SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING

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HYDRO-ELECTROMETALLURGICAL EXTRACTION OF ZINC FROM ZINC BEARING WASTES

By

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled "**Hydro-Electrometallurgical Extraction of Zinc from Zinc Bearing Wastes**". I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title of this for any other examining body or University.

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LIST OF ABBREVIATIONS

XRF	X-ray Flourescence
XRD	X-ray Diffraction
FE-SEM	Field Emission Scanning Electron Microscope
EDX	Energy-dispersive X-ray Spectroscopy
EAF	Electric Arc Furnace

LIST OF SYMBOLS

˚C	Degree celcius
%	Percent
Wt. %	Weight percent
g	Gram
m	Mass of deposits
M	Molar mass of the species
F	Faraday constant
I	Current
V	Voltage
A	Ampere
H	Leaching recovery
L	Liter
mins	Minute at time, t
mg/L	Miligram per liter
K	Kelvin
kWh	Kilowatt hour
hrs	Hour
ppm	Part per million

HiDRO-ELEKTROMETALURGI PENGEKSTRAKKAN ZINK DARIPADA SISA MENGANDUNGI ZINK

ABSTRAK

Penggalvanian adalah salah satu teknik penyaduran yang diamalkan pada masa kini juga menghasilkan sisa seperti proses metalurgi yang lain. Pengekstrakkan zink daripada sisa zink tergalvani adalah penting berikutan implimentasi undang-undang pemeliharaan alam sekitar sekaligus mengurangkan kesan yang negatif kepada persekitaran. Sisa zink penggalvanian yang digunakan dalam kajian ini terdiri daripada 64.8 peratus berat ZnO yang hadir bersama-sama mineral yang lain dengan peratus berat berlainan. Sebelum proses pelarutresapan sisa zink penggalvanian dijalankan, sampel telah dipanggang pada suhu 400˚C dan melalui proses pelarutresapan air panas. Sampel kemudiannya telah dilarutresap pada suhu (50, 70 dan 90˚C), kepekatan asid sulfurik (0.9, 1.8 dan 3.6 M) pada masa (1,2 dan 4 jam) yang berbeza. Dalam masa 2 jam proses pelarutresapan, pada suhu 70˚C, sebanyak 90.1% pengekstrakkan zink telah dicapai dengan kepekatan asid 1.8 M. Manakala pada suhu dan kepekatan yang sama tetapi pada masa yang lebih lama (4 jam), 98.58% pengekstrakkan zink telah dicapai. Walau bagaimanapun, apabila pelarutresapan dijalankan pada suhu 70˚C menggunakan 3.6 M asid sulfurik dalam tempoh dua jam, sebanyak 99.53% zink telah diekstrakkan. Larutan larutresap kemudiannya telah dirawat dengan menggunakan pemendakan besi dan pensimenan kuprum yang kemudiannya diikuti oleh proses elektrolehan. Proses electrolehan telah dijalankan dalam bikar 50 mL menggunakan anod plumbum dan katod aluminium dengan 12 cm jarak elektrod untuk mendapatkan arus kecekapan yang tinggi dengan tenaga yang rendah. Pada keadaan optimum proses elektrolehan,

endapan logam Zn berupa struktur kepingan didapati terendap pada katod Al dengan kecekapan arus dalam julat 93.9% hingga 98.5%. Tenaga elektrik yang diperlukan dalam proses electrowinning adalah dalam julat 2.13 ke 2.23 kWh/kg.

HYDRO-ELECTROMETALLURGICAL EXTRACTION OF ZINC FROM ZINC BEARING WASTES

ABSTRACT

Galvanizing, which is one of the coating techniques nowadays also produces wastes like all metallurgical process. Extracting the zinc back from the galvanizing zinc wastes is essential with the implementation of strict environmental protection regulations as well as to reduce the negative effects to the environment. The galvanizing zinc wastes used in this research consist of 64.80 wt% of zinc oxide occurring with other minerals of different wt%. Prior to leaching of the galvanizing zinc wastes, the sample was roasted at 400˚C and undergone hot-water leaching. The sample was then leached at varying temperatures (50,70 and 90˚C), concentration of H_2SO_4 (0.9, 1.8 and 3.6 M) and at time (1,2 and 4 hours). In 2 hrs leaching time, at 70˚C, about 90.10% of zinc recovery was achieved when leaching was conducted in 1.8 M sulfuric acid. While at the same leaching temperature and concentration of H_2SO_4 and at longer leaching time (4hrs), about 98.58% of zinc was recovered. However, when leaching was carried out at 70˚C with 3.6 M concentration of sulfuric acid conducted in 2 hrs, about 99.53% of zinc recovered. The pregnant leach solution was then purified by iron precipitation and copper cementation followed with electrowinning procedure. The electrowinning process was carried out in a 50mL beaker using lead anode and aluminium cathode with electrode distance was set to 12 cm to obtain high current efficiency with low energy requirement. At the optimum condition of electrowinning, zinc metal with a flake like structure was observed deposited at the aluminium cathode with a current efficiency between the range 93.9% and 98.5%. The electric energy requirement for the electrowinning process is in the range of 2.66 to 2.79 kWh/kg.

CHAPTER 1

INTRODUCTION

1.1 Research Background

Almost all metallurgical processes are dealing with the generation of wastes and residues that may be hazardous or non-hazardous in nature depending upon the criteria specified by institution such as Department of Environment of the Ministry of Natural Resources and Environment, etc. as discussed by Sahu, (2004). Wastes that are non-hazardous can be utilized for metal recovery of safe disposal. However, it is deemed be to be treated or disposed of the wastes containing heavy and toxic metals that are present beyond the permissible limits.

Zinc is an important base metal that has been used for various applications such metallurgical, chemical and textile industries. The zinc is mainly recovered from primary sulphide concentrates. The production of zinc around the globe are about 10 million tons per year, where 30% of zinc is produced from the secondary sources (Sahu, 2004). These secondary sources may come from zinc ash, zinc dross, flue dust of electric arc furnace, skimming and residues, automobile shredder scrap and rayon industry sludge. Jha,*et al.*, (2001) suggest that the secondary sources of zinc contain different level of impurities depending of their origins. The normal ranges of constituents in galvanizing zinc wastes and other sources are given in Table 1.1.

Recently, strengthen of environmental protection regulations cause the disposal of such materials is becoming expensive. Moreover, some of these particles are classified as hazardous wastes due to the presence of different metals.

Table 1.1: Composition of constituents presence in secondary zinc sources (Sahu, 2004)

Secondary Zn source	**Industry sector**	**Composition**				
		Zn	**Cu**	**Cd**	**Fe**	**Cl**
Zinc dross	Galvanizing	93-96		0-0.2	3-6	
Zinc ash	Galvanizing	50-75		0-0.1	0.2-1.5	1-6.5
Zinc skimmings	Galvanizing	50-60		0-0.2	0-1	10-25
Brass dross	Brass foundries	41-42	43-45	-	1-2	0.1-0.5
Brass ash	Brass foundries	20-30	4-8	-	1.5-2.5	0.1-0.3
Copper cement	Zinc plant	6.0-9.5	5.5-7.0	-	1-3	-
Flue dust	Pb & Cu smelters	30-32	5-6	-	1.5-2	7-8
Oxide dust	Waelz process	60-65	0.1-0.3	-	1-1.5	1.5-2
Steel fumes	Steel furnace	30-30.5	22-24	-	0.1-0.3	1.5-2

Industrially, pyrometallurgical and hydrometallurgical process are used for treating secondary zinc sources. Pyrometallurgy is a process in extracting and purifying metals with the use of high temperature. In the other hand, hydrometallurgy utilize the aqueous chemistry in extracting the metals from the ores or residual materials. As hydrometallurgy usually extract the metal in the solution, electrometallurgy is essential to be applied to extract the solid metal from the solution.

In this study, hydrometallurgical route was chosen as the method to produce pure zinc from galvanizing zinc wastes. Sulphuric acid leaching process have been investigated to recover zinc selectively from waste materials. The purification process also applied as a preparation of pure zinc sulphate ($ZnSO_4$) solution for electrowinning.

1.2 Problem Statement

Galvanizing is a technique of applying a protective zinc coating to steel or iron for industrial use as rusting inhibitors. However the galvanizing method also produce wastes like suggested by Sahu, (2004). The material produce could be disposed off or may be used to recover metallic values in it. However, the disposal of galvanizing zinc wastes is now becoming expensive due to implementation of environmental protection regulations. Due to that situation, extracting the zinc from the galvanizing zinc wastes is essential to be done.

In the industrial practices, hydrometallurgical and pyrometallurgical process are employed for treating such material. Pyrometallurgical method which use high temperature in extracting metal require high energy and need of gas cleaning system. Besides, expensive alloys need to be use as materials of construction if there is presence of chloride and fluoride salts that may causes severe corrosion problem (Jha, *et al.*, 2001).

The hydrometallurgical processes are more suitable because they are economical to treat even low zinc containing materials on small scale and environmental friendly as described by Jha *et al.*, (2001). On the other hand, the optimum condition of leaching need to be investigated in order to extract the zinc at maximum level.

1.3 Research Objective

The objectives of this study are:

1. To study the mineralogy and characteristics of the zinc bearing wastes.
2. To determine the factors affecting the leaching of zinc in sulphuric acid (H_2SO_4) such as temperature, acid concentration and leaching time.
3. To design an electrolytic cell for the electrochemical recovery/deposition of zinc from acid solution.
4. To determine the morphology and zinc recovery from the electrowinning process.

1.4 Scope of Study

The main focus of this research was to study the factors affecting the efficiency of leaching from galvanizing zinc and perform the electrowinning process using the pregnant leach solution. This study was carried out to understand and shed light on the factors affecting sulphuric acid leaching process in extracting zinc before electrowinning process.

Generally, in this study, there are three major steps involved. In this thesis,the characterization of galvanizing zinc sample was done by X-Ray Flourescene (XRF), X-Ray Diffraction (XRD), optical microscope, Scanning Electron Microscope (SEM) and Energy Dispersive X-ray (EDX). Roasting of the samples was done at high temperature to oxidized the sample. The sample is undergone dichlorination by leached it with hot water.

The filtered and dried sample are then leached with sulphuric acid solution. The parameters studied were particle sizes, time and temperature. Analysis of the leaching was done using Atomic Absorption Spectrometer (AAS) and XRF. In leach liquor, along with zinc, other impurities also go along into solution which are detrimental for subsequent electrolysis.

To remove the iron and copper, iron precipitation and copper cementation was done. The electrowinning experiment was done using the pregnant leach solution. The parameters of electrowinning were test first in pre-electrowinning stage using pure electrolyte of $ZnSO_4$ solution. The parameters considered in this step are the pH and electrode spacing. The results of this research will be discussed in Chapter 4.

1.5 Structure of the Thesis

This thesis is organized into five chapters:

- Chapter 1 is the introduction. The general idea of the current work was presented with an overview of the research background. The problem statement was highlighted and the related issues regarding the research was explained. Besides, the research objective was listed.
- Chapter 2 is the literature review. This section consists of a short introduction on secondary sources of zinc and its characteristics. A literature reviews on the hydro-electrometallurgical extraction of zinc was also presented. A brief review of the other researchers study on this topics was discussed. Finally, the reaction chemistry involved in this experiment was reviewed in detail.
- In Chapter 3, the methodology of the overall research was explained. The first part of the methodology was the sample preparation. This was followed by the characterization method of the sample. Next, the sample pre-treatment methods

before leaching was also be explained. Then, the methodology of leaching and electrowinning process was also provided.

- In Chapter 4, the research results are presented and discussed. Firstly, the mineralogical study was done by characterized by the raw sample of galvanizing zinc waste. Then, the results of zinc leaching with sulphuric acid was determined by using the AAS for the solution and XRF for leach residue. The pregnant leach solution is then treated on iron precipitation to remove iron and copper cementation to eliminate the copper. Both processes are characterized by XRD. The electrowinning of zinc from zinc sulphate solution was done and the current efficiency was calculated. The morphology of the deposited zinc was observed under the SEM and the element present was determined by EDX.
- In Chapter 5, a concise conclusion of the current study I presented and some recommendations for future work are suggested.

CHAPTER 2

LITERATURE REVIEW

2.1 Overview

In the galvanizing industries, iron or steel was applied with a protective zinc coating which will act as rusting inhibitors. However, just like the other metallurgical process, the galvanizing process will also produce waste. This waste may cause effect to the health as well as environment. Besides, the implementation of environmental protection regulation causes the disposal of such materials become expensive.

Therefore, it is crucial to extract the zinc from galvanizing zinc waste either by pyrometallurgical or hydrometallurgical(Jha *et al.*, 2001). However, due to the high cause and energy required in pyrometallurgy, hydrometallurgical route had been chosen in extracting the zinc. Several studies had been done by other reseachers before especially in extracting the zinc from secondary sources. The aim of this chapter is therefore to review existing process technologies especially in hydro-electrometallurgical extraction.

In this chapter, a brief review in zinc application is presented at the beginning of the chapter (Section 2.2) and focus on the alternative sources of the primary zinc (Section 2.3). Next, Section 2.4 discussed the introduction to the hydrometallurgy before proceed to the leaching of ores in Section 2.5. The overview of leaching the zinc dross in extracting the zinc was discussed in Section 2.6. Then in Section 2.7, the electrowinning process which will be conducted in this research was reviewed. Finally, in Section 2.8 the electrowinning of zinc from aqueous solution will be explained by reviewed the research work that had been done before.

2.2 Application of Zinc

Zinc is the fourth most commonly used metal after steel, aluminum and copper in the world. The zinc exhibits high tendency to form compound with other elements since it is chemically active. Due to that characteristics, consumption and its alloy has increased. Zinc has been widely used in galvanizing industries of base metals, paint pigment production for chemical industries and die casting zinc alloy production of brass. Figure 2.1 shows the proportions of world metallic zinc consumption. From the chart, it is clear that 50% of the world metallic zinc consumption come from galvanizing.

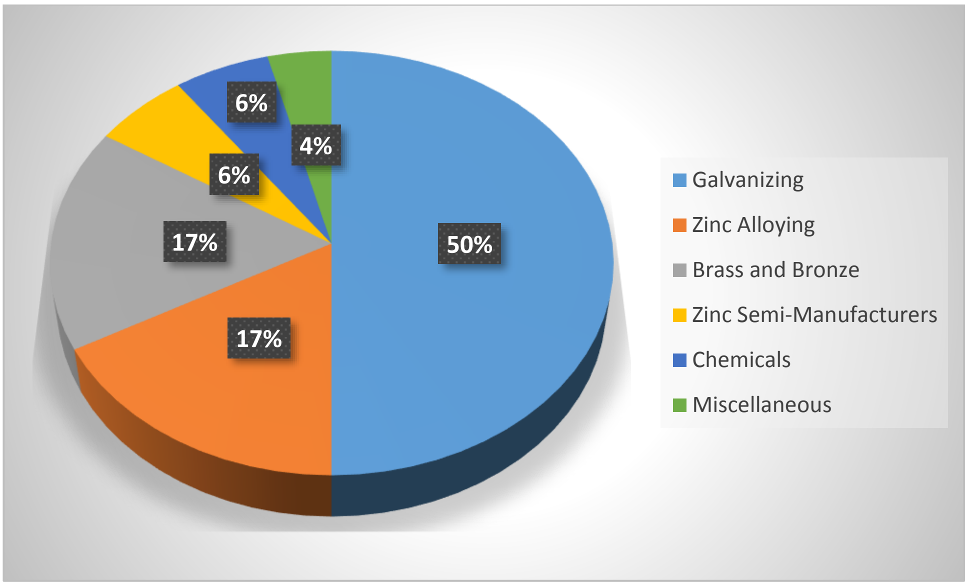

Figure 2.1: Proportions of World Metallic Zinc Consumption (Sunkar, 2005)

2.2.1 Zinc in Base-metal Coatings

Zinc is commonly used in coating process, especially for iron and steel due to its electropositive behavior. The galvanizing process is done on some metals such as iron and steel as they are prone to corrosion. Zinc coating methods used can be as follows:

I. Hot dip galvanizing
II. Electrogalvanizng
III. Sherardizing
IV. Metallizing – spraying with molten zinc droplets

2.2.2 Zinc and Zinc-based Alloys in Castings

Zinc alloys are classified as zinc-based alloys and alloys where zinc is an additive. The most important area that consumes zinc is brass production after coating applications. Brasses are widely used in telecommunication, construction, machinery and information technology sectors (Sunkar, 2005).

High percentage of metal such as copper, nickel, iron, magnesium, chromium and titanium in zinc-base alloys will cause it cannot be worked satisfactorily. Furthermore, low melting and boiling temperatures of zinc and its alloys trigger die-casting method. Consequently, some complex parts and/or specialty alloys can be given shape by utilizing close dimensional control feature of die-casting method for which zinc die-casting alloys are used. The most famous ones are Zamak™ and battery alloys that generally contain 4 % Al.

2.3 Alternative Sources of Primary Zinc

Nowadays, zinc is mainly recovered from zinc sulphide concentrates. As the demand for zinc is always increasing, the extraction was also be done from the secondary resources. There are various secondaries containing zinc are generated in metallurgical industries such as casting , smelting , galvanizing, scrap recycling etc. (Jha, *et al.*, 2001). Zinc present in secondaries is usually in the form of oxides, metal or alloy which contain different level of impurities according to their sources.

2.3.1 Zinc Ash and Zinc Dross

Zinc ash and dross are generated during the galvanizing of metal tubes or sheet (Subramanian, 1995). Zinc ash is obtained in the dry galvanizing process due to the oxidation of molten zinc on top of the bath and floats on the surface of the molten zinc. Jha, Kumar and Singh (2001) reported that the compositions of zinc ash are normally contains zinc oxides and free metallic zinc at a small percent with some impurities in wt% as 60-85 Zn, 2-12 Cl, 0.3-2.0 Pb, 0.2-1.5 Fe and 0-0.3 Al.

On the other hand, galvanizers dross is a material consisting of an alloy of Zn and Fe which settles down at the bottom of the zinc bath. It is the result of the reaction between molten zinc with the steel article and the steel kettle wall. Usually, the composition of the dross is 96% zinc and 4% iron.

2.3.2 Zinc Dust

Zinc dusts are generated in the electric arc furnace (EAF) from the smelting operation where different types of scrap are charged in the furnace for production of steel. Zinc metal is then evaporated with other metals before condensed during cooling. The chemical composition of the dusts depends on their origin. The EAF dust typically consist of 19.4% Zn, 4.5% Pb, 24.6% Fe, 0.42% Cu, 2.2% Mn, 1.2% Mg, 0.4% Ca, 6.8%Cl, 24.6% Fe and 1.4% Si.

2.4 Introduction to Hydrometallurgical Processing

Hydrometallurgy is essentially concerned with methods whereby metals, metals salts, or other metal compounds are produced by mean of chemical reactions involving aqueous and organic solutions. Hydrometallurgy process normally operate in the temperature ranging of 25 to 250˚C and can operate of only a few kilopascals (vacuum) to as high as 5000 kPa. It is a process of beneficiation as well as extraction. The hydrometallurgical route is usually taken on low grades ore where the pyrometallurgical operations are not feasible.

Hydrometallurgical processing involves the following steps (Ghosh, 1995):

1. Leaching: During leaching the desired elements in the ore are selectively dissolved in an appropriate solvent known as the leaching reagent or leachant. Proper leaching may call for some preliminary ore preparation operations such as grinding, sizing, physical beneficiation, roasting etc.

2. Separation of leach liquor: In this step, the solution i.e. the leach liquor is separated from solid residues by one or more of the various methods of materials separation, viz. settling, thickening, filtration, washing etc.

3. Recovery of metallic value from leach liquor: The desired solute or metal in elemental form is obtained in the recovery step. Methods employed to treat the enriched liquor include evaporation, distillation, precipitation, cementation, electrolysis, ion exchange, solvent extraction etc.

4. Reagent recovery: The leaching agent is generally recycled after purification and readjustment of composition.

Any hydrometallurgical process consisting of these steps may have one of the following objectives.

- To produce a pure compound which can be later processed to a metal by pyrometallurgical methods. Here hydrometallurgical is only a beneficiation step.

- To produce a metal from either crude metal or metal compound which has been prepared earlier by other methods.

- To produce a metal directly from an ore or concentrates.

The hydrometallurgical processing is characterized by several distinct advantages (Ghosh, 1995). These are listed.

1. Hydrometallurgical methods are suited for lean and complex ores. With gradual depletion of rich ore deposits, it is becoming increasingly difficult in many situations to apply conventional pyrometallurgical methods for metal extraction. If there is too much gangue, then the processing ores at high temperature causes wastages of energy as well as problems of slag disposal. The siliceous gangue in ores is unaffected by most leaching agents; whereas in pyrometallurgical smelting process, the gangue must be slagged.

2. Hydrometallurgy allows greater control over every step-in processing of ores resulting in recovery of valuable by-products. Metals may be obtained directly in pure from the leach liquor using one of several methods. Handling of materials is also easier.

3. Hydrometallurgical operations are often preferable from the point of view of environmental pollution. Thus, while pyrometallurgical processing of sulfide ores.
4. A hydrometallurgical process may start on a small scale and expand as required. However, a pyrometallurgical process usually must be designed as a large-scale operation for a reasons of process economy.

In the other hand, hydrometallurgical route also give some disadvantages as listed in "Hydrometallurgy in Extraction Process" (Gupta, 1990). These are listed.

1. Hydrometallurgical plants require sophisticated control schemes to maintain satisfactory operation. Hydrometallurgical plants operate more like chemical plants with the philosophy of control associated with chemical plants.

2. There is no economic gain in substituting a pyrometallurgical plant, processing a reasonably high-grade resource, with a hydrometallurgical one.

3. From the point of view of consumption of process materials, fuel, and electric power, hydrometallurgical processes are much more demanding than the pyrometallurgical ones because the latter use mostly oxygen of atmospheric air as a reagent and sulfur present in the ore as a source of heat.

4. Engineering of hydrometallurgical plants is more complex and requires the full understanding of scaleup relationships as well as processing requirements.

2.5 Leaching of Ores

2.5.1 Leaching Description

Leaching can be defined as the process by which a certain valuable soluble fraction is removed from the solid phase with which it is associated, into a solution. Thus, leaching aims at removing the component of interest from the solid phase particle into the solution, which can then be used for further processing.

The solid phase must be insoluble and is generally permeable, most often in the form of a particle with a porous surface or permeable cell walls (Perry and Green, 2008). This allows the leachant to enter into the particle, increasing the chemical reaction surface area. Selective dissolution is key to the leaching process, while diffusion may or may not be involved.

Several leaching mechanisms exist. In general, leaching can take place by one of two general types of mechanisms. The first of these types is merely a result of the solubility of the desired solid substance in a liquid. Chemical reactions are involved in the second type of leaching (Perry and Green, 2008).

There are several factors which influence the rate at which leaching takes place. Among these factors may include the chemical reaction rate (which is, in turn, influenced by several factors), the rate at which the solvent is transported to the site at which the substance of interest is located, the rate at which the substance of interest is leached into the solvent, and interfacial resistance (Perry and Green, 2008), to name but a few.

2.5.2 Essential Features of Leaching

i. The valuable metal must be soluble in an economically usable solvent,
ii. The metal must be economically recoverable from solution, and
iii. Any impurities elements which are co-extracted during leaching must be capable of further separation from the solution

2.5.3 Desirable Features of Leaching

i. The gangue minerals should not consume excessive amounts of solvent.
ii. The solvent should be recoverable (or capable of regeneration) for recycle.
iii. The feed material should be free of clay minerals, as these make separation of leach liquor from the treated solids difficult.
iv. The feed material should be permeable to the solution allowing direct contact between the solvent and the phase to be dissolved, and providing a high liquid/solid area for reaction for a given mass of material, and
v. the solvent should preferably be non-corrosive to materials used in plant equipment to minimize capital and maintenance costs, and should be non-toxic, to minimize any dangers to plant personnel.

2.5.4 Leaching Reagents

There are three common categories of leaching reagents which are water, acids and bases (Ghosh, 1995). To select an effective reagent, some criteria must be look into which are:

- Leaching by reagent must be as selective and as quick s possible
- It should be possible to dissolve the reagent in order to prepare a sufficiently strong leaching solution which can ensure a fast rate of leaching.

- The reagent should preferably be non-corrosive to materials used in plant equipment to minimize capital and maintenance cost, and should be nontoxic to minimize any damage to plant personnel.
- The reagent should be economical and preferably allow regeneration.

2.5.5 Kinetics of Leaching

The leaching process can be summarized in several steps listed below:

1. **Diffusion** of the lixiviant through the diffusion layer to surface of the particle occurs.
2. **Adsorption** of reactant onto the solid
3. **Chemical reaction** between solid and leachant which form product
4. **Desorption** of the product from the solid surface
5. **Diffusion** of the product from the solid surface through diffusion layer into the surrounding liquid.

A diagram illustrating the leaching process can be seen in Figure 2.2.

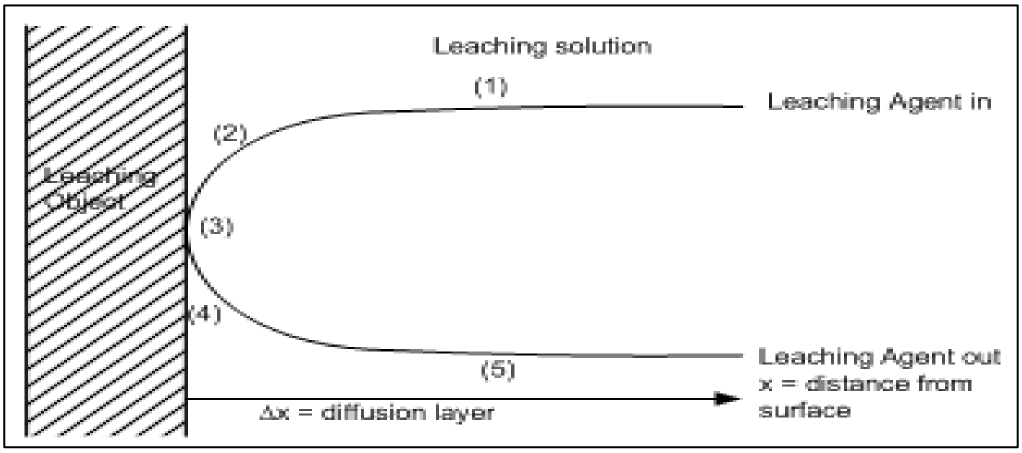

Figure 2.2: Summary of kinetics of the leaching process (A. Baba *et al.*, 2012)

2.5.6 Factors Affecting Rate of Reaction

Several factors can affect the rate of a reaction. These are as follows:

- The standard variables are concentration of reactants, temperature and catalyst, inhibitor or any other substance which affects the rate.
- Chemical reactions are generally very sensitive to temperature and must be studied at constant temperature.
- Rates of reactions in solution and unimolecular reactions in the gas phase are dependent on pressure.
- Some gas phase chain reactions have rates which are affected by the surface of the reaction vessel. Heterogeneous catalysis occurs when a surface increases the rate of the reaction.
- Photochemical reactions occur under the influence of radiation. Conventional sources of radiation, and modern flash and laser photolysis techniques, are both extensively used.
- Change of solvent, permittivity, viscosity and ionic strength can all affect the rates of reactions in solution.

2.6 Leaching of Zinc Dross for Recovery of Zinc

The waste sample obtained from Lab Zinc Company Sdn. Bhd., Ipoh is a zinc dross. Due to that, the composition of this materials was reviewed.

Zinc is molten in a bath during the hot dip galvanizing process. The surface of the molten which is exposed to the atmosphere, reacts with oxygen, forming an oxidized layer. To ensure good galvanizing coatings, the top dross (usually called zinc ash) must be removed. According to Shitov *et al.*, (2005), this zinc dross consists of estimately equal portions of oxidized and metallic zinc.

Dvořák and Jandová, (2005) had performed characterization of zinc ash from zinc dross and they found that the samples contained high percentage of simonkolleite ($Zn_5(OH)_8Cl_2.H_2O$), zincite (ZnO) and metallic zinc (in minority). However, the dross composition varies greatly, as the different stable phases formed in the dross are dependent on the temperature and bath chemistry in the galvanizing process.

Based on the study of the leaching of zinc dross and zinc ash by Rabah and El-Sayed (1995), they found that the zinc dross, with a lower percentage of fines, contained higher zinc. They conclude that finer particles have a great percentage of non-metallic inclusion than the coarser powder cuts. Thus, they suggest that it may be possible to recover more zinc from coarser particles than fines, at a slower rate of recovery.

Besides contain metal contaminants (e.g. Fe, Pb, Al, etc.), zinc dross and zinc ash usually contain significant quantities of chlorides due to flux addition during galvanizing. This means that the dross typically contains chloride compound (Dvořák and Jandová, 2005).

2.6.1 Factors Affecting Leaching Efficiency of Zinc Dross

There are several factors that effect that efficiency of leaching of zinc dross. These factors include temperature, reagent concentration and retention time.

a) Temperature

In the extraction of zinc dross and zinc ash, an uprising of temperature at a constant concentration of acid will increase the acid attack. This trend is consistently increasing up to the temperature of 80˚C which at this point there is no significant effect in zinc dissolution (Rabah and El-Sayed, 1995). The leaching experiment carried by Dvořák and Jandová (2005) at 40˚C found that 98% of zinc had been successfully extracted from the zinc dross in 30 minutes of reacting with 10% acid in a stirred vessel at atmospheric pressure.

In the study of leaching the Electric Arc Furnace Dust (EAFD), Havlík *et al.* (2006) observe that the optimum temperature for extracting zinc from EAFD is between the temperature of 70-90 ˚C where the zinc dissolution achieved was 72%. Moreover, they also found that the temperature had tremendous effect to the leaching efficiency without influenced by the solid/liquid ratio. However, the increasing temperature will negatively affect the iron dissolution.

Shawabkeh (2010) found that an increasing in solution temperature in the range 4-50˚C had increased the rate of zinc extraction. This was due to the increased of diffusivity, mass transfer coefficient and reaction constant.

In the first 20 minutes of zincite leaching, the raqte of dissolution was mainly effected by temperature as it was varied between 30 and 60˚C (Moradi and Monhemius, 2011). Despite that, the temperature effect had decreased during the second of 20 minutes of leaching time and afterward. According to Moradi and Monhemius (2011), this scenario occur probably due to the deposition of solid leaching product, adsorption of zinc onto gangue minerals or pore blocking by solid products. This proved that chemical reaction control occurs at the early stage, where later the leaching process become diffusion controlled.

b) Reagent Concentration

Rabah and El-Sayed (1995) reported that, increasing the concentration of sulphuric acid will gradually increase the amount of zinc dissolution up to 2M. However, a leaching investigation with EAFD done by Cruells, Roca and Núnẽz (1992) with equal range of acid concentration found that zinc leaching was essentially not affected by acid concentration. The residence time of this study was 24 hours which is long enough for maximum extraction to be achieved.

Increasing the acid concentration from 0.1 to 1 mol/L will increase the zinc recovery from 72% to 74.3% in the leaching of zinc from the EAFD (Shawabkeh, 2010). This corresponds well with the results from other resources, which suggest that acid concentration has a notable effect on zinc dissolution, but only up to a certain point. The situation occur as the result of increasing of the hydrogen ion flux across the particle boundaries as it increased the rate of reaction to produce zinc sulfate.

Havlík *et al.* (2006) also found that the acid concentration had the greatest effect on zinc extraction when leaching at atmospheric pressure, at an increasing temperature with the optimum acid concentration of 0.4 M. In 2006, the author conducted similar study using the acid in the range from 0.1 to 1 M. In this study, maximum recovery of 75% was achieved at 1 M (Havlík *et al.,* 2006).

Dvořák and Jandová (2005) achieved 98% of zinc extraction at the first 30 minutes of reaction time, which used 10% acid solution at a temperature of 40%. This method suggested that the concentration of acid has an effect on the leaching of zinc from galvanizing dross although many sources suggest that low temperature is unaffective to leaching.

Overall, it is important to note that the amount of acid added to the system will depend on the stoichiometry of the system reactions. It should be kept in mind that the solid/liquid ratio will therefore affect the amount of acid that should be added. In addition, the tendency of iron dissolution to increase with increasing acid concentration should be considered (Cruells, *et al.*, 1992).

c) Retention time

Rabah and El-Sayed, (1995) found that 98% of dissolution of zinc was achieved in 2M sulphuric acid within 30 minutes at the beginning of the study. The result show a slight increased with prolonged the residence time with the total dissolution of zinc was achieved after 20 hours. From the findings, it is probable to say that at a high temperature less residence time will be needed to achieve a complete dissolution.

However, the leaching zinc from EAFD was a very fast process using a sulphuric acid lixiviant (Havlík *et al.*, 2006). Almost all zinc was dissolved immediately after combining the solids with lixiviant. According to this study, they also found that as the experiment progressed, the amount of zinc extracted reduce with reaction time.

2.6.2 Reaction Chemistry of Zinc Dross Leaching

The leaching reaction between zincite and sulphuric acid are shown below as suggested by Havlík *et al.* (2006).

$$ZnO + H_2SO_4(aq) \rightarrow ZnSO_4 + H_2O \tag{2.1}$$

$$ZnFe_2O_4 + 4H_2SO_4 \rightarrow ZnSO_4(aq) + Fe_2(SO_4)_3(aq) + 4H_2O \tag{2.2}$$

$$ZnFe_2O_4 + H_2SO_4 \rightarrow ZnSO_4(aq) + Fe_2O_3 + H_2O \tag{2.3}$$

An alternative zinc ferrite leaching reaction was suggested by Havlík *et al.* (2006), as shown below.

$$ZnFe_2O_4 + H_2SO_4 + H_2O \rightarrow ZnSO_4(aq) + 2Fe(OH)_3 \tag{2.4}$$

Figure 2.3 and 2.4 below show the E_H-pH diagrams of Zn-Fe-H_2O system at temperature of 25˚C and 100˚C. Havlík *et al.* (2006) said that Reaction (2.2) is thermodynamically preferable over Reaction (2.3) and (2.4) for the leaching process at the temperature between 25 to 100˚C.

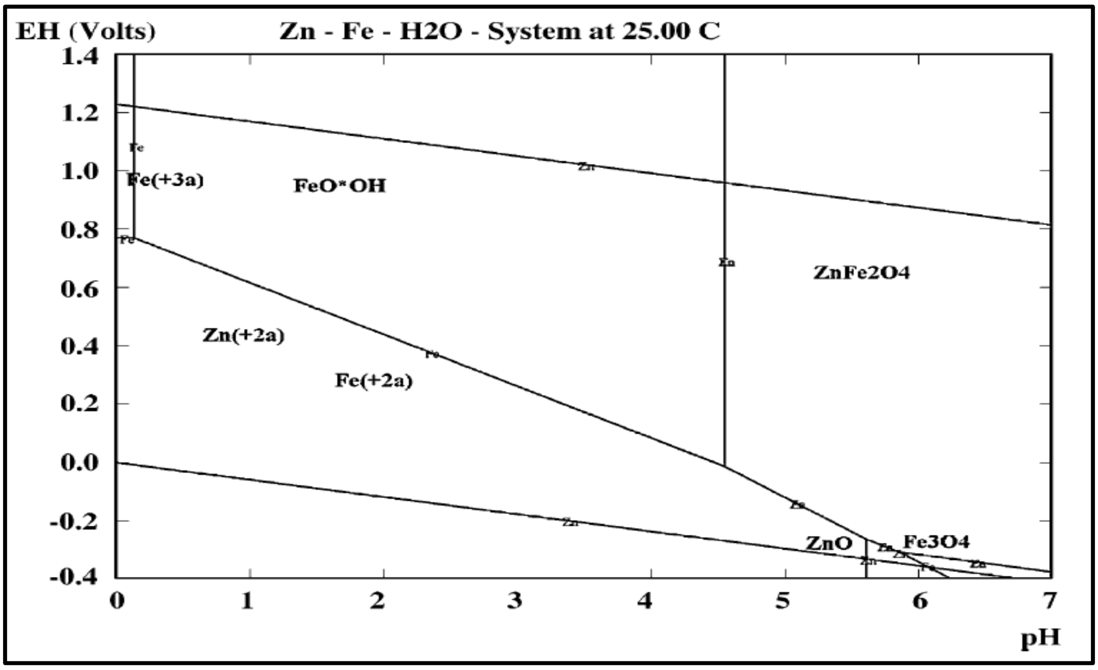

Figure 2.3: Zn-Fe-H_20 System at 25˚C (Havlík *et al.*, 2006)

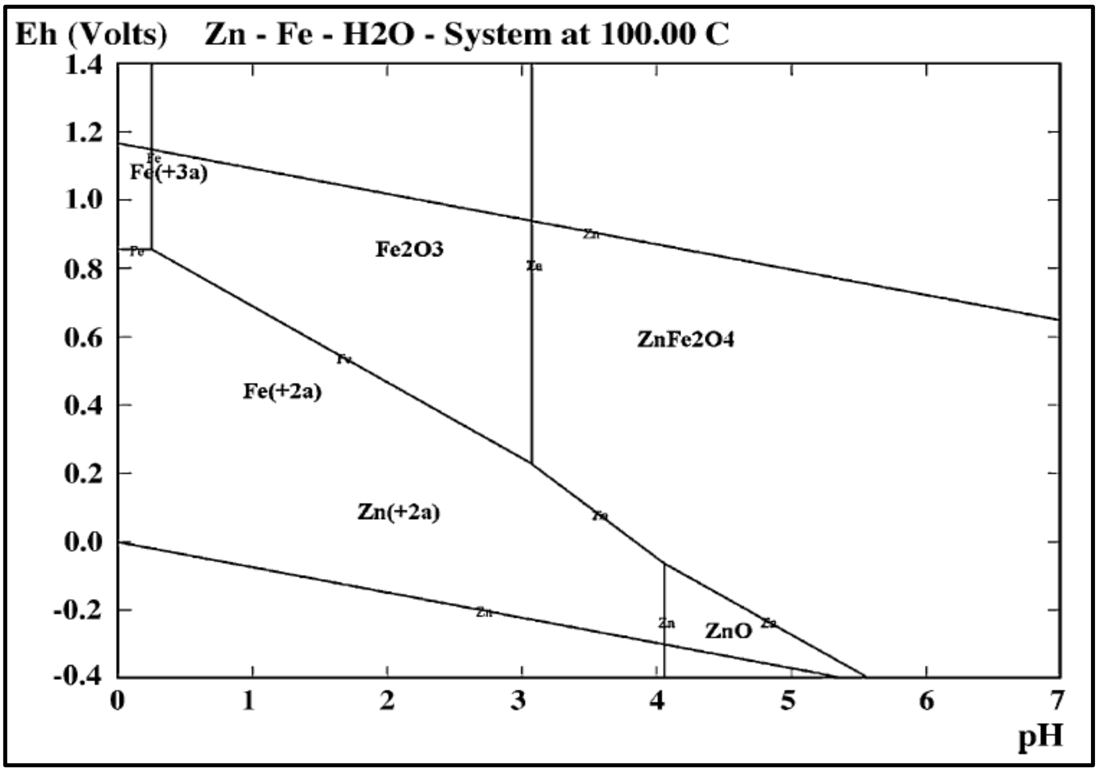

Figure 2.4: Zn-Fe-H_2O System at 100˚C (Havlík *et al.*, 2006)

Based on the Figure 2.2 and Figure 2.3, Fe^{2+} and Zn^{2+} are in the stability zone in the range of pH between 0 and 4 and potential of 0 to 0.8V. Decreasing potential and increasing the pH will precipitate the ferrous ion out of the solution. However, the zinc ions will remain in the solution (Havlík *et al.*, 2006).

Havlík *et al.* (2006) also suggested that as the temperature increase, the Fe^{3+} stability area is become bigger, where the Fe^{2+}/Fe^{3+} potential limit is moved towards higher redox potential. This will cause the iron to precipitate out of the solution.

Besides, magnetite mineral may also present in the sample. The reaction of magnetite with sulphuric acid was shown in the following way (Cruells, Roca and Núnẽz, 1992):

$$Fe_3O_4 + 4H_2SO_4 \rightarrow FeSO_4 + Fe_2(SO_4)_3 + 4H_2O \qquad (2.5)$$

According to Kukurugya, *et al.* (2015) as magnetite react with sulphuric acid in the presence of atmospheric oxygen, the reaction will occur as follows:

$$4Fe_3O_4 + 18H_2SO_4 + O_2(g) \rightarrow 6Fe_2(SO_4)_3 + 18H_2O \qquad (2.6)$$