RECOVERY OF SILVER FROM SILVER OXIDE BATTERIES:
A COMBINED EXPERIMENTAL AND COMPUTATIONAL STUDY

A MASTER'S THESIS

in

Chemical Engineering and Applied Chemistry

Atılım University

by

ABUBAKR BUSHRA ALİ MEHASİ

MAY 2017

RECOVERY OF SILVER FROM SILVER OXIDE BATTERIES: A COMBINED EXPERIMENTAL AND COMPUTATIONAL STUDY

A THESIS SUBMITTED TO

THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

OF

ATILIM UNIVERSITY

BY

ABUBAKR BUSHRA ALİ MEHASİ

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE

IN

THE DEPARTMENT OF CHEMICAL ENGINEERING

AND APPLIED CHEMISTRY

MAY 2017

Approval of the Graduate School of Natural and Applied Sciences, Atılım University.

____

Prof. Dr. İbrahim Akman

Director

I certify that this thesis satisfies all the requirements as a thesis for the degree of Master of Science.

____

Prof. Dr. Atilla Cihaner

Head of Department

This is to certify that we have read the thesis “Recovery of silver from silver oxide batteries: A combined experimental and computational study” submitted by “Abubakr Bushra Ali Mehasi” and that in our opinion it is fully adequate, in scope and quality, as a thesis for the degree of Master of Science.

____

Assist. Prof. Dr. Hakan Kayı

Supervisor

Examining Committee Members

Assoc. Prof. Dr. Murat Torun _______________________

Assoc. Prof. Dr. Seha Tirkeş _______________________

Assist. Prof. Dr. Hakan Kayı _______________________

Date: May 12, 2017

I declare and guarantee that all data, knowledge and information in this document has been obtained, processed and presented in accordance with academic rules and ethical conduct. Based on these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Name,Lastname: ABUBAKR BUSHRA ALİ MEHASİ

Signature:

ABSTRACT

RECOVERY OF SILVER FROM SILVER OXIDE BATTERIES: A COMBINED EXPERIMENTAL AND COMPUTATIONAL STUDY

Mehasi, Abubakr Bushra Ali
M.S, Chemical Engineering and Applied Chemistry
Supervisor: Assist. Prof. Dr. Hakan Kayı
May 2017, 42 pages

The purpose of this study is to recover pure silver from inactive and used silver oxide batteries and also model this process by using a software. Because, after the life cycles of batteries end, they become toxic contaminants and also yield incinerator emissions and ash.

Silver oxide batteries are used in wristwatches, clocks, remote controls of the various electronic devices, hearing aid devices, toys, and some other devices, and they are scrapped after they become spent. In this thesis, we collected spare batteries that contain silver and we use solid-liquid leaching as a separation process to recover the silver.

In our approach, we used leaching with nitric acid and precipitated silver by the help of copper plate and potassium chloride. Then after precipitate filtration, it was dried and then powder was smelted in a very high temperature (1000 °C) to produce metallic silver and also highly pure silver powder. Recovered silver can be utilized directly in different industrial applications.

Keywords: silver oxide batteries, modeling, leaching, silver recovery

ÖZ

GÜMÜŞÜN GÜMÜŞ OKSİT PİLLERDEN GERİ KAZANIMI: BİRLEŞİK BİR DENEYSEL VE HESAPLAMALI ÇALIŞMA

Mehasi, Abubakr Bushra Ali

Yüksek Lisans, Kimya Mühendisliği ve Uygulamalı Kimya

Tez Yöneticisi: Yrd. Doç. Dr. Hakan Kayı

Mayıs 2017, 42 sayfa

Bu çalışmanın amacı saf gümüşü aktif olmayan ve kullanılmış gümüş oksit pillerden geri kazanmak ve aynı zamanda bu süreci bir bilgisayar yazılımı ile modellemektir. Çünkü piller hayat döngüleri bittikten sonra toksik kirleticiler haline gelirler ve yakma fırını emisyonları ve kül açığa çıkartırlar.

Gümüş oksit piller, kol saatleri, saatler, çeşitli elektronik cihazların uzaktan kumandaları, işitme cihazları, oyuncaklar, ve bazı diğer cihazlarda kullanılır ve ömrü bittikten sonra atılırlar. Bu tezde, gümüş içeren atık piller toplandı ve gümüşü geri kazanmak için katı-sıvı özütlemesi bir ayırma işlemi olarak kullanıldı.

Yaklaşımımızda, nitrik asit kullanarak katı-sıvı özütlemesi yapıldı ve gümüş, bakır plaka ve potasyum klorür yardımıyla çöktürüldü. Çökeltinin süzülmesinden sonra bu çökelti kurutuldu ve sonra da metalik gümüş ve aynı zamanda yüksek saflıkta ince bir gümüş tozu elde etmek için çok yüksek bir sıcaklıkta (1000 °C) eritildi. Geri kazanılan gümüş, çeşitli endüstriyel uygulamalarda doğrudan kullanılabilir.

Anahtar kelimeler: gümüş oksit piller, modelleme, katıdan özütleme, gümüşün geri kazanımı

DEDICATION

To My Parents

ACKNOWLEDGMENTS

I would like to express my gratitude to my supervisor *Assist. Prof. Dr. HAKAN KAYI* for his support and guidance during my research. Her challenging approach in publication and presentation of the researches has profoundly influenced me. I am very grateful to him for his guidance, valuable advice throughout this study, for sharing his related experiences and opening his laboratory in which I feel like at home. His approach in solving problems will sure help me in my future academic life.

I would like to express my sincerely acknowledgements to my family and my friends for their fruitful help during the progress of my study.

Finally, I would like to extend my gratitude and offer sincere thanks to my parents, my brothers and my sisters for their continuous support during this period.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

For more than five thousand years, beauty of silver has had important role in the different sides of human life [1].

The accelerating high demand for electronic devices led to a progressive increase in the global demand for silver, and the global production of silver was around 25,000 metric tons in 2014. Compared to gold and platinum, silver is a less expensive, as silver presents limited amounts in the earth's crust and mostly connected with the ores of Cu, Zn, Pb, and Au [1].

Silver is mostly obtained from natural sources in general, as a byproduct with zinc, and co-produced with gold, lead, copper, etc. from metal processes. Recently it was noticed that the silver production costs increased suddenly, and the natural resource of silver decreased. The price of silver in markets has started to decrease although an the applications of silver has increased, such as, catalysis, silverware, photography, electrical, biomedical photonics, dental material, jewelry, radiography, batteries, electronics, medicines, food/beverages processes and disinfectants in wastewater treatment. Due to the increase of all their industries and the market demand for silver, scientists have been intense, studying the recovery and removal of silver [1]. The recovery of silver from spent source, poses an acute problem, while new economically, environmentally clean and more efficient, technologies are being used. The policy against environmental pollution of silver ion toxicity, have been phenomenally increased, because silver ion toxicity through chains for the microbial, vertebrate and invertebrate communities (including humans), have been causing a number of disorders and diseases [1].

Sources up to ppm level have been spent, as the recovery and removal of the silver ions (Ag^{+}) from industrial efflux, have become of great concern. Furthermore, environmentally and economically, recovery of silver is very important. Biometallurgical and hydrometallurgical routes have been used in the reclaim and recovery of silver. The first step of the hydrometallurgical method is leaching. Silver is recovered by various techniques which include, cementation, chemical precipitation, ion exchange, adsorption, electrocoagulation, biosorption, and extraction, etc.. These techniques are, indeed, quite important and cost effective with regards to silver recovery and extraction processes [1].

In order to solve stacking problems and to miniaturize battery packs, button cells were developed. These batteries are nowadays used in watches, clocks, toys, hearing aids, and thermometers, etc., among others, due to their high capacity per unit weight and long operation life**.** Zinc metal converts to zinc oxide and the silver oxide reduce to metallic silver when the battery is in use, and eqn(3) is given to the overall reaction as follows [2]:

$Ag_2O + H_2O + 2e^- \rightarrow 2Ag + 2OH^-$ (1)
$Zn + 2OH^- \rightarrow ZnO + H_2O + 2e^-$ (2)
Overall reaction: $Ag_2O(s) + Zn \rightarrow 2Ag + ZnO(s)$ (3)

On worldwide markets, the accumulation of used silver oxide batteries have been a broad pattern to their financial value. Because of the environmental point and financial reasons, battery recycling will be essential. There are only a couple of plants for battery recycling is available globally, and these plants apply for their own recycling procedures to recycle the important parts especially metals from used batteries, and they provide removal of some hazardous components in a safe way**.** It may be additionally known that used silver oxide batteries, might a chance to be fast sort program toward size. For instance mercury is distilled, toward those foray about silver oxide batteries in a Swiss battery recycling plant, and furthermore, silver is recovered after the sending of the remaining material to their silver recover refinery [1].

1.1. Electric Battery

An electrical battery works by converting chemical energy stored into electrical energy through built-in two or more electrochemical cells. Each cell contains a cathode and an anode [3]. The positive terminals have higher electrical energy than the negative ones, and are the source of electrons. Energy is produced when the electrons are connected to an external circuit and the energy will be delivered to an external device. Electrolytes gain the ability to move as ions. When the battery is connected to an external circuit, which allows the completion of the chemical reactions at apart terminals, and energy is transferred to the external circuits [4]. The current flows out the battery to perform the work due to the movement of the ions within the battery [4]. Single cells are also called batteries, although it is technically known that the name battery is given to devices with multiple cells [5].

Single or disposable batteries are referred to as primary batteries. These batteries are only used one time and then discarded, and during the discharge, electrode materials change irreversibly. Alkaline batteries which are mostly used in many different portable devices and flashlights are the common examples of primary batteries [6].

Rechargeable batteries are referred to as secondary batteries. It is possible to discharge and recharge this type of batteries multiple times, and the reverse current can restore the original composition of the electrodes. Lead acid batteries used in automobiles, trucks, etc., and the lithium ion batteries which are used in moveable devices are the examples of the secondary batteries. There are different size and shapes of batteries, from small button cell type used in hearing aids and wristwatches to room size battery banks which are normally used for telephone exchanges and computer data centers as standby power providers. Around ten years ago, it was estimated that the batteries industry generates $48 billion in sales annually worldwide and with a 6% annual growth. Compared to common fuels such as gasoline, the specific energy of the batteries are much lower per unit mass. This is fairly made up for producing more work in efficient electric motors compared with combustion engines [6].

1.2. Principles of Operation

Chemical energy is directly converted to electrical energy by batteries. Batteries consist of an amount of voltaic cells, and the voltaic cells consist of two and a half cells which are connected in chain, with the aid of a conductive electrolyte which contains cations and anions**.** Half of the cell contains an electrolyte and a negative electrode, to which the anions transfer and the other half contains an electrolyte and a positive electrode to which the cations transfer. The battery is powered by the redox reactions. During the charging process the cations are reduced at the cathode, while at the anode the anions are oxidized, and process is reversed during discharge [7]. The electrodes are electrically connected to each other by the electrolyte and they never touch each other. The electrolyte can be different in each half-cell, in such cases a separator is used to allow the ions migration between the half-cells and prevents the mixing of the electrolytes [7].

The capability of driving electric current from the internal to the external of the cell determines the electromotive force of each half-cell. Calculating the difference between the electromotive forces of the half cells gives us the net electromotive force of the cell. In case the electrodes have electromotive forces, from the difference between the reduction potentials of the half-reactions we can get the net electromotive force. Electrical driving force applies across the terminals of the cells. It is measured in volts and is referred to as the terminal voltage [7].

The open circuit voltage is the name given to the terminal voltage of the cell which does not charge or discharge, and equals the electromotive force of the cell. The terminal voltage of the cell which discharges is lesser in amount than the open circuit and the charging terminal voltage of the cell goes beyond the open-circuit voltage, and this is due to the internal resistance. Ideal cells maintain an invariable terminal voltage until exhaustion and then drop to zero due to its negligible internal resistance. Such cell would perform 1.5 joules of work on complete discharge, if it maintains 1.5 volts and has one Coulomb of charge. The open circuit decreases under discharge, and the internal resistance increases under discharge in actual cells. The graph would result as a curve, if the voltage and resistance are sketched on graph versus time and the curve changes following the chemistry and internal arrangements employed. The energy release of the chemical reactions of the electrodes and electrolyte determines the voltage developed across a cell's terminal. Some cells can have different chemistries but they have the same electromotive forces, like alkaline and zinc-carbon, with and electromotive force of 1.5 volts and nickel-cadmium (NiCd) and nickel metal hydride (NiMH) with an electromotive force of 1.2 volts. In the reactions of lithium compounds, high electrochemical potential changes yield lithium cells electromotive forces of 3 volts or above that [7].

1.3. Categories and Types of Batteries

Batteries can be classified to be primary and secondary.

In primary batteries chemical energy is transformed to electrical energy irreversibly. It is not possible to restore the energy to the battery, after the collapse of the supply reactants. In secondary batteries (which are rechargeable) the original composition can be approximately restored, by supplying electrical energy to the cell in order to reverse the chemical reactions. In some primary batteries, like the ones for telegraph circuits, the electrodes are replaced for the operation to be restored**.** Because of the loss of active materials and electrolyte, and due to internal corrosion in secondary batteries, they are considered to be indefinitely rechargeable [7, 8, and 9].

1.3.1. Primary Batteries

Current can be immediately produced after assembly in primary batteries. Such batteries are used commonly in transferable devices with low current drain, as an alternating source of energy, like in communication circuits where electrical power is occasionally available. Since the synthetic responses are not certainly reversible and additionally active materials might not profit, their first structures previously, disposable elementary cells, they can't make dependably recharged. Under high-drain requisitions with loads fewer than 75 ohms, disposable batteries don't charge great, despite the fact that they have higher vitality densities contrasted with rechargeable batteries [10, 11]

1.3.2. Secondary Batteries

Secondary batteries are generally mounted with active materials being discharged and hence must be charged before use. The chemical reactions that occur during the discharge in the secondary batteries are reversed by applying an electric current through chargers, and the reversion of the chemical reactions charges the battery [12]

Lead-acid batteries are the oldest form of rechargeable batteries. Liquid electrolyte in an unleashed container is contained in this technology, which requires the battery be hold in vertical position and the field needs to be ventilated good to provide safe hydrogen gas dispersion which produced at overcharging. The amount of electrical energy supplied by lead-acid batteries is relatively lighter than the battery itself. The cost of manufacturing of lead-acid batteries is low and its high surge current levels make it common, where its capacity (over 10Ah approx.) is more important than its weight and handling issues. Car batteries which can deliver a peak current of 450 amperes in general are a common application [12, 13].

In automotive industry valve regulated lead-acid batteries are popular as a replacement for the lead-acid wet cell. Such batteries use an immobilized sulfuric acid electrolyte, which reduces the chance of leakage and extending shelf life, plus electrolytes are solidify in valve regulated lead-acid batteries. There are two types of such cells. Gel cell batteries and absorbed glass mat batteries, in gel batteries, a semi-solid electrolyte is used and in the absorbed glass mats the electrolyte is absorbed in special fiberglass matting. A few fixed dry cell sorts about compact rechargeable batteries are advantageous in provisions, for example, in cell telephones and smartphone machines. These sorts of phones incorporate NiCd, nickel-zinc (NiZn), and NiMH batteries. Lithium-ion (Li-ion) cells will expanse energy thickness and expense. In the dry cell, Li-ion needs beyond question those most elevated impact. Because of NiMH's higher limit, it needs to be reinstated NiCd for the majority of applications. In any case over force tools, two-way radios and therapeutic supplies, NiCd is still utilized [12, 13].

Batteries for inserted hardware, for example, USBCELLs were included for late developments, What's more phones permits charging of an AA battery through USB connectors, nanoball batteries that consider a release rate regarding 100X more stupendous over current batteries, and advanced mobile battery packs for state-of-charge screens. Also battery security circuits prevent possible harm by looking into over-discharge. Optional units are permitted to make charged former on shipping toward low self-discharge [12, 13].

1.4. Battery Cell Types

Electrochemical cells have various types produced with varying chemical designs and processes, such as, fuel cells, flow cells, galvanic cell and voltaic piles [14].

1.4.1. Wet Cell

Batteries which have a liquid electrolyte are called wet cell batteries, or flooded cells, as all the internal parts of the cell are covered with liquid, or vented cell since the gases produced during the operation can escape to the air. Wet cells are commonly used as a learning tool for electrochemistry and dry cells were preceded by wet cells. Beakers and common laboratory supplies can be used in the building of wet cells. Beakers can be used to demonstrate how electrochemical cells work. Corrosion can be understood by a particular type of wet cells known as concentration cells [14].

Both grade and auxiliary phones have a chance to be showed on wet cells. The greater part of useful elementary batteries were manufactured likewise open-top glass jug wet cell, for example, Daniel cell, Grove cell, Bunsen cell, chromic corrosive cell, etc. Clinched alongside auto batteries What's more previously, business to standby force to switchgear, telecommunication alternately extensive uninterruptible force supplies, wet units are still used. Gel cell batteries have been utilized instep in large portions puts. Lead-acid alternately nickel-cadmium units would regularly utilize in these requisitions [14].

1.4.2. Dry Cell

A paste electrolyte with only enough moisture is used in dry cells in order to allow the flow of the current. For transportable equipment dry cell is more suitable than wet cells, as dry cells contain no free liquid and they can easily operate in any direction without spilling. Fragile glass containers with lead rods suspended from the open top were the first wet cells and they needed to be handled carefully in order to avoid spillage. Until the development of gel batteries, lead-acid batteries did not achieve the safety and portability of the dry cell. Zinc-carbon batteries (Leclanche cell), with a nominal voltage of 1.5 volts are common dry cells, alkaline batteries are also considered as common dry cells, since both types of cells use the same zinc manganese dioxide combination [14].

A zinc anode, typically in the structure of a barrel shaped pot, with a carbon cathode in the manifestation of a national pole, may be comprised concerning illustration a standard dry cell. Ammonium chloride in a paste form is the electrolyte located next to the bottom of the zinc. A second paste form which comprises of ammonium chloride and manganese dioxide takes the remaining space the middle of the electrolyte and the carbon cathode and the last goes about likewise a depolarizer. Zinc chloride replaces the ammonium chloride to a few outlines [14].

1.4.3. Molten Salt Batteries

These batteries utilize a dissolved salt as an electrolyte would allude as liquid salt batteries. These batteries activated in high temperatures by heating but can be kept for a long time at room temperature. These batteries provide high density of energy and power [14].

1.4.4. Reserve Batteries

Batteries which can be stored unassembled for long periods of time and inactivated without a power supply are referred to as reserve batteries. Reserve batteries can be assembled when needed, the battery becomes charged and ready to use immediately after assembly. The fuze of an electronic artillery battery can be activated by the impact of a firing gun, the battery is activated by the acceleration which breaks a capsule of the electrolyte. Then battery becomes activated and powers the circuits. This type of batteries are generally aimed to use for instantly, like seconds or minutes, after very long storage time. For oceanographic instruments and military applications water-activated batteries are used and they immediately activate on immersion in water [14].

1.5. Definition of Waste

Waste is an unusable, undesired or defective material which is indeed discarded after its primary use. The client needs no further utilization of these items. Wastes might be generated throughout the diverse phases about a generation, such as, throughout the extraction for crude materials process, those transforming from claiming crude materials under intermediate also final products, the utilization of final products, and other human activities.

1.6. Type of Wastes

There is a large number of waste sorts characterized by advanced frameworks for waste management, notably including:

• Metropolitan waste incorporates family unit waste, business waste, and obliteration waste.

• Dangerous waste incorporates mechanical waste.

• Biomedical waste incorporates medicinal services waste.

• Exceptional unsafe waste incorporates radioactive waste, explosives waste, and electronic waste.

1.7. Battery Recycling

The process of battery recycling may be defined as the process of reduction of batteries being disposed as municipal solid wastes. The heavy metals and toxic chemicals contained in batteries, has raised a concern over the soil contamination and water pollution while discarding [15].

1.7.1. Battery Recycling by Type

The recycling process can be done to most of the types of batteries. Lead-acid automotive batteries are more readily recycled than other types of cells, and they are nearly 90% recycled. Because the chemicals in button cells have high value and toxicity, they are also readily recycled. Alkaline and rechargeable batteries can also be recycled [15].

1.7.1.1. Lead-Acid Batteries

These batteries fuse regardless of needing aid not compelled to auto batteries, golf truck couch batteries, UPS batteries, mechanical forklift batteries, cruiser batteries, besides business batteries. These areas make all lead acid, settled lead acid, gel type batteries. These might be reused by crushing them, neutralizing the acid, separating the individual's polymers starting with the individuals lead. The individuals recouped materials might use inside a combination from asserting implementations with new batteries [16].

The lead on a lead-corrosive battery could a chance to be reused. Natural lead is lethal what more ought to further bolstering in this manner a chance to be kept out of the waste stream. A lot of people urban communities put the table battery reusing administrations for lead-acid batteries. Encountered with urban decay because of deindustrialization, engineering imagined government lodging. States in Canada wild rye provinces, a refundable store will be paid ahead batteries. This urges reusing for old batteries as opposed to abandonment or transfer with unit waste. In the United States, over 99% from claiming lead from utilized batteries may be recovered [16]. Organizations that offer new auto batteries might additionally gather utilized batteries (or be required will in this way by law) for reusing. Organizations accepting old batteries are looking into a "walk-in" basis, likewise restricted will in return to another battery. A large portion battery shops focuses on paying for scrap batteries. This could make a lucrative business, tempting particularly on risk-takers due to the wild variances in the worth of scrap lead that happen overnight. At lead costs try up, scrap batteries turn into focuses to thieves [16].

1.7.1.2. Silver Oxide Batteries

Utilized the greater part habitually over watches, toys, and etc., silver oxide batteries hold numerous a little measure from claiming mercury. The vast majority locales try to control and to decrease the release of mercury under nature's domain. Silver oxide batteries provide a chance to recover silver and also mercury.

1.7.1.3. Lithium Ion Batteries

Li-Ion and likewise Li-Phosphate batteries regularly hold numerous around different suitable metals extravagant copper and aluminum. To keep a future deficiency of cobalt, nickel also lithium and to empower a maintainable life cycle from claiming these technologies, recycled forms of lithium-ion batteries are required. These techniques must recover not main cobalt, nickel, copper and aluminum starting with used battery cells, as well as a huge stake about lithium. So as should accomplish this goal, a few unit operations need support consolidated with unpredictable procedure chains, particularly recognizing the assignment on improving rates about important materials for respect to included wellbeing issues. These unit operations are [17, 18].

Deactivation / discharging of the battery

1. Disassembly of battery systems
2. Mechanical Processes including crushing, sorting and sieving processes [18].
3. Hydro-metallurgical processes
4. Pyro-metallurgical processes

Particular hazard connected with lithium-ion battery reusing forms are electrical risk, compound dangers, smoldering reactions, also their possibility collaborations. An entangling component may be that water sensitivity: lithium hexafluorophosphate. After a while, electrolyte material will respond to water to form hydrofluoric acid. [17].

1.7.2. Battery Recycling by Location

1.7.2.1. European Union

In 2006, Battery Directive was passed by the EU and reported the plan as to higher the battery recycling rate. This directive stated that minimum of 45% of the batteries used by the EU must be gathered by 2016 and at least 50% of these must be recycled [19].

1.7.2.2. United Kingdom

The UK organization WRAP directed trials for applying different battery recycling routines in the country from 2005 to 2008. The routines tried include community drop-off, hospital, postal and fire station trials, and retail drop-off [20].

These trials helped to collect huge amount of battery mass, and the majority of people generally welcomed and comprehended them. The drop-off containers were spread around the neighborhood and trial was successful in collecting the used batteries.

Retail drop off trials was the also practically successful strategy. But also postal trials took that most noteworthy support from the community [21].

Batteries used in houses can have a chance to be recycled in the UK at committee recycling places and additionally at some shops and also shopping centers [22].

1.7.2.3. North America

In the US and Canada, rechargeable battery industry established the Rechargeable Battery Recycling Corporation (RBRC), which runs a battery recycling program called Call2Recycle. This corporation supplies businesses various shipping containers for batteries and in this way they help consumers to drop off batteries at different participating collection locations. It also alleges that no parts of any recycled battery ends up in a landfill.

An article in New York Times in November 2011 accounted for the batteries collected in the US are progressively being transported to Mexico for recycling due to the extending distance between the tough environmental and labor regulations between the two countries [23].

1.7.2.4. Japan

Japan hasn't brought an absolute national battery recycle law, so in the disposing of the batteries people are advised to pursue local and regional codes. Interestingly, the Battery Association of Japan advises the disposal of primary batteries (such as alkaline, zinc-carbon, and lithium) just like normal household waste. On the other hand, the Battery Association of Japan tries to increase the standardization of the procedures for recycling of button cell and secondary batteries [24].

1.7.2.5. Battery Recycling in Turkey

According to the data from 2004, each individual utilizes around three to four batteries every year in Turkey. In spite of the fact that the rate of utilization in European counties is about ten per person, using of batteries is actually increasing everyday with the improvements in technology. In Turkey, around 300 million different type of batteries are used annually with a market value of US$200 million. Each year over 10 000 metric tons of spent batteries were expected to pile up in Turkey in 2004 [25]. On the other hand, according to a United Nation Waste Management Report for Turkey, over 45 000 metric tons of batteries were accumulated by the year 2007, annually. Depending on the fast developing technology, only in 3 years the amount was increased drastically in Turkey. At the same time, according to the registration record, the amount of recollected spent batteries was only about the 2 percent of the all batteries supplied to the market in Turkey. By the year 2017, there are only a couple of battery recycle plant available in Turkey.

Producers of the batteries are normally responsible for the collection, transportation, and recycling of these waste materials. To be able to collect used batteries separately from the household waste, a particular collection commitment is presented for the manufacturers and exporters according to their marketing rates. To dispose scrap batteries separately from household wastes, local municipalities become responsible. The obligation regarding separate transfer of waste batteries from residential squanders lies with the regions. Designation of land for waste battery stockpiling locales with impenetrable conditions, of which the foundation and operational expenses will be conceived by battery makers, is additionally among the municipalities’ part and duty.

1.8. Study Objectives

- The overall goal of this study is to assess the feasibility of establishing a used silver oxide batteries collection and recycling program. This study objective has been pursued by:

- Literature review of the compositions of different types of batteries and their environmental impacts.
- Review the different options for used batteries collection channels and their practicability.
- Primary silver oxide batteries become a waste material after used.
- Reusing methods need aid necessary because of natural issues also to investment motivations.
- Those watch producers encounter issues in getting rid of the scrap batteries when they turn into dormant for long stockpiling.
- The recuperation of silver may be an alluring proposition Likewise it might mostly meet the interest for the metal clinched alongside nations.
- those watch commercial enterprises utilization silver oxide batteries for their products, Furthermore in spite of the fact that this batteries constitutes best 3% of the battery market, almost 1000 million from claiming utilized silver oxide batteries need aid created and offer scope to recuperation for around 25 tan /year from claiming silver.

CHAPTER 2

MATERIALS AND METHOD

2.1. Process Description

There are different types of precipitation processes to precipitate silver from silver oxide batteries [26, 27, 28, 29, 30, 31, 32].

2.1.1. Precipitation by Copper Plate:

The batteries were fed to the crusher to reduce it to small size then fed to the reactor with adding nitric acid solutions in 2h. The product is send to filter to filtrate the solution product. The solution product is then sent to copper precipitator tank to precipitate the silver in the bottom of the tank. Then the silver is washed with distilled water and then sends to smelting.

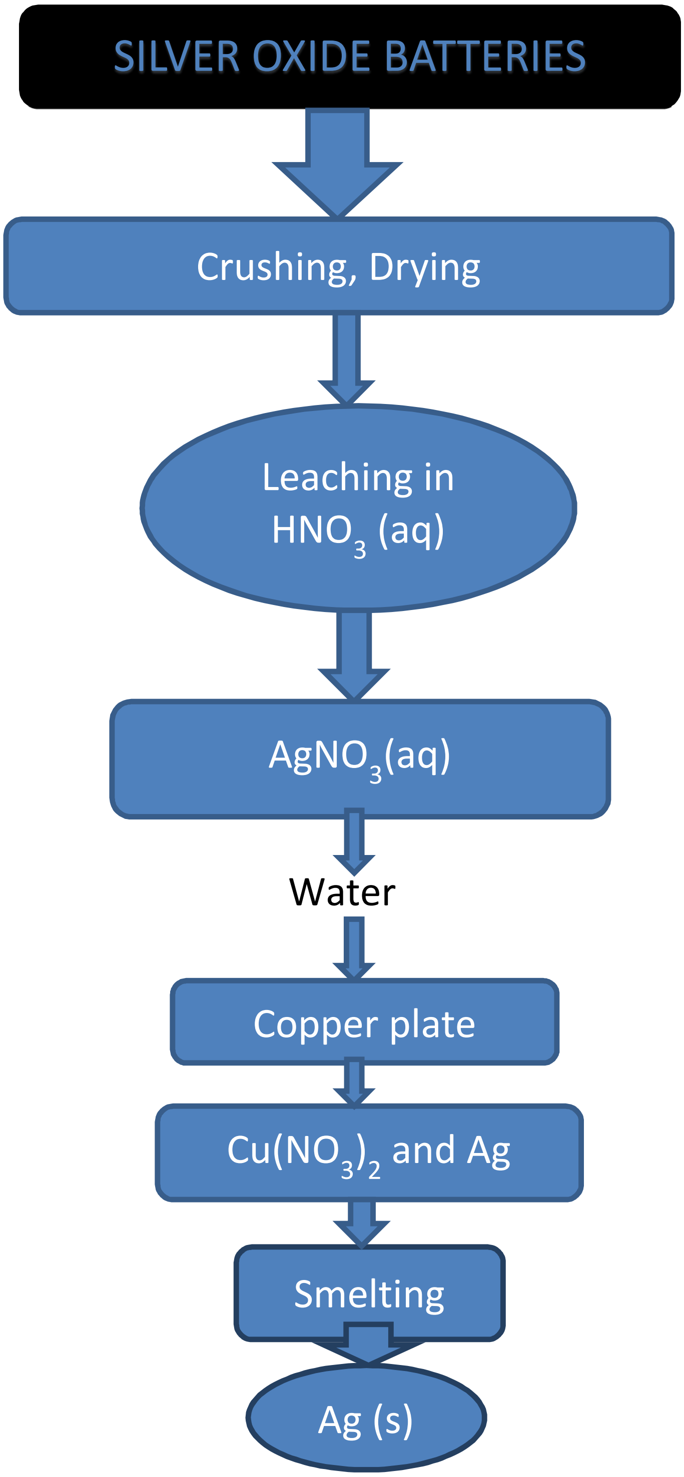

Figure 2.1 Precipitation by copper plate

2.1.2. Precipitation by KCl

The batteries were fed to the crusher to reduce it to small size then it feed to the reactor with adding nitric acid solutions in 2h. The product is sent to filter to filtrate the solution product. Then we added KCl to the solution product to precipitate the silver in the bottom in form of $AgNO_3$. Then the silver is washed with distilled water and then send to smelting.

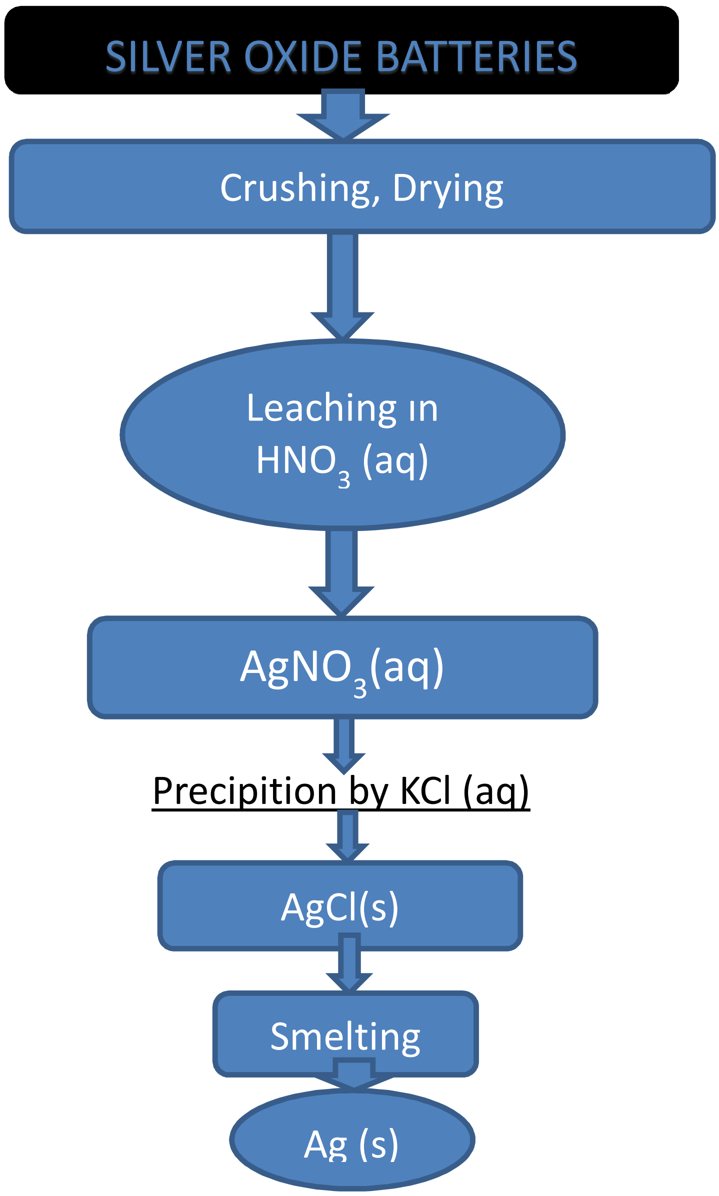

Figure 2.2 Precipitation by KCl

2.2. Silver Oxide Battery Construction

- Silver oxide batteries are created with flat circular cathodes and homogeneous gelled anodes [33].
- *Anodes* are electrolyte and a gelled mix of complex zinc powder.
- *Cathodes* are conductor and a mix of silver oxide (Ag_2O).
- *Separators* are especially material uses to avoid the migration of tiny solid particles in the battery.
- *Gaskets* are insulators and sealant molded of nylon.
- *Can* is the external battery surfaces made of nickel to avoid corrosion problem and be sure the electrical is contact.

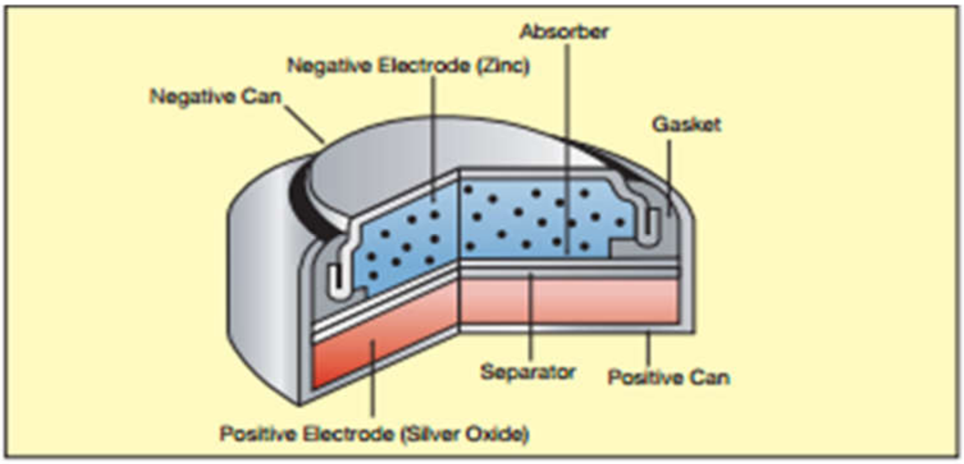

Figure 2.3 Battery construction [33].

CHAPTER 3

RESULTS AND DISCUSSION

A mix of a used up silver oxide batteries, that collected from repaired watch shops. The batteries were crushed and dried, and the chemical composition of this batteries powder is presented in Table 3.1.

Table 3.1 Typical chemical composition of silver oxide batteries [34].

Elements	Weight %
Fe	42%
Ni	2%
Mn	2%
Zn	9%
Hg	0.4%
Ag	44.6%

3.1. Materials and Variables Used

- Nitric acid (1.5 M).
- Silver oxide batteries.
- KCl.
- Copper plates.
- Temperature (room temperature).
- Pressure (1 atm).

3.2. Precipitation by KCl

By adding nitric acid to silver oxide batteries to form AgNO3, the following reactions take place:

Silver oxide and after silver oxide is reduced to metallic silver as given in eqn(3), they are dissolved in nitric acid to give aqueous AgNO3 according to the following reaction mechanisms [2]:

- $3Ag + 4HNO_3(aq) \rightarrow 3AgNO_3(aq) + 2H_2O(l) + NO(g)$ (4)
- $Ag_2O(s) + 2HNO_3(aq) \rightarrow 2AgNO_3(aq) + H_2O(l)$ (5)

Figure 3.1 Addition of nitric acid to crushed silver oxide batteries.

Figure 3.1 shows that when nitric acid was added to crushed silver oxide batteries, $AgNO_3$ and a dangerous smoke appeared. One needs to avoid this smoke. The temperature increases because of the exothermic reaction, and silver starts to be dissolved in nitric acid whose molarity was 1.5 M. This reaction takes about 3h.

Figure 3.2 Reaction mixture after water and KCl were added

After reaction became complete as shown in Figure 3.1, solution was filtered, some water and KCl was added. As shown in Figure 3.2, solution color changed to green and off-white powder (AgCl) was formed.

Figure 3.3 Dried AgCl powder

After solution shown in Figure 3.2 was filtered, the obtained AgCl filtrate was dried in the room temperature for 1 day long to obtain AgCl powder as shown in Figure 3.3. This powder was ready for smelting to extract metallic silver.

Figure 3.4 Final silver product after smelting.

Figure 3.4 shows the final product which is high purity metallic silver after smelting dry powder at more than 1000°C. In this procedure, 20.45 g of crushed batteries was used and 1.56 g of pure silver was produced by using KCl for precipitation. During the smelting process due to the high pressure of the burning gas and flame and blowing effect, considerable amount of silver powder and silver melt was spilled around and not possible to collect. Hence, the actual recovered amount of silver supposed to be higher.

3.3. Precipitation by Copper Plate

By the addition of nitric acid to crushed silver oxide batteries the reactions given by eqn(4) and eqn(5) take place and $AgNO_3$ is formed. When pure copper plate is added to this solution, the reaction below takes place and metallic silver is formed:

$$2Ag\,(NO_3) + Cu \rightarrow Cu(NO_3)_2 + 2Ag \quad (6)$$

Figure 3.5 Dissolution of crushed silver oxide batteries in nitric acid.

Figure 3.5 shows that when nitric acid was added to crushed silver oxide batteries, $AgNO_3$ is formed. The temperature increases due to exothermic reaction, and silver starts to be dissolved in nitric acid whose molarity was 1.5 M. This reaction takes about 3h.

Figure 3.6 Precipitate after copper plate immersed.

The brown powder in Figure 3.6 was formed after copper plate is immersed into $AgNO_3$ solution and reaction given by eqn(6) became complete. Indeed, distilled water was added to reaction mixture, then the solution was filtrated to extract large particles and finally dried.

Figure3.7 Final silver product after smelting.

Figure 3.7 presents the final product which is high purity metallic silver obtained after smelting of dry powder given in Figure 3.6 at more than 1000°C.

In this procedure, 15.23 g of crushed batteries was used to produce 0.164 g of silver by copper plate precipitation. During the smelting process due to the high pressure of the burning gas and flame and blowing effect, considerable amount of silver powder and silver melt was spilled around and lost. Hence, the actual recovered amount of silver supposed to be higher.

The experimental procedures outlined above can be used to recover the high percentage of the silver present in the spent silver oxide batteries as employed in this study.

CHAPTER 4

MODELING

4.1. Introduction to Design

Super pro designer is a software used for evaluation, modeling and optimization of integrated processes in a very wide range of industries (biotech, food, pharmaceutical, specialty chemical, consumer goods, microelectronics, mineral process, water purification, waste water treatment, air pollution control, etc.). In this study an evaluation version of this software was used.

The grouping of manufacturing and environmental process models in the same package enables the user at the same time to design and evaluate industries and end of pipe treatment process and practice waste minimization via pollution avoiding as well as pollution control.

This design program is very valuable tool for engineering, for scientists in process development, for manufacturing and process engineering. It is also a useful tool for dealing with environmental issues, such as, air pollution control, waste water treatment, pollution prevention and waste minimization. It is possible to build a model of around 140 unit operations. It contains elaborate reactor modules and allows performing mass and energy balances beside sizing and costing of the equipment by providing process economics. It also allows analyzing productivity and debottlenecking. It is possible to perform the characterization of the waste streams in the process and to assess the environmental impact.

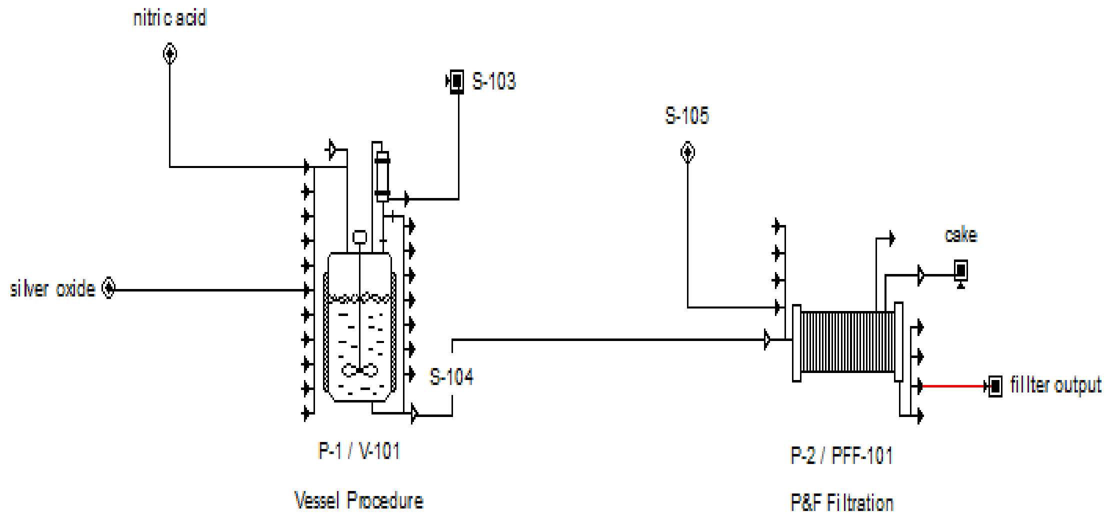

Figure 4.1 Overall recovery process

4.2. Process Outline

This process is carried out by using batch reactor and filter as explained in detail below.

4.2.1. Batch Reactor

A batch reactor may be that simplest sort of reactor vessels utilized to application of modern techniques. An ordinary batch reactor comprises a tank where the synthetic responses happen. These tanks can be equipped with an agitator and an interior warming or cooling framework [35].

- As shown in Figure 4.2, a batch reactor is used in our study, and the reaction takes 2h to be sure that all silver oxide batteries are completely dissolved in nitric acid under different parameters.

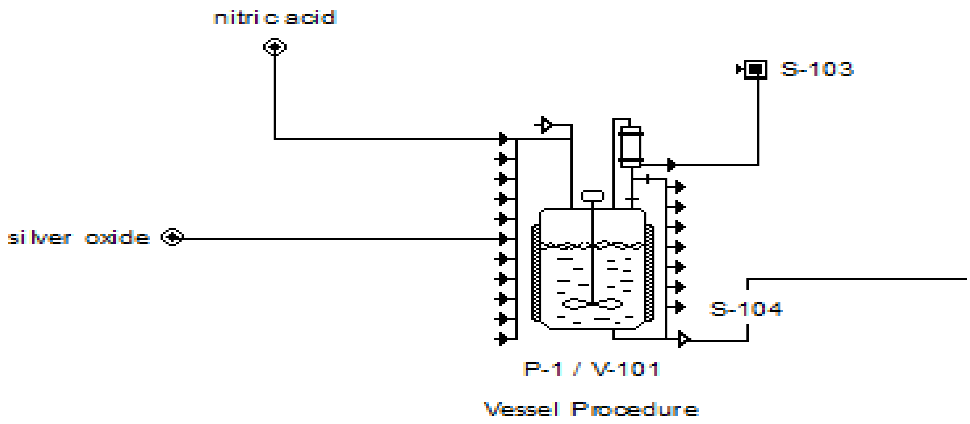

Figure 4.2 Batch reactor

Table 4.1 Input streams raw material amount and parameters of the batch reactor.

	Time Ref: Batch		nitric acid	silver oxide
	Type		Raw Material	Raw Material
	Total Flow	kg	7.5493	100.0000
	Temperature	°C	25.00	25.00
	Pressure	bar	1.013	1.013
	Liq/Sol Vol Flow	L	5.0000	10.9250
⊟	Total Contents	kg	7.5493	100.0000
	AgNo3		0.0000	0.0000
	Iron		0.0000	29.1100
	Manganese		0.0000	1.3960
	Mercury		0.0000	0.9960
	Nickel		0.0000	1.4560
	Nitric Acid		7.5493	0.0000
	Nitrog. Dioxide		0.0000	0.0000
	Nitrogen		0.0000	0.0000
	Oxygen		0.0000	0.0000
	Silver		0.0000	59.7400
	Water		0.0000	0.0000
	Zinc		0.0000	7.3020

4.2.2. Microfiltration (Feed and Bleed Operation)

Microfiltration is a pressure driven separation process for removing or separating colloidal and/or suspended particles from water. It fits in between conventional filtration techniques (particles of 1 - 40 micron) and ultrafiltration (normally macromolecules below 0.01 micron). Operation is in the cross-flow mode to minimize cake build-up and maximize product flux.

Traditionally microfiltration using porous polymeric sheets or tubes has been widely used in pharmaceutical and chemical industries for the removal of microfine species, and also to a wide range of application in water and wastewater filed [36].

General applications for microfiltration:

- Separation technique for colloidal / suspended solids,
- Thickening of weak sludge's,
- Pretreatment prior for reverse osmosis and electrodialysis,
- Removal of organic compounds from certain industrial effluents,
- Filtration of suspended solids solutions with poor settling characteristics.

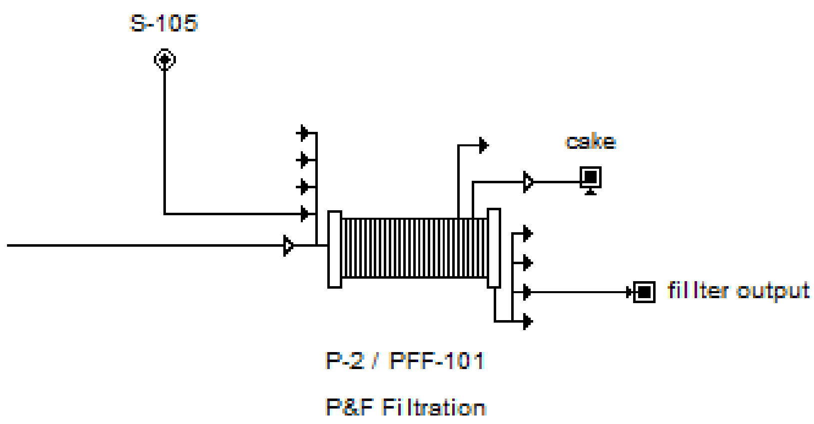

Figure 4.3 Microfiltration (feed and bleed operation).

Table 4.2 Filter output and process parameters.

	Time Ref: Batch		cake	fillter output
	Type			
	Total Flow	kg	60.7951	144.1351
	Temperature	°C	25.00	25.00
	Pressure	bar	1.013	1.013
	Liq/Sol Vol Flow	L	12.5561	100.5324
−	Total Contents	kg	60.7951	144.1351
	AgNo3		0.0000	9.6648
	Iron		0.0000	29.1100
	Manganese		0.0000	1.3960
	Mercury		0.0000	0.9960
	Nickel		0.0000	1.4560
	Nitric Acid		0.0000	0.3774
	Nitrog. Dioxide		0.0000	0.0000
	Nitrogen		0.0000	0.0000
	Oxygen		0.0000	0.0000
	Silver		53.6027	0.0000
	Water		7.1924	93.8328
	Zinc		0.0000	7.3020

CHAPTER 5

RECOMMENDATIONS

5.1. General

It is unlikely that municipal solid waste will ever be free of discarded batteries. So far, no satisfactory method has been found to extract all spent batteries from municipal solid waste all around the world. The Earth belongs to everyone. Each person has his or her role in the preservation of the environment. Reducing and recycling used batteries to reduce heavy metals that may become toxic contaminants and reduce the burden on requiring landfill areas are the responsibility of everyone. First o f all, the government should organize "one-day" program from time to time for one year to allow the people to accept this concept. Secondly, the government should put forward a mandatory deposit law and set up "permanent drop-off' centers. Producer/ distributor responsibility combined with deposit refund as enacted legislation will be most effective to achieve high recovery rates. This will provide a clear signal to producers, importers, suppliers and consumers to change their behavior on producing and consuming batteries. This will also provide a clear economic incentive to return batteries. The government could save money on waste collection and disposal and the life span of each landfill could be extended. However there would be potential administrative and enforcement costs for the government. On the other hand the polluter pays principle applies. The cost of dealing with waste is internalized for the waste generator allowing more economically efficient purchasing decisions [37].

5.2. Government’s Responsibility

Collecting and recycling is not a complete process unless the legal framework is included. Mandatory measures through legislation could be an effective means to reduce hazardous used batteries from our municipal solid waste stream. In addition, the government should use incentives to encourage recovery, charging schemes to discourage waste disposal and land allocation to assist recycling industries. Before any used battery recycling facility is established, waste exporters are required to apply for the necessary permits from the Environmental Protection Department. Therefore, the government should assist the exporters, in the meantime, to apply for the necessary permits. The government should be constantly monitoring and evaluating the strategies and programmers, which are adjusted and fine-tuned in the light of changing circumstances and evolving technologies in order to run the waste management services in the most effective and sustainable manner. The government should also encourage the use of recyclable products by developing green specification for government and organizing public awareness campaigns [37].

5.3. Manufacturer’s Responsibility

Many companies have a tendency t o follow the letter of the law rather than the intended spirit. This makes using legislation of limited success unless someone in management has the leadership, commitment and vision to do more than the minimum required and non-covered scope [37].

There may be a developing enthusiasm toward the utilization of incineration to decrease the volume o f robust wastes former will their last transfer or reprocessing. Of the degree that incinerator bolsters stocks hold numerous disposed of batteries, those harmful materials in the batteries will. Enter those incinerator flues alternately ashes. Better supplies on control air Also water. Contamination is, no doubt formed. It will be exceptionally alluring that poisonous materials in the flues Furthermore ashes make rendered safe. The elimination of cadmium and mercury are seen as an important contribution to protection of the environment. However, a further advanced step, which can be taken by the battery manufacturers, is to develop a truly environmentally safe battery in the near future. Source reduction actually prevents the generation of hazardous waste in the first place. In addition, rechargeable batteries, with materials that increase the life span, should take over a very significant part of the market currently occupied by primary batteries in order to reduce the waste volume. It will oblige organizations to use optional materials previously, result manufacturing also will configuration new items for not difficult dismantling and division about part materials [37].

5.4. Responsible Consumers

As a responsible consumer, one should internalize the cost of the potential environmental damages associated with the used battery disposal. One should be carefully [37]:

- Look for an "environmentally friendly" symbol on the packaging and
- Choose nontoxic alternatives or less toxic and recyclable batteries instead of primary batteries.
- Buy only what one needs to avoid leftover and think twice about what they throw away.
- Store and dispose all used batteries properly.
- Help to create a collection center for used batteries by participating.

CHAPTER 6

CONCLUSIONS

The procedures explained in the previous sections can be used to recover silver metal from used and spent silver oxide batteries. According to the various studies in the literature, it is possible that more than 99% of the silver metal available in the used and spent silver oxide batteries can be separated with the utilization of nitric acid (0. 5 M–2. 0 M) for the leaching. The silver can be specifically precipitated with KCl, or alternatively, by using a copper plate for the effectiveness guaranteeing that mercury and zinc stayed in the solution. It is possible to separate mercury from the solution by using distillation process which is not in the scope of this study.

According to the findings in our study,

- 20.45 g of crushed batteries was used to produce 1.56 g of pure silver by using KCl for precipitation.
- 15.23 g of crushed batteries was used to produce 0.164 g of silver by copper plate precipitation.
- By using the experimental procedures above, the amount of pure silver obtained (1.56 g and 0.164 g) may not seem to be a high recovery percentage. The main reason is, during the smelting process due to the high pressure of the burning gas and flame, considerable amount of silver powder and silver melt spilled around and not possible to collect them.
- Figure 4.1 describes the superpose design and the unit that we should use. And Table 4.1 show the amount of silver in the feed and the amount we extract. The feed is 100 kg crushed batteries including all construction parts of them, and

we theoretically extracted 55.67 kg of pure silver. The percentage of extraction is approximately 95%.

- Change in temperature does not affect the extraction noticeably, it just increases the speed of reaction.
- By using the above procedures, high purity silver powder can be obtained.

REFERENCES

[1] Syed, S. (2016). Silver recovery aqueous techniques from diverse sources:

Hydrometallurgy in recycling. Waste Management, 50, 234-256.

[2] Aktas, S. (2010). Silver recovery from spent silver oxide button cells. Hydrometallurgy, 104(1), 106-111.

[3] Pauling, Linus (1988). "15: Oxidation-Reduction Reactions; Electrolysis". General Chemistry. New York, Dover Publications, Inc. p. 539. ISBN 978-0-486-65622-9.

[4] "Battery - Definition of battery by Merriam-Webster". www.merriam-webster.com

[5] Pistoia, Gianfranco (2005-01-25). Batteries for Portable Devices. Elsevier. p. 1. ISBN 0080455565.

[6] Power Shift: DFJ on the lookout for more power source investments, Draper Fisher Jurvetson. Retrieved 20 November 2005.

[7] Zou, S., Dodd, R. Y., Stramer, S. L., & Strong, D. M. (2004). Probability of viremia with HBV, HCV, HIV, and HTLV among tissue donors in the United States. New England journal of medicine, 351(8), 751-759.

[8] Fink, D.G., Standard Handbook for Electrical Engineers, Sec. "Batteries and Fuel Cells.", 12th Edition, McGraw-Hill, New York, 1987.

[9] Franklin Leonard Pope, Modern Practice of the Electric Telegraph 15th Edition, D. Van Nostrand Company, New York, 1899, pages 7–11.

[10] Duracell: Battery Care, Retrieved 10 August 2008. https://www.duracell.com/en-us/technology/battery-care-use-and-disposal.

[11] Alkaline Manganese Dioxide Handbook and Application Manual, Energizer. Retrieved 25 August 2008. http://data.energizer.com/pdfs/alkaline_appman.pdf

[12] Dynasty VRLA Batteries and Their Application. C&D Technologies, Inc. Retrieved 26 August 2008. http://www.cdtechno.com/custserv/pdf/7327.pdf

[13] USBCELL – Revolutionary rechargeable USB battery that can charge from any USB port. Retrieved 6 November 2007. http://www.usbcell.com/

[14] "Spotlight on Photovoltaics & Fuel Cells: A Web-based Study & Comparison", pp. 1–2. Retrieved 14 March 2007.
http://www.pspb.org/e21/media/Compare_pvfc_v108_TN.pdf

[15] Bernardes, A. M.; Espinosa, D. C. R.; Tenorio, J. A. S. (3 May 2004). "Recycling of batteries: a review of current processes and technologies". Journal of Power Sources. 130 (1–2): 291–298. DOI:10.1016/j.jpowsour.2003.12.026. ISSN 0378-7753.

[16] "Recycling rate of lead from lead-acid batteries climbs to 99%", Battery Council International Report, 30 May 2014.

[17] Hanisch, C., Diekmann, J., Stieger, A., Haselrieder, W., Kwade, A. (2015) Handbook of Clean Energy Systems. Recycling of Lithium-Ion Batteries. John Wiley & Sons, Ltd. pp. 2865-2888. ISBN 9781118991978.

[18] Hanisch, Christian. "Recycling of Lithium-Ion Batteries". Presentation on Recycling of Lithium-Ion Batteries. Lion Engineering GmbH. Retrieved 22 July 2015. http://www.lion-eng.de/images/pdf/Recycling-of-Lithium-Ion-Batteries-LionEngineering.pdf

[19] "EU agrees battery recycling law" . *BBC Online*. 2006-05-03.

[20] "Waste and resources action programme (WRAP)", 20 March 2017, www.wrap.org.uk.

[21] Date, W. “UK on course to meet first battery collection target”, 19 September 2012, www.letsrecycle.com.

[22] Hickman, L. “Battery recycling and ethical living”, 13 December 2007, The Guardian Online.

[23] Rosenthal, E., Lehren, A. W., Zabludovsky, K., Agren, D. (8 Dec 2011), "Lead From Old US Batteries Sent to Mexico Raises Risks", The New York Times, nytimes.com.

[24] “Recycling portable rechargeable batteries”, the Battery Association of Japan (BAJ), 2010, www.baj.or.jp.

[25] Aktas, S., Sirkeci, A.A., Acma, E. (2004) Current situation of scrap batteries in Turkey. Journal of Power Resources, 130, 306-308.

[26] Aktas, S. (2008) Silver recovery from silver-rich photographic processing solutions by copper. Canadian Metallurgical Quarterly, 47 (1), 37-44.

[27] Sathaiyan, N., Nandakumar, V., Ramachandran P. (2006) Hydrometallurgical recovery of silver from waste silver oxide button cells. Journal of Power Sources, 161, 1-6.

[28] Aktas, S. and Morcali, M.H. (2011) Recovery of Mercury from Spent Silver Oxide Button Cells. *Minerals & Metallurgical Processing*, 28, 198-203.

[29] Sathaiyan, N. (2014) Reclamation of Mercury from Used Silver Oxide Watch Batteries. *ACES*, 4, 1-6.

[30] Hubicki, Z. and Hubicka, H. (1995) Studies of Extractive Removal of Silver (I) from Nitrate Solutions by Cyanex471X. *Hydrometallurgy*, **37**, 207-219.

[31] Ueneish, T. Japan. Patent No: 6036827, 1985

[32] Peter, R., Prax. Nat. Wiss. Chem. 34 (1985) 19–21.

[33] Ogawa, H., Inoue, K. and Fujiwara, A., Matsushita Electric Industrial Co., Ltd., 1978. Silver oxide primary cell. U.S. Patent 4,121,021.

[34] Fisher, K., Wallen, E., Laenen, P.P., Collins, M., Battery Waste Management Life Cycle Assessment, Environmental Resources Management Report, 18 October 2006

[35] Bonvin, D. (1998). Optimal operation of batch reactors—a personal view. Journal of process control, 8(5), 355-368.

[36] Treffry-Goatley, K., Groves, G.R. and Buckley, C.A., `The Application of a Cross-flow Microfiltration Unit to the Thickening of Water Works Alum Sludge, and Sewage Works Waste Activated Sludge', Institute of Water Pollution Control, Biennial Conference, Durban, South Africa, 27th-30th May 1985.

[37] Fung, K. Y. (1999). A feasibility study of the used battery collection programme in Hong Kong. 香港大學學位論文, 1-0.