SIMULATION AND MODELLING OF ZINC RECOVERY PROCESS FROM STEEL SCRAP

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In Partial Fulfillment of the Requirement
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This research project addressed a practical problem besetting electric arc furnace (EAF) steelmakers and environmentalists for many years. EAF dust is generated during the EAF steelmaking process, and it is designated as a hazardous waste in most industrialized countries because it contains zinc, which is hazardous for the environment. The purpose of this research was to develop a pre-treatment step that removes zinc coatings from galvanized steel scrap, leaving steel products with low or no zinc content, which can be used as a cheap source of feed materials for steel making industries that produce zinc-free EAF dust. Also, zinc consuming industries can use the recovered zinc to bridge the gap between the supply of and demand for zinc.

The zinc recovery process involves three major stages, namely: leaching, solvent extraction and electrowinning. A metallurgical simulator (METSIM) was used to simulate these processes. The leaching of the zinc coating from the galvanized scrap was carried out with sodium hydroxide because it cannot leach iron, which is the major component of the galvanized steel scrap. Sodium zincate was produced from this process, and black steel is recovered as a solid from the solid-liquid separator, which can be fed in the EAF to produce new steel. In the solvent extraction, 8-hydroxyquinoline (LIX-26) was used as an extractant because of its ability to extract zinc. Zinc quinoline and sodium hydroxide were produced as extract and raffinate, respectively. Concentrated sulfuric acid was used to strip the extract to produce zinc sulphate transferred to the electrowinning section. In electrowinning, metallic zinc was recovered from zinc ion deposited at the cathode and oxygen gas evolved from the stream.

This process's feed rate is 400 mt/yr of galvanized steel scrap with a feed component of 320 mt/yr and 80 mt/yr of iron and zinc, respectively. The amount of zinc recovered at the end of the process is 72.59 mt/yr, and the percentage is 90.74%. With this amount of zinc recovery, the steelmakers will be able to recycle the galvanized steel scrap with zero or minimal pollutants caused by zinc; also, the recovered zinc as a by-product will be used for other purposes in the zinc consuming industry.
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ABBREVIATIONS

BOF      Basic Oxygen Furnace
CFD      Computational fluid dynamics
EAF      Electric arc furnace
EAFD     Electric arc furnace Dust
ELC      Electrowinning cells
HTMR     High temperature metals recovery
IRM      Iron Rich Materials
ISP      Imperial smelting process
L/S      Liquid to solid ratio
METSIM   Metallurgical simulator
MRT      Molecular recognition technology
PLS      Pregnant leach solution
RLE      Roasting leaching electrowinning
SLS      Solid liquid separator
TNK      Tank
SYMBOLS

c: Concentration (mol m$^{-3}$)
D: Diffusivity of species (m$^2$ s$^{-1}$)
F: Faraday’s constant (C mol$^{-1}$)
g: Gravity (m s$^{-2}$)
i: Current density (A m$^2$)
i: Species
N: Flux density (mol m$^2$ s$^{-1}$)
p: Pressure (Pa)
R: Gas constant (J mol$^{-1}$ K$^{-1}$)
T: Temperature (K)
t: Time (s)
u: Mobility (m$^2$ V$^{-1}$ s$^{-1}$)
v: Velocity vector (m s$^{-1}$)
z: Charge (C)
$\alpha_a$: Anodic symmetry factor
$\alpha_c$: Cathodic symmetry factor
$\mu$: Viscosity (Pa s)
$\rho$: Density (kg m$^{-3}$)
$\Phi$: Electric field (V m$^{-1}$)
$\nabla$: Gradient
CHAPTER ONE
INTRODUCTION

1.0 Overview

Zinc (Zn) is a slightly brittle metal at room temperature and has a blue-silvery appearance when the protective oxide layer is removed. On the list of abundant elements in the earth's crust, zinc occupies the 24th position and has an average concentration of 65 g/t (Abkhoshk et al., 2014). It is mostly used to galvanize steel (an alloy of iron and carbon, and other elements) due to its ability to prevent corrosion. Galvanization is the process of preventing rusting of steel and iron by applying a protective zinc coating.

The primary source of zinc metal is from zinc sulphide ores; its use has increased rapidly in recent years. About 55% of zinc produced is used to galvanize steel, a significant component used in buildings, infrastructure, tools, ships, automobiles, and machines (Abkhoshk et al., 2014). They further stated that, after iron, aluminum, and copper, zinc is the next most widely consumed metal. The growth in the numbers of zinc-consuming industries will demand zinc to remain stable in the coming years. The zinc industry's primary concern is how to bridge the gap between the supply and demand of zinc because the zinc sulphide ores grade decreases as the consumption of zinc increases (Abkhoshk et al., 2014).

Pure zinc, in comparison, is much more amenable to chemical extraction and recovery. While galvanized scrap has bulk zinc concentrations lower than typical zinc ore, the zinc is in a relatively pure form in scrap. It is thought that this non-complex zinc feed can be selectively separated easier and more economically from the galvanized steel.

To meet the demand in the coming years, zinc needs to be recovered from the galvanized steel scrap. Although, the production of steel is associated with significant accumulation of wastes, such as slag, sludge, flue dust and gases. Some of these are recyclables, others are toxic, constituting hazardous wastes, which should be processed, to be reutilized or appropriately discarded to avoid environmental impact (Hagni et al., 1991). The primary concern related to steel production in electric arc furnaces (EAF) is the generation of a considerable amount of flue dust, which contains a variety of heavy metals. Lead, cadmium and chromium (IV) are the most hazardous species in the dust, whereas zinc is the most valuable component due to the relatively large amount present (Huber et al., 1999).
There are processes in place for recovering zinc from EAF through stabilization. These are pyrometallurgical, hydrometallurgical, or hybridization of both (Barrera-Godinez et al., 1992). However, finding a cost-effective and environmental-friendly process remains the major challenge. The pyrometallurgical process can process the EAF dust economically only when the zinc content is higher than 15-20% (Zunkel, 1999). The choice between pyrometallurgical and hydrometallurgical processing routes strongly depends on the dust characteristics, and these are the size of the particle, the number of valuable elements, and mineralogical phases. The mineralogical phases indicate leachable constituents (Lindblom et al., 2002). The presence of high energy consumption and the generation of worthless residues in pyrometallurgical processes constrain the viability of the procedures. However, hydrometallurgical processes offer an exciting alternative for zinc recovery as long as iron dissolution is controlled (Dutra et al., 2006).

1.1 Rationale

The rationale for developing this process is that galvanized steel scrap cannot be fed into a foundries furnace. This is due to safety and health concerns from zinc fuming. The diagrams regarding the treatment of galvanized steel block are shown in Figure 1.1 – 1.3. Figure 1.1 showed the recycling of steel without considering the recycling of zinc. Some of the zinc in the galvanized steel scrap were emitted to the atmosphere during the production of the steel (steelmakers), and the remaining zinc generated as dust were dumped in hazardous landfills. Although a human can handle a proportionately large zinc concentration, a very high zinc level can damage the pancreas and disturb protein metabolism. Figure 1.2 showed the recycling of steel and also the pyrometallurgical process for zinc recovery. The pyrometallurgical process recovered the zinc at the EAF/BOF dust was used for further galvanization of the steel. There is no dumping of zinc in a hazardous landfill, but zinc and some other element were emitted into the atmosphere. The hydrometallurgical process for the treatment of galvanized steel scrap is shown in Figure 1.3. This process leached the zinc present in the galvanized steel scrap, produced recycled steel with low or no zinc, and recycled the zinc to further galvanize steel without polluting the environment.
Fig 1.1. Block diagram showing the treatment of galvanized steel scrap (Alam, 2001).
Fig 1.2. Block diagram showing the pyrometallurgical process for treating galvanized steel scrap (Adapted from Alam, 2001).
Fig 1.3. Block diagram showing the hydrometallurgical process for treating galvanized steel scrap (Adapted from Alam, 2001).
The primary technology for recycling galvanized scrap is the use of electric arc furnace (EAF) in the steel making industry. Furnaces that can treat galvanized scrap need to have dust collection systems that drive up the cost of remelting scrap. For this reason, galvanized steel sells at a discount price compared to black steel. This difference can be significant, and it is thought that the economics may align to exploit this galvanized scrap source as a foundry feed.

1.2 Aims and objectives

The aim is to generate a saleable zinc product and to recycle the zinc coating. This project aimed to incorporate reagent recovery technologies to make this a zero discharge process. With increasingly tight environmental regulations and discharge permits put on chemical plants, there is a move towards zero discharge processes for economic and strategic reasons. The scope of this project was to develop a process to remove zinc from a galvanized steel and generate a dezinced ferrous scrap for use at a foundry using metallurgical simulator (METSIM).

The objectives of this research are:

I. To produce a zinc-free black steel from steel scrap that will be fed to steel makers.
II. To simulate and model the zinc recovery process from steel scrap.
III. Determine the effect of concentration of the lixiviant in the process.
IV. To recover metallic zinc from pregnant leached solution (PLS) by solvent extraction followed by electrowinning.

These objectives were achieved by using METSIM and COMSOL Multiphysics package. The model was validated with the experimental data obtained by Dr. Shafiq Alam, which is the only experiment done on zinc recovery from steel scrap using sodium hydroxide as the lixiviant. The modelling equations were developed for COMSOL Multiphysics package (modelling software) to use in future work.

1.3 Thesis outlines

The chapters of this research thesis are arranged as follows:

Chapter 1: Introduction
Chapter 2: Literature Review
Chapter 3: Materials and Method
Chapter 4: Results and Discussion
Chapter 5: Conclusions and Recommendations
CHAPTER TWO
LITERATURE REVIEW

2.0 Steel

Steel is an alloy consisting of iron and carbon and other elements such as nickel, copper, chromium and aluminum. Given its high tensile strength and low cost, it is a significant component used in buildings, tools, infrastructure, automobiles, ships, trains, machines, weapons, and appliances. The base material of steel is iron; the carbon content of steel is between 0.08 to 1.5 wt.%. Steel has an uncommon balance of hardness, flexibility and tensile strength. The making of steel requires iron ore to be heated and melted in furnaces where the impurities are removed, and carbon added. Presently, most steel is made using electric arc furnace.

2.1 Classification of steel

Carbon concentration is the baseline for classifying some of the more common steels. Plain carbon steels contain only residual concentrations of impurities aside from carbon and a touch manganese. For alloy steels, more alloying elements are intentionally added in specific concentrations (Callister and Rethwisch, 2010).

2.1.1 Low carbon steel

Of all the various steels, those produced within the most significant quantities fall within the low-carbon classification. These generally contain but about 0.25 wt.% wt.% C and are unresponsive to heat treatments intended to make martensite; strengthening is accomplished by cold work. Microstructures consist of ferrite and pearlite constituents. As a consequence, these alloys have outstanding ductility and toughness, although they are soft and weak. The typical applications include automobile body components, structural shapes, and sheets used in pipelines, buildings, bridges, and tin cans (Callister and Rethwisch, 2010).

2.1.2 Medium carbon steel

The medium carbon steels have between 0.25 and 0.60 wt.% carbon concentrations. These alloys could also be heat-treated by austenitizing, quenching, then tempering to enhance their mechanical properties. They are most frequently utilized within the tempered condition, having microstructures of tempered martensite. Plain medium carbon steels have low harden abilities and
may be successfully treated by heat only in very thin sections and with very successive quenching rates. Additions of chromium, nickel, and molybdenum improve those alloys' capacity to be heat-treated, giving rise to a spread of strength ductility combinations. The applications include railway wheels and tracks, gears, crankshafts, and other machine parts and high-strength structural components calling for a mixture of high strength, wear resistance, and toughness (Callister and Rethwisch, 2010).

2.1.3 High carbon steel

The high carbon steels, typically having carbon contents between 0.60 and 1.4 wt.%, are the toughest, strongest, and yet least ductile of the carbon steels. They are nearly always utilized in a hardened and tempered condition and, as such, are mostly wear-resistant and capable of holding a pointy leading edge. Examples of high carbon alloys are tool and die steels, usually containing chromium, vanadium, tungsten, and molybdenum. These alloying elements combine with carbon to make tough and wear-resistant carbide compounds. These steels are employed as cutting tools and dyes to form and shape materials, such as knives, razors, hacksaw blades, springs, and high strength wire (Callister and Rethwisch, 2010).

2.1.4 Stainless steel

The stainless steels are alloy steels and are highly resistant to corrosion (rusting) in diverse environments, especially the ambient atmosphere. Their predominant alloying element is chromium; a degree of a minimum of 11 wt.% Cr is required. Corrosion resistance may also be improved by adding nickel and molybdenum (Callister and Rethwisch, 2010).

2.2 Electric Arc Furnace (EAF)

Electric Arc Furnace (EAF) is mainly used to produce special quality steels that are alloyed with other metals. EAF can also be used to produce ordinary, non-alloyed steels. The feed materials such as scrap steel/black steel is tipped into the EAF from an overhead crane. When the furnace is full, the lid is swung shut, covering the top of the furnace. The lid contains electrodes that are lowered into the furnace. The electrodes are charged with a powerful electric current, which generates heat, thus melting the scrap. As the scrap melts, other metals known as ferroalloys are
added to the steel to give it the desired chemical composition. Lime and fluorspar are added to fuse with the impurities and form slag. The molten slag floats on the top of the molten steel and can be poured off by tilting the furnace. A range of special quality steels can be made in EAF by combining other metals to form steel alloys. The most widely used of these are stainless steel, which has chromium and nickel added to give it corrosion-resistant properties. Other special steels made in EAF include steels used in engineering, aerospace and armour plates (Metal Supermarket, 2015).

2.3 Steel scrap recycling

The recycling rates for steel are high; they are higher than most other metals. New scrap is produced during steel product fabrication, such as turning and stamping. Scrap automobiles are the primary and cheap sources of old scrap for steel production. In 2012, the recycling rate for automobiles was approximately 93% (Fenton, 2005).

The process routes for steel production are shown in Figure 2.1. Steel is produced from iron ore or recycled steel. The chief technology used to reduce iron ore to iron is a blast furnace. Electric arc furnaces are chiefly used to recycle steel by remelting it. The recycling of steel is economically advantageous as it is about half as energy-intensive as primary steel production, as displayed in Table 2.1. By recycling one ton of steel, 2500 lb. of iron ore, 1400 lb. of coal and 120 lb. of limestone are conserved (Javaid and Essadiqi, 2003).
Fig 2.1. Different process routes for steel production (UNEP, 2013).

Table 2.1: Energy Intensities for Process Route in Fig 2.1. (UNEP, 2013)

<table>
<thead>
<tr>
<th>Process Route</th>
<th>GJ/tonne</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary production via Blast Furnace and Open Heart Furnace (BF – OHF)</td>
<td>26.4 – 41.6</td>
</tr>
<tr>
<td>Primary production via Blast Furnace and Basic Oxygen Furnace (BF – BOF)</td>
<td>19.8 – 31.2</td>
</tr>
<tr>
<td>Primary production via Direct Reduction and Electric Arc Furnace (BF – EAF)</td>
<td>28.3 – 30.9</td>
</tr>
<tr>
<td>Recycling via Electric Arc Furnace (EAF)</td>
<td>9 – 12.5</td>
</tr>
</tbody>
</table>

2.4 Zinc deposit

Zinc is mainly used to galvanize steel (an alloy of iron and carbon, and other elements) due to its ability to prevent corrosion. Galvanization is the process of preventing rusting from steel and
iron by applying a protective zinc coating. There are approximately 55 known zinc minerals, but only a few have economic importance (Thompson, 2006). Table 2.2 is the list of the most common zinc minerals. The zinc mineral with the most significant amount is sphalerite (ZnS), it accounts for about 85% of zinc production. The global reserve of sulphide ore is expected to last for several decades, recovery of zinc from the steel scrap will be a significant alternative source for zinc metal production to meet the future demand of zinc. Zinc oxide is a general term that comprises a whole series of minerals. However, the only ones that have been considered so far to have economic importance for zinc extraction are the zinc carbonates, including smithsonite and hydrozincite and the zinc silicates hemimorphite and willemite (Boni et al., 2005; Large, 2001).

2.5 Zinc production methods

Zinc was first smelted about 1000 years ago in China and India; however, sophisticated technology for zinc production was developed in western civilization in the 18th century (Bond, 1999). At present, zinc can be produced through several processing techniques, which are classified into two categories. These are pyrometallurgical and hydrometallurgical methods. The former involves smelting of the ore or concentrate at high temperatures, while the latter involves leaching the ore or concentrate at relatively low temperatures.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Ideal formula</th>
<th>Wt.% Zn</th>
<th>Common associations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sphalerite</td>
<td>ZnS</td>
<td>67.09</td>
<td>Found in sulphide deposits</td>
</tr>
<tr>
<td>Smithsonite</td>
<td>ZnCO₃</td>
<td>52.14</td>
<td>Found in most oxide deposits</td>
</tr>
<tr>
<td>Hydrozincite</td>
<td>Zn₅(OH)₆(CO₃)₂</td>
<td>57.7</td>
<td>Present in many deposits might replace smithsonite</td>
</tr>
<tr>
<td>Hemimorphite</td>
<td>Zn₄Si₂O₇(OH)₂.2H₂O</td>
<td>54.3</td>
<td>Present in many oxide deposits common in the upper part of the calamine ore bodies</td>
</tr>
<tr>
<td>Willemite</td>
<td>Zn₂SiO₄</td>
<td>58.68</td>
<td>Typical of hypogene deposits</td>
</tr>
<tr>
<td>Sauconite</td>
<td>Na₀.₃(Zn, Mg)₃(Si, Al)₄.OH₂.nH₂O</td>
<td>-35</td>
<td>Present in many deposits especially in deposits associated with silicociates</td>
</tr>
</tbody>
</table>
2.5.1 Pyrometallurgical production of zinc metal

Direct smelting in extraction metallurgy refers to the production of metal directly from a sulphide ore without reliance on intermediate chemical reactions that form the metal oxide (Warner, 2009). In all smelting processes, the first step is to roast the concentrate in order to convert the zinc to zinc oxide (ZnO). Anthracite is usually used as a source of carbon to reduce zinc oxide in furnaces heated with natural gas or electricity. At a pressure of one atmosphere, carbon monoxide formed from the anthracite will reduce ZnO at a temperature as low as 920 °C. However, a temperature of 1100 °C is needed to make the reaction proceed at an acceptable rate. Since the boiling point of zinc is 907 °C, the metal form as a vapour, which must be protected from re-oxidation so that it can be collected as liquid zinc. Four techniques are used to reduce zinc oxide with carbon, i.e., a horizontal retort, a vertical retort, the imperial smelting process (ISP), and an electric furnace (Gordon et al., 2003).

Pyrometallurgical methods have various shortcomings, including high energy consumption, significant capital investments, and the production of harmful greenhouse gases. Although the pyrometallurgical and hydrometallurgical methods produced equal percentages of the world's supply of zinc in the 1960s, however, the present-day extractive metallurgy of zinc is dominated by the hydrometallurgical process (Harmer et al., 2007). Details of this process are given in section 3.2.

2.5.2 Hydrometallurgical production of zinc metal

Hydrometallurgical extraction of metals from their ores has significant advantages over the pyrometallurgical process because it is more attractive economically, environmentally, and technically. It is often less costly, and it is less harmful to the environment because it does not emit any hazardous gases. Also, metals can be obtained directly in pure form from a leach solution or recovered from the impure leach solution. Various factors make leaching preferable to high-temperature smelting are; low-temperature processing, low handling cost of leaching products, the possibility of treatment of low-grade ores, and the scale of operation (Al-Harahsheh and Kingman, 2004).

In 1880, the first patent application for electrolytic zinc production was submitted in Germany by C. Luckow of Danz (West-Sells, 1996). In 1915, Anaconda Electrolytic Zinc of Australia pioneered the first production of zinc by this method (West-Sells, 1996). Currently, more
than 80% of the world’s zinc metal output is produced by this process (Balarini et al., 2008; Harmer et al., 2007). This process includes three significant steps which are; roasting, leaching, and electrowinning (RLE).

The traditional RLE zinc production route was developed for the processing of zinc sulphide ores. Such ores are generally natural to enrich by using the time-proven flotation method of physical separation, producing a high-grade concentrate that can be treated by conventional processing. Extensive feasibility studies have shown that oxide-, silicate-, and carbonate-based zinc ores are not amenable to conventional processing. The reason is that non-sulphide minerals do not respond to recovery by flotation, which is the conventional process used to concentrate the zinc minerals before the electrolytic process and subsequent recovery as zinc metal (Boni et al., 2005; Cole and Sole, 2002). Although the pyrometallurgical process can treat low-grade ores, it has the disadvantage of causing extensive pollution, excessive quantities of energy, and high capital investment (Chen et al., 2009). Details of this process are given in section 3.3

2.6 Zinc recycling

The recycling rates for zinc are lower than for steel. This low end-of-life recycling rate is mostly due to zinc’s applications and the technologies used to recycle it. In the US, zinc has a recycling rate of around 30%. The new: old scrap recycling ratio is around 65:35. Brass alloys constitute the majority of recycled zinc and remain in use for alloys. The main form of old scrap is flue dust from steelmaking (Sibey, 2011).

Globally there is 80 – 200 kg of zinc per person in use in the developed world and 20 – 40 kg of zinc per person in use in the developing world (UNEP, 2010). The primary energy intensity of zinc production ranges from 49 – 55 GJ/tonne. Energy savings by recycling steel and zinc can range from 60 – 75% for both (Goodwill, 1994). Globally, about 20% of zinc becomes new scrap through continuous and batch galvanizing. Drosses and skimmings are used in die castings, and zinc oxide production due to their high zinc content, 80 – 90%. Approximately half of the continuous galvanizing zinc becoming scrap is the result of fabrication, such as stamping. This is considered new scrap but follows the recycling process routes of old scrap (Goodwill, 1994).
2.7 Galvanized steel

The galvanization process involves coating a steel substrate with a zinc layer that provides corrosion protection through acting as a physical boundary and galvanic protection (Zhang, 2013). Demand for galvanized comes from industries including automotive and construction. The galvanization of steel is a significant demand on zinc production. In 2011, about 55% of zinc produced in the US was used for galvanizing steel (Amy, 2012). In 2012 the US produced 3.4 million tons (3.08 million tonnes) of galvanized steel. Currently, there are approximately 95 galvanizing companies in North America, with over 165 plants (American Galvanizers Association, 2013). The global production of the galvanized steel sheet in 2012 was 32.5 million tonnes (World Steel Association, 2013).

2.8 Types of galvanizing of steel

Galvanization is a means of applying a zinc coating to the surface of steel or iron to prevent corrosion. There are a variety of zinc coatings, each having its unique characteristics and performance. The method by which the zinc coating is applied effects the coating characteristics. Hot-dip, or batch galvanization, differs from continuous galvanization in coating thickness, structure. Continuous galvanization is used to generate sheet, whereas a hot dip is used for structural shapes. The coating thickness of hot-dip galvanized pieces are more significant, and iron-zinc intermetallic layers are more pronounced. Fig 2.2 shows the microstructure of different zinc coating. The processes utilized for applying these zinc coatings are hot-dip galvanizing, thermal spraying, electrodeposition, sherardizing, and painting with zinc.

2.8.1 Hot-dip galvanizing

Hot-dipped galvanization was the first method developed for zinc coating steel and remains the most common method in use (Zhang, 2013). It is used mostly for steel sheets, fabricated articles, and tubes or wire. Zinc is coated to the steel substrate by dipping it in a molten bath of zinc, which forms metallurgically bonded coatings (Porter, 1991). These Zn-Fe intermetallic alloy layers are formed between the outmost zinc coating and steel substrate. The characteristics of the intermetallic alloys are dependent on the method and procedures used during the coating process. These processes can be broadly divided into two types, batch hot-dipped galvanization and continuous hot-dipped galvanization.
Batch galvanization is a process whereby the article to be coated immersed in a molten bath, at 445 – 454°C, for a while generally in the order of 3 – 6 minutes. Zinc, ammonium chloride fluxes are used to promote metal Fe-Zn contact by reacting with the Fe and Zn oxide surface films on the steel article and the molten bath, respectively. Batch galvanization can be further subdivided into either a wet or a dry process by the nature of the flux used. In the dry process, the steel article is covered and dried in the flux before immersion in a molten Zn bath, whereas in the wet process, a molten flux blanket covers the molten zinc, which the steel article must pass through during dipping (Zhang, 2013).

Continuous galvanization is a process whereby sheet steel is end to end welded into coils of steel that are coated at high speeds of 200 m/min. Continuous galvanization can be further subdivided into hot and cold processes. The main differences between them are the steel surface preparation between the cleaning stage and immersion in the molten zinc bath. The hot process involves the sheet steel being leached in an alkaline bath, then cleaned by mechanical brush, with final electrolytic alkaline cleaning before the sheet passing through a furnace with reducing conditions, hydrogen and nitrogen, to reduce any iron oxides on the steel surface. The steel is heated to temperatures slightly higher than needed for subcritical recrystallization and then cooled to the temperature of the molten zinc bath before immersion (Zhang, 2013). The cold process involves the sheet steel being cleaned, via alkaline solution, and pickled, via acid solution, continuously in line. The line then passes the sheet through a zinc ammonium chloride flux to be
coated, and dried, before immersion in the zinc bath. When the coated steel leaves the molten bath, excess molten zinc is removed from the surface by a stream of gas in the wiping dies. Air is used to lower the galvanized steel temperature to prevent coating damage from the turnaround roles, where the sheet is wound into coils (Zhang, 2013). Fig 2.3 shows the schematic diagram of continuous hot-dipped galvanizing and galvannealing process.

### 2.8.2 Galvannealing

This process involves the further treatment of hot-dipped galvanized steel. After coming out of the zinc bath, the sheet steel moves from the wiping dies to a vertical gas furnace where it is heated at about 500°C for approximately 10 seconds. This causes the iron and zinc in the coating to interdiffuse, forming an outer $\zeta$ phase rather than a $\eta$-Zn phase, which is rougher and more comfortable to paint (Zhang, 2013).

Fig 2.3. Diagram showing continuous hot-dip galvanizing and galvannealing process (Marder, 2000).
2.8.3 Electroplated coatings

This process uses an electric current that is passed through zinc-containing electrolytes, coating zinc on the cathodically charged steel. It is used for coating articles with zinc, and alloys such as nickel-zinc and highly uniform iron-zinc. Bath solutions use either cyanide, acid, alkaline, and neutral electrolytes. Each electrolytic solution has its benefits, with acid solutions being faster and cyanide solutions and having better ‘throwing power’, the throwing power is the ability of the electrolyte to coat the article uniformly (Porter, 1991). Before the 1980’s, the predominant method for electroplating was the use of alkaline cyanide baths.

Environmental concerns arising from the use of cyanide have led to zinc plating using acid baths, becoming the chief method used (Zhang, 2013). The size and shape of the article to be coated are the limiting factors, with some articles being too large to fit in the electrolyte bath, and some article shapes possessing areas that are recessed or too far away from the anode for the throwing power of the electrolyte. Electroplating is mostly used for articles requiring a very even smooth coating with a low tolerance for error. When coating thicknesses more significant than 15 μm are needed, electroplating becomes less economical than other coating methods (Porter, 1991).

2.8.4 Sherardizing

This process involves the intense agitation of the heated articles to be coated with zinc dust. This occurs at temperatures marginally below zincs melting temperature. The zinc is coated on the article by cementation or diffusion processes. This produces a hard coating of Zn-Fe intermetallic alloy layers with typical thicknesses of 30 μm. As a constant temperature is needed throughout the coating reactor, this process is generally limited to small, elaborate articles (Porter, 1991). This type of coating is used mainly for nuts, bolts, fastenings, nails and similar fittings (Zhang, 2013).

2.8.5 Mechanical Bonding

In this process, the steel articles to be coated are strongly agitated with zinc dust, and nonmetallic impactors at room temperature. This process is used as is does not embrittle the steel; however, a disadvantage of the process is that the zinc forms a mechanical bond, as opposed to a metallurgical alloyed bond (Porter, 1991).
2.8.6 Thermal Spraying

This process involves the melting of zinc dust or wire, and physically spraying the molten zinc onto a steel surface. The surface to be coated is abraded before coating as adhesion to the substrate's surface by the zinc coating is mechanical. It is possible to deposit alloy coatings by having some wires of different compositions (Porter, 1991). This process is mainly used for large steel structures that cannot be galvanized due to size constraints. It can also be used to repair and maintain existing galvanized articles that have incurred damage (Zhang, 2013).

2.9 Galvanized steel recycling

Galvanized steel is recycled in furnaces where the steel is melted and reformed. The flowsheet for this process is shown in Figure 2.1. The zinc is fumed off to form a speck of dust containing zinc ferrite (Kolta et al., 1980). Galvanized scrap, new and old, predominantly goes to Electric Arc Furnaces (EAF's), which have inputs containing 30 – 40% galvanized scrap, with some scrap going to basic oxygen furnaces (BOF's) which have inputs containing <10% galvanized scrap (Goodwill, 1994). Details on the technologies used are given in chapter 3.

Globally the end of the life-recycling rate of the steel component of galvanized scrap is very high and in the range of 70 – 90% (Reck et al, 2011). The fate of the zinc bearing dust from these steel recycling operations depends on the zinc content and the regulatory system at the generators' location. If the dust's zinc content is too low, it is landfilled instead of recycled to flow. If the zinc content is 20%, it is nearly all recycled. The fate of dust with intermediate zinc contents depends on the costs of landfill versus the cost of recycling, greatly affected by the jurisdictions' dust disposal regulations. Thus, recycling rates tend to be much higher in North America and Europe, with the end of life recycling rate of 60%. In contrast, jurisdictions with minimal regulation have an end of life-recycling rates of around 10%. This translates to a global end of life-recycling rate for the zinc in galvanized steel of around 35%, or of the 7 million tonnes of EAF dust generated globally. Only 2.5 million tonnes of it are recycled with the remainder landfilled (Goodwill, 1994).

Historically in the US, steel dusts were classified as standard waste with standard landfill charges. In 1986, EAF dust was deemed hazardous under a new K061RCRA hazardous designation if it exceeded thresholds in elements including arsenic, beryllium, cadmium, lead and
mercury. Interestingly enough, zinc is not included in the regulated elements. As EAF dusts invariably exceed these thresholds, their dust now needed to be disposed of as hazardous waste. As this increased the disposal costs substantially, it became more economical to pay zinc producers to take the dust (Goodwill, 1994).

In the US, if the zinc concentration in the dust is low, it is landfilled. If the concentration is above 10%, then the zinc is recovered using a pyrometallurgical technology such as a Waelz Kiln or Rotary Hearth Furnaces. Here, the zinc ferrite is roasted to form a zinc oxide gas phase that can be collected for further refining. The Horsehead Corporation operates 5 Waelz Kilns across the US with a capacity of treating upward of 500,000 tons of EAF dust per year with concentrations ranging from 10 – 20 % zinc (Amy, 2012).

2.10 Extractive metallurgy of zinc in electric arc furnace (EAF)

Zinc is one of the oldest used metals. In antiquity, it was not isolated in pure form, but rather by heating calamine (zinc oxide/zinc carbonate) with copper and carbon. The zinc was reduced and alloyed with the copper to produce brass. Commercial production of significant quantities began in Europe with a reduction (distillation process), which produced zinc distillate from roasted zinc blende (sphalerite) and/or calamine and carbon (Ingallis, 1936). This evolved into a variety of Retort Processes, which were common at the turn of the 20th century but have since been superseded by other technologies. The extractive metallurgy of zinc in this research is based on the treatment of galvanized steel scrap in an electric arc furnace (EAF).

2.11 Electric arc furnace (EAF) treatment technologies

The most logical of EAF dust would be in the iron and steelmaking process in which it is generated. Its iron-rich nature has resulted in attempts to directly recycle the dust to the various iron and steelmaking processes. However, its content of zinc, lead and other tramp elements such as copper, sulphur, sodium, potassium as well as halides make it impossible to recycle into the iron making process. Zinc is the cause of many troubles in blast furnace operation, such as refractory failure, scaffold formation in the stack, and complete filling of the gas offtake (Zunkel, 1996).

Consequently, the feed to an iron blast furnace must have a shallow zinc content. For example, the requirement for zinc content in iron ore, according to most specifications, is usually
less than 0.01% (Zunkel, 1996). Similarly, other tramp constituents are unwanted even at low concentration levels, since they either reduce furnace life and efficiency or are difficult to remove from the steel bath and lead to the production of inferior quality steel (Lu, 1974). EAF specks of dust have been recycled to the steelmaking process to recover portions of the iron and minimize the dust quantity, which eventually has to exit from the process. Due to a more substantial proportion of the fine dust particles in the feed, the amount of dust to be collected increases with each recycle. As the amount of recycled dust increases, the energy consumption also increases to reduce and melt the iron and the other constituents in the dust. Another negative factor influencing the recycling of dust is that the non-ferrous metals will build up with repeated recycling to such a point that they adversely affect the steel melting operation and the steel quality. As oxides present in the slag, they may attack the refractory lining of the furnace. In reduced form, these metals may enter the molten steel at concentrations higher than permissible to meet the specifications for the proper mechanical and physical properties of the steel. At this point, the dust has to be removed from the system (Lu, 1974). Traditionally, the dust has been disposed of in landfill sites.

As ever more stringent environmental regulations come into effect, landfiling is becoming a less viable option for steelmakers. Landfiling sites are costly, and the future liabilities of landfilled specks of dust are far from certain. With the depletion of the number of landfill sites, the total costs for landfills of the dust, including pretreatment, transportation and disposal, could exceed $200 per ton (James and Bounds, 1990). In 1992, only 11.2% of the EAF dust in the U.S. was landfilled, while in 1985, this number was as high as 73.0%. The landfill option may likely disappear soon (Goodwill, 1994). The options currently available for steelmakers are as follows: pyrometallurgical, hydrometallurgical, stabilization or vitrification processes, and other miscellaneous processes. Some of these processes have either been commercialized or commercialized for a period and then abandoned; many have only reached the pilot scale. The status of the pyrometallurgical and hydrometallurgical processes will be described in the following sections.

2.12 Pyrometallurgical process

Most of the commercially available processes, such as the rotary kiln processes, for the treatment of EAF specks of dust can be considered as pyrometallurgical. However, since rotary kiln processes usually require large tonnages of EAF dust to be treated to be economically
competitive, other technologies have also been developed, particularly those which aim at the
development of a small scale, on-site treatment process. Unfortunately, some of these processes
have proven to be too elaborate and energy-intensive, such as most plasma processes. Typically,
they all require a very well-designed condenser to recover zinc, lead, cadmium and salts such as
sodium and potassium chlorides. However, even if the elaborate operation regulations are strictly
followed, the efficiency of metal recovery is low. Therefore, it is not surprising that some of these
processes have been abandoned. As for the development of the small scale, on-site technologies,
however, remains to be seen if such efforts will provide a competitive option for dust treatment.
The primary process in pyrometallurgy, which are rotary kiln processes, High-Temperature Metal
Recovery (HTMR) plasma processes are discussed in the following sections.

2.12.1 Rotary kiln process

The major rotary kiln processes used in the treatment of EAF specks of dust are the Waelz
kiln process and the calcining kiln process. Other processes are the modification of significant
processes.

2.12.1.1 Waelz kiln process

The name Waelz was derived from the German verb "Walzen," meaning to trundle or roll,
the words which accurately describe the movement of the charge through the rotary kiln. As a
leading resource recycling Company, Horsehead Resource Development (HRD) Co., Inc. now has
its Waelz kiln facilities in Palmerton, PA, Calumet, IL, and Rockwood, TN, which treat about
80.85% of the dust from carbon steelmakers in the U. S. The specifications of HRD's rotary kilns
are summarized in Table 2.3.

The received EAF dust and/or other zinc bearing materials are conditioned to about 8 –
12% moisture, and the (CaO + MgO) : SiO₂ ratio is maintained above 1.35. Before being fed to
the kiln, the conditioned materials are blended with a carefully sized carbon source, typically
anthracite coal (Palmerton), petroleum coke (Chicago), or metallurgical coke fines (Rockwood);
or a combination of these sources. About one tonne of coal (dry basis) is needed for every five
 tonnes of zinc bearing feed. Several distinct reaction zones are observed within the kiln as follows:

i. Drying and preheating of feeds.

ii. Decomposition of limestone, if added.
iii. Volatilization of the halide compounds.
iv. Partial reduction of iron oxides.
v. Reduction/volatilization and reoxidation of lead, zinc and cadmium.

<table>
<thead>
<tr>
<th>Rotary Kiln</th>
<th>Location</th>
<th>Process</th>
<th>Length (Ft.)</th>
<th>Shell Diameter (Ft.)</th>
<th>Drive (HP)</th>
<th>Slope (%)</th>
<th>Rotation (RPM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Palmerton</td>
<td>Calcining</td>
<td>142</td>
<td>10.00</td>
<td>75</td>
<td>3 %</td>
<td>0.5</td>
</tr>
<tr>
<td>2</td>
<td>Palmerton</td>
<td>Waelzing</td>
<td>160</td>
<td>11.25</td>
<td>100</td>
<td>3 %</td>
<td>0.9</td>
</tr>
<tr>
<td>3</td>
<td>Palmerton</td>
<td>Waelzing</td>
<td>160</td>
<td>11.25</td>
<td>75</td>
<td>3 %</td>
<td>0.9</td>
</tr>
<tr>
<td>4</td>
<td>Palmerton</td>
<td>Waelzing or</td>
<td>160</td>
<td>12.00</td>
<td>125</td>
<td>3 %</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Calcining</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Palmerton</td>
<td>Calcining</td>
<td>160</td>
<td>12.00</td>
<td>125</td>
<td>3 %</td>
<td>0.8</td>
</tr>
<tr>
<td>6</td>
<td>Chicago</td>
<td>Waelzing</td>
<td>180</td>
<td>10.50</td>
<td>125</td>
<td>6 %</td>
<td>0.6</td>
</tr>
<tr>
<td>7</td>
<td>Rockwood</td>
<td>Waelzing</td>
<td>148</td>
<td>11.50</td>
<td>200</td>
<td>3 %</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Efficient kiln operation is achieved with a steady kiln temperature profile. This is accomplished by controlling kiln pressure through remotely operated louvres on the suction side of the hot fan (Palmerlon), or outlet dampers on the suction fan (Chicago and Rockwood). The kiln can be viewed as two reaction zones, the solid material charge zone (bed) and the free gas zone (freeboard). In the bed, the anthracite coal is oxidized, mainly by the Bouduard reaction as follows \( \text{CO}_2 + \text{C} \rightarrow 2\text{CO} \). This generates carbon monoxide, which reduces metal oxides. The reduced metals evaporate into the freeboard area and then are reoxidized.

Generally, the reactions are completed within ten feet of the discharge end of the kiln. The Waelz kiln has a natural gas burner at the Iron Rich Materials (IRM) discharge end of the unit. The burner is only used intermittently for temperature control since the anthracite coal combustion provides the thermal requirement. Some typical reactions in the kiln are given in Table 2.4 (James and Bounds, 1990).
Two products result from the Waelzing process: Crude Zinc Oxide and IRM. The Crude Zinc Oxide is collected in individually operated baghouses. The temperature of the exit gas from the kiln is reduced to approximately 423 – 453 K (150 – 180 °C) through evaporative cooling, dilution, and convective/radiant cooling. The evaporative cooling sprays are automatically activated by sensors in the baghouse to prevent bag damage from excessive temperatures. Nomex bags are used at all facilities. Clean furnace off-gas streams are maintained well within air permit specifications at all sites.

Table 2.4. Typical reaction in Waelz kiln (James and Bounds, 1990).

<table>
<thead>
<tr>
<th>Reaction Type</th>
<th>Reaction Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Combustion of Carbon</td>
<td>C + 0.5O₂ ⇌ CO, C + O₂ ⇌ CO₂, C + CO₂ ⇌ 2CO</td>
</tr>
<tr>
<td>Reduction</td>
<td>Fe₃O₄ + CO ⇌ 3FeO + CO₂, ZnO + CO ⇌ Zn + CO₂, CdO + CO ⇌ Cd + CO₂</td>
</tr>
<tr>
<td>Oxidation</td>
<td>CO + 0.5O₂ ⇌ CO₂, Zn + 0.5O₂ ⇌ ZnO, Cd + 0.5O₂ ⇌ CdO</td>
</tr>
<tr>
<td>PbS + 2O₂ ⇌ PbSO₄</td>
<td></td>
</tr>
</tbody>
</table>

Typical Waelzing feed and product compositions are given in Table 2.5. Crude zinc oxide produced at Chicago and Rockwood is discharged from the product baghouses directly to rail cars for delivery to customers or transferred to Palmerton. Crude Zinc Oxide produced at Palmerton is loaded directly into rail cars for sale or transferred to the calcining kiln feed bins for calcining.

Table 2.5. Typical Waelz kiln feeds and products (Moser et al., 1999).

<table>
<thead>
<tr>
<th>Element</th>
<th>EAF Dust (%)</th>
<th>Crude Zinc Oxide (%)</th>
<th>IRM (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>17.5</td>
<td>52.4</td>
<td>0.8</td>
</tr>
<tr>
<td>Fe</td>
<td>23.1</td>
<td>4.2</td>
<td>37.1</td>
</tr>
<tr>
<td>Ca</td>
<td>9.1</td>
<td>1.4</td>
<td>14.7</td>
</tr>
<tr>
<td>Si</td>
<td>1.7</td>
<td>NA</td>
<td>6.2</td>
</tr>
<tr>
<td>Na</td>
<td>0.64</td>
<td>1.2</td>
<td>0.8</td>
</tr>
<tr>
<td>K</td>
<td>0.47</td>
<td>0.48</td>
<td>NA</td>
</tr>
<tr>
<td>Mn</td>
<td>2.9</td>
<td>0.56</td>
<td>3.5</td>
</tr>
</tbody>
</table>


<table>
<thead>
<tr>
<th>Element</th>
<th>Calculated</th>
<th>Measured</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>1.9</td>
<td>0.39</td>
<td>2.6</td>
</tr>
<tr>
<td>Al</td>
<td>0.46</td>
<td>0.12</td>
<td>1.7</td>
</tr>
<tr>
<td>Pb</td>
<td>2.6</td>
<td>8.0</td>
<td>0.12</td>
</tr>
<tr>
<td>Cd</td>
<td>0.66</td>
<td>0.76</td>
<td>0.01</td>
</tr>
<tr>
<td>Cu</td>
<td>0.23</td>
<td>0.087</td>
<td>0.39</td>
</tr>
<tr>
<td>Cr</td>
<td>0.12</td>
<td>0.026</td>
<td>0.2</td>
</tr>
<tr>
<td>Ni</td>
<td>0.03</td>
<td>0.01</td>
<td>0.1</td>
</tr>
<tr>
<td>Sn</td>
<td>0.04</td>
<td>0.09</td>
<td>0.03</td>
</tr>
<tr>
<td>Cl</td>
<td>1.03</td>
<td>3.58</td>
<td>0.01</td>
</tr>
</tbody>
</table>

### 2.12.1.2 Calcining kiln process

To effect further metal separation, a separate rotary kiln is used to selectively volatilize cadmium, lead, chlorine and fluorine from the zinc oxide. Historically, rotary kilns employed in such a process were referred to as calcining or clinkering kilns. Calcining kilns are substantially identical to the Waelz kilns, as evidenced by the dual capability of Number 5 kiln to perform either Waelzing or calcining in Palmerton PA. However, the processing conditions are different. In contrast with the reducing conditions required for the Waelzing process, calcining is performed under an oxidizing atmosphere. Crude Zinc Oxide received from the Palmerton Waelzing process or the Chicago and/or the Rockwood operations, is conditioned with water for material handling purposes and conveyed to the kiln feed bin. Then the Crude Zinc Oxide is fed directly to the kiln without any reducing agent. Temperature profiles in the calcining kiln are also different from those employed for Waelzing. The temperature of the cold charge rises as it proceeds downkiln towards the discharge-end burner, where the maximum temperatures are reached in the neighbourhood of 1523 K (1250 °C). At such high temperatures, the lead and cadmium are formed as oxides, sulphides, and halides. These materials condense in the exit gas stream and are collected in a fabric filter bag collector. This lead/cadmium concentrate is transferred and bagged for shipment in fully enclosed facilities. Zinc Calcine, the remaining solid phase, is discharged from the kiln to a water quench and further transferred via a drag conveyor and loader for shipment (Dogan and Karayazic, 1994). Table 2.6 gives the typical composition for the Zinc Calcine and the Lead/Cadmium Concentrate.
2.12.1.3 Other rotary kiln process

All rotary kiln processes for the treatment of EAF specks of dust are the same in terms of process (physics and chemistry). However, some differences exist, such as feed preparation and Crude Zinc Oxide treatment. As discussed previously, burdened and mixed EAF dust feed is introduced directly into the Waelz kiln in America, while it is fed into the kiln in the form of pellets or briquettes in Europe and Japan (Kola, 1991). Since no Imperial Smelting Furnace (ISF) plants exist in America, then most Crude Zinc Oxide is further treated in rotary kilns to generate Zinc Calcine, which is sold to an electrothermic zinc smelter. While in Europe, Crude Zinc Oxide from the Waelz processes is either sold to ISP smelters directly or dehalogenated in a hydrometallurgical process before it is sold to ISP smelters in Japan (Tsuneyama et al., 1990). Another example of a modification of the Waelz kiln process is the Inclined Rotary Reduction Process (IRRP). The significant difference between the Waelz process and the IRRP is that the mixed oxide recovered in the bag filters is pelletized with high-quality coal powder and binder. It is then fed to a retort, which is heated externally by kiln off-gases. Zinc, lead and cadmium are fumed in the retort and recovered as zinc alloy (containing less than 1.5% Pb) and lead alloy (containing about 10% Zn and 1% Cd) in an ISP condenser. The balance of zinc, lead and cadmium is recovered from the off-gas as a mixed oxide in a baghouse and is recycled to the retort. An oxy-gas (CH₄/O₂) burner is employed in the kiln to reduce the volume of off-gas (Kotraba and Lanyi, 1991).

Table 2.6. Composition (%) of products from the calcining kiln (Moser et al., 1999).

<table>
<thead>
<tr>
<th>Element</th>
<th>Zinc Calcine</th>
<th>Pb/Cd Concentrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>55 – 66</td>
<td>5 – 10</td>
</tr>
<tr>
<td>Pb</td>
<td>0.5 – 1.5</td>
<td>35 – 50</td>
</tr>
<tr>
<td>Cd</td>
<td>0.05 – 0.15</td>
<td>1.2</td>
</tr>
<tr>
<td>Fe</td>
<td>4 – 9</td>
<td>0.5 – 1.5</td>
</tr>
<tr>
<td>Cl</td>
<td>0.15</td>
<td>15 – 25</td>
</tr>
</tbody>
</table>

2.12.1.3 Other rotary kiln process

All rotary kiln processes for the treatment of EAF specks of dust are the same in terms of process (physics and chemistry). However, some differences exist, such as feed preparation and Crude Zinc Oxide treatment. As discussed previously, burdened and mixed EAF dust feed is introduced directly into the Waelz kiln in America, while it is fed into the kiln in the form of pellets or briquettes in Europe and Japan (Kola, 1991). Since no Imperial Smelting Furnace (ISF) plants exist in America, then most Crude Zinc Oxide is further treated in rotary kilns to generate Zinc Calcine, which is sold to an electrothermic zinc smelter. While in Europe, Crude Zinc Oxide from the Waelz processes is either sold to ISP smelters directly or dehalogenated in a hydrometallurgical process before it is sold to ISP smelters in Japan (Tsuneyama et al., 1990). Another example of a modification of the Waelz kiln process is the Inclined Rotary Reduction Process (IRRP). The significant difference between the Waelz process and the IRRP is that the mixed oxide recovered in the bag filters is pelletized with high-quality coal powder and binder. It is then fed to a retort, which is heated externally by kiln off-gases. Zinc, lead and cadmium are fumed in the retort and recovered as zinc alloy (containing less than 1.5% Pb) and lead alloy (containing about 10% Zn and 1% Cd) in an ISP condenser. The balance of zinc, lead and cadmium is recovered from the off-gas as a mixed oxide in a baghouse and is recycled to the retort. An oxy-gas (CH₄/O₂) burner is employed in the kiln to reduce the volume of off-gas (Kotraba and Lanyi, 1991).
2.12.2 HTMR-plasma process

Intensive efforts have been made to develop plasma technologies for the treatment of electric arc furnace dust. They have involved both pilot scale and commercial production processes. However, the majority of these processes did not survive, mainly due to the problems encountered with the condensers’ operation. The high content of alkali and halide elements in the EAF dusts led to the formation of dross, which reduced the condensers’ efficiency. The existence of copper and sulphur in the dust made the iron-rich slag unacceptable for direct reuse in steelmaking processes (Best, 1994; Fauchias, 1997).

Also, the metallic zinc, which was obtained, was usually below Prime Western (PW) grade, and thus the processes were uneconomical. Furthermore, with the carry-over of slag forming materials and EAF dust into the off-gases as well as the evaporation of iron and/or iron oxides under the high operating temperatures (around 1873 K / 1600 °C), hard zinc was inevitably formed, which also reduced the efficiency of the condensers. The Tetronics Plasma Process is an example of a process that experienced some of these problems. It evolved into commercial use for a while but eventually had to be abandoned. The ScanDust Process, on the contrary, is relatively elaborate and more complex and attempted to solve the commonly encountered problems with plasma technology.

The Tetronics Plasma Process was developed jointly by International Mill Service, Inc. and Tetronics Research and Development Co. Ltd. Two commercial plants (the plant at Jackson, TN and the plant at Blytheville, AR.) were in operation in the United States for several years. However, both plants were shut down for various technical and/or economic reasons (Haenley and Cowx, 1997). This process is no longer being offered for sale.

A schematic diagram of the Tetronics Plasma Process is shown in Figure 2.4. The cylindrical furnace is made of mild steel and lined with carbon-impregnated magnesia bricks. The sealed furnace roof is cooled with water and is lined with a high-grade alumina castable refractory. The argon-stabilized plasma arc is transferred from the plasma torch to the furnace melt, which is in electrical contact with the mild steel anodes in the furnace hearth.

In operation, the pre-blended EAF dust, reductant and flux materials were dried and introduced through feed ports in the roof. As they descended through the furnace atmosphere, they were heated and then rapidly dissolved in the melt. Metal oxides were selectively reduced
carbothermically in the furnace slag, and the zinc, lead, and cadmium present was volatilized, leaving an iron-rich slag for disposal (Chapman et al., 1990).

An imperial smelting process (ISP) zinc splash condenser was used to recover the zinc, lead and cadmium from the gas mixture produced in the furnace. A mechanically rotated graphite impeller generated a spray of metal droplets of large surface area, to promote efficient condensation. The heat load in the condenser, produced by the exhaust gases and zinc condensation, was controlled by an immersed water cooling coil. All the metal vapours present were condensed by this mechanism, and the liquid in the condenser consisted of two layers, zinc and lead, with the cadmium partitioned between them.

The gases from the condenser's outlet were burned in a combustion chamber with an excess of air being employed to cool the gas stream entering the baghouse to below the specified baghouse temperature rating. A proportion of the zinc-rich baghouse fume may be recycled to the furnace to increase the zinc yield. The cleaned exhaust gases were vented to the atmosphere.

The Tetronics plasma process was simple because the pelleting or the agglomeration of the feed materials was not required. Flux materials were needed to make a high fluidity slag, which
had a CaO : SiO$_2$ basicity ratio of 1.0 – 1.2. The temperature was maintained at 1773 K (1500 °C) during the treatment process. The significant problems of this process were as follows:

1. Condenser efficiency was only about 75% for zinc.
2. Metals dispersion: dross (due to alkali and halide constituents present in the dust), hard zinc (due to volatilization of iron and iron oxides), new baghouse dust.
3. High operating temperatures: 1773 – 1873 K (1500 1600 °C).
4. Zinc metal produced was below PWG. New dust contained 60% zinc and other impurities.

Compared with the Tetronics plasma process, the plasmadust process developed by ScanArc Plasma Technologies AB was very elaborate in terms of process flowsheet and the requirement for the preparation of materials to be treated. This technology resulted in a commercial plant, which started operations in April 1984. Three MW plasma generators from SKF Steel were used (Santen, 1993).

The plant consisted of a material-handling system for dust, coal, coke and slag former, a shaft furnace, plasma generators, condensers for cooling and condensing zinc and lead, gas-cleaning units and tapping and casting equipment for zinc, lead, hot metal and slag. As-received dust was mixed with water to form a slurry with a solids content of about 50 percent. The slurry was pumped to two slurry mixers, each with a volume of 400 m$^3$ (14,000 ft$^3$), which were fitted with agitators to ensure satisfactory homogenization.

The slurry was then pumped to a 40 m$^3$ (1,400 ft$^3$) mixing tank, to which coal and slag former were added. The mixture then contained 50 percent solids and 50 percent water. After homogenization, it was pumped to a mechanical filter press, where the water content was reduced from 50 percent to between 15 and 20 percent. The filter cakes were stored for an interim period, during which the water content was further reduced, and was subsequently dried and crushed to a maximum of 2 mm (0.08 inch). The drying unit used some of the excess process gas. The dried and crushed material was then stored in a silo from which it was fed into three transfer hoppers. The material was blown from the hoppers to injection feeders near the shaft furnace, from where it was injected into the shaft’s reaction zone.

Coal and sand were balls milled to a grain size less than 0.1 mm (0.004 inch) for 80 percent of the product. Then they were water mixed, and the mixed slurry was pumped to a 30 m$^3$ (1,060 ft$^3$) slurry mixer for storage and was later added to the mixing tank in the correct quantities.
Commercial coke, with a grain size of 20 to 60 mm (0.8 – 2.4 inch), was used. The coke was charged to a silo and was then dried and screened before being fed to a conveyor for transport to the top of the shaft furnace. Coke fines were returned to the ball mill. The coke was charged at the shaft furnace top via a gas-tight valve system.

The mixture of EAF dust, coal and slag former was fed via three tuyeres with a total capacity of 8 – 12 tonnes per hour. A 6 MW plasma generator was mounted in each tuyere. The amount of hot metal produced varied from 200 to 600 kg (440-1,325 lbs.) per tonne of dust. The tapping temperature was approximately 1673 K (1400 °C). The hot metal was cast into pigs in a casting machine, and the liquid slag was tapped and cooled before disposal at a dump or delivery to a user. The amount of slag was 200 to 500 kg (440 – 1100 lbs.) per tonne of dust.

It was estimated that the furnace could be operated for 7,600 hours per year. Operating time was based on a 1 – 1.5-month round-the-clock operating cycle, before changing the feed material. The plant would be shut down for four weeks per year for maintenance. Plant availability was estimated at 95 percent.

The exit gas, a valuable form of energy, was cleaned and cooled after leaving the shaft. When smelting baghouse dust with low zinc content, the exhaust gas contained approximately 75 percent carbon monoxide, 24 percent hydrogen and 1 percent nitrogen. The temperature of the exhaust gas from the shaft furnace was approximately 1473 K (1200 °C). The gas passed through a venturi scrubber, where it was cleaned, and the temperature fell to approximately 313 K (40 °C). The venturi water was first led to a thickener and a cooling tower and was then recirculated. The thickener sludge was returned to the process.

For dust with high zinc and lead levels, three condensers were employed. The temperature of the gas entering the condensers was approximately 1473 K (1200 °C). This gas had a zinc content between 4 and 20 percent. The exhaust gas from the condensers had a low zinc content and a temperature of 773 – 873 K (500 – 600 °C). The gas then passed through the venturi scrubber and the exhaust ventilation system.

At a temperature of approximately 773 K (500 °C), zinc and lead flowed continuously from the condensers to a holding furnace. The amount of zinc typically contained in one tonne of dust varied from 200 to 400 kg (440 – 880 lbs.). Lead and zinc were cast into jumbo ingots or 25 kg (55 lbs.) slabs, according to customer requirements.
Some of the cleaned and cooled gas was recirculated as process gas after passing through a gas compressor. The excess gas was used as fuel for raw material drying, ladle preheating and a hot water boiler, connected to the local municipal district heating network. The hot water boiler also utilized energy in the cooling water from the shaft furnace, the plasma generators and the condensers. The annual quantity of thermal energy recovered amounts to approximately 65 GWh (220 billion Btu), which is equivalent to 6,500 m$^3$ (1.7 million gallons) of oil. From 70,000 tonnes of dust, 9,000 tonnes of coal, 3,600 tonnes of coke and 6,000 tonnes of sand which were to be processed annually, a total materials input of almost 90,000 tonnes, the following quantities of metals would be recovered:

<table>
<thead>
<tr>
<th>Recovered metals</th>
<th>Quantities (tonne)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc</td>
<td>15,000</td>
</tr>
<tr>
<td>Lead</td>
<td>2,800</td>
</tr>
<tr>
<td>Hot metal</td>
<td>13,800</td>
</tr>
<tr>
<td>Alloyed hot metal</td>
<td>3,700</td>
</tr>
</tbody>
</table>

The zinc was of Prime Western Grade, permitting it to be registered and sold on the London Metal Exchange. In addition to the recovery of metals, ScanDust also generated 30,000 tonnes of slag, which was used as filling material for construction projects and generated an excess energy equivalent to 65 GWh (220 billion Btu) per year (Herlitz et al., 1987).

### 2.13 Hydrometallurgical process

Hydrometallurgy refers to the extraction of metals and the production of inorganic substances from minerals through aqueous solutions. The advantages of hydrometallurgical processes for the treatment of EAF dust are that on a small scale, the on-site process could be economic, because of its low capital and operating costs and the recovery of the valuable metal-containing products. Also, there may be some environmental benefits of hydrometallurgical processes in comparison to pyrometallurgical processes. The primary process in hydrometallurgy which are the Molecular Recognition Technology (MRT) process, EZINEX process, CASHMAN process, sulfuric acid leach process, chloride leach process, chloride-sulphate leach process and caustic leach process area discussed in the following section.
2.13.1 MRT technology

The MRT process is the first commercial-use hydrometallurgical process for the treatment of EAF dust in North America. In 1995, MRT started operating a plant at Nucor Corporation’s minimill in Darlington, South Carolina, on a contract basis. Dust is leached with hot ammonium chloride to dissolve most of the zinc, lead and cadmium oxides in the dust. Leach slurry is filtered, and the unleached iron oxide, containing zinc ferrite, is filtered, washed, and recycled to the steel mill or stockpiled. Leach solution is treated with zinc dust to precipitate the dissolved lead and cadmium as cement, which is further separated into metallic lead and cadmium, which can be sold. The clean solution passes to a crystallizer where high purity zinc oxide crystals are produced for sale. Ammonium chloride solution is concentrated and recycled to the leaching process.

The plant has been operating reasonably since the startup problems were corrected. Improvements have been made and patented to increase zinc recovery and produce a value-added metallized iron product for recycle or sale using a pyrometallurgical rotary hearth pre-reduction step before leaching (Zunkel, 1996). The chemistry of this process is shown in table 2.7.

<table>
<thead>
<tr>
<th>Table 2.7. Chemistry for MRT process (Burrows, 1974).</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO + 2NH₄Cl ⇌ Zn(NH₃)₄Cl₂ + H₂O</td>
</tr>
<tr>
<td>Pb(NH₃)₂Cl₂ + Zn ⇌ Zn(NH₃)₄Cl₂ + Pb</td>
</tr>
<tr>
<td>Cd(NH₃)₂Cl₂ + Zn ⇌ Zn(NH₃)₄Cl₂ + Cd</td>
</tr>
<tr>
<td>Zn(NH₃)₄Cl₂ + H₂O ⇌ 2NH₄Cl + ZnO</td>
</tr>
</tbody>
</table>

2.13.2 EZINEX process

A 10,000 t/y EAF dust plant was constructed at Ferriere Nord in Osoppo, Italy and was commissioned in early 1996. This plant was reported to be operating satisfactorily. Worldwide opportunities for marketing this process are being sought. In this process, dust is leached in ammonium chloride solution to solubilize the zinc, lead and cadmium oxides. Leach solution is filtered and treated with zinc powder to cement the lead and cadmium, which can be sold (Zunkel, 1996). Unlike the MRT process in which the zinc is recovered as zinc oxide by crystallizing the cemented solution, zinc is electrowon from the purified solution in the EZINEX process. The spent electrolyte is recycled to the leaching stage. The iron-rich, zinc ferrite containing leach residue is dried, pelletized with coal, and recycled to the EAF. No other by-products are produced, which
require further disposal. A mixed NaCl-KCl salt is recovered by crystallization and can be sold as a flux (Zunkel, 1996).

2.13.3 CASHMAN process

This process was initially used for the treatment of arsenic-bearing ores and copper smelter specks of dust. It was then adapted for the treatment of electric arc furnace dust (EAFD) by American Metals Recovery Corp. Laboratory and small scale pilot plant tests were conducted.

In this process, zinc, which is not in the zinc ferrite, dong with lead and cadmium in the EAFD are pressure leached in a calcium chloride solution. The leached solution is purified by precipitation using zinc dust to remove the lead and cadmium. The cemented lead and cadmium mixture is separated and treated to produce metallic lead and cadmium using conventional procedures. High purity zinc oxide is precipitated from the purified solution. The leach residue is treated to recover residual zinc and produce an iron-rich residue suitable for recycling or disposal in a landfill. This process employs pressure leaching, but zinc recovery is not very high. Although the leachant is comparatively cheap, there can be some corrosion problems (Zunkel, 1996).

2.13.4 Sulfuric acid leach process

Experimental work on the sulfuric acid leaching of EAFD was performed at Warren Spring Laboratory in the U. K. The main findings of this work were that about 85 to 90% of the zinc could be extracted by sulfuric acid at pH 2 and 80% at pH 3 to 4. The significant problems reported were filtering and a high iron concentration in the solution (20 to 22 g/l) (Pearson, 1981).

Later, AMAX Extractive Research & Development, Inc. proposed an acid leach process, which is based on some results conducted on the leaching of laterite ores with sulfuric acid. These results showed that iron could be rejected from sulphate solutions as hematite at higher temperatures (Duyvesteyn et al., 1979; Jha and Duyvesteyn, 1985). In Japan, the Iijima Refinery of the EAFD Akita Zinc Company employs an autoclave process on a zinc-iron sulphate solution to precipitate iron as hematite. It involves two stages of the sulfuric acid leach process. In the first stage, is leached with a mild sulfuric acid solution at atmospheric pressure below the boiling point. The leachate, a low-iron, high-pH zinc sulphate solution, is sent to purification, and then the zinc is recovered. The solids are pressure leached in an autoclave to dissolve the residual zinc completely, leaving iron as an easy-settling hematite residue. After solid-liquid separation, the
solids are washed to recover zinc sulphate, while the solution goes to the first-stage leach step. The washed residue can be recycled back to the steel plant, or it can be further treated. Caustic or brine can be used to leach any lead present in the residue. The solids can be pelletized and recycled to the steel plant (Ohtsuka et al., 1978). The chemistry for this process is shown in Table 2.8.

### Table 2.8. Chemistry for sulfuric acid leach process (Duyvesteyn, 1986).

<table>
<thead>
<tr>
<th>Leaching Method</th>
<th>Reaction Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmospheric</td>
<td>( \text{ZnO} + \text{H}_2\text{SO}_4 \rightleftharpoons \text{ZnSO}_4 + \text{H}_2\text{O} )</td>
</tr>
<tr>
<td></td>
<td>( \text{PbO} + \text{H}_2\text{SO}_4 \rightleftharpoons \text{PbSO}_4 + \text{H}_2\text{O} )</td>
</tr>
<tr>
<td></td>
<td>( \text{Fe}^{3+} + 2\text{H}_2\text{O} \rightleftharpoons \text{FeOOH} + 3\text{H}^+ )</td>
</tr>
<tr>
<td>Pressure</td>
<td>( \text{ZnFe}_2\text{O}_4 \text{H}_2\text{SO}_4 \rightleftharpoons \text{ZnSO}_4 + \text{H}_2\text{O} + \text{Fe}_2\text{O}_3 )</td>
</tr>
</tbody>
</table>

Cruells et al. (1992) conducted a bench-scale study on the leaching of EAF dust using a sulfuric acid solution. They also did an extensive study on the characterization of the dust. Under the following optimum leaching conditions: 1 M \( \text{H}_2\text{SO}_4 \), a solid/liquid ratio 1:10, a leaching time 3 hours, at room temperature and a stirring speed 1000 min\(^{-1}\), they obtained 80% zinc recovery from the non-magnetic portion of EAFD and 40% of iron dissolved in the acid solution. The lead was not leached and was retained in the residue, while the iron was easily solubilized.

#### 2.13.5 Chloride leach process

This process uses dilute hydrochloric acid as leachant. The leaching reactions which occur at a pH of 4 are as follows:

\[
\begin{align*}
\text{ZnFe}_2\text{O}_4 + 2\text{HCl} & \rightleftharpoons \text{ZnCl}_2 + \text{Fe}_2\text{O}_3 + \text{H}_2\text{O} \\
\text{ZnO} + 2\text{HCl} & \rightleftharpoons \text{ZnCl}_2 + \text{H}_2\text{O} \\
\text{PbO} + 2\text{HCl} & \rightleftharpoons \text{PbCl}_2 + \text{H}_2\text{O}
\end{align*}
\]

By increasing the pH to 2 – 4, dissolved iron and lead are precipitated according to the reactions:

\[
\begin{align*}
\text{Cl}_2 + 2\text{FeCl}_2 + \text{H}_2\text{O} & \rightleftharpoons 2\text{FeOOH} + 6\text{HCl} \\
\text{PbCl}_2 \text{ (high temp)} & \rightleftharpoons \text{PbCl}_2 \text{ (low temp)}
\end{align*}
\]

Zinc is recovered from the solution by solvent extraction, using alkylphosphoric or alkylphosphonic acid as an extractant for zinc. Finally, zinc is electrowon as follow:
\[
\text{ZnCl}_2 \rightleftharpoons \text{Zn}^0 + \text{Cl}_2
\]

The process can produce cathode zinc, but the residue needs further treatment for detoxification (Duyvesteyn and Jha, 1986).

### 2.13.6 Chloride-sulfate leach process

In this process, EAFD is leached with hydrochloric and sulfuric acids at pH between 1 and 4. The reactions of this process is as follows:

\[
\begin{align*}
\text{ZnO} + 2\text{HCl} & \rightleftharpoons \text{ZnCl}_2 + \text{H}_2\text{O} \\
\text{PbO} + \text{H}_2\text{SO}_4 & \rightleftharpoons \text{PbSO}_4 + \text{H}_2\text{O} \\
\text{CaCO}_3 + \text{H}_2\text{SO}_4 & \rightleftharpoons \text{CaSO}_4 + \text{H}_2\text{O} + \text{CO}_2 \\
\text{CaO} + \text{H}_2\text{SO}_4 & \rightleftharpoons \text{CaSO}_4 + \text{H}_2\text{O} \\
\text{ZnFe}_2\text{O}_4 + 2\text{HCl} & \rightleftharpoons \text{ZnCl}_2 + \text{Fe}_2\text{O}_3 + \text{H}_2\text{O}
\end{align*}
\]

The residue from the first leaching step is leached again using hydroxide as the leachant:

\[
\begin{align*}
\text{PbSO}_4 + 4\text{NaOH} & \rightleftharpoons \text{Na}_2\text{PbO}_2 + \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O} \\
\text{CaSO}_4 + 2\text{NaOH} & \rightleftharpoons \text{CaO} + \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}
\end{align*}
\]

Dissolved iron and aluminum are removed by precipitation at elevated pHs

\[
\begin{align*}
\text{Fe}^{3+} + 2\text{H}_2\text{O} & \rightleftharpoons \text{FeOOH} + 3\text{H}^+ \\
\text{Al}^{3+} + 3\text{H}_2\text{O} & \rightleftharpoons \text{Al}_2\text{O}_3 + 6\text{H}^+
\end{align*}
\]

Solvent extraction is employed to recover the zinc from the pregnant solution phosphoric and phosphonic acids, and zinc is the electrowon. The residue needs to be detoxified to remove lead and cadmium before being discharged (Duyvesteyn and Jha, 1986).

### 2.13.7 Caustic leach process

This is the process used for this research because caustic lixiviants do not use the leach the iron that is present in large quantities in the EAFD. Details of the process are given in the next chapter.

The chemistry of the process can be described by the following reactions (Wheatley and Pooley, 1990):

Leaching reactions:

\[
\begin{align*}
\text{ZnO} + 2\text{NaOH} & \rightleftharpoons \text{Zn(ONa)}_2 + \text{H}_2\text{O}; \\
\text{PbO} + 2\text{NaOH} & \rightleftharpoons \text{Pb(ONa)}_2 + \text{H}_2\text{O};
\end{align*}
\]
SiO$_2$ + 2NaOH ⇌ Na$_2$SiO$_3$ + H$_2$O

Clarification reaction: Na$_2$SiO$_3$ + Ca(OH)$_2$ ⇌ CaSiO$_3$ + 2NaOH

Cementation reaction: Zn + PbO$_{2}^{2+}$ ⇌ Pb + ZnO$_2^{2-}$

Electrolysis reactions:

- In cathode: ZnO$_2^{2-}$ + 2H$_2$O + 2e$^-$ ⇌ Zn + 4OH$^-$
- In anode: 2OH$^-$ ⇌ 1/2O$_2$ + H$_2$O + 2e$^-$
- Overall: ZnO$_2^{2-}$ + H$_2$O ⇌ Zn + 1/2O$_2$ + 2OH$^-$

2.14 Process Flowsheet

The process flowsheet of the reactions that were simulated in METSIM is shown in Figure 2.5.

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Fig 2.5. Process flowsheet of zinc recovery from galvanized steel scrap (Adapted from Alam, 2001).
CHAPTER THREE
MATERIALS AND METHOD

3.0 Overview

In the 1980s, there are lots of interest in the recovery of zinc from galvanized steel due to the increased amounts of galvanized old scrap that started appearing. As the zinc-coated steel use in the automotive industry continues to increase, recycling galvanized scrap was identified as being a critical issue. Technology for dezinging of galvanized steel before melting was developed. Coated steels, be it a metallic coating or organic pose burdens on the remelting of scrap for recycling. Tramp elements or impurities are hazardous and require special procedures to collect them in an environmentally safe manner (Schneider et al., 1992).

All zinc-coated scraps, regardless of grade, are currently recycled via electric arc furnace (EAF), which are discussed in sections 2.10 and 2.11. With this in mind, the industry continues to search for an economical process to remove the zinc coating before melting the steel scrap. Between pyrometallurgical and hydrometallurgical processes, the latter is the best process for removing zinc before the steel is melted mostly because it is environmentally friendly and is the process used for this research.

Hydrometallurgy refers to the extraction of metals and the production of inorganic substances from minerals through aqueous solutions (acidic or alkaline). The hydrometallurgical process is divided into different stages, namely: leaching, solid-liquid separation, solvent extraction, stripping, electrowinning, precipitation, and so on. This research is the simulation and modelling of the experimental work conducted by Dr. Shafiq Alam (supervisor) for the recovery of zinc from galvanized steel scrap.

3.1 Leaching

Leaching means the dissolution of the metal value into a suitable reagent that may dissolve many other metals present in the ore. Before leaching, the ore may be subjected to preliminary treatments like crushing, grinding, and concentration by mineral beneficiation methods, which will not be dealt with here (Shamsuddin, 2016).

The choice of a particular technique depends on factors such as type of ore deposits, desired leaching rates, the composition of the ore, nature of the gangue associated with the ore, and the
subsequent separation and precipitation or extraction technique be adopted. A brief outline of each method is given below.

3.1.1 In-situ leaching

This leaching method, also known as solution mining, is used when very low-grade ore is left out in the worked-out mines and for the recovery of metals from low-grade deep-seated ore deposits. In this method, ore bodies are fractured at the surface for penetration of the lixiviant inside the mine and the resultant leach liquor is pumped out to recover the metal value. In-situ leaching has been successfully practiced for the recovery of copper and uranium in the Western United States (Shamsuddin, 2016).

3.1.2 Heap leaching

It is practiced by spraying a solvent over the ore lumps of less than 200 mm diameter, stacked in an open atmosphere with the facility for drainage for collection of the leach liquor. The process is slow, with low recovery (Shamsuddin, 2016).

3.1.3 Percolation leaching

It is adopted for crushed ore of 6–10 mm size placed in large tanks by percolating several solutions in increasing concentration. For effective leaching, the ore should be coarse enough so that the leaching solution can move freely through the voids. The method is also known as sand leaching because of the use of coarse particles. The tanks made of wood and concrete and lined with lead or asphalt are used. To facilitate the addition and withdrawal of leach solution and wash water, tanks are fitted with a filter at the bottom (Shamsuddin, 2016).

3.1.4 Agitation leaching

It is employed for ore fines ground to less than 0.4 mm in diameter. This is also known as slime leaching. The slime and the leach solution are agitated in one or more agitators until the ore minerals have dissolved. Some agitators have mechanically driven paddles or elevators inside the agitation tank that facilitate the pulp’s continuous circulation to achieve complete dissolution. For slime leaching, another type of tank known as pachuca in the form of a cylindrical vessel with a conical bottom fitted with a coaxial pipe, with both ends open, introduces compressed air for
agitation is more popular. In both types of tanks, the particles remain suspended in leach solution and are stirred mechanically or with jets of the compressed air. Though expensive, this is a faster and more efficient method than the percolation leaching (Shamsuddin, 2016).

3.1.5 Pressure leaching

Leaching is carried out in autoclaves at high pressure and relatively at a higher temperature than possible in open leaching tanks. High-pressure leaching is advantageous when gaseous reagents, for example, oxygen and ammonia, are involved. The amount of gas held in the solution increases with pressure (Shamsuddin, 2016).

3.1.6 Test work

Leaching can be done using acidic or alkaline lixiviant. The major elements present in galvanized steel scrap are iron and zinc. Because alkaline lixiviant does not leach iron, sodium hydroxide is used as the lixiviant for this process. In the leaching stage, only zinc was leached into the aqueous solution.

From the experiment, leaching tests were carried out batch-wise in a 4 liters stainless steel container at 90 °C. A 500 g zinc scrap was added to 1 liter 200 g/l of sodium hydroxide. Peroxide was used as an oxidizing agent. After 30 min. agitation, scrap was removed, and fresh 500 g scrap was added to the leached liquor, and leaching continued. Another two sets of 500 g scraps were added to the leached liquor, and the leaching duration was 2 hours. The percentage of zinc recovered in leach was 92.45%.

The overall reaction developed for the leaching process is shown in the equation (3.1). One mole of Zn reacted with two moles of sodium hydroxide in the presence of oxygen to give a mole of sodium zincate and water.

\[ \text{Zn} + 2\text{NaOH} + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{Zn(ONa)}_2 + \text{H}_2\text{O} \]  

(3.1)

3.2 Solvent extraction

This process involves bringing into contact the aqueous solution containing the metal value from leaching called pregnant leach solution (PLS) with a suitable organic solvent known as extractant. The metal value is distributed between the two phases. Under equilibrium, the
distribution coefficient $D$ is defined as $D = C_o/C_a$ where $C_o$ and $C_a$ are the concentration of a metal ion in the organic phase and that in the aqueous phase, respectively. The coefficient helps in assessing the extent of extraction in a given number of stages as total extraction does not occur in only one step. For a good separation that is required in the extraction as well as purification operations, the distribution should be larger or smaller than unity. After extraction, the metal value is recovered from the loaded organic phase in a subsequent step known as stripping where the solvent is brought into contact with a suitable aqueous stripping solution (Bewer et al., 1982).

### 3.2.1 Test work

A series of solvent extraction tests were carried out from the sodium zincate solution using different organic extractants containing oxine derivatives (e.g. Kelex 100 and LIX-26). Kelex 100 was a good extractant of zinc from caustic solution. However, since the production of Kelex 100 was stopped, LIX-26 was used.

The extraction of zinc from sodium zincate was carried out at 40 °C, using different concentrated extractant. It was found that LIX-26 best extracts zinc from its alkaline solution. The overall reaction developed for this process is given in equation (3.2).

$$\text{Zn(ONa)}_2 + 2\text{HQ} \rightleftharpoons \text{ZnQ}_2 + 2\text{NaOH} \quad (3.2)$$

where HQ represents the extractant, hydroxyiquinolin ($C_9H_7NO$). The test found that concentrated sulphuric acid is the most suitable stripping agent for zinc recovery from loaded LIX-26; this was carried out at room temperature. The reaction for the process is given in equation (3.3).

$$\text{H}_2\text{SO}_4 + \text{ZnQ}_2 \rightleftharpoons 2\text{HQ} + \text{ZnSO}_4 \quad (3.3)$$

From the test work, the zinc was recovered in the form of zinc carbonate, which was obtained from precipitation. Precipitation test was carried out at room temperature in which the zinc sulfate was stirred with sodium carbonate for about 30 minutes. The reaction for the process is given in equation (3.4).

$$\text{ZnSO}_4 + \text{Na}_2\text{CO}_3 \rightleftharpoons \text{ZnCO}_3 + \text{Na}_2\text{SO}_4 \quad (3.4)$$
However, in METSIM the solid zinc was recovered from zinc sulfate by electrowinning according to equation (3.5).

\[
2\text{ZnSO}_4 + 2\text{H}_2\text{O} \rightleftharpoons 2\text{Zn} + 2\text{H}_2\text{SO}_4 + \text{O}_2 \quad (3.5)
\]

3.3 METSIM

METSIM originated as a metallurgical process simulation program. It is written to perform mass and energy balances around the major unit operations of the process flow sheet. It stands out for its ability to deal with heterogeneous solutions, although it is not a user-friendly software when compared with other process simulators, such as Aspen, Hysys, ChemCad. METSIM was used for the simulation of zinc recovery from the galvanized steel scrap in this research. The following sections show how METSIM was used to develop a process flowsheet for this process, while Appendices A – C show all data input in the simulator to generate the flowsheet. The process flowsheet which is shown in Figure 2.5 is divided into three stages which are leaching, solvent extraction and electrowinning. Each stage will be discussed in the next sections.

3.3.1 Leaching process

As stated in the previous section, leaching is the process of a solute becoming detached or extracted from its carrier substance by a solvent. The flowsheet for this process is shown in Fig 3.1. The feed (galvanized steel scrap) for this process was 400 mt/yr, the weight composition of iron in galvanized steel is 70 – 90 %, and zinc is 30 – 10 %.
Fig 3.1. Flowsheet of the leaching process.

From the flowsheet shown in Fig. 3.1, stream 1 is 1576.2 mt/yr of fluid, it contained 1314 mt/yr of water and 262.2 mt/yr of air, and stream 2 is 326.7 mt/yr sodium hydroxide (sodium hydroxide and water with a weight fraction of 0.85 and 0.15, respectively). The two streams were mixed with an inline mixer (MXI 2) to produce stream 4, NaOH with a concentration of 200 gpl (pH of 14.7). The concentrated NaOH was split by a splitter stream (SPS) to streams 6, 7 and 8, which was connected to leaching tanks 5, 6 and 7, respectively. Stream 10 is the grounded feed which is 400 mt/yr of galvanized steel scrap, and the weight composition was assumed to be 80 % of iron and 20 % of zinc, that is, 320 mt/yr is iron, and 80 mt/yr is zinc. The feed reacts with concentrated NaOH according to the reaction provided in equation (3.1). As it was stated previously, only zinc will be leached by NaOH. Three leaching stages were required to obtain the maximum zinc leached in the pregnant leach solution (PLS). Stream 13 contained both the PLS
(sodium zincate) and tailing (iron), they were pumped to a solid-liquid separator (SLS) in which the sodium zincate (stream 15) was separated from the iron (stream 16). The composition of the streams are shown in appendix A.

3.3.2 Solvent extraction

It is a method to separate compounds based on their relative solubilities in two different immiscible liquids (Bewer et al., 1982). It involves solvent extraction and stripping, as shown in the flowsheet in Fig 3.2. Two stages of solvent extractions and stripping were used to achieve a maximum percentage of zinc recovery. The extractant is LIX-26 (8-hydroxyquinoline C₉H₇NO), and the diluent is kerosene (C₁₀H₂₂); the weight fraction is 0.2 and 0.8, respectively (stream 19). The sodium zincate (stream 15) was transferred to the extraction-1 and then move to extraction-2; the chemical reaction of this process, as shown in equation (3.2). The extract Zn(C₉H₆NO)₂ (stream 23) was transferred to the stripping stage, the raffinate NaOH (stream 18) leaves from the second extraction. In the stripping stage, concentrated H₂SO₄ (stream 26) was used to convert the extract into zinc sulfate according to equation (3.3). The extractant recovered (stream 25) was recycled to unit operation 11 (TNK). The zinc sulfate was transferred to the electrowinning stage.
Electrowinning is the electrochemical process of depositing metal from dissolved metal ions without the replacement of metal ions via anodic dissolution. It is the process of using electrolysis to extract a metallic element from its compound. Due to the nature of the electrochemical reactions, zinc electrowinning is an energy-intensive process that consumes a large amount of energy. Because of the large amount of electrolyte involved, the experimental approach of the zinc electrowinning process is not always practical and feasible. The flowsheet of the process is shown in Fig 3.3; it involves the electrodeposition of zinc ions on the cathode and oxygen evolution on the anode according to the reaction in equation (3.5).
From the flowsheet, zinc sulfate (stream 30) is transferred to the electrowinning cells (ELC), the reaction in the cell is based on equation (3.5). Metallic zinc is recovered from stream 34 as a result of zinc ion that has been deposited at the cathode, and oxygen gas is evolved from stream 35, concentrated H₂SO₄ is recovered from stream 36, and it recycled to stream 26 which is used for the stripping process.

3.4 Modelling

The modelling is based on the electrowinning section of zinc recovery. Zinc electrowinning involves a variety of complex physical and chemical processes. Several important electrode reactions are involved in the zinc electrowinning process, including the reduction of zinc ions on the cathode and the decomposition of water at the anode, as shown in equations (3.6) and (3.7).
To model the zinc electrowinning process as accurately as possible, these processes, including mass transfer, electrochemistry, fluid flow, and electrode reactions, must be considered. Furthermore, the interaction among these processes makes it harder to simulate the process. For example, as the electrochemical reactions consume or produce substances, these source terms affect the mass transfer process. In addition, the mass transfer process will affect the fluid flow in the electrowinning cell because of the density gradient created. The corresponding governing equations can describe these complexities, and they can be characterized and described by a model based on the computational fluid dynamics (CFD) module. The governing equations for the zinc electrowinning process are described below.

### 3.4.1 Governing equations

The equations that were used for the model are illustrated below.

#### 3.4.1.1 Mass transfer

In the zinc electrowinning process, the mass transfer comprises three processes: diffusion, migration, and convection. In the electrolyte, the governing equation for mass transfer in solution is the Nernst-Plank equation, as shown in equation (3.8).

\[
N_i = -z_i u_i F c_i \nabla \Phi_i - D_i \nabla c_i + c_i v
\]

where

- \(N_i\) = Flux density (mol m\(^{-2}\) s\(^{-1}\))
- \(z_i\) = charge (C)
- \(u_i\) = mobility (m\(^2\) V\(^{-1}\) s\(^{-1}\))
- \(F\) = Faraday’s constant (C mol\(^{-1}\))
- \(c_i\) = concentration (mol m\(^{-3}\))
- \(\nabla \Phi_i\) = electric field (V m\(^{-1}\))
- \(D_i\) = diffusivity of species
- \(\nabla c_i\) = concentration gradient (mol m\(^{-4}\))
\[ v = \text{velocity vector (m s}^{-1}) \]

The material balance in the electrolyte is governed by equation (3.9).

\[ \frac{\partial c_i}{\partial t} + \nabla N_i = 0 \quad (3.9) \]

Due to the electroneutrality of the electrolyte, the electrolyte current density is simplified and shown in equation (3.10).

\[ i_e = -F^2 \Phi_i \sum z_i^2 c_i v_i - F \sum z_i D_i \nabla c_i \quad (3.10) \]

where, \( i_e \) is the current density in the electrolyte and other variables were defined above.

**3.4.1.2 Fluid flow**

The fluid flow in zinc electrowinning cells is often affected by three factors: inlet and outlet flow, bubble movement and related flow, and electrolyte density gradient. The form of the bubbly flow equations used assumes that the fluid is non-compressible, and the fluid is laminar flow in the test electrowinning cell. The resulting equation is shown in equation (3.11).

\[ \phi_l \rho_l \frac{\partial v_i}{\partial t} + \phi_l \rho_l (v_i \cdot \nabla) v_i = \nabla \cdot \left[ -p 2I + \phi_l \rho_l (\nabla v_l + (\nabla v_l)^T) \right] + \phi_l \rho_l g + F \quad (3.11) \]

The continuity equation simplified via the low gas concentration assumption is shown in equation (3.12)

\[ \phi_l \nabla \cdot v_i = 0 \quad (3.12) \]

where,

\[ v_i = \text{velocity vector (m s}^{-1}) \]
\[ p = \text{pressure (Pa)} \]
\[ \phi_l = \text{phase volume fraction (m}^3\text{/m}^3) \]
\[ \rho_l = \text{density (kg m}^{-3}) \]
\[ g = \text{gravity vector (m s}^{-2}) \]
\[ F = \text{additional volume force (N m}^{-3}) \]
\[ I = \text{identity matrix} \]
3.4.1.3 Electrodes/Equilibrium potential

In order to determine the cell voltage, the equilibrium potential of both the anodic and cathodic reactions need to be calculated. The equilibrium potential $E$ is given by the Nernst equation, as in equation (3.13).

$$E = E^0 - \frac{2.303 \, RT}{nF} \log \left( \frac{n a_{\text{reduced species}}}{n a_{\text{oxidized species}}} \right) \quad (3.13)$$

This equation uses the standard thermodynamic potential along with the reduced species activities and the oxidized species activities to determine the equilibrium potential for a half-cell reaction.

3.4.1.4 Electrode kinetics

The local current density is calculated with an adapted Butler-Volmer equation shown in equation (3.14).

$$i_{loc} = i_0 \left( \frac{c_{RS}}{c_{RB}} \exp \left( \frac{\alpha_a zF}{RT} \eta \right) - \frac{c_{OS}}{c_{OB}} \exp \left( \frac{\alpha_c zF}{RT} \eta \right) \right) \quad (3.14)$$

where

- $i_{loc} =$ local current density at the interface (the charge transfer current density) (A m$^{-2}$)
- $i_0 =$ equilibrium exchange current density (A m$^{-2}$)
- $c_{RS} =$ surface concentration of the reduced species (mol m$^{-3}$)
- $c_{RB} =$ bulk concentration of the reduced species (mol m$^{-3}$)
- $c_{OS} =$ surface concentration of the oxidized species (mol m$^{-3}$)
- $c_{OB} =$ bulk concentration of the oxidized species (mol m$^{-3}$)
- $\alpha_a =$ anodic symmetry factor
- $\alpha_c =$ cathodic symmetry factor
- $z =$ number of electrons transferred in the rate-limiting step
- $F =$ Faraday’s constant (C mol$^{-1}$)
- $R =$ gas constant (J mol$^{-1}$ K$^{-1}$)
- $T =$ absolute temperature (T)
\[ \eta = \text{overpotential} \]

The corresponding standard electrode potential, the exchange current density, and the charge transfer coefficient for each reaction are shown in Table 3.1.

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Standard electrode potential E⁰ (V)</th>
<th>Exchange current density (i_0) (A m⁻²)</th>
<th>Anodic charge transfer coefficient</th>
<th>Cathodic charge transfer coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cathodic zinc reactions</td>
<td>-0.763</td>
<td>12.563</td>
<td>1.455</td>
<td>0.490</td>
</tr>
<tr>
<td>Anodic reaction</td>
<td>1.229</td>
<td>3.32 E⁻⁷</td>
<td>0.521</td>
<td>0.521</td>
</tr>
</tbody>
</table>

### 3.4.2 Electrolyte parameters

The main electrolyte parameters, i.e. electrolyte density and electrolyte viscosity, have an essential effect on the electrolyte fluid flow behaviour, and these parameters change with the operating conditions. Therefore, to get correct electrolyte parameters under different operation conditions, the relationship of electrolyte density and viscosity with a variety of operating parameters is taken into account. The density and viscosity of the electrolyte are generally affected by the ionic concentrations and the electrolyte temperature. Several researchers have studied the changes in density and viscosity within a certain range of ion concentration and temperature of the ZnSO₄ - H₂SO₄ - H₂O electrolyte system. In the literature, some empirical equations have been developed based on the experimental data. Among these equations, the following two equations were selected based on Guerra’s recommendations to calculate the electrolyte density and viscosity under different conditions in the model, as shown in equations (3.15) and (3.16) (Guerra and Bestetti, 2006).

\[
\rho = 1011.2 + 61.1C_{H_2SO_4}(1 - 0.08C_{Zn^{2+}}) + 156.8C_{Zn^{2+}} - (0.44 + 0.08C_{H_2SO_4} + 0.13C_{Zn^{2+}})(T - 273) \tag{3.15}
\]
\[
\mu = \left(17.7 + 4.1C_{H_2SO_4} - \left(1.0 + 2.5C_{H_2SO_4}C_{Zn^{2+}}\right)\right) \times \\
\exp\left(\frac{15200 + (1850 + 225C_{H_2SO_4}C_{Zn^{2+}})R_T}{RT}\right) \times 10^{-7}
\]

where,

- \(C_{Zn^{2+}}\) = zinc ion concentration (mol m\(^{-3}\))
- \(C_{H_2SO_4}\) = sulfuric acid concentration (mol m\(^{-3}\))
- \(T\) = electrolyte temperature (K)
- \(\rho\) = electrolyte density (kg m\(^{-3}\))
- \(\mu\) = electrolyte viscosity (Pa.s)
CHAPTER FOUR
RESULTS AND DISCUSSION

This chapter displays and discusses the results of this research project. The results are based on the simulation from METSIM and were compared with the results from the experiments carried out by Dr. Shafiq Alam and this is the only experiment performed on the recovery of zinc using NaOH as the lixiviant.

Previous chapters stated that concentrated sodium hydroxide was used to leach the steel scrap to avoid the leaching of iron. The feed rate is 400 mt/yr of galvanized steel scrap, with the composition of 320 mt/yr and 80 mt/yr of iron and zinc, respectively.

Using one leaching stage, about 60% of zinc was leached (47.52 mt/yr). The stage was increased to 2 leaching stages; the percentage of zinc leached was 83.68%. When the number of stages was increased to 3 leaching stages, 93.63% of zinc was leached (74.91 mt/yr). By increasing the number of leaching stages to 4, the percentage of zinc leached was 94.52%. It was concluded that three stages were the best for the leaching stage. From the experiment carried out by my supervisor, three stages were used for the leaching and the percentage of zinc leached was 92.45%.

The concentrations of sodium hydroxide were varied to know the best concentration needed for the leaching process. The concentration was varied from 40 g/l to 400 g/l, the overall percentage (3 stages of leaching) of the zinc leached with the increase in concentration is shown in Table 4.1. With a concentration of 40 g/l, the percentage of zinc leached was 54.06% (43.25 mt/yr), the percentage increases as the concentration increases. At the concentration of 200 g/l, the percentage of zinc leached is 93.63% (74.90 mt/yr). Increasing the concentration beyond 200 g/l, the percentage of zinc leached remains virtually constant. The temperature for the leaching process is 90.12 °C. It was concluded from the simulation that the best concentration of sodium hydroxide used for leaching of steel scrap is 200 g/l, which was confirmed with the results obtained from the experiment in section 3.1.6.

Figure 4.1 shows the effect of NaOH concentration on the percentage of Zn leached. From the figure the average concentration of sodium hydroxide is 220 g/l and the standard deviation is 121.11 g/l. From these values (average and standard deviation of the concentration), it can be observed that 200 g/l of sodium hydroxide gives the maximum amount of zinc leached because it in the range of the standard deviation with the average.
Table 4.1. Effect of NaOH concentration on the percentage of Zn leached.

<table>
<thead>
<tr>
<th>Concentration of NaOH (g/l)</th>
<th>Percentage of Zinc Leached (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>54.06</td>
</tr>
<tr>
<td>80</td>
<td>87.50</td>
</tr>
<tr>
<td>120</td>
<td>90.80</td>
</tr>
<tr>
<td>160</td>
<td>93.08</td>
</tr>
<tr>
<td>200</td>
<td>93.63</td>
</tr>
<tr>
<td>240</td>
<td>93.63</td>
</tr>
<tr>
<td>280</td>
<td>93.63</td>
</tr>
<tr>
<td>320</td>
<td>93.63</td>
</tr>
<tr>
<td>320</td>
<td>93.63</td>
</tr>
<tr>
<td>400</td>
<td>93.63</td>
</tr>
</tbody>
</table>

Fig 4.1. Effect of NaOH concentration on percentage of Zinc leached.
The effect of liquid to solid ratio (L/S) was used to determine the amount of feed that will give a maximum percentage of zinc leached at a concentration of 200 g/l of sodium hydroxide. The rate of the lixiviant is 1640 mt/yr, and it was left constant, the L/S ratio was varied from 1 to 10. For L/S of 1, it means the lixiviant and feed are 1640 mt/yr; meanwhile, for L/S of 10, it means the lixiviant and feed are 1640 mt/yr and 164 mt/yr, respectively, as the ratio increases the percentage of zinc leached increases as shown in Table 4.2. At the L/S ratio of 4, the percentage of zinc leached is 93.63%, as the L/S ratio continues to increase the percentage of zinc leached remains constant. It was concluded that 400 mt/yr of the feed gives the best percentage of zinc leached. In the solid-liquid separation process, the unleached iron is separated from sodium zincate. The amount of zinc that was transferred to the solvent extraction process was 74.88 mt/yr.

Table 4.2. Effect of L/S ratio on percentage of Zn leached at a concentration of 200 g/l of NaOH.

<table>
<thead>
<tr>
<th>Liquid to solid ratio (L/S)</th>
<th>Percentage of zinc leached (at 200 g/l NaOH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>70.92</td>
</tr>
<tr>
<td>2</td>
<td>89.88</td>
</tr>
<tr>
<td>3</td>
<td>92.66</td>
</tr>
<tr>
<td>4</td>
<td>93.63</td>
</tr>
<tr>
<td>5</td>
<td>93.64</td>
</tr>
<tr>
<td>6</td>
<td>93.64</td>
</tr>
<tr>
<td>7</td>
<td>93.64</td>
</tr>
<tr>
<td>8</td>
<td>93.64</td>
</tr>
<tr>
<td>9</td>
<td>93.64</td>
</tr>
<tr>
<td>10</td>
<td>93.64</td>
</tr>
</tbody>
</table>

Figure 4.2 shows the effects of liquid to solid ratio on the percentage of zinc leached at a concentration of 200 g/l. The average and standard deviation of L/S ratio is 5.5 and 3.03,
respectively. From these values, it can be observed and concluded that the L/S ratio of 4 is the best ratio to give the maximum amount of zinc leached.

Fig 4.2. Effect of L/S ratio on the percentage of zinc leached at a concentration of 200 g/l of NaOH.

In solvent extraction section, two stages of extraction and stripping were used to achieve the maximum extraction of zinc. The raffinate stream, which is mainly sodium hydroxide and water, contains 2.18 mt/yr, and the loaded organic has 72.69 mt/yr. The percentage of zinc transferred to the loaded organic is 96.94%. Concentrated sulfuric acid was used for stripping, and the amount of zinc stripped was 72.63 mt/yr. The total percentage of the zinc recovered in the solvent extraction section was 97%, at a temperature of 50 °C.

The metallic zinc was recovered in the electrowinning section at a temperature of 43 °C. The amount of zinc recovered in stream 34 is 72.59 mt/yr. The percentage of the zinc recovered in electrowinning is 99.94%. As stated earlier, the amount of zinc present in the galvanized steel scrap was 80 mt/yr, and the amount of zinc recovered at the end of the whole process is 72.59 mt/yr. The overall percentage of zinc recovered in the entire process is 90.74%.
5.0 Conclusions

In this thesis work, hydrometallurgical recovery of zinc from steel scrap using METSIM as the simulator was studied. The primary processes involved leaching, solvent extraction, stripping and electrowinning sections. These required a comprehensive understanding of the process solution and solid raw materials.

Leaching can be carried out with acidic or alkaline lixiviant; iron is the primary element in steel scrap. It must be separated from the zinc before the zinc can be recovered. To prevent the leaching of iron, alkaline leaching was used. The feed rate was 400 mt/yr, and it contained 320 mt/yr of iron and 80 mt/yr of zinc. The lixiviant for alkaline leaching was concentrated sodium hydroxide. The number of stages for the leaching was three; this gave the maximum amount of zinc recovery. The unleached iron was separated from sodium zincate (leached zinc) using solid-liquid separator before the PLS was transferred to the solvent extraction section. The amount of zinc recovered from leaching was 74.88 mt/yr, and the percentage was 93.60%.

In solvent extraction, the organic extractant was 8-hydroxyquinoline (LIX-26), while the diluent was kerosene. The extractant was used because it could extract zinc from a caustic solution. Two stages of extraction were used for the maximum recovery of zinc. At the stripping section, concentrated sulfuric acid was used as a stripping agent. The product after stripping was zinc sulphate. The amount of zinc recovered after extraction and stripping was 72.63 mt/yr at a temperature of 50 °C and the percentage of zinc recovered in extraction and stripping was 97%.

In electrowinning, metallic zinc was recovered from a zinc ion deposited at the cathode and oxygen gas was evolved from the anode. Concentrated sulfuric acid was produced from the electrowinning cell, and it was recycled to the stripping section to be used as a stripping agent. The amount of zinc recovered was 72.59 mt/yr; the overall percentage of zinc recovered in the entire process is 90.74%.

The percentage of zinc recovered is high; this method will reduce the pollutant generated from galvanized steel scrap that will be fed in the foundries for steel recycling. The zinc recovered can be used in a zinc-consuming industry, and it will address the primary concern in the zinc industry on how to bridge the gap between the supply and demand of zinc.
5.1 Recommendations

In this project, there are some areas of research that could expand our understanding of zinc recovery. This understanding would probably also have added benefit to industrial applications in terms of increased efficiency and capacity.

The alkaline (concentrated sodium hydroxide) used for leaching was recovered as raffinate after the extraction. This might be recycled to the leaching section, and it might increase the amount of feed used for the process.

The modelling of this simulation needs to be run with modelling software like the COMSOL Multiphysics package.
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APPENDICES

APPENDIX A

The figures showing the chemical reaction, rate and compositions of streams in leaching section.

Fig A.1: Aqueous composition of stream 1
Fig A.2: Gaseous composition of stream 1
Fig A.3: Concentration of sodium hydroxide in stream 5
Fig A.4: Composition of the steel scrap

Fig A.5: Chemical reaction in the leaching agitated tank.
Fig A.6: Solid components of the leached solution
Fig A.7: Aqueous component of the leached solution
Fig A.8: Steel recovered after solid-liquid separation (Tailing)
Fig A.9: Pregnant leached solution (PLS)
APPENDIX B

The figures showing the chemical reaction, rate and compositions of streams in solvent extraction section.

Fig B.1: Chemical reaction for the solvent extraction

\[ 2 \text{HQ} + \text{Zn}((\text{OH})_2) = \text{ZnQ}^2\text{+} + 2\text{NaOH} \]
Fig B.2: Composition of the extract
Fig B.3: Composition of the raffinate.

Fig B.4: Chemical reaction for the stripping.
Fig B.5: Chemical component of the stripped solution
APPENDIX C

The figures showing the chemical reaction, rate and compositions of streams in electrowinning section.

Fig C.1: Chemical reaction of zinc electrowinning.
Fig C.2: Amount of oxygen evolved at the anode.
Fig C.3: Amount of zinc recovered at the cathode