PRODUCTION OF NANO-LEAD(II)OXIDE FROM WASTE AUTOMOBILE LEAD-ACID BATTERY PASTE

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ABSTRACT

Recycling of Waste Lead-Acid Batteries (WLABs) by smelting produces high leaded materials which are harmful to the health of the populace. Hydrometallurgical process offers a better alternative of converting these materials to nanoparticle. Production of nano-lead(II)oxide (nano-PbO) from WLABs has been reported by few studies. However, in these studies the nano-PbO produced contains undesirable impurities such as sulphur, carbon, iron and this necessitates the need for impurity-free nano-PbO. The aim of this study therefore, was to produce and characterise high purity nano-PbO from waste automobile LABs.

Fifty (50) waste automobile LABs samples were collected, manually dismantled and the pastes were isolated, washed with distilled water and oven dried. A composite of the dried powdery material was made and analysed for chemical phases using X-ray diffraction (XRD). The morphological properties and elemental mapping were determined with Scanning Electron Microscope/Energy Dispersive X-ray (SEM/EDX). Samples were analysed for elemental composition by inductively coupled plasma optical emission spectroscopy. Concurrent leaching was optimised using citric, ethanoic, methanoic acids, sodium salt of citric acid, sodium salt of ethanoic acid and sodium salt of methanoic acid with hydrogen peroxide using a standard method. Leaching parameters (concentration of leachants, paste/leachant ratio, temperature, stirring rate and reaction time) were also optimised by standard method. The lead citrate precipitated from citric acid, sodium citrate, and hydrogen peroxide was characterised with XRD and SEM/EDX. Thermal decomposition/calcination temperature of the precipitate was identified by thermogravimetry-differential thermal analysis. The calcination product was characterised thereafter using the same methods. Data were analysed using descriptive statistics.

The major phases identified in the powdery material were lead sulphate ($PbSO_4$), lead(IV)oxide (PbO_2), lead(II)oxide (PbO) and lead oxide sulphate ($Pb_3O_2SO_4$) indicating high lead components/phases. The morphological and elemental composition/mapping of the powdery material revealed irregular bulk crystals consisting of 63.5% lead, 11.2% sulphur, 18.1% oxygen, 2.2% carbon and 5.0% iron. Concentration of lead in the fifty powdery samples ranged from 350,000 to 960,000 mg/kg. The optimum condition for leaching and precipitating lead citrate was 1 M citric acid, 2 M sodium citrate and 2 M hydrogen peroxide (2:1:2, v/v). Leaching parameters of 100 g/L, 30 ^{o}C, 500 rpm for 3 hours showed the highest lead recovery of 98.8%. The resulting sheet-shaped lead citrate precipitate contained 81.5% lead, 1.7% sulphur, 7.0% oxygen and 9.8% carbon. Calcinating the precipitate at 400 ^{o}C resulted into production of impurity-free spherical shaped nano-PbO of 85.2% lead and 14.8% oxygen. The calcination products were Massicot (α-PbO) and Litharge (β-PbO) with particle sizes ranging from 19 to 100 nm.

Highly purified nano-lead(II)oxide was produced from waste lead-acid battery paste. This could be an alternative material for the production of new lead-acid battery.

Keywords: Waste lead-acid battery, Citric acid leachants, Nano-Lead(II)oxide,
Thermal decomposition

Word Count: 437

CERTIFICATION

I certify that this project was carried out by Tope Damilola OGUNDELE in the Department of Chemistry, University of Ibadan.

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DEDICATION

The success of this work is solely ascribed to the Almighty God for His infinite mercies, knowledge and love towards me during the course of this programme.

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LIST OF ABBREVIATIONS

LAB	Lead-Acid Battery
SLAB	Spent lead-acid battery
WLAB	Waste lead- acid battery
ICPOES	Inductively Couple Plasma Optical Emission Spectroscopy
TTLC	Total Threshold Limit Concentration
PbO	Lead Oxide
XRD	X-ray Diffraction
SEM	Scanning Electron Microscopy
EDX	Energy Dispersive X ray Spectroscopy
FT-IR	Fourier Transmission Infra Red
TG	Thermo Gravimetry
DTA	Differential Thermal Analysis
EPSG	Electrical Power Generation and Storage
HEV	Hybrid Electric Vehicles
SOC	State of Charge
IOD	Intensity of Discharge
COH	Condition of Health
VRLA	Valve Regulated Lead Acid
TML	Tetramethyl lead
TEL	Tetraethyl lead
PVC	Polyvinylchloride
FIAM	Free Ion Activity Model
CNS	Central Nervous System
FWHM	Full Width at Half Maximum
SSA	Specific Surface Area
I_{cry})	Crystallinity Index
AAS	Atomic Absorption Spectrometer
EPGS	Electrical power generation and storage
TTLC	Total threshold limit concentration

CHAPTER ONE

INTRODUCTION

1.1 Background of the study

The growing environmental apprehension in the past few decades has given rise to stricter global environmental regulations, most especially those related to the disposal of harmful waste comprising heavy metals specifically, waste automobile batteries, rechargeable lantern, industrial installations, construction, demolition and agricultural waste (Houghton *et al.,* 2006). Waste can simply be referred to as unwanted, unusable, discarded materials after primary use ranging from industrial, municipal, agricultural, electrical and electronics, counterfeited pesticides, hazardous and radioactive materials.

Hazardous waste control by Basel convention for the trans-boundary waste and disposal Act 2 (1), of 1989, defines wastes as objects or substances unwanted in its present form, or intentionally thrown away or mandatory to be disposed of by the provision of the law (Choksi, 2001). Waste generation can be described as the amount of materials that enter the waste stream. It is inefficient use of material/resources for designated purposes and the principal cause of contamination/pollution and environmental degradation. The rate and composition of solid waste generation differs from place to place, depending on industrial activities, economic status, management regulations and lifestyle. Improper recovery of wastes constitutes environmental pollution (Houghton *et al.,* 2006).

Waste management/ recovery/ recycling/ re-use is a process of reclaiming useful recyclable substances from waste intended for disposal or for a specific next use. It is the processing of materials from waste stream that prevents environmental degradation. Waste management heavily depend on landfill for the disposal of waste. Over 90% of wastes are disposed of at landfill sites despite several management alternatives such as recycling (DEA, 2011). Disposal of hazardous wastes by landfill has limitation of environmental degradation as many of them are not properly managed. Environmental pollution by hazardous waste, such as battery waste, is of great concern as it contaminates, degrades the quality of environment and endangers public health by improper disposal. This is occurs through soil percolation/erosion of metal ions, sediment leachate/re-suspension and leaching of heavy metals. Recycling of waste, on the other hand, helps to preserve natural resources by making products from recycled materials rather from its naturally occurring form, thereby conserving land and reducing the need to mine for more minerals. Recycling waste battery requires less energy consumption than producing battery from the mineral ores. The production of secondary lead ingot requires less energy than primary lead. http://recycling.about.com/od/Recycling/a/Lead-Recycling.htm.

Recycling of wastes is believed to produce uncontaminated air and water. Generally, products from recycled materials generate less water and air pollution than generating products from the original materials. Recycling has the advantage of saving landfill area. Landfills area is conserved when used materials are recycled to generate new products. Recycling of waste is classified as the least expensive waste management options (USEPA, 2012).

Battery (waste lead-acid battery) is categorised as a harmful waste that contains inorganic elements predominantly and by its intrinsic physical, chemical or toxicological characteristics are detrimental to health and environment. Harmful waste can cause injury, illness and eventually death and devastation of the environment when it is not treated, stored, transported or discarded properly (DEA, 2009b). Toxic waste, such as waste lead-acid battery, contains heavy metals with metallic lead (Pb) as the main element and other metals at considerable minute level. Wastes such as lead slag and acidic sludge are major industrial wastes associated with lead-acid battery industries; and when in contact with the soil, it contaminates the soil and the growing plants thereby impacting negatively on the food chain.

Metallic lead (Pb) being one of the age long heavy metals known is naturally present in minerals explicitly as galena (PbS), Cerussite ($PbCO_3$) and anglesite ($PbSO_4$), constituting 86.6%, 77% and 68% lead respectively. This metal is also found in combination with other metals such as copper, silver and zinc which can be extracted as a co-product of these metals. However, metallic form of lead is generally required for industrial uses.

The prevalent occurrence, uncomplicated extraction method together with the desirable properties of lead metal made it suitable for various applications. Malleability of lead and its simplicity of smelting justified its use in pipes and lead sheeting manufacturing. It was used in paint and pigment industries until its environmental toxicity was pronounced. Large amount of lead industrially produced are employed in making batteries use in automobile vehicles and other energy storage device (USGS, 2016).

Lead industry reportedly produced about 2.5 MT of Pb globally and most of the Pb produced is utilised in automobile batteries. The rest is used to produce cable insulators, pesticides, ammunition and fuel additives, x-ray shielding. The global increase in the demand of lead acid batteries (LABs) as a result of increased automobile vehicles and the stringent environmental laws necessitated the need to relocate, modernise and re-convert processes for LABs manufacturing and Pb recycling to minimise their influence on the environment. LAB has lead alloy metal, lead sulphate, micro porous paper and plastic. Attempts to tackle the problems faced by the battery regulators and communities where it is produced, lead industry developed the green lead approach which emphasises sustainable practices in the LAB industry. This is because environmental metal contamination has increased ecological and global public health concern (USGS, 2016).

The importance of lead recovery from discarded LAB has been taken up for investigation as exploration of lead ore at the surface is becoming harder and the natural ore decreases over decades. Considerable efforts are being made by miners searching under the earth surface for lead deposits for it impending use. This operation is rigorous and harder to locate ore deposits, thus making recycling the future of the Pb industry. More than half of the lead consumed in the world now comes from secondary sources rather than mining (USGS, 2016). As for the challenges, there has been interest in developing efficient secondary recovering processes. Above all, two main processes of obtaining Pb in form of PbO from secondary LABs are pyrometallurgical and hydro-electrometallurgical processes. The first operation has suffered a major setback in its operation because of the residual effect of generating lead dust which is detrimental to the ecosystem. Generation of SO_2 gas is another challenge coupled with the high energy requirement of the process. The latter hydrometallurgical process seems to be environment friendly. It can treat the waste to low concentration of lead; less energy intensive and controllable leaching reagents (i.e. the process can be controlled). Different leaching/precipitating agents in the likes of Sulphuric acid, Nitric acid, Acetic acid, Citric acid and some other organic solvents have been employed by researchers.

This present work presents a hydrometallurgical route that avoided smelting by using unrefined and physically dismantled waste LAB paste. This was collected from markets in Nigeria to produce ultra fine particles of nano meter sizes suitable for the production of new LAB.

1.2 Aim and Objectives

The aim of this study was to produce/characterise high purity nano-lead(II)oxide from waste LABs which could serve as alternative material for the production of new LABs

. The study objectives were to:

i. Design questionnaire to assess battery types in Nigeria, their life span and end of life management.
ii. Study the flow of WLAB for recycling suitability and material estimation from the products;
iii. Characterise the waste battery paste for chemical contents and mineralogical phases;
iv. Study the effect of different lead precipitating agents to synthesise lead oxides precursor, using different organic precipitating reagents; and
v. Characterise chemical and structural properties of the synthesised lead(II)oxide precursor and nano-structured PbO.

1.3 Scope of the study

Span of this study, included determination of the presence and concentrations of some heavy metals in the waste LAB pastes, recovery of Pb from the battery paste, and production of ultra fine/nano PbO from the waste batteries by chemical methods which involve leaching, precipitation and calcination. Estimation of WLABs between 1980-2014 for material availability and product gain using substance flow analysis was also a focus in this study.

1.4 Knowledge gap

i. Usage of locally dismantled and untreated battery pastes.
ii. Provision of management database for LABs imported into Nigeria by substance flow analysis.
iii. Establishment of most efficient and environment friendly leaching reagents in appropriate ratios.
iv. Establishment of minima energy requiring recovery and recycling operation.
v. Production of impurity-free nano-PbO electrodes as active material.

1.5 Justification

All over the world, large demand for lead-acid battery (LAB) for various uses has resulted in production of billions of the product. When this product is spent, it constitutes environmental hazards. There is therefore the need for sound and green recovery and re-application of the valuable components in the battery. Development of recycling method was achieved in this research. The study gave possibility of resource conservation, prevention of environmental hazards and economic gain from waste to wealth.

CHAPTER TWO

LITERATURE REVIEW

2.1 General battery background

Battery is a storage device that produces electrical energy in a series of electro chemical reactions. The number of cells in a battery determines the capacity of the battery. Each of the cells contains cathode (positive terminal) and anode (negative terminal). Materials which are used in separation of batteries are mostly made of paperboard or polymeric materials. Electrolytes furnish ions that move between the electrodes, allowing the flow of current between the battery terminals for optimal performance (Bernardes *et al.,* 2004).

Many types of battery exist, and each of them is capable of delivering different desirable characteristics which makes it possible for particular applications of different battery. Characteristics and qualities of batteries are the determinants of the suitability of their applications. Batteries types may be differentiated according to their energy density. This can be used to measure the amount of energy each battery can deliver and at the same time considering their masses. Energy density can also be referred to as specific energy. Other suitable terms that described battery's properties are cycle life together with specific power (Bernardes *et al.,* 2004).

2.2 Automotive electrical work

2.2.1 Conventional operation of automobiles

In the conventional automotive electrical network, there are relatively few and simple functions which the Pb-acid battery serves. In general, Pb-acid battery is a device employed in kick-starting the engine by generating a huge current flow and helps to operate many devices requiring electrical energy. An automotive EPGS system is made up of a battery, voltage regulating device and alternator which serves all the electrical energy requiring items in a vehicle. An alternator is an electrical device which transmutes and converts mechanical energy into electrical energy. Through belt coupling, the alternator, which is a concurrent electrical device, receives energy from the mechanically propelled engine shaft. The alternator requires a rectification circuit because it produces an AC output which is implemented through solid-state rectifier. Also, voltage regulating device is controlled by the rectifier DC which gives desire energy yield to a designated specification, for the battery to sustain the desirable state of charge (Fasih, 2006).

Beyond huge current provision to kick-start an engine, the lead-acid batteries main function is to provide energy balance the alternator needed. The battery receives high frequent pulses generated by the alternator, and provides energy for the momentary energy needs when the electrical energy requiring devices are switched on and off while the alternator adjusts to the additional energy requirement. Furthermore, battery usually supplies the needed energy for any energy demands such as energy needed to play music which are occasional from the energy load of driving the vehicle and makes available supply of current required to kick-start an engine and also supply power to all electrical devices prior to alternator's take over (Fasih, 2006).

2.2.2 Hybrid electric vehicles

Hybrid electrical vehicles (HEV) are usually complex than the 12-Volt electrical devices explained in section 2.2.1. To achieve improved fuel economy and performance, HEV combines diverse energy converting systems (Internal Combustion engines and electrical converting machines) with energy loading systems. Therefore, apart from providing energy and power by the battery system in a HEV which is required in the conventional system, it also provides adhesive friction via electric rotating motors. The basic arrangements are series hybrid and parallel hybrid (Chehab, 2006).

In parallel hybrid arrangement via mechanical transmission, combustion engine and the electric rotating motors are attached to the wheels. Nearly every essential driving power is supplied by the combustion engine, and whenever a higher demand is required, electric motor is used; for instance, climbing hills and acceleration. This gives room for proper functioning of a smaller and effective combustion engine with the capacity of increasing fuel economy significantly. In a parallel hybrid, a generator is not required and in view of that, the electric rotating motor can be employed to charge the battery (Chehab, 2006).

The electric motor is directly connected to the wheels in a series hybrid whereas the combustion/ignition engine is attached to a generator device which can produce electrical energy that charges the battery and propel electric rotating motor. The ignition engine in series arrangement does not really power the vehicle but converts chemical energy to mechanical energy and then to electrical energy used in charging the batteries or for providing grip. During braking, the gripping/traction motors can be used as device to recuperate kinetic/motion energy. The advantage of the arrangements is that the combustion-starting engine is always active and it operates maximally with reduced emissions and fuel efficiency (Chehab, 2006).

2.2.3 Battery components and classifications

A battery as an electrochemical device converts electrochemical energy to electro-mechanical energy. It is made up of an electrolyte, an electrodes (anode and cathode) and separating rubber case as well as external rubber casing (Bernardes *et al.,* 2004). Batteries can be classified into two basic classes. They are:

I. **Primary Batteries:** Primary batteries are batteries that are non-rechargeable. When the electrical energy has been consumed, they are discharged. Examples of primary batteries include: zinc/carbon primary batteries, alkaline/manganese batteries, mercuric oxide batteries and silver oxide batteries.

II. **Secondary Batteries:** These are energy replenishing/rechargeable batteries which are widely used due to their capability of being recharged after they have discharged. Examples of secondary batteries include an automotive battery, that is, nickel-metal hydride batteries, nickel/cadmium batteries, lead-acid batteries and lithium ion (Li-ion) batteries.

2.2.4 Battery design

Based on a process known as electrolysis, a battery has related cells working together. Each cell consists of a positive and negative electrode. A cell produces electricity when parts of anode and cathode electrodes are immersed in electrolyte solution. However, diverse constituents of a cell will lead to many variations in structure and type which supply electrical energy. The electrolyte container could act as container and also as the anode or cathode. The arrangement of materials in battery cell affects a number of factors: the production rate, the amount of electricity produced, the voltage, and the ability of the cells to function at different temperature. Electrons are produced by a chemical reaction. For reaction to take place there must be flow of electrons from the battery to the wire and it must flow between the negative and the positive terminal. Electrical energy cannot be produced by a chemical reaction itself except it is connected in circuit (Bernardes *et al.,* 2004).

2.2.5 Battery operation

Every chemical battery has its basic characteristics. There exist four main components in each chemical battery:

- Anode: The negative electrode in battery is anode. Electrons flow from anode compartment.
- Cathode: The positive electrode is called cathode. It is the electrode in battery arrangement that receives electrons usually from the anode.
- Electrolyte solution: The electrolyte is the substance that conducts electrons amongst the electrodes. It provides the channel of transferring electrons between the positive and negative electrodes terminals.
- Separator: The separator is the substance that prevents transport of electrons when the battery is not in use.

Battery as a device stores energy in form of a voltage potential. Charge partitions between the electrodes can produce potential energy that will give rise to current flow in the incidence of electrical load. Chemical reactions occur at the electrodes interface during battery operation. These types of reactions are usually referred to as oxidation-reduction or REDOX reactions. Redox reaction is described as a chemical reaction by which there is an exchange of electrons, resulting into production of electrical energy. One of the advantages of secondary chemical batteries is the ability to rejuvenate or replenish their energy. During charging process, chemical reaction between the electrodes replenishes the energy lost during discharging to the battery by external energy means.

2.2.6 Properties of batteries

Certain features are used to describe and compare batteries. Battery’s operation can be explained by the following terms.

- **Battery’s Capacity**: This defines the amount of energy the battery can deliver at a given time or conditions. It describes the amount of energy in amp that a battery can deliver. For instance, 50 Amp per hour battery can deliver 50 amps of current per hour.
- **State of Charge (SOC):** The term SOC measures the amount of energy remaining in the battery at a certain time. It is usually describes as percentage of the battery’s actual capacity and it is usually affected by operating conditions (Battery usage) such as battery’s current loading and battery’s operating temperature.
- **Intensity of Discharge (IOD):** This is the reverse of SOC. The intensity of discharge describes the amount of energy lost by the battery. It also expresses the percentage of actual battery’s capacity. It corresponds to the total battery capacity being discharged.
- **Condition of Health (COH):** The condition of health of a battery defines the battery’s condition during use and gauge it ability or performance when compared to a new battery. This also describes the battery’s age.
- **Energy Specificity:** This describes the amount of energy contained in a specific mass of battery. It is the ratio of energy capability to its mass Wh/kg.
- **Specific Power:** This determines the amount of energy contained in a specified battery mass. It can be expressed as ratio of energy capability to mass Wh/kg.
- **Shelve Life:** It describes the duration of time the battery can deliver energy for maximum performance.
- **Cycle Life:** This is the number of reversible cycles a battery is able to undergo during it optimum usage and application.
- **Impedance:** The impedance of a battery defines its voltage and current relationships as a function of usage frequency alongside other variables, such as temperature and SOC. Batteries experience energy lost while discharging and these losses may be represented as resistance.

- **Power supply:** Battery's capacity to supply power is defined by its ability to supply desirable current. The quality and strength of a battery, is determined by the current it can discharge.

  Different battery types have various merits and demerits which can be described by their component features. Secondary chemical batteries have extremely diverse qualities depending on the type of chemicals used. Above features do not portray every aspect of battery's efficiency but elucidates on major differences in many battery types (Young *et al.,* 2013).

2.2.7 Types of batteries

Lead-acid batteries: These are mostly present in industries and automobile battery manufacturing. Pb- acid batteries often comprised of two plates of Pb alloy band, Pb-dioxide and sulphuric acid as the electrolyte primarily. In the process of discharge of Pb-acid battery, lead sulphate is formed (Espinosa *et al.,* 2004).

Lithium-ion battery: Li-ion type of battery is a type of battery that has no heavy metal such as mercury, cadmium, nickel, or lead as part of it composition. The battery configuration contains highly reactive and flammable electrolyte. Li-ion battery positive plate comprises of $LiXMA_2$ and graphite rod as the negative plate. The battery's electrolyte is composed of an organic liquid of $LISIO_4$ $LiBF_4$ and $LiPF_6$ (Bernardes *et al.,* 2004).

Nickel cadmium batteries: Of all rechargeable batteries, these are the most used batteries. This is a kind of secondary battery appropriately used for portable devices for many years. The battery uses cadmium as the cathode electrode. The anode plate is made up of Ni(OH) and the electrolyte is a combination of KOH and $LiOH_2$ (Bernardes *et al.,* 2004).

Nickel metal hydride (NiMH): This type of battery was developed to replace NiCd batteries. It has been discovered to effectively function in different ranges of temperature and it poses to have long lice and minima discharge rate. The anode electrode comprises of porous nickel plate and nickel hydroxide acting as activation agent. Ni-MH cathode made use of hydrogen alloy powder coated on metal mesh. The electrolyte used in Ni-MH battery is typically potassium hydroxide. A separator usually is a non-conducting insulating material used to separate the two electrodes (Bernardes *et al.,* 2004).

2.2.8 Lead acid battery

Pb-acid batteries (LABs) are the main supply of power intended for automobiles, lawn and garden tractors, motorcycles, forklifts, trucks, boats and golf carts. Pb-acid batteries also support a range of energy support systems in computers and any other products that requires a rechargeable battery. Some significant applications of lead acid batteries include powering electric vehicles, power sustaining devices (UPS) during power failure and supplying power for military operations which are important. The Pb-acid battery being an age long form of battery that is rechargeable and the innovation was first attempted in 1859 by French physicist Gaston Plante. Irrespective of minima energy/volume and energy/weight ratio, Pb-acid batteries supply of high surge currents implies that the cells in the batteries have comparatively large power/weight ratio. Apart from the battery's low cost, these features made the battery applicable for use in motor vehicles for high current required automobile starter motor.

The Pb- acid battery is made up of many materials and it is a complex industrial product. The actual components of a Pb-acid battery are; metallic connections, cathode-positive electrode consisting of PbO_2, metallic grids, active mass of anode-negative electrode comprising of metallic Pb, electrolyte-aqueous solution of H_2SO_4 and polypropylene casting box (Salomone *et al.,* 2005).

2.2.8.1 Lead-acid battery cell build-up

Construction of the Pb-acid battery is a little bit complex. The Pb-acid battery makes use of lead grid structure which is composed of Pb-oxide paste has the construction material for the electrodes. The Pb-oxide paste takes time to dry up when it is introduced to the lead alloy grid structure. The cell is thereafter soaked inside electrolyte made up of sulphuric acid and then enclosed in a polypropylene plastic in different sizes suitable for various uses. When current passes across the plates, the Pb-oxide is converted into Pb-dioxide at the positive plate, and Pb-oxide into Pb at the negative plate (Hansen, 1999).

2.2.8.2 Lead acid battery charged state

When battery is charged, elemental Pb is deposited at the negative plate and the positive plates becomes lead (IV) oxide (PbO_2) inside an electrolyte of about 33.5% v/v (4.2 mol/L) sulphuric acid (H_2SO_4). The charging process is characterised by the removal of electrons from the positive plate while the electrons are introduced to the negative plate by the charging process.

Reaction at Negative terminal:

$PbSO_{4(s)} + H^{+}_{(aq)} + 2e^{-} \rightarrow Pb_{(s)} + HSO_4{}^{-}_{(aq)}$

Reaction at Positive terminal:

$PbSO_{4(s)} + 2H_2O_{(1)} \rightarrow PbO_{2(s)} + HSO_4{}^{-}_{(aq)} + 3H_{(aq)} + 2e^{-}$

2.2.8.3 Lead acid battery discharged state

At the state of discharge, the two terminals (positive & negative) become $PbSO_4$. The discharge results into loss of electrolyte-sulphuric acid and becomes principally water. The discharge process is with transmission of electrons from the negative plate to the cell at the positive plate in an external circuit.

Reaction at the Negative plate:

$Pb_{(s)} + HSO_4{}^{-}_{(aq)} \rightarrow PbSO_4 + H^{+}_{(aq)} + 2e$

Reaction at the Positive plate:

$PbO_{2(s)} + HSO_4{}^{-}_{(aq)} + 3H_{(aq)} + 2e^{-} \rightarrow PbSO_{4(s)} + 2H_2O_{(1)}$

The overall reaction is:

$Pb_{(s)} + PbO_{2(s)} + 2H_2SO_{4(aq)} \rightarrow 2PbSO_{4(s)} + 2H_2O_{(1)}$

2.2.9 Peukert effect

Peukert law was presented in 1897 by Wilhelm Peukert. It expresses more or less the changes and reduction in capacity of rechargeable Pb-acid batteries at different discharge rates. According to Peukert effect, the capacity available in the battery reduces as the discharge rate increases. There is no linear correlation between the capacity and the rate of discharge in lead batteries. The lead battery experiences Peukert effect when exposed to higher discharge rates. The Peukert effect can be represented by equation relating accessible battery capacity and discharge current. It is largely modelled as an exponential function with different battery types having their Peukert constants suitable to be inputted into the equation. Pb-acid batteries is said to have 1.3 as Peukert (Buchmann, 2001). The less peukert effect of a particular battery is known when the number is nearer to 1.

$Q = K.I^{1-n}$ (Peukert Equation) – where Q stands for capacity while I stands for current. The K represents battery distinctive constant and n stands for the discharge rate sensitivity exponent. Peukert equation significantly elucidates and measures noticeable battery's capacity decrease to its discharge rate (Fasih, 2006). It also describes the internal resistivity of the battery according to its effectiveness. A peukert value nearest to 1 signifies an efficient battery effectiveness amounting to minima losses and by implication the battery has a lesser internal resistance (Buchmann, 2001).

2.2.10 Coup-de-fouet effect of lead-acid battery

The initial wash that often takes place in the lead-acid batteries discharge is referred to as the coup-de-fouet. This effect takes place in the process of loading the battery suddenly on a long-term float charge (Hansen, 1999). Float charge can be defined as drip or trickle charge and it is a term that finds common expression when operating Pb-acid batteries. This describes the charging procedure that constantly sustains the Pb-acid battery at full state of charge by charging the battery at equal rate it is discharging. The process of discharging the battery, Pb-dioxide is converted into Pb-sulphate. This sequential chemical reaction takes place when $PbSO_4$ molecule is produced at the electrodes. Specifically, during the early discharge of battery, the reaction is believed to be inefficient when compare to the time Pb-sulphate molecules are generated (Hansen, 1999). By implication, initial voltage drop is observed during discharge and the molecules are recovered when the chemical reaction progresses and becomes more efficient with the generation of $PbSO_4$.

2.2.11 Surface charge of lead-acid battery

Surface charge implies the pilling up of charges on the electrode surface when the battery is charging or discharging. Surface charge is predominantly common to Pb-acid battery compare to other battery types such as Ni-MH. Any scientific research dealing with dynamic testing, surface charge is usually an encountered issue. It present an efficient battery as inefficient and vis-versa via an open voltage measurement. When the voltage of a battery is measured directly after charging, the battery's voltage becomes extremely high even when the battery is over-charged beyond voltage limit. This happens as a result of charge pilling up on the surface of the electrodes. To measure an open circuit voltage, minimum of 4-12 hours should be observed to allow the charge that has piled up to dissolve. The higher the rate of charging or discharging, the larger the surface charge accumulated by the battery (Fasih, 2006).

2.2.12 Abusive use of lead-acid battery

LAB is recognised for its resilient abusive use. Pb-acid battery can withstand varied temperature limits. Nonetheless, an extremely high temperature reduces the lifespan of the battery (Buchmann, 2001). Certain conditions are capable of reducing and damaging the life span of battery. To a greater extent, discharging batteries beyond a certain limit damages and reduces the battery efficiency. The use of battery determines its cycle and calendar life, therefore adequate measures should be taken to elongate battery's life.

2.2.13 Over-charging of lead-acid battery

Adequate and efficient procedures of charging Pb-acid battery have been developed over the use of the product. One of the methods adopted by the commercial battery repairer/ chargers has been multi-stage charging method which initially regulates the charge current before controlling the voltage limit. Initially when the battery is connected to high current charging source, it charges rapidly to a particular voltage limit, then the charger changes to a controlled voltage such that the battery charges slowly to it full capacity.

Another procedure of charging a battery is the use of direct power supply. Pb-acid battery can be charged with a constant voltage threshold and then limit the current to a maximum ampere point. Other charging processes employs pulse charge methods which is reported to decrease the amount of cell corrosion during charging, it effectiveness has not being conventional (Buchmann, 2001).

Regardless of the method of charging, overcharging is hardly controlled and this causes cell corrosion at the electrodes which in turn causes permanent battery damages (Buchmann, 2001). There are two major ways of overcharging Pb-acid battery: voltage and current. Charging of Pb-acid battery at high current causes corrosion and overcharging, likewise charging the battery at high voltage will cause the same effect. Overcharging reportedly birth the breakdown of battery and this will lead to gassing eventually.

2.2.14 Over-discharging of lead-acid battery

To prevent cell damage, a Pb-acid battery should be able to abrogate itself when discharged at a specified voltage. This operating condition is usually restricted to 1.75V/cell (Buchmann, 2001). Therefore, a 12V battery should abrogate discharge at 10.5V. When this limit is exceeded, the battery becomes over-discharged. Over-discharging of battery results into cell reversal and short circuiting of the battery becomes inevitable.

2.2.15 Failure of lead-acid battery

Generally, batteries are associated with malfunctioning after a specific period of time and operating conditions. This malfunctioning is not limited to Pb-acid battery but common among other batteries such as Ni-MH batteries. The main malfunctioning of Pb-acid batteries is the corrosion of the battery components (positive grid, negative strap), dry out of water from the electrolyte, loss of active material, sulphation, cell exchange, high self discharge, hydration and thermal exhaustion.

Most battery degradations are due to corrosion of the positive grid. This malfunctioning is common to most operation of the battery, but abusive use of the battery accelerates the failure of the battery. Corrosion of the negative strap is often observed in

VRLA batteries. Corrosion of the negative strap can be minimised by avoiding complete immersion of the strap in an electrolyte solution as this will prevent untimely deadness of the battery. The negative plates depolarised to corrode and breakdown causing malfunctioning of the battery. Some manufacturing processes now put the negative strap in absorbed glass matt to prevent corrosion of the negative strap. The surface area of the battery is reduced by the effect of corrosion on the battery surface. The active area of the battery plates are prevented from interaction with the battery electrolyte (Hansen, 1999). This results in loss of capacity because the capacity to store charge by the battery is drastically reduced.

Water reduction or loss in battery electrolyte has great effect not only on Pb-acid batteries but also on other batteries using electrolyte solution. It reduces the chemical conductivity and this result in increase of internal resistance, consequently resulting in loss of potencies and power. Electrolyte plays very important role in battery's reactions and also accounts for loss of battery's capacity. Venting reduces the available water in the electrolyte. Loss of water also occurs by diffusion through battery casing. Vented (VRLA) has the capability of restoring water loss by the electrolyte but valve (VRLA) cannot restore water loss.

Capacity loss is associated with loss of active materials on the positive plate of a battery. This is usually observed during battery overcharging where excessive gassing ejects active material on partly corroded positive plate (Hansen, 1999).

Sulphation is another important consideration in Pb-acid battery as it occurs during discharge process and is eliminated during charging process. Sulphation can become permanent if the battery undergoes abusive conditions. When the rate of battery discharge is high, sulphation growth is inevitable. Sulphation growth is also observed when the battery is left at low level of charge while operating at high temperatures. Sulphation can generally be overcome by charging under suitable conditions.

Cell reversal and self-discharge are factors that are not commonly observed in Pb-acid batteries because of the high abuse tolerant of the battery (Buchmann, 2001). A Pb-acid battery is designed to self discharge at 5% on monthly basis which makes it advantageous to other batteries such as Ni-based and Li-based batteries. However, abusive cycling of the battery leads to an increase of its discharge.

Heat exhaustion is another associated parameter in Pb-acid battery. This refers to a condition where the battery generates internal heat thereby destroying itself. This usually happens during overcharging. When the battery is heated, more current is needed to keep the voltage at a moderate level. This supply of current generates more gas and thereby generating more heat (Hansen, 1999).

2.2.16 Life expectancy of lead-acid battery

Batteries are designed with life expectancy even when they are rated under best conditions. No matter how carefully a battery is operated, it does not guarantee how long the battery will supply energy. However, it is certain life expectancy of the battery is abridged under abusive operating conditions. Researches have been focused on loss of capacity rather than loss of power by Pb-acid batteries since the battery is designed to supply power. Batteries are judged to reach end of it life when the capacity drops below 80% for certain use. This percentage notwithstanding, Pb-acid batteries can still be functional by certain adjustment. Life expectancy of battery is comparatively related to the battery's IOD and operating temperature.

2.2.17 Application of Pb-acid batteries

Almost all (above 95%) of electric vehicles are powered by Lead-acid batteries, and this means of transportation has grown so much in the last few decades not exclusive to Africa but almost all over the world. An electric bicycle, tricycles, automobiles, motor-cycles and buses use Pb-acid batteries and have increased the demand for Pb used in Pb-acid batteries. LABs are mostly employed in electric power, telecommunication networks, energy storage systems (solar-wind power) because of numerous advantages of moderate price, stable performance, high voltage and favourable temperature range (Chang *et al.,* 2009).

2.3 Lead waste generated by industries

Metallic lead (Pb) can be grouped into primary and secondary ores. Principal Pb is directly mined from ores while secondary Pb can be obtained from scrap Pb products (automobile LABs). Various lead using industries generate lead containing waste in different capacities. Basically automobile lead acid battery industries generate the larger percentage of waste, comprising sulphuric acid, polypropylene plastics and furnace slag. Metallic waste of this kind is also associated with metallurgical operations. These wastes depend largely on the value of rudimentary materials used and management applied. Wastes are essentially of two types - hazardous and non-hazardous wastes which include toxic metals, heavy metals (Pb, Cd, Cr, Ni, Cu, Hg and Zn) depending on tolerable limit set for each metal.

2.4 Primary lead production

Galena (PbS) is the most essential form of lead ore. Others are formed from this ore. It is usually found in combination with zinc which has to be selectively extracted. The most common extraction method is froth flotation. The ore is pulverised in ball or roll mill and form fine suspension in water. In the presence of chemicals and well agitation, air is passed through the mixture and the required minerals connected to the air bubble which is passed to the surface to form mineral froth that can be easily skimmed off. Pyrometallurgical primary lead processing chart which modelled the ore processing unit is presented in (Figure 2.1). Sahu *et al.* (2000) presented a detailed typical primary lead facility waste produced, the amount, compositions and disposal approach of major plants. Dumping or stockpiling of Pb-discharge furnace residue, flue dust and imperial smelting furnace (ISF) residue is a usual practice of the primary plants which is no longer acceptable because of leachate generated in the long run thereby affecting the environment.

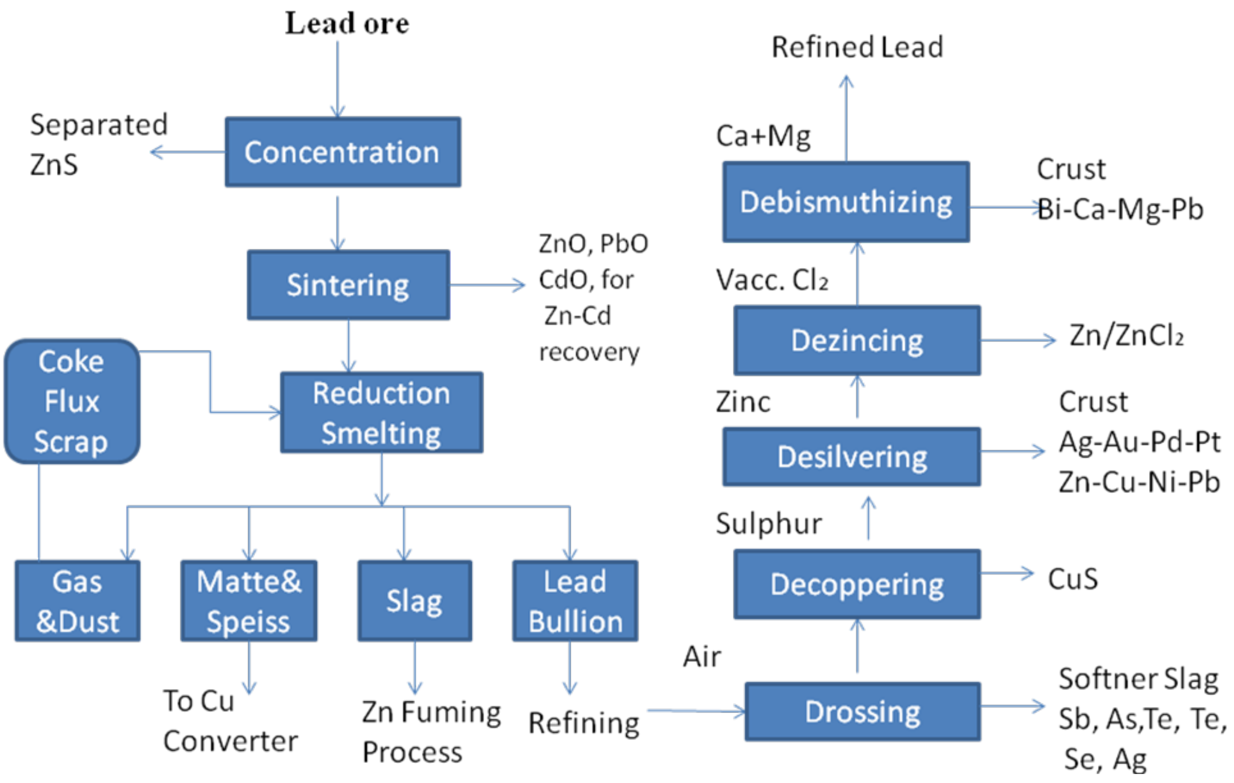


Figure 2.1: Recovery flow chart of primary lead ore

Source: Sahu, 2000.

A typical zinc-lead smelter is reported to generate blast furnace (BF) slag of 15,000 metric ton containing Pb=1.5-2.0%; SiO_2=20-22%; FeO=36-38%; MnO_2=3.0%; CaO=14%; MgO=2.0%; Al_2O_3=6-7%; Zn= 5-7%, and S = 2.0%.

Ordinary Cu dross contains Pb=83.0%; Ag=0.09%; Cu=2.0% and Zn=1.0%.

Antimony Dross Pb 7.0%, Ag 0.05%, Cu 0.3%, Zn 1.0%, Sb 2.0%.

Final Refinery Dross Pb 72.0%, Ag 0.03%, Cu 0.2%, Zn 5.2%, Sb 0.5%

Enriched Liquidation Silver Crust Pb 78.0%, Ag 5.8%, Cu 0.7%, Zn 14.0%, Sb 0.1%

Another of such primary plant that produces imperial smelting process (ISP) slag of 42,000 MT- Zn 6-9%, Pb 0.6-0.7%, Cu 0.19%, Sb 0.01%, Ag 19g/MT, Au 0.04g/MT, FeO 33%.

Matte and Speiss 1,300MT/Y Pb 17.3%, Cu 44.6%, Sb 1.2%, Ag 19.50g/MT, Au 1.9g/MT.

Silver Crust – 370 MT/Y Pb 24%, Cu 2.4%, Ag 15%, Au 0.012%.

At different levels, these wastes are treated to recover precious metals for different industrial purposes. By the conventional process, purified Pb will have purity of > 99.9% (Sahu *et al.,* 2000).

2.5 Secondary lead production

The single largest secondary producer of metallic lead (Pb) is in the automobile lead-acid batteries industry. Other sources include antifriction metals industry, solder and type metal. Lead (Pb) can be got from casing cables and inside layer of laboratory wash sinks. It is extensively found in plumbing. Pb can also be used as defensive sheet against X- ray and nuclear radiation. There are many compound of Pb of wide use. Lead oxides are of several commercial applications. Litharge- lead monoxide PbO, red lead - lead tetroxide Pb_3O_4; lead dioxide PbO_2, are utilised in making fire matches and as dye mordant in dye production . White Pb, $2PbCO_3 \cdot Pb(OH)_2$ (basic lead carbonate) is commonly used in manufacturing of paints and ceramics. Chrome yellow, $PbCrO_4$, is a bright yellow pigment. Sublimed white lead, $PbSO_4 \cdot Pb(OH)_2$ (basic lead sulphate), is also used as a pigment. Lead acetate (sugar of lead) is used as a mordant, and lead azide, $Pb(N_3)_2$, is employed as a detonator for explosives in ammunition. Lead arsenate is used in agrochemicals production as an insecticide. Tetraethyl lead was used as an antiknock compound in gasoline, which is now banned for its environmental consequences (Nriagu, 1983). Figure 2.2 illustrates the industrial application of lead in various capacities.

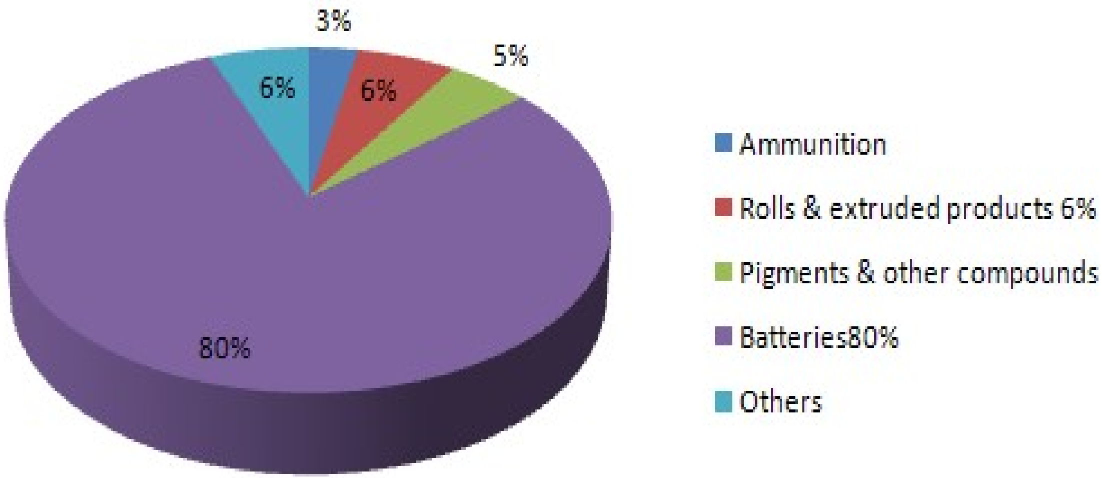


Figure 2.2: Industrial distribution of lead secondary industry

Source**:** http://www.expertsmind.com/questions/chemical-action-in-lead-acid-battery-30111769.

In secondary lead processing, batteries are dismantled and sorted into their chemistries. Polypropylene are recycled into battery cases, sulphuric acid is either neutralized or recycled for local use. Lead paste is desulphurised to reduce SO_2 emission and generation of waste sludge. This is usually done with soda ash, producing sodium sulphate as by product. A schematic flow chart is presented in Figure 2.3.

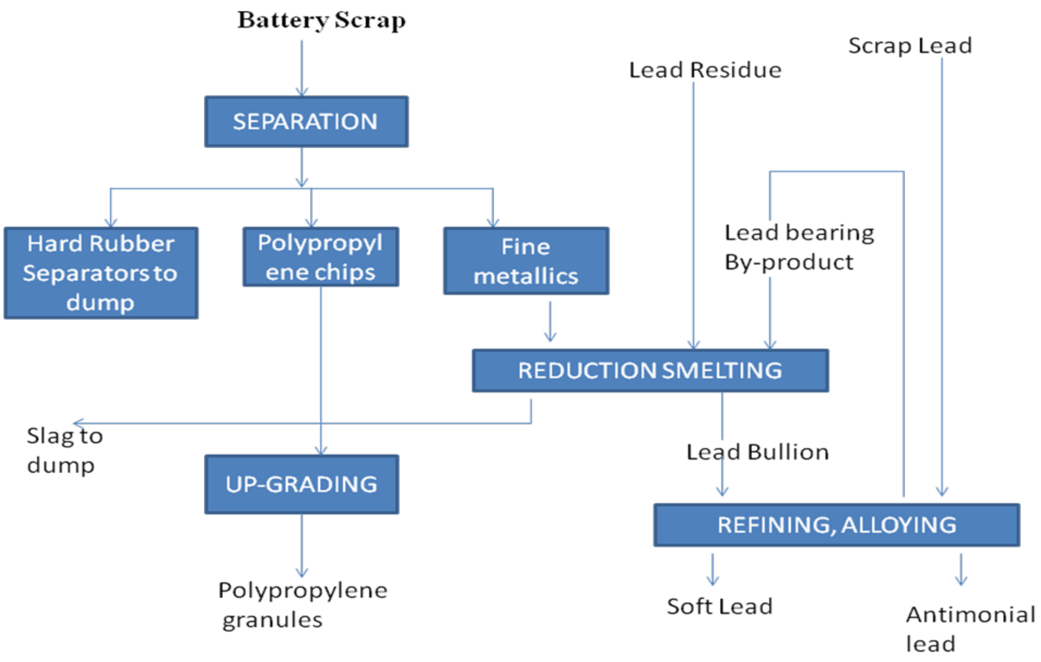


Figure 2.3: Pyrometallurgical flow chart of scraped lead

Source: Sahu, 2000.

Waste Pb-acid battery reprocessing/recycling

Subramanian (1995) reported that more than 90% of spent batteries are recycled in most developed nations and under recycled in developing nations. The rate of battery recycling is a factor of measuring the amount of lead recycled from batteries with the quantity available for recycling in a given year Table 2.1

Table 2.1: The Recovery Rate % of Secondary Lead in Some Developed Countries

Countries	**1986**	**1988**	**1989**	**1990**	**1991**
France	80	-	90	-	-
Germany	83	-	-	-	95
US	-	91	95	98	-
UK	84	-	-	-	93
Japan	93	92	94	92	-

Source: Subramanian, 1995.

Behrendt and Steil, (1997) reported that Pb-acid battery designed to start, lighten and ignite (SLI) an engine is primarily composed of the followings by mass Table 2.2. Sahu *et al.,* (2000) in his presentation reported a typical smelter that emits about 1 ton of Sulphur content into the atmosphere. A Stolberg Sinter/shaft till 1991 recorded the following as shown in Table 2.3.

Table 2.2: General Battery Composition

Components	**Wt.%**
Lead metal	34%
Lead Oxide Paste	39%
Polypropylene	5-6%
Electrolyte	11-12%

Source: Behrendt and Steil, 1997.

Table 2.3: Pb-SO_4 Emission by Technologies

Items	**Primary Pb Production**		**Secondary Pb Production MRV Technology**
	Sinter/Shaft Furnace	QSL Furnace energy recovery	
Energy MJ/MT Pb	10,000	7000	6000
SO_2 Emission-Air Kg/MT Pb	70	4	1
Lead Emission-Air g/MT Pb	140	40	7

Source: Sahu *et al.,* 2000. (QSL Queneau-Schuhmann-Lurgi furnace)

Deducing from the furnace emission rate in Table 2.3, it is not likely the informal recyclers have a functional furnace. The recovery rate of lead hardly gets up to 60% of lead from a spent battery. Therefore environmental pollution is inevitable by the open burning and recycling. (Viswanathan and Thamhani, 1991) reported that informal lead recyclers generate lead to air borne pollution up to 0.13 to 3.1mg/m^3. Typically, unrestrained emission of LABs stands at 8 kg of Pb per every thousand batteries. 80% emission is associated with recycling environment.

Anon MMR (1999) projected the demand for lead to rise to 161000MT in 1999-2000 and estimated the gap between demand and supply to be 81, 000 MT according to Table 2.4. 70% of lead produced is consumed in lead acid battery sector due to demand in automobile industry.

Table 2.4: Estimated Demand and Supply of Lead in '000 MT

Item	Actual	Years		Projected	Years	
	'94-95	'95-96	'96-97	'97-98	'98-99	'99-2000
Automobile	44	47	55	63	70	78
Railway & other sector	19	20	24	24	26	28
Total Battery Sector	**63**	**69**	**79**	**87**	**96**	**106**
Other Applications	34	35	41	45	50	55
Total Demand	**97**	**102**	**120**	**132**	**146**	**161**
Estimated Production	76	86	90	80	80	80
Demand & Supply Gap	21	16	30	52	66	81

Source: Anon MMR, 1999.

2.6 Heavy metal composition of discarded batteries

Lead acid storage batteries widely used in motor vehicle contain a high percentage of lead, cadmium, copper, zinc, manganese, mercury, nickel and lithium at considerable minimal amount. When spent, it becomes hazardous waste potentially dangerous to the health of the populace and ecosystem. Hazardous/toxic waste is any type of waste which contains organic and/or inorganic elements/compound which may have detrimental impact on health and environment, owing to the imminent chemical, physical, or toxicological qualities. Harmful waste can cause injury, illness, death and ruin of the environment when it is not treated, kept, transported or disposed properly. Harmful waste can contaminate the surface water, underground water, air or soil. Different categories of harmful unwanted substance are usually recognised ranging from organic to inorganic toxic chemicals. Waste information regulation classified hazardous waste into twenty-three categories (Table 2.5) according to the level of their risk (DEA, 2011).

Table 2.5: Classification of Hazardous Waste

Category	**Waste Type**
HW 01	Gaseous waste
HW 02	Mercury containing waste
HW 03	Batteries
HW 04	POP waste
HW 05	Pesticides containing waste
HW 06	Inorganic chemical waste
HW 07	Asbestos containing waste
HW 08	Waste oil
HW 09	Organic halogenated and/or sulphur containing solution
HW 10	Organic halogenated solid and compound with Sulphur
HW 11	Organic solvent without halogens and Sulphur
HW 12	Other organic substance without halogen and Sulphur
HW 13	Bituminous petroleum waste
HW 14	salt water
HW 15	Fly ash/residue and dust from diverse filter and sources
HW 16	base ash
HW 17	Residue
HW 18	Mineral waste
HW 19	Waste of electrical and electronic equipment (WEEE)
HW 20	Metal scrap
HW 21	Health care risk waste (HCRW)
HW 22	Sewage sludge
HW 99	Miscellaneous

Source: DEA, 2011

2.6.1 Lead

Metallic Pb is classified as an extensively use non-ferrous metallic element and it has a great number of industrial applications. Specific industries in which lead-containing solids dust and its fumes are encountered are the mining, petroleum industry and smelting of sulphide ores, cutlery and manufacture of storage batteries, paints and pigments, ceramics, glass, and ammunition. All soluble compounds of lead are poisonous. Toxicity increases as solubility increases. Acidity of the medium causes an increase in the solubility of lead. Therefore acidified streams and lakes due to mine leaching and rain would magnify the lead poisoning of aquatic life. Lead pollution in water may occur due to natural causes as well as domestic and industrial discard (plumbing, soldering waste). Lead is taken up through inhalation of air and intake of water, food, or dust. It has a tendency to accumulate in the body. Lead dust is absorbed primarily in the duodenum, bone and soft tissue. Once absorbed, lead is transported in the blood and binds to erythrocytes. As lead is not easily excreted, it interferes with the creation of blood cells (red) and results in a type of paralysis called lead palsy (Bhatia, 2005). A schematic flow of lead in human system is presented in Figure 2.4

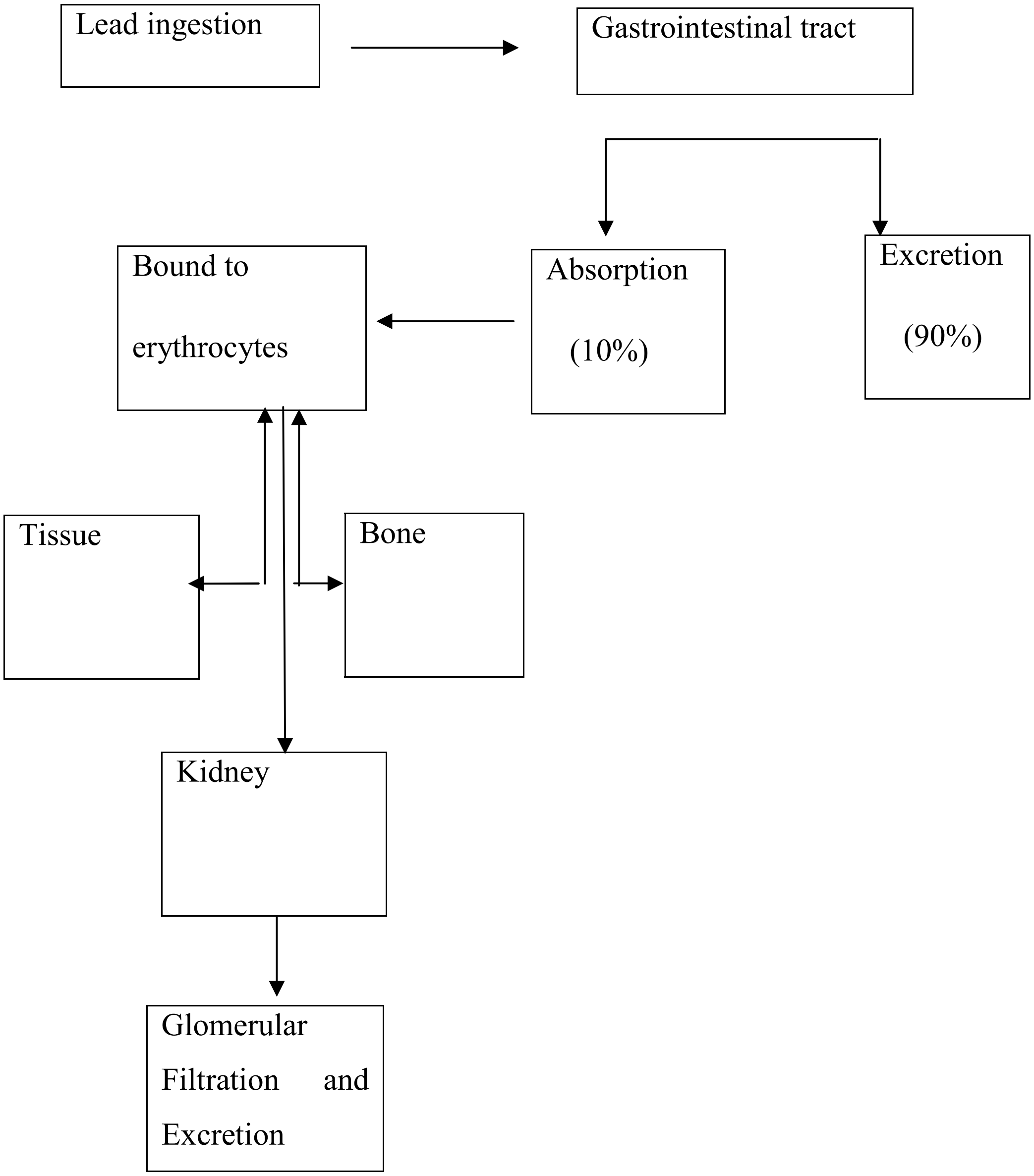


Figure 2.4: Schematic of lead transport in human system

Source: Bhatia, 2005

2.6.1.1 Sources of lead

Ash, auto exhaust, cigarette smoke, coal combustion, colour inks, pesticides, rainwater, food cans with lead solder sealing, toothpaste, wine, manufacturing batteries, cosmetics, hair dyes, lead pipes, liver, glazed ceramics, pencils, lead-based paint, industrial emissions.

Metallic Pb is relatively uncommon heavy metal relatively found in abundance in the earth's crust amounting to16 mg/kg (EPA, 1979). Out of over two hundred identified sources of Pb, three of them are significantly found in abundance which are- galena (PbS), anglesite ($PbSO_4$) and Cerussite ($PbCO_3$). Galena ore is the primary form of Pb in the natural state. Pb is closely associated with sphalerite (ZnS), pyrite (FeS_2), chalcopyrite ($CuFeS_2$), and other sulphur salts (May and McKinney, 1981).

2.6.1.2 Lead poisoning

Lead constitutes to metabolic toxin which impairs many health functionalities. Although exposure to Pb is minimal, continuous exposure to the metal causes affects the ecosystem and the health of the populace (Nriagu, 1978). Pb as mutagen and teratogen has been found out to be carcinogenic when the intakes exceed the permissible limits. It affects human reproductive system, destroys liver and interferes with central nervous system.

Ecological and toxicological attributes of Pb and its chemical counterparts (compounds) in the atmospheric, hydrological and lithospheric cycles have been comprehensively studied (Barth *et al.,* 1973). Concerned parties to the control of Pb had come up with five point of consideration on Pb toxicity. First, metallic Pb is classified as characteristic trace constituent of rocks, air particulate matter, weathered soils, plant parts and waste-water. Second consideration is that appropriately over four million metric tons of Pb is produced in different continents of the world for various applications such as the production of metal alloys, storage devices (batteries), colours, fuel additives and ammunition. Thirdly, Pb is not needed in effective growth and fruiting of plant and living organism. The fourth of the points is that Pb is deadly in whichever form. It is transferred through food chain. It can also be ingested, inhaled and dermally absorbed. Lastly, Pb is a bio-accumulating and fat soluble metabolic toxin that attacks behaviour, hematopoietic, vascular, central nervous system, kidney and human reproductive systems. Pb excessive intake results in decrease male fertility, miscarriages, inhibited development of foetuses, stillbirths, and sperm abnormality. This Pb exposure can also cause brain seizure, unconsciousness, and eventual death. Most children with acute Pb exposure end up having unrecoverable retarded growth or permanent neurological problem.

Plant growth is retarded by the uptake of Pb. Concentrations beyond tolerable limit in plant inhibit reproductivity, as well as reduced photosynthesis, division of cells and water absorption (Demayo *et al.,* 1982).

Pb has been regarded as most common causes of unintended death among domestic flora and fauna due to grassing on pastures contaminated by industrial lead activities, used crankcase oil, Pb-based paints, used oil filters, and Pb energy storage devices (Demayo *et al.,* 1982). Animals like horses, cattle grazing on the environment of Pb smelter in California exhibit traces of Pb pollution. Several cases of lead toxicosis in buffalos and cattle were reported in India as a result of grazing on grass grown near recycling Pb factories (Kwatra *et al.,* 1986). Apart from the complete reduction in milk production, there was also significant increase of miscarriages and foetus abortions in cattle that ingested and persistently graze on Pb-contaminated silage by Pb shot-pellet (Frape and Pringle, 1984).

2.6.1.3 Symptoms of lead poisoning

Symptoms of lead poisoning include Parkinson's disease, abdominal pain, renal dysfunction, restlessness, adrenal insufficiency, allergies, anaemia, impotence, liver dysfunction, anxiety, arthritis, blindness, headaches, hostility, nausea, numbness, cardiovascular dysfunctions, hypertension, colic, constipation, brain seizure, dyslexia, epilepsy, weakness, gout, hallucinations, hyperactivity, hypothyroidism, hyperkinesias, mental retardation, mood swings, menstrual problems, muscular dystrophy, multiple sclerosis, nephritis, nightmares, poor concentration, psychosis, schizophrenia, seizures, foetus death, tooth decay, vertigo and weight reduction (Radostits *et al.,* 2000).

2.6.1.4 Acute toxicity of lead

Pathologically, metallic Pb exhibit damaging consequence on haematopoiesis via imbalance of haemoglobin synthesis that cut short the life expectancy of red blood cell (erythrocytes) causing anaemia. Fundamental enzymes responsible for the formation of heme are Pb extremely sensitive. They are delta aminolevulinic acid dehydratase (ALAD), which catalyzes the dehydration of delta amino levulinic acid (ALA) to form porphobilinogen (PBG), and ferrochelatase heme synthetase (Barth *et al.,* 1973).

2.6.1.5 Mode of action of lead

The biochemical reaction of Pb alters the functionality of kidney, bone, CNS and the hematopoietic system that produces acute biochemical, histopathological, neuropsychological, fetotoxic, teratogenic, and reproductive effects (Boggess, 1977; Nriagu, 1978; De Michele, 1984). Pb in mammalian body enters the blood stream and attaches to the red blood cell. Blood effected with Pb spread between the extracellular fluids such that half of the ingested Pb stays in the blood stream after uptake. Although the site of storage of Pb in the body is unknown, it is believed that Pb is stored in the soft tissue and mainly in bone marrow. The average span of Pb in the blood is about 20 days. Twenty-eight (28) days in the human body and 600 to 3000 days in the bone marrow (De Michele, 1984).

Reaction pathway of Tetraalkyllead differs from the reaction pathway of metallic Pb. Tetraethyllead is lipo-soluble which makes it’s accumulation in body tissues easier. In spite of this, each of them stream into the bloodstream evenly between blood plasma and the red blood cells (Harrison and Laxen, 1981).

2.6.1.6 Permissible average daily intake of lead

Averagely, adult intake of lead on daily basis in the United Kingdom stands at about 1.6µg from the atmospheric pollution, 20 to 28µg from food chain. Although most Pb intake is from food, soil is another source of Pb contamination. Other sources such as waste water, air from industrial emission, soil, dust, paints. Lead (Pb) in the atmospheric air can contribute to soil lead levels by deposition through rain (Ferner, 2001).

Blood Pb concentrations among infants greater than 10mcg/dL raise great apprehension. Symptoms of Pb in adult blood become health challenge when the level exceeds 80mcg/dL (Dupler, 2001).

2.7 Effect of lead pollution

2.7.1 Harmful health impact of waste Pb-acid battery

LABs predominantly contained sulphuric acid together with large amount of lead. The acidic solution is extremely corrosive, it provides medium of reaction between the electrodes soluble lead and lead particulate. Lead is a toxic metal with severe health effects particularly in infants and young adult (Mansur *et al*., 2006).

Exposure to high levels of lead causes brain and kidney damage, impair hearing as well as other several related problems. On the usual, automobile battery on average weighs about 12 kilograms Pb. Ninety-six percent (96%) of mined lead is used in common Pb-acid battery, with the remaining 4% use for other application including weights for weighing scales and defensive coatings. Absorption of lead in significant concentrations in human body causes a considerable health risk. Whether exposure is single or prolong, lead poisoning occurs in major organs as the red blood cells, central and perial nervous system, and renal system (Rich, 1994). Acute lead poisoning causes severe kidney destruction/damage, central nervous system, liver, and the brain. It has been linked with carcinogenesis, reduced fertility, miscarriage, and spermatotoxicity. It causes anaemia, colic and mental disorders via defective memory, mental dullness, fatigue, nervousness, and anxiety. Lead exposure also results in hypertension that can lead to death. Uptake of lead by human body is very important. Between 48 to 64% of lead inhaled deposits in the lungs and gastrointestinal retain 15% of such inhaled Pb (Sahu *et al.,* 2000). The pollution control and enforcement authorities are well aware of the ill effect of lead but they lack enforcement (Thadhani, 1996).

2.8 Environmental impact of spent lead acid battery

Toxic substances such as spent LABs have varying effect on the immediate environment and mostly include consumption of natural resources, global warming and climate change, photochemical smog, ecotoxicity and water pollution.

Production of LABs generally ingest raw Pb resources, this contributes to an accelerated extinction of conserved natural resources.

Manufacturing of LABs produces particulate exhaust, SO_2 and other Pb pollutants into the atmosphere, thereby contributing to the pollution index. This is because potential chemical hazards are associated with Pb emission into aquatic ecosystems. Carelessness of waste batteries handling results in the release of corrosive liquids and dissolved metals that are toxic to plants and animals. Improper disposal of batteries in landfill sites can result in the release of toxic substances into groundwater and the environment (Michael, 2010). An emission control standards for lead operating plant are given in (Table 2.6).

Table 2.6: Emission Control Standard for Lead Plants

Countries	**Work place Pb mg/NCM**	**Blood Pb µg/100mL**	**Emission Pb mg/NCM**	**Effluent Pb mg/L**	**Atmospheric Pb mg/NCM**
Australia	0.15	70* 30**	10	0.05	1.5
Austria	0.10* 0.20*	30* 100**	10	0.05	-
Canada	0.15	70	29	1.5	-
Denmark	0.10	50	-	0.1-0.5	2.0
EEC	0.15	70	-	-	2.0
Germany	0.10	70* 30*	5	0.2	2.0
India	0.15	80	10	0.1	1.5
UK	0.15	70* 40**	10	Variable	2.0
US	0.1	50	Varied	Varied	1.5

* Men ** Women * maximum value for Plant (NCM – Normal Cubic Meter)

Source: Thadhani, 1996.

2.9 Collection of spent battery

An efficient way of collecting spent LABs boosts the availability of the material for recycling. Swedish System imposed an environmental fee of about $8 on each battery sold in the home market. The fee is administered by the government to meet the cost arising from collection companies and recycling companies. In US like other developed countries, it is compulsory for a battery manufacturer to take back old batteries for new ones. Battery manufacturers/dealers must be required by law to collect the same numbers of battery sold through their dealers in the market as part of their social responsibilities. Some strict legislation with fiscal incentives and penalties are required.

Large consumers of lead acid batteries (LABs) such as railways, defence, transport sector, power units should discontinue the practice of disposing batteries without proper accountability. Collection of spent battery should be administered by some independent agencies or manufacturers themselves and should be financed by implementing additional tax on the new battery which could be used to subsidise the collection and transportation of spent battery to the formal sector. A corporative collection centred in different zones is an alternative. This will ease the stress of collection (Qianyu, 2013).

2.9.1 Creation of waste LABs in Africa

According to the International Lead Association, metallic Pb being a metal with optimum rate of re-utilisation of all material commonly used in daily activities, higher than the recycling rate of glass or newspaper. Amongst other factors, there is basically no degradation in the recycled lead compared to the lead from primary mining (ILA, 2016).

In many African countries, recycling of LABs is economically attractive because of its high lead-content. Due to inappropriate practices in most parts of Africa, the recycling of spent LABs is believed to have detrimental impact on the health of the populace and the environment (Manhart and Schleicher, 2015). Availability of statistical data on generated/spent lead acid batteries is difficult in many African countries. However, a consistent data base is needed to be generated. The OICA gives a consistent annual overview on the amount of vehicles still in use worldwide by continent and country. This applies to the figures in “World Commercial Vehicle still in use" by country and the type between 2005-2013 and “World Passenger Cars still in use" by country and the type between 2005-2013 as released by OICA in March 2015. The term V*ehicles in use* comprises all registered vehicles on the road.

According to OICA, the figures are collected via NTO (National Trade Oorganization), OICA members and its correspondents, National Offices of Statistics, Ministries of Transport. (OICA, 2016a). Two types of vehicles were considered:

i. **Passenger Cars**: Passenger vehicles are motor vehicles, not including motor cycle, meant for conveying of passengers and designed to accommodate at least nine persons at a time.

ii. **Commercial Cars**: Commercial vehicles are light-weight duty vehicles, weighty trucks, rail vehicle and buses.

In estimating the total sum of waste lead acid batteries (WLABs) in use in vehicles, the following formula was applied:

Generation of WLABs from vehicles (t/a) = passenger cars in use (n) ∗ LABs per vehicle (n) ∗ weight of LAB (t) / service life of LAB (a) + commercial vehicles in use (n) ∗ LABs per vehicle (n) ∗ weight of LAB (t) / service life of LAB (a)

This survey makes available approximately the WLABs generated in Africa continent per year. The calculation predominantly depend on data obtained from the International Organization of Motor Vehicle Manufacturers for the amount of vehicles still in use in Africa and assumptions of service live, weights and Pb content of WLABs.

Table 2.7 gives an overview on the number of passenger cars in use in Africa from 2007 to 2013 and the average annual rate of growth of each country. The annual numbers are given by OICA. The average yearly rate of growth is calculated on the basis of the individual annual growth rates from 2007 to 2013 (OICA, 2016a).

Table 2.7: Passengers Vehicles in Use in Africa (1000 Units)

Countries	**2007**	**2008**	**2009**	**2010**	**2011**	**2012**	**2013**	**Average Annual Growth Rate**
Algeria	2,212	2,395	2,593	2,691	2,800	3,050	3,268	6.7
Angola	400	566	574	590	610	640	670	9.8
Benin	146	153	160	167	170	180	190	4.5
Botswana	105	121	135	177	180	190	210	12.6
BurkinaFaso	105	109	112	116	120	130	140	4.9
Burundi	16	16	16	17	18	20	20	3.9
Cameroon	184	193	201	210	220	230	240	4.5
DR Congo	911	914	917	920	943	982	1,000	1.6
Egypt	2,400	2,546	3,000	3,437	3,600	3,800	4,000	9.0
Ethiopia	73	75	76	77	79	82	90	3.6
Ghana	370	500	440	450	470	490	510	6.4
Ivory Cost	298	312	326	340	350	370	390	4.6
Kenya	450	578	500	520	540	570	620	6.2
Liberia	16	13	13	13	14	15	20	4.9
Libya	1,400	1,420	1,430	1,436	1,500	1,600	1,700	3.3
Madagascar	110	146	141	150	160	170	180	9.1
Malawi	44	55	55	60	60	60	60	5.7
Mali	98	116	119	124	130	140	150	7.5
Mauritania	13	13	13	14	15	16	20	7.8
Mauritius	100	110	118	127	136	148	160	8.2
Morocco	1,644	1,721	1,798	1,875	2,000	2,100	2,200	5.0
Mozambique	156	156	204	233	240	250	270	10.0
Nigeria	2,200	2,250	2,288	2,400	2,500	2,600	2,700	3.5
Senegal	172	189	197	206	210	266	270	8.1
South Africa	5,161	5,276	5,411	5,596	5,832	6,111	6,377	3.6
Sudan	40	40	41	41	42	44	50	3.9
Tanzania	80	177	180	190	200	210	220	23.9
Togo	105	105	106	108	111	116	120	2.3
Tunisia	830	787	820	848	855	862	900	1.4
Uganda	91	94	97	101	110	120	130	6.2
Zambia	200	135	190	200	210	220	230	4.6
Zimbabwe	610	617	626	650	680	710	750	3.5
Africa	**20,740**	**21,898**	**22,897**	**24,084**	**25,105**	**26,492**	**7,855**	
Annual Growth Rate	5.6	4.6	5.2	4.2	5.5	5.1	5.0	
Estimated figures own calculation								

Source: OICA, 2016c. [Annual Growth Rate and Average Growth Rate calculated

Going by the calculated average yearly growth rate at hand, the quantity of passenger cars in use is extrapolated until 2016. Table 2.8 shows this forecast for passenger cars in use in the indicated African countries for years 2014, 2015 and 2016. In total, it is estimated that in the indicated countries around 32.7 million passenger cars are in use.

Table 2.8: Passenger Cars in Use in Africa Estimated between 2014 to 2016 (1000 units)

Country	**2014**	**2015**	**2016**
Algeria	3,488	3,723	3,974
Angola	736	808	886
Benin	199	207	217
Botswana	236	266	300
Burkina Faso	147	154	162
Burundi	21	22	22
Cameroon	251	262	274
DR Congo	1,016	1,032	1,048
Egypt	4,360	4,753	5,181
Ethiopia	93	97	100
Ghana	542	577	614
Ivory Cost	408	427	446
Kenya	658	699	742
Liberia	21	22	23
Libya	1,756	1,815	1,875
Madagascar	196	214	234
Malawi	63	67	71
Mali	161	173	186
Mauritania	22	23	25
Mauritius	173	187	202
Morocco	2,310	2,424	2,545
Mozambique	297	327	360
Nigeria	2,794	2,891	2,992
Senegal	292	316	341
South Africa	6,606	6,844	7,089
Sudan	52	54	56
Tanzania	273	338	419
Togo	123	125	128
Tunisia	913	926	939
Uganda	138	147	156
Zambia	241	252	263
Zimbabwe	776	804	832
Africa	**29,362**	**30,975**	**32,704**
Annual growth rate *own calculation*	5.4	5.5	5.6

Source: OICA, 2016a

Table 2.9 provides an overview on the number of commercial vehicles in use in selected African countries from 2007 to 2013 and the average annual growth rate of each country. The annual numbers are given by OICA. The average yearly rate of growth is calculated on the basis of the individual annual growth rates from 2007 to 2013.

Table 2.9: Commercial Vehicles in Use in Africa (1000 Units)

Country	**2007**	**2008**	**2009**	**2010**	**2011**	**2012**	**2013**	**Average Annual Growth Rate**
Algeria	1,100	1,150	1,254	1,290	1,330	1,483	1,567	6.1
Angola	90	124	126	130	130	130	133	7.5
Benin	20	38	39	40	41	40	41	16.3
Botswana	106	114	118	120	120	120	120	2.1
BurkinaFaso	44	46	49	51	52	50	52	2.9
Burundi	30	34	34	35	36	40	41	5.5
Cameroon	63	67	69	71	73	80	82	4.5
DR Congo	704	708	709	711	726	741	760	1.3
Egypt	750	931	940	954	980	1,010	1,030	5.7
Ethiopia	55	56	57	58	59	60	61	1.7
Ghana	200	280	270	280	290	300	310	8.4
Ivory Cost	373	403	414	424	440	450	470	3.9
Kenya	280	237	396	400	410	420	440	10.4
Liberia	40	38	39	40	41	40	41	0.5
Libya	400	410	420	430	440	450	470	2.7
Madagascar	160	365	370	380	390	400	420	23.7
Malawi	50	68	69	70	72	70	73	7.2
Mali	30	28	29	30	31	30	31	0.6
Mauritania	19	20	21	21	22	20	20	1.0
Mauritius	41	42	43	43	44	43	45	1.6
Morocco	512	553	569	582	600	620	730	6.2
Mozambique	57	57	72	82	84	90	94	9.0
Nigeria	660	670	679	690	710	730	740	1.9
Senegal	229	259	266	273	280	290	300	4.7
South Africa	2,642	2,741	2,810	2,876	2,962	3,057	3,149	3.0
Sudan	50	50	52	53	54	55	57	2.2
Tanzania	80	135	137	140	140	140	140	12.1
Togo	48	49	49	50	51	52	54	2.0
Tunisia	220	390	400	411	414	417	430	14.5
Uganda	212	219	259	265	270	280	300	6.1
Zambia	80	83	108	110	110	110	113	6.4
Zimbabwe	90	93	95	97	100	100	103	2.3
Africa	**9,435**	**0,458**	**10,962**	**11,207**	**11,502**	**11,918**	**12,417**	
Annual growth rate	10.8	4.8	2.2	2.6	3.6	4.2	4.7	

Source: Own compilation with data from OICA, 2016d.
Annual growth rate and average yearly growth rate calculated.

With calculated average yearly growth rate the number of commercial vehicles in use is extrapolated until 2016. Table 2.10 shows the forecast for commercial vehicles in use in the indicated African countries for 2014, 2015 and 2016. This sums-up to around 14.7 million commercial vehicles for all of the African countries analysed in 2016.

Table 2.10: Commercial Cars in Use in Africa Estimated between 2014 to 2016 (1000 units)

Country	2014	2015	2016
Algeria	1,663	1,765	1,873
Angola	143	154	165
Benin	48	55	64
Botswana	123	125	128
Burkina Faso	53	55	57
Burundi	43	46	48
Cameroon	86	90	94
DR Congo	770	780	790
Egypt	1,089	1,151	1,217
Ethiopia	62	63	64
Ghana	336	364	395
Ivory Cost	489	508	528
Kenya	486	536	592
Liberia	41	41	42
Libya	483	496	510
Madagascar	520	643	796
Malawi	78	84	90
Mali	31	31	32
Mauritania	20	20	21
Mauritius	46	46	47
Morocco	775	824	875
Mozambique	102	112	122
Nigeria	754	769	784
Senegal	314	329	344
South Africa	3,243	3,339	3,438
Sudan	58	60	61
Tanzania	157	176	197
Togo	55	56	57
Tunisia	492	564	646
Uganda	318	338	358
Zambia	120	128	136
Zimbabwe	105	108	110
Africa	13,104	13,855	14,679
Annual growth rate *own calculation*	5.5	5.7	5.9

Source: Own compilation with data from OICA, 2016d.
Yearly growth rate and average yearly growth rate calculated.

In order to estimate the yearly generation of WLAB in Africa on the basis of number of vehicles in use the following information and assumptions are taken into account; Lead acid battery for passenger car weighs 20kg and commercial weighs 50kg. It is estimated that a passenger car carries one battery and commercial vehicles carry minimum of two batteries. The life span of these vehicles is estimated to be two years and the lead content estimated to be 65%.

In Table 2.11 the calculated estimation of the total weight of WLABs per year and country is shown. WLABs generated by passenger cars in use in Africa in 2016 have a weight of about 330,000 tons. The commercial vehicles in use in Africa in 2016 are estimated to generate SLABs weighing round about 730,000 tons. In total, the generation of SLABs from the use in vehicles sums up to be more than 1 million tons in 2016.

Table 2.11: Total Annual Generation of SLABs from Vehicles in Africa 2016 (t/a)

	PCs in use2016 (‘000 unit)	Gene. of SLABs (‘000 unit)	Weight of SLABs (t/a)	CVs in use 2016 (‘000 unit)	Gene. of SLABs	Weight of SLABs (t/a)	Total Weight (t/a)
Algeria	3,974	1,987	39,744	1,873	1,873	93,637	**133,382**
Angola	886	443	8,865	165	165	8,256	**17,121**
Benin	217	108	2,168	64	64	3,224	**5,392**
Botswana	300	150	2,999	128	128	6,391	**9,390**
BurkinaFaso	162	81	1,618	57	57	2,831	**4,449**
Burundi	22	11	224	48	48	2,404	**2,628**
Cameroon	274	137	2,741	94	94	4,682	**7,423**
DR Congo	1,048	524	10,480	790	790	39,488	**49,968**
Egypt	5,181	2,591	51,811	1,217	1,217	60,863	**112,674**
Ethiopia	100	50	1,000	64	64	3,212	**4,213**
Ghana	614	307	6,137	395	395	19,751	**25,888**
Ivory Cost	446	223	4,462	528	528	26,393	**30,856**
Kenya	742	371	7,423	592	592	29,608	**37,032**
Liberia	23	12	231	42	42	2,078	**2,309**
Libya	1,875	938	18,751	510	510	25,476	**44,226**
Madagascar	234	117	2,336	796	796	39,780	**42,116**
Malawi	71	35	708	90	90	4,498	**5,207**
Mali	186	93	1,862	32	32	1,580	**3,442**
Mauritania	25	13	250	21	21	1,030	**1,280**
Mauritius	202	101	2,024	47	47	2,359	**4,383**
Morocco	2,545	1,273	25,452	875	875	43,750	**69,202**
Mozambique	360	180	3,596	122	122	6,093	**9,689**
Nigeria	2,992	1,496	29,917	784	784	39,181	**69,097**
Senegal	341	171	3,414	344	344	17,201	**20,615**
South Africa	7.089	3,545	70,894	3,438	3,438	171,900	**242,794**
Sudan	56	28	561	61	61	3,044	**3,604**
Tanzania	419	209	4,187	197	197	9,853	**14,040**
Togo	128	64	1,283	57	57	2,864	**4,148**
Tunisia	939	469	9,387	646	646	32,297	**41,684**
Uganda	156	78	1,555	358	358	17,917	**19,473**
Zambia	263	132	2,635	136	136	6,807	**9,442**
Zimbabwe	832	416	8,319	110	110	5,510	**13,830**
Africa	**32,704**	**16,352**	**327,036**	**14,679**	**14,679**	**733,960**	**1.060,996**

Source: Own compilation with data from OICA, 2016d.
Yearly growth rate and average yearly growth rate as calculated.

2.9.2 Generation of waste lead-acid batteries in United States

Estimation of consumption of raw material such as ore concentrate and refined metals is often not available. Apparently, consumption of raw material as defined is mine production + secondary refined production + imports (concentrates and refined metal) – exports (concentrates and refined metal) + adjustments for government and industry stock changes. The propounded calculation do not specifically provide exact amount of mineral commodity in products imported to or export out of the United State.

Although it expected to add the mineral in manufactured products as part of consumption estimate, it is sometimes difficult to collect and estimate such data (Biviano et al., 1999). To understand the consumption pattern of Pb and its compound, each sector end use and trade available data must be obtained. The calculation draws upon the findings of an earlier Pb consumption findings (Biviano et al., 1999) by the USGS for the period of 1984 to 1993.

Figure 2.5 reveals the quantity of materials in United State total consumption of Pb metal from domestic and foreign industrial sectors in 2004, according to trade data reported by the USGS and the U.S. International Trade Commission (USITC).

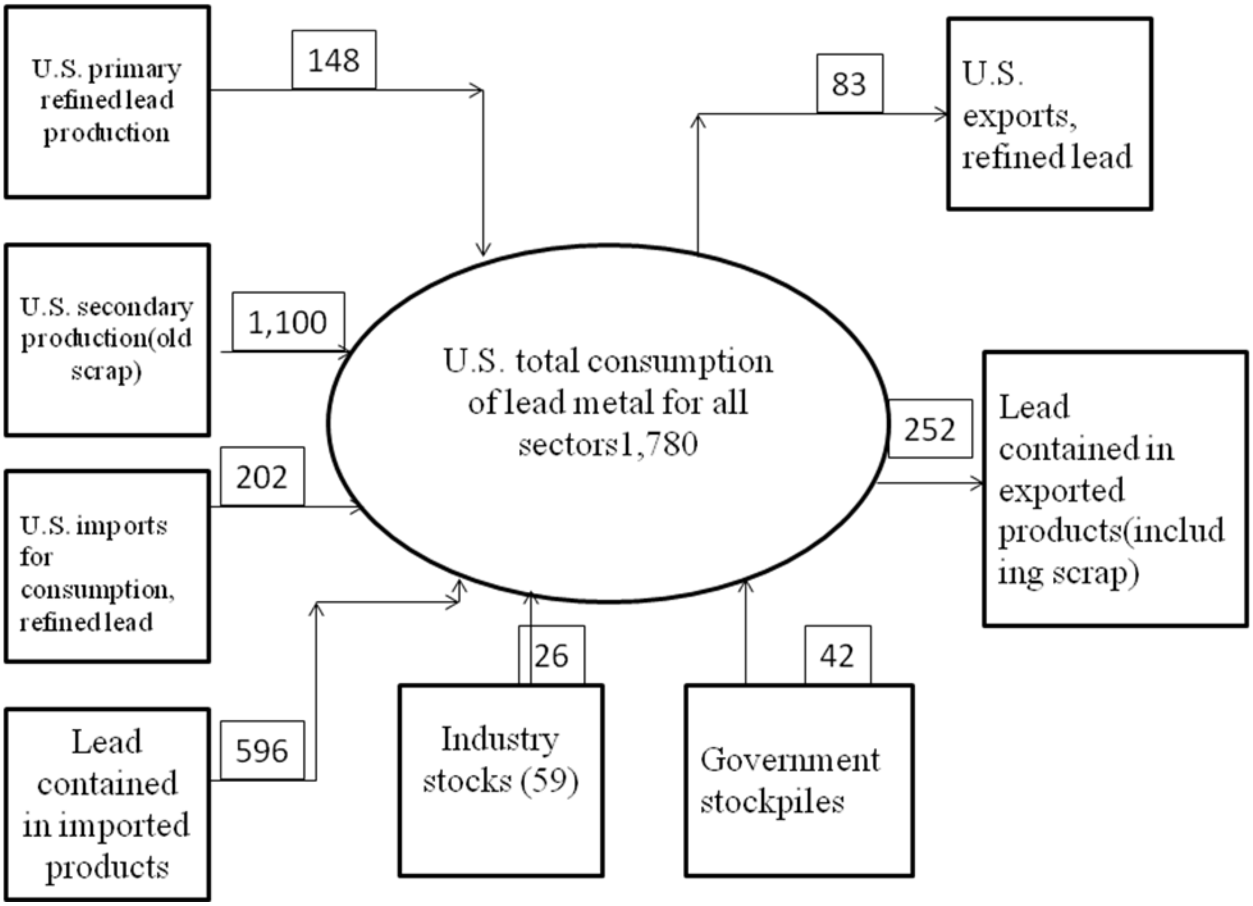


Figure 2.5: Flow chart of total Pb consumption in United State for 2004.

Source: USGS, 2016.

Total consumption has shown in the chart above is primary and secondary refined lead production + refined metal imports for consumption + refined lead contained in imported products – refined lead exports – refined lead contained in exported products + adjustments for government and industry stock changes.

Estimates of the average number of lead in different battery categories are enumerated in Table 2.12. The quantity of lead in Pb-acid batteries varies appreciably with battery types and slightly by manufacturers. Estimation of the average Pb content of battery was obtained by the Pb values for each of the battery classification.

Table 2.12: Average Lead Content Estimates

Classification	**Pb-acid battery types**	**Weight of Pb in battery, in pounds**	**Weight of Pb in battery, in kilograms**
Golf car	Golf carts or similar vehicles	41.1	18.6
Marine	Speed boats, trolling craft	30.9	14.0
Military vehicle	Motorized fighting vehicles, tanks	44.0	20.0
Heavy stationary	Uninterruptible power supply equipment	1,800	816
Small motive	Airline ground equipment or similar motive equipment	38.0	17.2
Passenger car/ light truck	Passenger cars, light trucks	21.5	9.7
Specialty vehicle	Industrial forklifts, mining equipment, or similar equipment	25.0	11.3
Tractor	Tractors	33.0	15.0
Truck and heavy duty	Trucks, heavy duty vehicles	38.7	17.5
Utility	Special purpose motor vehicles	9.1	4.1

(Pb (lbs) by Battery Council International 2005; Pb in (kg) by 2.2046 lbs/kg conversion factor.

2.9.3 Pb- acid batteries recycling processes

Spent/discarded lead-acid batteries may be recycled by processing in conventional lead smelter operations and by chemical conversion. Although the present trend is towards recycling batteries wastes in dedicated facilities operated by the manufacturer or by independent reprocessors that is environment friendly, cost effective and less energy consuming. Different recycling methodologies have been employed in recovering valuable metals from secondary waste as spent batteries among which are: crude smelting, pyrometallurgical processes, hydrometallurgical processes, lead mining and hydro-electrometallurgy (Li *et al*., 2012).

2.9.3.1 Thermal processing (Crude smelting)

The most simplest processes for recuperating Pb from LABs is the thermal processing developed by Varta. Spent batteries are drained and feed to a blast furnace operated under reducing conditions to convert lead compounds to metallic lead and to convert sulphate to iron sulphide. The bottoms removed from the furnace are a mixture of molten lead, iron sulphide, and slag, all of which can be separated mechanically. The crude lead with its content of antimony in older batteries is sent to a lead smelter for refining. The iron sulphide may be disposed off or reprocessed to recover iron and sulphuric acid. Environmental challenges have been a major disadvantage of this process. Soil pollution and under-ground water contamination occurs via acid spill when batteries are opened, Pb dust blown when mechanically dismantled battery scrap is stored without safety measures. Atmospheric emissions of Pb dust, soot, SO_2, chlorides and dioxins are associated environmental challenges. When spent battery is heated by crude processing method, the organic components (casing, PVC separators) inevitably release gases and vapours as illustrated in Plate 2.1 (Qianyu, 2013).

Plate 2.1: Crude smelting of used lead acid batteries

Source: Qianyu, 2013.

2.9.3.2 Pyrometallurgy processing

Pyrometallurgical processing of waste LABs is thermal treatment of battery in rotary furnace designed to recuperate Pb from it contained source. It requires specially expensive designed equipment because of the high corrosive nature of the material and the need for cleaning system of associated gases and liquid waste. A blast furnace is usually required in this process. It is a large oven built to accomplish the smelting processes. This process is applicable to processing of primary lead and secondary lead. Primary lead which is usually gotten from galena and other sources as shown in Figure 2.6 can be roasted (oxidized) as it can aid the removal of the sulphur component of the metal sulphide. The general pyrometallurgical method is simply describe in Figure 2.7

Roasting of sulphide ore in air oxidised the metal sulphide to a metal oxide or metal alone. The produced lead II oxide PbO subsequently reacts with coke to obtain refined lead as shown by the equations below.

$2PbS + 3O_2 \quad \rightarrow 2PbO + 2SO_2$

$PbO + C \qquad \rightarrow Pb + CO_2$

Galena and battery materials can also be smelted by roasting to oxidize sulphur and create metal oxide out of galena.

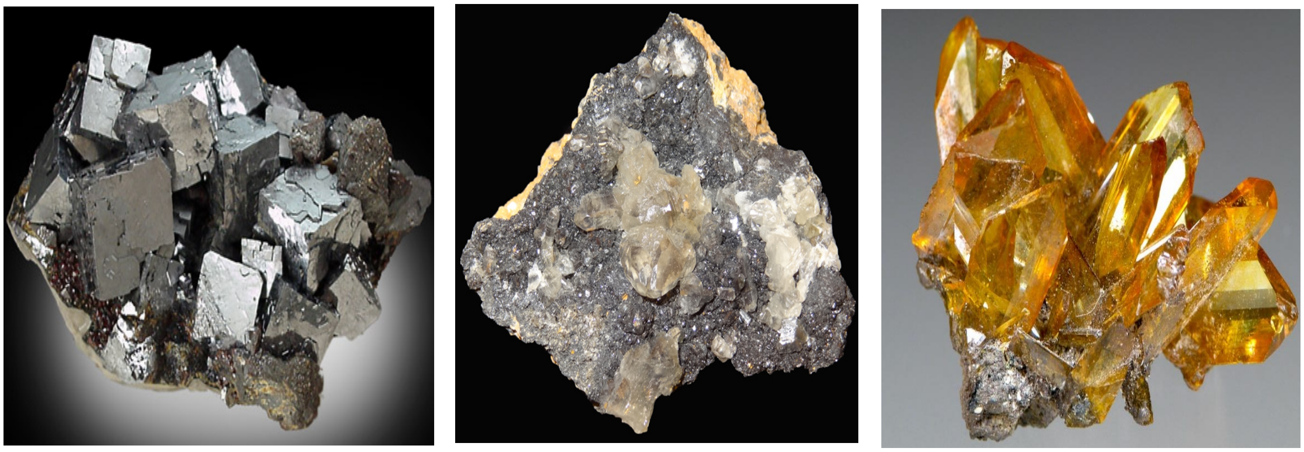
$2PbS + 3O_2 \quad \rightarrow 2PbO + 2SO_2$

The raw ore is then added to the products and is further heated.

$2PbO + PbS \quad \rightarrow 3Pb + SO_2$

http://www.worldresourcesforum.org/resource-snapshot-6-lead.

One of the recent advanced pyrometallurgical methods is ISASMELT Process presented in Figure 2.8. This process is suitable for treating secondary lead especially waste batteries processed ores and concentrates in an environmentally acceptable way but not without challenges such as expensive equipment to curb the environmental challenges and where this is not obtainable, it result in the release of hazardous substance into the air and water channels. As a result aforementioned challenges, more suitable methods are required (Sahu *et al.,* 2000).



(a) Galena (PbS) (b) Cerussite ($PbCO_3$) (c) Anglesite ($PbSO_4$)

Figure 2.6: Major minerals containing lead

Source: http://metapedia.asianmetal.com/mineral/indexen.shtml

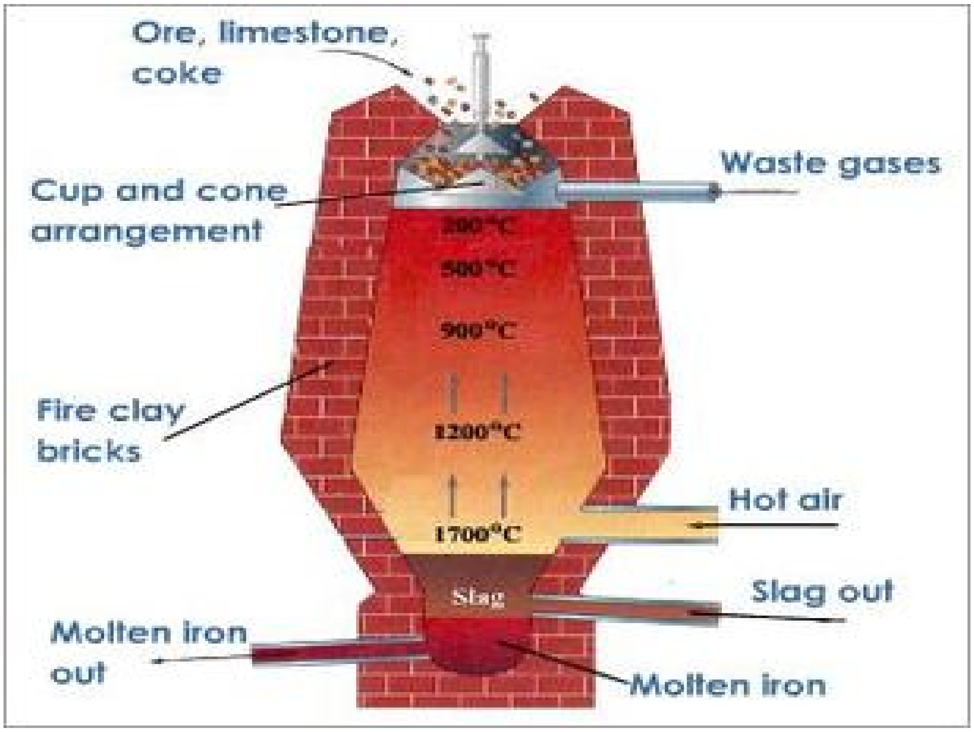


Figure 2.7: Pyrometallurgy lead smelting furnace

Source: http://www.worldresourcesforum.org/resource-snapshot-6-lead

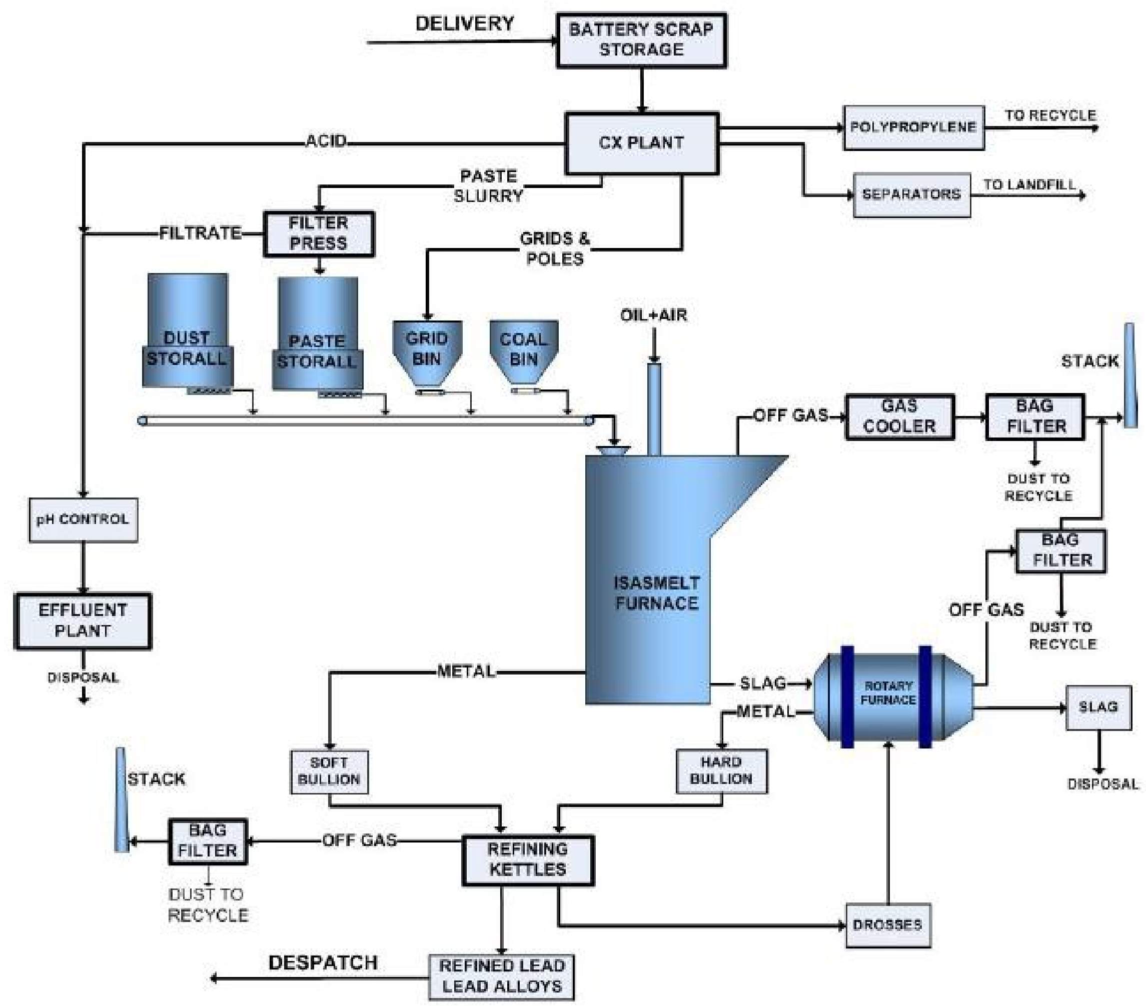


Figure 2.8: ISASMELT pyrometallurgical furnace

Source: Sahu, 2000

2.9.3.3 Lead refining (Separation by unit operation)

Refining method is basically used for industrial batteries such as waste lead-acid batteries. Treatment of the batteries separates materials of interest from other materials for further use during recovery processes. Treatment is habitually the first step of the recycling activity where the scraps are treated for latter recycling operations as illustrated in Figure 2.9 (Espinosa *et al.,* 2004).

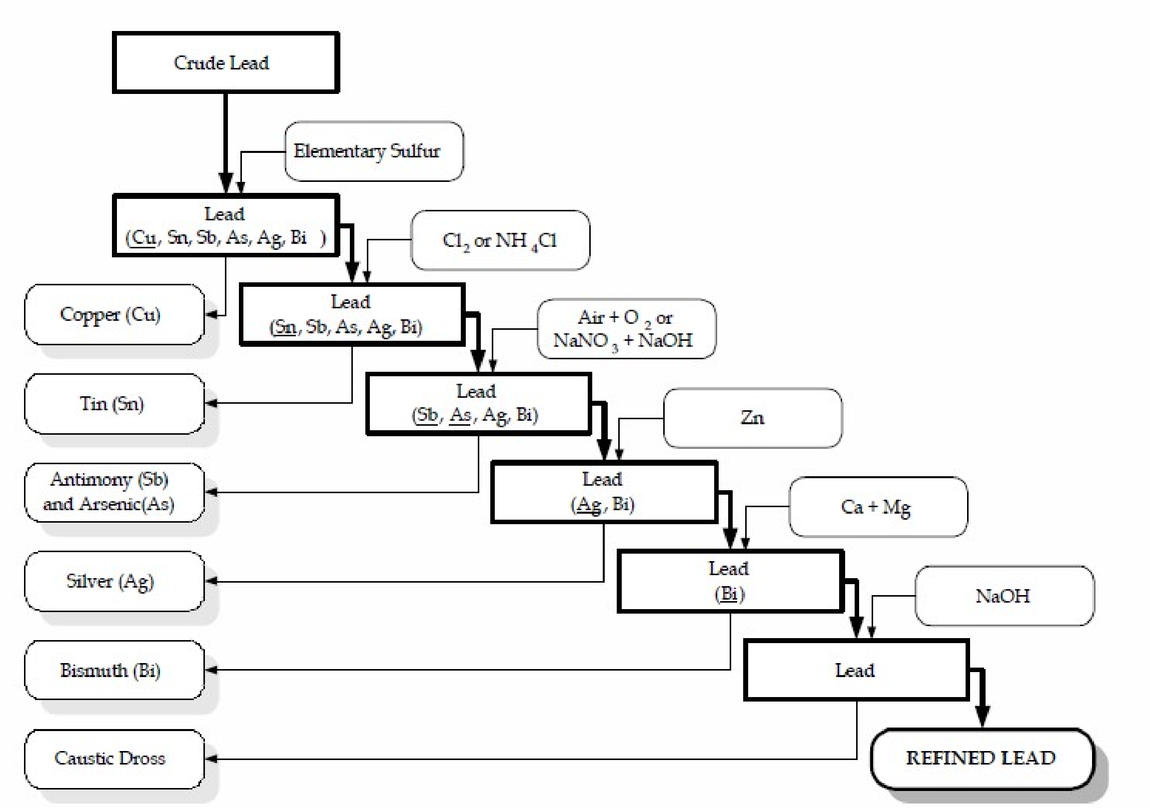


Figure 2.9: Lead refining by unit operation

Source: Espinosa, 2004

2.9.3.4 Hydro-Electrometallurgy processing

Electrometallurgy is an electrolytic method of recovering metals (lead) from its solution. It is a hydrometallurgical or chemical solubilisation of metal that is accompanied by electro-winning of the soluble metals. Recovering Pb via hydro-electrometallurgical pathway, Pb electro-winning plays a crucial role. Different electrolytes have been employed in pilot plants for Pb electro-winning. Table 2.13 shows merits and demerits of some proposed and tested electro-winning processes to recuperate Pb from spent LABs.

Ferracin *et al.* (2002) studied alkaline and acidic electro-winning using three electrolytes including fluoroboric acid, glycerol and sodium hydroxide(NaOH), and sodium potassium tartrate and sodium hydroxide. Each electrolyte contained three electrodes. For acidic fluoroborate electrolyte, two graphite anodes and one stainless steel foil cathode. For alkaline electrolyte, two cathodes and one anode were made of the same stainless steel foil.

The main challenge of the electrolytic processes has to do with the life span of the anodes plate. Well designed anodes are required to give off oxygen from the highly corrosive fluoride medium. Many anode materials experimented had shown satisfactory performance on pilot scale. Despite the favourable performance, virtually all of the anode materials have proven to be capable of maximum efficiency of two years of life span. The major problem has to do with deposition of PbO_2 which reduces the quantity of Pb produced and shortens the life expectancy of the anode plate (Cole *et al.,* 1983).

Table 2.13: Comparison of Various Lead Electro-Winning Processes

		Advantages				Disadvantages
Classification	Electrolyte	Current efficiency/ %	Energy consumption KWh/tPb	Purity/ %	Others	
Acid media	HBF$_4$	99	800	99.89	reduce cost	PbO$_2$ formation on the anodes. (graphite collapse).
	HBF$_4$ with Fe^{+3}/Fe^{+2}	High	500	99.99	desulfurization not needed	Diaphragm cell with membranes
Basic media	NaOH-glycerol	85-90	400-500	99.98	anodes of stainless steel, desulfurization not needed	PbO$_2$ produced on the anodes and cost of chemicals
	NaOH-NaKC$_4$H$_4$O$_6$	>98	400-500	99.99	anodes of stainless steel, desulfurization not needed	PbO$_2$ formation on the anodes and cost of chemicals

Source: Ferracin *et al.,* 2002.

2.9.3.5 Hydrometallurgical processing

Hydrometallurgical processing is a recent trend in chemical conversion that recycles almost all the materials in spent lead acid batteries, and it produces minimal discharges by virtue of the extensive use of internal recycling of process streams. The method starts from the physical separation of the batteries solids from the electrolyte and screening, followed by the separation of the various solids by floatation and hydrodynamics separation techniques. The metallic lead collected is smelted and refined to produce a re-usable lead grid alloy. The lead compounds in the slurry from the screening operation are digested chemically to produce a soluble lead salt that is electrolysed to give high purity lead. The sodium sulphate solution generated in the slurry digestor is electrolysed to produce battery grade sulphuric acid and a sodium hydroxide solution that is recycled to the slurry digestor (Sequeira, 1994).

These technologies are suitable for treating secondary lead materials especially spent batteries. As a result of some environmental challenges such as emission of SO_2, high energy requirement, lead fume generation and expensive equipments, a proficient and environmental responsive hydrometallurgical process have been employed to process LAB pastes. Majority of these methods are on laboratory scale and others at pilot scale of production.

Revere smelting and refining (RSR) process

In RSR process, the paste is reacted alongside ammonium carbonate resulting into lead carbonate and ammonium sulphate

$$PbSO_4 + (NH_4)_2CO_3 \rightarrow PbCO_3 + (NH_4)_2SO_4 \quad (1)$$

Other alkali carbonates like Li, K, Na follow the same. Reduction of PbO_2 (insoluble) to become soluble can be achieved in two ways. Firstly, by the reaction between SO_2 and an alkali/ammonium carbonates to produce alkali sulphite/ bisulphate that can react with PbO_2 resulting in $PbSO_4$. The sulphite and bisulphite are oxidized to sulphate and Pb precipitated as $PbCO_3$ or $PbCO_3.Pb(OH)_2$

$$PbSO_4 + PbO_2 + (NH_4)_2CO_3 + H_2O \rightarrow PbCO_3.Pb(OH)_2 + 2(NH_4)_2SO_4 \quad (2)$$

Secondly, battery paste is heated to 290°C in the presence of some organics. The treated paste leached in H_2SiF_6 and HBF_4 and lead is electro won. About 500 ppm of arsenic is added to the electrolyte in order to prevent PbO_2 deposition on the anode. The solution may have 70-200 g/L lead and 50 g/L of free acid (Sahu *et al.,* 2000).

Bureau of mines process

This process is comparable to RSR process where the paste lead sulphate and lead dioxide ($PbSO_4$ and PbO_2) are initially treated in ammonium carbonate so as to desulphurised $PbSO_4$ while reduction of PbO_2 is by addition of metallic Pb powder when leaching by H_2SiF_6. The challenge associated with this process is when large quantity of the powder in form of PbO_2 (35- 40%) is required to be recycled. This process utilizes PbO_2 coated titanium anode and lead cathode of about 2 g/L phosphorus to stop PbO_2 deposition on the cathode. The Pb metal deposited inside the electrolyte may be as high as 150 g/L (Sahu *et al.,* 2000).

Engitech process

In engitech process, subsequent to desulphurisation of $PbSO_4$, part of the battery paste with Na_2CO_3 and NaOH, the paste comprising of the followings Pb, $PbCO_3$, PbO, PbO_2, and $Pb(OH)_2$ can be leached using fluoroboric acid (HBF_4). The PbO_2 and Pb hardly solubilised. PbO_2 is initially reduced and is further solubilised. Hydrogen peroxide helps in the reduction of PbO_2 as shown in equations (3) and (4). The dissolution kinetic is controlled by acid, H_2O_2 content and temperature of the solution.

$$PbO_2 + Pb + HBF_4 \rightarrow 2\ Pb(BF_4)_2 + H_2O \tag{3}$$

$$PbO_2 + H_2O_2\ HBF_4 \rightarrow 2\ Pb(BF_4)_2 + 2H_2O + O_2 \tag{4}$$

In order to prevent PbO_2 deposition at the anode, the engitech process uses composite anode specially designed to operate at an enormously high anode current density 320 A/m^3 (Sahu et al., 2000).

Ginata process

The process utilises neither desulphurisation nor leaching of the battery paste components to solubilise lead components. Similar to the charging cycle, Pb-acid batteries (LABs) electrolytically converts $PbSO_4$ in dilute H_2SO_4 to sulphuric acid (H_2SO_4). When this takes place, electrode plates are short circuited in fluoroboric acid electrolyte during which oxidation of the lead and reduction of the PbO_2 takes place together with soluble fluoroborate being produced. Consequentially, fluoroborate electrolyte is electro won when closely 200 ppm cobalt is added as additives which eliminate the giving off of oxygen and thereafter, minimises the dilapidation of graphite anode. The electro wining process is advisably undertaken by cyclic reverse current that can oxidise antimony in the electrolyte to valence of five precipitated from the electrolyte when the concentration is slightly above 3000 ppm. Pure lead cathode is produced in the process (Sahu *et al.,* 2000).

Ammoniacal ammonium sulphate (A.A.S) process

In AAS process, ammoniacal ammonium sulphate solution is predominantly used for the leaching of the waste battery scrap. The process is designed in such a way that the whole crushed batteries are ingested into the vertically designed leaching column. The upward moving AAS solution in the column floats the battery casing and separators off the column. The Pb components of the paste are separated as clean fraction, suspended and dissolved. The PbO together with $PbSO_4$ solubilise in AAS solution and the remaining PbO_2 that has not dissolved is separated, converted to $PbSO_4$ using 50% H_2SO_4 at high temperature. The produced $PbSO_4$ is returned back to the AAS column leaching process. The Pb is electro won to obtain spongy Pb. Ammonia and water are used as feed and $(NH_4)_2SO_4$ recovered through bleed stream (Sahu *et al.,* 2000).

$PbSO_4$ slurry process

This methodology requires direct electro wining of Pb in the battery paste. The solid divalent particles of the $PbSO_4$ /PbO of the battery paste are deposited into the ion selective case compartment of the cell. Cathode compartment electrolyte is made up of the sludge of $PbSO_4$, PbO, H_2SO_4, Na_2SO_4 and NaOH including complexing agent like EDTA, oxalic acid. The fluidised bed cathode made of particles is merged with current accumulator. During electro wining procedure, the paste is in contact with the cathode and it is converted to metallic Pb. The sulphate ions generated passes through the compartment resulting into H_2SO_4. When PbO_2 is in contacted with SO_2 in form of Na_2SO_3 it produces $PbSO_4$ that can be regenerated in the cathode compartment. In this procedure the paste is turned into metallic Pb and sulphuric acid (Sahu *et al.,* 2000).

Placid treatment

The route encompasses chloride leaching instead of desulphurisation by leaching with HBF_4 or H_2SiF_6. The procedure can be illustrated with chemical equations.

$$PbO + 2HCl \rightarrow PbCl_2 + H_2O \tag{5}$$

$$Pb + PbO_2 + 4HCl \rightarrow PbCl_2 + H_2O \tag{6}$$

$$PbSO_4 + NaCl \rightarrow PbCl_2 + Na_2SO_4 \tag{7}$$

Resulting Pb powder precipitates dissolved impurities. The $PbCl_2$ produced solubilised in hydrochloric acid (HCl) and passes through the cathode partition of the diaphragm for electro wining. Though the treatment seem direct and simple, it is not environmentally secured and bulk Pb is produced and extremely large quantity of PbO_2 is required (Sahu *et al.,* 2000).

Plint process

The process, as described by (Andrews *et al.,* 2000) is almost the same as placid process. The only difference is in principles. In Plint process, electro wining is replaced by precipitation. Initially, decomposed hydroxide is reacted with hard coal resulting in purified Pb. This procedure temperature is similar to the temperature required during casting and alloying.

Environmentally, lead recovered in the battery paste through hydrometallurgical/electro wining plants is attractive. There is need for full scale operation of these processes to bridge the gap of demand and supply, and attaining a safe environment from pollution. This is rather desirable than limiting efforts to pilot and small scale levels (Sahu *et al.,* 2000).

2.9.4 Comparison of different processing route of spent lead-acid battery

Frias *et al.* (2006) presented a preliminary evaluation of a clean lead process by hydrometallurgical route and compared it with the conventional pyrometallurgical process of recycling lead-acid battery. The novel route aimed at achieving sustainable lead acid battery recycling activities for the 21st century. It equally achieved zero emission process, avoiding environmental damage, disposal cost and producing re-usable valuable product. Saving energy in the smelting process and producing stable re-usable slag instead of toxic slag in the conventional operation was targeted, and developing a new energy low hydrometallurgical process in alkaline media to obtain pure PbO or pure electrolytic lead. Clean Lead hydrometallurgical route promises to deliver a Zero- waste generation technology in lead-acid battery recycling against conventional process as illustrated in Table 2.7.

Thermal conversion (Pyrometallurgy) has been widely used industrially but it has high environmental effect and high energy cost. Hydro-electrometallurgy by electro-winning in acidic media HBF_4 has the advantages of minima environmental consequence, 99% current efficient, 300 kWh/t of Pb, 99.98% purity and minima cost. This acidic media has the disadvantages of forming PbO_2 deposit on the electrode (anode). Electro-winning in NaOH-glycerol has the advantages of minima environmental impact, 85-90% current, 400-500 kWh/t of Pb energy, 99.98% purity, stainless steel anodes and it is void of desulphation. It has the disadvantages of forming PbO_2 on the electrode (anode) and expensive chemicals are required.

Electro-winning in $NaOH\text{-}NaKC_4H_4O_6$ solution has the advantages of reduce environmental effect, >98% current, 400-500 kWh/t of Pb, 99.99% purity, anodes made of stainless steel with desulphating not necessary. It has the disadvantages of depositing PbO_2 on the electrode (anode) and expensive chemicals are required. Electro-winning in acidic solution together with $Fe^{2+/}Fe^{3+}$ has the advantages of minima environmental consequence, 500 kWh/t of Pb, purity of 99.99% and does not require desulphating. It posed the disadvantage of diaphragm cell with membrane (Cole *et al.* 1983). Considering these challenges of the methods described, a new hydrometallurgical method that recovers lead by precipitation is required.

Table 2.14: Environmental Features of Conventional Process against Clean Lead Process

Parameter	**Unit**	**Conventional Process**	**Clean Lead Process**
Energy Consumption	MWh/t Pb	1.5	1.0
Battery Breaking Waste (plastics)	t/t Pb	0.1	0.1
Toxic Slag		0.3	0
Exhausted Gases	Nm3/t Pb	70,000	5,000
Drained Acid Sludge	t/t Pb	0.2	0
Gypsum Product	t/t Pb	0	0.4

Source: Frias *et al.,* 2006.

2.9.5 Nanotechnology

It is the attempt and art of controlling or manipulating materials at small scale to obtain microscopic dimension. Nanotechnology could be described as the existence, control of matters at dimension within the range of 1 to 100nm, with distinctive phenomena for novel application. Nano-metre size is one-billionth meters in dimension. A sheet of paper has dimension 100,000 nano-metres in thickness. Dimension between one and hundred nm are regarded as nanoscale. Usually changes in properties (physical, chemical, and biological) are peculiar to materials at nano-meter scale. The properties varied distinctively from bulk material to single atom or molecules.

Nano-science is the study of phenomenon of manipulating materials at atomic, molecular scale having different properties from those on large scale. Metals with dimension sizes of around 10 nanometres are usually rigid and tougher compare with the same metals at hundreds (100) of nanometres. The changes in properties observed in nano materials against bulk material could be due to quantum effect. The bulk properties of a material are the summation of quantum forces of all the atoms of that material. As the materials reduces in sizes, their chemical reactivity increases.

The properties of materials differ at nano dimension for two reasons:

a. Nano materials possess larger surface area compared to mass of materials produced in a larger form. It increases the chemical reactivity of materials. Inert materials can be activated at nano dimension for improved reactivity.

b. Quantum effect controls the behaviour of matter at the nano scale. Materials that are produced at nano scale in one dimension (1D material- thin surface coating), 2 Dimension (nano wires and nanotubes) or 3 Dimension (nano-particles) exhibit this effect. http://www.nanowerk.com/nanotechnology/introduction/introduction-to-nanotechnology-1.htm.

2.9.6 Hydrometallurgical synthesis of nano lead oxide

Hydrometallurgy can be defined as a process whereby metals are recuperated from ores/minerals. An extractive approach that involves aqueous reactions to recover metals from ores, concentrates and recycled materials (Brent, 2000; Habashi, 2009). Hydrometallurgy is a metal processing technique that is complemented by

Pyrometallurgy, vapour metallurgy and hydro-electrometallurgy discussed in previous section. Hydrometallurgy typically encompasses the following areas as illustrated in Figure. 2.10. Leaching is similar to extraction whereby aqueous solutions are used to extract metal in materials presumed to contain the metal of interest. For optimum leaching, the solution pH, oxidation-reduction potential, chelating agent and reaction temperature are factors to be optimised for phase transfer from the material into the extracting solution (Peter *et al.,* 2007).

Prior to recovery of desired metal, leach liquor undergoes solution concentration. Undesirable metals may be present as impurities which must be masked or removed. Precipitation provides a means of separating a desire metal or the interfered metal in it compound form.

Cementation is another way of converting the metal ion into metal by redox reaction. Solvent extraction, ion exchange and gas reduction are ways of solution concentration among others. Metal recovery is the final step of hydrometallurgical process. At the instance of producing ultra-fine metals, refining is a further required step. The major primary metal recovery routes are via electrolysis, gaseous reduction and precipitation.

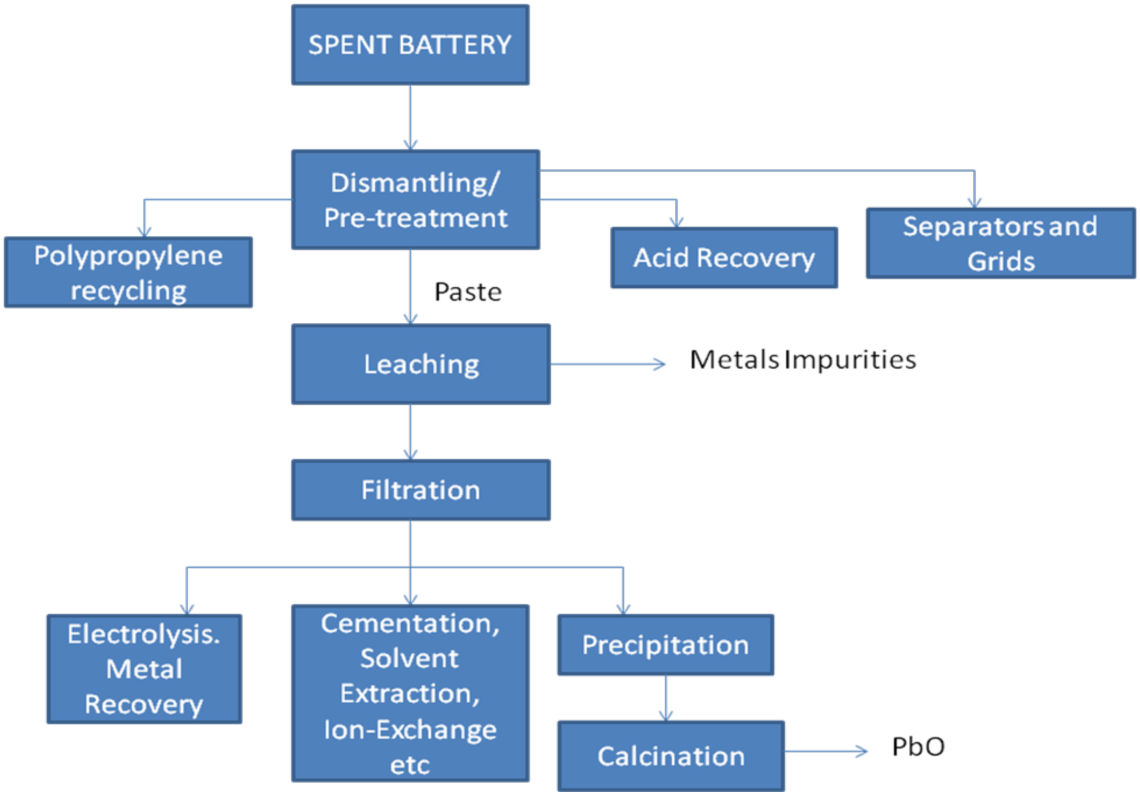


Figure 2.10: Hydrometallurgical route of recovering lead from scrap battery.

Source: Habashi, 2009

Many researchers have used different routes to produce nano PbO which can be employed as starting materials in producing lead acid battery as presented in Table 2.15. Sonmez and Kumar, (2009a) through hydrometallurgical pathway produced lead citrate via PbO and PbO_2 chemicals. The attempt was to avoid smelting and electro wining in conventional Pyrometallurgy and electrometallurgy respectively. Citric acid reagent in solution was reacted with PbO, PbO_2 together with H_2O_2. The process resulted into ($Pb(C_6H_6O_7).H_2O$) characterised differently by analytical techniques. In another of his articles citric acid reagent was reacted with $PbSO_4$ in solution to achieve lead citrate recovery and desulphurisation concurrently. He noted that leaching with citric acid and sodium citrate produced uncontaminated Pb citrate which could be a precursor for the production of PbO nano particles.

Li *et al.,* (2012) in a publication investigated low temperature calcination of lead citrate powder as precursor for PbO from waste lead acid battery. The Pb citrate and oxide were characterised by thermo-gravimetry differential thermal analysis. The obtained Pb citrate precipitate was heated in Nitrogen gas and in Air. Mixtures of orthorhombic (PbO), tetragonal (PbO) and metallic (Pb) having particle sizes of 100- 200 nm . The properties of the nano structure were investigated by electrochemical techniques. This was a step ahead of the previous work.

Pengran *et al.,* (2013) Solvothermally produced α-PbO from powder of PbO_2 and tested its cyclic performance when used in coating positive electrode plate. He researched the solvo-thermal behaviour of PbO_2 in methanol at temperature above the boiling point of methanol (140^{o}C) and subsequent calcination of the product. Lead II oxide (PbO) and lead oxide carbonate ($PbO.CO_3$) were produced which was calcined below 500^{o}C to produce alpha PbO. This demonstrated a way of reusing PbO_2 in waste lead acid battery to produce highly active PbO.

Pengran *et al.,* (2013) in another work demonstrated methano-thermal behaviour of carbonated mixture of $PbSO_4$ with PbO_2 to produce alpha PbO for LABs. Mixture of $PbSO_4$ with PbO_2 in different ratios was firstly desulphated and solvothermally processed in methanol to form alpha PbO. This was investigated using the spent lead acid battery. These authors in another work investigated methano-thermal reduction of mixture of $PbSO_4$ and PbO_2 to synthesis ultra-fine alpha PbO powder for LAB. $PbO.PbSO_4$ produced was calcined to produce alpha PbO by reacting artificial mixture of $PbSO_4$ and PbO_2 solvothermally and treated in methanol at 140°C for 24 hours. The mixture was desulphated with ammonium carbonate and produced $PbCO_3$.

Sadeghzadeh et al., (2009) reported ultrasonic- supported production separate new nano controlled 3D lead II coordinating polymer a precursor for producing PbO nano structure. In this approach, $[Pb_2(4\text{-pyc})_2]I_2(H_2O)n$ 4-Hpyc 4-pyridinecarboxylic acid and $Pb_2(3\text{-pyc})I]n$ 3-Hpyc 3-pyridinecarboxylic acid were produced. The nano materials were characterised. Block PbO structure was obtained by heating of the two compounds at 400°C.

Zohreh and Morsal, (2009) sonochemically produced nano dimensional porous lead (II) coordination polymer as precursor for preparation of lead(II)Oxide nano particles. Pb(bpacb)(OAc)-DMF]n-bpacb3,5-bis[(4-pyridylamino)Carbonyl]benzoic acid was synthesized sonochemically. The nano material produced was characterised by scanning electron microscope, x-ray diffraction, $^{13}{}_{1}$CNMR, infra-red spectroscopy.

Liu *et al.,* (2014) investigated Nano crosses of Pb-sulphate as the negative active material of LABs. He demonstrated how lead sulphate which is usually the cause of failure of battery can be made electrochemically active by reacting aqueous lead acetate and sodium sulphate. He achieved cross-like particles with diameter of each arm being 100nm to 3 µm.. Karami *et al.,* (2008) elucidated on the production of micro nano meter lead oxide by sol- gel pyrolysis and it can be used as cathode and anode of LAB. Lead acetate and polyvinylalcohol (PVA) 2.5 wt% lead acetate, 8 wt% PVA and water/alcohol (40/60 v/v) to obtained sol which was heated to produce gel that was calcined at 500°C for 5hr. This process produced lead oxide nano powder.

Xinfeng *et al.,* (2012) prepared lead carbonate from waste paste via chemical conversion. He produced PbO and Pb_3O_4 through a four step procedures. This process is believed to be enormous and chemical consuming compare to the previous ones. Masoumeh and Mohammad, (2011) combusted citrate and nitrate gel produced from reaction of citric acid and lead acetate, citric acid with metal nitrate.

Morale *et al.,* (2006) examined four samples of PbO_2 prepared by different synthetic pathways. PbO_2 was produced by the hydrolysis of lead acetate $Pb(CH_3COO)_4$ precursor. He obtained another sample of lead oxide by hydrothermal treatment of obtained sample in an autoclave 175^oC within 4 days. Samples from positive plate of a commercial battery and chemically synthesised were characterised. Thin lead dioxide positive electrodes were prepared using the materials produced by spray deposition technique.

Cruz *et al.,* (2002) used spray pyrolysis method to prepare PbO. He prepared a positive plate using precursor method to deposit lead II solution onto lead foil of 0.35mm in thickness. An aqueous solution of 0.5M Pb $(CH_3COO)_2.$ H_2O was used to obtain thick lead films by depositing it into lead sheet at 150^oC. The conversion of the oxide produced was accomplished by heating the Pb film obtained at 260^oC for 24 hours.

Cheng *et al.* (2015) propounded a method using oxalate and sodium oxalate for treating WLABs. The pure lead oxalate precursor of PbC_2O_4 was crystallised in the leaching set up. Pb-oxalate crystallised out of the solution owing to its reduced solubility index and combusted directly to produce lead oxide as a precursor for making new battery pastes.

Table 2.15: Scientific Contribution

Samples	Reagents	Leaching time (Min)	Temp. (°C)	Solid/ Liquid. S/L	Recovery %	Mixing rate	Methods	References
Battery Paste	99.5%Citric acid,99% Trisodium citrate,30% H_2O_2	1440	22°C	1/5	96.0%	650 rpm	Chemical precipitation	Li et al., 2012
Paste	0.2M Na_2CO_3		60°C	3/25			Chemical precipitation	Chen and Dutrizac, 1996
Lead Oxide&	1M citric acid	15	20°C	1/3	99.8%	250 rpm	Chemical precipitation	Sonmez et al., 2009a.
PbO_2	4Mcitric acid, 2MH_2O_2	60	20°c	1/5	99.0%	250 rpm		Sonmez et al., 2009a
Lead Sulphate	6Mcitric acid, 2MH_2O_2, 2M sodium citrate	60	20°C	1/5	98%	250 rpm	Chemical precipitation	Sonmez et al., 2009b
Lead Sulphate	0.01M, Pb acetate, 0.1M Na_2SO_4,0.3wt% PSS,SDS,PVP	10	70°C				Chemical Reaction	Liu et al.,2014
Lead oxide	99.5%20ml methanol	120	140°C				Solvothermal synthesis	Pengranet al.,2013
Prepare αPbO	0.5M lead acetate trihydrate	1440	260°C				Spray Pyrolysis	Cruz et al., 2002
Lead oxide	Pb acetate	5760					Hydrolysis	Morale et al., 2006
PbO2	PbO_2	5760					Hydrothermal treatment	Morale et al., 2006
Pb acetate	0.1M lead acetate,-0.1M 4Hpyc, 0.1M 3Hpyc.		300°C				Sonochemical method	Sadeghzadeh et al., 2009
Battery Paste	Na_2CO_3, $NaHCO_3$, $(NH_4)_2CO_3$, 1M citric-acid, H_2O_2	60	35°c	1/10, 1/5	99.0%		Chemical Conversion	Xinfeng Zhu et al., 2012

CHAPTER THREE

METHODOLOGY

3.1 Study Design

The study was carried out in phases as each of the phases is connected. Survey of automobile battery types in South-West markets in Nigeria and gathering of data for Material Flow Analysis/ stock inventory of imported motor vehicles in Nigeria was the first phase. Collection of different waste lead-acid batteries according to types was another phase followed by characterisation of the WLABs. Optimisation of synthesis parameters was design to produce PbO precursor and nano structured lead(II)oxide (nano-PbO) which was structurally characterised. The study design block is presented in Figure 3.1.

The design of the experiment is illustrated by the flow chart presented in Figure 3.2. The design spanned from the collection of the waste batteries to the dismantling of the products, separation of components, calcination and characterisation.

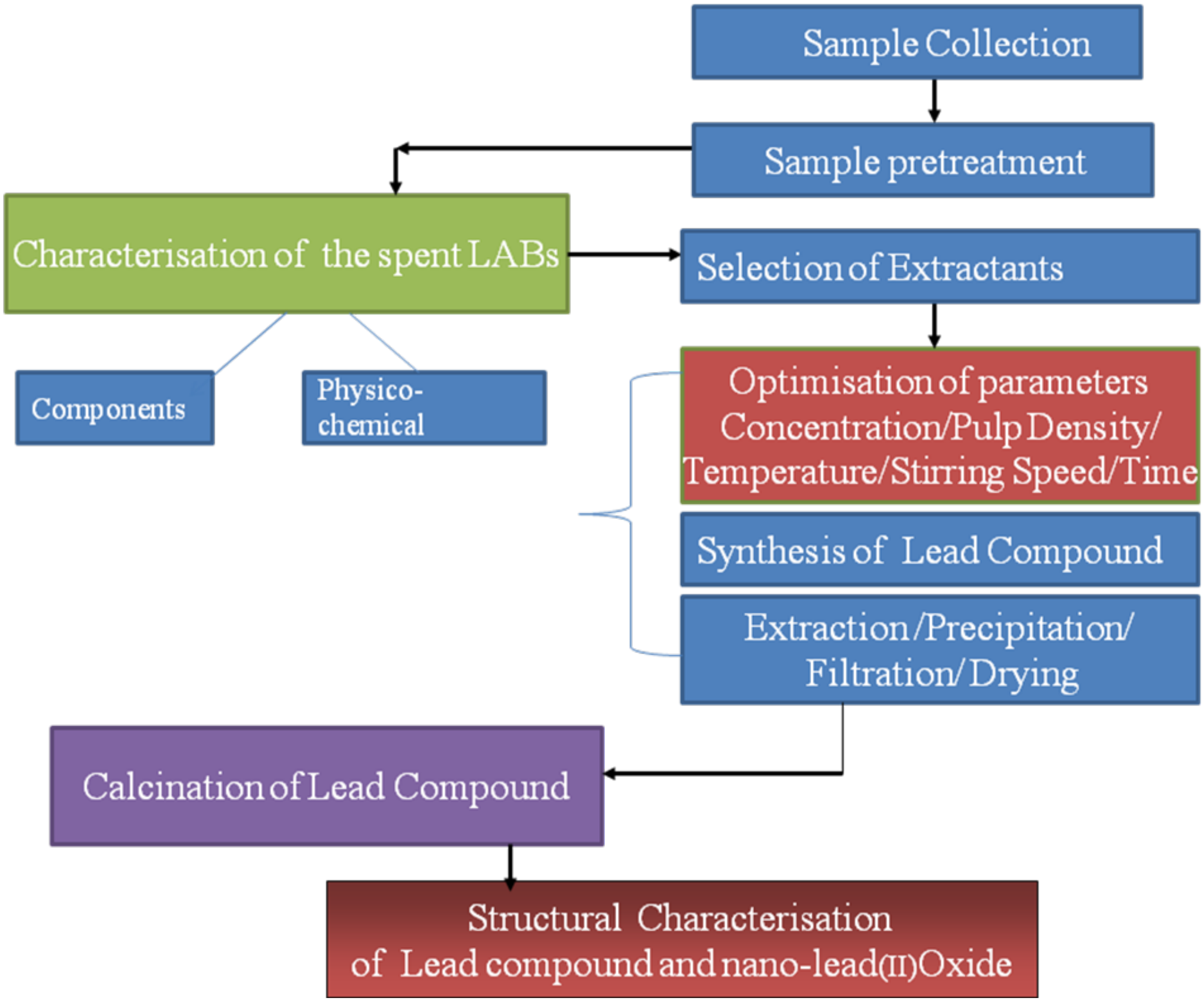


Figure 3.1: Study design flow chart

3.2 Experimental design

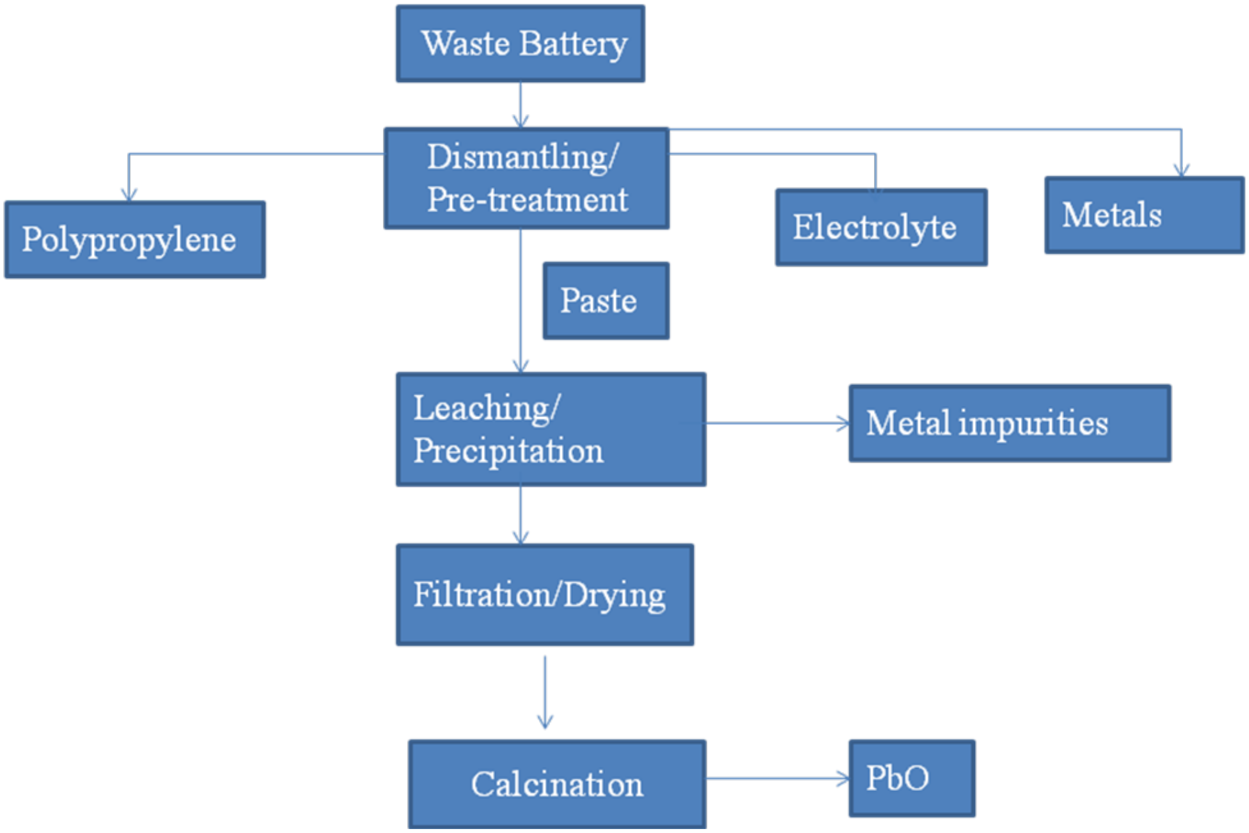


Figure 3.2: Schematic flow sheet of the experimental design

3.2.1 Description of the study Locations

Nigeria is one of the countries in the West African coast on latitude 4^0N and 14^0N of the equator and longitude 30^0E and 14^0E. Nigeria borders with Benin republic and Niger, Cameroon and Chad. Nigeria lies within the area of 923,768.64 sqkm. The major five geographic regions in Nigeria include: a low coastal zone along the Gulf of Guinea; hills and low plateaus north of the coastal zone; the Niger-Benue river valley; a broad stepped plateau stretching to the northern border that has elevations exceeding 1,200 meters and a mountainous zone along the eastern border, which includes the country's highest point, Chappal Waddi (2,419 meters). Vegetation in Nigeria varies at both the national and local level in relation to climate, soil, elevation, and human impact on the environment. In the low-lying coastal region, mangroves line the brackish lagoons and creeks, while swamp forest grows where the water is fresh. The vegetation of Nigeria gives way to tropical forest, with its many species of tropical hardwoods, including mahogany, iroko, and obeche (Oyegun, 1983). Geographical coordinates of locations where samples were collected is summarised in Table 3.1

Kwara State is one of the States in Nigeria and Ilorin as the capital was one of the selected study areas because of the similarity in types of lead acid batteries in Nigeria as revealed by the survey carried out in this study. Figure 3.3 shows the map of the state with locations where samples were collected. The city which lies between latitudes 8° 24' and 8° 36' north and longitudes 4° 10' and 4° 36' east (Oyegun, 1983).

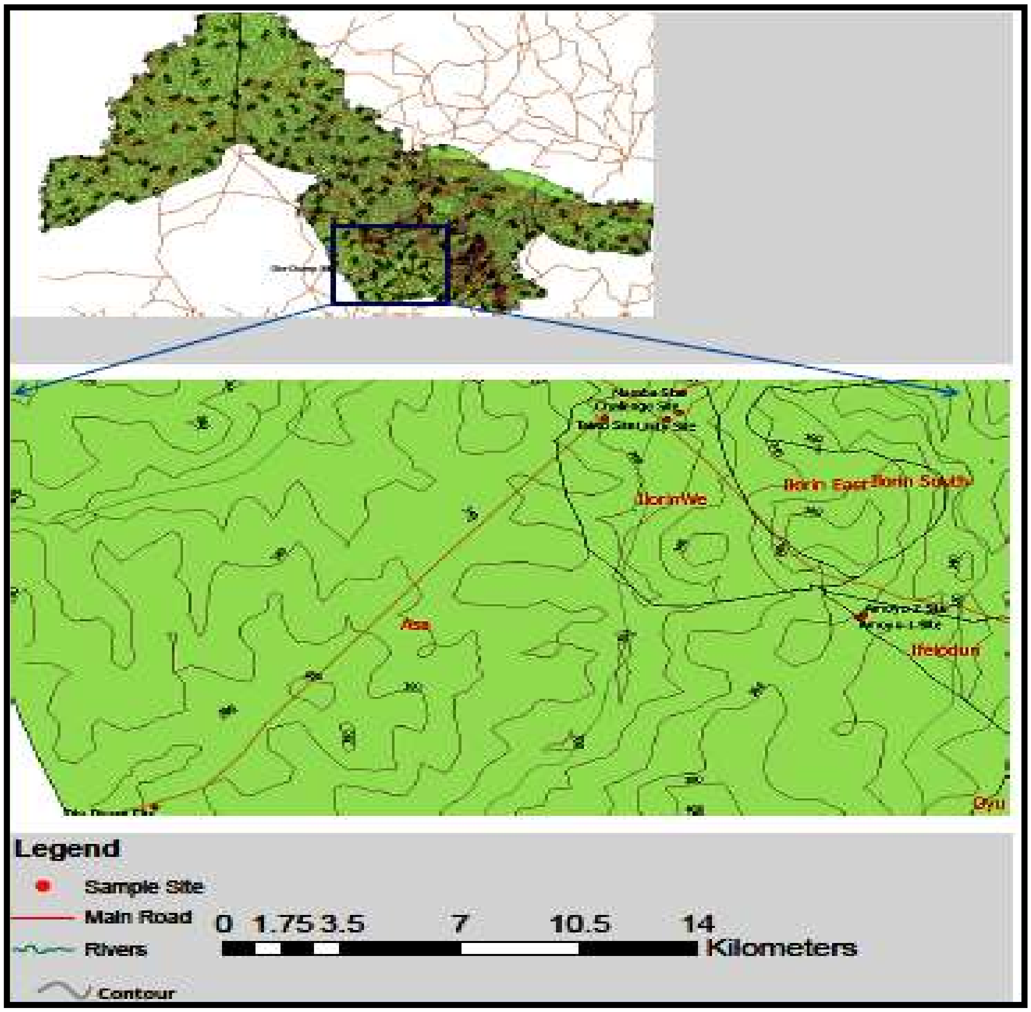


Figure 3.3: Map of Kwara State showing sampling locations

Source:Oyegun,1983

Ekiti State (Ado-Ekiti) was another study area situated at about 48 kilometers North of Akure, Ondo State capital, 344 kilometers north of Lagos and about 750 kilometers south west of Abuja (FCT). Ado -Ekiti is the Capital city of Ekiti State and also serves as a Local Government Headquarter in one of the sixteen Local Government Areas in Ekiti state as shown in Figure 3.4. Ado-Ekiti, lies within Latitude 7° 10' and 7° 45' North of the Equator and Longitudes 5° 10 ' and 5° 28 ' east of the Greenwich meridian. The town is situated on a fairly high level with about 390 meters above sea level in the south eastern part of Ireje stream and about 540 meters above sea level in the north eastern limits of the town. The landscape is dotted with rounded inselbergs and steep sided hills with gradients ranging from 33° to 44°.

The climatic condition of Ado-Ekiti is similar to the general climate of the South Western Nigeria characterised by seasonal wet and dry seasons with double maxima rainfall occurring in July and September. The onset and cessation of the rainy season are often marked by severe thunderstorms which are mainly experienced in the afternoons and occasionally at night (Adebayo, 1993).

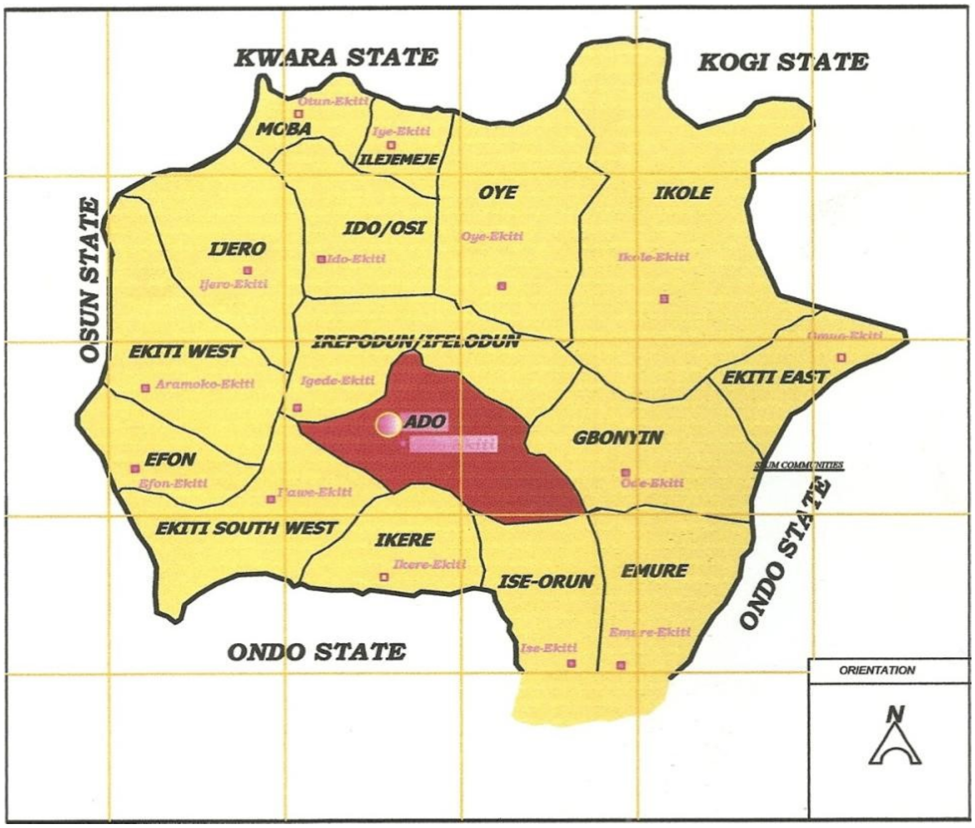


Figure 3.4: Map of Ekiti state showing sampling locations

Source:Adebayo,1993

3.2.2 Survey of battery types in Nigeria

Research survey was designed to obtain information on the battery types in Nigeria, life span of automobile LAB, and end of life management of the products. Closed ended question format was adopted to gather information for the survey as compiled in Appendix X. Random sampling technique was employed to select the major stakeholders in the automobile LAB businesses in Nigeria. The stakeholders include battery sellers, battery users and battery repairers/chargers/scavengers. An average of three hundred structured questionnaires was categorically administered to the three selected factions in Southwest Nigeria because of restrictions among the practitioners.

3.2.3 Gathering of data for substance flow analysis

Material and substance flow analysis (M/SFA) is a designed method used for tracing the flow of a selected group of substances through definite system. The MFA was embarked upon in order to determine the quantity of LABs imported to Nigeria within a particular period of time. Availability of materials that justify the efficacy of recycling the product when spent is expected from such substances flow analysis. Then data used for material flow analysis contained the amount of officially registered motor cars, buses and trucks imported into Nigeria between 1980 and 2014. Motor vehicles official statistics in Nigeria from 1980 to 2014 as acquired from national statistics and literature. Data on the inflow of vehicles that carry LABs was obtained from literatures, Federal Road Safety Corps, national sources, Lagos State motor vehicle data, international trade data as well as reports from Nigerian transport sector (Babayemi *et al.* 2016). Relevant stakeholders (battery sellers, battery users and battery repairers) who were involved in the management and handling of used LABs were also consulted. The inflow of vehicles to Nigeria has drastically increased within few decades. Nigeria, being the number one importer of vehicles in Africa, acquires an average of 70,000 vehicles yearly (Bevorward, 2014). Eighty-five percent of vehicles imported into Nigeria are second-hand vehicles which aged between 5 to 15 years in spite of the 7 years prohibition of vehicles entering into Nigeria (Agbo, 2011).

The MFA was conducted by the use of STAN 2 software designed by Technical University of Vienna to perform the analysis approved by the Austrian Standard O Norm

S 2096 (Material/Substance flow analysis-application for waste management) (http://www.stan2web.net/) in order to estimate the environmental/health impact that could be generated, if WLABs are not properly managed.

3.2.3.1 End-of-Life and current fleet of motor vehicles in Nigeria

The number of vehicles imported, those in current use and those that have reached End-of-life (EoL) between 1980-2010 were obtained from existing literature and data base Babayemi *et al.,* (2016). Data for import of motor vehicles in 2011-2014 were obtained from UN Comtrade database. This information from existing literature and the database was used for further calculations in this study, using equation (1) for simple estimation.

$n_{u\,(2010)} = n_i - n_e$ …………………………………. equation (1)

$n_{u\,(2010)}$ is the number in use up to 2010;
n_i is the number of motor vehicles imported (1980 – 2010);
n_e is the number in EoL.

It was assumed that motor vehicles imported from 2010 to 2014 were still in use currently in 2014, considering that the average period of motor vehicles in Nigeria to be 30 years.

3.2.3.2 Lead-acid battery components of motor vehicles in Nigeria

Given that the average life span of motor vehicles in Nigeria is 30 years, the number of motor vehicles in EoL between 1980 and 2010 were estimated; and others (between 2011 and 2014) were assumed to still be in current use. From these, the total number of batteries used by motor vehicles in Nigeria (1980-2014) was calculated using the relationships in equations (2) to (4). This was done in two steps: one, for motor vehicles that reached EoL within this period of time; and two, for those in use up to the inventory year 2014, using the same relationships.

$n_b = {}^{t_1}/_{t_2}$ ………………………………………….. equation (2)

$n = n_v \times {}^{t_1}/_{t_2}$ ……………………………………. equation (3)

$m = n_v \times {}^{t_1}/_{t_2} \times w$ ………………………………. equation (4)

where n_b is the number of battery used per vehicle;
t_1 and t_2 are the life span of vehicle and battery respectively;
n is the total number of battery used by a category of vehicle;
n_v is the number of vehicles in a category;
m is the total amount (tons) of battery used by a category of vehicle;
w is the average weight (tons) of battery.

However, the amounts of motor vehicles imported to Nigeria between 2011 and 2014 were reported in weights (not in number). Knowing the average percentage of lead acid battery per category of vehicle, the amount of battery was calculated. The average weight of battery by categories and percentage fraction of battery were reported by U.S. Federal Transit Administration (2012).

3.2.3.3 Amount of elements in lead-acid battery in different life cycle stages

This was estimated using equation (5).

$m_s = cm$ ………………………………………… equation (5)

giving c as the concentration (in percentage) of each element in the battery;
m is the total amount (tons) of battery used by a category of vehicle in a particular life cycle stage.

3.3 Analytical processes

The study was carried out in phases. The first phase was the collection, pre-treatment and characterisation of waste lead-acid battery. The second phase was solubilisation of metals in the paste of waste batteries. Selection of paste leaching/desulphurisation/reduction/precipitation system was the next phase followed by reaction conditions of the selected desulphurisation, leaching, reducing and precipitating system and production of Pb citrate precursor and production of nano-PbO.

3.3.1 Battery sampling plan by types (Alloys) in Nigeria

A survey of automobile battery types was carried out in markets that are situated in South-West geopolitical zone of Nigeria (i.e. in Lagos, Ogun, Oyo, Osun, Ondo and Ekiti States) through the use of questionnaires. In each of these States, one hundred (100) questionnaires were distributed out of which an average of fifty (50) was retrieved from the respondents. The respondents are battery sellers, battery repairers/recyclers and battery users. The questionnaire elicited information to assess the types of lead acid battery (LABs) in the market, their life span, and end of life management.

3.3.2 Collection of waste lead-acid batteries

Fifty (50) different brands of waste lead-acid batteries were randomly collected in Ilorin metropolis of Kwara State and Ado Ekiti in Ekiti State (Figures 3.3 and 3.4) based on the similarity of types revealed by the survey. The samples were collected from the heaps gathered by the scavengers who transport/export them for recycling based on the brands and the types shown in Plate 3.1.

3.3.3 Sample dismantling

The waste batteries were transported to the site where they were dismantled individually. Prior to the dismantling of the waste batteries, they were discharged by touching the terminals of the batteries with electrical wires to ensure neutrality of the terminals. Dismantling of the battery was done using hammer, saw blade, hand gloves, and a pair of pliers into different components, as shown in Plate 3.2.

3.3.4 Sample characterisation

The different components were separated and classified accordingly into polypropylene plastics, metal grids, wire gauze, electrolyte, and lead paste, as shown in Plate 3.3. Each component was carefully handled to avoid environmental and human contamination. The battery pastes were air dried for 48 hours before grinding to remove residual moisture. The dried battery pastes were packed into polythene bags for further treatment. The battery pastes were obtained by pulverising the electrodes (i.e. $PbSO_4$, PbO_2, PbO, & Pb) in a mortar for uniform appearance of the sample.

Prepared reddish brown samples were screened for particle size analysis, using mesh sieve of different sizes on mechanical shaker for 20 minutes. Sample which was screened to less than 0.35mm (-48 mesh) was employed for homogeneity of the sample. Part of the sample was slurred in 70 ^{o}C water for 1 hour on magnetic stirrer operated at 450 rpm on hot plate; vacuum filtrated and dried in a furnace in order to check for residual acidity. The solution pH after washing was 7.27 at room temperature. Subsequent characterisation and leaching/crystallisation were done using the prepared sample.

Plate 3.1: Waste automobile lead acid batteries stockpile in Ilorin Nigeria

Plate 3.2: Dismantled automobile waste lead acid batteries

Plate 3.3: Material components of waste lead acid battery (LAB)

3.4 Metal characterisation of the pastes (Digestion)

Fifty samples of waste lead-acid battery paste were prepared for determination of elemental composition. Digestion method was adapted from Anton Pear's multiwave 3000 micro wave digestion system. The dissolution of the 50 waste battery samples was done by weighing accurately 0.2 g of each sample into digestion flasks and adding 10 mL concentrated nitric acid (HNO_3). The samples solution was drastically reduced by heating. Ten (10) mL concentrated hydrochloric acid (HCl) was added to the sample flask and also heated to near dryness. Ten (10) mL Perchloric acid ($HClO_4$) was added to almost dryness and another 10 mL conc. HCl was finally added. After the dissolution, the digested samples were filtered and transferred into pre-cleaned 250 mL standard flasks and it was made up to 250 mL by double distilled water addition. The digests were analysed for Pb, Cd, Ag, As, Co, Ca, Cr, Cu, Fe, Mn, Ni, Sb, Se, and Te by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES: 7600 thermo scientific, Austria). All the chemicals used, (nitric, hydrochloric and Perchloric acids) were of laboratory grade (Grade: GR, supplied by Merck, India).

3.4.1 Metal characterisation of composite paste

The composite paste was prepared by taking 2 g each of the 50 battery pastes samples, homogenised and digested for metal characterisation using the same digestion procedure.

3.5 Structural and micro-structural characterisation of the paste

3.5.1 X-ray diffraction analysis

The chemical phases of the pastes were determined using X-Ray diffraction (XRD). A known weight 2 g of composite sample of the paste was sieved to 0.35 mm finely-oriented powder, part of which was mounted on the XRD sample holder and analysed with Bruker X-ray diffractometer (D8 Discovery, US) using 2θ range with scan rate of $0.02^{o}/0.5$ sec. The CuKα radiation (λ 1.5406 Å) at 40KV and 40mA. The XRD patterns were analysed using Diffrac.EVA V2.1 software.

3.5.2 SEM/EDX analysis

Scanning electron microscope (SEM) is an analytical instrument used for obtaining information about the morphology of materials. It can be used for point analysis and elemental mapping (bulk or area) when connected to Energy Dispersive X-ray Spectrometer (EDX). A finely-sieved and homogenised powder sample of WLAB paste mounted on an aluminum holder using adhesive tape. The mounted samples were coated with silver under vacuum using sputtering coater. The morphology of the samples was examined using Field emission gun-scanning electron microscope (Model FEI 430) fitted with energy dispersive X-ray spectrometer (FEG-SEM/EDAX) and operated at 15.0 KV. The EDX spectra were collected on EDX SDD Apollo 40 Resolution 131.44 Model FEI 430.

3.5.3 Fourier transformed infrared spectroscopic analysis

The bonding properties of waste lead-acid battery paste was determined with Fourier transformed infrared spectrometer (FTIR). A minute amount of the samples powders (about 0.1 – 2% of KBr) was mixed with KBr, homogenised and pressed into pellets. A thin and transparent KBr pellets (windows) were obtained. The pellet in a collar was mounted on the sample holder of FTIR spectrometer (Nicolet 5700 FTIR, Thermo Electron Corporation), and FTIR spectra were obtained.

3.6 Quality control and assurance

Atomic absorption spectroscopic digestion procedures and ICP-OES analysis were adhered to by performing blank and triplicate analysis.

3.7 Statistical analysis

All standard analysis of average, standard deviation (SD) and coefficient of variation CV were obtained by SPSS 14.0. A non-parametric equivalent of one-way analysis of variance (ANOVA) called Kruskal-Wallis rank sum test was adopted (Hollander and Wolfe, 1973) to test the null hypothesis. Multiple comparisons test for median concentrations of the thirteen heavy metals in lead-acid battery (LAB) pastes was also conducted to investigate which pair of the thirteen heavy metals has significantly different median concentrations for the fifty paste samples.

The Kruskal Wallis test is a non parametric test, which means that the test does not assume that data comes from a particular distribution. The test statistic used in this test is called the H statistic. The hypotheses for the test are:

- H_0: population medians are equal.
- H_1: population medians are not equal.

3.8 Preparation of reagents

Preparation of 1M $C_6H_8O_7.H_2O$ (99.5%)

1M Citric Acid solution was prepared by dissolving 210.14g in 1litre of de-ionised water. Subsequent solutions were prepared by this procedure.

Preparation of 1M $Na_3C_6H_5O_7.2H_2O$

1M tri-sodium citrate dihydrate solution was prepared by dissolving 294.10g in 1litre of de-ionised water. Subsequent solutions were prepared by this procedure

Preparation of 1M Hydrogen Peroxide (30%)

1M solution of H_2O_2 was prepared by serial dilution of 30% 9.8M stock solution in 250mL volumetric flask and subsequent solutions were prepared by this procedure.

Preparation of 1M Methanoic acid (85%)

1M Methanoic Acid solution was prepared by dissolving 46.03g molecular weight in 1litre of de-ionized water. Subsequent solutions were prepared by this procedure.

Preparation of 1M sodium Methanoate

1M sodium methanoate solution was prepared by dissolving 68.01g in 1litre of de-ionised water. Subsequent solutions were prepared by this procedure

Preparation of 1M CH_3COOH from 17.4M stock solution of 99.5%

1M Ethanoic Acid solution was prepared by serial dilution of 57ml into 600ml de-ionised water and made up in 1litre with de-ionised water. Subsequent solutions were prepared by this procedure.

Preparation of 1M CH_3COONa (99.0%)

1M Sodium ethanoate solution was prepared by dissolving 136.02g in 1litre of de-ionised water. Subsequent solutions were prepared by this procedure.

3.9 Production of the lead precursors

3.9.1 Selection of extractant

The recovery of lead was performed in the form of simultaneous leaching and precipitation using an environment friendly, green chemistry, and relatively low cost organic acids and salts of organic acids. Among factors that influence chemical reaction is the physical nature of the reactants, concentration, stirring speed, reaction durations and temperature at which reaction occurs. The selection of leaching/precipitating agents lies largely on some factors as physical and chemical behaviour of the materials to be extracted, selectivity of the reagents, and chemical expenses. The efficiency of different organic acids and its salts were investigated by using citric acid and sodium citrate, ethanoic acid and sodium ethanoate, and methanoic acid and sodium methanoate under identical conditions. Maximum extraction/ leaching is best achieved under certain extraction conditions such as: Solution concentrations, pulp density or Solid/Liquid mixture, Temperature, Stirring speed and Reaction time.

Lead components of the paste was leached, desulphurised, reduced and precipitated as lead organic compounds using three different low molecular weight carboxylic acids (Methanoic acid, ethanoic acid and citric acid), their salts (sodium methanoate, sodium ethanoate and sodium citrate) and 30% hydrogen peroxide solutions with concentrations ranging from 1-2 M maintained at pH 3.9. Each of the combined solutions was prepared by mixing the acid, salt of the acid solution inside a closed, three-necked Pyrex flask glass reactor either as the three solutions combined before the addition of the paste or as acids and their salts solutions combined, then addition of paste follows by the addition of hydrogen peroxide. The ratio of the paste to the solution was 1:10(^{w}/v). The reaction mixtures was kept stirred at room temperature for a period of 30 minutes to obtain Pb precipitate precursors. Affirming completion of the reaction, the precipitate was isolated by vacuum filter and the filtrate collected for analyses to determine unreacted Pb.

Operating by the latter option of the addition of reactants, the viscosity of the slurry was reduced and precipitation enhanced.

Procedure

10 g of WLAB paste was leached, desulphurised and reduced by 100 mL each of the three types of systems: (1) 1M citric acid, 2 M trisodium citrate and 2M 30% hydrogen peroxide (2) 1M ethanoic acid, 2M sodium ethanoate, and 2M 30% hydrogen peroxide; and (3) 1M methanoic acid, 2M sodium methanoate and 2M 30% hydrogen peroxide in the ratio 2:1:2 by volume respectively. Citric acid monohydrate $(C_6H_8O_7).H_2O$ 99.5% purity of laboratory reagent grade (HI-PURE Rankem) chemicals was employed for the preparation of citric acid solution in double distilled water. Trisodium citrate dihydrate $C_6H_5Na_3O_{7}._2H_2O$ (HI-PURE Rankem) and Hydrogen Peroxide H_2O_2 30% w/v served as the desulphating agent and reducing agent respectively. Citric acid provided leaching medium; Sodium citrate was used as the desulphating agent during leaching experiment of LAB paste; and hydrogen peroxide was used as the reductant. Ethanoic acid (CH_3COOH), Sodium ethanoate, and 30% hydrogen peroxide, methanoic acid, Sodium methanoate and 30% hydrogen peroxide Extra Pure reagents were also used.

3.9.2 Optimisation parameters for citric acid system

Varied solution concentrations (1 – 3M) of citric acids, sodium citrate and hydrogen peroxide prepared through standard reagent preparation procedures were tested for optimum leaching conditions. Different solid/liquid ratios of 30 g/L -200 g/L were examined at varied temperatures (30^o C – 40 ^oC). Stirring rate of (500 – 700 rpm) at different reaction time between 30 – 240 minutes was investigated

3.9.3 Precipitation of lead precursor

The leaching of WLAB paste was carried out in a closed three-necked Pyrex flask glass reactor. The sample was introduced into the leachants of pre-determined pH of 3.94 for optimum leaching and precipitation in ratio 2:1:2 in different conditions determined 1M citric acid, 2M sodium citrate, and 2M hydrogen peroxides.

Shaking of the sample mixtures was achieved by magnetic stirring adequate enough to ignore mass transfer loss effect during the leaching experiment. Samples were pipetted at a desire time interval, filtered and taken for analysis by AAS. On completion of each experiment, the precipitates were vacuum filtrated and dried at 70 ^{o}C in temperature-controlled oven for 1 hour. The filtrate was analysed for metals remaining in the solution. Mass balance by calculations for each round of leaching experiment was obtained.

3.9.4 Leaching/extraction kinetics study

Leaching Kinetics was done to study the mechanism of dissolution of the battery paste in citric acid. Kinetic study helps to confirm the certainty of leaching temperature, energy consumption, and to validate the morphology obtained from the SEM spectra. Shrinking core models equations were tested during the kinetics leaching experiments. These models elucidating on the solid-fluid reaction of dense particles.

$X = K_c t$ *Film diffusion control dense constant size small particles – all Geometrics 1

$1 - (1 - X)^{2/3} = K_c t$ *Film diffusion control dense shrinking spheres 2

$1 - (1 - X)^{1/2} = K_c t$ *Chemical reaction control dense constant size cylindrical particles 3

$1 - (1 - X)^{1/3} = K_c t$ *Chemical reaction control dense constant size or shrinking spheres 4

$1 - 3(1 - X)^{2/3} + 2(1 - X) = K_c t$ *Ash diffusion control dense constant size-spherical particles 5

where K_c = reaction rate constant (min^{-1});
t = time (min);
X = fraction reacted of Pb (% extraction/100).

3.10 Product characterisation

3.10.1 X-ray diffraction analysis (XRD)

Synthesised lead compound and nano-PbO were characterised by X-ray diffraction (XRD) analysis by Bruker X-ray diffractometer (D8 Discovery, US) using 2θ range with scan rate of 0.02°/0.5 sec. The CuKα radiation (λ 1.5406 Å) was generated at 40KV and 40mA. The XRD patterns were analysed using Diffrac.EVA V2.1 software.

3.10.2 Scanning electron microscopic/Energy dispersive spectroscopic analysis

The morphology of the precursor and nano-PbO produced were examined using Field emission gun-scanning electron microscope (Model FEI 430) fitted with energy dispersive X-ray spectrometer (FEG-SEM/EDAX) and operated at 15.0 KV, after coating the sample on carbon tape. The EDX spectra were collected on SEM/EDX SDD Apollo 40 Resolution 131.44 Model FEI 430.

3.10.3 Thermogravimetry-differential thermal analysis

Thermogravimetry-differential thermal analysis measures the heat flow and weight loss against temperature in a sample. Specific heat capacity of a sample can be obtained by TG/DTA. The peaks observed in DTA shows chemical reactions occurring in a sample as it changes from one phase to another either as endothermic or exothermic. Thermogravimetry measures weight loss of the sample during the heating process. It decreases as exothermic reaction occurs. Thermal investigation of the Pb precursor determine by Thermo-Gravimetry-Differential Thermal Analysis using HITACHI STA 7300 analyser to determine the temperature at which the precursor lost its organic content and obtain a stable mass of the product. Thermal analyses were conducted on lead citrate compound by placing the precipitate in platinum crucible and alumina reference recorded on HITACHI STA 7300 in static air by heating at ambient temperature to 800 °C at 10 °C min^{-1}.

3.10.4 Fourier transformed infrared spectroscopic analysis

Bonding properties of the precursor and nano PbO produced were determined with Fourier transformed infrared spectrometer (FTIR).

3.11 Calcination and thermal analyses of lead precipitate

The Pb-citrate produced was heated in static air at 400 ^{o}C for 30 minutes at heating rate of 10 ^{o}C min^{-1}. The weight loss was determined for the experiment. Calcination temperature was determined based on TG-DTA data.

3.12 Structural characterisation of the products

Chemical phase composition of the lead precursor and the nano-lead oxide was done using X-ray diffraction with Bruker X-ray diffractometer (D8 Discovery, US) with CuKα radiation (λ 1.5406 Å) generated at 40KV and 40mA. The imaging and elemental mapping of the products were examined using Field emission gun-scanning electron microscope (Model FEI 430) fitted with energy dispersive X-ray spectrometer (FEG-SEM/EDAX) and operated at 15.0 KV after coating the sample with silver. The EDX spectra were collected on SEM/EDX SDD Apollo 40 Resolution 131.44 Model FEI 430. Fourier transformed infra-red spectra were recorded on a Nicolet 5700 spectrometer using KBr pellet method.

3.13 Further characterisation of nano-PbO

A. XRD-particle size

An XRD examination of the prepared PbO was carried out using X'pert PRO PANalytical diffractometer, Cu-Kα X-rays of wave-length (λ) 1.5406Å. The average sizes of the product were calculated using Debye-Scherrer formula (Arulmozhi *et al.,* 2013).

$$D = 0.9\lambda/\beta \cos \theta$$

where D is the mean particle size;
λ is wavelength of CuKα -1.5406Å;
β is the full width at half maximum (FWHM); and
θ is bragg's diffraction angle.

B. Sample surface area

This is one of the properties of solids which can be described as the total area of a material per unit mass. It is scientifically derived and it helps to determine the types and material properties. It has a wide range of applications in catalysis, adsorption and reaction on material surfaces. It was determined by the formula:

$$SSA = SA_{part}/V_{part} \times \text{Density}$$

where SSA is the specific surface area;
SA part is surface area of the particle;
V part is particle volume; and
Density is the theoretical density of lead Oxide.

SSA can also be calculated using the formula:

$$S = 6 \times 10^3/Dp$$

where S is the specific surface area;
D is the mean particle size; and
p is the density of lead Oxide.

C. Crystallinity index (I_{cry})

Crystallinity of a solid defines the extend of structural arrangement in solid. It is evaluated by comparing particle size measured from XRD data with particle size from SEM/TEM measurement. It is usually expressed:

$$I_{cry} = Dp/D$$

where D*p* is the particle size from SEM/TEM; and
D is the particle size from Scherrer formula.

If I_{cry} value is near 1, the particle size is monocrystalline; and where it is greater than or much larger, it is assumed to be polycrystalline.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Environmental management of waste lead acid battery

Analysis of the study survey revealed the types of LABs in the market, their life expectancy and end of life management. Table 4.1 showed the percentages of active stakeholders in the management of WLABs. Eleven percent (11.5%) of the respondents identified themselves as battery sellers; battery repairers were 17.5%; scavenger/recyclers 22.3%; and battery users 48.5%. These percentages may not be generalised in the distribution of LABs among these groups nevertheless they present a trend in it distributions. Figure 4.1 shows the percentage distribution of end of life management of WLABs among groups. About 8.5% of the respondents disposed the waste battery indiscriminately, 70.8% disposed the waste battery using dumpsites, 1.5% burns the spent products, 13.1% returns the waste battery to the sellers and 6.2% cannot account for the management of the spent products. The survey in Figure 4.2 revealed about 98% of automobile batteries as calcium ion (Ca^{2+}) batteries which represent the majority of the LABs as calcium ion in types. Figure 4.3 revealed the life span of lead acid battery. Twenty-five percent of the respondents used batteries for three years, fifty-eight percent used the batteries for five years and sixteen percent for seven years.

Table 4.2 shows variation in the components weight of different waste lead acid batteries (WLABs) that were studied. The weight differs according to models, number of cells and voltage capacities of the batteries.

Table 4.1: Stakeholders in LABs management

		Frequency	Percent	Valid Percent	Cumulative %
Valid	Local Recyclers	29	22.3	22.3	22.3
	Battery Seller	15	11.5	11.5	33.8
	Battery Repairers	23	17.7	17.7	51.5
	Battery Users	63	48.5	48.5	100.0
	Total	130	100.0	100.0	

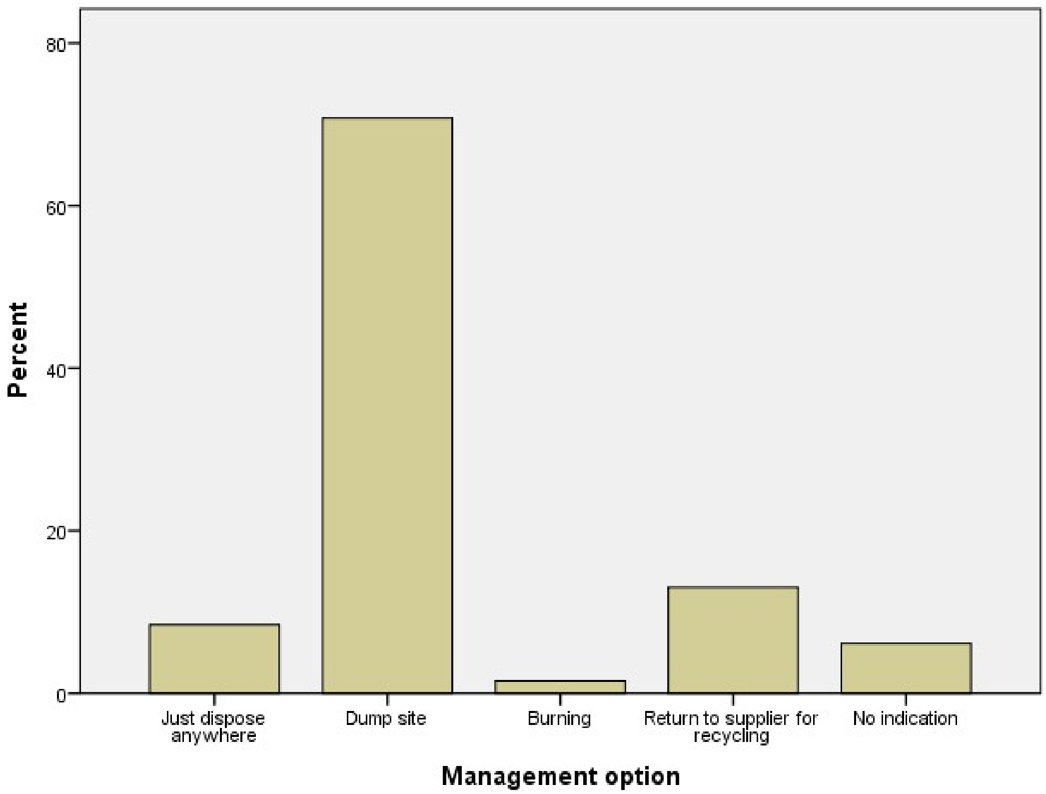


Figure 4.1: Percentage distribution of end-of-life management of WLABs among groups

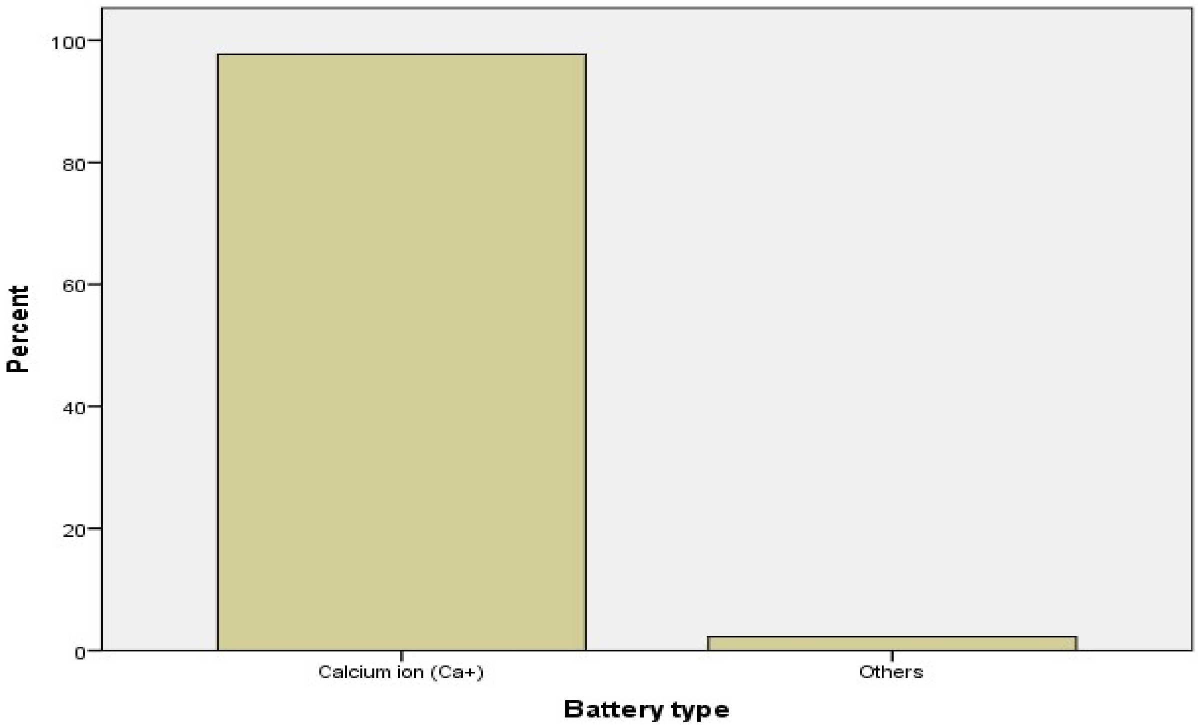


Figure 4.2: Types of Lead-acid battery in Nigeria markets

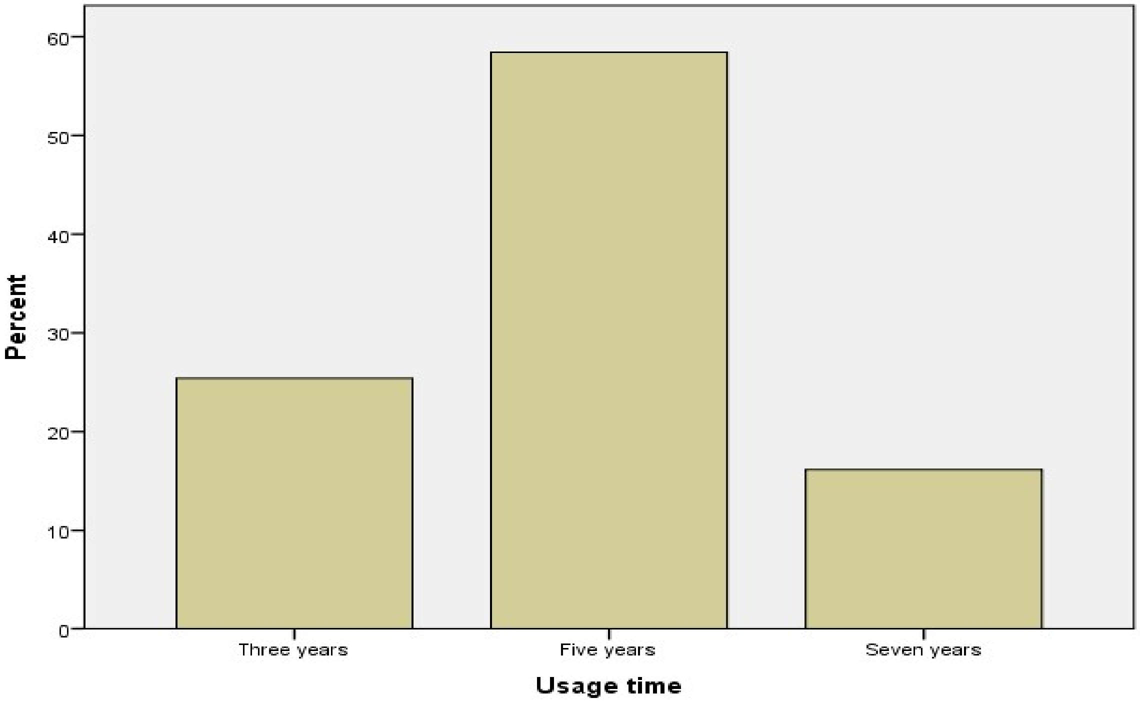


Figure 4.3: Duration of use of Lead-acid batteries

Table 4.2: Weights (g) of Components of Different Models of LABs

S/n	Sample code	Metal & Paste	Plastics
1	LAB Model 1	980	850
2	LAB Model 2	570	650
3	LAB Model 3	1020	920
4	LAB Model 4	1590	1190
5	LAB Model 5	3290	720
6	LAB Model 6	2120	1020
7	LAB Model 7	1390	1080
8	LAB Model 8	2010	1540
9	LAB Model 9	880	1650
10	LAB Model 10	1370	810
11	LAB Model 11	750	690
12	LAB Model 12	990	680
13	LAB Model 13	1390	860
14	LAB Model 14	2130	1210
15	LAB Model 15	1250	1380
16	LAB Model 16	1210	960
17	LAB Model 17	1210	1500
18	LAB Model 18	1070	1000
19	LAB Model 19	1320	880
20	LAB Model 20	1540	1450
21	LAB Model 21	970	670
22	LAB Model 22	590	1020
23	LAB Model 23	730	820
24	LAB Model 24	760	1020
25	LAB Model 25	920	1020
26	LAB Model 26	910	890
27	LAB Model 27	890	1040
28	LAB Model 28	790	1250
29	LAB Model 29	1060	830
30	LAB Model 30	780	870
31	LAB Model 31	1050	770
32	LAB Model 32	1830	940

Table 4.2: Weights (g) of Components of Different Models of LABs (continued)

S/n	Sample Code	Metals & Paste	Plastics
33	LAB Model 33	1350	860
34	LAB Model 34	1380	860
35	LAB Model 35	1390	1200
36	LAB Model 36	1070	1380
37	LAB Model 37	1510	1640
38	LAB Model 38	1820	690
39	LAB Model 39	1180	860
40	LAB Model 40	1190	800
41	LAB Model 41	1190	1250
42	LAB Model 42	980	1000
43	LAB Model 43	850	630
44	LAB Model 44	950	820
45	LAB Model 45	870	1710
46	LAB Model 46	930	1140
47	LAB Model 47	1180	1130
48	LAB Model 48	1340	1110
49	LAB Model 49	1180	740
50	LAB Model 50	1480	970

4.2 Material flow of motor vehicles in Nigeria (1980-2014)

Estimate of registered automobile vehicles in Nigeria within 1980 and 2010 was obtained. For this span of vehicle life, 13 million cars, 6 million buses and 190 thousand trucks were estimated to be imported to Nigeria. About 2.4 million cars, 984 725 buses and 34 229 trucks were estimated to be the amount of vehicles in end of life up to 2004 (Babayemi *et al.,* 2016). Up to 2010, over 10 million cars, 5 million buses and about 160 thousand trucks were in use from the estimated vehicles reported to have entered Nigeria between 1980 and 2010.

The estimates of LABs in end-of-life up to 2004 are depicted in Table 4.3. About 2.4 million cars estimated to have reached end-of-life produced almost 300 thousand (tons) of WLABs. Almost 1 million buses produced close to 120 thousand (tons) of waste batteries and 34 thousand trucks produced 4 thousand (tons) of waste batteries. Almost 400 thousand (tons) of WLABs were estimated to have reached end-of-life between 1980 and 2004.

The estimated distributions of LABs in motor vehicles in use up to 2010 is presented in Table 4.4. Over 10 million cars carried about 1.5 million (tons) of LABs. About 5 million buses in use till 2010 have almost 700 thousand (tons) of batteries while 155 thousand trucks carried about 22 thousand (tons) of LABs.

Estimated amount of vehicles (in weights) between 2011 and 2014 are shown in Table 4.5. Almost 4 billion cars, about 1.5 billion buses and about 1.4 billion trucks in this period are in use. Motor vehicles imported from 2010 to 2014 are still in use currently till 2014, since a vehicle can span up to 30 years in Nigeria.

Table 4.3: Numbers of Vehicles Registered in Nigeria

Vehicle	*Number Imported (1980 – 2010) (n_i)	*Number in End-of-Life up to 2004 (n_e)	Number in Use up to 2010 ($n_{u\,(2010)}$)
Cars	13,000,000	2 395 912	10 604 088
Buses	6,000,000	984 725	5 015 275
Trucks	190,000	34 225	155 775

* **Source**: Babayemi *et al.,* 2016

4.3 Material flow of LABs of motor vehicles in Nigeria (1980 – 2014)

The results of the estimates amount of LABs imported to Nigeria through buses, cars and truck between the years 2011 – 2014 are shown in (Table 4.7). Approximately 6.7 Mt of motor vehicle imported within this period used approximately 53 883 tons of LABs during this period.

The result of LABs between the year 1980 and 2014, approximately 4.8 million tons (Mt) LAB were used via motor vehicles in Nigeria; of which approximately 2.6 million (Mt) have reached E-o-L; while approximately 2.2 million (Mt) were in current use in 2014 as shown in (Table 4.8). Out of these batteries in E-o-L, approximately 2.3 Mt were calculated to be recycled and 0.3 Mt land-filled. Given an average life span of lead acid battery of motor vehicles in Nigeria to be 5 years based on the survey in (Figure 4.3) and reported average life span of 5 years from the literature, this implies that by the year 2019, approximately 2.2 Mt will be added to the amount in E-o-L. This is summarised by the flow chart (Figure 4.4).

Table 4.4: Estimated distributions of LABs in End-of-Life up to 2004

Vehicle	Number (n_v) in end-of-life up to 2004 (t_1=25yrs)	Battery lifespan (yr) (t_2)	Number of battery used per vehicle (t_1/t_2)	Total Number of battery used n_v x (t_1/t_2)	Average weight of battery (kg) (w)	Total amount of battery (tons) n_v x (t_1/t_2) x w
Cars	2 395 912	5	5	11 979 560	22.7	271 936
Buses	984 725	5	5	4 923 625	22.7	111 766
Trucks	34 225	5	5	171 125	24	4107
Total						387 809

Table 4.5: Estimated Distributions of LABs in Motor Vehicles in Use up to 2010

Vehicle	*Number (n_v) in use up to 2010 (t_1=30 years)	Battery lifespan (yr) (t_2)	Number of battery used per vehicle (t_1/t_2)	Total Number of battery used n_v x (t_1/t_2)	Average weight (kg) of battery (w)	Total amount of battery (tons) n_v x (t_1/t_2) x w
Cars	10 604 088	5	6	63 624 528	22.7	1 444 277
Buses	5 015 275	5	6	30 091 650	22.7	683 080
Trucks	155 775	5	6	934 650	24	22 432
Total						2 149 789

* **Source**: Babayemi *et al.,* 2016

Table 4.6: Amount (kg) of Buses, Cars and Trucks Imported to Nigeria (2011 – 2014)

Period	Net Weight (kg)		
	Buses	Cars	Trucks
2011	1,114,913,120	1,526,360,204	552604406
2012	343,081,497	1,550,482,497	527426823
2013	85,147,701	583,364,153	228836281
2014	33,599,107	112,080,943	84856638
Total	1,576,741,425	3,772,287,797	1,393,724,148

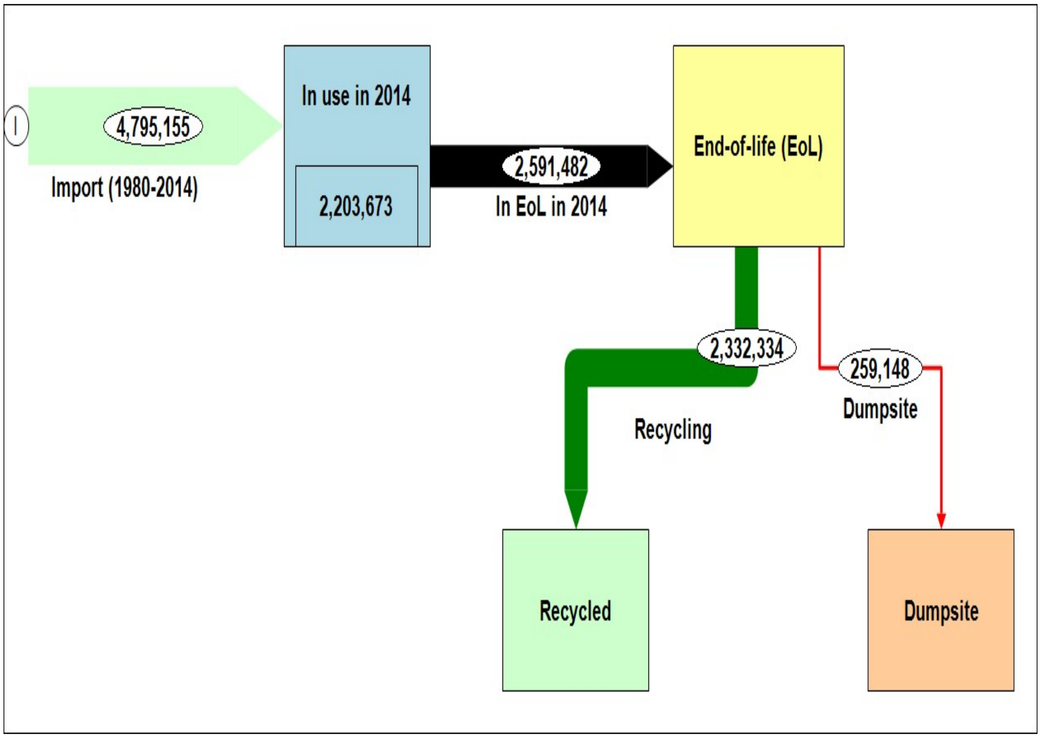


Figure 4.4: Material/Substance flow chart of LABs motor vehicles imported to Nigeria (1980 – 2014), stock for inventory 2014.

Table 4.7: Amount of Battery (tons) Imported via Buses, Cars and Trucks into Nigeria (2011 – 2014)

Vehicle	Amount of Vehicles (kg)	Fraction of Battery (%)	Amount of Battery (tons)
Cars	3,772,287,797	1.25	47,154
Buses	1,576,741,425	0.25	3,942
Trucks	1,393,724,148	0.20	2,787
Total	6,742753370		53,883

Table 4.8: Total Amount (tons) of LABs Used via Buses, Cars and Trucks in Nigeria (1980 – 2014)

Vehicle	Amount in EoL vehicles (1980 – 2010) (a)	Amount in Use up to 2010 (b)	Amount in Use (2011 – 2014) (c)	Amount of Vehicles in Current Use (2014) (b + c)	Total Amount Used in History (1980 – 2014) (a + b + c)
Cars	271 936	1 444 277	47 154	1 491 431	3 254 798
Buses	111 766	683 080	3 942	687 022	1 485 810
Trucks	4 107	22 432	2 787	25 220	54 547
Total	387 809	2 149 789	53 883	2 203 673	4 795 155

4.4 Substance flow analysis of valuable and toxic elements in lead acid battery of motor vehicles in Nigeria

The results of amount of valuable and toxic elements generated in different life cycles of lead acid batteries (LABs) in Nigeria are presented in (Table 4.9). Metallic lead, being the major element in the battery, gave the highest amount of 3.5 million tonnes between 1980 and 2014. Recycling/ recovering these toxic and valuable elements will not only protect the environment and health, but also it is economically viable as secondary materials for other industrial uses.

Table 4.9: Substance Flow Analysis of Valuable and Toxic Elements in LABs

Heavy Metallic elements	Amount (tons) in Batteries of Motor Vehicles (1980 – 2014)			Amount (tons) in Different Life Cycle Stages		
	Cars	Buses	Trucks	Total Amount in History (1980-2014)	Amount in E-o-L (1980-2014)	Amount in Current Use (2014)
Pb	2 346 709	1 071269	39 328	3 457 306	279 610	1 588 848
Cd	25.7	11.7	0.4	37.8	3.1	17.4
Ag	43.6	20.0	0.7	64.3	5.2	29.5
As	19.5	8.9	0.3	28.7	2.3	13.2
Co	32.5	14.9	0.5	47.9	3.9	22
Ca	290	132	4.9	427	35	196
Cr	3.58	1.6	0.06	5.24	0.4	2.4
Cu	1009	461	17	1 487	120	683
Fe	2 767	1 263	46	4 076	330	1 873
Mn	176	80	3	259	21	119
Sb	553	253	9.3	815	66	375
Se	2	1	0.03	3.03	0.2	1.3
Te	4.6	2.1	0.08	6.78	0.5	3.1

4.5 Heavy metal composition of WLABs

The elemental compositions of fifty different brands of LABs are presented in Table 4.10. The results of Pb, Cd, Ag, As, Ca, Co, Cr, Cu, Fe, Mn, Ni, Sb, Se, and Te concentration in the spent batteries paste reveal that the paste contained other elements in minute concentration. Some of these elements are added as binder intentionally in the manufacturing of LAB. The percentage weight of Pb in the paste was 72% (721,000 ±38.2 mg/kg). The concentration of lead in waste lead acid batteries indiscriminately dumped by individuals and illegally refined by unauthorised local refiners is extremely high. Recycling of lead from these waste products is extremely viable from the perspective of urban mining, turning of waste to wealth and environmental/ health safety (Abdul-wahab and Marikar, 2011).

In classifying the waste batteries paste as hazardous or non-hazardous, the concentrations limit should either exceed or below the TTLC. The concentration of Pb in each sample exceeded the permissible limit of 1000 mg/kg by TTLC. Lead metal in various degrees has resulted in various environmental and health issue most especially in developing countries like Nigeria and India. A popular case is Zamfara lead poisoning that led to the death of many. Due to the consequences of Pb in the environment and impact on human health, its use in many products had largely been regulated and constrained majorly to the production of Automobile vehicles. The directives were conveyed by the ECRoHS Directive 2002/95/EC 17 (Ogundiran *et al.,* 2015). The levels of other metals studied were found to be below the TTLC values as reported in Table 4.10. Freiberg, (1986) reported that materials containing such high concentration of metals above these levels of TTLC may be regarded as unsafe.

Therefore, there is need for safe environmental and green approach to the management of spent lead acid battery. Recovery of Pb from spent lead acid batteries has reached advance stage in advanced continents which are very unpopular in developing continent. The most available methods are pyrometallurgy and hydrometallurgy (Ogundiran et al., 2015). The pyrometallurgical system involves the smelting of the batteries paste at high temperature to recover the valuable material (Qianyu, 2013). This method is used by most legal refining plants and crude method commonly used in developing countries has also been abused by the local illegal refiners. This poses great environmental and health effects on the ecosystem. Hydrometallurgical method on the other hand uses chemicals for the recuperation of the valuable metal at very low temperature when compared with the pyrometallurgical method which is energy intensive, emission of SO_2 and dust into the environment. It is therefore advisable that the regulatory and the manufacturers of the lead acid battery should establish an environment friendly way of recovering Pb from waste lead-acid batteries.

Table 4.10: Average Concentration of Heavy Metals in mg/kg in LABs and TTLC Values

Heavy Metals	**Samples Mean ± S.E (mg/kg)**	**TTLC (mg/kg) and *µg/kg**
Pb	721,000 ± 38.2	1000
Cd	7.90 ± 7.0	100
Ag	13.4 ± 7.4	500
As	6.00 ± 3.0	500
Co	10.00 ± 6.0	8000
Ca	89.00 ± 0.2	-
Cr	1.10 ±0.8	2,500
Cu	310 ± 255.8	2,500
Fe	850 ± 248.0	1000
Mn	54.0 ± 38.0	2,500
Ni	< nd	2000
Sb	170 ± 42.0	500
Se	0.6 ± 0.3	100
Te	1.40 ± 0.5	*100

Total Threshold Limit Concentration (TTLC) by California Department of Toxic Substances Control. Code of Regulation; 22 sections 66261.24.

The results of Pb concentrations in the 50 samples are presented in Figure 4.5. Since we have more than two samples (metals) to compare and no doubt, data values under all of them do not have equal variance and they do not assume normal distribution, a nonparametric ANOVA known as Kruskal-Wallis rank sum test was adopted (Hollander and Wolfe, 1973). Table 4.11 to test the null hypothesis that no detectable difference between median concentration of heavy metal (%wt) statistically in lead acid batteries, across all the 50 samples.

Kruskal-Wallis distribution free test is a nonparametric test used when the assumptions of equal variance of one-way ANOVA in the thirteen heavy metals in the 50 samples was not accomplished. Kruskal-Wallis test and one-way ANOVA assess for significant differences on a continuous dependent variable by a categorical independent variable (with two or more groups). In the ANOVA, we assume that the dependent variable is normally distributed and there is approximately equal variance on the scores across groups. However, when this assumption was not met, using the Kruskal-Wallis Test becomes the alternative when none of the assumptions holds.

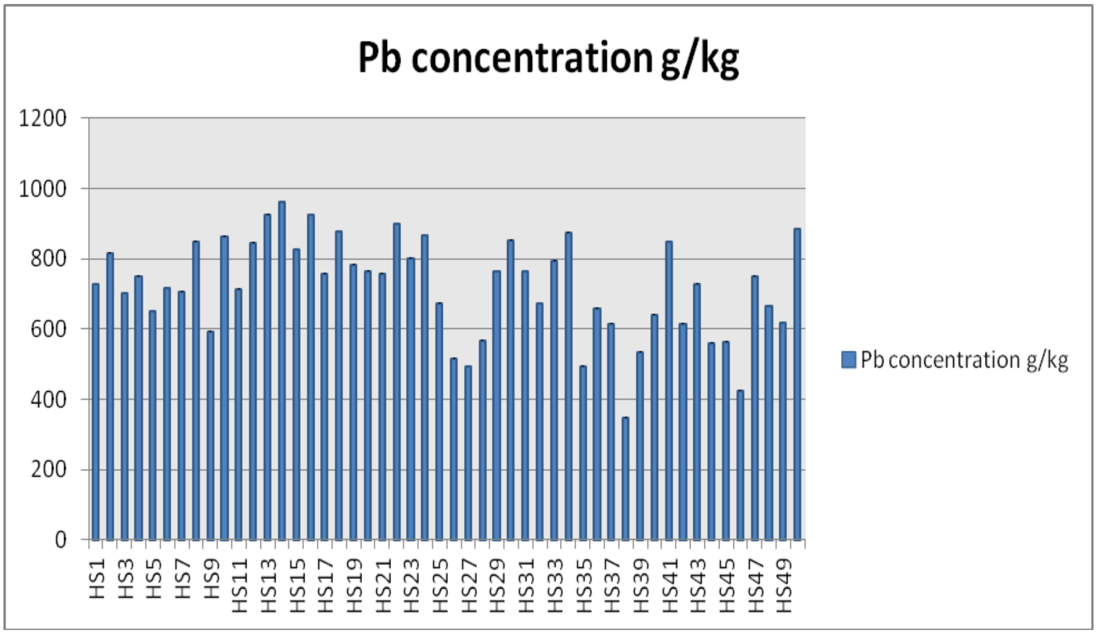


Figure 4.5: Pb concentrations in 50 samples of waste LAB paste

Table 4.11: Kruskal-Wallis Rank Sum Test

Data	Chi-squared	Degree of Freedom	p-value	Decision	Inference
Metal Concentration	404.7652	12	2.2e-16	Reject H_0	Median metal concentrations are statistically different

From Table 4.11, it is evident that concentrations data is sufficient to reject the null hypothesis of equal median concentrations of the fourteen heavy metals in lead acid batteries (LABs) across all the fifty elemental samples, since the test p-value 2.2e-16 is lesser than the critical value α = 0.05at 95% significance level. This implies that at least one of the heavy metals has concentrations higher than other metals in LABs. To investigate which pair of the thirteen heavy metals has significantly different median concentrations for the fifty elemental samples, a test of multiple comparisons for median concentrations of the thirteen heavy metals in LABs was conducted.

All pairs of heavy metals with observed differences greater or equal to corresponding critical differences are said to have significantly different concentrations in lead-acid batteries (LABs) while those with smaller observed difference than the critical differences are said to be identical in terms of their concentrations in LABs.

This inference is further evident in (Figure 4.6) with each box representing five number summaries deposit of each metal type including minimum (inverted T), lower statistical value (lower end of box), median (middle tick line), upper statistical value (upper end of box) and maximum (T on top of each box) deposit of each metal. All metals whose boxes overlap do not have statistically detectable difference in their deposit while those whose boxes are not overlapping (significance) have statistically different median concentrations in LABs among the 50 samples.

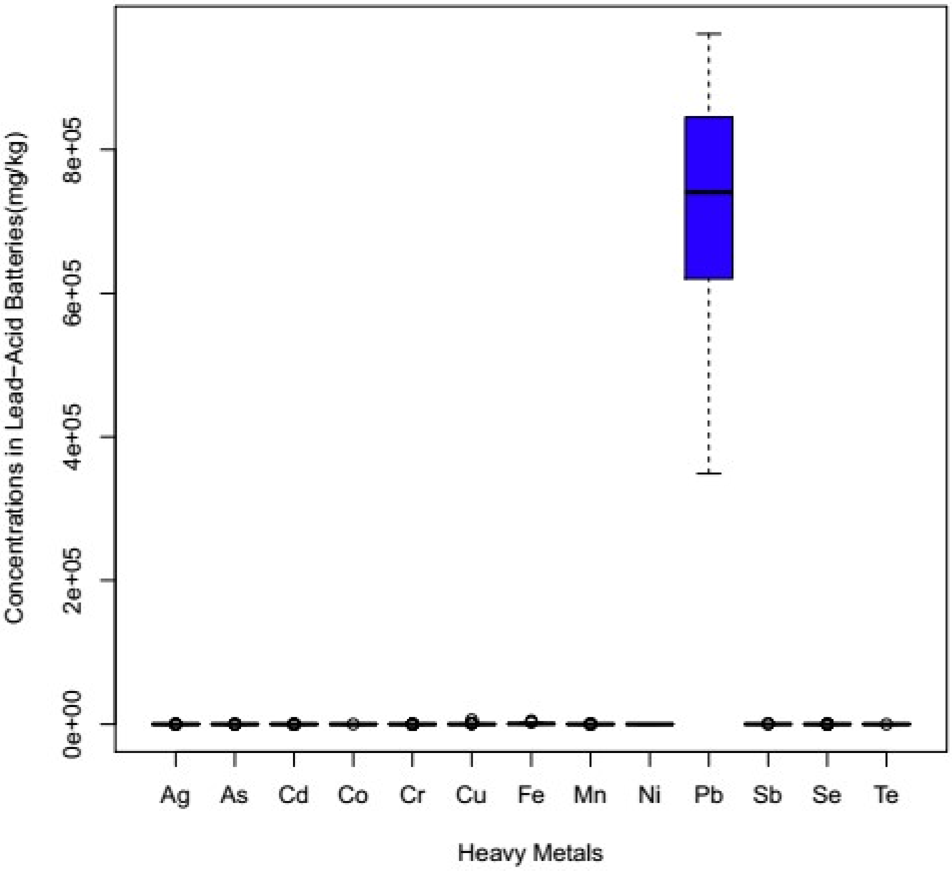


Figure 4.6: Box plot showing median metals concentrations in LABs

4.6 Characterisation of battery paste

4.6.1 X-ray diffractometric characterisation of the LAB paste

The chemical phases identified in the waste Pb-acid battery paste are shown in Figure 4.7. The result reveals different phases of Pb as lead sulphate ($PbSO_4$), lead (IV) oxide (PbO_2), lead oxide (PbO), metallic Pb and lead oxide sulphate ($Pb_3O_2SO_4$). When the battery is in charged state, it is basically composed of lead (IV) oxide, the electrolyte (H_2SO_4) and lead. The chemical phases in Figure 4.7 clearly showed that the battery has been discharged and spent. The XRD spectrum reveals the dominant phases in the paste as lead sulphates and lead (IV) oxides.

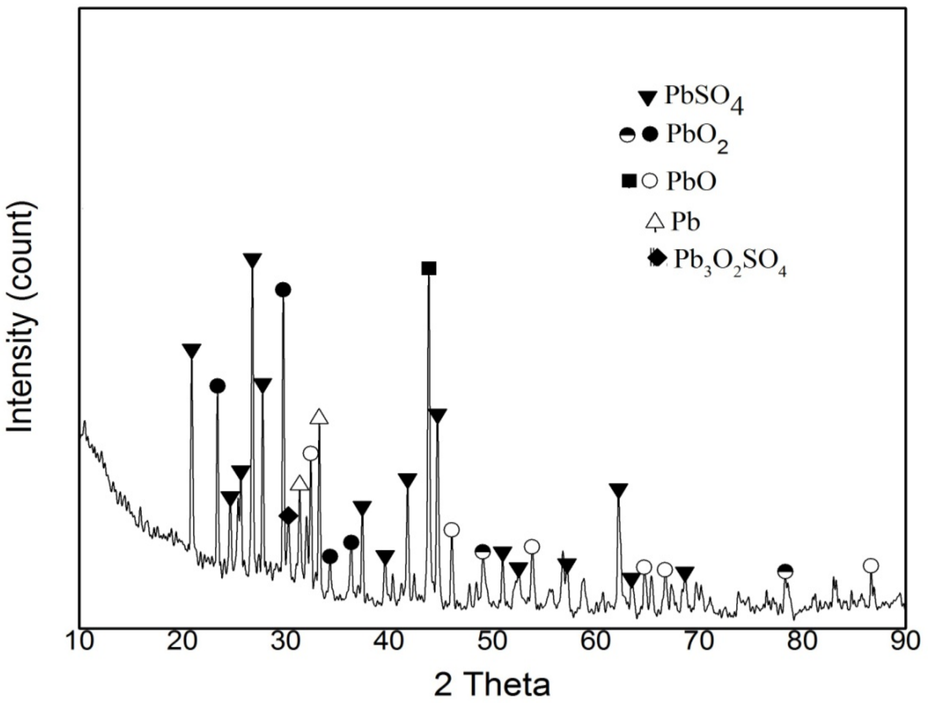


Figure 4.7: XRD pattern of waste LAB paste

4.7 SEM-EDX morphology of LAB paste

The morphology of the paste was investigated prior to leaching/desulphurisation and precipitation to observe any significant material changes in physical and chemical properties. Area and point imaging/mapping of the paste showed lead, oxygen and sulphur. The traces of carbon is believed to have been from the carbon tape used in coating the sample on the sample holder and the iron may be present as impurity. The bulk images in the paste revealed that lead sulphate was densely distributed. The result of the scanning electron microscope SEM obtained in this study matched well with the morphology of $PbSO_4$ observed by Sajadi, (2011) in his research on Pb sulphate and Pb oxide sulphate morphology and thermal decomposition. Figure 4.8 picture SEM image of the paste indicating bulk of $PbSO_4$ as confirmed by the Energy dispersive spectroscopy attached to the scanning microscope in Figure 4.9. The results confirmed the presence of $PbSO_4$ as the major phases in the paste as shown by XRD diffraction. This implies that desulphurisation is the major process to obtain lead in nano oxide form.

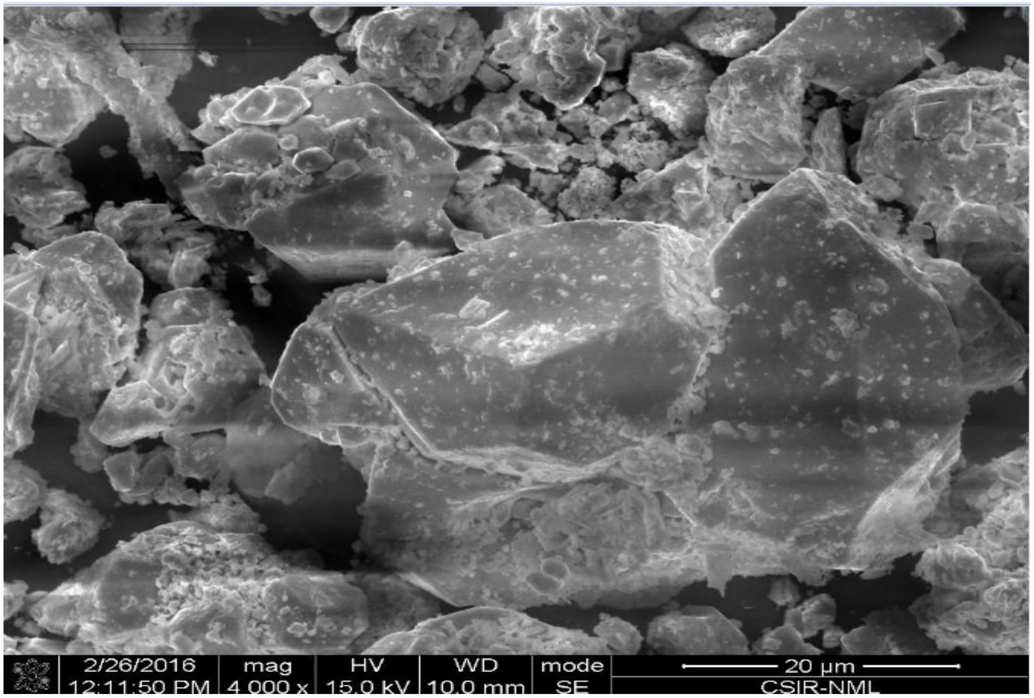
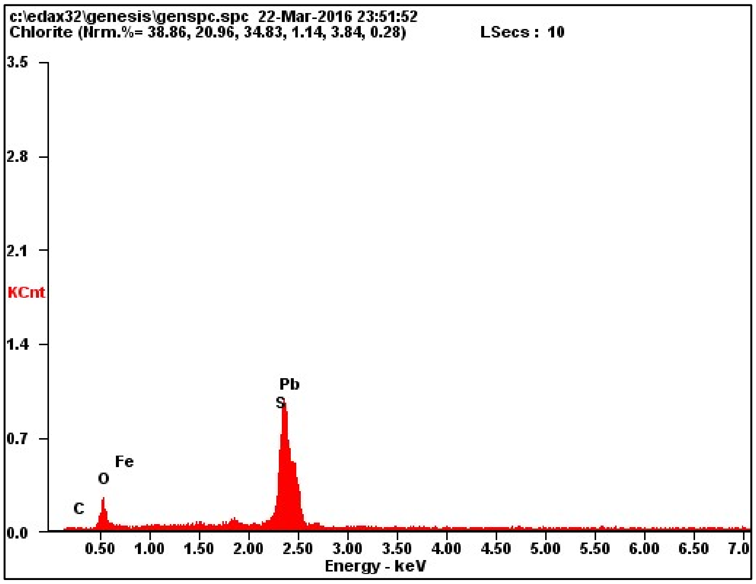


Figure 4.8: Scanning electron microscopic photograph of lead acid battery paste



Elements	***Wt %***	***At %***
C K	02.17	08.80
O K	18.10	54.96
FeL	05.08	04.42
S K	11.18	16.94
PbL	63.46	14.88

Figure 4.9: EDX spectra of lead acid battery paste

The energy dispersive spectra of point analysis obtained confirmed the presence of Pb, O, S, Fe, as dominant elements in the paste and trace amount of carbon resulting from carbon tape used to coat the sample. The percentages of Pb 63%, sulphur 11%, oxygen 18% and iron 5% showed that the material is predominantly lead sulphate with traces of iron.

4.8 FT-IR spectra of lead acid battery paste

Figure 4.10 illustrates the spectra peak of battery paste. The absorption peak of 441 cm^{-1} and Pb-O stretching vibration correlated. The peaks at about 1114 cm^{-1} and 595 cm^{-1} indicated absorption band of lead sulphate ($PbSO_4$). Peaks at 3467 cm^{-1}, represent O-H stretching (Arulmozhi and Mythili, 2013).

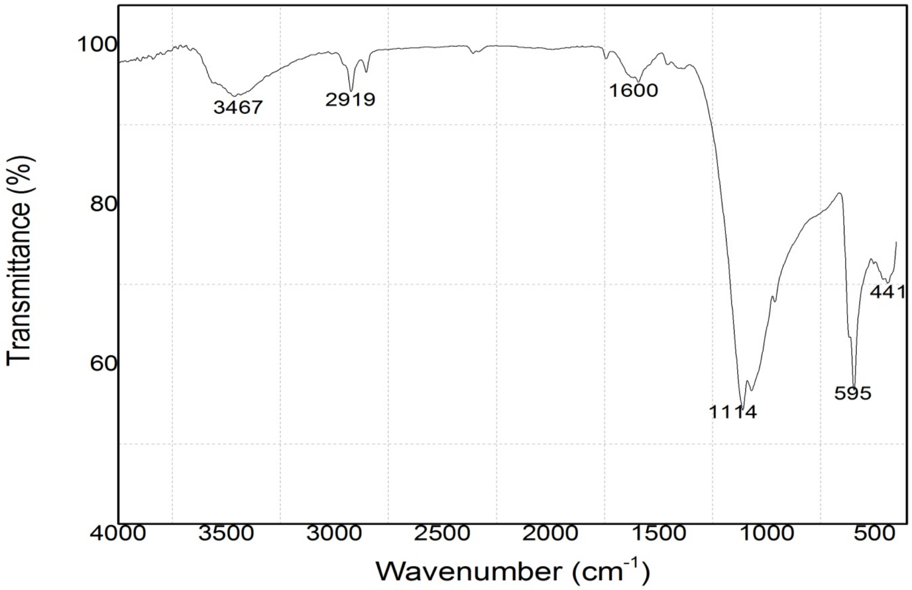


Figure 4.10: FT-IR spectra of raw paste

4.9 Heavy metal compositions of composite lead paste

The results of heavy metals components of the composited paste as measured by wet digestion are presented in (Table 4.12 and Figure 4.11). Lead was observed to have the highest concentration.

Table 4.12: Heavy Metal Composition of Composited Paste (% Weight)

Pb	Cd	Ag	As	Co	Cr	Cu	Fe	Mn	Ni	Sb	Se	Te
61.8	0	0	0.001	0	0	0	0.04	0.05	0	0.004	0	0

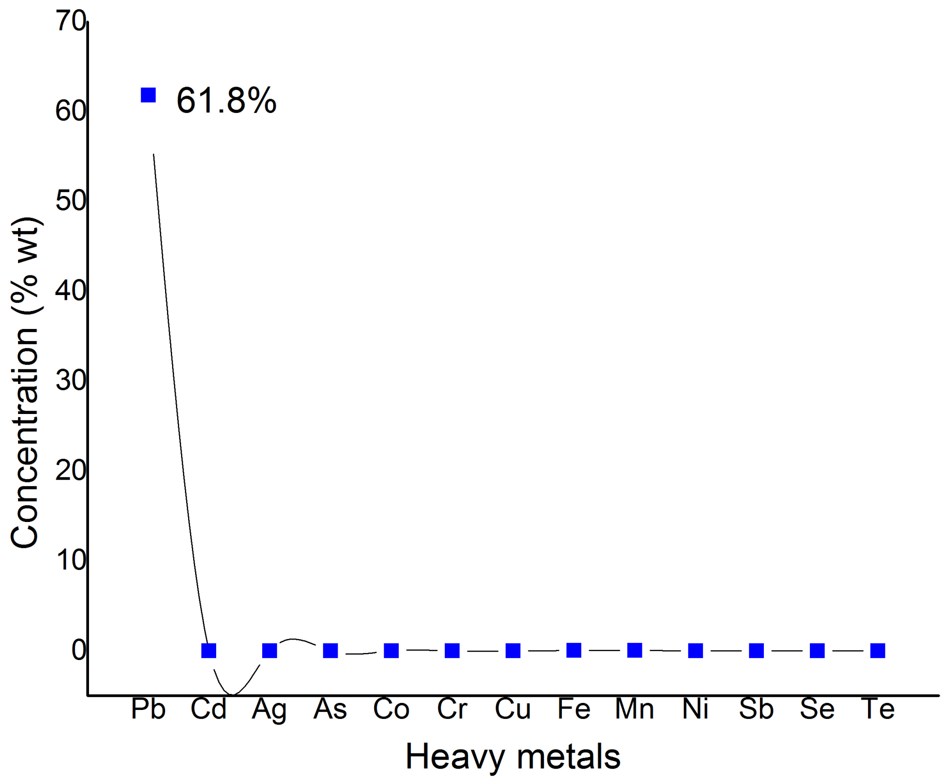


Figure 4.11: Percentage weight (% wt) of heavy metals in the battery paste

4.9.1 Simultaneous extraction and precipitation

The results in (Figures 4.12-4.15) show extractions with different organic acids at varied concentrations to determine the acid with optimal extraction appropriate for lead to precipitate in the paste. The result presented in Figure 4.13 shows that citric acid showed recovery of 98.8%, methanoic acid 81%, and ethanoic acid 61% at 30°C for 30 minutes. Citric acid has high efficiency in leaching and precipitating Pb from the paste at concentration of 1M citric acid, 2M sodium citrate, and 2M hydrogen peroxide, 30°C for 30 minutes than other tested acids. Thus, citric acid was found suitable for the leaching/precipitation because of its selectivity and ease of precipitation/filtration properties with lead as against ethanoic acid, the precipitate of which was difficult to filter with lead as observed during the experiments. It also has considerable advantages over other acids in terms of its source of production (fruit plant acid), low cost and environmental friendliness. Citric acid provided the leaching environment as its dissociation reaction releases 3 H^+ during leaching. This result is in line with the choice of citric acid as leaching agent by (Zhu *et al.,* 2012).

$C_6H_8O_7 \rightarrow C_6H_7O_7^- + H^+ \qquad K\alpha_1 = 7.4 \times 10^{-4}$

$C_6H_7O_7^- \rightarrow C_6H_6O_7^{2-} + H^+ \qquad K\alpha_2 = 1.7 \times 10^{-5}$

$C_6H_6O_7^{2-} \rightarrow C_5H_5O_7^{3-} + H^+ \qquad K\alpha_3 = 4.0 \times 10^{-7}$

The sodium citrate functioned as desulphating agent and acid-buffer reagent and the hydrogen peroxide served as the reductant to reduce Pb (IV) to Pb (II).

$PbO + C_6H_8O_7.H_2O \rightarrow Pb(C_6H_6O_7).H_2O + H_2O$

$PbO_2 + C_6H_8O_7.H_2O + H_2O_2 \rightarrow Pb(C_6H_6O_7).H_2O + 2H_2O + O_2$

$3PbSO_4 + 2(Na_3C_6H_5O_7.2H_2O) \rightarrow Pb_3(C_6H_5O_7)_2.3H_2O + 3Na_2SO_4 + H_2O$

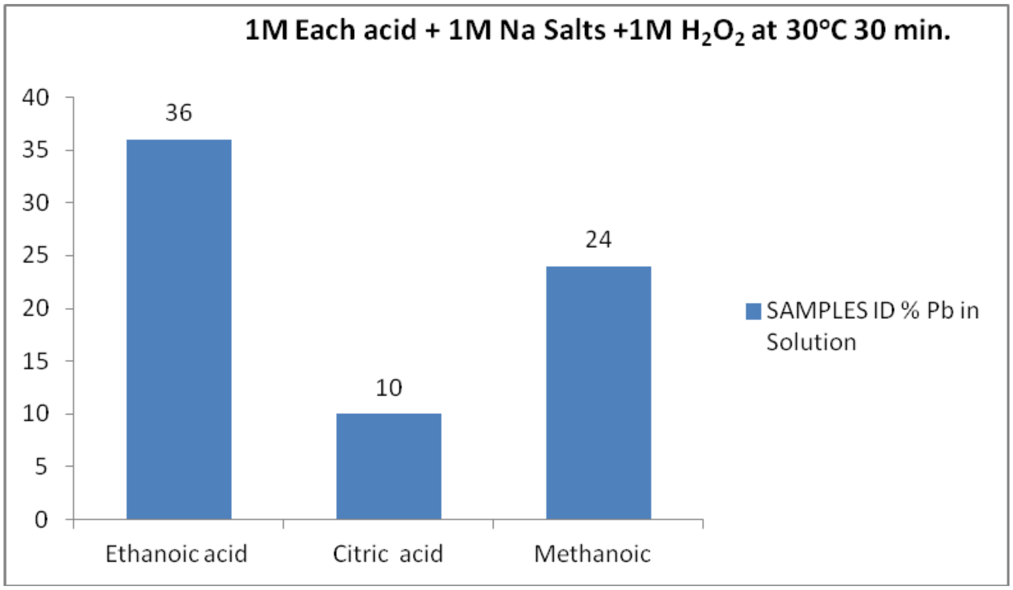


Figure 4.12: Selection of leachants/precipitants, at S/L 100 g/L, 1M concentrations, 30 °C, 500 rpm, 30 mins.

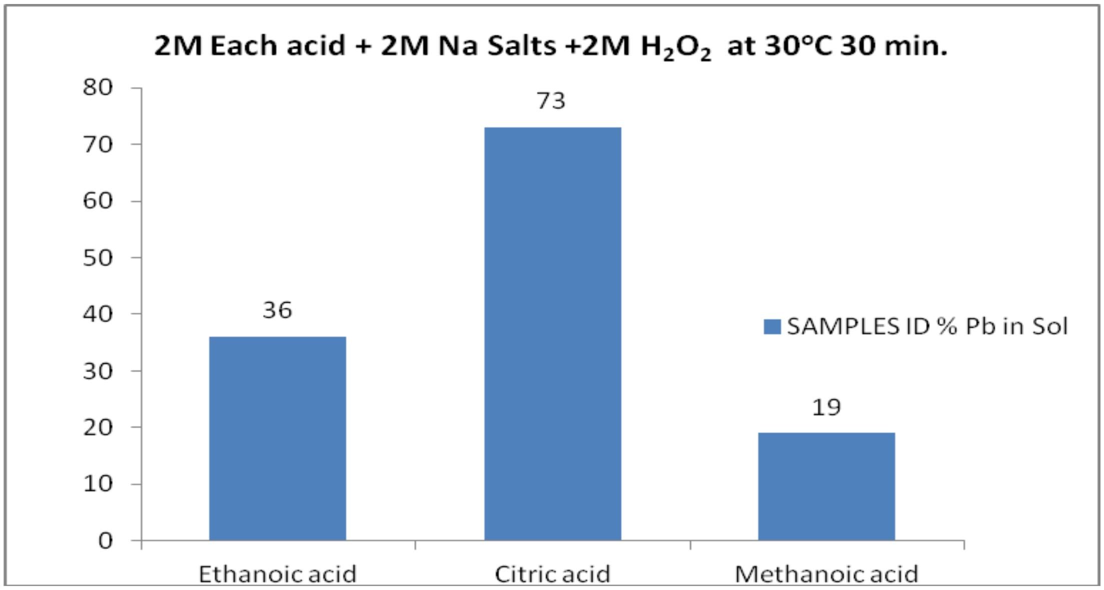


Figure 4.13: Selection of leachants/precipitants at S/L 100 g/L, 2M concentrations, 30 °C, 500 rpm, 30 mins.

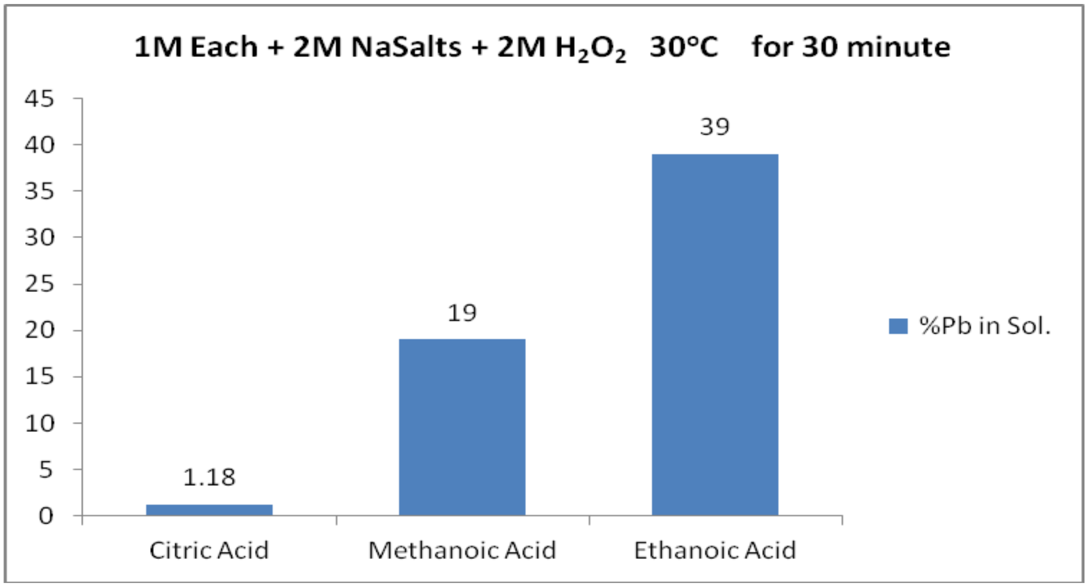


Figure 4.14: Selection of leachants/precipitants at S/L 100 g/L, 1M concentrations, 2M sodium salts and 2M H_2O_2, 30 ^{o}C, 500 rpm , 30 mins.

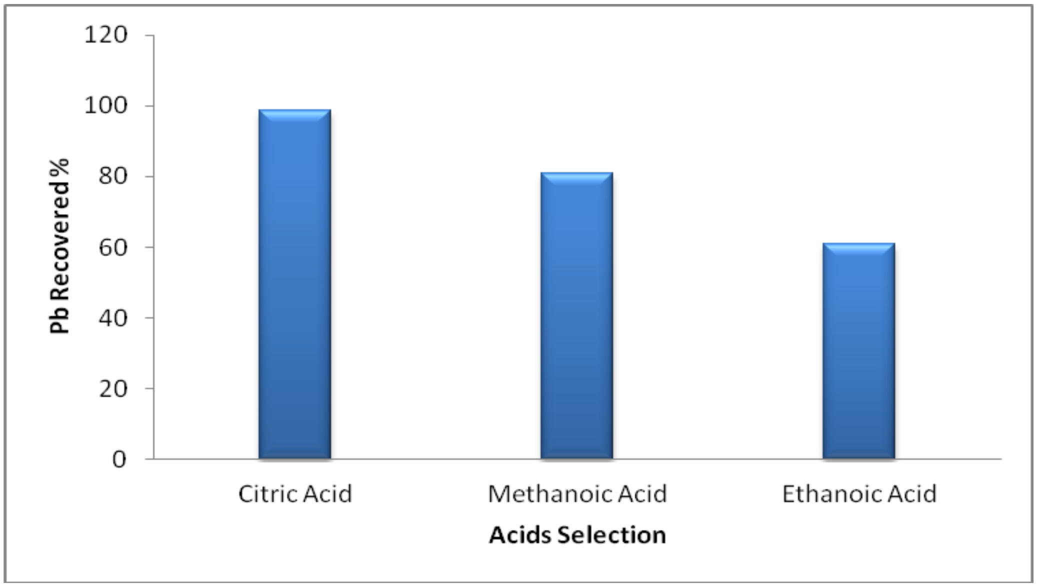


Figure 4.15: Selection of leachants/precipitants, S/L 100 g/L, 1M concentrations, 2M Na-salts, 2M H_2O_2, 30 °C, 500 rpm , 30 mins

4.9.2 Parameters/conditions optimisation for the selected reagents

4.9.2.1 Effect of acid concentrations

The results of varied concentrations of citric acid are presented in Figure 4.16. 1M solution of citric acid left about 1.1 % of unrecovered Pb in the solution resulting in about 98.8% precipitated Pb. At 2M and 3M concentrations of citric acid, recovery of about 97% and 96.5% respectively was attained. It was observed that the higher the solution concentration, the higher the percentage of Pb in the filtrate. It could be inferred that precipitated lead re-dissolved at higher acid concentrations. Concentration of acid or reagents has profound effect on leaching and subsequent precipitation during metal extraction in general. Investigation of appropriate acid concentration was carried out to obtain an optimum leaching acid condition. Different molarities of citric acid and 2M sodium citrate together with 2M hydrogen peroxide volume ratio (2:1:2) was optimized under identical conditions of room temperature 30 ^{o}C, pulp density (S/L) 100 g/L, reaction time of 30 minutes, and stirring speed of 500 rpm. Figure 4.16 shows the concentrations range from 1 M to 3 M from which the recovery was calculated based on the concentration of Pb in the leached paste. After each of the experiments, the filtrate was analysed for the remaining unrecovered Pb ions in the solutions. 1M solution was selected as the optimum concentration as it was left with about 1% Pb in the solution resulting in about 99% Pb recovery as against 3.0 M solution with above 3% Pb in solution and recovery of less than 96% Pb. Shawabkeh, (2010) reported this phenomenon that when acid concentration increases, the H^+ ion across the particle boundaries increases thereby the rate of dissolution of precursor /precipitate formed. Zhu *et al.,* (2012) observed similar results as the concentration ratio increased, the Pb ion in the solution increased. Also Jha *et al.,* (2012) observed a similar trend until certain extent during leaching experiment. Thus, this could be as a result of certain solubility of lead citrate in citric acid solution. Therefore, it is very paramount to bring to minimal quantity of Pb ion in the solution for higher recovery of lead and to minimise waste hazard of lead.

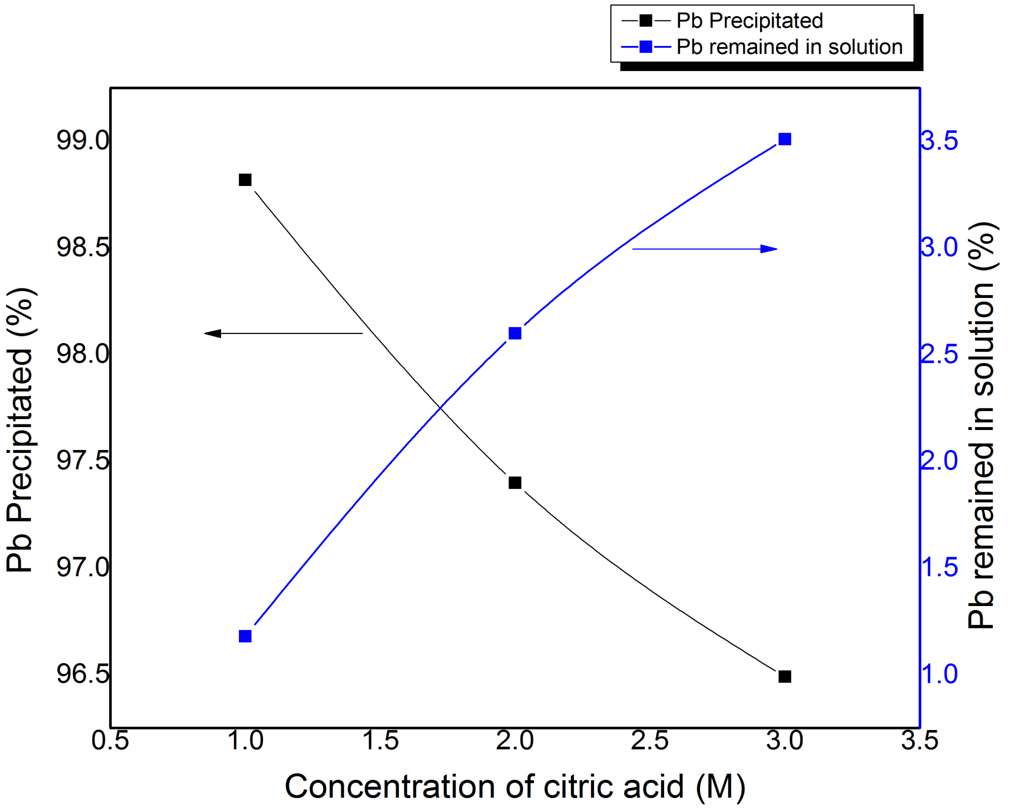


Figure 4.16: Effect of citric acid and sodium citrate concentration during experiment at S/L 100 g/L, 30 °C, 500 rpm, 30 mins.

4.9.2.2 Pulp density effect

The results of leaching at different pulp densities are presented in (Figure 4.17). Recovery of above 99% was achieved at 100 g/L as against 30, 50, 70 and 200 g/L. The leaching and precipitation of lead significantly depend on the solid-liquid ratio (pulp density). It helps to increase the surface area per unit volume of the solution and recovery of metals is enhanced within a specific time. The physical states of reactants play a major role in leaching/precipitation efficiency and reaction chemistry. Solid-liquid ratio of 100 g/L was selected as the optimum density as shown in (Figure 4.17). Increase in pulp densities was found to be relatively proportional to the recovery of lead but slightly decreased on further loading of the solution with the paste as its reactivity with the acid in 200 g/L may not provide adequate leaching/precipitating media (Sonmez *et al.,* 2009a). This observation could be due to the formation of precipitate at higher solid-liquid density which increased until super saturation is presumed.

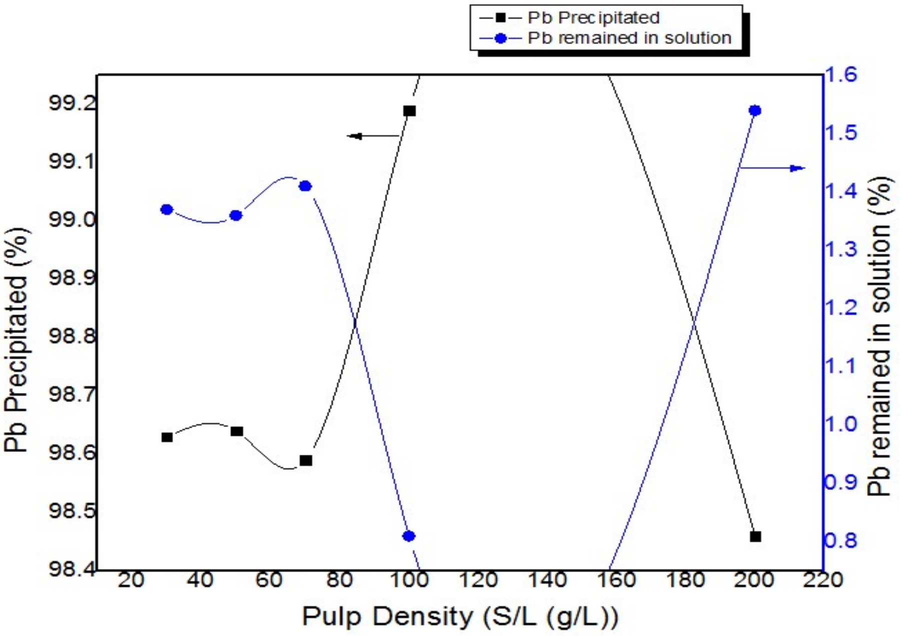


Figure 4.17: Effect of pulp densities during reaction. Concentration 1M, 30 ^{o}C, 500 rpm, 30 mins.

4.9.2.3 Effect of temperature

The results of leaching temperature are shown in (Figure 4.18). Leaching at room temperature of 30 °C gave the best Pb recovery as against the 35 °C and 40 °C. Increase in temperature is presumed to aid the re-dissolution of the precipitate formed. Leaching/precipitation experiment was carried out at various temperatures ranging from room temperature to 40 °C under identical conditions. Generally, corresponding rise in temperature is supposed to increase the rate of chemical reaction during leaching experiment but it was observed in this simultaneous leaching/precipitation experiment that the opposite is the case. The Pb^{2+} in the filtered solution increased with increased temperature from about 0.8% at room temperature to about 1.5% at 40 °C. This observation was in line with the previous report by Sonmez *et al.,* (2009a). The precursor lead citrate formed reacted further with citric acid and resulted in mass transfer and diffusivity of Pb^{2+} into the solution. This was contrary to the observation in leaching experiment alone mostly with mineral acids. (Figure 4.18) illustrates this observation.

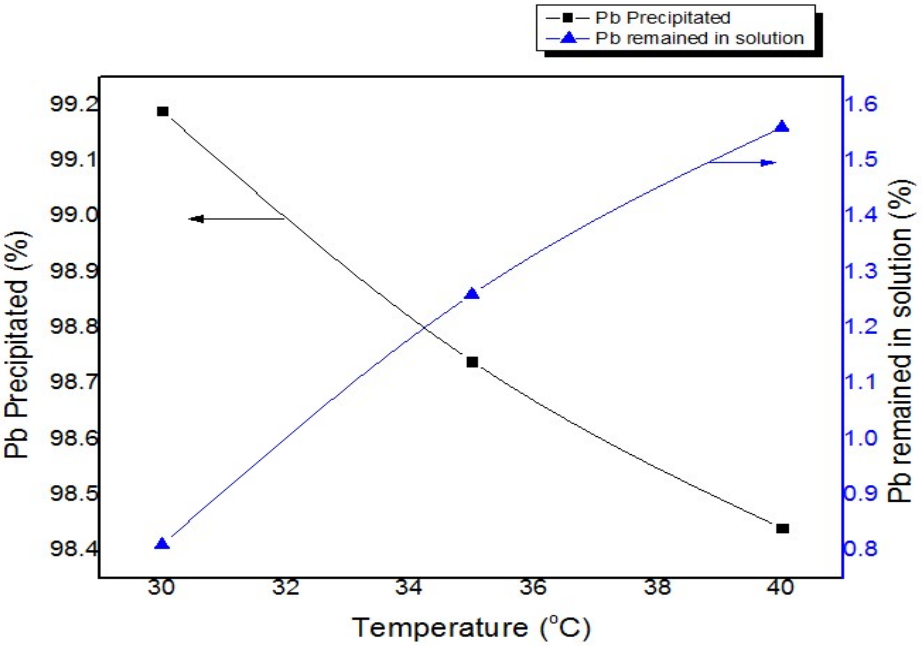


Figure 4.18: Effect of temperature during reaction at S/L 100 g/L, concentrations 1M, 500 rpm, 30 mins.

4.9.2.4 Effect of mixture agitation

The results of different speed of stirring the mixture are presented in (Figure 4.19). The range of rpm tested was 500, 600 and 700 rpm. It was observed that the ranged gave a very similar yield of recovered Pb leaving very minute percentage of unrecovered Pb in the solution. Effective mixing of solid particles with solution required proper agitation for efficient mass transfer and proper precipitation. The suspended solid particles was agitated at varied speed for optimum stirring speed to investigate sufficient speed and excessive speed at which lead citrate precipitated diffused back into the solution. The stirring speed in this experiment was in the range of 500 to 700 rpm. All the sets of experiments were carried out under identical conditions. It was discovered that an increase in the stirring speed in the selected range resulted in almost the same recovery of Pb^{2+} in the solution. Excessive speed is reported to increase the diffusion of the acid through to the sample matrix thereby eliminating the resistance that could be created by the solute boundary layer for efficient mixing. The excessive increase in stirring speed can diffused the particles of lead citrate precipitated in citric acid. Stirring the mixture at speed of 500 rpm (98.6%) was suitable enough to ignore mass diffusion though 700 rpm (98.9%) gave the highest recovery. This was maintained throughout the experiments as shown in Figure 4.19.

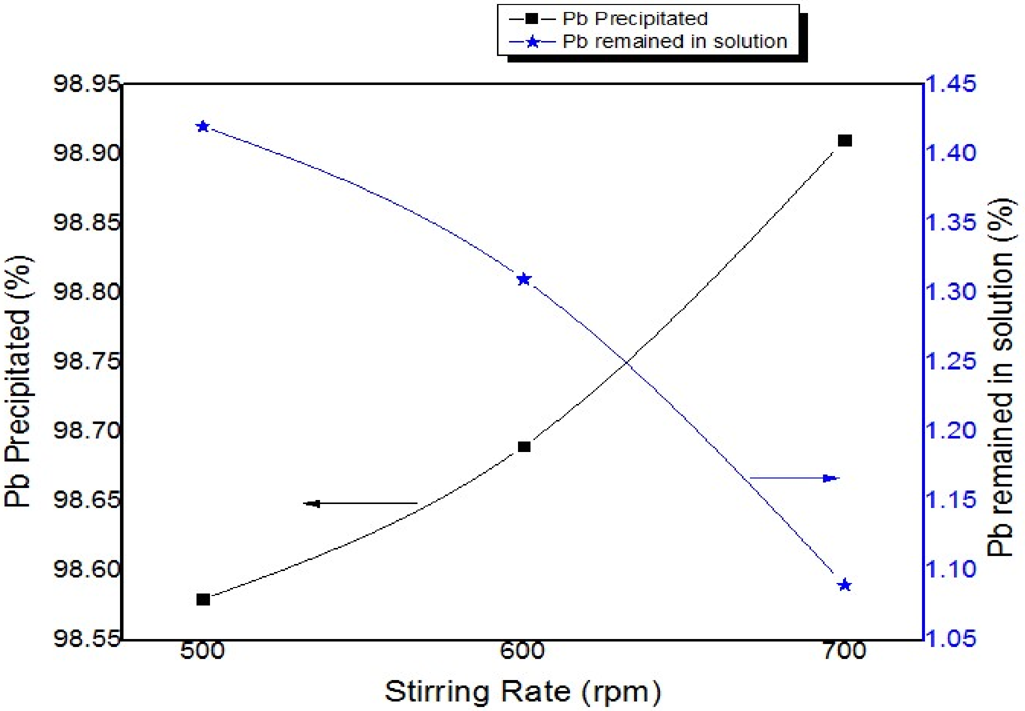


Figure 4.19: Effect of Stirring speed during reaction at S/L 100 g/L, concentrations 1M, 30 °C, 30 mins.

4.9.2.5 Effect of reaction time

Results of reaction time is presented in (Figure 4.20). The effect of reaction time was investigated for each set of experiment ranging from 30 to 240 minutes. Increase in reaction time resulted in increased recovery of Pb until 180 minute (99%) when increase in time does not have significant effect in the recovery 240 minutes (99%). There was no significant recovery above 180 minutes of reaction as the lead ion in solution barely differ appreciably. For this experiment, recovery of little above 99% was achieved at 180 minutes. Therefore, 180 minute was used as the optimum leaching/precipitation reaction time shown in Figure 4.20.

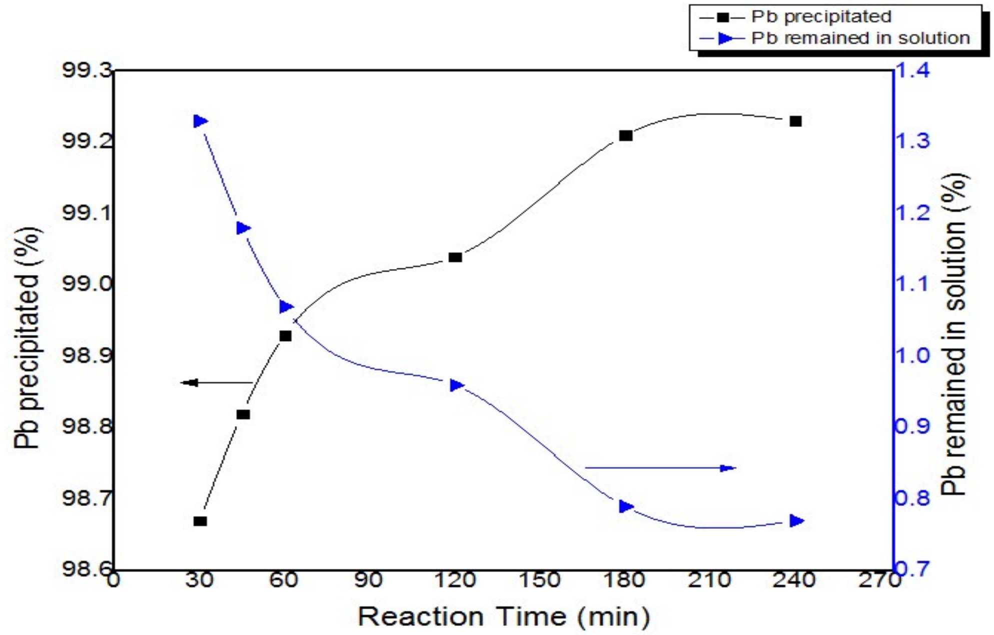


Figure 4.20: Effect of reaction time during experiment at S/L 100 g/L, concentrations 1M, 30 °C, 500 rpm.

Lead citrate precursor was produced by the optimised conditions in the sets of optimisation experiments. The mass balance ratio was calculated and recovery of 97.7% was achieved. The sets of results achieved in optimisation experiments were maintained for the leaching/precipitation of paste sample used for the synthesis of lead citrate as a precursor for the production of ultra-fine PbO particles.

4.9.3 Extraction kinetics

The leaching kinetics of the paste was attempted by leaching/extracting at different time interval to different acid concentrations (1-3M) and S/L ratio of 100 g/L. The result is presented in Figure 4.21. An increase in acid concentration increased the lead in solution at varied time. All standard equations of shrinking core models were tested for reaction kinetics of lead dissolution.

$X = K_c t$ *Film diffusion control dense constant size small particles – all Geometrics (1)

$1 - (1 - X)^{2/3} = K_c t$ *Film diffusion control dense shrinking spheres (2)

$1 - (1 - X)^{1/2} = K_c t$ *Chemical reaction control dense constant size cylindrical particles (3)

$1 - (1 - X)^{1/3} = K_c t$ *Chemical reaction control dense constant size or shrinking spheres (4)

$1 - 3(1 - X)^{2/3} + 2(1 - X) = K_c t$ *Ash diffusion control dense constant size- spherical particles (5)

where K_c = reaction rate constant (min^{-1});

t = time (min); and

X = fraction reacted of Pb (%extraction/100).

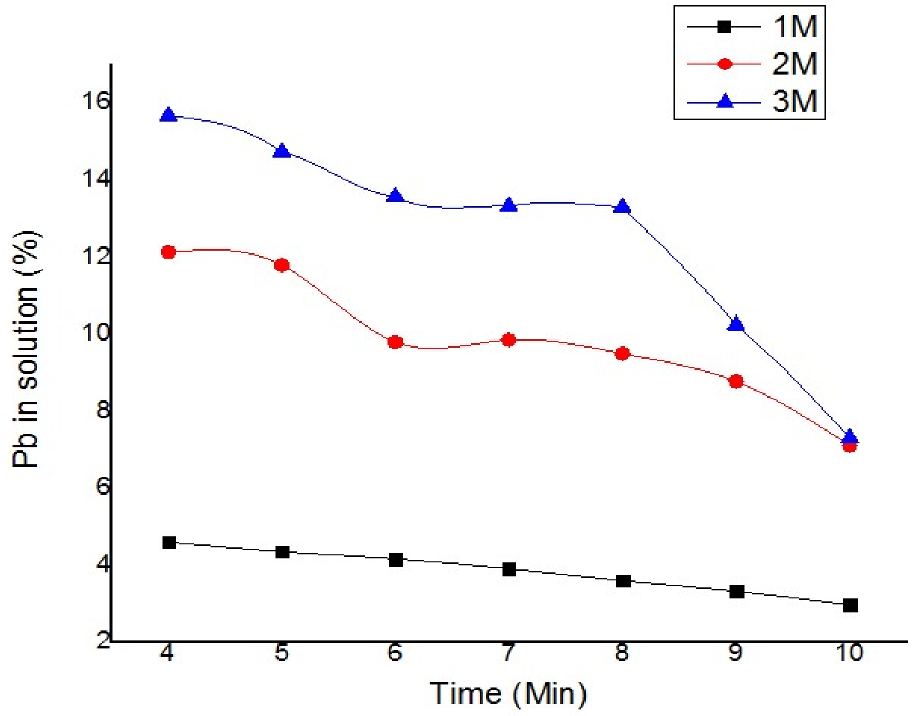


Figure 4.21: Kinetics of Pb leaching at 100g/L with citric acid

On examination of experimental results in all the models with the above equations, the kinetics followed ash diffusion control model i.e, $1 - 3(1 - X)^{2/3} + 2(1 - X) = K_ct$ (Figure 4.21 and Table 4.13) for 1M and 3M citric acid concentration; while at 2M concentration, chemical reaction control model was best fitted. The ash diffusion model was tested appropriate by the SEM/EDX studies of lead precursor obtained after leaching. The porous structure of the leached residue revealed that elemental Pb was deposited few minutes of leaching reaction. The precipitated Pb created a porous layer permitting ash diffusion-control reaction kinetics, the SEM image is shown in Figure 4.22. The model fitted at 2M citric acid with $1 - (1 - X)^{1/2} = K_ct$ chemical reaction control dense cylindrical particles.

This is indicated in SEM photograph in Figure 4.22 which confirmed the model of the reaction. The equations well suited for the reaction was chosen on the premises of highest values of R^2 – the regression coefficient in each study presented in Figure 2.23. The activation energy of the ash diffusion control model was calculated to be 8.3 KJ/Mol and chemical control model was 33.3 KJ/Mol. Michael (2013) reported that aqueous diffusion control reaction often have low activation energies of less than 15,000 J/mol. and that chemical control has larger activation energies. The reactions in this study are not strongly influenced by temperature as room temperature was found suitable for the experiments which confirmed kinetic reaction processes.

Table 4.13: Regression Coefficient Values for Different Shrinking Core Models for the Kinetics of Leaching of Lead Acid Battery Paste

S/n	Citric Acid conc. (M)	X	$1-(1-X)^{2/3}$	$1-(1-X)^{1/2}$	$1-(1-X)^{1/3}$	$1-3(1-X)^{2/3} + 2(1-X)$	Model selected
A	1	0.9927	0.9928	0.9929	0.9929	0.9979	$1-3(1-X)^{2/3}+2(1-X)$
B	2	0.9207	0.9209	0.921	0.921	0.9199	$1-(1-X)^{1/2}$
C	3	0.8409	0.8533	0.8546	0.8287	0.8983	$1-3(1-X)^{2/3}+2(1-X)$

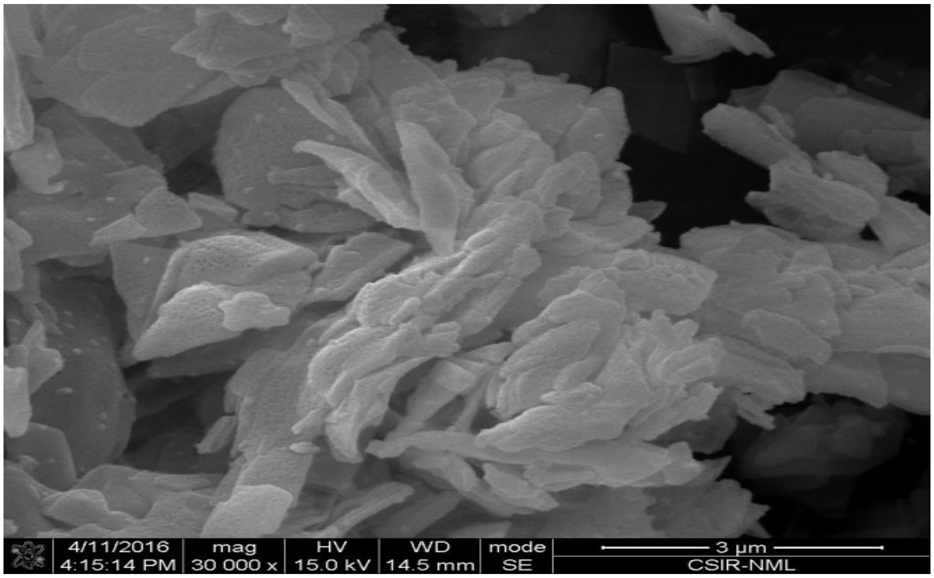


Figure 4.22: SEM images of leached residue for kinetics studies

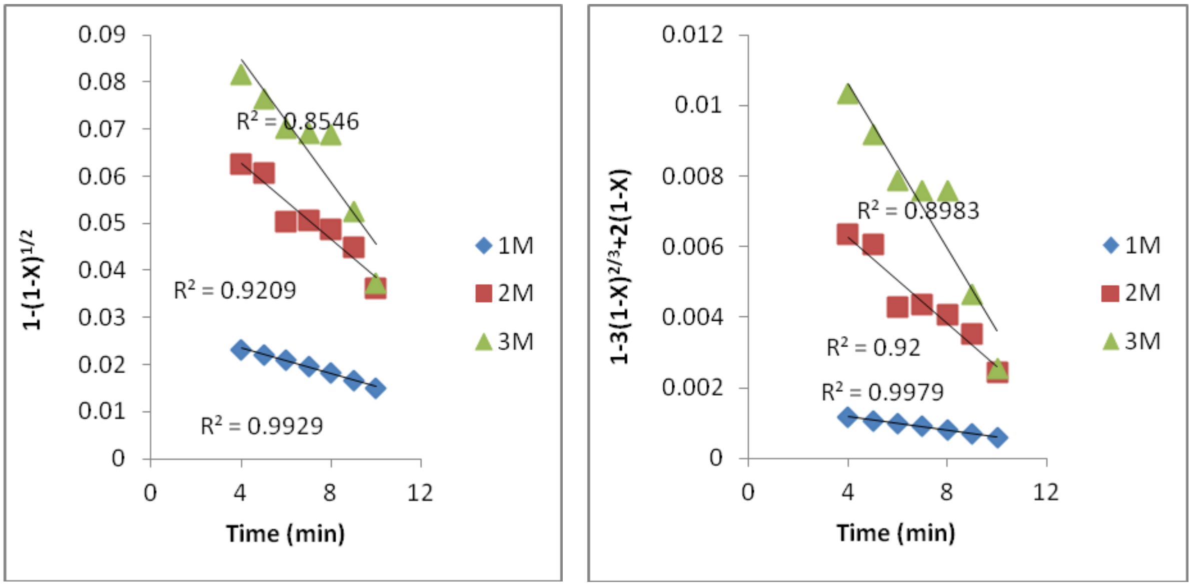


Figure 4.23: Fittings of lead conversion into shrinking core model equations for lead acid battery paste:

(i) Chemical reaction control dense constant size cylindrical particles

(ii) Ash diffusion control dense constant size-spherical particles

4.10 Characterisation of synthesised lead citrate precursor

The morphology of the paste was block-like but in lead citrate is sheet-like which was significantly different from the morphology of the battery paste prior to leaching/precipitation experiment. Figure 4.24 reveals the shape of the citrate crystal which was similar to the observed morphology by Li *et al.,* (2012).

4.10.1 XRD pattern of lead citrate

X-ray diffraction of Pb citrate powder is shown in (Figure 4.25). The XRD pattern observed is totally different from the phases observed in the starting paste Figure 4.7. It can be deduced that desulphurisation was almost completed as the lead sulphate and oxides phases identified in the x-ray diffractometric characterisation of the paste differed from the precursor produced. The existing X-ray diffraction analysis programme (PCPDFWIN) software did not contain any matching data but when compared with the existing data, the product was a kind of $PbC_6H_6O_7.H_2O$. The powdered lead citrate precursor pattern almost matched with the pattern observed for lead citrate precursor by (Zhu *et al.,* 2012) and the standard lead citrate reported.

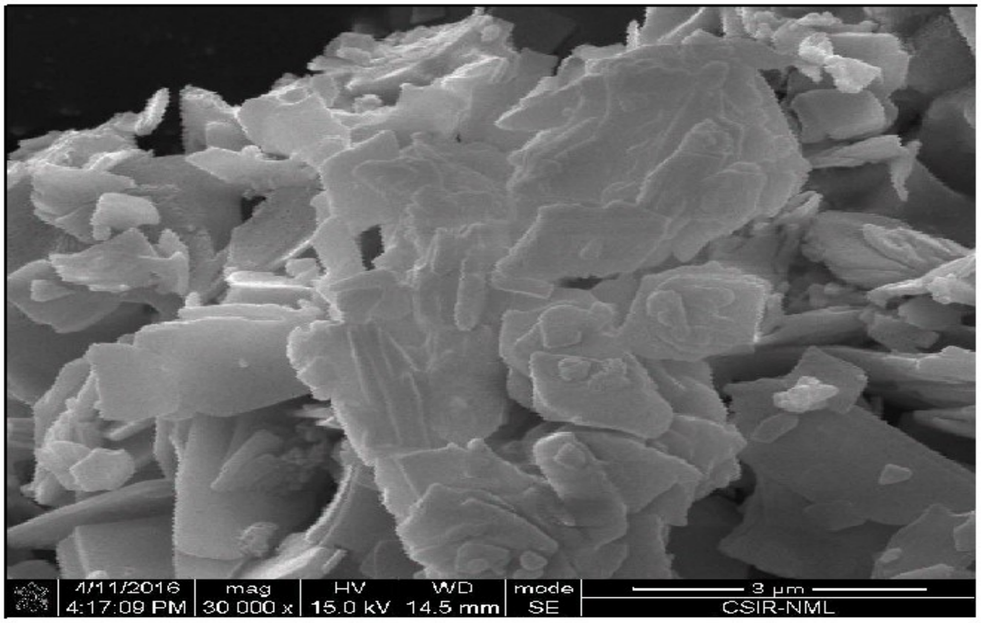


Figure 4.24: Scanning image of Pb citrate produced

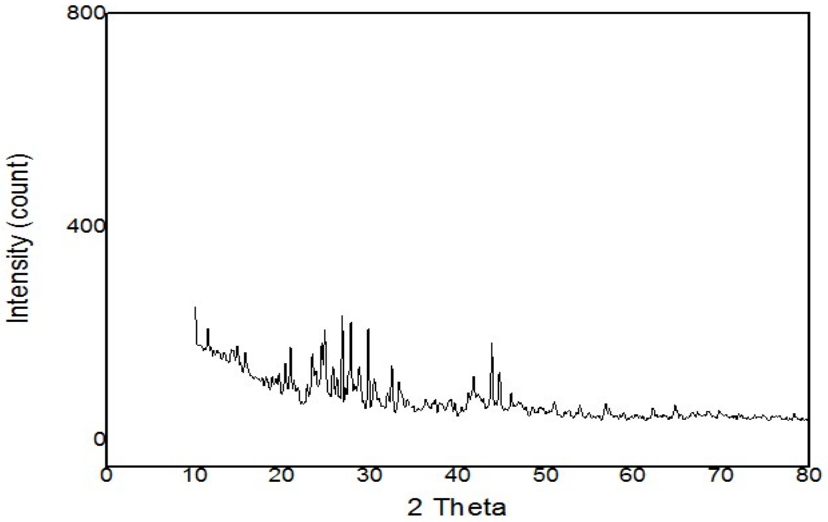


Figure 4.25: XRD pattern of Pb citrate precursor with 1M citric acid, 100 g/L pulp density, 30 ^{o}C, reaction time 3 hr, and 500 rpm stirring speed

4.10.2 Lead paste and lead citrate

The photograph of the starting paste and resulting powder of lead citrate is shown in Figure 4.26 a & b. The physical appearance of the resulting powder changed from reddish brown of the raw battery paste to white appearance in lead citrate.

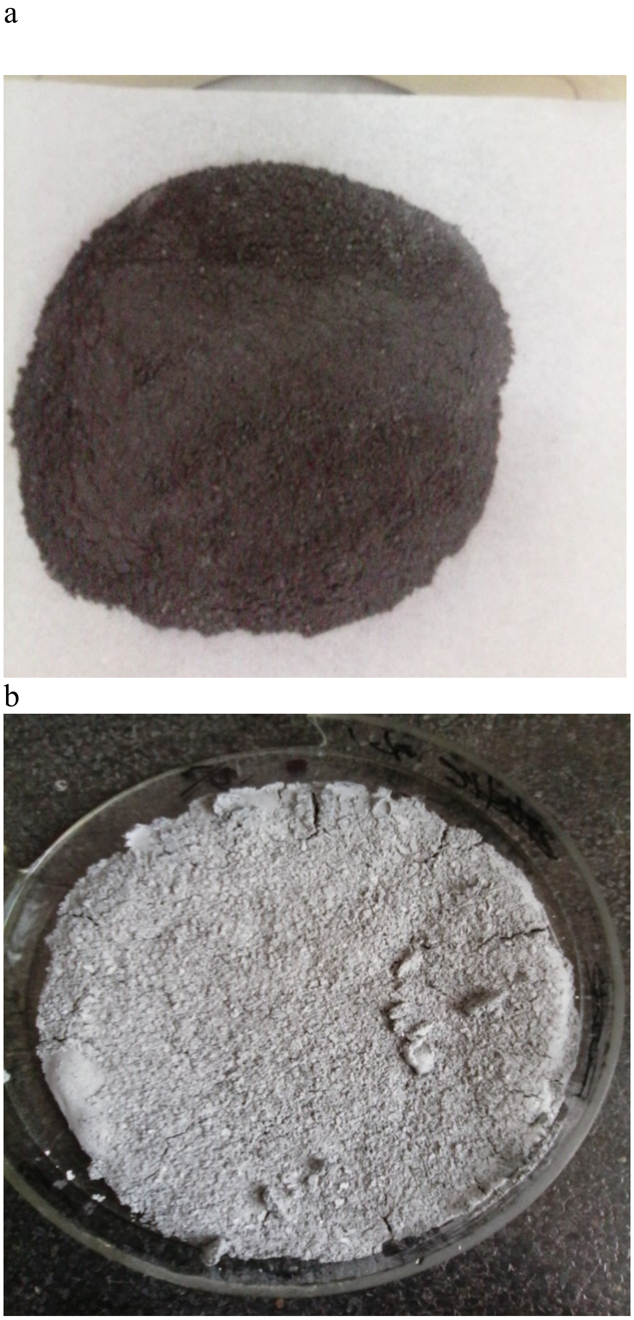
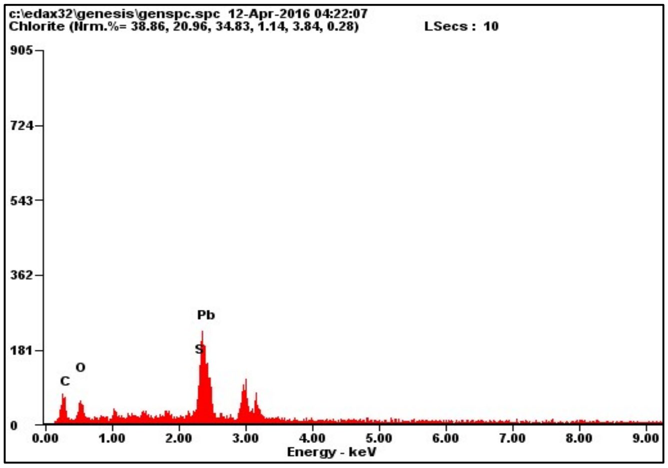


Figure 4.26: Photographs of LAB paste before (a) and after leaching/precipitation (b)



Element	***Wt %***	***At %***
C K	09.75	47.76
O K	07.06	25.97
S K	01.70	03.11
PbL	81.50	23.15

Figure 4.27: EDX spectra of lead citrate precursor

Energy dispersive spectra of the lead citrate gave the percentages of elements present in the precursor as lead 81%, sulphur 1%, oxygen 7%, and carbon 9% (as revealed in Figure 4.27) as against the percentages of these elements in the paste lead 63%, sulphur 11%, iron 5%, oxygen 18%, and carbon 2% (shown in Figure 4.9). Deducing from these results, sulphur in the paste has been reduced drastically from 11% to 1% which was the major process (desulphurisation). It was discovered that the paste contained iron but has been eliminated in the precursor probably as iron-sulphate. This observation affirms the purity of the precursor synthesised. The lead citrate precursor was used to synthesise the desired PbO nano sized particles.

Fourier transformed infra-red analysis shown in (Figure 4.28) presents strong absorption of carboxylate structure. The band at 3415 cm^{-1} revealed O-H strong stretching. Symmetric vibration of the range 1567 cm^{-1} to 1400 cm^{-1} belonged to carboxylate group. The weak bands of 1268 cm^{-1} to 1074cm^{-1} stands for C=O stretching from citric acid. The band 622 cm^{-1} denotes Pb-O-Pb bond. Strong intense peak of 1400 cm^{-1} are as a result of O-H bending vibration in adsorbed water (Arulmozhi and Mythili, 2013).

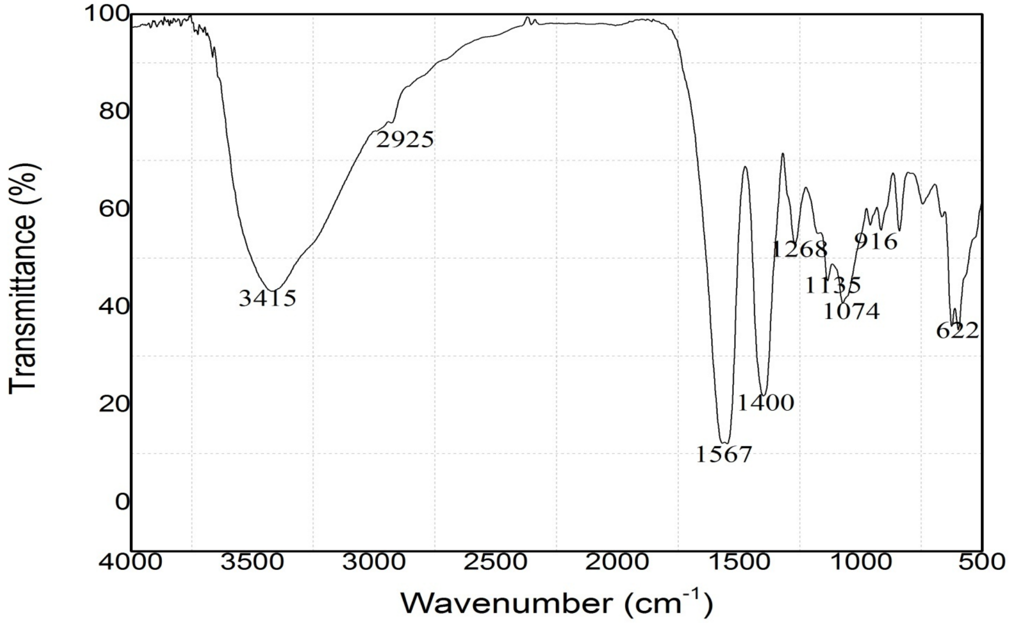
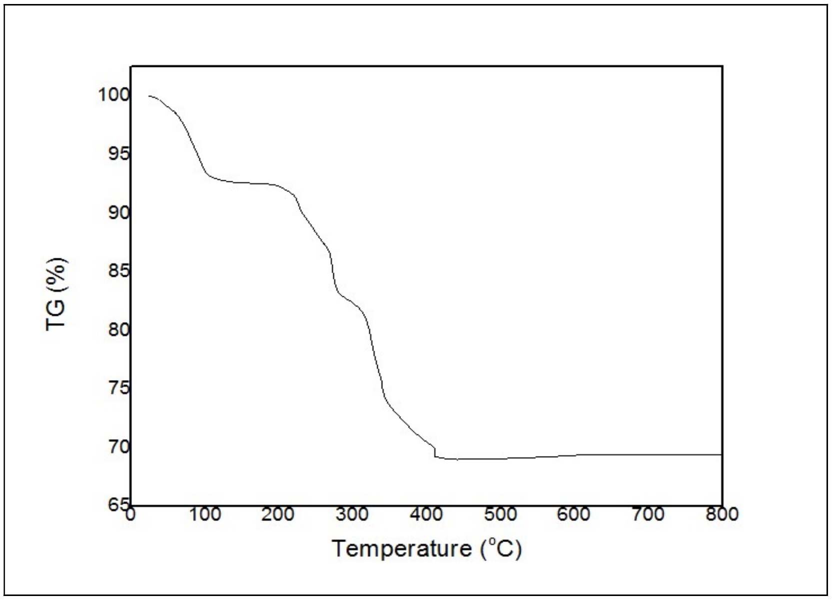


Figure 4.28: FT-IR spectra of lead citrate product

4.11 Thermal analysis

Thermal decomposition temperature point of Pb citrate was derived from the thermo-Gravimetry Diffraction Analysis curve obtained in static air as shown in (Figure 4.29) from room temperature to 800 ^{o}C. Oxygen is believed to aid combustion or oxidation of the citrate. The initial weight loss was observed between 20 ^{o}C – 100 ^{o}C. This was slightly shown by an endothermic peak around 100 ^{o}C. This temperature point denotes dehydration of lead citrate. Another temperature point of weight loss was observed between 220 – 410 ^{o}C. The total weight loss in the thermal reaction amounted to about 32%. When the temperature was above 400 ^{o}C, the heat flow and weight loss became relatively stable. The exothermic peak observed at around 400 ^{o}C revealed the decomposition stage of the lead citrate. Therefore, the calcination temperature was set at 400 ^{o}C to prepare PbO in the subsequent experiment.



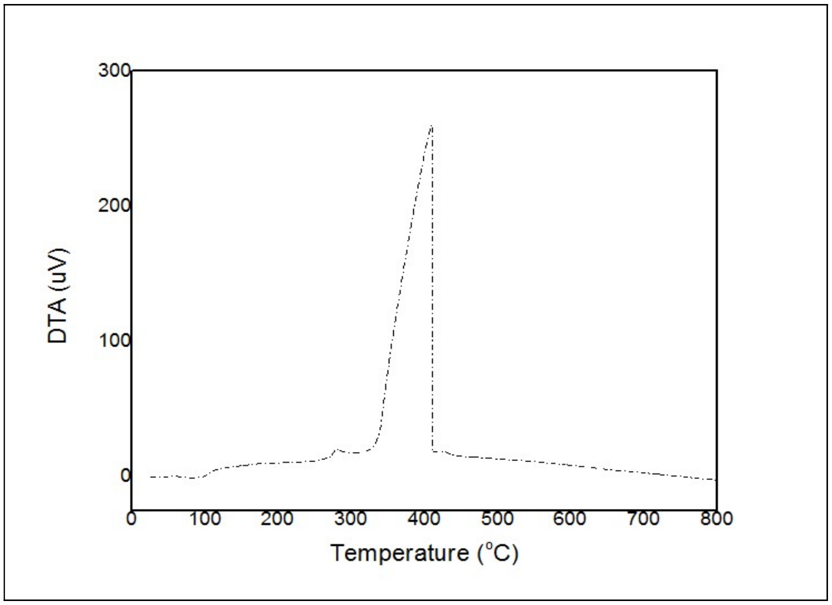


Figure 4.29: TG-DTA of Pb citrate

4.12 Structural characterisation of calcination-combustion product

X-ray diffraction of the prepared lead oxide shown by (Figure 4.30) at 400 ^{o}C showed that the products mainly are orthorhombic massicot lead oxide and tetragonal litharge lead oxide.

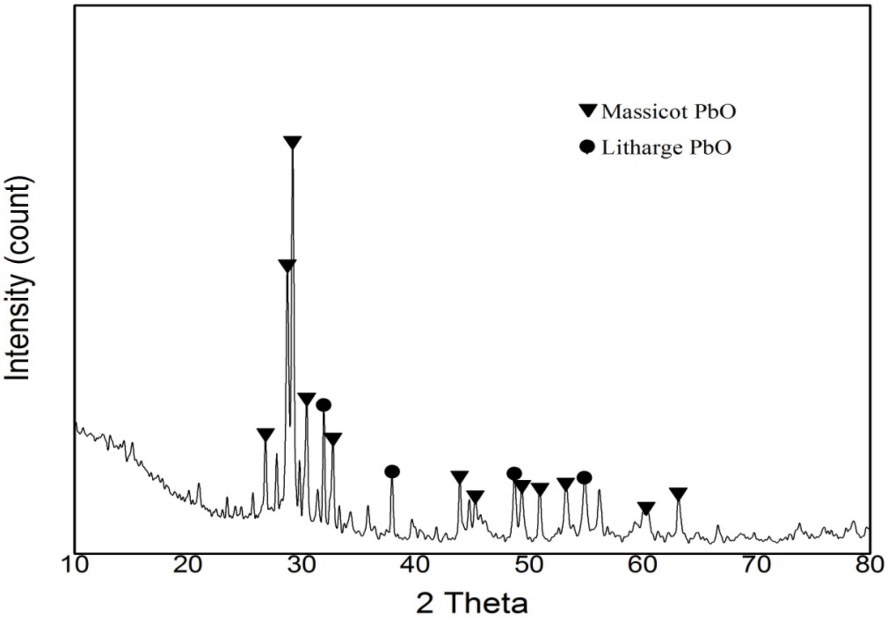


Figure 4.30: XRD spectra of calcination-combustion products

The SEM morphology of the products as shown in (Figure 4.31) revealed the particle sizes of the products as less than 100 nm. The morphology of the lead citrate was observed to have changed from sheet-like structure with the calcination temperature. The particles were agglomerated at the 400 ^{o}C. The EDX spectra as shown in Figure 4.32 also showed that the products were mainly lead oxides. The colour of the products changed from the whitish colour of the lead citrate (Figure 4.26) prior to calcination to yellow products of nano lead oxides as shown in Figure 4.33. The FT-IR spectra studied was employed to analyse the vibration of lead oxide products (Figure 4.34). The band at 3399 cm^{-1} is the characteristic OH stretching vibrations of adsorbed water. The sharp peak around 601 cm $^{-1}$ denotes asymmetric bending vibration of Pb-O-Pb bond (Arulmozhi and Mythili, 2013).

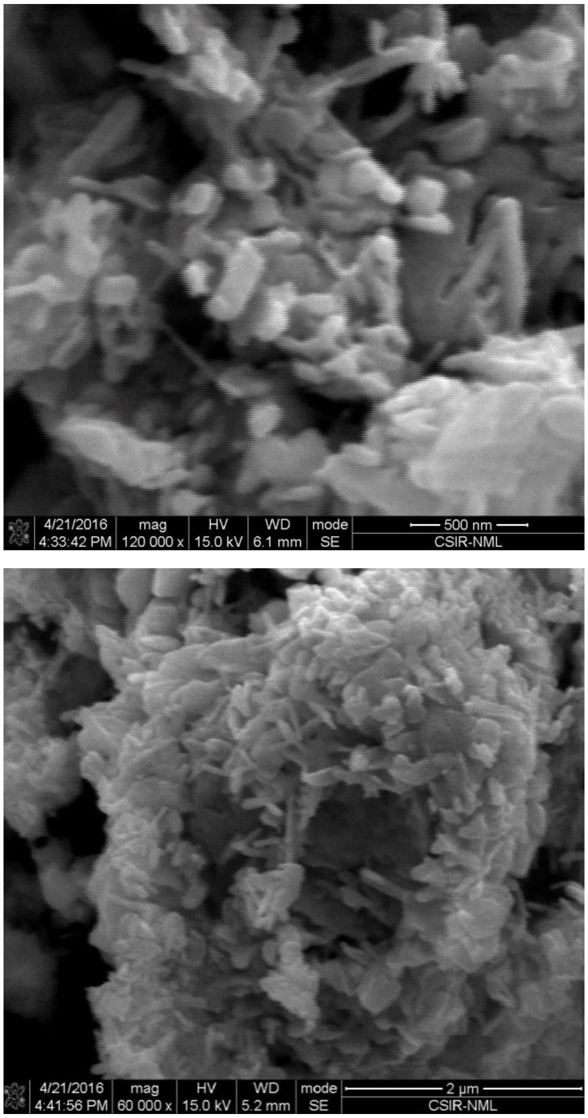
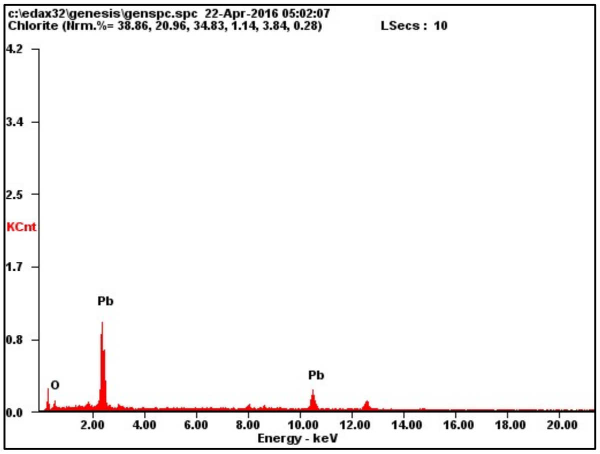


Figure 4.31: SEM-EDX of calcined PbO



Element	*Wt%*	*At%*
O K	14.80	69.22
Pb L	85.20	30.78

Figure 4.32: SEM-EDX of calcined PbO

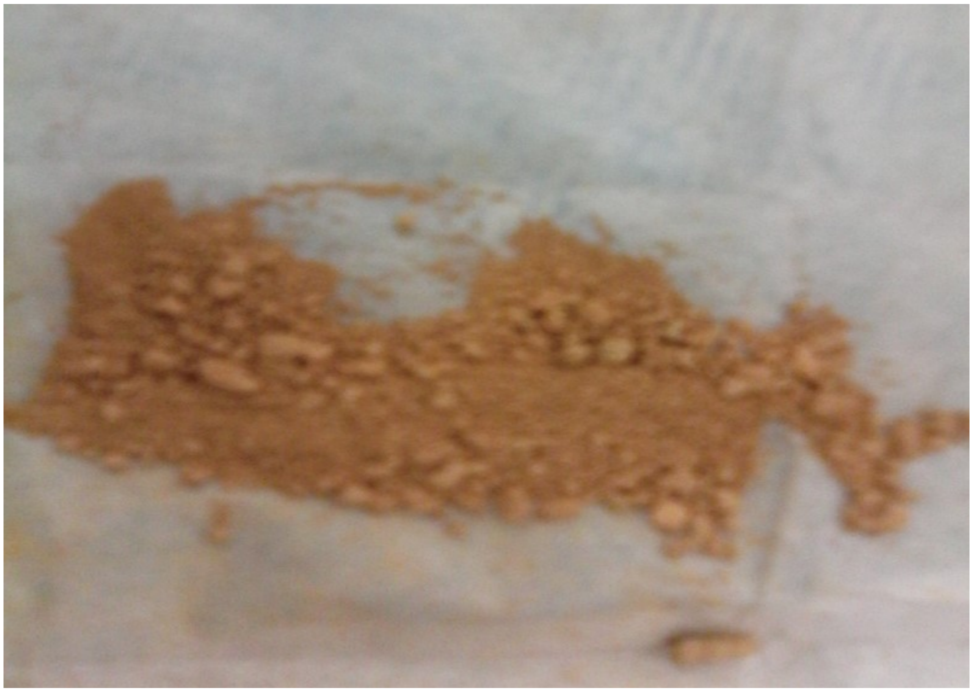


Figure 4.33: Calcination product (PbO)

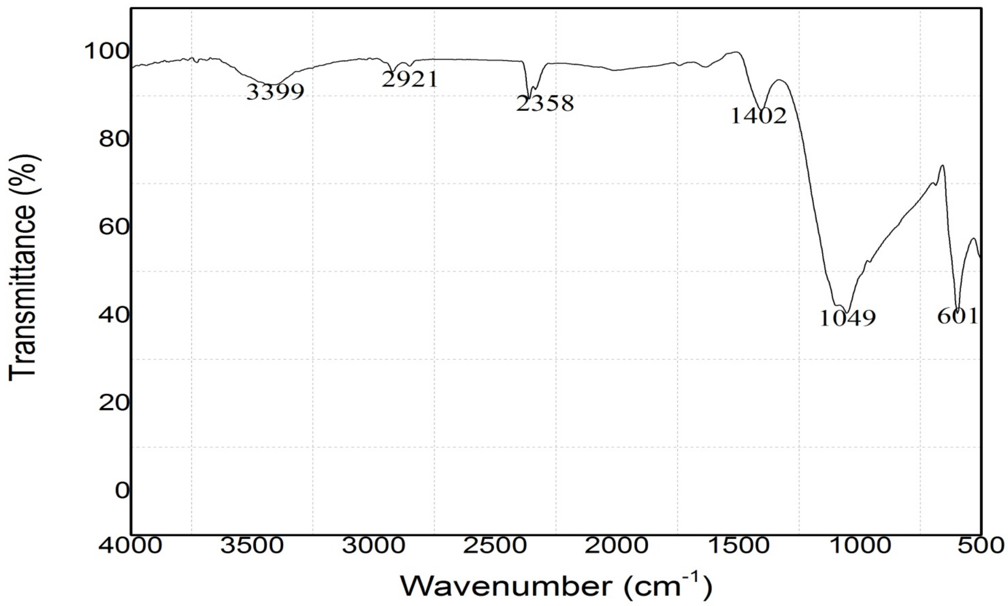


Figure 4.34: FT-IR spectra of calcined lead oxide

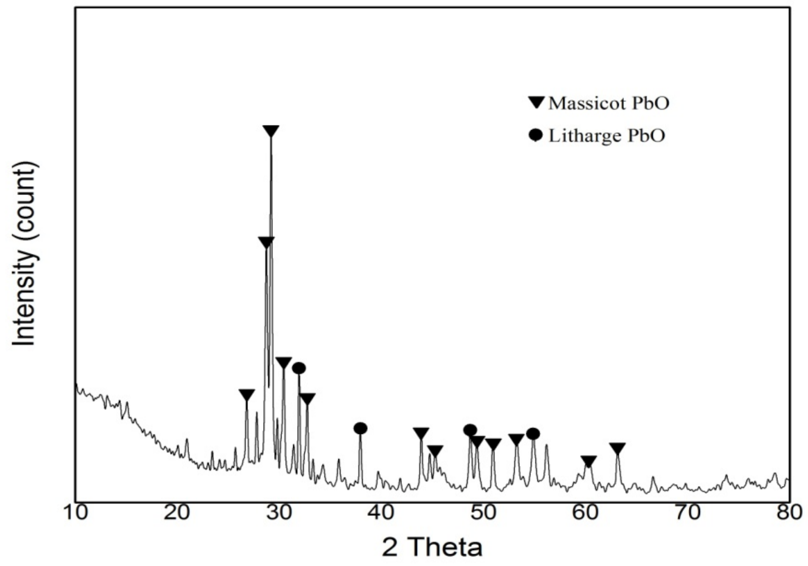


Figure 4.35: XRD spectra of nano PbO

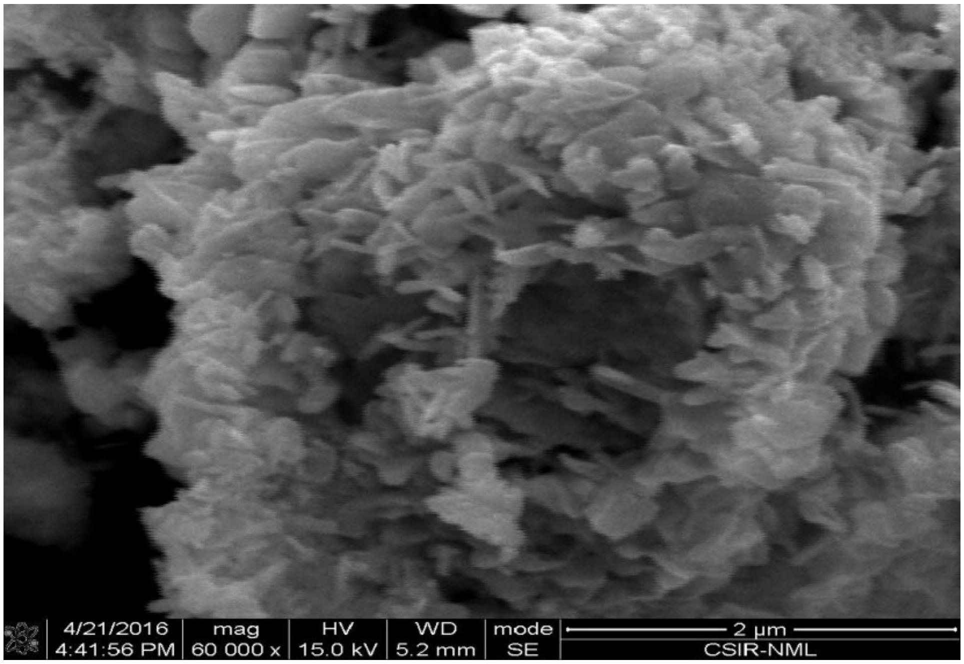


Figure 4.36: SEM image of nano PbO

4.13 Further characterization of nano-PbO

D. XRD-particle size

An XRD pattern of Lead Oxide nanoparticle prepared is shown in (Figure 4.35). The average sizes of the product were calculated using Debye-Scherrer formula (Arulmozhi *et al.,* 2013).

$$D = 0.9\lambda/\beta \cos \theta$$

where D is the mean particle size;
λ is wavelength of CuKα -1.5406Å;
β is the full width at half maximum (FWHM); and
θ is bragg's diffraction angle.

The particle sizes calculated by the above formula were 19 nm.

E. Sample surface area

The material surface area was calculated by the formula:

$$SSA = SA_{part}/V_{part} \text{ x Density}$$

where SSA is the specific surface area;
SA part is surface area of the particle;
V part is particle volume; and
Density is the theoretical density of lead Oxide.

SSA can also be calculated using the formula:

$$S = 6 \text{ x } 10^3/Dp$$

where S is the specific surface area;
D is the mean particle size; and
p is the density of lead Oxide.

The expressions give same value for the equations . SSA calculated by the formula was $33m^2/g$.

F. Crystallinity index (I_{cry})

Crystallinity index of the nano-PbO produced was determined by

$$I_{cry} = Dp/D$$

where D*p* is the particle size from SEM/TEM; and
D is the particle size from Scherrer formula.

If I_{cry} value is near 1, the particle size is monocrystalline; and where it is greater than or much larger, it is assumed to be polycrystalline. The calculated Crystallinity index was 3, which implied that the product was polycrystalline in nature.

CHAPTER FIVE

SUMMARY, CONCLUSION AND RECOMMENDATION

5.1 Summary of findings

Deducing from the administered questionnaires, lead acid batteries (LABs) with calcium alloy (98%) is the most prevalent automobile batteries in Nigerian markets. Proper management of waste lead-acid batteries is not popular in Nigeria. Waste batteries in end of life amounted to 4.8 million tons (Mt) and elemental lead that could be generated from these products amounted to about 3.5 million (Mt).

Waste batteries basically contained elemental lead and other metals in trace concentrations as additives which are intentionally added as binders in the course of producing LABs. Synthesis of precursor from the paste by citric acid, citrate salt and hydrogen peroxide (2:1:2) by volume gave the best extraction among the organic acids studied. Citric acid provided leaching medium, sodium citrate served as the desulphating agent during leaching while hydrogen peroxide was used as reductant. The synthesised lead citrate was calcined at $400^{o}C$ to produce lead oxides (litharge and massicot) in nano sizes.

All chemical and structural characterisations of the products ascertained the final products as nano PbO that can effectively be used as an starting material in the production of new LAB.

5.2 Conclusion

In this study, an innovative, environment friendly approach was developed as a better option to the pyrometallurgical smelting treatment of WLAB paste via hydrometallurgical processing of WLABs to produce a new starting material of PbO in nano meter sizes due to the special properties of the material.

Hydrometallurgical method showed several advantages compared to smelting method by elimination of emissions through chemical conversion. Reduced energy usage was achieved during leaching was achieved in this process as the reaction was best at room temperature. The ultra fine lead oxide powder showed increased surface area from the locally dismantled WLAB as it was found in nano-meter size.

The following points should be considered: WLABs which in some parts of the world are discarded without accountability should be maximally collected in order to recover Pb in oxide form via hydrometallurgical processes. These processes have been considered more environmental friendly and they produce filtrate which can be further processed to obtain valuable products that are environment and human friendly. Leaching and precipitating with organic reagents, many of which are on bench scale, pilot scale and partially commercialised form should be industrialised and localised. In the course of choosing leaching and precipitating agents, environment friendliness, cost effectiveness, reagent minimisation should be the key factors to be considered. Organic reagent seems attractive due to environmental consideration and ease of availability for the recovery of lead in oxides form than the mineral acids.

5.3 Recommendation

Hydrometallurgical approach should be encouraged to treat spent paste. Most of the hydrometallurgical synthesis has been based on laboratory reagents. Few are targeted directly on the spent battery. There should be more studies to provide detailed information on this approach using spent batteries directly.

There should be an environmental campaign on the environmental and health risk involved in improper handling of LABs. People who are involved in crude or unlicensed activities of refining lead from LABs should be shown a better way of managing the products in hydrometallurgical way to prevent the long run effect on the environment and health.

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APPENDICES

Appendix I: Calculation

The concentration of the analyte for heavy metal was obtained by the following calculations.

Concentration (Percentage %) = (PPM *100 * V) / (Ms * 1000000)

PPM- concentration of analyte in the sample (mg/L)

V- Volume make up

Ms - Mass of the sample (g)

To calculate or convert the % Pb to mg/kg

%Pb *10000 =mg/kg or PPM *Vol. make up /Wt of sample

For example % Pb remaining in solution after leaching

Ppm-736.49

V- 250ml

Ms Pb- 15.5g

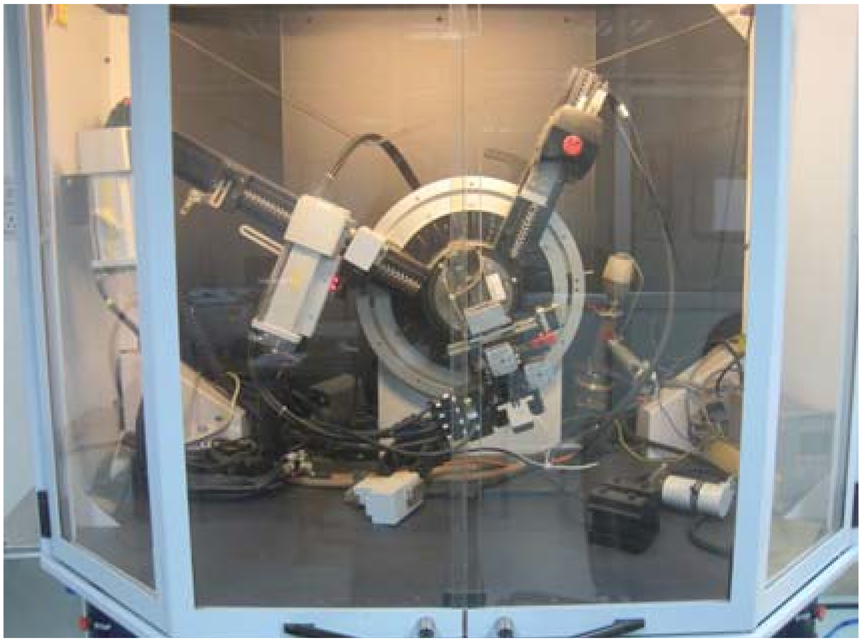
Concentration (Percentage %) = (PPM *100 * V) / (Ms Pb * 1000000)

Ms Pb- Mass of the analyte in the sample digests (g)

% Pb= 736.49 *100*250 / 15.5*1000000

= 1.18%

Appendix II: X-ray diffractometer



XRD samples, sample holder and Bruker X-ray diffractometer (D8 Discovery)

Appendix: III

Estimate of Vehicles in End-of-Life (Vehicles Registered 1980 – 2004)

Year	Category	Estimate of vehicles registered	Percentage in end-of-life	Estimate of vehicles in end-of-life	Estimate of vehicles entering current transport fleet
1980-1985	Cars	1 133 002	90	1 019 702	113 300
	Trucks	16 186		14 567	1 619
	Buses	469 386		422 447	46 939
1986-1990	Cars	122 676	75	92 007	30 669
	Trucks	1 753		1 315	438
	Buses	40 335		30 251	10 084
1991-1995	Cars	492 905	50	246 453	246 453
	Trucks	7 042		3 521	3 521
	Buses	204 204		102 102	102 102
1996-2000	Cars	3 395 000	25	848 750	2 546 250
	Trucks	48 500		12 125	36 375
	Buses	1 406 500		351 625	1 054 875
2001-2004	Cars	1 890 000	10	189 000	1 701 000
	Trucks	27 000		2 700	24 300
	Buses	783 000		78 300	704 700
Total	Cars			2 395 912	4 637 672
	Trucks			34 228	66 253
	Buses			984 725	1 918 700

Source: Babayemi *et al.,* 2016

Appendix: IV

Post-Hoc Test for Median Metal Deposit

Pair of Metals	Observed Difference	Critical difference	Difference
Ag-As	4.78	128.2045783	FALSE
Ag-Cd	53.85	128.2045783	FALSE
Ag-Co	5.59	128.2045783	FALSE
Ag-Cr	103	128.2045783	FALSE
Ag-Cu	1.72	128.2045783	FALSE
Ag-Fe	251.41	128.2045783	TRUE
Ag-Mn	109.74	128.2045783	FALSE
Ag-Ni	144.33	128.2045783	TRUE
Ag-Pb	339.17	128.2045783	TRUE
Ag-Sb	222.73	128.2045783	TRUE
Ag-Se	80.24	128.2045783	FALSE
Ag-Te	33.33	128.2045783	FALSE
As-Cd	58.63	128.2045783	FALSE
As-Co	10.37	128.2045783	FALSE
As-Cr	107.78	128.2045783	FALSE
As-Cu	3.06	128.2045783	FALSE
As-Fe	246.63	128.2045783	TRUE
As-Mn	104.96	128.2045783	FALSE
As-Ni	149.11	128.2045783	TRUE
As-Pb	334.39	128.2045783	TRUE
As-Sb	217.95	128.2045783	TRUE
As-Se	85.02	128.2045783	FALSE

Appendix V: Post-Hoc Test for Median Metal Deposit (Continued)

Pair of Metals	Observed Difference	Critical Difference	Difference
As-Te	38.11	128.2045783	FALSE
Cd-Co	48.26	128.2045783	FALSE
Cd-Cr	49.15	128.2045783	FALSE
Cd-Cu	55.57	128.2045783	FALSE
Cd-Fe	305.26	128.2045783	TRUE
Cd-Mn	163.59	128.2045783	TRUE
Cd-Ni	90.48	128.2045783	FALSE
Cd-Pb	393.02	128.2045783	TRUE
Cd-Sb	276.58	128.2045783	TRUE
Cd-Se	26.39	128.2045783	FALSE
Cd-Te	20.52	128.2045783	FALSE
Co-Cr	97.41	128.2045783	FALSE
Co-Cu	7.31	128.2045783	FALSE
Co-Fe	257	128.2045783	TRUE
Co-Mn	115.33	128.2045783	FALSE
Co-Ni	138.74	128.2045783	TRUE
Co-Pb	344.76	128.2045783	TRUE
Co-Sb	228.32	128.2045783	TRUE
Co-Se	74.65	128.2045783	FALSE
Co-Te	27.74	128.2045783	FALSE
Cr-Cu	104.72	128.2045783	FALSE
Cr-Fe	354.41	128.2045783	TRUE

Appendix VI: Post-Hoc Test for Median Metal Deposit (Continued)

Pair of Metals	Observed Difference	Critical Difference	Difference
Cr-Mn	212.74	128.2045783	TRUE
Cr-Ni	41.33	128.2045783	FALSE
Cr-Pb	442.17	128.2045783	TRUE
Cr-Sb	325.73	128.2045783	TRUE
Cr-Se	22.76	128.2045783	FALSE
Cr-Te	69.67	128.2045783	FALSE
Cu-Fe	249.69	128.2045783	TRUE
Cu-Mn	108.02	128.2045783	FALSE
Cu-Ni	146.05	128.2045783	TRUE
Cu-Pb	337.45	128.2045783	TRUE
Cu-Sb	221.01	128.2045783	TRUE
Cu-Se	81.96	128.2045783	FALSE
Cu-Te	35.05	128.2045783	FALSE
Fe-Mn	141.67	128.2045783	TRUE
Fe-Ni	395.74	128.2045783	TRUE
Fe-Pb	87.76	128.2045783	FALSE
Fe-Sb	28.68	128.2045783	FALSE
Fe-Se	331.65	128.2045783	TRUE
Fe-Te	284.74	128.2045783	TRUE
Mn-Ni	254.07	128.2045783	TRUE
Mn-Pb	229.43	128.2045783	TRUE
Mn-Sb	112.99	128.2045783	FALSE
Mn-Se	189.98	128.2045783	TRUE

Pair of Metals	Observed Difference	Critical Difference	Difference
Mn-Te	143.07	128.2045783	TRUE
Ni-Pb	483.5	128.2045783	TRUE
Ni-Sb	367.06	128.2045783	TRUE
Ni-Se	64.09	128.2045783	FALSE
Ni-Te	111	128.2045783	FALSE
Pb-Sb	116.44	128.2045783	FALSE
Pb-Se	419.41	128.2045783	TRUE
Pb-Te	372.5	128.2045783	TRUE
Sb-Se	302.97	128.2045783	TRUE
Sb-Te	256.06	128.2045783	TRUE
Se-Te	46.91	128.2045783	FALSE

Appendix VIII: Heavy Metal Concentrations of 50 Samples of SLABs (mg/kg)

Pb	Cd	Ag	As	Co	Cr	Cu	Fe	Mn	Sb	Se	Te
730250	115	8.75	Nd	Nd	Nd	1217.5	1437.5	Nd	181.7875	2.175	4.3875
816863	130	22.5	0.4625	2.5	Nd	292.5	550	Nd	53.1	Nd	3.0875
704450	42.5	25	2.125	Nd	Nd	372.5	1550	Nd	156.1	Nd	4.175
750625	65	5	Nd	Nd	Nd	Nd	500	Nd	77.25	1.3375	1.75
653450	2.5	5	Nd	13.75	Nd	Nd	1137.5	Nd	199.25	0.375	2.625
71623	Nd	21.25	Nd	17.5	1.25	38.75	387.5	Nd	67.675	Nd	6.625
707488	7.5	1.25	Nd	32.5	Nd	Nd	737.5	15	7.6	4.1	Nd
848700	Nd	142.5	Nd	13.75	Nd	207.5	625	11.25	99	Nd	1.7375
592863	1.25	Nd	14.25	10	5	Nd	1500	5	114.575	0.5375	Nd
864750	Nd	10	0.4125	8.75	2.5	630	2825	6.25	155.475	1.4	Nd
715000	Nd	2.5	Nd	17.5	Nd	Nd	712.5	8.75	66.6375	Nd	0.5125
845075	7.5	107.5	21.025	12.5	Nd	Nd	3037.5	11.25	95.6	Nd	1.35
925850	Nd	48.75	Nd	30	15	6312.5	637.5	135	116.25	0.4625	Nd
961250	Nd	5	0.9125	33.75	8.75	1027.5	550	195	93.7	2.8875	Nd
826500	Nd	16.25	Nd	17.5	11.25	1118.75	387.5	130	102.7375	0.3625	Nd
924875	Nd	11.25	0.7375	22.5	2.5	Nd	450	131.25	102.075	Nd	Nd
758500	Nd	26.25	10.65	Nd	5	Nd	1100	123.75	130.2	Nd	3.8
877012.5	Nd	Nd	Nd	Nd	Nd	Nd	875	40	215.1375	0.3375	Nd
783875	Nd	10	Nd	2.5	2.5	Nd	425	37.5	127.6375	Nd	2.3375
765000	Nd	Nd	1.6	3.75	Nd	Nd	5087.5	70	87.125	Nd	1.9375
758475	Nd	Nd	Nd	5	Nd	Nd	575	151.25	108.725	Nd	2.6125
899375	Nd	48.75	Nd	Nd	Nd	Nd	362.5	38.75	141.9625	0.575	Nd
802000	Nd	2.5	Nd	Nd	Nd	Nd	525	21.25	81.225	1.0375	Nd
866125	1.25	20	12.0375	1.25	Nd	30	2025	70	238.1125	5.1	1.9875
674687.5	Nd	3.75	Nd	Nd	Nd	865	1500	25	65.3875	4.275	Nd
517243.8	Nd	Nd	2.26625	Nd	Nd	Nd	512.5	11.25	108.5	Nd	2.70875
493097.5	1.25	Nd	1.485	Nd	Nd	Nd	1128.75	20	152.9563	3.2975	2.63125
567945	1.25	Nd	2.155	Nd	Nd	350	458.75	7.5	36.895	Nd	Nd
764433.8	Nd	Nd	6.93625	Nd	Nd	Nd	392.5	21.25	263.0438	0.16125	3.8225

Appendix IX: Heavy Metals Analysis of the Raw 50 Samples of SLABs (mg/kg) (Continued)

Pb	Cd	Ag	As	Co	Cr	Cu	Fe	Mn	Sb	Se	Te
852750	Nd	Nd	6.93625	Nd	Nd	Nd	255	1.25	231.6713	Nd	2.5925
764500	2.5	Nd	Nd	147.5	Nd	Nd	1085	13.75	213.1638	Nd	Nd
672007.5	1.25	51.25	54.11	Nd	Nd	60	942.5	12.5	982.8938	0.205	4.3725
794750	Nd	6.25	9.66375	Nd	Nd	301.25	907.5	Nd	337.8338	Nd	Nd
874435	1.25	Nd	10.895	25	Nd	Nd	441.25	35	332.6713	1.37875	Nd
494445	Nd	Nd	3.0275	1.25	Nd	Nd	646.25	18.75	435.8088	Nd	0.51375
659600	Nd	Nd	41.11625	Nd	Nd	Nd	2088.75	17.5	378.135	Nd	Nd
615698.8	Nd	Nd	5.82	Nd	Nd	Nd	307.5	57.5	176.6225	Nd	1.22125
348745	Nd	Nd	39.925	Nd	Nd	Nd	727.5	5	196.3025	Nd	Nd
535698.8	1.25	Nd	1.09375	Nd	Nd	Nd	667.5	2.5	56.4375	Nd	Nd
641496.3	3.75	42.5	2.3975	2.5	Nd	315	786.25	47.5	101.575	Nd	Nd
847375	2.5	Nd	2.8775	12.5	Nd	388.75	258.75	32.5	61.70875	Nd	1.43875
616405	Nd	11.25	22.235	15	Nd	Nd	56.25	28.75	356.36	Nd	1.0475
729770	Nd	Nd	3.24125	30	Nd	Nd	Nd	Nd	212.7875	Nd	Nd
561172.5	1.25	Nd	5.175	Nd	Nd	Nd	Nd	3.75	185.3738	Nd	2.8825
564738.8	Nd	Nd	1.12125	8.75	Nd	Nd	105	25	184.9275	Nd	0.4125
424907.5	2.5	Nd	6.685	Nd	Nd	Nd	Nd	10	32.90625	Nd	5.05
751567.5	Nd	Nd	0.605	Nd	Nd	Nd	95	16.25	126.745	Nd	Nd
664972.5	3.75	Nd	Nd	Nd	Nd	Nd	61.25	36.25	37.06375	Nd	2.38
620558.8	Nd	13.75	1.27875	Nd	Nd	1162.5	102.5	37.5	91.01375	Nd	0.63625
884908.8	Nd	Nd	4.05125	6.25	Nd	633.75	915	978.75	193.2163	Nd	Nd
618157.5	Nd	Nd	1.07625	1.25	Nd	Nd	377.5	493.75	42.17375	Nd	Nd

Detection limit- Ag-0.003 mg/L, As-0.012, Cd-0.0015, Co- 0.005, Cr- 0.004, Cu- 0.002, Fe- 0.0015, Mn-0.0003, Ni- 0.0055, Pb-0.014, Sb-0.018, Se-0.037mg/L

Appendix X: Research questionnaire

Survey Questionnaire

Section A: Personal Data
Please tick as appropriate:

Sex: Male [1] Female [2] Age: below 20 [1] above 30[2]

Occupation: Battery Importers/Sellers [1] Battery Repairers [2]

Battery User [3] Local Recyclers (waste scavenging) [4]

Section B:
Please tick as appropriate

D = Disagree/No (1) AG = Agree/Yes (2)

S/N	Questions	Disagree No	Agree Yes	Others (specify)
1	Do you know Pb-acid battery?	1	2	
2	How many Pb-acid battery have you used?	1	2	
3	What brand/types of lead acid battery do you like/use?	1	2	
4	Do you receive used LAB and how many do you receive from customer in a year...........?	1	2	
5	How long do the battery last? Specify years	1	2	
6	Do you know that People engage in manual recycling of LABs	1	2	
7	What are they looking for in the battery? a. lead Pb b. Acids c. Plastic	1	2	
8.	Are you aware of Spent Lead acid battery recycling	1	2	

	facilities/company in Nigeria			
9	Do you have a Car/Motor cycle/Bus/ mini bus(Akoto) that use lead acid battery	1	2	
10	There is market for used battery waste, thus scavenging is lucrative	1	2	
11	Do you know that foreign countries where these used batteries are being imported prohibit the burning or manual recycling?	1	2	
12	Have you ever repaired your battery?	1	2	
13	How many times have you changed your car battery? a. once b. twice c. thrice	1	2	
14	Have you ever left your used battery with battery chargers	1	2	
15	Have you dumped your used battery in the waste bin before	1	2	
16	Do you have used battery in your surrounding or Garage	1	2	
17	Have you at one time or the other dumped battery in dumpsites	1	2	