Recovery of Lithium from Spent Lithium Ion Batteries

Gabriel Chinyama Luzendu

Chemical Engineering, masters level
2016

Luleå University of Technology
Department of Engineering Sciences and Mathematics
RECOVERY OF LITHIUM FROM SPENT LITHIUM ION BATTERIES

Author: Gabriel Chinyama Luzendu
Supervisors: Fredrik Engström & Jakob Kero
Examiner: Caisa Samuelsson
31/08/2016

Division of Minerals and Metallurgical Engineering
Department of Civil, Environmental & Natural Resource Engineering
Luleå University of Technology
Luleå, Sweden
Declaration

By submitting this thesis, I solemnly declare that the work contained therein is my own original work and that I am the sole author thereof and that it contains no material that has been accepted for the award of any other degree or diploma in any university. I also wish to declare that to the very best of my knowledge, it contains no material published previously or inscribed by another person, except where due reference is made in the text and that publication by Luleå University of Technology will not infringe any third party rights.

Gabriel Chinyama Luzendu

August, 2016
Acknowledgement

This thesis has been carried out at Luleå University of Technology, Division of Minerals and Metallurgical Research Laboratory. Further acknowledgement goes to the Swedish Institute for the financial support through the scholarship for my studies.

I also wish to acknowledge my examiner Associate Professor Fredrik Engström and Jakob Kero for the knowledge, guidance and advice they shared with me during this thesis. Special thanks go to Professor Caisa Samuelsson for the opportunity to do the thesis in the department.

Special appreciations go to all my friends Fortune Munodawafa, Makame Makame, Joyce Viklund and Dr. Stephen Mayowa Famurewa and his family for their encouragement, support company and prayers.

I would also like to extend my appreciations to my parents Mr. and Mrs. Luzendu and Mr. and Mrs. Manda for their moral and spiritual support. My brothers Elliot, Debby, Clifford, Kelvin and sister Emma are also acknowledged for their support.

My heartfelt gratitude goes to my lovely wife Chimwemwe Manda Luzendu and my son Gabriel Chinyama Luzendu (Jr) for their understanding and complete tolerance when I had to undertake my studies far away from them.

Finally, all my strength and help comes from God. Indeed, I can do all things through Christ Jesus who strengthens me.

June 2016

Gabriel Chinyama Luzendu
Abstract

Batteries have found wide use in many household and industrial applications and since the 1990s, they have continued to rapidly shape the economy and social landscape of humans. Lithium ion batteries, a type of rechargeable batteries, have experienced a leap-frog development at technology and market share due to their prominent performance and environmental advantages and therefore, different forecasts have been made on the future trend for the lithium ion batteries in-terms of their use. The steady growth of energy demand for consumer electronics (CE) and electric vehicles (EV) have resulted in the increase of battery consumption and the electric vehicle (EV) market is the most promising market as it will consume a large amount of the lithium ion batteries and research in this area has reached advanced stages. This will consequently be resulting in an increase of metal-containing hazardous waste. Thus, to help prevent environmental and raw materials consumption, the recycling and recovery of the major valuable components of the spent lithium ion batteries appears to be beneficial.

In this thesis, it was attempted to recover lithium from a synthetic slag produced using pyrometallurgy processing and later treated using hydrometallurgy. The entire work was done in the laboratory to mimic a base metal smelting slag. The samples used were smelted in a Tamman furnace under inert atmosphere until 1250°C was reached and then maintained at this temperature for two hours. The furnace was then switched off to cool for four hours and the temperature gradient during cooling was from 1250°C to 50°C. Lime was added as one of the sample materials to change the properties of the slag and eventually ease the possibility of selectively leaching lithium from the slag. It was observed after smelting that the slag samples had a colour ranging from dark grey to whitish grey among the samples.

The X-ray diffractions done on the slag samples revealed that the main phases identified included fayalite (Fe₂SiO₄), magnetite (Fe₃O₄), ferrobustamine (CaFeO₆Si₂), Kilchoanite (Ca₃Si₂O₇), iron oxide (FeOₙₙₙₙO) and quartz (SiO₂). The addition of lime created new compound in the slag with the calcium replacing the iron. The new phases formed included hedenbergite (Ca₀.₅Fe₁.₅Si₆O₁₈), ferrobustamine (CaFeO₆Si₂), Kilchoanite (Ca₃Si₂O₇) while the addition of lithium carbonate created lithium iron (II) silicate (FeLi₂O₄Si) and dilithium iron silicate (FeLi₂O₄Si) phases.
The Scanning Electron Microscopy (SEM) micrographs of the slag consisted mainly of Fe, Si and O while the Ca was minor. Elemental compositions obtained after analysis was used to identify the different phases in all the slag samples. The main phases identified were the same as those identified by the XRD analysis above except no phase with lithium was identified. No lithium was detected by SEM due to the design of the equipment as it uses beryllium planchets which prevent the detection of lithium.

Leaching experiments were done on three slag samples (4, 5 and 6) that had lithium carbonate additions. Leaching was done for four hours using water, 1 molar HCl and 1 molar H$_2$SO$_4$ as leaching reagents at room temperature. Mixing was done using a magnetic stirrer. The recoveries obtained after leaching with water gave a lithium recovery of 0.4%. Leaching with HCl gave a recovery of 8.3% while a recovery of 9.4% was obtained after leaching with H$_2$SO$_4$.

It can be concluded that the percentage of lithium recovered in this study was very low and therefore it would not be economically feasible. It can also be said that the recovery of lithium from the slag system studied in this work is very difficult because of the low recoveries obtained. It is recommended that test works be done on spent lithium ion batteries so as to get a better understanding of the possibilities of lithium recovery as spent lithium ion batteries contain other compounds unlike the ones investigated in this study.

**Key words:** Lithium ion batteries; Slag; Recycling; Pyrometallurgy; Hydrometallurgy; Leaching.
Nomenclature

Ni – Cd = Nickel Cadmium

NiMH = Nickel metal hydride

HEVs = hybrid electric vehicles

EV = electric vehicles

PHEVs = plug in hybrid electric vehicles

LIBs = lithium ion batteries

mAh = milliampere – hour

Ah = ampere hour

UPS = uninterruptible power supply

SLI = starting, lighting and igniting

VRLA = valve – regulated lead-acid battery

Wh = watt hour

SEI = solid electrolyte interface

PPO = polyphenylene oxide

MJ = mega joules

VTR = Vacuum thermal treatment

LiCoO₂ = lithium cobaltate
# Table of Contents

**CHAPTER ONE** .......................................................................................................................... 12

1 **Introduction** ............................................................................................................................... 12
   1.1 Background ............................................................................................................................... 13
   1.2 Purpose of study ......................................................................................................................... 16

**CHAPTER TWO** ............................................................................................................................ 17

2 **History of batteries** .................................................................................................................... 17
   2.1 Categories of batteries .............................................................................................................. 18
   2.2 Primary batteries ....................................................................................................................... 18
      2.2.1 Types of primary batteries ............................................................................................... 19
   2.3 Secondary or rechargeable batteries ......................................................................................... 22
      2.3.1 Types of secondary batteries ............................................................................................ 23
   2.4 Summary of advantages and disadvantages ............................................................................ 28

**CHAPTER THREE** .......................................................................................................................... 30

3 **Lithium metal** ............................................................................................................................. 30
   3.1 Lithium applications ................................................................................................................. 30
      3.1.1 Chemical applications for lithium ..................................................................................... 30
      3.1.2 Technical applications ...................................................................................................... 31
   3.2 Generations of lithium ion batteries ......................................................................................... 33
      3.2.1 First generation lithium ion batteries ............................................................................... 33
      3.2.2 Second generation lithium ion batteries .......................................................................... 34
      3.2.3 Third generation lithium ion batteries ............................................................................. 35
   3.3 Difference between lithium and lithium ion batteries ............................................................. 36
   3.4 Advantages and disadvantages of lithium ion batteries ......................................................... 36
      3.4.1 Uses of lithium ion batteries ............................................................................................ 37
   3.5 Lithium ion batteries designs .................................................................................................. 39
3.6 Lithium ion batteries chemistry................................................................................. 40

CHAPTER FOUR ................................................................................................................. 42

4 Lithium ion battery components .................................................................................. 42

4.1 Cathode ...................................................................................................................... 42

4.2 Anode ......................................................................................................................... 44

4.3 Electrolyte .................................................................................................................. 46

4.4 Binder ......................................................................................................................... 47

4.5 Separator ..................................................................................................................... 47

4.6 Electronic circuit ......................................................................................................... 48

4.7 Casing ......................................................................................................................... 48

4.8 Lithium ion battery sizes ........................................................................................... 48

CHAPTER FIVE .................................................................................................................. 50

5 Lithium ion battery materials ....................................................................................... 50

5.1 Typical material composition of a battery pack ......................................................... 50

5.2 Safety and environmental issues of spent lithium ion batteries ............................... 51

5.3 Battery raw materials ............................................................................................... 52

CHAPTER SIX ................................................................................................................... 56

6 Principals of lithium ion battery recycling.................................................................... 56

6.1 Recycling of lithium ion batteries ............................................................................. 56

6.1.1 Reduced dependency from primary resources ....................................................... 56

6.1.2 Reduced dependency from countries with mineral reserves ............................... 57

6.1.3 Reduction in scrap volumes .................................................................................. 57

6.1.4 Valuable components ............................................................................................ 57

6.1.5 Environmental legal requirement .......................................................................... 57

6.2 Lithium ion batteries recycling methods or routes .................................................... 58
### CHAPTER SEVEN

#### Existing lithium ion battery recycling companies

- **7.1.1 The Umicore process (Belgium)** ........................................ 69
- **7.1.2 The Sony-Sumitomo process (Japan)** ................................... 69
- **7.1.3 The Toxco process (Canada)** ............................................. 70
- **7.1.4 The Recupyl process** ......................................................... 70
- **7.1.5 The Accurec GmbH (Germany)** .......................................... 71
- **7.1.6 Akkuser OY (Finland)** ....................................................... 71
- **7.1.7 Batrec Industrie AG (Switzerland)** ...................................... 71
- **7.1.8 Falconbridge International Ltd (Canada and Norway)** ............. 72

### CHAPTER EIGHT

#### Material and methodology

- **8.1 Material description** .............................................................. 73
- **8.2 Sample preparation** ............................................................. 74
- **8.3 Equipment** ........................................................................ 75
  - **8.3.1 Tamman furnace** ............................................................. 75
  - **8.3.2 Scan electron microscopy** ............................................... 75
  - **8.3.3 X-ray diffraction** ............................................................ 76
- **8.4 Experimental procedure** ...................................................... 77
14.5 XRD sample preparation ................................................................. 105
14.6 SEM Images and elemental composition .......................................... 106
14.7 Leaching test preparation ................................................................. 112
  14.7.1 ICP standard analysis preparation ............................................... 112
14.8 XRD ................................................................................................. 113
CHAPTER ONE

1 Introduction

Batteries have found wide use in many household and industrial applications and since the 1990s, they have continued to rapidly shape the economy and social landscape of humans. Batteries are currently being developed to help power an increasing different range of applications from cars to microchips (Zeng, et al., 2014). However, since batteries are inherently simple in their concept, it is surprising that their development has progressed very slowly compared to other areas of electronics and they are often viewed as the heaviest, costliest, and least green components of any electronic device (Armand & Tarascon, 2008).

Batteries can be divided into two categories namely primary batteries and secondary or rechargeable batteries, mainly including the lead-acid batteries, nickel-cadmium (Ni-Cd) batteries, nickel-metal hydride (NiMH) batteries, and lithium ion batteries (LIBs). A comparison between rechargeable batteries shows that some lithium batteries do have a high energy density, less memory effect, high cell voltage, low self-discharge, very good life and are environmentally sound and easier to charge and maintain (Zeng, et al., 2014). The lithium batteries, both primary and rechargeable batteries, since 1990s, have widely been used in communication and portable instruments and are also considered as battery of choice in powering the next generation of hybrid electric vehicles (HEVs) as well as plug-in hybrids (PHEVs) as long as improvements could be made in performance, cost and safety (Dunn, et al., 2011). The primary lithium batteries have been on the market for about 35 years now while the lithium ion batteries have been on the market less than 20 years but they have experienced a leap-frog development at technology and market share due to their prominent performance and environmental advantages (Lankey & McMicheal, 2000).

The world population has continued to grow at a very fast rate. With continuous growth in populations, comes demand for more products to be used. The more products the world population consumes, the more waste that it produces. Waste is produced at different stages including when companies manufacture products, during the use of the products and eventually when the product has come to the end of its life. A report by the WORDBANK estimates that a total of 1.3 billion tonnes per year (as of 2015) of waste is being produced
and that by the year 2025 the amount of waste produced will increase to about 2.2 billion tonnes per year (WorldBank, 2012). With this in mind, there has been a public concern about how the environment can be safe guarded and has resulted in stricter regulations worldwide especially with the destination of hazardous wastes containing heavy metals e.g. cobalt, nickel from spent batteries (Xu, et al., 2008).

The steady growth of energy demand for consumer electronics (CE) and electric vehicles (EV) have resulted in the increase of battery consumption and consequently resulting in an increase of metal-containing hazardous waste. At the end of their life, the lithium ion batteries are discarded just as common as other electronic wastes globally undergoing from e-wonderland to e-wasteland in the absence of suitable policy and feasible technology (Ogunseitan, et al., 2009). Thus, to help prevent environmental and raw materials consumption, the recycling and recovery of the major valuable components of the spent lithium ion batteries appears to be beneficial (Zeng, et al., 2014).

1.1 Background

Different forecasts have been made on the future trend for the lithium ion batteries in terms of their use. The electric vehicle (EV) market is the most promising market as it will consume a large amount of the lithium ion batteries and research in this area has reached advanced stages. It is forecasted that an estimated 20 million electric vehicles will be produced and sold worldwide by 2020 (USGS, 2012) while the International Energy Agency (IEA) projects that there will be 100 million electric vehicles annually by 2050 (Sonoc, et al., 2015). Currently, there are many different types of lithium ion batteries on the market and there is continuing development of the metals used in order to make the batteries cheaper. Most of the electric vehicles manufacturers use the nickel-metal hydride (NiMH) batteries for the powering but the lithium ion batteries do offer significant better performance than the NiMH batteries. They have a high charge-to-weight ratio making them much lighter and therefore more desirable for the powering of electric vehicles. They also offer constant voltage output and long lifetime (Ekermo, 2009). The lithium ion batteries in the cars are also estimated to last between 8-10 years (Battery, 2003). The lithium ion batteries do not have the memory effect problem experienced by the NiMH batteries. However, lithium ion batteries are expensive and there are concerns with safety and also wide temperature range of operation (Wang & Friedrich, 2015).
In automotive applications, different cells are connected typically together in different configuration and packages with the associated control and safety circuitry to form a module of battery. The lithium ion batteries are currently small and research has been directed towards improving lithium ion battery technology at the cell level but research is also likely to be directed towards the determination of the most effective configuration and packaging. As the replacing of the internal combustion with electric vehicles continues, there will be a large demand for lithium. According to William, (2007) he stated that if the 60 million vehicles produced worldwide each year were to be replaced by plug-in hybrids, with each having a 5-kilowatt battery which requires about 1.4 kg of lithium carbonate, the demand for lithium carbonate would be 420,000 tonnes annually, which is approximately 5 times the current lithium carbonate production (William, 2007). It is also projected that for the mid and near future (today towards 2030) that the only batteries based on lithium chemistry will satisfy the requirements of electric vehicles. Unfortunately given the projected increase in demand for lithium needed in the batteries, even the most optimistic supply scenario will not be able to meet the demand in 2023 (Sonoc, et al., 2015). The estimated demand for lithium are very high and therefore there is need to finding ways of alternative sources of lithium (Wang & Friedrich, 2015).

The supply crunch in lithium could be averted if lithium ion batteries were recycled. At 100% recycling rate with a minimum lithium recovery of 90%, this would ensure that an adequate supply for all of the 21st century demand is met. However, only about 3% of the lithium ion batteries are recycled and lithium recovery is still very limited as more focus is placed on the other metal components such as cobalt and nickel which have a higher economic value (Sonoc, et al., 2015). Lithium is still inexpensive to mine and the demand has not reached a point where the supply is decreasing hence the low price. If attention is only on the recovery of valuable materials while recycling lithium ion batteries; two problems could be encountered. Firstly, it is true to say that without lithium there would be no lithium ion batteries. The fact that as the high density, easily accessible lithium deposits become scarce, the value of lithium will increase and will cause for an improvement in the recoveries in the current recycling processes, by then, the price of lithium ion batteries will have increased. Since Lithium ion batteries are expensive, they already make up a large part of the cost of electric vehicles at the present low lithium carbonate prices; a significant
increase in the price of the batteries will eventually stall the electrification of the world’s electric vehicles. Secondly, cell manufacturers are switching to using cheaper cathode materials including lithium manganese oxide and lithium iron phosphate so as to lower the price of batteries (Sonoc, et al., 2015).

The recycling of the spent lithium ion batteries can be done by physical separation processes, leaching and also by thermal treatment. The recycling of the spent batteries using thermal treatment is usually geared towards the complete meltdown of the entire battery and obtaining an alloy containing mainly cobalt and nickel and because of this, a complete separation of the metal components from the batteries is never carried out. Lithium and aluminium is often lost and reports in the slag from the thermal treatment processing and the slag is usually used in applications with lower requirements including cement (Wang & Friedrich, 2015).
1.2 Purpose of study

The purpose of this thesis was to evaluate the potential of recycling lithium from the spent lithium ion batteries in order to be able to reuse the lithium and thereby close the loop. From literature studies and survey, lithium reports to the slag during a pyrometallurgical processing and therefore in this study an iron silicate based slag was created mimicking the slag system used in the base metal smelting. The base metal smelting is already an established operation and the lithium ion batteries would be added during the smelting and then the produced iron silicate based slag would then be studied. The slag would be produced pyrometallurgically and then it would be leached to recover the lithium. The investigations conducted in this thesis were aimed at analysing the following;

i. The effect of addition of lime to the iron silicate based slag. The iron based silicate slag is a stable slag system and the addition of lime was aimed at changing the properties of the slag.

ii. Selective leaching of lithium from the slag

The work to be done in this thesis was based on:

i. A detailed literature review and survey about the lithium ion batteries which included; history, application, recycling and processing plants.

ii. Based on the literature review and survey, a plan of how to conduct the experiments in the laboratory was done and finally a written report about the findings was submitted.
CHAPTER TWO

2 History of batteries

A battery\(^1\) is a device capable of converting the stored chemical energy in the active materials straight into electric energy through an electrochemical oxidation-reduction (redox) reaction. A battery is made up of basic electrochemical units called cells. A battery consists of one or more of the cells that are connected in series or parallel or both. The connection is dependent upon the desired output voltage and capacity (Linden & Reddy, 2002). Just a few decades ago, the world was not as we know it today where people are able to enjoy the comfort, communicate easily and have such immense power. It is true to say that engineering accomplishment such as self-propelled automobiles, nuclear energy, electronics etc. had not even been imagined (Zito, 2010).

In the past, the storage of energy was hardly important as primary sources of energy such as electricity were scarce. Before 1830, the only artificial powering system for transportation was steam-power and with the discovery of electromagnetic induction by Michael Faraday in 1831, lead to the invention of DC-engine. Nevertheless, by 1870 most of the machinery still used only coal and fuel. Therefore, there was no need for a secondary system such as a battery, to store the necessary electrical energy. Plante invented a lead-acid cell, or battery, in about 1860 which was and still is an excellent electrochemical cell for storing energy for prolonged periods of time at fairly inexpensive costs as it was rechargeable. The principal interest of the battery was for primary sources, since electrical energy remained scare, to be able to power up telegraph lines and other special purpose systems (Zito, 2010). With the introduction of the internal combustion engine and the electric car (with the advent of the electric starter) in about 1912, the use of the battery increased rapidly otherwise it would have stayed dormant for a long time (Zito, 2010). The battery was and still is the only low-cost device capable with a power density of starting a large internal combustion engine to get ignition for a long time (Ekermo, 2009).

---

\(^1\) A battery consists of one or more electrochemical cells, electrically connected in an appropriate series/parallel arrangement to provide the required operating voltage and current levels, including, if any, monitors, controls and other ancillary components (e.g. fuses, diodes), case, terminal and markings. (Linden & Reddy, 2002)
In 1860 a primary battery called the Leclanche´ cell was invented whose earlier forms were wet cells with zinc as the reducing agent and manganese dioxides as the oxidizer (initially called depolarizer). The cell had ammonium chloride acting as the electrolyte and is still in use today (Batterien, 2007). This was in the mid and late nineteenth century which has been described as exciting and very eventful with regards to aspects of engineering and applied electricity (pre-electronic era of vacuum tubes and semiconductors). When countless technology demands where needed especially in warfare and increase in power needs of societies, more effort were made to provide power sources to the evolving machinery that required immense electrical power for short periods of time leading to development of silver/zinc cell and zinc/dichromate cells which were powerful and expensive batteries. These batteries were able to provide the needed large amounts of power such as being able to propel a torpedo to its enemy ship but were very costly to make and required careful handling by trained personnel (Zito, 2010).

The first rechargeable battery-type of the lead-acid batteries were developed around 1859 and since then a lot of different batteries have been made. Currently, there are a lot of batteries of the type nickel cadmium and the nickel-metal hydride system but there is an increasing demand and use of the lithium ion batteries type because of the high electrochemical potential of the lithium (Ekermo, 2009).The recent development in battery production is now focused in the development of lithium cells which are mostly used in small portable electronic products requiring small amounts of stored energy.

2.1 Categories of batteries
Batteries can be categorised as either primary or secondary based on their technical construction and properties. Batteries can also be categorised as being portable (household) batteries, vehicle batteries or industrial batteries.

2.2 Primary batteries
Primary batteries are conveniently, cheap, lightweight source of packaged power for portable electronic and electric devices, photographic equipment, toys, lighting, memory backup, and a host of other application which give freedom from utility power. Primary batteries are designed to only be used once and thereafter discarded. They irreversibly transform chemical energy to electrical energy and thereby produce current immediately on
assembly. Their discharge results in a displacement reaction where the lattice of the anode gets disrupted and a new stable (solid) phase is formed. They have higher energy densities than rechargeable batteries (Wakihara & Yamamoto, 2008). There are many different types and characteristic of primary batteries. The following are the types of primary batteries from the first batteries produced to date (Linden & Reddy, 2002).

2.2.1 Types of primary batteries

2.2.1.1 Zinc-Carbon Battery

The Leclanche´ (named after its developer) or zinc-carbon dry cell battery was the first battery to be developed and has been in existence for over 100 years and therefore has been the most used of all the different types of dry cell batteries. The reason the zinc-carbon battery was widely used include its low cost, relatively good performance, and readily accessible. Cells and batteries of different sizes and characteristics have been manufactured so as to meet the requirements of a wide variety of applications. A lot of important developments in the capacity and also the shelf life had been made with this type of battery system between the period 1945 and 1965. The developments included the use of new materials such as the beneficiated manganese dioxide and zinc chloride electrolyte, and also cell designs such as the paper-lined in the cell. The major attraction of the Leclanche´ battery has been its low cost, but it has lost substantial market share, except in the developing countries where it is still used quite highly. This is because of the newer type of primary batteries with superior performance characteristics which developed later (Linden & Reddy, 2002).

2.2.1.2 Zinc/Alkaline/Manganese Dioxide Battery

During the past decade, there had been an increased portion in the use of primary batteries and the market shifted to the Zn/ alkaline /MnO2 battery. The system Zn/alkaline/MnO2 battery had become the battery of choice among many users because of its superior performance such as its higher current drains and low temperature performances and also its better shelf life. Batteries function best at room temperature. For instance, a battery that provides 100% capacity at 27°C will only deliver 50% at -18°C. The operating temperature for this type of battery was between -20°C to 60°C. Though they were more expensive than the Leclanche´ battery on a unit basis, they were actually more cost-effective for those applications requiring the high-rate or low temperature capability. The alkaline nature of the
battery could outperform the Leclanche battery by a factor of 2 to 10. The Zn/alkaline/MnO₂ battery’s better shelf life is often selected for applications where the batteries are used occasionally and exposed to storage conditions which are uncontrolled (such as consumer flashlights and smoke alarms), but are required to perform reliably when required. The most recent advances in research have been to design batteries that provide better-quality rate of performance for use in cameras and other consumer electronics requiring this high power capability (Linden & Reddy, 2002).

2.2.1.3 Zinc/Mercuric Oxide Battery
Another important zinc anode primary system developed was the zinc/mercuric oxide battery. This type of battery was developed during World War II specifically for military communication applications. The main reason was because of its good shelf life and a higher volumetric energy density. In the post-war period, the battery system was mainly used in small button, flat, or cylindrical configurations such as the power source in electronic watches, hearing aids, calculators, photographic equipment, and similar applications that required a dependable long-life miniature power source. The use of the mercuric oxide battery ended in the last decade mainly due to environmental problems that are associated with mercury and also the development of other battery systems, such as the zinc/air and lithium batteries, which offered superior performance for numerous applications (Linden & Reddy, 2002).

2.2.1.4 Cadmium/Mercuric Oxide Battery
The zinc in the zinc/mercuric oxide battery system was replaced with cadmium to produce the cadmium/mercuric oxide battery system. This resulted in a lower voltage but gave a very stable system with a shelf life of up to 10 and also improved performance at both high and low temperatures. Due to the low voltage, the watthour capacity of this battery system was roughly 60% of that of zinc/mercuric oxide battery capacity. The use of this battery system has also been limited due to hazardous nature of the cadmium (Linden & Reddy, 2002).

2.2.1.5 Zinc/Silver Oxide Battery
The design of the primary zinc/silver oxide battery is similar to that of the small zinc /mercuric oxide button cell, except that it has a higher energy density (on a weight basis) and also the ability to accomplishes better performance at low temperatures. Because of these characteristics, the battery system is desirable for use in photographic applications,
hearing aids, and electronic watches. The high cost of this battery system and the
development of other battery systems has caused its use as a primary battery to be limited
mainly to small button battery applications in which the higher cost is justified (Linden &
Reddy, 2002).

2.2.1.6 Zinc/Air Battery
The zinc/air battery system is renowned for its high energy density, but had only been
used in larger low-power batteries such as those for signalling and navigational-aid applications.
The development of improved air electrode meant that the high-rate capability of the
system was improved and therefore the small button-type batteries are now used broadly in
electronics, hearing aids, and similar applications. This zinc/air battery system has a very
high energy density reason being that there is no active cathode material needed. The wider
use of this battery system has been slow because of their performance limitations which
include their sensitivity to extreme temperatures, humidity and other environmental
factors, and also have poor activated shelf life and very low power density. However, they
are being considered for a number of application from the portable consumer electronic
because of their attractive energy density. They will also be considered eventually for larger
devices such as electric vehicles, possibly in a reserve ²or mechanically rechargeable
³configuration because of their energy density (Linden & Reddy, 2002).

2.2.1.7 Magnesium Batteries
Although magnesium has attractive electrochemical properties, there has been relatively
little commercial interest in magnesium primary batteries due to the generation of hydrogen
gas during discharge and their fairly modest storage-ability of a partially discharged cell. The
magnesium dry cell batteries have successfully been used in military communications
equipment. This has been applied by taking advantage of the long shelf life they possess in
an undischarged condition, including at high temperatures and also its high energy density.
Magnesium is still employed as an anode material for reserve type and metal/air batteries
(Linden & Reddy, 2002).

² Batteries which use highly active component materials to obtain the required high energy, high power,
and/or low-temperature performance are often designed in a reserve construction to withstand deterioration
in storage and to eliminate self-discharge prior to use. One key component of the cell is separated from the
remainder of the cell until activation. Activation is done by adding the missing components just prior to use
(Linden & Reddy, 2002).
³ A mechanically rechargeable battery is one where the discharged electrode is physically removed and
replaced with a fresh one. Recharging of the battery is done remotely from the battery
2.2.1.8 Aluminium Batteries

Aluminium is another suitable metal for the anode with a high theoretical energy density, but has problems such as polarization and parasitic corrosion which has inhibited the development of a fully commercial product. It is being considered for a future number of applications, with the best promise as a reserve or mechanically rechargeable battery (Linden & Reddy, 2002).

2.2.1.9 Lithium Batteries

The lithium anode batteries are a relatively recent development (since 1970). They have advantages including highest energy density, wide temperature range operation and long shelf life, and have slowly replaced the conventional battery systems. They have capacity ranging from less than 5 mAh to 10,000 Ah, with various designs and chemistries, but having, in common, the use of lithium metal as the anode. The lithium primary batteries are classified into three groups. The smallest are the low-power solid-state batteries that have excellent shelf life, and are mostly used in applications such as cardiac pacemakers and battery backup for volatile computer memory, where steadfastness and long shelf life are paramount requirements. The second category is the solid-cathode batteries, which are designed in coin or small cylindrical configurations. These batteries have substituted the conventional primary batteries in watches, calculators, photographic equipment, memory circuits, communication devices, and other such applications which require high energy density and long shelf life as being critical. The soluble-cathode batteries (using gases or liquid cathode materials) make-up the third category. They are typically constructed in a cylindrical configuration, like flat disks, or in prismatic containers with flat plates. These batteries, up to about 35 Ah in size, are used in military and industrial applications, lighting products, and other different devices where small size, small weight, and operation over a wide temperature range are critical. The larger batteries are being developed for special military applications or as standby emergency power sources (Linden & Reddy, 2002).

2.3 Secondary or rechargeable batteries

Secondary batteries can be used more than once because they can be recharged. These types of batteries are easily recharged electrically after discharge to their original condition by passing a current through them in the opposite direction to that of the discharging current. This is due to them having their chemical reactions reversed by supplying electrical
energy to the cell and thereby restoring their original composition (Nazril & Pistoia, 2008). The reversibility of the charge is because of insertion or intercalation\(^4\) of ions in the anode. In the secondary batteries, the positive ions from the cathode do occupy existing spaces within the crystal lattice of the anode giving only minimal structure change (Linden & Reddy, 2002). They have high power density, high discharge rate, flat discharge curves and good low temperature performance. They are used as storage device of electrical energy and are sometimes called storage batteries or accumulators (Linden & Reddy, 2002). The application of these batteries falls in two groups:

1. Applications where the battery is used as an energy-storage device, where it is electrically connected to and is being charged by a primary energy source and then supplying its energy to the load on demand. This is the case in automotive, hybrid electric cars, aircraft systems, stationery energy storage (SES) and also emergency no-fail and standby (Uninterruptible Power Supply-UPS).
2. Applications where the battery is being used or discharged basically as a primary battery but it is recharged after being used rather than being discarded. Examples where the secondary batteries are used in this manner include; portable tools, electric vehicles and also portable consumer electronics.

The important characteristics of secondary batteries are that, the charge and discharge should be able to proceed in a reversible way, they should be energy efficient, and that they should show minimal change physically that can limit their life cycle. They should not have a chemical action which might result in deterioration of the cell’s component, cause of life or loss of energy (Linden & Reddy, 2002).

The following are the types of secondary or rechargeable batteries;

2.3.1 Types of secondary batteries

2.3.1.1 Lead-Acid Batteries

The lead-acid battery system fulfils many of the characteristics mentioned above. The charging-discharging process is principally reversible, the system is not affected by any deleterious chemical action, and although the system has low energy density and specific energy, it is able to perform reliably over a varied temperature range. The most important

---

\(^4\) Intercalation is a type of reversible insertion reaction where the intercalated atom or molecule is inserted between the other atom in a crystal lattice.
factor for its popularity and dominant position is due to its low cost with good performance and cycle-life (Linden & Reddy, 2002).

The battery system is designed in many configurations ranging from small sealed cells with a capacity of 1 Ah to large cells, up to 12,000 Ah of capacity. The automotive starting, lighting and igniting (SLI) battery is the most popular and the most widely used. The most significant advances in SLI battery design has been in the use of lighter-weight plastic containers, perfection in shelf life, the “dry-charge” process, and the “maintenance-free” design (Al-Qasem, 2012). The loss of water while charging (minimizing the need for water addition) has been reduced by the use of calcium-lead or low-antimony grids, and further improvement in the reduction of the self-discharge rate so that the batteries can be shipped or stored in a wet, charged state for a much longer period (Linden & Reddy, 2002).

The lead-acid batteries used for industrial storage are normally larger than the SLI batteries and are stronger and are constructed of higher-quality. The industrial batteries application falls in several categories (Al-Qasem, 2012). The first category is the motive power traction types which are used in materials-handling trucks, mining vehicles, tractors, and, to a limited extent, golf carts and personnel carriers, although the majority in use are automotive-type batteries. The second category is the diesel locomotive engine starting and the rapid-transit batteries which have replaced the nickel-iron battery in the newer applications. The third category is the stationary service, where they are used for electric utilities for operating power distribution controls, for telecommunications systems, for emergency and standby power systems, UPS, and in rail-roads, signalling and car power systems (Linden & Reddy, 2002).

One of the important developments in the lead-acid battery technology has been the development of the Valve-Regulated Lead-Acid battery (VRLA). This type of batteries operates on the principle of oxygen recombination, using a “starved” or immobilized electrolyte. The oxygen that is generated at the positive electrode during charging is able to diffuse to the negative electrode, where it is capable of reacting with the freshly formed lead, in the presence of sulphuric acid. The VRLA design has proven to minimise gas emission by over 95%. This is due to the suppression of hydrogen gas. Oxygen recombination is eased by the use of a pressure-relief valve, which is normally closed when in operation (Al-Qasem, 2012). The build-up of pressure causes the valve to open at a predetermined value, venting the gases. Before cell pressure decreases to atmospheric pressure, the valve reseals. The
VRLA battery has found application in over 70% of the total telecommunication batteries and also in about 80% of the UPS applications (Linden & Reddy, 2002). Smaller sealed lead-acid cells have found applications in emergency lighting and in devices like portable instruments and tools, and various consumer-type applications and similar devices that require backup power in an event of a power failure. They are constructed in two different types of configurations, prismatic cells that have parallel plates and ranges in capacity from 1 to 30 Ah, and the cylindrical cells which are similar in appearance to the nowadays popular primary alkaline cells and ranging in capacity up to about 25 Ah. The electrolyte is acid and either gelled or absorbed onto the plates and the separators are highly porous so that operation can be done virtually without the danger of leakage (Linden & Reddy, 2002). The grids used are of lead-calcium-tin alloy though some use grids of pure lead or a lead-tin alloy. These cells are capable of oxygen recombination and are considered to be VRLA batteries (Al-Qasem, 2012).

Lead-acid batteries are also used in other types of applications which include submarine service where they are for reserve power in marine applications, and in areas where engine-generators cannot be used, such as indoors and in mining equipment (Al-Qasem, 2012). The new applications must take advantage of the cost effectiveness of this battery type including its load levelling for utilities and solar photovoltaic systems. However, the new applications will require improvements in the energy and power density of the lead-acid battery to be used effectively (Linden & Reddy, 2002).

2.3.1.2 Alkaline Secondary Batteries

The other conventional types of secondary rechargeable batteries use an aqueous alkaline solution (KOH or NaOH) as the electrolyte. Electrode materials used are less reactive with alkaline electrolytes compared with acid electrolytes. Additionally, the charge-discharge mechanism in the alkaline electrolyte consists only of the transportation of oxygen or hydroxyl ions from one end of electrode to the other; henceforth the composition or concentration of the electrolyte is not affected during charge and discharge (Linden & Reddy, 2002). The following are the types of alkaline secondary batteries and their characteristics:
2.3.1.2.1 Nickel-Cadmium Batteries

The nickel-cadmium secondary battery was the most popular alkaline secondary battery and was available in different cell designs and wide variety of sizes. The construction used was the pocket-plate for the original design. They had very long lives and required little maintenances afar from occasional toppings with water. The nickel-cadmium secondary battery was mainly used in heavy-duty industrial applications, such as in mining vehicles, railway signalling, materials-handling trucks, emergency or standby power, and diesel engine starting. The recent development has been the sintered-plate construction which has higher energy density and provides high performance than the pocket-plate type design at lower temperatures and higher discharge rates (Al-Qasem, 2012). The disadvantage is that it’s more expensive. It has found applications, such as starting engines for aircraft and also in communications and electronics equipment, which requires lighter weight and where superior performance is required. The third design is a sealed cell which uses an oxygen-recombination feature almost the same as that used in sealed lead acid batteries to inhibit the build-up of pressure that is caused by gassing while charging. They are available in prismatic, button, and cylindrical configurations and are used in consumer and small industrial applications (Linden & Reddy, 2002).

2.3.1.2.2 Nickel-Iron Batteries

The nickel-iron batteries were used mainly in materials-handling trucks, mining and underground vehicles, railroad and rapid-transit cars, and in stationary applications before it lost its market share to the lead acid batteries. Its main advantages, with its major cell components of nickel-plated steel, were its extremely rugged construction, long life, and resilience or durability (Al-Qasem, 2012). However, its limitations included, poor charge retention, low specific energy, and poor low-temperature performance, and its high cost of manufacture compared with the lead-acid battery leading to its decline in usage (Linden & Reddy, 2002).

2.3.1.2.3 Silver Oxide Batteries

The silver-zinc (zinc / silver oxide) battery is renowned for its high energy density, its low internal resistance desirable for high-rate discharge, and a flat second discharge plateau. The battery system has been useful in applications where high energy density has been a prime requisite, such as in electronic news gathering equipment, submarine and training
target propulsion, and other military and space uses. However, it has not been employed for general storage battery applications due to its high cost, its cycle life and activated life are equally limited, and its performance at low temperatures falls off more markedly than with other secondary battery systems types (Al-Qasem, 2012). The silver-cadmium (cadmium/silver oxide) battery has a significant longer cycle life and a much better low-temperature performance than the silver-zinc battery but it’s also inferior in these characteristics when compared with the nickel-cadmium battery including its energy density, too, which is between that of the nickel-cadmium and the silver-zinc batteries. The battery is also very expensive as it uses two of the costlier electrode materials. As a result, the silver-cadmium battery was never developed commercially but found special applications in, areas such as nonmagnetic batteries and space applications. Other silver battery systems, such as silver-hydrogen and silver-metal hydride couples, have been the subject of development activity but have not reached commercial viability (Linden & Reddy, 2002).

2.3.1.2.4 Nickel-Zinc Batteries
The characteristics of the nickel-zinc (zinc/nickel oxide) batteries are midway between those of the nickel-cadmium and the silver-zinc battery systems. It’s energy density is almost twice that of the nickel-cadmium battery, but has limited cycle life initially due to the tendency of the zinc electrode toward shape change which decreases capacity and dendrite formations, which is the basis for internal short-circuiting (Al-Qasem, 2012). The recent development work has been able to extend the cycle life of nickel-zinc batteries through the use of additives in the negative electrode in conjunction with the use of a reduced concentration of KOH to repress zinc solubility in the electrolyte. These modifications have been able to extend the cycle life of this battery system such that it’s now being marketed for use in scooters, electric bicycles and trolling motors (Linden & Reddy, 2002).

2.3.1.2.5 Hydrogen Electrode Batteries
Another secondary battery system type uses hydrogen as the active negative material (with a fuel-cell-type electrode) and a conventional positive electrode, such as nickel oxide. These batteries are nowadays being used exclusively for the aerospace programs which require long cycle life at low depth of discharge (Al-Qasem, 2012). The major advantage of this battery system is that it has significantly higher specific energy and energy density than that of the nickel-cadmium battery. The sealed nickel-metal hydride batteries, manufactured in
small cylindrical and prismatic cells, are being used in portable electronic devices and are being actively used for other applications which include hybrid electric vehicles. The larger sizes of these batteries are finding use in electric vehicles (Linden & Reddy, 2002).

2.3.1.2.6 Zinc/Manganese Dioxide Batteries

A lot of the conventional primary battery systems have been manufactured as secondary rechargeable batteries before, but currently the manufacturing is focused on the cylindrical cell using the zinc/alkaline-manganese dioxide chemistry (Al-Qasem, 2012). The major advantage of this type of battery system is that it has a higher capacity than the conventional secondary batteries and has an initial low cost, nonetheless its cycle life and rate capability are limited (Linden & Reddy, 2002).

2.3.1.2.7 Lithium ion batteries

The lithium ion batteries have emerged in the last decade and have managed to capture over half of the sales value of the secondary consumer market and have found applications in devices such as laptop computers, cell phones and camcorders (known as the “Three-C” market). Production capacity has recently been estimated to be over 75 million cells per month (Al-Qasem, 2012). The advantages of these cells is that they provide high energy density and specific energy and long cycle life, typically greater than 1000 cycles at 80% depth of discharge. When built into batteries, battery management circuitry is required to avoid over charge and over discharge, both of which are harmful to performance. The circuits might also provide an indication of state-of-charge and safety features in the case of an over-current or an over-heating condition (Linden & Reddy, 2002).

2.4 Summary of advantages and disadvantages

The summary of the advantages and disadvantages of both the primary and secondary batteries are outlined in Table 1
Table 1. Summary of the advantages between secondary and primary batteries *(Linden & Reddy, 2002)*

<table>
<thead>
<tr>
<th>Conditions of use</th>
<th>Secondary batteries</th>
<th>Primary batteries</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Assuming acceptable load capability</td>
<td><strong>Frequent use, repeated cycling</strong> Lower life-cycle cost ($/kWh) if charging is convenient and inexpensive (work force and equipment)</td>
<td><strong>Lighter or smaller – or longer service per “charge” or replacement</strong> No maintenance or recharging Ready available (for replacement)</td>
</tr>
<tr>
<td>2. Assuming high discharge rates</td>
<td><strong>Frequent use, low drain capacity</strong> Aqueous secondary batteries have poor charge retention: have to be charged periodically</td>
<td><strong>Long service per “charge”; cost advantages of secondary disappears</strong> Infrequent replacement, cost advantage of secondary disappears Good charge retention; no need for charging or maintenance</td>
</tr>
<tr>
<td></td>
<td><strong>Infrequent use</strong> Li-ion batteries have better charge retention, but still require charge</td>
<td><strong>Hybrid battery system may provide longer service, freedom from line power</strong></td>
</tr>
</tbody>
</table>
CHAPTER THREE

3 Lithium metal

The metal lithium is one of the chemical elements with the symbol Li and has an atomic number 3, atomic mass of 6.941 g/mol and an electronegativity of 1.0 according to Pauling (LENNTECH, 2016). It belongs to the alkaline group elements in the periodic table. Lithium is a soft, silver-white and under standard conditions is the lightest metal with less density of only 0.535g/cm³. It has a melting point of 180.5°C and a boiling point of 1342°C. It is a highly reactive and very flammable metal. Lithium also has a high standard electrode potential in aqueous solution at 25°C of -3.04 V. These properties make lithium to be used in the lithium ion batteries especially towards the end of the 20th century when the lithium was used as the anode material in lithium batteries (USGS, 2012).

3.1 Lithium applications

The application of lithium can be divided into two categories namely chemical applications and technical applications.

3.1.1 Chemical applications for lithium

Lithium could be processed to form a lot of different chemicals, including lithium carbonate, lithium bromide, butyl lithium, lithium chloride and lithium hydroxide (Fox Davies Captial, 2013). The chemical applications of lithium include in; batteries, lubricants, aluminium smelting, air treatment and pharmaceuticals. The reasons for the use of lithium are as follows.

i. Batteries – the fastest growing and also the second largest market for lithium is for use in batteries both primary and secondary (rechargeable). This is because lithium batteries have a high energy density superior to the other types of alkaline batteries (DAKOTA, 2016).

ii. Aluminium Smelting – lithium is added during the aluminium smelting to help minimise the overall power consumption, helps to increase the bath for the electrical conductivity and helps minimizes fluorine emissions (TALISON, 2011).
iii. Lubricants – lithium is added to the grease so that it acts as a thickener. This is done so that lubrication properties in the grease are sustained during the entire of temperatures ranges (Fox Davies Captial, 2013).

iv. Air treatment – in industrial refrigeration, humidity and drying systems, lithium is used as an absorption medium to destroy the microorganisms and bacteria and also helps remove carbon dioxide from the air (Rockwood, 2016).

v. Pharmaceuticals - lithium is used in the treatment for bi-polar disorder as a prophylactic agent. Lithium has also shown signs that it is effective in stopping onset mood. Lithium has also found applications in other pharmaceutical applications such as treatments of major depression, schizophrenia and some psychiatric disorders in children (Nenade & Dombeck, 2009).

3.1.2 Technical applications

The products of lithium can also be used directly in technical applications. They are usually concentrated to about 5% and then sold for use in glass and ceramics. The lithium product used in this way must have low iron concentrations which are necessary to meet the highly specialised needs of the end users (DAKOTA, 2016). The technical applications of lithium include in ceramics, glass and also in specialty applications. It is also used in metallurgical applications of both steel castings and iron castings. The largest worldwide use of lithium has been in glass and ceramics (Fox Davies Captial, 2013). The reasons why lithium is used in the technical applications include the following:

i. Ceramics – lithium is added during the production of ceramics as it helps to lower the firing temperature as well as the thermal expansion while it helps increase the strength of the ceramic bodies and also heatproof ceramic cookware (DAKOTA, 2016). The types of ceramics where lithium is added include ceramics bodies, glazes, frits and heatproof ceramics cookware. Lithium is also added to glazes to help improve the colour, strength and lustre. It is added also to improve the viscosity for coating (TALISON, 2011).
ii. Glass – during the production of glass, lithium is added because of its ability to provide the needed durability, corrosion resistance and also high temperature use in particular critical resistance to thermal shock (DAKOTA, 2016). The types of glass where lithium is added during the production include; flat glass, container glass, specialty glass, pharmaceutical glass and fiberglass. The addition of lithium helps to improve the rate at which the glass melts and reduces both the viscosity and the melt temperature and the overall results being higher output, improved moulding benefits and energy savings (Fox Davies Captial, 2013).

iii. Specialty Applications – lithium, because of its high coefficient of thermal expansion makes it ideal to be used in specialty applications (TALISON, 2011). The extremely high coefficient of thermal expansion of lithium enables its application in induction cook tops and cookware to be resistant to the shock imposed by thermal and imparts high mechanical strength (Fox Davies Captial, 2013).

iv. Steel casting – lithium when added during the continuous casting mould fluxes process of steel enables the much needed thermal insulation to be available. The objective of mould fluxes in relation to thermal insulation is to avoid heat loss that might cause premature solidification of the liquid steel (Brandaleze, et al., 2012). Lithium when added during continuous casting also causes the easy of lubrication of surface of steel (TALISON, 2011).

v. Iron casting – during the production of engine blocks, the addition of lithium helps to avert veining and thereby minimise the production of defective casts during iron casting (Fox Davies Captial, 2013).

---

5 Mould fluxes are synthetic slags constituted by a complex mix of oxides, minerals and carbonaceous materials
6 Veining is the occurrence of a sheet like casting defect, which is usually produced as a result of molten metal being poured into a sand mould.
Figure 1 shows the main applications of lithium.

![Applications of lithium](image)

**Figure 1. Main applications of lithium (Janvoda, et al., 2011)**

3.2 Generations of lithium ion batteries

The generations of the lithium ion batteries can be categorised as being first, second and third generation and the description are as follows:

3.2.1 First generation lithium ion batteries

The first primary lithium batteries were produced around 1970 and attempts were then made to develop a rechargeable lithium battery but were not successful because of the high safety reason due to the reactive nature of the lithium metal. Research was then shifted to non-metallic lithium battery using lithium ions (Battery, 2003). Scrosati and Lazzari, (1980) were the first to introduce the term “rocking-chair” batteries in 1980 (Scrosati & Lazzari, 1980). This pioneered the concept which came to be known as the first generation of the rocking-chair batteries\(^7\) and gave birth to the first generation of lithium ion batteries which

\(^7\) Rocking chair batteries, another name for the lithium ion batteries, named so because the batteries can be charged and discharged many times.
were then introduced in the market around 1991. In this generation of batteries, both electrodes intercalate the lithium reversibly by showing a back and forth motion of the lithium ions during cell charge and discharge (Tirado, 2003). The anodic material in these systems was lithium insertion compound, such as Li$_x$Fe$_2$O$_3$. The elementary requirement for the rocking-chair cell was the presence of two intercalation compounds that were stable within different potential ranges. The intercalation/insertion reactions were required to be highly reversible and desirable so as to provide adequately large cell voltages (Wei, 2011). The active material for the negative electrodes was graphitization carbon (the so called soft carbon). The diameter of the cell was 20 mm with length 50 mm and had a voltage of about 4.1 V with an energy density of 80 Wh/kg. The voltage and energy density was higher when compared to the nickel-metal hydride or Ni-Cd cells. The first generation lithium ion batteries found application in cellular phones and needed two cells to be connected in series for each phone because of the poor power output of the lithium ion batteries during those days. It was therefore difficult to use lithium ion batteries of the first generation at low ambient temperatures (Pistoia, 2013).

3.2.2 Second generation lithium ion batteries

Research at Sony Energytech during the late 1980s, were able to develop the first patents and commercial products that could be considered as the advert of the second generation of rocking-chair cells. The introduction of the second generation lithium ion batteries on the market came around 1992 whose active material for the negative electrodes was a hard carbon as the anode. The advantage with the hard carbon as the anode was that the fading during the charge cycle of lithium ion batteries was reduced and therefore the batteries could now be charged at 4.2 V (Pistoia, 2013). Simultaneously during this period, the term “lithium ion” started to be used to describe the batteries that were using a carbon-based material as the anode that was inserting lithium at low voltage during the charging of the cell, and Li$_{1-x}$CoO$_2$ as cathode material. With this type of battery generation, larger specific capacities and higher cell voltages were obtained, compared with the first generation batteries (Wei, 2011). The second generation lithium ion batteries had an energy density of 120 Wh/kg, a ~50% increase compared to soft carbon used in the first generation lithium ion batteries and the diameter of the cell was 18 mm with 65 mm as length and were called 18650 cell size (Pistoia, 2013).
Remarkable efforts have been made by many research groups during the past 10 years in order to help improve the performance of the electrodes and the electrolyte of the lithium ion battery. There are two lines of research that can be distinguished; first one has been the improvement of LiCoO$_2$ and carbon based materials and secondly, the replacement of the electrode materials with others having different composition and structure (Tirado, 2003). The replacement of LiCoO$_2$ for the positive electrode has proved to be a difficult task and therefore, there has been new research which has suggested development of the rocking-chair batteries by using LiMn$_2$O$_4$ as the cathode. The most promising candidates up to now include lithium manganese spinel oxide and olivine LiFePO$_4$. These materials useful electrochemical reaction falls in the range between 3 – 4 V, which is appropriate when combined with a negative electrode whose potential is sufficiently close to lithium (Wei, 2011).

3.2.3 Third generation lithium ion batteries

The third generation lithium ion batteries were developed so as to catch up with the higher required volumetric energy density. This was done by introducing a graphite negative electrode to the cells. The energy density increased from 120 Wh/kg in the second generation to that of the latest 18650 cell type with 230 Wh/kg and 620 Wh/dm$^3$ in the third generation lithium ion batteries (Pistoia, 2013).

More recently, the development of 5 V material have emerged offering a different option, e.g. LiNi$_{0.5}$Mn$_{0.5}$O$_4$ and LiCoPO$_4$. The high working potential of this type of material makes it possible with a high-voltage anode material such as TiO$_2$. A cell built according to this concept belongs to the category of third generation lithium ion batteries (Wei, 2011). Figure 2 shows the comparisons of voltage in the three lithium ion batteries generations.
3.3 Difference between lithium and lithium ion batteries

Two types of lithium batteries exist namely primary lithium batteries and lithium ion batteries (LIBs) as already said above. The important difference between primary lithium batteries and lithium ion batteries is that the primary lithium batteries use metallic lithium as cathode and do not contain any toxic metals: however, a possibility of fire does occur if metallic lithium is exposed to moisture while the cells are corroding. The lithium ion secondary rechargeable batteries on the other hand do not contain any metallic lithium but lithium ions (Xu, et al., 2008).

3.4 Advantages and disadvantages of lithium ion batteries

The lithium ion batteries have a significant advantage over the other types of batteries. The higher volumetric and gravimetric energy storage capability are key characteristic of the lithium ion battery system compared to the conventional sealed nickel-cadmium (Ni-Cd), nickel-metal hydride (Ni-MH), and valve-regulated lead acid (VRLA) battery system as shown in Figure 3, their cell voltage for a single cell at 3.6 V compared to the other types of cells at 1.2 V for the nickel-metal hydride battery type and 2.1 V for the lead-acid battery type (Masaki, et al., 2009). The other most important advantages is that they do not possess memory effect, they have a very slow self-discharge and their charge cycles can be made

---

Memory effect which is typically sometimes known as battery effect, battery memory, lazy battery effect, is an effect that has been seen in batteries made from nickel cadmium and nickel metal hydride rechargeable batteries causing them to store less charge.
to a sufficiently high level to last a lifetime of say a vehicle (Battery, 2003). The lithium ion batteries also have some disadvantages (Battery, 2003) which include; being expensive to produce, they are safety cautious, they are sensitive to either over-charge or over-discharge requiring an electronic protection circuit to help control the charging and discharging. They are also prone to aging even when not in use (Electronics, n.d.).

Figure 3. Energy density (Wh/l) and specific energy (Wh/kg) for the major small-sealed rechargeable battery systems (Masaki, et al., 2009).

3.4.1 Uses of lithium ion batteries
The lithium ion batteries are used widely almost in all gadgets including laptop computers, cordless heavy-duty power tools, hand-held electronic devices, cell phones, cameras communication equipment and also equipment used in medicine (Zeng, et al., 2014). Lithium ion batteries have also found application in the electric and hybrid vehicle batteries and also for the alternative energy production such as solar batteries (USGS, 2012).

The use of lithium ion batteries in electric vehicles has continued to rise for the past 25 years and will continue to increase as the path to reduce the dependence on oil consumption continues. It is believed that as of 2007, the major consumption of lithium has been in the production of batteries. The lithium ion batteries continue to replace other types of batteries causing their consumption to further increase. The lithium consumption has been compelled by robust growth in the transportation sector where it is estimated that the introduction of plug-in hybrid (PHEV), electric (EV) and hybrid (HEV) vehicles into the market
by 2020 will be around 20% (O’Rourke, 2010). Figure 4 shows the actual and estimated consumption of lithium contained products. It can clearly be seen that estimated consumption of lithium products especially in batteries increases drastically.

Figure 4. Actual and forecasted breakdown of lithium- contained demand (O’Rourke, 2010)

The worldwide production of lithium ion batteries in 2000 reached about 500 million cells and based on this consumption, it is estimated that annually between 200 – 500 million tonnes (MT) of LIB waste was produced with a metal content of 5 – 15 wt.% Co and 2 – 7 wt.% Li (Lee & Rhee, 2002). The annual production of lithium ion batteries increased by about 800% between 2000 and 2010 and the United Nations estimated that the total production of mobile phones was 12.7 billion, laptop computers was 94.4 million and digital cameras was 768.9 million (Wanger, 2011). Due to the increase in the electric vehicle industry, it is further estimated that the quantity and weight of spent lithium ion batteries in 2020 will exceed 25 billion units and 500 thousand tonnes respectively. Further, China which is a populous and rapid developing country has become an important producer, consumer and supplier of lithium ion batteries and therefore will have a rapid speed of discarding lithium ion batteries than the total global level (Zeng, et al., 2012). A global outlook for EV/HEV/PHEV market growth is shown in Figure 5.
Figure 5 shows the global changing of lithium industry so as to emphasise the auto electrification impact on it. It can be seen that the total lithium demand is presented to increase from 0.3% in 2010 to about 40.3% in 2020. It can also be indicated that HEV will dominate in all the auto electrification although EV shows a more rapid increase than HEV and PHEV (Zeng, et al., 2014).

3.5 Lithium ion batteries designs

There are two different geometrical battery designs for the lithium ion batteries. The two designs are the cylindrical type and the prismatic battery type. The common case in both is that the electrodes consist of foils covered with active materials. In the cylindrical type, the foils are rolled up forming a cylinder hence called cylindrical type while in the prismatic type; the foil is layered and pressed forming a square shape (Gaines & Roy, 2000). Figure 6 and Figure 7 shows the design of a cylindrical design and the prismatic design of a battery respectively.
3.6 Lithium ion batteries chemistry

The term lithium ion battery refers to the different family of battery chemistries. The main feature in the lithium ion batteries is the intercalation, where lithium ions are incorporated into the structure of the electrode. In this way, the current is carried by the lithium ions (Li\(^+\)) from the positive electrode (cathode) to the negative electrode (anode) during charging and from negative to positive during discharging. When the current is carried by the lithium ions, it gives rise to reduction/oxidation of the active electrode materials (Gaines & Roy, 2000). The battery chemistry and design are the same for all types of the lithium ion automotive...
batteries, however, most lithium ion batteries available today differ in the composition of their positive electrode (cathode) (Lighting Africa, 2012).

All the lithium ion batteries work in more or less the same way. When charging the battery, the lithium based cathode withdraws some of its lithium ions, which moves through the electrolyte and reach the anode and remain there (Gaines & Roy, 2000). In this way, the battery stores energy. During discharging, the lithium ions move back across the electrolyte to the cathode, producing the energy that powers the battery (Mehul, et al., 2010). The reactions taking place are shown below:

The overall reaction is

\[
\text{Li}_x\text{M}_y\text{O}_z + 6\text{C} \rightarrow \text{Li}_x\text{C}_6 + \text{Li}_{1-x}\text{M}_y\text{O}_z
\]

The cathode reaction during charging is governed by:

\[
\text{LiM}_y\text{O}_z \rightarrow \text{Li}_{1-x}\text{M}_y\text{O}_z + x\text{Li}^+ + xe^-
\]

The anode reaction during charge is governed by:

\[
6\text{C} + x\text{Li} \rightarrow \text{C}_6\text{Li}_x
\]

For example, in the charge reaction of a cathode with LiCoO\(_2\), the reaction is

\[
\text{LiCoO}_2 + 6\text{C} \rightarrow \text{Li}_x\text{C}_6 + \text{Li}_{1-x}\text{CoO}_2
\]

The mechanism showing the above reactions is shown in Figure 8

![Figure 8. Representation of lithium ion reaction mechanism (McDowall, 2008)](image)

The vice versa of the above reactions is what happens during the discharging of the lithium ion battery (Xu, et al., 2008).
CHAPTER FOUR

4 Lithium ion battery components

The typical composition of the battery is an anode, cathode, binder to attach the lithium metal oxide to the cathode, electrolyte for ion transfer, separator between the anode and the cathode to prevent short circuiting (McDowall, 2008). The description of the battery components is discussed in the sections below.

4.1 Cathode

The conductor plate is made from aluminium but the material displays far more variability than the anode. The cathode material in most cases is lithiated\(^9\) metal oxide of the form \(\text{Li}_x\text{M}_y\text{O}_z\) such as \(\text{LiCoO}_2\) or \(\text{LiMn}_2\text{O}_4\), carbon and PVDF\(^{10}\) binder coated on aluminium foil. LiCoO\(_2\) is the most used positive material as it is relatively easy to prepare an electrode with a layered structure of extremely high quality (Osiak, et al., 2014). The batteries using LiCoO\(_2\) have very high energy densities and cycle life but when the batteries are abused, they are prone to releasing large amounts of energy which can result in fire (McDowall, 2008). Latest developments are gaining ground in producing material for the cathode with composition \(\text{LiFePO}_4\). Improvements in the cathode material in-terms of safety, is to move from the oxide materials to phosphates. Phosphate bonds are much stronger than the bonds in the oxide (McDowall, 2008), with the result that when abusively over-charged, \(\text{LiFePO}_4\) batteries release very little energy (Xu, et al., 2008). Cells that use \(\text{LiFePO}_4\) have reasonable calendar life and very good cycling characteristics as long as they are operated at moderate temperatures.

In future hybrid electric vehicle batteries, cobalt is very unlikely to be used in large quantities because it is quite expensive and therefore, there is consideration for substitution with cheaper materials. Currently, cathode materials that are based on nickel and manganese systems are being developed for the vehicles for the short term while iron phosphate is the most probable material for use in the longer term (Gaines & Roy, 2000).

---

\(^9\) Treated with or containing lithium

\(^{10}\) PVDF is polyvinylidene fluoride
Table 2 shows the different composition of the active material and where the batteries are used.

Table 2. Cathode material in Li-ion batteries *(Battery, 2003)*

<table>
<thead>
<tr>
<th>Chemical name</th>
<th>Material</th>
<th>Abbreviation</th>
<th>Voltage nominal (V)</th>
<th>Short form</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium Cobalt Oxide (Also Lithium Cobaltate or lithium ion-cobalt)</td>
<td>LiCoO$_2$ (60% Co)</td>
<td>LCO</td>
<td>3.6</td>
<td>Li-cobalt</td>
<td>Cell phone, laptop, camera</td>
</tr>
<tr>
<td>Lithium Manganese Oxide. (Also Lithium Manganate or lithium ion manganese)</td>
<td>LiMn$_2$O$_4$</td>
<td>LMO</td>
<td>3.7</td>
<td>Li-manganese, or spinel</td>
<td>Power tools, e-bikes, EV, medical, hobbyist</td>
</tr>
<tr>
<td>Lithium Iron Phosphate</td>
<td>LiFePO$_4$</td>
<td>LFP</td>
<td>3.6, 3.7</td>
<td>Li-phosphate</td>
<td></td>
</tr>
<tr>
<td>Lithium Nickel Manganese Cobalt Oxide, (also lithium-manganese-cobalt-oxide)</td>
<td>LiNiMnCoO$_2$ (10-20% Co)</td>
<td>NMC</td>
<td>3.2, 3.3</td>
<td>NMC</td>
<td></td>
</tr>
<tr>
<td>Lithium Nickel Cobalt</td>
<td>LiNiCoAlO$_2$ (9% Co)</td>
<td>NCA</td>
<td>3.6</td>
<td>NCA</td>
<td>Gaining</td>
</tr>
</tbody>
</table>
Aluminium Oxide

Lithium Titanate

| Aluminium Oxide | Li$_4$Ti$_5$O$_{12}$ | LTO | 2.4 | Li-titanate | importance in electric powertrain and grid storage |

Figure 9. Typical specific energy of lead-, nickel- and lithium-based batteries

*Figure 9* the typical specific energy of lead, nickel and lithium ion batteries and it can be seen that NCA is the best in storing more battery capacity\(^{11}\) than the other systems but this only applies to specific energy\(^{12}\). For specific power\(^{13}\) and the thermal stability\(^{14}\), LMO and LFP are the best. LTO has low capacity but the chemistry outlives most of the other batteries in terms of life span and also has the best cold temperature performance (Battery, 2003).

4.2 Anode

The anode also called the negative active material, contains graphite as the active material, PVDF binder, additives and conductor coated on copper foil (Gaines & Roy, 2000). The anode has a layer denoted ‘SEI’ for ‘Solid-Electrolyte Interface. The SEI is the significant enabling feature for lithium ion technology since the graphite electrode potential is very low

---

\(^{11}\) Battery capacity is a measure (typically in Amp-hr) of the charge stored by the battery, and is determined by the mass of active material contained in the battery.

\(^{12}\) Specific energy or gravimetric energy density is energy per unit mass. Also called energy density

\(^{13}\) Specific power or gravimetric power density indicates loading capability

\(^{14}\) Thermal stability is the stability of a molecule at high temperatures; a molecule with more stability has more resistance to decomposition at high temperatures
and therefore the intercalated lithium ions are expected to react immediately with the solvent of the electrolyte. During the first charge cycle when the electrolyte decomposes, a permanent passivation layer, the SEI, gets formed on the negative electrode which then protects the lithium ions in the negative. The quality of the SEI affects the battery performance, irreversible charge “loss”, rate capability, exfoliation of graphite and safety of the battery (Verma, et al., 2010). The SEI is permeable to the lithium ions and not to the electrolyte and its stability is very essential for the long life operation of the battery (McDowall, 2008).

The SEI is very stable at ambient temperature but breaks down when heated to around 110°C allowing uncontrolled reactions between the lithium ions and the electrolyte (common known as thermal runaway \(^{15}\)). This process of uncontrolled reactions occurs regardless of the positive material used as the cathode but depending on the cathode material used and the thermal characteristics of the cell and battery, the positive material used as the cathode may be destabilized and result in fire due to the heat released (McDowall, 2008).

Another material for the anode is lithium titanate which is better than graphite as it operates at a higher (less negative) voltage and therefore the lithium ions are more stable with respect to the electrolyte. With this type of anode, the SEI does not form and the problem encountered with overheating for the anode is eliminated. The lithium titanate has additional benefits including its ability for faster charging (McDowall, 2008).

In the conventional graphite anodes, they operate at a voltage of only about 150 mV higher than the one for lithium metal. The SEI on the anodes has a certain resistance to the lithium ions passing and when the charge current exceeds the value resulting in 150 mV drop across the SEI, this results in lithium ions depositing on the surface of the SEI instead of passing through. The plating of the lithium does not result or constitute a safety risk when not taken to extremes but it is capable of damaging the cell and reduces its life. The lithium titanate when used as anode in lithium ion batteries can be charged at a much higher and faster rate as fast as 5 minutes due to its high voltage compared to when graphite is used. The higher

\(^{15}\) Thermal runaway refers to a situation where an increase in temperature changes the conditions in a way that causes a further increase in temperature, often leading to a destructive result. It is a kind of uncontrolled positive feedback.
negative electrode voltage leads to a low cell voltage and affects the energy and power density. The cells with lithium titanate negatives are of little practical value except just in a few applications where faster charging is very important (McDowall, 2008).

4.3 Electrolyte

The movement or transportation of ions between electrodes is via the electrolyte. The voltage in a lithium ion cell (~3.6 V) is higher than that of the standard potential of the electrolysis of water (1.23 V at 25°C) and therefore a non-aqueous solvent is necessary (Zeng, et al., 2014). Usually solvents that have high dielectric constants16 are needed and the electrolyte also contains lithium salts for ionic transportation (Gaines & Roy, 2000).

The common solvents used are mainly of carbonate form such as propylene carbonate (PC), ethylene carbonate (EC) and dimethyl sulfoxide (DMSO). All these solvents are able to dissolve several lithium salts. These solvents have very high viscosities which make the ionic transfers to give very low conductivity (Zeng, et al., 2014). The problem of low conductivity is overcome by having empirical mixtures also containing low viscosity solvents in the actual electrolyte fluids such as dimethyl carbonate (DMC) and also methyl ethyl carbonate (MEC). The electrolyte salts used include LiPF$_6$, LiBF$_4$, LiCF$_3$SO$_3$, and Li(SO$_2$CF$_3$)$_2$. Lithium hexafluorophosphate (LiPF$_6$) is the most widely used lithium salt (Zeng, et al., 2014). The solvents used should be formulated to match the electrode materials used. For instance, a cobalt-based cell with a full-charge voltage of 4.2 V and the electrolyte should be able to withstand this level; the resulting electrolyte formulation could be quite different from that of a lower-voltage phosphate-based cell. Some electrolyte constituents could contribute to stabilization of the SEI such as vinylene carbonate which is quite effective in this regard. There is also a possibility to fine-tune the electrolyte so that it can be operated at lower or higher temperatures (McDowall, 2008).

In consumer cells, the electrolyte often includes so-called overcharge additives. These are compounds that are envisioned to decompose during moderate overcharge and generating a gas which increases the internal cell pressure resulting in an internal circuit breaker to open. In this way, the cell is sacrificed and further overcharge is prevented (Zeng, et al., 2014). There has been evidence in floating operations that overcharge additives can

---

16 Dielectric constant is a quantity of measuring the ability of a substance to store electrical energy in an electric field.
polymerize while under normal operations causing catastrophic increase in cell impedance. The solvent of the electrolyte is very flammable and that in itself is a safety concern (McDowall, 2008).

4.4 Binder
The active electrode materials consist of granules which are attached onto a collector plate using a binder. The environment inside the battery is very reactive and therefore the binder should be able to withstand the heat generated and also the electricity (Zeng, et al., 2014). The most common used binder is polyvinylidene fluoride (PVDF) which is the preferred choice because of its good electrochemical stability and binding capability, as well as its ability to absorb electrolyte for facile transport of the lithium ions to the active material surface or cathode (Chou, et al., 2014). The PVDF offers other properties include the high ability for thermos resistant and non-reactive properties (Ekermo, 2009). The PVDF however, requires the usage of toxic and quite expensive solvents. Other binders that are available include carboxymethyl cellulose (MCM), polyacrylic acid (PAA) and polyethylene glycol (PEG) which are naturally available and can easily be dissolved in water making the electrode preparation process cheap and environmentally friendly. Quite recently, aqueous binders have been slowly replacing the PVDF binder especially for the anode. The advantages of the aqueous binders include the following: they have low cost, they pose no pollution problem, they are able to enhance the active material in the cell owing to the reduction of binder content, they do not require strict control of the processing humidity and they have fast drying speed (Chou, et al., 2014).

4.5 Separator
To keep the space between the anode and the cathode, a separator is used. The separator is usually a microporous film made from polymers such as polyethylene (PE) or polypropylene (PP). The separator serves two functions with the main purpose being to prevent the direct short circuits between the electrodes. It also functions as a safety device in such a way that if the cell is to overheating, the porous film should smelt and irreversibly seals the electrodes from each other. In a normal circumstance, the electronic device disconnects the cells before this happens, since the cell cannot be reused once the shutdown separator melts (Zeng, et al., 2014). Separators for either the high-energy or high-power lithium ion
batteries are usually made from polyolefins using about 3- to 8- µm layers (PP/PE\textsuperscript{17}/PE or just PE) with 50% porosity (Gaines & Roy, 2000).

4.6 Electronic circuit

The electronic circuit is a built-in circuit which serves as a guard when charging and discharging of the battery to prevent overcharging and over discharging. The risk with overcharging is that it causes plating on the electrodes surfaces resulting in the production of metallic lithium. The plating of the electrodes with lithium does not only affect the performance of the cell but it also poses as a safety risk of explosion in an event that the cell ruptured. The lithium ion battery either always carry some charge or the charging capacity might be lost due to the structure and chemical (irreversible) changes in the electrode material. It is therefore not advised to recharge a battery after structural changes due to over-discharging as the risk is great (Gaines & Roy, 2000).

4.7 Casing

The casing which houses the functional parts of the cell is mainly of metallic form made from either stainless steel or aluminium. The cells and the electronic are contained in a plastic shell and the plastic shell is usually made of a halogen free polymer. It is often the case that the outer plastic coheres with the material of the product where the battery is being used. For example, in a PPO\textsuperscript{18} computer case the battery also has a PPO shell (Gaines & Roy, 2000).

4.8 Lithium ion battery sizes

From the total number of lithium ion batteries used world-wide, about 95% of them have sizes (weight) that range between 5 – 75 grams while from this same size range about 85% have size ranging from 5 – 25 grams and 15% have sizes ranging from 25 – 75 grams. The widest applications for the lithium ion batteries are in mobile phones and laptop computers. In the mobile phones, only a single cell battery is used with an average cell size at 22 grams while in the laptop computer usually six cells having an average cell weight of 45 grams are used (Espinosa, et al., 2004).

\textsuperscript{17} PP = polypropylene, PE = propylene
\textsuperscript{18} PPO means Polyphenylene oxide and it is a high-temperature thermoplastic. It is a rarely used in its pure form due to its difficulties in processing and therefore it is mainly bled with polystyrene, high impact styrene-butadiene copolymer or polyamide commonly used in computers.
The case for electric vehicles is different in that larger cell sizes are used in the order of hundreds of grams per cell. The cells are packed together into a unit so-called ‘module’ and usually the electric battery is composed of several modules (Wang & Friedrich, 2015). A typical hybrid electric vehicle battery could use battery cells of between 300 – 400 grams. However, the number of cells in each battery is dependent on the type of hybrid model but in a fully hybrid\(^\text{19}\) electric vehicle, the battery supplies around 300 – 400 volts corresponding to 100 cells in series. In a hybrid vehicle, the lithium ion battery would be up to 50 kilograms including the casing and the electronics (Gaines & Roy, 2000).

---

\(^{19}\) A fully hybrid vehicle is one that is able to drive with only battery power as opposed to a power assist hybrid vehicle that uses an electric power to assist the primary motor during acceleration.
CHAPTER FIVE

5 Lithium ion battery materials

In the lithium ion batteries, the nature of the active materials is of primary importance to the subsequent cell energy. The most important features of the active material which determines the cell energy are the number of electrons that it can store per volume or weight (volumetric capacity or specific capacity), and also the electrochemical potential they are capable of producing (Broussely & Archdale, 2004). The material contents of lithium ion batteries vary depending on the type of active cathode material used as described in section 4.1. The current lithium ion batteries are dominated by the small batteries which normally use cobalt cathodes but other batteries do exist that have manganese or iron phosphate. The market for bigger batteries for the electric vehicles is less certain but continuous research is being carried out on new electroactive compounds, with improved properties such as manganese and nickel based cathode or lithium iron phosphate instead of cobalt as explained in section 4.1 (ELIBAMA, 2015). Almost in all lithium ion batteries, the anode is usually made from graphite as described in section 4.2.

5.1 Typical material composition of a battery pack

A lithium ion battery has the following typical material composition:

i. Plastic casing and electrical contacts – Plastics, electronics
ii. Steel or aluminium casing – Steel (Fe, Cr, Ni), aluminium
iii. Anode – Carbon, aluminium and PVDF
iv. Cathode – Lithium, cobalt, nickel, manganese, iron and copper and PVDF
v. Electrolyte – Lithium salts and organic solvents.

Table 3 shows the average composition of lithium ion batteries as summarised by Paulino et al. (2008) and Elibama, (2015).
Table 3. Average composition of lithium ion batteries

<table>
<thead>
<tr>
<th>Component</th>
<th>Amount (wt.-%) (Paulino, et al., 2008)</th>
<th>Component</th>
<th>Amount (wt.-%) (ELIBAMA, 2015)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cathode, anode and electrolyte</td>
<td>39.1 ± 1.1</td>
<td>Battery cells</td>
<td>32.0</td>
</tr>
<tr>
<td>Plastic case</td>
<td>22.9 ± 0.7</td>
<td>Steel</td>
<td>30.0</td>
</tr>
<tr>
<td>Steel case</td>
<td>10.5 ± 1.1</td>
<td>Plastics (PP, PA)</td>
<td>30.0</td>
</tr>
<tr>
<td>Copper foil</td>
<td>8.9 ± 0.3</td>
<td>Aluminium</td>
<td>8.4</td>
</tr>
<tr>
<td>Aluminium foil</td>
<td>6.1 ± 0.6</td>
<td>Copper</td>
<td>2.8</td>
</tr>
<tr>
<td>Polymer foil and electrolyte</td>
<td>5.2 ± 0.4</td>
<td>Electronic components (BMS, FUSES,...)</td>
<td>0.92</td>
</tr>
<tr>
<td>Solvent (non-aqueous)</td>
<td>4.7 ± 0.2</td>
<td>Elastomers</td>
<td>1.44</td>
</tr>
<tr>
<td>Electrical contacts</td>
<td>2.0 ± 0.5</td>
<td>Composite materials</td>
<td>14.04</td>
</tr>
</tbody>
</table>

From Table 3, it can be seen that the active mass (cathode, anode and electrolyte) for component A comprises almost about 40% of the total battery weight while from this weight, the weight of the carbon from the anode is about 30% (Paulino, et al., 2008). Component B is for an HEV battery with a weight of 250 kg. It is expected that the percentage of the cells for the EV is expected to be about 60% (ELIBAMA, 2015).

5.2 Safety and environmental issues of spent lithium ion batteries

The concern about the health and safety of workers and the impact on the environment is growing coupled with an increase in company reporting and accountability. The lithium ion batteries have high amounts of stored energy and toxic components and therefore possess potential risks when the batteries are mistreated or damaged. In comparison to other batteries chemistries, the lithium ion batteries are relatively innocuous. However, there are environmental considerations with the lithium ion batteries to be looked at in order to know how to treat the batteries from production to consumption and eventually until the battery becomes spent (Zeng, et al., 2014).
Batteries that do carry charge contain lithium intercalated in the anode graphite and therefore the end of life batteries will continue to have some lithium in the anode even after being discharged. The reaction of the intercalated lithium with water produces lithium hydroxide ($\text{LiOH}$) and hydrogen gas ($\text{H}_2$), however the reaction isn’t as violate as the case is with lithium metals. Batteries that are subjected to overcharge do obtain lithium plating on their anode surface. It is not unlikely that used batteries are disposed as a result of malfunction and therefore the presence of lithium metal cannot be discarded in recycling processes. Besides the hazard of lithium metals, the other risks are somewhat dependent of the design of the battery. The electrolytes contained in the lithium ion batteries are usually considered to comprise the main toxicity and flammability (Zeng, et al., 2014). However, a study by Aral and Vecchio-Sadus, (2008) on the toxicity of lithium to humans and environment found that lithium is not expected to bio-accumulate and that its environmental and human toxicity are low (Aral & Vecchio-Sandus, 2008).

5.3 Battery raw materials

Most of the raw materials used in lithium ion batteries are from ores with the main focus being mostly on cobalt and lithium as they have the largest market share that is dedicated to the production of batteries (Gaines & Roy, 2000). Below is the summary of some raw materials used in the production of lithium ion batteries.

**Cobalt**

Cobalt is usually found in ores accompanied by copper or nickel and some with arsenic and silver. Cobalt is low in concentration and is mostly produced as a by-product from another metal. The production of cobalt can be split roughly as 50% from nickel industry, 44% from copper industry and other and finally 6% from primary cobalt operations. The major producers of cobalt until recently have been African countries and in particular Democratic Republic of Congo (DRC) and Zambia while other important producers include Australia, Brazil, Cuba, Russia, Canada, Madagascar and China. The approximate refined quantity of cobalt as of 2014 was about 92,000 tonnes with a reserve of about 13 million tonnes, it is reported that cobalt is surviving in a more severe situation due to its increased use (CDI, 2014). On the market, the cobalt amount is modest but the total production of cobalt is by mass twice that of lithium while the atomic amount is only one fourth (USGS, 2016). There have been two major shifts patterns in the demand for cobalt. The first one being that the
demand for cobalt has moved from the United States of America and Europe to Asia. Since 2002, there has been more cobalt demand in Asia which has increased rapidly while demand in USA and Europe has almost been steady. Secondly, the rise in the cobalt demand is attributed to the increases in chemical applications, most notably rechargeable batteries and catalysts with an estimate being 54% for the chemical applications and 46% in metallurgical applications (Zeng, et al., 2014).

Copper
The production of copper as of 2015 was estimated to be about 19 million tonnes (USGS, 2016). The outlook for copper is mainly focused on China. The copper demand is currently slow due to low demand from the slower economic growth in China. However, the future prospects show that the demand for copper will improve especially that the economy for China will continue to grow at a slower but safer and more sustainable growth with an estimated economic growth of 6.3% in 2016 and 6.0% in 2017 (IMF, 2015). The volumes of copper used in the production of batteries are too insignificant to be able to upset the market demands for the copper.

Nickel
Most of the nickel produced is used in the production of stainless steels, non-ferrous alloys, super alloys, alloy steels and electroplating. The 2015 nickel production was about 0.08 million tonnes more at 2.53 million tonnes than in 2014 at 2.45 million tonnes despite the weak prices attributed to decline in the growth rate for global production of austenitic stainless steel and also the commissioning of nickel refineries in Madagascar and Canada and also the ramp up of production at the new ferronickel smelters in Brazil and New Caledonia (USGS, 2016). A small part of the nickel is used in the battery material for the nickel metal hydride (NiMH). The nickel production and recycling is still very extensive (USGS, 2016).

Manganese
The major producers and suppliers of manganese are South Africa, Gabon and China. South Africa is reported to account for 75% of the world resources and Ukraine with 10% (though the production from Ukraine is low). Steelmaking including the ironmaking component accounts for most of the manganese demand ranging from 85% to 90% (USGS, 2016).
Manganese metal is still produced from ores containing manganese oxides mainly by electrothermal decomposition of the ore itself or by electrolysis of aqueous manganese salts (USGS, 2016). Other leading end uses of manganese include; products for construction, machinery, and transportation. It is also a key component of the widely used aluminium alloys, in oxide form, dry cell batteries, animal feeds, in plant fertilizers, and as brick coolant (USGS, 2016).

**Lithium**

The current world production of lithium is about 32,500 tonnes annually. The main producers of lithium are Chile and Australia which accounts for the majority of the world production. China is also emerging as a major producer and it was able to produce lithium carbonate, lithium hydroxide and lithium chloride. The estimated reserves for lithium are about 14 million tonnes which is dominated by South America where Chile has about 53% and Argentina at 14%. China has an estimated reserve of about 23% of the total world reserves (USGS, 2016).

Lithium has mainly been produced from subsurface brines due to low cost of production but with the current demand of lithium, mineral-sourced lithium has been able to regain market share and it is estimated to have accounted for one-half of the world’s lithium supply in 2015. The supply security of lithium is now a top priority for technology companies in the United States of America and Asia and therefore strategic alliances and joint ventures are being created between technology companies and exploration companies. This is being done to ensure a reliable, diversified supply of lithium for battery suppliers and vehicle manufacturers (USGS, 2016).

The rechargeable batteries have been the largest potential growth for the lithium compounds as there has been more demand for the lithium rechargeable batteries than the other type of rechargeable batteries. For example, a leading electric car manufacturer was setting up a lithium ion battery processing plant that will be capable of producing about 500,000 lithium ion vehicle batteries every year in the United States of America. With such high lithium demand, the demand for lithium will continue to increase (USGS, 2016).
Iron

The world-wide production of iron is very vast and the resources are estimated to being over 230 billion tonnes iron contained in over 800 billion tonnes crude ores. It is mined in about 50 countries with Australia and Brazil being the main exporters. Iron is also the fourth most abundant element in the earth’s crust. Iron ores mainly occur in the form of iron oxides, with the primary oxides being hematite (Fe$_2$O$_3$) and magnetite (Fe$_3$O$_4$). The production of iron is by subjecting the iron ore to high temperatures in a presence of a reducing agent such as carbon supplied by burning the coke. Almost all the iron produced (98%) is used in the production of steel (USGS, 2016).

Aluminium

Aluminium is the second most abundant metallic element found in the earth’s crust after silicon. When measured in terms of its quantity or value, aluminium exceeds any other metal except iron. It is used almost in all different sectors of the economy with wide applications being in transportation (automobiles, airplanes, trucks, railcars, etc.), packaging (cans, foil, etc.), construction (windows, doors, etc.), consumer durables (appliances, cooking utensils etc.), electrical transmissions lines, machinery etc. The global resources for bauxite, the aluminium ore which is the world’s main source of aluminium, are estimated to be between 55 to 75 billion tonnes and are therefore sufficient to meet the demand for the aluminium well into the future (USGS, 2016).
CHAPTER SIX

6 Principals of lithium ion battery recycling

Recycling is the process by which materials or products that have reached their end of life including lithium ion 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 (ECOCYCLE, n.d.). 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 way (Ekermo, 2009).

6.1 Recycling of lithium ion batteries

Lithium ion batteries are recycled for several reasons including: reduction on the dependency from mining and countries with reserves, reduction in scrap volumes, recovery of major valuable resources and environment legal requirement.

6.1.1 Reduced dependency from primary resources

Recycling of lithium ion batteries could try and help save the primary resources for future use though it won’t be able to provide the metals needed. This means therefore that the shortage of resources is avoided and further results in an increase in the stability of prices of raw materials (Gaines, 2009).
6.1.2 Reduced dependency from countries with mineral reserves

If the recycling is enhanced for lithium ion batteries, there will be less dependency on the countries with mineral reserves. This reduction of dependency from countries can act as a strategy for future use (ELIBAMA, 2015).

6.1.3 Reduction in scrap volumes

Lithium ion batteries recycling will help in the reduction of the continuous stockpiling of spent batteries and therefore keep the scrap volumes low and eliminate or reduce the danger of the spent waste batteries to environment (Xu, et al., 2008).

6.1.4 Valuable components

Lithium ion batteries as already stated contains metals such as cobalt, aluminium, copper, nickel and lithium and therefore, there is need to recycle these metals. However, lithium ion recycling is driven by price and hence materials components are recovered only when they are economically viable to recover (Kumar, 2011). The price of the valuables components in lithium ion batteries like cobalt, nickel and copper are high on the market and therefore these metals make recycling of the batteries economical.

6.1.5 Environmental legal requirement

There has been an increase in public concern about the environment in the last decade resulting in stricter regulations throughout the world on the destination of hazardous residues containing heavy metals such as those coming from spent portable batteries (Xu, et al., 2008). To help prevent the lithium ion batteries from ending up in landfill, collection regulations and recycling rates for the batteries are mandatory in some places. For instance, in the European Union (EU), there is a directive 2006/66/EC which regulates the management of batteries at the end of life making the disposal in landfills or incineration of waste industrial and automotive batteries and accumulators prohibited. This legislative framework enforces and ensures that producers and traders of all kinds of batteries take the spent batteries back and assure a state-of-art treatment and recycling. It states that for lithium ion batteries, recycling must reach a similar yield of at least 50% of products or products for other purposes by weight (European Union, 2006). In the United States of America, the laws to do with the collection and recycling of batteries differ between states and only New York and California have laws that cover lithium ion batteries. They classify lithium ion batteries as being miscellaneous hazardous waste. This means that there are
detailed requirements to do with packaging, labelling and shipping (Gaines, 2014). With such environmental regulation in place, the recycling of lithium ion batteries contributes to reduction in both CO$_2$ and the hazardous substances that are brought into the environment (ELIBAMA, 2015).

6.2 Lithium ion batteries recycling methods or routes

The allowing of e-waste$^{20}$ to be landfilled is not ideal as it has the potential threat when considering the battery composition. The alternative to landfilling of batteries is recycling. If the batteries are not properly landfilled, they may leach the toxic metal contents into the soil and pollute the groundwater. Therefore, the toxic and hazardous materials in batteries may require specialised facilities to be able to recover them (Bernardes, et al., 2004). Lithium ion batteries on the other hand, contain less toxic material than other batteries or are classified as less dangerous waste (Xu, et al., 2008), but there is still need to find ways of preventing them from being landfilled so as to enable the recovery of the valuable elements (Boyden, 2014). Recycling of the lithium ion batteries is necessary as this will help the environment by; reducing pollution and also acting as a source of the valuable raw materials. Recycling of lithium ion batteries has proven to being a more energy efficient process than obtaining the minerals like nickel and cobalt from their primary sources. Recycling also has proven to release less CO$_2$ compared to the mining of the minerals (Morinos & Mishra, 2015). The more the lithium ion batteries are used, the more scrap that will be generated in both the production as well as when the battery life comes to an end. There is need to close the loop and allow for the returning back of the spent batteries in order to produce new ones.

The recycling process of the spent lithium ion batteries are categorised into three stages namely; the pre-treatment, which is focused with the removal of some hazardous sources and being able to separate the individual components of the lithium ion batteries. The second stage, is the stage which focuses on the separation of the individual components and also being able to dissolve the compositions of the spent lithium ion batteries. The final stage, is the stage which is employed to recovering the valuable products such as Cu, Al, Fe, Co, Li, Ni, Mn, C, and plastics (Zeng, et al., 2014).

---

$^{20}$ E-waste is any refuse that is created by discarded electronic devices and components including substances involved in their manufacture or use. The disposal of electronics has become a growing problem because electronic equipment frequently contains hazardous substances
Literature study and review has shown that; mechanical processing, pyrometallurgical processing, and hydrometallurgical processing are the major recycling approaches employed for the recycling of spent lithium ion batteries (Zeng, et al., 2014). Mostly, the techniques above are combined to be able to recover the different materials. Figure 10 shows the analysis of recycling methods from literature that are mainly used in the recycling of batteries which include both paper publications as well as patents.

Figure 10. Global concerns and focus from main publications related to spent Lithium ion batteries (Zeng, et al., 2014).

The survey of literature shows that the research of the spent lithium ion batteries is becoming a hotspot and that there is an intensified global concern of the spent lithium ion batteries. Figure 10 shows that hydrometallurgy is the most used process with 57.25% followed by mechanical treatment at 22.9% and pyrometallurgy at 16.79% (Zeng, et al., 2014).

6.3 Mechanical processing

Spent Lithium ion batteries still have a little power in them and therefore they can blow up during the recycling process. The lithium ion batteries first have to be discharged to prevent short-circuiting and also self-ignition. After being discharged, they are dismantled and then
separated either manually or mechanically. The dismantling is usually done either by crushing or shredding. They are crushed until small size fractions are obtained (Georgi-Maschler, et al., 2012). The crushing or shredding of the spent lithium ion batteries is usually done in inert or cryogenic atmospheres so as to prevent the violent reaction of lithium (which forms when the intercalated lithium reacts with water to produce either lithium hydroxide, LiOH and hydrogen gas, H₂). Batteries that are overcharged are prone to obtaining lithium plating on the anode surface. The other reasons for crushing or shredding in inert atmosphere is that the electrolyte contains the main toxic and flammable compounds and therefore minimises the risks from the organic present in the batteries. There are intense exothermic reactions when metallic lithium comes into contact with water or moisture salts (Zeng, et al., 2014).

Once the lithium ion batteries have successfully been crushed and reduced to small sizes, they are separated by sorting the materials according to their physical properties. Separation by density methods can be employed to remove the plastics which are lighter than the other components. This can also be done by using vibrating tables or flotation. The lighter components can also be recovered from the heavy ones by differences in their densities. To remove ferrous components, a magnetic separator can be employed. Mechanical processing can be used entirely to recycle lithium ion batteries, in this case after crushing; this should be followed by grinding so as to liberate the active materials in the spent lithium ion batteries and being able to liberate them from their substrates. After liberation, the valuable components can be recovered and concentrated using the standard mineral processing operations (Al-Thyabet, et al., 2013).

6.4 Pyrometallurgical processing

In pyrometallurgical processing, the recovery of the valuables metals is done with the application of high temperatures and is usually associated with high amounts of atmospheric emissions control because of the dioxins, chloride compounds and volatile metals (such as mercury and zinc if present) that can be generated during the process (ELIBAMA, 2015) At slightly lower temperatures, the reaction involves the phase transitions and the structural changes while at high temperature chemical reactions are involved to a greater extent. As a result of the higher temperatures employed, the batteries can be smelted with the addition of slag formers easily giving a metallic fraction, a slag and gases. The processes that are used
in pyrometallurgical lithium ion batteries recycling route include; pyrolysis, smelting, distillation and refining (Bernardes, et al., 2004).

**Pyrolysis**

The pyrolysis process also called calcination, is the thermochemical decomposition of organic matter when temperatures are elevated in the absence of oxygen. The organic compounds are thermally destroyed and then emitted as a gas together with water vapour. The pyrolysis process is also capable of deactivating certain batteries of their energy (SNAM, 2016). Pyrolysis can also be done in vacuum in order to decrease the boiling temperature and therefore prevent chemical reactions from occurring. The reactions occurring during pyrolysis are the internal reactions involving the material itself only. When temperature reaches around 700°C, the organic components of the cells start to decompose and if the atmosphere is controlled, the carbon remain as the rest of the organics while the metallic components are stable in the metallic or oxidized form (ELIBAMA, 2015). Snam recycling company uses pyrolysis method for two reasons namely; deactivating certain batteries as they may still contain their residue energy and also eliminating organic matter (plastic, paper, cardboard) and solvents (electrolytes) (SNAM, 2016).

**Smelting**

Smelting involves the application of heat and chemical reduction to produce metals either as the element or just as a simple compound by heating beyond the melting point. A slag former is added before or during smelting to produces a slag carrying almost all the waste and off gases (ELIBAMA, 2015).

**Distillation treatment**

The distillation treatment is a thermal process used in the separation by evaporating the different metals in the batteries (SNAM, 2016). The metals are separated at different temperatures and then they are condensed. This is done for metals with low boiling points (Sequeira & Moffat, 1998).

**Refining**

The refining is a thermal treatment process for obtaining a very pure metal where the remaining impurities are eliminated (SNAM, 2016).
Pyrometallurgical processes are fast and easy to handle. There is usually no safety risk with the electrolyte from the batteries. There is a reduction of the fuel consumption by burning the plastics, electrolyte and carbonates during the processing. The pyrometallurgical processing route requires large amounts of energy because of the high temperatures needed. The major disadvantage of the pyrometallurgical processing is its inability to recover lithium as it is always oxidized and reports to the slag (Georgi-Maschler, et al., 2012). Pyrometallurgical processing releases a lot of gas emissions which can include carbon dioxide, carbon monoxide, sulphur dioxide, volatile organic compounds and a lot of dust due to the high temperatures utilised and therefore there is need to control the emissions to avoid leakage to the environment. The off-gas is purified by costly gas cleaning systems (Bernardes, et al., 2004). In order to recover the lithium from the slag, a combination of pyro- and hydrometallurgical processing are usually employed (Bernardes, et al., 2004). The organic compounds including carbon are burned and used as reducing agents while ignoble metals end up in the slag (such as aluminium) and not recovered (Georgi-Maschler, et al., 2012).

6.5 Hydrometallurgical processing
In hydrometallurgical processing, it involves the dissolving of the spent lithium ion batteries and then selectively separating them from the leach liquor which is then purified to obtain the required valuable metals. Crushing and shredding are usually used as pre-treatment operations for hydrometallurgical processing so that the materials are easily liberated and therefore most processing plants have incorporated mechanical processing together with hydrometallurgical processing. Studies have shown that hydrometallurgical recovery of metals from spent lithium ion batteries is suitable as it has good advantages such as high recovery of the metals with high purity, low energy requirement and very minimum gas emissions. However, liquid effluents are also produced during the process. Hydrometallurgical processing can be used to successfully recovery lithium from the spent lithium ion batteries (Jha, et al., 2013). The hydrometallurgical process can also be highly selective and that direct separation and retrieval of several materials at high efficiency is reached (ELIBAMA, 2015). The processes used in hydrometallurgical route include; leaching, precipitation, ion exchange, solvent extraction and electrochemical separation.
Leaching
Leaching is the extracting of a soluble element (often metal) from a solid with a solvent. It is used to get the metals into solution but it can also be selective for specific elements. Sulphuric acid is the most used leaching agent or solvent because it is easily available, less costly and also less hazardous to the environment compared to other acids like nitric or hydrochloric acids. The selectivity or leaching efficiency depends on the type of leaching media used either acidic or basic but it can also depend on other configurations. For instance, reduction leaching improves the efficiency by changing the oxidation state of a metal cobalt $\text{Co}^{2+}$ much more water soluble than $\text{Co}^{3+}$ (ELIBAMA, 2015). Leaching efficiency can also be improved by complexometric leaching, which is a method where an extractant is allowed to form complexes with the leached components. The formation of complexes removes the solvated metal from the leach liquor and keeps the concentration low. The low metal concentration increases the leaching efficiency by changing the phase equilibrium (Li, et al., 2008). Leaching can be done on the electrode of the material immediately after crushing and it is also possible to leach the slag remaining from pyrometallurgical treatment. However, the recovery of lithium from the slag is neither economical nor energy efficient and it is therefore not very effective (Gaines, 2014).

Precipitation
Precipitation is used to get elements out of the solution by producing insoluble compounds and follows immediately after leaching. This is usually done by adding other chemicals that are able to react with solvated species forming insoluble salt that precipitates. The precipitate can then be recovered by centrifugation or filtration. One advantage with precipitation is that the material can be re-used if a suitable solidifying agent is used. The disadvantage is a possible rest solubility of the connection and the soiling of the metal connections which makes an additional cleaning step necessary (Xu, et al., 2008).

Ion exchange
Ion exchange is where a solution with metal (or other ionic compounds) in solution is passed through a bed of resin with high affinity for certain ions. The affinity is usually limited to either cations or anions (Xu, et al., 2008). The selective sorption of a metal may be achieved depending on the affinity properties of the resins material. Ion exchange is also used for concentrating metal solutions by passing large volumes of low concentrated metal through
the ion exchanger and there after washing with a small volume of suitable eluent (Xu, et al., 2008).

**Solvent extraction**

In solvent extraction, two immiscible phase systems consisting of an organic phase and an aqueous phase are made use of. There is uneven distribution of a substance between the two phases leading in separation. The metals in the aqueous solution are present as charged species and therefore not soluble in the organic non-polar solvent (Habashi, 1969).

The addition of complexing agents to the solution makes it possible to form uncharged species. The hydrophobic complexes get easily transferred to the organic phase giving uneven distribution of the metals and eventually allowing them to separate. If a complexing agent has a higher selectivity towards forming complexes with a specific metal, the metal selectivity will also be improved. Solvent extraction can be utilised even if the selectivity is slightly higher for one metal than the other and obtain good separation by using multiple stages. Elements that belong to the same group of the periodic table do have the same or close chemical properties making their separation difficult (Habashi, 1969). The advantage with solvent extraction is that it is selective. It is possible to be able to extract single metal ions e.g. lithium ions, from the solution. The complexes regained often have a higher quality than precipitated complexes. The major disadvantage is the high price and the toxicity of the solvents such as benzene, toluene, kerosene, etc. (Xu, et al., 2008).

**Electrochemical separation**

To extract metal species or components out of a solution and achieve the necessary reduction, electrowinning can be used. It involves the supply of energy into two electrodes used in the solution yielding oxidation and reduction of the ions in solution. To be successful, the method requires that the metals present in the solution have differing reductive and oxidative potentials. Once the metals have been separated into different solutions by solvent extraction, electrochemical deposition can then be used to produce high purity metals (Habashi, 1969). Also an electrolysis cell can be used in which the electrodes are separated by a membrane where the membrane only allows metal ions to pass thorough. On the side of the cathode, the metal ions are concentrated until the solubility product is exceeded and the solid metal hydroxides are precipitated (Xu, et al.,
In another technique, gaseous carbon dioxide is introduced into the electrolysis cell initiating the precipitation of lithium carbonate at the cathode side. The electrochemical processes are slow and their productivity are also slow (ELIBAMA, 2015).

### 6.6 Chlorine metallurgy

In chlorine metallurgy, the idea is to form metals chlorides which are easily able to be leached. This is usually done by a mechanochemical treatment where the batteries are first reduced into small size fractions and then grinding the battery material waste are ground together with chlorine containing compounds such as polyvinyl chloride (PVC) in air. The products from this open air grinding reaction produce lithium and cobalt chlorides and then subsequent leaching with water of the ground products to extract cobalt and lithium. The grinding is very important as it improves the yield (Xu, et al., 2008).

### 6.7 Summary of advantages and disadvantages of mechanical, pyrometallurgical and hydrometallurgical processes

The advantages and disadvantages of the recycling methods described above are summarised in the Table 4:

Table 4. Comparisons of advantages and disadvantages of recycling methods (*Boyden, 2014*)

<table>
<thead>
<tr>
<th>Process</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mechanical</td>
<td>• The composition of the material remains the same.</td>
<td>• There are risks of explosions from the batteries.</td>
</tr>
<tr>
<td></td>
<td>• There are risks of explosions from the batteries.</td>
<td>• The process requires a uniform feed as it is difficult to separate components from each other.</td>
</tr>
<tr>
<td></td>
<td>• The process requires a uniform feed as it is difficult to separate components from each other.</td>
<td>• Energy requirements are high due to crushing and grinding operations.</td>
</tr>
</tbody>
</table>
### Hydrometallurgical
- Requires low energy for operation.
- Has high recovery and high purity components.
- Very minimal gas emissions are released.
- There is wastewater produced from the processing.
- The process is sensitive to process input.

### Pyrometallurgical
- Simple operation
- There is often no need for sorting.
- Can handle any input or mixture of inputs in high volumes.
- Lithium cannot be recovered.
- Plastics and other organic materials are not recovered.
- Requires high energy for smelting.
- High gas emissions and therefore high cost of gas control.

---

**6.8 Previous work of lithium ion batteries recycling done in lab scale**

Work that has been done in the recycling and recovery of the valuable materials from the spent lithium ion batteries in particular lithium and cobalt include the following: ZHU, et.al. (2012) conducted a study on how to recover Co and Li metals from the spent lithium ion batteries by combining both acid leaching and chemical precipitation. They dissolved the active substance which they had separated from the cathode of the spent lithium ion batteries in H₂SO₄ and H₂O₂ solutions and were able to precipitate CoC₂O₄.2H₂O micro particles with the addition of (NH₄)₂C₂O₄. The CoC₂O₄.2H₂O was obtained after filtering the suspension while Na₂CO₃ was added to precipitate LiCO₃. Their results showed that 96.3% of Co (mass fraction) and 87.5% of Li could be dissolved in the solution made of 2 mole per litre H₂SO₄ and 2.0% H₂O₂ (volume fraction), and also that 94.7% of Co and 71% of Li could be recovered respectively in the form of CoC₂O₄.2H₂O and LiCO₃ (ZHÜ, et al., 2012).
In another study by Wang and Freidrich, (2015) on the efficient and product-oriented hydrometallurgical recycling process for automotive Li-ion batteries where a pre-treatment was developed to handle the Li–ion batteries from the automotive after being used up. Their study’s main focus was on the possibility of recovering the high-grade graphite, cathode metal salts and lithium carbonate successfully. Their developments for the process route included leaching, solution purifying, to precipitate the cathode metals and finally being able to crystallise the lithium as lithium carbonate. The results from leaching efficiencies obtained of valuable metals (Co, Ni, Cu and Li) were in the range of 98.6 – 99.9 % while the conditions used were optimum at: 80°C, 50 grams per litre of hydrogen peroxide, 2 moles per litre of sulphuric acid or 4 moles per litre of hydrochloric acid in 2 hours. The graphite was filtered and had a purity of about 99.8 %. The optimal condition for the cementation of copper was found to be at 60°C while the calculated activation energy for the cementation reaction was 12.9 kJ/mole. During hydroxide precipitation, a pH range of 3.5 – 4 was recommended for aluminium and iron to be effectively removed while a pH of 10 was recommended to be high enough for the cathode metal (Co, Ni and Mn) salts precipitation. They found that the carbonate and sulphide precipitation methods were quite successful. The conclusion from their study showed that several marketable products were obtained including graphite, Cu powder, cathode metal salts and lithium obtained as lithium carbonate (Wang & Friedrich, 2015).

The study on the recovery of lithium from waste materials was done by Jandova, et al. (2011). They based their processes on roasting, leaching, crystallization and finally condensation-precipitation steps for successful separation of Li$_2$CO$_3$ from Li/MnO$_2$ batteries and lithium-containing wastewaters. They roasted spent Li/MnO$_2$ batteries in reduced pressure at about 650°C causing the casting to split and deactivating the batteries by reducing the LiMnO$_2$ and MnO$_2$ with the residual lithium metal and graphite forming MnO and Li$_2$CO$_3$. The lithium carbonate obtained was selectively soluble in water while the manganese remained in the water. 99.5% of Li$_2$CO$_3$ was obtained after the water was evaporated at about 95%. In their study of lithium-containing alkaline wastewaters from the production of rubber, they were able to condense the lithium concentration up to 12 - 13 grams per litre and then, they did a two-step precipitation of lithium carbonate with CO$_2$ as a precipitating agent. They produced Li$_2$CO$_3$ that was sparingly soluble at 95°C in their second step with most of the impurities remaining in the solution. The lithium carbonate
obtained in their study contained an average of about 99.5% Li$_2$CO$_3$ with the lithium efficiency being about 90% (Janvoda, et al., 2011).
CHAPTER SEVEN

7 Existing lithium ion battery recycling companies

Different facilities exist for the recycling of the lithium ion batteries. The major industrial recycling processes for lithium ion batteries include; Umicore process, the Sony-Sumitomo process, and the Toxco process. There has also been a new plant that has been commercialised called the Recupyl process. The main aim of the recycling processes both those at the industrial and lab scales, is to recover the cobalt and nickel because these do have the highest value while the recovery of lithium is usually not a priority (Sonoc, et al., 2015).

7.1.1 The Umicore process (Belgium)

The capacity of the Umicore industrial operation is 7,000 tonnes of batteries per year which is equivalent to about 150,000 (H)EV batteries or about 250 million mobile phones batteries (ELIBAMA, 2015). The Umicore process represents a dedicated recycling route which combines both pyro- and hydrometallurgical battery recycling routes for end of life lithium ion batteries and nickel metal hydride batteries. The portable or smaller batteries are directly smelted without pre-treatment while the bigger batteries from hybrid and full electric cars are first dismantled in a dedicated dismantling line. The process starts with pyrometallurgical treatment where an alloy of valuable materials (Co, Ni, Cu, Fe) is obtained (Sonoc, et al., 2015). Plastics, solvent and graphite are burnt and leave as gases. The alloy is further treatment hydrometallurgically. The alloy is leached with acid in particular sulphuric acid followed by chemical precipitation to metal salts. The lithium, aluminium and manganese are not recovered and end up in the slag (Georgi-Maschler, et al., 2012). The Umicore process is also a producer of cathode materials for the lithium ion batteries and therefore the recycling aims at a closed loop recovery of cobalt and nickel in the form of LiCoO2 and Ni(OH)2 (Sonoc, et al., 2015).

7.1.2 The Sony-Sumitomo process (Japan)

Sony of Japan in conjunction with Sumitomo Metals Mining Company have developed a process specifically devoted to the recovery of cobalt oxide from the spent lithium ion batteries. The batteries are incinerated at 1000°C in a furnace. In the process of incineration, the cells do open; inflammable components such as organic solvents, plastic casing, lithium
and fluoride are lost as fly ash. The residue is metallic and metal pieces of iron, copper and aluminium can be separated magnetically (Sonoc, et al., 2015). The remaining fraction of material is a powder containing mainly the active cathode material and graphite or carbon which is processed hydrometallurgically to recover the cobalt (Ekermo, 2009).

7.1.3 The Toxco process (Canada)

Two processing methods are used by the Toxco process namely mechanical and hydrometallurgical process to recover metal values from the spent lithium ion batteries. In the Toxco process both lithium metal primary batteries and the lithium ion secondary batteries are recycled. Residual electrical energy in the spent batteries is removed from both the larger and more reactive batteries (Georgi-Maschler, et al., 2012). This is done by cryogenically cooling the batteries in liquid hydrogen to about -200°C. The lithium which is normally explosive at room temperature, behave almost inert at this low temperature. The batteries are then shredded safely and crushed using a hammer mill and then water is added via a shaker table. The homogenates are recovered in an alkaline solution so as to neutralize the acid compounds emitted and also to hydrolyse the organic solvents. The resultant lithium salts formed are separated from the metallic and plastics materials. Sodium carbonate is added to the slurry to enable the precipitation of lithium carbonate which is taken for purification and recrystallization (Tedjar & Foundraz, 2010).

7.1.4 The Recupyl process

The lithium ion batteries are shredded by a rotary shearing machine and they are crushed in an air tight enclosure filled with an inert atmosphere of argon and carbon dioxide. The inert atmosphere of argon and carbon dioxide helps to prevent the violent reaction of the lithium. There is continuous monitoring of the residual oxygen content and pressure and the information recorded is used to determine the injection rate of the gas. After shredding different fractions are obtained which include; a fines fraction that is rich in metal oxides and carbon, a fraction composed of the casings which are magnetic, a denser fraction made up of copper and aluminium which is non-magnetic, and a fraction made up of plastics and paper which is of low density. These fractions are separated while they are still in inert atmosphere. The fines fraction is added to water where the lithium reacts with water and releases hydrogen. The water is heavily stirred and the addition of the fines is done in a very well controlled manner to avoid an explosion while the atmosphere above is maintained.
with poor oxygen. The water then becomes rich in lithium hydroxide and the lithium is recovered by adding sodium carbonate or phosphoric acid. The rest of the materials are recovered using hydrometallurgical means (Sonoc, et al., 2015).

Other recycling companies that have come up include:

7.1.5  The Accurec GmbH (Germany)
The Accurec GmbH process uses mechanical treatment to first extract the electrode material which then is processed by pyrometallurgy to recover cobalt manganese alloy and lithium chloride. The process starts with the removal of electronics and plastic casings and then its followed by (VTR) vacuum thermal treatment and pyrolysis to ensure the electrolyte and the conductive salts are taken care of (ACCUREC, 2016). The batteries are crushed and then aluminium, copper, steel and binder polymer are removed using the combinations of sieving, magnetic separation and air separation. Binder is then added to the remaining electrode material and then agglomerated and pressed to form briquettes which are put in a smelting furnace for reduction. Two fractions are obtained from the furnace namely a metallic cobalt manganese alloy and a slag that contains the lithium. The slag is leached with acid and the lithium is precipitated as lithium chloride (Ekermo, 2009).

7.1.6  Akkuser OY (Finland)
The Akkuser process uses a very different process from others in that they employ a dry process altogether without the addition of any chemicals (AKKUSER, 2016). There is a thoroughly sorting of batteries so as to avoid the contamination of the batteries chemistry as this is essential for the business. The lithium ion batteries are crushed and ground into fine dust where gases are removed and closely monitored and the dust is then further treated by extensive mechanical separation. The lighter fraction of plastics and paper are separated while the metallic fractions are divided according to their class. The metals recovered are then sent to lithium ion battery manufacturers (Ekermo, 2009).

7.1.7  Batrec Industrie AG (Switzerland)
The spent lithium ion batteries are first crushed in a controlled atmosphere where the lithium released is neutralised. The fractions obtained after mechanical treatment results in; Ni-scrap (chrome-nickel steel), non-ferrous metals, cobalt, manganese oxides and plastics (Pistoia, et al., 2001). The fractions obtained are not pure such that the lithium ends up in
the cobalt fraction. The products are then sold to materials producers for further treatment (Georgi-Maschler, et al., 2012).

7.1.8 Falconbridge International Ltd (Canada and Norway)

The lithium ion batteries are partly treated in a smelting furnace together with other wastes in a pyrometallurgical process in Canada. The metallic alloy obtained is granulated and mainly contains copper, cobalt and nickel. The material is then shipped to Norway where it is pulverised and leached using a chlorine-leach hydrometallurgical process. The leached fractions are then introduced in other processes for purification and then refined into products using liquid extraction and electrowinning (Ekermo, 2009).
CHAPTER EIGHT

8 Material and methodology

8.1 Material description

Lithium as already mentioned above in section 1.2 reports to the slag phase during a pyrometallurgical processing route in a base metal smelting because it is easily oxidised. In this thesis, a combined route of both pyrometallurgy and hydrometallurgy processing will be employed. A synthetic slag to mimic a slag produced in a base metal smelter was to be produced in the laboratory. A slag used in a base metal smelting is mainly composed of silica and iron oxide. The amount of silica was the same in all samples while that of iron oxide was adjusted with the addition of the lime. The lime was added as a slag additive so that it would be able to change the properties of the slag and enable the leaching of the lithium to be easier from the slag. A composition of lithium in lithium ion batteries is less than 2% and in this thesis a composition of 4% of lithium in the samples was used. This was done so that the lithium could be detected in the analytical technique by XRD. The samples were produced using the following chemicals:

- Lithium carbonate, pure Li$_2$CO$_3$
- Iron powder, 99% Fe
- Hematite, 99.5% Fe$_2$O$_3$
- Lime, 99.5% CaO
- Silica, 99.5% SiO$_2$

The slag used in this thesis was created according to the equations below. Firstly, iron oxide (FeO), was made by mixing iron powder with hematite according to the equation:

$$ Fe (S) + Fe_2O_3(S) \rightarrow 3 FeO (S) $$

Secondly, the iron oxide produced was mixed with silica to produce a slag according to the equation below:

$$ SiO_2 (S) + 2FeO(S) \rightarrow Fe_2SiO_4(S) $$
### 8.2 Sample preparation

Each sample was weighed in a beaker and then carefully mixed to ensure that no lumps were present. After mixing, the sample was put in a silica carbide crucible ready to be put in the furnace. Figure 11 shows the mixed sample material in the crucible. Table 5 shows the material proportion of each sample. The material balance is shown in section 14.1 of the Appendix.

![Mixed sample material](image)

**Figure 11.** Mixed material in the crucible

**Table 5.** Material proportion for each sample

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fe (g)</th>
<th>Fe₂O₃ (g)</th>
<th>SiO₂ (g)</th>
<th>CaO (g)</th>
<th>Li₂CO₃ (g)</th>
<th>Sum (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>18.27</td>
<td>52.24</td>
<td>29.49</td>
<td>0</td>
<td>0</td>
<td>100.00</td>
</tr>
<tr>
<td>2</td>
<td>16.46</td>
<td>47.06</td>
<td>29.49</td>
<td>7</td>
<td>0</td>
<td>100.00</td>
</tr>
<tr>
<td>3</td>
<td>14.64</td>
<td>41.87</td>
<td>29.49</td>
<td>14</td>
<td>0</td>
<td>100.00</td>
</tr>
<tr>
<td>4</td>
<td>18.27</td>
<td>52.24</td>
<td>29.49</td>
<td>0</td>
<td>27.05</td>
<td>127.05</td>
</tr>
<tr>
<td>5</td>
<td>16.46</td>
<td>47.06</td>
<td>29.49</td>
<td>7</td>
<td>27.05</td>
<td>127.05</td>
</tr>
<tr>
<td>6</td>
<td>14.64</td>
<td>41.87</td>
<td>29.49</td>
<td>14</td>
<td>27.05</td>
<td>127.05</td>
</tr>
</tbody>
</table>

The first three samples had a sum of 100 grams while the last three samples had a sum of 127.1 grams. This was because in the first samples no lithium carbonate was added. The lithium in the lithium carbonate was calculated to being 5.1% while the lithium in the total sample was 4% as already explained. The CaO had a maximum composition of 14% in 100-gram sample and 11% and 127.1-gram sample.
8.3 Equipment

8.3.1 Tamman furnace

Tamman furnace is a high temperature furnace wherein a cylindrical carbon material is employed and electrodes provided at both ends thereof across which electric current is supplied for the heating. The heating tube is made of carbon material surrounded by a thermal insulating material and the inside of the tube is the heat treatment chamber. The furnace can reach high temperatures and the inside of the furnace is maintained under an inert atmosphere. This is done in order to suppress oxidation of a sample to be thermally treated and the heating tube. Figure 12 shows how a picture of the Tamman furnace used.

Figure 12. Tamman furnace. [1] is the nitrogen gas pipe, [2] is water cooling pipes, [3] is the heating furnace and [4] is the electrode at both sides of the furnace

8.3.2 Scan electron microscopy

A scanning electron microscopy is an electronic microscopy capable of producing images of samples after scanning the sample with focused beams of electrons. Once a focused beam of electrons is introduced on the sample, they will interact with the atoms of the sample and produce signals that contain information about the samples surface topography and composition. The SEM equipment used is shown in Figure 50 in the Appendix.
8.3.2.1 Slag sample preparation for Scan electron microscopy analysis

After smelting in the Tamman furnace, slag samples were crushed to obtain small samples to be used for qualitative characterisation using SEM as shown in Figure 27 in the Appendix section. Random samples were selected and mounted in 25 mm diameter cups used to prepare epoxy. The epoxy samples before and after polishing are shown in section 14.4 in the Appendix. After polishing, the samples were carbon-coated to prevent the samples from charging due to the interaction with the electron beam.

8.3.2.2 Characterisation of slag samples using SEM/EDX

The characterisation was conducted using a ZEISS-Merlin with Oxford INCA Mineral software installed on a computer for EDS spectra processing. Before the Backscatter Electron Detector (BSE) images and analysis were taken from the samples, the following were done:

i. The voltage on the Electron High Tension (EHT) was set at 20 kV.

ii. The distance for working between the sample and the low portion of the lens was set at 8.5 mm.

iii. A copper reference was mounted on the sample and used for calibration.

After the procedure above was done, the samples were placed in the sample holders in the SEM and various sites of interest were chosen representing the different phases observed in the slag sample using the ‘Point and ID’ analysis. Images and compositions of the different positions were obtained and are shown in section 9.3 of the Results and Analysis and the rest of the images are shown in section 14.6 of the Appendix.

8.3.3 X-ray diffraction

X-ray diffraction is an analytical technique that is primarily used for phase identification of a crystalline material. It is able to provide information about the unit cell dimensions of the sample. The samples for XRD analysis were first ground in a ring mill for 20 seconds. A small amount of slag sample of about 50 grams was used when grinding. The powder obtained after grinding was then used.

The samples were placed into the sample holder and then the sample holder was mounted in the X-ray diffractometer. The X-ray diffraction analysis was run between 5 and 70 degrees 2-theta. The XRD analysis was run using a PANalytical Empyrean diffractometer and the sampling was done in Gonio mode. Each sample was analysed for one hour. After the analysis, a diffractogram was received from each slag sample. Software “High Score Core
Plus” by PANalytic was used to identify phases present in each sample. The identification of the phases was done by choosing the expected elements in the software and then matching their peaks in the diffractogram with corresponding reference patterns. The elements that were chosen in the software included; Ca, Fe, Si, Li and O as these were the elements present in the slag samples. Section 14.5 in the Appendix shows the slag before and after being put in the sample holder.

8.4 Experimental procedure

8.4.1 Tamman furnace

8.4.1.1 Before each experimental run

A graphite crucible was put inside the furnace and then the silica carbide crucible with the prepared sample was put in the graphite crucible. The silica carbide crucible was then covered with a lid.

The temperature probe and the argon gas lance were then attached and inserted inside the chamber and an isolation brick was used to prevent heat losses during smelting. A ventilation hood was then placed on top of the furnace. The tube for nitrogen was attached to the bottom of the furnace. The setup of the furnace in readiness for the run is shown in Figure 13.

Once switched on, the furnace was run until 1250oC and then maintained at this temperature for two hours. Then it was switched off and allowed to cool for four hours. The temperature during cooling dropped from 1250oC to 50oC in the four hours of cooling and the furnace was switched off. During the entire process of running the furnace, close monitoring was being done to ensure that cooling water was available and that the protection gas was on. The experiment was run in an inert atmosphere.
8.4.2 Leaching tests

Samples for leaching were first ground in a ring mill for 25 seconds. Leaching tests were done on the slag samples with Li₂CO₃ additions; these being sample 4, sample 5 and sample 6 as shown in Table 5. A 20-gram weight of sample was measured from each of samples 4, 5 and 6 and the sample was divided into four parts with a weight of 5-gram each. Three of the 5-gram slag samples were used in the leaching tests while the other 5-gram slag sample was taken for analysis at ALS Scandinavia AB for chemical composition. Three leaching reagents were used as shown in Table 6. Analysis using ICP was later done on the leachate. The standard used in the ICP analysis was prepared as outlined in section 14.7.1 of the Appendix.
Table 6. Leaching test material

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Weight of sample (g)</th>
<th>Leaching agent used</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>5</td>
<td>Water</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>1 molar HCL</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>1 molar H₂SO₄</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>Water</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>1 molar HCL</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>1 molar H₂SO₄</td>
</tr>
<tr>
<td>6</td>
<td>5</td>
<td>1 molar HCL</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>1 molar H₂SO₄</td>
</tr>
</tbody>
</table>

8.4.2.1 Leaching with water

5-gram slag sample was put in a beaker and then a volume of 100 ml of water was added. A magnetic stirrer was used for mixing. Leaching was done for four hours at room temperature. The pH was measured at the end of leaching. A sample from the leached solution was first filtered and then stored in a container for analysis. The procedure was repeated for all water leaching tests. The setup of the test work is shown in Figure 14.

Figure 14. Water leaching setup. [1] is slag in beaker while leaching and [2] is magnetic mixer

8.4.2.2 Leaching with 1 molar HCL and 1 molar H₂SO₄

For leaching with either HCL or H₂SO₄, 5-gram of slag was put in a beaker and then a volume of 100 ml of water was added. A magnetic stirrer was used for mixing. A pH meter was inserted inside the solution to monitor the pH. Either 1 molar HCL or H₂SO₄ was added
using a pipette to maintain a pH of 7 during the entire time. A pH of 7 was chosen so as to selectively leach lithium. Leaching was done for four hours at room temperature. After leaching, a sample was obtained from the leachate, filtered and put in a container for analysis. The total volume of acid used was measured at the end. The setup of the leaching with either HCL or H2SO4 is shown in Figure 15.

Figure 15. Setup for leaching with either 1 molar HCL or 1 molar H2SO4. [1] is pH meter, [2] is beaker with sample material during leaching, [3] is pH electrode, [4] is cylinder with acid for leaching and [5] is temperature electrode though temperature used was room temperature.
CHAPTER NINE

9 Results and Analysis

9.1 Smelting material balance

The material balance for the samples before and after smelting is shown in Table 7. The weight of the material sample after smelting showed a decrease with sample 1 and 6 having the highest percent loss of 14.1 % and 17.0 % respectively.

Table 7. Material balance before and after smelting

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Material weight of sample in (g)</th>
<th>Material weight of sample out (g)</th>
<th>Weight of sample material loss (g)</th>
<th>Weight percent of material loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100.07</td>
<td>85.99</td>
<td>14.08</td>
<td>14.07</td>
</tr>
<tr>
<td>2</td>
<td>100.07</td>
<td>95.67</td>
<td>4.40</td>
<td>4.40</td>
</tr>
<tr>
<td>3</td>
<td>100.07</td>
<td>96.63</td>
<td>3.44</td>
<td>3.44</td>
</tr>
<tr>
<td>4</td>
<td>127.04</td>
<td>109.40</td>
<td>17.64</td>
<td>13.89</td>
</tr>
<tr>
<td>5</td>
<td>127.08</td>
<td>109.50</td>
<td>17.58</td>
<td>13.83</td>
</tr>
<tr>
<td>6</td>
<td>127.00</td>
<td>105.47</td>
<td>21.53</td>
<td>16.95</td>
</tr>
</tbody>
</table>

The crucible used in all smelting tests was the same and weight difference before and after smelting were taken into consideration.
9.2 XRD analysis

Figure 16 shows the diffractogram from the XRD analysis for Sample 1. The analysis showed that the dominant phases that could be identified in Sample 1 were fayalite and quartz with minor christobalite and iron. Table 8 shows the phases identified in slag samples 2 and 3 while the diffractograms are shown in Figure 41 and Figure 43 in the Appendix.

![Figure 16. XRD diffractogram for Sample 1](image)

Table 8. Phases identified in slag samples 2 and 3

<table>
<thead>
<tr>
<th>Slag sample #</th>
<th>Main phases identified</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Hedenbergite ($Ca_{0.5}Fe_{1.5}Si_2O_6$), quartz ($SiO_2$), fayalite ($Fe_2SiO_4$), Calcium Diferrite ($CaFe_2O_4$) &amp; Iron oxide ($Fe_{0.974}O$).</td>
</tr>
<tr>
<td>3</td>
<td>Magnetite ($Fe_3O_4$), Ferrobustamine ($CaFeSi_2O_6$), Silicon dioxide ($SiO_2$) &amp; Calcium Disilicate ($CaO_6Si_2$)</td>
</tr>
</tbody>
</table>
**Slag Sample 6**

Figure 17 shows the diffractogram from XRD for Sample 6. The main phases identified in Sample 6 were dilithium iron silicate, quartz and kilchoanite. Table 9 shows the phases identified in slag samples 4 and 5 while their diffractograms are shown in Figure 45 and Figure 47 in the Appendix.

![Diffractogram](image)

**Figure 17. XRD diffractogram for Sample 6**

**Table 9. Phases identified in slag samples 4 and 5**

<table>
<thead>
<tr>
<th>Slag sample</th>
<th>Main phases identified</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>Lithium Iron Silicate (FeLi$_2$SiO$_4$) and fayalite (Fe$_2$SiO$_4$)</td>
</tr>
<tr>
<td>5</td>
<td>Dilithium Iron Silicate (FeLi$_2$SiO$_4$) and Lithium Iron Silicate (FeLiSiO$_4$)</td>
</tr>
</tbody>
</table>
9.3 SEM analysis

**Slag Sample 1**

In Figure 18, spectrums 1, 2 and 3 could be pure iron droplets in the slag while spectrums 4, 5 and 6 could be phases of either quartz or cristobalite. Spectrums 7 - 12 could be fayalite phases. Spectrums 13 and 14 could also be some fayalite phase. Using the stoichiometric compositions, the results from SEM were in agreement with the results obtained in the XRD analysis shown in Figure 16. The micrographs for slag samples 2 and 3 are shown in Table 10. Point analysis for site of interests for slag sample 1. Oxygen by stoichiometric (Normalised) except spectrum 1 – 3 which were all element analysed and all results in atomic %.

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>Na</th>
<th>Al</th>
<th>Si</th>
<th>S</th>
<th>K</th>
<th>Ca</th>
<th>Ti</th>
<th>Fe</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectrum 1</td>
<td>0.95</td>
<td>6.5</td>
<td>19.48</td>
<td>1.34</td>
<td>0.09</td>
<td>0.8</td>
<td>0.27</td>
<td>7.97</td>
<td>62.59</td>
</tr>
<tr>
<td>Spectrum 2</td>
<td>0.97</td>
<td>6.91</td>
<td>20.42</td>
<td>0.72</td>
<td>0.13</td>
<td>0.84</td>
<td>0.28</td>
<td>7.2</td>
<td>62.52</td>
</tr>
<tr>
<td>Spectrum 3</td>
<td>0.95</td>
<td>6.89</td>
<td>20.84</td>
<td>0.5</td>
<td>0.1</td>
<td>0.92</td>
<td>0.32</td>
<td>6.94</td>
<td>62.54</td>
</tr>
<tr>
<td>Spectrum 4</td>
<td>0.64</td>
<td>18.75</td>
<td>0.11</td>
<td>21</td>
<td>59.51</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spectrum 5</td>
<td>0.51</td>
<td>18.3</td>
<td>21.91</td>
<td>59.28</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spectrum 6</td>
<td>0.56</td>
<td>18.45</td>
<td>21.62</td>
<td>59.37</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spectrum 7</td>
<td>0.45</td>
<td>18.07</td>
<td>22.33</td>
<td>59.15</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spectrum 8</td>
<td>0.59</td>
<td>18.46</td>
<td>0.09</td>
<td>21.51</td>
<td>59.35</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spectrum 9</td>
<td>0.46</td>
<td>18.24</td>
<td>22.06</td>
<td>59.24</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spectrum 10</td>
<td>0.8</td>
<td>2.77</td>
<td>13.8</td>
<td>0.1</td>
<td>17.14</td>
<td>65.39</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spectrum 11</td>
<td>0.4</td>
<td>1.38</td>
<td>14.21</td>
<td>18.99</td>
<td>65.01</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
**Slag Sample 6**

Figure 19. Site of interests for slag sample 6, SEM-EDS analysis

Spectrums 1 could represent some phase of pure iron while 2 - 4 could be iron oxide as shown in Figure 19. Spectrums 5 – 7 could be calcium silicate while spectrums 8 – 10 could represents iron silicate phases. Hedenbergite could be represented by spectrums 11 – 13. The micrographs for slag sample 4 and 5 are shown in Figure 37 and Figure 38 in the Appendix.

Table 11. Point analysis for site of interests for slag sample 6. Oxygen by stoichiometric (Normalised) except spectrum 1 – 3 which were all element analysed and all results in atomic %

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>Al</th>
<th>Si</th>
<th>Ca</th>
<th>Fe</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectrum 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>100</td>
</tr>
<tr>
<td>Spectrum 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>100</td>
</tr>
<tr>
<td>Spectrum 3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>100</td>
</tr>
<tr>
<td>Spectrum 4</td>
<td></td>
<td>0.19</td>
<td>49.81</td>
<td></td>
<td>50</td>
</tr>
<tr>
<td>Spectrum 5</td>
<td>17.43</td>
<td>22.73</td>
<td>1.12</td>
<td></td>
<td>58.72</td>
</tr>
<tr>
<td>Spectrum 6</td>
<td>17.33</td>
<td>22.87</td>
<td>1.14</td>
<td></td>
<td>58.66</td>
</tr>
<tr>
<td>Spectrum 7</td>
<td>17.43</td>
<td>22.79</td>
<td>1.07</td>
<td></td>
<td>58.71</td>
</tr>
<tr>
<td>Spectrum 8</td>
<td>0.34</td>
<td>21.12</td>
<td>0.13</td>
<td>17.76</td>
<td>60.65</td>
</tr>
<tr>
<td>Spectrum 9</td>
<td>0.32</td>
<td>21.21</td>
<td></td>
<td>17.79</td>
<td>60.68</td>
</tr>
<tr>
<td>Spectrum 10</td>
<td>0.44</td>
<td>21.23</td>
<td>0.11</td>
<td>17.49</td>
<td>60.73</td>
</tr>
<tr>
<td>Spectrum 11</td>
<td>15.07</td>
<td>14.99</td>
<td>12.41</td>
<td></td>
<td>57.53</td>
</tr>
<tr>
<td>Spectrum 12</td>
<td>15.25</td>
<td>15.78</td>
<td>11.35</td>
<td></td>
<td>57.62</td>
</tr>
<tr>
<td>Spectrum 13</td>
<td>15.38</td>
<td>15.8</td>
<td>11.13</td>
<td></td>
<td>57.69</td>
</tr>
</tbody>
</table>
9.4 Leaching tests

The results for the chemical composition done by ALS Scandinavia is shown in Table 12 for the main elements of interest. Slag samples 4 and 5 had the lithium content of 40000 mg/kg while sample 6 had 30000 mg/kg.

Table 12. Chemical composition of the elements as analysed by ALS Scandinavia

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Li (mg/kg)</th>
<th>Fe2O3 (%)</th>
<th>CaO (%)</th>
<th>SiO₂ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>40000</td>
<td>64.4</td>
<td>&lt;0.08</td>
<td>28.9</td>
</tr>
<tr>
<td>5</td>
<td>40000</td>
<td>57.0</td>
<td>6.38</td>
<td>31.2</td>
</tr>
<tr>
<td>6</td>
<td>30000</td>
<td>55.9</td>
<td>11.7</td>
<td>29.3</td>
</tr>
</tbody>
</table>

The leaching with both water and either 1 molar HCl or H₂SO₄ was conducted as described in section 8.4.2 of the Material and methodology. The final pH, volume of acid consumed and recoveries after four hours of leaching are shown in the Table 13.

Table 13. Leaching results

<table>
<thead>
<tr>
<th></th>
<th>Water leaching</th>
<th>Leaching with either 1 molar HCl or H₂SO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Slag sample #</td>
<td>Final pH</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>11.16</td>
<td>0.35</td>
</tr>
<tr>
<td>5</td>
<td>11.02</td>
<td>0.31</td>
</tr>
<tr>
<td>6</td>
<td>11.04</td>
<td>0.35</td>
</tr>
</tbody>
</table>

86
Graph of leaching recoveries

The summary of the leaching recoveries for slag samples 4, 5 and 6 are shown in Figure 20 with the highest recovery being for slag sample 6.

Figure 20. Summary of leaching recoveries
CHAPTER TEN

10 Discussion

10.1 Tamman furnace smelting

After smelting, it was observed that there were colour changes in the slag samples with sample 1 having a very dark grey colour while sample 6 had a whitish grey colour. This could be due to the addition of both lime and lithium carbonate to the slag. The colour change of the samples is shown in Figure 25 in the Appendix.

The mass balance shown in Table 7 reveals that the weight loss in grams after smelting was highest in samples 1 at 14.1% and sample 6 at 17.0% weight loss. It was expected that the loss should be the same in all samples since the similar conditions were used. The loss could have been due to that some of the sample remained on the crucible walls as it was difficult to remove the sample after smelting from the crucible since the same crucible was used in all tests. Some slag samples could also have been lost while trying to remove from the crucible and during the crushing when reducing the sample sizes. The loss especially in samples with lithium carbonate additions could also be attributed to the dissociation of lithium carbonate and releasing carbon dioxide gas during smelting.

10.2 XRD and SEM analysis

The slag samples were analysed in XRD in order to investigate the mineral compositions and phases present as a result of the different samples mixtures. As already stated in section 9.2 and 9.3 it could be seen that most of the phases present were mostly oxides of silicon, iron and calcium. The main phases present from samples 1 were fayalite and quartz with minor phases of christobalite and iron while the phases that could be identified by SEM might be phases of fayalite, either quartz or christobalite and also pure iron droplets. This was in agreement with the phases identified in XRD. In sample 2, XRD was able to detect phases of hedenbergite, quartz and fayalite as main phases while the phases that might be of hedenbergite or fayalite and quartz were detected by SEM. Slag sample 3 had magnetite, ferrobustamine, iron (II) oxide, silicon dioxide and calcium disilicate as the main phases detected by XRD. The phases that might be for either hedenbergite or fayalite or ferrobustamine were detected by SEM analysis according to their stoichiometric composition. These were in agreement with the phases identified by XRD although it was
not possible to detect either magnetite or iron (ii) oxide. The peak list for slag samples 1 – 3 are shown in Figure 40, Figure 42 and Figure 44 in the Appendix.

Slag sample 4 had the phases lithium iron (II) silicate and fayalite detected by XRD while the phases that might be for iron oxide, fayalite and also pure iron droplets were detected by SEM. The only phase that was in agreement with XRD was the fayalite. In slag samples 5 and 6, XRD was able to detect dilithium iron silicate, Kilchoanite and lithium iron silicate as the main phases while the phases that might be for iron oxide, fayalite, some calcium silicate and also hedenbergite were detected by SEM. The only phase in agreement with XRD was the iron silicate phase for fayalite and the calcium silicate phases for Kilchoanite. The peak lists for the slag sample 4 – 6 are shown in Figure 46, Figure 48 and Figure 49 in the Appendix.

The addition of lime to the slag was able to create new phases such as hedenbergite and ferrobustamine by replacing some of the iron in the slag lattice. No lithium was detected by SEM due to the design of the equipment as it uses beryllium planchets which prevent the detection of lithium. However, there are new EDS detectors which are able to detect lithium in samples. From the diffractograms for slag samples 4, 5 and 6, it is clear that lithium was reporting in the fayalite phase. The presence of lime could also be the reason why magnetite was only identified in sample 3 as it had the highest lime addition. Slag sample 6 also had a high lime addition of 14% but maybe due to the addition of lithium carbonate, this affected the detection of the magnetite.

10.3 Leaching tests

A higher pH of 11.2 was obtained after leaching slag with water for sample 4 while pH for sample 5 and 6 was both at 11. This may be due to the pH meter that was used or due to an error while the pH was being measured. The leaching with either 1 molar HCl or H2SO4 showed that sample 5 consumed the lowest amount of both acids as shown in Table 13.

From Figure 20, which shows the graph of recoveries for water, HCL and H2SO4 leaching, it can be seen that the highest recovery for lithium was obtained after leaching with 1 molar H2SO4 at 9.4%. Leaching with water gave the lowest recoveries for all slag samples. This could have been due to the low solubility of the formed lithium iron silicate phases in water at room temperature. Low leaching recoveries were obtained for sample 5 for both with HCl
and H\textsubscript{2}SO\textsubscript{4} leaching as compared to recoveries for both samples 4 and 6. It was also noticed that only sample 5 had a slightly higher recovery after leaching with HCl of 2% as compared to H\textsubscript{2}SO\textsubscript{4} leaching of 1.4%. It could also be seen that the higher the volume of acid consumed, the higher the recovery of lithium that was obtained with both HCl and H\textsubscript{2}SO\textsubscript{4} leaching.
CHAPTER ELEVEN

11 Conclusion

A synthetic slag, mimicking a slag from base metal smelting was produced in the laboratory. As stated in section 1.2, lithium reports to the slag phase during pyrometallurgical processing and since the base metal smelting is already an established operation, the lithium ion batteries could be charged during base metal smelting and the lithium recovered from the produced slag by hydrometallurgy. Lime was successfully added to influence the properties of the slag and also to replace the iron in the fayalite lattice. From this work the following could be concluded:

- The dominant phases identified by both XRD and SEM were fayalite, hedenbergite, quartz and ferrobustamine.
- The addition of lime created new dominant phase of hedenbergite and ferrobustamine.
- XRD was able to detect lithium in the slag phases as lithium iron silicates.
- SEM was not able to detect any lithium from the samples.
- Leaching with water gave very low recoveries. This could be due to the low solubility of the formed lithium iron silicate phases in water at room temperature.
- The highest recovery was obtained after leaching with H2SO4.
- Under the conditions tested within this study, the selective recovery of lithium from a slag is very difficult due to the low recoveries obtained.
CHAPTER TWELVE

12 Recommendation

Further investigations that need to be done should be related to the following:

- The smelting of the sample materials in this study was done up to a maximum temperature of 1250°C. There is therefore, need to investigate smelting at lower or higher temperature and study the distribution of the compounds in the formed slag.

- Also in this thesis, the slag samples were slowly cooled. It would be ideal to study the effect of fast cooling.

- Slag contains other basic and acidic oxides like alumina and magnesia and therefore it would be interesting to investigate how they might affect the lithium distribution and eventually the recovery.

- There is also a need to investigate other slag systems apart from the slag system investigated in this thesis.

- Leaching in this thesis was done at room temperature. The effect of leaching at higher temperature should be investigated.

- In this thesis the pH was maintained at 7. A different pH should be investigated to see if it’s possible to selectively leach lithium.

- It is highly recommended that tests are also done on spent lithium ion batteries so as to get a better understanding of the possibilities of lithium recovery as spent lithium ion batteries contain other compounds unlike the ones investigated in this study.
CHAPTER THIRTEEN

13 Bibliography

ACCUREC, G., 2016. ACCUREC RECYCLING GMBH. [Online]
Available at: http://www.accurec.de/treatment-and-recycling
[Accessed 7 3 2016].

AKKUSER, 2016. AKKUSER - True recycling. [Online]
Available at: http://www.akkuser.fi/en/service.htm
[Accessed 7 3 2016].


BATREC, n.d. BATREC-Swiss quality recycling solution. [Online]
Available at: http://www.batrec.ch/en/Recycling-Services#Batteries
[Accessed 7 3 2016].

Available at: http://www.grs-batterien.de/
[Accessed 3 2 2016].

Available at: http://batteryuniversity.com/learn/article/is_lithiumIon_the_ideal_battery
[Accessed 5 2 2016].


ELIBAMA, E. L.-I. B. A. M. F. E., 2015. Li-ion batteries recycling - the batteries end of life., s.l.: ELIBAMA.


Jha, M. K. et al., 2013. Recovery of lithium and cobalt from waste lithium ion batteries. *Journal of Waste management,* 14 6, Volume 33, pp. 1890-1897.


Available at: http://www.lightingafrica.org/resources/briefing-notes.html
[Accessed 18 3 2016].


McDowall, J., 2008. Understanding lithium-ion technology, Marco island, FL: Battcon.


Available at: https://www.mentalhelp.net/articles/bipolar-disorder-treatment-lithium/
[Accessed 25 04 2016].

O’Rourke, J., 2010. The market oracle. [Online]
Available at: http://www.marketoracle.co.uk/Article18127.html
[Accessed 5 2 2016].


batteries-vital-sustainability
[Accessed 02 05 2016].


USGS, U. S. G. S. -, 2012. Lithium in batteries, Virginia, USA: USGS.


CHAPTER FOURTEEN

14 Appendix

14.1 Sample preparation mass balance

<table>
<thead>
<tr>
<th>g/mol</th>
<th>Molar mass</th>
<th>FeO wt.%</th>
<th>Fe₂SiO₄ Mass balance</th>
<th>Mass</th>
<th>100 gram</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1</td>
<td>2  3</td>
</tr>
<tr>
<td>Fe</td>
<td>55.85</td>
<td>1</td>
<td>25.91</td>
<td></td>
<td>18.27 16.46 14.64</td>
</tr>
<tr>
<td>FeO</td>
<td>71.85</td>
<td>3</td>
<td>100</td>
<td>2</td>
<td>70.51 63.51 56.51</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>159.7</td>
<td>3</td>
<td>100</td>
<td>3</td>
<td>52.24 47.06 41.87</td>
</tr>
<tr>
<td>Fe₂SiO₄</td>
<td>203.79</td>
<td>1</td>
<td>100</td>
<td>4</td>
<td>100.00 93.00 86.00</td>
</tr>
<tr>
<td>SiO₂</td>
<td>60.09</td>
<td>1</td>
<td>29.49</td>
<td></td>
<td>29.49 29.49 29.49</td>
</tr>
<tr>
<td>Si</td>
<td>28.09</td>
<td></td>
<td></td>
<td>2</td>
<td>29.49 29.49 29.49</td>
</tr>
<tr>
<td>CaO</td>
<td>56.08</td>
<td>0</td>
<td>7</td>
<td></td>
<td>0  7 14</td>
</tr>
<tr>
<td>Ca</td>
<td>40.08</td>
<td></td>
<td></td>
<td>3</td>
<td>0  7 14</td>
</tr>
<tr>
<td>Li₂O</td>
<td>75.89</td>
<td>0</td>
<td>0.00</td>
<td></td>
<td>0.00 27.05 27.05</td>
</tr>
<tr>
<td>Li</td>
<td>6.94</td>
<td>0</td>
<td>0</td>
<td></td>
<td>0  5.08 5.08</td>
</tr>
<tr>
<td>O</td>
<td>16</td>
<td>0</td>
<td>18</td>
<td></td>
<td>18 5.08 5.08</td>
</tr>
<tr>
<td>C</td>
<td>12.011</td>
<td>14</td>
<td>Tot. wt.</td>
<td></td>
<td>100.00 100.00 100.00</td>
</tr>
<tr>
<td>Li</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>127.05 127.05 127.05</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4.00 4.00 4.00</td>
</tr>
</tbody>
</table>

Figure 21. Material balance

14.2 Tamman furnace

Figure 22. Complete Tamman furnace
Figure 23. Crucible with sample inside the Tamman furnace  

Figure 24. After smelting

Figure 25. Slag samples after being ground in the roll mill showing different colours

14.3 Tamman furnace slag samples after smelting

Figure 26. Slag sample after smelting and cooling  

Figure 27. Crushed slag sample
14.4 Epoxy sample preparation

Figure 28. Filled epoxy sample cups

Figure 29. Epoxy samples after hardening overnight

Figure 30. Epoxy samples after polishing  Figure 31. Set of discs used in polishing
14.5 XRD sample preparation

Figure 32. Slag sample being put in sample holder

Figure 33. Slag in sample holder
**14.6 SEM Images and elemental composition**

**Slag sample 1**

![SEM Image](image)

Figure 34. Site of interests for slag sample 1, SEM-EDS analysis

**Table 14. Point analysis for site of interests for slag sample 1. Oxygen by stoichiometry (Normalised) and all results in atomic %**

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>Na</th>
<th>Al</th>
<th>Si</th>
<th>K</th>
<th>Fe</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectrum 1</td>
<td>0.56</td>
<td>18.45</td>
<td>0.1</td>
<td>21.55</td>
<td>59.34</td>
<td></td>
</tr>
<tr>
<td>Spectrum 2</td>
<td>0.54</td>
<td>0.46</td>
<td>18.65</td>
<td>0.09</td>
<td>20.98</td>
<td>59.28</td>
</tr>
<tr>
<td>Spectrum 3</td>
<td>0.32</td>
<td>0.65</td>
<td>18.96</td>
<td>0.11</td>
<td>20.43</td>
<td>59.53</td>
</tr>
<tr>
<td>Spectrum 4</td>
<td>0.6</td>
<td>0.6</td>
<td>19.98</td>
<td>0.12</td>
<td>18.74</td>
<td>59.96</td>
</tr>
<tr>
<td>Spectrum 5</td>
<td>0.37</td>
<td>0.48</td>
<td>18.62</td>
<td>21.19</td>
<td>59.34</td>
<td></td>
</tr>
<tr>
<td>Spectrum 6</td>
<td>0.53</td>
<td>1.07</td>
<td>20.88</td>
<td>0.16</td>
<td>16.81</td>
<td>60.54</td>
</tr>
<tr>
<td>Spectrum 7</td>
<td>0.58</td>
<td>0.7</td>
<td>18.88</td>
<td>0.22</td>
<td>20.2</td>
<td>59.42</td>
</tr>
</tbody>
</table>
Figure 35. Site of interests for slag sample 2, SEM-EDS analysis

Table 15. Point analysis for site of interests for slag sample 2. Oxygen by stoichiometry (Normalised) and all results in atomic %

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>Al</th>
<th>Si</th>
<th>S</th>
<th>K</th>
<th>Ca</th>
<th>Fe</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectrum 1</td>
<td>1.43</td>
<td>19.31</td>
<td>0.3</td>
<td>0.1</td>
<td>3.28</td>
<td>15.28</td>
<td>60.29</td>
</tr>
<tr>
<td>Spectrum 2</td>
<td>1.08</td>
<td>19.82</td>
<td>0.16</td>
<td>0.1</td>
<td>4.03</td>
<td>14.57</td>
<td>60.34</td>
</tr>
<tr>
<td>Spectrum 3</td>
<td>1.47</td>
<td>19.16</td>
<td>0.43</td>
<td>0.09</td>
<td>3.05</td>
<td>15.44</td>
<td>60.36</td>
</tr>
<tr>
<td>Spectrum 4</td>
<td>1.23</td>
<td>20.31</td>
<td>0.29</td>
<td></td>
<td>7.18</td>
<td>10.24</td>
<td>60.75</td>
</tr>
<tr>
<td>Spectrum 5</td>
<td>1.53</td>
<td>21.08</td>
<td>0.44</td>
<td>0.08</td>
<td>6.4</td>
<td>9.12</td>
<td>61.34</td>
</tr>
<tr>
<td>Spectrum 6</td>
<td>1.60</td>
<td>20.93</td>
<td>0.46</td>
<td></td>
<td>6.17</td>
<td>9.53</td>
<td>61.32</td>
</tr>
<tr>
<td>Spectrum 7</td>
<td>1.16</td>
<td>19.42</td>
<td>0.34</td>
<td>0.14</td>
<td>2.83</td>
<td>15.8</td>
<td>60.31</td>
</tr>
<tr>
<td>Spectrum 8</td>
<td>1.03</td>
<td>19.39</td>
<td>0.16</td>
<td>0.11</td>
<td>2.2</td>
<td>17.01</td>
<td>60.09</td>
</tr>
<tr>
<td>Spectrum 9</td>
<td>1.06</td>
<td>19.49</td>
<td>0.15</td>
<td></td>
<td>3.06</td>
<td>16.08</td>
<td>60.16</td>
</tr>
<tr>
<td>Spectrum 10</td>
<td>0.4</td>
<td>6.46</td>
<td>11.14</td>
<td></td>
<td>1.15</td>
<td>16.39</td>
<td>64.47</td>
</tr>
<tr>
<td>Spectrum 11</td>
<td>0.66</td>
<td>11.74</td>
<td>6.11</td>
<td></td>
<td>2.11</td>
<td>17.22</td>
<td>62.15</td>
</tr>
<tr>
<td>Spectrum 12</td>
<td>0.49</td>
<td>8.1</td>
<td>9.76</td>
<td></td>
<td>1.17</td>
<td>16.57</td>
<td>63.93</td>
</tr>
</tbody>
</table>
Slag sample 3

Figure 36. Site of interests for slag sample 3, SEM-EDS analysis

Table 16. Point analysis for site of interests for slag sample 3. Oxygen by stoichiometry (Normalised) and all results in atomic %

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>Al</th>
<th>Si</th>
<th>S</th>
<th>K</th>
<th>Ca</th>
<th>Ti</th>
<th>V</th>
<th>Cr</th>
<th>Fe</th>
<th>Cu</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectrum 1</td>
<td>14.93</td>
<td>0.35</td>
<td>0.44</td>
<td>0.34</td>
<td>0.28</td>
<td>45.38</td>
<td>51.27</td>
<td>65.94</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spectrum 2</td>
<td>15.01</td>
<td>0.39</td>
<td>0.43</td>
<td>0.38</td>
<td>0.33</td>
<td>45.23</td>
<td>51.31</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spectrum 3</td>
<td>15.02</td>
<td>0.2</td>
<td>15.84</td>
<td>0.14</td>
<td></td>
<td>17.79</td>
<td>0.09</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spectrum 4</td>
<td>1.63</td>
<td>0.98</td>
<td>0.96</td>
<td>0.96</td>
<td></td>
<td></td>
<td>41.67</td>
<td>53.09</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spectrum 5</td>
<td>1.38</td>
<td>0.98</td>
<td>0.96</td>
<td>0.96</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spectrum 6</td>
<td>1.46</td>
<td>0.98</td>
<td>0.96</td>
<td>0.96</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spectrum 7</td>
<td>0.98</td>
<td>0.98</td>
<td>0.96</td>
<td>0.96</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spectrum 8</td>
<td>0.98</td>
<td>0.98</td>
<td>0.96</td>
<td>0.96</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spectrum 9</td>
<td>0.98</td>
<td>0.98</td>
<td>0.96</td>
<td>0.96</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spectrum 10</td>
<td>1.69</td>
<td>0.57</td>
<td>2.09</td>
<td>0.32</td>
<td>0.58</td>
<td>41.67</td>
<td>53.09</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spectrum 11</td>
<td>0.12</td>
<td>0.5</td>
<td>14.76</td>
<td>0.17</td>
<td>0.29</td>
<td>18.85</td>
<td>0.32</td>
<td>64.99</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 37. Site of interests for slag sample 4, SEM-EDS analysis

Table 17. Point analysis for site of interests for slag sample 4. Oxygen by stoichiometry except spectrums 1 – 3 except spectrum 1 – 3 which were all element analysed (Normalised) and all results in atomic %. All elements analysed (Normalised) and all results in atomic %

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>Na</th>
<th>Al</th>
<th>Si</th>
<th>K</th>
<th>Ca</th>
<th>Fe</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectrum 1</td>
<td>50</td>
<td>50</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>50</td>
</tr>
<tr>
<td>Spectrum 2</td>
<td>50</td>
<td>50</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>50</td>
</tr>
<tr>
<td>Spectrum 3</td>
<td>50</td>
<td>50</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>50</td>
</tr>
<tr>
<td>Spectrum 4</td>
<td></td>
<td></td>
<td>14.88</td>
<td></td>
<td>27.68</td>
<td>57.44</td>
<td></td>
</tr>
<tr>
<td>Spectrum 5</td>
<td></td>
<td></td>
<td>14.98</td>
<td></td>
<td>27.53</td>
<td>57.49</td>
<td></td>
</tr>
<tr>
<td>Spectrum 6</td>
<td></td>
<td></td>
<td>14.93</td>
<td></td>
<td>27.6</td>
<td>57.47</td>
<td></td>
</tr>
<tr>
<td>Spectrum 7</td>
<td></td>
<td></td>
<td>14.96</td>
<td></td>
<td>27.56</td>
<td>57.48</td>
<td></td>
</tr>
<tr>
<td>Spectrum 8</td>
<td>0.28</td>
<td></td>
<td>20.76</td>
<td></td>
<td>18.52</td>
<td>60.45</td>
<td></td>
</tr>
<tr>
<td>Spectrum 9</td>
<td></td>
<td></td>
<td>20.82</td>
<td></td>
<td>18.77</td>
<td>60.41</td>
<td></td>
</tr>
<tr>
<td>Spectrum 10</td>
<td></td>
<td></td>
<td>20.96</td>
<td></td>
<td>18.56</td>
<td>60.48</td>
<td></td>
</tr>
<tr>
<td>Spectrum 11</td>
<td></td>
<td></td>
<td>14.9</td>
<td></td>
<td>27.65</td>
<td>57.45</td>
<td></td>
</tr>
<tr>
<td>Spectrum 12</td>
<td>0.79</td>
<td>0.77</td>
<td>14.14</td>
<td>0.27</td>
<td>0.15</td>
<td>26.87</td>
<td>57</td>
</tr>
</tbody>
</table>
Figure 38. Site of interests for slag sample 5, SEM-EDS analysis

Table 18. Point analysis for site of interests for slag sample 5. Oxygen by stoichiometry (Normalised) and all results in atomic %
Figure 39. Site of interests for slag sample 6, SEM-EDS analysis

Table 19. Point analysis for site of interests for slag sample 6. Oxygen by stoichiometry except spectrum 1 which was all elements analysed (Normalised) and all results in atomic %

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>Al</th>
<th>Si</th>
<th>S</th>
<th>Ca</th>
<th>Cr</th>
<th>Fe</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectrum 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>Spectrum 2</td>
<td></td>
<td></td>
<td></td>
<td>0.14</td>
<td></td>
<td>49.82</td>
<td>50.04</td>
</tr>
<tr>
<td>Spectrum 3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Spectrum 4</td>
<td></td>
<td>21.19</td>
<td></td>
<td>0.19</td>
<td></td>
<td>18.03</td>
<td>60.59</td>
</tr>
<tr>
<td>Spectrum 5</td>
<td>0.23</td>
<td></td>
<td>21.11</td>
<td>0.16</td>
<td></td>
<td>17.89</td>
<td>60.61</td>
</tr>
<tr>
<td>Spectrum 6</td>
<td>0.26</td>
<td></td>
<td>21.16</td>
<td>0.2</td>
<td></td>
<td>17.72</td>
<td>60.65</td>
</tr>
<tr>
<td>Spectrum 7</td>
<td></td>
<td>15.11</td>
<td></td>
<td>15.62</td>
<td></td>
<td>11.72</td>
<td>57.56</td>
</tr>
<tr>
<td>Spectrum 8</td>
<td>0.4</td>
<td>17.16</td>
<td>0.39</td>
<td>14.31</td>
<td></td>
<td>8.66</td>
<td>59.08</td>
</tr>
</tbody>
</table>
14.7 Leaching test preparation

14.7.1 ICP standard analysis preparation

To prepare standards for using when analysing the leached slag samples, concentrations for each element to be analysed was done. This was done by first calculating the content of each element if the 5-gram sample, then the total leaching volume was measured and the concentration of the element was calculated. Then it was determined that the least concentration should be 1% of the highest concentration. This was done for all elements to be analysed. The results of the calculated concentrations are shown in Table 20.

Table 20. Calculated concentrations for elements in 5-gram slag sample

<table>
<thead>
<tr>
<th>Element</th>
<th>Highest calculated concentration (g/L)</th>
<th>Lowest calculated concentration (g/L)</th>
<th>Concentration used for preparing the standard (g/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>2.00 Water 1.67 HCL 1.78 H2SO4</td>
<td>0.02 Water 0.02 HCL 0.02 H2SO4</td>
<td>2</td>
</tr>
<tr>
<td>Fe</td>
<td>21.57 Water 17.98 HCL 19.17 H2SO4</td>
<td>0.22 Water 0.18 HCL 0.19 H2SO4</td>
<td>20</td>
</tr>
<tr>
<td>Si</td>
<td>5.43 Water 4.52 HCL 4.82 H2SO4</td>
<td>0.05 Water 0.05 HCL 0.05 H2SO4</td>
<td>10</td>
</tr>
<tr>
<td>Ca</td>
<td>3.94 Water 3.28 HCL 3.50 H2SO4</td>
<td>0.04 Water 0.04 HCL 0.04 H2SO4</td>
<td>10</td>
</tr>
</tbody>
</table>

Standard solutions of the elements to be analysed were taken and then the dilution factor was calculated so that the highest analysis concentration could be reached. The standard concentrations of the elements are shown in Table 21.

Table 21. Concentrations for standard elements

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration (µg/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>1000</td>
</tr>
<tr>
<td>Fe</td>
<td>10000</td>
</tr>
<tr>
<td>Si</td>
<td>10000</td>
</tr>
<tr>
<td>Ca</td>
<td>10000</td>
</tr>
</tbody>
</table>

Using the information from Table 20 and Table 21, dilution factors were calculated. These are 500 for Li, 50 for Fe and 1000 for both Si and Ca. The volume of the flask used was 100ml and with these dilution factors, the volume of each standard needed was calculated. The volumes of the standards needed were: Li = 0.2 ml, Fe = 0.2 ml, Si = 0.1 ml and Ca = 0.1 ml.
14.8 XRD

Slag sample 1 Peak list

Figure 40. Slag sample 1 peak list

Slag sample 2 micrograph

Figure 41. XRD diffractogram for sample 2
Slag sample 2 Peak list

Figure 42. Slag sample 2 peak list

Slag sample 3 micrograph

Figure 43. XRD diffractogram for sample 3
Slag sample 3 Peak list

Figure 44. Slag sample 3 peak list

Slag sample 4 micrograph

Figure 45. XRD diffractogram for Sample 4
Slag sample 4 Peak list

Figure 46. Slag sample 4 peak list

Slag sample 5 micrograph

Figure 47. XRD diffractogram for Sample 5
Slag sample 5 Peak list

Figure 48. slag sample 5 peak list

Slag sample 6 Peak list

Figure 49. slag sample 6 peak list
Figure 50. SEM equipment used