RECOVERY OF VALUE METALS FROM SPENT ZINC-CARBON BATTERIES

By

Jarumi Akila MANGEY
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NIGERIA

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Declaration

I declare that the work in this dissertation titled **"RECOVERY OF VALUE METALS FROM SPENT ZINC-CARBON BATTERIES"** has been carried out by me and is a record of my own research work under the supervision of Dr. M.A. Ajibike and Prof. A. Isma'il. All the information derived from literatures has been duly acknowledged in the text and a list of references provided. No part of this dissertation was previously presented for another degree or diploma at this or any other institution.

Name of Student	Signature	Date

Certification

This dissertation titled **"RECOVERY OF VALUE METALS FROM SPENT ZINC-CARBON BATTERIES"** by **MANGEY, Jarumi Akila** meets the regulations governing the award of Master of Science degree in the Department of Water Resources and Environmental Engineering, Ahmadu Bello University, Zaria, Kaduna State.

Dr. M.A. Ajibike Chairman, Supervisory Committee	Signature	Date
Prof. A. Isma'il Member, Supervisory Committee	Signature	Date
Prof. A. Isma'il Head of Department	Signature	Date
Prof. S.Z. Abubakar Dean, School of Postgraduate Studies	Signature	Date

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Dedication

To Mr. Ronald A.B Mangey, Mrs. Comfort R.A. Mangey and Mrs. Biairatu Abubakar

Abstract

Spent primary batteries are known to contain metallic compounds that could be of value if recycled as well as harmful to man and the environment if not properly disposed. Also, the recovery of these value metals from the used batteries can reduce limited natural resource (ore) depletion. This research was carried out to investigate the recovery potential of Zinc and Manganese from spent zinc-carbon battery paste. Spent battery samples were collected around Samaru area of Sabon-gari LGA of Kaduna State. The samples were crushed, ground, sieved, washed and oven-dried. Quantities of dry samples were taken for x-ray fluorescence (XRF) analysis and chemical digestion. Chemical digestion (leaching) was done by studying some variable parameters: acid concentration, reducing agent concentration, temperature, stirring speed, solid-liquid ratio and time. Leached samples were then filtered and the filtrate taken for quantitative analysis of dissolved metals using atomic absorption spectrophotometer (AAS) analysis. Results show traces of heavy metals (lead, mercury and cadmium) and also significant amount of zinc and manganese in the solution. The optimum conditions for selective dissolution of zinc was found to be 2M nitric acid concentration, 10% hydrogen peroxide, 60^0C, 400rpm, 1:5 S/L and 1.5hrs, which yielded 4788.323mg/lit. For manganese, it was 1M nitric acid, 5% hydrogen peroxide, 60^0C, 400rpm, 1:5 S/L ratio and 1.5hrs giving a yield of 18042.67mg/lit while the optimum condition for simultaneous dissolution of zinc and manganese was found to be 1M nitric acid concentration, 5% hydrogen peroxide, 60^0C, 400rpm, 1:5 S/L ratio and 1.5hrs with a yield of 1225.648mg/lit zinc and 18042.67mg/lit manganese. The study therefore, showed that there is reasonable potential of zinc and manganese recovery from spent zinc-carbon battery.

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CHAPTER ONE

1.0 INTRODUCTION

1.1 Background to Study

Large amount of primary cell batteries are discarded annually across the globe. In most West African countries, zinc-carbon and alkaline-zinc-manganese dioxide batteries have traditionally been the most popular among the rural folks and lately among the low to middle income populace in the urban areas owing to erratic power supply (Dankwah *et al.*, 2015).

Primary batteries are the most common household portable energy source. They are also known as single-use batteries because they cannot be recharged and are disposed of after use, therefore, are considered the most common source of household hazardous wastes. The environmental impact of battery is not limited to the waste stream. Environmental impacts occur in the production, distribution and end-of-life phases of the batteries. Single-use batteries have significant environmental impact at every stage of their life cycle. Secondary batteries are rechargeable as they can be used repeatedly upon being recharged. Recharging occurs when electrical current is applied to the battery, reversing the chemical reactions that occur during battery use (Linden and Reddy, 2002).

Owing to its popularity and short lifespan, spent primary cells such as zinc-carbon and alkaline-zinc-manganese dioxide batteries can considerably function effectively as energy source to power household gadgets such as flash lights, television remote controls, radio receivers, etc. if recycled (Dittrich *et al.*, 2012).

IRR (1992) stated that the logistics and viability of recycling household battery collection systems is mainly influenced by the current status of battery recycling technology for the various battery systems and the cost of battery recycling. Such knowledge will aid in evaluating the feasibility of implementing battery recycling programs. In fact, it is believed that the collection and recycling of used household batteries poses several unanswered technical and economic problems that need to be resolved before any widespread and implementation of such a program.

The metals of potential concern in the household batteries studies are cadmium, manganese, mercury, nickel, and zinc. In whatever disposal or management practice that is adopted for used household batteries, there is the potential for the release of one or more of these metals into the environment which may affect human health directly or indirectly or which may negatively impact the environment. Currently, used household batteries are almost exclusively disposed of in domestic waste, which is eventually incinerated or landfilled. Lately, the idea of used battery collection, separation and possible recycling is becoming another focus of attention (Veloso *et al.*, 2005).

Any decision to recycle primary batteries must carefully weigh several factors including the low toxicity of the battery materials (e.g. steel, zinc and manganese), total energy requirement and the environmental impact associated with the collection, transport and recycling of the batteries, the amount and value of the metals recovered and the overall cost (Meskers *et al.*, 2009).

According to NEMA (2002), landfill disposal of primary cell batteries does not pose a significant health or environmental risk based on over 20 years of battery experience and the results of various scientific studies. Almost a decade later, Khan and Kurny (2012) reported that "when zinc-carbon batteries (primary cells) are disposed of in a landfill, the elements of the spent

batteries can undergo natural leaching, seep into the ground water, change water pH and cause contamination". Further stated that the incineration of batteries also poses two major potential environmental concerns. The first is the release of metals (Zn, Pb and Hg if present) into the ambient air and the second is the concentration of metals in the ashes that must be land-filled. The stabilization process of the landfill on the other hand, is a costly process (Bernardes *et al.*, 2004).

EPBA (2006) reported that the disposal of spent batteries represents an increasing environmental problem in terms of heavy metal contents when these devices are disposed of inadequately. This environmental problem is closely related to the battery market evolution; in 2003 the total portable battery weight in the East and West Europe was about 164,000 tons of which 50,197 and 99,138 tons were zinc-carbon and alkaline batteries respectively (30% and 60% of the total annual sales).

According to Nindhia *et al.* (2016), spent primary cell still contains ammonium chloride (NH_4Cl_2) which is mildly acidic that can disturb the balance of nature if the battery is carelessly discarded. Manganese dioxide (MnO_2) is known as a hazardous material that can stain the human skin.

1.2 Statement of the Research Problem

Whilst the exact chemical make-up varies from type to type, most batteries contain heavy metals, which are the main cause for environmental concern. When disposed of incorrectly, these heavy metals may leak into the ground when the battery casing corrodes. This can contribute to soil and water pollution and endanger life. In Nigeria, only a very small percentage of consumer disposable batteries are recycled and most are disposed of with house wastes in landfill sites.

Lead-acid automobile batteries are types of rechargeable batteries recycled by local blacksmiths to produce household utensils such as pots, spoons, tools, etc. Population growth is a global issue which is currently addressed by nations to reduce depletion of our limited resources because of increased demand for day-to-day products such batteries.

1.3 Justification

Zinc and Manganese represent the greatest percentage of metals in primary batteries powder; therefore they are of interest when it comes to the recycling of these batteries (Mihailova, 2015).

However, so many works have been done on the recovery of value metals from spent primary batteries using reductive-acid leaching process such as hydrochloric and sulfuric acid media; and some organic and inorganic acids such as oxalic acid, citric acid and hydrogen peroxide as reducing agents. The present research attempts to fill the gaps and update the knowledge on the recycling and value metals recovery from spent zinc-carbon battery using nitric acid and hydrogen peroxide as reducing agent.

This research will attempt to evaluate the leaching process conditions using data obtained from leach sample analysis. To the best of my knowledge no work has been carried out in the present area of study and hence prompted me to carry out this research.

1.4 Aim and Objectives

The aim of this work is to study the Recovery Potential of Value Metals (zinc and manganese) from spent zinc-carbon battery through the following objectives:

i. To characterize the carbon paste in spent zinc-carbon batteries by X-Ray Fluorescence (XRF) analysis;

ii. To treat used zinc carbon batteries by hydrometallurgical process in order to extract zinc and manganese.

iii. To chemically leach zinc and manganese from used zinc-carbon battery powder using nitric acid and hydrogen peroxide for qualitative analysis.

iv. To examine the cost and benefits of recycling zinc-carbon batteries using nitric acid and hydrogen peroxide as leaching agents.

1.5 Scope and Limitation of the Study

This research work is limited to the qualitative and quantitative analysis of zinc-carbon battery using hydrometallurgical process of samples, collected from Samaru Area of Sabon-Gari Local Government Area of Kaduna State. Also, it does not involve purification of the metals in solution form and life cycle analysis (LCA).

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Electronic-waste Recycling

Recycling is the process by which materials or products that have reached their end of life including batteries are processed into new and useful products. Recycling is very important as it reduces the use of the raw materials that would eventually have been used. Most of the waste materials are usually taken to landfill and therefore recycling aims to provide a way of cleaning up the environment in which we live. Recycling enables the ability to recover the non-renewable resources such as minerals. Recycling processes aims at achieving the separation of constituents into their different fractions where they will be reintroduced into production more easily. The purer and better defined fraction after separation, the more valuable the products will be compared to mixed and impure ones. Separating all the different elements in their respective fractions and eventually breaking the chemical bonds could be seen as an ideal recovery process but this is far from ideal because of high energy requirements. The real goal and effort of recycling is therefore to be able to produce useable products, reduce the amount of waste, transform hazardous substances and being able to do all this in an energy efficient and cost effective sway (Ekermo, 2009;).

The demand of electrical and electronic equipment (EEE) has increased dramatically with the advancement in technology. Drastic innovations on the electrical and electronic technologies further shortened the life, and thus enhanced the generation of waste from electrical and electronic equipment (WEEE) or electronic waste (e-waste). The global production of e-waste/WEEE is increasing rapidly and is expected to accelerate in the near future. Currently, 20

to 25 million tons per year of e-waste are being generated globally with major share of Europe, USA and Australasia (Khaliq *et al.,* 2014) However, China, Eastern Europe and Latin America are expected to become significant e-waste producers in the next decade (Robinson, 2009). In Europe, it is expected that the production of e-waste will increase by 45% between 1995 and 2020. Therefore, a three pillars strategy of waste prevention, recycling and reuse has been suggested to minimize the environmental impact and promote the efficient utilization of wasted resources (EP, 2003).

E-waste is classified as hazardous material therefore should be managed properly. However, the presence of metals in e-waste such as gold (Au), silver (Ag), platinum (Pt), zinc (Zn), Manganese, Lithium (Li), Iron (Fe), Gallium (Ga), palladium (Pd), tantalum (Ta), tellurium (Te), germanium (Ge) and selenium (Se) makes it attractive for recycling. Industrially, different metallurgical routes are used to extract valuable metals from e-waste. Both pyrometallurgical and hydrometallurgical processes are commonly employed to recover value metals.

There is no standard definition for WEEE or e-waste. E-waste or WEEE embraces various forms of EEE that have no value to their owners. The reported definitions of e-waste in literature are described here:

European WEEE Directive

“Electrical or electronic equipment which is waste, including all components, sub-assemblies and consumables, which are part of the product at the time of discarding.” (EP, 2003; EP, 2012).

Basel Action Network

“E-waste encompasses a broad and growing range of electronic devices ranging from large household devices such as refrigerators, air conditioners, cell phones, personal stereos, and

consumers electronics to computers which have been discarded by their users." (Puckett *et al.*, 2002).

WEEE or e-waste is divided into ten categories based on the European WEEE Directives 2002/96/EC and 2012/19/EU (EP, 2003; EP, 2012) and is given in Table 2.1. The scope of each category is detailed elsewhere (EP, 2003; EP, 2012). E-waste is a complex mixture composed of ferrous, nonferrous, plastic and ceramic materials. According to the Association of Plastics Manufacturers in Europe (APME), material consumption in electric and electronic equipment is summarized in Table 2.2 (APME, 2004).

Table 2.1**:** Categories of **w**aste from electrical and electronic equipment (WEEE) (EP, 2003; EP, 2012).

No.	Category	Label
1	Large household appliances	Large HH
2	Small household appliances	Small HH
3	IT and telecommunications equipment	ICT
4	Consumer equipment	CE
5	Lighting equipment	Lighting
6	Electrical and Electronic tools (with the exceptions of large-scale stationary industrial tools)	E & E tools
7	Toys, leisure and sport equipment	Toys
8	Medical Devices	Medical equipment
9	Monitoring and Control instruments	M & C
10	Automatic Dispensers	Dispensers

Table 2.2**:** Main materials found in waste from electrical and electronic equipment (WEEE) (APME, 2004).

No	Material	Percentage
1	Ferrous	38
2	Non-ferrous	28
3	Plastics	19
4	Glass	4
5	Wood	1
6	Other	10

Generally, metals in e-waste can be grouped into precious metals (PMs), platinum group metals (PGMs), base metals (BMs), metals of concern (MCs), and scarce elements (SEs), such as the following (Hagelüken, 2006):

PMs: Au, Ag;

PGMs: Pd, Pt, Rh, Ir and Ru;

BMs: Cu, Al, Ni, Sn, Zn and Fe;

MCs (Hazardous): Hg, Be, In, Pb, Cd, As and Sb;

SEs: Te, Ga, Se, Ta and Ge.

2.2 General Driving Force for E-Waste Processing

There are three general reasons for e-waste processing: environmental concerns, energy savings and resource efficiency. These are explained in more detail in the following subsections.

2.2.1 Environmental Concerns

E-waste is composed of a large number of components of various sizes, shapes and chemistry. Some of them contain hazardous metals including Hg, Pb and Cd. Such components are removed through separate treatment and recycling processes. In the European directives (2002/96/EC and 2012/19/EU) (EP, 2003; EP, 2012), e-waste is classified as hazardous material. Major hazardous components in e-waste are summarized in Table 2.3.

Table 2.3: Major hazardous components and materials in WEEE (EP, 2003; EP, 2012).

No.	Materials and Components	Description
1	Batteries	Heavy metals such as lead, mercury and cadmium are present in batteries
2	Cathode ray tubes (CRTs)	Lead in the cone glass and fluorescent coating cover the inside of panel glass
3	Mercury containing components such as switches	Mercury is used in thermostats, sensors, relays and switches (e.g., on PCBs and in measuring equipment and discharge lamps). It is also used in medical equipment, data transmission, telecommunication, and mobile phones
4	Asbestos waste	Asbestos waste has to be treated selectively
5	Toner cartridges, liquid and pasty, as well as color toner	Toner and toner cartridges have to be removed from any separately collected WEEE
6	PCBs	In PCBs, cadmium occurs in certain components, such as SMD chip resistors, infrared detectors and semiconductors
7	Polychlorinated biphenyl (PCB) containing capacitors	PCB-containing capacitors have to be removed for safe destruction
8	Polychlorinated biphenyl (PCB) containing capacitors	LCDs of a surface greater than 100 cm2 have to be removed from WEEE
9	Plastics containing halogenated flame retardants	During incineration/combustion of the plastics, halogenated flame retardants can produce toxic components
10	Equipment containing chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs) or hydrofluorocarbons (HFCs)	CFCs present in foam and refrigerating circuit must be properly extracted and destroyed. HCFCs or CFCs present in foam and refrigerating circuit must be properly extracted and destroyed or recycled
11	Gas discharge lamps	Mercury has to be removed

Traditionally, most of the e-waste ends up as landfill. According to the U.S Environmental Protection Agency report on e-waste management (EPA, 2008), 19% of e-waste is combusted

and 81% is disposed in landfills. The disposal of e-waste underground has multiple disadvantages including the contamination of underground water and soil, and wasting a potential source of valuable metals.

In the last decade many countries have formulated legislations on e-waste management (EP, 2003; EP, 2012; Puckett *et al.*, 2002). Several investigators reported on the individual countries and global legislations on managing and handling of e-waste (Robinson, 2009; Widmer *et al.*, 2005; Kang *et al.*, 2005; Kahhat *et al.*, 2008; Lee *et al.*, 2007; Huang *et al.*, 2009; Hischier *et al.*, 2005; Dalrymple *et al.*, 2007; Khaliq *et al.*, 2014). It is no longer permissible to dispose e-waste underground or burn it in incinerators without isolating the hazardous materials. Moreover, exporting e-waste to underdeveloped countries is not permissible according to the international regulations (Puckett *et al.*, 2002). Disposing underground, burning in air and acid leaching will deteriorate the environment by spoiling drinking water and releasing toxic gases into the atmosphere (Luda, 2010; Guo *et al.*, 2009; Huang *et al.*, 2009). Therefore, recycling of e-waste is crucial from the perspective of minimizing environmental pollution and resource management.

2.2.2 Energy and Resource Conservation

Recycling of e-waste for metal recovery is also important from the perspective of saving energy. The U.S Environmental Protection Agency (EPA, 2008) has identified seven main benefits for using recycled Fe and steel over their virgin materials. One of the major benefits is a significant energy saving using recycled materials compared to virgin materials. The energy savings for a number of common metals and materials are summarized in Table 2.4.

Table 2.4: Recycled materials energy savings over virgin materials (ISRI, 2003; Cui and Forssberg, 2003)

No	Materials	Energy savings (%)
1	Aluminum	95
2	Copper	85
3	Iron and steel	74
4	Lead	65
5	Zinc	60
6	Paper	64
7	Plastics	>80

Moreover, processing of e-waste will reduce burden on mining ores for primary metals. Therefore, scarce resources especially for metals could be conserved, e.g., metals that exist at low concentrations in primary ores and consume significant energy during extraction.

2.2.3 Economic Value of Selected Value Metals

The recovery of precious and base metals is important for e-waste management, recycling, sustainability and resource conservation. The value distribution of PMs in PCBs and calculators is more than 80%. After PMs, copper is the next highest value metal to be extracted from e-waste (Hagelüken, 2006). It is worth noting that sustainable resource management demands the isolation of hazardous metals from e-waste and also maximizes the recovery of metals

2.3 E-Waste Processing

E-waste recycling consists of three main steps: collection, preprocessing and end processing (Meskers *et al.*, 2009). Each step is critical for the recovery of metals and recycling economy. E-waste collection is facilitated by appropriate government policies, effective advertisement for public awareness, and by installing separate collection facilities at public places. End of life

electronic components are sorted at the collection facility where useable components are returned to the consumer supply chain.

Preprocessing of e-waste is one of the most important steps in the recycling chain. The expired equipment are manually dismantled at collection facilities and individual components are tested and isolated from e-waste. During the early stage, housing, wiring boards and drives, and other components are liberated. Mechanical processing is an integrated part of this stage where e-waste scrap is shredded into pieces using hammer mills (Meskers *et al.*, 2009). Metals and non-metals are separated during this stage using techniques similar to that used in the mineral dressing, e.g., screening, magnetic, eddy current and density separation techniques.

The final stage in the recycling chain of e-waste is the end processing, where the non-metal and metal fractions of e-waste are further processed.

The metallic fraction of e-waste can be further processed to separate or extract minor metals/elements using various metallurgical processes. The following sections will explain in more detail the metallurgical processes to extract metals from e-waste.

2.4 Metallurgical Processes for the Extraction of Metals from E-Waste

The metal fractions separated from e-waste during preprocessing can be further processed using hydrometallurgical, pyrometallurgical, electrometallurgical, biometallurgical processes, and their combinations. The hydrometallurgical and pyrometallurgical processes are the major routes for processing of e-waste. These routes may be followed by electrometallurgical/electrochemical processes (for example electrorefining or electrowinning) for selected metal separation and recovery. Currently, there are only limited laboratory studies for e-waste processing through biometallurgical routes, e.g., bioleaching of metals from e-waste. Nevertheless, this route has a potential for further development.

The preprocessing of e-waste is not always required for pyrometallurgical routes. For example, complex electronic equipment such as mobile phones and MP3 players can be treated directly during smelting processes (Anindya, 2012). However for hydrometallurgical routes, preprocessing is required to separate metal fractions from other fractions. This will enhance the efficiency of each step associated with hydrometallurgical routes. Each route has advantages and disadvantages that should be considered for the selection of an appropriate recycling process.

2.4.1 Hydrometallurgical Processes

Various investigators studied the extraction of metals from e-waste using hydrometallurgical routes (Chehade *et al.*, 2012; Dhawan *et al.*, 2008; Dhawan *et al.*, 2009; Delfini *et al.*, 2011; Park *et al.*, 2009). These routes are based on traditional hydrometallurgical technology of metals extractions from their primary ores. Similar steps of acid or caustic leaching are employed for selective dissolution of metals from e-waste. The pregnant solution is separated and purified for the enrichment of metal content thereby impurities are removed as gangue materials. The isolation of metal of interest is conducted through solvent extraction, adsorption and ion exchange enrichment processes. Finally, metals are recovered from solution through electrorefining (electrometallurgy) or chemical reduction processes (Sadegh *et al.*, 2007; Ritcey, 2006; Yang, 1994; Shamsuddin, 1986; Tavlarides, 1985). Cui and Zhang (2008) reviewed the processes for recovering metals from e-waste. Hydro- and pyrometallurgical processes were evaluated and discussed. It has been reported that hydrometallurgical processes have additional benefits compared to pyrometallurgical processes because they are more exact, predictable, and easily controllable (Paretsky *et al.*, 2004).

Solvents especially halides, cyanides, thiourea and thiosulfates are used for the leaching of PMs from their primary ores. Process factors including pH, temperature and stirring control the

dissolution of metals from their primary ores. The recovery of PMs from the leached solution is carried out by cementation, solvent extraction, adsorption on activated carbon, and ion exchange methods. Similar techniques could be employed for extracting metals from e-waste, however, its complex nature makes the process complicated compare to natural ores.

Park *et al.* (2009) proposed a hydrometallurgical method for recovering PMs from e-waste. Aqua regia was used as leachant and a fixed ratio of 1/20 between metals and leachant was exercised. Silver and palladium were extracted during the first stage with 98% and 93% recovery, respectively. For gold, a liquid-liquid extraction method was adopted with toluene and a recovery of 97% was reported.

It is noted that HNO3, H2SO4, and HCl-based solutions are commonly employed for dissolving metals from e-waste. From the leachants, metals are recovered employing methods similar to those used in the mineral industry.

2.4.1.1 Limitations of Hydrometallurgy Route

Hydrometallurgical routes have been successfully used to recover metals from e-waste. However, these processes are associated with certain disadvantages that limit their application on the industrial scale. Some common limitations of hydrometallurgical methods for recovering metals from e-waste are listed here (Cui and Zhang, 2008; Hilson *et al.*, 2006; La Brooy *et al.*, 1994):

i. Overall, hydrometallurgical routes are slow and time consuming and impact recycling economy. There are concerns regarding the economy of hydrometallurgical routes compared to pyrometallurgical processes for the extraction of metals from e-waste.

ii. Mechanical processing of e-waste takes longer to reduce size for efficient dissolution. It is reported that 20% PM is lost by mechanical force during the liberation process that contributes to a significant loss in the overall revenue.

iii. Cyanide is a dangerous leachant and should therefore be used with high safety standards. It can cause contamination of rivers and seawater, especially near gold mines, which poses serious health risks to the inhabitants.

iv. Halide leaching is difficult to implement due to strong corrosive acids and oxidizing conditions. Specialized equipment made of stainless steel and rubbers is required for leaching of gold using halide agents from e-waste.

v. The consumption of leachate is comparatively higher and the overall process is slower, which limits its application for metals extraction from ores as well as from e-waste.

vi. There are risks of metal loss during dissolution and subsequent steps, therefore the overall recovery of metals will be affected.

2.4.2 Pyrometallurgical Processes

Pyrometallurgical processes for recovering metals from various waste materials have been used during the last two decades. Smelting in furnaces, incineration, combustion and pyrolysis are typical e-waste recycling processes. State-of-the-art smelters and refineries can extract value metals and isolate hazardous substances efficiently. Such recycling facilities can close the loop of value metals and reduce environmental impact arising from large quantities of e-waste. Currently, e-waste recycling is dominated by pyrometallurgical routes (Antrekowitsch *et al.*, 2006), whereas the steel industry embraces the ferrous fractions for the recovery of iron, and the secondary aluminum industry takes the aluminum fractions. Pyrometallurgical processes work with the steps of liberation, separation/upgrading and

purification that are fundamentally similar to those of mechanical or hydrometallurgical routes. However, the liberation of valuable metals is not achieved by leaching, crushing or grinding but by smelting in furnaces at high temperatures. In these processes, metals are sorted by exploiting their chemical and metallurgical properties, e.g., PMs are segregated into a solvent metal phase (copper or lead).

2.4.2.1 Limitations of Pyrometallurgical Processes

Pyrometallurgical routes are generally more economical, eco-efficient and maximize the recovery of metals, however, they have certain limitations that are summarized here (EPA, 2008; Cui and Zhang, 2008):

i. Recovery of plastics is not possible because plastics replace coke as a source of energy;

ii. Iron and aluminum recovery is not easy as they end up in the slag phase as oxides;

iii. Hazardous emissions such as dioxins are generated during smelting of feed materials containing halogenated flame retardants. Therefore special installations are required to minimize environmental pollution;

iv. A large investment is required for installing integrated e-waste recycling plants that maximize the recovery of valuable metals and also protect the environment by controlling hazardous gas emissions;

v. Instant burning of fine dust of organic materials (e.g., non-metallic fractions of e-waste) can occur before reaching the metal bath. In such cases, agglomeration may be required to effectively harness the energy content and also to minimize the health risk posed by fine dust particles;

vi. Ceramic components in feed material can increase the volume of slag generated in the blast furnaces, which thereby increases the risk of losing PMs from BMs;

vii. Partial recovery and purity of metals are achieved by pyrometallurgical routes. Therefore, subsequent hydrometallurgical and electrochemical techniques are necessary to extract pure metals from BMs;

viii. Handling the process of smelting and refining is challenging due to complex feed materials. The expertise in process handling and the thermodynamics of possible reactions will be difficult.

2.4.3 Microbial Biotechnological Approaches to Recover Metals from Waste

Biohydrometallurgy is based on the application of microbially catalysed processes for the extraction of metals from different raw materials. Biotechnological approaches cover all cutting-edge areas of biohydrometallurgy, which include bioleaching, bioprecipitation, bioflotation bioflocculation, biooxidation, biosorption, bioreduction, bioaccumulation and the application of biosensors in analytics (Sivasubramanian, 2016). At the early stage of applying bioprocesses at an industrial scale, bioleaching and biooxidation were widely used to extract metals from natural ores (e.g. sulfides) (Hunter, 2002; Watling, 2006).

With the rise of environmental awareness in our society, people have started to expand the application of microbial biotechnology into waste treatment and metal extraction from waste. Such biotechnological approaches could not only reduce the toxicity of various waste streams, such as mining wastes, e-wastes and even municipal waste sludge, but also unearth the potential of those wastes as secondary materials for metal recovery (Mishra *et al.*, 2005; Shin *et al.*, 2015; Awasthi *et al.*, 2016; Palomo-Briones *et al.*, 2016).

These microbial biotechnological approaches are promising for economically recycling of metals and have the potential to be not only cost-effective but also environmentally friendly (Sivasubramanian, 2016). Recycling metals from wastes is an important subject not only from the point of the recovery aspect of valuable materials but also from the point of waste management. For example, it would be very beneficial if toxic metals can be easily removed from waste so that the waste can be used for secondary purposes, e.g. in construction.

2.4.3.1 Contribution of microbial biotechnology to the recovery of precious metals from waste

Applications of biohydrometallurgy for extraction of precious metals from natural ore deposits have been developed and applied in a few cases (Chandraprabha *et al.,* 2002; Sun *et al.,* 2012). Yet, another application of microbial biotechnology is the bioprocessing of industrial and other wastes to first recover metals from the waste and second to add value to a 'clean' or at

least a less toxic waste product (Cui *et al.,* 2008; Ilyas *et al.,* 2010; Maes *et al.,* 2016). The availability of high-grade ores of precious metals on Earth is not endless, and the ongoing consumption of these limited resources will eventually lead to a rapid depletion of high-quality ores. By viewing metal-containing waste as secondary 'ores', we can avoid exhausting natural resources. Industries can potentially also enhance their profits by applying microbial biotechnology processes, which can be cost-effective and have a low energy requirement. In addition, several environmental benefits could be achieved.

2.5 Design for Resource (DfR) Efficiency

One of the key factors in the e-waste management and recycling is the DfR efficiency. It refers to the product designs that strive for minimum loss of resources at the end of product life. Similarly, a DfR efficiency for electrical and electronics equipment ensures effective recovery of

metals during processing. The recycling of e-waste initiates with collection, dismantling and sorting and is followed by preprocessing and final processing for the recovery of metals. The role of DfR is important in e-waste recycling at all stages such as dismantling, sorting, preprocessing and final processing. For example, aluminum is used as a heat dissipater in electronic equipment that could be designed for easy manual extraction. This could prevent the loss of aluminum in recycling of e-waste in the integrated smelting facility to recover metals. The recovery of metals during e-waste smelting could also be improved by designing products for recycling. The recycling efficiency will be dictated by the mineralogy of the input materials. Metals with similar thermodynamic properties should be kept together to maximize their recovery and resource efficiency. For example, product designers should use silver and gold with copper rather than nickel or lead that can be treated in the copper smelters.

The DfR efficiency comes under the policy framework that could be implemented by the producers. Over the years, many countries have adopted extended producer responsibilities (EPR) regulations that require the EEE producers to take back and recycle their products that have reached the end of their life (Tanskanen, 2013). Moreover, public policy can influence manufacturers to design products for recycling that will also encourage material innovation without impeding the functionality of the components (Reuter, 2013). Overall, the role of DfR efficiency in the electrical and electronic industry is important for the recycling of e-waste and extraction of metals, and this approach could be expanded around the world.

2.6 Batteries

A battery is a device that converts the chemical energy contained in its active materials directly into electrical energy by means of an electrochemical oxidation-reduction (redox) reaction. In the

case of a rechargeable system, the battery is recharged by a reversal of the process (Linden and Reddy, 2002). While the term “battery” is often used, the basic electrochemical unit being referred to is the “cell”. The cell consists of three major components (Linden and Reddy, 2002):

1. The anode or negative electrode — which gives up electrons to the external circuit and is oxidized during the electrochemical reaction.

2. The cathode or positive electrode — which accepts electrons from the external circuit and is reduced during the electrochemical reaction.

3. The electrolyte—the ionic conductor—which provides the medium for transfer of charge, as ions, inside the cell between the anode and cathode. The electrolyte is typically a liquid, such as water or other solvents, with dissolved salts, acids, or alkalis to impart ionic conductivity. Some batteries use solid electrolytes which are ionic conductors at the operating temperature of the cell

2.7 Classification of Batteries

Batteries can be classified into two broad types, namely primary and secondary batteries depending on the recharging ability. Reserve battery and fuel cells are other classifications that do not strictly limit to the primary and secondary batteries (Khan and Kurny, 2012). All of these classifications are briefly described below. Depending on the nature of electrolyte, batteries can also be classified as wet cell and dry cell. Present day batteries are mostly dry cell types (Linden and Reddy, 2002).

2.7.1 Primary batteries

Primary batteries irreversibly (within limits of practicality) transform chemical energy to electrical energy. When the initial supply of reactants is exhausted, energy cannot be readily

restored to the battery by electrical means. Hence, primary batteries are not rechargeable and come gradually to the spent condition with time of using. Even if never taken out of the original package, disposable (or "primary") batteries can lose 8 to 20 percent of their original charge every year at a temperature of about 20°–30°C (Khan and Kurni, 2012). This is known as the "self-discharge" rate and is due to non-current-producing "side" chemical reactions, which occur within the cell even if no load is applied to it. The rate of the side reactions is reduced if the batteries are stored at low temperature, although some batteries can be damaged by freezing. High or low temperatures may reduce battery performance (Linden and Reddy, 2002). Different types of primary batteries are available of which zinc-carbon dry cell batteries are the most prominent. Alkaline zinc-carbon batteries however are currently replacing the old zinc-carbon type in many countries due to their higher life time and energy density. Common types of primary batteries according to Linden and Reddy (2002) include:

a. Zinc-carbon batteries

Zinc carbon batteries are packaged in zinc can that serves as both a container and anode. Zinc carbon batteries are the least expensive batteries and thus a popular choice by manufacturers when devices are sold with batteries included. The primary electrolyte in zinc carbon type nowadays is $ZnCl_2$ with a small amount of NH_4Cl. They can be used in remote controls, flashlights, toys, or transistor radios (Linden and Reddy, 2002).

b. Alkaline batteries

Alkaline batteries are a type of power cell dependent upon the reaction between zinc and manganese dioxide (Zn/MnO_2). Alkaline batteries have a higher energy density and longer shelf-life compared to the carbon zinc batteries. The primary electrolyte in alkaline batteries is

potassium hydroxide (KOH) and this electrolyte type differentiates the primary and alkaline batteries. These batteries can be used in cassettes players, radios, or other appliances (Linden and Reddy, 2002).

c. Zinc-air batteries

Zinc-air batteries are electro-chemical batteries powered by the oxidation of zinc with oxygen from the air. These batteries have high energy densities and are relatively inexpensive to produce. They are used in hearing aids and in experimental electric vehicles. These batteries may become an important contributor in the future high energy and long cycle battery designs (Linden and Reddy, 2002).

d. Silver oxide batteries

Silver oxide batteries have a long life and very high energy/weight ratio, but a prohibitive cost for most applications due to the high price of silver. They are available in either very small sizes as button cells where the amount of silver used is small, or in large custom design batteries where the superior performance characteristics of the silver oxide chemistry outweigh cost considerations (Linden and Reddy, 2002).

2.7.2 Secondary Batteries

Secondary batteries can be recharged; that is, they can have their chemical reactions reversed by supplying electrical energy to the cell, restoring their original composition. Rechargeable batteries, especially nickel-based batteries self-discharge more rapidly than primary batteries. A freshly charged NiCd loses 10% of its charge in the first 24 hours, and thereafter discharges at a rate of about 10% a month. However, modern lithium ion battery designs have reduced the self-

discharge rate to a relatively low level (but still high compared to the primary batteries) (Linden and Reddy, 2002). Lithium ion batteries are now dominant in the mobile industry. Lead acid heavy duty batteries are very commonly used in transportation. Other batteries of rechargeable types are generally Nickel-cadmium (NiCd) battery, Nickel-Metal-Hydride (NiMH) battery, Nickel-zinc (NiZn) battery etc. Common type of secondary batteries according to Linden and Reddy (2002) include:

a. Lead-acid automobile batteries

Lead-Acid automobile batteries are types of rechargeable batteries usually used on the automobiles. Lead acid batteries are rechargeable batteries made of lead plates situated in a 'bath' of sulfuric acid within a plastic casing. Almost ninety percent of the lead acid batteries can be recycled (Linden and Reddy, 2002).

b. Non-automotive lead-based batteries

Gel cells and sealed lead-acid batteries are commonly used to power industrial equipment, emergency lighting, and alarm systems. The same recycling process applies as with automotive batteries. An automotive store or a local waste agency may accept the batteries for recycling (Linden and Reddy, 2002).

c. Lithium batteries

In these types, lithium ions move from the negative electrode to the positive electrode during discharge and back when charging. During discharge, lithium ions (Li^+) carry the current from the negative to the positive electrode, through the non-aqueous electrolyte and separator diaphragm. Lithium metal or lithium compounds are used as an anode in lithium batteries.

Depending on the design and chemical compounds used, lithium cells can produce voltages from 1.5 V to about 3 V, twice the voltage of an ordinary zinc-carbon battery or alkaline cell. Lithium batteries are used in many portable consumer electronic devices, and are widely used in industries (Linden and Reddy, 2002).

d. Nickel-Cadmium batteries

The Nickel-Cadmium battery (commonly abbreviated NiCd) is a type of rechargeable battery using nickel oxyhydroxide and metallic cadmium as electrodes. However, due to the hazardous element cadmium, the use of these batteries are banned in many countries and lithium ion batteries are currently replacing them (Linden and Reddy, 2002).

e. Nickel-Metal-Hydride (NiMH) batteries

The rechargeable sealed nickel-metal hydride battery is a relatively new technology with characteristics similar to those of the sealed nickel-cadmium battery. The principal difference is that the nickel-metal hydride battery uses hydrogen, absorbed in a metal alloy, for the active negative material in place of the cadmium used in the nickel-cadmium battery (Muchnick and Hurd, 1993). A NiMH battery can have two to three times the capacity of an equivalent size nickel-cadmium battery. These batteries are used in electric vehicles, consumer electronics etc (Linden and Reddy, 2002).

f. Nickel-zinc batteries

The nickel-zinc battery system uses the nickel /nickel oxide electrode (also known as the nickel-hydroxide/nickel oxyhydroxide electrode) as the positive and the zinc / zinc oxide electrode as the negative. This kind of batteries may be used in cordless power tools, cordless telephone,

digital cameras, battery operated lawn and garden tools, professional photography, electric bike, and light electric vehicle sectors.

2.7.3 Reserve batteries

Also called deferred-action batteries, these are special purpose primary batteries usually designed for emergency use. The electrolyte is usually stored separately from the electrodes which remain in a dry inactive state. The battery is only activated when it is actually needed by introducing the electrolyte into the active cell area. This has the double benefit of avoiding deterioration of the active materials during storage and at the same time it eliminates the loss of capacity due to self-discharge until the battery is called into use. They can thus be stored for 10 years or more yet provide full power in an instant when it is required. The reserve batteries can be classified by the type of activating medium or mechanism that is involved in the activation (Linden and Reddy, 2002) as seen below:

- *Water-activated batteries:* Activation by fresh- or seawater.
- *Electrolyte-activated batteries:* Activation by the complete electrolyte or with the electrolyte solvent. The electrolyte solute is contained in or formed in the cell.
- *Gas-activated batteries:* Activation by introducing a gas into the cell. The gas can be either the active cathode material or part of the electrolyte.
- *Heat-activated batteries:* A solid salt electrolyte is heated to the molten condition and becomes ionically conductive, thus activating the cell. These are known as thermal batteries.

These batteries are used, for example, to deliver high power for relatively short periods of time, in missiles, torpedoes, projectiles and bomb fuses, and various weapon systems (Linden and Reddy, 2002).

2.7.4 Fuel Cell

A fuel cell is a device that converts the chemical energy of a fuel (hydrogen, natural gas, methanol, gasoline, etc.) and an oxidant (air or oxygen) into electricity. In principle, a fuel cell operates like a battery. Unlike a battery however, a fuel cell does not run down or require recharging. It will produce electricity and heat as long as fuel and an oxidizer are supplied. Fuel cell construction generally consists of a fuel electrode (anode) and an oxidant electrode (cathode) separated by an ion-conducting membrane. Oxygen passes over one electrode and hydrogen over the other, generating electricity, water and heat. Fuel cells chemically combine the molecules of a fuel and oxidizer without burning or having to dispense with the inefficiencies and pollution of traditional combustion (Linden and Reddy, 2002).

2.8 Zinc carbon dry cell battery

A zinc carbon dry cell battery consists of zinc can with a porous plastic layer next to zinc and a carbon rod in the center as an electrode. The space between the carbon rod and the plastic separator is filled with a hard (hammered down), barely moist cathode mixture. This mixture consist of carbon (acetylene black, graphite), manganese-dioxide and a water solution of ammonium-chloride and zinc-chloride salt. This means it is technically a "Lechlance" cell, but it is usually called "carbon cell" because both the current collecting central carbon rod and part of the cathode mix are made of types of carbon products. The main components of a zinc-carbon battery are shown in Figure 2.1 and they include:

1. Zinc- anode

2. MnO_2 and C – cathode mix

3. Carbon rod- current collector

4. Paste of $ZnCl_2$ and/or NH_4Cl as the electrolyte

5. Porous paper- separates the paste from the Zn casing, also allows for the diffusion of ions.

6. Wax seal that prevents the evaporation of water.

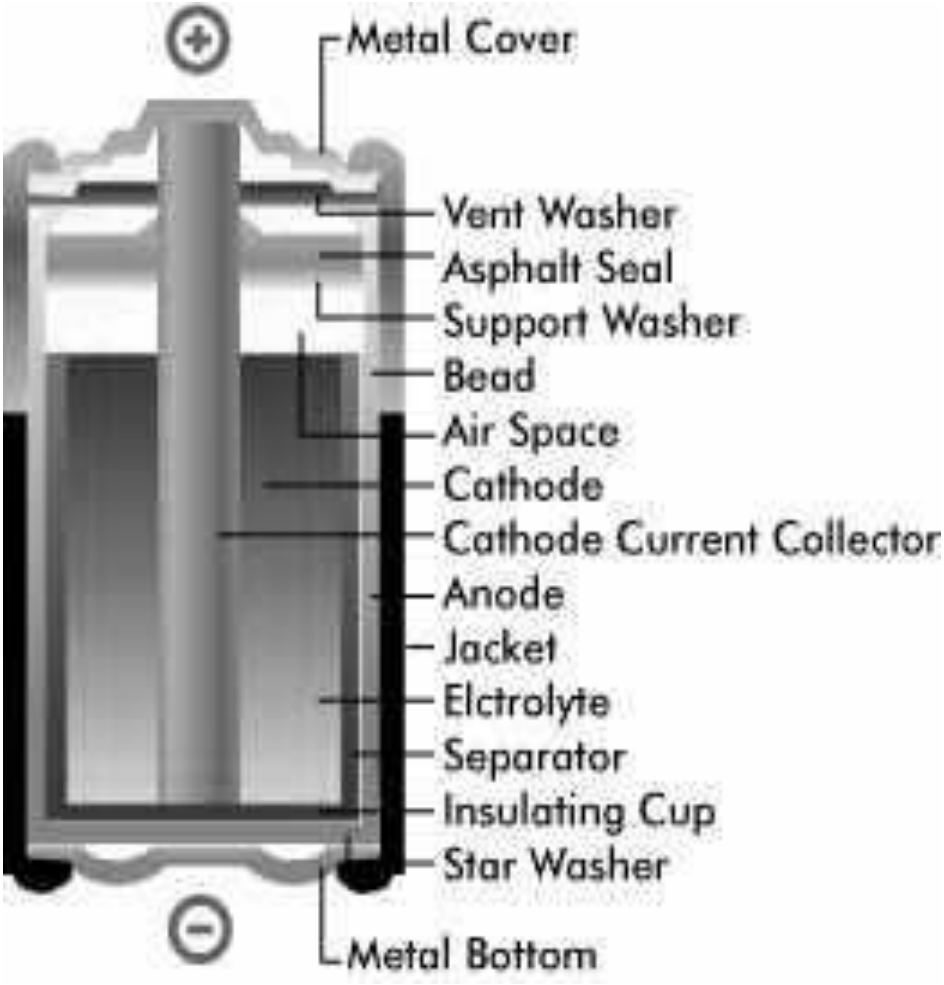


Figure 2.1: Zinc-carbon dry cell battery (Khan and Kurni, 2012)

The cell is usually closed by filling the top of the zinc can with pitch through which the carbon rod protrudes. Thus sealed, the structure is resistant to shock and vibration and storage (shelf) life is very good. When the plastic separator is eventually replaced with a cereal-paste-coated heavy paper, each cell (Figure 2.1) could provide about twenty watts of direct electrical current (dc) for short periods without electrical noise (Linden and Reddy, 2002). Five types of Zinc carbon dry cell batteries (AAA, AA, C, D, 9V) are available in the market. NH_4Cl electrolyte is predominant in Lechlance type cells. Most of the battery manufacturers nowadays use $ZnCl_2$ as the primary electrolyte with little or no addition of NH_4Cl. Nowadays, acetylene black is commonly used in combination with graphite due to the high electrical conductivity and the ability to retain moisture of acetylene black powders (Linden and Reddy, 2002).

Zinc-carbon and alkaline dry-cell batteries are the most used types of batteries and constitute approximately 80% of waste dry-cell stream (Cynthia *et al.*, 2007). In the recent past, mercury and cadmium with lead were the main hazardous components in a zinc-carbon battery. In recent years, mercury and cadmium are not used in zinc-carbon and alkaline manganese batteries (Shin *et al.*, 2007). However, a small amount of lead is still being used in these batteries (Khan and Kurny, 2012).

Baba et al (2009) stated that in most sub Saharan African countries, zinc-carbon constitute by far the dominant portion of household batteries used. Figure 2.2 shows a common type of zinc-carbon battery used in Nigeria. A recent systematic case study on the inventory of disposal batteries carried out in Cameroon showed that more than 98% of all the non-rechargeable exhausted batteries are made up of the zinc-carbon battery type because of their easy use, good discharge characteristic per ratio and the fact that the supply of electricity is still epileptic in

most African countries. More than 300,000 tons of zinc-carbon batteries are sold per year (Bernardes *et al.,* 2004).



Figure 2.2: A typical zinc-carbon battery commonly used in Nigeria

2.9 Chemistry of zinc-carbon dry cell batteries

The oxidation at the zinc electrode (the anode) is straight forward and similar to that in other cells like the Danielle cell. The other reactions involve the MnO_2 which is contained near the carbon center rod and the NH_4Cl and $ZnCl_2$ which make up the bulk of the paste between the cathode and anode. The chemical reactions in this cell may be expressed as:

$Zn\ (s) \rightarrow Zn^{2+}\ (aq) + 2e^-$ (Anode) …… (1)

$2NH_4^+\ (aq) + 2MnO_2\ (s) + 2e^- \rightarrow Mn_2O_3\ (s) + H_2O\ (l) + 2NH_3\ (g)$ (Cathode) …… (2)

Some of the complexity of this reaction comes from the fact that the reduction of the ammonium ion produces two gaseous products which must be absorbed to prevent the buildup of gas pressure.

$2NH_4^+ (aq) + 2e^- \rightarrow 2NH_3 (g) + H_2 (g)$ …… (3)

That is accomplished with two further reactions in the paste electrolyte. Zinc chloride reacts with ammonia to form solid zinc ammonium chloride and manganese dioxide reacts with hydrogen to form solid dimanganese trioxide plus water.

$2ZnCl_2 (aq) + 2NH_3 (g) \rightarrow 2Zn (NH_3)Cl_2 (s)$ …… (4)

$2MnO_2 (s) + H_2 (g) \rightarrow Mn_2O_3 (s) + H_2O (l)$ ……. (5)

The overall reaction that occurs in the zinc-carbon batteries can be expressed as follows.

$Zn + 2MnO_2 \rightarrow ZnO.Mn_2O_3$ ……. (6)

The exact reaction mechanism is sometimes complex in nature. According to Linden and Reddy (2002), the reactions that occur in a dry cell battery having $ZnCl_2$ as the primary electrolyte are as follows:

Light discharge:

$Zn + 2MnO_2 + ZnCl_2 + 2H_2O \rightarrow 2MnOOH + 2Zn(OH)Cl$ …….. (7)

Heavy discharge:

$4Zn + 8MnO_2 + 9H_2O + ZnCl_2 \rightarrow 8MnOOH + ZnCl_2.4ZnO.5H_2O$ …… (8)

Prolonged discharge:

$Zn + 6MnOOH + 2Zn(OH)Cl \rightarrow 2Mn_3O_4 + ZnCl_2.2ZnO.4H_2O$ …… (9)

For cells having ammonium chloride as the primary electrolyte, the reactions can occur as follows:

Light discharge:

$Zn + 2MnO_2 + 2NH_4Cl \rightarrow 2MnOOH + Zn(NH_3)_2Cl_2$ …… (10)

Heavy discharge:

$Zn + 2MnO_2 + NH_4Cl + H_2O \rightarrow 2MnOOH + NH_3 + Zn(OH)Cl$ ……. (11)

Prolonged discharge:

$Zn + 6MnOOH \rightarrow 2Mn_3O_4 + ZnO + 3H_2O$ ……. (12)

The voltage of this cell is initially about 1.5 volts, but decreases as energy is taken from the cell. It also has a short shelf life and deteriorates rapidly in cold weather. Oxidation of the zinc wall eventually causes the contents to leak out, so such batteries should not be left in electric equipment for long periods.

2.10 Background of Battery Recycling

Information obtained from the European Union market of portable primary batteries, approximately 160,000 tonnes of portable batteries every year are produced and ultimately disposed of. However, portable primary batteries do not necessarily cause serious damaging environmental impacts during their use phase, these batteries contain metals, which can pollute the environment at the end of their life cycle. Mercury, lead and cadmium are the most dangerous substances present in batteries. The other batteries on the European Union market are

estimated to be around 800,000 tonnes of automotive batteries and 190,000 tonnes of industrial batteries. (Mudgal *et al*., 2010; Popita *et al.,* 2010)

The batteries containing reusable metals are as such far too good material source to be wasted. According to Dittrich *et al.* (2012), study between years 1980 and 2008, global consumption of metals increased by around 87 %. Some metals, such as aluminium or copper, are used in large quantities and for a wide scale of applications. Others, such as indium, are used in small quantities but in everyday high-tech products. With the increasing demand, even more metals are exploited, with the related environmental implications such as the degradation of ecosystems through metal mining and emissions to water and soil (Dittrich *et al.,* 2012).

Due to a strongly increased demand in the period 2000 to 2008, world primary metal production increased by 95% and world primary industrial mineral production 27%. In the year 2008, more than 50% of world metal production was concentrated in only one country for 16 metals, and more than 80% of world production was concentrated in only three countries for a further eight metals. China is the number one producer of 19 metals as it is also the main user for many metals (Monier *et al.,* 2011).

Roughly over 5 billion batteries went to the market in year 2009 according European Portable Battery Association (EPBA) with alkaline manganese batteries accounting for the largest market share. The statistics for the rechargeable segment only includes batteries sold in the most popular D, C, AA, AAA and 9V sizes, and not batteries or battery packs sold with devices like mobile phones, computers, MP3 players, power tools, etc. (EPBA 2010)

2.11 Previous Works on Battery Recycling

Muchnick et.al (1993), estimated around 20% Zn, 30% MnO_2 and 5% C in the electrolyte paste of the zinc-carbon type dry cell batteries. Authors such as Devi *et al.*, (1997), Salgado *et al.*, (2003), De Souza and Tenorio (2004) and Veloso *et al.*, (2005) investigated reductive acid leaching process using sulfuric acid and hydrogen peroxide. Rabah *et al*., (1999) dissembled the different type of batteries manually and estimated the weight percentage of different component parts. They also mentioned the crystalline phases that may be present in zinc-carbon type batteries. Gega and Walkowiak (2001) determined the composition of zinc-carbon batteries while Linden and Reddy (2002) gave detailed description of the types of carbon, manganese dioxide and zinc chloride generally used in zinc-carbon batteries.

However, a comprehensive characterization of AA household alkaline batteries was done by Almeida *et al.* (2006). They estimated the moisture content, ash content, zinc and zinc oxide amount on the anode, weight percentage analysis of the different component parts. They also identified the percentage metal and non-metal values in the batteries. Eterigho and Adediran (2004) investigated spent zinc-carbon dry cells as a potential source of manganese. Xi *et al.* (2004) proposed a process for the production of manganese-zinc ferrites using spent alkaline batteries. Barnardes *et al.* (2004) reviewed processes and technologies in recycling of batteries, and thereafter suggested alternatives to the final disposition of batteries as landfill, stabilization, incineration and recycling. Nan *et al.* (2006) also proposed similar process. Ferella *et al.* (2006) studied leaching systems for the recovery of zinc and manganese from spent alkaline and zinc-carbon batteries and proposed hydrometallurgical process for the recycling of alkaline and zinc carbon batteries. Guerra *et al.* (2008) characterized the Zn-MnO_2 type batteries after sorting and shredding of the batteries and found that zinc and manganese constituted around 19% and 25 %

respectively of the total weight of these batteries. They also obtained 90 percent of the size fractions below 4mm under sieving. Shin *et al.* (2008) studied a selective leaching of zinc from spent zinc-carbon battery with ammoniacal ammonium carbonate and got high zinc and manganese leaching efficiency and overall high zinc recovery (88%). Baba *et al.* (2009) studied the development of a combined hydro- and pyro-metallurgical route to recycling spent zinc-carbon batteries and found out that iron has been effectively separated by precipitation prior to extraction using ammoniacal solution. Sayilgan *et al*. (2009) studied leaching of battery samples by sulfuric and hydrochloric acids in the presence of oxalic acid as reducing agent. Ferella *et al.* (2010) extracted zinc and manganese from alkaline and zinc-carbon batteries using citric-sulfuric acid solution. Samuel and Gilbert (2010) carried out a preliminary inventory of pollutants entering into the local environment from exhausted portable batteries collected from the uncontrolled dumping in Younde, Cameroon and found that most of the non-rechargeable, exhausted batteries belong to the zinc-carbon (98.12 %) batteries class. Gega and Walkowiak (2010) evaluated the leaching behavior of zinc and manganese and their compounds of interest under different conditions and found that the leaching recovery of zinc and manganese increases with increasing sulfuric acid concentration. They also found out that the rate of zinc leaching is higher than that of manganese and the rate of both reactions increases with temperature as well as with a decrease of the solid/liquid ratio.

Khan and Kurny (2012) characterized spent zinc-carbon dry cell batteries to identify the potential of recovering values metal from these batteries and found out that the outer steel were tin-plated, and steel, zinc and manganese consisted of more than half the total weight of the spent batteries. Presence of small percentage of lead was found in both the zinc anode and electrolyte paste of the batteries. Sridhar and Hammed (2014) reviewed the current waste management

practiced in Nigeria and suggested strategies for its improvement. They recommended sustainable integrated waste management to achieve these specific waste management goals. Al Mahbub *et al.* (2014) did similar work. Zeytuncu (2015) studied the dissolution of alkaline batteries in reductive acidic media of sulfuric acid and sulfur (IV) oxide as reducing agent.

Dankwah *et al.* (2015) investigated the recycling of spent primary cells for the synthesis of spinel zinc manganese oxides ($ZnMn_3O_4$) using waste polypropylene as reductant in a domestic microwave oven and found traces of $ZnMn_2O_4$ and SiO_2 and uncombined ZnO and Mn_3O_4. Mihailova (2015) investigated the hydrometallurgical treatment of spent alkaline and zinc-carbon batteries and arrived at optimal values of leaching efficiency. Celikler and Aksan (2015) carried out an evaluation from an educational perspective of the effects of waste batteries on the environment and later proposed that waste batteries that have detrimental effects on the environment can be prevented by collecting them in containers specifically designed for waste batteries. Nindhia *et al.* (2016) investigated the reuse of carbon paste from spent zinc-carbon battery for biogas desulfurizer with clay as a binder and found out that carbon powder from spent zinc-carbon battery is an excellent desulfurizer.

2.12 Heavy Metal Effects.

Common story of lead, mercury and cadmium is that none has known useful function in biological organisms (E.P, 2002).

Lead is of most concern in particular due to the possible impacts on children. Lead influences the nervous system, slowing down nerve response. This influences learning abilities and behaviour. Children are exposed to lead right from their birth, as children in the embryonic stage receive lead from their mothers through the blood. Children are, furthermore, exposed to lead via dust

and soil contaminated by deposition from air and other sources. In the environment lead is known to be toxic to plants, animals and microorganisms. Effects are generally limited to specially contaminated areas.

Concerning mercury, the primary focus is on methyl mercury originating from the diet in particular through the consumption of fish and fish products. In humans, methyl mercury affects among other organs the brain, and it is documented that children in the embryonic stage receive mercury via the placenta causing persistent effects on children's mental development.

In the environment animals placed highly in the food chain and in particular the marine food chain are assumed to be exposed to mercury poisoning due to the ability of methyl mercury to concentrate via the food chain.

Cadmium accumulates especially in the kidneys leading to dysfunction of the kidney with increased secretion of e.g. proteins in urine (proteinuri) and other effects. Intake of cadmium is generally based on the diet, in particular vegetables and corn products. The concern of this pathway is based on the knowledge that an increase in the content of cadmium in agricultural soil will result in an increased uptake of cadmium by plants. However, for smokers the use of tobacco is of concern.

In the environment cadmium is reported toxic to especially animals and microorganisms. Also for animals kidney damage is the dominating effect. Concerning microorganisms, cadmium is known to significantly influence leaf litter decomposition.

Recycling of the heavy metals is generally regarded as a preferred option compared to incineration or landfilling as recycling may reduce the loss of heavy metals to the environment and at the same time avoid virgin heavy metals entry into circulation. No matter whether

recycling is the preferred option or not, a number of obstacles to increased collection and recycling of the heavy metals exists.

The strategy for minimization of the effects of heavy metals in waste is partly to reduce today and future environmental and human exposure to the heavy metals in the waste. Strategies for treatment of heavy metals apart from waste recycling has until now been based on two basic principles: dilution and retention.

Due to elemental nature of the metals, they will remain after treatment of the waste and will sooner or later be released to the environment. To prevent human and environmental exposure to the heavy metals at levels where harmful effects may occur, the metals are either diluted in large quantities of media or the release of the metals is retained. During the last decade, there has been a tendency away from the dilution strategy towards the retention strategy as exemplified by the application of flue gas cleaning technology.

The basis for the retention strategy is that by retaining the heavy metals, they can be released over time at a controlled and environmentally acceptable rate. This strategy may quite well apply to degradable substances or a situation where a limited amount of contaminated waste is produced within a limited space of time. But what will happen if there is a continued production of contaminated persistent waste over a wider space of time?

About 50% of global lead consumption is derived from recycled or reused materials; the figure is higher in Europe (60%) and the USA (70%) (Scoullos *et al.*, 2001). The main source of lead for recycling is used batteries. Lead may be used for small scale manufacturing of yatch keels, fishing equipment etc.

According to Masters (1997) about 700-900 tonnes/year of mercury was recycled globally of which about 200-400 tones originated from spent mercury-containing products, and the rest mainly coming from clor-alkali facilities.

Recovery of mercury is normally done by distillation in a closed system. The process is applied to most mercury containing wastes inclusive metallic mercury, batteries as well as residues from e.g laboratories. The volatile nature of mercury means that the greatest concern of the distillation process as well as other collection and recovery processes generally will be paid to the risk of air emission.

The total amount of cadmium recovered by recycling worldwide in 1998 is estimated at approximately 1500 tonnes (Scoullos *et al.,* 2001). Secondary cadmium production is based on recovery from flue gas filter dust, slag and residue arising from primary cadmium production as well as discarded materials and treatment of wastes and sludge. Most existing secondary production is from recycling of spent cadmium containing batteries.

2.13 Environmental Hazards of Household Batteries

Batteries contain heavy metals such as mercury, lead, cadmium, and nickel, which can pollute the environment when they are improperly disposed of. Cadmium, for example, can be toxic to aquatic invertebrates and can bio-accumulate in fish, which damages ecosystems and makes them unfit for human consumption. Some batteries, such as button cell batteries, also contain mercury, which has similar hazardous properties. Mercury is no longer being used in the manufacture of non-rechargeable batteries, except button cells where it is a functional component.

Batteries may produce the following environmental hazards:

i. Burning the batteries in public area will pollute the lakes and streams as the metals vaporize into the air when burned and it may cause burns or danger to eyes and skin.

ii. Landfilling batteries contribute to heavy metals that may potentially leach from solid waste landfills.

iii. Batteries waste in riverside will pollute the water with strong acid and make it unfit for drinking.

2.14 Cost of Recycling Waste

Uncertainty is associated with all future costs and benefits. Data from a variety of sources are combined and reasonable assumptions are made. Although recycling programs have become a key component in waste management policies of most nations around the world, recycling programs are in fact one of the most costly methods of waste disposal. According to Black (2006) "in San Jose, California, it costs $28 per ton to landfill waste compared with $147 a ton to recycle". He went further to say in Atlantic County, New Jersey, selling recyclable goods brings in $2.45 million. However, the cost of collecting and sorting these recycled materials plus interest payments on the recycling facility costs the county over $3 million. With the time, money, and energy spent collecting and processing recycled goods, the price of recycling is much higher than discarding waste into landfills or incinerators which in turn have adverse environmental effects. Figure 2.3 and Figure 2.4 shows trends in costs of zinc and manganese respectively



Figure 2.3: Recent trends in price of Zinc



Figure 2.3: Recent trends in price of Manganese

2.15 Battery Reprocessing

Batteries contain a range of metals which can be used as secondary raw materials. There are well-established methods for the recycling of most batteries containing lead, zinc, nickel-cadmium, nickel hydride and mercury. For some, such as newer nickel-hydride and lithium systems, recycling is still in the early stages.

There are a number of different recycling processes for batteries, which are aimed at recovering a variety of materials (Almeida *et al.*, 2006):

i. Lead can be recovered by either separating the different materials that make up the battery (lead, plastics, acid, etc.) prior to metallurgical processing. Alternatively, batteries can be processed as a whole through heat treatment in a particular type of furnace with metals being recovered at the end of this process.

ii. NiCd batteries can be reprocessed through a similar thermal technique, which recovers cadmium and iron-nickel for steel production.

iii. Batteries containing mercury (button cells) are most commonly processed using a vacuum-thermal treatment, in which the mercury vaporizes. It condenses when temperatures are reduced and can then be reintroduced into the material cycle.

iv. NiMH batteries are reprocessed by mechanically separating the individual materials (plastic, hydrogen and nickel) within a vacuum chamber to prevent the escape of hydrogen. The output of this process is a product with high nickel content which can be used in the manufacture of stainless steel.

v. Li-Ion batteries are currently reprocessed through hydrometallurgical routes to recover the primary metals.

vi. Zinc-carbon/air and alkaline-manganese batteries can be reprocessed using a number of different methods, which include smelting and other thermal-metallurgical processes to recover the metal contents (particularly zinc and manganese).

CHAPTER THREE

3.0 MATERIALS AND METHOD

3.1 Materials Used

Powder paste obtained from collected spent zinc-carbon batteries were used after dismantling the batteries. Chemical reagents used are Nitric acid (HNO_3) (16M concentration, 95% purity) and Hydrogen Peroxide (H_2O_2). These reagents were obtained from commercial chemical suppliers in Zaria town. Distilled water prepared in the Ahmadu Bello University Multiuser Laboratory was also used in chemical preparations and washing.

3.1.1 Equipment Used

The following are equipment used in the whole research process. Some of the equipment are seen in Plates I, II, III, IV, V and VI. They include:

i. Hotplate Magnetic stirrer (IKA C-MAG HS-7 220/240Volts, 1000W)
ii. Oven (Gallenkamp Hotbox Oven Size One, 220/240Volts, 2.3Amps, 50/60Hz)
iii. Suction pump (EDWARDS, SPEEDIVAC 2 Model A134-51-912 fitted with Tyco Electronics Campton Small Motors, 220-240Volts, 1425rpm 50Hz, Phase I, BS5000.III)
iv. Desiccators
v. Pliers, scissors, cutters and screwdrivers
vi. Gloves and masks
vii. Fume cupboard
viii. Mortar and pestle
ix. Pipette

x. Thermometer

xi. Conical flask

xii. Beakers

xiii. X-Ray Fluorescence (XRF) machine ((RIGAKU-ZSX PRIMERS XRF Machine (IMMM) 220/240V 50/60Hz)

xiv. Atomic Absorption Spectrophotometre (AAS) machine (Varian AA-240FS 220/240V 50/60Hz)

xv. Funnel and filter papers

xvi. Sieve (BS410/1986 Stainless Steel, brass aperture 355 micrometer)

xvii. Digital weighing balance (Denver InstrumentsXP-600 15Volts D.C 100mA)

xviii. Plastic containers

xix. Masking tape

xx. Measuring cylinder

3.2 Methods

This research was carried out according to procedures described by Khan and Kurni (2012), Shalchian *et al.,* (2014), Mihailova (2015). Figure 3.1 shows a summary of the workflow of the treatment process. The following steps were followed:

i. Sample collection, separation and dismantling

ii. Leaching and filtration of samples

iii. Analyses of leached and unleached samples using AAS and XRF

iv. Analysis of Variance (ANOVA) of AAS results

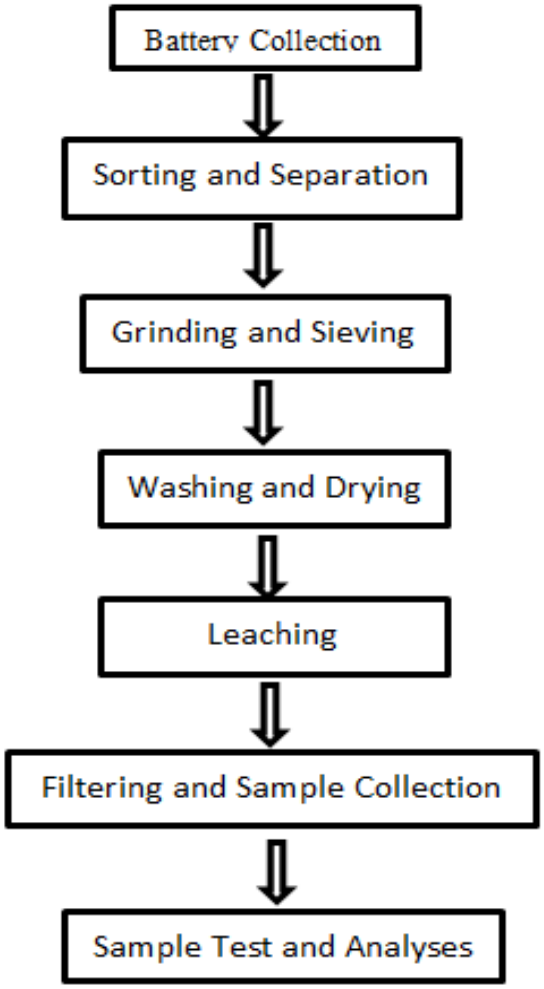


Figure 3.1: Workflow of Treatment Process of the Spent Zinc-carbon Battery

3.2.1 Pretreatment and Characterization

The pretreatment and characterization of the samples involved batteries collection, separation, dismantling, weighing, moisture content determination, grinding and sieving. Spent zinc-carbon batteries of the commercially available and most common Tiger Brand batteries (sizes AAA, AA and D types) were collected from streets, residents and dump sites/refuses of Samaru area of Sabon-Gari Local Government, Kaduna State. About 3077 pieces (9231g) of zinc-carbon batteries of combined sizes obtained were manually and carefully dismantled and separated into different component parts (rods, plastics, papers, steel covers, carbon powder, etc.) using pliers, cutters, screwdrivers and hammers. These components were later weighed using digital weighing balance and the carbon powder were poured into a black polythene bag to prevent light penetration and stored for subsequent process analyses.

Powder paste sample weighing 5838.92g was extracted from the dismantled batteries. The average weight of component parts, moisture content of carbon powder, particle size by grinding and sieving, composition of powder by XRF analysis were determined afterwards.

Weight of all component parts were taken using digital weighing balance (Denver Instruments XP-600). The weighing tray was clean of dirt and other particles and was set to zero reading after which each battery component was weighed. This was repeated for every weight measurement and records taken.

Moisture content of carbon powder was determined after weighing and oven-drying. This was done by recording the weight and then drying in the oven (Gallenkamp Hotbox Oven) at 110 ^{0}C until a constant weight was attained by checking weight every day. This took about four days

because of unstable power supply. The powder was always placed in the desiccator when not in use so as to avoid absorption of moisture from the environment (see Plate I).

After complete drying, the powder sample which was in clods was ground using agate mortar and pestle after which it was sieved using 355 micrometer sieve. The essence of grinding and sieving is to increase surface area of contact for effective dissolution during leaching as well as to have a homogenous particle size distribution. A fine fraction of the powder was taken for XRF analysis.

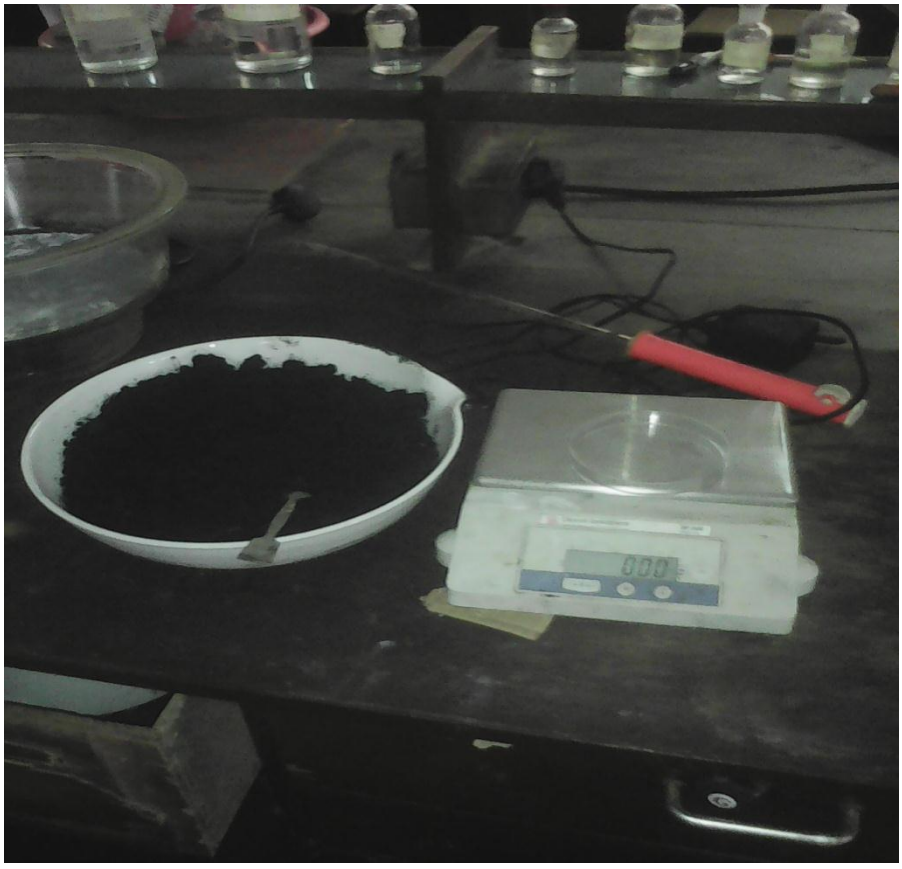


Plate I: Dry Carbon Battery Sample Removed from Desiccator ready for Weighing

3.2.2 Leaching Test

Leaching test was conducted in two stages:

i. Neutral leaching stage and

ii. Acid leaching stage

In the neutral leaching stage, the dry homogenous carbon powder sample was washed in distilled water (prepared and collected from the Multi User Science Research Laboratory, Department of Chemistry Ahmadu Bello University, Zaria.) and continuously stirred for 1hour at 60^0C after which the mixture was filtered. The filtered residue was oven-dried at 110^0C for about seven days until completely dry and was used in acid leaching stage. A fraction of the filtered residue was also collected for XRF analysis. The washing is to avoid interference due to salts which reduces process yield. Also, salt removal from the powder is to reduce acid consumption during acid leaching test.

Acid leaching involves the dissolution of the homogenous powder in a selected and suitable acid of known concentration. For this research, nitric acid (HNO_3) was the chosen solvent with hydrogen peroxide (H_2O_2) as the reducing agent. Independent factors which include nitric acid concentration, hydrogen peroxide concentration, temperature, stirring speed, time and solid/liquid ratio were studied and were the variables in some range. During acid leaching, these variable factors took the following conditions as shown in Table 3.1.

Table 3.1: Parameters studied in acid leaching process

Experiment Number	**Parameters studied**	**Parameter value**	**Constant Parameters**
1	HNO_3 Concentration	1.0M	Temp.60^0C, H_2O_2 Conc.5%, Stirring Speed 400rpm, Solid/Liquid ratio 1:5, Time 1.5hours
2		2.0M	
3		3.0M	
4	H_2O_2 Concentration	3%	Temp.60^0C, HNO_3 Conc.2M, Stirring Speed 400rpm, Solid/Liquid ratio 1:5, Time 1.5hours
5		5%	
6		10%	
7	Temperature	40^0C	HNO_3 Concentration 2M, H_2O_2 Conc.5%, Stirring Speed 400rpm, Solid/Liquid ratio 1:5, Time 1.5hours
8		60^0C	
9		80^0C	
10	Stirring Speed	200rpm	HNO_3 Concentration 2M, H_2O_2 Conc.5%, Temperature 60^0C, Solid/Liquid ratio 1:5, Time 1.5hours
11		400rpm	
12		600rpm	
13	Solid/Liquid ratio	1:5	HNO_3 Concentration 2M, H_2O_2 Conc.5%, Stirring Speed 400rpm, Temperature 60^0C, Time 1.5hours
14		1:10	
15		1:15	
16	Time	1hour	HNO_3 Concentration 2M, H_2O_2 Conc.5%, Stirring Speed 400rpm, Temperature 60^0C, Solid/Liquid ratio 1:5
17		1.5hours	
18		2hours	

All chemicals used were of analytical reagent (AR) grade. They include

1. Nitric acid (HNO_3) 16M
2. Hydrogen peroxide

These chemicals were prepared into solutions of desired concentrations.

For nitric acid

$$M_1V_1 = M_2V_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (13)$$

Where

M_1 is molarity of concentrated acid = 16M

V_1 is volume of concentrated acid

M_2 is molarity of dilute acid = 1M, 2M and 3M

V_2 is volume of dilute acid = 2litres

For hydrogen peroxide

3% = 97ml distill water + 3ml H_2O_2

5% = 95ml distill water + 5ml H_2O_2

10% = 90ml distill water + 10ml H_2O_2

Having prepared chemicals to the required concentration, the mixture was poured into a conical flask and placed on a hotplate magnetic stirrer and allowed to heat up to 40^0C by observing with a thermometer. At the required temperature, stirring was activated at 200rpm for 1hour (see

Plates III and IV). After heating and stirring simultaneously for 1hour, the process was stopped, removed from the hotplate and allowed to cool. Cooling is important so as to avoid precipitation during filtration. The mixture was then filtered using a filter paper, funnel and suction pump (see Plate VI). The filtrate was collected in washed plastic containers and taken for quantitative analysis using Atomic Absorption Spectrophotometer (AAS). The same process was carried out for different parameter values until all parameters variables were determined.



Plate II: Concentrated Chemical Reagent Grade (RG) Used



Plate III: Prepared Dilute Chemical Reagent Grade (RG) Used



Plate IV: Measuring Chemical Amount for Digestion

z 

Plate V: Sample Mixture Setup Ready for Digestion



Plate VI: Filtration of Digested Mixture

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 Pre-treatment and characterization

Sample of zinc-carbon batteries collected were dismantled and separated into different component parts as shown in Table 4.1. It is seen that carbon paste has the highest percentage weight (52.83 %), metallic parts has 29.91 %, plastic and membrane 6.33 %, other parts 8.22 % and 2.71 % loss. Similar result was obtained by Shalchian *et al.* (2014), Shin *et al.* (2008), Khan and Kurni (2012) and Zeytuncu (2016). The paste moisture content was also determined after oven-drying to constant weight and found to be 13%. This is similar to results obtained by Bartolozzi *et al.* (1994) (11.2 %) and Khan and Kurni (2012) (12.32 %). It is also seen that the spent zinc-carbon batteries are heavier in weight than new. This may be due to swelling of discharged battery elements as well as foreign particles at dump sites.

Table 4.1: Average weights of components of new and used zinc-carbon batteries

s/n	Component	Size AAA		Size AA		Size D	
		New (gram)	Used (gram)	New (gram)	Used (gram)	New (gram)	Used (gram)
1	Whole Battery	7.30	7.34	17.45	17.82	90.02	91.63
2	Metallic Parts	2.183	2.195	5.219	5.330	26.92	27.41
3	Powder Paste	3.857	3.878	9.219	9.414	47.56	48.41
4	Plastic & Membrane Parts	0.462	0.465	1.105	1.128	5.70	5.80
5	Other Parts	0.600	0.603	1.434	1.465	7.40	7.53
6	Loss	0.198	0.199	0.473	0.483	2.44	2.48

Table 4.2: Average percentage weight of component of used zinc-carbon batteries

Component Parts	Weight (%)
Metallic part	29.91%
Battery paste	52.83%
Plastic and membrane	6.33%
Others	8.22
Loss	2.71%

Result of the XRF analysis is presented in Table 4.3. It is observed that values of zinc and manganese in the washed samples increased compared to the unwashed and constitute about 45% of the metal content of the paste. Washing results in salt (chlorine) removal which interfered with spectrophotometer reading, hence the expressive increase in Mn and Zn values. Removal of salt also reduces acid consumption during leaching. The presence of salt in the sample is attributed to the ammonium chloride and/or zinc chloride in the electrolyte paste of the battery. Ferella et al (2006), Veloso et al (2005) and De Souza and Tenorio (2004) reported similar results.

Table 4.3: Elemental Composition of Samples using X-Ray Fluorescence (XRF)

Element	Sample 1 (Unwashed) (%)	Sample 2 (Washed) (%)
Mg	BDL	BDL
Al	1.363	1.833
Bal	44.935	38.72
Si	4.362	5.024
P	BDL	BDL
S	0.07	0.079
Cl	**6.912**	**2.442**
K	0.307	0.281
Ca	0.383	0.203
Ti	0.045	0.069
V	BDL	0.014
Cr	0.017	0.023
Mn	**18.861**	**30.408**
Fe	3.716	6.277
Co	BDL	BDL
Ni	0.014	0.025
Cu	0.01	0.01
Zn	**14.77**	**18.326**
As	0.003	0.006
Se	BDL	BDL
Rb	BDL	BDL
Sr	0.012	0.012
Zr	0.002	0.003
Nb	BDL	BDL
Mo	BDL	BDL
Pd	BDL	BDL
Ag	BDL	BDL
Cd	0.004	BDL
Sn	BDL	BDL
Sb	BDL	BDL
Ba	0.175	0.214
W	BDL	BDL
Au	BDL	BDL
Pb	0.03	0.029
Bi	BDL	BDL
Total	99.991	99.998

BDL= Below Detection Level

4.2 Leaching Effects of Studied Parameters on Metals Extraction

Electrolyte paste of the spent battery was leached in nitric acid. A small amount of hydrogen per oxide was added to nitric acid. Hydrogen per oxide acts as a reducing agent for manganese in presence of manganese dioxide in solution. Particle size was kept at a fixed value in all the experiments. Table 4.4 is AAS results of the vale metals (zinc and manganese) recovered as well as possible trace of heavy metals (mercury, lead and cadmium) detected. The effect of nitric acid concentration, hydrogen peroxide concentration, temperature, stirring speed and solid/liquid ratios and time were determined in the leaching experiment. The different variable parameters and their influence on leaching experiments are discussed below.

Table 4.4: AAS result of recovered metal concentration in leached samples

Sample ID	Hg (mg/l)	Pb (mg/l)	Cd (mg/l)	Zn (mg/l)	Mn (mg/l)
Sample 1	0.153	0.802	2.361	1225.648	18042.67
Sample 2	0.209	0.139	1.493	1363.597	16286.91
Sample 3	0.000	0.294	2.195	1165.097	15253.57
Sample 4	0.011	0.159	1.437	1112.213	1189.996
Sample 5	0.000	0.164	1.061	4788.323	8443.77
Sample 6	0.077	0.204	1.308	1991.45	7707.73
Sample 7	0.020	0.293	2.164	3436.144	8383.24
Sample 8	0.000	0.233	1.543	2788.212	7793.69
Sample 9	0.064	0.295	2.391	4149.492	8560.65
Sample 10	0.031	0.263	0.62	1677.464	8365.43
Sample 11	0.119	0.235	0.324	678.051	5452.61
Sample 12	0.238	0.292	1.182	2189.564	4085.55
Sample 13	0.170	0.296	1.334	3177.882	3969.96

Table 4.5: ANOVA result of recovered value metals concentration in leached samples

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Zn(mg/l)	13	29743.137	2287.934	1647160.384
Mn(mg/l)	13	949469.006	73036.077	53737316085

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	32534449004	1	32534449004	1.211	0.282	4.260
Within Groups	6.449E+11	24	26869481623			
Total	6.774E+11	25				

Table 4.5 shows the results for the amount of zinc and manganese extracted from the sample leaching experiment. Important aspects of the analysis of variance (ANOVA) tables are the between groups, within groups, total variation, sum of squares, degree of freedom, mean square, F-statistic, P-value and F-critical.

With P-value = 0.282 which is greater than the agreed significance level ($\alpha = 0.05$), the null hypothesis (which assumed that there is no significant difference between the means of amount of zinc and manganese extracted) will not be rejected.

4.2.1 Effect of Nitric Acid Concentration on Metal Extraction from Paste solution

Washed zinc-carbon battery powder was treated with nitric acid (HNO_3) by setting its concentrations at 1M, 2M and 3M. During the treatment, hydrogen peroxide (H_2O_2) concentration, temperature, stirring speed, solid-liquid ratio and time were kept constant at 5%,

60^0C, 400rpm, 1:5 and 1.5hr respectively. As can be seen from Table 4.5, the recovery of zinc increased with increase in HNO_3 concentration up to 2M. At 3M concentration, it dropped, hence there was no need to increase acid concentration since high dissolution yield is realized at 2M concentration. This can be said to be the optimum concentration for zinc extraction.

The dissolution of manganese also did not show significant increase in its yield. It is therefore more economical to dissolve manganese at 1M concentration of HNO_3 with given conditions of other given parameters. A similar trend of effect of sulfuric acid concentration on extraction of zinc and manganese from used zinc-carbon battery was observed by Khan and Kurni (2012) and Gega and Walkowiak (2011). It is therefore understood that acid concentration affects zinc and manganese dissolution considerably.

Table 4.6: Amount of Metals Extracted with Nitric Acid Concentration

HNO_3 Concentration	**Amount Extracted/Dissolved (ppm)**	
	Zinc	**Manganese**
1M	1225.648	18042.67
2M	1363.597	16286.91
3M	1165.097	15253.57

4.2.2 Effect of Hydrogen peroxide Concentration on Metal Extraction from Paste solution

Hydrogen peroxide is an oxidizing agent, but in the presence of stronger oxidizing agent such as MnO_2 and Mn_2O_3 it serves as reducing agent. After varying its concentration to 3%, 5% and 10% while keeping nitric acid concentration at 2M, solid-liquid ratio at 1:5, temperature at 60^0C and time at 1.5hr, zinc dissolution greatly increased. The dissolution increased up to 4700ppm (at 3% H_2O_2) from 1112ppm (at 10 % H_2O_2). But this is not the case in the dissolution of manganese. It increased from 3% to 5% and significantly decreased at 10 %. This may be due to swelling in the

carbon paste by formation of carbon dioxide (CO_2) in the mixture (Khan and Kurni, 2012). According to Zeytuncu (2016), zinc dissolution is not dependent on the amount of reducing agent, but because it can improve the leaching power of the media, perhaps the expressive increase in zinc dissolution.

Table 4.7: Amount of Metals Extracted with Hydrogen peroxide Concentration

H_2O_2 Concentration	**Amount Extracted/Dissolved (ppm)**	
	Zinc	**Manganese**
3%	1112.213	1189.996
5%	1363.597	16286.91
10%	4788.323	8443.77

Probable Reaction Equations due to nitric acid and hydrogen peroxide effects are as follows:

$$Mn + 2HNO_3 \rightarrow Mn(NO_3)_2 + H_2 \quad \text{(14)}$$

$$Zn + 2HNO_3 \rightarrow Zn(NO_3)_2 + H_2 \quad \text{(15)}$$

$$MnO_2 + 2HNO_3 + H_2O_2 \rightarrow Mn(NO_3)_2 + 2H_2O \quad \text{(16)}$$

$$Mn_2O_3 + 2HNO_3 + H_2O_2 \rightarrow 2Mn(NO_3)_2 + 2H_2O \quad \text{(17)}$$

4.2.3 Effect of Temperature on Metal Extraction from Paste solution

Effect of temperature was determined at 40^0C, 60^0C and 80^0C while keeping nitric acid concentration, hydrogen peroxide concentration, stirring speed, solid-liquid ratio and time fixed. As can be seen from Table 4.8, zinc dissolution increases with increase in temperature up to 80^0C. Above this temperature, it may drop as was observed by Khan and Kurni (2012) and Souza et al (2001).

The dissolution of manganese was fast during leaching, rising rapidly from 7707.73ppm at 40^0C to 16286ppm at 60^0C. However, at 80^0C, manganese dissolution fell drastically. The drastic fall may probably be due to hydrogen peroxide decomposition at higher temperature (Khan and Kurni, 2012). The result therefore shows that higher dissolution of zinc can be achieved by increasing temperature up to 80^0C -100^0C (Zeytuncu, 2016).

Table 4.8: Amount of Metals Extracted with Temperature

Temperature	**Amount Extracted/Dissolved (ppm)**	
	Zinc	**Manganese**
40^0C	1363.597	7707.73
60^0C	1991.450	16286.91
80^0C	3436.144	8383.24

4.2.4 Effect of Stirring speed on Metal Extraction from Paste solution

Stirring speed effect on the dissolution of zinc and manganese was investigated at 2M nitric acid concentration, 5% hydrogen peroxide concentration, 60^0C temperature, 1:5 solid-liquid ratio and 1.5hr time. It was varied from 200rpm to 600rpm. For both zinc and manganese dissolution, there was increase with increase in stirring speed from 200rpm to 400rpm. At speed above 400rpm, it may be difficult to get high dissolution because of the high tendency of the mixture to spill; hence 400 rpm is the optimum stirring speed for the process (Khan and Kurni, 2012).

Table 4.9: Amount of Metals Extracted with Stirring speed

Stirring Speed	Amount Extracted/Dissolved (ppm)	
	Zinc	Manganese
200rpm	2788.212	7793.69
400rpm	4149.492	16286.91
600rpm	1363.597	8560.65

4.2.5 Effect of Solid-liquid Ratio on Metal Extraction from Paste solution

As with the previous parameters discussed, the effect of solid-liquid ratio was investigated at various values while keeping other parameter values constant. At 1:5 solid-liquid ratios, the dissolution of both zinc and manganese was observed to drop. In the case of zinc, drop was gradual until at 1:15 while in manganese it was sudden. The reason for the drop in amount of zinc and manganese dissolved may perhaps be related to decrease in the molar concentration of the reactants, Shin et al (2008), (Khan and Kurni, 2012) and Mihailova (2015).

Table 4.10: Amount of Metals Extracted with Solid/Liquid Ratio

Solid-Liquid Ratio	**Amount Extracted/Dissolved (ppm)**	
	Zinc	**Manganese**
1:5	1677.464	16286.91
1:10	1363.597	8365.43
1:15	678.051	5452.61

4.2.6 Effect of time on Metal Extraction from Paste solution

At various time intervals keeping other given parameter values constant, the effect of time was determined. Although the results do not perfectly agree with the expected behavior i.e increase in dissolution amount with time, the results at 1.5hr seem to have the optimum yield in nearly all experiments. This agrees with findings by Mihailova (2015).

Table 4.11: Amount of Metals Extracted with Time

Time	Amount Extracted/Dissolved (ppm)	
	Zinc	Manganese
1hr	1363.597	4085.59
1.5hr	2189.564	16286.91
2hrs	3177.882	3969.96

4.3 Highest and Optimum Dissolution Conditions

High dissolution yield does not necessarily mean optimum dissolution. Optimum dissolution implies highest possible yield with least amount of chemical and/or energy requirement since recycling tries to cut cost.

Therefore, highest amount of zinc dissolved was observed at 2M HNO_3, 10% H_2O_2, 60^0C, 400rpm, 1:5 S/L ratio and 1.5hrs. Conditions which yielded 4788.323ppm (4788.323mg/lit) of zinc. Highest quantity of manganese dissolved was observed at 1M HNO_3, 5% H_2O_2, 60^0C, 400rpm, 1:5 S/L ratio and 1.5hrs with yield of 18042mg/lit.

The optimum condition for simultaneous dissolution of zinc and manganese is 1M nitric acid concentration, 5% hydrogen peroxide, 60^0C, 400rpm, 1:5 S/L ratio and 1.5hrs with a yield of 1225.648 mg/lit zinc and 18042.67 mg/lit manganese.

4.4 Cost Estimate for Recycling Zinc-Carbon Batteries

The study also examined the costs and benefits of recycling zinc-carbon battery using nitric acid to address the issues of economic costs and benefits of diverting zinc-carbon batteries waste streams from current disposal practice. It also looks into the economic effect of recovery level of this battery in terms of costs and benefits comparison. Table 4.12 and shows the cost estimate of the recycling process carried out. All costs were as at September 2016.

Table 4.12: Cost Estimate of Zinc-Carbon Batteries Recycling

s/n	Item	Rate	Quantity	Total Cost
1	HNO_3	N3000/litre	0.25 litre	N750.00
2	H_2O_2	N3000/litre	0.1 litre	N3000.00
3	Electricity	N26.37/unit	160kWhr	N2,109.60
4	Waste Battery Collection		3077 pieces	N2,000.00
5	Overall Coat	N1,500	1 piece	N1,500.00
6	Plastic Container	N50/piece	25 pieces	N1,250.00
7	Nose mask	N100/piece	10 pieces	N1,000.00
8	Hand Gloves	N100/piece	10 pieces	N1,000.00
9	Use of laboratory and other equipment			N15,000.00
		Total		N27,609.60

Table 4.13: Comparison of Cost of Recycling and Market Value of Recovered Metals

Metal	Quantity Recovered (g/lit)	*Cost of Recovered Metals/g	*Cost of Recovered Metals/kg	*Cost of Virgin Metals
Zinc	4.788	N4.32	N902.26	N900.44/kg
Manganese	18.042	N10.59	N587.96	N586.38/kg

*Market cost as at March, 2017 for zinc and as at December 2016 for manganese

Table 4.12 shows the estimated cost of the recycled zinc-carbon batteries using nitric acid and hydrogen peroxide. The total cost is N27,609.60. About 9321g of battery powder was generated from 3077 pieces of batteries dismantled. At the end 4.788 g/lit of zinc and 18.042 g/lit of manganese were recovered. According to online market price source, Infomine (2017), the price

of zinc as at March, 2017 is N900.44/kg and N587.38/kg as at December, 2016 for manganese. As mentioned in the study limitations, the recovered metals are in solution form, and if they were to be further treated and the same amount of the metals solution be obtained in solid form, it means 0.0048 kg of zinc and 0.018 kg of manganese is recovered. This will imply N902.26 worth of zinc and N587.96 worth of manganese (Table 4.13). Looking at the energy, time and money spent in the whole recycling process, it is obvious buying virgin metals is less costly economically. Despite the high costs of recycling, proponents of recycling argue that the environmental and health benefits of recycling outweigh the economic costs. Recycling advocates believe that recycling is more than just an issue of economics; it is essential to caring for human health (which is wealth) and environmental sustainability. Therefore, because of the environmental and health benefits of recycling to its high costs, nations must offset several of the cost of recycling, hence, waste reduction techniques such as reducing and reusing must become a commonplace component of these countries' waste management.

CHAPTER FIVE

5.0 SUMMARY, CONCLUSION AND RECOMMENDATIONS

5.1 Summary and Conclusion

This work was done to investigate the recovery potential of value metal (zinc and manganese) from used zinc-carbon battery paste. It has been carried out by separation and dismantling of spent zinc-carbon batteries, leaching and analyzing sample collected.

The characterization involves collection, sorting, sieving, weighing, moisture content determination and XRF analysis of the paste powder. Leaching consists of dissolving the washed sample in prepared acid solution by stirring at a given temperature, time, solid-liquid ratio and concentration after which it was filtered. Lastly, the filtered samples were quantitatively analyzed using AAS. The following conclusions were drawn from the results obtained:

i. The powder paste constitute 52.83% of the total battery weight and has 13% moisture content;

ii. Zinc and Manganese are 48.73% of the total weight of the electrolyte paste and can be substantially recovered by leaching;

iii. The optimum conditions for selective dissolution of zinc is 2M nitric acid concentration, 10% hydrogen peroxide, 60^0C, 400rpm, 1:5 S/L and 1.5hrs, which yielded 4788.323 g/lit. For manganese it is 1M nitric acid, 5% hydrogen peroxide, 600C, 400rpm, 1:5 S/L ratio and 1.5hrs giving a yield of 18042.67 g/lit;

iv. The optimum condition for simultaneous dissolution of zinc and manganese is 1M nitric acid concentration, 5% hydrogen peroxide, 60^0C, 400rpm, 1:5 S/L ratio and 1.5hrs with a yield of 1225.648 g/lit zinc and 18042.67 g/lit manganese;

v. Traces of heavy metals such as lead (Pb), cadmium (Cd) and mercury (Hg) were detected;

vi. It was discovered that cost of recycling zinc-carbon batteries in the presence of nitric acid and hydrogen peroxide to recover zinc and manganese is higher than buying the ore (virgin) metals. However, the environmental impact in terms of limited natural resources depletion and the introduction of hazardous metals makes recycling a better option that cannot be compromised.

5.2 Recommendations

Having carried out the investigation and drawn the above conclusions, the following recommendations are given for further research:

i. Further study can be carried out to investigate the feasibility of recycling other component parts of the used battery such as plastics, metals, papers, etc.

ii. Research can be carried out to recycle a mixture of both zinc-carbon and alkaline batteries' powder using nitric acid and other mineral acids since they have almost the same chemical content.

iii. A project can be undertaken to investigate the application of these recovered metals (zinc and manganese) in other manufacturing processes such as battery production, medicine, water treatment, etc.

iv. Study can be done on the separation and purification of the value metals from the solution.

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