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SELECTIVE LIQUID-LIQUID EXTRACTION OF PRECIOUS METALS FROM SEMICONDUCTOR WASTES

(PENGEKSTRAKAN CECAIR-CECAIR TERPILIH LOGAM BERHARGA DARI SISA SEMIKONDUKTOR)

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ABSTRACT

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(Keywords: Liquid-liquid extraction, semiconductor wastes, precious metals, silver)

Semiconductor waste can cause a serious problem in term of storage and pollution since it contains high concentration of heavy metals. One of the possible alternatives is to treat this waste by recovering the precious metals such as silver. In this study, an attempt was made to remove the silver selectively from selected semiconductor waste using leaching, precipitation and liquid-liquid extraction processes. From the characterization study, it was found that the semiconductor waste contains 5.92 % of silver which mostly existed in the form of Ag and AgCl compounds. Therefore, chloride leaching has been selected to leach silver from the waste by forming soluble silver chloro complexes. The extent of silver leaching increases with increasing the chloride concentration which could be achieved by either increasing the HCl concentration or addition of high NaCl concentration. The process involved could be explained using shrinking-core model which indicated that the leaching rate was controlled by outward diffusion of silver chloro complexes from the particle surface. These complexes are stable especially at pH 12. Thus, pH adjustment on leaching solution was successfully recovered silver selectively and removed copper and iron precipitate through centrifugation. In the liquid-liquid extraction studies, the extent of silver extraction using Cyanex 272 from leaching solution is low and independent of pH. This result might due to high stability of silver chloro complexes. Therefore, dithizone has been selected due to its soft donor atom of sulfur which is capable to bind with soft acid of silver by forming silver dithizonate. This extraction process was able to extract silver selectively up to almost 100 % and dependence of pH. As an overall, the proposed silver recovery procedure can remove more than 45 % of silver from the selected semiconductor waste.

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ABSTRAK

PENGEKSTRAKAN CECAIR-CECAIR TERPILIH LOGAM BERHARGA DARI SISA SEMIKONDUKTOR

(Kata kunci: Pengekstrakan cecair-cecai, sisa semikonduktor, logam berharga, logam perak)

Sisa semikonduktor boleh mendatangkan masalah dari segi penyimpanan dan pencemaran akibat dari kandungan logam beratnya yang tinggi. Salah satu penyelesaian masalah ini adalah merawat sisa tersebut bagi memperolehi semula logam berharga seperti argentum. Dalam kajian ini, penggunaan kaedah pencernaan, pemendakan dan pengekstrakan cecair-cecair telah dijalankan bagi tujuan perolehan semula logam argentum dari sisa semikonduktor yang terpilih. Melalui pencirian sisa semikonduktor ini, didapati ia mengandungi 5.92 % argentum dan kebanyakannya wujud dalam bentuk Ag dan AgCl. Jadi, pencernaan argentum melalui pembentukan komplex argentum kloro telah digunakan. Tahap pencernaanya boleh diperbaiki dengan meningkatkan kepekatan klorida sama ada melalui peningkatan kepekatan HCl atau penambahan NaCl yang pekat. Penggunaan model 'shrinking-core' menunjukkan kadar pencernaan argentum adalah dikawal oleh resapan keluar komplek kloro argentum dari permukaan partikel. Komplex ini adalah stabil terutamanya pada pH 12. Jadi, melalui pengubahsuaian pH, ia berjaya memperolehi semula argentum secara terpilih. Bagi kajian pengektrakan cecair-cecair, didapati tahap pengektrakan argentum oleh Cyanex 272 adalah rendah dan tidak bergantung kepada pH. Ini adalah disebabkan oleh kestabilan komplek kloro argentum. Maka, dithizone telah digunakan kerana ia berupaya mengikat argentum melalui penderma atomnya, sulfur. Proses pengektrakan ini berjaya mengekstrak argentum secara terpilih menghampiri 100 % dan bergantung pada pH. Secara keseluruhannya, kaedah yang dicadangkan dapat memperolehi semula argentum melebihi 45 % dari sisa semikonductor yang terpilih.

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[AgCl]	AgCl concentration
[M]	Metal concentration
AAS	Atomic absorption spectrophotometry
$AgCl_n^{-(n-1)}$	Silver chloro complexes
$AgHA_2$	$AgH(POO)_2$
AgHDz	Silver dithizonate
EDAX	Energy dispersive x-ray analysis
H_2Dz	Dithizone
HSAB	Hard soft acid base principles
L/S	Liquid (ml)/ solid (g) ratio
PCB	Printed circuit board
XRD	X-ray diffraction
XRF	X-ray fluorescence
δ	Boundary layer thickness (m)
ρ	Degree of association of the extractant
$\mathrm{\rho}$	Density (gm^{-3})
α	Fractional conversion
τ	Required time for complete conversion (s)
ρ_B	Molar density of solid reactant (molm^{-3})
β_n	Overall stability constant
A	Surface area of particle (m^2)
b	Stoichiometric factor
C	Bulk solution concentration (molm^{-3})
C_A	Concentration of A in solution at time, t
C_o	Concentration of A in solution at time = 0

C_s	Surface concentration ($molm^{-3}$)
D	Coefficient diffusion (m^2s^{-1})
D_c	Distribution coefficient
E	Percentage of extraction (%)
K	Mass transfer coefficient (ms^{-1})
k’	First order rate constant (m^3s^{-1})
k_d	Acid dissociation constant of dithizone
K_{ex}	Equilibrium constant
k_o	Concentration of potentially reactive surface sites ($molm^{-2}$)
k_s	First order rate constant (ms^{-1})
K_{sp}	Solubility product
M	Molecular weight ($gmol^{-1}$)
n	Number of moles
n	Valence state of metal
p_c	Partition coefficient of silver dithizonate
p_d	Partition constant of dithizone
$pH_{1/2}$	pH at $D_c = 1$
pH_{eq}	pH at equilibrium
pH_o	Initial pH
pK_a	-log K_a where K_a is acid dissociation constant
r	Radius of sphere particle (m)
Re	Reynold number
r_o	Initial radius of particle (m)
Sc	Schmit number
t	Time (s)
V	Solution volume (m^3)
V	Volume of a particle (m^3)
V_m	Molar volume (m^3mol^{-1})

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CHAPTER I

INTRODUCTION

1.1 Background

Current emphasis on industrialization and rapid growth of technology has led to the development of silver uses. This development of silver uses is commonly found such as in alloys, batteries and cells, bio-medical, brazing and soldering, catalysis, ceramics, contacts, conductors, fibers, lubrication and bearing, mirroring and photo-electric, photography, plating, powders, sterling ware and collectibles, tarnish and corrosion resistance [1]. As a result, the world's industrial consumption of silver had increased from 900 metric tons in 1916 to 12,900 metric tons in 1971 [2]. Due to the high demand of silver consumption, the price of silver had increased substantially. For instance, the price from just under US$0.07 per gram during 1971 and 1972 had increased to more than US$0.14 per gram during 1974, and went up to US$1.77 per gram during early 1980 [3].

For the past decades, silver source was mainly found from the earth's crust. The silver-rich ores were discovered in Mexico, Peru and Bolivia in the 16th century and in the USA in the 19th century [2]. The most common silver ore is sulfide mineral called 'galena' found in South America, Western USA, Australia and Norway [4]. However, this type of silver source becomes exhausted due to increment of silver consumption. Furthermore, the silver recovery involves high operating costs due to its occurrences in a great variety of geological environments. Therefore, until the recent past, silver recovery from the waste had been widely practiced to overcome the exhausted of this natural resource. For instances, the silver recovery from photographic waste [5], electronic scrap [6], copper smelter flue dust [7] and jewelry manufacturing waste [8] have been reported. These silver recovery practices give to several beneficial results, such as economic benefits from the silver recovered, nonrenewable resources of silver will be recycled for use of society and there will be significantly less hazardous material to be disposed in landfills.

Semiconductor waste is one of the potential silver recovery sources. This is because silver is normally used to plate the semiconductor components in order to improve the electrical contact of the component. In Malaysia, the rapid growth of semiconductor industry has accelerated the waste generation. This waste causes a serious environmental problem due to the high heavy metal content. At present, most of the local semiconductor industries have practiced the waste minimization by converting their processing waste stream into sludge form. However, some of sludge generated are not passing the leaching test and not allowed by government to send for landfill. Therefore, their sludge has being stored and accumulated at factory site and this will give another problem to the company. In order to solve this problem, some of the companies have sent their waste oversea for treatment such as Japan, Australia and United State. This might consume high cost of transportation and service charges. According to one of US semiconductor industries, such treatment can cost them RM 400,000 by treating 300 MT of sludge [9].

Currently, Malaysia is lack of treatment technologies especially treating the semiconductor sludge and there is very limited information available. Furthermore, the multi-elements of the semiconductor waste make the studied system more complex. Therefore, the study on treatment of semiconductor waste in order to recover silver is significantly important.

Based on the literature study, several silver recovery technologies have been reported. These include the flotation techniques which consumes high volume of feed material in order to be used economically, pyrometallurgical technique which is energy intensive, biological process using microorganisms that exhibit low selectivity and operative only at low silver concentration, and electrometallurgical technology which is not applicable in metal complexation system (detail of each recovery technologies can be reviewed in Section 2.3). However, the extraction technique which is widely used in hydrometallurgy field, has shown numerous advantages for silver recovery. Its operation performed easily and economically, and provides high selectivity and purity of silver recovery.

1.2 Research Objective and Scopes

The objective of this study was to develop an appropriate procedure to recover silver selectively from the selected semiconductor waste.

In order to achieve the underlying objective, research scopes were designed as following:

1. to characterize the waste by determining the physical properties which include water and organic matter content, density and particle size; and then identify its chemical composition by using XRF, EDAX and XRD;
2. to study the effect of leaching agent types, HCl and NaCl concentration and liquid/solid ratio on the leaching process and understand the process involved by studying the kinetics of leaching process;
3. to study the effect of pH and extractant types (Cyanex 272 and dithizone) on silver extraction. The metal solubility is influenced by the pH of the solution. Therefore, the effect of pH on metal precipitation was also being studied.

1.3 Outline of the Report

The organization of the report is reflects the sequence of the objectives as discussed previously and entails five chapters. Chapter I is presented to give a brief description of the background of the study which leads to define the research objectives and scopes.

In order to provide some background on the fundamentals and the state of the art of the subject under study, a literature review on semiconductor waste and its wastewater treatment, silver recovery technologies with emphasis on the topics of leaching and liquid-liquid extraction processes will be discussed in Chapter II.

In order to achieve the underline objective and scopes of this study, Chapter III is then presented to describe the materials and methods used throughout the study.

The results and discussions of the study are presented in Chapter IV. In this chapter, the results of waste characterization followed by leaching, liquid-liquid extraction and precipitation processes are discussed in some details as defined in the research scopes.

Finally in Chapter V, based on the results obtained, a conceptual silver recovery procedure from semiconductor waste is proposed and concluded. Some recommendations for future work are also included in this chapter.

1.4 Summary

Idea of silver reuse has attracted much attention recently due to the exhausted of silver source from earth’s crust, increasing of silver price and environmental problems. One of the potential silver recovery sources is from semiconductor waste. There are a number of silver recovery technologies have been reported, but the solvent extraction which is widely used in metal extraction can provide a good and potential technique for silver recovery from semiconductor waste.

CHAPTER II

LITERATURE REVIEW

2.1 Semiconductor Waste

Semiconductor industry is a part of the electronic component manufacturing industry such as the manufacture of integrated circuit and printed circuit board (PCB). Figure 2.1 shows the process flow of manufacturing these two components. It is nearly 140 new semiconductor manufacturing plants will be built worldwide before the turn of the century [10] and Malaysia becomes one of the most attractive country for investors to invest in this industry. In Malaysia, from a total of just four companies with 577 employees [11] and a total output value of RM 25 million in 1970, the industry had expanded to comprise more than 850 companies in production, employing 302,000 workers in 1995 with a total estimated output value of RM 67.4 billion. The performance of the electronics industry during the period 1988-1994 had been particularly remarkable, registering an output growth of 30.3 % per annum.

With the rapid growth of semiconductor industry, Malaysia faces the problem of waste accumulation and disposal. Hayhurst [10] reported that the production of one fingernail-width silicon wafer can produce 17,000 litres of wastewater, 12 kg of chemicals, 0.6 m^3 of hazardous gases and 4 kg of hazardous solid waste. Apart from that, the annual manufacturing capacity of PCB created estimated annual revenue of US$0.50 billion can generate up to 100,000 metric tons of sludge [9].

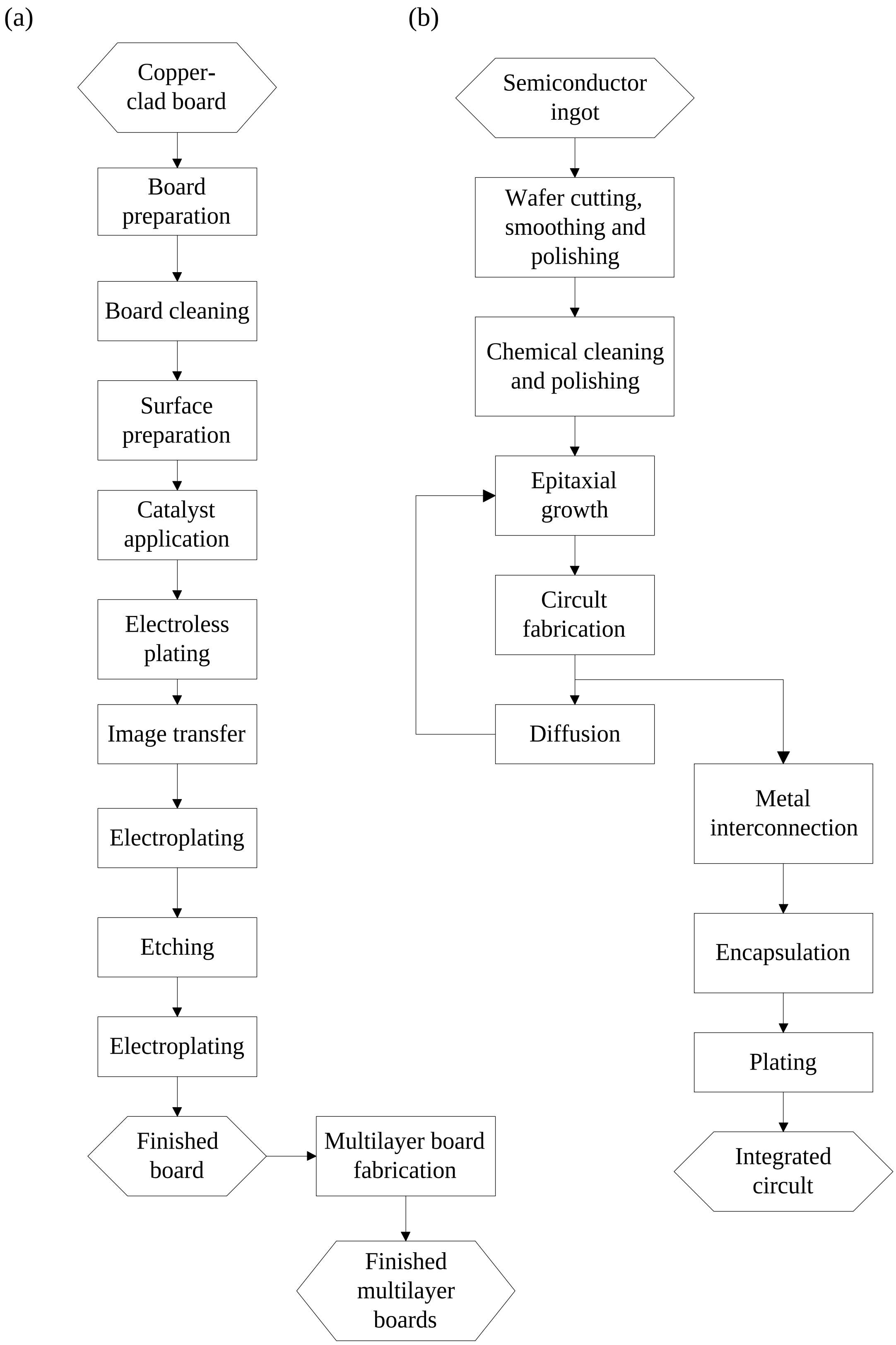


Figure 2.1: A process flow of the manufacture of printed circuit board (a) and integrated circuit (b) in semiconductor industry [12, 13].

Generally, the growth rate of waste generation in the electronic and semiconductor sector in Malaysia had estimated at 5 % per annum out of the total industrial waste generation for the period from 1987-1992 [14]. Recently, the Department of Environment of Johor had reported that the rate of generation of metal hydroxide sludge from semiconductor industry is about 0.45 to 4.0 metric tons per month [15]. Table 2.1 shows the generation of scheduled waste, metal hydroxide sludge (N151) for each of the states in Malaysia except Sabah and Sarawak.

Table 2.1: Scheduled Wastes (N151) generated by several states in Malaysia reported in 1987 and 1992 (cubic meters per annum) [14]

States	1987	1992	States	1987	1992
Perlis	0	0	N. Sembilan	1307	1735
Kedah	1468	1962	Melaka	519	750
Penang	9460	12001	Johor	15414	19788
Perak	16146	21428	Pahang	0	0
Selangor	10713	10159	Kelantan	1	1
Federal Territory	1297	1403	Trengganu	60	70

The major waste from the semiconductor industry can be categorized into two types; spent organic solvent and metals-containing waste [12]. Organic solvents are used for wafer / board cleaning and for the developing and stripping of photoresist materials used in the image transfer and / or circuit fabrication processes. Whereas the metals are introduced into the waste stream through the disposal of concentrated plating baths, running rinses and chemical etch step utilized as part of the electroplating preclean operations. Rinse water contains heavy metal and precleaning chemical such as acid, alkaline, cyanide and other metal salts. There are several types of plating utilized in semiconductor industry, for instance, silver plating, nickel plating, tin plating, copper plating and tin-lead plating. Therefore, the metals-containing waste vary depends on the types of plating process used.

2.2 Wastewater Treatment in Semiconductor Industry

Basically, prime objectives of wastewater treatment process in semiconductor industry are for cyanide reduction, heavy metal removal and neutralization. The treatment process for cyanide removal is generally carried out chemically via conversion of cyanide (CN^-) to cyanate (NCO^-) at pH 9.0 or above and followed by decomposition of cyanate to N_2 and CO_2 at pH 7.5 or below [16]. Cyanide removal is normally conducted by oxidation with chlorine using either sodium hypochlorite (NaOCl) or chlorine gas. For instance, the oxidation of sodium cyanide using sodium hypochlorite (NaOCl) can be written as:

$$NaOCl + NaCN \longrightarrow NaCNO + NaCl$$

$$2NaCNO + 4NaOCl \longrightarrow 2CO_2 + N_2 + 4NaCl + 2NaOH$$

However, some metal-complexed cyanide species are very stable and need to be further decomposed by reduction process using sodium bisulphite ($NaHSO_3$) and coagulated by $Cu(OH)_2$ which is formed according to the following reaction:

$$CuSO_4 + 2NaOH \longrightarrow Cu(OH)_2 + Na_2SO_4$$

Coagulant such as $Al_2(SO_4)_3.18H_2O$ is also added to neutralize the colloid matter and to form aggregates which will be settled down in the settling tank.

Any heavy metal in the waste liquor can normally be precipitated through pH adjustment to form their hydrous oxides which occurs at high pH. This process is normally carried out in the pH-adjusting tank where the lime, $Ca(OH)_2$ and $FeCl_3$ are added. The $Fe(OH)_3$ precipitate is added to produce flocs that has an extensive adsorptive capacity for transition metal ions and some of their complexes. The sediment then will go through thickening and filter press to form metal hydroxide sludge. Meanwhile the treated water will be neutralized before discharge. Figure 2.2 illustrates a general flow diagram for the wastewater treatment system used in the semiconductor industry.

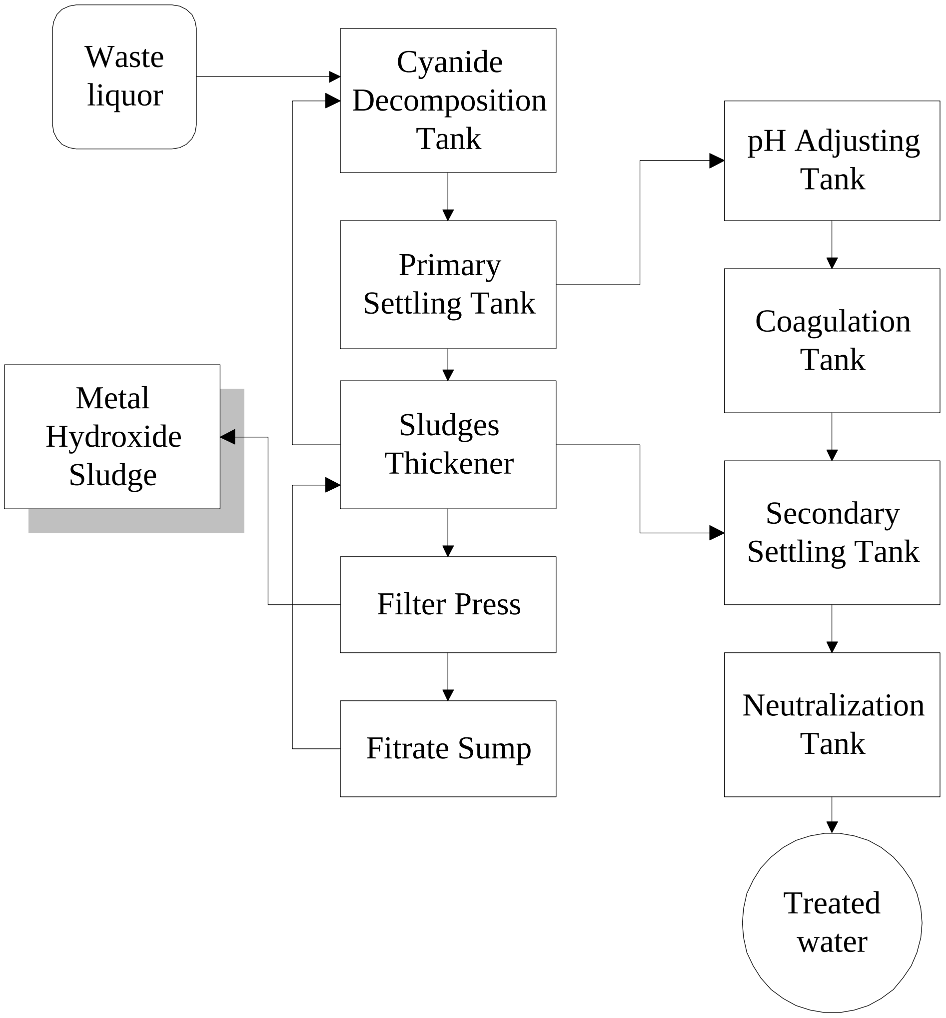


Figure 2.2: A typical process flowchart of wastewater treatment system in semiconductor industry [17].

2.3 Silver Recovery Technologies

The consumption of silver has increased due to the rapid economic development. However, with the current limited silver ores from the earth's crust, it leads to the development of silver recovery techniques to recover silver from low-grade ores and waste. Numerous methods have been developed to recover silver from various sources such as processing waste and metal scrap. The most common and potential methods for silver recovery such as the flotation technique, pyrometallurgical process, biological process, electrometallurgical process and hydrometallurgical process will be discussed briefly in the following sections.

2.3.1 Flotation

Flotation is widely used in wastewater treatment to remove suspended matter and to concentrate biological sludge [18]. However, it is also being used in the silver recovery process. Beyzavi et al. [19] reported that their process for the silver recovery by flotation from the residue of wet extraction of zinc had successfully resulted in a silver yield of more than 89.5 %.

Flotation is referred to a unit operation which is applying bubbles to attach the particulate matter and the buoyant force of the combined particle and gas bubbles is great enough to cause the particle to rise to the surface [18]. The process depends on the selective affinity of the reagents used to form gas bubbles. In general, the reagents which increase the angle of contact between the liquid and the materials, are known as collectors. Collectors are materials which form surface films on the particles. Frothing agent is used to produce a froth, which must have sufficient stability to retain the particles in the surface so that they can be discharged.

Flotation process is very useful for the removal of the light particles. However, this process consumes high volume of feed material in order to be used economically. Furthermore its operation is more complex due to consumption of different types of chemical which must be well controlled.

2.3.2 Pyrometallurgical Process

Pyrometallurgical process for precious metals treatment and recovery is also being used commercially. Eastern Smelting & Refining Corp. [8] has practiced the method in processing of most types of scrap, waste and residues containing silver. Van Hecke et al. [20] reported that 91 % of silver recovery from catalytic and electrical scraps using air roast techniques at pyrometallurgy temperature of 1400 °C was obtained.

Pyrometallurgical process is a thermal decomposition of metal which involves incineration, smelting and refining [21]. Basically, the incineration of the raw materials such as slime, low-grade metals and scraps is carried out to remove the volatile fraction. It followed by smelting of the ash produced in the incineration step. From the smelting process, bullion that contains the metal is recovered and refined using the standard electrolytic process to recover the metals.

The primary disadvantage to the method is a large of capital is required for the processing equipment. For instance the complicated lead blast furnace operation required for reprocessing waste containing high Al_2O_3 results in high energy and time consumption [6]. The low precious-metal contents of the starting material represent a further problem to the application of this technique. It also can not handle waste in the liquid form.

2.3.3 Biological Process

Another promising emerging technology for silver removal is based on biological process. Certain types of microbial biomass can retain relatively high quantities of metal ions by ‘passive’ sorption and/or complexation. This is commonly known as biosorption [22]. Basically, biosorption may be classified into metabolic and non-metabolic dependence [23].

Metabolic dependence biosorption process or commonly known as bioaccumulation is an intracellular accumulation process which involves the transport of the metal across the cell membrane [23]. Bioaccumulation of silver has been documented in numerous studies. Pooley [24] reported that bioaccumulation of silver by a mixed culture of *T. ferroxidans* and *T. thiooxidans* occurs during the leaching of sulfide ore minerals. *Pseudomonas stutzeri* AG259 and *Streptomyces albus* have been used by Mattushka and coworkers to study the silver accumulation [25]. They reported that the accumulation of silver from a mixed metal solution was 142 μmol Ag g^{-1} dry weight of *P. stutzeri* AG259 and the selectivity, however was not satisfactory. Another study which conducted by Charley and Bull have shown a great capacity for silver bioaccumulation by the community of *P. maltophilia*, *S. aureus* and a *coryneform* organism [26].

Non-metabolic biosorption process involves the physicochemical interaction between the metal and functional groups of cell walls (mainly composed of carboxylate, hydroxyl, sulphate, phosphate and amino groups) [23]. Normally, the biosorption process has been conducted by immobilization of biomass in solid structures as columns or beads in a manner similar to ion exchange resins and activated carbons [27]. Brierley et al. [28] have developed a process called AMT-BIOCLAIM^{TM} for fixing biomass into fine granules to accumulate silver. Another important developments are BIO-FIX process [29] and AlgaSORB^{TM} process [23].

Biosorption is becoming important component in the silver recovery technologies. However, up to date, its application is limited. It is due to the fact that this biological process can not provide high selectivity and capacity, and it can only operate at a very low metals concentration.

2.3.4 Electrometallurgical Process

Electrometallurgical process is an electrolytic method to extract metal from metal bearing solution. This technique is based on the oxidation-reduction reaction which takes place at the surface of conductive electrodes (cathode and anode). Basically, the process comprises of three steps [30]. First is the creation of concentration gradient due to the applied current. Second is the electron transfer to the metal ion and forms the metal atom. Third is the surface diffusion of the adsorbed atom on the growing crystal lattice of the metallic deposit.

This electrolytic recovery of metal especially silver is of considerable interest and extensively studied. It is because this process gives several advantages which include the high purity of silver recovery, elimination of toxic heavy metals and sludge, and equipment maintenance is minimal [31]. Kirk and coworkers [32] have found that by using electrolytic process to leach silver from silver arsenopyrite, they obtained the silver extraction up to 57 % compared with 15 to 25 % with acids or acid and chlorine leaches. They observed that more silver was dissolved as the anode voltage was increased to about 1.74 V. Silver has also been widely electrolytically recovered from photographic waste [33,34]. Grau and Bisang [34] have suggested that the cathodic potential must more than –0.6 V to avoid the darkening of deposits due to the formation of Ag_2S. Therefore, the main factor that influences the physical characteristic of deposits is current density.

In practice, however, electrometallurgical process has faced several constraints. The electrolytic recovery is operative only down to solution concentration of 100-500 mgL^{-1} [35] and for diluted solution, cathodic polarization problem is arisen. In such system, as the metal is plated at the electrode, the layer of solution next to the electrode forms a polarized layer that offers high resistance to metal migration to the electrode [31]. Apart from that, the complexation of metal in solution can also cause a problem.

2.3.5 Hydrometallurgical Process

Hydrometallurgical process involves the dissolution of metal from solid matrix by an aqueous solution and subsequently precipitating or isolating the required metal [21]. From the literature, the hydrometallurgical processes which are potentially used in silver recovery include precipitation, liquid membrane, liquid ion exchange, solid-liquid and liquid-liquid extraction processes. These processes will be presented in the following sections except the solid-liquid and liquid-liquid extraction processes which will be reviewed in Section 2.4 and Section 2.5 respectively.

2.3.5.1 Precipitation

Precipitation is the most common method used for removal of inorganic heavy metals from industrial waste effluents. Precipitation of a heavy metal ion occurs when the metal salt reaches its solubility limit or defined as solubility products, K_{sp} [36]. In the case of silver metal, several types of precipitation processes such as hydroxide, chloride and sulfide precipitate are commonly used in metal separation.

Netzer and coworkers [37] have reported that the minimum silver hydroxide solubility is achieved at the level of 0.2 mgL^{-1} at pH 11.1. However, by the lime precipitation at pH 11.5, it was able reduced the residual soluble silver level from 500 to 21 μgL^{-1} and filtration provided further removal to 14.5 μgL^{-1} [38].

Silver chloride, AgCl has very low solubility (K_{sp} = 1.82 x 10^{-10} [39]) and can be used as effective technique to precipitate silver from solution. Such precipitation is commonly found in plating wastewater treatment [40]. The oxidation of silver cyanide for instance with chlorine, release chloride ions into solution, which in turn react with silver ions to from AgCl. However, in the excess of chloride ions, it will increase the solubility of silver through the formation of soluble silver chloro complexes [41]. In the AgCl precipitation process, ferric chloride is commonly added to the solution as a coagulant. Hannah et al. [38] have reported that 95 % of silver concentration in the solution can be precipitated by addition of $FeCl_3$ at pH 6.2 - 6.4.

Silver sulfide has extremely low solubility (K_{sp} = 6 x 10^{-50} [39]). Therefore, it can be used to separate silver from the waste. Use of sulfide for silver precipitation from photographic waste has reported by Fusco [42]. However, the addition of sulfide to the wastewater is considered disadvantage due to the formation of noxious hydrogen sulfide gas.

Silver can also be precipitated in the form of mixed sulfate-oxide. This can be achieved by addition of magnesium and lime to the silver solution [43]. The use of lime and ozone has also reported in order to increase the silver oxidation state from +1 to either +2 or +3 which are less soluble precipitate than does Ag^+[44].

Although precipitation has provided an effective technique for silver recovery, in practical, it has faced several problems. Industrial effluents contain complexing agents which might tie to the silver metal. This metal complex is sometime very stable and not be able precipitated by precipitation. Furthermore, when two or more metals are found in the same waste stream, the problem becomes even more complex [36].

2.3.5.2 Liquid Membrane Extraction

Liquid membranes separation processes are attracting attention in recent years due to their potential for low capital cost and energy efficiency. Liquid membranes can be of two kinds; the supported or immobilized liquid membranes and the liquid surfactant or emulsion liquid membranes. The supported liquid membranes configuration has the organic-phase liquid (containing the metal complexing agent) immobilized in the pores of a microporous membrane with the aqueous strip phase on the other side [45]. Emulsion liquid membranes are formed by dispersing a water-immiscible emulsion in water or an oil-immiscible emulsion in oil. The emulsion consists of an encapsulated phase (stripping phase) emulsified in the membrane phase with the use of surfactants. The emulsion is then dispersed in the continuous phase by agitation to yield globules of 0.1-2.0 mm diameter [46].

The large number of membranes with different formulation give a variety of applications, including metal recovery. Metzner and coworkers [47] have discovered that emulsion liquid membrane technique recovered the copper at low concentration selectively by using LIX extractant. Emulsion liquid membranes using thioDEHPA and dithioDEHPA have recovered zinc [48] and copper from waste stream [49]. However, up to now, there have been no report with regard to the application of liquid membrane for silver recovery.

Emulsion liquid membranes can offer greater areas for transport and thus have an advantage over the supported liquid membranes. Though the liquid surfactant membrane systems have several advantages over a conventional solvent extraction process such as extraction and stripping occur simultaneously that increase the capacity of process and result in lower operating costs, however this low capital costs can be somewhat offset by the need for separate emulsifier and coalescer units. Another problems generated from this system are encapsulated phase leakage caused by instability of emulsion and presence of osmotic pressure gradient [45,46].

2.3.5.3 Ion-exchange

Nowadays, much attention has been paid to the ion-exchange process since the ion-exchange resins are sufficiently inexpensive and effective technique to recover silver. Modern ion-exchange resins are synthetic polymers in which hydrocarbon groups (either strong acid or strong base) make up a three-dimensional network to enable the exchange process. Ion-exchange process can be defined as reversible exchange of ions between solid (resin) and a liquid (water containing ionized metal salts) [50].

Several ion-exchange technologies used to recover silver especially from photographic rinse water have been developed. Jansen and coworkers [51] have invented a silver recovery resin bed which comprised of strong base anion exchange resin. This resin exchanges the silver thiosulphate to release chloride ion while capturing the silver complex. Riveros and Cooper [52] examined two main categories of applicable ion-exchangers, weak base and strong base anionic. They found that only the strong base resins loaded significant amounts of silver but they are more difficult to elute. Apart from that, Hubicki and Hubicka [53] has tested six different selective ion-exchangers which included the functional group of thiol, thiourea, isothiourea and polyphenol. The ion-exchanger with -SH functional group on a skeleton of styrene copolymer with divinylbenzene (Duolite ES-465) showed the highest recovery factor of silver (I), the shortest period of ion-exchange equilibrium time and the most effective of selectivity ion-exchanger for silver removal.

Though the ion exchange technology is well established, there are still some drawbacks that limit its application. The ion-exchange resin cannot be heavily loaded and the consequent resin regenerate will not be sufficiently concentrated in metal to warrant recovery. Recovery is further hampered by the relatively non-selective nature of most commercially available resins, resulting in the accumulation in the regenerant of secondary and undesired contaminating ions.

2.4 Solid-liquid Extraction (Leaching) Process

Solid-liquid extraction is also called as leaching process. It is a process that involves dissolving the required metal from a solid substance into a solution. This process involves three different steps. First, the change of phase of the solute as it dissolves in the solvent. Second, its diffusion through the solvent in the pores of the solid to the outside of the particles and third, the transfer of the solute from the solution in contact with the particles to the main bulk of the solution [54].

In the leaching process, there are several aspects that need to be considered. However, in this study, four aspects will be highlighted. They are types of leaching agent, leaching agent concentration, liquid/solid ratio and kinetics aspects.

2.4.1 Types of Leaching Agent

Several potential leaching agents for silver removal have been reported in literature. These include cyanide, thiourea, chloride and acids. The selection of leaching agents is important to ensure a good silver leaching with high capacity and selectivity.

2.4.1.1 Cyanide

Cyanide reagent has been widely used in well-established treatment such as cyanidation process of primary ores and concentrated [55]. In the mining industry, the conventional cyanidation has been used to treat the silver ores with alkaline cyanide solutions in order to dissolve the silver in the form of $Ag(CN)_2^-$. Then the soluble ions are extracted from the solution by adsorption on activated carbon or known as carbon-in-pulp (CIP) [56]. The extent of silver leaching from the ores depends on the silver mineralization in the ore and some modifications have been used to improve the silver dissolution. Nunez and coworkers [57] has reported that the sulphidization of sodium sulphide prior to cyanide leaching on argentojarosite, $AgFe_3(SO_4)_2(OH)_6$ made it possible to improve the silver recovery from 40 % to 55 - 67 %. For the silver ores that disseminated in sulphidic minerals, it is necessary to oxidize this type of ores in order to break down the sulphidic part before cyanidation [58]. In the kinetic study by Maudos et al. [59], they found that the chloridation of silver from jeweler workshop sweeps prior to cyanide leaching has able to speed out the silver dissolution. Nevertheless, it has reported that the use of cyanide in alkaline media is recommended only when the silver is in carbonate or oxide form [60].

From the above review, even though cyanide leaching is widely used on a commercial scale, this process has several known disadvantages. The stability of $Ag(CN)_2^-$ is quite low [55], therefore, the cyanidation reaction requiring high cyanide concentration which is unfavorable process due to its high toxicity. Apart from that, the reaction involves a low leaching rate (24 – 72 hours contact time) and the process must be carefully monitored and controlled, and the spent cyanide leaching solutions must be treated before being discharged to the environment [58].

2.4.1.2 Thiourea

The utilization of thiourea ($CS(NH_2)_2$) as leaching agent has been reported for the treatment of refractory type precious metal ores [58,61], polymetallic complex ores [60] and jeweler workshop sweeps and exhausted batteries [59]. Thiourea is stable up to pH 2. It forms single cationic complexes with silver as $Ag[CS(NH_2)_2]_3^+$ [62]. Numerous reagents have been used as oxidizing agents such as hydrogen peroxide and Fe(III) in thiourea leaching which operated at pH 1 – 3. Iron (III) has shown to give the fastest silver leaching rate [58,59,61]. However, due to the fact that iron (III) forms complexs with thiourea which might increase the thiourea consumption [63], the thiourea concentration and the redox potential must be controlled. Electrochemical study has shown that the most active dissolution of silver is obtained in acidic solution (pH ~ 1) at redox potential 100 – 150 mV [62]. At redox potential above 200 mV, oxidation of the thiourea to formamidine disulphide (FDS) and then decomposition of the FDS to cyanamide and elemental sulfur will occur [64]. These formations might decrease the dissolution rate of silver due to degradation of thiourea and adsorption of silver thiourea complexes to sulfur product [62]. For the practical purposes, hydrogen peroxide is considered to be a better oxidant [64].

Another attempts to improve the thiourea leaching rate that has been reported was chloridation prior thiourea leaching either calcined the ores in the presence of NaCl or addition of sea water [59,60]. In the presence of Cl^- ions, the silver dissolution occurs according to the following equation:

$$Ag + Cl^- + 3\ CS(NH_2)_2 + Fe^{3+} \rightarrow Ag[CS(NH_2)_2]_3^+ + Fe^{2+} + Cl^-$$

The free energy, ΔG^o of the reaction becomes lower and indicates that the reaction is favorable [59].

Leaching in thiourea solutions, has potential advantages over conventional cyanidation. These include the acidic medium of thiourea leaching, cationic complexes formed by thiourea, faster reaction rates and no detrimental environment impact. However, the thiourea leaching is facing the difficulty in controlling the oxidation condition during the leaching process.

2.4.1.3 Chloride

Lately, ferric chloride ($FeCl_3$) leaching process is being widely used for the treatment of base-metal sulphide concentrates and other metallurgical products to recover by product such as silver [65]. Such process offers an advantage such as the formation of elemental sulfur rather than hazardous gas of sulfur dioxide. However, the dissolution of silver is often limited due to the diverse forms of silver mineralization such as native silver (Ag), argentian tetrahedrite, acanthite (Ag_2S) and chloragyrite (AgCl) [66]. Numerous works have been carried out on studying the dissolution of these silver forms using chloride-leaching agents. These include the studies of the Ag-$FeCl_3$ / $CuCl_2$-HCl system [67], Ag_2S-$FeCl_3$-HCl system [68] and AgCl-$FeCl_3$-HCl system [41,66]. The essence of these chloride leaching is the progressive formation of soluble silver chloro complexes of $AgCl_n^{-(n-1)}$ as given by the following reaction [66]:

$$Ag + nCl^- \Leftrightarrow AgCl_n^{-(n-1)} + e \qquad n = 1, 2, 3, 4$$

However, this reaction involves the low equilibrium constant which indicates that the concentrated chloride solution is required to achieve any significant silver dissolution. This result is in agreement with several published works [7,66,68]. In the simple AgCl-HCl-H_2O system, at the HCl concentration below 0.5 M, the $AgCl_2^-$ complex is expected to form, whereas at HCl concentration between 0.5 to 1.5 M, $AgCl_3^{2-}$ complex is dominant. The $AgCl_4^{3-}$ complex is formed only in higher concentrated chloride media [66].

Although $FeCl_3$ has been widely used as oxidant in silver dissolution, Dutrizac [66] found that this oxidant is not required in the reaction of chloro complexation of silver. Instead, it can be replaced by several other chloride salts such as $CaCl_3$, NaCl, KCl [66] and $CuCl_2$ [67]. However, sodium chloride, NaCl is the least costly of the common salts, easily found and frequently added to chloride leaching media to elevate the boiling point of the solution and the most important, is to increase the solubility of AgCl [41].

2.4.1.4 Acids

The oxidative property of acid makes it possible to digest wide range of metal compounds. Sulfuric acid has been used to leach nickel and magnesium from serpentine ore [69], manganese from manganese carbonate ore [70] and zinc oxide [71]. Lo and Chen [72] have found that the use of H_2SO_4 has successfully removed cadmium, chromium, nickel and zinc from industrial sludge. Nitric acid, hydrochloric acid and aqua regia have been widely used in leaching of precious metals such as gold, silver, platinum and ruthenium from electronic scrap [6,73].

Apart from that, acid has attracted much attention in the waste pretreatment [74]. It is because acid reduces the interference of organic matter and converts metals that associate with particulate to free metals. Therefore, acid digestion has been recommended as a standard method for the wastewater analysis [75]. Furthermore, sorption loss of silver on the surface of glassware is reduced in the presence of acidic medium [76]. It is important in order to get good analytical accuracy.

In the dissolution studies of Ag and AgCl by HCl [66,67] or H_2SO_4 [77], it has found that the chloride medium produced more stable soluble silver than in sulphate medium. However, in term of kinetic, silver dissolves faster in sulphate medium than chloride medium [77]. In the ferric chloride leaching system, HCl is required to prevent the hydrolysis and precipitation of iron which might reduce the efficiency of silver dissolution [66]. But still, the acid concentration used can not be too high that might cause the decreasing of it dissociation degree [60].

2.4.2 Leaching Agent Concentration

An efficient leaching process is very depends on how well the leaching agent itself can perform [54]. One of the critical aspects that affect its performance is leaching agent concentration. Generally, a leaching process is initiated by chemical reaction where the leaching agent reacts with metal to form soluble metal compounds. Therefore, the more leaching agent concentration is introduced into the leaching process, the more rapid and effective of the process can perform and the more yield of extracted metal can be obtained [59,60]. In the previous works on silver leaching [41,66-68], it was found practically on using chloride to extract silver especially in the form of AgCl and Ag from the solid waste. A study of silver recovery from copper smelter flue dust [7] deduced that the minimum NaCl concentration required was 125 g/L in order to obtain a significant silver removal. Similar works that have been carried out by other researchers [66,68] also showed the same results. These come to the conclusion that a significant silver dissolution required a minimum of 2 M of NaCl leaching system. However, the variable of HCl concentration showed minor effect on silver recover [7].

2.4.3 Liquid/Solid Ratio

Liquid/solid ratio is a term used to indicate the mixture ratio of the solid in liquid which has been widely used in hydrometallurgy field especially in the leaching process. This ratio affects the degree of solution viscosity and the total surface area of the particle contact to the leaching agent [54]. Liquid/solid ratio must be well tuned in order to provide a sufficient low viscosity for the leaching solution to circulate freely. Nunez and coworkers [7] have found that the silver recovery of 15 mg Ag/kg waste was achieved at the liquid/solid ratio of 20 (10 g of solid waste in 200 ml of leaching agent). The decrease of the ratio did not result in an increase of the amount of silver dissolved. It deduced that when the leaching system has reached a maximum particle surface contact with leaching solution, the increase of leaching agent volume will not affect the leaching process.

2.4.4 Kinetic Modeling of Leaching Process

Kinetic modeling of leaching process is very important in order to get better understanding on the mechanism involved as well as to get engineering parameters for scale up of the process. In the leaching process especially for metal leaching from mineral ores or processing waste, the process generally occurs through heterogeneous reactions involving two different phases. A liquid is brought into contact with a solid, react with it, and transform it into product. The overall reaction rates may be influenced by the individual steps that illustrated in Figure 2.3.

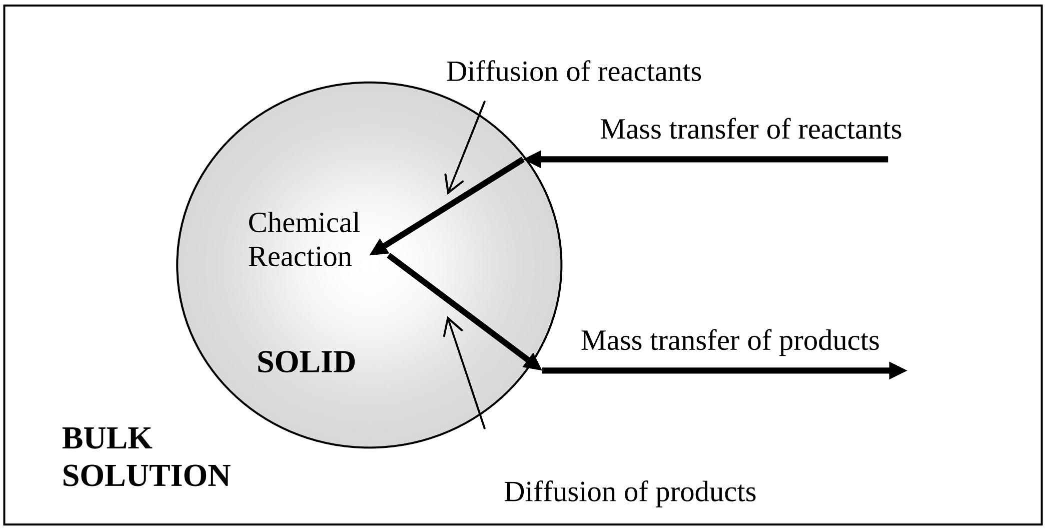


Figure 2.3: A schematic diagram of the overall reaction involved in leaching process [78].

Kinetic of the leaching process involving noncatalytic reaction of particles with surrounding liquid, can basically be described by either progressive-conversion model or shrinking-unreacted-core model [79]. The former model assumes that the reactant enters throughout the particle at all times. As a result, the solid reactant is converted progressively. However, the latter model assumes that the reaction occurs first at the outer skin of the particle and the zone of reaction then moves deeper into the solid. Thus, at any time there exists an unreacted core of material that shrinking during reaction.

In leaching process, evidence from wide variety of conditions as reported in the literature indicates that the shrinking unreacted-core model is capable to describe the process more closely to what observed experimentally. Therefore, it has been chosen in this study. Basically, the shrinking core model of leaching process can be classified further into chemical reaction and diffusion through liquid films control models.

2.4.4.1 Chemical Reaction Control

A leaching system to be said in controlled by chemical reaction when the leaching rate is not influenced by the stirring speed. It is because at this condition, no matter how diffusion thickness it is (vary the stirring speed), the rate-controlling step still governed by the slow chemical reaction that occurs at the interface. From the literature, it was found that two types of models had been used to describe the kinetic of leaching process controlled by chemical reaction.

Wadsworth [78] proposed the kinetic model based on the facts that the reaction rate, dn/dt rely on the total surface, $4\pi r^2$ and the number of reactive sites per unit area available for reaction, k_o. n, the number of moles is equal to $4\pi r^3/(3V_m)$ where V_m is the molar volume of solute. Of course, the concentration of reactant, C and the rate constant of first-order reaction, k' also affect the reaction rate. The general rate expression for a sphere with radius r is given by

$$dn/dt = -4\pi r^2 C k_o k' \quad \text{.......} \quad 2.1$$

which rearranged into

$$dr/dt = -V_m C k_o k' \quad \text{.......} \quad 2.2$$

If r_0 is the initial radius of the sphere, the fractional conversion α can be written as

$$\alpha = 1-(r/r_o)^3 \quad \text{.......} \quad 2.3$$

The differentiation of Equation 2.3 with respect to time and combined with Equation 2.2 gives

$$d\alpha/dt = (3V_m C k_o k'/r_o)(1-\alpha)^{-2/3} \quad \text{.......} \quad 2.4$$

For the condition $\alpha = 0$, when $t = 0$, Equation 2.4 may be integrated for constant concentration giving

$$\mathbf{1 - (1-\alpha)^{1/3} = (V_mCk_ok'/r_o)t} \quad \ldots\ldots 2.5$$

This final equation represents the kinetic model proposed by Wadsworth which can predict the leaching process controlled by chemical reaction.

Levenspiel [79] has proposed the other kinetic model that describes the leaching rate by chemical reaction. In his approach, the author assumed that the decrease in volume or radius of unreacted core was accompanying by the disappearance of *d*n moles of solid reactant which lead to the rate expression as

$$dn/dt = -4\pi r^2bk_sC \quad \ldots\ldots 2.6$$

where b is a stoichiometric factor and k_s is a first order reaction rate constant. However, the author defined n as $4\pi r^3\rho_B$ where ρ_B is a molar density of solid reactant. By rearrangement of Equation 2.6 with respect to ρ_B, it gives

$$dr/dt = -bk_sC/\rho_B \quad \ldots\ldots 2.7$$

and the correlation between α and t then expressed as

$$\mathbf{1-(1-\alpha)^{1/3} = (bk_sC/\rho_Br_o)t} \quad \ldots\ldots 2.8$$

Actually, the approach in developing these two kinetic models is similar. The only different is, in the former model, it considers the concentration of potentially reactive surface sites, while in the latter model, stoichiometric factor was considered.

2.4.4.2 Diffusion through Liquid Film Controls

In most hydrometallurgical systems involving dissolution or precipitation of a solid and diffusion through a zone adjacent to solid-liquid interface might often be rate controlling step [78]. Diffusion is a process which tends to equalize concentration within a single phase. Under this condition, when the stirring speed is changed, the leaching rate also being changed. It is due to the change of diffusion thickness which affects the rate of species diffused. As reported from literature, three common kinetic models have been used to describe the leaching process controlled by diffusion.

In the kinetic expression by Wadsworth [78], he included the stoichiometric factor, b and the limiting boundary layer thickness, δ. It is because, the rate of disappearance of reactants or the rate of appearance of products depends upon the overall stoichiometry of the reaction. Therefore, the author has replaced the Equation 2.1 to express the reaction rate as

$$dn/dt = -4\pi r^2 DC/b\delta \quad \ldots\ldots 2.9$$

where D is a diffusion coefficient which independent of concentration. Since

$$D/b\delta = k_o k' \quad \ldots\ldots 2.10$$

Equation 2.9 then can b expressed as

$$\mathbf{1-(1-\alpha)^{1/3} = (CV_mD/\delta br_o)t} \quad \ldots\ldots 2.11$$

Levenspiel [79] in his model, expressed that if the mass transfer step is rate-controlling, then

$$dn/dt = -4\pi r^2 bKC \quad \ldots\ldots 2.12$$

where K, mass transfer coefficient which is equal to D/r (in Stokes regime). By replacing K and integrating of Equation 2.12, it gives

$$t = (\rho_B r_o^2/2bCD)[1-(r/r_o)^2] \quad \ldots\ldots 2.13$$

The time for complete disappearance of a particle is thus

$$\tau = (\rho_B r_o^2/2bCD) \quad \ldots\ldots 2.14$$

and on combining we obtain

$$\mathbf{1-(1-\alpha)^{2/3} = (2bCD/\rho_B r_o^2)t} \quad \ldots\ldots 2.15$$

For the third model proposed by Geankoplis [80], the rate of mass transfer is expressed as

$dn/dt = -AK(C_s - C_t)$ ………………………………………….…………….... 2.16

where dn defined as Vdc (V is solution volume), A is a total surface area of particles and, C_s and C_t are the concentration of solute at $t = \infty$ and $t = t$ respectively. Equation 2.16 then rearranged and integrated from t = 0 and t = t, and C_o and C_t respectively, it gives

$(C_s - C_t)/(C_s - C_o) = \exp -(KA/V)t$ ……………………………….………. 2.17

If pure solvent is used initially, C_o = O, then we obtain

$\mathbf{\ln (1- \alpha) = -(KA/V)t}$ …………………………………………………..…. 2.18

Basically, three kinetic models described above have similar concept on establishing their models. The rate of reactant disappearance is depend on surface area, reactant concentration and mass transfer coefficient or diffusion coefficient. However, in attempt to express these parameters, they represent those parameters in different way. Instead of K, Wadsworth [78] has replaced it by considered the effect of diffusion thickness and stochiometric factor. In the kinetic model developed by Levenspiel [79], the term of molar density is used in the rate expression. While Geankoplish [80] has considered the volume of liquid reactant that diffuse to the surface of reaction.

Overall, however, the different rate expression of these models might cause the deviation from actual experimental data. If a model corresponds closely to what really takes place, then its rate expression will closely predict and describe the actual kinetics. Table 2.2 is summarizes the leaching kinetic models either describing the rate controlled by chemical reaction or diffusion.

Table 2.2: Summary of chemical and diffusion control kinetic leaching models.

Chemical Reaction Control Model	Diffusion Through Liquid Film Control Model
$1 - (1-\alpha)^{1/3} = (VCk_ok'/r_o)t$ $1-(1-\alpha)^{1/3} = (bk_sC/\rho_B r_o)t$	$1-(1-\alpha)^{1/3} = (CVD/\delta\sigma r_o)t$ $1-(1-\alpha)^{2/3} = (2bCD/\rho_B r_o^2)t$ $\ln (1- \alpha) = -(KA/V)t$

2.5 Liquid-liquid Extraction Process

The use of liquid-liquid extraction as a unit operation in hydrometallurgy now extends to a wide range of metals from a variety of feed materials including low-grade ores, scrap and waste and diluted aqueous solutions. A considerable amount of work has been carried out on liquid-liquid extraction of silver. Schweitzer et al. [81,82] have carried out an extensive study on silver extraction using dithizone. Recently, much consideration also paid to study the silver removal by liquid-liquid extraction using sulfur-containing extractant [83,84,85]. Liquid-liquid extraction is widely used nowadays due to its operation can perform easily, environmental friendly, less energy intensive energy and provides high purity of product.

Liquid-liquid extraction or referred to as solvent extraction involves separating the solutes from the liquid, normally aqueous solution by adding the immiscible or partially miscible liquid refer to as solvent or diluents. It is an equilibrium process which can be simply described by following reaction,

$$M + E \Leftrightarrow ME$$

In the first step (extraction step), the metal, M is transferred from an aqueous phase to an organic phase by the extractant, E as complex ME. The second step is the reverse of the first step, that is the metal is transferred from the organic phase to an aqueous phase (stripping stage). So, basically the solvent extraction of metals is a simple operation requiring only a shift in the equilibrium between the extraction and stripping processes.

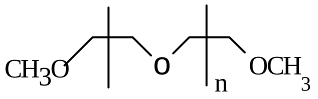
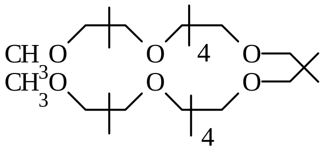
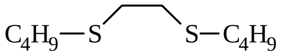
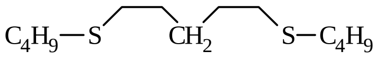
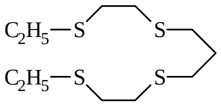
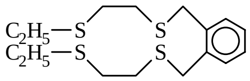
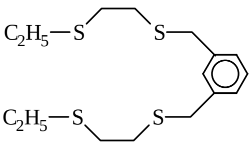
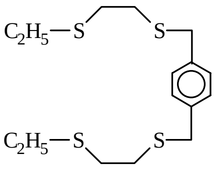
However, normally a metal ion exists in aqueous solution with little or no tendency to transfer to an organic phase. Thus in order to achieve the required transfer, the metal ion has to be modified by converting a hydrophilic species into an extractable hydrophobic species and this can be done by using solvation, anion-exchange or cation-exchange extractants. The selection of extractant is very crucial in order to get a good selectivity and high loaded metal capacity.

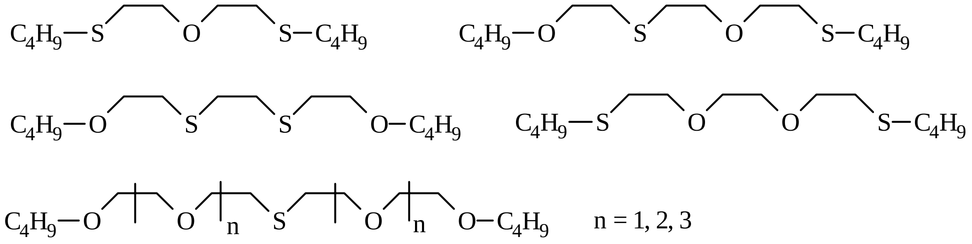
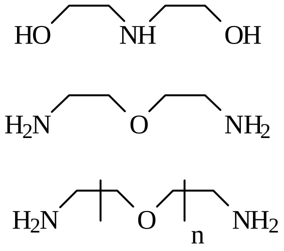
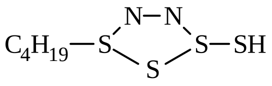
2.5.1 Silver Extractant

According to the principle of hard and soft acid base (HSAB) developed by Pearson [86], silver ion is a soft acid and therefore should show a great affinity towards soft base atom. Many researchers have prepared and studied a various extractants that possess these characteristics.

Sulfur-containing extractant is among the most familiar one since it has a Pauling electronegativity of 2.58 compared to 3.41 for oxygen, making it is a highly polarizable soft donor atom. These types of extractant have studied by Sole and coworkers [84,87]. They observed that replacing the oxygen of R_2PO_2H (Cyanex 272 : R represents 2,4,4-trimethylpentyl) by sulfur atom forming R_2PSOH (Cyanex 302) and R_2PS_2H (Cyanex 301) have shifted the silver extraction to lower pH and it was found that Ag-Cyanex 301 complex exhibited a great stability among the others. Apart from these extractants, Cyanex 471X (triisobutylphosphine sulphide) will also give a promising result towards silver extraction selectivity [83]. The high selectivity of Cyanex 471X for Ag (I) is because of its strong complex with silver. Paiva [88] reviewed some of silver extractants and concluded that extractant containing sulfur and nitrogen atoms including thiourea and its derivatives could be potentially good extractability for silver. Dithizone is among the most famous silver extractant that commonly used as analytical reagent for photometric determination of trace amount of silver. Meanwhile, Shetkar and Shinde [89] discovered that by using triphenylphosphine sulphide, 99.66 % of silver extraction could be achieved. As analogous sulfur ligands, Dietze and coworkers [90] studied the complex formation and extraction properties of some oxathia-alkanes with silver. By comparison the stability constants of the thia-alkanes, it was found that the introduction of oxygen atoms will increase the stability of the compounds especially when the oxygen atoms are placed at the center of the molecule. Paiva [88] reviewed some other open-chain silver extractants as given in Table 2.3.

Table 2.3: Open chain extractants for silver extraction [88].

TYPES OF SILVER EXTRACTANT
Oxygen atom
 n = 3, 4, 5 Oxa-alkanes
 Oxa-alkanes
Monensin
Sulfur atom
Hexyl sulfide
1,2-Bis-(hexylthio)ethane
$RS(CH_2)_nSR$ Cis-R'-SCH=CHS-R' $O-C_6H_4-(SCH_3)_2$
$C_4H_9-S-C_4H_9$ Dibutyl sulfide  1,2-(butylthio)-etane 
    Acyclic tetrathioethers
Phosphorus atom
Tributylphosphate
Synergistic mixture of bis-(2-ethylhexyl)-phosphoric acid and 4-sec-butyl-2-(2-methylbenzyl)-phenol
Bis-(2-ethylhexyl)-phosphoric acid

di-n-butyl-phosphorothioic O,O'-di-n-butyl-phosphorodithioic
bis-(2-ethylhexyl)-dithiophosphoric acid
Nitrogen atom
Triaurylamine
N1923 (primary amine)
Oxygen and Sulfur atoms
$S[(CH_2)_nCO_2H]_2$ n = 1, 2 $HO_2C\text{-}CH_2\text{-}S\text{-}(CH_2)_n\text{-}S\text{-}CH_2\text{-}CO_2H$ n = 1, 2
Octylthiomethylacetophenone
 Oxathia-alkanes
Oxygen and Nitrogen atoms
 n = 2, 3
Sulfur and Nitrogen atoms
Diantipyrylthiourea Diphenylthiourea
bis-(O-tolyl)-thiourea
N,N'-diphenylthiourea
2-alkylthiopyridine
2-octylthiopyridine
t-dodecylthiopyridine

R-CS-NHR' (R, R'= alkyl, aryl)

2.5.2 Extraction of Silver by Using Dithizone

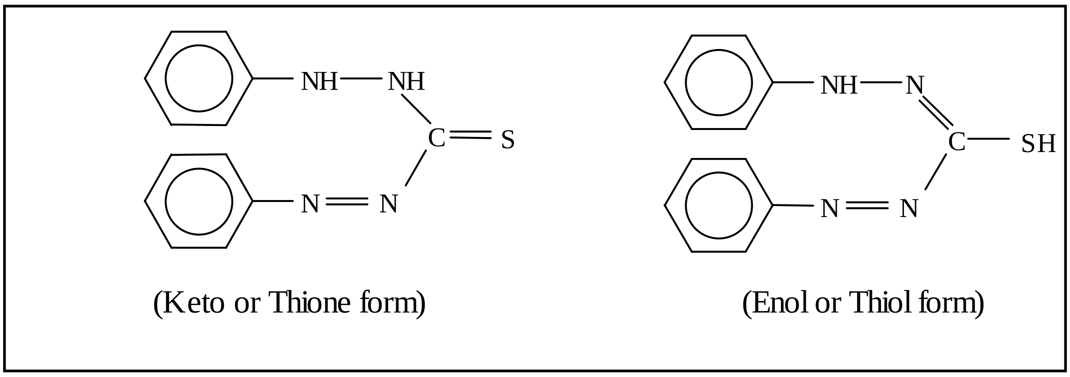
2.5.2.1 Introduction

A comprehensive review of dithizone properties by Irving [91] and Pearson [86] showed that the dithizone is the most suitable extractant for silver. A systematically study of silver dithizonates which carried out by Schweitzer and Dyer [81] gave a clear understanding of silver behaviour during the extraction process. Besides that, dithizone is widely used in the field of quantitative chemical analysis using photometric method [92,93,94]. Grote and Kettrup [95] also discovered that dithizone exhibits excellent chelating abilities for silver metal.

2.5.2.2 Physical and Chemical Properties of Dithizone

Pure dithizone (diphenylthiocarbazone/ H_2Dz: $C_{13}H_{12}N_4S$) is a violet-black crystalline powder having molecular weight of 256.3 $gmol^{-1}$ and the density of 1.35 gml^{-1}. Though H_2Dz possesses a high melting point of 169 °C but the solution is unstable towards heat, strong light and oxidants. From the solubility data reported by the researchers, Irving [91] concluded that H_2Dz shows a low solubility in paraffinic and alicyclic hydrocarbons but the highest solubility was reported in aromatic hydrocarbons. Dithizone has very high solubility in chlorinated paraffins (Appendix A). The solubility of dithizone in water is very low ($\approx 5x10^{-5}\ gL^{-1}$) and thus making it suitable for extraction process.

Dithizone exits in two tautomeric forms, the keto (monoprotic) and the enol (diprotic) as given in Figure 2.4. Dithizone has two H atoms which can be replaced by heavy metals to form either primary and secondary dithizonates. However, only few metals can form secondary dithizonates because these metal complexes are labile and less soluble in organic solvent. Most of the reactions to form metal complex require a very weakly acidic or slightly basic conditions for getting satisfactory extraction (Figure 2.5).



(Keto or Thione form)   (Enol or Thiol form)

Figure 2.4: Tautomeric forms of dithizone [91].

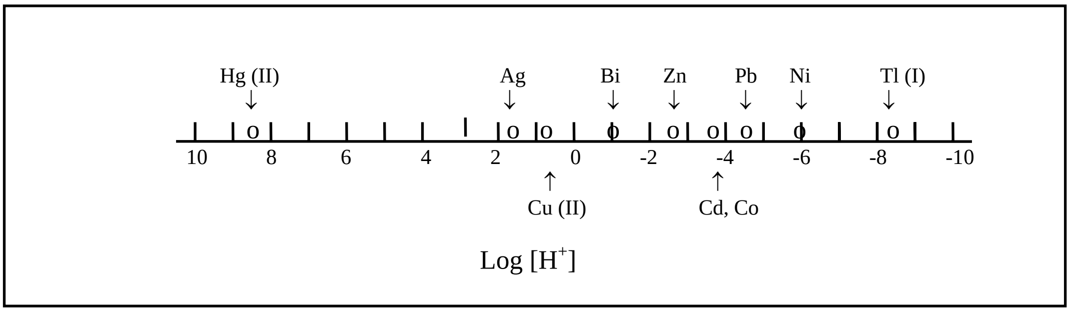


Figure 2.5: pH of metal extraction by dithizone [92].

Silver reacts with dithizone in acidic solution to form the primary dithizonate, Ag(HDz) which dissolves in CCl_4 or $CHCl_3$ to give a yellow solution. However, in neutral or basic medium, the red-violet secondary dithizonate (Ag_2Dz) is formed and virtually insoluble in CCl_4 and slightly soluble in $CHCl_3$ [94]. This red-violet solution is readily converted into yellow by adding excess of H_2Dz and acidifying the aqueous phase. It has been reported that to prevent the co-extraction of other elements, complexing agents such as EDTA may be added to the aqueous solution of silver to complex Cu, Bi, Cd, Zn, Pb but not Hg [92].

2.5.2.3 Effect of pH on Silver Extraction by Dithizone

The various equilibrium reactions that govern the extraction of primary silver dithizonate are shown in Figure 2.6:

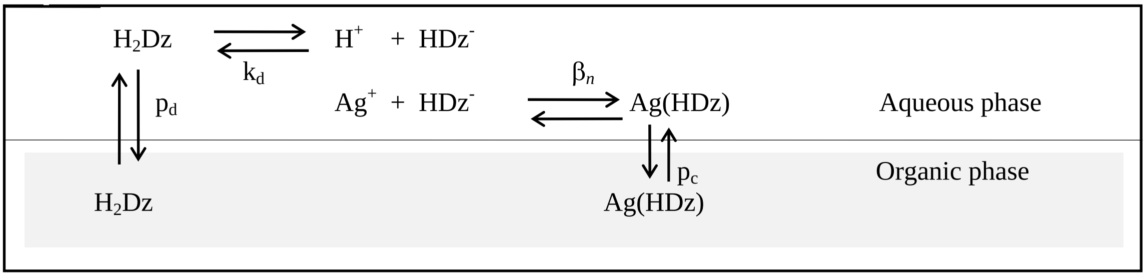


Figure 2.6: Various equilibrium reactions involved in the silver extraction by dithizone [91].

where $k_d = [H^+][HDz^-] / [H_2Dz]$ and $p_d = [H_2Dz]_o / [H_2Dz]$ are the (first) acid dissociation constant and partition constant for dithizone respectively, $\beta_n = [Ag^+][HDz^-] / [Ag(HDz)]$ is the overall stability constant of the metal dithizonate, and $p_c = [Ag(HDz)]_o / [Ag(HDz)]$ is the partition coefficient.

The fundamental equation for silver extraction using dithizone is given by,

$$Ag^+ + H_2Dz\ (org) \overset{K_{ex}}{\Leftrightarrow} Ag(HDz)\ (org) + H^+$$

$$K_{ex} = \frac{[Ag(HDz)]_o[H^+]}{[Ag^+][H_2Dz]_o} = \frac{p_c k_d}{\beta_n p_d} \quad \text{…..……………………………………} \quad 2.19$$

According to Equation 2.19, the extraction equilibrium constant, K_{ex} increases with decreasing ionization of the chelate in the aqueous phase and its increasing partitioning into the organic phase, and with increasing ionization of the chelating agent and its increasing partitioning into the aqueous phase [92].

Distribution coefficient, D_c is given by:

$D_c = [Ag(HDz)]_o/[Ag^+] = K_{ex}[H_2Dz]_o/[H^+]$ ……………………………...…… 2.20

and

$\log D_c = \log K_{ex} + pH + \log [H_2Dz]_o$ …………………………………… 2.21

Equation 2.21 indicates that a ten-fold change in $[H_2Dz]_o$ can compensated by the unit change in pH and so it is obviously that control of pH will be a dominant factor.

pH at 50 % of extraction donates as $pH_{1/2}$. Therefore, at $pH_{1/2}$ one should have $D_c = 1$ and Equation 2.21 becomes,

$0 = \log 1 = \log K_{ex} + pH_{1/2} + \log [H_2Dz]_o$

whence

$\Delta pH = pH_{1/2} - pH = - \log D_c = \log (100-E)/E$ ……………………………..…….2.22

where E is the percentage of extraction. It follows that:

$E = 50 (1-\tanh 1.1513\ \Delta pH)$ …………………………………………..….. 2.23

showing that plots of E against pH should be sigmoid and centrosymmetric about the mid-point as shown in Figure 2.7 [91].

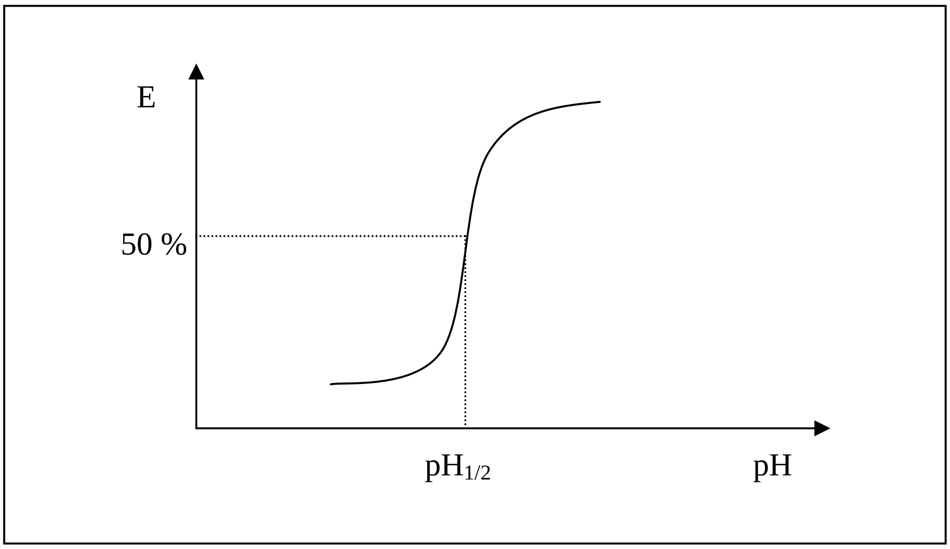


Figure 2.7: A sigmoid curve of the metal extraction.

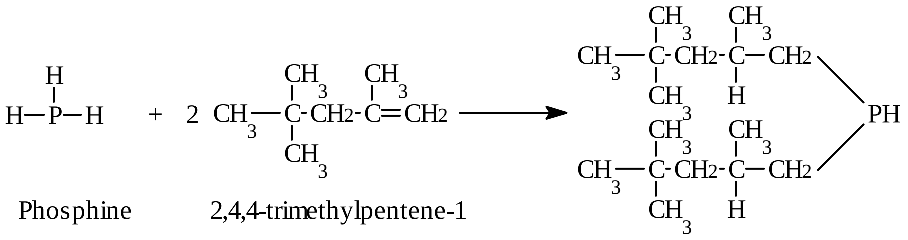
Extraction process is significantly affected by the pH of the solution as described above. However, other factors such as temperature, extractant concentration, organic/aqueous ratio and hydrodynamic parameters also contribute to the extent and rate of extraction. The detail discussion on the effect of these parameters, however, will not be included in this review.

2.5.3 Silver Extraction by Cyanex 272

2.5.3.1 Introduction

Organophosphorus acid compounds have been widely used as an extractant in recent years in solvent extraction of many metal ions on a commercial scale. Among these, bis (2,4,4-trimethylpentyl) phosphinic acid has been widely studied, particularly with respect to cobalt-nickel separation [96,97] and silver extraction [84].

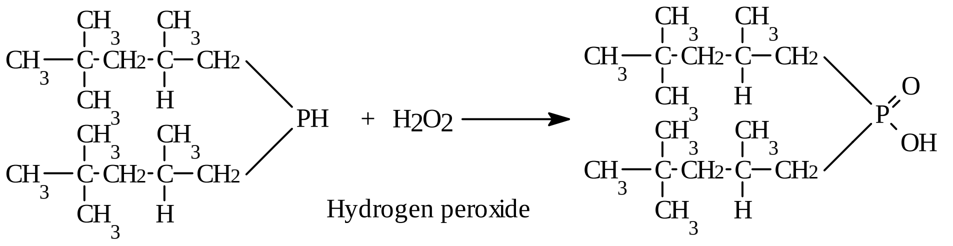
Bis (2,4,4-trimethylpentyl) phosphinic acid or commonly known as Cyanex 272 is manufactured from phosphine in a two stages process [98]. Initially, phosphine is reacted with 2,4,4-trimethylpentene-1 to form bis (2,4,4-trimethylpentyl) phosphine.



Phosphine 2,4,4-trimethylpentene-1

Bis (2,4,4-trimethylpentyl) phosphine

This intermediate product is then oxidized with hydrogen peroxide to produce phosphinic acid.



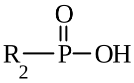
Hydrogen peroxide

Bis (2,4,4-trimethylpentyl) phosphine Bis (2,4,4-trimethylpentyl) phosphinic acid

2.5.3.2 Physical and Chemical Properties of Cyanex 272

Cyanex 272 is a clear, light-amber, viscous liquid which is totally miscible in common aliphatic and aromatic diluents. The basic physical and chemical properties of Cyanex 272 are given in Table 2.4.

Table 2.4: Cyanex 272 structural and properties at 24 °C [99].

* Structural Formula	pK_a in H_2O	Density (kgm^{-3})	Viscosity ($kgm^{-1}s^{-1}$)	Molar Mass ($gmol^{-1}$)	Aqueous Solubility (mgL^{-1})
 $R_2-\overset{O}{\overset{\Vert}{P}}-OH$	6.37	910	14.2	290	38

* R represents the 2,4,4-trimethylpentyl group

Cyanex 272 can exist either in the forms of monomer or dimer which indicated by two major peaks of the ^{13}P-NMR spectra at 59.6 ppm and 59.9 ppm [87]. However, Sole and Hiskey [99] reported that Cyanex 272 exists primarily as self-associated species (dimer) due to the formation of hydrogen bonding by proton acceptor of oxygen in Cyanex 272.

2.5.3.3 Effect of pH on Silver Extraction by Cyanex 272

The silver extraction by Cyanex 272 may be written as:

$$Ag^+ + \overline{m(R_2POOH)_p} \Leftrightarrow \overline{Ag((R_2POO)_pH)_n(R_2POOH)_{p(m-n)}} + nH^+$$

where m is the stoichiometric ratio, p is the degree of association of the extractant, n is the valence state of metal and overlining represents organic-phase species [84]. The equilibrium constant for the reaction is then given by:

$$K_{ex} = \frac{[\overline{Ag((R_2POO)_pH)_n(R_2POOH)_{p(m-n)}}][H^+]^n}{[Ag]^+[\overline{(R_2POOH)_p}]^m} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots 2.24$$

It is then readily shown that

$$\log K_{ex} = \log D_c - npH - m\log[(R_2POOH)_p] \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 2.25$$

At $pH_{1/2}$, $D_c = 1$ and with $n = 1$, Equation 2.25 becomes

$$pH_{1/2} = -m \log [(R_2POOH)_p] - \log K_{ex} \quad \ldots\ldots 2.26$$

Therefore, a plot of $pH_{1/2}$ against $\log [(R_2POOH)_p]$ as shown in Figure 2.8 should give a straight line with slope $-m$ and a y-intercept of $-\log K_{ex}$.

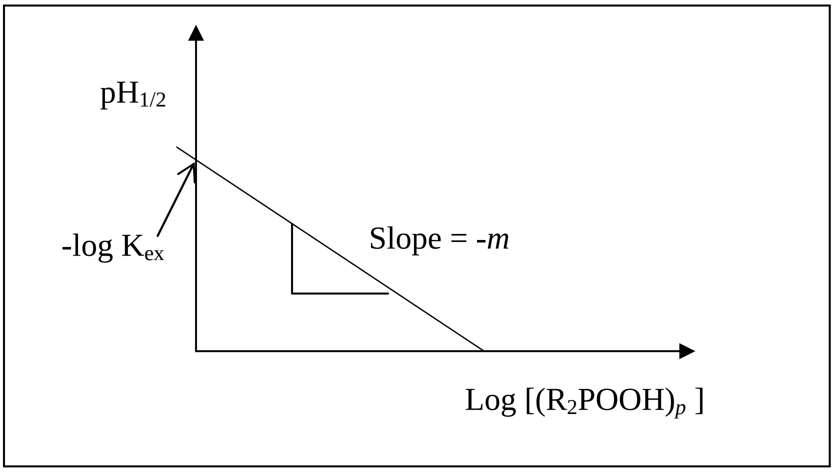


Figure 2.8: A straight line of $pH_{1/2}$ versus logarithm extractant concentration.

The Equations 2.24, 2.25 and 2.26 indicate the important of pH and extractant concentration on the extent of silver extraction. Other factors such as shaking speed, temperature and organic/ aqueous phase ratio are also important but they will not be reviewed here since they are not the subjects of the current study.

2.6 Summary

A rapid growth of semiconductor industry, in turn, generates huge quantity of waste inevitably. However, this semiconductor waste provides a great opportunity to recover silver. Several silver recovery technologies have been reported and hydrometallurgical process has attracted great attention among the others due to its advantages. It comprises the use of leaching and liquid-liquid extraction process. Several aspects of leaching process have been reviewed such as types of leaching agent, leaching agent concentration, liquid/solid ratio and kinetics of the process. The kinetics modeling has also been included. In the liquid-liquid extraction process, some of the common silver extractants were reviewed with special emphasis on dithizone and Cyanex 272. As overall, this section provides a fundamental background of the subject under study.

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CHAPTER II

LITERATURE REVIEW

2.1 Semiconductor Waste

Semiconductor industry is a part of the electronic component manufacturing industry such as the manufacture of integrated circuit and printed circuit board (PCB). Figure 2.1 shows the process flow of manufacturing these two components. It is nearly 140 new semiconductor manufacturing plants will be built worldwide before the turn of the century [1] and Malaysia becomes one of the most attractive country for investors to invest in this industry. In Malaysia, from a total of just four companies with 577 employees [2] and a total output value of RM 25 million in 1970, the industry had expanded to comprise more than 850 companies in production, employing 302,000 workers in 1995 with a total estimated output value of RM 67.4 billion. The performance of the electronics industry during the period 1988-1994 had been particularly remarkable, registering an output growth of 30.3 % per annum.

With the rapid growth of semiconductor industry, Malaysia faces the problem of waste accumulation and disposal. Hayhurst [1] reported that the production of one fingernail-width silicon wafer can produce 17,000 litres of wastewater, 12 kg of chemicals, 0.6 m^3 of hazardous gases and 4 kg of hazardous solid waste. Apart from that, the annual manufacturing capacity of PCB created estimated annual revenue of US$0.50 billion can generate up to 100,000 metric tons of sludge [**Error! Bookmark not defined.**].

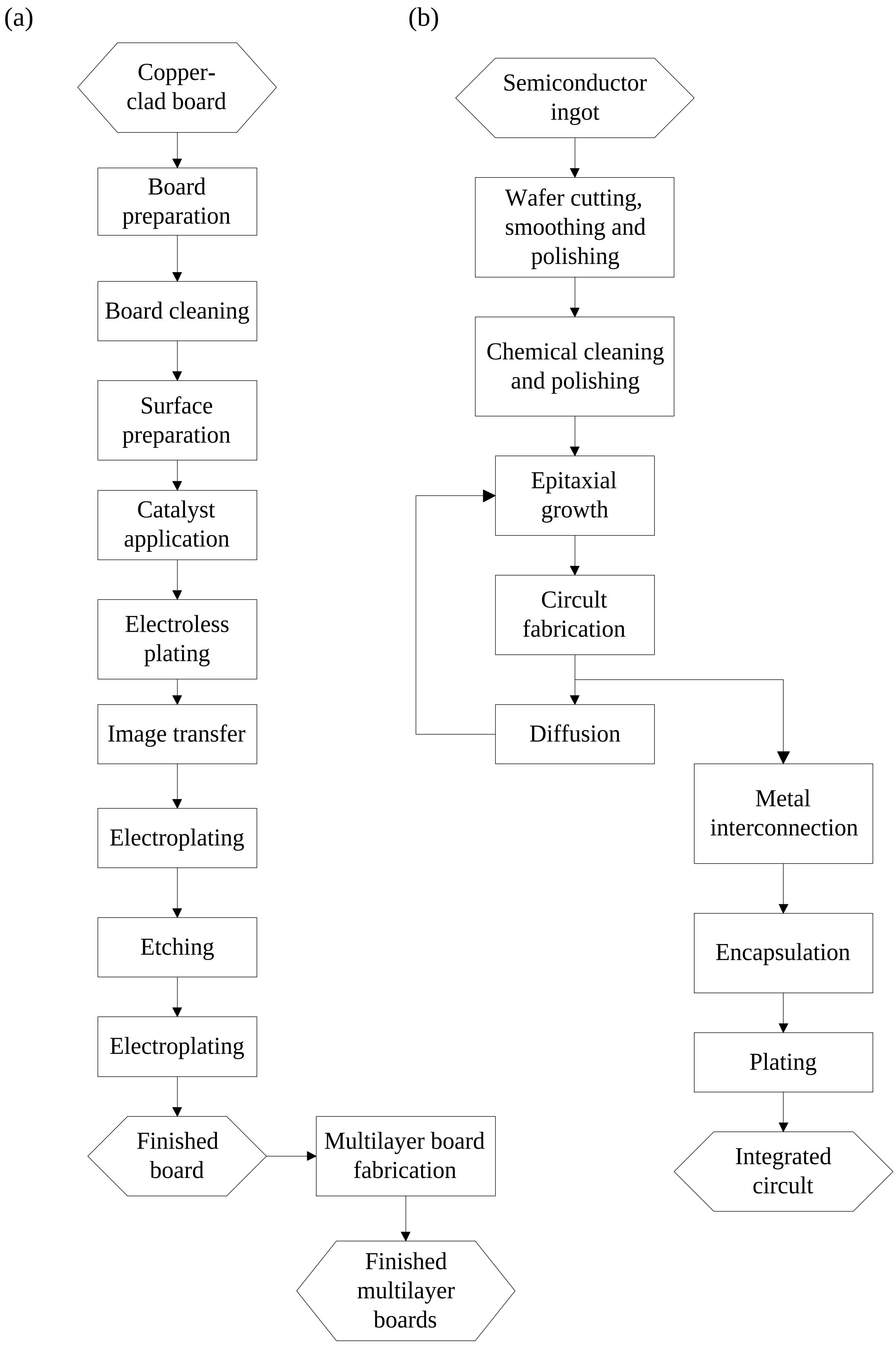


Figure 2.1: A process flow of the manufacture of printed circuit board (a) and integrated circuit (b) in semiconductor industry [3, 4].

Generally, the growth rate of waste generation in the electronic and semiconductor sector in Malaysia had estimated at 5 % per annum out of the total industrial waste generation for the period from 1987-1992 [5]. Recently, the Department of Environment of Johor had reported that the rate of generation of metal hydroxide sludge from semiconductor industry is about 0.45 to 4.0 metric tons per month [6]. Table 2.1 shows the generation of scheduled waste, metal hydroxide sludge (N151) for each of the states in Malaysia except Sabah and Sarawak.

Table 2.1: Scheduled Wastes (N151) generated by several states in Malaysia reported in 1987 and 1992 (cubic meters per annum) [5]

States	1987	1992	States	1987	1992
Perlis	0	0	N. Sembilan	1307	1735
Kedah	1468	1962	Melaka	519	750
Penang	9460	12001	Johor	15414	19788
Perak	16146	21428	Pahang	0	0
Selangor	10713	10159	Kelantan	1	1
Federal Territory	1297	1403	Trengganu	60	70

The major waste from the semiconductor industry can be categorized into two types; spent organic solvent and metals-containing waste [3]. Organic solvents are used for wafer / board cleaning and for the developing and stripping of photoresist materials used in the image transfer and / or circuit fabrication processes. Whereas the metals are introduced into the waste stream through the disposal of concentrated plating baths, running rinses and chemical etch step utilized as part of the electroplating preclean operations. Rinse water contains heavy metal and precleaning chemical such as acid, alkaline, cyanide and other metal salts. There are several types of plating utilized in semiconductor industry, for instance, silver plating, nickel plating, tin plating, copper plating and tin-lead plating. Therefore, the metals-containing waste vary depends on the types of plating process used.

2.2 Wastewater Treatment in Semiconductor Industry

Basically, prime objectives of wastewater treatment process in semiconductor industry are for cyanide reduction, heavy metal removal and neutralization. The treatment process for cyanide removal is generally carried out chemically via conversion of cyanide (CN^-) to cyanate (NCO^-) at pH 9.0 or above and followed by decomposition of cyanate to N_2 and CO_2 at pH 7.5 or below [7]. Cyanide removal is normally conducted by oxidation with chlorine using either sodium hypochlorite (NaOCl) or chlorine gas. For instance, the oxidation of sodium cyanide using sodium hypochlorite (NaOCl) can be written as:

$$NaOCl + NaCN \longrightarrow NaCNO + NaCl$$

$$2NaCNO + 4NaOCl \longrightarrow 2CO_2 + N_2 + 4NaCl + 2NaOH$$

However, some metal-complexed cyanide species are very stable and need to be further decomposed by reduction process using sodium bisulphite ($NaHSO_3$) and coagulated by $Cu(OH)_2$ which is formed according to the following reaction:

$$CuSO_4 + 2NaOH \longrightarrow Cu(OH)_2 + Na_2SO_4$$

Coagulant such as $Al_2(SO_4)_3.18H_2O$ is also added to neutralize the colloid matter and to form aggregates which will be settled down in the settling tank.

Any heavy metal in the waste liquor can normally be precipitated through pH adjustment to form their hydrous oxides which occurs at high pH. This process is normally carried out in the pH-adjusting tank where the lime, $Ca(OH)_2$ and $FeCl_3$ are added. The $Fe(OH)_3$ precipitate is added to produce flocs that has an extensive adsorptive capacity for transition metal ions and some of their complexes. The sediment then will go through thickening and filter press to form metal hydroxide sludge. Meanwhile the treated water will be neutralized before discharge. Figure 2.2 illustrates a general flow diagram for the wastewater treatment system used in the semiconductor industry.

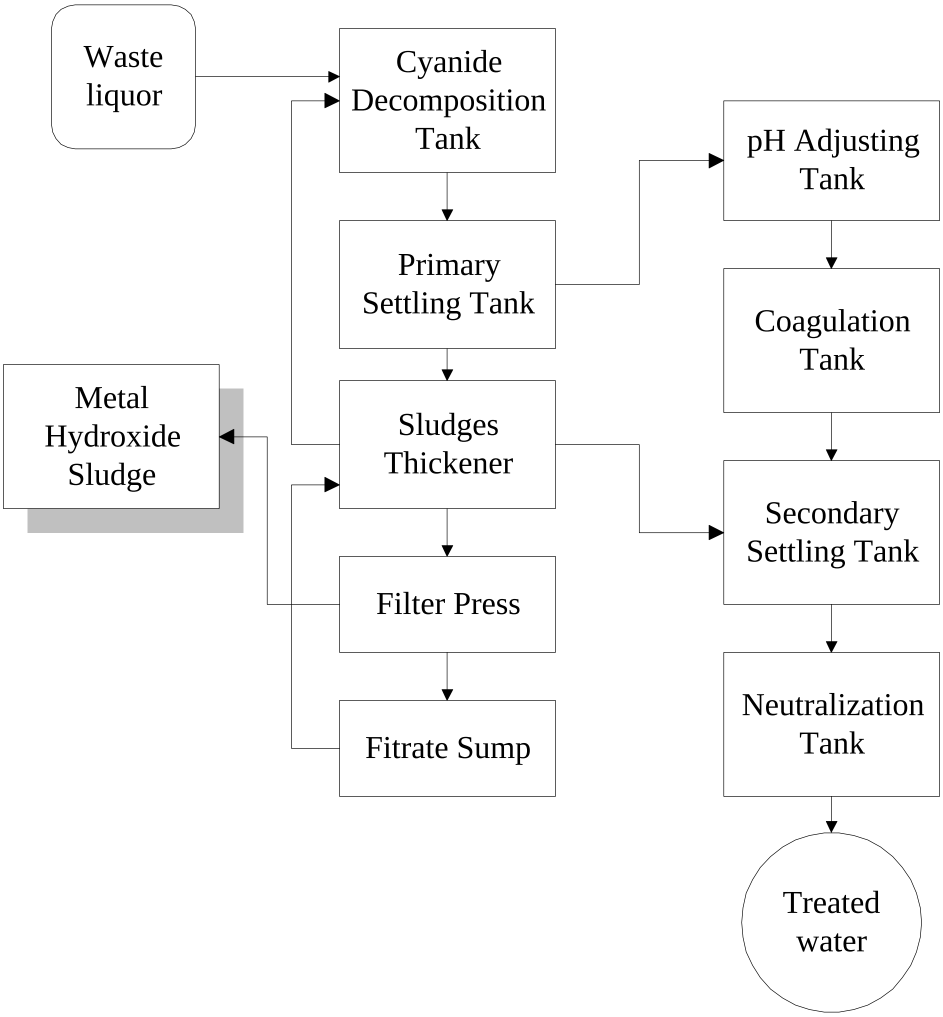


Figure 2.2: A typical process flowchart of wastewater treatment system in semiconductor industry [8].

2.3 Silver Recovery Technologies

The consumption of silver has increased due to the rapid economic development. However, with the current limited silver ores from the earth’s crust, it leads to the development of silver recovery techniques to recover silver from low-grade ores and waste. Numerous methods have been developed to recover silver from various sources such as processing waste and metal scrap. The most common and potential methods for silver recovery such as the flotation technique, pyrometallurgical process, biological process, electrometallurgical process and hydrometallurgical process will be discussed briefly in the following sections.

2.3.1 Flotation

Flotation is widely used in wastewater treatment to remove suspended matter and to concentrate biological sludge [9]. However, it is also being used in the silver recovery process. Beyzavi et al. [10] reported that their process for the silver recovery by flotation from the residue of wet extraction of zinc had successfully resulted in a silver yield of more than 89.5 %.

Flotation is referred to a unit operation which is applying bubbles to attach the particulate matter and the buoyant force of the combined particle and gas bubbles is great enough to cause the particle to rise to the surface [9]. The process depends on the selective affinity of the reagents used to form gas bubbles. In general, the reagents which increase the angle of contact between the liquid and the materials, are known as collectors. Collectors are materials which form surface films on the particles. Frothing agent is used to produce a froth, which must have sufficient stability to retain the particles in the surface so that they can be discharged.

Flotation process is very useful for the removal of the light particles. However, this process consumes high volume of feed material in order to be used economically. Furthermore its operation is more complex due to consumption of different types of chemical which must be well controlled.

2.3.2 Pyrometallurgical Process

Pyrometallurgical process for precious metals treatment and recovery is also being used commercially. Eastern Smelting & Refining Corp. [**Error! Bookmark not defined.**] has practiced the method in processing of most types of scrap, waste and residues containing silver. Van Hecke et al. [11] reported that 91 % of silver recovery from catalytic and electrical scraps using air roast techniques at pyrometallurgy temperature of 1400 °C was obtained.

Pyrometallurgical process is a thermal decomposition of metal which involves incineration, smelting and refining [12]. Basically, the incineration of the raw materials such as slime, low-grade metals and scraps is carried out to remove the volatile fraction. It followed by smelting of the ash produced in the incineration step. From the smelting process, bullion that contains the metal is recovered and refined using the standard electrolytic process to recover the metals.

The primary disadvantage to the method is a large of capital is required for the processing equipment. For instance the complicated lead blast furnace operation required for reprocessing waste containing high Al_2O_3 results in high energy and time consumption [**Error! Bookmark not defined.**]. The low precious-metal contents of the starting material represent a further problem to the application of this technique. It also can not handle waste in the liquid form.

2.3.3 Biological Process

Another promising emerging technology for silver removal is based on biological process. Certain types of microbial biomass can retain relatively high quantities of metal ions by ‘passive’ sorption and/or complexation. This is commonly known as biosorption [13]. Basically, biosorption may be classified into metabolic and non-metabolic dependence [14].

Metabolic dependence biosorption process or commonly known as bioaccumulation is an intracellular accumulation process which involves the transport of the metal across the cell membrane [14]. Bioaccumulation of silver has been documented in numerous studies. Pooley [15] reported that bioaccumulation of silver by a mixed culture of *T. ferroxidans* and *T. thiooxidans* occurs during the leaching of sulfide ore minerals. *Pseudomonas stutzeri* AG259 and *Streptomyces albus* have been used by Mattushka and coworkers to study the silver accumulation [16]. They reported that the accumulation of silver from a mixed metal solution was 142 μmol Ag g^{-1} dry weight of *P. stutzeri* AG259 and the selectivity, however was not satisfactory. Another study which conducted by Charley and Bull have shown a great capacity for silver bioaccumulation by the community of *P. maltophilia*, *S. aureus* and a *coryneform* organism [17].

Non-metabolic biosorption process involves the physicochemical interaction between the metal and functional groups of cell walls (mainly composed of carboxylate, hydroxyl, sulphate, phosphate and amino groups) [14]. Normally, the biosorption process has been conducted by immobilization of biomass in solid structures as columns or beads in a manner similar to ion exchange resins and activated carbons [18]. Brierley et al. [19] have developed a process called AMT-BIOCLAIM^{TM} for fixing biomass into fine granules to accumulate silver. Another important developments are BIO-FIX process [20] and AlgaSORB^{TM} process [14].

Biosorption is becoming important component in the silver recovery technologies. However, up to date, its application is limited. It is due to the fact that this biological process can not provide high selectivity and capacity, and it can only operate at a very low metals concentration.

2.3.4 Electrometallurgical Process

Electrometallurgical process is an electrolytic method to extract metal from metal bearing solution. This technique is based on the oxidation-reduction reaction which takes place at the surface of conductive electrodes (cathode and anode). Basically, the process comprises of three steps [21]. First is the creation of concentration gradient due to the applied current. Second is the electron transfer to the metal ion and forms the metal atom. Third is the surface diffusion of the adsorbed atom on the growing crystal lattice of the metallic deposit.

This electrolytic recovery of metal especially silver is of considerable interest and extensively studied. It is because this process gives several advantages which include the high purity of silver recovery, elimination of toxic heavy metals and sludge, and equipment maintenance is minimal [22]. Kirk and coworkers [23] have found that by using electrolytic process to leach silver from silver arsenopyrite, they obtained the silver extraction up to 57 % compared with 15 to 25 % with acids or acid and chlorine leaches. They observed that more silver was dissolved as the anode voltage was increased to about 1.74 V. Silver has also been widely electrolytically recovered from photographic waste [24,25]. Grau and Bisang [25] have suggested that the cathodic potential must more than –0.6 V to avoid the darkening of deposits due to the formation of Ag_2S. Therefore, the main factor that influences the physical characteristic of deposits is current density.

In practice, however, electrometallurgical process has faced several constraints. The electrolytic recovery is operative only down to solution concentration of 100-500 mgL^{-1} [26] and for diluted solution, cathodic polarization problem is arisen. In such system, as the metal is plated at the electrode, the layer of solution next to the electrode forms a polarized layer that offers high resistance to metal migration to the electrode [22]. Apart from that, the complexation of metal in solution can also cause a problem.

2.3.5 Hydrometallurgical Process

Hydrometallurgical process involves the dissolution of metal from solid matrix by an aqueous solution and subsequently precipitating or isolating the required metal [12]. From the literature, the hydrometallurgical processes which are potentially used in silver recovery include precipitation, liquid membrane, liquid ion exchange, solid-liquid and liquid-liquid extraction processes. These processes will be presented in the following sections except the solid-liquid and liquid-liquid extraction processes which will be reviewed in Section 2.4 and Section 2.5 respectively.

2.3.5.1 Precipitation

Precipitation is the most common method used for removal of inorganic heavy metals from industrial waste effluents. Precipitation of a heavy metal ion occurs when the metal salt reaches its solubility limit or defined as solubility products, K_{sp} [27]. In the case of silver metal, several types of precipitation processes such as hydroxide, chloride and sulfide precipitate are commonly used in metal separation.

Netzer and coworkers [28] have reported that the minimum silver hydroxide solubility is achieved at the level of 0.2 mgL^{-1} at pH 11.1. However, by the lime precipitation at pH 11.5, it was able reduced the residual soluble silver level from 500 to 21 μgL^{-1} and filtration provided further removal to 14.5 μgL^{-1} [29].

Silver chloride, AgCl has very low solubility (K_{sp} = 1.82 x 10^{-10} [30]) and can be used as effective technique to precipitate silver from solution. Such precipitation is commonly found in plating wastewater treatment [31]. The oxidation of silver cyanide for instance with chlorine, release chloride ions into solution, which in turn react with silver ions to from AgCl. However, in the excess of chloride ions, it will increase the solubility of silver through the formation of soluble silver chloro complexes [32]. In the AgCl precipitation process, ferric chloride is commonly added to the solution as a coagulant. Hannah et al. [29] have reported that 95 % of silver concentration in the solution can be precipitated by addition of $FeCl_3$ at pH 6.2 - 6.4.

Silver sulfide has extremely low solubility (K_{sp} = 6 x 10^{-50} [30]). Therefore, it can be used to separate silver from the waste. Use of sulfide for silver precipitation from photographic waste has reported by Fusco [33]. However, the addition of sulfide to the wastewater is considered disadvantage due to the formation of noxious hydrogen sulfide gas.

Silver can also be precipitated in the form of mixed sulfate-oxide. This can be achieved by addition of magnesium and lime to the silver solution [34]. The use of lime and ozone has also reported in order to increase the silver oxidation state from +1 to either +2 or +3 which are less soluble precipitate than does Ag^+[35].

Although precipitation has provided an effective technique for silver recovery, in practical, it has faced several problems. Industrial effluents contain complexing agents which might tie to the silver metal. This metal complex is sometime very stable and not be able precipitated by precipitation. Furthermore, when two or more metals are found in the same waste stream, the problem becomes even more complex [27].

2.3.5.2 Liquid Membrane Extraction

Liquid membranes separation processes are attracting attention in recent years due to their potential for low capital cost and energy efficiency. Liquid membranes can be of two kinds; the supported or immobilized liquid membranes and the liquid surfactant or emulsion liquid membranes. The supported liquid membranes configuration has the organic-phase liquid (containing the metal complexing agent) immobilized in the pores of a microporous membrane with the aqueous strip phase on the other side [36]. Emulsion liquid membranes are formed by dispersing a water-immiscible emulsion in water or an oil-immiscible emulsion in oil. The emulsion consists of an encapsulated phase (stripping phase) emulsified in the membrane phase with the use of surfactants. The emulsion is then dispersed in the continuous phase by agitation to yield globules of 0.1-2.0 mm diameter [37].

The large number of membranes with different formulation give a variety of applications, including metal recovery. Metzner and coworkers [38] have discovered that emulsion liquid membrane technique recovered the copper at low concentration selectively by using LIX extractant. Emulsion liquid membranes using thioDEHPA and dithioDEHPA have recovered zinc [39] and copper from waste stream [40]. However, up to now, there have been no report with regard to the application of liquid membrane for silver recovery.

Emulsion liquid membranes can offer greater areas for transport and thus have an advantage over the supported liquid membranes. Though the liquid surfactant membrane systems have several advantages over a conventional solvent extraction process such as extraction and stripping occur simultaneously that increase the capacity of process and result in lower operating costs, however this low capital costs can be somewhat offset by the need for separate emulsifier and coalescer units. Another problems generated from this system are encapsulated phase leakage caused by instability of emulsion and presence of osmotic pressure gradient [36,37].

2.3.5.3 Ion-exchange

Nowadays, much attention has been paid to the ion-exchange process since the ion-exchange resins are sufficiently inexpensive and effective technique to recover silver. Modern ion-exchange resins are synthetic polymers in which hydrocarbon groups (either strong acid or strong base) make up a three-dimensional network to enable the exchange process. Ion-exchange process can be defined as reversible exchange of ions between solid (resin) and a liquid (water containing ionized metal salts) [41].

Several ion-exchange technologies used to recover silver especially from photographic rinse water have been developed. Jansen and coworkers [42] have invented a silver recovery resin bed which comprised of strong base anion exchange resin. This resin exchanges the silver thiosulphate to release chloride ion while capturing the silver complex. Riveros and Cooper [43] examined two main categories of applicable ion-exchangers, weak base and strong base anionic. They found that only the strong base resins loaded significant amounts of silver but they are more difficult to elute. Apart from that, Hubicki and Hubicka [44] has tested six different selective ion-exchangers which included the functional group of thiol, thiourea, isothiourea and polyphenol. The ion-exchanger with -SH functional group on a skeleton of styrene copolymer with divinylbenzene (Duolite ES-465) showed the highest recovery factor of silver (I), the shortest period of ion-exchange equilibrium time and the most effective of selectivity ion-exchanger for silver removal.

Though the ion exchange technology is well established, there are still some drawbacks that limit its application. The ion-exchange resin cannot be heavily loaded and the consequent resin regenerate will not be sufficiently concentrated in metal to warrant recovery. Recovery is further hampered by the relatively non-selective nature of most commercially available resins, resulting in the accumulation in the regenerant of secondary and undesired contaminating ions.

2.4 Solid-liquid Extraction (Leaching) Process

Solid-liquid extraction is also called as leaching process. It is a process that involves dissolving the required metal from a solid substance into a solution. This process involves three different steps. First, the change of phase of the solute as it dissolves in the solvent. Second, its diffusion through the solvent in the pores of the solid to the outside of the particles and third, the transfer of the solute from the solution in contact with the particles to the main bulk of the solution [45].

In the leaching process, there are several aspects that need to be considered. However, in this study, four aspects will be highlighted. They are types of leaching agent, leaching agent concentration, liquid/solid ratio and kinetics aspects.

2.4.1 Types of Leaching Agent

Several potential leaching agents for silver removal have been reported in literature. These include cyanide, thiourea, chloride and acids. The selection of leaching agents is important to ensure a good silver leaching with high capacity and selectivity.

2.4.1.1 Cyanide

Cyanide reagent has been widely used in well-established treatment such as cyanidation process of primary ores and concentrated [46]. In the mining industry, the conventional cyanidation has been used to treat the silver ores with alkaline cyanide solutions in order to dissolve the silver in the form of $Ag(CN)_2^-$. Then the soluble ions are extracted from the solution by adsorption on activated carbon or known as carbon-in-pulp (CIP) [47]. The extent of silver leaching from the ores depends on the silver mineralization in the ore and some modifications have been used to improve the silver dissolution. Nunez and coworkers [48] has reported that the sulphidization of sodium sulphide prior to cyanide leaching on argentojarosite, $AgFe_3(SO_4)_2(OH)_6$ made it possible to improve the silver recovery from 40 % to 55 - 67 %. For the silver ores that disseminated in sulphidic minerals, it is necessary to oxidize this type of ores in order to break down the sulphidic part before cyanidation [49]. In the kinetic study by Maudos et al. [50], they found that the chloridation of silver from jeweler workshop sweeps prior to cyanide leaching has able to speed out the silver dissolution. Nevertheless, it has reported that the use of cyanide in alkaline media is recommended only when the silver is in carbonate or oxide form [51].

From the above review, even though cyanide leaching is widely used on a commercial scale, this process has several known disadvantages. The stability of $Ag(CN)_2^-$ is quite low [46], therefore, the cyanidation reaction requiring high cyanide concentration which is unfavorable process due to its high toxicity. Apart from that, the reaction involves a low leaching rate (24 – 72 hours contact time) and the process must be carefully monitored and controlled, and the spent cyanide leaching solutions must be treated before being discharged to the environment [49].

2.4.1.2 Thiourea

The utilization of thiourea ($CS(NH_2)_2$) as leaching agent has been reported for the treatment of refractory type precious metal ores [49,52], polymetallic complex ores [51] and jeweler workshop sweeps and exhausted batteries [50]. Thiourea is stable up to pH 2. It forms single cationic complexes with silver as $Ag[CS(NH_2)_2]_3^+$ [53]. Numerous reagents have been used as oxidizing agents such as hydrogen peroxide and Fe(III) in thiourea leaching which operated at pH 1 – 3. Iron (III) has shown to give the fastest silver leaching rate [49,50,52]. However, due to the fact that iron (III) forms complexs with thiourea which might increase the thiourea consumption [54], the thiourea concentration and the redox potential must be controlled. Electrochemical study has shown that the most active dissolution of silver is obtained in acidic solution (pH ~ 1) at redox potential 100 – 150 mV [53]. At redox potential above 200 mV, oxidation of the thiourea to formamidine disulphide (FDS) and then decomposition of the FDS to cyanamide and elemental sulfur will occur [55]. These formations might decrease the dissolution rate of silver due to degradation of thiourea and adsorption of silver thiourea complexes to sulfur product [53]. For the practical purposes, hydrogen peroxide is considered to be a better oxidant [55].

Another attempts to improve the thiourea leaching rate that has been reported was chloridation prior thiourea leaching either calcined the ores in the presence of NaCl or addition of sea water [50,51]. In the presence of Cl^- ions, the silver dissolution occurs according to the following equation:

$$Ag + Cl^- + 3\ CS(NH_2)_2 + Fe^{3+} \rightarrow Ag[CS(NH_2)_2]_3^+ + Fe^{2+} + Cl^-$$

The free energy, ΔG^o of the reaction becomes lower and indicates that the reaction is favorable [50].

Leaching in thiourea solutions, has potential advantages over conventional cyanidation. These include the acidic medium of thiourea leaching, cationic complexes formed by thiourea, faster reaction rates and no detrimental environment impact. However, the thiourea leaching is facing the difficulty in controlling the oxidation condition during the leaching process.

2.4.1.3 Chloride

Lately, ferric chloride ($FeCl_3$) leaching process is being widely used for the treatment of base-metal sulphide concentrates and other metallurgical products to recover by product such as silver [56]. Such process offers an advantage such as the formation of elemental sulfur rather than hazardous gas of sulfur dioxide. However, the dissolution of silver is often limited due to the diverse forms of silver mineralization such as native silver (Ag), argentian tetrahedrite, acanthite (Ag_2S) and chloragyrite (AgCl) [57]. Numerous works have been carried out on studying the dissolution of these silver forms using chloride-leaching agents. These include the studies of the Ag-$FeCl_3$ / $CuCl_2$-HCl system [58], Ag_2S-$FeCl_3$-HCl system [59] and AgCl-$FeCl_3$-HCl system [32,57]. The essence of these chloride leaching is the progressive formation of soluble silver chloro complexes of $AgCl_n^{-(n-1)}$ as given by the following reaction [57]:

$$Ag + nCl^- \Leftrightarrow AgCl_n^{-(n-1)} + e \qquad n = 1, 2, 3, 4$$

However, this reaction involves the low equilibrium constant which indicates that the concentrated chloride solution is required to achieve any significant silver dissolution. This result is in agreement with several published works [**Error! Bookmark not defined.**,57,59]. In the simple AgCl-HCl-H_2O system, at the HCl concentration below 0.5 M, the $AgCl_2^-$ complex is expected to form, whereas at HCl concentration between 0.5 to 1.5 M, $AgCl_3^{2-}$ complex is dominant. The $AgCl_4^{3-}$ complex is formed only in higher concentrated chloride media [57].

Although $FeCl_3$ has been widely used as oxidant in silver dissolution, Dutrizac [57] found that this oxidant is not required in the reaction of chloro complexation of silver. Instead, it can be replaced by several other chloride salts such as $CaCl_3$, NaCl, KCl [57] and $CuCl_2$ [58]. However, sodium chloride, NaCl is the least costly of the common salts, easily found and frequently added to chloride leaching media to elevate the boiling point of the solution and the most important, is to increase the solubility of AgCl [41].

2.4.1.4 Acids

The oxidative property of acid makes it possible to digest wide range of metal compounds. Sulfuric acid has been used to leach nickel and magnesium from serpentine ore [60], manganese from manganese carbonate ore [61] and zinc oxide [62]. Lo and Chen [63] have found that the use of H_2SO_4 has successfully removed cadmium, chromium, nickel and zinc from industrial sludge. Nitric acid, hydrochloric acid and aqua regia have been widely used in leaching of precious metals such as gold, silver, platinum and ruthenium from electronic scrap [**Error! Bookmark not defined.**,64].

Apart from that, acid has attracted much attention in the waste pretreatment [65]. It is because acid reduces the interference of organic matter and converts metals that associate with particulate to free metals. Therefore, acid digestion has been recommended as a standard method for the wastewater analysis [66]. Furthermore, sorption loss of silver on the surface of glassware is reduced in the presence of acidic medium [67]. It is important in order to get good analytical accuracy.

In the dissolution studies of Ag and AgCl by HCl [57,58] or H_2SO_4 [68], it has found that the chloride medium produced more stable soluble silver than in sulphate medium. However, in term of kinetic, silver dissolves faster in sulphate medium than chloride medium [68]. In the ferric chloride leaching system, HCl is required to prevent the hydrolysis and precipitation of iron which might reduce the efficiency of silver dissolution [57]. But still, the acid concentration used can not be too high that might cause the decreasing of it dissociation degree [51].

2.4.2 Leaching Agent Concentration

An efficient leaching process is very depends on how well the leaching agent itself can perform [54]. One of the critical aspects that affect its performance is leaching agent concentration. Generally, a leaching process is initiated by chemical reaction where the leaching agent reacts with metal to form soluble metal compounds. Therefore, the more leaching agent concentration is introduced into the leaching process, the more rapid and effective of the process can perform and the more yield of extracted metal can be obtained [50,51]. In the previous works on silver leaching [32,66-68], it was found practically on using chloride to extract silver especially in the form of AgCl and Ag from the solid waste. A study of silver recovery from copper smelter flue dust [**Error! Bookmark not defined.**] deduced that the minimum NaCl concentration required was 125 g/L in order to obtain a significant silver removal. Similar works that have been carried out by other researchers [57,59] also showed the same results. These come to the conclusion that a significant silver dissolution required a minimum of 2 M of NaCl leaching system. However, the variable of HCl concentration showed minor effect on silver recover [**Error! Bookmark not defined.**].

2.4.3 Liquid/Solid Ratio

Liquid/solid ratio is a term used to indicate the mixture ratio of the solid in liquid which has been widely used in hydrometallurgy field especially in the leaching process. This ratio affects the degree of solution viscosity and the total surface area of the particle contact to the leaching agent [45]. Liquid/solid ratio must be well tuned in order to provide a sufficient low viscosity for the leaching solution to circulate freely. Nunez and coworkers [**Error! Bookmark not defined.**] have found that the silver recovery of 15 mg Ag/kg waste was achieved at the liquid/solid ratio of 20 (10 g of solid waste in 200 ml of leaching agent). The decrease of the ratio did not result in an increase of the amount of silver dissolved. It deduced that when the leaching system has reached a maximum particle surface contact with leaching solution, the increase of leaching agent volume will not affect the leaching process.

2.4.4 Kinetic Modeling of Leaching Process

Kinetic modeling of leaching process is very important in order to get better understanding on the mechanism involved as well as to get engineering parameters for scale up of the process. In the leaching process especially for metal leaching from mineral ores or processing waste, the process generally occurs through heterogeneous reactions involving two different phases. A liquid is brought into contact with a solid, react with it, and transform it into product. The overall reaction rates may be influenced by the individual steps that illustrated in Figure 2.3.

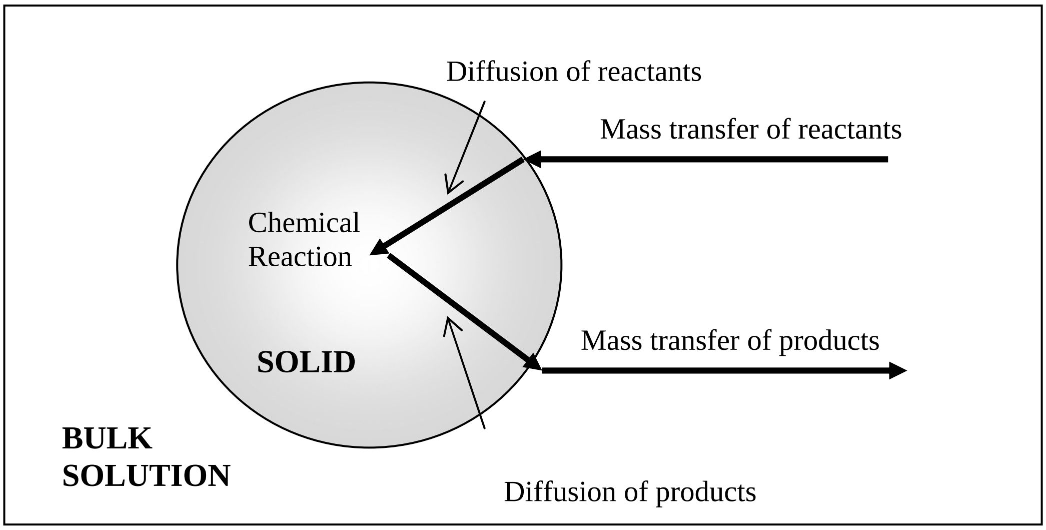


Figure 2.3: A schematic diagram of the overall reaction involved in leaching process [69].

Kinetic of the leaching process involving noncatalytic reaction of particles with surrounding liquid, can basically be described by either progressive-conversion model or shrinking-unreacted-core model [70]. The former model assumes that the reactant enters throughout the particle at all times. As a result, the solid reactant is converted progressively. However, the latter model assumes that the reaction occurs first at the outer skin of the particle and the zone of reaction then moves deeper into the solid. Thus, at any time there exists an unreacted core of material that shrinking during reaction.

In leaching process, evidence from wide variety of conditions as reported in the literature indicates that the shrinking unreacted-core model is capable to describe the process more closely to what observed experimentally. Therefore, it has been chosen in this study. Basically, the shrinking core model of leaching process can be classified further into chemical reaction and diffusion through liquid films control models.

2.4.4.1 Chemical Reaction Control

A leaching system to be said in controlled by chemical reaction when the leaching rate is not influenced by the stirring speed. It is because at this condition, no matter how diffusion thickness it is (vary the stirring speed), the rate-controlling step still governed by the slow chemical reaction that occurs at the interface. From the literature, it was found that two types of models had been used to describe the kinetic of leaching process controlled by chemical reaction.

Wadsworth [69] proposed the kinetic model based on the facts that the reaction rate, dn/dt rely on the total surface, $4\pi r^2$ and the number of reactive sites per unit area available for reaction, k_o. n, the number of moles is equal to $4\pi r^3/(3V_m)$ where V_m is the molar volume of solute. Of course, the concentration of reactant, C and the rate constant of first-order reaction, k' also affect the reaction rate. The general rate expression for a sphere with radius r is given by

$$dn/dt = -4\pi r^2 C k_o k' \quad \text{.......} \quad 2.1$$

which rearranged into

$$dr/dt = -V_m C k_o k' \quad \text{.......} \quad 2.2$$

If r_0 is the initial radius of the sphere, the fractional conversion α can be written as

$$\alpha = 1-(r/r_o)^3 \quad \text{.......} \quad 2.3$$

The differentiation of Equation 2.3 with respect to time and combined with Equation 2.2 gives

$$d\alpha/dt = (3V_m C k_o k'/r_o)(1-\alpha)^{-2/3} \quad \text{.......} \quad 2.4$$

For the condition $\alpha = 0$, when $t = 0$, Equation 2.4 may be integrated for constant concentration giving

$$\mathbf{1 - (1-\alpha)^{1/3} = (V_m C k_o k'/r_o)t} \quad \ldots\ldots 2.5$$

This final equation represents the kinetic model proposed by Wadsworth which can predict the leaching process controlled by chemical reaction.

Levenspiel [70] has proposed the other kinetic model that describes the leaching rate by chemical reaction. In his approach, the author assumed that the decrease in volume or radius of unreacted core was accompanying by the disappearance of *d*n moles of solid reactant which lead to the rate expression as

$$dn/dt = -4\pi r^2 b k_s C \quad \ldots\ldots 2.6$$

where b is a stoichiometric factor and k_s is a first order reaction rate constant. However, the author defined n as $4\pi r^3 \rho_B$ where ρ_B is a molar density of solid reactant. By rearrangement of Equation 2.6 with respect to ρ_B, it gives

$$dr/dt = -b k_s C/\rho_B \quad \ldots\ldots 2.7$$

and the correlation between α and t then expressed as

$$\mathbf{1-(1-\alpha)^{1/3} = (b k_s C/\rho_B r_o)t} \quad \ldots\ldots 2.8$$

Actually, the approach in developing these two kinetic models is similar. The only different is, in the former model, it considers the concentration of potentially reactive surface sites, while in the latter model, stoichiometric factor was considered.

2.4.4.2 Diffusion through Liquid Film Controls

In most hydrometallurgical systems involving dissolution or precipitation of a solid and diffusion through a zone adjacent to solid-liquid interface might often be rate controlling step [69]. Diffusion is a process which tends to equalize concentration within a single phase. Under this condition, when the stirring speed is changed, the leaching rate also being changed. It is due to the change of diffusion thickness which affects the rate of species diffused. As reported from literature, three common kinetic models have been used to describe the leaching process controlled by diffusion.

In the kinetic expression by Wadsworth [69], he included the stoichiometric factor, b and the limiting boundary layer thickness, δ. It is because, the rate of disappearance of reactants or the rate of appearance of products depends upon the overall stoichiometry of the reaction. Therefore, the author has replaced the Equation 2.1 to express the reaction rate as

$$dn/dt = -4\pi r^2 DC/b\delta \quad \ldots\ldots 2.9$$

where D is a diffusion coefficient which independent of concentration. Since

$$D/b\delta = k_o k' \quad \ldots\ldots 2.10$$

Equation 2.9 then can b expressed as

$$\mathbf{1-(1-\alpha)^{1/3} = (CV_m D/\delta b r_o)t} \quad \ldots\ldots 2.11$$

Levenspiel [70] in his model, expressed that if the mass transfer step is rate-controlling, then

$$dn/dt = -4\pi r^2 bKC \quad \ldots\ldots 2.12$$

where K, mass transfer coefficient which is equal to D/r (in Stokes regime). By replacing K and integrating of Equation 2.12, it gives

$$t = (\rho_B r_o^2/2bCD)[1-(r/r_o)^2] \quad \ldots\ldots 2.13$$

The time for complete disappearance of a particle is thus

$$\tau = (\rho_B r_o^2/2bCD) \quad \ldots\ldots 2.14$$

and on combining we obtain

$$\mathbf{1-(1-\alpha)^{2/3} = (2bCD/\rho_B r_o^2)t} \quad \ldots\ldots 2.15$$

For the third model proposed by Geankoplis [71], the rate of mass transfer is expressed as

$dn/dt = -AK(C_s – C_t)$ ……………………………….……………..... 2.16

where dn defined as Vdc (V is solution volume), A is a total surface area of particles and, C_s and C_t are the concentration of solute at $t = \infty$ and $t = t$ respectively. Equation 2.16 then rearranged and integrated from t = 0 and t = t, and C_o and C_t respectively, it gives

$(C_s - C_t)/(C_s - C_o) = \exp -(KA/V)t$ ……………………………….………. 2.17

If pure solvent is used initially, $C_o = O$, then we obtain

$\mathbf{\ln (1- \alpha) = -(KA/V)t}$ …………………………………………….…. 2.18

Basically, three kinetic models described above have similar concept on establishing their models. The rate of reactant disappearance is depend on surface area, reactant concentration and mass transfer coefficient or diffusion coefficient. However, in attempt to express these parameters, they represent those parameters in different way. Instead of K, Wadsworth [69] has replaced it by considered the effect of diffusion thickness and stochiometric factor. In the kinetic model developed by Levenspiel [70], the term of molar density is used in the rate expression. While Geankoplish [71] has considered the volume of liquid reactant that diffuse to the surface of reaction.

Overall, however, the different rate expression of these models might cause the deviation from actual experimental data. If a model corresponds closely to what really takes place, then its rate expression will closely predict and describe the actual kinetics. Table 2.2 is summarizes the leaching kinetic models either describing the rate controlled by chemical reaction or diffusion.

Table 2.2: Summary of chemical and diffusion control kinetic leaching models.

Chemical Reaction Control Model	Diffusion Through Liquid Film Control Model
$1 - (1-\alpha)^{1/3} = (VCk_ok'/r_o)t$	$1-(1-\alpha)^{1/3} = (CVD/\delta\sigma r_o)t$
$1-(1-\alpha)^{1/3} = (bk_sC/\rho_B r_o)t$	$1-(1-\alpha)^{2/3} = (2bCD/\rho_B r_o^2)t$
	$\ln (1- \alpha) = -(KA/V)t$

2.5 Liquid-liquid Extraction Process

The use of liquid-liquid extraction as a unit operation in hydrometallurgy now extends to a wide range of metals from a variety of feed materials including low-grade ores, scrap and waste and diluted aqueous solutions. A considerable amount of work has been carried out on liquid-liquid extraction of silver. Schweitzer et al. [72,73] have carried out an extensive study on silver extraction using dithizone. Recently, much consideration also paid to study the silver removal by liquid-liquid extraction using sulfur-containing extractant [74,75,76]. Liquid-liquid extraction is widely used nowadays due to its operation can perform easily, environmental friendly, less energy intensive energy and provides high purity of product.

Liquid-liquid extraction or referred to as solvent extraction involves separating the solutes from the liquid, normally aqueous solution by adding the immiscible or partially miscible liquid refer to as solvent or diluents. It is an equilibrium process which can be simply described by following reaction,

$$M + E \Leftrightarrow ME$$

In the first step (extraction step), the metal, M is transferred from an aqueous phase to an organic phase by the extractant, E as complex ME. The second step is the reverse of the first step, that is the metal is transferred from the organic phase to an aqueous phase (stripping stage). So, basically the solvent extraction of metals is a simple operation requiring only a shift in the equilibrium between the extraction and stripping processes.

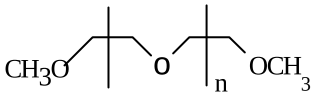
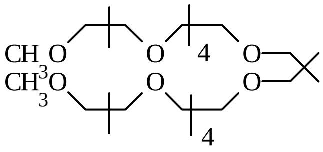
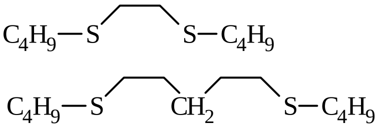
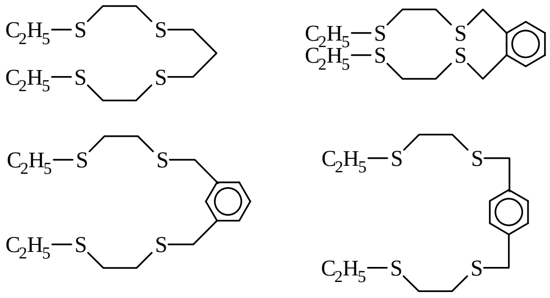
However, normally a metal ion exists in aqueous solution with little or no tendency to transfer to an organic phase. Thus in order to achieve the required transfer, the metal ion has to be modified by converting a hydrophilic species into an extractable hydrophobic species and this can be done by using solvation, anion-exchange or cation-exchange extractants. The selection of extractant is very crucial in order to get a good selectivity and high loaded metal capacity.

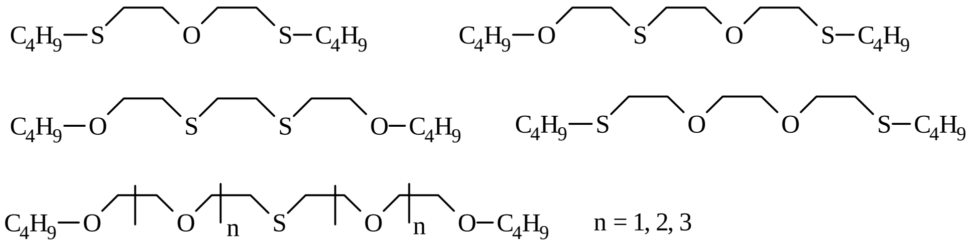
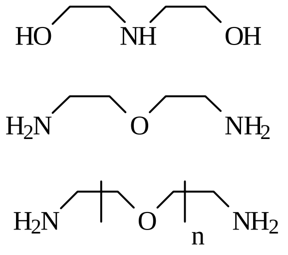
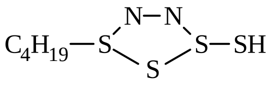
2.5.1 Silver Extractant

According to the principle of hard and soft acid base (HSAB) developed by Pearson [77], silver ion is a soft acid and therefore should show a great affinity towards soft base atom. Many researchers have prepared and studied a various extractants that possess these characteristics.

Sulfur-containing extractant is among the most familiar one since it has a Pauling electronegativity of 2.58 compared to 3.41 for oxygen, making it is a highly polarizable soft donor atom. These types of extractant have studied by Sole and coworkers [75,78]. They observed that replacing the oxygen of R_2PO_2H (Cyanex 272 : R represents 2,4,4-trimethylpentyl) by sulfur atom forming R_2PSOH (Cyanex 302) and R_2PS_2H (Cyanex 301) have shifted the silver extraction to lower pH and it was found that Ag-Cyanex 301 complex exhibited a great stability among the others. Apart from these extractants, Cyanex 471X (triisobutylphosphine sulphide) will also give a promising result towards silver extraction selectivity [74]. The high selectivity of Cyanex 471X for Ag (I) is because of its strong complex with silver. Paiva [79] reviewed some of silver extractants and concluded that extractant containing sulfur and nitrogen atoms including thiourea and its derivatives could be potentially good extractability for silver. Dithizone is among the most famous silver extractant that commonly used as analytical reagent for photometric determination of trace amount of silver. Meanwhile, Shetkar and Shinde [80] discovered that by using triphenylphosphine sulphide, 99.66 % of silver extraction could be achieved. As analogous sulfur ligands, Dietze and coworkers [81] studied the complex formation and extraction properties of some oxathia-alkanes with silver. By comparison the stability constants of the thia-alkanes, it was found that the introduction of oxygen atoms will increase the stability of the compounds especially when the oxygen atoms are placed at the center of the molecule. Paiva [79] reviewed some other open-chain silver extractants as given in Table 2.3.

Table 2.3: Open chain extractants for silver extraction [79].

TYPES OF SILVER EXTRACTANT
Oxygen atom
 n = 3, 4, 5 Oxa-alkanes
 Oxa-alkanes
Monensin
Sulfur atom
Hexyl sulfide
1,2-Bis-(hexylthio)ethane
$RS(CH_2)_nSR$ Cis-R'-SCH=CHS-R' $O\text{-}C_6H_4\text{-}(SCH_3)_2$
$C_4H_9\text{-}S\text{-}C_4H_9$ Dibutyl sulfide  1,2-(butylthio)-etane
 Acyclic tetrathioethers
Phosphorus atom
Tributylphosphate
Synergistic mixture of bis-(2-ethylhexyl)-phosphoric acid and 4-sec-butyl-2-(2-methylbenzyl)-phenol
Bis-(2-ethylhexyl)-phosphoric acid

di-n-butyl-phosphorothioic O,O’-di-n-butyl-phosphorodithioic
bis-(2-ethylhexyl)-dithiophosphoric acid
Nitrogen atom
Triaurylamine
N1923 (primary amine)
Oxygen and Sulfur atoms
$S[(CH_2)_nCO_2H]_2$ n = 1, 2 $HO_2C\text{-}CH_2\text{-}S\text{-}(CH_2)_n\text{-}S\text{-}CH_2\text{-}CO_2H$ n = 1, 2
Octylthiomethylacetophenone
 Oxathia-alkanes
Oxygen and Nitrogen atoms
 n = 2, 3
Sulfur and Nitrogen atoms
Diantipyrylthiourea Diphenylthiourea
bis-(O-tolyl)-thiourea
N,N’-diphenylthiourea
2-alkylthiopyridine
2-octylthiopyridine
t-dodecylthiopyridine

R-CS-NHR’ (R, R’= alkyl, aryl)

2.5.2 Extraction of Silver by Using Dithizone

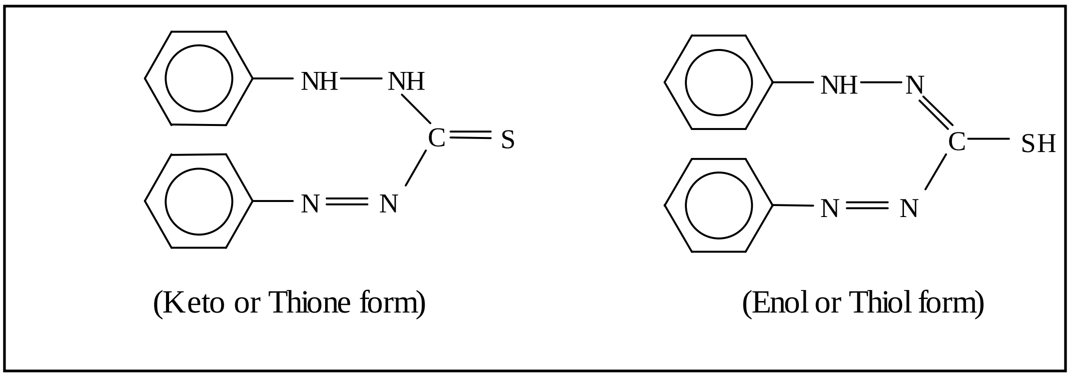
2.5.2.1 Introduction

A comprehensive review of dithizone properties by Irving [82] and Pearson [77] showed that the dithizone is the most suitable extractant for silver. A systematically study of silver dithizonates which carried out by Schweitzer and Dyer [72] gave a clear understanding of silver behaviour during the extraction process. Besides that, dithizone is widely used in the field of quantitative chemical analysis using photometric method [83,84,85]. Grote and Kettrup [86] also discovered that dithizone exhibits excellent chelating abilities for silver metal.

2.5.2.2 Physical and Chemical Properties of Dithizone

Pure dithizone (diphenylthiocarbazone/ H_2Dz: $C_{13}H_{12}N_4S$) is a violet-black crystalline powder having molecular weight of 256.3 $gmol^{-1}$ and the density of 1.35 gml^{-1}. Though H_2Dz possesses a high melting point of 169 °C but the solution is unstable towards heat, strong light and oxidants. From the solubility data reported by the researchers, Irving [82] concluded that H_2Dz shows a low solubility in paraffinic and alicyclic hydrocarbons but the highest solubility was reported in aromatic hydrocarbons. Dithizone has very high solubility in chlorinated paraffins (Appendix A). The solubility of dithizone in water is very low ($\approx 5x10^{-5}$ gL^{-1}) and thus making it suitable for extraction process.

Dithizone exits in two tautomeric forms, the keto (monoprotic) and the enol (diprotic) as given in Figure 2.4. Dithizone has two H atoms which can be replaced by heavy metals to form either primary and secondary dithizonates. However, only few metals can form secondary dithizonates because these metal complexes are labile and less soluble in organic solvent. Most of the reactions to form metal complex require a very weakly acidic or slightly basic conditions for getting satisfactory extraction (Figure 2.5).



(Keto or Thione form) (Enol or Thiol form)

Figure 2.4: Tautomeric forms of dithizone [82].

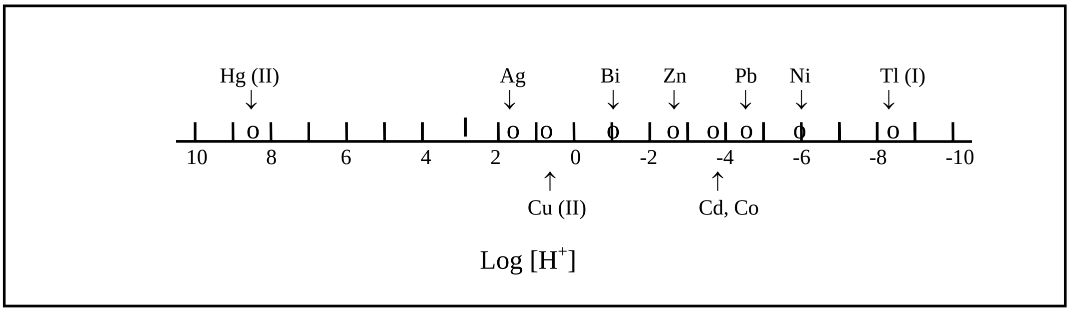


Figure 2.5: pH of metal extraction by dithizone [83].

Silver reacts with dithizone in acidic solution to form the primary dithizonate, Ag(HDz) which dissolves in CCl_4 or $CHCl_3$ to give a yellow solution. However, in neutral or basic medium, the red-violet secondary dithizonate (Ag_2Dz) is formed and virtually insoluble in CCl_4 and slightly soluble in $CHCl_3$ [85]. This red-violet solution is readily converted into yellow by adding excess of H_2Dz and acidifying the aqueous phase. It has been reported that to prevent the co-extraction of other elements, complexing agents such as EDTA may be added to the aqueous solution of silver to complex Cu, Bi, Cd, Zn, Pb but not Hg [83].

2.5.2.3 Effect of pH on Silver Extraction by Dithizone

The various equilibrium reactions that govern the extraction of primary silver dithizonate are shown in Figure 2.6:

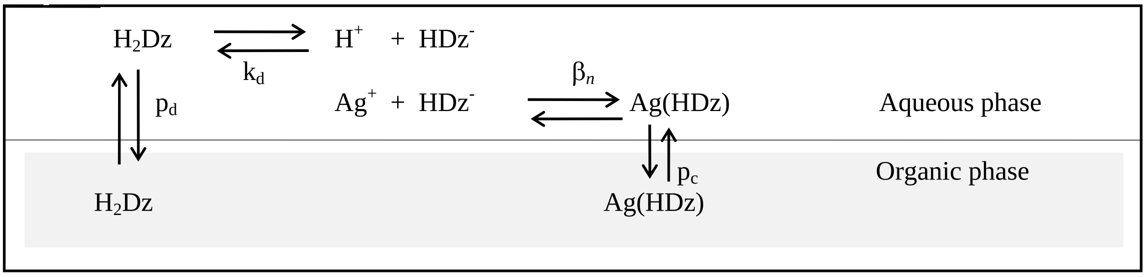


Figure 2.6: Various equilibrium reactions involved in the silver extraction by dithizone [82].

where $k_d = [H^+][HDz^-] / [H_2Dz]$ and $p_d = [H_2Dz]_o / [H_2Dz]$ are the (first) acid dissociation constant and partition constant for dithizone respectively, $\beta_n = [Ag^+][HDz^-] / [Ag(HDz)]$ is the overall stability constant of the metal dithizonate, and $p_c = [Ag(HDz)]_o / [Ag(HDz)]$ is the partition coefficient.

The fundamental equation for silver extraction using dithizone is given by,

$$Ag^+ + H_2Dz\ (org) \overset{K_{ex}}{\Leftrightarrow} Ag(HDz)\ (org) + H^+$$

$$K_{ex} = \frac{[Ag(HDz)]_o[H^+]}{[Ag^+][H_2Dz]_o} = \frac{p_c k_d}{\beta_n p_d} \quad \text{…..……………………………………} \quad 2.19$$

According to Equation 2.19, the extraction equilibrium constant, K_{ex} increases with decreasing ionization of the chelate in the aqueous phase and its increasing partitioning into the organic phase, and with increasing ionization of the chelating agent and its increasing partitioning into the aqueous phase [83].

Distribution coefficient, D_c is given by:

$$D_c = [Ag(HDz)]_o/[Ag^+] = K_{ex}[H_2Dz]_o/[H^+] \quad \text{……………………….....…… } 2.20$$

and

$\log D_c = \log K_{ex} + pH + \log [H_2Dz]_o$ …………………………………… 2.21

Equation 2.21 indicates that a ten-fold change in $[H_2Dz]_o$ can compensated by the unit change in pH and so it is obviously that control of pH will be a dominant factor.

pH at 50 % of extraction donates as $pH_{1/2}$. Therefore, at $pH_{1/2}$ one should have $D_c = 1$ and Equation 2.21 becomes,

$0 = \log 1 = \log K_{ex} + pH_{1/2} + \log [H_2Dz]_o$

whence

$\Delta pH = pH_{1/2} - pH = -\log D_c = \log (100-E)/E$ …………………………….…….2.22

where E is the percentage of extraction. It follows that:

$E = 50\,(1 - \tanh 1.1513\,\Delta pH)$ ……………………………………….….. 2.23

showing that plots of E against pH should be sigmoid and centrosymmetric about the mid-point as shown in Figure 2.7 [82].

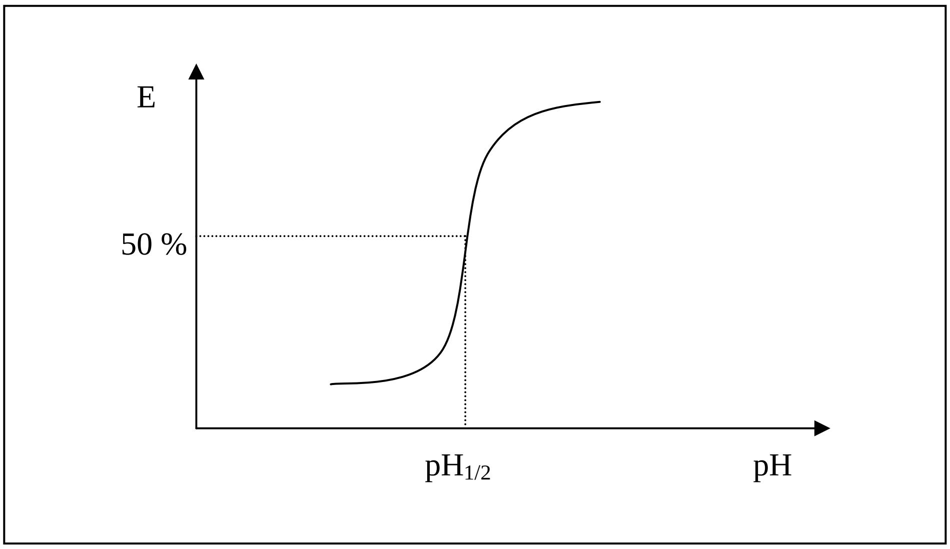


Figure 2.7: A sigmoid curve of the metal extraction.

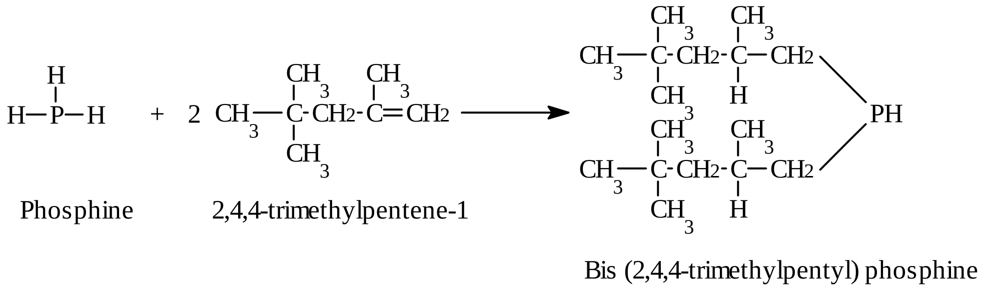
Extraction process is significantly affected by the pH of the solution as described above. However, other factors such as temperature, extractant concentration, organic/aqueous ratio and hydrodynamic parameters also contribute to the extent and rate of extraction. The detail discussion on the effect of these parameters, however, will not be included in this review.

2.5.3 Silver Extraction by Cyanex 272

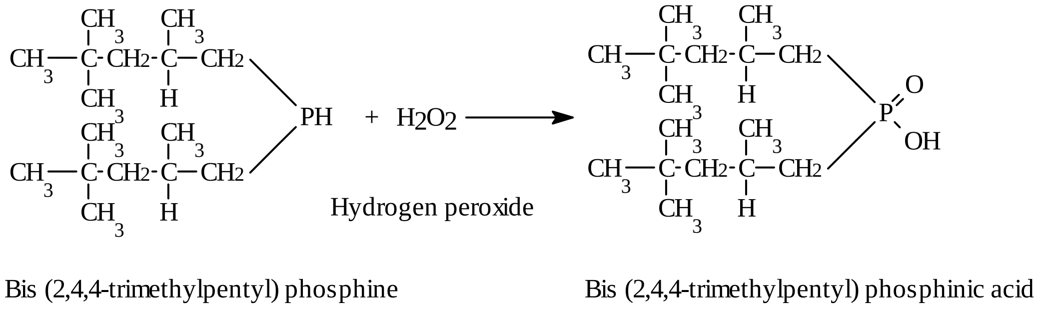
2.5.3.1 Introduction

Organophosphorus acid compounds have been widely used as an extractant in recent years in solvent extraction of many metal ions on a commercial scale. Among these, bis (2,4,4-trimethylpentyl) phosphinic acid has been widely studied, particularly with respect to cobalt-nickel separation [87,88] and silver extraction [75].

Bis (2,4,4-trimethylpentyl) phosphinic acid or commonly known as Cyanex 272 is manufactured from phosphine in a two stages process [89]. Initially, phosphine is reacted with 2,4,4-trimethylpentene-1 to form bis (2,4,4-trimethylpentyl) phosphine.



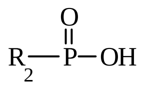
This intermediate product is then oxidized with hydrogen peroxide to produce phosphinic acid.



2.5.3.2 Physical and Chemical Properties of Cyanex 272

Cyanex 272 is a clear, light-amber, viscous liquid which is totally miscible in common aliphatic and aromatic diluents. The basic physical and chemical properties of Cyanex 272 are given in Table 2.4.

Table 2.4: Cyanex 272 structural and properties at 24 °C [90].

* Structural Formula	pK_a in H_2O	Density (kgm^{-3})	Viscosity ($kgm^{-1}s^{-1}$)	Molar Mass ($gmol^{-1}$)	Aqueous Solubility (mgL^{-1})
 $R_2-\overset{\overset{O}{\parallel}}{P}-OH$	6.37	910	14.2	290	38

* R represents the 2,4,4-trimethylpentyl group

Cyanex 272 can exist either in the forms of monomer or dimer which indicated by two major peaks of the ^{13}P-NMR spectra at 59.6 ppm and 59.9 ppm [78]. However, Sole and Hiskey [90] reported that Cyanex 272 exists primarily as self-associated species (dimer) due to the formation of hydrogen bonding by proton acceptor of oxygen in Cyanex 272.

2.5.3.3 Effect of pH on Silver Extraction by Cyanex 272

The silver extraction by Cyanex 272 may be written as:

$$Ag^+ + \overline{m(R_2POOH)_p} \Leftrightarrow \overline{Ag((R_2POO)_pH)_n(R_2POOH)_{p(m-n)}} + nH^+$$

where m is the stoichiometric ratio, p is the degree of association of the extractant, n is the valence state of metal and overlining represents organic-phase species [75]. The equilibrium constant for the reaction is then given by:

$$K_{ex} = \frac{[\overline{Ag((R_2POO)_pH)_n(R_2POOH)_{p(m-n)}}][H^+]^n}{[Ag]^+[\overline{(R_2POOH)_p}]^m} \quad \text{……………….. 2.24}$$

It is then readily shown that

$$\log K_{ex} = \log D_c - npH - m\log[(R_2POOH)_p] \quad \text{…….……………………. 2.25}$$

At $pH_{1/2}$, $D_c = 1$ and with $n = 1$, Equation 2.25 becomes

$$pH_{1/2} = -m \log [(R_2POOH)_p] - \log K_{ex} \qquad 2.26$$

Therefore, a plot of $pH_{1/2}$ against log $[(R_2POOH)_p]$ as shown in Figure 2.8 should give a straight line with slope $-m$ and a y-intercept of $-\log K_{ex}$.

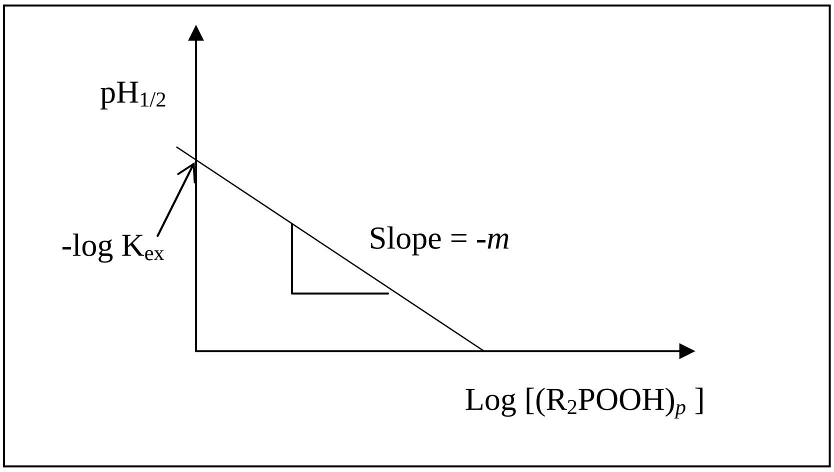


Figure 2.8: A straight line of $pH_{1/2}$ versus logarithm extractant concentration.

The Equations 2.24, 2.25 and 2.26 indicate the important of pH and extractant concentration on the extent of silver extraction. Other factors such as shaking speed, temperature and organic/ aqueous phase ratio are also important but they will not be reviewed here since they are not the subjects of the current study.

2.6 Summary

A rapid growth of semiconductor industry, in turn, generates huge quantity of waste inevitably. However, this semiconductor waste provides a great opportunity to recover silver. Several silver recovery technologies have been reported and hydrometallurgical process has attracted great attention among the others due to its advantages. It comprises the use of leaching and liquid-liquid extraction process. Several aspects of leaching process have been reviewed such as types of leaching agent, leaching agent concentration, liquid/solid ratio and kinetics of the process. The kinetics modeling has also been included. In the liquid-liquid extraction process, some of the common silver extractants were reviewed with special emphasis on dithizone and Cyanex 272. As overall, this section provides a fundamental background of the subject under study.

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CHAPTER III

MATERIALS AND METHODS

3.1 Materials

3.1.1 General Chemicals

Throughout the experiments, Silver (Ag), Ferum (Fe), Cuprum (Cu), Stanum (Sn) and Calcium (Ca) Nitrate solutions of 1000 ppm obtained from BDH Limited were used as standard solutions for Atomic Absorption Spectroscopy calibration. Aqueous solutions were prepared using distilled and deionized water of 18 MΩcm purity. Sodium hydroxide, NaOH (99.0 % purity) and hydrochloric acid, HCl (37 % purity) obtained from R & M Chemical and nitric acid, HNO_3 (69.1 % purity) obtained from Fischer Chemical, were used for pH adjustment. All the chemicals were used as received.

3.1.2 Sample of Semiconductor Waste

Two types of semiconductor wastes were collected from wastewater treatment plant of the same local semiconductor industry (Figure 3.1). Sample A was collected directly after filter press which is in the form of semi solid and clay-like clumps. While the sample B was taken after the dryer which is in the form of dry solid comprising of various particle sizes. Both samples are brownish green and odorless. Throughout the leaching process, the sample B which preheated at 105 °C to remove the water content was used as dry sample.

Figure 3.1: Samples A and B of semiconductor wastes collected from local semiconductor industry.

This waste existed as a metal hydroxide sludge is categorized under classification number N151 of the Environmental Quality (Scheduled Waste) Regulation 1989 [100]. Excessive oral intake of this kind of waste might result in acute or chronic poisoning. It will also affect the blood, digestive, respiratory, lungs, liver, and kidneys if it is chronic overexposure. By continued excessive contact with the waste might cause dermal irritation [15].

3.1.3 Leaching Agents

In the leaching process, the conventional acid leaching was used. The leaching agents used were hydrochloric acid, HCl (37 % purity), sulfuric acid, H_2SO_4 (95-97 % purity) and nitric acid, HNO_3 (69.1 % purity) obtained from R&M Chemical, MERCK and Fischer Chemical respectively. All the leaching solutions were prepared using distilled and deionized water to obtain the required concentration. Sodium chloride, NaCl (99.5 % purity) obtained from R&M Chemical was used as an additional source of chloride ion in leaching process. All the leaching agents used as received.

3.1.4 Extractants

In the extraction processes, two extractants were used; diphenyl thiocarbazone or commonly known as dithizone (97 % purity) and diisooctylphosphinic acid (90 % purity) or commercially known as Cyanex 272 obtained from Fischer Chemical and Fluka Chemika respectively. The extractants were used without any further purification. Kerosene and chloroform obtained from Fluka Chemika and MERCK respectively were used as diluents and were used as received.

3.2 Experimental Methods

3.2.1 Semiconductor Waste Characterization- Physical Properties

3.2.1.1 Water Content

In this work, both sample A and sample B were used to determine the water content. The water content of each semiconductor waste was carried out in triplicate by drying the sample at 105 °C in oven until the constant weight was achieved. The loss in weight corresponds to the amount of water content in the sample [74].

3.2.1.2 Organic Content

The organic content of semiconductor waste was determined by heating the dry sample B, first by means of soft flame and then the temperature raised to about 420 °C and left for overnight. This process was repeated until the sample achieved a constant weight. The organic matter content was then calculated based on the weight losses after heating [74]. The experiment was carried out in triplicate.

3.2.1.3 Density

Determination of sample density was carried out by multipycnometer (Quantachrome). Approximate 2.00 g of sample B was filled into the sample cup. The density was then calculated based on the measured pressures as shown in the calculation sheet in Appendix B. The experiment was carried out in triplicate.

3.2.1.4 Granulometric Analysis

A granulometric analysis was carried out using approximate 1 kg of the sample waste. It was performed by mechanical shaker (Pascall Engineering) which the sieves were stacking in ascending order of aperture size. The sieve sizes used in granulometric analysis were 75 μm, 150 μm, 250 μm, 500 μm, 710 μm, 1000 μm and 2380 μm. The sample was placed on the top sieve and the stack was then vibrated for 60 minutes which well enough for the screening process. The residue weight of sample on each sieve size was determined.

3.2.2 Semiconductor Waste Characterization- Chemical Properties

Generally, there were three stages involved in mineralogical analysis for determination of chemical composition of the sample. Firstly the qualitative analysis which was carried out by using x-ray fluorescence spectrophotometer, followed by quantitative analysis by energy dispersive x-ray spectrophotometer and lastly the determination of existing compounds in the sample using x-ray diffraction spectrophotometer.

3.2.2.1 X-ray Fluorescence Analysis

In this work, the qualitative analysis of semiconductor waste was carried out by using The Siemens SRS 300 X-Ray Fluorescence Spectrometer (XRF). The sample was ground to a fine powder and subsequently compressed into a circular pellet 40 mm in diameter and 2 mm in thickness. In this experiment, 3 types of analyzer crystals had been used. They were Lithiumfluoride (LiF100), Pentaerythrite (PET) and OVO-55. A continuous spectrum will show the intensity and position of each spectral line which representing the existed metal.

3.2.2.2 Energy Dispersive X-ray Analysis

The quantitative determination of elemental compositions was carried out by Philips PV 9900 Energy Dispersive X-ray (EDAX) Spectrophotometer. In this study, the sample was prepared by grinding to form fine powder and subsequently compressed into pallet form with 13 mm in diameter and 1.5 mm of thickness. The sample then treated with gold sputtering to ensure a high conductivity of the samples. The composition of each element would be given as weight percentage of total solid weight.

3.2.2.3 X-ray Diffraction Analysis

The Siemens D5000 X-ray Diffraction (XRD) Spectrophotometer was used to identify the structure and thus to determine the existing compounds in the semiconductor waste. In this study, the sample was prepared by grinding to a fine powder, which was then spread uniformly over the hole of sample plate. The experiment was running for 30 minutes in the range of $10° < 2\theta < 70°$.

3.2.3 Solid-liquid Extraction (Leaching) Experiment

In leaching experiment, four parameters were investigated such as types of leaching agent, HCl concentration, NaCl concentration and liquid/solid ratio, L/S (defined as leaching solution volume in ml over sample weight in g). The stirring speed was studied in order to understand the kinetics of the leaching process.

Throughout the experiment, the dry sample B was added into 500 ml beaker at specified L/S ratio containing 300 ml of leaching agent. The mixture was then stirred by magnetic stirring at selected stirring speed. During the stirring, 5 ml of leaching solution was withdrawn by pipette at selected time intervals (0, 1, 3, 5, 10, 15, 30, 60, 90, 120 and 180 min). This small quantity of sample taken is important to ensure that no significant changing in volume as well as solid sample. Initial study to determine the equilibrium time showed that mixing time of 15 minutes was well enough to achieve equilibrium. The samples were then separated by centrifuge (model: Hettich Zentrifuger EBA 12) at 4500 rpm for 15 minutes which was enough to separate the mixture completely. The collected supernatants were then used for metal determination by using Atomic Absorption Spectroscopy (model: Philips PU9200X). Table 3.1 is presented to summarize the experimental conditions of different sets of leaching experiment.

Table 3.1: Experimental conditions of different sets of leaching experiment

Studied parameter	Experimental condition	
	Varied	Fixed
Leaching agent type	HCl (4 M) H_2SO_4 (4 M) HNO_3 (4 M) 4 M HCl (3) + 4 M HNO_3 (1)	L/S: 200 Temperature: 29.5 °C Stirring speed: 500 rpm
HCl concentration	0.5 M, 1.0 M, 2.0 M, 3.0 M and 4.0 M	L/S: 200 Temperature: 29.5 °C Stirring speed: 500 rpm
NaCl concentration	1.0 M, 1.5 M, 2.0 M, 2.5 M and 3.0 M	L/S: 200 Temperature: 29.5 °C Stirring speed: 500 rpm Leaching medium: 0.5 M HCl
Liquid/solid ratio	60, 100, 200 and 1200	Temperature: 29.5 °C Stirring speed: 500 rpm Leaching agent: 3.0 M NaCl in 0.5 M HCl
Stirring speed	200 rpm and 500 rpm	L/S: 200 Temperature: 29.5 °C Leaching agent: 3.0 M NaCl in 0.5 M HCl

3.2.4 Liquid-liquid Extraction Experiment

Liquid-liquid extraction experiments were carried out using dithizone and Cyanex 272 for silver extraction from leached solution. The effect of pH and extractant was also studied. The pure silver system comprising of either silver chloro complexes or silver nitrate, $AgNO_3$ solutions were used in order to verify the results. However, the solubility of extractant in selected diluent was first determined in order to obtain a suitable diluent for silver extraction.

3.2.4.1 Solubility of Extractant in Diluent

The determination of extractant solubility in different diluent was studied. Initially, the solubility of dithizone in kerosene was carried out by dissolving the 0.70 g of dithizone in 250 ml of kerosene in 500 ml of conical flask. The mixture then stirred at vigorous speed for one hour. Thereafter, the saturated solution was filtered by vacuum pump and the filtrate was collected for determination of dithizone concentration. At the meantime, three standards of dithizone in kerosene with the concentration of 4.40×10^{-3} gL^{-1}, 1.00×10^{-2} gL^{-1} and 2.16×10^{-2} gL^{-1} were prepared. The calibration curve was then prepared at pre-determined wavelength of 447.5 nm using the UV-Visible Spectrophotometer (model: UV-160 Shimadzu) and the unknown dithizone concentration in kerosene was measured.

3.2.4.2 Preparation of Stock Solutions

a) Pure Silver Nitrate Solution

1000 ppm of silver nitrate solution was used as pure $AgNO_3$ solution. The required concentration of $AgNO_3$ was then prepared by diluting the certain quantity of 1000 ppm with deionized distilled water. However, these $AgNO_3$ solutions were precipitated during the pH adjustment. Therefore, these precipitates were removed by centrifugation and the collected supernatants were then used as aqueous phase and the determination of initial silver concentration was carried out using AAS.

b) Pure Silver Chloro Complex Solution

Approximately 200 ppm of Ag^+ was prepared by dissolving the 0.1145 g of AgCl in 300 ml of 0.5 M HCl-3.0 M NaCl leaching agent under vigorous stirring at 500 rpm. The solubility of the AgCl was increased by increasing the temperature to 70 °C in order to obtain the required concentration of Ag^+ at 120 minutes. The undissolved AgCl was removed from the solution by vacuum pump to ensure a constant concentration of Ag^+ in solution. The aqueous phase that used for extraction process must be cleared from any precipitate. Centrifuge was used to separate the precipitate. Since the formation of precipitate was occurred at certain pH. The initial silver concentration of each solution was determined using AAS.

c) Leaching Solution

1.5 g of sample waste was dissolved in 0.5 M HCl-3.0 M NaCl under vigorous stirring at 500 rpm for 120 min. The leaching solution was then filtrated by vacuum pump to separate the solid particles. The filtrate was then used as an aqueous phase for extraction experiment. The aqueous solution, however, must clear from any precipitate that might form during pH adjustment. The initial silver concentration of each aqueous solution was determined.

d) Dithizone in Kerosene

Saturated dithizone in kerosene solution was prepared by dissolving 0.700 g of dithizone in 250 ml kerosene. The dissolution process was conducted at 29.5 ± 0.5 °C under vigorous stirring condition. The saturated solution then filtrated by vacuum pump in order to determine the dithizone solubility. The color of the filtrate was light green.

e) Dithizone in Chloroform

The solubility of dithizone in chloroform at 30 °C is 20.3 $mgml^{-1}$ [91]. Therefore the 0.02 M dithizone in chloroform was prepared by dissolving 0.7689 g in 150 ml $CHCl_3$. The dissolution process was rapid and only need a low stirring speed to achieve a complete dissolution within 1 minute. The color of dithizone solution was in dark green.

f) Cyanex 272 in Kerosene

The initial concentration of the stock Cyanex 272 solution is 2.8385 M. In order to get the 0.02 M of Cyanex 272 in kerosene, 1.7615 ml of Cyanex 272 was diluted in kerosene using 250 ml volumetric flask. The Cyanex 272 solution was colorless.

3.2.4.3 Extraction Experiment

In extraction experiments, a series of aqueous phases were prepared comprising of different pH that adjusted by concentrated NaOH, diluted HCl or HNO_3. An additional of small portions of acid or alkaline to the solution is important to avoid any significant change of the solution volume. The solutions were then left for overnight and thereafter, separated by centrifugation at the rotating speed of 4500 rpm for 10 minutes. Only the supernatants had been used as aqueous phase for extraction processes.

Throughout the extraction experiments, 10.0 ml each of aqueous and organic solution were introduced into 50 ml separating funnel. The separating funnel then tided to the mechanical shaker (Lab-Line) for the shaking process as illustrated in Figure 3.2. 20 minutes of shaking time was enough for the extraction process to achieve equilibrium. In order to get a complete phase separation of organic and aqueous phases, the mixture was left for one hour. The aqueous samples were then taken for metal concentration determination using AAS. The metal contents of the organic phases were determined by mass balance. The pH of the initial and equilibrated aqueous phase was measured using a calibrated pH meter (model: F series of Horiba). All the extraction experiments were performed at room temperature of 29.5 ± 0.5 °C and the detail conditions of the experiments were stated in Chapter IV.

Figure 3.2: Separating funnel tided to the mechanical shaker for extraction process

3.2.5 Analytical and Spectroscopic Methods

3.2.5.1 Determination of Metal Concentrations by AAS

Metal contents of the aqueous phases were determined by Atomic Absorption Spectrophotometer, AAS (model: Philips PU9200X). Organic-phase metal contents were determined by mass balance. Five metals were considered throughout this study which consist of silver, iron, copper, stanum and calcium. Basically, the instrument was instructed by following the five-step procedures. Firstly, the turret is defined to locate the analyzed element. It followed by optical setup and flame setup to give a pathway to plot the standard calibration curve. Lastly, the instrument is readily used to determine the metal contents of the samples. Table 3.2 shows all the relevant parameters for metal determination during the setting of AAS.

Table 3.2: Instrumental setting for metal determination using AAS.

Metals	Wavelength (nm)	Flame	Calibration Curve (ppm)	Sensitivity (ppm)
Silver, Ag	328.1	Air-Acetylene	2-10	0.06
Iron, Fe	248.3	Air-Acetylene	2-10	0.12
Copper, Cu	324.8	Air-Acetylene	2-10	0.1
Stanum, Sn	224.6	Air-Acetylene	10-300	4
Calcium, Ca	422.7	Air-Acetylene	2-10	0.08

Some precautions must be taken into consideration during the analysis of sample using AAS. A preliminary experiment was conducted to study the effects of aging phenomenon and dilution factor on silver determination. The results indicate that the silver determination must be held immediately after the dilution especially for the solution containing AgCl. It is because when adding the distilled water, it will decrease the solubility of AgCl and consequently forms the cloudy solution, which indicates the existence of the AgCl. However, the results indicate that the dilution factor does not contribute to the fluctuation of reading if the analysis was conducted immediately. In metal content determination, 5 ml was withdrawn from leaching solution. The conditions of the leaching solution were assumed to be constant throughout the experiment.

3.2.5.2 Determination of Extractant Concentration by UV-visible Spectrophotometer

The concentration of dithizone in kerosene was determined using UV-visible spectrophotometer model Shimadzu UV-60. The measurement of the wavelength was first determined by measuring the absorbance of the 1.00 x 10^{-3} gL^{-1} dithizone solution at wavelength ranging from 300-700 nm. It was found that the maximum absorbance was observed at wavelength 447.5 nm. Therefore, this wavelength was used as reference wavelength in determination of dithizone concentration in the solution. The dithizone standard solutions which are 4.40 x 10^{-3} gL^{-1}, 1.00 x 10^{-2} gL^{-1} and 2.16 x 10^{-2} gL^{-1} were used. It was found that their absorbance was depended on the concentration which can be represented by the following equation.

$$C = 0.0126\,A + 0.0002 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 3.1$$

where C is the concentration in gL^{-1} and A is the absorbance.

3.2.5.3 pH Measurement

All pH measurements throughout this study were performed by pH meters (model: F series of Horiba). The pH meter was first verified with standard buffers of pH 4, pH 7 and pH 9. Then it was readily used to measure the pH of solution. During the pH measurements, the solution level must at least 5 cm from the tip of the electrode and performed under stirring condition. This has been done to ensure an accurate measurement of pH. The accuracy of pH measurement is ± 0.005.

CHAPTER IV

RESULTS AND DISCUSSIONS

4.1 Characterization of Semiconductor Waste

In order to get better understanding of the characteristics of waste sample, it is essentially to determine the physical and chemical properties of the sample. The physical properties such as water and organic contents, density and the particle size, while the chemical properties such as elemental compositions and chemical compound were analyzed in this study.

4.1.1 Physical Properties

Several physical properties such as water and organic contents, density and particle size were measured in these studies in order to determine the sample characteristics.

The water content of the sample A and sample B is 34.57 ± 0.33 % and 21.57 ± 0.09 % respectively. Between these two samples, sample B had been chosen for the whole studies considering the ease of its handling. In determination of the organic content, it was found that the sample consists of 14.73 ± 0.29 % organic matter. This organic matter might probably come from the organic solvent such as 1,1,1-

trichloroetylene used in the solder plating processing. The density of sample B was calculated based on the procedure described in Appendix B. The density of the waste is 2.87 ± 0.07 gcm^{-3}.

As stated earlier, the sample B consists of various particle sizes. In order to get particle size distribution of the sample, granulometric analysis was carried out as described in Section 3.2.1.4. The result from granulometric analysis is shown in Table 4.1. It indicates that most of the particle sizes distributed below 500 μm. By using statistical calculation (Appendix C), the mean size of the semiconductor sample is 441.01 μm. The specific surface area of the particle was calculated based on measured particle size and density, and it was found to be 47.12 cm^2g^{-1} (Appendix D). Table 4.2 shows the physical properties of the semiconductor waste.

Table 4.1: Granulometric analysis of the sample B.

Aperture width, μm	% (w/w)
0-75	16.03
75-150	19.91
150-250	16.69
250-500	19.19
500-710	8.80
710-1000	8.44
1000-2380	10.94

Table 4.2: The physical properties of the sample B.

Properties	Quantity
Water content (% w/w)	21.57
Organic content (% w/w)	14.73
Density (gcm^{-3})	2.87
Mean particle size (μm)	444.01
Specific surface area (cm^2g^{-1})	47.12

4.1.2 Chemical Compositions

The semiconductor waste consists of complex combination of various substances which can affect the extraction process. Thus, it is important to determine the chemical compositions of the semiconductor waste. In this study, three spectroscopic techniques were used sequentially starting with x-ray fluorescence, EDAX and x-ray diffraction techniques in order to determine the elemental composition and metal compounds existing in the sample. The analytical procedures used were described in Section 3.2.2.

Based on analysis of the x-ray fluorescence spectrum as given in Appendix E, it qualitatively indicates that the major element existed in the sample are copper (Cu), calcium (Ca), iron (Fe), silver (Ag) and stanum (Sn). This result however was supported and confirmed again by the quantitative analysis of EDAX which is clearly shown in Table 4.3 and EDAX spectrum in Appendix F. The silver content of the sample B is 7.55 % by dry sample weight or 5.92 % of wet sample weight. Ag, Cu and Sn were detected in the sample due to their use in electroplating process to improve the electrical contact of semiconductor components. While the existed Fe and Ca in the sample might be due to their use as coagulant in wastewater treatment process.

Table 4.3: Elemental composition of semiconductor waste sample determined by EDAX

Element	% w/w	Element	% w/w	Element	% w/w
O	21.05	S	1.37	Ca	3.44
Al	3.15	Cl	1.64	Fe	5.15
Si	0.19	Ag	7.55	Ni	1.59
P	2.07	Sn	17.83	Cu	34.96

In the x-ray diffraction study, there are some significant peaks shown in the diffractogram (Appendix G) that be able to determine the existing compounds in the sample. By using the matching techniques as shown in Table 4.4, it is successfully to identify the existing of Ag and AgCl. So, it is to be said that silver exists in the sample mostly in the form of cubical Ag and AgCl. By considering the percentage weight of Ag^+ and Cl^- as 7.55 % and 1.64 % respectively and assuming that the only silver compounds existed in the sample were Ag and AgCl, it is then found that 1.50 g of sample might contain 9.95×10^{-2} g AgCl and 3.84×10^{-2} g Ag, which the calculation is shown in Appendix I. AgCl is found in the sample resulted from the reaction of Cl^- ions produced from the cyanide decomposition and the Ag^+ ion in the solution. While the existed Ag might be due to the limitation of chloride ions available and therefore, the free Ag^+ ions are then reduced by other potential reducing agents to form Ag. However, in general, the diffractogram is very complicated and overlapping which is very difficult to analyze for other metals. These characterizations of diffractogram indicate that the sample is an amorphous.

Table 4.4: Strong lines matching of the sample and reference peaks.

Silver compounds		——— Strong lines decrease ——→				
Ag (Cubic)	Reference (Appendix H)	2.36	2.04	1.23	1.45	0.94
	Sample	2.3542	2.0392		1.4423	
AgCl (Cubic)	Reference (Appendix H)	2.77	3.20	1.96	1.67	1.60
	Sample	2.7689	3.197	1.9580		1.5992

4.2 Leaching Process

Generally, the leaching process involves dissolving the required metals existed in the ore, concentrate or process waste by a suitable reagents. It usually leaches many coexist metals into solution at the same time. In this study, the leaching experiment was designed to leach silver from the semiconductor waste and attempt to establish a selective leaching procedure was considered.

4.2.1 Effect of Leaching Agent Types

As reported in the literature, different types of leaching agents have affected the extent of solute leaching. Several types of leaching agents were studied in this work. Table 4.5 shows the effect of leaching agents on metal leaching capability and their color observation of the leaching solutions. At similar leaching agent concentration, HCl shows the highest silver leaching compared to the other leaching agents. Similar behavior is also observed for copper, stanum and calcium except iron.

Table 4.5: Effect of leaching agent types on the extent of metals leaching from semiconductor waste and color observations of the leaching solutions.

Leaching Agent	Leached metal concentration, ppm (%)*					Color observation
	Ag	Cu	Fe	Sn	Ca	
HCl (4 M)	197 (52.19)	905 (51.77)	176 (68.35)	210.2 (23.58)	14.7 (8.56)	Green yellowish
HNO_3 (4 M) (1) + HCl (4 M) (3)	167 (44.24)	886 (50.69)	258 (100.00)	164.2 (18.42)	0.0 (0.00)	Green yellowish
HNO_3 (4 M)	132 (34.97)	843 (48.23)	252 (97.86)	58.4 (6.55)	0.0 (0.00)	Grey
H_2SO_4 (4 M)	116 (30.73)	850 (48.63)	258 (100.00)	65.6 (7.36)	0.0 (0.00)	Grey

* Values in brackets are % of metals leached

Hydrochloric acid shows a good leaching power for silver because of the existence of free chloride ions produced by HCl. These Cl^- ions can increase the solubility of AgCl and Ag by forming silver chloro complexes according to the following reactions [41,66],

$$AgCl + nCl^- \rightarrow AgCl_{n+1}^{-n}$$

$$Ag + nCl^- \rightarrow AgCl_n^{-(n-1)} + e$$

However, the effect of chloride ion on silver leaching is observed decrease when replacing with HNO_3-HCl. But it still performs better silver leaching compared to HNO_3. This result again indicates the important of chloride ion on silver leaching from the semiconductor waste.

HCl is the best leaching agent among the others, however, the silver leaching is only achieved at 52.19 %. The low percentage of silver leaching might due to the limitations of the available of free chloride ions contributed by HCl. Based on data obtained from Dinardo and Dutrizac [41], it showed that the AgCl solubility in 4.0 M HCl at 30 °C should be 428.47 ppm. However, the value obtained from the experiment shows only 197 ppm. It suggests that the free chloride ions contributed by dissociation of HCl are limited or the free Cl^- might react with other metal compound that coexisted in the sample. One of the possibilities is the formation of copper chloro complexes by the reaction of Cl^- with the coexisted $CuCl_2.2H_2O$ in the sample. It is because, during the leaching process by either HCl or HNO_3-HCl, the green yellowish solution was observed. This green yellowish solution occurred due to the presence of complex anion $[CuCl_4]^{2-}$ (yellow) and complex cation $[Cu(H_2O)_4]^{2+}$ (blue), both are in equilibrium [101]:

$$2[Cu.4H_2O]Cl_2 \Leftrightarrow [Cu(H_2O)_4]^{2+} + [CuCl_4]^{2-} + 4\ H_2O$$

Apparently, the chloride ions which might increase the solubility of Ag and AgCl were partially reacted with other compounds and consequently reduced the concentration of Cl^- available for the formation of soluble silver chloro complexes.

In the case of HNO_3, 34.97 % of silver leaching is obtained. This can be explained by referring to the initial content of silver in the sample where 1.50 g of sample contain 3.84×10^{-2} g of Ag and 9.95×10^{-2} g of AgCl (assume that silver existed only in these two forms). In this case, the formation of silver chloro complex does not occur since the Cl^- was not present. Therefore the solubility of AgCl in HNO_3 is assumed equally to the solubility of AgCl in H_2O as 4.85 ppm [41]. This assumption was proved correctly when pure AgCl dissolved in 4.0 M HNO_3 was able to produce 5.00 ppm only. However, in excess of NO_3^-, the anions might react totally with existed amount of Ag to form soluble $AgNO_3$ which theoretically, produces the leached silver concentration of 128.01 ppm. The reaction is shown below [101],

$$3Ag + 4HNO_3 \rightarrow 3AgNO_3 + 2H_2O + NO$$

Thus, the total solubility of silver in HNO_3 system might contain 132.86 ppm which is in agreement with the value obtained by experiment (132 ppm). This also proves that silver exists in the form of Ag and AgCl in the semiconductor waste sample.

In the leaching system performed by H_2SO_4 (4.0 M), the leaching percentage of silver from the waste is only 30.73 %. This probably due to the formation of solid Ag_2SO_4 which dissolves extremely slow according to the following reaction [60,69],

$$2Ag + 2H_2SO_4 \rightarrow Ag_2SO_4 + 2H_2O + SO_2$$

Apart from that, the low solubility of AgCl in H_2SO_4 medium also contributes to the low silver leaching. It was reported that the solubility of AgCl in 4.0 M H_2SO_4 is less than 50 ppm [102]. Therefore, the extractability of H_2SO_4 in silver leaching is the lowest among these four types of leaching agents.

HCl is a good leaching agent on silver removal from the semiconductor waste. However, in term of selectivity, HCl could not provide an appreciable criterion. It has leached along the other undesirable metals such as Cu, Fe, Sn and Ca. But still, among the four types of leaching agent, HCl shows selectivity on silver leaching over iron metal. It is important since the presence of iron metal in leaching solution might affect the efficiency of silver liquid-liquid extraction process using extractants such as Cyanex 272 and dithizone.

4.2.2 Effect of Hydrochloric Acid Concentration

As discussed above, the extent of silver leaching was mainly due to the presence of Cl^- ions. Therefore, in order to understand the effect of these Cl^- ions on silver leaching, the study on the effect of HCl concentration was carried out. Figure 4.1 is presented to show the effect of HCl concentration on silver leaching. The results show that the extent of silver leaching increases fairly gradually to about 2.0 M HCl, but thereafter rises rapidly with increasing the acid concentration.

The increase of silver leaching is due to the dissolution of AgCl in chloride medium as a result of the progressive formation of soluble silver chloro complexes which can be shown by the following reactions:

$$AgCl + Cl^- \Leftrightarrow AgCl_2^-$$

$$AgCl_2^- + Cl^- \Leftrightarrow AgCl_3^{-2}$$

$$AgCl_3^{-2} + Cl^- \Leftrightarrow AgCl_4^{-3}$$

However, these reactions involve very low equilibrium constant [41]. Therefore, in this study, it found that a concentrated chloride solution is required (more than 2.0 M) to achieve any significant silver solubility. At this high Cl^- concentration, the equilibrium is forced to generate more soluble silver chloro complexes which follow the Le Chatelier principles.

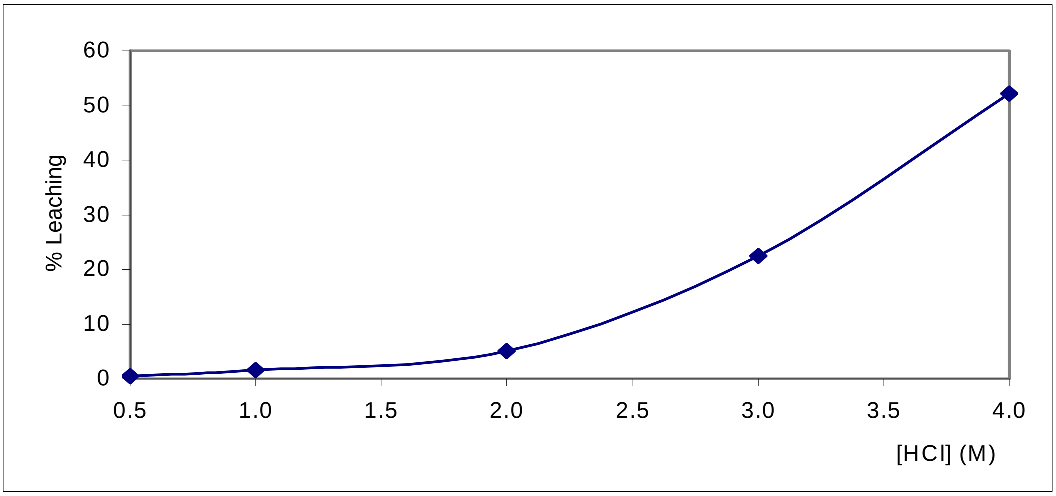


Figure 4.1: Effect of HCl concentration on the extent of silver leaching. The conditions used were: L/S of 200, stirring speed of 500 rpm and 29.5 °C .

4.2.3 Effect of Sodium Chloride Concentration

Although concentrated HCl could leach high extent of silver from semiconductor waste, it is not preferable in industrial application. It is because the concentrated HCl can cause a serious corrosion problem to the piping. Thus, chloride source was replaced by sodium chloride. The effect of NaCl concentration on silver leaching was investigated and the results is presented in Figure 4.2.

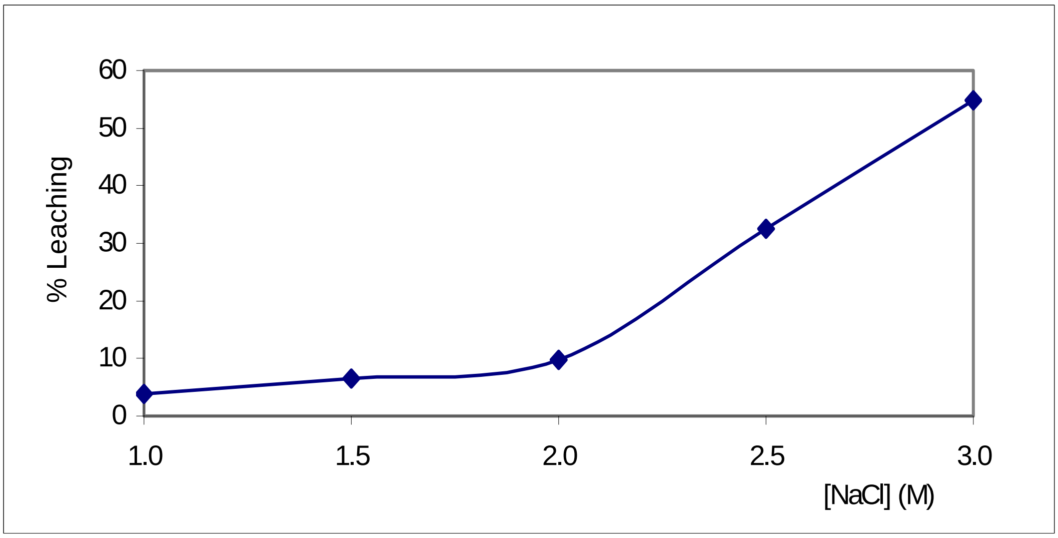


Figure 4.2: Effect of NaCl concentration on the extent of silver leaching. The experimental conditions used were 0.5 M HCl at L/S of 200, 500 rpm of stirring speed and 29.5 °C .

From Figure 4.2, the silver leaching behaviour in HCl-NaCl system is similar to HCl leaching medium. This suggests that the basic mechanism of the formation of soluble silver chloro complexes is not influenced by the addition of cationic ion from sodium chloride salts. As reported by Dinardo [41], the commercial $FeCl_3$ leaching medium would likely contain more than 2.0 M NaCl to give substantial increase of AgCl solubility. This is in agreement with the results obtained from the experiment as shown in Figure 4.2. It shows that the effect of NaCl concentration on silver leaching is significantly at higher NaCl concentration (> 2.0 M NaCl).

4.2.4 Comparison between HCl and HCl-NaCl Leaching Systems

The results presented above indicated consistently the importance of concentrated chloride ions of HCl and HCl-NaCl for high silver leaching. But there are still some aspects should be looked into between these two leaching systems which help to clarify the leaching behavior. Therefore, the following discussion will try to compare the HCl and HCl-NaCl leaching systems in three aspects: effect of total chloride concentration contributed by these two different systems on silver leaching, effect of other metals, and the selectivity of these two systems.

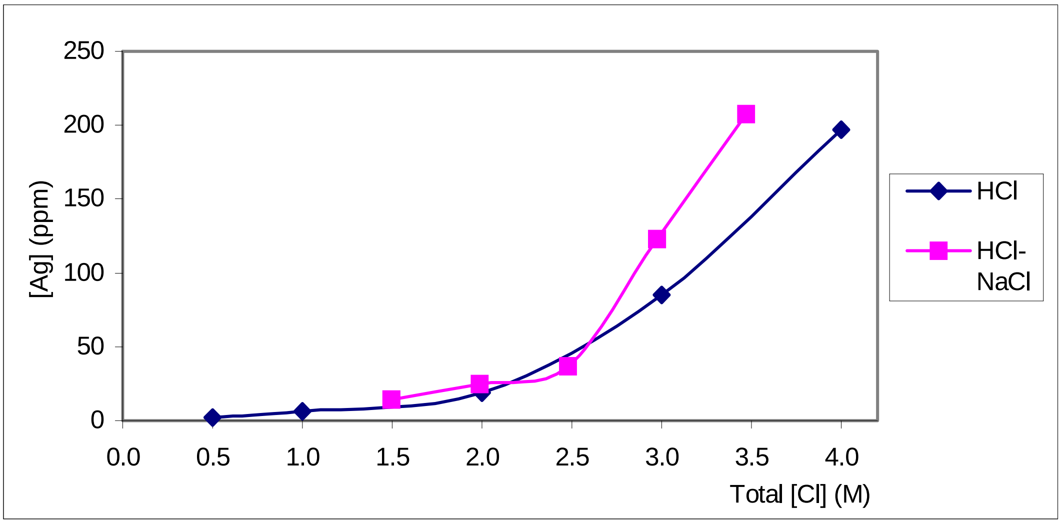


Figure 4.3: Effect of total Cl^- concentration contributed by HCl and HCl-NaCl on silver leaching.

Figure 4.3 shows the leached silver concentration as a function of total chloride concentration for different leaching systems. The total chloride concentration was calculated based on the assumption that HCl and NaCl dissociated completely and did not involve any chemical reactions between these two electrolytes. From Figure 4.3, a similar behavior on silver leaching is observed between these two systems especially at the chloride concentration below 2.5 M. Then the silver leaching rises more rapidly by HCl-NaCl compared to HCl system at higher chloride ions concentration. Based on this observation, it can generally conclude that H^+ ions do not play a direct role in the leaching reaction of Ag and AgCl. Hence, the influence of HCl on the leaching reaction is probably related to its effect on the total chloride concentration in the solution. However, in term of total chloride contributed by these two leaching systems, HCl-NaCl produces much higher of free Cl^- ions compared to HCl system. It is because at the same Cl^- concentration, HCl-NaCl performs very well on silver leaching due to the increment of formation of soluble silver chloro complexes. It was found that, at concentrated Cl^- ions, HCl has leached high amounts of other metal compounds compared to HCl-NaCl system, which in turn forming the soluble complex with free Cl^-. And the lack of free Cl^- available in HCl leaching medium might reduce the formation of soluble silver chloro complex which leads to low silver leaching as found in Figure 4.3 by HCl medium.

During the leaching process performed by HCl and HCl-NaCl leaching medium, other coexisted metals in sample were also being leached into solution. Their behaviors in these two mediums are separately illustrated in Figure 4.4 and Figure 4.5.

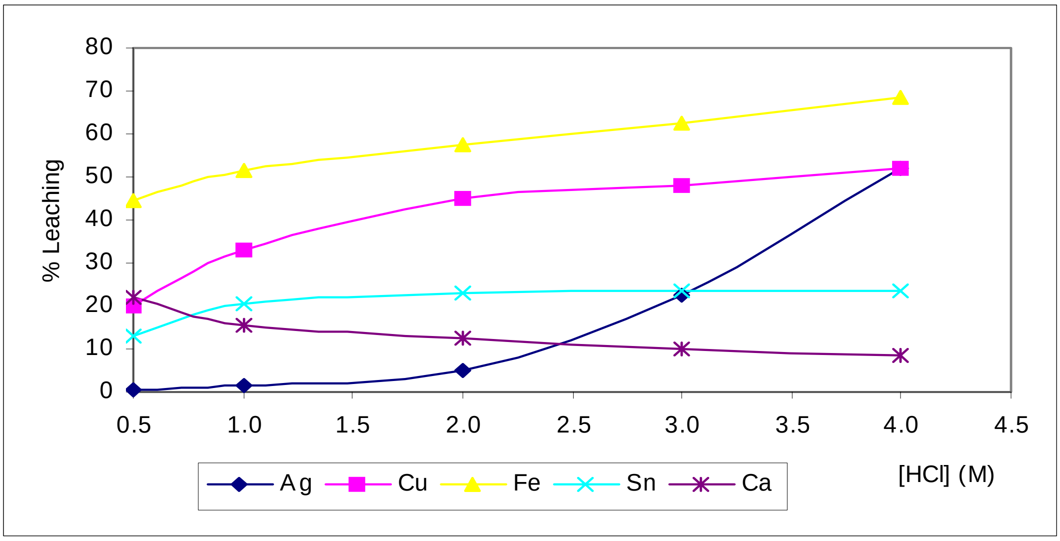


Figure 4.4: Effect of HCl concentration on the extent of metals leaching at 200 of L/S, 500 rpm and 29.5 °C.

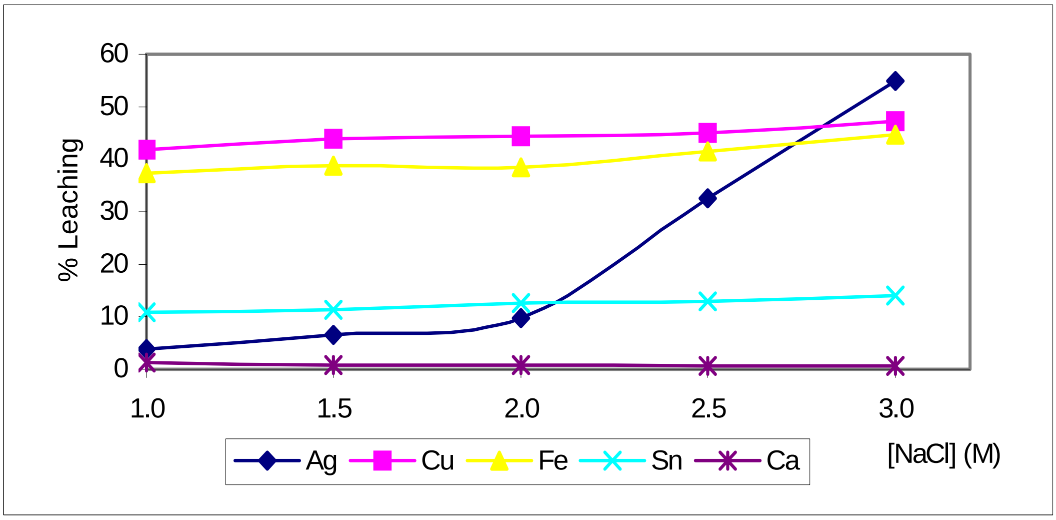


Figure 4.5: Effect of NaCl concentration on the extent of metals leaching in 0.5 M HCl at 200 of L/S, 500 rpm and 29.5 °C.

By comparing these two figures, acid has affected the metal leaching especially iron and copper. It is because at constant acid concentration (0.5 M) of HCl-NaCl leaching system, the percentages of these metal leachings are almost constant. But when increasing the acid concentration, these metal leachings have increased accordingly as shown in Figure 4.4. It suggests that most of these metals in sample wastes must be in the form of hydroxides, which are readily leached by acid. However, in this regard, we must consider the high copper leaching is also observed even at low acid concentration of 0.5 M HCl-1.0 M NaCl as illustrated in Figure 4.5. It could be explained that the copper compounds are partially existed in the form of chloro species which react with Cl^- to form soluble complexes. Therefore, the percentage copper leaching achieves more than 40 % at 0.5 M HCl-1.0 M NaCl compared to 20 % at 0.5 M HCl which is in lower Cl^- concentration. Based on this explanation, again, we might say that the low silver leaching at lower Cl^- concentration is possibly affected by limited free Cl^- available. It is because, at this limited circumstances, high concentration of $CuCl_2.2H_2O$ will compete with Ag or AgCl to form soluble complexes of $[Cu(H_2O)_4]^{2+}$ and $[CuCl_4]^{2-}$.

HCl-NaCl leaching system has proved to be efficient for silver leaching from semiconductor waste. Apart from that, the use of low concentration of acid mixed with NaCl provided a more selective process on silver leaching compare to HCl alone. For instance, 4.0 M HCl provides the percentage leaching of Ag, Cu, Fe, Sn and Ca as 52.18, 51.77, 68.35, 23.58 and 8.56 % respectively. However, 0.5 M HCl-3.0 M NaCl provides the 54.89 % of silver, 47.31 % of Cu, 44.66 % of Fe, 14.10 % of Sn and 0.60 % of Ca. It shows that at similar chloride concentration, HCl-NaCl leaching system has successfully increased the silver leaching and at the same time reduced the undesired metals which leached together with silver metal.

4.2.5 Effect of Liquid/Solid Ratio

The effect of the liquid/solid ratio (defined as the ratio of leaching solution volume in ml to sample weight in g) on metal leaching is shown in Table 4.6. The results are clearly show that decreasing the liquid/solid ratio would increase the metals leaching. As we know, leaching mechanism is partly controlled by the gradient of the silver in the system. Hence, by increasing the sample quantity, it will give rises to the silver gradient and encourage the transfer of silver from solid into bulk solution by an appropriate chemical reaction. However, if too much sample has been used, it might create the perturbation of high concentration of other coexisted metals which leached along with silver ions as shown in Table 4.6. These metals might affect the silver extraction process.

Table 4.6: Effect of liquid/solid ratio on the extent of metals leaching.

Sample weight (g) in 300 ml of leaching agent	L/S	Leached Metal Concentration (ppm)				
		Ag	Cu	Fe	Sn	Ca
0.25	1200	39.7	197.0	22.0	54.3	0.0
1.50	200	206.0	815.0	113.0	118.9	0.9
3.00	100	291.0	1583.0	214.0	251.6	1.7
5.00	60	281.0	2407.0	349.0	266.7	5.6

Figure 4.6 is presented to illustrate the correlation between percentage of metal leaching and L/S ratio. The percentage of metal leaching was calculated based on the data stated in Table 4.7. Figure 4.6 shows that increasing in L/S results increasing in the leaching percentage of metals. A sharp increases in silver leaching was observed from 60 to 200 of L/S. This observation shows that by increasing the L/S would avoid any impediment circulation of the particle in the bulk leaching solution that might affect the transfer of solute into bulk solution. Therefore, in the leaching process, high L/S is necessary to ensure a complete solute transferring by mixing process. In this study, the required L/S ratio is at least at L/S of 200.

Table 4.7: Metal concentration leached completely by 300 ml of 0.5 M HCl-3.0 M NaCl leaching agent using different weight of sample.

Solid weight (g) in 300 ml leaching agent	Leached Metal Concentration (ppm)				
	Ag	Cu	Fe	Sn	Ca
0.25	62.9	291.3	42.9	148.6	28.7
1.50	377.5	1748.0	257.5	891.5	172.0
3.00	755.0	3496.0	515.0	1783.0	344.0
5.00	1258.3	5826.7	858.3	2971.7	573.3

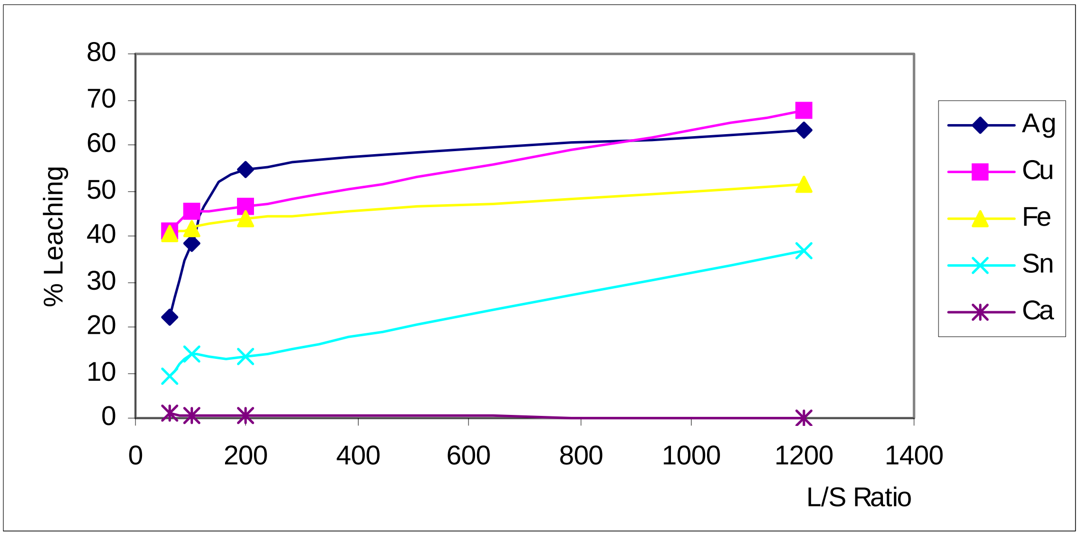


Figure 4.6: Effect of L/S ratio on the extent of metals leaching in 0.5 M HCl-3.0 M NaCl at 500 rpm and 29.5 °C.

4.2.6 Kinetics of Leaching Process

The kinetic study of leaching process gives an indication on how fast the leaching process attains the equilibrium state and how the reaction might occur during the leaching process. The study will be discussed and concentrated on several aspects. Firstly, factors affecting the kinetics of leaching process followed by the kinetic modeling and lastly, the development of the possible mechanistic model for silver leaching from semiconductor waste.

4.2.6.1 Factors Affecting the Leaching Kinetics of Silver

The kinetics of silver leaching from semiconductor waste is affected by several parameters which include leaching agent types, HCl and NaCl concentrations, liquid/solid ratio and stirring speed of leaching process. Therefore, the following discussion will try to look into these effects which will help to clarify the mechanistic behavior of silver leaching. Basically, the leaching kinetics of silver from semiconductor waste was attained equilibrium rapidly at 500 rpm of stirring speed. With the available data, the following kinetic study will consider until the leaching time of 60 seconds.

a) Effect of Leaching Agent Types

Figure 4.7 and Table 4.8 are presented to illustrate the effect of leaching agent types on silver leaching and initial rate of leaching from semiconductor waste. The silver leaching process attains equilibrium even at 60 seconds indicating that the silver leaching reaction is rapid. Apart from that, Figure 4.7 also indicates that the acid anions affect the kinetics of silver leaching. Chloride anions from HCl are enhancing the kinetics of silver leaching process compared to other anions. It is because Cl^- ions are take part in the formation of soluble silver chloro complex and thus increase the initial rate of silver leaching as shown in Table 4.8.

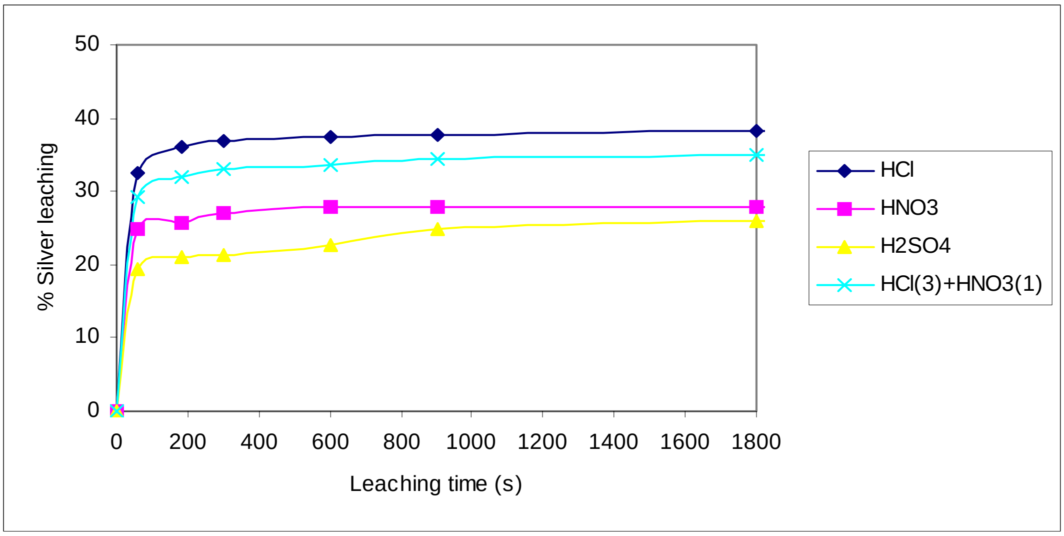


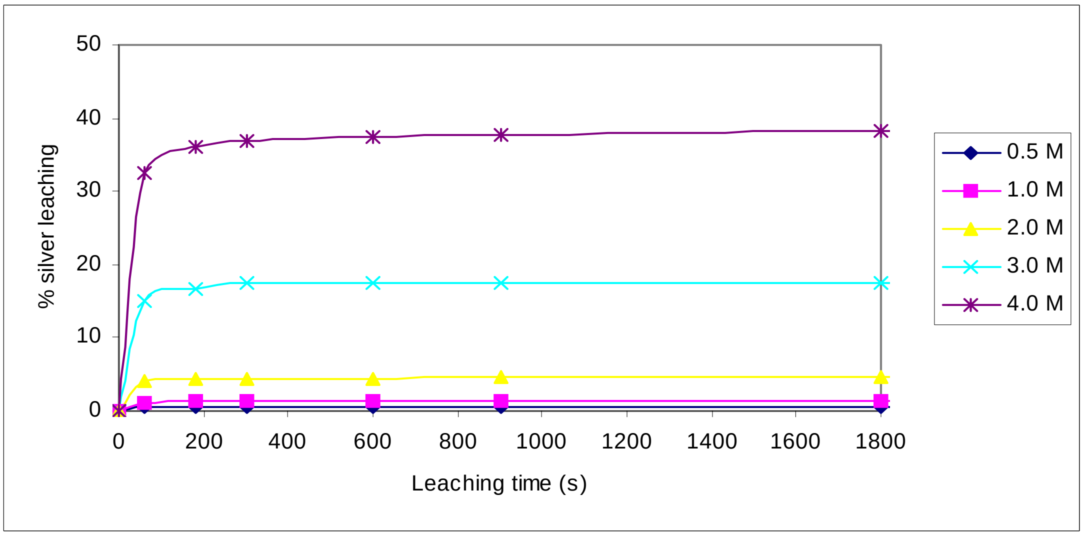
Figure 4.7: Effect of leaching agent types on the extent of silver leaching at 500 rpm, 29.5 °C and 200 of L/S.

Table 4.8: Initial rate of silver leaching from different type of leaching agents.

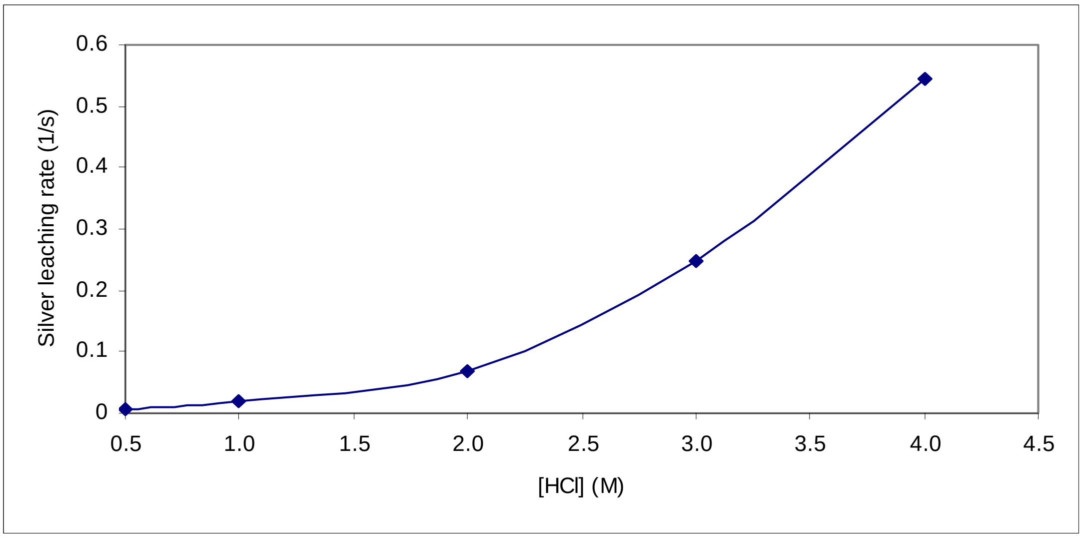
Leaching agents	Initial silver leaching rate (s^{-1})
HCl	0.543
HCl (3) + HNO_3 (1)	0.486
HNO_3	0.415
H_2SO_4	0.322

b) Effect of HCl Concentration

In order to investigate the effect of Cl^- on silver leaching kinetics, Figure 4.8 is presented to illustrate the effect of HCl concentration on silver leaching rate. Figure 4.8(b) shows an exponential correlation between the initial leaching rate and HCl concentration. A significant effect of acid concentration is observed at the concentration higher than 2.0 M. It gives an indication that the leaching rates are readily affected by the high concentration of reactant either the H^+ or Cl^- ions that surrounding the surface of the sample particles. The higher gradient of the reactant concentration between the surface and bulk solution will increase the leaching rate of the solute from solid. It is because, when the H^+ or Cl^- is increased in bulk solution, the driving force of these species diffuse to the surface will increase accordingly. Therefore, the leaching rate is increased. As found previously, the low leaching rate of silver below 2.0 M of HCl concentration, might due to the limitation of the available free chloride ions. It is because the existence of chloro copper species has competed with silver compound to form soluble chloro complex.



(a)



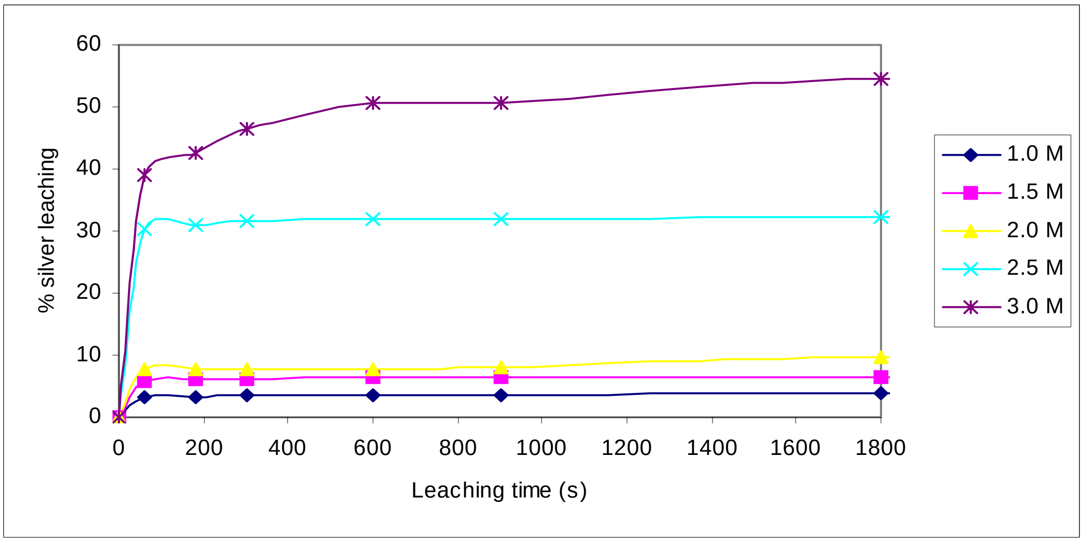
(b)

Figure 4.8: (a) Effect of HCl concentration on the extent of silver leaching at different leaching time. (b) Effect of HCl concentration on the initial leaching rate of silver at temperature, 29.5 °C; stirring speed, 500 rpm; L/S, 200.

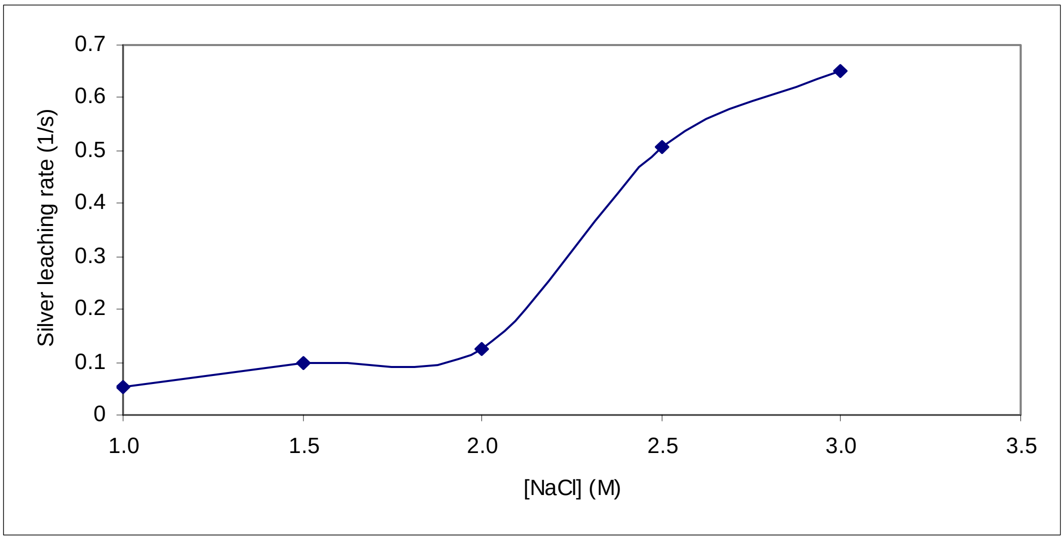
c) Effect of NaCl Concentration

Figure 4.9 (a) illustrates the effect of NaCl concentration on silver leaching at different leaching time while Figure 4.9 (b) shows the initial silver leaching rate at various concentration of NaCl in 0.5 M HCl. A similar behaviour is observed both in Figure 4.8 (b) and Figure 4.9 (b). It indicates that the existence of H^+ does not give an appreciable variance on silver leaching kinetics. It is because at constant H^+ concentration, HCl-NaCl still be able to increase the rate of silver leaching. Apparently, the total chloride contributed by either HCl or NaCl is directly influences the rate of silver removal from solid sample.

From Figure 4.8 (b) and Figure 4.9 (b), HCl-NaCl leaching system provides higher silver leaching rate compared to HCl alone at the same total chloride concentration. It could be explained that the strength of Na^+ to draw the anion of silver chloro complex away from particle surface is much higher than H^+. Therefore, the silver leaching rate increases in the existence of NaCl. Thus, from the curves of Figure 4.8 (b) and Figure 4.9 (b), suggest that the minimum chloride concentration required to achieve a significant leaching rate of Ag and AgCl is 2.0 M.



(a)



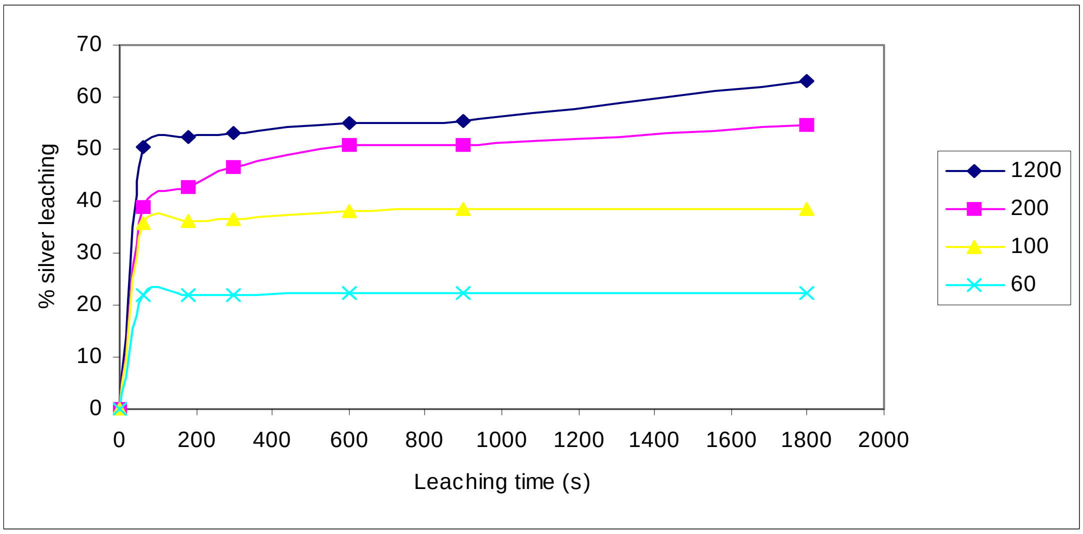
(b)

Figure 4.9: (a) Effect of NaCl concentration on the extent of silver leaching at different leaching time. (b) Effect of NaCl concentration on the initial leaching rate of silver. Experimental conditions: Leachant, 0.5 M HCl; temperature, 29.5 °C; stirring speed, 500 rpm; L/S, 200.

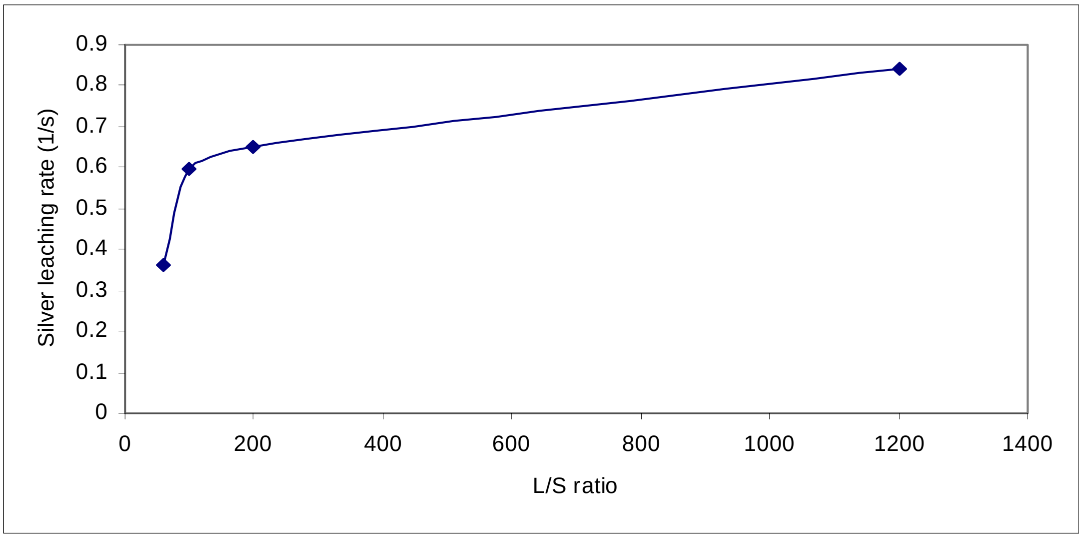
d) Effect of Liquid/Solid Ratio

Generally, the initial solute content in solid particle will affect the leaching process of the solute. Therefore, in order to understand this phenomenon, the effect of liquid/solid ratio was carried out. The result is presented in Figure 4.10. Figure 4.10 (b) illustrates the function of initial leaching rate to L/S ratio. It shows a proportional effect of liquid/solid ratio on silver leaching rate. However, the rate is increased rapidly at low L/S ratio but gradually from 100 to 1200 of L/S ratio.

The above phenomenon explains that when at the constant concentration of Cl^- reactant, the increase of silver content will reduce the rate of silver leaching due to insufficient available free Cl^- ions around the sample particle. Furthermore, at high solid content in the leaching system, it might reduce the efficiency of mixing process due to the impediment of particle circulation. As a result, the leaching rate is reduced as observed in Figure 4.10 (b).



(a)

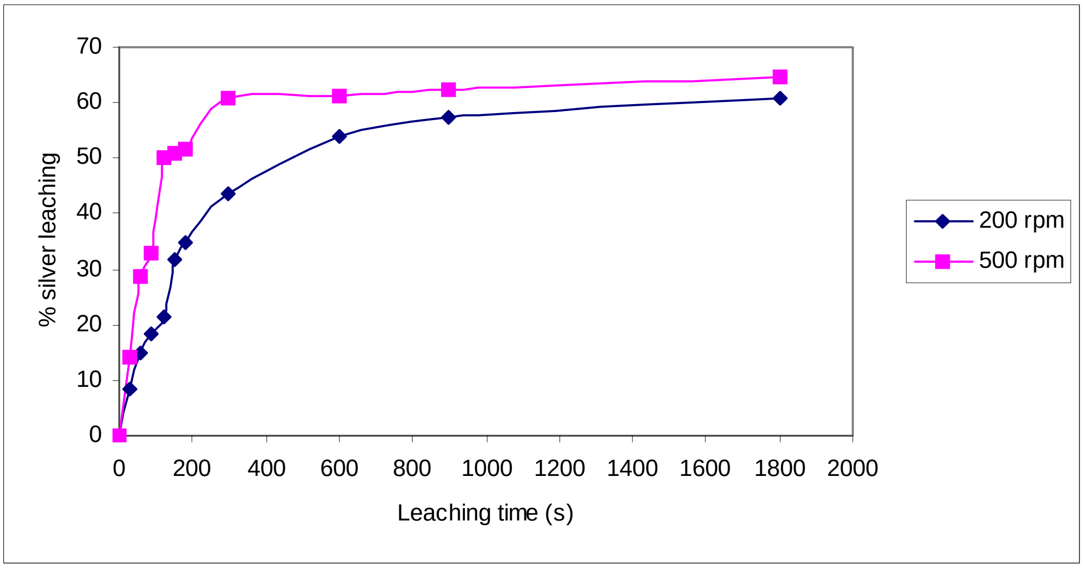


(b)

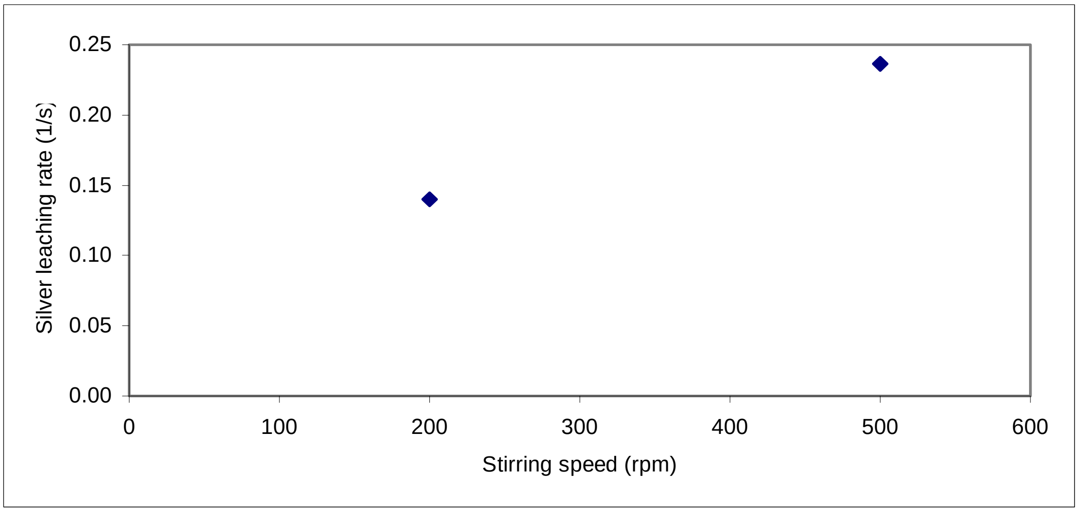
Figure 4.10: (a) Effect of L/S ratio on the extent of silver leaching at different leaching time. (b) Effect of L/S ratio on the initial leaching rate of silver. Experimental conditions: Leachant, 0.5 M HCl-3.0 M NaCl; temperature, 29.5 °C; stirring speed, 500 rpm.

e) Effect of Stirring Speed

Figure 4.11 illustrates the effect of stirring speed on silver leaching. Figure 4.11 (b) shows that the initial silver leaching rate increases with increasing in stirring speed. It is consistently with the correlation of mass transfer coefficient, K depends on Reynolds number, Re [79] and Re is proportional to stirring speed [80]. The linear dependence of rate on stirring speed suggests that the leaching process of silver might control by the diffusion of some species through the liquid boundary layer adjacent to the surface of the stirred particles or the diffusion of product species out from the surface. Based on the film theory, the simplest theory of interfacial mass transfer assumes that a stagnant film exists near every interface [103]. This film also called an "unstirred layer". When the stirring speed increases, it will reduce this stagnant layer. Hence, the distance of reactant species diffused inward surface or product diffused outward from surface will be decreased. As a result, it seem that the rate of silver leaching will be increased.



(a)



(b)

Figure 4.11: (a) Effect of stirring speed on the extent of silver leaching at different leaching time. (b) Effect of stirring speed on the initial silver leaching rate. Experimental conditions: Leachant, 0.5 M-3.0 M NaCl; temperature, 29.5 °C; L/S, 200.

4.2.6.2 Kinetic Modeling of Silver Leaching Process

a) Model Description and Selection

Kinetic modeling is used to predict and describe the actual kinetics of the process. In this study, attempts to describe the leaching of silver from semiconductor waste will be carried out. Five selected models from literature that stated in Table 4.9 were used to fit the experimental data in order to develop the kinetics of the silver leaching process. Among these five models, two of them have been developed with the assumption that the silver dissolution controlled by chemical reaction, while the other three as diffusion controlled models. Details of these models however have been reviewed in Section 2.4.4.1.

Table 4.9: Summary of the five selected kinetic leaching models.

Kinetic Model			Designation
Chemical Reaction Control	$1-(1-\alpha)^{1/3} = (V_mCk_ok'/r_o)t$	$\alpha = 1-[1-(V_mCk_ok't/r_o)]^3$	Model 1
	$1-(1-\alpha)^{1/3} = (k_sC/b\rho_Br_o)t$	$\alpha = 1-[1-(k_sCt/b\rho_B r_o)]^3$	Model 2
Diffusion Through Liquid Film Control	$1-(1-\alpha)^{1/3} =(CV_mD/\delta br_o)t$	$\alpha = 1-[1-(CV_mDt/\delta br_o)]^3$	Model 3
	$1-(1-\alpha)^{2/3} =(2CD/b\rho_Br_o^2)t$	$\alpha = 1-[1-(2CDt/b\rho_Br_o^2)]^{3/2}$	Model 4
	$\ln (1-\alpha) = -(KA/V)t$	$\alpha = 1-\exp[-(KAt/V)]$	Model 5

As described earlier, these models have been developed using different approaches. Therefore, the selection of the representative model of the silver leaching kinetics from semiconductor waste will consider several factors, such as chemical or diffusion control, effect of stoichiometric and diffusion thickness on silver leaching. Throughout this kinetic study, several assumptions are made. They are:

a) The particles are essentially spherical with the same initial radius;
b) The surface roughness factor does not change during leaching;
c) Ag and AgCl compounds existed in the sample;
d) The reaction involves the chloro complexation of the silver.

i) Chemical versus Diffusion

Initially, each of the kinetic models with their parameters that had been defined in Appendix J is plotted as conversion against leaching time. Figure 4.12 illustrates the behaviour of Model 1 to Model 5 along with the silver leaching experiment data. The experiment data was obtained at 200 of L/S ratio and 200 rpm of stirring speed using 0.5 M HCl-3.0 M NaCl leaching medium. Analysis of the silver leaching data given in Figure 4.12 shows that the experimental data deviates greatly from Model 1 and Model 2, but close to the diffusion-controlled models. So, it suggests that the silver leaching kinetics under chloride medium could be possibly controlled by diffusion through liquid boundary layer rather than chemical reaction.

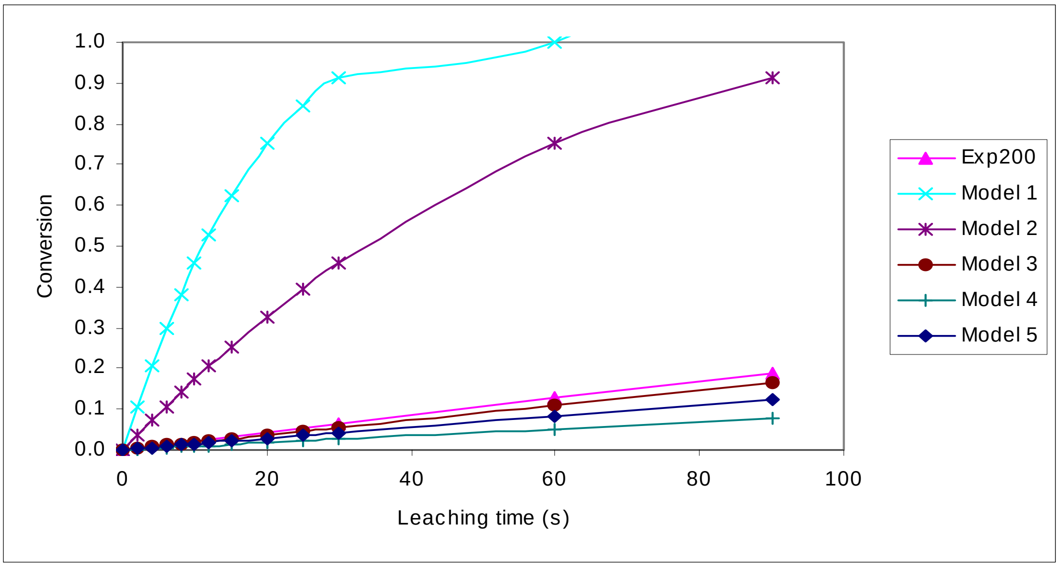


Figure 4.12: A comparison of conversion at various leaching time for different models and experimental data.

ii) Effect of Stoichiometric Factor

From the Figure 4.12, though the Model 3 correlates well with the experimental data, there is still no assurance to eliminate the possibility of Model 4 to be the selected kinetic model. It is because the unknown stoichiometric factor that involved in the equation has not been well defined. However, the elimination of Model 5 is reasonable due to its high deviation from the experimental data. Moreover, there are no other undefined parameters that can be studied in this model.

Figure 4.13 tries to investigate the effect of stoichiometric factor of Model 4 on silver leaching process. From the previous discussion, the silver leaching process needs a high concentration of chloride medium to achieve any significant dissolution. Dutrizac [41] has reported that in the concentrated chloride medium, the dominant form of silver chloro complex is $AgCl_4^{3-}$. Therefore, the silver leaching reaction might involve a high stoichiometric factor to form $AgCl_4^{3-}$. However, by the illustration of Figure 4.13, it is clearly indicates that the Model 4 is unacceptable to be the kinetic model for silver leaching process from semiconductor waste. It is because the experimental data is only fitted between the low stoichiometric factor of 1 and 2.

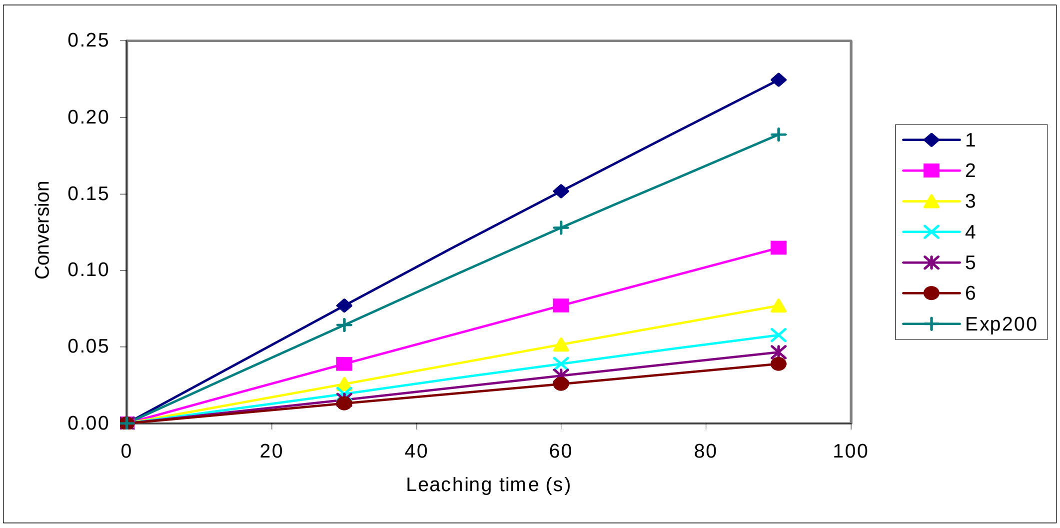


Figure 4.13: Effect of stoichiometric factor on conversion at various leaching time for Model 4.

Further investigation was carried out on the effect of stoichiometric factor on Model 3 and their correlation are presented in Figure 4.14 with the assumption that the diffusion thickness to be 1 x 10^{-4} m, an approximate thickness for the unstirred condition [78]. Figure 4.14 indicates that the silver leaching reaction is preferable with the formation of silver chloro complexes, $AgCl_3^{2-}$, $AgCl_4^{3-}$ which generally described by the following reactions:

$$Ag + 3Cl^- \rightarrow AgCl_3^{2-} + e$$

$$AgCl + 3Cl^- \rightarrow AgCl_4^{3-}$$

The result is in agreement with the results reported by Dinardo and Dutrizac [41].

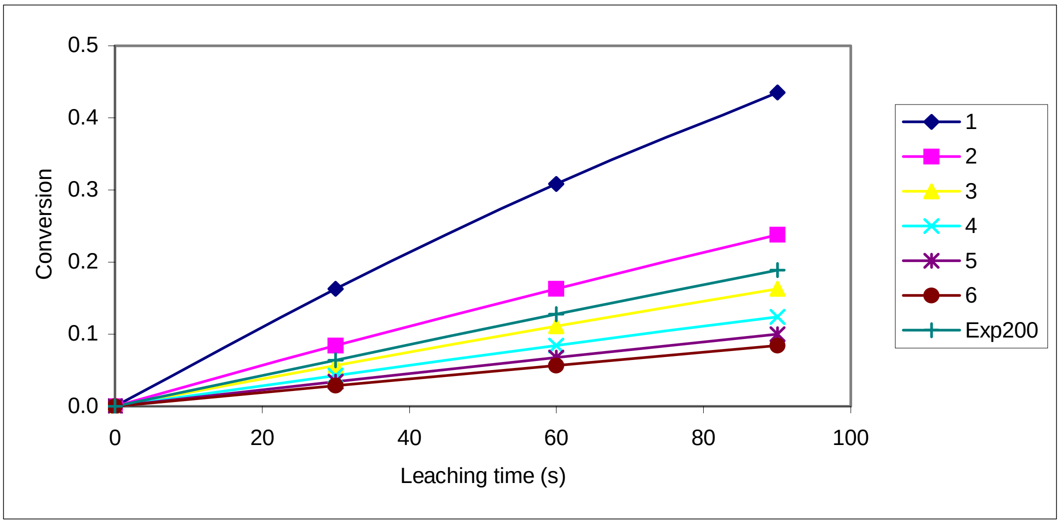


Figure 4.14: Effect of stoichiometric factor on conversion at various leaching time for Model 3.

iii) Effect of Diffusion Thickness (Stirring Speed)

Interpretation of silver leaching reaction has been moderately described using Model 3. However, the selection of Model 3 has not been decided without studying the effect of diffusion thickness. Therefore, the next analysis was carried out on the effect of diffusion thickness on silver leaching kinetics. Sohn and Wadsworth [78] have reviewed that the diffusion boundary in unstirred solutions was approximately 0.05 cm and diminishing to approximately 0.001 cm under condition of violent agitation. By using this range of thickness and the value of stoichiometric factor as 3 fitted into Model 3, the $1-(1-\alpha)^{1/3}$ against leaching time at different thickness is given in Figure 4.15.

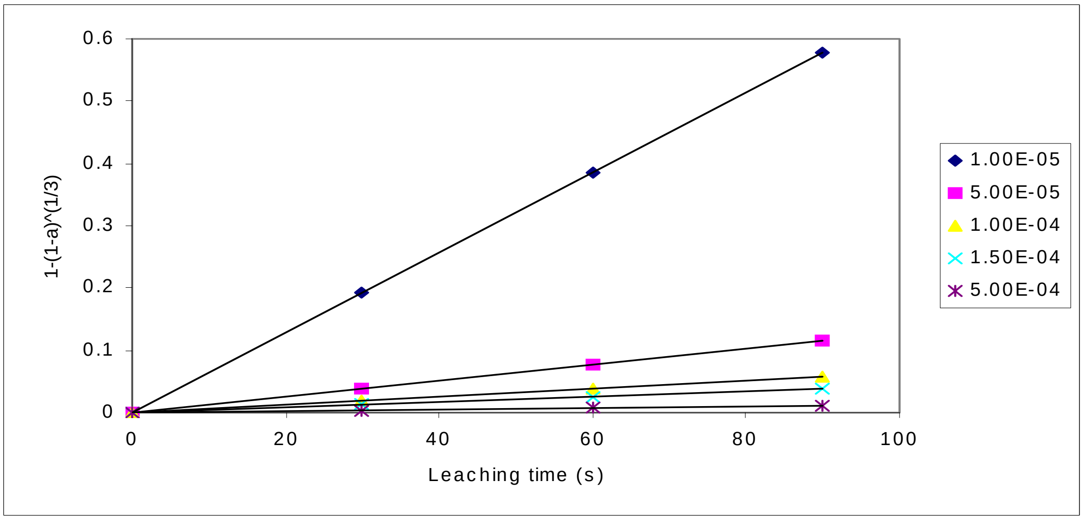


Figure 4.15: Effect of diffusion thickness on silver leaching under 0.5 M HCl-3.0 M NaCl (Theoretical correlation of Model 3).

Figure 4.15 illustrates the theoretical correlation between the diffusion thickness, δ and rate constant, k_i (slope) based on Model 3, which the derived k_i are then plotted against the boundary thickness shown in Figure 4.16. From the linear regression analysis, the correlation between k_i and δ is given by

$$k_i = \frac{6.4 \times 10^{-8}}{\delta} - 1.05 \times 10^{-6} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \; 4.1$$

which indicates that the rate constant is inversely proportional to the diffusion thickness.

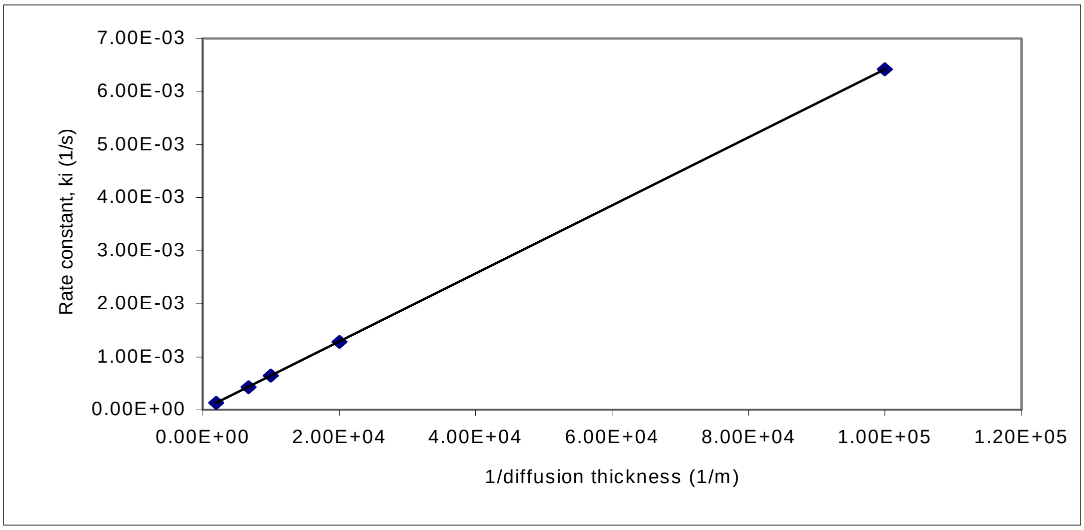


Figure 4.16: Linear correlation between 1 / diffusion thickness and the rate constant based on Model 3.

Generally, as stirring speed is increased, it reduces the diffusion boundary layer adjacent to the solid surface and affects the rate constant of the leaching process. Therefore, in order to understand the effect of stirring speed on rate constant, a series of experiments at different stirring speed were carried out. The data is presented in the form of $1-(1-\alpha)^{1/3}$ versus leaching time as shown in Figure 4.17.

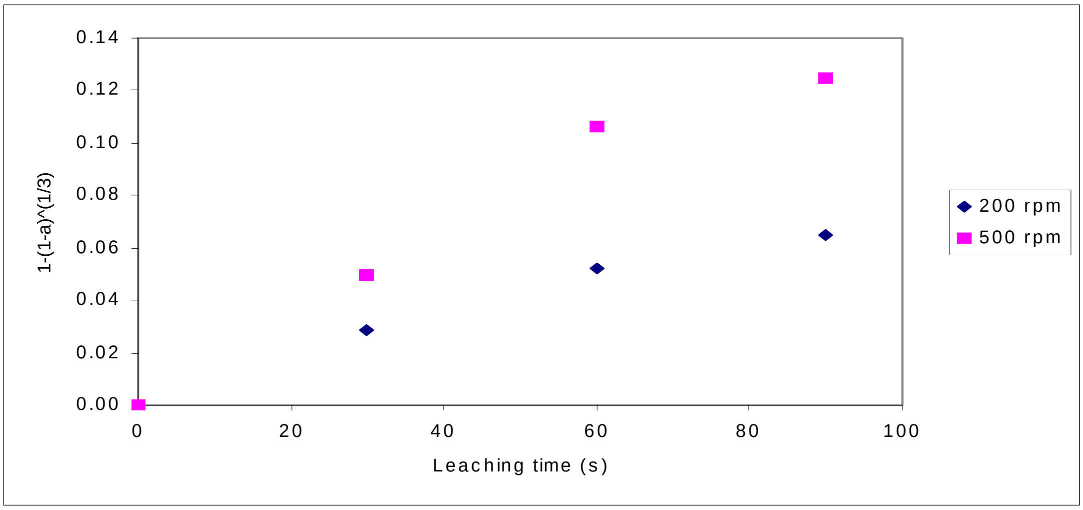


Figure 4.17: Plot of $1-(1-\alpha)^{1/3}$ versus. leaching time for silver leaching at 200 and 500 rpm in 0.5 M HCl- 3.0 M NaCl.

The linear correlation coefficients, r at different stirring speeds are more than 0.96. These results imply that the silver leaching kinetic is likely described by Model 3 and indicates that the rate constant is directly proportional to stirring speeds which in agreement with the model.

Using the Equation 4.1 and the derived rate constant obtained from Figure 4.17, it leads to the determination of boundary layer at 200 rpm and 500 rpm (in 0.5 M HCl-3.0 m NaCl under 200 L/S ratio at 29.5 °C) as 7.99 x 10^{-5} m and 4.26 x 10^{-5} m, respectively. By these thickness values, the application of Model 3 to experiment data at different stirring speeds are plotted as shown in Figure 4.18 which clearly shows that, at a given stirring speed, Model 3 shows great correlation to describe the silver behaviour during chloride leaching.

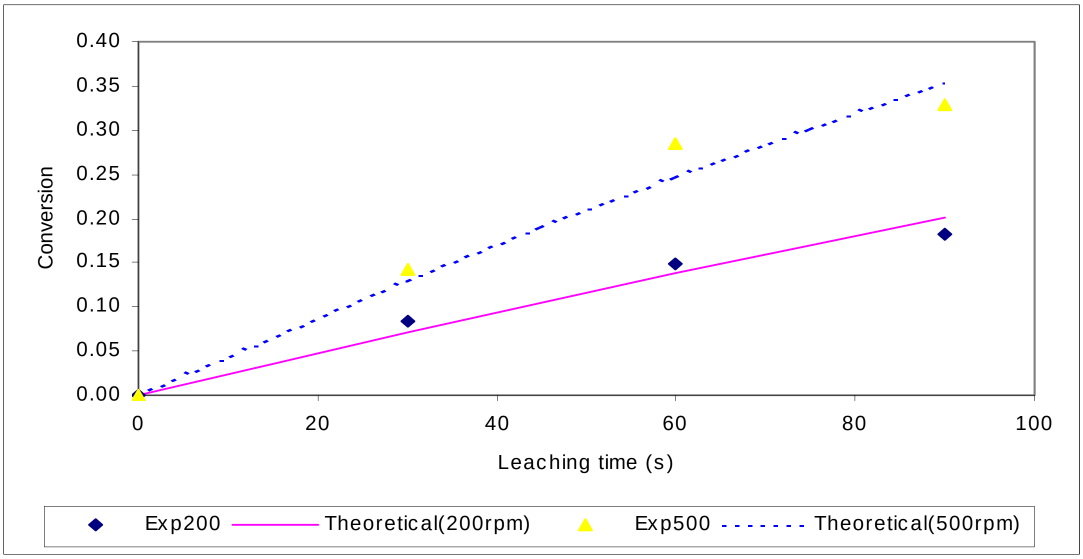


Figure 4.18: Comparison of theoretical and experimental conversion of silver at different leaching time for stirring speed of 200 and 500 rpm.

b) Mass Transfer Coefficient Determination

Based on previous discussion, Model 3 has been selected to describe the silver leaching behavior as discussed in Section 4.2.6.2 (a). The leaching reaction involves stoichiometric factor as high as 3 to cause the progressive formation of silver chloro complex. Therefore, the following will use the Model 3 to determine the mass transfer coefficient of the silver leaching at different stirring speeds.

In order to estimate theoretical mass transfer limited reaction rate, it is necessary to calculate the limiting diffusion boundary layer thickness, δ. Monhemius and Katungu [71] have defined the δ as Equation 4.2:

$$\delta = Di / (2 + 0.6\,Re^{0.5}\,Sc^{0.33}) \quad \ldots\ldots 4.2$$

where $Re = \left(\frac{4\,g^2(dp - ds)^2 Di^3}{225\,ds^2\,\upsilon}\right)^{0.33} \frac{Di}{\upsilon}$

and $Sc = \frac{\upsilon}{D}$

and the other parameters are defined as; Di is particle diameter (m), Re and Sc is Reynold and Schmidt number respectively, g is 9.807 ms^{-1}, dp and ds is solid and fluid density (kgm^{-3}) respectively, ν is kinematic viscosity (m^2s^{-1}) and D is diffusion (m^2s^{-1}).

Using the correlation of $K = D/\delta$ and a value of 6.4×10^{-10} m^2s^{-1} for the diffusion coefficient of Ag(I) in concentrated brine [66], the diffusion boundary layer thickness for the system at 500 rpm was calculated as 1.06×10^{-5} m, which leads to a theoretical mass transfer coefficient of 6.03×10^{-5} ms^{-1}. However, based on the Model 3, the calculated mass transfer coefficients of 200 rpm and 500 rpm are 8.01×10^{-6} and 1.50×10^{-5} ms^{-1} respectively as shown in Table 4.10.

Table 4.10: Calculated mass transfer coefficient of silver leaching at 200 and 500 rpm under 0.5 M HCl-3.0 M NaCl leaching medium.

Stirring speed (rpm)	Diffusion thickness (m)	Mass transfer coefficient (ms^{-1})
200	7.99×10^{-5}	8.01×10^{-6}
500	4.26×10^{-5}	1.50×10^{-5}

4.2.6.3 Mechanistic Model of Silver Leaching

The results obtained in the previous section indicate consistently the important of the total chloride concentration on the rate of silver leaching from semiconductor waste. It also eliminates the possibility of H^+ diffusion to be the rate control species. The silver leaching rate is significantly increased at high concentration of chloride ions. This has been proven by the application of Model 3 that showing three equivalents of chloride ions per mole of silver (I) chloro complexes involved. Therefore, in general, the silver dissolution from semiconductor waste can be expressed by the following reactions:

$$Ag + 3Cl^- \rightarrow AgCl_3^{2-} + e$$

$$AgCl + 3Cl^- \rightarrow AgCl_4^{3-}$$

From the previous analysis of several kinetic models, it has evidently indicated that the silver leaching process was controlled by the diffusion of some species through the liquid boundary layer adjacent to the reacting surface. From the above reactions, it might suggest that the rate-controlling diffusing species is either chloride ion or the Ag(I) chloro-complex. However, if the author uses the diffusion of Cl^- as controlled species (diffusion coefficient of chloride ions as 1.61×10^{-9} m^2s^{-1}) [104], experimental data is deviates greatly from Model 3 as shown in Figure 4.19. But when the silver chloro complex is chosen as diffusion controlled species (D as 6.40×10^{-10} m^2s^{-1}), it gives a good agreement to illustrate the silver leaching behaviour as described in Figure 4.18. Therefore, it implies that the silver leaching rate is controlled by the outward diffusion of Ag(I) chloro-complexes through liquid boundary layer into the bulk solution.

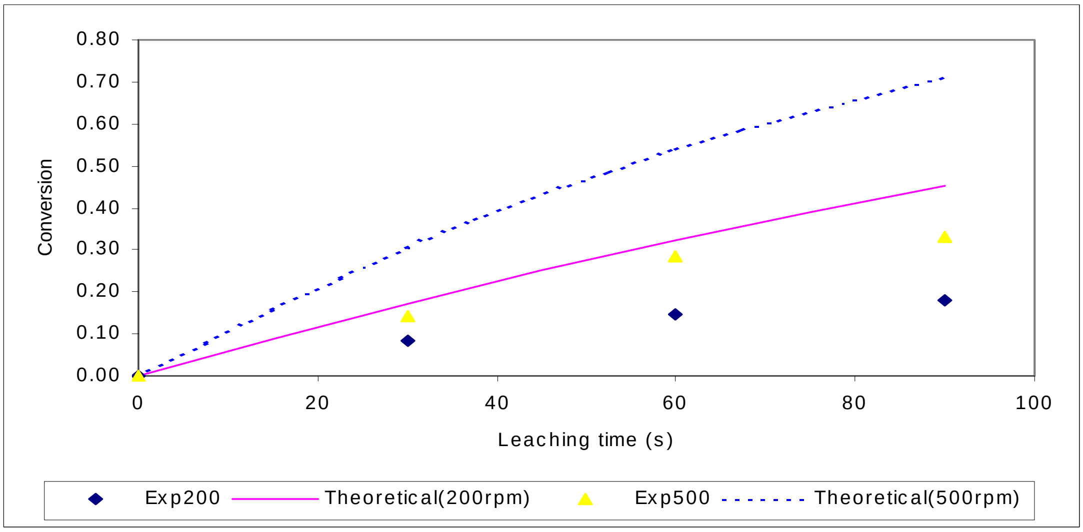


Figure 4.19: Comparison of theoretical and experimental conversions of silver leaching at different leaching time for 200 and 500 rpm of stirring speed. Theoretical conversion was calculated using D as 1.61 x 10^{-9} m^2s^{-1}.

4.2.7 Concluding Remarks

Several factors affecting the thermodynamics and kinetics of leaching process have been discussed such as leaching agent types, HCl and NaCl concentration, liquid/solid ratio and stirring speed. The results of the study have provided the basic background for predicting the leaching behavior of silver metal from semiconductor waste. In kinetic modeling, the shrinking core model was able to describe the silver leaching behavior and indicated that the outward diffusion of silver chloro complex is the rate-controlling step.

4.3 Liquid-liquid Extraction of Silver

The liquid-liquid extraction of silver from leaching solution using two types of extractant: Cyanex 272 and dithizone was carried out and discussed. In order to understand the silver extraction behavior, two types of pure silver solutions: $AgNO_3$ and silver chloro complex were also studied. Throughout these studies, the effect of pH and other metals on silver extraction were highlighted. However, during the preliminary study of extraction process, the formation of third phase was occurred due to the metal precipitate during pH adjustment. This third phase was very stable even at low pH. Therefore, the removal of metal precipitate was carried out and the detail discussion of the metal precipitation will be discussed in Section 4.4. Apart from that, the effect of calcium ion would not be studied and considered to be negligible because its concentration in leaching solution is too low (1.03 ppm).

4.3.1 Solubilities of Extractant in Diluent

In liquid-liquid extraction, several factors used to consider in selecting the right diluent. One of the factors is the solubility of extractant in organic diluent which is important when discussing its behavior in two-phase extraction systems. In this study, the selection of suitable diluent for Cyanex 272 and dithizone was first carried out. Kerosene is among the diluents that attracts great interest in this study. It is due to its low cost, easily found and low solubility in aqueous phase. From the experiment that had been carried out, Cyanex 272 was easily mixed well in kerosene while the solubility of dithizone in kerosene is very low at 3.93×10^{-2} gL^{-1}. The detailed procedure to determine the dithizone solubility was already discussed in Section 3.2.5.2, and some calculation procedures are given in Appendix K. Since the solubility of dithizone in kerosene is very low, therefore, chloroform, $CHCl_3$ was used as diluent in preparing the dithizone solution. Solubility of dithizone in $CHCl_3$ is 20.3 gL^{-1} at 30 °C [91].

4.3.2 Extraction of Silver Using Cyanex 272

Recently, the Cyanex reagents have came to the forefront as silver extractant. Of these, Cyanex 272 or bis (2,4,4-trimethylpentyl) phosphoric acid has proven to be good extractant for silver [84] as well as for cobalt and nickel [96,97]. However, there have been very little studies on silver extraction by Cyanex 272 from mixed metals system with chloride medium. Thus the following section is presented to discuss the effect of pH and other metals on silver extraction from leaching solution by Cyanex 272. Two types of pure silver solution were used to verify the silver extraction behavior from leaching solution.

4.3.2.1 Effect of pH on Silver Extraction Using Cyanex 272

Figure 4.20 shows the effect of pH on silver extraction from leaching solution using 0.02 M Cyanex 272 in kerosene. Silver extraction attains not more than 20 % and not much influenced by the pH. The low extractability of silver might due to the existence of silver chloro complex which is very stable in excessive chloride ions in leaching solution. This unextractable silver chloro complex was also found in several extraction systems which have been reported in literature [105,106]. While the minor effect of pH on silver extraction, however, suggesting that the extraction might occur through coordination mechanism instead of proton exchange reaction [105]. The outer shell electron configuration of silver in silver chloro complex is $d^{10}s^2$. The hybridization of these orbital then provide vacancies for the donor atom of Cyanex 272 which substitutes for chloro ligands, and forming the extractable species [105]. Such mechanism does not involve the replacement of proton. Therefore, pH does not influence the silver extraction. But the extractable complexes might not be stable and as a result low percentage of silver extraction was observed (Figure 4.20).

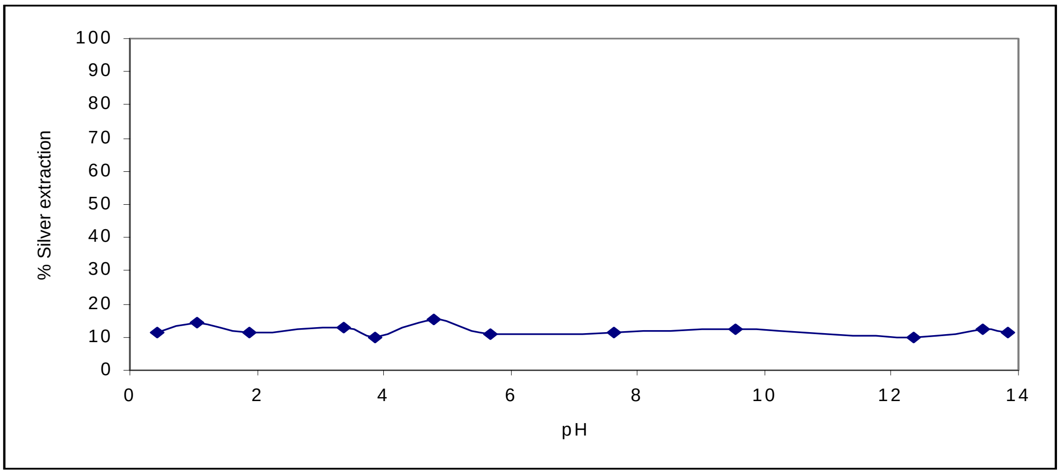


Figure 4.20: Silver extraction from leaching solution by 0.02 M Cyanex 272

In order to have a better understanding of the silver extraction from leaching solution, the extraction was also carried out on pure silver solutions; $AgNO_3$ and silver chloro complex solution. The results are presented along with silver extraction from leaching solution which is given in Figure 4.21. It is clearly shows that the similar trend of silver extraction behavior is observed between pure silver chloro complex and leaching solution. It proves that the existence of unextractable silver chloro complex in leaching solution contributes to the low extractability of silver. Several studies have been reported on silver extraction from chloride medium by

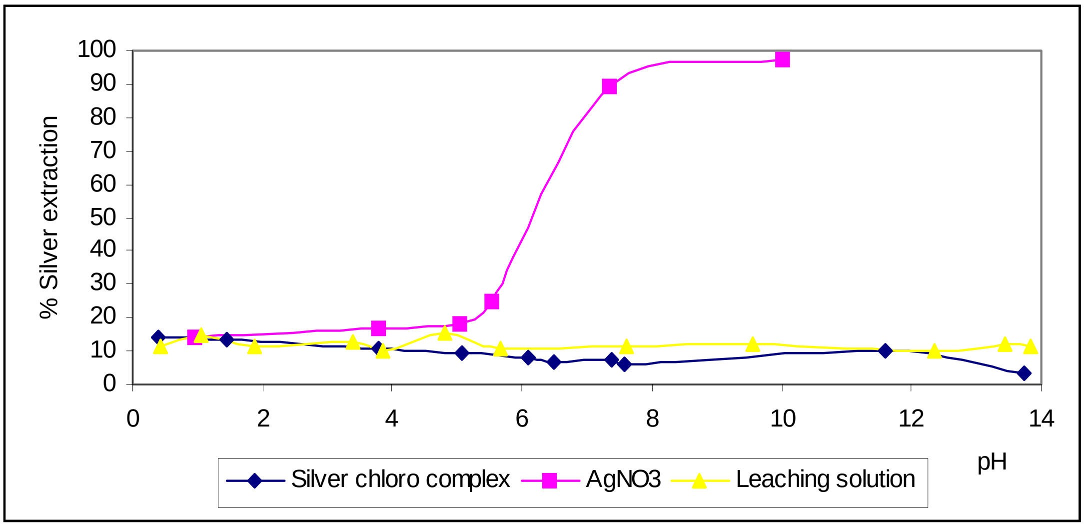


Figure 4.21: Silver extraction in different aqueous systems by 0.02 M Cyanex 272

Cyanex reagents [105,106]. They found that the silver chloro complex tend to form metal chelate through coordination mechanism. Again, it is possible to deduce that the reaction is follows the coordination mechanism.

In pure $AgNO_3$, however, the silver extraction by Cyanex 272 is preferable and achieves almost 100 % extraction at pH more than 8. The extraction occurs through proton exchange mechanism which has been reported by Sole and coworkers [84]. Therefore, at acidic medium, the equilibrium of reaction is shifted and the formation of silver complex is reduced in organic phase. While at alkali medium, the equilibrium is forced to generate more silver complexes to achieve another stage of equilibrium which increases the silver extraction as illustrated in Figure 4.21.

However, by the principle of Hard Soft Acid Base, the hard-base oxygen donor ligand rarely form complexes with silver, therefore, the low stability of this complex is not unexpected (K_{ex} = 5.7 x 10^{-4} [84]). The postulated structure of silver (I) complexes is in dimeric 8-membered ring which the metal coordinate in linear geometry between an oxygen donor atom from each molecule as illustrated in Figure 4.22.

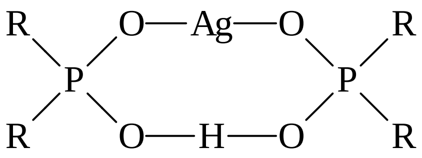


Figure 4.22: Structure of silver (I) complexes, $AgHA_2$ formed by Cyanex 272; A denotes as R_2POO and R denotes as 2,4,4-trimethylpentyl [84].

From the above study of pure silver solution, it indicates that the anions of silver compounds are greatly affects the extraction behavior of silver by Cyanex 272.

4.3.2.2 Cyanex 272 Selectivity to Metals

Extractant is normally exhibits a good selectivity on particular metal during extraction process. In this section, the study on the effect of other metals on silver extraction from leaching solution using Cyanex 272 was carried out. The results as shown in Figure 4.23 represents the percentage of metal extraction as a function of pH. It indicates that the extraction efficiency follows the order of iron > copper > stanum > silver. Details of the results are shown in Table 4.11. This order may due to extraction equilibrium constant of iron complex (3.16 x 10^{-4} [107]) is much higher than copper complex (2.5 x 10^{-7} [99]). Although these two studies of anionic mediums are not similar to leaching solution, but it still gives indication that the iron complex is more stable. Moreover, the existence of stable copper chloro complex which identified in previous discussion, limits the copper ion to be extracted into organic phase. At higher pH, copper ions become hydrolyzed and forming a strong complex with H_2O which leads to the decrease of copper extraction as illustrated in Figure 4.23. The behavior of stanum extraction, however, is difficult to be explained. It might be due to the existence of several complex forms of stanum compound in leaching solution which disturbs the extraction process. In the case of silver extraction, the other possible effect contributes to low extraction may be due to the

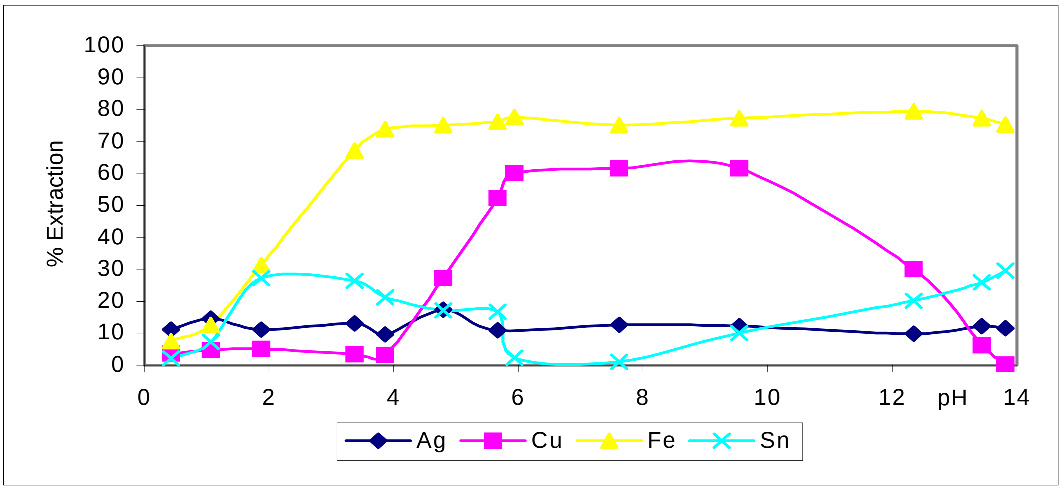


Figure 4.23: Percentage of metal extraction from leaching solution using 0.02 M Cyanex 272 at different pHs.

effect of sodium ion. This is because during the pH adjustment, a high concentrated sodium hydroxide was added. However, this possibility is eliminated since low extraction of sodium at different pHs have been detected.

Table 4.11: Metal concentration in aqueous phase before extraction and in organic phase after extraction at different pH by Cyanex 272.

pH		[Metal] in aqueous phase before extraction (ppm)				[Metal] in organic phase after extraction (ppm)			
pH$_{o}$	pH$_{eq}$	Ag	Cu	Fe	Sn	Ag	Cu	Fe	Sn
0.43	0.43	186.5	830.5	134.5	143.5	21.0	31.0	10.0	3.0
1.09	1.07	161.0	825.0	106.5	62.0	23.5	39.5	13.0	4.5
1.97	1.88	148.0	811.0	73.5	40.5	16.5	42.5	23.0	11.0
3.78	3.38	142.0	804.5	12.5	26.5	18.5	28.0	8.3	7.0
4.49	3.86	143.5	687.0	4.4	23.5	14.0	22.0	3.2	5.0
5.67	4.80	161.5	27.5	3.2	20.5	28.0	7.5	2.4	3.5
8.57	5.67	146.5	10.5	3.1	19.0	16.0	5.5	2.4	3.2
8.62	5.94	148.5	7.5	3.1	17.2	17.5	4.5	2.4	0.4
9.92	7.62	150.5	6.5	3.2	22.5	23.5	4.0	2.4	0.2
11.51	9.54	186.5	6.5	3.3	54.0	23.0	4.0	2.5	5.5
12.59	12.34	186.5	10.0	3.4	63.0	17.5	3.0	2.7	12.7
13.49	13.44	171.5	71.5	3.7	86.5	21.0	4.5	2.9	22.5
13.83	13.82	155.5	523.5	4.2	98.5	18.0	1.0	3.2	29.2

Overall, the low silver extraction from leaching solution by Cyanex 272 is not affected by the existence of other metals. Instead, it is due to the presence of high stability of silver chloro complex which is unextracted into organic phase. Apart from that, Cyanex 272 has shown high selectivity for the extraction of copper and iron over silver and stanum at pH between 6 to 10 from leaching solution. Thus, Cyanex 272 is not suitable for the selective extraction of silver from leaching solution.

4.3.3 Extraction of Silver Using Dithizone

Dithizone is another promising silver extractants which has been widely used in photometric analysis [92,93,94]. Therefore, the extraction study was carried out to investigate the effect of pH and other metals on silver extraction using dithizone. Pure $AgNO_3$ and silver chloro complex solutions were used to verify the silver behavior in leaching solution.

4.3.3.1 Effect of pH on Silver Extraction by Dithizone

The behaviors of silver extraction by dithizone from leaching solution, $AgNO_3$ and silver chloro complex were studied. The effect of pH on silver extraction from these three different types of systems is presented in Figure 4.24. It shows that more than 95 % of silver extraction from leaching solution is achieved. A similar extraction result was also observed in pure silver chloro complex solution. These indicate that the basic mechanism involved in silver extraction reaction from these two systems is similar. However, at pH lower than 2, silver extraction from leaching

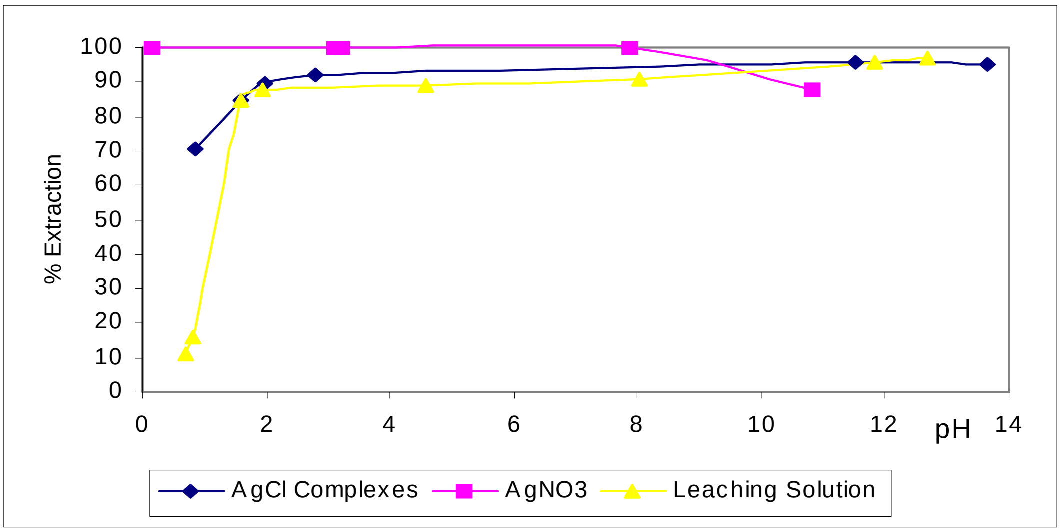


Figure 4.24: Percentage of silver extraction from different systems using 0.02 M dithizone.

solution is much lower than pure silver chloro complex solution. This phenomenon could be explained by considering the effect of other metals which would be discussed in Section 4.3.3.2. Basically, dithizone exhibits a good silver extraction at wide range of pH. It is because dithizone with the low pK_a value of 4.55 is able to provide an acidic medium even at pH less than 2 for silver extraction [108].

In the silver extraction from pure $AgNO_3$ solution, Figure 4.17 shows that the silver ions in $AgNO_3$ solution are easily extracted and achieve 100 % of extraction though slightly drop at higher pH. It is due to the fact that at higher ionization of $AgNO_3$, it generates huge amount of free Ag^+ ions which are easily reacted with HDz^- forming the extractable complex of AgHDz. The overall reaction involved in silver extraction from $AgNO_3$ by dithizone can be represented by the following reaction:

$$Ag^+ + H_2Dz\ (org) \Leftrightarrow AgHDz\ (org) + H^+$$

Based on 0.02 M H_2Dz and log K_{ex} of 5.8 [105], Equation 2.21 gives 100 % of silver extraction covering the whole range of pH. It is consistently obtained in this study as shown in Figure 4.24. However, a slightly drop of silver extraction found in pH more than 8, might be due to the dissolving of silver complexes in aqueous phase which gave a reddish orange of AgHDz in aqueous phase as observed during the extraction experiment [91].

4.3.3.2 Dithizone Selectivity to Metals

Figure 4.25 illustrates the effect of other metals on silver extraction at different pHs. It indicates that the extraction efficiency of dithizone follows the order of Ag > Cu > Fe > Sn. Based on the HSAB principle [86], the sulfur atom of dithizone shows great affinity towards soft acids of Ag and Cu compared to Fe and Sn as shown in Figure 4.25. The silver and copper extractions are observed more than 80 %, while the iron and stanum ions do not show any significant extraction. As stated previously, the high stability of silver chloro complex which existed in leaching solution was not extracted into organic phase by Cyanex 272. However, in the case of dithizone, the silver atom shows a great affinity to bind with donor atom of sulfur. It is true due to the fact that the stability constant of AgHDz and $AgCl_4^{3-}$ is 6.31×10^5 and 3.02×10^{-5} respectively [41,84].

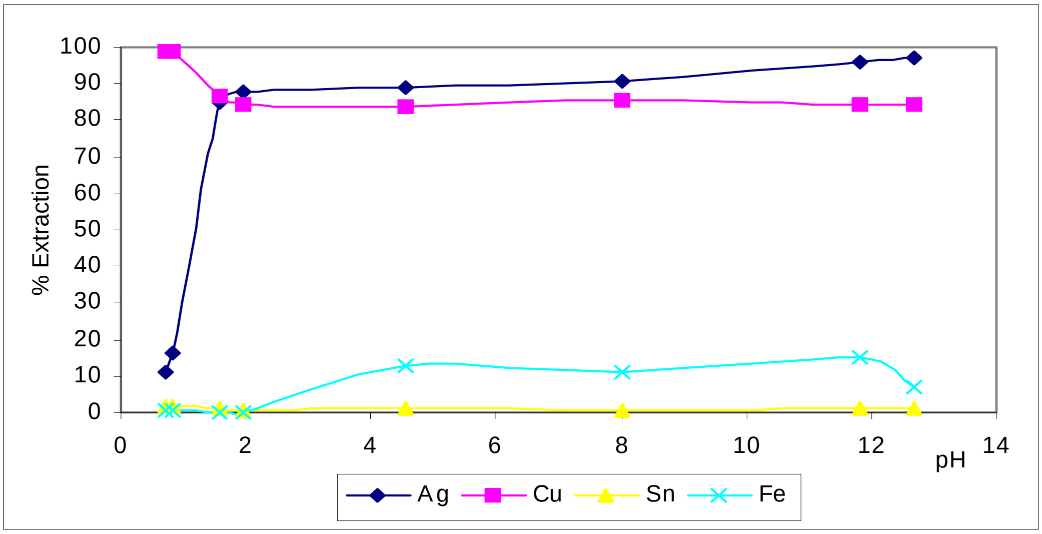


Figure 4.25: Percentage of metal extraction from leaching solution by 0.02 M Dithizone at different pHs.

At pH equilibrium below 1, the initial concentration of copper ion in aqueous phase as shown in Table 4.12 was more than 700 ppm. This high concentration of copper ions might compete strongly with the high stability of silver chloro complex to form the violet primary copper dithizonate, $Cu(HDz)_2$ as observed during experiment. Furthermore, the 0.02 M of dithizone is not in excess since the stoichiometric reaction required two mole of dithizone per one mole of copper ions. This is the reason why the low extractability of silver at pH lower than 1 is observed. However, when the copper started to precipitate (at pH equilibrium more than 1), the extent of silver extraction increased sharply due to the availability of dithizone in the system. This result again can explain the differences of silver extraction at pH lower than 1 between leaching solution and pure silver chloro complex solution.

Table 4.12: Metal concentration in aqueous phase before extraction and in organic phase after extraction at different pH by dithizone.

pH		[Metal] in aqueous phase before extraction (ppm)				[Metal] in organic phase after extraction (ppm)			
pH_o	pH_{eq}	Ag	Cu	Fe	Sn	Ag	Cu	Fe	Sn
3.22	0.70	147.0	809.5	14.5	32.5	16.0	802.0	0.1	0.5
4.20	0.83	145.0	705.0	6.3	26.5	23.5	697.0	0.1	0.5
5.04	1.59	159.0	30.5	4.5	24.3	135.0	26.5	0.0	0.3
5.78	1.95	162.0	17.5	3.2	23.2	142.5	14.8	0.0	0.2
8.75	4.56	156.0	8.5	3.2	20.4	139.0	7.1	0.4	0.2
9.23	8.03	153.0	7.0	3.3	24.0	139.0	6.0	0.4	0.2
12.05	11.81	187.0	9.5	3.3	62.5	179.5	8.0	0.5	0.7
12.70	12.61	188.0	25.0	3.5	75.5	182.0	21.1	0.3	1.0

In term of selectivity, dithizone shows great affinity towards silver. At pH equilibrium of 11.81 (Table 4.12), it shows that 179.5 ppm of silver was extracted from leaching solution together with only 8.0 ppm of copper and negligible concentration of Fe and Sn. Therefore, it indicates that dithizone capable to extract silver selectively from leaching solution.

4.3.4 Effect of Extractant Type on Silver Extraction

Silver extraction by Cyanex 272 and dithizone has been discussed separately in the previous sections. It showed that these two extractants behaved differently on silver extraction. A close comparison of their different extraction behaviors can be observed in Figure 4.26.

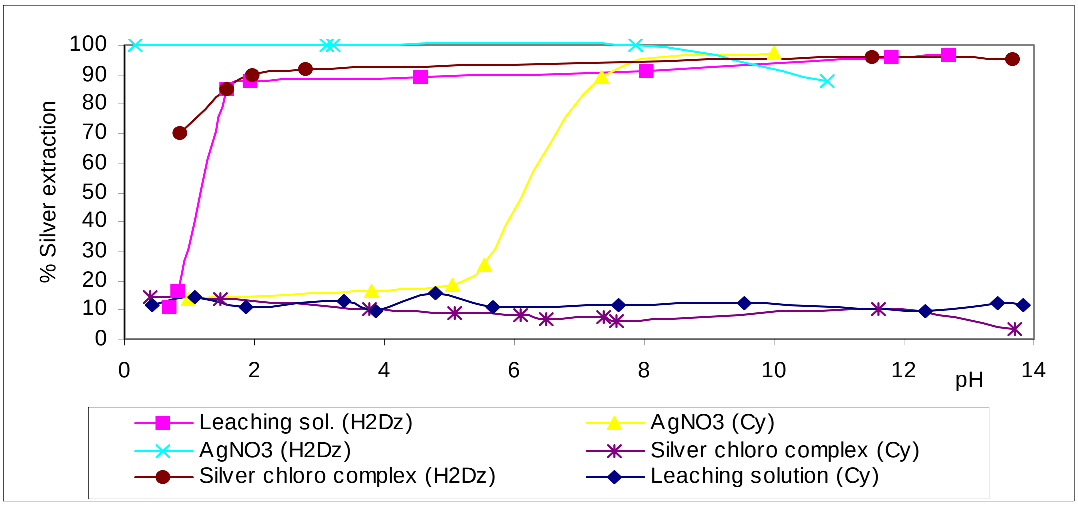


Figure 4.26: Effect of extractant type on silver extraction in pure and leached silver solution. Cy: Cyanex 272; H_2Dz: dithizone

From the Figure 4.26, it shows that the dithizone can extract silver quite well at wide range of pH either from pure silver system or leached silver system. However, silver extraction by Cyanex 272 can only observe high percentage of silver extraction from pure $AgNO_3$ system at pH more than 8 but not from pure silver chloro complexes and leached silver system.

In order to illustrate the observed phenomenon, we have to compare the equilibrium constants of some silver chelating complexes, which formed during the extraction process. These complexes with their constants are as follows:

$Ag^+ + H_2A_2 \Leftrightarrow AgHA_2 + H^+$ $K_{ex} = 5.70 \times 10^{-4}$ [84]

$Ag^+ + H_2Dz \Leftrightarrow AgHDz + H^+$ $K_{ex} = 6.31 \times 10^{5}$ [91]

$AgCl + 3Cl^- \Leftrightarrow AgCl_4^{3-}$ $K_{ex} = 3.02 \times 10^{-5}$ [41]

Since the stability of AgHDz is much higher than the $AgCl_4^{3-}$, the formation of silver chelates of AgHDz is preferable. As a result, silver extraction by dithizone could achieve higher percentage in the pure silver chloro complexes and leached silver systems. However, in the case of Cyanex 272, the comparable stability of $AgHA_2$ and $AgCl_4^{3-}$ causes the low extractability of silver from solutions containing silver chloro complexes as illustrated in Figure 4.26.

Apart from this, Figure 4.26 shows that a sigmoid curve with $pH_{1/2}$ of ~ 6.0 is observed in the silver extraction of $AgNO_3$ by Cyanex 272, but in the case of dithizone, high silver extraction is observed even at very low pH medium. This can be explained by considering the acidity of the extractants. The pK_a of Cyanex 272 and dithizone are as following:

$H_2A \Leftrightarrow H^+ + HA^-$ $pK_a = 6.37$ [87]

$H_2Dz \Leftrightarrow H^+ + HDz^-$ $pK_a = 4.55$ [108]

Form the value of pK_a, it shows that the extraction by Cyanex 272 should occur at pH higher than dithizone. And this was found in agreement with the experiment results.

4.3.5 Concluding Remarks

Liquid-liquid extraction performed by Cyanex 272 and dithizone has been studied and discussed. Cyanex 272 has provided low extractability on silver extraction from leaching solution compared to dithizone due to the existence of silver chloro complexes species. This has been verified by the study of pure silver chloro complexes solutions. However, dithizone has shown great affinity to bind with silver due to its soft donor atom of sulfur compared to oxygen from Cyanex 272.

4.4 Metal Precipitation Process

During the liquid-liquid extraction studies, pH adjustment of the leaching solution was formed some metals precipitate. In order to understand the phenomenon occurred, the effects of pH on metal precipitation and selectivity were studied. Pure silver solution of $AgNO_3$ and silver chloro complex were again used to verify the silver precipitation behavior from leaching solution.

4.4.1 Effect of pH in Metal Precipitation

A study on the effect of pH on silver precipitation was carried out for leaching solution, pure silver chloro complexes and silver nitrate. Figure 4.27 shows the silver precipitation behavior for these three different systems at various pH mediums. It shows that the silver precipitation behavior from leaching solution is analogous to pure silver chloro complex solution. For both systems, only less than 25 % of silver was precipitated. Figure 4.28 also shows a sharply increase of silver precipitation from $AgNO_3$ at pH more than 10 which is almost 100 % of silver precipitation.

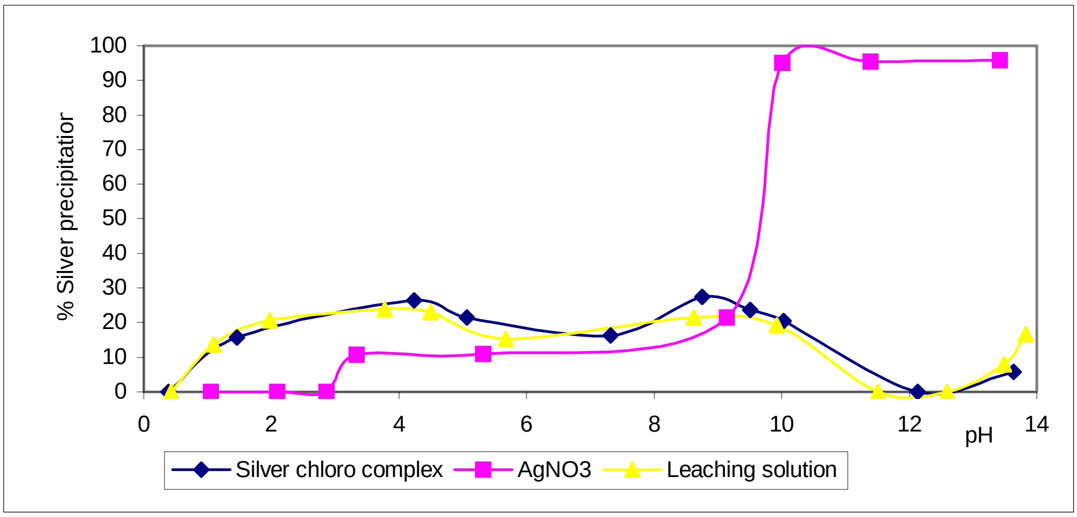


Figure 4.27: Effect of pH on the extent of silver precipitation from different systems.

In the precipitation process, by knowing the solubility product (K_{sp}) of the precipitate, it is possible to find the pH value at which precipitation will start to occur for a given concentration of the metal ion. In this study, AgOH was formed by the reaction of $AgNO_3$ and NaOH as shown below:

$$AgNO_3 + NaOH \rightarrow AgOH + NaNO_3$$

and the defined solubility product, K_{sp} of AgOH is

$$AgOH \Leftrightarrow Ag^+ + OH^-$$

$$K_{sp} = [Ag^+][OH^-] \quad \ldots\ldots\ldots\ldots \quad 4.3$$

pK_{sp} of AgOH is 7.7 [39] and the metal ion concentration in the silver nitrate solution was 204.5 ppm (1.8958×10^{-3} M). By the calculation below,

$$pK_{sp} = -\log K_{sp} \quad \ldots\ldots\ldots\ldots \quad 4.4$$

So, $$[OH^-] = \frac{1.9952 \times 10^{-8}}{1.8958 \times 10^{-3}} = 1.0524 \times 10^{-5}\ M$$

$$pH = 14 - (-\log [OH^-])$$

$$= 9.02$$

it shows that the silver precipitation would start at pH 9.02. This is in agreement with the experimental observation that the brown precipitate (AgOH) started to form at pH 9.14 in the $AgNO_3$ system.

However, this observation is not found in silver chloro complexes system. Instead, the white precipitate was formed at pH from 5 to 12 and brown precipitate was found at pH 13.64. It happens due to the high stability of silver chloro complexes in excessive of chloride ion medium. By progressively additional of NaOH which might decrease the solubility of AgCl and thus formed the white silver chloride precipitate. This is because when increasing the Na^+, it will react with the free Cl^- to form NaCl. Therefore, the equilibrium of AgCl chlorination reaction will shift to the left and reduce the solubility of AgCl by forming white precipitate of AgCl.

$$AgCl + nCl^- \Leftrightarrow AgCl_{n+1}^{-n}$$

With the progressively increment of NaOH concentration, the product of AgCl will then reacted with NaOH to form brown precipitate of Ag_2O by the following reaction.

$$2AgCl + 2NaOH \rightarrow Ag_2O + H_2O + 2NaCl$$

From the silver precipitation behavior of $AgNO_3$ and silver chloro complex, it proves that the leaching solution contains silver chloro complex compound which has similar behavior of silver precipitation with pure silver chloro complex.

4.4.2 Effect of Other Metals and Selectivity on Silver Precipitation

The effect of other metals on silver precipitation at different pHs medium is illustrated in Figure 4.28. The results show that the iron is significantly removed at the pH more than 4.0, whereas copper at pH more than 6.0, and suddenly drop at pH 14. Stanum precipitated at pH range of 2 to 10 at more than 70 %.

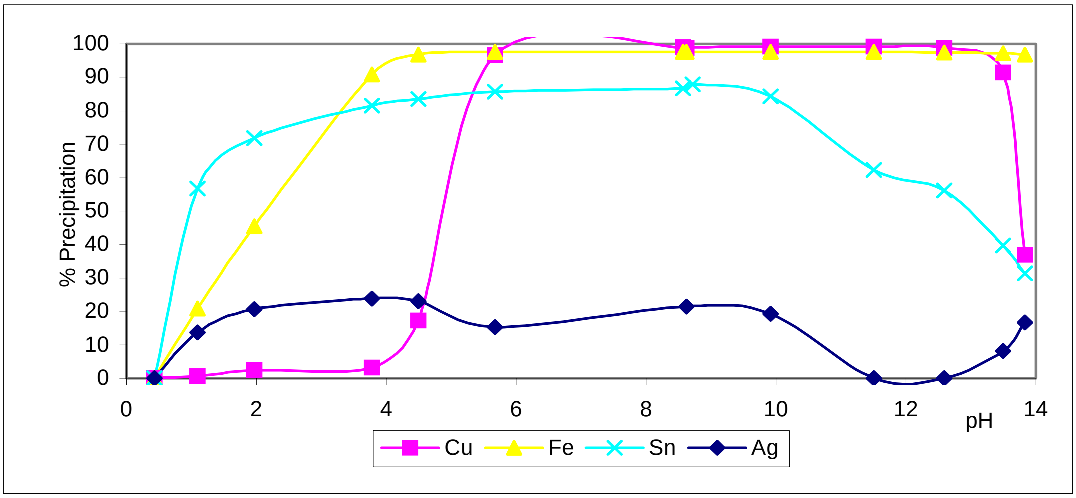


Figure 4.28: Effect of pH on the extent of metals precipitation from leaching solution.

So, in order to explain the above phenomenon, iron precipitate is assumed to be either $Fe(OH)_2$ or $Fe(OH)_3$,and copper is $Cu(OH)_2$. According to their solubility product and the initial metal concentration in the leaching solution, the pH at which the precipitate started to form is determined as shown in Table 4.13.

Table 4.13: Solubility products and predicted pH of metal precipitates.

Reaction	K_{sp} [39]	$[M]_{initial}$ (M)	pH
$Fe(OH)_2 \Leftrightarrow Fe^{2+} + 2OH^-$	$[Fe^{3+}][OH^-]^2 = 8 \times 10^{-16}$	2.408×10^{-3}	7.76
$Fe(OH)_3 \Leftrightarrow Fe^{3+} + 3OH^-$	$[Fe^{2+}][OH^-]^3 = 4 \times 10^{-38}$	2.408×10^{-3}	2.41
$Cu(OH)_2 \Leftrightarrow Cu^{2+} + 2OH^-$	$[Cu^{2+}][OH^-]^2 = 1.6 \times 10^{-19}$	1.307×10^{-2}	5.54

From Table 4.13, $Fe(OH)_2$ and $Fe(OH)_3$ are formed at pH 7.76 and 2.41 respectively. Initially we might conclude that the formation of $Fe(OH)_3$ is reasonable in agreement with the curve found in Figure 4.28. But, when considering the precipitate color as shown in Figure 4.29 and Figure 4.30, it indicates that the existence of green precipitate of $Fe(OH)_2$ but not $Fe(OH)_3$. However, there have the possibility that the green precipitate might consist of various metal compounds that formed during the pH adjustment.

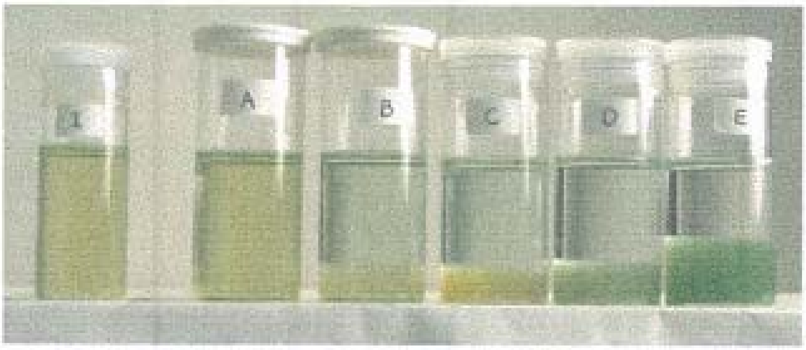


Figure 4.29: Changes during pH adjustment in leaching solution; 1(without adjusted at pH 0.46), A(1.14), B(2.52), C(3.56), D(3.86) and E(5.35).

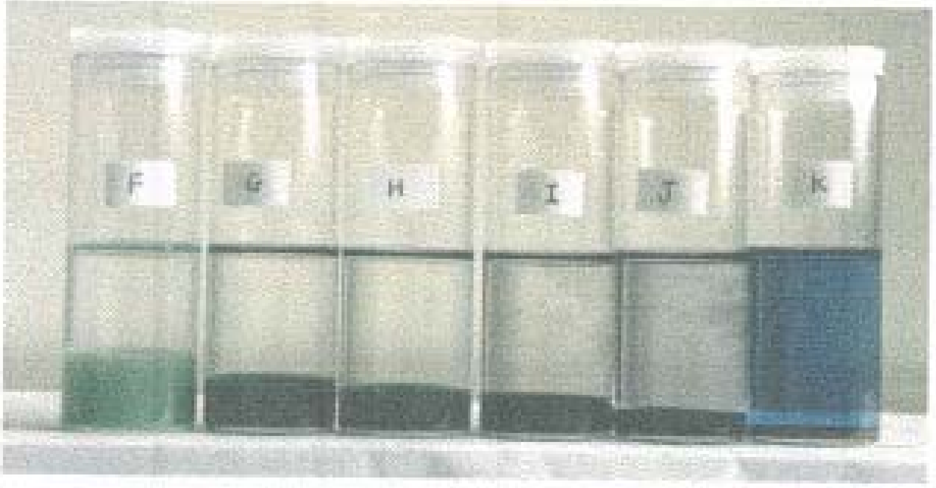


Figure 4.30: Changes during pH adjustment in leaching solution; F(6.16), G(10.40), H(12.36), I(12.81), J(13.17) and K(13.77)

Copper started to precipitate at pH 5.54 which showed consistently with the curve obtained in Figure 4.28. However, the copper precipitation drops at higher pH more than 13.0. The apparent increase in solubility at higher pH values is probably due to peptisation, which refers to the process by which a coagulated colloid reverts to its original dispersed state. And at this pH, the solution was turned into blue. It suggested that by increasing the OH^- concentration, it might hydrolyze the Cu^{2+} ions to form the blue complexes $[Cu(H_2O)_6]^{2+}$.

Of greater significance, the silver removal was not high compared to the other metals and fluctuated along the pH range as shown in Figure 4.28. The silver precipitation is not more than 25 %. This might due to the existence of high stability of silver chloro complex as discussed before. But there is still a great interesting that the silver do not precipitate at pH around 12 which indicates that the precipitation method is able to establish a selective silver removal from semiconductor waste leaving the other metals as precipitates.

4.4.3 Concluding Remarks

Metals precipitation from $AgNO_3$, silver chloro complex and leaching solution have been carried out and discussed. It has found that significant metal removals especially copper and iron have been obtained. However, in the case of silver metals, low precipitation was obtained. This is due to the high stability of silver chloro complex in the excessive medium of chloride ions which proven by the study of pure silver solution.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Semiconductor waste from the selected local semiconductor industry contains 5.92 % of silver which mostly existed in the form of cubical Ag and AgCl. The waste was then proceeded to the treatment process comprising of leaching, precipitation and liquid-liquid extraction processes. The results showed a promising outcome and lead to propose a preliminary conceptual silver recovery strategy from semiconductor waste. An appropriate selective silver recovery procedure from semiconductor waste is then developed as following.

Initially, the semiconductor waste is treated in a solution of 0.5 M HCl-3.0 M NaCl with a liquid/solid ratio of 200. The low acid concentration is preferable in industrial application because it can reduce any risk of corrosion in piping system. While, the high concentration of chloride ion from NaCl is used to activate the progressive formation of soluble silver chloro complexes, $AgCl_n^{-(n-1)}$ from Ag and AgCl. The process involved is actually controlled by the outward diffusion of Ag(I) chloro complex through liquid boundary layer into bulk leaching solution. The process is conducted under room temperature to reduce the operating cost and 500 rpm of stirring speed is good enough to provide a reasonable speed to achieve equilibrium rapidly. In term of selectivity, 0.5 M HCl-3.0 M NaCl of leaching system was able to perform better than HCl alone at any leaching agent concentration.

The leaching solution is then adjusted to pH around 12 by adding the concentrated sodium hydroxide. In this study, NaOH is added to precipitate the copper and iron by formation of metal hydroxides. Almost 100 % of copper and iron are remove successfully. At pH around 12, the maximum solubility of silver is being detected by AAS. This phenomenon is important to ensure a very selective silver removal over other undesired metals.

The solution is left for overnight to ensure a complete precipitation to be achieved. Thereafter, the precipitate is removed by centrifugation at 4500 rpm for 10 minutes which provided an easily and complete separating process. The collected supernatant then being used in the extraction process, which conducted by mixing the equal volume of supernatant (aqueous phase) and organic phase. The organic phase is prepared stoichiometric amounts by dissolving dithizone into chloroform, which is 0.02 M. The equilibrium extraction time is around 15 minutes which able to extract silver ions into organic phase and left behind the stanum ions in aqueous phase. This is because silver ion as soft acid would likely bind with soft donor atom of sulfur from dithizone. High selectivity is achieved towards silver recovery where a pure silver dithizonate has been extracted into the organic phase.

Overall, this conceptual strategy of silver recovery procedure make it possible to recover silver selectively and more than 45 % of silver was successfully removed from selected semiconductor waste.

5.2 Recommendations

Throughout the work, it was found that several parts of the study could be improved. Therefore, the followings are recommended for future study in order to obtain a better silver recovery from semiconductor waste.

Waste characterization is used to determine the properties of the waste and thus be able to identify its behavior. In this study, semiconductor waste was well characterized and determination of silver compounds was successfully being carried out. However, the identification of other coexisted metal compounds is facing difficulty due to the complicated analysis of EDAX spectrum. Therefore, it is recommended for future study to determine the other metal compounds using other techniques which can give a better understanding of the sample.

In the leaching process, the mixture of HCl and NaCl provided the best leaching power on silver removal compared to other leaching agents. However, it could only achieve at 55 % of silver removal from the waste that limited the overall silver recovery efficiency. Therefore, it is recommended to use other leaching agents such as thiourea. Thiourea is a nontoxic chemical and has been widely used to dissolve AgCl. Therefore, it is suspected that thiourea can perform well on silver leaching from semiconductor waste.

In the liquid-liquid extraction process, there are several aspects need to be studied further in order to get a better understanding and to improve the silver recovery process from semiconductor waste. From the experiment, it was found that dithizone could extract silver from leaching solution very well. However, it is still doubtful of the stoichiometric factor that involves in the extraction reaction. Therefore, it is recommended to vary the dithizone concentration and using the slope analysis technique to verify its stoichiometric factor. Apart from that, it also suggested to vary the chloride concentration in the aqueous phase in order to study the effect of chloride ions on silver extraction by dithizone.

Based on the present results, precipitation can be used to precipitate metals in leaching solution. Hence, further study is required. In this study, metal precipitation was carried out by varying the pH solution by NaOH. However, NaOH caused the redissolution of $Cu(OH)_2$ at higher pH. Therefore, it is recommended to use calcium hydroxide, $Ca(OH)_2$ which provide the minimum solubility of $Cu(OH)_2$ at higher pH [16]. It is important since the soft acid atom of copper might be coextracted into the organic phase by dithizone at higher pH and thus affected the efficiency of silver extraction.

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APPENDIX A

Solubility of Dithizone in Organic Solvents

No.	Solvent	Solubility (gL^{-1})	
		20°C	30°C
1	Dichloroethane	21.66	-
2	Chloroform	16.9	20.3
3	Dichloromethane	-	12.6
4	α-Bromonaphthalene	2.97	-
5	Carbon disulphide	2.83	-
6	Nitrobenzene	-	-
7	*o*- Dichlorobenzene	1.74	-
8	Chlorobenzene	1.43	2.5
9	Benzene	1.24	4.24
10	Acetonitrile	1.0	-
11	Toluene	0.95	4.52
12	Acetone	0.93	-
13	Methyl isobutyl ketone	0.805	-
14	Isopentyl formate	0.80	-
15	Isopentyl ethanoate	0.65	24.3
16	Carbon tetrachloride	0.512	0.74
17	Dioxan	0.349	-
18	Diethyl ether	0.4	-
19	Ethanol	0.3	-
20	*n*-Pentanol	0.054	-
21	Cyclohexane	0.014	-
22	Methylcyclohexane	0.01	-
23	*n*-Hexane	0.04	-
24	Water	5×10^{-5}	-

APPENDIX B

Multipycnometer Density Worksheet

Sampel I.D.	SWaste(B)	Date	23/3/1998
Source	M-SMM Electronics Sdn. Bhd.	Operator	B. S. Tang
Total weight	3.7707 g	Reference volume (V_R)	6.28 cm^3
Tare weight	1.5485 g	Cell volume (V_C)	11.67 cm^3

Operational Equation

$$V_P = V_C - V_R \left(\frac{P_1}{P_2} - 1 \right)$$

V_P = Volume of powder (cm^3)

V_C = Volume of sample cell (cm^3)

V_R = Reference volume (cm^3)

P_1 = Pressure reading after pressurizing the reference volume

P_2 = Pressure reading after including V_C

Data

	Run 1	Run 2	Run 3
P_1	17.178	17.193	17.140
P_2	6.276	6.294	6.265
V_P	0.7611	0.7952	0.7690
Density	2.9199	2.7944	2.8899

Average density = **2.87 ± 0.07 gcm^{-3}**

APPENDIX C

Determination of Mean Particle Size

Sieve size (μm)	Sieve weight (g)	(Sieve + sample) weight (g)	Sample weight	% w/w (K_i)	X_i	K_iX_i
0-75	379.3	546.8	167.5	16.03	37.5	601.02
75-150	293.5	501.6	208.1	19.92	112.5	2240.10
150-250	297.9	472.3	174.4	16.69	200.0	3337.48
250-500	315.0	515.6	200.6	19.19	375.0	7197.88
500-710	337.0	429.0	92.0	8.80	605.0	5325.81
710-1000	370.1	458.3	88.2	8.44	855.0	7215.67
1000-2380	385.0	499.3	114.3	10.94	1690.0	18483.11
		Total	1045.1	100		44401.06

$$\text{Mean particle size} = \frac{\sum K_i X_i}{\sum K_i}$$

$$= \frac{44401.06}{100}$$

$$= \mathbf{444.01\ \mu m}$$

APPENDIX D

Calculation of Specific Surface Area

Sample weight = 1.50 g

Particles diameter = 444.0106 x 10^{-6} m

Density of particle = 2.8681 gcm^{-3}

Therefore,

Total surface area = number of particle x particle surface area

$$= \frac{\text{total volume sample}}{\text{particle volume}} \text{ x particle surface area}$$

$$= \frac{\text{sample weight}/\text{particle density}}{\frac{4}{3}\Pi j^3} \text{ x } 4\Pi j^2$$

$$= \frac{3 \text{ x } 1.50 \text{ g}}{2.8681 \text{ x } 10^6 \text{ gm}^{-3}} \text{ x } \frac{2}{444.0106 \text{ x } 10^{-6} \text{ m}}$$

$$= 7.0673 \text{ x } 10^{-3} \text{ m}^2$$

$$\text{Specific surface area} = \frac{\text{total surface area}}{\text{total sample weight}}$$

$$= \frac{7.0673 \text{ x } 10^{-3} \text{ m}^2}{1.50 \text{ g}}$$

= **47.12 cm^2g^{-1}**

APPENDIX E

Spectrum of the X-ray Fluorescence Analysis

APPENDIX F

Spectrum of the Energy Dispersive X-ray Analysis

APPENDIX G

Diffractogram of X-ray Diffraction Analysis

Angle 2 Theta °	d value Angstrom	Intensity Cps %	Intensity %
23.092	3.848	61.2	38.5
27.888	3.197	105	65.7
32.304	2.7689	159	100.0
37.566	2.3923	60.0	37.7
38.196	2.3542	114	71.9
44.386	2.0392	73.6	46.3
46.331	1.9580	93.6	58.8
55.869	1.6443	54.6	34.3
57.590	1.5992	61.6	38.7
58.175	1.5845	51.9	32.6
60.680	1.5249	53.5	33.6
62.666	1.4813	51.2	32.2
64.560	1.4423	62.7	39.4

APPENDIX H

Standard Diffraction Pattern of Ag and AgCl (JCPDS)

APPENDIX I

Weight Calculation of Ag and AgCl in 1.50 g of Sample Waste

From EDAX:

% Ag = 7.55 %

% Cl = 1.64 %

Assumption: 100 % of Cl^- combines with Ag^+ to form AgCl

Therefore, 1.50 g sample might contain,

$$W_{Cl^-} = \frac{0.0164\ g\ Cl^-}{1.0\ g\ sample} \times 1.5\ g\ sample$$

$$= 0.0246\ g\ Cl^-$$

$$Mol_{\ Cl^-} = \frac{0.0246\ g\ Cl^-}{35.453\ gmol^{-1}\ Cl^-}$$

$$= 6.9388 \times 10^{-4}\ mol\ Cl^-$$

With the stoichiometry of $Ag^+ + Cl^- \longrightarrow AgCl$

Therefore,

$$[AgCl] = 6.9388 \times 10^{-4}\ mol\ AgCl$$

$$W_{AgCl} = 6.9388 \times 10^{-4}\ mol\ AgCl \times 143.351\ gmol^{-1}\ AgCl$$

$$= \mathbf{9.9468 \times 10^{-2}\ g\ AgCl\ in\ 1.50\ g\ sample}$$

Assumption: sample contained two form of silver compounds; Ag and AgCl

Therefore, 1.50 g sample might contain

$$Mol_{\ Ag} = \left(\frac{0.0755\ g\ Ag}{1.0\ g\ sample} \times \frac{1.50\ g\ sample}{107.868\ gmol^{-1} Ag} \right) - 6.9388 \times 10^{-4}\ mol\ Ag$$

$$= 3.5602 \times 10^{-4}\ mol\ Ag$$

$$W_{Ag} = 3.5602 \times 10^{-4}\ mol\ Ag \times 107.868\ gmol^{-1}\ Ag$$

$$= \mathbf{3.8403 \times 10^{-2}\ g\ Ag\ in\ 1.50\ sample}$$

APPENDIX J

Defined Parameters in Kinetic Models

α	reacted fraction or conversion	
V_m	molar volume of unreacted Ag + AgCl (M/ρ), m^3mol^{-1}	1.92×10^{-5}
M	molecular weight of Ag + AgCl, $kgmol^{-1}$	1.33×10^{-1}
ρ	density of Ag + AgCl, kgm^{-3}	6.94×10^{3}
C	concentration of Cl^-, $molm^{-3}$	3.47×10^{3}
k_o	number of reactive sites per unit area, m^{-2}	
k'	rate constant, m^3s^{-1}	
K	mass transfer coefficient (k_ok'), ms^{-1} (predicted as shown in next page)	6.16×10^{-5}
r_o	radius of solid sphere, m	2.22×10^{-4}
t	time, s	
k_s	first order reaction rate constant, ms^{-1} (assume to be same as K)	6.16×10^{-5}
b	stoichiometric factor	
ρ_B	molar density of Ag + AgCl in solid (ρ/M), $molm^{-3}$	5.20×10^{4}
D	diffusion coefficient, m^2s^{-1}	6.40×10^{-10} [66]
δ	diffusion boundary layer thickness, m	1.00×10^{-4} [78]
A	total surface area of particle, m^2	7.07×10^{-3}
V	total volume of solution, m^3	3.00×10^{-4}

Predicted K was calculated as following:

$$K = \frac{2D}{D_p} + 0.31 N_{SC}^{-2/3}\left(\frac{\Delta p \mu_C g}{p_C^{\,2}}\right)^{1/3}$$

where,

$$N_{SC} = \frac{\mu_C}{p_C\, D}$$

$$\Delta p = |\, p_p - p_c \,|$$

D - diffusity coefficient (m^2s^{-1})
D_p - diameter of particle (m)
N_{SC} - Schmidt number
p_p - density of particle (kgm^{-3})
p_c - density of solution (kgm^{-3})
μ_C - viscosity of solution ($kgm^{-1}s^{-1}$)
g - 9.80665 ms^{-2}
R - diameter of solute (m)

$$N_{SC} = \frac{\mu_C}{p_C D}$$

$$= \frac{1.0355 \times 10^{-3}\ kgm^{-1}s^{-1}}{1.1153 \times 10^{3}\ kgm^{-3} \times 6.4 \times 10^{-10}\ m^2s^{-1}}$$

$$= 1450.7027$$

Therefore,

$$K = \frac{2 \times 6.4 \times 10^{-10}}{444.0106 \times 10^{-6}} + 0.31(1450.7027)^{-2/3} \times$$

$$\left[\frac{(2.8681 - 1.1153) \times 10^{3} \times 1.0355 \times 10^{-3} \times 9.8067}{(1.1153 \times 10^{3})^2}\right]^{1/3}$$

$$= \mathbf{6.16 \times 10^{-5}\ ms^{-1}}$$

APPENDIX K

Determination of Dithizone Solubility in Kerosene

Figure K(1): Absorption spectra of dithizone in kerosene

Figure K(2): Calibration curve of dithizone in kerosene

Calculation of dithizone solubility in kerosene

Dilution factor, DF = 5

Absorbance, A = 0.608

Concentration of dithizone in kerosene = (0.0126 A + 0.0002) DF

= [0.0126 (0.608) + 0.0002] 5

= 3.9304×10^{-2} gL^{-1}

Therefore, the dithizone solubility in kerosene is **3.9304×10^{-2} gL^{-1}**.

APPENDIX L

Raw Experimental Data of Waste Characterization, Leaching, Precipitation and Extraction

A) Characterization

Table A1(i): Water content of sample 1.

Plate (g)	Plate + Sample (g)	Plate + dry sample (g)	% Water
96.7804	118.5054	104.2358	34.32
97.1112	124.5334	106.6948	34.95
98.1478	127.4739	108.2498	34.45

% Water = (34.57 ± 0.33) %

Table A1(ii): Water content of sample 2.

Plate (g)	Plate + Sample (g)	Plate + dry sample (g)	% Water
97.9137	115.3603	111.5830	21.65
97.9167	117.9788	113.6464	21.59
97.8073	115.1174	111.4001	21.47

% Water = (21.57 ± 0.09) %

Table A2: Organic content of sample 2.

Plate (g)	Plate + Sample (g)	Plate + dry sample (g)	% Organic
78.5618	92.6206	90.5956	14.40
72.6534	85.9331	83.9472	14.95
77.9300	89.3544	87.6577	14.85

% Organic = (14.73 ± 0.29) %

Table A3: Density of sample 2.

	Run 1	Run 2	Run 3
P_1	17.178	17.193	17.140
P_2	6.276	6.294	6.265
V_p (cm^3)	0.7611	0.7952	0.7690
Density	2.9199	2.7944	2.8899

Density = (2.87 ± 0.07) gcm^{-3}

B) Leaching

Table B1(i): Leached silver concentration using different types of acid (4.0 M).

Experimental conditions: L/S= 200, T= 29.5°C, stirring speed= 500 rpm.

[Ag] (ppm)				
Leaching time (min)	HCl	HNO_3	H_2SO_4	Aqua Regia
0	0	0	0	0
1	123	94	73	110
3	136	97	79	121
5	139	102	80	125
10	141	105	86	127
15	142	105	94	130
30	144	105	98	132
60	146	110	102	135
90	171	116	108	142
120	182	131	115	165
180	197	132	116	167

Table B1(ii): Leached copper concentration using different types of acid (4.0 M).

Experimental conditions: L/S= 200, T= 29.5°C, stirring speed= 500 rpm.

[Cu] (ppm)				
Leaching time (min)	HCl	HNO_3	H_2SO_4	Aqua Regia
0	0	0	0	0
1	874	818	759	852
3	880	825	819	871
5	880	826	821	872
10	882	828	828	874
15	882	829	828	880
30	884	829	829	880
60	886	839	832	881
90	886	841	842	881
120	896	842	850	885
180	905	843	850	886

Table B1(iii): Leached iron concentration using different types of acid (4.0 M).

Experimental conditions: L/S= 200, T= 29.5°C, stirring speed= 500 rpm.

[Fe] (ppm)				
Leaching time (min)	HCl	HNO_3	H_2SO_4	Aqua Regia
0	0	0	0	0
1	149	214	245	240
3	156	219	247	242
5	157	224	249	245
10	159	229	250	248
15	160	232	252	250
30	162	235	252	254
60	169	243	254	254
90	168	244	256	256
120	170	252	258	256
180	176	252	258	258

Table B1(iv): Leached stanum concentration using different types of acid (4.0 M).

Experimental conditions: L/S= 200, T= 29.5°C, stirring speed= 500 rpm.

[Sn] (ppm)				
Leaching time (min)	HCl	HNO_3	H_2SO_4	Aqua Regia
0	0.0	0.0	0.0	0.0
1	184.5	93.0	55.0	143.7
3	192.1	90.9	61.1	145.9
5	194.1	90.5	61.2	147.1
10	194.4	88.7	61.7	149.6
15	195.8	82.8	61.9	151.5
30	201.1	77.4	62.2	155.4
60	204.5	68.4	62.2	161.0
90	207.5	64.4	64.6	162.1
120	209.3	60.5	65.0	163.8
180	210.2	58.4	65.6	164.2

Table B1(v): Leached calcium concentration using different types of acid (4.0 M). Experimental conditions: L/S= 200, T= 29.5°C, stirring speed= 500 rpm.

[Ca] (ppm)				
Leaching time (min)	HCl	HNO_3	H_2SO_4	Aqua Regia
0	0.00	0.00	0.00	0.00
1	13.91	0.00	0.00	0.00
3	14.01	0.00	0.00	0.00
5	14.08	0.00	0.00	0.00
10	14.08	0.00	0.00	0.00
15	14.13	0.00	0.00	0.00
30	14.28	0.00	0.00	0.00
60	14.28	0.00	0.00	0.00
90	14.53	0.00	0.00	0.00
120	14.60	0.00	0.00	0.00
180	14.73	0.00	0.00	0.00

Table B2(i): Leached silver concentration using different HCl concentrations.

Experimental conditions: L/S= 200, T= 29.5°C, stirring speed= 500 rpm.

[Ag] (ppm)					
Leaching time (min)	0.5 M	1.0 M	2.0 M	3.0 M	4.0 M
0	0.00	0.00	0.00	0.00	0.00
1	1.65	4.60	15.75	56.50	123.00
3	1.70	4.70	16.00	63.00	136.00
5	1.80	5.10	16.00	66.00	139.00
10	1.80	5.20	17.00	66.00	141.00
15	1.85	5.20	17.75	66.50	142.00
30	1.90	5.40	17.75	66.50	144.00
60	1.90	5.50	18.25	67.50	146.00
90	1.95	5.90	18.25	75.50	171.00
120	2.00	6.00	18.75	84.50	182.00
180	2.05	6.20	19.00	85.00	197.00

Table B2(ii): Leached copper concentration using different HCl concentrations.

Experimental conditions: L/S= 200, T= 29.5°C, stirring speed= 500 rpm.

[Cu] (ppm)					
Leaching time (min)	0.5 M	1.0 M	2.0 M	3.0 M	4.0 M
1	338.20	550.40	760.00	797.00	874.00
3	344.40	556.70	766.00	814.00	880.00
5	345.75	568.00	770.50	821.50	880.00
10	346.85	568.40	771.50	823.00	882.00
15	348.15	569.70	773.00	828.00	882.00
30	348.20	570.90	777.50	829.00	884.00
60	348.45	571.70	778.25	834.00	886.00
90	348.55	573.00	778.25	835.00	886.00
120	348.55	575.90	785.50	835.50	896.00
180	348.75	576.00	786.00	836.50	905.00

Table B2(iii): Leached iron concentration using different HCl concentrations.

Experimental conditions: L/S= 200, T= 29.5°C, stirring speed= 500 rpm.

[Fe] (ppm)					
Leaching time (min)	0.5 M	1.0 M	2.0 M	3.0 M	4.0 M
1	99.30	121.70	138.50	149.00	149.00
3	106.75	127.40	140.75	155.00	156.00
5	107.30	127.50	141.75	156.00	157.00
10	111.85	127.70	143.00	156.00	159.00
15	112.00	130.60	143.00	156.50	160.00
30	112.90	131.10	144.00	156.50	162.00
60	113.10	131.20	144.25	157.00	169.00
90	113.20	131.70	145.25	158.00	168.00
120	114.70	132.10	148.00	159.00	170.00
180	114.90	132.80	148.50	160.50	176.00

Table B2(iv): Leached stanum concentration using different HCl concentrations.

Experimental conditions: L/S= 200, T= 29.5°C, stirring speed= 500 rpm.

[Sn] (ppm)					
Leaching time (min)	0.5 M	1.0 M	2.0 M	3.0 M	4.0 M
1	99.00	152.90	182.10	183.80	184.50
3	106.60	161.70	182.40	188.30	192.10
5	107.00	161.90	183.10	188.70	194.10
10	107.10	162.80	184.30	189.20	194.40
15	109.40	165.20	184.80	189.40	195.80
30	109.90	171.20	188.60	199.30	201.10
60	110.60	173.50	197.20	201.90	204.50
90	112.00	178.40	206.60	206.70	207.50
120	113.70	182.60	206.60	208.60	209.30
180	114.50	183.40	206.80	209.50	210.20

Table B2(v): Leached calcium concentration using different HCl concentrations.

Experimental conditions: L/S= 200, T= 29.5°C, stirring speed= 500 rpm.

[Ca] (ppm)					
Leaching time (min)	0.5 M	1.0 M	2.0 M	3.0 M	4.0 M
1	31.93	23.56	19.34	15.49	13.91
3	34.73	25.27	20.24	16.62	14.01
5	34.79	25.31	20.28	16.76	14.08
10	34.82	25.46	20.29	16.80	14.08
15	35.33	25.65	20.32	16.91	14.13
30	35.77	25.71	20.41	17.01	14.28
60	35.81	25.71	20.42	17.03	14.28
90	36.70	25.85	20.51	17.33	14.53
120	37.71	26.18	20.82	17.42	14.60
180	37.80	26.85	21.20	17.60	14.73

Table B3(i): Leached silver concentration using different NaCl concentrations. Experimental conditions: 0.5 M HCl, L/S= 200, T= 29.5°C, stirring speed= 500 rpm.

[Ag] (ppm)					
Leaching time (min)	1.0 M	1.5 M	2.0 M	2.5 M	3.0 M
1	11.84	22.29	28.70	114.90	147.00
3	12.21	22.89	28.80	116.40	161.00
5	12.92	23.41	29.25	119.40	175.00
10	13.41	23.77	29.55	120.20	191.00
15	13.71	24.08	30.55	120.80	191.00
30	14.01	24.55	36.75	121.80	206.00
60	14.24	24.65	36.80	122.40	206.40
90	14.30	24.80	36.82	122.76	207.00
120	14.30	24.82	36.90	122.80	207.20

Table B3(ii): Leached copper concentration using different NaCl concentrations. Experimental conditions: 0.5 M HCl, L/S= 200, T= 29.5°C, stirring speed= 500 rpm.

[Cu] (ppm)					
Leaching time (min)	1.0 M	1.5 M	2.0 M	2.5 M	3.0 M
1	697.00	678.00	679.00	694.00	744.00
3	701.00	746.00	732.00	773.00	793.00
5	703.00	747.00	737.00	777.00	802.00
10	704.00	748.00	750.00	778.00	809.00
15	705.00	755.00	761.00	779.00	814.00
30	707.00	761.00	765.00	779.00	815.00
60	716.00	764.00	767.00	780.00	821.00
90	716.00	765.00	767.00	786.00	827.00
120	732.00	767.00	776.00	787.00	827.00

Table B3(iii): Leached iron concentration using different NaCl concentrations. Experimental conditions: 0.5 M HCl, L/S= 200, T= 29.5°C, stirring speed= 500 rpm.

[Fe] (ppm)					
Leaching time (min)	1.0 M	1.5 M	2.0 M	2.5 M	3.0 M
1	84.00	88.00	85.00	92.00	106.00
3	91.00	95.00	92.00	97.00	107.00
5	91.00	95.00	95.00	99.00	108.00
10	93.00	96.00	95.00	100.00	110.00
15	94.00	96.00	97.00	100.00	110.00
30	94.00	98.00	98.00	101.00	113.00
60	95.00	99.00	98.00	102.00	113.00
90	95.00	100.00	98.00	106.00	114.00
120	96.00	100.00	99.00	107.00	115.00

Table B3(iv): Leached stanum concentration using different NaCl concentration. Experimental conditions: 0.5 M HCl, L/S= 200, T= 29.5°C, stirring speed= 500 rpm.

[Sn] (ppm)					
Leaching time (min)	1.0 M	1.5 M	2.0 M	2.5 M	3.0 M
1	75.00	89.30	84.20	100.30	105.70
3	83.80	92.30	93.80	102.80	106.60
5	84.60	97.50	95.00	107.20	111.10
10	85.30	97.70	100.40	109.70	117.10
15	87.20	98.40	100.80	109.90	118.90
30	89.20	98.60	103.70	112.00	118.90
60	89.30	99.80	104.40	112.50	123.20
90	93.70	99.80	109.30	115.20	124.70
120	96.20	101.60	112.70	115.90	125.70

Table B3(v): Leached calcium concentration using different NaCl concentration. Experimental conditions: 0.5 M HCl, L/S= 200, T= 29.5°C, stirring speed= 500 rpm.

[Ca] (ppm)					
Leaching time (min)	1.0 M	1.5 M	2.0 M	2.5 M	3.0 M
1	1.79	1.32	1.11	0.81	0.71
3	1.80	1.35	1.12	0.82	0.88
5	1.87	1.36	1.13	0.84	0.92
10	1.89	1.39	1.18	0.96	0.92
15	1.90	1.40	1.19	0.99	0.93
30	1.96	1.42	1.19	1.02	0.96
60	1.98	1.43	1.20	1.03	1.00
90	2.05	1.45	1.27	1.10	1.03
120	2.06	1.48	1.30	1.16	1.03

Table B4(i): Leached silver concentration using different liquid/solid ratio. Experimental conditions: 0.5 M HCl-3.0 M NaCl, T= 29.5°C, stirring speed= 500 rpm.

[Ag] (ppm)				
Leaching time (min)	0.25 g	1.50 g	3.00 g	5.00 g
0	0.00	0.00	0.00	0.00
1	31.70	147.00	270.00	274.00
3	32.80	161.00	273.00	276.00
5	33.30	175.00	276.00	278.00
10	34.55	191.00	288.00	280.00
15	34.80	191.00	290.00	280.00
30	39.70	206.00	291.00	281.00

Table B4(ii): Leached copper concentration using different liquid/solid ratio. Experimental conditions: 0.5 M HCl-3.0 M NaCl, T= 29.5°C, stirring speed= 500 rpm.

[Cu] (ppm)				
Leaching time (min)	0.25 g	1.50 g	3.00 g	5.00 g
0	0.00	0.00	0.00	0.00
1	179.00	744.00	1372.00	2150.00
3	181.00	793.00	1500.00	2307.00
5	182.00	802.00	1514.00	2325.00
10	184.00	809.00	1530.00	2372.00
15	189.00	814.00	1557.00	2400.00
30	197.00	815.00	1583.00	2407.00

Table B4(iii): Leached iron concentration using different liquid/solid ratio. Experimental conditions: 0.5 M HCl-3.0 M NaCl, T= 29.5°C, stirring speed= 500 rpm.

[Fe] (ppm)				
Leaching time (min)	0.25 g	1.50 g	3.00 g	5.00 g
0	0.00	0.00	0.00	0.00
1	12.52	106.00	179.00	311.00
3	12.62	107.00	197.00	314.00
5	12.73	108.00	207.00	328.00
10	13.01	110.00	209.00	336.00
15	13.53	110.00	212.00	347.00
30	13.76	113.00	214.00	349.00

Table B4(iv): Leached stanum concentration using different liquid/solid ratio. Experimental conditions: 0.5 M HCl-3.0 M NaCl, T= 29.5°C, stirring speed= 500 rpm.

[Sn] (ppm)				
Leaching time (min)	0.25 g	1.50 g	3.00 g	5.00 g
0	0.00	0.00	0.00	0.00
1	33.80	105.70	152.10	219.20
3	38.50	106.60	173.80	243.90
5	44.30	111.10	184.80	257.30
10	46.70	117.10	194.00	258.20
15	53.60	118.90	237.70	259.90
30	54.30	118.90	251.60	266.70

Table B4(v): Leached calcium concentration using different liquid/solid ratio.

Experimental conditions: 0.5 M HCl-3.0 M NaCl, T= 29.5°C, stirring speed= 500 rpm.

[Ca] (ppm)				
Leaching time (min)	0.25 g	1.50 g	3.00 g	5.00 g
0	0.00	0.00	0.00	0.00
1	0.00	0.71	1.35	2.43
3	0.00	0.88	1.47	4.18
5	0.00	0.92	1.51	4.82
10	0.00	0.92	1.52	5.23
15	0.00	0.93	1.63	5.41
30	0.00	0.96	1.66	5.59

Table B5: Leached silver concentration using different stirring speed.

Experimental conditions: 0.5 M HCl-3.0 M NaCl, L/S= 200, T= 29.5°C.

[Ag] (ppm)		
Leaching time (s)	200 rpm	500 rpm
0	0.00	0.00
30	31.75	53.50
60	55.75	107.75
90	68.75	124.25
120	80.50	189.50
150	120.00	192.00
180	131.00	195.50
300	165.25	229.25
600	204.00	231.00
900	216.50	235.00
1800	230.00	244.00
3600	235.00	

C) Extraction

Table C1(i): Metal concentration in leaching solution before extraction and in organic phase after extraction using 0.02 M Cyanex 272 in kerosene.

pH		[Metal] in aqueous phase before extraction (ppm)				[Metal] in organic phase after extraction (ppm)			
pH_o	pH_{eq}	Ag	Cu	Fe	Sn	Ag	Cu	Fe	Sn
0.43	0.43	186.5	830.5	134.50	143.50	21.0	31.0	10.00	3.00
1.09	1.07	161.0	825.0	106.50	62.00	23.5	39.5	13.50	4.50
1.97	1.88	148.0	811.0	73.50	40.50	16.5	42.5	23.00	11.00
3.78	3.38	142.0	804.5	12.35	26.50	18.5	28.0	8.30	7.00
4.49	3.86	143.5	687.0	4.40	23.50	14.0	22.0	3.25	5.00
5.67	4.80	161.5	27.5	3.20	20.50	28.0	7.5	2.40	3.50
8.57	5.67	146.5	10.5	3.15	19.00	16.0	5.5	2.40	3.20
8.62	5.94	148.5	7.5	3.15	17.25	17.5	4.5	2.45	0.40
9.92	7.62	150.5	6.5	3.20	22.50	23.5	4.0	2.40	0.25
11.51	9.54	186.5	6.5	3.30	54.00	23.0	4.0	2.55	5.50
12.59	12.34	186.5	10.0	3.40	63.00	17.5	3.0	2.70	12.75
13.49	13.44	171.5	71.5	3.75	86.50	21.0	4.5	2.90	22.50
13.83	13.82	155.5	523.5	4.25	98.50	18.0	1.0	3.20	29.25

Table C1(ii): Silver concentration in silver nitrate solution before extraction and in organic phase after extraction using 0.02 M Cyanex 272 in kerosene.

pH_o	pH_{eq}	[Ag] in aqueous phase before extraction (ppm)	[Ag] in organic phase after extraction (ppm)
0.96	0.97	211.25	29.38
3.37	3.79	209.85	34.85
5.20	5.05	201.88	36.63
9.10	5.53	170.80	42.60
10.89	7.34	14.08	12.53
12.81	10.00	6.95	6.78

Table C1(iii): Silver concentration in silver nitrate solution at different pH.

pH	[Ag] in $AgNO_3$ (ppm)
1.05	204.50
2.09	204.50
2.86	204.50
3.34	182.50
5.32	182.00
9.14	160.50
10.01	10.00
11.39	9.50
13.42	8.50

Table C1(iv): Silver concentration in silver chloro complexes solution before extraction and in organic phase after extraction using 0.02 M Cyanex 272 in kerosene.

pH_o	pH_{eq}	[Ag] in aqueous phase before extraction (ppm)	[Ag] in organic phase after extraction (ppm)
0.39	0.39	202.50	28.50
1.46	1.46	170.50	23.00
4.24	3.78	149.00	15.50
5.06	5.08	159.00	14.50
7.32	6.11	169.50	14.00
8.75	6.49	147.00	10.00
9.50	7.37	154.50	11.50
10.03	7.56	161.00	9.50
12.13	11.60	202.50	20.50
13.64	13.72	191.00	7.00

Table C2(i): Metal concentration in leaching solution before extraction and in organic phase after extraction using 0.02 M dithizone in chloroform.

pH		[Metal] in aqueous phase before extraction (ppm)				[Metal] in organic phase after extraction (ppm)			
pH_o	pH_{eq}	Ag	Cu	Fe	Sn	Ag	Cu	Fe	Sn
3.22	0.70	147.0	809.5	14.50	32.5	16.0	802.0	0.05	0.5
4.20	0.83	145.0	705.0	6.25	26.5	23.5	697.0	0.05	0.5
5.04	1.59	159.0	30.5	4.50	24.3	135.0	26.5	0.00	0.3
5.78	1.95	162.0	17.5	3.20	23.2	142.5	14.8	0.00	0.2
8.75	4.56	156.0	8.5	3.15	20.4	139.0	7.1	0.40	0.2
9.23	8.03	153.0	7.0	3.25	24.0	139.0	6.0	0.35	0.2
12.05	11.81	187.0	9.5	3.30	62.5	179.5	8.0	0.50	0.7
12.70	12.61	188.0	25.0	3.45	75.5	182.0	21.1	0.25	1.0

Table C2(ii): Silver concentration in silver nitrate solution before extraction and in organic phase after extraction using 0.02 M dithizone in chloroform.

pH_o	pH_{eq}	[Ag] in aqueous phase before extraction (ppm)	[Ag] in organic phase after extraction (ppm)
3.37	0.15	209.85	209.85
5.20	3.11	201.88	201.88
9.10	3.22	170.80	170.80
10.78	7.87	14.08	14.08
12.81	10.81	6.95	6.10

Table C2(iii): Silver concentration in silver chloro complexes solution before extraction and in organic phase after extraction using 0.02 M dithizone in chloroform.

pH_o	pH_{eq}	[Ag] in aqueous phase before extraction (ppm)	[Ag] in organic phase after extraction (ppm)
1.25	0.86	202	142
2.47	1.59	205	174
4.73	1.96	233	209
8.11	2.80	224	206
11.95	11.51	390	373
13.44	13.67	353	335

Lampiran 20

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UNIVERSITI TEKNOLOGI MALAYSIA

BORANG PENGESAHAN
LAPORAN AKHIR PENYELIDIKAN

TAJUK PROJEK : **Pengekstrakan Cecair-Cecair Terpilih Logam Berharga Dari Sisa Semikonduktor**

Saya **PROF. MADYA DR. HANAPI BIN MAT**
(HURUF BESAR)

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Tarikh: 12 hb. Jun 2006

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