at the buffer vessel. The amount of lithium depleted was calculated using the equation:

$$\text{Number of moles of electrons transferred} = \frac{\text{It}}{\text{F}} \qquad 3.1$$

Where,

I = current,
t = time,
F = Faraday’s constant = 96485C/mol.

The quantitative aspects of electrolysis developed by Faraday, (1907), Strong, (1961) and Ehl, (1954), as summarized the equations below.

The anode reaction includes: $\mathrm{Cl^- \rightarrow Cl_2 + 2e^-}$ 3.2

The cathode reaction includes: $\mathrm{Li^+ + e^- \rightarrow Li}$ 3.3

The overall reaction: $\mathrm{\mathbf{2}LiCl \rightarrow 2Li + Cl_2}$ 3.4

Mass of lithium deposited was calculated using the equation;

$$\frac{Q}{F} \times \frac{M}{Z} \frac{(3.54 \times 3600)}{96485} \times \frac{6.947}{1} \qquad 3.5$$

Where

Q = charge; F = Faradays constant; M = RMM of Lithium metal and Z = number of electrons.

The total charge, Q, which passes through an electrolytic cell can be expressed as the current *It* or *nF*. These equations were used to determine amount of materials used or generated during electrolysis, the reaction time and the current.

3.9 Preparation of standard solutions (stock solutions)

3.9.1 Phosphate solution

Potassium dihydrogen phosphate (0.2198 g) was accurately weighed and transferred into a 1000 ml volumetric flask. It was dissolved in deionized water and the volume was made up to 1000 ml mark. The working phosphate solutions of different concentrations were prepared by serial dilution of the stock solution (Skoog, (2004).

3.9.2 Ammonium molybdate solution

Warm water (100 ml) was used to dissolve ammonium molybdate (1.708 g); cooled and transferred into 250 ml volumetric flask and diluted to the mark using deionized water, 50 ml of this ammonium molybdate reagent was transferred again to 100 ml volumetric flask and diluted to the mark using distilled water (Skoog, (2004).

3.9.3 Molar sulphuric acid solution

Concentrated sulphuric acid solution (280 ml, specific gravity = 1.84 g/l) was diluted to 1000 ml in a 1000 ml of volumetric flask. It was used to precipitate the $Ca^{2+}$from the digested bones.

3.9.4 Hydrazine sulphate solution

Hydrazine sulphate (1.5 g) was accurately weighed and dissolved with distilled water in a clean beaker then transferred to 1000 ml volumetric flask and made up to calibrated mark. It was used to test for phosphates in both soil and fertilizer samples (Skoog, (2004).

3.9.5 Preparation of the phosphorus standards

A standard phosphate stock solution was prepared by measuring 0.2198 g of potassium di – hydrogen phosphate as highlighted by Skoog, (2004) 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 stock solution to 100 ml volumetric flasks and diluted to the mark with deionized water. 25 ml of each was transferred to the 50 ml volumetric flasks, 5 ml of of molybdate solution was added followed by 2.0 ml of hydrazinium sulphate and diluted to the mark (Skoog, (2004). The flasks were then immersed in boiling water bath for thirty minutes, removed and immerced in ice for twenty minutes to cool rapidly (Skoog, (2004). The volumes were adjusted to the mark using deionized water and absorbances measured using a U.V spectrophotometer at a wavelength of 830 nm against the blank. A calibration curve was plotted and the equation used to calculate the concentration of phosphate in the solutions.

3.10 Bone phosphate extraction

This was done following the procedure highlighted in the article Manufacture of phosphoric acid from hydroxyl apatite contained in the ashes of the incinerated meat – bone ashes by Kinga Krupa – Zuczek *et al*., 2008. The process of evaluating the lowest concentration of phosphoric acid for total dissolution of bones was carried out by varying the concentrations from 0.1 M, 0.2 M, 0.25 M, 0.275 M and 0.3 M. The concentrations were each exposed to 10 g of bones each at 75 ^oC and agitated for two hours. The concentrates were filtered, the unreacted bones were rinsed with deionized water and dried by squeezing between two filter papers. The filtrate was reacted with 6 M H_2SO_4 acid to precipitate the Ca^{2+}. It was filtered and the acid concentration in the filtrate determined by back titration. The % P in the filtrate was determined and results recorded in Table 4.3. From the results it was determined that the lowest concentration of phosphosric acid to completely dissolve bones was 0.275 M. Therefore, volumes of 10000 ml of 0.275 M phosphoric acid were used to dissolve 10 kg of bones in plastic containers for a period of seven days. A stirring bar was used for stirring the solutions after every twenty four hours to ensure that all the bones were dissolved. The laboratory temperatures varied between 21 – 25 ^oC during this period of experiment. Ten twenty-litre plastic containers were used in dissolution of bones and replicate measurements were done for a period of two months to dissolve about 130 kg of bones and to confirm the solubility data. The resulting mixture was filtered and stored. 5.0 ml of the sample was measured and dissolved in 50 ml of deionized water each. The solution was then transferred to three 100 ml of volumetric flasks separately and diluted up to the mark with deionized water (Amponsah *et al*., (2014). A solution of each sample (1.0 ml) was transferred to a 25 ml volumetric flask followed by 2 ml of 2.5 % ammonium molybdate and 0.5 ml of 1 M sulphuric acid solutions. The mixture was shaken before adding 1.0 ml of 0.5 M hydrazine hydrate solution and the volume made up to mark with deionized water (Amponsah *et* *al*., (2014). Colour developed fully when the solution was allowed to stand for 45 minutes. Absorbance was taken at a wavelength of 830 nm (Amponsah *et al*., (2014). A calibration curve (Figure 4.1) for the standard phosphate solutions was used to calculate the concentration of phosphate in the enhanced phosphoric acid. The values obtained for PO_4^{3-} were converted to Total phosphorus by multiplying with 0.3261 and the values were converted to P_2O_5 by multiplying by 2.2915. The results were recorded in Table 4.6.

3.11 Synthesis of Diammonium Phosphate

An average amount (156.09 g) of lithium nitride was ground in a mortar and placed in a flat bottomed flask and a separatory funnel attached to the flask. 150 ml of deionized water was added to the flat-bottomed flask through the separatory funnel to initiate hydrolysis. The ammonia gas produced passed through a delivery tube to a beaker containing 200 ml of 4.58 M H_3PO_4 extracted from bones as described in Section 3.10. This experiment was repeated eight times to enable use of all the lithium nitride solid that had been prepared. The beaker containing 4.58 M phosphoric acid (200 ml) was immersed in basin containing ice because the reaction was highly 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 at room temperature for seven days and weighed. A total of 3170.60g of the crystals formed were analysed for percentage composition of phosphorus spectrophotometrically as described in below.

3.11.1 Characterization of diammonium phosphate fertilizer

Determination of phosphorus in the fertilizer

The sample of synthesized fertilizer (5.0 g) was weighed out and dissolved in 50 ml of deionized water. The solution was then filtered through a Whatmann-41 filter paper and the filtrate transferred to a 100 ml of volumetric flask and diluted up to the mark with deionized water (Amponsah *et al*., (2014). A solution of sample (1.0 ml) was transferred to a 25 ml volumetric flask followed by 2 ml of 2.5 % ammonium molybdate and 0.5 ml of 1 M sulphuric acid solution (Amponsah *et al*., (2014). The mixture was shaken before adding 1.0 ml of 0.5 M hydrazine hydrate solution and the volume made up to mark with deionized water. The solution was allowed to stand for about 45 minutes for maximum colour development (Amponsah *et al*., (2014). Absorbance was taken at a wavelength of 830 nm. Similarly, the absorbance values for the fertilizer samples were measured and the corresponding concentrations of phosphorus were obtained using the equation from the calibration curve (Amponsah *et al*., (2014). The procedure was replicated for the commercial fertilizer. From the experimentally determined phosphorus concentration, the percentage P_2O_5 in the fertilizer was calculated from the equation:

$$\%P_2O_5 = Conc\ of\ P(g/l) \times \frac{100l}{g\ of\ fertilizer} \times 10^{-6}\ g/mg \times M_r of\ \frac{P_2O_5}{2g}.at.wt.P$$

Where g. of fert = weight of fertilizer measured

M_r of P_2O_5 = Molecular weight of phosphorus pentoxide

g. at. wt. of P = gram atomic weight of phosphorus

Three replicate determinations were obtained for each different fertilizer. The comparison between the value percentage P_2O_5 and to the commercial fertilizer were done.

Determination of Nitrogen in the fertilizer

The nitrogen in the fertilizer samples was determined by the Kjeldahl method. A mass of 1.0 g of the diammonium phosphate fertilizer prepared was weighed and transferred to a two-necked digestion flask and set up for distillation. A receiver flask containing 25.0 ml of 4% boric acid solution was attached to the distillation unit. About 50.0 cm^3 of NaOH (40%) solution added to the fertilizer in the flask to initiate evolution of ammonia which was absorbed into the boric acid in the receiver flask. Distillation took 20 minutes after which the receiver flask was removed; 5 drops of screened methyl red indicator solution were added to the distillate receiver flask and titrated against 0.05 M sulphuric acid to a grey end point. The procedure was repeated three times and results averaged. Two blank titrations were run and the average blank value used for subsequent calculations. The content of nitrogen, (W_N), in milligrams per gram, was calculated using the formula:

$$\frac{(V_1 - V_0) x [H^+] x M_N x 100}{(m x m_t)} = W_N$$ Where,

V_1 = the volume, in ml of the sulphuric acid used in the titration of the sample

V_0 = the volume, in ml of the sulphuric acid used in the titration of the blank test

$[H^+]$ = the concentration of H^+ in the sulphuric acid in moles per litre (e.g. if 0.01 mol/l sulphuric acid is used, $[H^+]$ = 0.01 mol/l)

M_N = the molar mass of nitrogen, in grams per mole (=14)

m = the mass of test sample

m_t = the dry residue, expressed as g / 100g on the basis of oven dried material according to the standard of the special material.

Determination of Moisture in the fertilizer

The moisture content of the fertilizer prepared was determined gravimetrically (Masayoshi Koshino, 1998). About 50 g of the sample was transferred to a weighing dish and first dried in a desiccator for twenty four hours to a constant mass before subjecting it to the oven temperature. It is believed that the sample would “crawl” if dried rapidly hence cause inaccurate results (Masayoshi Koshino, 1998). The sample was then placed in an oven set at 110 °C for five hours and dried to a constant mass. It was then transferred to a desiccator for cooling. Five replications were done using the same procedure. The % moisture content was calculated using the equation

$$\frac{(\text{Mass of initial sample } - \text{Mass of dried sample})}{\text{Mass of initial sample}} \times 100$$

3.12 Efficacy evaluation of diammonium phosphate

The efficacy of the diammonium phosphate fertilizer prepared in the laboratory was evaluated by growing tomatoes in the greenhouse with the commercially obtained fertilizer as the positive control.

3.12.1 The seedbed

A Nursery seedbed site, 1 m x 1 m was prepared under a tree whose soils were pulverised and sieved. The seeds were mixed with sand at a volume ratio of one to one and sown in shallow farrows in seed beds that were raised 15 cm in depth. Tomato seeds being so tiny and difficult to handle, care and precaution was taken to avoid ending up with a pile of seeds on the seed plot. Piling of seeds could also lead to reduction in germination rates and increase in time spent on thinning. Hence, mixing seed with sand helped in spreading the seeds hence a less likelihood of droping to drop many seeds in any one spot. It was difficult to estimate the spread of soil to four times the size of the seed, hence, need to mix with sand provided a thin cover to avoid drying immediately the seeds sprouts and also help to avoid seeds being buried so deeply as they would die before they emerge from its blanket of soil. The bed was covered with dry leaves to reduce moisture loss and splashing effect during watering. Watering was done twice a day during early morning and evening. After two weeks after sprouting, spacing was done by thinning to avoid weakening of the seedlings. The seedlings were then transplanted to the greenhouse after four weeks.

3.12.2 The greenhouse

The greenhouse measuring 6 m x 10 m (Fig. 3.3) that was used during the study was built at Kenyatta University Appropriate Technology Centre.

Figure 3.3: Greenhouse

Quantitative test for phosphorus of the soils in the green house

The surface of the plots in the green house were first cleared off the litter. A spade was used to scoop soil from each of the three plots (at the middle of each plot) to a depth of 25 cm. The samples were then mixed thoroughly with the spade, air-dried for 3 days and sieved. A portion of the dried soil (2.0 g) was accurately weighed and transferred to a 250 ml conical flask followed by 60 ml of *aqua regia*. The mixture was shaken in a mechanical shaker for 30 min and left to stand for 6 h 30 min. The mixture was then filtered using filter paper Whatman No. 41 (Amponsah *et al*., (2014).

About 15 ml of the filtrate was transferred to a 25 ml volumetric flask followed by 3 ml of ammonium molybdate and 2 ml of hydrazine sulphate and the mixture made to the mark with distilled water (Amponsah *et al.*, (2014). The mixture was then kept in a water bath for 30 min (Amponsah *et al.*, (2014). The intensity of the blue colour observed was measured spectrophotometrically on a UV/Vis spectrophotometer (Oladeji *et al.*, 2016; Fummilayalo and Oladeji, 2016). The amount of available phosphorus (PO_4^{3-}) in the soil was found to be 198ppm

Quantitative determination of total nitrogen in the soils

A soil sample (0.2 g) was dried and ground then transferred to the digestion flask followed by 10 ml of sulphuric acid and swirling until the acid was thoroughly mixed with the sample. The mixture was allowed to stand and cool to room temperature; 2.5 g of the catalyst mixture (made by mixing and thoroughly grinding together 200 g of potassium sulphate, 20 g of copper sulphate pentahydrate and 20 g of titanium dioxide) was added to the mixture and heated until the digestion mixture became clear. The mixture was then boiled gently for up to 5 hours to allow the sulphuric acid to condense about ⅓ of the way up to the neck of the flask.

The flask was allowed to cool after which 20 ml of deionized water was added slowly while shaking. The flask was swirled to bring any insoluble material into suspension and the contents transferred to the distillation apparatus. The flask was rinsed three times with deionized water to complete the transfer. Boric acid (5.0 ml) was transferred to a 200 ml conical flask which was then placed under the condenser of the distillation apparatus in such a way that the end of the condenser dipped into the solution. Sodium hydroxide solution (20 ml) was added slowly into the distillation chamber. About 100 ml of condensate was distilled off and collected. The three drops of mixed indicator was added to the distillate which was then titrated against 0.5 M sulphuric acid to a violet endpoint. The means were as a result of four determinations each. The results for the content of plant available nitrogen gave the amount of nitrogen directly available in soils for subsequent uptake by plants. It also guided in determining adequate fertilizer application.

Division of the plots

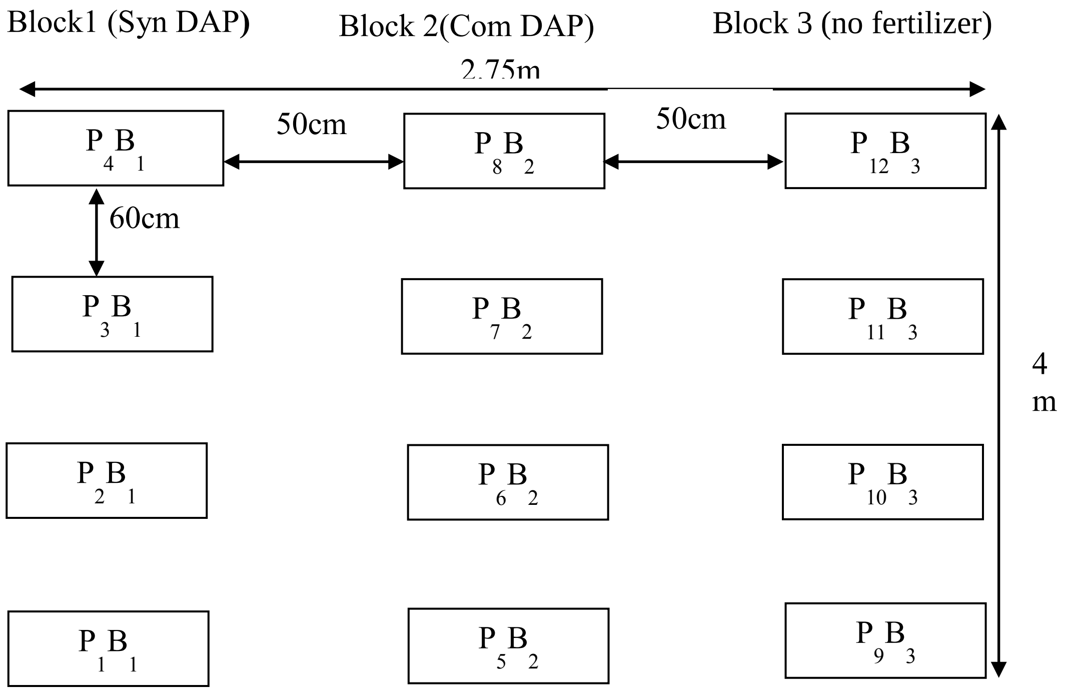


Figure 3.4: Diagrammatic representation of plots in the greenhouse

The green house was divided into three blocks, B$_1$, B$_2$, and B$_3$ measuring 4 m x 2.75 m each with a space of 50 cm between the blocks. Each block was divided into four plots measuring 90 cm x 180 cm, each with a distance of 60cm between the plots as shown in Fig. 3.4. In block B$_1$, tomato plants were grown with synthesized DAP fertilizer, in B$_2$, tomato plants were grown with commercial DAP fertilizer while in B$_3$, tomato plants were grown without fertilizer. In each plot seedlings were planted in 2 rows spaced 35 cm apart. Each row contained 5 plants hence one plot contained 10 plants. Irrigation was done by installing a trickle watering system. A hose was placed along the plots and connected to the water tank (FAO of the United Nations, Rome. 2013). A thermostat was installed to register maximum and minimum temperatures.

Transplanting of seedlings.

The main plots in the greenhouse were thoroughly prepared before transplanting because the roots of tomatoes are very weak. Reduction in soil compaction and maximum root growth was achieved by raising the beds of the soils. The rows to which the seedlings were to be transplanted were uniformly applied with fertilizers and covered with fine soil of approximately 2 cm depth before applying water.to curb the edge effects, more tomato seedlings were planted along the borders. All standard practises such as removal of weeds, controlling diseases (done every after six weeks), pest control (greenhouse was completely sealed and the opening of the door controlled as a way of controlling pest attack) and irrigation (done continuously) were performed during the duration of growth.

The plants that were to be used for data collection were coded in such a way that they could be distinguished from the rest of the population. They were coded by attaching colourful strings to make the plants easier to be identified. The five plants were used for data collection throughout the experiment period. A piece of wood of length 1 m and of size 1’ x 1’ was marked in centimetres and placed alongside the yardstick onto which the sisal twine was used to track the height of the tomato plants. This process was repeated for collecting data for each tomato plant that was tagged.

Measurement of plant heights in centimetres was done from the base to the top of mature leaf. The change in root lengths were determined using the core broken method where visible roots were extracted from the broken soil column and measured directly. The leaves from the plants selected for data collection were also coded. Measurement of leaf lengths was done from the lamina and petiole and the width was measured from the end of the tips and the distance between the widest lamina lobes. The data was taken every after one week for the first two weeks then after every after two weeks from week two to week twelve and comprehensive results recorded in the *Tables 4.9 – 4.12* in the *Section 4.8*.

CHAPTER 4

4 Results and discussion

4.1 Introduction

The goal of this study was to prepare diammonium phosphate fertilizer using bone phosphate-enriched phosphoric acid and ammonia obtained by hydrolysis of lithium nitride. This chapter presents results for processes of separating nitrogen from air and its conversion to lithium nitride and hydrolysis of the nitride to ammonia. The results of extraction of bone phosphate into phosphoric acid and the reaction of bone phosphate enriched phosphoric acid with ammonia to give diammonium phosphate fertilizer, characterization of the fertilizer prepared and determination of the efficacy of the same in the growing of tomatoes in the green house are also presented and discussed.

4.2 Separation of nitrogen from air

This was achieved by removing oxygen, CO_2 and water vapour from air. The optimum working temperature for maximum oxygen removal from the air was determined by varying the working temperature and measuring the percent oxygen removal. Table 4.1 gives results of percentage O_2 separated when air was passed over heated a constant mass of copper filings (850g) for 300 seconds at different temperatures.

Table 4.1: Mean of O_2 (%) removed from air at different temperatures

Temperature ^{o}C	Volume of air passed (ml)/sec	Total volume of air passed for 5 minutes(ml)	Mass of copper oxide formed (g)	Initial mass of copper granules (ml)	Volume of nitrogen extracted	Mean % (±SD) O_2 percentage separated
200	293.34	88002	874.51	850	68641.56	92.70 ± 1.375^{a}
250	291.72	87516	875.05	850	68262.48	95.43 ± 1.809^{b}
300	291.48	87444	875.26	850	68206.32	$96.31\ 1.577^{bd}$
350	291.12	87336	875.10	850	68122.08	95.89 ± 1.481^{cbd}
400	290.61	87183	875.83	850	68002.74	98.79 ± 1.297^{ed}

Values with similar superscript letters indicate no significant difference.

From the results in Table 4.1, the amount of oxygen separated generally increased with increase in temperature. However, there was no significant increase in oxygen separated between 250 ^{o}C and 350 ^{o}C, though the increase in percentage oxygen separated between 350 ^{o}C and 400 ^{o}C was significant at (p-values = 0.000 < 0.05). The temperature of 400 ^{o}C was, therefore, used in the separation of oxygen from air. The percentages of oxygen separated ranged from 92.7 to 98.8 %, indicating that there was effective diffusion of oxygen into copper from 200 to 400 ^{o}C. However, all oxygen was supposed to be separated from air in order to get pure nitrogen which was supposed to react with lithium. To ensure that no traces of oxygen that passed without reacting with the heated copper fillings reached the reaction vessel that contained heated lithium, the gas was passed through a solution of sodium naphthalide. From the total volume of 8700 ml of air passed at a temperature of 400 ^{o}C, the volume of oxygen separated was 18081 ml (98.96 % separation) and 67860 ml of nitrogen extracted.

4.3 Reaction of nitrogen with lithium

About 1.25 kg of lithium formed during electrolysis reacted with nitrogen gas at 250 ^{o}C, giving 1980.09 g (94.75 %) conversion to lithium nitride as a reddish brown solid. When hydrolysed there was a conversion of 94.75 % of Li_3N to ammonia that reacted directly with bone phosphate enriched phosphoric acid to form 3170 g of diammonium phosphate fertilizer. Heated lithium glowed within the first one minute of the reaction an indication of rapid diffusion of nitrogen through molten lithium. The diatomic molecule dissociates on absorption then diffuses in the atomic form.

4.4 Pre – electrolysis and electrolysis of LiCl – KCl mixture

The working conditions that is, applied voltage, time and current density were obtained and recorded as summarized in Table 4.2.

Table 4.2: Change in voltage and current with time

Cell voltage (V)	Current density(A)/M^2	Current (A)	Time (min)	Resistance	Current efficiency (%)
1.20	0.85	4.49	17.4	0.267	89.0
1.40	0.94	4.06	21.3	0.345	87.9
1.53	1.06	3.60	27.6	0.425	88.0
1.85	1.08	3.54	46.5	0.522	89.9
2.00	1.09	3.50	43.9	0.571	81.6
2.19	1.18	3.24	42.2	0.676	78.9
2.20	1.57	2.43	42.4	0.905	75.0
2.27	1.32	2.89	42.7	0.978	73.0

The observations made indicate that the efficieny of current passed decreased with decreasing current that was applied from 89.0 – 73.0 %) and that efficiency of current was decreasing as time and voltage was increasing. This was as a result of electrolyte depletetion and increase in current density that increased molecular movements hence reducing the contact time of the electrolyte with the electrodes. The high current efficiency was also influenced by lower viscosity of the electrolyte which also influences mass transport including delivery of ions to the electrodes. The best current observed in production of lithium was 3.54 A.

The decreasing current from 4.49 A is an indication of a higher electric conductivity of the salt at increased potential.this shows that more the current was being passed through the salt, the more it was being wasted. It was also noted that the energy being consumed during electrolysis was highly dependent on the current. The voltage also changed marginally as the current decreased rapidly an indicator that the system resistance was very low. After establishing the voltage (1.85V) and current (3.54A) to be applied on the electrolysis cell, the process of electrolysing lithium chloride/ potassium chloride mixture was allowed to run continuously for five days and the mass of lithium was collected by overflow method.

4.5 Extraction of bone phosphate

The evaluation of the effect of change of concentration of phosphoric acid on bone dissolution was as shown in Table 4.3

Table 4.3: Change of acid concentration on bone dissolution

Molarity of phosphoric acid (g/l)	Bones: Volume of acid ratio (g: ml)	Acid concentration after dissolution (g/l)	Mass of unreacted bones (g)	% P in the filtrate	Concentration of H_2SO_4 used (g/l)
0.1	10:35	0.135	4.3	19.41	6
0.2	10:35	0.241	4.0	19.39	6
0.25	10:35	0.290	4.0	19.78	6
0.27	10:35	0.355	0.0	19.84	6
0.3	10:35	0.356	0.0	19.83	6

Dissolution of bones was not complete when concentrations of 0.1, 0.2, 0.25 M H_3PO_4 was used. Complete dissolution was observed when 0.275 M and 0.3 M were used. This indicated that the concentration of phosphoric acid used determined the extend of dissolution of bones. The mass of dissolved bones in the solvent was expressed as the difference between the initial mass of bones weighed before the experiment and the mass of unreacted bones. The calculation done for the dissolved bones gave the following results % P (19.45), % P_2O_5 (44.58) and concentration of phosphoric acid was raised from 0.275 M to 4.58 M signifying significant phosphate enrichment.

4.6 Determination of (% N and PO_4^{-3}) in the soil

The determination of % N and PO_4^{-3} of the soil used for growing tomatoes in the greenhouse was done and results obtained are as shown in Table 4.4.

Table 4.4: % N and PO_4^{-3} determinations

Soil samples	Mean % N	S.E	Mean PO_4^{-3}(ppm)	S.E
1	0.0303	0.0001	198	0.0001
2	0.0305	0.0001	198	0.0001
3	0.0302	0.0002	198	0.0001

The results indicate low levels of available phosphates (198 ppm) and very low percent nitrogen levels (0.0303). these results are an indication that plants grown without fertilizer can have adverse stunted growth. The results are confirmed by minimal growth rates of tomato plants grown without fertilizer as shown in *Tables 4.9 – 4.12*.

4.7 Synthesis and characterization of diammonium phosphate fertilizer

The yield of the dissolved phosphorus in g/l was determined as a mass percentage of the phosphorus content of the crushed bone which was equivalent to 28.11 % P_2O_5. Reaction of phosphoric acid with ammonia in the ratio of 1.4:1 was a very exothermic reaction with temperatures recorded reaching 95 ^oC. The reaction was exothermic with the highest temperature recorded during the reaction as 95 ^oC but the crystals formed at 51^oC. After the reaction, the temperatures of the reaction vessel were allowed to cool to 26 ^oC. The crystals were filtered from the mother liquor and dried in air giving a mass of 3170.60 g of diammonium phosphate, equivalent to 48.06 % yield.

The calibration curve for the standard solutions was calibrated and the equation used to calculate the concentrations of PO_4^{3-} in the fertilizer prepared and commercially obtained fertilizer.

The values for PO_4^{3-} obtained were converted to Total Phosphorus by multiplying with 0.3261 where as, Total Phosphorus was converted to P_2O_5 by multiplying the values obtained by 2.2915. Table 4.5 shows the average absorbance and concentrations of the standard solutions while Figure 4.1 shows the calibration curve.

Table 4.5: Average absorbance and concentrations of standard solution

Volume (ml) of standards	Average absorbance	Concentration of PO_4^{3-}(ppm)
1	0.2295	0.5580
2	0.3904	1.0204
3	0.5605	1.5092
4	0.7313	2.0000
5	0.9185	2.5379
6	1.0990	3.0566
7	1.2550	3.5049
8	1.3970	3.9129

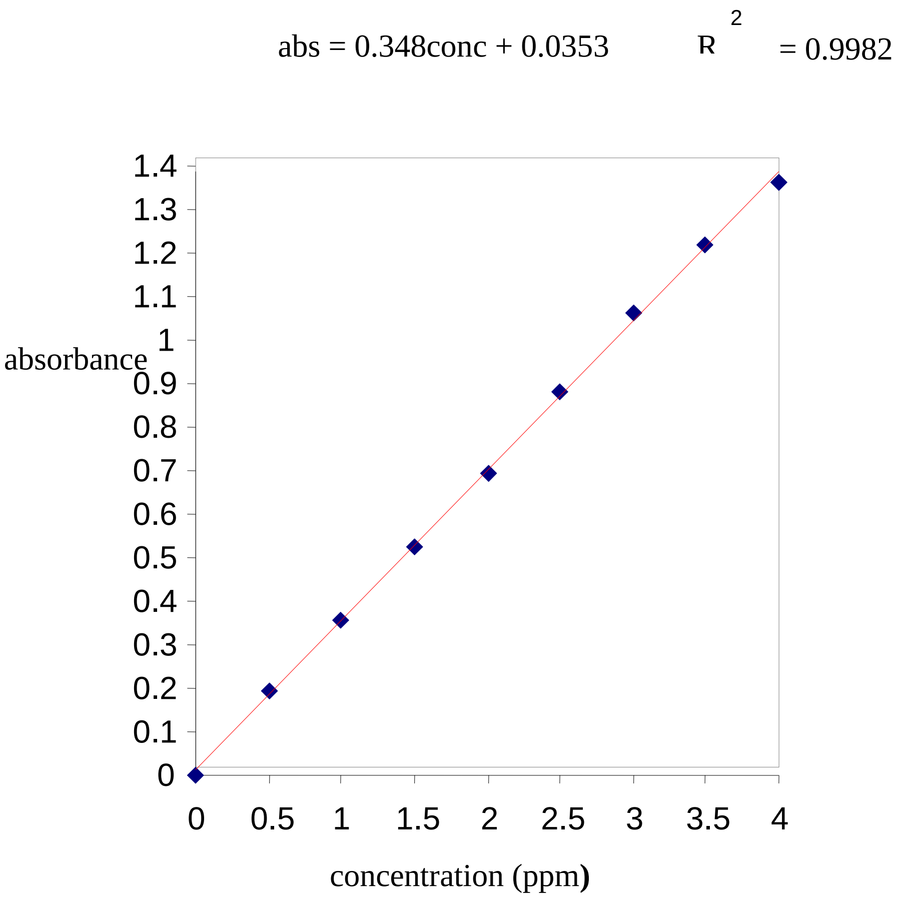


Figure 4.1: Calibration curve for phosphorus standards

Concentration of phosphate levels in the fertilizer was determined using the equation of the calibration curve and results recorded in Table 4.6.

Table 4.6: Levels of % P_2O_5 in Synthesized DAP and commercial DAP

Synthesized DAP	Absorbance	Concentration (ppm)	% P_2O_5	Commercial DAP	Absorbance	Concentration (ppm)	% P_2O_5
Sample 1	0.2428	0.5964	44.56	Sample 1	0.2467	0.6082	45.45
Sample 2	0.2433	0.5976	44.66	Sample 2	0.2471	0.6086	45.48
Sample 3	0.2426	0.5957	44.52	Sample 3	0.2470	0.6083	45.46
Average	-	-	44.58	Average	-	-	45.46
Rsd (%)	-	-	0.23	Rsd (%)	-	-	0.23

Synthesized DAP contained 44.58 % P_2O_5 as compared to 45.46 % P_2O_5 for commercial DAP. The difference could be accounted for by the fact that bones contain 15 – 19 % P and rock phosphate contains 15 ± 1 % P (Coutand *et al.*, 2008). The % N levels in the prepared DAP and commercial DAP were analysed using Kjeldahl process and results recorded in Table 4.7

Table 4.7: Levels of % nitrogen in Synthesized and commercial DAP

Laboratory fertilizer	M_{sample} (g)	V_{sample}(ml)	%N	Commercial fertilizer	M_{sample} (g)	V_{sample}(ml)	%N
Sample 1	0.6034	14.73	17.07	Sample 1	0.6680	16.55	17.35
Sample 2	0.5787	14.22	17.21	Sample 2	0.6979	17.14	17.20
Sample 3	0.6045	14.94	17.31	Sample 3	0.6758	16.78	17.39
Average	-	-	17.19	Average	-	-	17.31
Rsd (%)	-	-	0.77	Rsd (%)	-	-	0.77

Synthesized DAP contained 17.19 % N as compared to commercial DAP (17.39 % N). this could probably be as a result of the effect of poor storage facilitis for the synthesized DAP where some levels of ammonia were lost. The values for the moisture content for the fertilizers determined was recorded in Table 4.8.

Table 4.8: Percentage moisture content in synthesized and commercial DAP

	Mean Weight of Wet Fertilizer (g)	Mean Weight of Dry Fertilizer (g)	% Moisture content
Synthesized DAP	50	23.5	0.53 ± 0.14
Commercial DAP	50	30.5	0.39± 0.06

The synthesized fertilizer contained a higher percentage of moisture (0.53 ± 0.14) as compared to the commercial fertilizer (0.39 ± 0.06). This could be attributed to the solubility levels of the fertilizer. It is assumed that commercial fertilizer contained low moisture content due to the treatment to which it was subjected to in the process of manufacture.

The results for P_2O_5 in synthesized DAP compare well with the results by David, (2016) who observed that the phosphate content of phosphorite varied strongly from 4 % - 20 % P_2O_5 after being enriched or beneficiated to 28 % P_2O_5 through magnetic separation or floatation. Similar efforts to maximize extraction conditions to obtain maximum concentration of P_2O_5 from rock phosphate have also been done by Muhammad *et al*. (2012) in which phosphoric acid is concentrated from 4.8 % P_2O_5 to 65 % P_2O_5.

4.8 Efficacy of the prepared DAP in tomato growth

This was evaluated by applying the fertilizer to tomato plants in a greenhouse and monitoring growth parameters including, height, length of leaf, width of leaf and length of root over a period of twelve weeks. Commercial fertilizer was used as positive control. Tomatoes grown without fertilizer were used as the negative control.

4.8.1 Height of tomato plants

The changes in height of tomatoes planted with lab fertilizer, commercial fertilizer and without fertilizer were measured over a period of twelve weeks. The plant heights were measured weekly for the first two weeks and then every two weeks until the twelfth week. Table 4.9 summarises the results obtained.

Table 4.9: Change in heights of tomato plants with time

Fertilizer/Plant	Tomato plant Heights (cm)							
	Week 1	Week 2	Week 4	Week 6	Week 8	Week 10	Week 12	Margin
Synthesized fertilizer	9.59±0.29^{c}	21.52 ±0.29^{c}	31.42 ±0.29^{c}	33.72 ±0.29^{c}	42.11 ±0.29^{c}	47.93 ±0.29^{c}	51.61 ±0.29^{c}	34.02±0.19
Commercial fertilizer	10.27 ±0.29^{c}	22.33 ±0.29^{c}	28.99 ±0.29^{c}	33.79 ±0.29^{c}	42.446 ±0.29^{c}	49.43 ±0.29^{c}	53.3 ±0.29^{c}	34.37±0.19
No fertilizer	5.69± 0.29^{c}	10.22±0.29^{c}	17.70± 0.29^{c}	18.80± 0.29^{c}	20.04±0.29^{c}	20.04±0.29^{c}	20.41±0.29^{c}	16.13±0.19

It can be seen from the table that the height of the tomato plants which were planted with synthesized fertilizer increased with time from week one reaching max at week twelve. The height attained was not significantly different from what was observed with tomatoes planted with commercial fertilizer (p-values = $0.000 < 0.05$). The height attained in tomatoes planted with synthesized fertilizer was significantly different from the height attained in tomatoes planted without fertilizer (i.e. the negative control). There was increase in heights of tomato plants grown without fertilizers up to week four then reduction in growth as shown by the rates between week six and twelve. This could be attributed to decreasing availability of native phosphorus in the soil. Plants grown with commercial fertilizer gave the largest increase in height, although the increase was not significantly different from change in heights of plants grown with laboratory prepared fertilizer. The relatively high amounts of % N and % P_2O_5 in commercial fertilizer (17.31, 45.46) respectively could be the main reason for the consistently better performance of commercial DAP. The highest height was recorded at week twelve. There was significant decrease in the rate of increase in plant heights after week six in all treatments. This could probably be due to decrease in the levels of nitrogen and phosphorus as plants grew. The rate of increase in height was calculated as an average of the values between two weeks divided by time. For the first interval (between week one and two) growth rate was calculated as the increase in total length per day.

4.8.2 Root length of the tomatoes

The changes in root length of tomatoes planted with synthesized fertilizer, commercial fertilizer and with no fertilizer were measured over a period of twelve weeks. The root length was measured weekly for the first two weeks and then every two weeks until the twelfth week. Table 4.10 summarizes the obtained results.

Table 4.10: Root length of tomato plants

Fertilizer/Plant	Root Length (cm)							
	W_1	W_2	W_4	W_6	W_8	W_{10}	W_{12}	Margin
Average change in root length (Synthesized fertilizer)	2.44±0.423^{c}	13.12±0.423^{c}	14.6±0.423^{c}	16.12 ±0.423^{c}	17.16±0.423^{c}	18.0 ±0.423^{c}	19.0±0.423^{c}	13.917±0.027
Average change in root length (commercial fertilizer)	2.5 ±0.423^{c}	13.12±0.423^{c}	14.70±0.423^{c}	15.94 ± 0.423^{c}	17.20±0.423^{c}	18.96±0.423^{c}	19.62±0.423^{c}	14.388±0.027
Average change in root length (Zero fertilizer)	2.02±0.423^{c}	2.74± 0.423^{c}	3.3± 0.423^{c}	3.98± 0.423^{c}	4.64±0.423^{c}	5.16±0.423^{c}	5.58±0.423^{c}	14.588±0.027

It can be seen from the table that the root length of the tomato plants which were planted with synthesized fertilizer increased from week one and reached maximum at week twelve. There was also increase in root lengths in plants grown with commercial fertilizer from week one to week twelve. The rate of increase in root length was more at the beginning of the planting period, that is, week one and week two than towards the end (week 10 and week twelve). This shows that roots have the greatest demand for phosphorus at early stages of root development. There was suppressed change in root length for plant grown without fertilizers with time as shown by decrease in rate of growth, an indication of phosphorus deficiency. The change in root length for plants grown with synthesized fertilizer was not significantly (p-values = 0.000 < 0.05) different from the change in root length in plants grown with commercial fertilizer. Messele, (2016) describes phosphorus as a stimulant for early root formation and growth that helps in absorption of essential minerals and water.

4.8.3 Variation of leaf length of the tomato plants

The change in leaf length of tomatoes planted with synthesized fertilizer, commercial fertilizer and with no fertilizer was measured over a period of twelve weeks. The leaf length was measured weekly for the first two weeks after transplanting and then after every two weeks until the twelfth week, Table 4.11 summarizes the results obtained. The leaf length continued to increase from week one to week twelve for plants grown with synthesized fertilizer, but the rate of increase of leaf length decreased with time. For example, the leaf length increased from 2.51 cm to 5.67 cm from week one to week two which was equivalent to the rate of change of 0.45cm/day and between week two and week three, the leaf length increased from 5.67 cm to 7.54 cm which was equivalent to a rate of 0.13 cm/day. The leaf length of plants grown with commercial fertilizer also increased from week one to week twelve. The rate of increase of leaf length in cm/day also decreased with time

Table 4.11: Leaf length of tomato plants

Fertilizer/Plant	Leaf Length (cm)							
	W_1	W_2	W_4	W_6	W_8	W_{10}	W_{12}	Margin
Average change in leaf length(synthesized fertilizer)	2.51±0.08 ^{c}	5.67±0.08 ^{c}	7.54±0.08 ^{c}	9.46±0.08 ^{c}	10.55±0.08 ^{c}	11.67±0.08 ^{c}	12.42±0.08 ^{c}	8.549±0.529
Average change in leaf length(commercial fertilizer)	2.39±0.08 ^{c}	5.74±0.08 ^{c}	7.94±0.08 ^{c}	9.48±0.08 ^{c}	10.83±0.08 ^{c}	11.88±0.08 ^{c}	13.06±0.08 ^{c}	8.763±0.529
Average change in leaf length(zero fertilizer)	2.10±0.08 ^{c}	2.92±0.08 ^{c}	3.92±0.08 ^{c}	4.82±0.08 ^{c}	5.24±0.08 ^{c}	5.60 ±0.08 ^{c}	5.88± 0.08 ^{c}	4.355±0.529

For example, between week one and week two, the leaf length increased from 2.10 cm to 2.92 cm giving an increase in rate as 0.11 m/day whereas between week two and week three, there was an increased rate of 0.071 cm/day. Plants to which the fertilizers were applied yielded higher leaf length values as compared to plants where no fertilizer was applied. For the two fertilizers (synthesized and commercial), plants grown with commercial fertilizers yielded higher leaf length values as compared to plants grown with laboratory fertilizer, though, the two fertilizers were not significantly different (p-values = 0.000 < 0.05). Previous research has shown that diammonium phosphate fertilizer has nitrogen which has a promoting effect on the leaf growth (Marschner, 2002).

4.8.4 Leaf width of the tomatoes

The change in leaf width of tomatoes planted with synthesized fertilizer, commercial fertilizer and with no fertilizer was measured over a period of twelve weeks. The leaf width was measured weekly for the first two weeks and then every two weeks until the twelve weeks. Table 4.12 summarizes the results obtained.

Table 4.12: Variation of leaf width of tomato plants

Fertilizer/Plant	Leaf Width (cm) Periods							
	W_1	W_2	W_4	W_6	W_8	W_{10}	W_{12}	Margin
Average change in leaf width (synthesized fertilizer)	1.24± 0.043 ^{c}	2.8± 0.043 ^{c}	3.74±0.043^c	4.60±0.043^c	5.24 ± 0.043 ^{c}	5.74± 0.043 ^{c}	6.20± 0.043 ^{c}	4.222±0.028
Average change in leaf width (commercial fertilizer)	1.2 ±0.043^c	2.84±0.043^c	3.94±0.043^c	4.7 ±0.043^c	5.36 ±0.043^c	5.92±0.043^c	6.5 ±0.043^c	4.348±0.028
Average change in leaf width (zero fertilizer)	1.02 ±0.043^c	1.44 ±0.043^c	1.96 ±0.043^c	2.3 ±0.043^c	2.6 ±0.043^c	2.78 ±0.043^c	2.92 ±0.043^c	2.145±0.028

The leaf width progressively increased from week one to week twelve for plants grown with synthesized fertilizer. The rate of increase in leaf width decreased with time. For example, between week one and week two, the rate was 0.82 cm/day, between week two and week three, the rate was 0.078 cm/day and between week three and week four, the rate was 0.061 cm/day. The leaf width of plants grown with commercial fertilizer also increased from week one to week twelve. The rate of increase in leaf width also decreased from week 1 to week twelve, for example, between week one and week two, the rate of growth was 0.23 cm/day, between week two and week three, the rate was 0.078 cm/day and between week three and week four, the rate was 0.054 cm/day.

The leaf width of plants grown without fertilizer also increased marginally. For example, between week one and week two, the leaf width increased from 1.02 cm to 1 .44 cm giving an increased rate of 0.06 cm/day and between week two and week three, there was an increased rate of 0.03(cm/day). Plants to which the fertilizers were applied yielded higher leaf width values as compared to plants where no fertilizer was applied. Plants grown with commercial fertilizer showed higher leaf width values than plants grown with synthesized fertilizer, but the leaf widths were not significantly different at (p-values = 0.000 < 0.05). Previous research (Marschner, 2002), has shown that the width of tomato leaves increase over time when planted with diammonium phosphate fertilizer. Shah Jahan Leghari *et al.*, (2016) also observes that a significant reduction in the rate of increase in leaf width is as a result of reduced phosphorus over time which leads to reduction in cell division and leaf expansion.

CHAPTER 5

5 Conclusions and Recommendations

5.1 Conclusions

The DAP fertilizer was synthesized, characterized and used to grow tomatoes in a greenhouse with commercial DAP as the positive control. Tomato plants grown without fertilizers served as the negative control. Based on the results discussed in this thesis, the following conclusions can be made:

i) Nitrogen was successfully separated from air and used to generate Li_3N which was hydrolysed to NH_3 for DAP production.

ii) An electrolysis cell was fabricated, optimized and used to recycle LiOH produced in the hydrolysis of Li_3N. It was powered by a solar/ wind hybrid system.

iii) Bone phosphate was successfully extracted by acid hydrolysis thereby enriching commercial phosphoric acid from 0.275 M phosphoric acid to 4.58 M.

iv) DAP fertilizer was sucessfuly prepared by reacting NH_3 from hydrolysis of Li_3N and bone phosphate enriched phosphoric acid.

v) The DAP obtained was as efficacious as the commercial DAP in growing tomatoes in the green house.

5.2 Recommendations from the study

While a stepwise reaction scheme has been developed, it is recommended that a continuous process be employed during implementation.

References

Amponsha, D. Etsey, G and Nagai, H (2014). Determination of amount of Phosphate and Siulphate in Soil Samples from University of Cape Coast Farm. *International Journal of Science and Technology*. (3) 7: 9 – 11.

Appl, Max (2005), "Ammonia", Ullman's Encyclopaedia of Industrial Chemistry, 40 Volume set. 7th Ed. Weinheim: Wiley-VCH. (27989 – 28005).

Ball Jeff, (2007). Back to Basics: The Roles of N, P, K and Their Sources. *International Journal of Current. Microbiology and Applied Sciences*. (3) 6: 1085 – 1095.

Brink, J.W. (1977). World resources of phosphorus. Ciba Found. Symposium. 57: 23-48.

Cauyela, M. Markus W., Ribbe and Yilin, Hu. (2009). Mineralization dynamical and biochemical properties during initial decomposition of plant and animal residues in soil. *Journal of Applied Soil Ecology*. 41:118-127.

Christopher, H. Vegna, R and Jorana, H. (2018). Phosphorus as a bottleneck for a suitable food supply. *Contemporary Agriculture*. (2) 67: 117 -182.

Considine, M. (1994). Chemical and Process Technology Encyclopedia. McGraw-Hill Book Publishers Ltd. 869- 871).

Cordell, D. White Markus W., Ribbe and Yilin, Hu, S. (2009). The story of Phosphorus! Global Food Security and Food for Thought. *Global Environmental Change.* 19: 292-305.

Cordell, D and Stewart, W. (2011). Peak Phosphorus: Clarifying the key issues of a vigorous Debate about long term phosphorus security and sustainability. *Sustainability*. 3: 2022 – 2049.

Cordell, D. Schroder, J. Smith, A and Rose Mavin. (2010). Sustainable use of phosphorus. *Plant Research International Report*. 357

Coutand, M. Markus W., Ribbe and Yilin, Hu. (2008). Characteristics of Industrial and Laboratory Meat and Bone Meal ashes and their potential application. *Journal of Hazard Materials.* 150: 522- 532.

David R (2016). World Ammonia Production. *Nature Geoscience*. (1)10: 636-639.

Deryl, P and Anderson, B. (2007). Peak Phosphorus. *Energy Bulletin*. 33164.

Driver, J., Lijmbach, D. and Steen, I. (1999). Why Recover Phosphorus for Recycling and How? *Environmental Technology*. (7) 20: 651 – 662

EcoSanRes, (2003). Closing the loop on Phosphorus. Stockholm, Stockholm Environment Institute (SEI) funded by SIDA: 2. EEA, 2009.

Ehl, R.G and Ihde, A. (1954). Faradays' Electrochemical laws and the determination of Equivalent weights. *Journal of Chemical Education*. 31: 226 – 232

Emsley, J. (2000). The 13th Element: The Sordid Tale of Munde, Fire and Phosphorus: John Wiley & Sons: New York, NY, USA; ISB: 0 – 471. 39455 -6.

FAO, (2017). World Fertilizer Trends and Outlook to 2018. Food and Agricultural Organization of the United Nations. Rome.

FAO, (2018). The Role of Agriculture in Economic Development. In Proceedings in the International Conference on Agriculture and Economic Development, Rome, Italy. 3-5 May, 2018. FAO of the United Nations, Rome, Italy.

FAO, (2013). Good Agricultural Practices for Greenhouse Vegetable crops. Principles of Mediterranean climate areas. United Nations, Rome. 2013.

FAO, (2006). Food Security and Agricultural Development in Sub – Saharan Africa. FAO of the United Nations, Rome. Italy.

Faraday, M. (1934). Faraday's Laws of Electrolysis. Encyclopedia Britannica. 7th Ed. 2267.

Feed The Future People. U.S. Agency for International Development, The U.S Department of Agriculture and U.S African Development Foundation, reported into Feed the Future's Central Monitoring system for fiscal year, 2019.

Filippelli, G. (2011). Phosphate Rock Formation and Marine Phosphorus Geochemistry: The Deep Time Perspective. Chemosphere. 84: 759-766.

Funmilayo, E. and Oladeji, S. (2016). Spectroscopic Analysis of Phosphate Concentration in Agricultural Soil Samples and Water Samples using Molybdenum Blue method. *Brazilian Journal of Biological Sciences*. (3) 6: 407 – 412.

Fryzuk, D.M and Samuel, A.J. (2000). The Continuous Story of Dinitrogen Activation. *Coordination Chemistry Reviews*. 200 – 202. 379 – 409.

Gergely, G., Weber, F., Lukacs, I., Toth, L., Howarth, E., Mihaly, J., and Balazi, C. (2010). Preparation and characterization of hydroxyl apatite from eggshell. *Ceramic International Journal of Material Sciences.* (2) 36: 803 – 806.

Greenwood, N.N and Earnshaw, A. (1984). 'The Cyanamide Industry in Chemistry of Elements'. Pergamon, New York. 537-558.

Housing and Population Census (2017). Population and Household Distribution by Social Economic Characteristics. Kenya National bureau of Statistics. 11: 397 – 398.

IFFRI, (2013) Green Revolution: Curse or Blessing! International Food Policy Research Institute: Washington, DC. USA.

International Plant Nutrition Institute, (2015). Natural Source Specifics: Diammonium Phosphate. 17: 11040.

Jahn, G. (2004). Multitrophic Interactions in Soil and Integrated Control. *International Organization for Biological Control (IOBC) WPRS bulletin* (1) 27:115-122.

Jasinski, S.M. (2009). Phosphate Rock, Mineral Commodity Summaries, US Geological Survey: Reston, VA, USA, 2009.

Jean - Michel Verier, Serge Jacubert, Jean Grosbois and Jean – Yves Dumousseau. (1986). Continuous Electrolysis of LiCl into Lithium Metal. US Patent Number 4617098.

Johnson, A.E (2000). Soil and Plant Phosphates: International Fertilizer Industry Association (IFA): Paris, France.

Jogi, A.H (2002). Studies on Phosphate Solubilizing Yeasts of Saline Agricultural Soils and their Use as Biofertilizer. Shodhganga: A Reservoir of Indian Theses @ INFLIBNET.

Kenya, Government of, 'Annual Import Fertilizer Costs 2016'. Kenya National Bureau of Statistics. February, 2017.

Kenya, Government of, Fertilizer Statistics Overview, Kenya. 2012 – 2015. Kenya National Bureau of Statistics. Data validated on 4th Oct. 2016.

Kinga Krupa – Zuczek. (2008). Manufacturing of phosphoric acid from hydroxyl apatite contained in the ashes of the incerated meat – bone ashes. *Polish Journal of Chemical Technology.* (3) 10: 13.

Kirchmann, H Gunnar, B, Katterer, T and Yariv Cohen, (2017). From Agricultural Use of Sewage Slurge to Nutrient Extraction. *A Soil Science Outlook*. 46: 143 – 154.

Knox, A. Su, X. Enowashu, E and Mondini, C. (2006). Phosphate sources and their suitability for remediation of contaminated soils. *Science Total Environment*. 357: 271-279.

Lapedes, M. (1997). Encyclopedia of Food, Agriculture and Nutrition. McGraw-Hill Publishers Ltd.

Larsen, T.A, Maurer, M. Udert, K.M, and Lienert, I. (2007). Nutrient cycles and Waste Water treatment technology. *Water Science and Technology*. (5) 56: 229 – 237.

Leyshon, D. (1999). (Jacob Engineering), Phosphate: Looking Back – Early Phosphate Technology, 14th Regional Phosphate Conference, Lakeland Centre, and Lakeland, Florida.

LeGeros R.Z. (1991). Calcium phosphates in oral biology and medicine. Monographs in Oral Science. Karger, Basel. 15:201.

Lide D.R. (2005). The CRC handbook of chemistry and physics. CRC Press, Boca Raton, Florida. 86:2544.
Mårald, E. I Mötet Mellan Jordbruk Och Kemi. (1998). Agrikulturkemins Framväxt på Lantbruksakademiens Experimentalfält 1850–1907; Institutionen för idéhistoria, University of Umeå, Sweden.

Marschner, H. (2002). Mineral Nutrition and Yield Response. Mineral Nutrition of Higher Plants. 2nd Ed. Academic Press. London. UK. 184 – 200.

Marshall, S. (1979). Processes, Polution Control and Energy. Fertilizer Industry. Noyes Data Corporation. 57 -59.

Messele, B. (2016). Effects of Nitrogen and Phosphorus rates on Growth Yield and Quality of Onion. *Journal of Agricultural Research & Technology. Ethiopia*. Issue: 1(3) 1: 23 -26.

Mills. F. A. (1995). Basic heat and Mass Transfer. University of California at Los Angeles. IRWIN.

Mondini, C. Su, X. Enowashu, E and Schorr, M. (2008). Soil application of meat and bone meal. Short term effects of mineralization dynamics and soil microbiological properties. *Journal of Soil Biology and Biochemistry*. 40: 462 – 474.

Mosayoshi Koshino, (1988). Second Revision of the Methods of Analysis of Fertilizers. Yokendo, Tokyo. 20 - 23.

Muhammad, K. Muhammad, A. Imtiaz -UD-DIN, Mohammed, K. and Nida, A. (2012). Phosphoric Acid Manufacturing Through Hydrochloric Acid Route by Solvent Extraction. Research Institute of Chemistry, International Center for Chemical and Biological Sciences, University of Karachi, Karachi-75270, Pakistan Institute of Chemistry, International Center for Chemical and Biological Sciences, University of Karachi, Karachi-75270, Pakistan.

Nishibayashi, Y. (2018). Catalytic nitrogen fixation using Molybdenum dinitrogen complexes. *The Royal Chemical Science*. 10: 543 – 557.

Oladeji, S., Adelowo, F. and Odelade, K. (2016). Evaluation of Phosphate level in Water Samples using UV- visible spectrophotometric method. *International Journal of Science Research and Environmental Science.* (4) 4: 102-108.

Prothero Donald R and Schwab, F. (2003). Sedimentary Geology. Macmillan Publishers Ltd. 265–269.

Qureshi, G. Stecher, M. U. Qureshi, T. Sultana and Bonn, G. K. (2012). Methods of Producing Phosphoric acid. *Journal of the Chemical Society of Pakistan*. 34: 168.

Runge – Metzger, A. (1995). Closing the cycle: Obstacles to efficient Phosphorus management for improved global food security. SCOPE 54 – Phosphorus in the global Environment – Transfers, cycles & management.

Sayma, S. and Sharba, K. (2019). Phosphorus fertilizer: The original and commercial Sources, Phosphorus – Recovery and Recycling. Tao Zhang. IntechOpen. DOI: 10.5772.

Schorr, M. and Lin, J. (1997). Wet Process Phosphoric acid Production. Problems and Solutions. Industrial Mines. 355: 61 -71.

Schroder, J.J, Cordell, D. and Smit A, L. (2009). Sustainable use of Phosphorus. Plant Research International. ENV. Tender. BI/ EIV/ 0025.

Shah Jahan Leghari, Niaz, A.W, Ghulam, M.L, Abdul, H.L, (2016). Role of Nitrogen for Plant Growth and Development. *Advances in Environmental Biology* (9) 10:209-218.

Shen, Y. and Wolsky, M. (1980). Energy and Materials Flows in the Production of Liquid and Gaseous Oxygen. US Dept. of Energy. (1) 117: 121 – 134.

Skoog, D. (2004). Fundamentals of Analytical Chemistry. Thomson Book Collection. Mexico. 8th ed. Chapter 37. 1059- 1075.

Sneddon, I., Enowashu, E and Mondini, C. (2006). Use of Bone Meal Amendments to Immobilize Pb, Zn, and Cd in soil: a leaching column study. *Journal of Environment and Pollution.* 144: 816 – 825.

Steen, I. (1998). Phosphorus availability in the 21st Century Management of a non-renewable resource. Phosphorus and Potassium. 217: 25 – 31.

Stewart, W., Hammond, L and Kauwenberg, S. (2005). Phosphorus as a natural Resource. Phosphorus: Agriculture and the Environment. Agronomy Monograph No. 46. American Society of Agronomy, Crop Science Society of America, Soil Science of America. Madison, WI, USA

Strong, F.C (1961). Faraday's laws in one Equation. *Journal of Chemical Education*. (38) 89: 112-114.

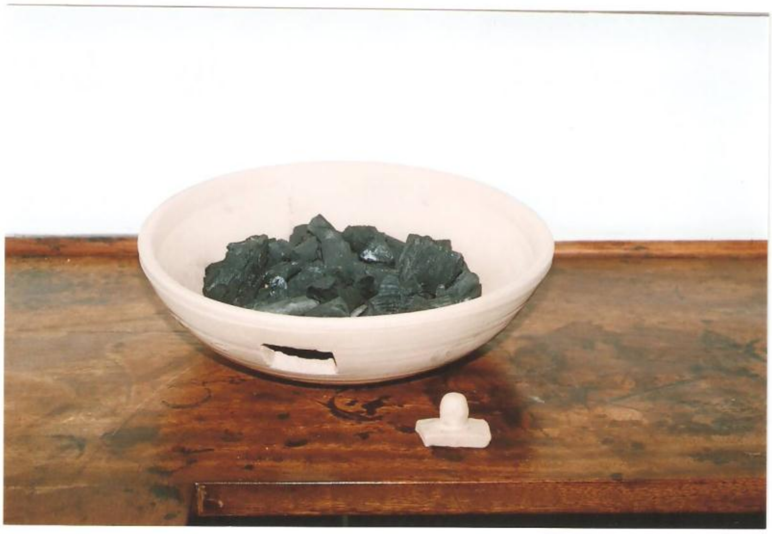
United Nations DESA, (2015). Transforming the world: The 2030 Agenda for Sustainable Development. Envision 2030.

White, P.J and Hammond, J.P (2005). The Ecophysiology of Plant – Phosphorus Interractions. Springer Science + Business Media B.V.

World Development Prospects, 2020. United Nations Department of Economic and Social Affairs Population Division. "World Population Clock".

Appendices

Appendix 1: A clay *jiko*



Appendix 2: Effect of varying temperatures on separation of oxygen from air

Experiment 1

Volume of air passed (sec)	Time (sec)	Temp (^{o}C)	Total volume of air passed(ml)	Mass of copper granules(g)	Mass of copper oxide formed (g)	Mass of oxide formed (g)	% separation of oxygen from air
295.08	300	200	88564	850	875.30	25.3	95.25
291.27	300	200	87381	850	874.38	24.38	93.01
295.83	300	200	88749	850	874.29	24.29	91.24
291.76	300	200	87528	850	874.19	24.19	92.15
293.75	300	200	88125	850	874.37	24.37	92.20
292.39	300	200	88617	850	874.53	24.53	92.28

Experiment 2

Volume of air passed (sec)	Time (sec)	Temp (^{o}C)	Total volume of air passed (ml)	Mass of copper granules(g)	Mass of copper oxide formed (g)	Mass of oxide formed (g)	% separation of oxygen from air
290.01	300	250	87003	850	875.11	25.11	96.2
292.35	300	250	87705	850	875.63	25.63	97.41
292.08	300	250	87624	850	874.79	24.79	94.33
291.90	300	250	87570	850	874.26	24.26	92.34
293.15	300	250	87945	850	875.35	25.35	96.09
290.80	300	250	87240	850	875.19	25.19	96.25

Experiment 3

Volume of air passed (sec)	Time (sec)	Temp (^{o}C)	Total volume of air passed (ml)	Mass of copper granules(g)	Mass of copper oxide formed (g)	Mass of oxide formed (g)	% separation of oxygen from air
291.56	300	300	87468	850	875.16	25.16	95.88
292.12	300	300	87636	850	874.98	24.18	95.01
292.45	300	300	87735	850	875.58	25.58	97.18
290.67	300	300	87201	850	875.44	25.44	97.24
291.33	300	300	87399	850	874.69	24.68	94.16
290.80	300	300	87240	850	875.75	25.75	98.39

Experiment 4

Volume of air passed (sec)	Time (sec)	Temp (^oC)	Total volume of air passed (ml)	Mass of copper granules(g)	Mass of copper oxide formed (g)	Mass of oxide formed (g)	% separation of oxygen from air
290.98	300	350	87294	850	875.70	25.70	98.16
291.08	300	350	87324	850	874.68	24.68	94.23
291.21	300	350	87363	850	874.81	24.81	94.69
290.68	300	350	87204	850	875.16	25.16	96.17
292.01	300	350	87608	850	875.39	25.39	96.91
290.77	300	350	87231	850	874.90	24.90	95.18

Experiment 5

Volume of air passed (sec)	Time (sec)	Temp (^oC)	Total volume of air passed (ml)	Mass of copper granules(g)	Mass of copper oxide formed (g)	Mass of oxide formed (g)	% separation of oxygen from air
290.11	300	400	87033	850	876.01	26.01	99.65
290.19	300	400	87057	850	875.93	25.93	99.31
290.68	300	400	87204	850	875.61	25.61	97.89
291.01	300	400	87303	850	876.11	26.11	99.69
291.38	300	400	87414	850	875.32	25.32	96.56
290.32	300	400	87097	850	876.04	26.04	99.69

Appendix 3: Electrolysis of LiCl – KCl mixtuure

Mass of lithium collected during electrolysis

Exp.no.	Time (hrs)	Electrolyte	Temp ^{o}C	Mass of lithium deposited(g)
1	120	LiCl - KCl	450	109.80
2	120	LiCl - KCl	450	110.50
3	120	LiCl - KCl	450	105.60
4	120	LiCl - KCl	450	110.90
5	120	LiCl - KCl	450	111.00
6	120	LiCl - KCl	450	112.10
7	120	LiCl - KCl	450	112.00
8	120	LiCl - KCl	450	102.60
9	120	LiCl - KCl	450	105.30
10	120	LiCl - KCl	450	103.50

Appendix 4: Lowest H_3PO_4 concentration for total dissolution of bones

Molarity of H_3PO_4	Mass of bones: volume of H_3PO_4	Dissolution	Acid concentration after dissolution	Mass of unreacted bones
0.1	10g;35ml	Not totally dissolved	0.135	4.3
0.1	10g:34ml	Not totally dissolved	0.133	4.2
0.1	10g;33ml	Not totally dissolved	0.137	4.0
0.1	10g:32ml	Not totally dissolved	0.137	4.0
0.1	10g:31ml	Not totally dissolved	0.136	3.9
0.2	10g:35ml	Not totally dissolved	0.241	4.0
0.2	10g:34ml	Not totally dissolved	0.241	4.0
0.2	10g:33ml	Not totally dissolved	0.246	4.1
0.2	10g:32ml	Not totally dissolved	0.250	3.9
0.2	10g:31ml	Not totally dissolved	0.255	3.8
0.3	10g:35ml	Totally dissolved	0.356	0
0.3	10g:34ml	Totally dissolved	0.355	0
0.3	10g:33ml	Totally dissolved	0.350	0
0.3	10g:32ml	Totally dissolved	0.350	0
0.3	10g:31ml	Totally dissolved	0.351	0
0.25	10g:35ml	Not totally dissolved	0.286	3.7
0.25	10g:34ml	Not totally dissolved	0.289	3.9
0.25	10g:33ml	Not totally dissolved	0.290	4.0
0.25	10g:32ml	Not totally dissolved	0.290	4.0
0.25	10g:31ml	Not totally dissolve	0.286	3.9
0.275	10g:34ml	Totally dissolved	0.355	0
0.275	10g:33ml	Totally dissolved	0.350	0
0.275	10g:32ml	Totally dissolved	0.350	0
0.275	10g:31ml	Totally dissolved	0.351	0

Appendix 5: Quantitative determination of phosphorus in synthesized fertilizer

In the spectroscopic method, the phosphormolybdate ions react with phosphorus as the central coordinating atom as shown in the equations;

$$\mathbf{H_3PO_4 + 12H_2MoO_4 \rightarrow H_3P(Mo_3O_{10}) + 10H_2O}$$

$PO_4^{3-} + 12(NH_4)2MoO_4 + 24H^+ \rightarrow$

$(NH_4)3PO_4.12MoO_3 + NH_4 + 12H_2O(NH_4)3PO_4.12MoO_3 + N_2H_4.H_2O \rightarrow$

molybdenum blue.

At effective analytical conditions, the intensity of the blue colour (absorbance) is directly proportional to the concentration of phosphorus in the sample. The % concentration of phosphorus was calculated using the equation;

$$\%\mathbf{P} = (\frac{\mathbf{concentration}}{\mathbf{mass}} \times \mathbf{dilution\ factor}) \times \mathbf{100}$$

Appendix 6: Preparation of fused LiCl – KCl mixture

The masses LiCl – KCl of were arrived at from the following calculations;

(i) Surface area of anode = $2\pi r^2 + 2\pi rh$

$= (3.14 \times 7.5 \times 7.5 \times 2) + (2 \times 3.14 \times 7.5 \times 10)$

$= 353.22 + 471.0$

$= 824.22 cm^2$

(ii) Surface area of cathode = $2\pi rh$

$= 2 \times 3.14 \times 8.5 \times 10$

$= 533.8 cm^2$

(iii) Interpolar distance between the cathode and anode = 2cm

(iv) Battery is 12V

V = I x R; where, I = current and R = resistance

12 = 200Ah x R

R = 0.06 ohms

(v) Surface area occupied by the electrolyte = $\pi r^2 + 2\pi rh$

$= (3.14 \times 8.5 \times 8.5) + (2 \times 3.14 \times 8.5 \times 15)$

$= 226.865 + 800.7$

$= 1027.565 cm^2$

(vi) Volume of the electrolyser = $\pi r^2 h$

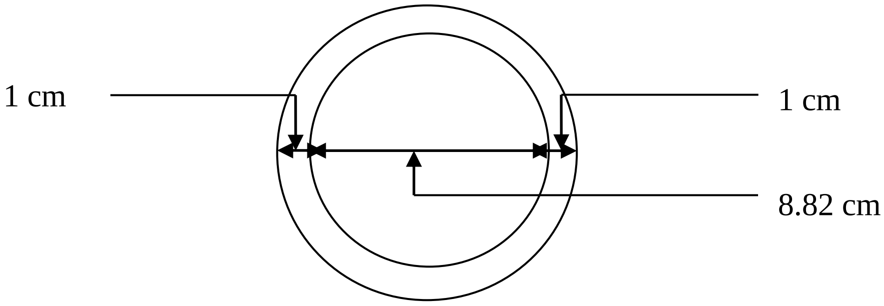
$= 3.14 \times 8.5 \times 8.5 \times 15$

$= 3402.975 cm^3$

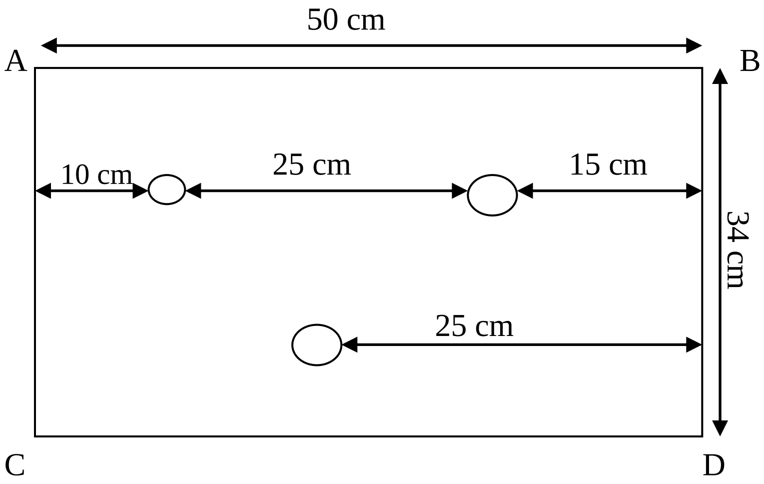
Appendix 7: Fabricated main electrolysis cell

Appendix 8: The fabrication of the electrolysis cell from stainless sheets

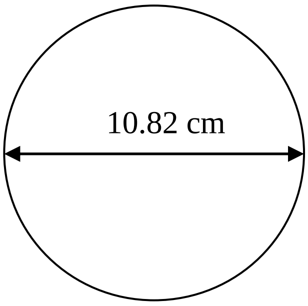
TOP LID



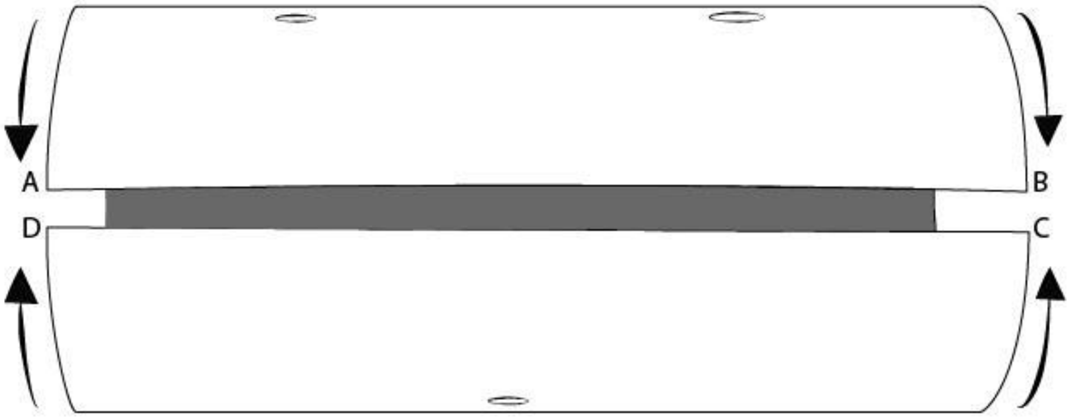
MAIN CELL



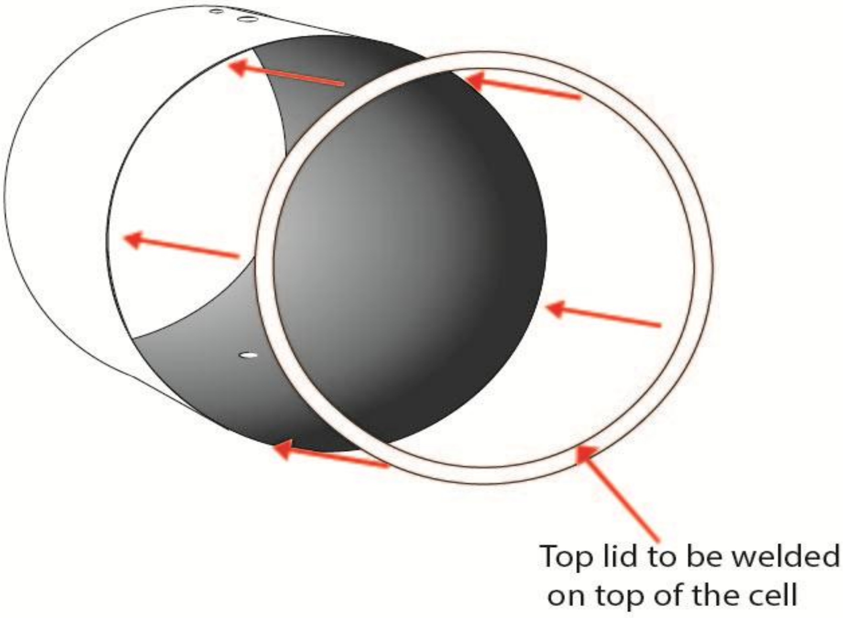
BOTTOM LID



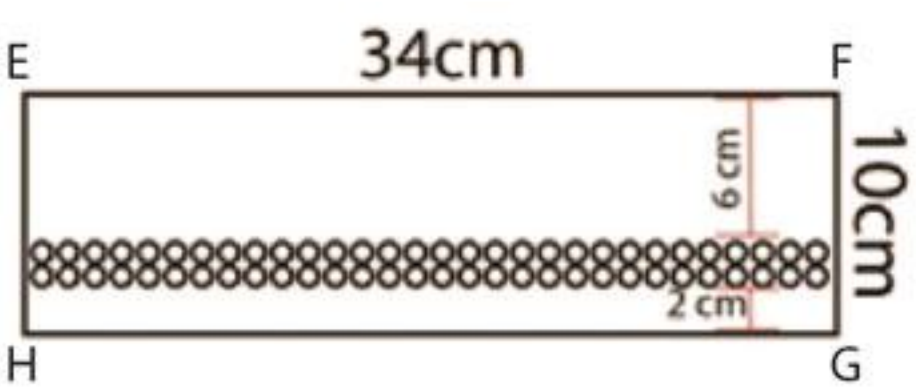
The 50 (length) x 34 (width) cm sheet was folded as shown below and welded along AB – CD line to create a cylindrical body.



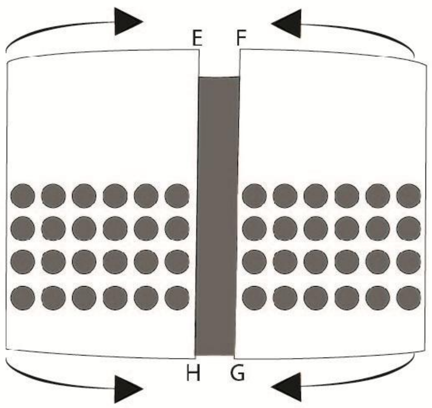
Two lids were cut, circular in shape with a diameter of 10.82 cm. They were labelled as top and bottom lids. A hole was made in the top lid of diameter 8.82 cm as shown below which would later accommodate a graphite electrode. The 1 cm ring remaining was welded to the cylindrical main body part of the cell as the top lid.



Another stainless-steel sheet 10 cm x 34 cm was cut out of the remaining sheet as shown;



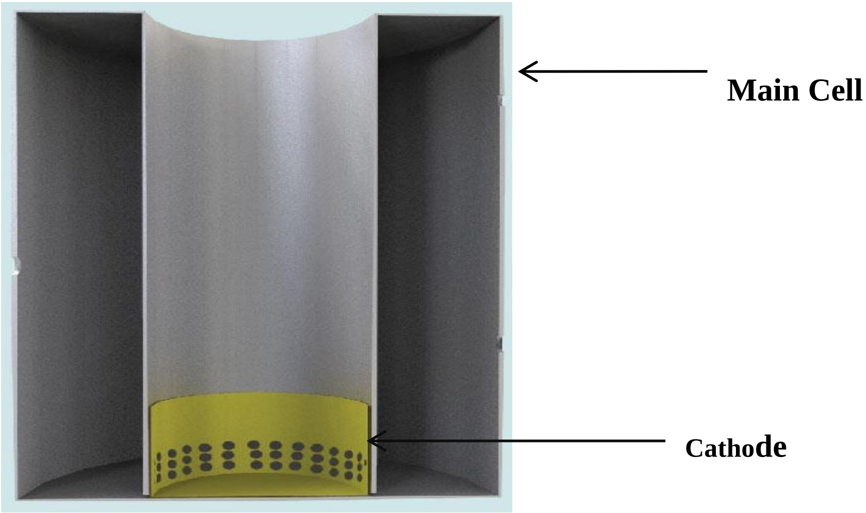
Lines EH and FG were joined and wielded into a cylindrical shape as shown in below,



The cylindrical piece was then wielded to the bottom lid before the lid was welded to the main cell.

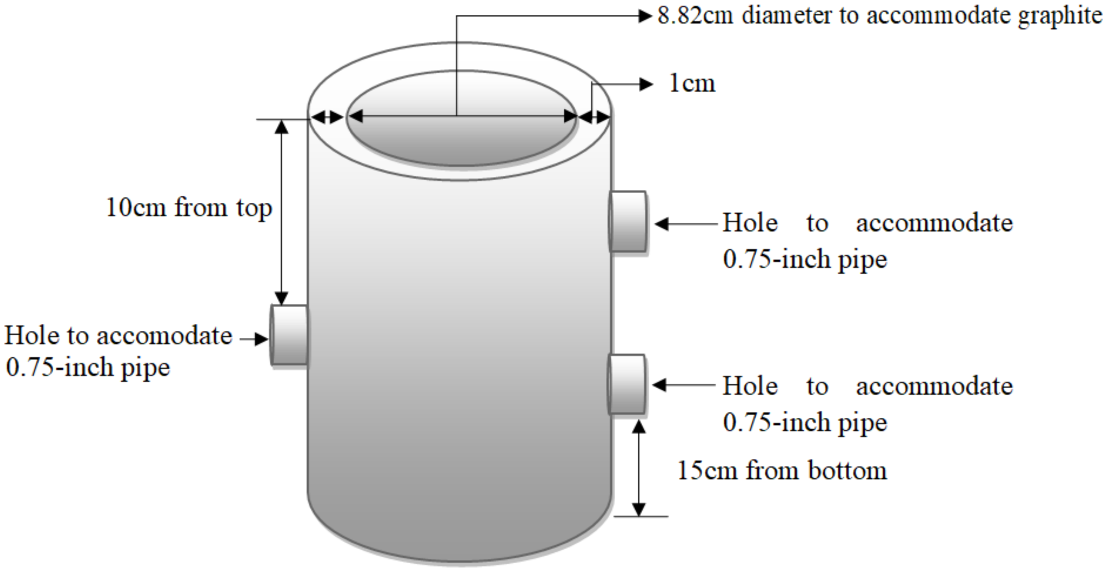
The cathode attached to the bottom lid before wielding to the main body

MAIN

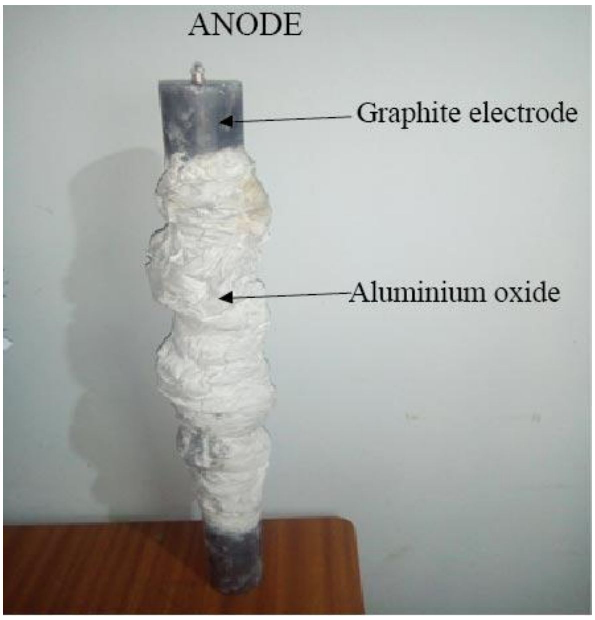


The cross section view of the electrolysis cell showing the cathode in yellow colour

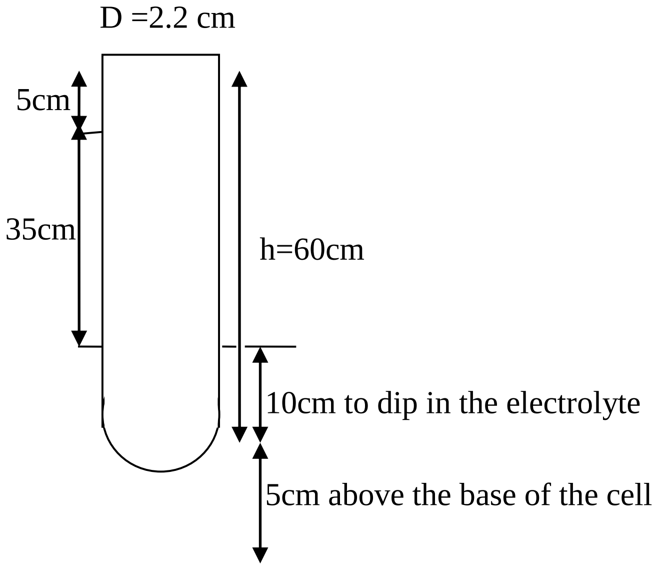
After the welding of the top and bottom lids as well as the inlet and outlet pipes, the main cell appeared as shown in below.



Insulated graphite elctrode



Cross – sectional diagram of a graphite electrode

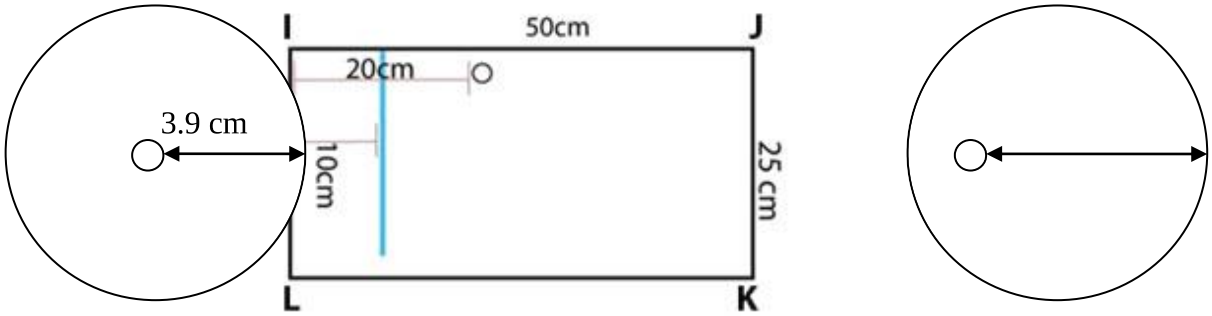


A thin layer of vermiculite clay/cement mould was smeared round the top of electrode to hold the graphite tightly when it was finally inserted in the main cell.

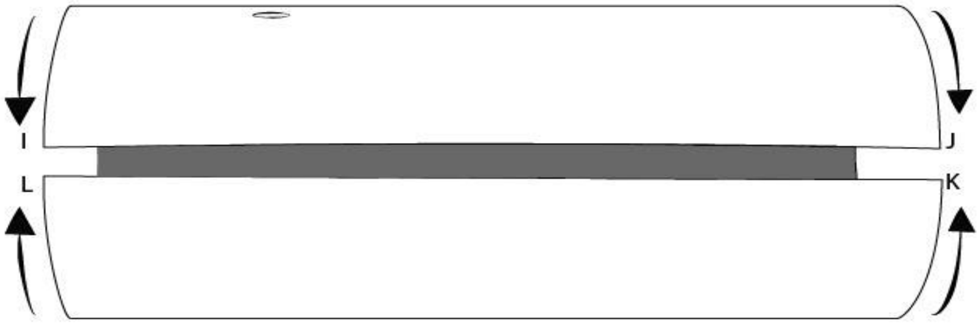
The Separator

The separator comprised of a decantation compartment, an outlet for discharging the upper light phase (the lithium metal) by overflow and an outlet for discharging the dense bottom phase that is the mixture of molten salts for recycling. It was made by cutting a rectangular sheet of stainless steel sheet measuring 50 cm x 25 cm labelled as IJKL. A hole was drilled 20 cm from IL side to accommodate a 0.75 cm pipe that would act as an inlet for withdrawal of lithium from the main cell during electrolysis. The line IJ and LK would then be joined and wielded to give a cylindrical shape.

Sideway lid (1) Separator Sideway lid (2)



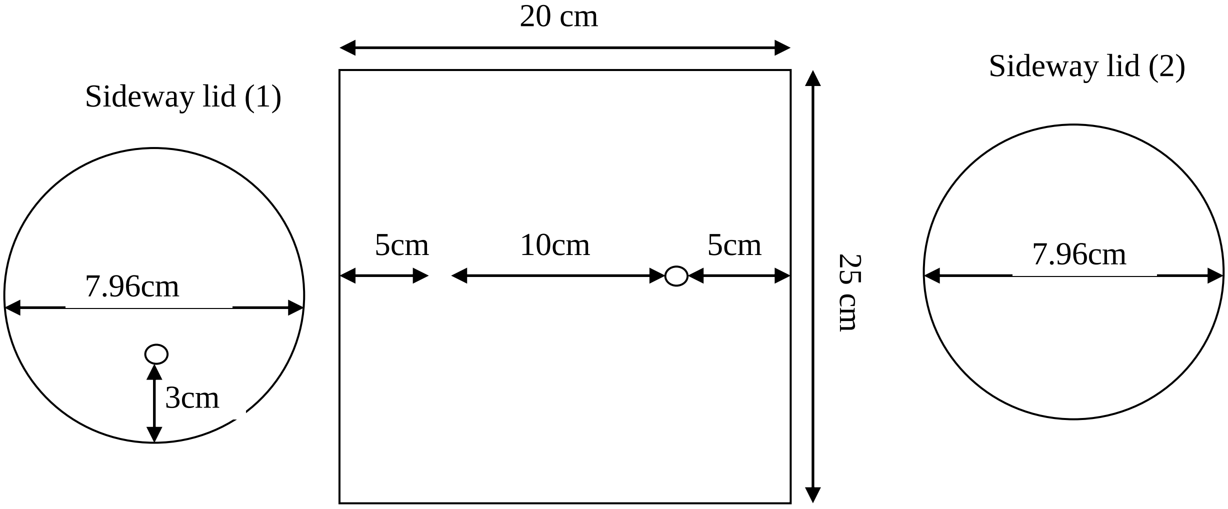
A thin circular shaped sheet cut as shown was then inserted 3.9 cm from side IJ which would act as a separator for the light and denser phase of the electrolyte. Two sideway lids were also cut circular in shape. A hole was made in each as shown in below. They were later to be wielded on the sides. 0.75” diameter pipes were fitted as shown in the diagram



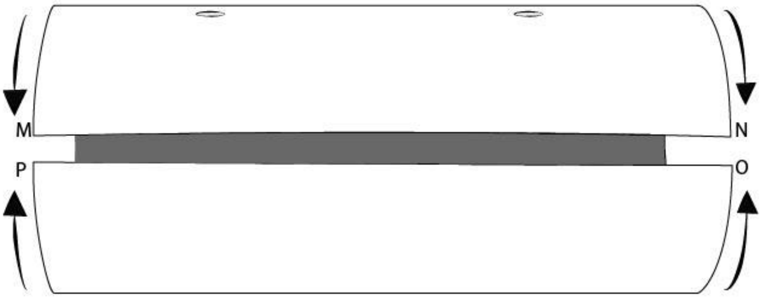
The Buffer

The buffer vessel was made from a rectangular stainless steel sheet measuring 25 cm x 20 cm and labelled as MNOP. Two holes were made, hole A to accommodate a pipe from the separator and hole B to accommodate a pipe that would be used to feed the depleted electrolyte. Lid 1 and 2 were welded on the opposite sides to give a buffer container.

Buffer

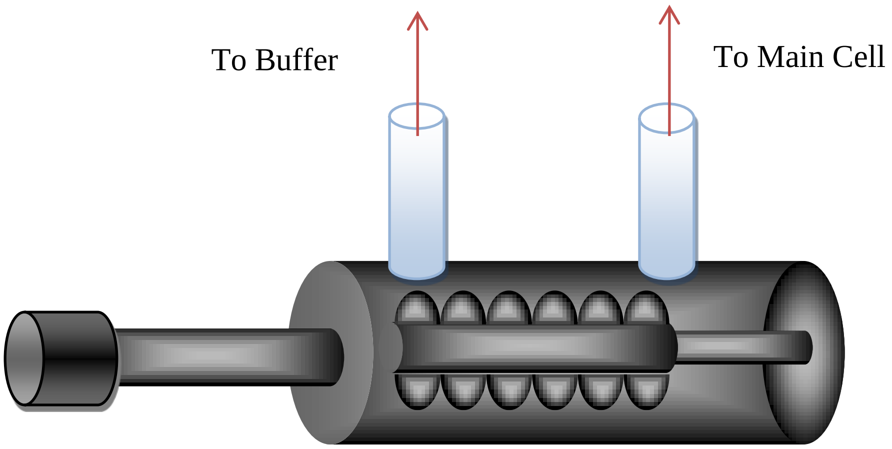


Two circular side lids of circumference of 25 cm were cut. A hole was made on sideway lid 1 to accommodate a 0.75” diameter pipe as shown. It was later connected to the pump. The two lids were then wielded on both ends as shown.



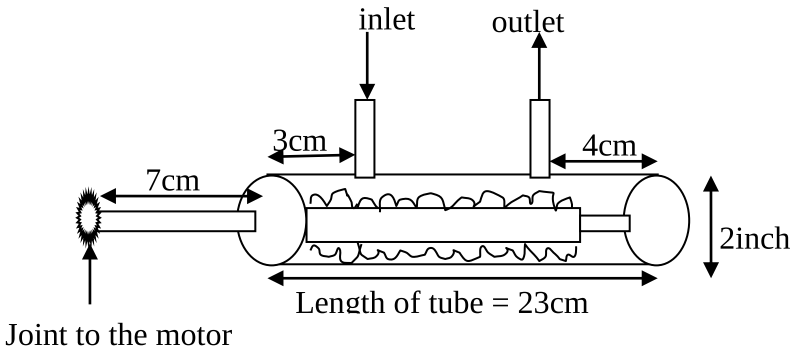
Cross-sectional diagram of assembled buffer

PUMP



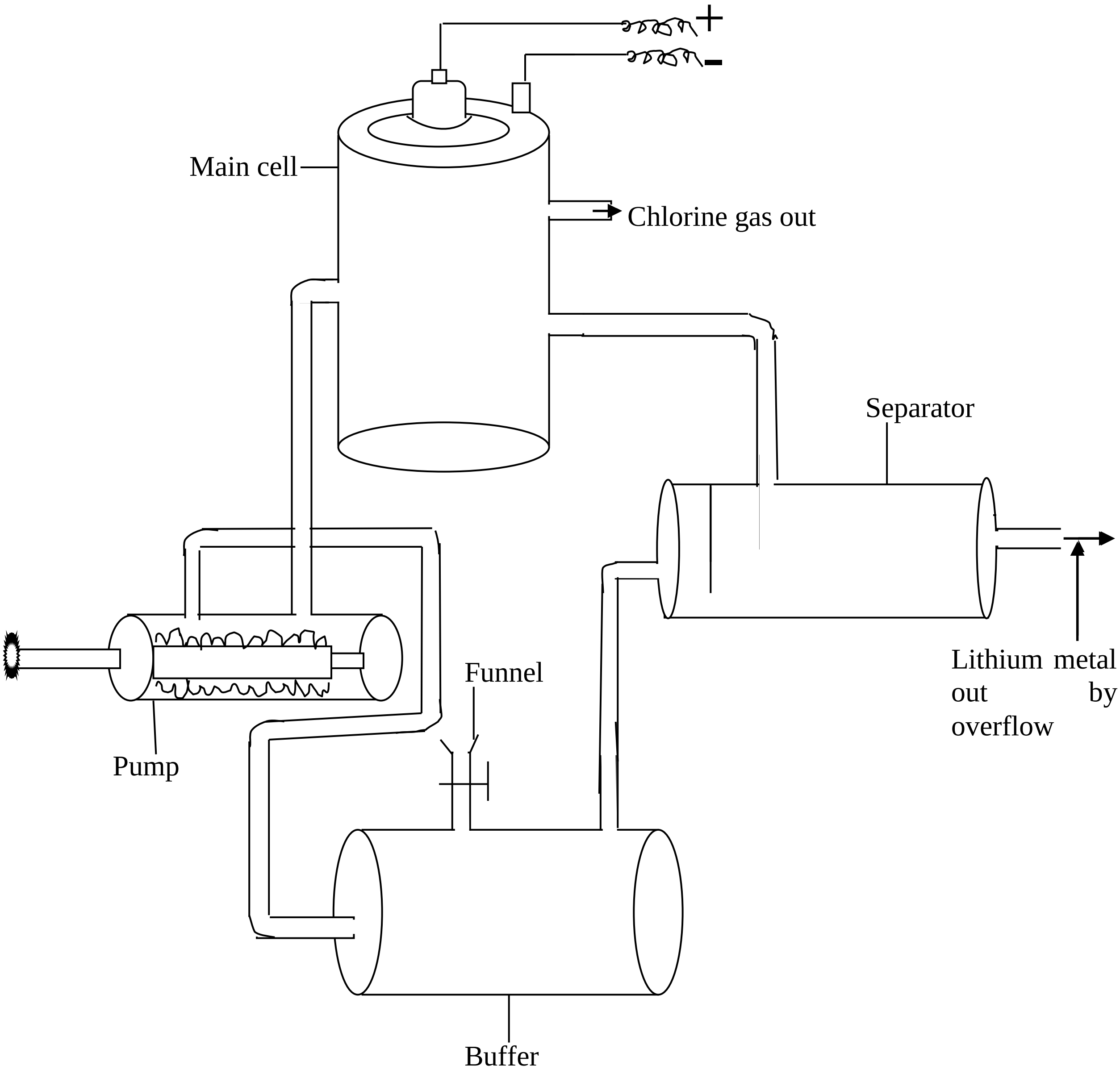
The pump facilitated the circulation of the molten medium back into the electrolyser.

The pump



Schematic diagram of the pump

Appendix 9: Electrolysis cell showing all components assembled



Appendix 10: The green house

The greenhouse that was used during the study was built at Kenyatta University Appropriate Centre using the following materials and procedure.

Summary of the materials used in construction of the greenhouse

Materials	Tools
Six concrete blocks	Digging tools
Two boxes exterior screws	Safety gloves and glasses
Six 5x10"galvanised screws	Drill and drill bits
Five 2 x 4"12 feet boards	Hammer
Ten 2 x 4" 6 feet boards	Spirit level
Sixteen 2 x 4" 8 feet boards	Carpentry level
Two rolls of 12 feet sheets of greenhouse plastic	Measuring level
Temperature control system	
Thermometer	

Six holes of about 6" deep were dug for the concrete blocks to make a rectangle 8 feet 4 x 12" in size. A hammer was used to level them into the earth. A frame for the front was built by laying 28 feet 2 x 4" boards parallel to each other 8 feet apart. Exterior screws were used to attach 3 more 8 feet 2 x 4" boards to them to have a square with a 2 x 4" running up and down the centre of it. This was repeated for the back frame. Two 12 feet 2 x 4" boards were laid down parallel to each other 8 feet apart. Exterior screws were used to attach five 8 feet 2 x 4" between them, one at each end and three evenly spaced in the middle. The bottom of the back was placed on the concrete blocks and raised until vertical and screwed into the concrete blocks.

This procedure was repeated for the side and front. The frames were screwed into the side frames. Twenty-one ½ feet 2 x 4" boards were cut and exterior screws used to toenail them to the centre of the end frames. 12 feet 2 x 4" boards were cut and placed on top of these 2 x 4" boards and toe nailed in place. They were about 5 x 1½" long at an angle of 32.75^{o}. They were screwed using the drill. The door 5" wide was installed in the front and the greenhouse enclosed with the plastic using a drill and screws to secure it to the wood. This construction was done with the assistance of carpenters and technicians from the science workshop and appropriate technology, Kenyatta University.

Appendix 11: Photo showing length of seedlings

After 25 days, the plants were in the range of 2cm to 3cm tall and had on average 3 leaves.

The leaves of about 5 to 10 leaves were about 5 cm long and presented a transpiring surface of 0.4 cm^2. The stem of the plant at the ground line was 0.5 cm in diameter.

Appendix 12: Data collected for tomatoes in the green house

	Plant Height							**Root Length**						
Fertilizer Type	Height for w	Height for w	After 30days	After 45days	After 60days	After 75days	After 90days	Root Length	Root Length	After 30days	After 45days	After 60days	After 75days	After 90days
1	9.76	20.45	30.62	33.31	42.17	47.97	51	2.6	13.3	14.8	16.2	17.2	18.3	19.2
1	9.83	20.11	31.25	33.37	42.33	47.73	51.66	2.2	12.9	14.8	16.1	17.3	18	19.1
1	9.9	21.66	30.52	33.03	41.33	48.53	51.5	2.6	13.2	14.5	16.2	17.3	18.3	19.2
1	9.83	22.7	32.67	34.67	43	48.13	52	2.4	13	14.7	15.9	16.9	18	18.9
1	9.67	22.71	32.06	34.25	41.76	47.33	51.9	2.4	13.2	14.6	16.2	17.1	18.1	18.9
Totals	48.99	107.63	157.12	168.63	210.59	239.69	258.06	12.2	65.6	73.4	80.6	85.8	90.7	95.3
Average	9.798	21.526	31.424	33.726	42.118	47.938	51.612	2.44	13.12	14.68	16.12	17.16	18.14	19.06
2	10.6	22.67	32.33	33.3	41.39	48.2	53.3	2.4	13.1	14.6	15.9	17.2	18.5	19.3
2	9.15	23.67	29.33	33.47	42.84	48.53	52.4	2.4	12.9	14.7	15.9	17.5	19	19.5
2	10.65	21.33	31.33	35.73	43.06	49.95	53.6	2.8	13.3	14.8	16	17.3	18.7	19.4
2	10.93	20.67	28.67	32.11	43.25	50.5	54.1	2.6	13.2	14.7	16	17.2	19.6	20.3
2	10.03	23.33	32	34.38	41.69	50	53.1	2.3	13.1	14.8	15.9	17.1	19	19.6
Totals	51.36	111.67	153.66	168.99	212.23	247.18	266.5	12.5	65.6	73.6	79.7	86.3	94.8	98.1
Average	10.272	22.334	30.732	33.798	42.446	49.436	53.3	2.5	13.12	14.72	15.94	17.26	18.96	19.62
3	5.86	10.91	17.69	18.39	19.06	19.9	20.2	2.2	2.8	3.3	4	4.7	5.3	5.7
3	6.04	11.07	17.65	18.65	19.4	19.66	20	1.9	2.7	3.3	3.9	4.6	5.1	5.4
3	5.54	10.6	17.75	19.5	19.9	20.37	20.66	1.7	2.6	3.3	4.1	4.8	5.2	5.6
3	4.31	8.2	17.39	18.9	19.06	19.4	20	2.1	2.7	3.2	3.9	4.5	5	5.5
3	5.73	10.3	18.03	19.66	20.37	20.9	21.2	2.2	2.9	3.4	4	4.6	5.2	5.7
Totals	**27.48**	**51.08**	**88.51**	**95.1**	**97.79**	**100.23**	**102.06**	**10.1**	**13.7**	**16.5**	**19.9**	**23.2**	**25.8**	**27.9**
Average	5.496	10.216	17.702	19.02	19.558	20.046	20.412	2.02	2.74	3.3	3.98	4.64	5.16	5.58

Leaf Length							**Leaf width**						
Leaf Length wk	Leaf Length wk	After 30days	After 45days	After 60days	After 75days	After 90days	Leaf width wk1	Leaf width wk2	After 30days	After 45days	After 60days	After 75days	After 90days
2.21	4.57	6.27	8.31	9.69	10.85	12	1.1	2.3	3.1	4.1	4.8	5.4	6
2.43	5.86	7.1	8.97	10	10.9	11.1	1.2	2.9	3.5	4.4	5	5.4	5.6
2.37	5.54	7.47	9.67	11.32	12.05	13.1	1.2	2.7	3.7	4.8	5.6	6	6.5
2.82	6.04	8.22	10.01	11.22	12.4	13	1.4	3	4.1	5.1	5.6	6.2	6.5
2.72	6.37	8.67	10.38	10.54	11.7	12.9	1.3	3.1	4.3	4.6	5.2	5.7	6.4
12.55	28.38	37.73	47.34	52.77	57.9	62.1	6.2	14	18.7	23	26.2	28.7	31
2.51	5.676	7.546	9.468	10.554	11.58	12.42	1.24	2.8	3.74	4.6	5.24	5.74	6.2
2.28	4.31	6.6	8.52	9.74	10.9	12	1.1	2.1	3.3	4.2	4.8	5.4	6
2.24	5.72	7.4	9.42	10.67	11.8	13.2	1.1	2.8	3.7	4.7	5.3	5.9	6.6
2.38	6.01	8.32	9.75	11.1	12	13.1	1.2	3	4.1	4.8	5.5	6	6.5
2.42	6.64	8.9	10.1	11.5	12.3	13.6	1.2	3.3	4.4	5.2	5.7	6.1	6.7
2.66	6.03	8.52	9.65	11.15	12.4	13.4	1.3	3	4.2	4.6	5.5	6.2	6.7
11.98	28.71	39.74	47.44	54.16	59.4	65.3	5.9	14.2	19.7	23.5	26.8	29.6	32.5
2.396	5.742	7.948	9.488	10.832	11.88	13.06	1.18	2.84	3.94	4.7	5.36	5.92	6.5
1.79	2.42	3.8	4.6	5	5.4	5.6	0.8	1.2	1.9	2.3	2.5	2.7	2.8
1.91	2.66	3.6	4.7	5.1	5.5	5.9	0.9	1.3	1.8	2.3	2.5	2.7	2.9
2.22	3.29	4.1	5	5.4	5.7	5.9	1.1	1.6	2.1	2.5	2.7	2.8	2.9
2.14	3.4	4.3	5.2	5.7	6	6.2	1.1	1.7	2.1	2.1	2.8	3	3.1
2.46	2.86	3.8	4.6	5	5.4	5.8	1.2	1.4	1.9	2.3	2.5	2.7	2.9
10.52	**14.63**	**19.6**	**24.1**	**26.2**	**28**	**29.4**	**5.1**	**7.2**	**9.8**	**11.5**	**13**	**13.9**	**14.6**
2.104	2.926	3.92	4.82	5.24	5.6	5.88	1.02	1.44	1.96	2.3	2.6	2.78	2.92