

# **A Study of Recovery and Separation of Heavy Metal Ions from Waste Solutions Using Precipitate Flotation**

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of the degree of Doctor of Philosophy (Ph.D)

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## Statement of Authorship

Except where explicit reference is made in the text of the thesis, this thesis contains no material published elsewhere or extracted in whole or in part from a thesis by which I have qualified for or been awarded another degree or diploma. No other person's work has been relied upon or used without due acknowledgment in the main text and bibliography of the thesis.

A handwritten signature in black ink, appearing to be 'Xiang Ren', written in a cursive style with a long horizontal stroke extending to the right.

Xiang Ren

09 May, 1999

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## Abstract

An important industrial problem is the production of wastewater containing a large amount of heavy metal ions. The study described in this thesis is trying to use precipitate flotation technology to explore techniques for not only removing heavy metal ions from the solution, but also selectively separating them to recycle of the recovered metal value from industry wastewater.

Zinc and copper hydroxide precipitation and flotation behaviour have been studied. It shows that it is almost impossible to separate copper and zinc ion using hydroxide precipitate flotation when the solution contains  $\text{Fe}^{3+}$  or  $\text{Al}^{3+}$  ions. The influence of additional ions such as  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , and other electrolytes on the flotation and separation have been studied. DLVO theory has been used to explain the mechanisms occurring in the process.

A new process, named "self-carrier" precipitate flotation using anionic surfactants, has been developed to improve the flotation recovery and reduce the consumption of collector. The mechanism of the process is discussed in detail with reference to data collected from Optical Microscopy, Scanning Electron Microscopy and Zeta Potential Measurement.

The xanthates are the most commonly used class of sulphide mineral collectors. This study investigated the copper sulphide precipitate reactions and the aggregation behaviour, the influence of oxidation, additional ions etc., and successfully used xanthate to float the sulphide precipitates. The mechanisms occurring in this process have been discussed. The investigation of the sulphide precipitate flotation behavior using a cationic collector has also been carried out to discover the possibility of copper and zinc separation.

An important application of this study is the flotation and separation of copper and zinc ions from industry wastewater. The tailing wastewater from a mineral processing plant, Woodlawn Mines (N.S.W., Australia), which contains high concentrations of harmful heavy metal ions was used to test the flotation and separation of the heavy metal ions. Both xanthate and cationic collectors have been investigated for the flotation separation. Effective separation has been achieved.



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**Appendix 2 Calculation of Aggregation and Dispersion of Fine Particles**

**Appendix 3 List of Publications produced During Ph.D Study**

**Appendix 4 Copy of Main Publication**

*– A Study of “Self-Carrier” Precipitate Flotation for the removal  
of Heavy Metal Ions from Solution*

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## List of Abbreviations

SDS	Sodium Dodecyl Sulfate
SDBS	Sodium DodecylBenzeneSulphonate
EXt	Sodium Ethyl Xanthate
IBXt	Sodium IsoButyl Xanthate
MAA	Methyl Amyl Alcohol
DAA	Dodecylammonium acetate
$pH_{pi}$	The pH at which the precipitation increases
$pH_{pd}$	The pH at which the precipitation decreases
$pH_{fi}$	The pH at which the precipitate flotation recovery increases
$pH_{fd}$	The pH at which the precipitate flotation recovery decreases
$[Cu^{2+}]_{ini}$	The initial copper concentration
$[Zn^{2+}]_{ini}$	The initial zinc concentration
$[S]_{total}$	The total concentration of added sodium sulphide precipitant
$V_A$	London-van der Waals forces
$V_R$	Overlapping of electric double layers
$V_T$	The total energy
$A$	The Hamaker constant; ;
$R_1$ and $R_2$	The radii of the two colloid spheres
$h$	The distance between the spheres
$\kappa$	The Debye-Huckel parameter ( $m^{-1}$ )
$\epsilon_r$	The relative permittivity
$\psi_1$ and $\psi_2$	The zeta or Stern potential of particles 1 and 2
$e$	The electronic charge
$N_A$	The Avogadro constant
$k$	The Boltzmann's constant
$T$	The absolute temperature
$z_i$	The valency
$M_i$	The molar concentration
$\kappa^{-1}$	The "thickness" of the double layer
SCPF	"Self-carrier" precipitate flotation

## Chapter I Introduction

### 1.1 Problem

An important industrial problem is the production of wastewater containing a large amount of heavy metal ions. Heavy metal ions such as mercury and cadmium exhibit toxicity in humans at extremely low concentrations. Elements such as copper, zinc, lead, chromium and silver are also very toxic to humans and animals although concentrations of these elements can be higher before they are considered dangerous. Allowable concentrations, of some heavy metals in potential water supplies were suggested by Dickinson (1974) and Morictor (1994) as follows:

Heavy Metals	Dickinson (1974)	Morictor (1994)
Lead	Not more than 0.05 mg/litre	Not more than 0.01 mg/litre
Chromium	Not more than 0.05 mg/litre	Not more than 0.05 mg/litre
Cadmium	Not more than 0.01 mg/litre	Not more than 0.002 mg/litre
Copper	Not more than 1.0 mg/litre	Not more than 1.0 mg/litre
Zinc	Not more than 5.0 mg/litre	Not more than 3.0 mg/litre

Heavy metal ions are insidious pollutants of our environment. They are not biodegradable and through the food chain, they can be highly bio-accumulated, remaining in human and animal bodies and causing a number of diseases. The most publicized example of such pollution occurred in Japan about 40 years ago (Anon, 1971). Mercury from a plastic manufacturing factory was discharged into Minamato Bay and through microorganisms and fish passed on to local people, causing diseases of severe chronic mercury poisoning.

The sources of heavy metal ions in industrial wastewater can be traced to metal processing, metal finishing, electroplating, mining and mineral processing waste. The first three sources normally contain appreciable quantities of heavy metal ions such as nickel, chromium, copper, and zinc, as well as two specific types of salts which are considered to be particularly toxic, namely chromates and cyanides. Before being discharged, they are

usually required to be treated until the total concentration of toxic materials in less than a few parts per million (Baier, 1974). Some acid mine drainage and mineral processing tailings wastewater may also contain significant quantities of dissolved copper, zinc and lead. Thus at the Woodlawn Mines (N.S.W., Australia), the tailings from mineral processing plant are stored in a conventional water-storage type dam, the wastewater in the tailing dam is very acidic (pH value is about 2.7) and contains high concentrations of harmful heavy metal ions, such as zinc (>2000ppm), copper (>100ppm) and cadmium (>10ppm).

The recovery or removal of heavy metal ions from waste water or aqueous solutions may be achieved by applying a variety of methods, e.g., chemical precipitation, coagulation and flocculation, ion exchange and solvent extraction, complexation, cementation, electrochemical processes, biological processes, adsorption, flotation, evaporation, filtration, and membrane processes (Peters, Ku and Bhattacharyya, 1985). The industrial sources and treatment technologies for different heavy metal ions, as well as some other toxic elements, have been well documented (Patterson, 1985).

By far the most widely used purification process for wastewater containing heavy metal ions is that of chemical precipitation, followed by sedimentation or coagulation and flocculation. It has been reported that approximately 75% of electroplating facilities employ precipitation treatment using either hydroxide, carbonate, or sulfide treatment, or some combination of these treatments (Patterson and Minear, 1975). Among these, the most common precipitation technique is hydroxide treatment due to its relative simplicity and the low cost of the lime precipitant (Peters, Ku and Bhattacharyya, 1985). Although this treatment method can, when operating at peak efficiency, give good results for each heavy metal ion, under normal operating conditions the effluent often exceeds the established limits required for disposal to sewer (Sanciolo, Harding, and Mainwaring, 1989). Another disadvantage of this method is the large quantity of hydroxide sludge produced and the very slow settling rate of this sludge. This sludge normally can not be reused and a secondary treatment may be required, such as packing and deep landfill disposal which probably generate a secondary pollution. Clearly, there is a need for a more reliable and effective means for the treatment of wastewater containing heavy metal ions.

Flotation is well known as a most effective separation method in mineral processing. A rough estimate of the quantity of crushed ore treated by flotation is about  $9 \times 10^9$  tons annually (Matis and Zouboulis, 1995). Ion, precipitate and adsorbing colloid flotation are relatively new foam separation techniques aimed at the removal of metal ions, charged species and fine particulate materials from aqueous solutions. A brief review is given in the next chapter. Compared with precipitation and sedimentation, the advantages of these methods are that they are very fast processes, capable of application at different scales, requires very limited space and produces a relatively small amount of sludge. These techniques have been well reviewed in each decade and almost every type of heavy metal ion has been examined (Sebba, 1962a; Pinfold, 1972a, b; Clark and Wilson, 1983; Zouboulis, Matis and Stalidis, 1992). Nevertheless, a great deal of work still needs to be done to develop the process to its full potential.

Any ideal technique for the heavy metal wastewater treatment has to not only remove heavy metal ions from the solution, but must also selectively separate them to enable the recycling of the recovered metal value and subsequently achieve a non-waste technique. In recent years, some studies have appeared in this area, mainly using ion flotation technique (Matis and Mavros, 1991). As opposed to precipitate flotation, ion flotation requires stoichiometric or greater amounts of the collector since the ion and the collector actually form a compound and this will increase the cost of the process and restrict its usage.

The purpose of the study described in this thesis is to examine the precipitate flotation process in detail to postulate ideas and consider techniques for more efficient recovery and separation of heavy metal ions, firstly from artificial solution and then from industrial waste water. The tailing wastewater from a mineral processing plant, Woodlawn Mines (N.S.W., Australia), was chosen as an industrial waste solution for examination. The technique proposed is not restricted to the wastewater from this particular company, as the fundamental aspects of the precipitation and flotation have been studied in detail. The mechanisms involved in the process, such as the reactions among ions, the phase equilibrium in the solution; the presence of other ions and electrolytes and the electrochemistry of the flotation process, have been studied by using and applying a variety of modern physical-chemistry calculations and instrumental techniques.

## 2.2 Aim

To investigate the precipitate flotation method for recovery and separation of heavy metal ions and to understand the mechanisms involved in the process.

## 2.3 Objectives

- To investigate the precipitation and flotation behavior of zinc and copper hydroxide; to discover the possibility of separation of these two heavy metals; to study the influence of pH and the presence of other ions and electrolytes on the flotation and separation; to explain the processes involved; and to discuss the possible mechanisms.
- To develop a new process which can improve the precipitate flotation technique, and is less sensitive to changes in flotation conditions. To understand the mechanisms occurring in the process.
- To investigate the heavy metal sulphide precipitate flotation behavior using xanthate as collector for the separation of heavy metal ions. To discover the mechanisms occurring in this process and to further develop this new process.
- To study sulphide precipitate flotation using a cationic collector for flotation and separation. To investigate the possibility of selective separation of copper and zinc sulphide precipitate.
- To investigate the possibility of flotation and separation of industrial waste water (from the Woodlawn Mines); to recommend the direction of future research in this area.

## Chapter II Research Background

In recent decades, flotation has come to be used extensively in wastewater treatment, chemical technology, hydrometallurgy, the petroleum industry, seawater treatment, sea manganese nodule treatment, etc. The heavy metal ions produced as a result of metal processing, metal finishing, electroplating, chemical reactions, hydrometallurgy leaching, mining and mineral processing in the industrial waste solution are potentially able to be recovered or removed by flotation processes, such as ion flotation, precipitate flotation and adsorbing colloid flotation methods.

The purpose of this chapter is to review the flotation processes currently available for the treatment of wastewater laden with heavy metals. Chemical precipitation followed by sedimentation, the most widely used process for removal of heavy metals from solution, will also briefly be described. The applications reviewed will serve as examples, to explain the different techniques, highlight significant contributions to the field and indicate the problems remaining. It is not intended to cover the entire literature.

### 2.1 Existing Methods for Heavy Metal Wastewater Treatment

A number of specialized processes for the removal of metal ions from waste solution have been developed. These processes include: *chemical precipitation* (Jenkins et al., 1964; Linstedt et al., 1971; Patterson et al., 1977; Bhattacharyya et al., 1981), *coagulation/flocculation* (Daniels, 1975), *ion exchange/solvent extraction* (Knocke, 1977; Clevenger and Novak, 1983; McDonald and Bajaw, 1977), *complexation* (Jellinek and Sangel, 1972; Swanson, 1973), *electrochemical operations* (Farkas and Mitchell, 1984), biological operations (Chang et al., 1984), *membrane processes* (Bhattacharyya and Grieves, 1977) and *flotation*. So far, the most widely used process for removal of heavy metal ions from waste solution is that of chemical precipitation, followed by filtration or sedimentation. In accordance with the research topic of this study, only chemical precipitation, using either hydroxide or sulphide precipitant, have been briefly reviewed here.

### 2.1.1 Hydroxide Precipitation

The most commonly used chemical precipitation technique is hydroxide precipitation, due to its relative simplicity, low cost of precipitant (lime is normally used as precipitant) and ease of automatic pH control (Peters, Ku and Bhattacharyya, 1985). When this method of treatment operates at peak efficiency, good results for each heavy metal ion can be obtained (Sanciolo et al., 1989).

Dean et al. (1972) point out that iron, manganese, copper, zinc, nickel and cobalt can be almost completely removed by hydroxide precipitation, with almost no special modification required. However, the precipitation of mercury, cadmium and lead may be slow and incomplete. When chromium is present, a reduction of the solution with sodium metabisulphite, ferrous sulphate or metallic iron prior to hydroxide precipitation is required.

Peters and Ku (1984) studied hydroxide precipitation of zinc, cadmium and nickel for various pH conditions, reaction times and concentration of complexing agents. It was found that the metal hydroxide precipitates tend to be colloidal and amorphous, causing the resulting sludge to be voluminous. It was furthermore observed that the presence of complexing agents severely inhibited metal hydroxide precipitation, and that higher pH conditions enhance the nucleation rate and the particle size distribution. With the absence of chelating agents, results of  $\text{Zn} < 0.5\text{ppm}$  and  $\text{Cd} < 0.3\text{ppm}$  could be obtained.

A process of hydroxide precipitation for the recovery of chromium from spent tan liquor was reported by Arumugam (1976). The removal of chromium exceeded 98% at  $\text{pH}=6.6$  using lime as precipitant. The precipitated chromium hydroxide was separated from the solution by settling, filtered and then redissolved in sulphuric acid to form chromium sulphate which could be recycled for further tanning.

Different heavy metal ions in a waste solution may require different optimum pH for precipitation of each metal ion. Lanouette (1977) pointed out that it may be possible to precipitate one or more of the metal ions separately at one pH and treat the remaining

solution at another pH to achieve the separation of different metal ion from the waste solution.

Peters et al. (1984) have pointed out the limitations of hydroxide precipitation for removal of heavy metal ions from waste solutions as follows:

- Hydroxide precipitates tend to resolubilize if the solution pH is changed.
- Chromium (VI) is not removed by hydroxide precipitation.
- Removal of metals in mixed metal wastes by hydroxide precipitation may not be effective because minimum solubilities occur at different pH conditions for different metals.
- The presence of complexing agents may have an adverse effect on metal removal.
- Cyanide interferes with heavy metal removal by hydroxide precipitation.
- Hydroxide sludge quantities can be substantial and are generally difficult to dewater due to the amorphous particle structure.

### 2.1.2 Sulphide Precipitation

Sulphide precipitation is an effective method to achieve a high degree of separation of various heavy metals from industrial wastewater. The high reactivity of sulphide ions ( $S^{2-}$  and  $HS^-$ ) with most heavy metal ions and the very low solubility of heavy metal sulphides over a broad pH range are attractive features when compared to the corresponding hydroxide precipitation process (see Fig. 2-1-1).

Sulphide precipitation is known to present some advantages (Peters, et al., 1985), such as:

- Low solubility of metal sulphides over a broad pH range (see Fig. 2-1-1).
- Low reactive time requirement because of the high reactivities of sulphides.
- Feasibility of selective metal removal and recovery.
- Fewer products with high enrichment. This makes it possible to reuse the products and achieve selective separation from different ions.



- Better sludge thickening and dewatering than the corresponding metal hydroxide sludges.

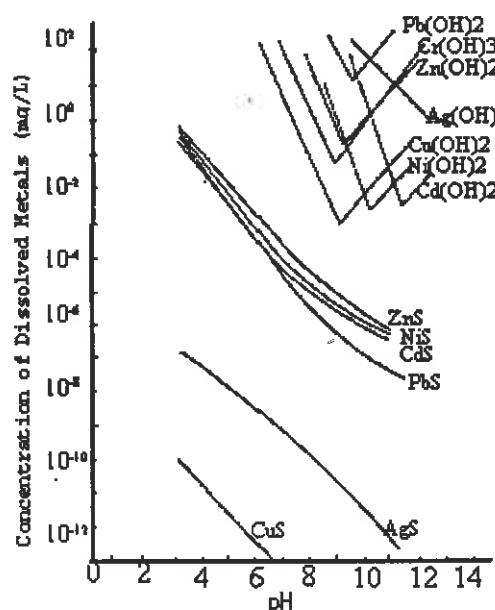


Fig. 2-1-1 Solubility of metal hydroxides and sulphides as a function of pH (Palmer et al., 1988)

Currently, there are two main processes for sulphide precipitation of heavy metal ions from wastewater: Soluble sulphide precipitation (SSP) and insoluble sulphide precipitation (ISP). In the SSP process, sulphide is added in the form of a water soluble sulphide reagent, such as sodium sulphide ( $\text{Na}_2\text{S}$ ) or sodium hydrosulphide ( $\text{NaHS}$ ). In the ISP process, a slightly soluble sulphide precipitant such as ferrous sulphide ( $\text{FeS}$ ) or calcium sulphide ( $\text{CaS}$ ) is added into the wastewater to precipitate the heavy metal ions as sulphide precipitates, as most heavy metal sulphides are less soluble than ferrous sulphide or calcium sulphide.

The main advantages of the SSP process comprise the facts that only a small amount of precipitant (stoichiometric or a slight surplus) is required, that the reaction speed is fast and that small quantities of the sludge contain high metal grade. The potential of  $\text{H}_2\text{S}$  gas evolution in acidic solution and the very fine colloidal precipitate particles, which may cause difficulty in the subsequent settling or filtering process are to be counted among the

disadvantages of this process. In currently operated soluble sulphide systems, the process tanks are always enclosed and vacuum evacuated to minimize the  $H_2S$  gas problem.

The use of the SSP process for the removal of heavy metal ions has gained considerable industrial importance (Robinson, 1978; Schlauch and Epstein, 1977). A full scale SSP treatment plant for an electroplating facility in the U.S.A. was constructed to remove different heavy metals from wastewater (Resta et al., 1978; Whang et al., 1982). Removals of Cd, Cr, Cu, Ni and Zn exceeding 90% were observed with over 80% of Pb removal.

The SSP process has been used to obtain better precipitation for heavy metal wastewater containing some complexing agents, such as ammonia and EDTA. Peters and Ku (1984) compared the precipitation of zinc, cadmium and nickel using both hydroxide and sulphide precipitation at various pH conditions with and without complexing agents. Enhanced removals were achieved using sulphide precipitation in the presence of complexing agents (particularly for EDTA), as compared to similar hydroxide precipitation conditions. The presence of ammonia had a minimal effect on metal sulphide removal and precipitation kinetics. The effect of chelants on metal sulphide precipitation was addressed by Peters et al. (1984). EDTA forms strong metal chelates which interfere with zinc sulphide precipitation. However, the removal of copper ion from wastewater was close to completion, even in the presence of EDTA.

The SSP process was also used for selective separation of different heavy metals from wastewater in accordance with the different solubility products of metal sulphide precipitates. Bhattacharyya et al. (1979) found sulphide precipitation using  $Na_2S$  to be highly effective in obtaining a high degree of separation of heavy metal cations (Cd, Zn, Cu, and Pb) and of the oxyanions of arsenic and selenium from a dilute synthetic mixture and from the wastewater of an actual copper smelting plant. Optimum overall separation of arsenic and other heavy metals as well as optimum precipitate settling rates at sulphide dosages of about 60% of the theoretical values and at a final pH greater than 8.0 were achieved. The removals of Cd, Zn, and Cu from the actual wastewaters were greater than 99%. As and Se removals were 98% and >92%, respectively. The metal separations and

settling rates obtained with conventional hydroxide precipitation (lime) were considerably lower than those obtained with sulphide precipitation.

Compared to the SSP process, a significant advantage of the ISP process is the absence of any detectable  $H_2S$  gas. The disadvantages of this process include considerable larger than stoichiometric precipitant consumption and a large quantity of sludge due to the iron hydroxide formation.

Schlauch and Epstein (1977) studied the use of ferrous sulphide for the removal of heavy metals (Cu, Cd, Cr and Zn) from an influent wastewater.  $FeS$  was found to be superior to the conventional hydroxide precipitation which employed lime as the precipitant.

Kim (1983) found that calcium sulphide slurries, prepared by reacting lime with either hydrogen sulphide or sodium hydrosulphide, were effective for metal sulphide precipitation. The addition of  $CaS$  was controlled in most cases by adjusting the pH. Wastewater containing oil emulsions and dissolved copper was effectively treated using  $CaS$  precipitant (Kim and Amodeo, 1983). The  $CaS$  particles acted as nucleisites for the production of the metal sulphide precipitates. The dissolved calcium also functioned as a coagulant. Since the calcium added in the form of  $CaS$  was dissolved in the wastewater after reaction, the increase in sludge volume was minimal.

### 2.1.3 Other Precipitation Methods

Carbonate precipitation is an alternative method for hydroxide precipitation. In some cases, it has some advantages of conventional hydroxide precipitation, such as lower pH condition and better sludge filtration characteristics.

Patterson et al. (1977) indicated that in the case of nickel and zinc precipitation, no benefit was derived by using carbonate precipitation as opposed to hydroxide precipitation. However, for cadmium and lead removals, comparable residual cadmium concentration was observed approximately 2 pH units lower in carbonate than in hydroxide treatment. The filtration rate of the cadmium carbonate precipitate was approximately twice that of the cadmium hydroxide precipitate. Lead carbonate precipitation was also shown to

require lower pH and to result in better filtration than was the case in lead hydroxide precipitate. Cho and Kim (1991) studied selective precipitation of cadmium from synthetic wastewater containing cadmium and copper ions through carbonate infusion. The optimum condition for selective precipitation of the cadmium from the mixed solutions were around pH 9 at a mixing rate of 100 rpm.

Combined hydroxide, sulphide or carbonate precipitation for heavy metal wastewater treatment has some times been used to obtain more effective removal of heavy metals. McAnnally et al. (1984) used a combined soluble sulphide and carbonate precipitation method for the removal of nickel from a synthetic nickel plating wastewater. Good results were obtained for the nickel removal from the synthetic wastewater at a pH range of 10 to 11. Optimum removal occurred at pH 11 where a residual total nickel concentration of 0.1ppm was obtained. Talbot (1981) described a combined hydroxide-sulphide treatment process using less than the stoichiometric addition of sulphide precipitant. Less than 0.05 ppm Cd can be obtained from a solution initially containing 15 ppm Cd by using this process, while the conventional hydroxide precipitation provided a residual concentration of 4.8 ppm Cd.

It was found that the addition of ferrous sulphate improved the precipitation of chromium, nickel and cadmium using sulphide as precipitant (Higgins and Slater, 1984). Such treatment was very effective in reducing hexavalent chromium to trivalent chromium. An addition of ferrous sulphate to the alkaline solution ( $7 \leq \text{pH} \leq 10$ ) caused the iron to precipitate as iron hydroxide and increased the flocculation of other sulphide precipitates.

Brantner and Cichon (1981) compared the hydroxide, carbonate and sulphide precipitation treatments for removal of heavy metals (Zn, Cr, Cd, Cu, and Pb). Precipitation of zinc, cadmium and copper was effectively achieved by all three processes. However, effective removal of chromium was only achieved by sulphide precipitation. Removal of lead was effectively achieved by both carbonate and sulphide precipitation causing a residual filtered lead concentration of  $<0.1\text{ppm}$ , while hydroxide precipitation resulted in a mean effluent level of  $0.2\text{ppm}$ . Of the three precipitation processes, carbonate precipitation produced the smallest sludge volume, while the sulphide precipitation was most stable in acidic solution.

## 2.2 The Development of the Flotation Method for the Removal of Heavy Metal Ions from Waste Solution

The techniques of ion, precipitate and adsorbing colloid flotation are physical methods for the removal of the ions present in dilute liquors. The ions in the liquor, with the aid of suitable reagents and surfactant, are concentrated using bubbles and removed as a froth product. Flotation, offering higher rates and a better effluent quality, is also an alternative solid-liquid separation method to sedimentation or filtration after the precipitation process.

Compared with precipitation and sedimentation, flotation offers several distinct advantages (Peters et al., 1985):

- Simplicity.
- Flexibility and effectiveness of operation.
- Limited space requirements due to rapid reactions.
- Production of small and concentrated volumes of sludge.
- Moderate costs comparable to that of lime precipitation, and low costs in terms of labor, equipment, energy and chemicals.
- Capability of application on small, intermediate and large scales.
- Capability of reducing the contaminant concentrations well below the standards established by regulatory agencies.

### 2.2.1 Nomenclature

The nomenclature applied to the ion flotation, precipitate flotation and adsorbing colloid flotation causes considerable confusion in different research papers.

*Ion flotation* was first introduced by Sebba (1959a), and the basic principles of technique were outlined in subsequent publications (Sebba, 1959b, 1960, 1962). He gave the following descriptor definition of ion flotation: *a surface-active ion, of opposite charge to the ion that is to be concentrated, is added to the solution and gas bubbles are introduced*

*well below the surface.* These bubbles collect the surface-active material, which carries with it the opposite charged ion, to form a froth on the surface. The froth subsequently collapses to produce a scum which contains the collected ion in the concentrated form. The product of the surface-active ion (called the *collector*) and the target surface-inactive ion (called the *colligend*) is known as the *sublate*, and when it ultimately reaches the surface of the solution, it is always present as a solid. When concentrations of collector and colligend are low (about  $10^{-5} M$ ), the flotation occurs from a true solution. Increasing the concentrations of the collector and the colligend may lead to precipitation of sublate before gas is passed into the solution and on this basis it is considered that ion flotation is a form of precipitate flotation (Pinfold, 1972a). On the other hand, some authors e.g. Shimoizaka (1973) have defined ion flotation broadly as the removal of the colligend from the solution, using flotation. In this definition, ion flotation includes the concepts of precipitate flotation and adsorbing colloid flotation.

*Precipitate flotation*, as defined by Baarson and Ray (1963), occurs when: a precipitate is formed and then foamed off. Pinfold (1972b) in his excellent review of precipitate flotation defined it as: *the process in which an ionic species is concentrated from an aqueous solution by forming a precipitate which is subsequently removed by flotation.* He distinguished three variations of the process.

1. *Precipitate flotation of the first kind* involving the flotation of precipitate particles by a surface-active species where the latter is not a chemical constituent of the precipitate substance and occurs only on the surface of the particles.
2. *Precipitate flotation of the second kind* using no surfactant to float the particles but involving two hydrophilic ions, which precipitate to form a solid with a hydrophobic surface.
3. *A form of ion flotation* in which ions are precipitated by surfactants, and the resulting particles are floated, which is in effect the definition of ion flotation.

*Adsorbing colloid flotation* has been defined by Grieves et al. (1969) as: *a separation of a solute through adsorption on colloidal particles which are then removed by flotation.* It is not clear whether the removal of a solute is by adsorption on or coprecipitation with colloidal particles, hence it is difficult to distinguish it from the precipitate flotation as defined above.

Although the above classification of the diverse flotation processes is probably the most famous, it has not universally been accepted, as the definitions tend to overlap causing considerable confusion. Ferguson, et al. (1974) presented a more common sense classification:

- *If the surfactant, also known as collector, forms an insoluble product with the nonsurface-active material, the process is known as ion flotation.*
- *If the nonsurface-active material forms a precipitate with something other than the collector, which is in turn made surface active by the collector, the process is called precipitate flotation.*
- *Adsorbing colloid flotation is defined as the removal of dissolved material by adsorption on colloidal particles followed by the removal of the colloidal particle, dissolved material.*

For reasons of clarity the latter definitions have been adopted for this study.

### 2.2.2 Ion Flotation

The ion flotation technique has been regularly reviewed since the sixties, almost every decade (Sebba, 1962; Pinfold, 1972; Clark and Wilson, 1983; Matis and Mavtos, 1991). It is neither possible nor necessary to include all past researches and applications of ion flotation, suffice it to highlight some of the more significant contributions to the development of this technique, particularly in the recent years.

#### 2.2.2.1 Removal of metal ions by ion flotation

The removal of most common heavy metal ions, such as copper, zinc, cadmium, lead, etc., from waste solution using the ion flotation process has been well researched in the past forty years. In particular, Clark and Wilson (1983) have made an excellent review. As most heavy metal ions are positively charged in aqueous solution, negatively charged anionic surfactants are commonly used as collector. Sodium lauryl sulphate (denoted as NLS, SLS, or SDS when lauryl is dodecyl) and sodium dodecylbenzenesulphonate (SDBS) are widely used anionic collectors in the ion flotation process.

Jurkiewicz (1984-85) investigated ion flotation of cadmium cations with sodium lauryl sulphate and sodium laurate from sulphate and nitrate solution. Sodium lauryl sulphate was ineffective for the cadmium removal. However, sodium laurate was highly effective for cadmium ion flotation. The presence of electrolyte in the solution was found to have a negative influence on ion flotation.

Bernasconi et al. (1987a) studied barium ion flotation using sodium lauryl sulphate. It was found that the nature of the chemical interactions between the barium ions and the collector is independent of the pH. In fact, the reaction is controlled by the solubility product equation. The adsorption of collector in the precipitated phase of barium lauryl sulphate corresponds to the successive deposition of two monolayers: when the surface coverage is close to or less than the monolayer of surfactant, the solid particles are flocculated and float easily. After the adsorption of the second layer of collector, the solid particles disperse and float badly: the ionic groups of the second layer of surfactants are orientated towards the solution. A mathematical model (Bernasconi et al., 1987b) was also used to estimate the recovery curves and particularly the optimal recovery conditions as a function of nitric acid content and initial barium concentration.

Bernasconi, et al. (1988) also published their research on the removal of zirconium from uranyl nitrate solutions by ion flotation, in which alkylsulphate of various chain length (C10, C12, C14) were used as collectors. It was indicated that Zr can be removed from highly concentrated acid uranyl nitrate solutions and that the alkyl chain length is an optimisation factor of the ion flotation process. It was further established that the recovery rate decreases when the ionic strength increases.

Thiol collectors such as O-alkyl dithiolcarbonates (usually termed xanthates) are known to exhibit a high level of chemical reactivity for heavy metals, both in solution and at sulphide mineral surfaces (Fuerstenau, 1976). Xue et al. (1990) studied the effects of commonly accompanying ions such as  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Cu}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  and  $\text{CO}_3^{2-}$  on nickel ion flotation using sodium butyl xanthate as collector. The  $\text{Mn}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{Na}^+$  ions promoted the floatability of Ni-Butyl Xanthate (Ni-BuX), due to the improvement of the Ni-BuX coagulation. Extraneous  $\text{Cu}^{2+}$  ion decreased the nickel flotation recovery as

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copper ion can react with xanthate ion more strongly than nickel ion.  $\text{Fe}^{2+}$  ion depressed the Ni-BuX flotation when the concentration of ferrous was above 30ppm, and  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  ions did not influence the flotation recovery. In the presence of carbonate ion, the nickel ion flotation recovery decreased.

Wang et al. (1990) used the coordination chemistry calculation method to predict the effect of carbonate ion on nickel and cobalt ion flotation using sodium butyl xanthate or sodium diethyldithiocarbonate as collector. When nickel ion flotation was conducted in a concentrated carbonate solution at pH 8.5-9.5, high flotation recovery could be obtained using either of the two collectors. However, in the case of cobalt ion flotation when carbonate ion was present, sodium butyl xanthate was ineffective as a collector.

Some metals are present as negatively charged anionic ions in solution, and, according to the concept of ion flotation, they can be floated using cationic collectors. A simple system for illustrating anionic ion flotation using cationic collector is perhaps the removal of the hexavalent chromium ions from dilute aqueous solutions. Grieves (1973) investigated the ion flotation of hexavalent chromium species as a function of pH, ionic strength, mixing time, and temperature, using a cationic surfactant. A sharp increase in the flotation stoichiometry from 1.0 to 2.0 over pH 6-8 was observed.

Jurkiewicz (1990) studied the flotation removal of the tetrahedral zinc complex using cetyltrimethylammonium as collector. The effectiveness of zinc flotation increases with an increase in chloride, bromide, iodide, and thiocyanate concentration and in relation to the nature of the ligands it follows the order:  $\text{Zn}(\text{Cl})_4^{2-} < \text{Zn}(\text{Br})_4^{2-} < \text{Zn}(\text{SCN})_4^{2-} < \text{Zn}(\text{I})_4^{2-}$ . The experiments show the separation sequence:  $\text{Co}(\text{SCN})_4^{2-} < \text{Zn}(\text{SCN})_4^{2-} < \text{Cd}(\text{SCN})_4^{2-}$ . In the presence of acids, the zinc thiocyanate complex removal (and the amounts of zinc in the sublate) decrease with increasing acid concentration in the following sequence:  $\text{HClO}_4 < \text{H}_3\text{PO}_4 < \text{HCl} < \text{H}_2\text{SO}_4 < \text{no acid}$ . The interpretation of the effectiveness of the zinc complex removal as well as the changes in interface phenomena are based on the analysis of interactions in the foam separation medium.

Yang et al. (1990) investigated the feasibility flotation of an Nb-containing converter slag, and suggested two technological methods: alkaline melting water leaching, followed by

ion flotation, and sulfatizing roasting – acid leaching – ion flotation. The niobium complexes, in the alkaline leaching solution formed as  $\text{Nb}_6\text{O}_{19}^{8-}$  and in the acid leaching solution as  $[\text{H}_5\text{Nb}_6\text{O}_{11}(\text{SO}_4)_5]^{3-}$ , both were very well floated using the cationic collector dodecylamine.

Zhao et al. (1996) studied the ion flotation of arsenic (V) and molybdenum (VI), using dodecylamine as collector. It was found that when the initial  $[\text{Mo}]/[\text{As}]$  molar ratio was above 6, both these two ions were effectively removed over an optimum pH range of 2.5-4.5. The arsenate ion was considered to be floated as molybdoarsenic formation, and its removal was directly related to the presence of molybdenum.

Currently Australian research endeavours have focused on recovering gold from extremely dilute alkaline cyanide solution using recoverable gold-selective reagents. The gold ion flotation (GIF) process was developed to provide an economic means of replacing the carbon adsorption and stripping sections of the conventional gold processing operation (Nicol et al., 1992; Engel et al., 1992).

Engel et al. (1991) developed an ion flotation process for the recovery of gold cyanide from different alkaline solutions, such as reclaimed residue dam water and the carbon-in pulp (CIL) liquor from the processing plant adjacent to a BHP gold mine in Australia, using a quaternary ammonium surfactant. The flotation results indicated that optimum gold upgrade occurred when a low airflow, high-throughput system was used. In multistage flotation operation, a combined gold concentration of 6.0ppm with 86% recovery was obtained. A detailed cost study of a GIF facility was made. It was found in general, GIF technology is capital cost competitive with carbon adsorption methods when treating clear leaching solutions. The ion flotation process recovering gold from a heap leach mine feed liquor was also reported (Galvin et al., 1993). Recovery of precious metals such as gold and silver from solution were reported elsewhere (Torem and Rangel, 1997; Zouboulis, 1995; Zouboulis et al., 1993).

Although ion flotation has been thoroughly investigated, only a limited number of reports on its industrial applications for removal heavy metal ions from wastewater exist. One industrial usage of ion flotation for removal of cadmium ion from the wastewater of a

copper smelting plant was reported in Japan (Ito and Shinoda, 1973). The wastewater containing 1-3 ppm cadmium, 1-2ppm copper, 5-6ppm zinc and 0.02-0.15ppm lead at pH 3.5-4.0 had a volume of 3000 cubic meters per day. Six Wemco 66-type mechanical flotation cells with slight adjustment were used for the ion flotation process. Potassium amyl xanthate was used as collector. Although potassium amyl xanthate is more expensive than potassium ethyl xanthate, it was found that ethyl xanthate and amyl xanthate could not be used in combination for the flotation and that only amyl xanthate could achieve effective cadmium removal. On completion of the ion flotation process, the cadmium concentration in the treated water was less than 0.05ppm, which met the industrial discharge standard. The floated product was directly mixed with the copper concentrate for further filtering and smelting. The COD of the wastewater after ion flotation treatment was less than 20mg/liter, which was an acceptable level. This industrial system commenced operation in January 1971 and was successfully used until the wastewater from the smelting plant no longer contained cadmium ion (Sasaki, 1982).

#### *2.2.2.2 Selective separation of metal ions by ion flotation*

One of the most important characteristics and advantages of ion (or precipitate) flotation is that it can work selectively, contributing in this way to the recycling of the recovered metal values (Matis and Zouboulis, 1995). In the nineties, the selective separation of metal ion using the ion flotation method has attracted much attention.

Walkowiak (1991, 1992) investigated the mechanism and selectivity of ion flotation in the case of transition metal cations and anions from dilute aqueous solutions, using cationic and anionic surfactants. It was determined that ion-water and cation-surface active anion interactions govern the ion flotation selectivity, when a sublate was not formed in the bulk solution. The selective sequences for the affinity of metal cations to anionic surfactants were correlated with the ionic potentials. It was concluded that according to a theory, based on the Gouy-Chapman diffuse double layer model, the ion flotation selectivity of metal cations could be predicted. The flotation selectivity orders of anions were correlated with the experimentally-determined viscosity coefficients. It was found that, if sublate precipitation takes place in the bulk solution, the surface charge of sublate was the key factor influencing the floatability of an ion.

Uranium ores contain impurities such as Zr and Mo in variable amounts depending on their origins. These impurities, along with uranium, are solubilized during an alkaline leaching process using sodium carbonate. Jdid and Blazy (1990) studied the selective separation of zirconium from uranium in a carbonate solution. The selective removal of zirconium contained in industrial carbonate solutions from uranium was easily achieved by ion flotation using octylhydroxamic acid as the collector. The Zr/U ratio of the solution was reduced from 2.04 to 0.02%, with only a 0.5% loss of uranium.

Stalidis et al. (1989) studied the selective separation of copper, zinc, and arsenic ions from a dilute aqueous synthesized solution. Phase separation was accomplished by applying dissolved-air flotation. Ion flotation of copper using potassium ethyl xanthate (with 10% excess of the stoichiometric amount and at pH 3.0-5.0) was carried out, followed by ion flotation of zinc by a stoichiometric amount of diethyl dithiocarbamate at the same pH. Arsenic was finally removed by adsorbing colloid flotation on hydrolyzed ferric sulphate at pH 5.0 without a surfactant.

Germanium is known to be a scattered element occurring in traces in other ores, mainly mixed sulphides and coal. In many countries, fly ash is used as raw material for germanium, since the combustion process concentrates germanium. Matis et al. (1987) investigated the selective recovery of germanium from arsenic ions in dilute aqueous solution, using pyrogallol as activator and laurylamine as collector. Over 95% of the germanium flotation recovery was obtained while the arsenic remained in solution. The separation of germanium from lead in solution was also reported (Zoumboulis et al., 1990; Zoumboulis and Matis, 1995). The lead ion was floated as the hydroxide precipitate, using dodecylamine as collector at pH 10, germanium was further concentrated as a second stage by ion flotation at pH 7.

### ***2.2.2.3 The recycling of collectors***

Ion flotation requires collectors present in at least stoichiometric amounts. As the large quantity of collectors and its high costs restricted the usage of this technique (Golman, 1988), the recycling of collectors became increasingly important.

Soon after the ion flotation process was introduced, recycling techniques of collectors were studied. Liu (1982) reviewed the recycling techniques used in ion flotation. In the two main methods of xanthate recycling: sulphide or hydroxide salts were used. Sulphide or hydroxide ion can react with the metal xanthate, producing metal sulphide or hydroxide precipitate and replacing the xanthate ion into the solution. The reactions are as follows:



*Where, RXt<sup>-</sup> is xanthate ion; Me is heavy metal ion (using divalent ion as example)*

The heavy metal sulphide or hydroxide precipitate was recovered, using a filtration process and the filtrate containing the recycled xanthate in the aqueous solution could be reused. It was reported (Liu, 1982) that when either the sulphide or the hydroxide recycling processes were used, the recovery of xanthate reached above 90%.

As the industrial application of ion flotation was applied in Japan for the removal of cadmium ions using xanthate as collector, the recycling technique of xanthate using the sulphide process was studied at the same time. It was reported (Ito and Shinoda, 1972) that the xanthate ion could be recycled effectively, but that the particle size of the cadmium sulphide was so fine that subsequent filtration became difficult.

Cationic collectors (normally fatty amine) have been used for the recovery of anions by ion flotation. Guo et al. (1990) introduced a recycle method in a hot alkaline solution (80-90°C). A fatty amine with a carbon chain (R) length of C11-13 normally used for molybdenum ion flotation was applied. The reaction was as follows:



The recycling ratio of amine reached 70%. The quality of the recycled amine was even better than that purchased from commercial markets.

Galvin et al. (1994) described a pilot scale field trial of recycling a cationic collector from the ion flotation process, as applied to the recovery of gold. The principal objectives of this trial were to establish the technical feasibility of long-term reagent recycle and to quantify the recyclability of the reagent, an essential specification in the determination of the economic viability of the technology which could not be sensibly established at the laboratory scale. The trial involved a total of 13 reagent recycle stages. The results indicated that the recyclability of the reagent was about 80%.

Although anionic collectors have widely been used in ion flotation studies for recovering cationic metal ions from a solution, the recycling method of this kind of surfactants has not been thoroughly investigated. Liu (1982) has briefly reported on recycling a type of carboxylic acid collector in copper ion flotation using acid to re-dissolve the sublate. The reaction was:



The copper ion was re-dissolved into the solution with a 20-25 times enrichment. The carboxylic acid was separated from the solution and recycled as an oleic phase.

### 2.2.3 Precipitate Flotation

Precipitate flotation is a technique used to remove fine precipitates from aqueous dispersion. The most significant advantage of precipitate flotation over ion flotation, which requires stoichiometric or greater amounts of the collector since the ion and the collector actually form a compound, is the low surfactant requirement. Perez and Aplan (1975) compared ion flotation with precipitate flotation for the removal of copper and iron from a solution. They concluded that precipitate flotation was superior to ion flotation. For ion flotation, roughly one mole of collector was required for every mole of metal ion removed, whereas in precipitate flotation only about 1/100 mole of surfactant was needed for every mole of metal ion removed. Kawalec-Pietrenko (1984-85) investigated the kinetics of removal of trivalent chromium salts from aqueous solutions using both ion and precipitate methods. It was indicated that precipitate flotation is a considerably more rapid process than ion flotation.

### *2.2.3.1 Removal of metal ions by precipitate flotation*

As reviewed above, in industrial wastewater treatment, the conventional method for the removal of heavy metals is to precipitate the ions as hydroxide followed by sedimentation or filtration of precipitates. Although this process is slow and inefficient, because of its cheap and easy to use, hydroxide precipitate flotation has been most widely studied.

In earlier studies (e.g., Saab, 1962; Rubin and Johnson, 1967; Rubin and Lapp, 1971; Rubin, 1972, Chen et al., 1986) dealing with hydroxide precipitate flotation for the removal of different metal cations, the flotation results were interpreted as involving hydrolysis reactions. Clark and Wilson (1983) have thoroughly reviewed the hydroxide precipitate flotation of most metals.

Jurkiewicz (1984-85) studied the hydroxide precipitate flotation of cadmium in relation to the pH from solutions of different metal concentrations using lauryl sulphate as collector. The precipitate flotation results reflected the precipitation of the metal in the form of a hydroxide. The precipitation pH values calculated amounted to approximately 50% of cadmium removal. The presence of electrolytes proved to have a negative effect on the results of the precipitate flotation of cadmium hydroxide with lauryl sulphate.

Hydroxide precipitate flotation is usually applied to a solution containing various inorganic electrolytes. Jurkiewicz (1986, 1990) investigated the influence of electrolytes on cobalt and zinc hydroxide precipitate flotation. It was found that increased electrolyte concentration negatively affects the cobalt and zinc hydroxide flotation with a lauryl sulphate collector, but that it enhances hydroxide flotation with a cetyltrimethylammonium collector. Lauryl sulphate collector adsorption on the hydroxide precipitate decreased with increasing electrolyte concentration, whereas cetyltrimethylammonium collector adsorption increased. The isoelectric points (IEP) of the cobalt and zinc hydroxide in water were close to pH 9.8 and pH 9, respectively. In the presence of the lauryl sulphate collector and electrolyte anions, the zeta potential of the precipitates decreased, shifting the IEP to lower pH values. However, in the presence of the cetyltrimethylammonium collector the zeta potential of the hydroxides increased.

Since the metal hydroxide precipitation is a function of pH, the equilibria between metal ions and the hydroxyl ion are very important for understanding the precipitation and subsequent flotation process. Wakamatsu (1973) introduced some methods for the calculation of the equilibrium of metal ions in the solution, and the influence of some accompanying anionic ions on the precipitation. Numata and Wakamatsu (1978) studied the removal of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Fe}^{3+}$  by hydroxide precipitate flotation, using anionic surfactants such as sodium lauryl sulphate and sodium dodecylbenzenesulphonate (SDBS) as well as cationic surfactants, such as cetyltrimethylammonium bromide as collectors. It was found that the pH range at which flotation occurred corresponded well with the calculated precipitation pH range. Guo (1984, 1986) carried out similar equilibrium and flotation tests, arriving at much the same conclusions.

One major problem is that, in hydroxide precipitation, the minimum solubility for various metals occurs at different pH values and that the hydroxide precipitates are amphoteric in nature. Also, the presence of complexing agents, such as ammonia or EDTA, prevents effective precipitation (Peters and Ku, 1984; Matis and Mavros, 1991). Because of these reasons, hydroxide precipitate flotation sometimes can not achieve effective removal of heavy metals from wastewater.

The sulphide precipitate flotation process as explained previously, is known to present some advantages as compared to hydroxide precipitate flotation: A smaller amount of precipitating agent is required for precipitation at low concentrations, even in acidic solutions. Moreover, the use of sulphide may enable selective removal of some highly insoluble metal cations of sulphide, such as copper from other cations (Beitelshees et al., 1981). As for the sludge that is produced, it exhibits better thickening properties and dewaterability, and is less subject to leaching than metal hydroxide sludge, therefore final disposal is easier and safer (Whang et al., 1982).

Perez and Aplan (1975) comparing hydroxide and sulphide precipitate flotation concluded that metal sulphide precipitate flotation had advantages over hydroxide precipitate flotation in its selectivity between species, in the reduction of froth volumes, and in the



usage of a broad variety of additional surfactants, especially the sulphhydryl compounds as collector.

However, conclusions with regard to such comparisons varied with different circumstances. Charewicz and Walkowlak (1982) reported a comparative study on hydroxide, sulphide and carbonate precipitate flotation process of copper industry wastewaters (containing copper, nickel, and other metal ions), applying both the glass flotation column technique and a flotation machine, as well as the sedimentation process. The precipitate flotation process proved to be highly effective in the removal of metals in the form of hydroxides, carbonates, and sulphides, resulting both in higher metal recoveries and reduced sludge volume ratios, except for the removal of sulphides from acidic solutions. Considering efficiency of the wastewater treatment and the process duration time as well as the treatment costs, the application of lime as precipitant and anionic surfactants as collector was recommended in the precipitate flotation.

Ghazy (1995) investigated the removal of Cd(II), Pb(II), Hg(II), Sn(II), Sn(IV), Sb(III), Sb(V), As(III), and As(V) from aqueous solutions by sulphide precipitate flotation using oleic acid (HOI) as the surfactant. The complete flotation (about 100%) of these elements was attained at pH values of 5.5-6.5, 3-6.5,  $\leq 1$ , 1-4, 0.5-3, and  $\leq 2$ , respectively. It was found that neither temperature nor ionic strength has an appreciable effect on the flotation efficiency of the metal ions investigated. The method was successfully applied to remove completely these metal ions added to 1L samples of drinking and seawater, in optimum conditions for each element.

Beitelshees et al. (1981) studied two amphoteric surfactants, cationic at low pH and anionic at high pH, as collector for the removal of copper from dilute aqueous solution (100-500 ppm) using sulphide precipitate flotation. It was found that a negatively charged surface, rather than neutral was required for efficient surfactant recovery. Amphoterger K-2 was identified as a suitable surfactant for CuS precipitate with sulphide ion in excess. These surfactants could be recycled from the flotation foam products. Tests established that 95% of adsorbed Amphoterger K-2 could be recovered by raising the pH to 11 and by boiling the suspension for one hour, which was followed by decanting. The solids of the foam settled rapidly, which helped to reduce the consumption of chemicals for the pH

change. Column flotation studies were carried out using Amphoterger K-2 for recovery of  $\text{Cu}^{2+}$  present at 100 ppm and  $\text{pH} = 2$ . High removals of CuS could be obtained at concentrations of surfactant above about 25 ppm. In these conditions a substantial fraction of the surfactant remained in the solution rather than being adsorbed onto the CuS. The recovery of CuS was improved by introducing the surfactant in a separate feed, below the feed of CuS suspension. These variations gave an even better recovery of CuS (99.8%) at sufficiently high surfactant loadings.

A very interesting study on the removal of copper ions from dilute aqueous solutions by the addition of fine mineral (pyrite) particles, followed by dissolved-air flotation for solid/liquid separation, was reported by Zouboulis et al. (1992). They found that finely ground pyrite (0.5 g/L or above) in the solution increased the copper flotation recovery. The pyrite was therefore suggested for use in utilization wastewater treatment. Various collectors for pyrite flotation were also examined.

#### ***2.2.3.2 Selective separation by precipitate flotation***

Selective flotation and separation of different metal ions from wastewater by the flotation method has probably been the greatest challenge for researchers who aimed at achieving a maximum potential usage of metal ions.

Acid mine drainage from a base metal mine sometimes contains very high concentrations of iron and sulphate ions. After neutralization by lime, ferric hydroxide precipitate and gypsum (calcium sulphate precipitate) are produced. Xue and Mamiya (1982) investigated the flotation separation of ferric hydroxide precipitate and gypsum from an artificial acid mine wastewater which contained 1000mg/L ferric ions and 6000 mg/L sulphate ions. The artificial wastewater was neutralized by calcium carbonate until the pH reached about 5.0. Selective separation of gypsum from ferric hydroxide precipitate was achieved by using dodecylammonium acetate (DAA) as collector and starch as modifier. Starch acted as a depressant for ferric hydroxide precipitate as well as a selective flocculant for gypsum. 90% gypsum was recovered in the flotation foam while 92% of ferric hydroxide precipitate remained in the solution. Similar studies on the flotation separation of aluminum hydroxide and gypsum, as well as germanium hydroxide and gypsum,

precipitated in the neutralization process from mining wastewater and a leaching solution, have also been reported (Xue et al., 1983; Xue, 1990).

The above precipitate separation studies provide good guidelines for the application of the hydroxide precipitate flotation technique to wastewater treatment. However, the separation of different metal ions by hydroxide precipitate flotation methods was not mentioned. Sulphide precipitate flotation may enable selective precipitation of different metal ions from a solution, and subsequent flotation separation.

Stalidis et al. (1988) studied the precipitate flotation of copper and zinc, as sulphides, by cationic surfactants (mainly laurylamine) at a pH of about 2, as a selective separation method for the two dissolved metals from dilute aqueous solutions. The dissolved-air flotation technique was used to produce fine bubbles and copper sulphide was found in the foam layer. Two series of batch experiments were introduced: an initial (first-order) series having as basic parameters a copper-ion concentration, pH, and concentrations of sodium sulphide and amine added; and a second-order series, with the concentrations of copper and zinc ions and a preliminary stirring speed as parameters. The separation results obtained were considered promising; copper recovery was over 90%, while about 10-20% of zinc was included in the concentrate.

Further studies of precipitate flotation separation of copper and zinc as sulphides in dilute aqueous solutions (50-250 ppm metal ion concentration), using a continuous flow, laboratory dispersed-air flotation system, were reported (Stalidis et al., 1989). A selective recovery of copper sulphide of the order of 95% in a high acidic pH region (of 1.7), by a laurylamine as collector and with the addition of cetyl-pyridinium chloride as frother, was achieved with a zinc recovery in the foam layer under 6%. The precipitate flotation of zinc sulphide was then accomplished with the same method at a pH of 5.0 as a second separation stage (in the presence of minor amounts of copper). Over 95% zinc recovery was obtained in the second stage flotation.

#### 2.2.4 Adsorbing Colloid Flotation

Adsorbing colloid flotation, sometimes referred to as co-precipitate flotation, was a later development after ion and precipitate flotation. The process generally involves the production of a hydroxide precipitate of metal ions by adsorption and/or co-precipitation with a floc generating material such as  $\text{Fe}(\text{OH})_3$  or  $\text{Al}(\text{OH})_3$ , rendering removal by flotation with air bubbles (Sanciolo et al., 1989b). It should be noted that the processes of adsorption, co-precipitation and occlusion are difficult to distinguish and are often non-selective, thus making it difficult the possibility for the recovery of one metal from a mixture of metals in solution (Matis and Mavros, 1991).

Wilson (1977) indicated that, compared with conventional precipitation, followed by sedimentation, adsorbing colloid flotation has a number of attractive features (similar to precipitate flotation): (a) low energy requirement; (b) high removal efficiency; (c) reasonable capital requirements; (d) comparatively low maintenance and operating costs, thereby potentially providing a low cost method of heavy metals recovery from industrial wastewater.

Numerous studies have been carried out with regard to adsorbing colloid flotation. Earlier studies included: removal of zinc and copper (Kim and Zeitlin, 1972), phosphate and arsenate from seawater (Chaine and Zeitlin, 1974); removal of copper, lead, zinc and cadmium from mining wastewater (Muigeru and Nakahiro, 1972; Fujii, 1974; Robertson et al., 1976; Allen et al., 1979); flotation of fluoride ion by aluminum hydroxide in aqueous media (Clarke and Wilson, 1975). Wilson and his co-authors also published a series of research papers on electrical aspects of adsorbing colloid flotation (Brown and Wilson, 1981; Wilson, 1982; Kiefer et al., 1982; Abraham et al., 1987). Clark and Wilson (1983) published an excellent review of this process.

Metal ions can be efficiently removed by adsorbing colloid flotation using  $\text{Fe}(\text{OH})_3$  as the adsorbing floc. It was found that the flotation recovery could even be highly improved by adding a specific amount of  $\text{Al}(\text{III})$  as activator. Huang et al. (1984-85) reported the effect of  $\text{Al}(\text{III})$  on adsorbing colloid flotation using  $\text{Fe}(\text{OH})_3$  as the coprecipitant and sodium lauryl sulphate as the collector. It was found that when  $\text{Al}(\text{III})$  was used as an activator, the zeta potential of the floc was more positive, which presumably gave the floc a stronger affinity for anionic surfactant adsorption, resulting in better separation efficiency. The

working range of pH for an effective separation was extended and good separation efficiency was achieved at pH values closer to neutral with the aid of Al(III). The separation efficiency was significantly improved for solutions containing interfering ions, such as sulphate, by using Al(III) as an activator.

A full-scale pilot plant has been built for wastewater treatment using adsorbing colloid flotation methods (McIntyre et al., 1982a, b). The simulated wastewater contained 20 mg/L of each of Cu(II), Zn(II) and Cr(III) ions; after adsorbing colloid flotation, the residual concentrations of ions amounted to less than 0.1 mg/L (Cu), 0.5 mg/L (Zn), and 0.2 mg/L (Cr) under optimal conditions. Sodium dodecyl sulphate was used as the collector; and Fe(OH)<sub>3</sub>, Al(OH)<sub>3</sub>, and mixtures of the two were used as the carrier floc. The capital costs were calculated. The costs comparison of adsorbing colloid flotation with lime precipitation was \$0.51/1000L versus \$0.60/1000L (the cost of a filtration step in the lime precipitation plant was not included). Clearly, adsorbing colloid flotation was the cheaper alternative.

In Australia, Sancio et al. (1989a, b) studied the removal of heavy metal ions (Cr<sup>3+</sup>, Ce<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup>, Co<sup>2+</sup>) from electroplating wastewater by adsorbing colloid flotation. Good results were obtained. A pilot plant with a capacity of 1000 litres per hour was designed, and the cost was calculated. It was reported that the overall operating cost for adsorbing colloid flotation appeared to be very similar to conventional precipitation and sedimentation. However considering the running costs of sludge disposal, adsorbing colloid flotation would be cheaper than the conventional processing.

Mehta and Han (1984) reported the results of a very interesting study on the coprecipitation of cobalt(II) and nickel(II) in ammoniacal solutions with manganese rather than Fe(III) or Al(III). It was found that cobalt and nickel were precipitated with the aid of manganese at pH 9.3-10.2. However, the rate of precipitation of manganese was about five times that of cobalt. The recovery of these divalent ions by precipitation increased as the pH of the solution increased, while the selectivity of cobalt against nickel decreased with the increase of pH. The partial pressure of oxygen also played an important role in the precipitation of manganese and cobalt but had little effect on the recovery of nickel. As the oxygen pressure was increased, manganese and cobalt oxidized at a fast rate and

the rate of coprecipitation of cobalt with manganese increased. Typically, more than 90% of cobalt was recovered readily by coprecipitation with manganese, while very little nickel was removed from the solution.

The mechanism of colloidal adsorption/coprecipitation of divalent ions with highly valent ions was also studied. Early investigations (Kolthoff and Overholser, 1939a, b) suggested that the coprecipitation could be interpreted as an ionic adsorption phenomenon. Later, Han et al. (1982) explained this phenomenon not as a simple adsorption process but as direct association of the divalent ions with the lattice of the precipitates of trivalent ions. The studies indicated that the amount of divalent ions associated with coprecipitated products was very much affected by the solution conditions under which precipitation took place.

The aging process of coprecipitated products also contributed significantly to the stability of precipitates and recovery. Research has shown that X-ray patterns become clearer with aging of precipitates (Han et al., 1987) and this may influence precipitate stability and recovery.

Narita et al. (1990) investigated the crystal structure and chemical composition of the coprecipitated products of Al(III) with Co(II) and Ni(II) in ammoniacal solutions using X-ray diffraction analyses. It was found that the pH of the solution was an important factor in determining the nature of the precipitated product. The capacity of Al(III) to incorporate Co(II) and Ni(II) in the precipitated product was extraordinarily high. The X-ray patterns of Co(II)/Al(III) precipitate showed a partially crystalline hydrotalcite-type layered structure. Those of the Ni(II)/Al(III) precipitate formed a hydrotalcite-type layered structure when precipitated at pH 6.3-8.3. However a bayerite structure was exhibited when the precipitate formed at pH 9.5-10.5. The coprecipitated amount of divalent species decreased in the following order: chloride > sulphate > carbonate.

## **2.3 Bubble Generation Methods**

The flotation process requires a large number of air bubbles in the solution, which attach to the solid particles and subsequently float to the surface. According to the method used

for generating the gas bubbles, three categories of flotation for wastewater treatment can be distinguished: dispersed-air flotation, dissolved-air flotation, and electrolytic flotation.

### 2.3.1 Dispersed-Air Flotation

This method generates bubbles by introducing air directly into the flotation cell. The most popular dispersed-air flotation cells used in wastewater treatment are the mechanically agitated flotation cells and column flotation cells.

#### 2.3.1.1 Mechanically agitated flotation

The mechanically agitated flotation cells are the oldest and the most common flotation cells used in flotation plants of mineral processing. A mechanically driven impeller agitates the slurry and the air is sucked in or injected into the slurry, usually through a separate piping system or an impeller shaft. A large number of bubbles are obtained mainly by the shearing effect of impellers. It was reported that the higher the stirring strength, the smaller the bubbles generated (Lu and Weng, 1992).

The mechanically agitated flotation cells have been used for more than one hundred years and countless papers have described different cells. Reviewing these studies in the context of this study would be of little relevance. The most interesting development in recent decades is probably that of enlarging the cell size. The largest cell size found so far is the 127.5 m<sup>3</sup> WEMCO SmartCELL™ (Nelson and Redden, 1997). Some advantages of the mechanically agitated flotation cells are easy maintenance, low equipment cost and easy settlement, etc.

Mechanically agitated flotation has been adopted for some laboratory research (Numata and Wakamatsu, 1978; Xue et al., 1983; Xue, 1990) and for industrial practice (Ito and Shinoda, 1973) in wastewater treatment. However, as this bubble generation method involves high turbulence, which breaks up the fragile flocs formed during the chemical pretreatment, the method is regarded as unsuitable for ion, precipitate and adsorbing colloid flotation. Another serious disadvantage is that the bubble sizes generated by this method are too large for wastewater flotation.

### *2.3.1.2 Column flotation*

Column flotation is considered to be one of the most significant achievements in the field of mineral processing in recent decades (Rubinstein, 1997). The first column apparatus was developed more than 70 years ago. However, activation of practical research work in the field of column flotation began only in the mid seventies. The advantages of column flotation are higher selectivity of the process, and low power and metal requirement. The column flotation design, research and practice have been extensively introduced and reviewed (Rubinstein, 1994; Finch and Dobby, 1990).

Conventional flotation columns use spargers at the base of the columns. The material used for the spargers can be porous ceramic, stainless-steel, polyethylene, filter, rubber etc. Air injected through the spargers generates a large amount of bubbles. The size of the bubbles depends upon the sparger pore size. In the early stage of the development of this method, the performance of porous spargers tended to deteriorate due to pore plugging (Matis and Mavros, 1991). However, in the past twenty years, this problem has been solved by the introduction of new materials and by improved design of the air-water mixture system. A microgas dispersion flotation system (Ciriello et al., 1982) was reported for the removal of heavy metals from aqueous solutions. Reports on studies and practices of the recently developed jet flotation systems have also been published (Guney et al., 1997; Seinmuller et al., 1997; Sanchez et al., 1997; Evans et al., 1992).

Most of the studies relating to ion, precipitate and adsorbing colloid flotation were carried out in conventional laboratory column flotation systems (Jurkiewicz, 1986, 1990; Sanciolo et al., 1989b), due to its ease of control and simplicity of the system, as well as its greater effectiveness in fine particles flotation, as compared to the mechanically agitated flotation. However, the bubble size produced from the spargers (normally 1-5mm) is much larger than that generated by dissolved-air flotation or electrolytic flotation (20-100 $\mu$ m). For ion, precipitate and adsorbing colloid flotation in wastewater treatment, the column flotation system is less effective than the two flotation systems, discussed below. Nevertheless, column flotation continues to have great potential for wastewater treatment because of its low cost in equipment and operation, its easy maintenance and



controllability, and its large capacity. The overall efficiency of column flotation for wastewater treatment is normally good enough for the removal of heavy metal ions.

### 2.3.2 Dissolved-Air Flotation

Dissolved-air flotation is a very effective solid-liquid separation process used in water treatment, as an alternative to sedimentation before granular filtration. This enables filters to be operated more effectively and is cost efficient in producing a filtered water quality suitable for potable supply. It was reported that more than 50 plants were in operation or under construction in the Scandinavian countries and the United Kingdom (Zabel, 1992).

In dissolved-air flotation, the bubbles are produced by a pressure reduction in a water stream saturated with air. The amount of air dissolved in the water at a given pressure may be easily calculated using Henry's law. The two main types of dissolved-air flotation are vacuum flotation and pressure flotation.

#### 2.3.2.1 Vacuum flotation

In vacuum flotation, the water to be treated is saturated with air at atmospheric pressure. A vacuum is then applied to the flotation tank releasing the air as small bubbles. However, the amount of air available for flotation is limited by the achievable vacuum. This process is being applied only in the paper industry for the recovery of fibres. It is being replaced by pressure flotation (Zabel, 1992).

#### 2.3.2.2 Pressure flotation

Pressure flotation is currently the most widely used dissolved-air flotation process in wastewater treatment. Initially, water is saturated with air at a relatively high pressure. When this water is introduced in the flotation vessel, the change to normal atmospheric pressure releases the air bubbles. As vacuum flotation is not used very often, the pressure flotation normally represents dissolved-air flotation. Three basic dissolved-air flotation processes can be used: full-flow pressure flotation, split-flow pressure flotation, and recycle-flow pressure flotation. Zabel (1992) introduced pressure flotation in detail and indicated that recycle-flow pressure flotation was the most appropriate system due to the

fact that the flocs would be destroyed by the high shear experienced during the pressure release in the case of the other two dissolved-air flotation processes.

Stalidis and Matis and their co-authors (Stalidis et al., 1988, 1989a, b) in Greece investigated a series of ion, precipitate and adsorbing colloid flotation using dissolved-air flotation. Lazaridis et al. (1992) studied the removal of metal ions (copper, nickel, zinc, and ferric ions) from dilute aqueous solutions by dissolved-air flotation. The ions were either precipitated as sulphides or floated (as ions) by xanthates. It was found that copper sulphide precipitate could be floated without collectors under specific conditions.

Dissolved-air (pressure) flotation has the advantages of a large capacity and of generating extremely fine bubbles of diameter of 0.05-0.1mm, for this reason, this flotation method will no doubt be more widely used in water and wastewater treatment. However, apart from the fact that the process is more complex than column flotation, it cannot treat dispersions of high density, and furthermore requires a high recycle ratio (of the order of 50%) (Matis and Zouboulis, 1995).

#### 2.3.4 Electrolytic Flotation

The basis of electrolytic flotation (also known as electro-flotation) is the generation of bubbles of hydrogen and oxygen in a dilute aqueous solution by passing a direct current between two electrodes (Barett, 1975). The electrolytic reactions at the two electrodes are as follows:



The size of the bubbles generated by the electrolytic reactions is in the range of 8-15  $\mu\text{m}$ , and they are not easily merged, thus it is very efficient for small particle flotation. It has also been reported that the bubble surfaces were electrically charged and that this could be maintained for a specific period of time, which improved the selectivity of flotation (Lu and Wong, 1992).

Alexandrova et al. (1994) investigated the possibility of removal of metal ions from mining wastewaters through ion flotation by electroflotation for obtaining a gaseous phase with sufficient volume and high dispersity, using an potassium oleate surfactant. The metal ions present in the wastewater were successfully removed. The removal of chromium from dilute solutions by electrolytic flotation, using dodecylamine or cetyltrimethyl-ammonium bromide as collector, at a current density of  $200 \text{ Am}^{-2}$  and 18 V, was also achieved (Zouboulis and Matis, 1989).

The disadvantages of this process are that the electrodes need periodic replacement, fouling of the electrodes is a frequent problem, and the capacity is small. The application of electro-flotation has been restricted mainly to sludge thickening and small effluent treatment plants (Zabel, 1992).

## 2.4 Research Questions and Methodology

The main challenge for ion, precipitate and adsorbing colloid flotation is the selective separation of different metal ions from waste solution to achieve the maximum potential in wastewater treatment. A number of studies have been undertaken in this area, using the ion flotation method. However, little attention has been given by researchers to selective separation in precipitate flotation. As it is superior to ion flotation because of the requirement of less amounts of collector, some work should to be undertaken in this area.

### 2.4.1 Research Questions

- *Is selective separation of different heavy metal ions from waste solutions by hydroxide precipitate flotation possible?*

Different heavy metal ions in a waste solution may require different optimum pH for precipitation of each metal ion. It was suggested (Lanouette, 1977) that heavy metal ions may be selectively precipitated by controlling the pH, and subsequently separation may be achieved. However, selective separation of different heavy metal ions from waste solution by hydroxide precipitate flotation has rarely been reported, nor has the possible influence of the presence of other ions and

electrolytes on flotation and separation. All of which is a matter for investigation in this study.

- *How to improve precipitate flotation?*

The particle sizes of heavy metal precipitates, either hydroxide or sulphide precipitate, have been reported as extremely fine and amorphous. This requires large quantities of collectors and causes several problems in flotation separation. In the precipitation process, a so-called activated-sludge process, in which a portion of the settled product is recycled to the reactor has been used extensively in the biological treatment of wastewater. This process can significantly improve floc formation and increase the kinetics of sedimentation. The recycling techniques of collectors for ion flotation have been reported as being very successful. Is it possible to combine these two processes together to develop a new process to improve the precipitate flotation? One of the aims in this study is to develop a new flotation process to improve the precipitate flotation recovery and to reduce the consumption of collector.

- *Can xanthates be used as collector for metal sulphide precipitate flotation in wastewater treatment?*

Xanthate is the most commonly used collector in the sulphide mineral flotation area. It has also been used in ion flotation for the removal of cadmium or copper ion from wastewater (Ito and Shinoda, 1973; Stalidis et al., 1989). Can this collector be used in sulphide precipitate flotation? Few research attempts have been made to answer this important question which will be investigated in the context of this study.

- *Is it possible for selective separation of heavy metal ions from industrial mining wastewater by precipitate flotation?*

Most selective separation studies have been carried out in synthetic wastewater flotation. Studies dealing with real industrial wastewater are rare, particularly for

flotation separation using the precipitate flotation method. Industrial wastewater, unlike synthetic wastewater, normally contains some other ions and suspended solids, which probably influence flotation and separation. This study will encompass the flotation separation of different heavy metal ions from a mining wastewater.

## 2.4.2 Methodology

### 2.4.2.1 Selection of the flotation process

As ion flotation requires stoichiometric or greater amounts of collector, the cost of this process is much higher than that of the precipitate flotation process. The adsorbing colloid flotation is often non-selective, which is problematic for selective separation of different metal ions. The precipitate flotation process was chosen for the purposes of this particular study. However, for comparison purposes, in some cases, ion flotation will also be investigated.

### 2.4.2.2 Selection of heavy metal ions

Zinc and copper are the common toxic metals encountered in mining wastewater, dilute leach solutions, spent process streams, and liquid effluents in industry (Winnicki et al., 1975; Patterson, 1985). The solubility products\* of zinc and copper hydroxide precipitates are  $5.2 \times 10^{-17}$  and  $5.6 \times 10^{-20}$  respectively, and those of zinc and copper sulphide precipitates are  $1.6 \times 10^{-24}$  and  $1.3 \times 10^{-36}$  respectively. The solubility of most other heavy ions are within the solubility range of zinc and copper precipitates. Moreover, the heavy metal ions in the tailing wastewater from the mineral processing plant, Woodlawn Mines Pty. (N.S.W., Australia), to be used for the final separation tests, mainly contains zinc and copper ions. Thus, zinc and copper were chosen as examples of heavy metal ions in this work.

### 2.4.2.3 Selection of the bubble generation method

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\* Solubility products were calculated using Outokumpu HSC Chemistry® for Windows software Version 3.0

The dissolved-air (pressure) flotation method is probably more suitable for water and wastewater treatment because of the extremely fine bubbles generated by this method. However, since the purpose of this work is to investigate the flotation and separation behaviours of zinc and copper precipitates, the conventional laboratory flotation column system was considered adequate for the task. Moreover, the fact that the flotation column has the advantages of easy control and simple design, was an additional reason for this choice of flotation system.

## Chapter III Experimental

### 3.1 Samples

#### 3.1.1 Copper and Zinc Solution

The initial copper solution and the initial zinc solution were produced from cupric sulphate and zinc sulphate (for chemical details, see Table 3-2-1). A bulk of 20 liters of 50ppm copper (or zinc) solution was prepared and stored in a 25 liter container. Before tests, the container was well shaken for five minutes after which several beakers of 250ml solution were prepared for the precipitation and flotation tests.

#### 3.1.2 Woodlawn Wastewater

Woodlawn Mines is situated 70km northeast of Canberra, A.C.T., and 50 km south of Goulburn, N.S.W., Australia. The tailings from its mineral processing plant are stored in a conventional water-storage type dam. The Woodlawn wastewater sample was obtained from its Evaporation Dam No.1, and stored in a 25 liter container. A typical analysis of this wastewater, supplied by Denehurst Analytical Services Pty. Ltd., and our analysis are shown below (Table 3-1-1).

Table 3-1-1 Woodlawn Mines Wastewater (from Evaporation Dam No.1)\*

Name	Cu	Pb	Zn	Fe	Cd	Al	Mn	Ca	Na	K	Mg	SO <sub>4</sub> <sup>2-</sup>
Dam1*	115	<0.03	2440	180	13	470	115	480	770	2.1	1440	13750
Dam1#	122	-	1935	-	12	-	-	-	-	-	-	-

\*Analysis supplied by Denehurst Analytical Services Pty. Ltd., Australia; units in ppm

#Our own analysis, ppm

The pH value of this wastewater was 2.85. Our analysis of zinc concentration of the wastewater used in this study is somewhat different to the above value. Our analysis for zinc is 1935ppm. Our analysis data was used for the calculations of the flotation recovery for the Woodlawn wastewater tests.

### 3.1.3 Synthetic Waste Solution

The synthetic waste solution was prepared in accordance with the chemical analysis of the tailing wastewater from the Woodlawn Mines (Table 3-1-1). For the concentrations of ions and pH, see Table 3-1-2 below. For the chemical reagents, see Table 3-2-1.

*Table 3-1-2 The synthetic waste solution (ppm)*

pH	Cu <sup>2+</sup>	Zn <sup>2+</sup>	Fe <sup>3+</sup>	Cd <sup>2+</sup>	Al <sup>3+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	SO <sub>4</sub> <sup>2-</sup>
2.6	100	2000	150	10	45	450	1000	13090

In order to keep the flotation tests stable, ten liters of the synthetic waste solution were prepared in a container for all the tests.

## 3.2 Water and Reagents

### 3.2.1 Water

Since this study deals specifically with the water treatment area, the purity of the water used in the research is extremely important. All water used was type-I ultra-pure reagent grade water, produced by a Milli-Q Reagent-Grade Water System. This system, manufactured by Millipore Corporation (Bedford, Mass.), is a "polishing" system, designed to further purify pretreated water (double distilled water here) to ultrapure levels.

The Milli-Q system employs a three-step purification process. The initial purification is provided by the Q-Gard purification pack, tailored to the specific feedwater source. Secondary purification is carried out by a Quantum ultrapure cartridge, designed to remove ionic and organic contaminants. The final water purification is handled at the point of use by a pharmaceutical-grade, absolute 0.22 mm Millipak Filter Unit.

The water thus purified effectively met the requirements of the tests as determined by conductivity measurements. For more information about the water system and its performance, visit Millipore Corporation web site at: <http://millispider.millipore.com/>



### 3.2.2 Flotation Collectors and Frother

One anionic collector used for the hydroxide precipitate flotation was Sodium Dodecyl Sulfate (denoted as **SDS**), analytical grade, chemical formula  $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}$  (Aldrich Chemical Company, Inc. USA); another was Sodium DodecylBenzeneSulphonate (denoted as **SDBS**), chemical formula  $\text{C}_{12}\text{H}_{25}\text{C}_6\text{H}_4\text{SO}_3\text{Na}$  (Aldrich Chemical Company, Inc. USA).

The xanthate collectors used in the sulphide precipitate flotation were Sodium Ethyl Xanthate (denoted as **EXt**, chemical formula  $\text{C}_2\text{H}_5\text{OCSSNa}$ ) and Sodium IsoButyl Xanthate (denoted as **IBXt**, chemical formula  $(\text{CH}_3)_2\text{CHCH}_2\text{OCSSNa}$ ). Both of these reagents were purified from commercial products. The purification process was carried out according to Harris (1988); the xanthate was dissolved in dry acetone and the inorganic impurities were removed by filtration, ether was then added to the filtrate, and the precipitated xanthates recovered by filtration. This process was repeated three times. As xanthate is oxidized easily in aqueous solution, the xanthate solution was prepared daily prior to the tests.

Three frothers, Methyl IsoButyl Carbinol (MIBC), pine oil and Methyl Amyl Alcohol were tested for compatibility with xanthate collectors. It was found that the bubbles produced by MIBC broke easily and that those from pine oil were too sticky. Methyl Amyl Alcohol (denoted as **MAA**) was chosen as a suitable frother for sulphide precipitate flotation using xanthate as collector because of the suitable features of its bubbles.

The cationic collector used for the sulphide precipitate flotation was DodecylAmmonium Acetate (denoted as **DAA**), produced from reaction of the DodecylAmine (chemical formula  $\text{CH}_3(\text{CH}_2)_{11}\text{NH}_2$ , analytical grade, Aldrich Chemical Company, Inc. USA) with the acetic acid. In the preparation process, the appropriate amount of dodecylamine was dissolved in water, slowly neutralized dropwise with acetic acid till the  $\text{pH}=7$ , then diluted into the required volume. The resultant solution is referred to as dodecylammonium acetate (**DAA**).

### 3.2.3 Other Reagents

Other reagents used in this work are listed in Table 3-2-1. All these reagents are analytical grade.

*Table 3-2-1 Other reagents used in this work*

Reagent Name	Formula	Purity/Assay*	Supplier
Cupric Sulphate Gran.	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	98.5%	May & Baker LTD.
Zinc Sulphate	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	>99.0%	AJAX Chemicals
Sodium Sulphide	$\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$	>98.0%	AJAX Chemicals
Sodium Hydroxide	$\text{NaOH}$	97.0%	AJAX Chemicals
Nitric Acid	$\text{HNO}_3$	Analytical Reagent 69.0- 71.0% w/w	AJAX Chemicals
Iron(III) Chloride	$\text{FeCl}_3$	97%	Aldrich Chemicals
Aluminium Sulphate	$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$	>98%	AJAX Chemicals
Ferrous Sulphate	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	98%	B.D.H. Chemicals
Calcium Chloride	$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	>98%	AJAX Chemicals
Magnesium Chloride	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	>98.0%	AJAX Chemicals
Cadmium Sulphate	$\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$	>98.0%	AJAX Chemicals
Sodium Sulphate	$\text{Na}_2\text{SO}_4$	>99.5%	B.D.H. Chemicals
Potassium Chloride	$\text{KCl}$	>98.0%	AJAX Chemicals
Sodium Chloride	$\text{NaCl}$	>98.0%	AJAX Chemicals
Hydrogen Peroxide	$\text{H}_2\text{O}_2$	Analytical Reagent 29.0- 31.0% w/w	AJAX Chemicals
Acetone	$\text{CH}_3\text{COCH}_3$	99.5+%	Aldrich Chemicals
Diethyl Ether	$(\text{C}_2\text{H}_5)_2\text{O}$	Analytical Reagent	AJAX Chemicals

*\*Analysis data for all reagents described by the suppliers*

Some reagent solutions such as sodium sulphide and hydrogen peroxide solutions, become easily oxidized and for this reason were prepared daily prior to the tests. Others were prepared monthly.

### 3.3 Precipitation and Flotation

#### 3.3.1 Precipitation Test

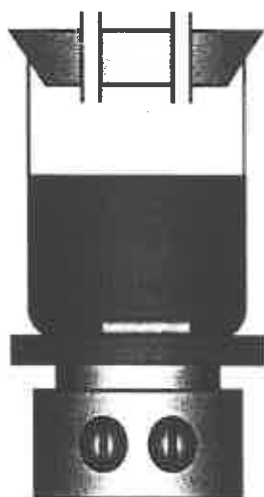
In the precipitation test for hydroxide precipitate, the hydroxide precipitant was added to the feed solution (250ml), and magnetically stirred for twenty minutes (stirring apparatus, see Fig. 3-3-1A), after which the pH was measured. The solution was then transferred into a centrifugal separator to centrifuge for twenty minutes at 4000rpm. This was followed by an analysis of the top clear solution and calculation of the precipitation percentage.

#### 3.3.2 Sedimentation Test

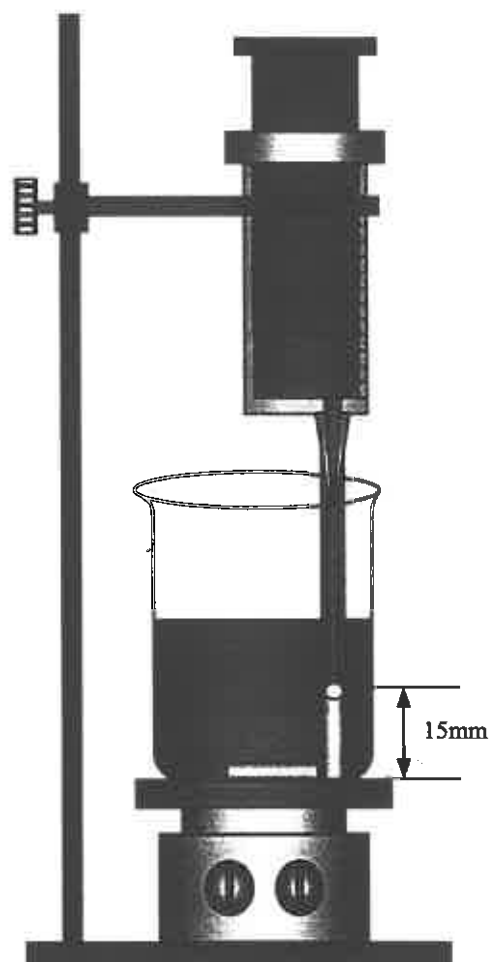
The sedimentation test of hydroxide precipitate was carried out in a specially designed apparatus shown in Fig. 3-3-1B.

In the sedimentation process, the precipitant was added to the feed solution (250ml) and magnetically stirred for twenty minutes, after which additional ion was added and stirred for a further ten minutes (if no additional ion was added, the solution was directly stirred for a total of thirty minutes). The precipitate was allowed to settle for fifteen minutes, time being counted immediately upon cessation of the stirring. The solution, after settling being 15mm above the bottom of the beaker, was withdrawn using a syringe connected with a specially designed plastic tube with two holes 15mm from its end (see Fig. 3-3-1B). To ensure the solution was only removed from 15mm above the bottom of the beaker, the tube was sealed using silicone sealant from the end to the two holes. The slurry thus obtained was analyzed and the percentage sedimentation calculated.

As the copper or zinc is present in fairly low concentrations in the solution (50ppm), the percentage sedimentation is influenced by the settling speed and the degree of aggregation of the precipitate.



*Fig. 3-3-1A Normal Stirring*



*Fig. 3-3-1B Sedimentation Test Apparatus*

*Fig. 3-3-1 Schematic representation of apparatus for normal stirring and the sedimentation test*

### 3.3.3 Flotation Test

#### 3.3.3.1 Flotation Apparatus

Flotation was carried out in a laboratory flotation column apparatus, which is similar to that described by Jurkiewicz (1990a, 1990b), as shown in Fig. 3-3-2.

When valve 1 is opened, the water from the constant water tank, elevated three meters above the rest of the apparatus, flows into the constant air pressure tank and the air is

forced out through a flow meter into the flotation column. This generates a large number of fine bubbles as it passes through the sintered glass frit at the bottom of the flotation column. The flotation process was conducted for five minutes at a constant airflow rate of  $70 \text{ cm}^3/\text{min}$ . The floated precipitate was collected at the top of the column. When the water level in the constant air pressure tank was more than two-thirds, the water could be discharged by closing valve 1 and opening valve 2 and valve 3.

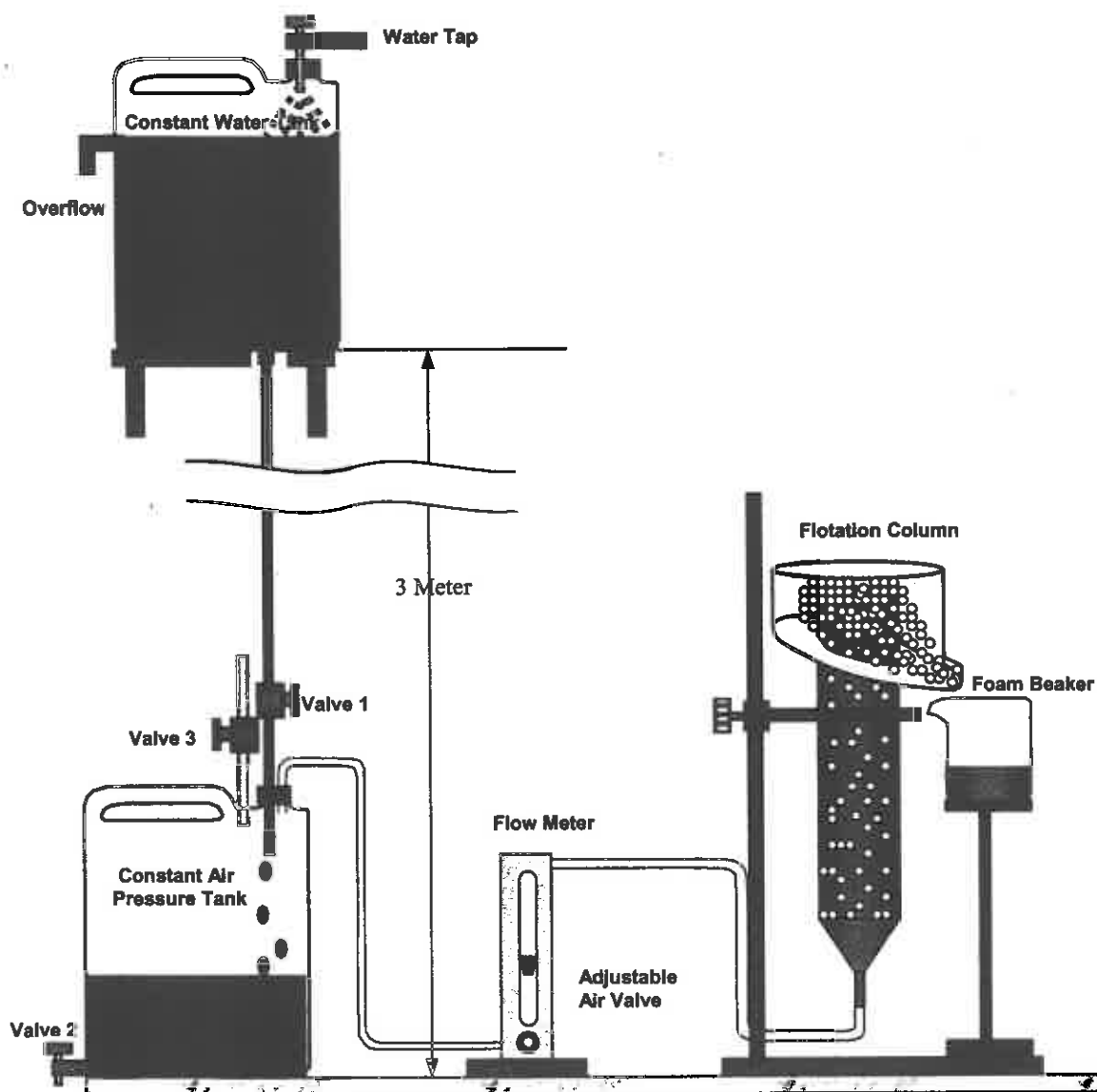


Fig. 3-3-2 Schematic presentation of the precipitate flotation apparatuses

### 3.3.3.2 Flotation Column

The flotation column was a 320mm high glass column, with a volume of 250ml and a G-3 sinter (15-40  $\mu\text{m}$  nominal porosity) at the base. For a detailed schematic presentation of the flotation column, see Fig. 3-3-3 below.

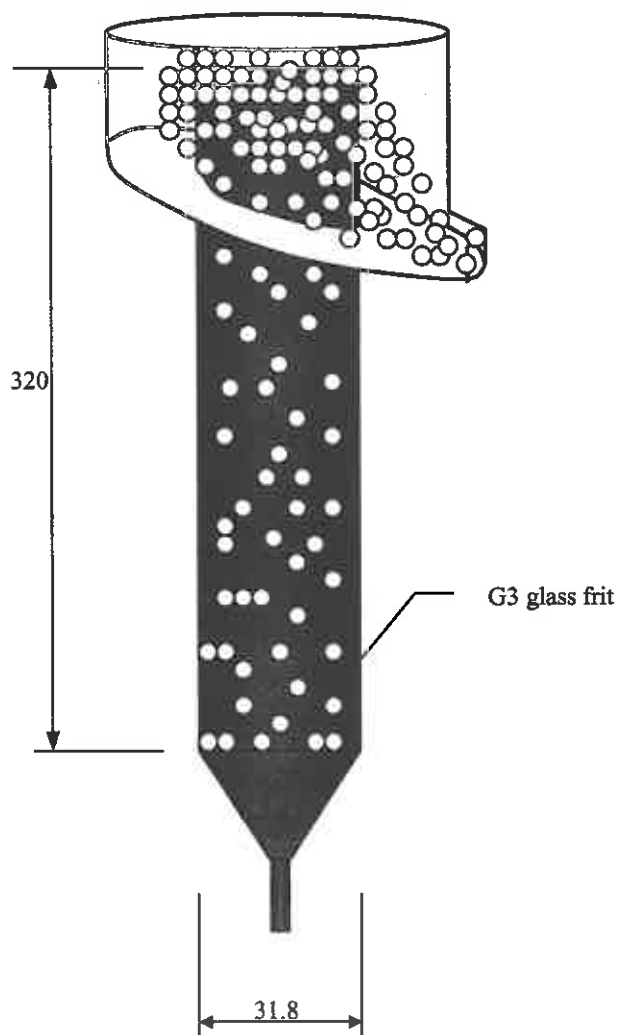
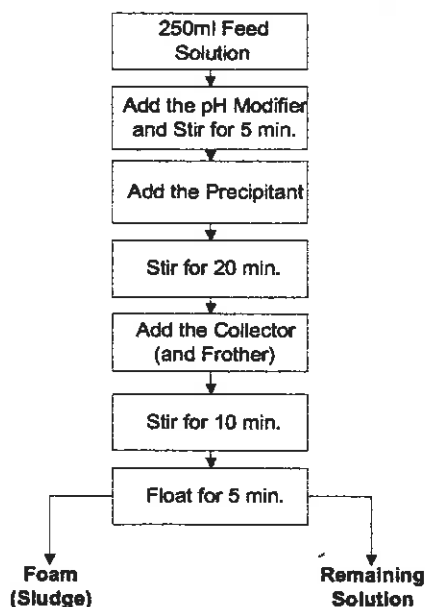


Fig. 3-3-3 Detailed schematic presentation of the flotation column

### 3.3.3.3 Flotation Process

A general flowsheet of the precipitate flotation process is represented in Fig. 3-3-4.



*Fig .3-3-4 General flowsheet of precipitate flotation process*

A conditioning stage preceded the flotation operation, during this stage a small volume of a concentrated aqueous solution of pH modifiers ( $\text{HNO}_3$  or  $\text{NaOH}$ ) was added to the feed solution (250ml) and stirred (magnetic stirring) for five minutes. The precipitant ( $\text{NaOH}$  or  $\text{Na}_2\text{S}$ ) was then added. After it had been stirred for twenty minutes, the collector (and the frother if required) was added and stirred for a further ten minutes. This solution was then transferred to the flotation column and floated for five minutes at a constant airflow rate of  $70 \text{ cm}^3/\text{min}$ . The pH of the feed solution was measured before the flotation process. Ambient temperature conditions were used ( $20 \pm 2^\circ\text{C}$ ).

In some cases, where the flotation process was other than that above, a description has been given in the relevant section.

### 3.3.4 Recovery Calculation

The extent of the recovery of metal ion/collector species was determined by measuring the target ion residual concentrations in the solution remaining in the flotation column. This solution was diluted and acidified ( $\text{HNO}_3$  2%w/w) in order to ensure complete solution of the target ions and the unfloated precipitate. The recovery was calculated as follows:

$$R(\%) = (1 - C/C_0) \times 100 \quad \text{---(3.1)}$$

where,  $C$  is the total concentration of target ions in the remaining solution after being treated (in the dissolved and precipitated state);  $C_0$  is the initial concentration of target ions in the feed solution.

### 3.4 Measurements

- 900P Microprocessor pH Meter (T.P.S. Pty Ltd, Australia) was used to measure the pH and temperature of solution.
- Varian SpectrAA-20 atomic absorption spectrophotometer was used to analyze the metal ions (such as copper and zinc). Before measurement, the solutions were diluted and acidified ( $\text{HNO}_3$  2%w/w).
- Nikon Labophot-Pol Microscope was used to investigate the coagulation and dispersion of the precipitates and to take optical photographs. VideoVue Image Capture Adapter (Video Associates Labs) was used to capture the computer images directly from the Sony SSC-DC38P digital video camera placed at the camera port of the microscope.
- Jeol JSM-6300 Scanning Electron Microscope (denoted as SEM) was used to investigate the structure of the precipitates, to analyze the elements in the flotation products and to take photographs. In the sample preparation process for the SEM, a few drops of precipitate (or flotation product) were caught directly on a carbon holder and kept in a vacuum receptacle, containing a desiccant at  $-92$  Kpa. Once dried, the sample was coated with gold and investigated in the SEM.
- Coulter 440 Laser Zeta potential meter was used to measure the zeta potential of precipitates with the assistance of the staff at the University of Melbourne. In the



sample preparation process, for the zeta potential determination of “fresh” precipitate after twenty minutes precipitation, a drop of precipitate was caught and immediately placed into the measurement cell for immediate determination of the zeta potential.

- Seimens Model 501 X-ray diffraction (XRD) was used to identify the flotation products. In the sample preparation process, the flotation products were washed three times in purified water and then centrifuged, the centrifuge “cakes” were moved onto the XRD glass holders and kept in a vacuum receptacle, containing a desiccant at -92 Kpa. Once dried, the samples were investigated under XRD.

## Chapter IV Results and Discussion

### Section 1 Precipitation and Flotation of Zinc and Copper Hydroxide

#### 1.1 Zinc and copper hydroxide precipitation and flotation behaviour

##### 1.1.1 Results

##### *1.1.1.1 Influence of pH on hydroxide precipitation and flotation*

pH is a key issue for hydroxide precipitation and subsequently flotation. Hydroxide precipitates will tend to dissolve if the pH is (in the case of amphoteric hydroxides) increased. The dispersion, aggregation and flotation behavior of hydroxide precipitates are thus affected by the pH value.

The effect of pH on copper and zinc hydroxide precipitation was examined under the following conditions: reaction for 20 minutes; centrifugal separation at 4000rpm for 20 minutes; initial copper or zinc concentration 50ppm (detailed operation see Chapter III, page 42). The results are summarized in Fig. 4-1-1. The precipitation of copper starts to increase at approximately  $\text{pH}_{\text{pi}}^*$  5.2 and the maximum precipitation of over 95% is reached in the pH range of 6.5 to 11.5. The  $\text{pH}_{\text{pi}}$  value for zinc hydroxide precipitation is at about 6.8 with the significant precipitation in the pH range of 8.5-11.5. When the pH value ( $\text{pH}_{\text{pd}}^\dagger$ ) is above 11.0, the percent precipitation decreases as the precipitate redissolves due to its amphoteric character.

The effects of pH on the flotation recoveries of copper and zinc hydroxide precipitate using the ionic collectors, SDS and SDBS at  $4 \times 10^{-4}$  M were examined (detailed

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\*  $\text{pH}_{\text{pi}}$  is the pH at which the precipitation increases.

†  $\text{pH}_{\text{pd}}$  is the pH at which the precipitation decreases.

description see Chapter III, page 43) and the results are shown in Fig. 4-1-2 and Fig. 4-1-3.

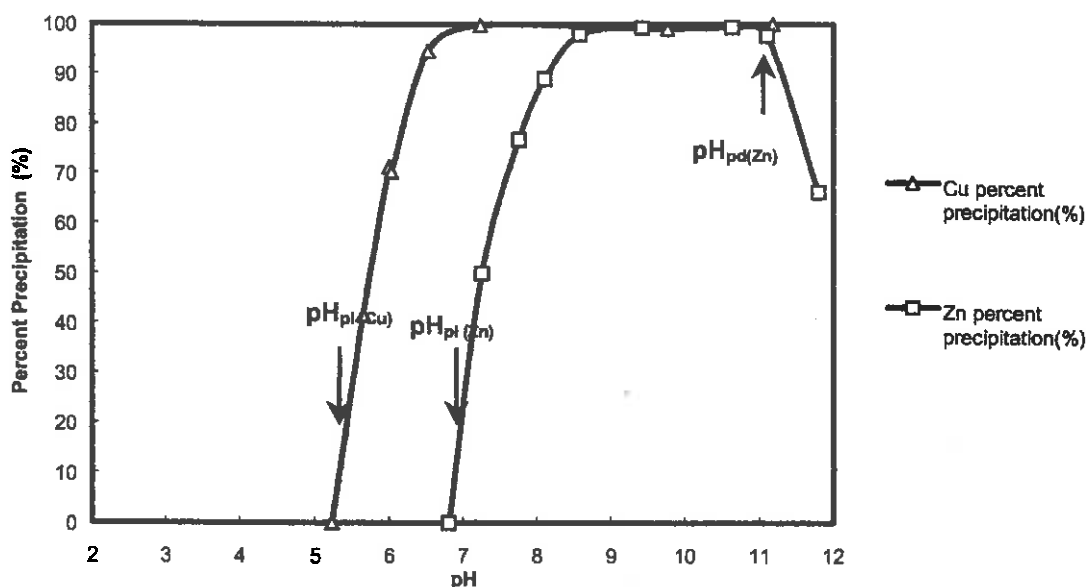


Fig. 4-1-1 The effect of pH on copper and zinc hydroxide precipitation (centrifugal separation 4000rpm 20 min.,  $[Cu^{2+}]_{ini}^*$  and  $[Zn^{2+}]_{ini}^†$  50ppm)

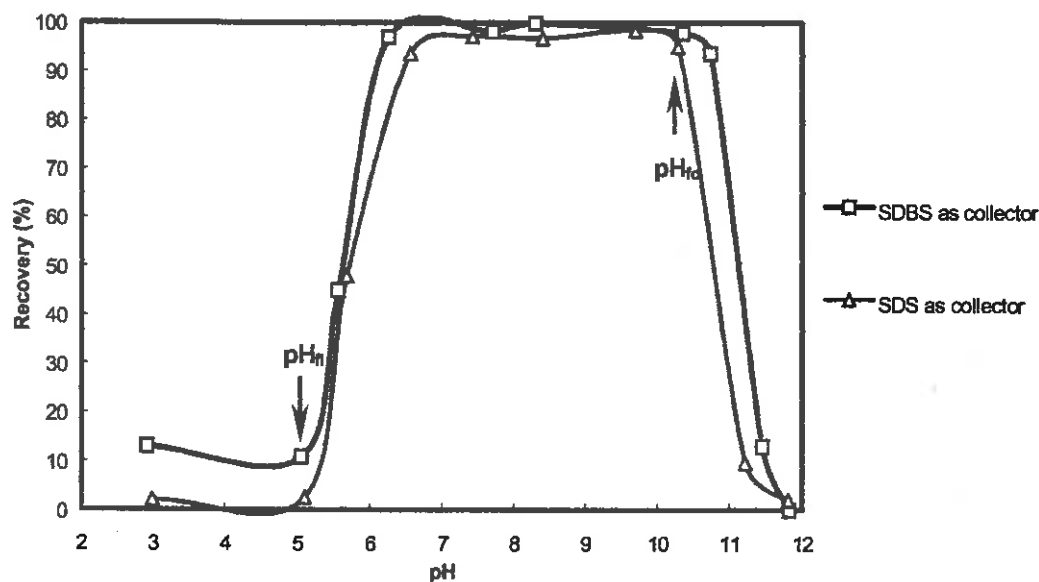


Fig. 4-1-2 The effect of pH on the flotation recoveries of copper hydroxide precipitate ( $[Cu^{2+}]_{ini}$  50ppm, SDS or SDBS as collector  $4 \times 10^{-4}$  M).

\*  $[Cu^{2+}]_{ini}$  is the initial copper concentration.

†  $[Zn^{2+}]_{ini}$  is the initial zinc concentration.

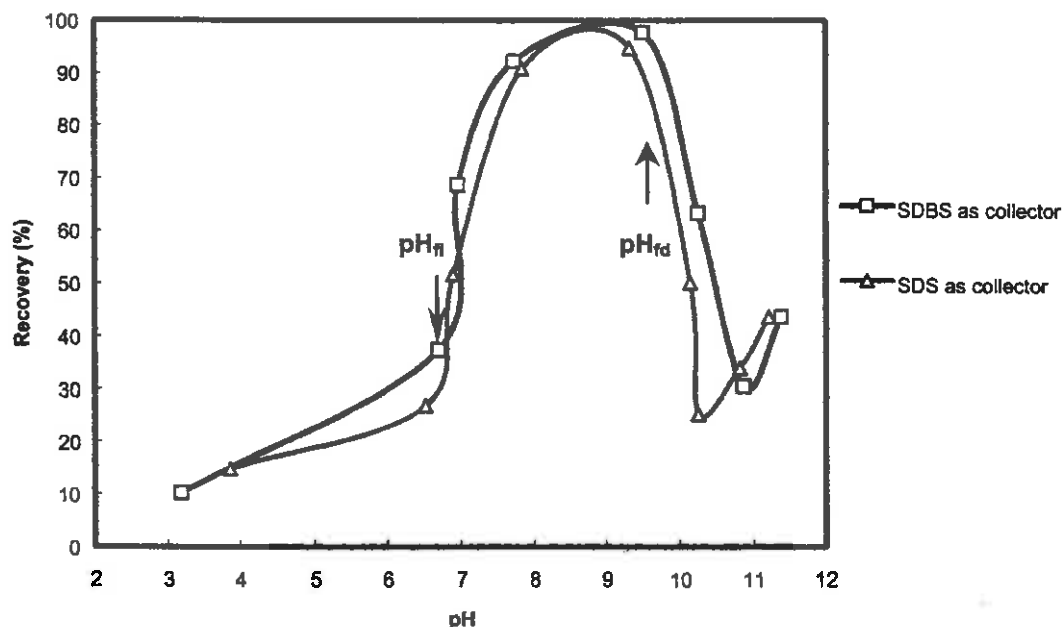


Fig. 4-1-3 The effect of pH on the flotation recoveries of zinc hydroxide precipitate ( $[Zn^{2+}]_{ini}$  50ppm, SDS or SDBS as collector  $4 \times 10^{-4}$  M).

It can be seen from Fig. 4-1-2 that the increase of copper flotation removal starts around  $pH_{fi}^* = 5$  and the maximum flotation with 95% copper removal is reached in the pH range of 6.5 to 10.5. However, with precipitation results, the flotation recovery drops down markedly when the pH value ( $pH_{fd}^\dagger$ ) is over 10.2.

The zinc hydroxide precipitate flotation recovery (Fig. 4-1-3) increasing point ( $pH_{fi}$ ) is 6.5, which is close to the precipitation increasing point ( $pH_{pi}$ ). The maximum flotation recovery is in the pH range of 8.0-9.5. When the pH value ( $pH_{fd}$ ) is above 9.5 (not at  $pH_{pd}=11.3$ ), the flotation recovery significantly decreases.

Fig. 4-1-4 and Fig. 4-1-5 illustrate the influence of concentration of SDBS and SDS on the flotation recoveries of copper and zinc hydroxide precipitates (note the different mole ratio scale). No drop in recovery is obtained for  $Cu^{2+}$ , at higher mole ratios, hence different scales for  $Cu^{2+}$  and  $Zn^{2+}$  were used.

\*  $pH_{fi}$  is the pH at which the precipitate flotation recovery increases.

†  $pH_{fd}$  is the pH at which the precipitate flotation recovery decreases.

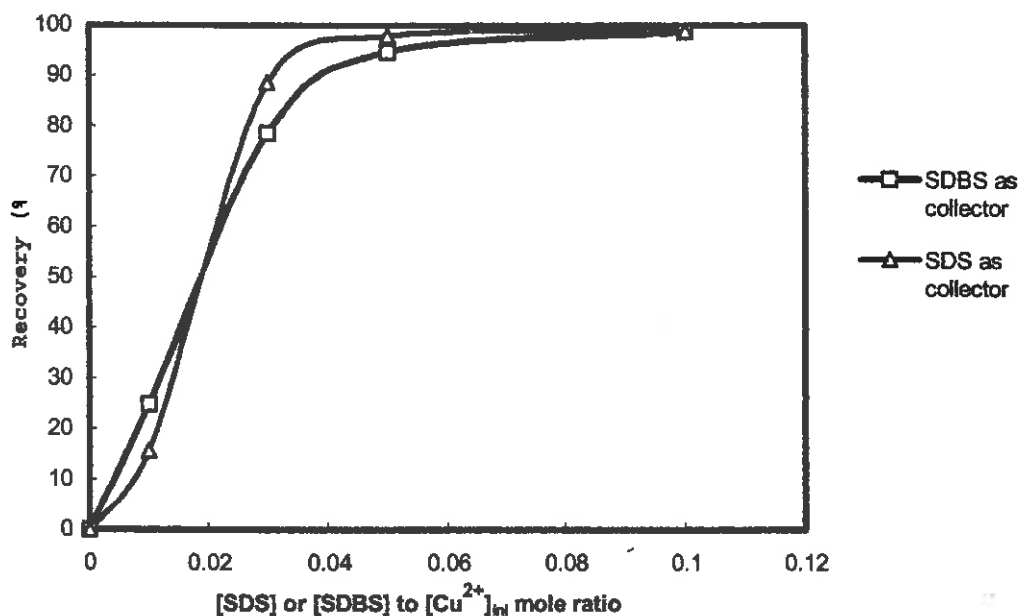


Fig. 4-1-4 Effect of concentration of SDBS and SDS on the flotation recovery of copper hydroxide precipitate flotation ( $[Cu^{2+}]_{ini}$  50ppm; pH  $8.0 \pm 0.2$ ).

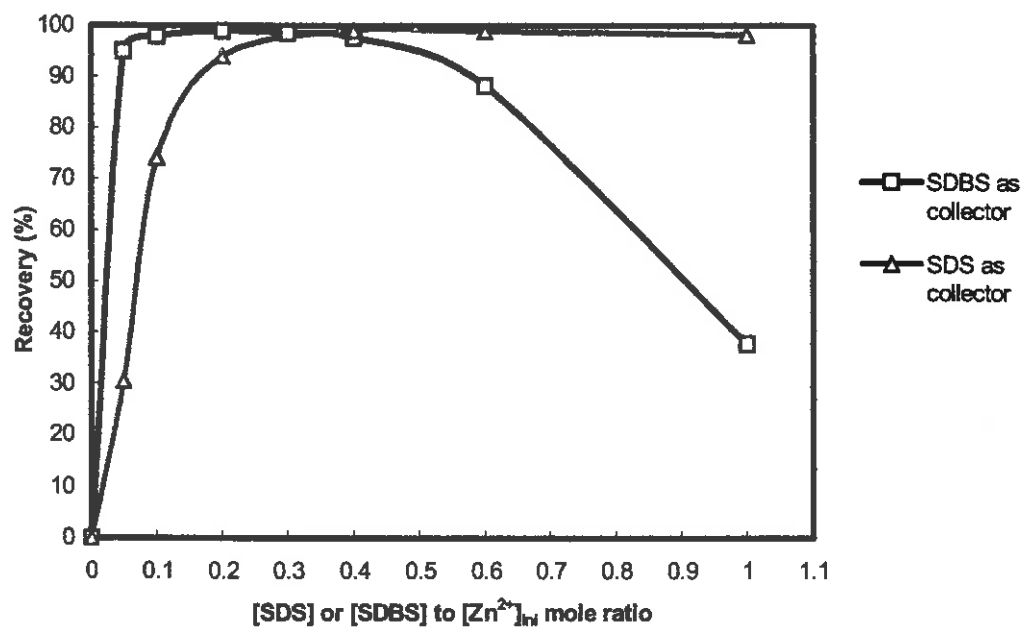


Fig. 4-1-5 Effect of concentration of SDBS and SDS on the flotation recovery of zinc hydroxide precipitate flotation ( $[Zn^{2+}]_{ini}$  50ppm; pH  $8.8 \pm 0.2$ ).

Fig. 4-1-4 and Fig. 4-1-5 show that the floatability of copper hydroxide is better than that of zinc hydroxide. In copper hydroxide precipitate flotation, when the mole ratio of the

concentration SDBS or SDS to copper is more than 0.03, a high recovery of copper can be obtained. SDBS as collector for zinc seems much more efficient than SDS. When the mole ratio of SDBS to zinc is about 0.05, more than 90% recovery can be obtained. While using SDS, a mole ratio of SDS to zinc of  $> 0.2$  is required to achieve the same recovery. The requirement of such a small quantity of collector to achieve high recovery is the main advantage of precipitate flotation compared with the ion flotation technique, which normally needs the mole ratio of the collector to be more than 1:1 to the target heavy metal ions. These observations are consistent with previous work (Guo, 1984).

Both anionic collectors, SDBS and SDS, are efficacious for copper and zinc hydroxide precipitate flotation. Comparing these two anionic collectors, SDBS is slightly better than SDS, probably because SDBS behaves as a better frother than that of SDS.

#### ***1.1.1.2 The influence of variation of sequence of the adding precipitant and collector on the flotation***

The hydroxide precipitate flotation method adopted in this study was to use an amount of hydroxide precipitant (normally sodium hydroxide) to form the heavy metal hydroxide precipitate, to stir for 20 minutes, then add the required amount of collector(s), followed by further stirring and finally transfer into the column for flotation. For a detailed flowsheet of this process see Fig. 4-1-6, flowsheet 1-3.

A question arises, does the sequence of precipitant and collector(s) affect the hydroxide precipitate flotation recovery? The other two flowsheets (flowsheet 1-1 and flowsheet 1-2 of Fig. 4-1-6) were tested to compare results of the typical hydroxide precipitate flotation process.

Flowsheet 1-1 involved firstly the addition of collector, stirring for 20 minutes, followed by the addition of the hydroxide precipitant and further stirring for 10 minutes to give the total time of 30 minutes stirring, then transferring into the column for flotation. Flowsheet 1-2 demonstrated the addition of collector and the hydroxide precipitant together into the solution, stirring for a total of 30 minutes, and followed by flotation. Flowsheet 1-3 has been described as above.

The zinc flotation results as shown in Fig. 4-1-7 and Fig. 4-1-8 have been derived from the flowsheets shown in Fig. 4-1-6.

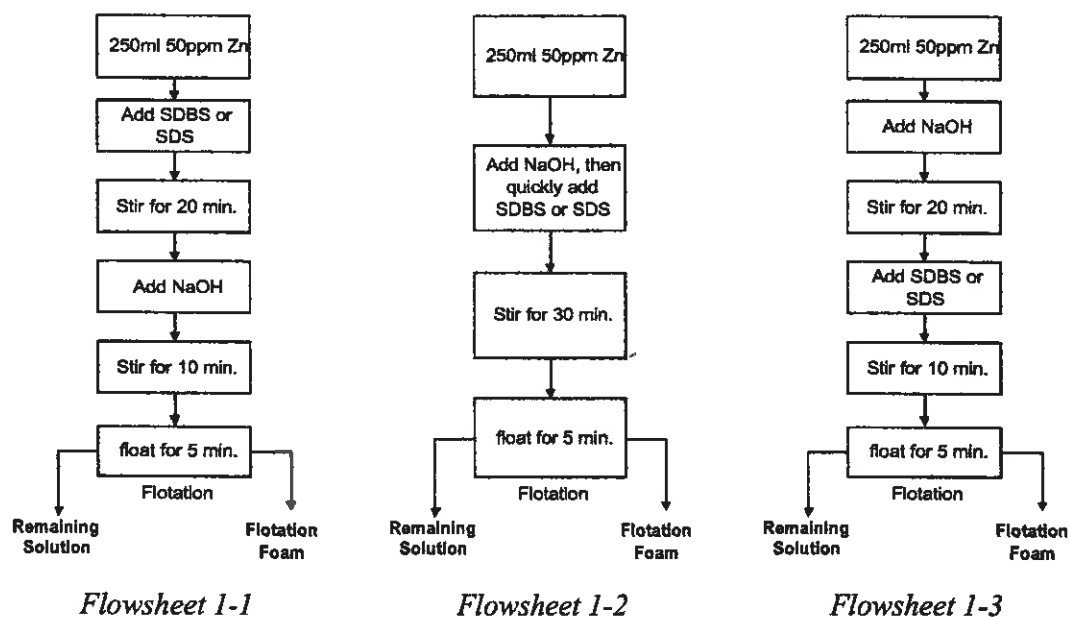


Fig. 4-1-6 Three flowsheets used to determine the influence of the variation of sequence of addition of reagents on flotation recovery of zinc hydroxide.

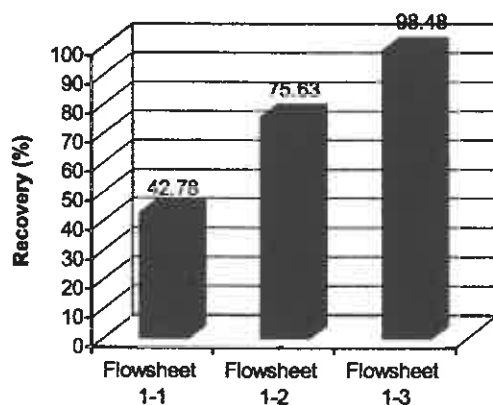


Fig. 4-1-7 Effect on zinc flotation recovery by the variation of sequence of addition of reagents using SDS as collector (SDS:Zn mole ratio 0.4:1).

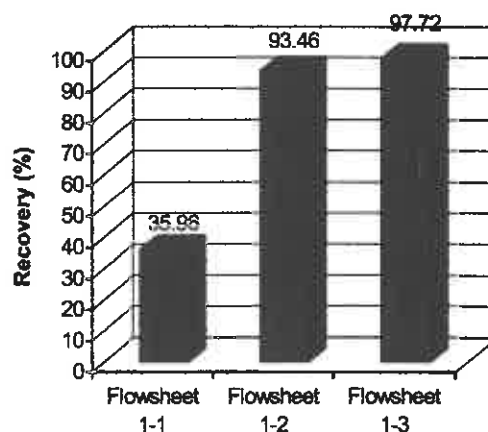


Fig. 4-1-8 Effect on zinc flotation recovery by the variation of sequence of addition of reagents using SDBS as collector (SDBS:Zn mole ratio 0.4:1).

Fig. 4-1-7 and Fig. 4-1-8 show that the sequence of addition of precipitant and collector significantly affects zinc recovery from the solution. When the mole ratio of collector to zinc ions is 0.4:1, and using flowsheet 1-1, the flotation recoveries of both SDS and SDBS are approximately the same, at about 40 per cent. In flowsheet 1-3 with the typical hydroxide precipitate flotation process, using SDBS and SDS as collectors, the recovery of zinc can reach more than 95 per cent. The zinc recovery using flowsheet 1-2 shows that when precipitant and collector are being added simultaneously, the percentage of recovery will be between the recoveries obtained using flowsheet 1-1 and flowsheet 1-3.

Further investigation with regard to flowsheet 1-1 has been carried out. Fig. 4-1-9 illustrates the influence of the stirring time on flotation after adding NaOH, using SDS and SDBS as collectors. As the stirring time increases after adding NaOH, the recovery of zinc ions from the solution increases. A comparison of the two curves shows that using SDS as the collector, the zinc recovery is more rapid than when SDBS is used as the collector. The reason for this will be discussed in the following section.

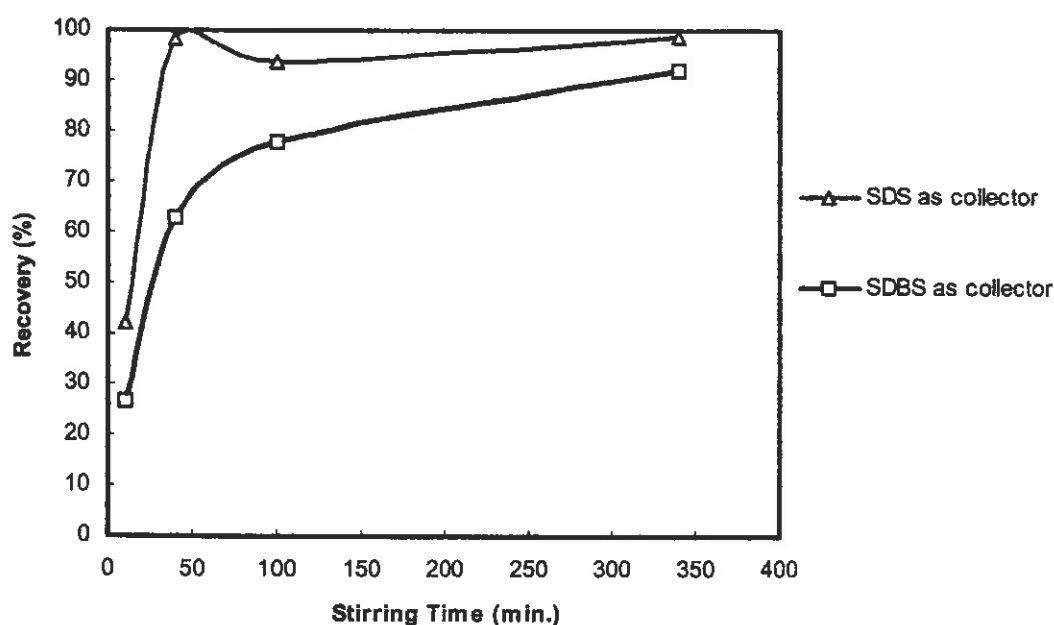


Fig. 4-1-9 The influence of stirring time on zinc flotation recovery after adding NaOH with the flowsheet 1-1 using SDS or SDBS as collectors ( $[SDS]$  or  $[SDBS]$  to  $[Zn^{2+}]_{ini}$  mole ratio 0.4:1).

### 1.1.1.3 The mutual influence of copper and zinc on precipitation and flotation



Copper and zinc ions usually exist together in waste solution, therefore the separation of the two ions is the main objective. The precipitation and flotation behavior of copper and zinc mixed solutions has been investigated.

Fig. 4-1-10 shows the pH effect on the precipitation of the initial copper (50ppm) and zinc (50ppm) mixed solution. The dotted lines are the precipitation curves for copper or zinc ion alone in solution (see Fig. 4-1-1). The precipitation behavior for copper ions in the mixed solution is very similar to the behavior of copper ion alone in solution. The precipitation behavior for zinc is somewhat different. Fig. 4-1-10 shows that the precipitation of zinc hydroxide from the mixed solution occurs over a slightly wider pH range (8.0 - 11.5) compared to the solution of zinc alone.

The effect of pH on the flotation recoveries of zinc and copper hydroxide precipitate from copper/zinc mixed solution is shown in Fig. 4-1-11 using SDBS as collector.

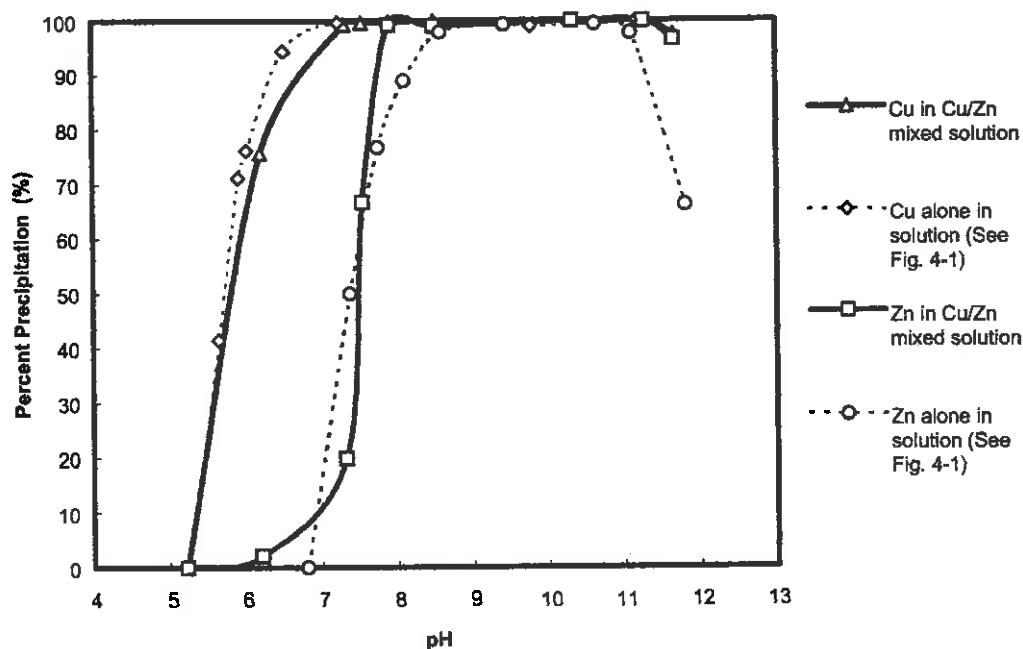


Fig. 4-1-10 The effect of pH on the precipitation of copper and zinc hydroxide from a copper/zinc mixed solution (centrifugal separation 4000rpm 20 min.,  $[Cu^{2+}]_{ini}$  50ppm,  $[Zn^{2+}]_{ini}$  50ppm).

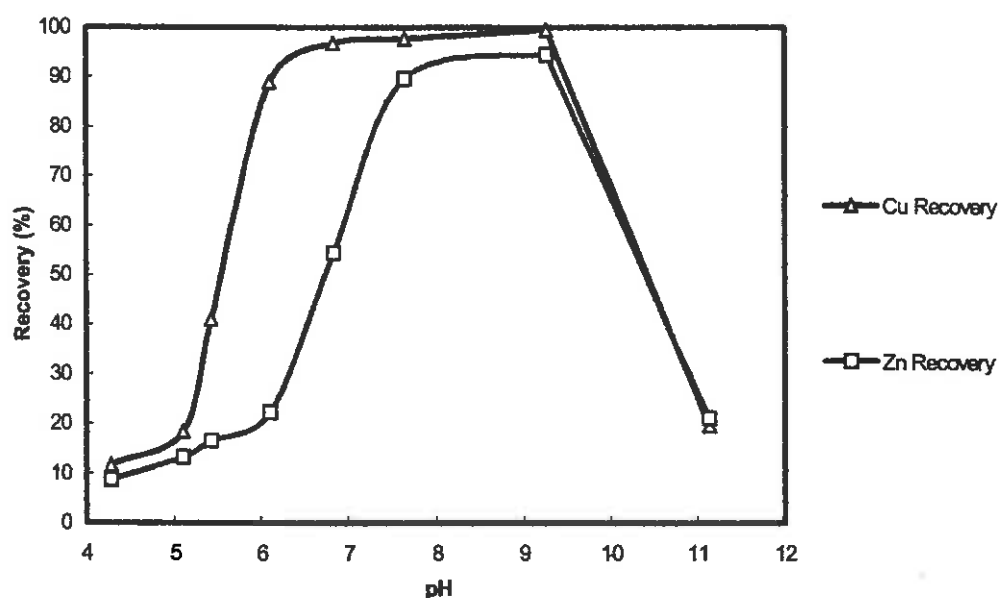


Fig. 4-1-11 The effect of pH on the flotation recoveries of copper and zinc hydroxide from a copper/zinc mixed solution using SDBS as the collector ( $[Cu^{2+}]_{ini}$  50ppm,  $[Zn^{2+}]_{ini}$  50ppm, SDBS  $4 \times 10^{-4}$  M).

The results in Fig. 4-1-11 show that the optimum pH range for the flotation separation of copper and zinc hydroxide is only in a very narrow pH range of 6.0 to 6.5. At pH=6.1 there is a difference in flotation recovery of approximately 66% between copper and zinc hydroxide precipitates, thus reasonable flotation separation of copper and zinc from solution can be obtained at this pH value.

### 1.1.2 Discussion

#### 1.1.2.1 Ionic Equilibrium Diagrams

Most heavy metal ions in water will produce a series of complexes with hydroxyl ions. Study of these metal hydroxo-complexes is very important for understanding the dissolution, precipitation and re-dissolving of metal hydroxide in the solution.

The reactions of zinc ions with hydroxyl ions have been shown to be as follows at 25°C (Wang and Hu, 1988):

Reactions	Ks	
$\text{Zn}^{2+} + \text{OH}^- \leftrightarrow \text{Zn}(\text{OH})^+$	$10^{5.0}$	(a)
$\text{ZnOH}^+ + \text{OH}^- \leftrightarrow \text{Zn}(\text{OH})_{2(\text{aq})}$	$10^{6.1}$	(b)
$\text{Zn}(\text{OH})_{2(\text{aq})} + \text{OH}^- \leftrightarrow \text{Zn}(\text{OH})_3^-$	$10^{2.5}$	(c)
$\text{Zn}(\text{OH})_3^- + \text{OH}^- \leftrightarrow \text{Zn}(\text{OH})_4^{2-}$	$10^{1.2}$	(d)
$\text{Zn}(\text{OH})_{2(\text{solid})} \leftrightarrow \text{Zn}^{2+} + 2\text{OH}^-$	$10^{-16.46}$	(e)

Reactions of copper ions with hydroxyl ion are slightly different from those of zinc ions. Two or more copper ions can also react with hydroxyl ion and produce hydroxo complexes. The reactions and K values are shown as follows (Wang and Hu, 1988):

Reactions	Ks	
$\text{Cu}^{2+} + \text{OH}^- \leftrightarrow \text{CuOH}^+$	$10^{6.3}$	(a1)
$\text{Cu}^{2+} + 2\text{OH}^- \leftrightarrow \text{Cu}(\text{OH})_{2(\text{aq})}$	$10^{12.8}$	(b1)
$\text{Cu}^{2+} + 3\text{OH}^- \leftrightarrow \text{Cu}(\text{OH})_3^-$	$10^{14.5}$	(c1)*
$\text{Cu}^{2+} + 4\text{OH}^- \leftrightarrow \text{Cu}(\text{OH})_4^{2-}$	$10^{16.4}$	(d1)*
$\text{Cu}(\text{OH})_{2(\text{solid})} \leftrightarrow \text{Cu}^{2+} + 2\text{OH}^-$	$10^{-19.32}$	(g1)

\*Note: In some references (Wakamatsu, 1973; Guo and Chui, 1986)  $\text{Cu}(\text{OH})_3^-$  and  $\text{Cu}(\text{OH})_4^{2-}$  are also known as  $\text{CuO}_2\text{H}^-$  and  $\text{CuO}_2^{2-}$ .

According to the above reactions, the distributions of copper and zinc hydroxo complexes versus pH have been calculated as shown in the diagrams in Fig. 4-1-12. and Fig. 4-1-13. A specific computer program, developed by the author, was used to do these calculations and graphical presentation (See Appendix 1).

For the zinc hydroxo complex, Fig. 4-1-12 shows that:

- $\text{pH} < 8.5$ , the major zinc hydroxo complex is  $\text{Zn}^{2+}$ ;
- $8.5 < \text{pH} < 11$ , the major complex is  $\text{Zn}(\text{OH})_{2(\text{aq})}$ ;
- $11 < \text{pH} < 13$ , the major complex is  $\text{Zn}(\text{OH})_3^-$ ;
- $\text{pH} > 13$ , the major complex is  $\text{Zn}(\text{OH})_4^{2-}$ .

For the copper hydroxo complex, Fig. 4-1-13 indicates that:

- $\text{pH} < 6$ , the major copper hydroxo complex is  $\text{Cu}^{2+}$ ;
- $6 < \text{pH} < 9$ , the major copper hydroxo complex is  $\text{CuOH}^+$ ;
- $9 < \text{pH} < 11.2$ , the major copper hydroxo complex is  $\text{Cu}(\text{OH})_2(\text{aq})$ ;
- $11.2 < \text{pH} < 13$ , the major copper hydroxo complex is  $\text{Cu}(\text{OH})_3^-$  (or  $\text{CuO}_2\text{H}^-$ );
- $\text{pH} > 13$ , the major copper hydroxo complex is  $\text{Cu}(\text{OH})_4^{2-}$  (or  $\text{CuO}_2^{2-}$ ).

The theoretical percentage hydroxide precipitation and total soluble concentration of zinc and copper at the initial concentration of 50ppm as a function of pH have been calculated. The diagrams of the calculation results are shown in Fig. 4-1-14 and Fig. 4-1-15.

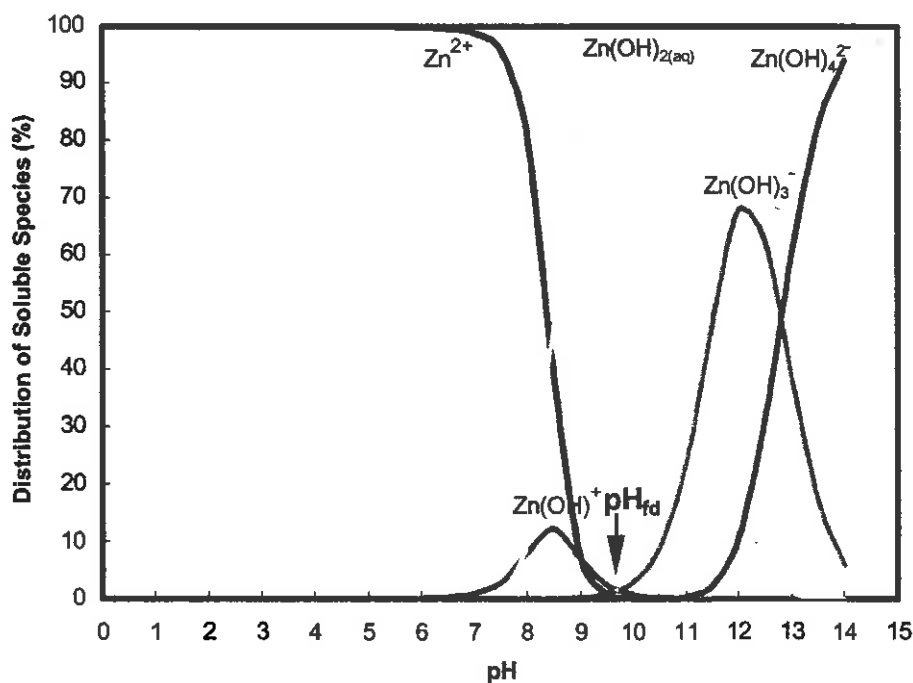


Fig. 4-1-12 Distribution of soluble zinc species versus pH in aqueous solution

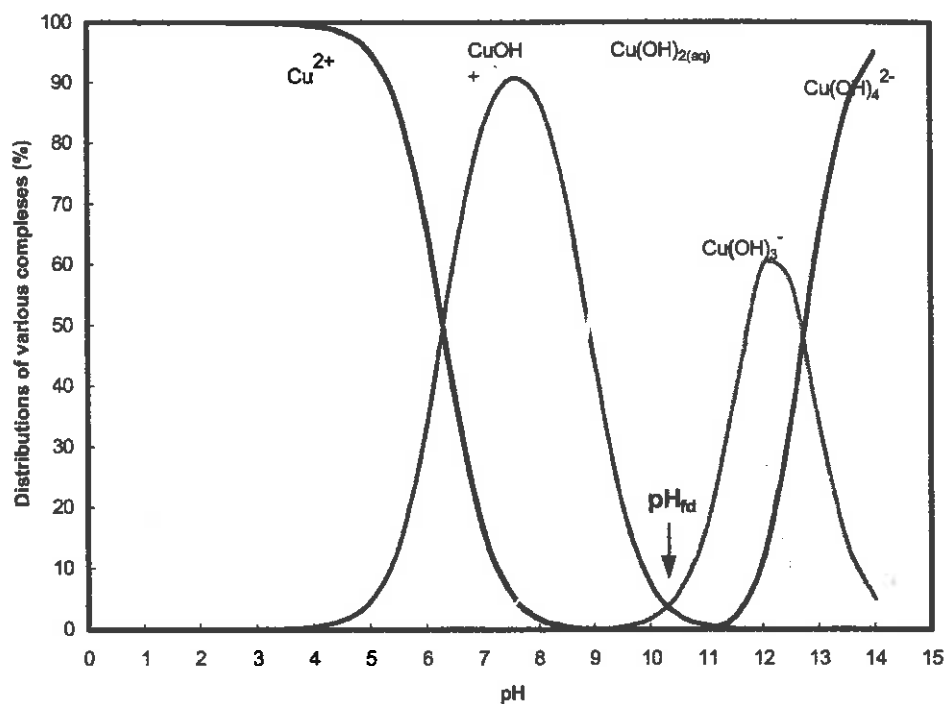


Fig. 4-1-13 Distribution of soluble copper species versus pH in aqueous solution

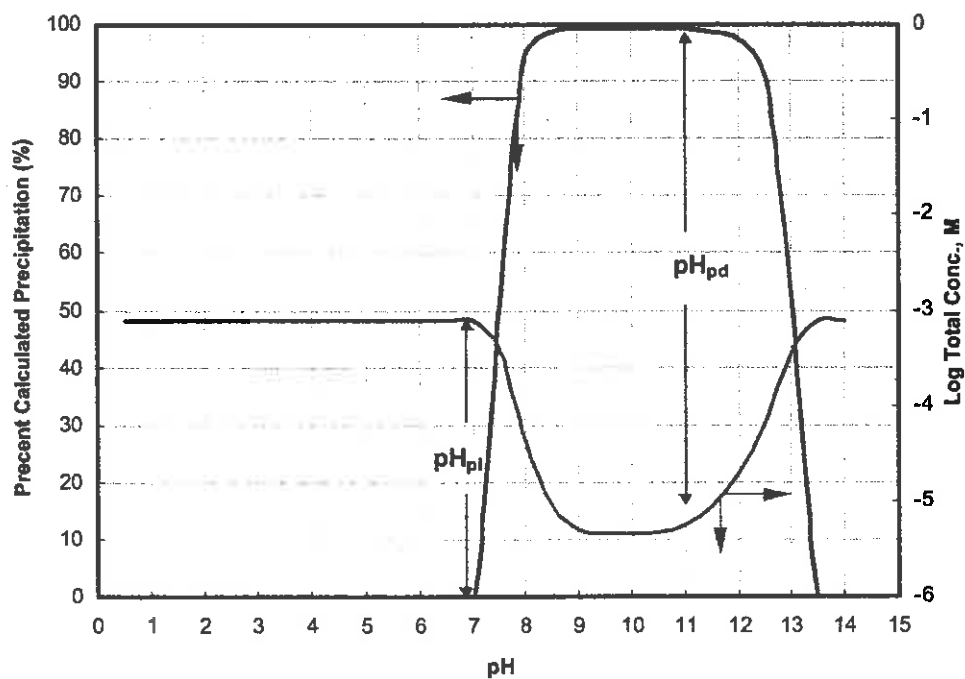


Fig. 4-1-14 Calculated zinc percentage precipitation and total soluble zinc species concentration as a function of pH ( $[\text{Zn}^{2+}]_{\text{ini}} 50\text{ppm}$ )

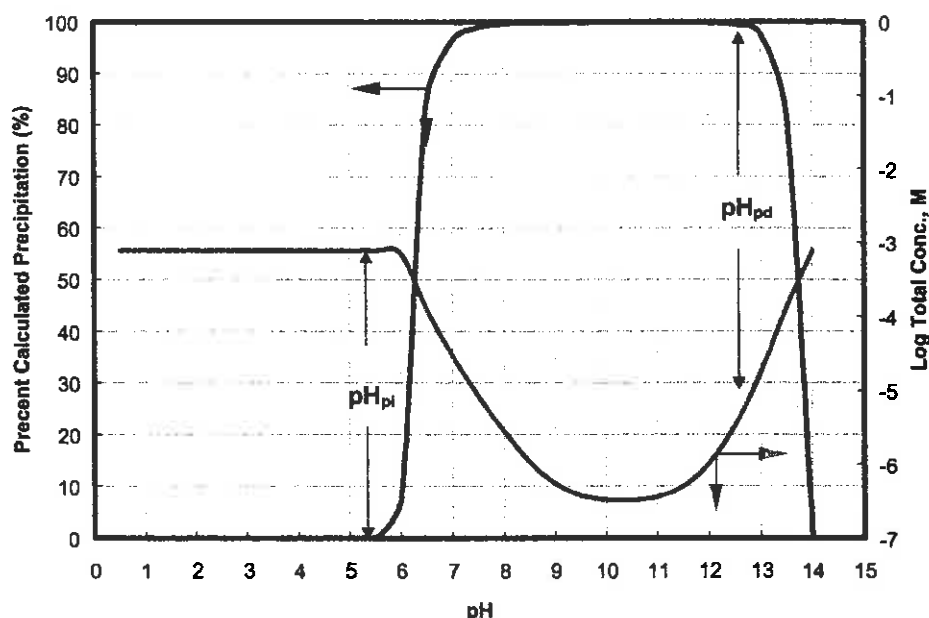


Fig. 4-1-15 Calculated copper percentage precipitation and total soluble copper species concentration as a function of pH ( $[Cu^{2+}]_{ini}$  50ppm)

#### 1.1.2.2 Mechanisms of the influence of pH on hydroxide precipitation and flotation

Combining data for the measured percentage precipitation (Fig. 4-1-1), flotation recovery (Fig. 4-1-2 and Fig. 4-1-3) and the calculated percentage precipitation (Fig. 4-1-14 and Fig. 4-1-15), the results are summarized in Fig. 4-1-16 and Fig. 4-1-17.

It is evident that:

- The results of precipitation and flotation of both zinc and copper hydroxide as a function of pH corresponded well to the theoretical calculated percentage precipitation. The flotation recovery increasing pH points ( $pH_{fi}$ ) and the actual measured hydroxide percentage precipitation increasing pH points ( $pH_{pi}$ ) are very close to the calculated pH range of hydroxide precipitate formation.
- The flotation recovery decreasing pH points ( $pH_{fd}$ ) are lower than the measured and calculated hydroxide percentage precipitation decreasing pH points ( $pH_{pd}$ ).
- The highest flotation recoveries are obtained in the pH range of the maximum hydroxide precipitate formation.

- (d) When the pH value is lower than the hydroxide precipitate existing point, a small amount of zinc and copper ions can still be removed by flotation.

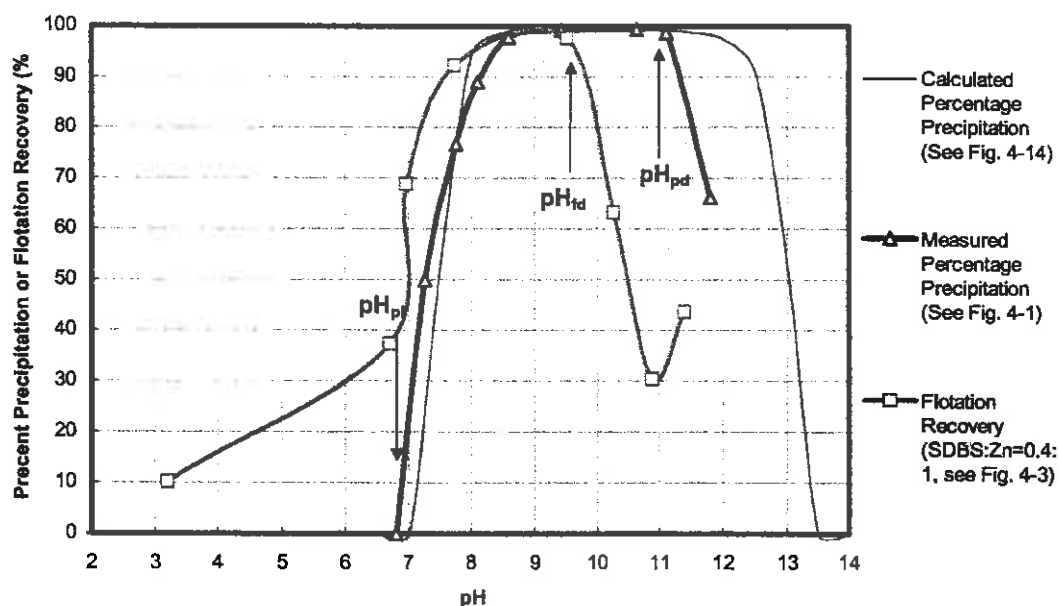


Fig. 4-1-16 The flotation recovery, actual measured percentage precipitation and theoretical calculated percentage precipitation of zinc hydroxide as a function of pH ( $[Zn^{2+}]_{ini}$  50ppm)

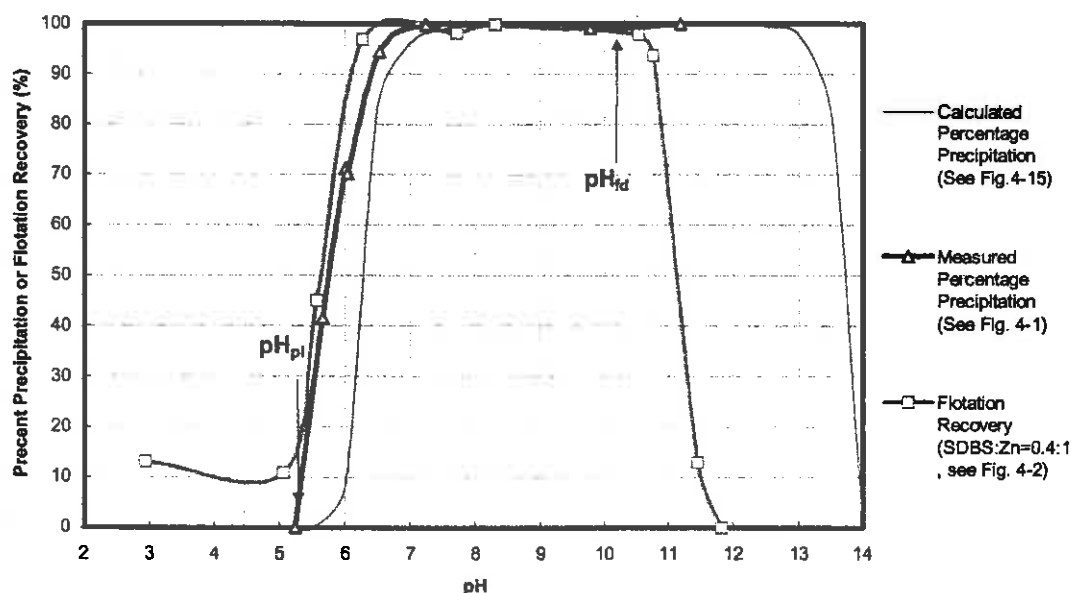


Fig. 4-1-17 The flotation recovery, actual measured percentage precipitation and theoretical calculated percentage precipitation of copper hydroxide as a function of pH ( $[Cu^{2+}]_{ini}$  50ppm)

From Fig. 4-1-12 and Fig. 4-1-13, it can be seen that, for zinc ion, when the pH is greater than 9.5 ( $pH_{fd}$ ), the concentration of the negatively charged complexes ( $Zn(OH)_3^-$  and  $Zn(OH)_4^{2-}$ ) become the majority of the soluble zinc complexes in the aqueous solution; for copper ion when the pH is greater than 10.2 ( $pH_{fd}$ ), the concentration of the negatively charged complexes ( $Cu(OH)_3^-$  and  $Cu(OH)_4^{2-}$ ) become the majority. This means that when the pH value is more than  $pH_{fd}$ , although the hydroxide precipitate is well formed, the precipitate surfaces become more and more negatively charged (Rubin, 1972; Basak and Charewicz, 1986), and the negatively charged collector will be unable to adsorb on the precipitate surface, and the precipitate particles will become dispersed and hence the flotation recovery decreases.

It is also noticed (Fig. 4-1-16 and Fig. 4-1-17) that the flotation increasing pH points ( $pH_f$ ) and the measured hydroxide precipitation increasing pH point ( $pH_{pi}$ ) are slightly lower than the theoretical calculated hydroxide precipitate existing point. It is estimated that the high concentration of sodium hydroxide ( $2 \times 10^{-2}$  M) added in the solution causes an initial hydroxyl ion surplus and forms a heavy metal hydroxide precipitate even though the bulk pH is lower than the hydroxide precipitate existing point. As the stirring time is not long enough to totally re-dissolve the precipitate, and the reaction speed at the pH near the hydroxide precipitate existing point is slow, the pH values ( $pH_f$  and  $pH_{pi}$ ) of flotation and precipitation occur earlier than the calculated precipitate existing point. Jurkiewicz (1990) indicated another possible reason for the difference in the pH values; he believed it caused to be by the presence of lauryl sulphate (collector) in the foam separation medium, as this causes faster precipitation of the hydroxide.

The flotation recovery which occurred at a pH value lower than the hydroxide precipitate increasing point ( $pH_{pi}$ , more accurately, flotation increasing pH point,  $pH_f$ ), is considered as such because of a kind of ion flotation. At this pH value, the heavy metal ions, appearing as cationic ions, can react with the anionic collector and form the sublate and then be floated out.



### *1.1.2.3 Discussion of the influence of variation of sequence of the adding precipitant and collector to the flotation*

The tests of the variation of sequence of the adding precipitant and collector illustrate the difference between ion flotation and precipitate flotation. Flowsheet 1-3 (Fig. 4-1-6) shows the typical hydroxide precipitate flotation process, as zinc ion reacts with hydroxide ion and forms zinc hydroxide precipitate first, the collector (SDS or SDBS) adsorbs only on a part of the precipitate particle surface and causes it become hydrophobic and then to be floated out. Therefore, although the mole ratio of collector to zinc ion is 0.4:1, the recovery of zinc ion from the solution is more than 97%.

Flowsheet 1-1 (Fig. 4-1-6) demonstrates a kind of ion flotation with a small amount of precipitate flotation. As the collectors, SDS and SDBS, are univalent ions and the zinc ion is divalent, the mole ratio is 0.4, which means, from the strictly ion flotation point of view that the maximum flotation recovery should be 20%. However, the recoveries reached 35-40%, the additional recovery is considered to have resulted from the subsequent hydroxide precipitant addition, which probably causes some zinc hydroxide precipitate.

Flowsheet 1-1 shows that the recoveries of zinc ion rise with an increase in stirring time after adding hydroxide precipitant (Fig. 4-1-9). It is considered that the sublate (the product of collector and zinc ion) is re-dissolved. The more the stirring time is increased, the more zinc hydroxide is formed. The re-dissolved collector ion can then adsorb onto the zinc precipitate surface and cause it to float as precipitate flotation. Hence, the flotation recoveries increase. It can be seen from Fig. 4-1-9 that the recovery increases much more quickly with an increase in stirring time when SDS is used as collector than when SDBS is used as collector. This is because SDBS more readily reacts with zinc ion than SDS. When zinc dodecylbenzenesulphonate sublate is produced, it is not easy to be replaced by hydroxide ion.

It can be concluded that the variation of sequence of the adding precipitant and collector does influence the flotation recovery. Precipitate flotation can obtain better flotation recovery and requires much less collector than ion flotation.

### 1.1.3 Summary

Both zinc and copper hydroxide precipitate can be efficaciously floated using an anionic collector, such as SDBS and SDS. The results of precipitation and flotation of zinc and copper as a function of pH can be well explained by the calculation of hydrolysis reactions. The pH value of the flotation decreasing point corresponds to the pH point that the negatively charged heavy metal complexes become a majority.

The variation of sequence of the adding precipitant and collector is very important to the flotation recovery. Precipitate flotation is more effective than ion flotation.

Reasonable hydroxide precipitate flotation separation of copper and zinc ion from solution can be obtained at a pH of 6.1 in pure water, however very close control of pH is necessary.

## 1.2 The Effect of Extraneous Ions and Electrolytes on Zinc and Copper Hydroxide Precipitation and Flotation

### 1.2.1 Results

#### 1.2.1.1 Influence of $\text{CaCl}_2$ and $\text{MgCl}_2$ on sedimentation and flotation behaviour

Calcium and magnesium are the most common ions existing in both natural water and in wastewater systems. In order to understand more about zinc and copper flotation separation, it is important to investigate the influence of the presence of calcium and magnesium ions on the zinc and copper hydroxide precipitate sedimentation and flotation behavior. The sedimentation test method has been described in Chapter 3.

Fig. 4-1-18 and Fig. 4-1-19 show the influence of calcium and magnesium ions on the zinc and copper hydroxide precipitate sedimentation behavior.

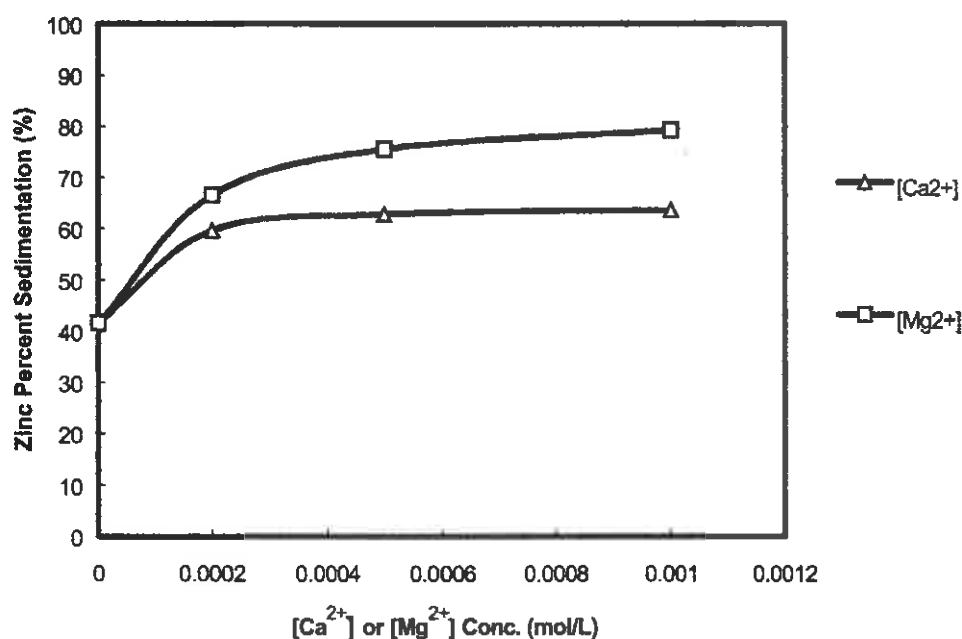


Fig. 4-1-18 The influence of  $\text{CaCl}_2$  and  $\text{MgCl}_2$  salts on zinc hydroxide precipitate sedimentation ( $[\text{Zn}^{2+}]_{\text{ini}}$  50ppm; pH  $8.8 \pm 0.2$ )

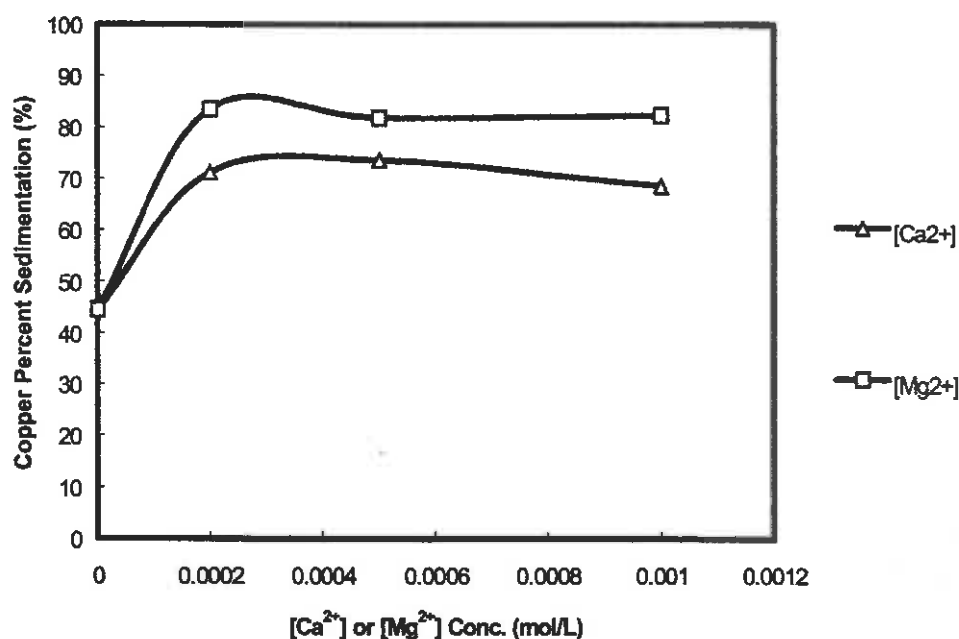


Fig. 4-1-19 The influence of  $\text{CaCl}_2$  and  $\text{MgCl}_2$  salts on the copper hydroxide precipitate sedimentation ( $[\text{Cu}^{2+}]_{\text{ini}} 50\text{ppm}$ ;  $\text{pH } 8.0 \pm 0.2$ )

From Fig. 4-1-18 and Fig. 4-1-19 it can be seen that both  $\text{CaCl}_2$  and  $\text{MgCl}_2$  salts can improve the percentage sedimentation of zinc and copper hydroxide precipitate. When the concentration of  $\text{CaCl}_2$  or  $\text{MgCl}_2$  is  $2 \times 10^{-4}$  molar/litre, the percentage sedimentation of zinc or copper hydroxide precipitate increases from around 40% to 60-85%. However, when the concentration of  $\text{CaCl}_2$  or  $\text{MgCl}_2$  is more than  $2 \times 10^{-4}$  molar/litre, there is no further increase in the percentage sedimentation. When calcium ion is compared with magnesium, the magnesium ion appears to influence the hydroxide sedimentation more than does the calcium for both copper and zinc hydroxide precipitate.

The effect of the concentration of  $\text{CaCl}_2$  and  $\text{MgCl}_2$  salts on zinc and copper hydroxide precipitate flotation recovery is presented in Fig. 4-1-20 and Fig. 4-1-21. It can be seen that in the absence of the  $\text{CaCl}_2$  or  $\text{MgCl}_2$  salts, the flotation recovery for copper is only about 25% and for zinc is about 10%.

Fig. 4-1-20 and Fig. 4-1-21 illustrate that both  $\text{CaCl}_2$  and  $\text{MgCl}_2$  can improve the zinc and copper hydroxide precipitate flotation recovery. By increasing the  $\text{CaCl}_2$  and  $\text{MgCl}_2$  concentration from 0 to  $2 \times 10^{-4}$  M, the flotation recovery of copper can increase from

about 25% to around 80% and of zinc from 10% to 60% ( $\text{CaCl}_2$ ) and 75% ( $\text{MgCl}_2$ ). In the concentration range of the  $\text{CaCl}_2$  or  $\text{MgCl}_2$   $2 \times 10^{-4}$  to  $1 \times 10^{-3}$  M, the flotation recovery slightly decreases as the concentration of  $\text{CaCl}_2$  or  $\text{MgCl}_2$  increases.

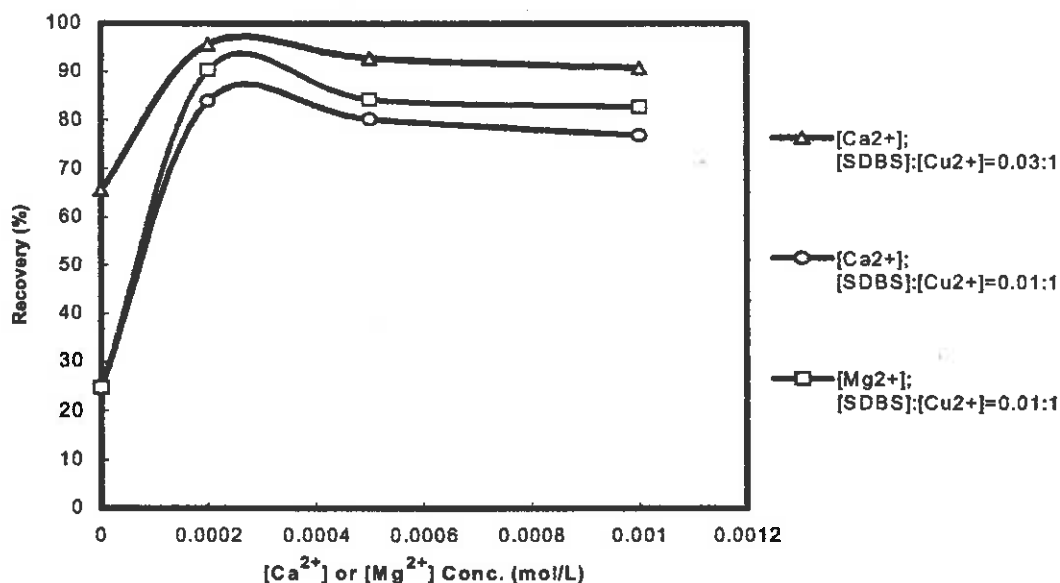


Fig. 4-1-20 The effect of concentration of  $\text{CaCl}_2$  and  $\text{MgCl}_2$  salts on copper hydroxide precipitate flotation recovery ( $[\text{Cu}^{2+}]_{\text{ini}}$  50ppm, pH  $8.0 \pm 0.2$ )

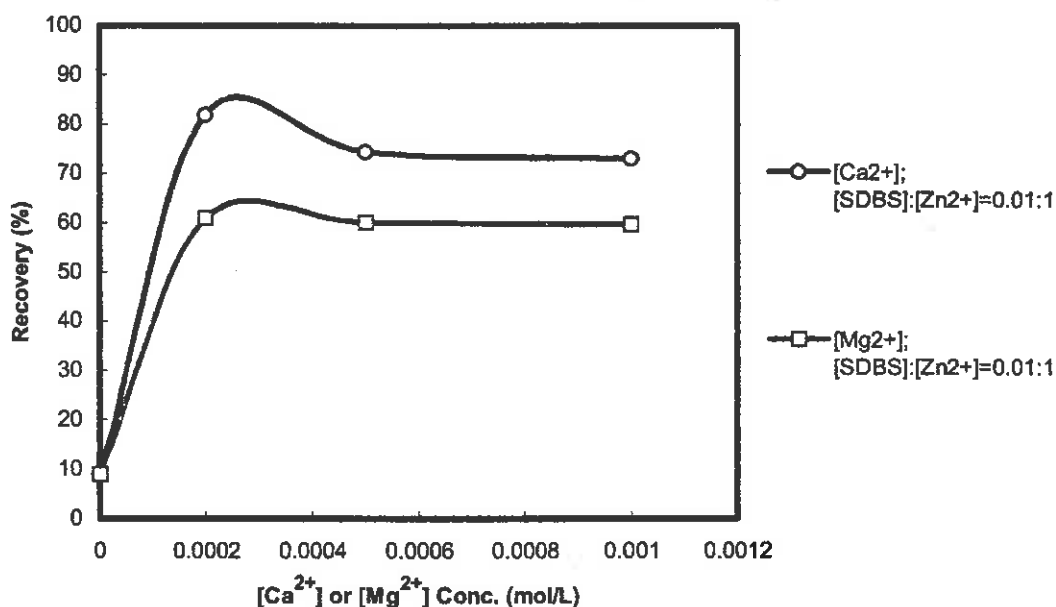


Fig. 4-1-21 The effect of concentration of  $\text{CaCl}_2$  and  $\text{MgCl}_2$  salts on zinc hydroxide precipitate flotation recovery ( $[\text{Zn}^{2+}]_{\text{ini}}$  50ppm, pH  $8.8 \pm 0.2$ )

### 1.2.1.2 Influence of electrolytes on hydroxide precipitate sedimentation and flotation

The effect of sodium sulphate, potassium chloride and sodium chloride additions on the precipitate percentage sedimentation of zinc and copper hydroxide is presented in Fig. 4-1-22 and Fig. 4-1-23.

Fig. 4-1-22 shows that all of the above electrolytes can improve the precipitate percentage sedimentation of zinc hydroxide. At a concentration of  $5 \times 10^{-4}$  to  $5 \times 10^{-3}$  M of KCl and NaCl, the percentage sedimentation of zinc hydroxide becomes almost constant at 72% compared with 40% in the absence of electrolytes. For  $\text{Na}_2\text{SO}_4$ , at concentrations between  $1 \times 10^{-4}$  and  $5 \times 10^{-3}$  M, the precipitate percentage sedimentation increases from 40% to more than 80%, which is slightly better than in the presence of KCl and NaCl.

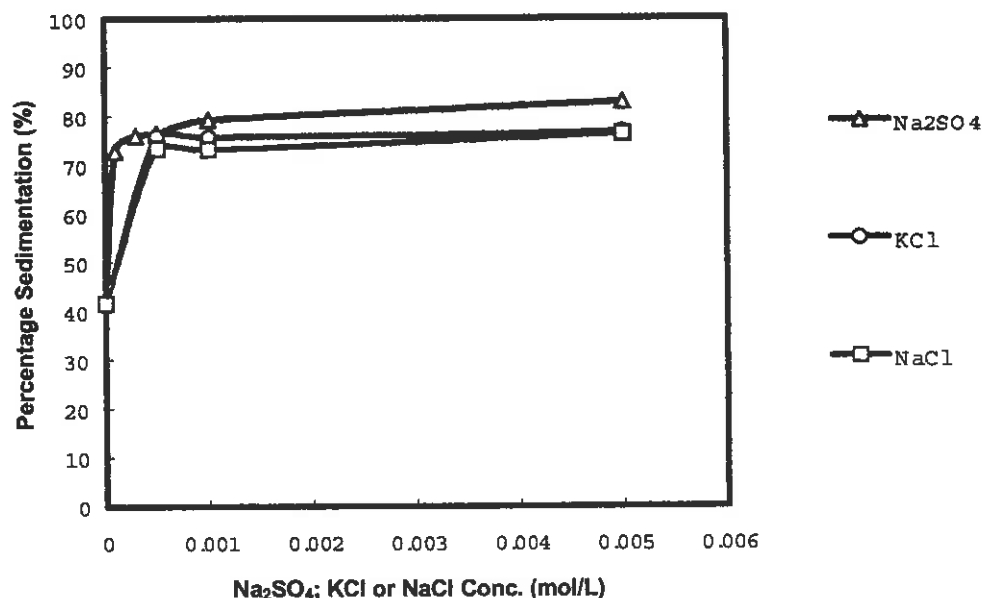


Fig. 4-1-22 The effect of increasing concentrations of sodium sulphate, potassium chloride and sodium chloride on the precipitate percentage sedimentation of zinc hydroxide ( $[\text{Zn}^{2+}]_{\text{ini}} 50\text{ppm}$ ,  $\text{pH } 8.8 \pm 0.2$ )

The behavior of copper in the presence of electrolytes is similar to that of zinc. Fig. 4-1-23 shows that the precipitate percentage sedimentation of copper hydroxide increases from 45% to 73% when the concentration of KCl or NaCl is increased from 0 to  $5 \times 10^{-4}$

M. The percentage sedimentation of copper hydroxide varies with concentration somewhat differently with  $\text{Na}_2\text{SO}_4$ . When the concentration of  $\text{Na}_2\text{SO}_4$  increases from 0 to  $5 \times 10^{-3} \text{M}$ , the percentage sedimentation first increases in the concentration range of  $\text{Na}_2\text{SO}_4$   $1 \times 10^{-4}$  to  $3 \times 10^{-4} \text{M}$ , then the percentage sedimentation decreases quickly to even lower than the initial copper percentage sedimentation when the concentration of  $\text{Na}_2\text{SO}_4$  is more than  $3 \times 10^{-4} \text{M}$ . This means the copper hydroxide precipitate becomes more disperse. This phenomenon will be discussed later.

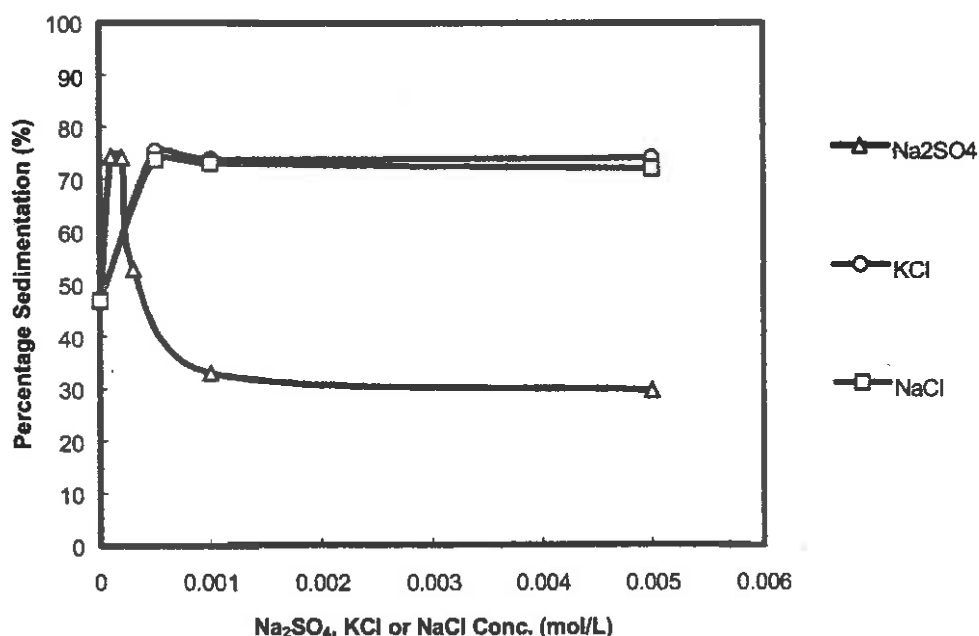


Fig. 4-1-23 The effect of increasing concentrations of sodium sulphate, potassium chloride and sodium chloride on the precipitate percentage sedimentation of copper hydroxide ( $[\text{Cu}^{2+}]_{\text{ini}}$  50ppm, pH  $8.8 \pm 0.2$ )

Fig. 4-1-24 and Fig. 4-1-25 illustrate the influence of increasing concentrations of sodium sulphate, potassium chloride and sodium chloride on zinc and copper hydroxide precipitate flotation recovery.

Fig. 4-1-24 shows that in the case of zinc hydroxide precipitate flotation, an increase in the sodium sulphate, potassium chloride and sodium chloride concentration can significantly increase the flotation recovery. When the concentration of potassium chloride and sodium chloride is  $5 \times 10^{-4}$  to  $5 \times 10^{-3} \text{M}$ , the flotation recovery can increase

from around 10% to 60%. The same amount of sodium sulphate concentration can achieve a higher recovery; when the concentration of sodium sulphate is  $5 \times 10^{-4}$  to  $5 \times 10^{-3}$  M, the flotation recovery can reach about 80%.

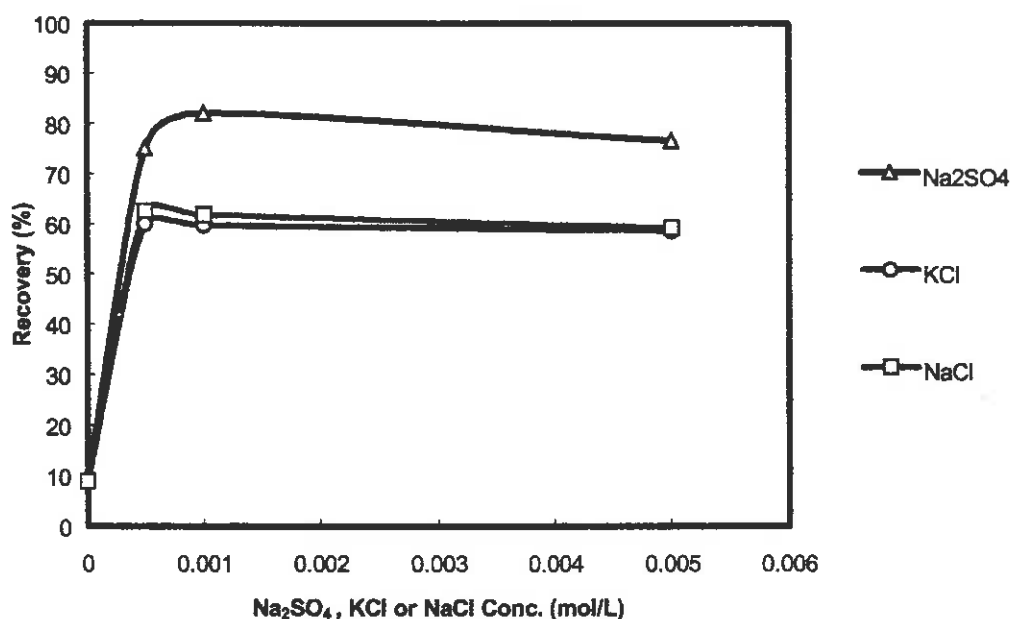


Fig. 4-1-24 The influence of sodium sulphate, potassium chloride and sodium chloride concentration on zinc hydroxide precipitate flotation recovery ( $[Zn^{2+}]_{ini}$  50ppm, pH is  $8.8 \pm 0.2$ ,  $[SDBS]:[Zn^{2+}]_{ini}=0.01:1$ ).

As with zinc hydroxide precipitate flotation (Fig. 4-1-24), the copper hydroxide precipitate flotation recovery improved with increasing amounts of sodium sulphate, potassium chloride and sodium chloride concentrations (see Fig. 4-1-25). When the concentration of potassium chloride and sodium chloride is 0 to  $5 \times 10^{-4}$  M, the flotation recovery can increase from around 25% to 70%. However, in a manner similar to the copper hydroxide sedimentation test results (shown in Fig. 4-1-21), when the concentration of  $Na_2SO_4$  is  $5 \times 10^{-4}$  M, the flotation recovery reaches the highest level and when the concentration of  $Na_2SO_4$  is more than  $5 \times 10^{-4}$  M, the flotation recovery decreases. Nevertheless, when the concentration of  $Na_2SO_4$  is in the range of  $5 \times 10^{-4}$  to  $5 \times 10^{-3}$  M, the copper hydroxide precipitate flotation recovery is significantly better than without  $Na_2SO_4$  additions.



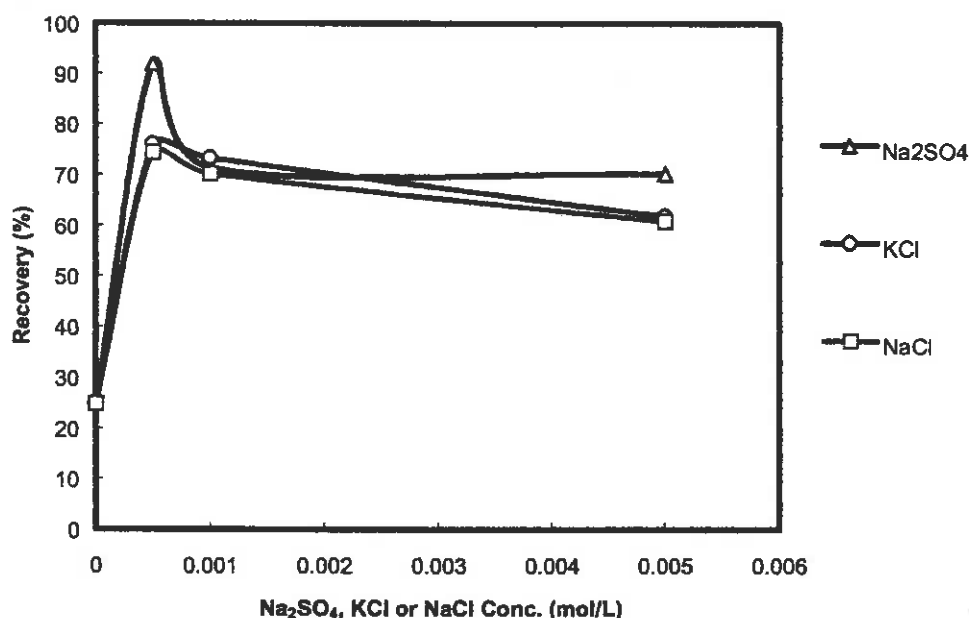


Fig. 4-1-25 The influence of a sodium sulphate, potassium chloride and sodium chloride concentration on copper hydroxide precipitate flotation recovery ( $[Cu^{2+}]_{ini}$  50ppm, pH is  $8.0 \pm 0.2$ ).

### 1.2.1.3 Influence of ferric and aluminum ions on copper and zinc hydroxide precipitation

$Fe^{3+}$  and  $Al^{3+}$  are commonly present in industrial wastewater. They are also extensively used as co-precipitants in adsorption colloid precipitate flotation for removal of heavy metal ions from waste solution (see Chapter II). It is important therefore to investigate the effect of  $Fe^{3+}$  and  $Al^{3+}$  on the precipitation and flotation of heavy metal ions.

The influence of  $Fe^{3+}$  ion on the precipitation of copper and zinc hydroxide has been investigated in this work and the results are shown in Fig. 4-1-26 and Fig. 4-1-27. Comparison of Fig 4-1-26 and Fig. 4-1-27 shows that ferric ion at a concentration of 44ppm in which the mole ratio to 50ppm copper is 1:1 does not affect the precipitation of copper hydroxide. However, in the case of the precipitation of zinc hydroxide (see Fig. 4-1-1 and Fig. 4-1-27), the presence of ferric ion can significantly influence the zinc hydroxide precipitation, the zinc will start to produce hydroxide precipitate at a lower pH

level than in the pure solution. It can also be seen that the greater the increase in ferric ion concentration, the more likely zinc hydroxide will precipitate at a lower pH value.

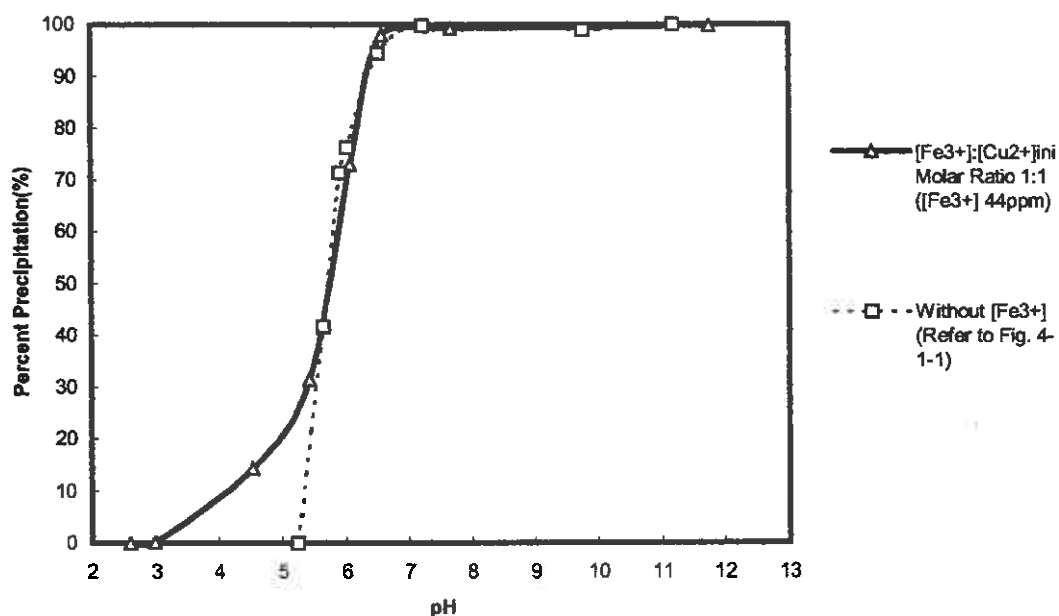


Fig. 4-1-26 The influence of  $[\text{Fe}^{3+}]$  on the precipitation of copper hydroxide (Centrifugal separation 4000rpm 20 min.,  $[\text{Cu}^{2+}]_{\text{ini}}$  50ppm)

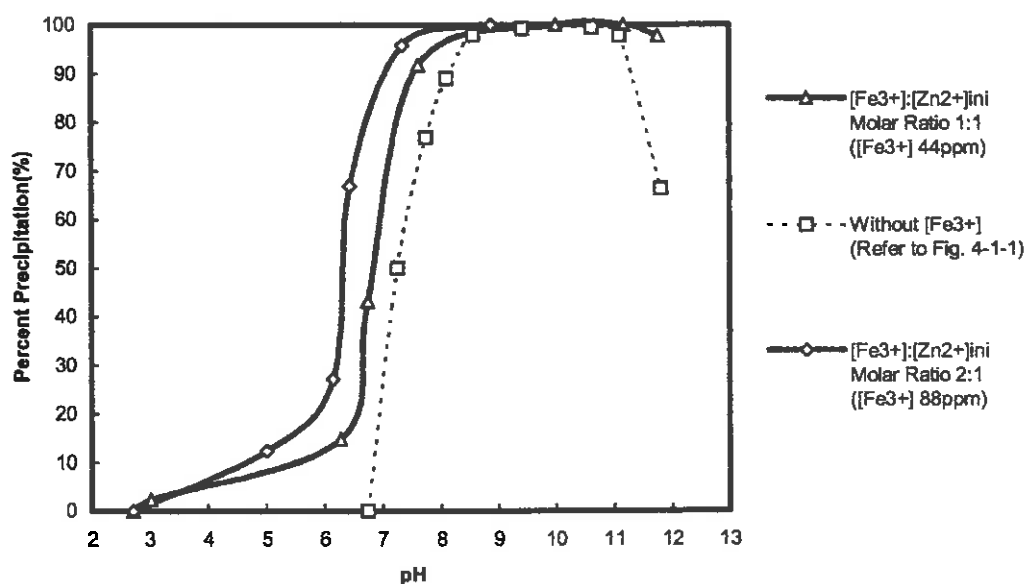


Fig. 4-1-27 The influence of  $[\text{Fe}^{3+}]$  on the precipitation of zinc hydroxide (Centrifugal separation 4000rpm 20 min.,  $[\text{Zn}^{2+}]_{\text{ini}}$  50ppm)

Fig. 4-1-28 and Fig. 4-1-29 show the test results of the influence of  $Al^{3+}$  on the precipitation of copper and zinc hydroxide.

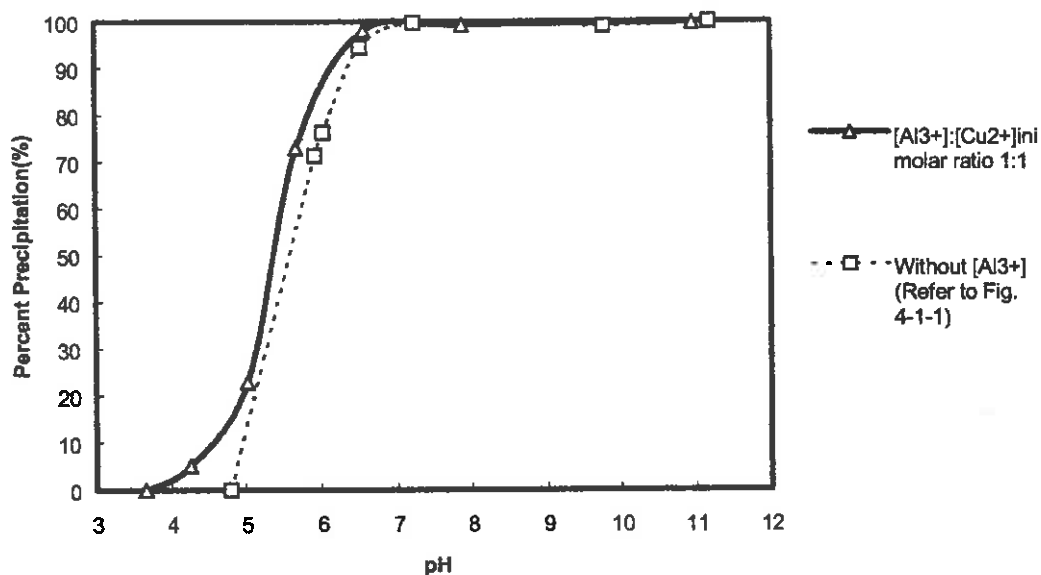


Fig. 4-1-28 The influence of  $[Al^{3+}]$  on the precipitation of copper hydroxide (Centrifugal separation 4000rpm 20 min.,  $[Cu^{2+}]_{ini}$  50ppm)

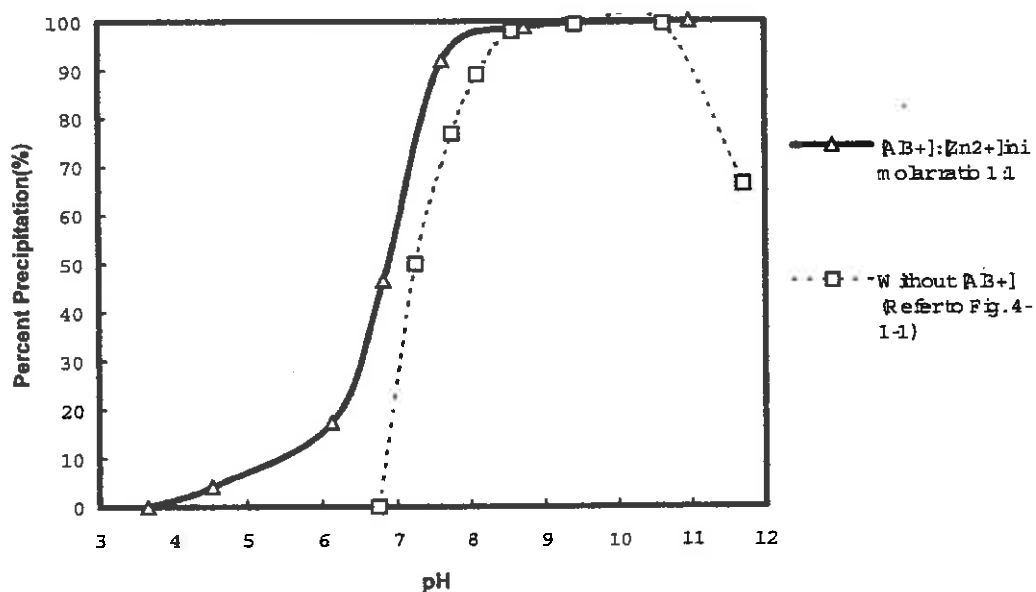


Fig. 4-1-29 The influence of  $[Al^{3+}]$  on the precipitation of zinc hydroxide (centrifugal separation 4000rpm 20 min.,  $[Zn^{2+}]_{ini}$  50ppm)

From Fig. 4-1-28 and Fig. 4-1-29 it can be seen that the precipitation pH curves of both copper and zinc shift to the left when the  $\text{Al}^{3+}$  ion is present in the solution. This means that a hydroxide precipitate will start to form at a lower pH level than in the pure solution. However, the precipitation of zinc hydroxide (Fig. 4-1-29) is more significantly influenced by the  $[\text{Al}^{3+}]$  ion than is copper hydroxide precipitation.

The above studies show that when  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  ions are present in solution, the precipitation will be influenced. Here, the influences of  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  ions on the precipitation of copper and zinc hydroxide from a copper/zinc mixed solution have been investigated.

Fig. 4-1-30 shows the influence of pH on the percentage precipitation of 50ppm zinc, 50ppm copper and ferric ion ( $[\text{Fe}^{3+}]:[\text{Cu}^{2+}]=1:1$ ) mixed solution. The percentage precipitation of 50ppm zinc, 50ppm copper and 44ppm aluminum mixed solution vs. pH value are illustrated in Fig. 4-1-31.

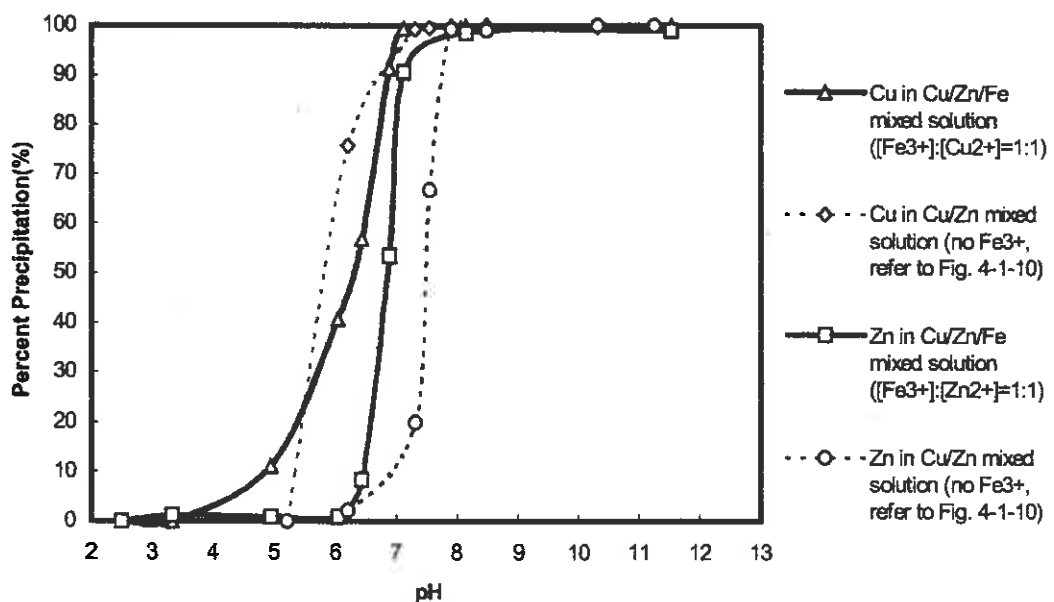


Fig. 4-1-30 The precipitation percentage of zinc, copper and  $[\text{Fe}^{3+}]$  mixed solution as a function of pH ( $[\text{Zn}^{2+}]_{\text{ini}} 50\text{ppm}$ ,  $[\text{Cu}^{2+}]_{\text{ini}} 50\text{ppm}$ ,  $[\text{Fe}^{3+}]:[\text{Cu}^{2+}]_{\text{ini}}=1:1$  when present)

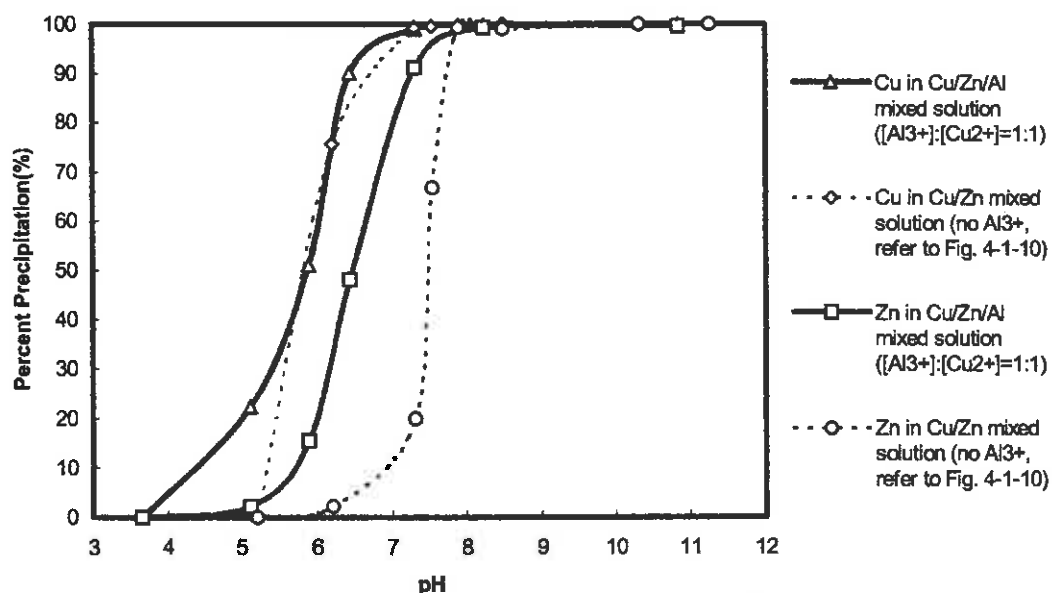


Fig. 4-1-31 The precipitation percentage of zinc, copper and  $[Al^{3+}]$  mixed solution vs. pH value ( $[Zn^{2+}]_{ini}$  50ppm,  $[Cu^{2+}]_{ini}$  50ppm,  $[Al^{3+}]:[Cu^{2+}]_{ini}=1:1$  when present)

Fig. 4-1-30 and Fig. 4-1-31 indicate that where  $Fe^{3+}$  or  $Al^{3+}$  ions are present, the differences in copper and zinc precipitation become less; the maximum difference in precipitation percentage is from 80% in the absence of  $Fe^{3+}$  or  $Al^{3+}$  ions (Fig. 4-1-10) to only 40-50%. This means that, using the hydroxide precipitation method it is impossible to separate copper and zinc efficiently when specific amounts of  $Fe^{3+}$  or  $Al^{3+}$  ions are present in the solution.

#### 1.2.1.4 Influence of ferric and aluminum ions on the flotation of copper and zinc hydroxide from a copper/zinc mixed solution

The flotation of copper and zinc hydroxide with ferric or aluminum ions present in the solution have been carried out using SDBS as collector at  $4 \times 10^{-4}$  M and the results are shown in Fig. 4-1-32 and Fig. 4-1-33.

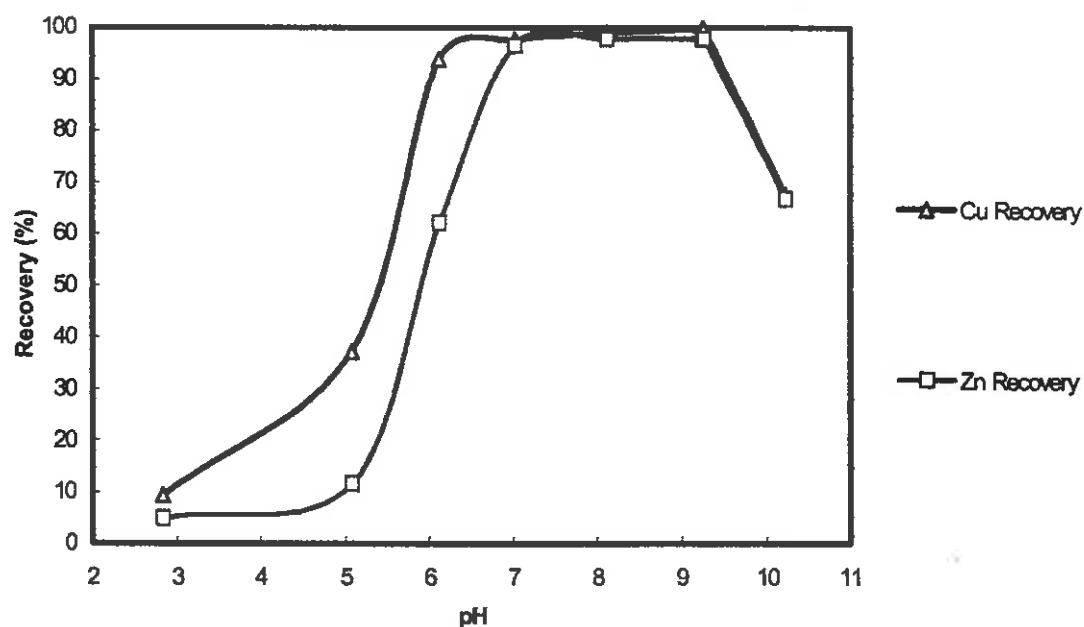


Fig. 4-1-32 The flotation recovery of copper and zinc hydroxides in the presence of ferric ion ( $[\text{Fe}^{3+}]:[\text{Cu}^{2+}]=1:1$ ) in solution as a function of pH ( $[\text{Zn}^{2+}]_{\text{ini}} 50\text{ppm}$ ,  $[\text{Cu}^{2+}]_{\text{ini}} 50\text{ppm}$ ,  $[\text{Fe}^{3+}]:[\text{Cu}^{2+}]_{\text{ini}}=1:1$ , SDBS  $4 \times 10^{-4} \text{ M}$ )

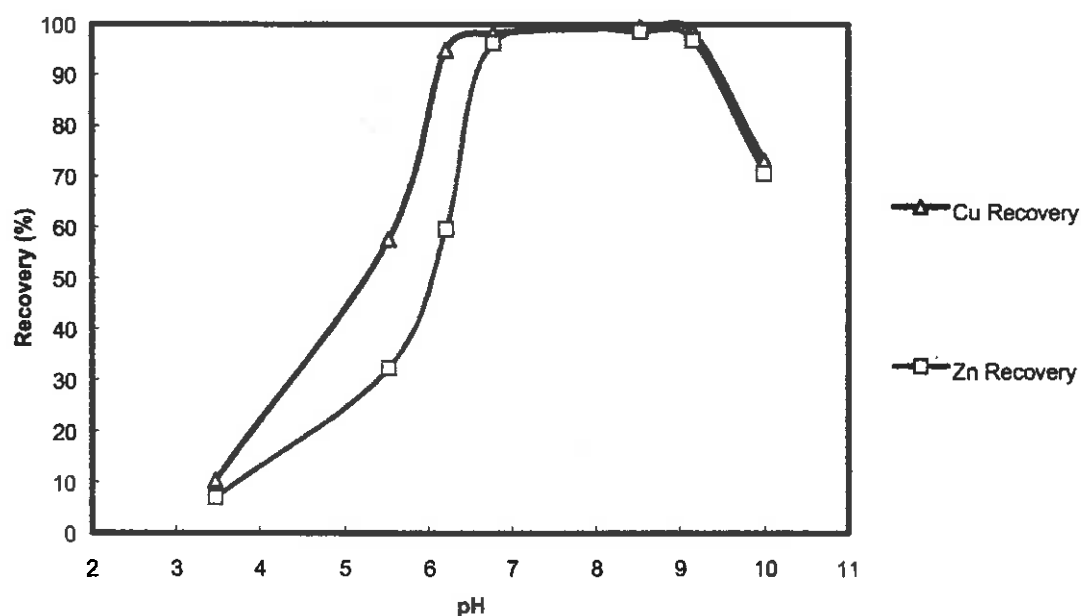


Fig. 4-1-33 The flotation recovery of copper and zinc hydroxides in the presence of aluminum ion ( $[\text{Al}^{3+}]:[\text{Cu}^{2+}]=1:1$ ) in solution as a function of pH ( $[\text{Zn}^{2+}]_{\text{ini}} 50\text{ppm}$ ,  $[\text{Cu}^{2+}]_{\text{ini}} 50\text{ppm}$ ,  $[\text{Al}^{3+}]:[\text{Cu}^{2+}]_{\text{ini}}=1:1$ , SDBS  $4 \times 10^{-4} \text{ M}$ )

The flotation results show (See Fig. 4-1-32 and Fig. 4-1-33) that where ferric or aluminum ions are present, the differences between copper and zinc hydroxide precipitate flotation recoveries become smaller. The maximum difference in copper and zinc recovery in the presence of ferric ion ( $[\text{Fe}^{3+}]:[\text{Cu}^{2+}]=1:1$ ) is only 31.62% (at pH 6.1) (Fig. 4-1-32); and in the presence of aluminum ion ( $[\text{Al}^{3+}]:[\text{Cu}^{2+}]=1:1$ ) the difference in recovery is only 35.30% (at pH 6.2) (Fig. 4-1-33).

## 1.2.2 Discussion

### 1.2.2.1 Aggregation and dispersion of precipitates and the DLVO theory\*

The Scanning Electron Microscopy photographs (see Page 107, Fig. 4-2-10) demonstrate that the “fresh” precipitate produced from the hydroxide precipitation process consists of colloidal amorphous particles in the order of 0.01-0.5 micron in size. In order to understand the phenomena which occurs in flocculation and flotation, it is necessary to consider the conditions of dispersion and aggregation of colloidal particles.

A most important physical property of colloidal dispersions is the tendency of the particles to aggregate. Encounters between particles dispersed in liquid media occur frequently as a result of Brownian motion and the stability of the dispersion is determined by the interaction between the particles during these encounters.

In the 1940s, Derjaguin and Landau (1941) and Verwey and Overbeek (1948) independently developed a comprehensive theory of the interaction potential between colloidal particles. This so-called “DLVO theory” involves estimations of the energy of attraction (London-van der Waals forces,  $V_A$ ) and the energy of repulsion (overlapping of electric double layers,  $V_R$ ) in terms of inter-particle distance. According to the classical DLVO theory, the total energy ( $V_T$ ) between two particles can be described as:

$$V_T = V_A + V_R \quad \text{---(4.1)}$$

---

\* For more detail, see “Appendix 2. Aggregation and Dispersion of Fine Particles”.

The London-van der Waals forces ( $V_A$ ) are attractive forces due to dipoles, induced dipoles and London forces. They may be modified by the presence of adsorbed layers. Schenkel and Kitchener (1960) gave a reasonably accurate expression for the magnitude of the interaction by taking into account the effects of retardation.

For  $P_0 < 0.5$ :

$$V_A = -\frac{AR_1R_2}{6(R_1 + R_2)h} \left( \frac{1}{1 + 1.77P_0} \right) \quad \text{---- (4.2)}$$

For  $P_0 = 0.5$  to  $\infty$  and  $h \ll R_1$  or  $R_2$ :

$$V_A = -\frac{AR_1R_2}{6(R_1 + R_2)h} 12 \left[ -\frac{2.45}{60P_0} + \frac{2.17}{180P_0^2} - \frac{0.59}{420P_0^3} \right] \quad \text{---- (4.3)}$$

Where  $P_0 = 2\pi h/\lambda$ ;  $A$  is the Hamaker constant;  $R_1$  and  $R_2$  are the radii of the two colloid spheres;  $h$  is the distance between the spheres (see Fig. 4-1-34).

The interaction between two spheres is shown in Fig. 4-1-34.

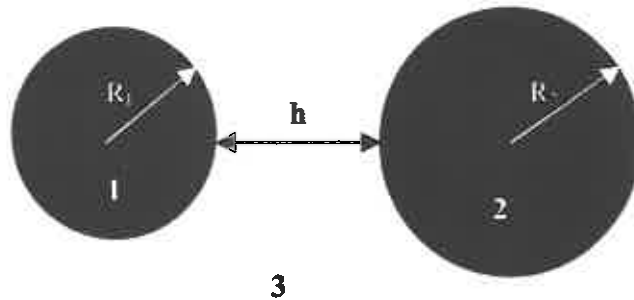


Fig 4-1-34 Interaction between two colloid spheres

The range of values of the Hamaker constant for substances immersed in water can be summarized as follows (Hunter, 1987):



$$\begin{array}{ll}
 \text{Metals:} & A = 10 - 30 \times 10^{-20} \text{ J} \\
 \text{Oxides and halides:} & A = 1 - 3 \times 10^{-20} \text{ J} \\
 \text{Hydrocarbons:} & A \leq 0.3 \times 10^{-20} \text{ J}
 \end{array}
 \quad \text{----(4.4)}$$

These figures reflect the differences in the polarizabilities of various materials, on which  $A$  largely depends. For approximate calculations, the above information may be sufficiently accurate.

The electrical double layer interactions ( $V_R$ ) arise due to the charges on the particles and the overlap of the ionic double layers. When two colloidal particles or two double-layer systems approach one another, electrical interactions will occur. In the case of the same type of particles, the forces will always be repulsive; in the case of particles of different types, the interactive forces can be either repulsive or attractive, depending on the differences of the charges on the particle surfaces.

These forces are very important because they can be controlled by the changes of conditions or (and) the use of reagents, and can subsequently control the aggregation or dispersion of the particles. The principal parameters determining the magnitude of these forces are the relevant potential at the particle surface and the Stern plane. The parameter is important in colloid stability and this can, in many cases, be shown to be approximately equal to the potential measured by electrokinetic measurements, namely the zeta potential.

The interaction between two spherical particles has been given by Hogg et al. (1966):

For constant potential interaction:

$$V_R = \frac{\pi \epsilon_0 \epsilon_r R_1 R_2 (\psi_1^2 + \psi_2^2)}{(R_1 + R_2)} \left\{ \frac{2\psi_1 \psi_2}{(\psi_1^2 + \psi_2^2)} \ln \left[ \frac{1 + \exp(-\kappa h)}{1 - \exp(-\kappa h)} \right] + \ln[1 - \exp(-2\kappa h)] \right\} \quad \text{----(4.5)}$$

For constant charge interactions:

$$V_R = \frac{\pi \epsilon_0 \epsilon_r R_1 R_2 (\psi_1^2 + \psi_2^2)}{(R_1 + R_2)} \left\{ \frac{2\psi_1 \psi_2}{(\psi_1^2 + \psi_2^2)} \ln \left[ \frac{1 + \exp(-\kappa h)}{1 - \exp(-\kappa h)} \right] - \ln[1 - \exp(-2\kappa h)] \right\} \quad (4.6)$$

Where  $\kappa$  is the Debye-Huckel parameter ( $\text{m}^{-1}$ );  $\epsilon_r$  is the relative permittivity;  $\psi_1$  and  $\psi_2$  are the zeta or Stern potential of particles 1 and 2;  $R_1$  and  $R_2$  are the radii of the two colloid spheres;  $h$  is the distance between the spheres (see Fig. 4-1-34).

The Debye-Huckel parameter reciprocal  $\kappa^{-1}$  is often called the "thickness" of the double layer. All distances within the double layer are judged large or small relative to this thickness. The  $\kappa$  can be calculated as (Hiemenz, 1986):

$$\kappa = \left( \frac{1000e^2 N_A}{\epsilon k T} \sum_i z_i^2 M_i \right)^{1/2} \quad (4.7)$$

where  $e$  is the electronic charge;  $N_A$  is the Avogadro constant;  $k$  is the Boltzmann's constant;  $T$  is the absolute temperature;  $z_i$  is the valency, and  $M_i$  is the molar concentration.

As the total ionic strength in the solution  $I$  is a function of  $\sum_i z_i^2 M_i$ , therefore, from Eq. (4.7), when the ionic strength increases, the value of  $\kappa$  increases and the double layer thickness decreases. Subsequently, from Eq. (4.5) and Eq. (4.6), the repulsive energy will decrease, in other words, the particles will be more easy to aggregate.

The classical DLVO theory has successfully established the base of the colloid stability theory and has clearly explained the phenomena of aggregation and dispersion of many electrostatic colloidal systems. Our precipitate system is quite a simple system fitting the classical DLVO theory. The above knowledge will be used to explain the phenomenon of the influence of the  $\text{CaCl}_2$ ,  $\text{MgCl}_2$  and electrolytes on hydroxide precipitation and flotation.

### 1.2.2.2 The mechanisms of the influence of $\text{CaCl}_2$ , $\text{MgCl}_2$ and electrolytes on hydroxide precipitation and flotation

Using Eq. (4.7), the numerical substitutions of the zinc and copper hydroxide precipitate systems have been examined. The precipitate tests are normally carried out at the room temperature, which is approximately 25°C, the absolute temperature  $T$  is 298 K. At this temperature  $\epsilon_r = 78.54 \text{ C}^2\text{J}^{-1}\text{m}^{-1}$  for water. The electronic charge  $e$  is  $1.60 \times 10^{-19} \text{ C}$ ; the Avogadro constant  $N_A$  is  $6.02 \times 10^{23} \text{ mol}^{-1}$ , the Boltzmann's constant  $k$  is  $1.38 \times 10^{-23} \text{ JK}^{-1}$ . Recalling  $\epsilon = \epsilon_r \epsilon_0$ , it can be written that:

$$\kappa = \left( \frac{(1000)(1.60 \times 10^{-19})^2 (6.02 \times 10^{23})}{(78.54)(8.85 \times 10^{-12})(1.38 \times 10^{-23})(298)} \sum_i z_i^2 M_i \right)^{1/2} \quad \text{---- (4.8)}$$

$$= 2.32 \times 10^9 (\sum_i z_i^2 M_i)^{1/2} \quad \text{m}^{-1}$$

and:

$$\kappa^{-1} = 4.31 \times 10^{-10} (\sum_i z_i^2 M_i)^{-1/2} \quad \text{m} \quad \text{---- (4.9)}$$

The initial 50ppm zinc and copper solution are  $7.65 \times 10^{-4} \text{ M}$  and  $7.87 \times 10^{-4} \text{ M}$  respectively, prepared from sulphate salts. The precipitant is sodium hydroxide. When zinc or copper hydroxide is produced, the stoichiometric molar concentration of sulphate and sodium ions can be expected to remain in the solution. Here, we are using the zinc hydroxide precipitate as the example, the summation in Eq. (4.8) for the initial zinc solution, if we take into account the stoichiometry of dissociation, is:

$$\sum_i z_i^2 M_i = 2 \times 1^2 \times 7.65 \times 10^{-4} + 1 \times 2^2 \times 7.65 \times 10^{-4} = 4.59 \times 10^{-3}$$

Therefore, from Eq.(2.8) and Eq.(4.9) we can get:

$$\kappa = 1.57 \times 10^8 \text{ m}^{-1} \quad \text{and} \quad \kappa^{-1} = 6.36 \times 10^{-9} \text{ m} = 6.36 \text{ nm}$$

When additional  $\text{CaCl}_2$ ,  $\text{MgCl}_2$  or electrolytes are added to the zinc solution, the summation in Eq. (4.8) will be changed. For symmetrical 1:1 electrolytes such as  $\text{KCl}$  and  $\text{NaCl}$ , the changeable additional concentration is  $M_c$ :

$$\sum_i z_i^2 M_i = 4.59 \times 10^{-3} + 2 \times M_c \quad \text{----(4.10)}$$

For asymmetrical 1:2 or 2:1 electrolytes such as  $\text{CaCl}_2$ ,  $\text{MgCl}_2$  and  $\text{Na}_2\text{SO}_4$ :

$$\sum_i z_i^2 M_i = 4.59 \times 10^{-3} + (1 \times 2^2 + 2 \times 1^2) M_c = 4.59 \times 10^{-3} + 6 \times M_c \quad \text{----(4.11)}$$

Combining Eq.(4.10), Eq.(4.11) with Eq.(2.8) and Eq.(4.9), it can easily be calculated that the Debye-Huckel parameter  $\kappa$  and the "thickness" of the double layer  $\kappa^{-1}$  vary with the concentration of extraneous electrolytes. Fig. 4-1-35 shows the calculation results of the "thickness" of the double layer  $\kappa^{-1}$  versus the concentration of  $\text{CaCl}_2$ ,  $\text{MgCl}_2$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{KCl}$  and  $\text{NaCl}$ .

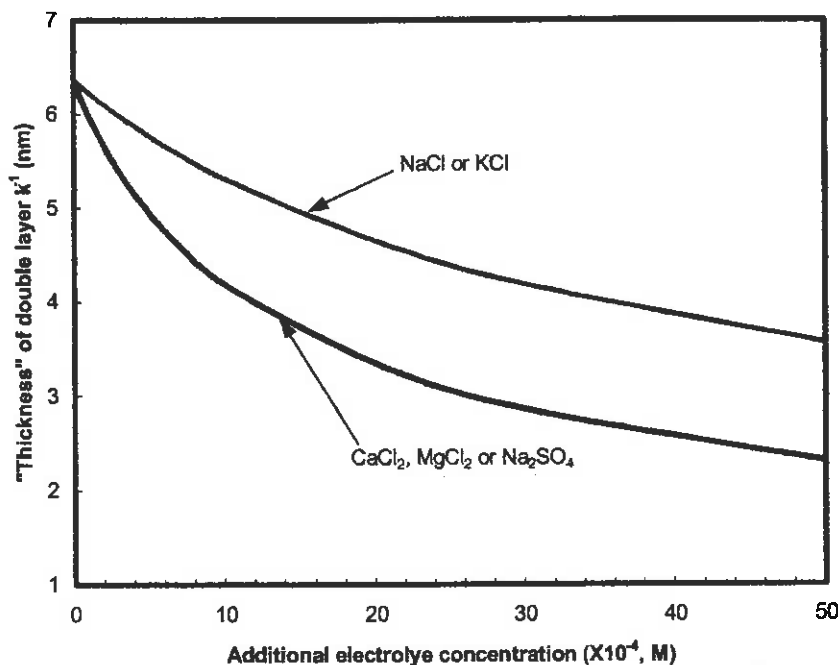


Fig. 4-1-35 The "thickness" of the double layer  $\kappa^{-1}$  in zinc hydroxide precipitate solution versus the concentration of extraneous  $\text{CaCl}_2$ ,  $\text{MgCl}_2$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{KCl}$  and  $\text{NaCl}$ .

It can be seen (Fig. 4-1-35) that the “thickness” of the double layer  $\kappa^{-1}$  drops significantly when the concentration of extraneous electrolytes is increased. This means that the hydroxide precipitate particles will aggregate more easily. Hence the flotation recovery is increased. This explains the test results of the influence of extraneous  $\text{CaCl}_2$ ,  $\text{MgCl}_2$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{KCl}$  and  $\text{NaCl}$  concentration on the sedimentation and flotation. When the 2:1 ( $\text{CaCl}_2$  and  $\text{MgCl}_2$ ) and the 1:2 ( $\text{Na}_2\text{SO}_4$ ) types of electrolytes are compared with the 1:1 type electrolytes ( $\text{KCl}$  and  $\text{NaCl}$ ), at the same molar concentration, the 2:1 and 1:2 types of electrolytes much more efficiently reduce the “thickness” of double layer than the 1:1 electrolytes. This is the reason why  $\text{CaCl}_2$ ,  $\text{MgCl}_2$  and  $\text{Na}_2\text{SO}_4$  are able to increase the sedimentation percentage and flotation recovery to a greater extent than the same molar concentration of  $\text{KCl}$  and  $\text{NaCl}$ .

The classic DLVO theory is also used to explore how the electrolytes influence the total energy between two precipitate particles, the precipitate dispersion and aggregation, and subsequently the sedimentation and flotation recovery.

The potential at the particle surface and the Stern plane (approximately the zeta potential) is a very important aspect of the DLVO calculation. However, in the presence of added electrolytes, the zinc hydroxide precipitate tends to aggregate very quickly, and it is extremely difficult to measure the zeta potential, which varies with the concentration of added electrolytes. The zeta potential of zinc hydroxide precipitate has been measured without extraneous electrolytes (see Fig. 4-2-25, page 102), however it proved difficult to obtain data in the case of extraneous electrolytes. Our purpose here is to explore the influence on the concentration of extraneous electrolytes to the interactive energy of precipitate particles. Our results show that the isoelectric point (IEP) of “fresh” zinc hydroxide precipitate is at  $\text{pH}=8.6-8.7$ , similar to that reported by Jurkiewicz (1990b). As the zinc precipitate sedimentation and flotation are normally tested at  $\text{pH}=8.8-9.0$ , the zinc hydroxide precipitate particle zeta potential of  $-10\text{mv}$  was used to calculate the interactive energies. It is assumed that this zeta potential remains constant with the variation of the added electrolyte concentrations.

The magnitude of the Hamaker constant also needs to be decided before calculations proceed. According to the expression (4.4) and referring to the values of other materials given by Gregory (1969), Visser (1972), Hunter (1987), and Lu and Weng (1992), the Hamaker constant  $A=2\times 10^{-20}$  J was chosen for the zinc hydroxide precipitate. The zinc hydroxide precipitate size is assumed to be 0.05 micron, according to the Scanning Electron Microscopy photographs (see page 107, Fig. 4-2-10). Combining all this information and Eq.(4.1), Eq.(4.2), Eq.(4.5) as well as Eq.(4.8), we can calculate the total energy between the two precipitate particles. For a diagram of calculation results see Fig. 4-1-36 and Fig. 4-1-37.

Fig. 4-1-36 and Fig. 4-1-37 show that in the absence of added electrolytes, the total potential energy of interaction of two zinc hydroxide precipitate spherical particles has a positive energy peak, positive meaning repulsion. This energy peak however is very small and can easily be overcome so that the precipitate particles at this condition still tend to aggregate. However, in the presence of extraneous electrolytes, the energy peak becomes smaller and smaller, even disappearing and becoming negative. This means that not only is there no repulsive energy among the precipitate particles but that in fact these particles have attractive forces towards each other. This leaves no doubt that where the electrolytes are present the precipitates will flocculate more strongly and generate large aggregates.

Fig. 4-1-38 shows the optical microphotographs of zinc and copper hydroxide precipitate in the absence or presence of an added electrolyte. It can be seen that in the absence of an added electrolyte zinc and copper hydroxide precipitate are only slightly agglomerated. (Fig.4-1-38A and Fig. 4-1-38C). With the  $\text{CaCl}_2$  (added electrolyte) present, the precipitates were agglomerated and become larger aggregates (Fig.4-1-38B and Fig. 4-1-38D). Hence the total precipitate surface area is decreased and the flotation recovery can be improved.

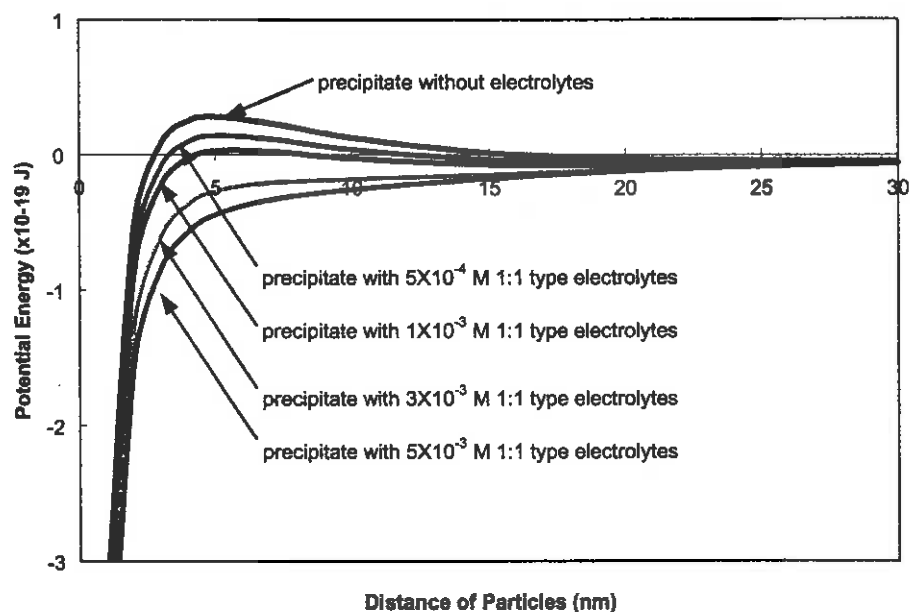


Fig. 4-1-36 The influence of added 1:1 type electrolytes on the total potential energy of interaction of two zinc hydroxide precipitate spherical particles ( $R_1 = R_2 = 5 \times 10^{-7} \text{ m}$ ,  $A = 2 \times 10^{-20} \text{ J}$ ,  $T = 298 \text{ K}$ ,  $\psi_1 = \psi_2 = -10 \text{ mV}$ )

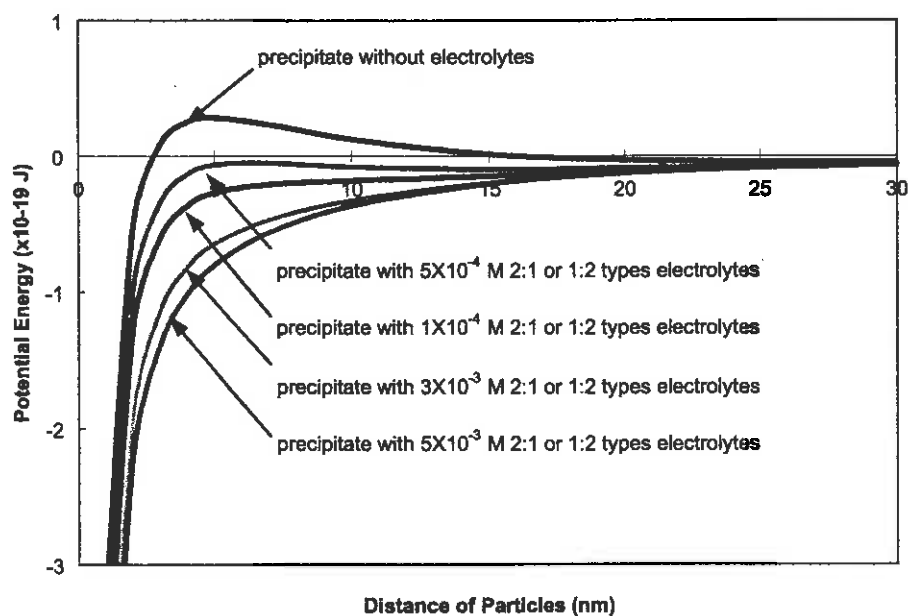
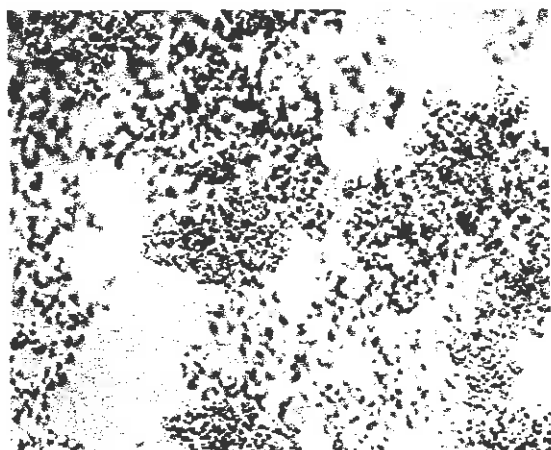


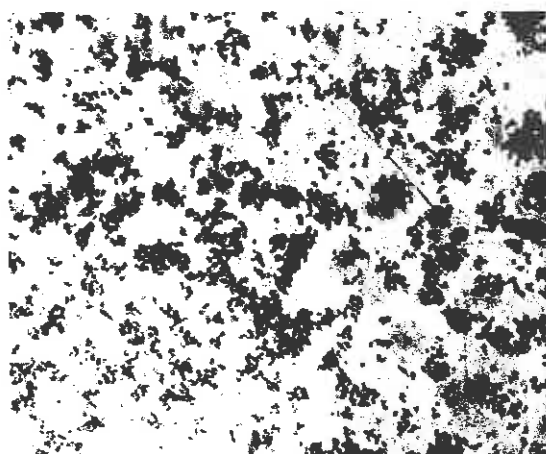
Fig. 4-1-37 The influence of added 2:1 or 1:2 type electrolytes on the total potential energy of interaction of two zinc hydroxide precipitate spherical particles ( $R_1 = R_2 = 5 \times 10^{-7} \text{ m}$ ,  $A = 2 \times 10^{-20} \text{ J}$ ,  $T = 298 \text{ K}$ ,  $\psi_1 = \psi_2 = -10 \text{ mV}$ )



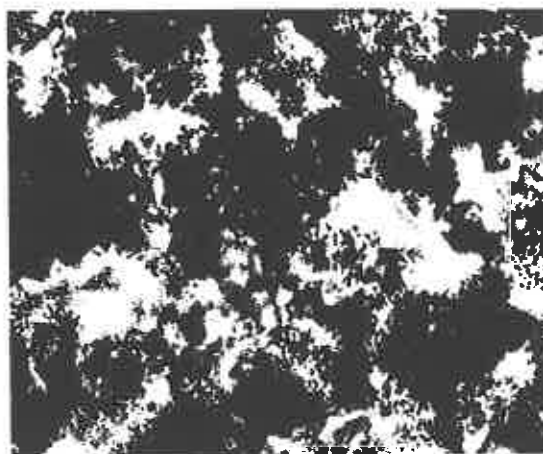
*Fig. 4-1-38A Zinc hydroxide precipitate in the absence of an added electrolyte*



*Fig. 4-1-38B Zinc hydroxide precipitate in the solution containing  $5 \times 10^{-4} \text{ M CaCl}_2$*



*Fig. 4-1-38C Copper hydroxide precipitate in absence of an added electrolyte*



*Fig. 4-1-38D Copper hydroxide precipitate in the solution containing  $5 \times 10^{-4} \text{ M CaCl}_2$*

*Fig. 4-1-38 Optical microphotographs of hydroxide precipitate in the solution*

The above discussions have demonstrated the mechanisms of influence of electrolytes on hydroxide precipitation and flotation. The following discusses in some detail the phenomena observed in the tests.

It can be seen from Fig. 4-1-20 and Fig. 4-1-21 that when the concentration of  $\text{CaCl}_2$  or  $\text{MgCl}_2$  increases, the recovery of zinc or copper increases rapidly. When more  $\text{CaCl}_2$  or  $\text{MgCl}_2$  is added, this process slightly decreases. It is suggested that when the concentration of calcium or magnesium ions in the solution is very high, the calcium or



magnesium ions can react with the ionic collector and produce a sublate, subsequently reducing the adsorption of the collector on the hydroxide precipitate surface and decreasing the flotation recovery.

The influence of  $\text{Na}_2\text{SO}_4$  on copper hydroxide precipitate sedimentation and flotation shown in Fig. 4-1-23 and Fig. 4-1-25 is somewhat unusual. When the concentration of  $\text{Na}_2\text{SO}_4$  increases, the copper hydroxide precipitate sedimentation percentage increases initially, then decreases rapidly. It is assumed that a small amount of sulphate ions can decrease the "thickness" of double layer and improve the precipitation and flotation. However, when the concentration of sulphate ions in the solution becomes high, sulphate ions can specifically adsorb on the copper precipitate surface, changing its zeta potential and subsequently increase the total potential energy of copper hydroxide precipitate particles. Unfortunately, as the precipitate is dispersed and the particle is too small, we are unable to measure its zeta potential value. Nevertheless, with an increase in sulphate ions, the "thickness" of double layer can still be reduced, which will improve the collector ion attachment to the hydroxide precipitate surface and increase the flotation recovery in comparison to the process without extraneous  $\text{Na}_2\text{SO}_4$ . Using the same concentration of  $\text{Na}_2\text{SO}_4$  (1:2 type of electrolyte), better zinc hydroxide precipitate flocculation and flotation recovery can be obtained than with  $\text{NaCl}$  or  $\text{KCl}$  (1:1 type of electrolytes) as shown in Fig. 4-1-22. The above calculation can provide an adequate explanation for Fig. 4-1-24.

#### *1.2.2.3 Discussion of the influence of ferric and aluminum ions on the hydroxide precipitation and flotation*

Although ferric and aluminum ions used as the main co-precipitants have been widely studied in coprecipitation and colloid adsorption flotation (see Chapter 2. Research Background), the mechanisms of coprecipitation or adsorption and the structure of the co-precipitate are still not very clear. The two possible mechanisms are considered as follows:

- Adsorption or post adsorption. In this hypothesis, the ferric or aluminum ion firstly form a hydroxide precipitate and then adsorb the heavy metal ions or

hydroxo species on to its surface. Although the ferric hydroxide precipitate is known to be positively charged in the pH range from approximately 2.5 to 9.0 (Lemlich, 1972), according to the DLVO theory however it is still possible to adsorb the positively charged heavy metal ions on to the surface.

- Co-precipitation. It is assumed that the ferric (or aluminum) ion combines the heavy metal ions in solution and forms a kind of ferric (or aluminum) heavy metal hydroxo complex (co-precipitate). The possible structure of the co-precipitate is  $(\text{Fe})_x(\text{Heavy Metal})_y(\text{OH})_z$ .

The processes of adsorption and co-precipitation are very difficult to distinguish. Scanning Electron Microscope has been used in this study to explore the co-precipitate structure. Fig. 4-1-39 shows the SEM microphotographs of ferric, copper and zinc hydroxide precipitate. Elemental analysis indicates that the iron, zinc and copper are even distributed. This probably means the precipitate is more likely formed by co-precipitation. However, as the precipitate particle is very amorphous and the particle size is very fine (see Fig. 4-1-39A and Fig. 4-1-39B) and it is impossible to identify individual precipitate particles under the Scanning Electron Microscope, the possibility of adsorption still remains.

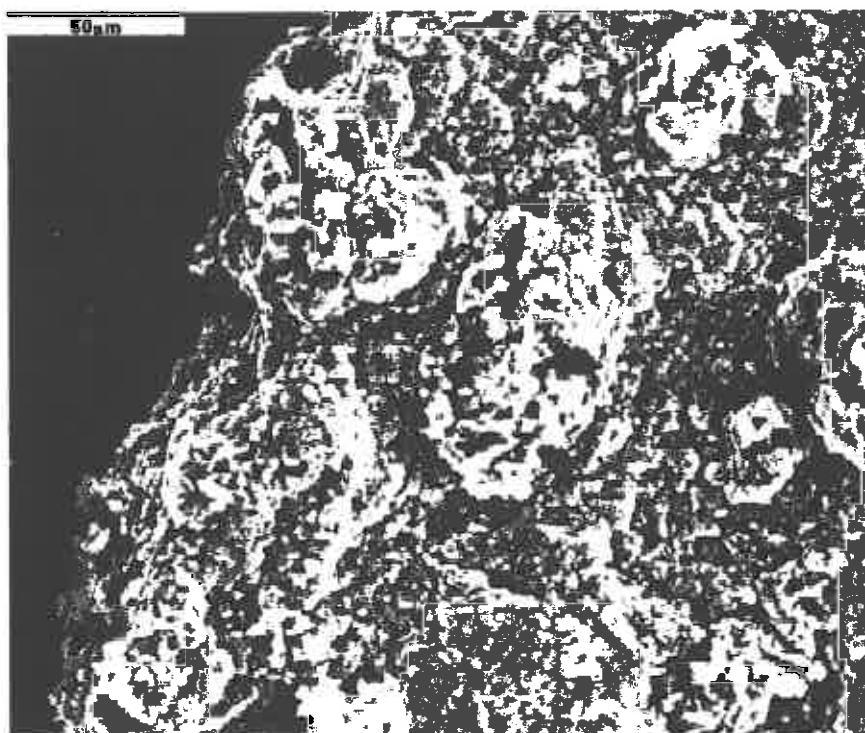


Fig. 4-1-39A

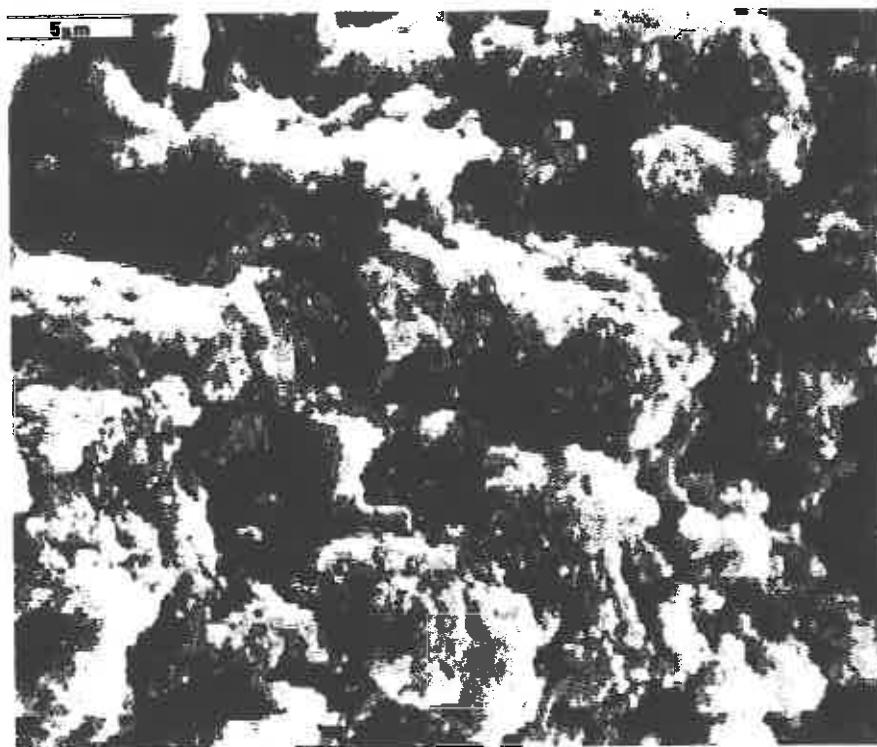


Fig. 4-1-39B

Fig. 4-1-39 SEM microphotographs of ferric, copper and zinc hydroxide precipitate.

X-ray Diffraction has also been used to explore the co-precipitate structure. Unfortunately, as the precipitate is very amorphous, not enough information from X-ray Diffraction could be obtained to form a clear identification of the co-precipitate structure. To arrive at a better understanding of the mechanisms of the influence of ferric and aluminum ions on the hydroxide precipitation and flotation, better methods and instrumental tests need to be developed in future studies.

### 1.2.3 Brief Summary

Extraneous electrolytes can improve the zinc and copper hydroxide precipitate flocculation and flotation. Using the same concentration of  $\text{CaCl}_2$ ,  $\text{MgCl}_2$  (2:1 type of electrolytes) or  $\text{Na}_2\text{SO}_4$  (1:2 type of electrolyte) better hydroxide precipitate flocculation and flotation recovery can be obtained than when  $\text{NaCl}$  or  $\text{KCl}$  (1:1 type of electrolytes) are used. However, high concentrations of  $\text{CaCl}_2$  or  $\text{MgCl}_2$  will decrease the flotation

recovery due to the fact that the calcium or magnesium will consume the flotation collector.

The mechanisms of the influence of extraneous electrolytes on the hydroxide flocculation and flotation recovery can be adequately explained by using the classic DLVO theory calculation. The calculation results show that the "thickness" of the double layer and the total energy peak between two hydroxide precipitate particles drop significantly when the concentration of extraneous electrolytes is increased. The 2:1 and 1:2 types of electrolytes are much more efficient in reducing the "thickness" of double layer and the total energy peak than the 1:1 types of electrolytes.

With the presence of ferric or aluminum ions in solution, the differences in copper and zinc precipitation and flotation recovery become less and less. It is impossible to separate copper and zinc efficiently when specific amounts of ferric or aluminum ions are present in a solution using hydroxide precipitation and flotation. The mechanisms involved are not very clear.

### 1.3 Section Conclusion

- Anionic collectors, such as SDBS and SDS, are efficient collectors for both zinc and copper hydroxide precipitate flotation. The results of the precipitation and flotation of zinc and copper as a function of pH can be demonstrated by the calculation of the hydrolysis reactions. The pH value of the flotation decreasing point corresponds to the pH point at which the negatively charged heavy metal complexes become the majority.
- A reasonable hydroxide precipitate flotation separation of copper and zinc ion from solution can be obtained at a pH of 6.1 in pure water. However, when ferric or aluminum ions are present in the solution, the differences in copper and zinc precipitation and flotation recovery become less and less. Using hydroxide precipitation and flotation, it is impossible to separate copper and zinc efficiently when specific amounts of ferric or aluminum ions are present in the solution.
- The zinc and copper hydroxide precipitate flocculation and flotation can be improved with extraneous electrolytes. Using the same concentration of 2:1 type or 1:2 type of electrolytes, better hydroxide precipitate flocculation and flotation recovery can be obtained than when 1:1 type electrolytes are used. High concentrations of  $\text{CaCl}_2$  or  $\text{MgCl}_2$  will decrease the flotation recovery due to the fact that the calcium or magnesium will consume the flotation collector.
- The mechanisms of this influence of extraneous electrolytes on the hydroxide flocculation and flotation recovery can be adequately explained by using the classic DLVO theory calculation. The calculation results show that the "thickness" of the double layer and the total energy peak between two hydroxide precipitate particles drop significantly with an increased concentration of extraneous electrolytes. The 2:1 and 1:2 types of electrolytes are much more efficient in reducing the "thickness" of the double layer and the total energy peak than the 1:1 types of electrolytes.

## Section 2 "Self-Carrier" Precipitate Flotation<sup>\*</sup>

The precipitate particle sizes of heavy metal hydroxide are normally very fine (in the range 0.01-0.5 micron). This requires large quantities of collectors and causes several problems in flotation separation.

In order to overcome these problems, a new process, named "self-carrier" precipitate flotation (SCPF) using anionic surfactants, has been developed to improve the flotation recovery and reduce the consumption of collector. This work describes the SCPF methods for the removal of zinc ions from pure water. The mechanism of the SCPF process is also proposed.

### 2.1 Introduction

The so-called activated-sludge process in which a portion of the settled product is recycled to the reactor has been used extensively in biological treatment of wastewater (Tchobanoglous, 1983). This process can significantly improve floc formation and increase the kinetics of sedimentation.

Hydroxide precipitation of heavy metals followed by settling of the precipitates is most often used to treat industrial wastewater (Peters, Ku and Bhattacharyya, 1985; Patterson and Minear, 1975). A hydroxide precipitation process, which returns part of the precipitate slurry to the precipitate reaction cell, has been briefly introduced (Wang and Jiang, 1993) and it is claimed that good results have been obtained in copper and zinc industrial wastewater treatment in Japan.

Carrier flotation has been considered as one efficient way for recovering fine minerals in mineral processing (Subrahmanyam and Eric Forssberg, 1990). It has been noticed that autogenous or ramification carrier flotation (Hu, Wang and Jin, 1982; Hu, Wang and Qu,

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<sup>\*</sup> The main part of this section has been published at: Ren, X., Brady, K.T., Jay, W.H., & Schrieke, R.R. (1997). A study of "self-carrier" precipitate flotation for the removal of heavy metal ions from solution. In: H. Hoberg, & H. Blottnitz (Eds.), Proceedings of the XX IMPC (Volume 4) (pp. 693-704). Aachen.

1987), which used the same pre-conditioned coarse mineral particles instead of externally added minerals as a carrier, has achieved a higher recovery and better separation efficiency with the reagent consumption markedly reduced. The optimum size of carrier using this process is 25 to 36 microns (Hu, Wang and Qu, 1988). This size range however is not applicable for the precipitate flotation process.

Precipitate flotation has been extensively studied (see Chapter 2 "Research Background"). However, very few papers have been devoted to the actual precipitation process. In this section, the self-carrier precipitate flotation process has been developed to improve the precipitate flotation process and the mechanism occurring in this process has been clarified. Zinc ion was used as an example of heavy metal ions in this section.

## 2.2 Results and Discussion

### 2.2.1 Concept of Self-Carrier Precipitate Flotation

Self-Carrier Precipitate Flotation (SCPF) is a new process in precipitate flotation for the removal of heavy metal ion from a solution. In this process, the floated foam (heavy metal precipitate) is treated and returned to the flotation column and used as a self-carrier for adsorbing the heavy metal ions from the fresh solution prior to re-flotation.

The principle of Self-Carrier Precipitate Flotation is shown in Fig. 4-2-1:

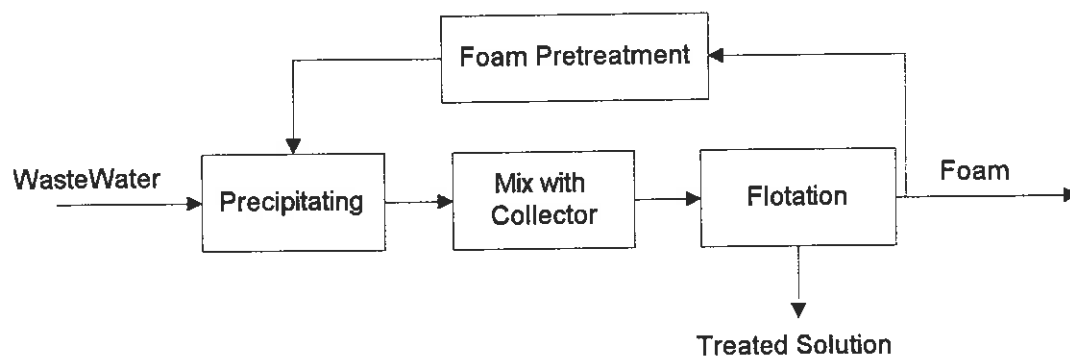
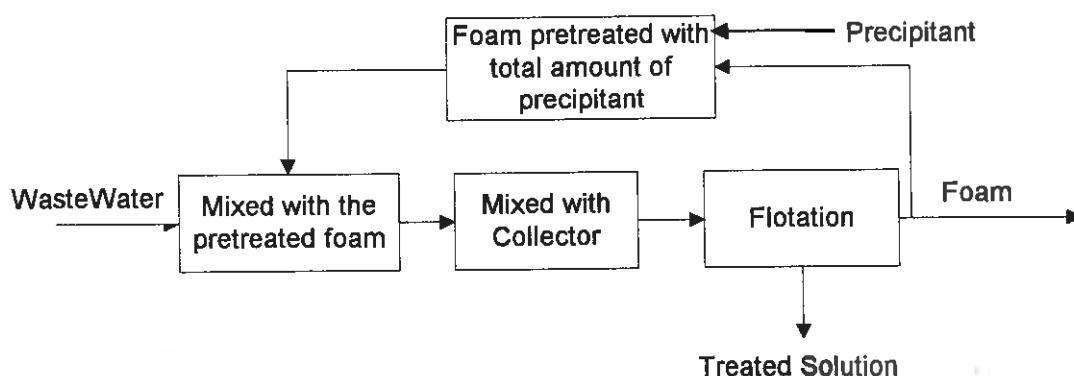
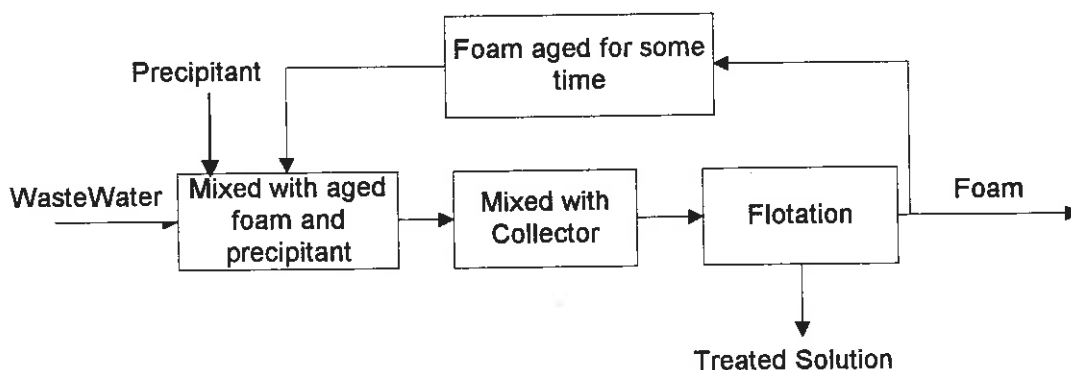


Fig. 4-2-1 The fundamental flowsheet of the Self-Carrier precipitate flotation process

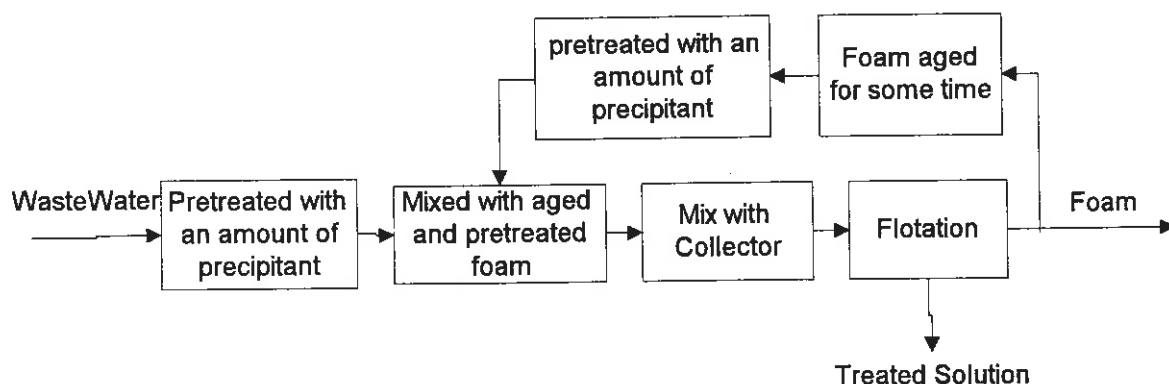
Based on the fundamental flowsheet, taking into account the hydroxide precipitate surface charge and the precipitate crystal size, three types of flowsheet are presented below (Fig. 4-2-2).



(a) The foam pretreated with the total amount of the precipitant without aging



(b) The aged foam without precipitant pretreatment



(c) The aged foam and pretreated precipitant mixed with precipitant pretreated wastewater.

Fig. 4-2-2 The extended flowsheets of the Self-Carrier precipitate flotation process.



Fig. 4-2-2a shows that the floated foam pretreated with precipitant (here sodium hydroxide) mixes with the wastewater. The collector adsorbing on the surface of the heavy metal precipitate of the foam mixed with the solution and can then be re-used. The pretreated precipitate becomes highly negatively charged at high pH. The positively charged heavy metal ions in the waste solution can easily be adsorbed, precipitating on the surfaces of the pretreated precipitates (the self-carrier), hence flotation recovery can be increased. However, the disadvantage of this situation is that the self-carrier itself is too fine for flotation.

Fig. 4-2-2b shows the floated foam, aged for a specific period of time to allow the precipitates to grow larger, then mixed with the waste solution and the precipitant. As the size of the self-carrier precipitate increases, the fresh precipitate rather than heavy metal ions is easily adsorbed or precipitated on the surface of the self-carrier, improving the flotation recovery.

Fig. 4-2-2c shows that the floated foam was aged for a specific period of time to allow the precipitates to grow larger, then pretreated with a part amount of precipitant and subsequently mixed with the waste solution which had itself been pretreated with another portion of precipitant. This process therefore combines the advantages of Fig. 4-2-2a and Fig. 4-2-2b. The self-carrier size increases; the pretreated precipitant is able to release the collector ions adsorbing on the surface of the self-carrier, causing it to become highly negatively charged. The "fresh" precipitate in the waste solution, which is normally positively charged due to insufficient precipitant, is pretreated with another portion of precipitant. When the pretreated self-carrier and the pretreated waste solution mix, the negatively charged large self-carrier particle will strongly adsorb the positively charged "fresh" precipitate and hence increase flotation recovery.

All three forms of the self-carrier precipitate flotation process have been investigated in the following tests and are the subject of more detailed discussion.

### 2.2.2 Flotation Behavior

The effect of pH on the flotation recoveries of zinc from three solutions of different initial zinc ion concentration is shown in Fig. 4-2-3. A smaller amount of anionic collector SDBS (compared with Fig. 4-1-3) was used in the flotation described in Fig. 4-2-3.

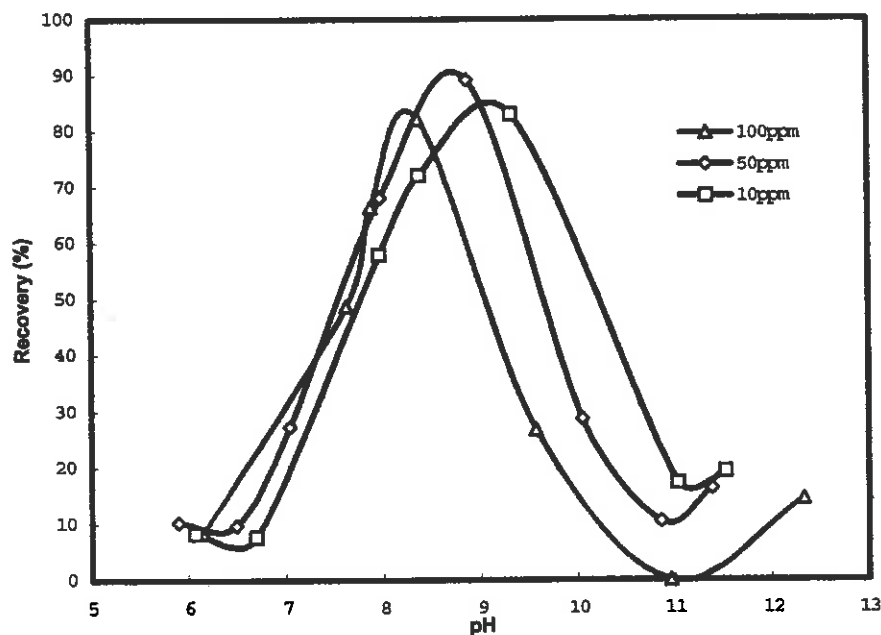


Fig. 4-2-3 The effect of pH on the flotation recoveries of zinc from three solutions of different initial zinc ion concentration using SDBS as collector at  $3 \times 10^{-5}$  M.

Fig. 4-2-3 shows that maximum removal of zinc can be obtained in the pH range 8.5-9.5. Thus, with reference to Fig. 4-1-14, it can be seen that the highest recovery can be obtained in the pH range at which the solubility of zinc hydroxide is the lowest. The initial concentration of zinc ion in the solution is not influencing the recovery significantly, at these levels.

However, when the pH is above 9.5, for example pH=10, the recovery decreases although the solubility of zinc hydroxide is still very low at this pH (see Fig. 4-1-14). Let us review the reason for this. When the pH>9.5, the concentration of the negatively charged complexes ( $\text{Zn}(\text{OH})_3^-$ ,  $\text{Zn}(\text{OH})_4^{2-}$ ) becomes more significant (see Fig. 4-1-12.), the zeta potential of the precipitate becomes more negative (See Fig. 4-2-5) which will impede the negatively charged anionic collector ions (SDBS) from adsorbing onto the surface of the

precipitate. This explanation was also suggested by Rubin (1972), Basak and Charewicz (1986) and Jurkiewicz (1990).

### 2.2.3 Self-Carrier Precipitate Flotation Results

Based on the extended flowsheets of Self-Carrier Precipitate Flotation (Fig. 4-2-2), four detailed flowsheets have been developed (see Fig. 4-2-4).

Fig. 4-2-4A, a detailed flowsheet of Fig. 4-2-2a, shows that the foam from the first stage precipitate flotation was treated with sodium hydroxide after which it was immediately added to the second flotation stage. Fig. 4-2-4B (refer to Fig. 4-2-2b) shows that the first stage foam had been aged (without stirring) for 24 hours and was then added to the second flotation stage without any sodium hydroxide pre-treatment. Fig. 4-2-4C (refer to Fig. 4-2-2c) shows that the first stage foam had been aged for 24 hours and after being treated with half the amount of sodium hydroxide was added to the second flotation stage which had been pre-treated with another half amount of sodium hydroxide.

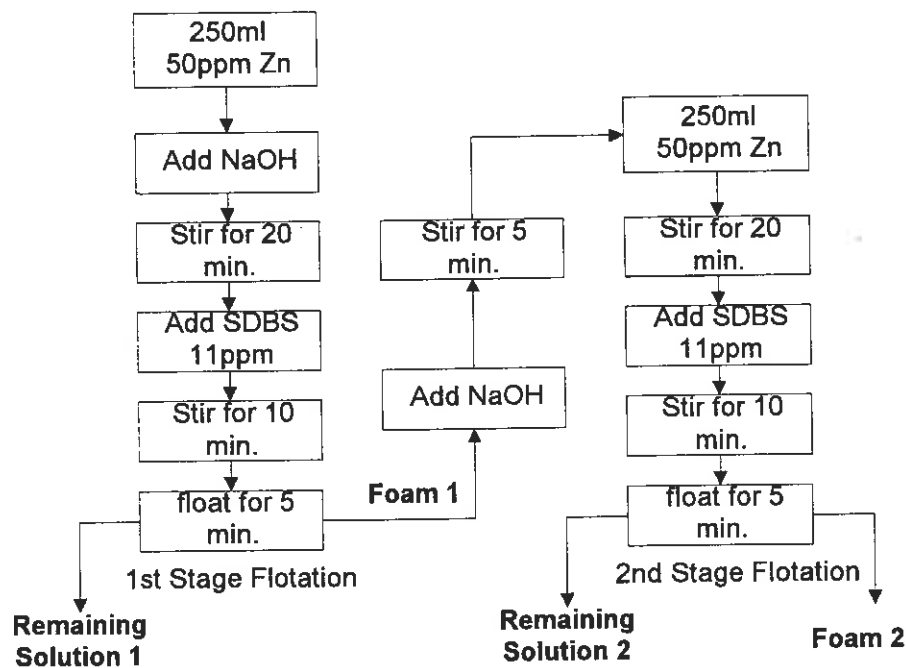


Fig. 4-2-4A

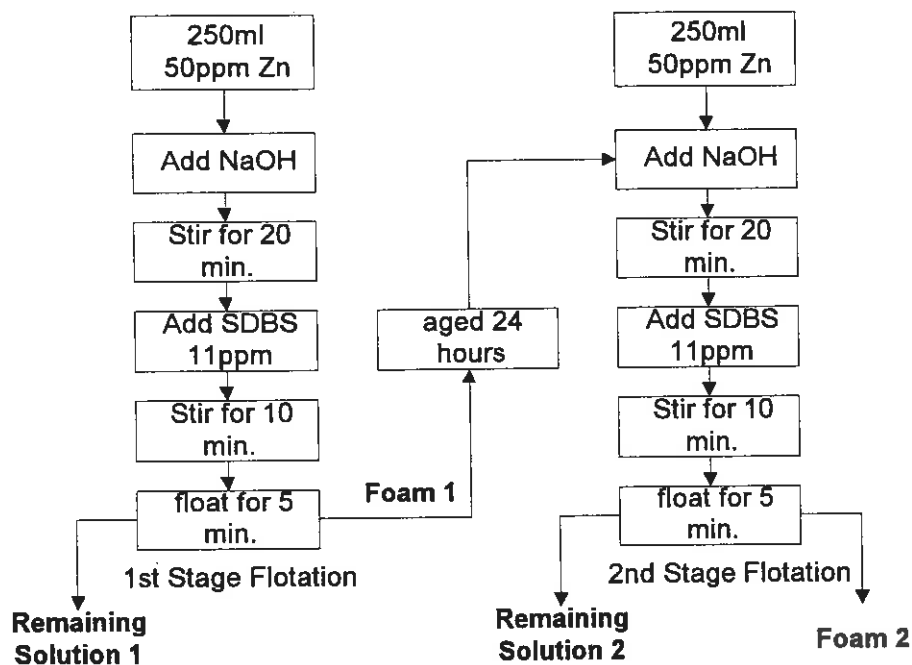


Fig. 4-2-4B

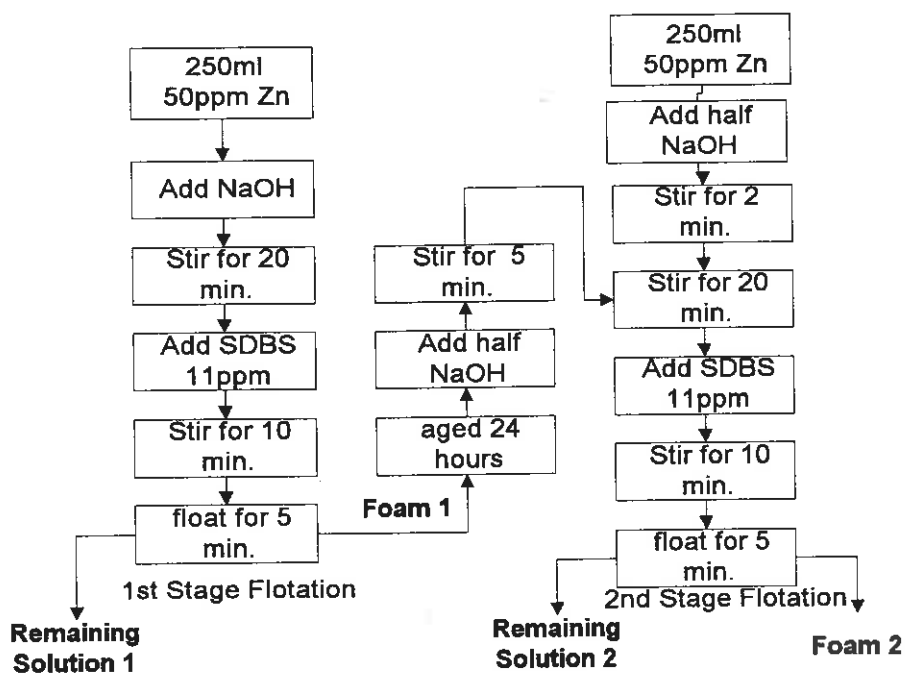


Fig. 4-2-4C

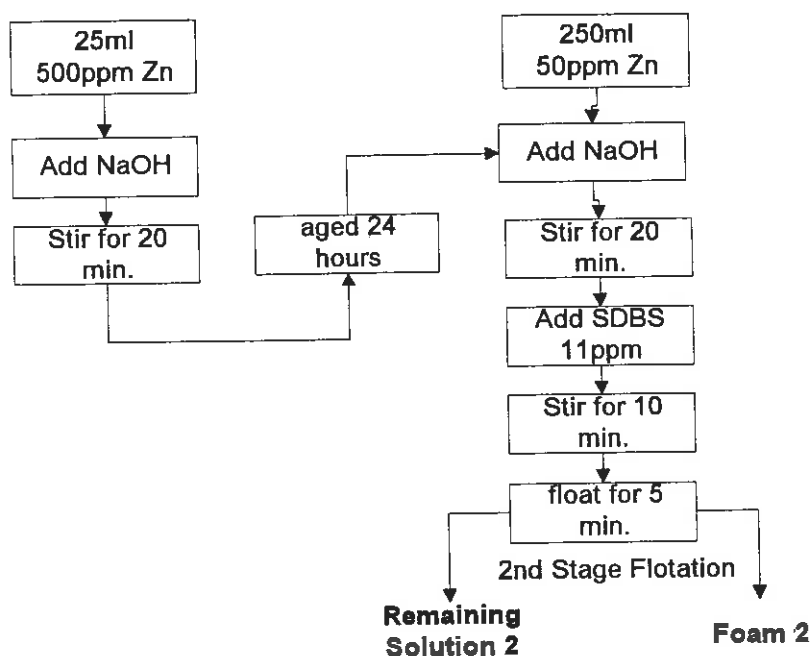


Fig. 4-2-4D

Fig. 4-2-4 Self-Carrier Precipitate Flotation Flowsheets

However, in order to simplify the laboratory tests, Fig. 4-2-4D was developed to simulate Fig. 4-2-4C. The flowsheet shows that a high initial zinc concentration was used to make the  $\text{Zn}(\text{OH})_2$  precipitate followed by 24 hrs of aging prior to its addition into the flotation process. In all these situations, the flotation pH was controlled at  $8.8 \pm 0.2$ .

The self-carrier precipitate flotation (SCPF) results for the above processes are shown in Table 4-1.

From Table 4-2-1 it can be seen that all four SCPF processes obtained much better recoveries than was the case in the conventional precipitate flotation. Using the SCPF process presented in Fig. 4-2-4A, the recovery of zinc can increase from 91.49% for the conventional precipitate flotation to 95.40%, and the remaining zinc concentration in solution decreases from 4.26ppm to 2.30ppm. From the SCPF process presented in Fig. 4-2-4B, a better recovery (96.34%) and lower remaining concentration of zinc in solution (1.83ppm) can be obtained. However, when the four processes are compared it is clear that, the best results can be obtained from the process presented in Fig. 4-2-4C, that of the aged pretreated self-carrier mixed with the pretreated waste solution. The recovery of zinc can reach up to 97.44 % and the concentration of zinc remaining in the solution decreases

to 1.28ppm. The results presented in Table 4-2-1 from the process of Fig. 4-2-4D are similar to those from process of Fig. 4-2-4C. The average recovery is 97.21% and the average concentration of zinc remaining in the solution is 1.39ppm.

*Table 4-2-1 Self-carrier precipitate flotation results (2nd Stage Flotation) compared with the conventional precipitate flotation results (1st Stage Flotation). SDBS  $3 \times 10^{-5}$  M.*

Flowsheet	Tests	Zn Conc. of Remaining Solution1(ppm)	Zn Conc. of Remaining Solution2(ppm)	Recovery (%) (1st Stage Flotation )	Recovery (%) (2nd Stage Flotation)
Fig. 4A	1	5.01	2.30	89.97	95.40
Fig. 4A	2	3.50	2.30	93.00	95.41
<b>Average</b>		4.26	2.30	91.49	95.40
Fig. 4B	1	5.69	1.74	88.62	96.52
Fig. 4B	2	3.02	1.45	93.97	97.10
Fig. 4B	3	2.60	1.61	94.79	96.77
Fig. 4B	4	5.11	2.53	89.78	94.95
<b>Average</b>		4.11	1.83	91.79	96.34
Fig. 4C	1	4.60	1.53	90.80	96.95
Fig. 4C	2	4.05	1.17	91.90	97.67
Fig. 4C	3	3.66	1.43	92.69	97.15
Fig. 4C	4	3.68	1.01	92.63	97.97
<b>Average</b>		4.00	1.28	92.00	97.44
Fig. 4D	1		1.35		97.28
Fig. 4D	2		1.43		97.14
<b>Average</b>			1.39		97.21

Fig. 4-2-5 shows the difference in zeta potential between the "fresh" (stirring 20 minutes) and aged (24 hours) zinc hydroxide precipitate. Compared with the "fresh" precipitate, the zeta potential of aged zinc hydroxide precipitate seems less positive or negative respectively in the pH range 7.5 to 11 than the "fresh" precipitate. For "fresh" precipitate, when  $\text{pH} < 8.7$ , it is positively charged and when  $\text{pH} > 8.7$ , it becomes negatively charged.

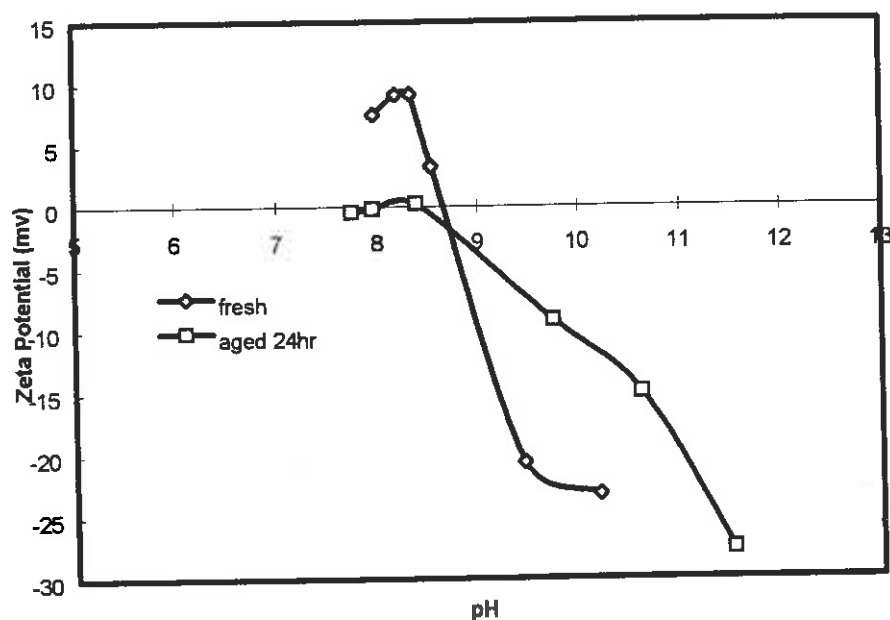


Fig. 4-2-5 Zeta potential of the "fresh" (stirring 20 minutes) and aged (24 hours) zinc hydroxide precipitate

Flowsheet Fig. 4-2-4C illustrates that, when the self-carrier precipitate (aged 24 hours) was treated using half the amount of sodium hydroxide, the pH was raised to 11.5 and the zeta potential of the precipitate was about -27mV. At the same time, the bulk solution was treated using the other half of the sodium hydroxide, before the self-carrier precipitate was added. The pH of the solution was  $8 \pm 0.2$  and the zeta potential of the "fresh" zinc precipitate was about +8mV. When the carrier precipitate was added, the negatively charged carrier strongly adsorbed the positively charged "fresh" zinc precipitate and a better flotation recovery was achieved.

No evidence has been found that the reagent (collector) carried over from the concentrate foam (self-carrier) has improved the zinc recovery (see the results of Fig. 4-2-4B and Fig. 4-2-4D). This is probably because the influence of additional collector at an SDBS:Zn ratio above 0.04 is very small. (see Fig. 4-2-6).

Since the results shown in flowsheet Fig. 4-2-4D are similar to those in Fig. 4-2-4C, flowsheet Fig. 4-2-4D was drawn up to develop SCPF data for Fig. 4-2-6, Fig. 4-2-7 and

Fig. 4-2-8, as the conditions in that process are more easily controlled in the laboratory than those in Fig. 4-2-4C.

Fig. 4-2-6 illustrates the effect of concentration of SDBS on the zinc recovery in the case of the conventional precipitate flotation and in the case of SCPF. The effect of pH on the zinc recovery in both cases is shown in Fig. 4-2-7. Compared with the conventional precipitate flotation, the SCPF process has a much wider adaptability to the change of pH and collector concentration, over which a high recovery is obtained and a lower collector concentration can be used. When the SDBS:Zn mole ratio is 0.02 and 0.03, for the conventional precipitate flotation the precipitate is difficult to float, but when the SCPF process is applied reasonable recoveries can be obtained (Fig. 4-2-6).

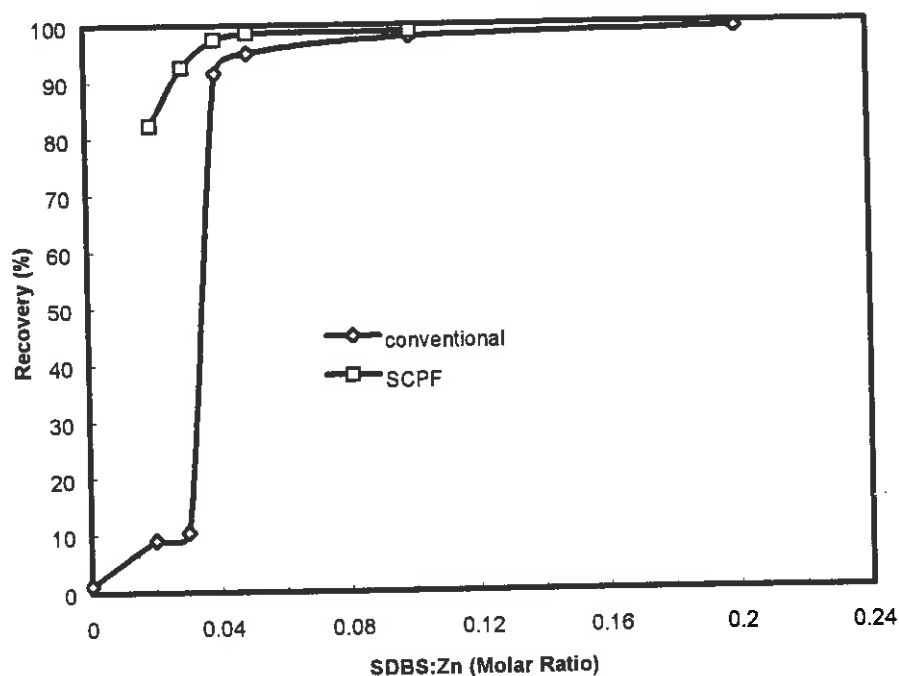


Fig. 4-2-6 Effect of concentration of SDBS on the zinc recovery in the case of the conventional precipitate flotation and in the case of SCPF.



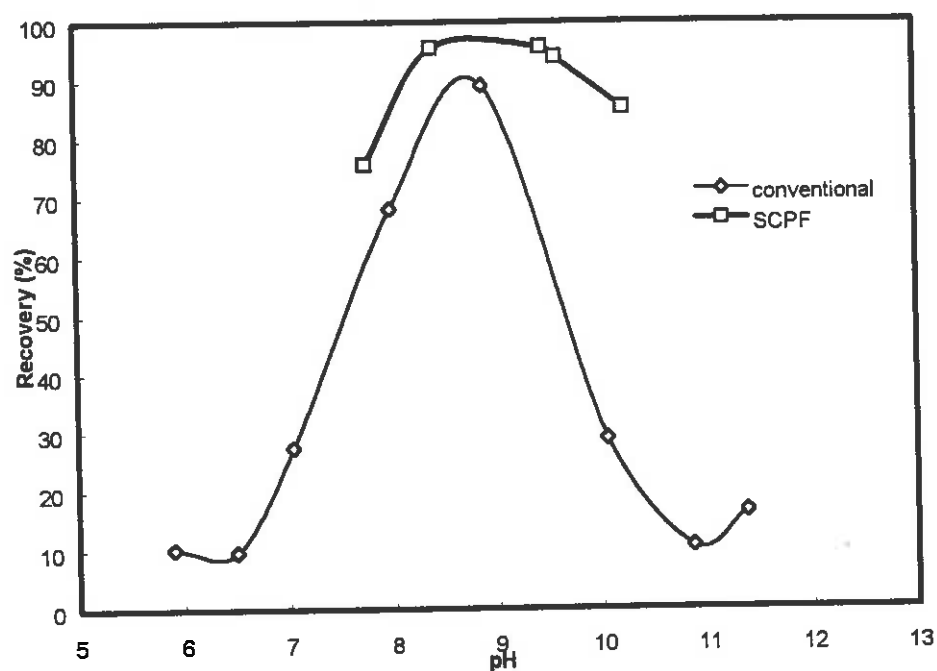


Fig. 4-2-7 Effect of pH on the zinc recovery in the case of the conventional precipitate flotation and in the case of SCPF (SDBS  $3 \times 10^{-5}$  M).

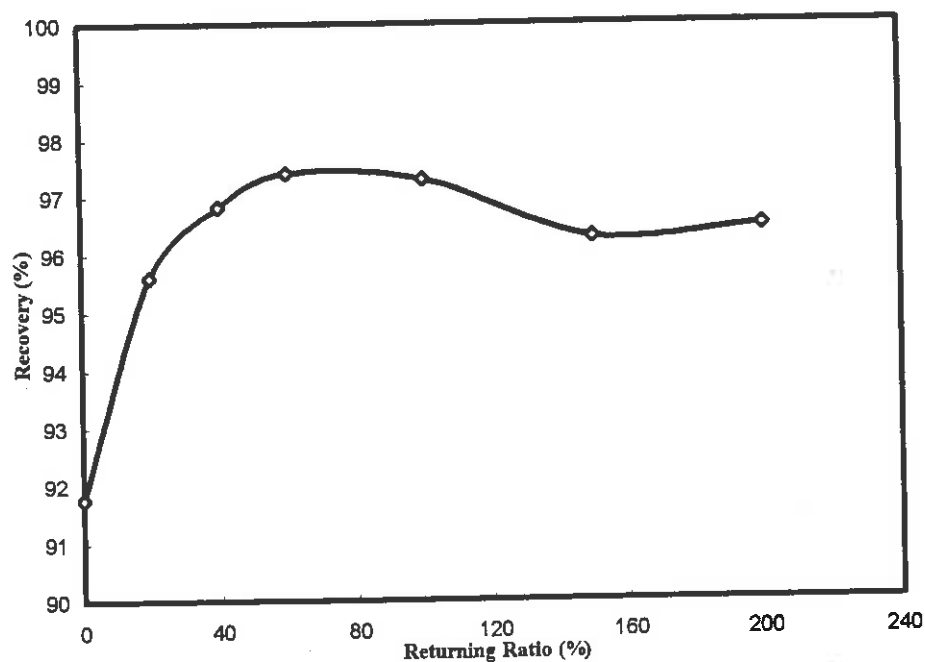


Fig. 4-2-8 The effect of the self-carrier returning ratio of SCPF on the zinc recovery (SDBS  $3 \times 10^{-5}$  M).

The effect of the self-carrier returning ratio on the zinc recovery using the process presented in the Fig. 4-2-4D has been tested and the results are shown in Fig. 4-2-8.

The returning ratio is defined as the amount of zinc contained in the aged solution (25 ml, 500ppm, as in Fig. 4-2-4D) compared with the amount of zinc in the flotation feed stream (250ml, 50ppm, as in Fig. 4-2-4D). This particular combination of concentrations and volumes gives a returning ratio of 100%. Fig. 4-2-8 shows that good results can be obtained even when the returning ratio of the self-carrier to the target ion in the solution varies from 20-200%.

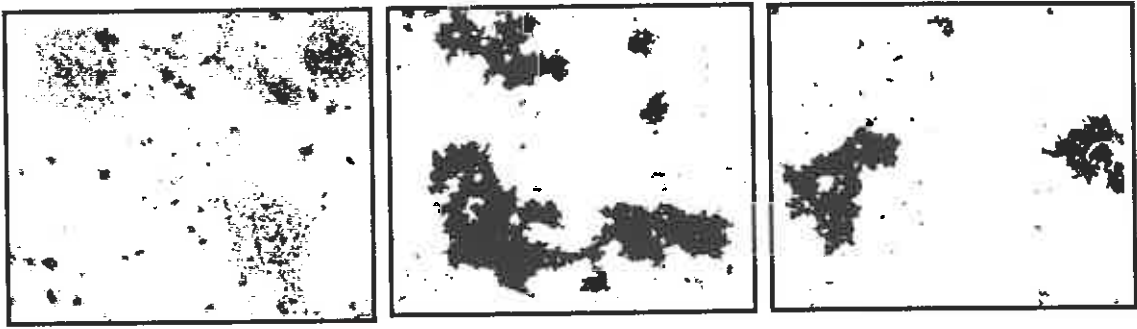
The SCPF process is tolerant to a wide range of flotation conditions (see Fig. 4-2-6, Fig. 4-2-7 and Fig. 4-2-8). This process is therefore likely to be more readily accepted and more widely used in the future.

#### 2.2.4 Microphotographs and Discussion

In order to understand how the SCPF process works, Optical Microscopy and Scanning Electron Microscopy were used to investigate the precipitate changes during the process.

Fig. 4-2-9 shows the optical microphotographs of precipitate in various conditions. It can be seen that the "fresh" zinc hydroxide precipitate is very fine and only slightly agglomerated. (Fig. 4-2-9A). When the self-carrier precipitate (aged 24 hours) was added, the precipitate agglomerated and became larger aggregates (Fig. 4-2-9B). This is very similar to the appearance of "fresh" precipitate with some collector (SDBS) added (Fig. 4-2-9C).

The fine structures of precipitates and aggregates were revealed by Scanning Electron Microscopy, as shown in Fig. 4-2-10, Fig. 4-2-11, Fig. 4-2-12 and Fig. 4-2-13.



*Fig. 4-2-9A "Fresh"  
precipitate (20 minutes  
stirring)*

*Fig. 4-2-9B "Fresh"  
precipitate plus 24 hours  
aged self-carrier, without  
collector*

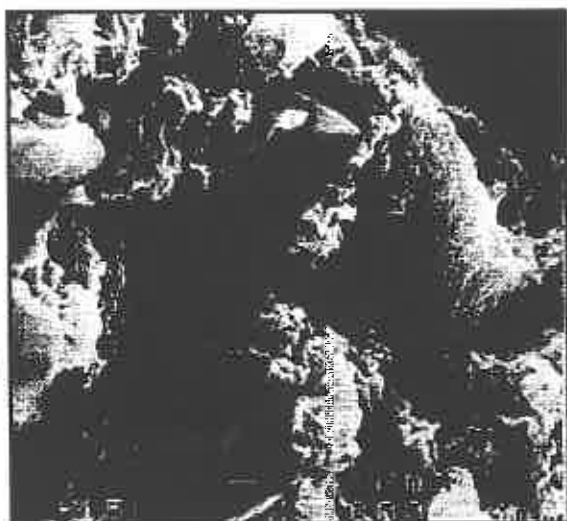
*Fig. 4-2-9C "Fresh"  
precipitate with 11mg/l  
collector without self-  
carrier*

*Fig. 4-2-9 Optical microphotographs of precipitate in various conditions ( $pH=8.8\pm0.2$ )*

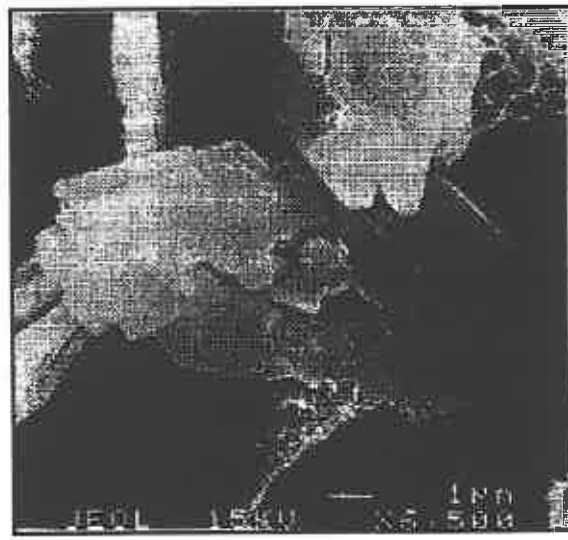
Fig. 4-2-10A illustrates that the "fresh" precipitate is amorphous with a particle size around 0.05-0.2 micron. Fig. 4-2-10B shows that even enlarged to 20,000 times, the size and structure of "fresh" zinc hydroxide precipitate are still unclear. However, after 24 hours aging, most of the precipitate (self-carrier) grows and becomes plate like crystals with a size of around 5-10 microns, although a small amount of amorphous precipitate still can still be found (Fig. 4-2-11A). Fig. 4-2-11B illustrates the microstructure of plate like precipitate. It can clearly be seen that there are some steps onto the crystals' surface, on which the zinc ion in the solution can easily precipitate.

When the 24 hour aged self-carrier precipitate was put into the "fresh" precipitate, the plate-shape crystals became larger and thicker and it also adsorbed (combined) a lot of small amorphous precipitates (Fig. 4-2-12A, B). This increased the precipitate size and decreased the total precipitate surface area and subsequently reduced the consumption of collector.

When the small amorphous precipitates were combined with the aid of the collector, very few large plate-shaped crystals were found (see Fig. 4-2-13A, B). This means that part of the function of the collector in this system is to combine the fine precipitate.

*Fig. 4-2-10A**Fig. 4-2-10B*

*Fig. 4-2-10 SEM microphotographs of "Fresh" zinc precipitate ( $pH=8.8\pm0.2$ )*

*Fig. 4-2-11A**Fig. 4-2-11B*

*Fig. 4-2-11 SEM microphotographs of 24 hours aged self-carrier ( $pH=8.8\pm0.2$ )*



Fig. 4-2-12A



Fig. 4-2-12B

Fig. 4-2-12 SEM microphotographs of "Fresh" precipitate plus 24 hours aged self-carrier, without collector ( $\text{pH}=8.8\pm0.2$ )



Fig. 4-2-13A

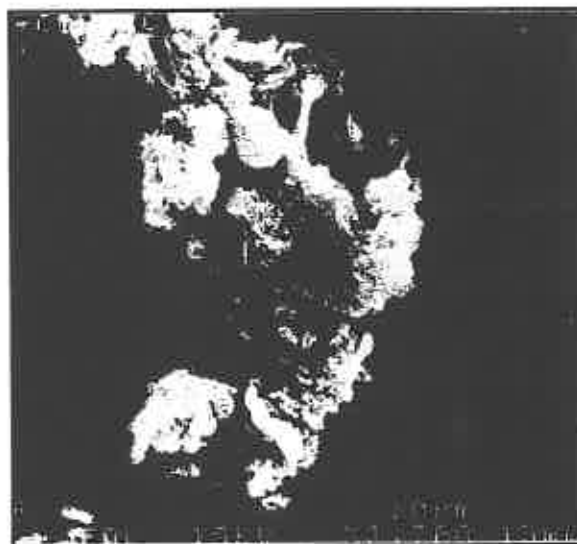


Fig. 4-2-13B

Fig. 4-2-13 SEM microphotographs of "Fresh" precipitate with  $3\times10^{-5}\text{M}$  collector without self-carrier ( $\text{pH}=8.8\pm0.2$ )

The classical DLVO theory was used to calculate the total energy between two "fresh" zinc hydroxide precipitate particles and between the "fresh" zinc hydroxide precipitate particle and the aged pretreated self-carrier particle. The calculation methods can be seen in Section 4.1.2.2 and Appendix 2. The calculation results are shown in Fig. 4-2-14.

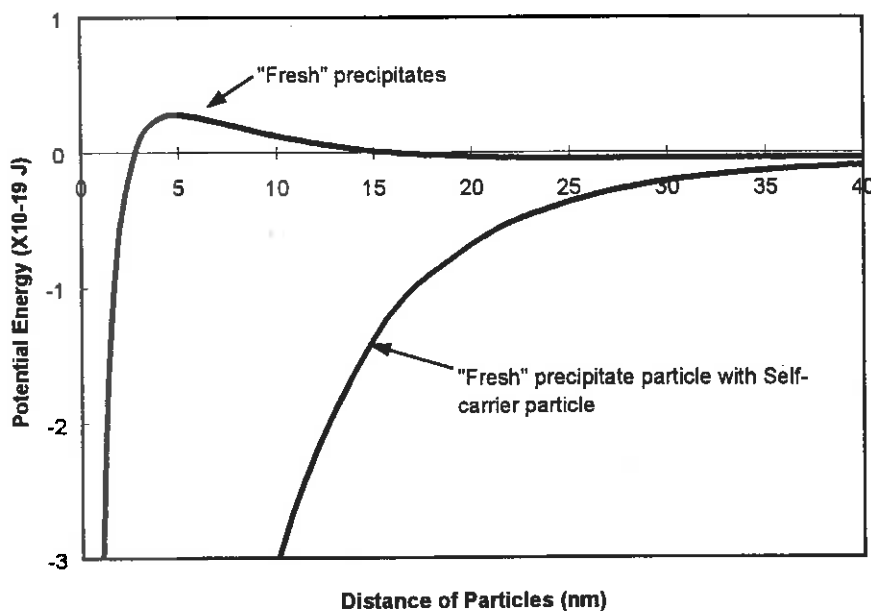


Fig. 4-2-14 The total potential energy of interaction of two "fresh" zinc hydroxide precipitate spherical particles and the "fresh" zinc hydroxide precipitate particle with the aged pretreated self-carrier particle ( $A=2 \times 10^{-20}$  J,  $T=298K$ , For the "fresh" zinc hydroxide precipitate particle:  $\psi = +8mV$ ,  $R=5 \times 10^{-7}m$ ; For the aged pretreated self-carrier particle:  $\psi = -27mV$ ,  $R=1 \times 10^{-4}m$ )

The total potential energy of interaction of two "fresh" zinc hydroxide precipitate spherical particles has a small positive energy peak (see Fig. 4-2-14). However, the total potential energy between the "fresh" zinc hydroxide precipitate particle and the aged pretreated self-carrier particle is highly negative. This indicates that when the self-carrier is added, it strongly attracts the "fresh" zinc hydroxide precipitate particles and generates a large aggregate, thus increasing the flotation recovery.

In summary, it is proposed that the mechanism for SCPF involves the formation of a second stage of hydroxide precipitate on the surface of the self-carrier, thus acting like a

seed crystal. Secondly the carrier adsorbs the "fresh" precipitate that already exists in the solution and produces larger aggregates. This partly replaces the function of the collector and hence improves the flotation recovery.

### 2.3 Section Conclusions

- The self-carrier precipitate flotation (SCPF) process is a new process for the removal of heavy metal ion from a solution. The laboratory tests have shown that this process can improve the zinc hydroxide precipitate flotation results.
- The SCPF process is less sensitive to changes in flotation conditions (pH and collector concentration) than conventional precipitate flotation.
- The SCPF mechanism is considered to be that the carrier precipitate behaves as a seed crystal to aid aggregation and to combine the fine precipitate particles.
- Classical DLVO calculations show that, at the instance of mixing these solutions, a strong attractive force exists between the "fresh" zinc hydroxide precipitate particles and the aged "self-carrier" zinc hydroxide particles.

## Section 3 Copper And Zinc Sulphide Precipitate Flotation Using Xanthate as Collector

Thiol collectors such as O-alkyl dithiocarbonates (usually termed xanthates) are the most commonly used class of sulphide mineral collectors (Aplan and Chander, 1987; Harris, 1987). They are known to exhibit a high level of chemical reactivity towards heavy metals, either in solution or at a sulphide mineral surface. It has been established that the consumption of xanthate in sulphide mineral flotation is millions of tonnes annually.

Xanthates have been used for copper ion removal by the so-called IPU (ion-precipitate-ultrafine) process (Nagahama, 1974) or ion flotation (Stalidis, Matis and Lazaridis, 1989). The results of sulphide precipitate flotation of copper and zinc from dilute aqueous solutions, using cationic collectors, have also been reported (Stalidis, Lazaridis and Matis, 1989).

This study investigates copper sulphide precipitate flotation behavior using xanthate as collector. It explores the influence of stirring time and oxidation on the copper sulphide precipitate flotation. It establishes the influence of the presence of extraneous ions on the flotation and postulates the mechanisms occurring in the process. Zinc sulphide precipitate flotation behavior is also investigated. Purified sodium O-ethyl-dithiocarbonate (denoted hereafter as xanthate, NaEtX, or EtX<sup>-</sup>) has been used as a flotation collector in all the flotation tests.

### 3.1 Copper sulphide precipitate flotation behavior

#### 3.1.1 Results

##### *3.1.1.1 Copper ion flotation using xanthate as collector*

It is well known that copper ion in solution can react with xanthate ion and form a copper xanthate compound, which will precipitate out of the solution as a sublate:





Eq. (3.1) shows that twice the molar concentration of xanthate to that of copper is required in the solution to form a stoichiometric reaction of ion flotation.

In this work, the effect of increasing concentration of sodium ethyl xanthate on the ion flotation recovery of copper was examined (detailed operation see Chapter III, page 45) and the results are shown in Fig. 4-3-1.

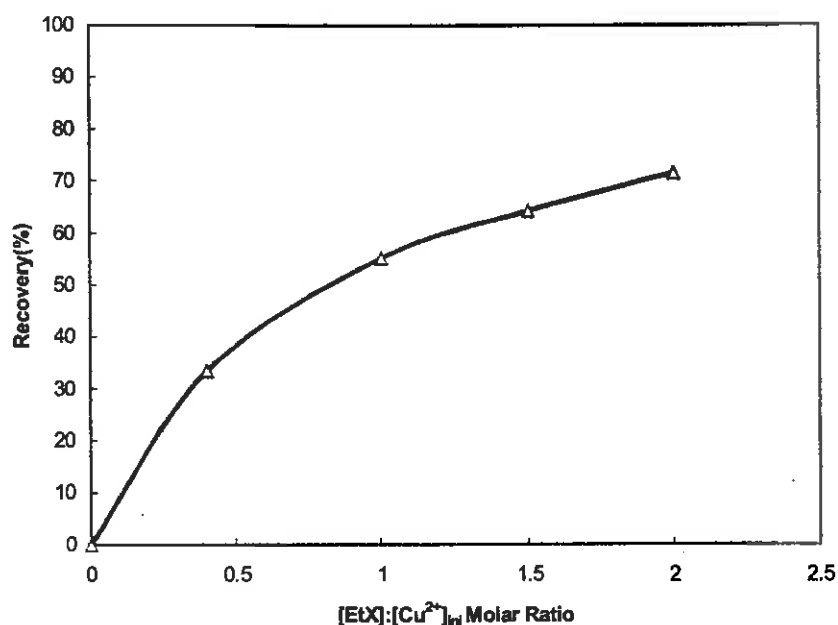


Fig. 4-3-1 Effect of sodium ethyl xanthate concentration on the ion flotation recovery of copper ( $[\text{Cu}^{2+}]_{\text{ini}} 50\text{ppm}$ , MAA\* 9.25ppm, pH  $6.5 \pm 0.2$ )

Fig. 4-3-1 shows that the copper ion flotation recovery increases with increased NaEtX concentration. However, when the  $[\text{EtX}]:[\text{Cu}^{2+}]_{\text{ini}}$  mole ratio is 2:1, which is the stoichiometric amount of reaction, the flotation recovery reaches only around 70%. This is lower than the near 90% flotation recovery of copper ions obtained by other authors (Stalidis, Matis and Lazaridis, 1989). The most probable reason for this rests in the different method used for generating air bubbles in the flotation process. The particle sizes of  $\text{Cu}(\text{EtX})_2$  or  $\text{CuEtX}$  sublates are so fine that it is difficult to identify them under

\* MAA: Methyl Amyl Alcohol, frother.

microscope. Since the bubble size is one of the most important parameters in fine particle flotation, the finer the particle size, the smaller the bubble size required. The bubble size of the dispersed air flotation method adopted in this study is normally in the range of 1-5 mm, which is much larger than that of the dissolved air flotation bubble (size 20-100 micron) used by Stalidis et al.(1989). Therefore, it is not surprising that the dispersed air flotation in our tests obtained lower recovery than in the case of the dissolved air flotation. (details on dissolved air flotation, see Chapter I, page 32).

The effects of pH on the ion flotation recovery of copper using sodium ethyl xanthate as collector at  $[\text{EtX}]:[\text{Cu}^{2+}]_{\text{ini}}$  mole ratio 1:1 and 0.4:1 were examined and the results are shown in Fig. 4-3-2.

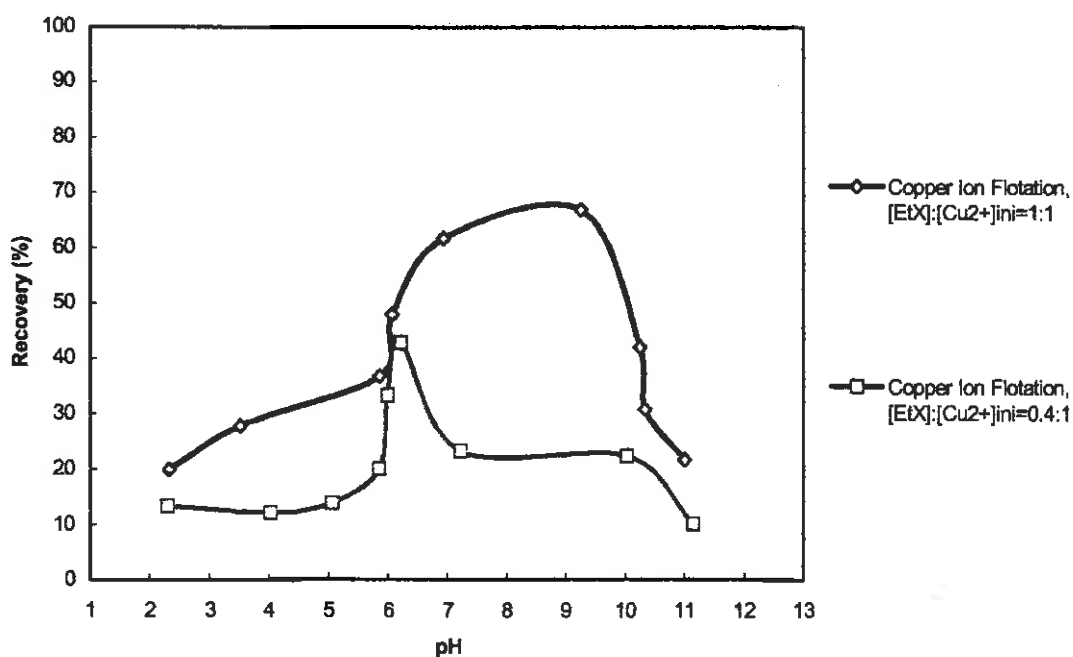
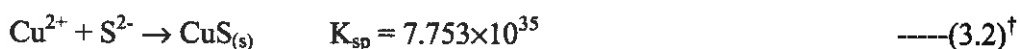


Fig. 4-3-2 Effect of pH on the ion flotation recovery of copper using sodium ethyl xanthate as collector ( $[\text{Cu}^{2+}]_{\text{ini}}$  50ppm, MAA 9.25ppm)

The recovery of copper ion flotation, using xanthate as collector, is slightly better in the pH range 5.5 to 9.5 (see Fig. 4-3-2). However, as the stoichiometric amount of xanthate needs to be double that of the copper concentration, even if the flotation recovery were high, the consumption of collector would be unacceptable from the economic point of view. Definitely, a new more cost efficient way needs to be found.

### 3.1.1.2 Copper sulphide precipitate flotation behavior using xanthate as collector

Sulphide ion can strongly react with copper ion in solution and produce a very insoluble copper sulphide precipitate. The reaction is shown as follows:



Compared with copper hydroxide precipitate  $K_{sp}=10^{19.32}$  (see Section 1, page 58), this is  $10^{16.78}$  times lower. Hence sulphide precipitant would seem to be more efficient to form copper sulphide precipitate and subsequent flotation than hydroxide precipitant for copper hydroxide precipitate.

Our calculation results (see Fig. 4-3-13) show that a very small surplus of sulphide precipitant significantly improves the percentage of the copper sulphide precipitation. In order to ensure such a surplus of sulphide ion, the total concentration of added sodium sulphide precipitant to the initial copper concentration (normally 50ppm) mole ratio  $[\text{S}]_{\text{total}}^\ddagger : [\text{Cu}^{2+}]_{\text{ini}} = 1.016:1$  was used for copper sulphide precipitation and flotation. To simplify the symbols, hereafter,  $[\text{S}^{2-}]$  will be used to represent the total concentration of added sodium sulphide precipitant  $[\text{S}]_{\text{total}}$ , and  $[\text{S}^{2-}] : [\text{Cu}^{2+}]_{\text{ini}} = 1:1$  for the  $[\text{S}]_{\text{total}} : [\text{Cu}^{2+}]_{\text{ini}} = 1.016:1$ .

The effect of pH on copper sulphide precipitate flotation using sodium ethyl xanthate as collector is shown in Fig. 4-3-3.

Although the reaction between copper ions and sulphide ions is quick and complete, the size of the precipitate particles is so fine and so dispersed that the only observable phenomenon of the reaction is a change in the colour of the solution after the sulphide precipitant has been added. The copper sulphide precipitate particle size, checked by using the microfilter method, was around 0.05 micron (Stalidis, et al, 1988, 1989). Clearly, in the pH range of 2.5-11.5, it is almost impossible to float copper sulphide precipitate using NaEtX as collector (see Fig. 4-3-3). It would appear that the strong

<sup>†</sup>  $K_{sp}$  was calculated using Outokumpu HSC Chemistry® for Windows software Version 3.0.

<sup>‡</sup>  $[\text{S}]_{\text{total}}$  is the total concentration of added sodium sulphide precipitant.

negatively charged copper sulphide precipitate resists the negatively charged xanthate ions attaching to its surface and therefore does not float.

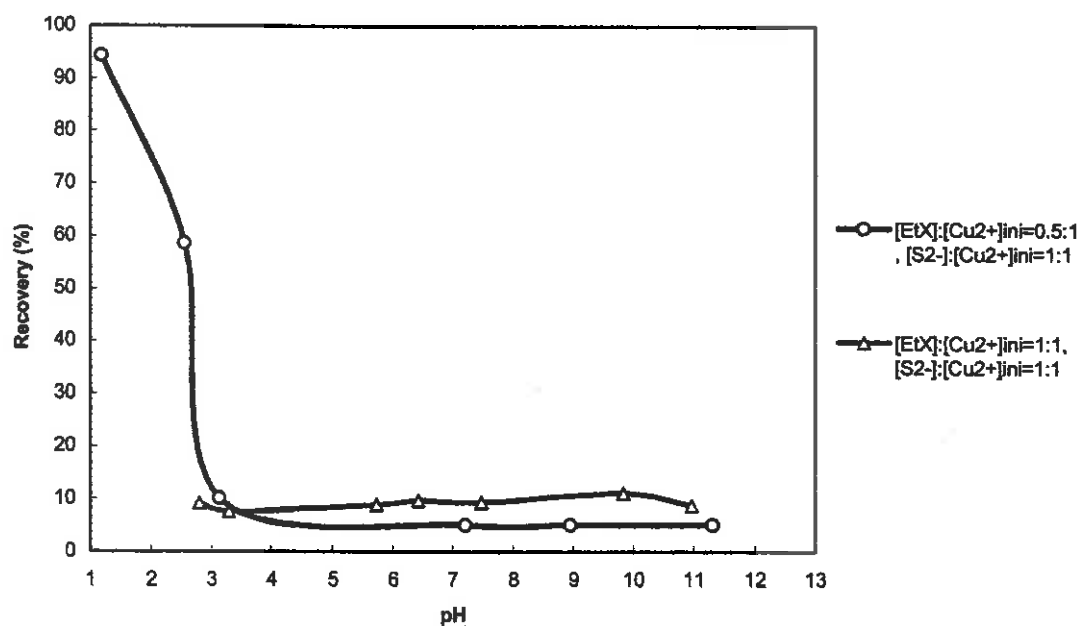


Fig. 4-3-3 Effect of pH on copper sulphide precipitate flotation using sodium ethyl xanthate as collector ( $[Cu^{2+}]_{ini}$  50ppm,  $[S^{2-}]:[Cu^{2+}]_{ini}=1:1$ , MAA 9.25ppm )

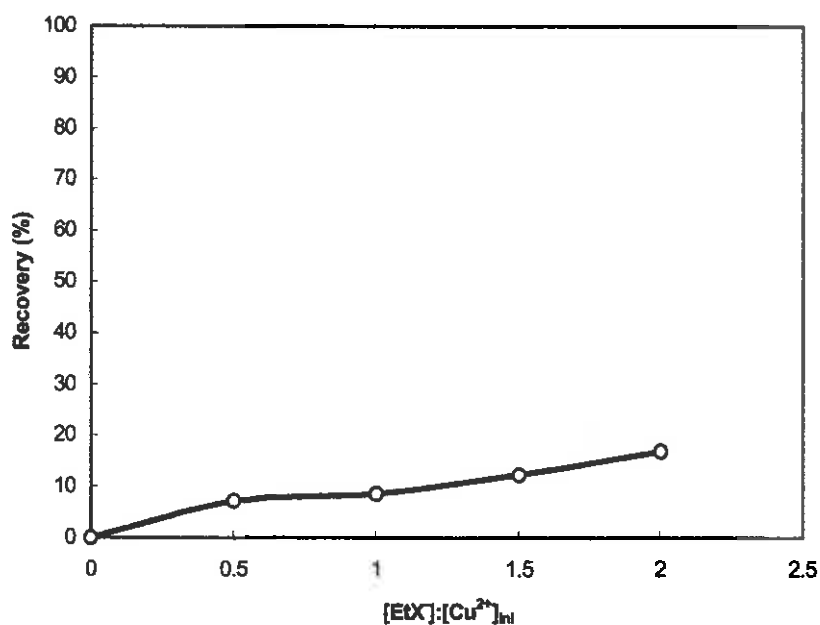


Fig. 4-3-4 Effect of a concentration of sodium ethyl xanthate on copper sulphide precipitate flotation ( $[Cu^{2+}]_{ini}$  50ppm,  $[S^{2-}]:[Cu^{2+}]_{ini}=1:1$ , MAA 9.25ppm, pH  $6.5 \pm 0.2$ )

The effects of the NaEtX concentration on the copper sulphide precipitate flotation are demonstrated in Fig. 4-3-4. The flotation recovery of the copper sulphide precipitate is very low, even when the molar concentration of  $[EtX^-]$  is twice that of the copper ions (stoichiometric amount), the flotation recovery remains less than 20%.

The effect of a sodium sulphide precipitant concentration on the copper sulphide precipitate flotation, using xanthate as collector, is shown in Fig. 4-3-5. Fig. 4-3-6 provides more detailed flotation test results showing the effect of sodium sulphide concentration on copper sulphide flotation recovery.

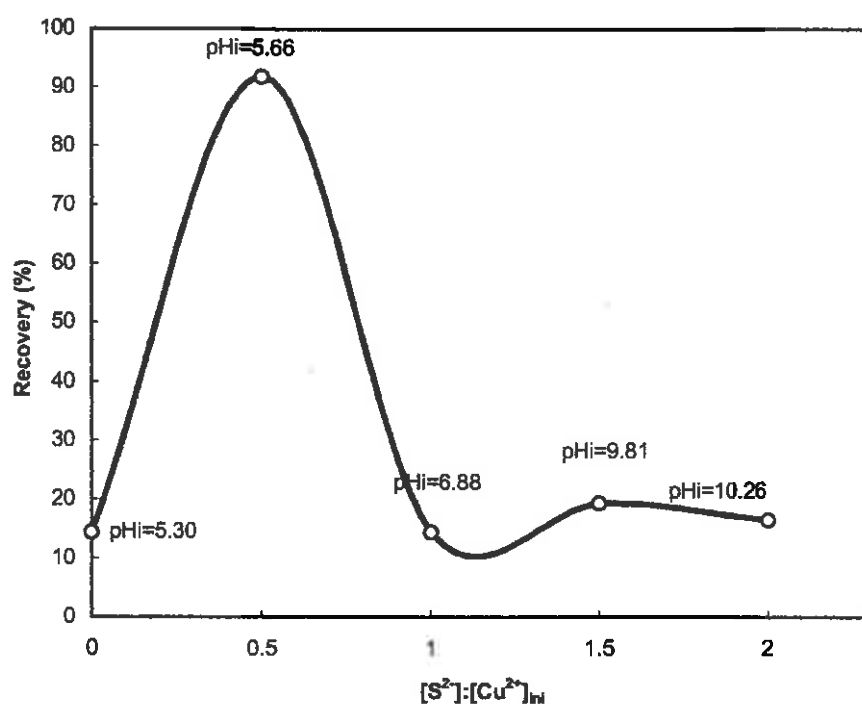


Fig. 4-3-5 Effect of the sodium sulphide concentration on copper sulphide precipitate flotation ( $[Cu^{2+}]_{ini}$  50ppm,  $[EtX^-]:[Cu^{2+}]_{ini}=1:1$ , MAA 9.25ppm)

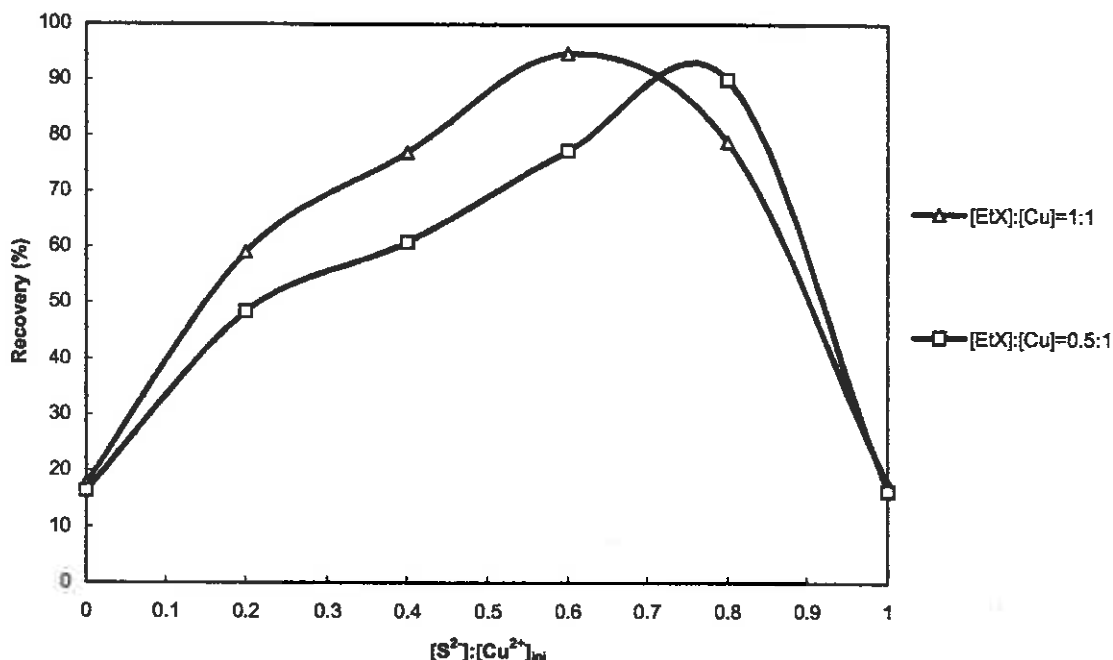


Fig. 4-3-6 Effect of the sodium sulphide concentration on copper sulphide precipitate flotation ( $[Cu^{2+}]_{ini}$  50ppm, MAA 9.25ppm, pH  $6.0 \pm 0.5$ )

It was found that when the  $[S^{2+}]:[Cu^{2+}]_{ini}$  mole ratio was 1:1 or more, the flotation recovery was less than 20%, however, when the  $[S^{2+}]:[Cu^{2+}]_{ini}$  mole ratio was 0.5:1 and the  $[EtX]:[Cu^{2+}]_{ini}$  mole ratio was 1:1, the flotation recovery was more than 90% (see Fig. 4-3-5). This indicates that it is possible to float copper sulphide precipitate under this condition using xanthate as collector.

The detailed flotation results in Fig. 4-3-5 show that the maximum flotation recovery of copper sulphide precipitate is the function of both the  $[S^{2+}]$  to  $[Cu^{2+}]_{ini}$  and the  $[EtX^-]$  to  $[Cu^{2+}]_{ini}$  mole ratio. When the  $[EtX^-]$  to  $[Cu^{2+}]_{ini}$  mole ratio is 1:1, the maximum copper flotation recovery can be obtained at  $[S^{2+}]:[Cu^{2+}]_{ini} = 0.5:1$ , whereas, when the  $[EtX^-]$  to  $[Cu^{2+}]_{ini}$  mole ratio is 0.5:1, the maximum copper flotation recovery is at  $[S^{2+}]:[Cu^{2+}]_{ini} = 0.8:1$ .

After the mole ratio of  $[S^{2+}]$  to  $[Cu^{2+}]_{ini}$  had been fixed at 0.8:1, the flotation tests of the effect of the ethyl xanthate concentration and pH on the copper sulphide precipitate flotation were carried out. The results of these tests have been graphically presented in Fig. 4-3-7 and Fig. 4-3-8.

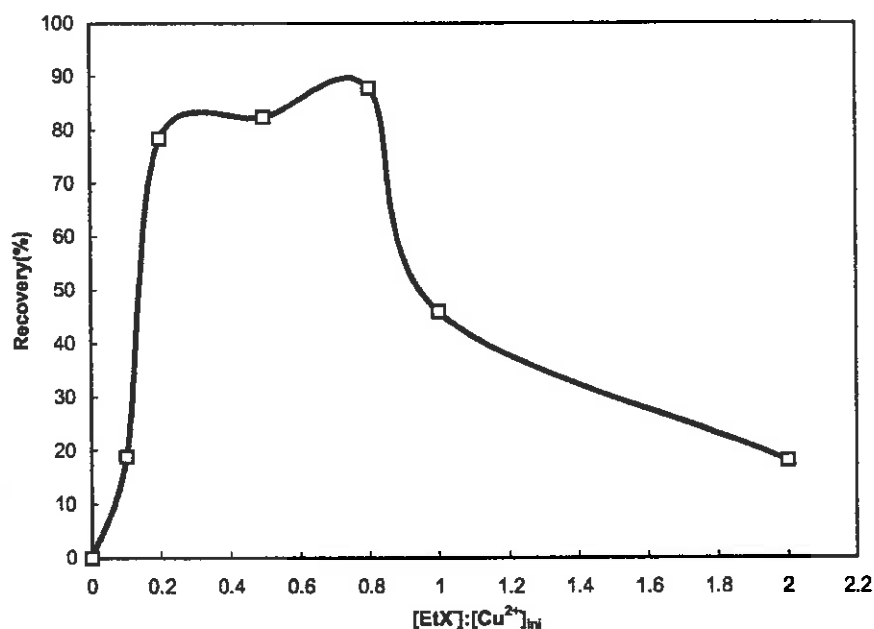


Fig. 4-3-7 Effect of concentration of sodium ethyl xanthate on copper sulphide precipitate flotation ( $[Cu^{2+}]_{ini}$  50ppm,  $[S^{2-}]:[Cu^{2+}]_{ini}=0.8:1$ , MAA 9.25ppm, pH  $6.5 \pm 0.2$ )

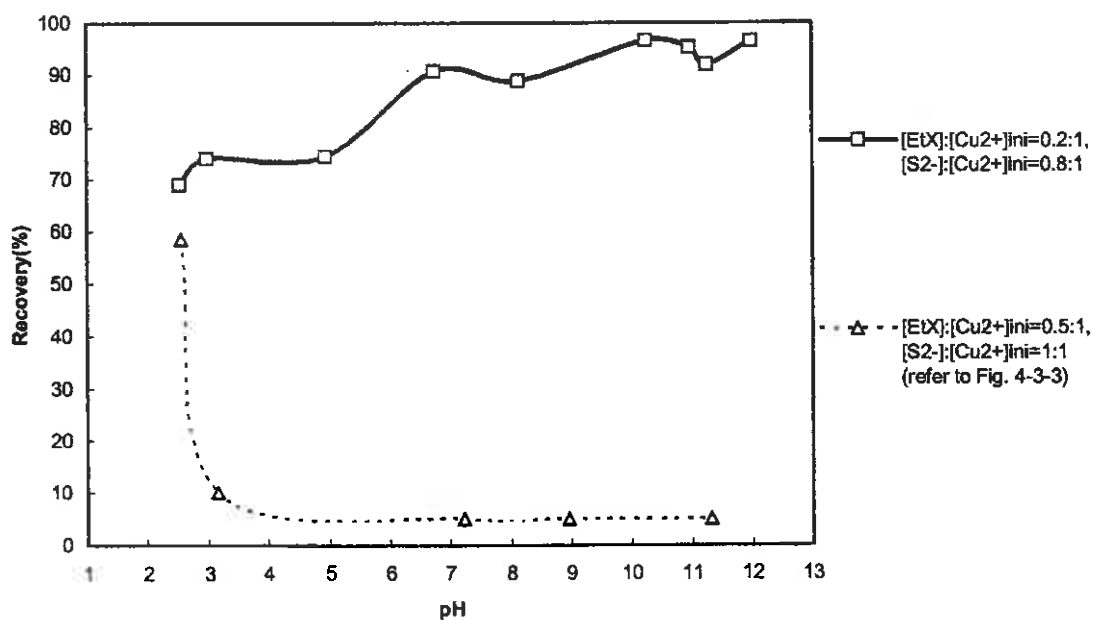


Fig. 4-3-8 Effect of pH on copper sulphide precipitate flotation using sodium ethyl xanthate as collector ( $[Cu^{2+}]_{ini}$  50ppm,  $[S^{2-}]:[Cu^{2+}]_{ini}=0.8:1$ ,  $[EtX]:[Cu^{2+}]_{ini}=0.2:1$ , MAA 9.25ppm)

Fig. 4-3-7 shows that when the mole ratio of  $[\text{EtX}]:[\text{Cu}^{2+}]_{\text{ini}}$  is in the range of 0.2:1 to 0.8:1, the flotation recovery can reach more than 80% while  $[\text{S}^{2-}]$  to  $[\text{Cu}^{2+}]_{\text{ini}}$  is fixed at 0.8:1. Compared to the copper ion flotation (refer to Fig. 4-3-1), the consumption of xanthate was ten times less.

Fig. 4-3-8 illustrates that when  $[\text{S}^{2-}]:[\text{Cu}^{2+}]_{\text{ini}}=0.8:1$  and  $[\text{EtX}]:[\text{Cu}^{2+}]_{\text{ini}}=0.2:1$ , the copper sulphide precipitate flotation was good and the recoveries were more than 75% in the pH range of 3 to 12, particularly, when in the pH range of 7 to 12 (the medium and high pH value), the flotation recoveries were more than 90%. In comparison, when  $[\text{S}^{2-}]:[\text{Cu}^{2+}]_{\text{ini}}=1:1$  and  $[\text{EtX}]:[\text{Cu}^{2+}]_{\text{ini}}=0.5:1$ , there was almost no flotation in the pH range of 3 to 12 (see Fig. 4-3-3).

### ***3.1.1.3 Effect of added copper ion on copper sulphide precipitate flotation using xanthate as collector***

Fig. 4-3-6 and Fig. 4-3-8 show that the copper sulphide precipitate can be floated using xanthate as collector when the sulphide precipitant molar concentration is less than the stoichiometric amount of copper ion concentration. In order to understand more about the mechanism of this phenomenon, the effect of added copper ion on the flotation recovery of copper sulphide precipitate ( $[\text{S}^{2-}]:[\text{Cu}^{2+}]_{\text{ini}}$  mole ratio 1:1) was studied. The flowsheet of the effect of added copper ion on the flotation is shown in Fig. 4-3-9.

The flowsheet shows how the copper solution was mixed with a stoichiometric amount of sulphide precipitant (here sodium sulphide), stirred for 20 minutes to form the copper sulphide precipitate, an additional amount of copper ion was then added and stirred for a further 10 minutes. Finally the collector (NaEtX) and the frother (MAA) were added to the solution after which flotation took place.



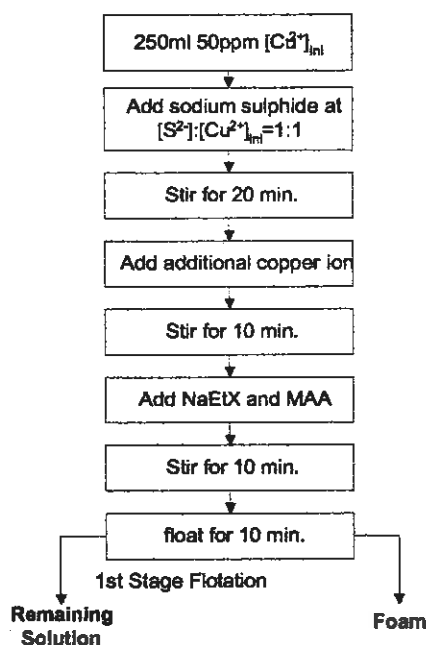


Fig. 4-3-9 Flowsheet to test the effect of added copper ion on the flotation recovery of copper sulphide precipitate ( $[S^{2-}]:[Cu^{2+}]_{ini}$  mole ratio 1:1) using xanthate as collector

When additional copper ion was added to the solution, the total concentration of copper ion in the solution changed with the quantity of added copper ion. The recoveries shown in Fig.4-3-10 were calculated using the following two methods:

For recovery of the total copper ion in the solution:

$$Recovery(\%) = \left(1 - \frac{[Cu^{2+}]_{rem}}{[Cu^{2+}]_{ini} + [Cu^{2+}]_{add}}\right) \times 100\% \quad \text{---(3.3)}$$

For recovery only to the  $[Cu^{2+}]_{ini}$ :

$$Recovery(\%) = \left(1 - \frac{[Cu^{2+}]_{rem} - [Cu^{2+}]_{add}}{[Cu^{2+}]_{ini}}\right) \times 100\% \quad \text{----(3.4)}$$

$[Cu^{2+}]_{rem}$  is the measured copper concentration remaining in solution after flotation;  $[Cu^{2+}]_{add}$  is the added copper concentration;  $[Cu^{2+}]_{ini}$  is the initial copper concentration (50ppm).

The effects of added copper concentration on copper sulphide precipitate flotation, using xanthate as collector, have been graphically presented in Fig.4-3-10 below.

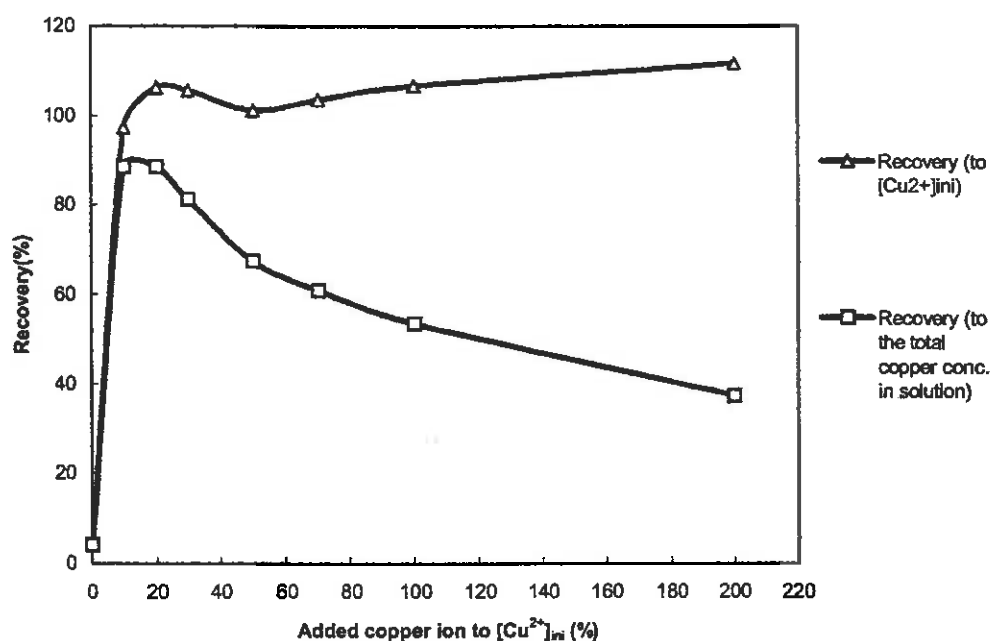


Fig. 4-3-10 Effect of added copper concentration on copper sulphide precipitate flotation using xanthate as collector ( $[Cu^{2+}]_{ini}$  50ppm,  $[S^{2-}]:[Cu^{2+}]_{ini}=1:1$ ,  $[ElX]:[Cu^{2+}]_{ini}=0.2:1$ , MAA 9.25ppm, pH  $6.0 \pm 0.5$ )

The above figure shows that where copper ion was added to the  $[Cu^{2+}]_{ini}$  concentration at a level of 10-20 %, the flotation recovery to the total copper concentration increased from less than 10% to approximately 90%. When the added copper ion was more than 30%, the sulphide precipitant molar concentration was significantly lower than the total copper concentration in the solution, the flotation recovery to the total copper concentration having decreased. However, the recovery to the initial copper concentration ( $[Cu^{2+}]_{ini}$ ) was approximately 105-110% when the added copper ion was more than 10% (in the range of 20-200%). It was also found that after flotation, the solution became clear (before flotation, the solution was black red, due to the copper sulphide precipitate colour). This means that almost all copper sulphide precipitate can be floated using xanthate as collector with the assistance of a wide range of additional copper ion.

The effect of pH after the 20% copper ion had been added, on the copper sulphide precipitate flotation, using xanthate as collector is shown in Fig.4-3-11 (the copper flotation recovery is the recovery to the total copper ion in the solution, calculated using Eq.(3.3)).

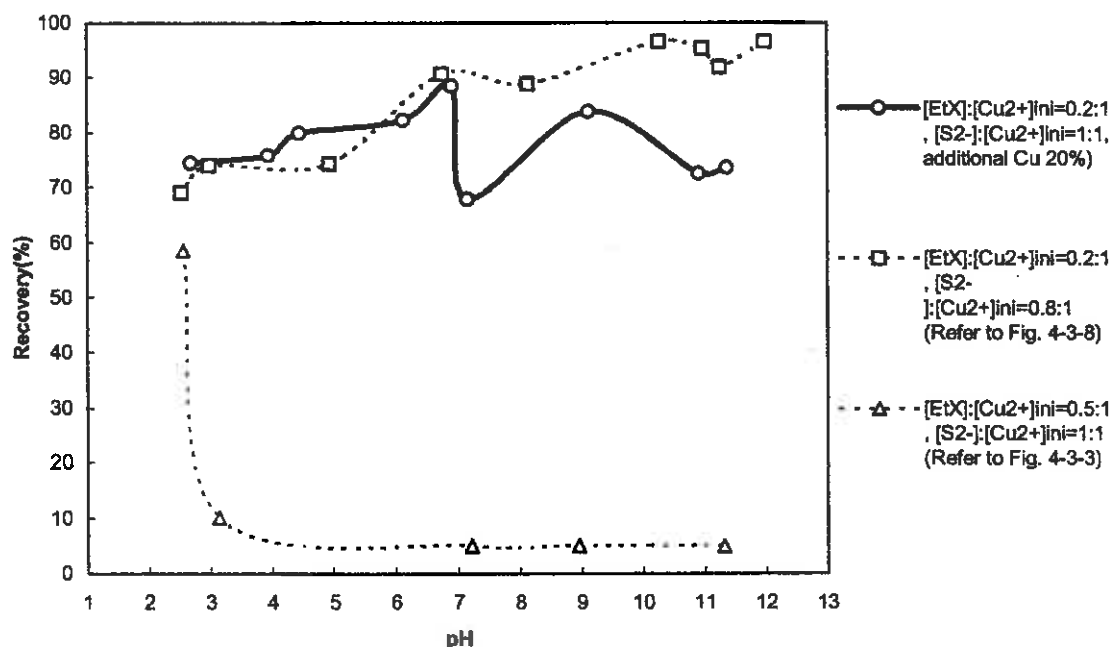


Fig. 4-3-11 Effect of pH with the 20% added copper ion on the copper sulphide precipitate flotation using xanthate as collector ( $[Cu^{2+}]_{ini}$  50ppm,  $[S^{2-}]:[Cu^{2+}]_{ini}=1:1$ ,  $[EtX]:[Cu^{2+}]_{ini}=0.2:1$ , MAA 9.25ppm)

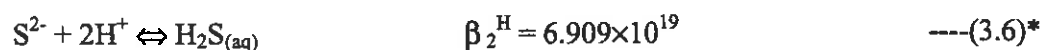
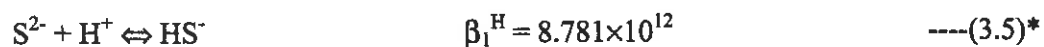
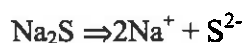
It can be seen (Fig. 4-3-11) that, with 20% added copper ion, the flotation recovery of copper sulphide precipitate ( $[S^{2-}]:[Cu^{2+}]_{ini}$  mole ratio 1:1) is reasonably good at a pH range of 2.5 to 11.5. When the pH is lower than 7, the flotation recovery is very close to that when the  $[S^{2-}]:[Cu^{2+}]_{ini}$  mole ratio is 0.8:1, however, it is slightly lower when the pH is more than 7.

### 3.1.2 Discussion

#### 3.1.2.1 Copper Sulphide Precipitation Calculation<sup>§</sup>

<sup>§</sup> For more detail, see "Appendix 1. Solution Chemistry Calculation"

It was already known that copper ion in water can form a series of soluble complexes with hydroxyl ions (see Section 1, page 58). Sodium sulphide precipitant in water can also involve a range of reactions, which may be listed as follows:



\*Note:  $\beta_1^H$  and  $\beta_2^H$  were calculated using Outokumpu HSC Chemistry® for Windows software Version 3.0.

According to the above reactions, the distributions of  $\text{S}^{2-}$ ,  $\text{HS}^-$  and  $\text{H}_2\text{S}_{(\text{aq})}$  complexes as a function of pH have been calculated and the results are shown in Fig. 4-3-12.

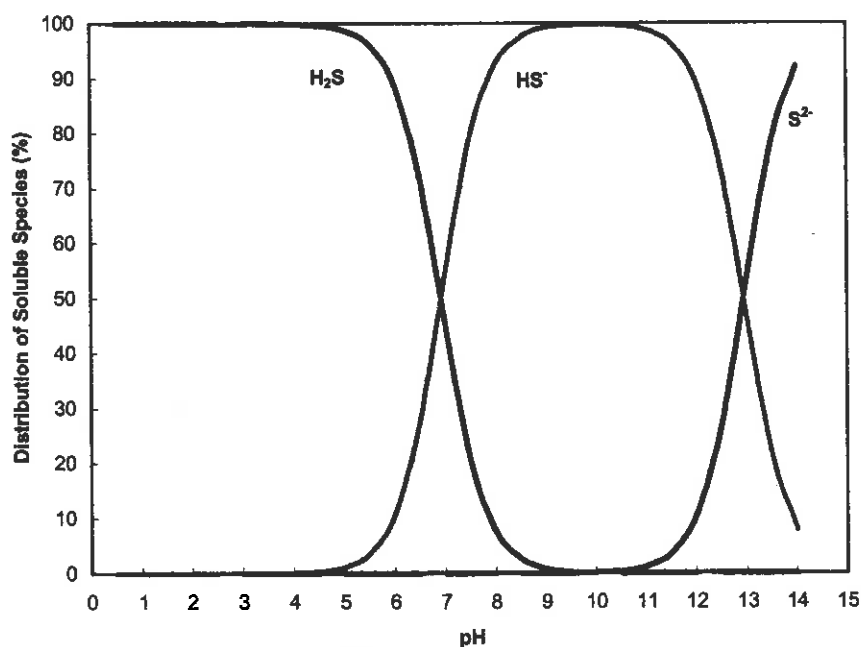


Fig. 4-3-12 Distributions of  $\text{S}^{2-}$ ,  $\text{HS}^-$  and  $\text{H}_2\text{S}_{(\text{aq})}$  complexes as a function of pH

Fig. 4-3-12 shows that:

- $\text{pH} < 6.5$ , the major sulphide complexes is  $\text{H}_2\text{S}_{(\text{aq})}$ ;
- $6.5 < \text{pH} < 12.8$ , the major sulphide complexes is  $\text{HS}^-$ ;

- $\text{pH} > 12.8$ , the major sulphide complexes is  $\text{S}^{2-}$ .

When in an acidic solution, if the  $\text{H}_2\text{S}_{(\text{aq})}$  concentration is high enough,  $\text{H}_2\text{S}$  gas will be formed which is itself a kind of pollution. This was listed as one of the disadvantages for using sulphide precipitation in flotation. However, using modern technology, the precipitation containers could be sealed well, and the  $\text{H}_2\text{S}$  gas can be easily absorbed and re-used by applying an alkaline solution. It would therefore not be difficult to solve this problem.

Fig. 4-3-13 shows the calculated results, with the help of a comprehensive calculation method (see Appendix 1) which takes into account the relative stability of both copper sulphide and copper hydroxide, of the total remaining soluble copper concentration of various sodium sulphide concentrations after sulphide precipitation. Fig. 4-3-14 shows the calculated results of the copper sulphide percentage precipitation, after sulphide precipitation as a function of pH.

Fig. 4-3-13 and Fig. 4-3-14 indicate that:

- Without the sodium sulphide precipitant, the lowest total remaining copper soluble concentration is  $3.3 \times 10^{-7}$  M in the pH range of 10.0-10.5 (refer to Fig. 4-3-13 line 1). With the stoichiometric amount of sodium sulphide precipitant ( $[\text{Na}_2\text{S}]:[\text{Cu}^{2+}]_{\text{ini}} = 1:1$ ), the total remaining copper soluble concentration can be decreased to as low as  $2.0\text{-}2.2 \times 10^{-15}$  M at the pH range of 7.5-8.5 (refer to Fig. 4-3-13 line 3).
- With a very slight surplus of sodium sulphide precipitant, the total remaining copper soluble concentration can be further significantly decreased. For example, when  $[\text{Na}_2\text{S}]:[\text{Cu}^{2+}]_{\text{ini}} = 1.016:1$ , the total remaining copper soluble concentration is  $3.2\text{-}3.6 \times 10^{-25}$  M at pH 7.5-8.5 (refer to Fig. 4-3-13 line 4). However, when the sodium sulphide concentration is increased more, the decreasing of the total remaining copper soluble concentration slows down. For instance, when  $[\text{Na}_2\text{S}]:[\text{Cu}^{2+}]_{\text{ini}} = 1.1:1$ , the total remaining copper soluble concentration is  $6.0\text{-}6.2 \times 10^{-26}$  M in the pH range of 7.5-8.5 (refer to Fig. 4-3-

13 line 5); when  $[\text{Na}_2\text{S}]:[\text{Cu}^{2+}]_{\text{ini}} = 1.5:1$ , the total remaining concentration is  $6.0-6.2 \times 10^{-27}$  M (refer to Fig. 4-3-13 line 6).

- When  $[\text{Na}_2\text{S}]:[\text{Cu}^{2+}]_{\text{ini}} \geq 1:1$ , the copper sulphide percentage precipitation is approximately 100% in all pH ranges (refer to Fig. 4-3-14 line 1), which is possible for sulphide precipitation and subsequent flotation in acid solution.
- With  $[\text{Na}_2\text{S}]:[\text{Cu}^{2+}]_{\text{ini}} = 0.8:1$ , when the  $\text{pH} < 6.5$ , it can form approximately 80% copper sulphide precipitate; when the  $\text{pH} \geq 6.5$ , a copper sulphide precipitate and copper hydroxide precipitate mixture will be formed (refer to Fig. 4-3-14 line 2).

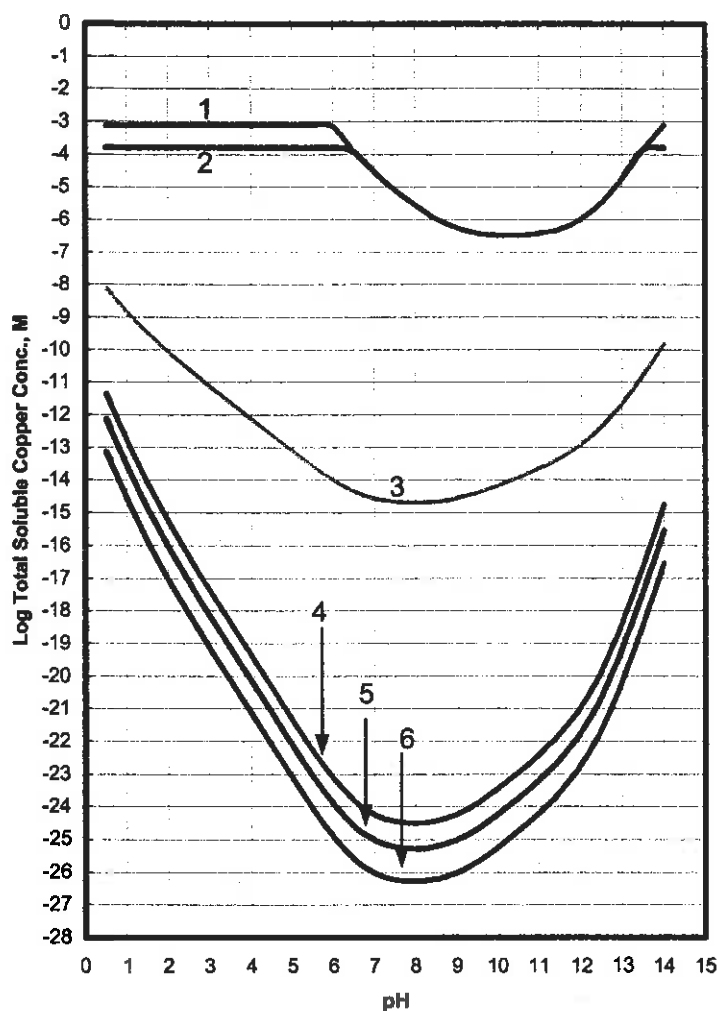


Fig. 4-3-13 Calculated total remaining soluble copper concentration after sulphide precipitation at  $[\text{Cu}^{2+}]_{\text{ini}} = 7.87 \times 10^{-4}$  M (50ppm) as a function of pH

1 ----  $[\text{Na}_2\text{S}] = 0$                       2 ----  $[\text{Na}_2\text{S}]:[\text{Cu}^{2+}]_{\text{ini}} = 0.8:1$                       3 ----  $[\text{Na}_2\text{S}]:[\text{Cu}^{2+}]_{\text{ini}} = 1:1$   
 4 ----  $[\text{Na}_2\text{S}]:[\text{Cu}^{2+}]_{\text{ini}} = 1.016:1$                       5 ----  $[\text{Na}_2\text{S}]:[\text{Cu}^{2+}]_{\text{ini}} = 1.1:1$                       6 ----  $[\text{Na}_2\text{S}]:[\text{Cu}^{2+}]_{\text{ini}} = 1.5:1$

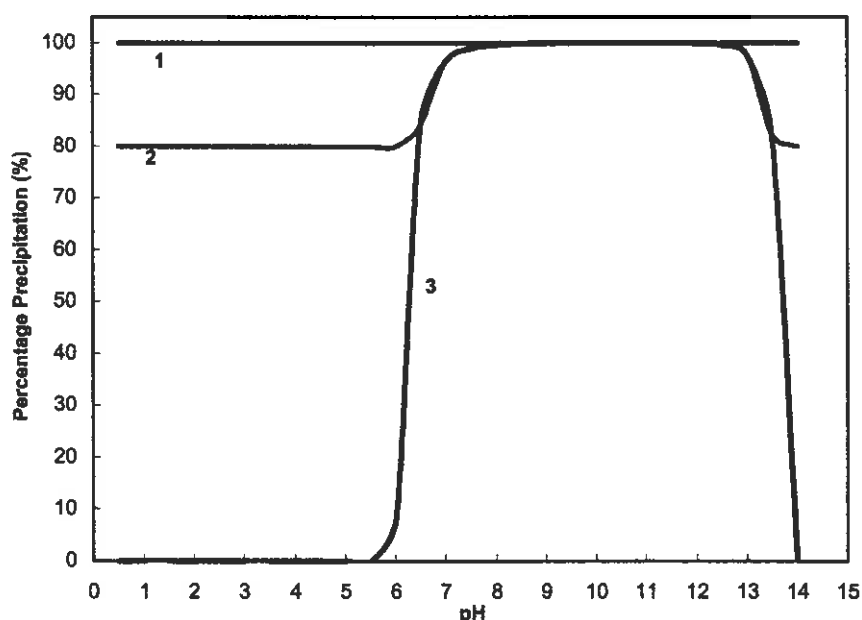


Fig. 4-3-14 Calculated copper sulphide percentage precipitation after sulphide precipitation at  $[Cu^{2+}]_{ini} = 7.87 \times 10^{-4} M$  (50ppm) as a function of pH

1 ---  $[Na_2S]:[Cu^{2+}]_{ini} \geq 1:1$     2 ---  $[Na_2S]:[Cu^{2+}]_{ini} = 0.8:1$     3 ---  $[Na_2S] = 0$

### 3.1.2.2 Mechanism of Copper Sulphide Precipitate Flotation Using Xanthate as Collector

From the above calculations, it is clear that with a very slight surplus of sodium sulphide precipitant, the total remaining copper soluble concentration can be significantly decreased. However, when  $[S^{2-}]:[Cu^{2+}]_{ini} = 1:1$  (a slight surplus of  $[Na_2S]$ ), the copper sulphide precipitate cannot be floated using xanthate as collector in the whole pH range of 2.5 to 11.5 (refer to Fig. 4-3-3). It is assumed that the excess  $HS^-$  or  $S^{2-}$  ions cover the precipitate surface and make it highly negatively charged (see Fig. 4-3-15). The negatively charged xanthate ion is obstructed from attaching onto the sulphide precipitate surface, therefore, the copper sulphide precipitate flotation is depressed. This mechanism is similar to when sodium sulphide is used as depressant in sulphide mineral flotation.

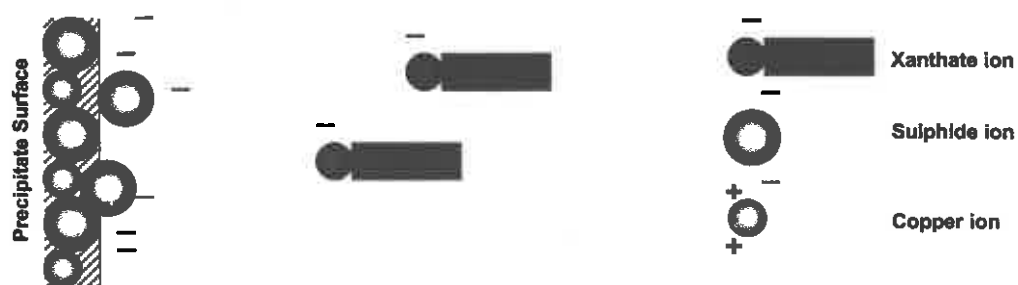


Fig. 4-3-15 Schematic representation of negatively charged copper sulphide precipitate surface obstructs the attachment of xanthate ion

However, when  $[S^{2-}] < [Cu^{2+}]_{ini}$  or  $[S^{2-}]:[Cu^{2+}]_{ini} = 1:1$  with extraneous copper ion added, the copper sulphide precipitate can be floated (see Fig. 4-3-6, Fig. 4-3-7 and Fig. 4-3-11). It would appear that the surplus of copper ion adsorbs (more likely to be chemisorption) on the copper sulphide precipitate surface, decreases the magnitude of its negative charge, improves the adsorption of xanthate ion onto the sulphide precipitate surface, and therefore increases the copper sulphide precipitate flotation. A schematic representation of the process can be seen in Fig. 4-3-16.



Fig. 4-3-16 Schematic representation of excessive copper ions improve the attachment of xanthate ion onto the copper sulphide precipitate surface

In addition to the process seen in the above model, the surplus of copper ion may combine with the strong negatively charged copper sulphide precipitate particles and form aggregates. As extra copper ions are involved in the aggregates, the magnitude of the negative charge on the surface decreases, the xanthate ions can then attach to the precipitate surface and subsequently float it out.



A schematic representation of excessive copper ion combining the copper sulphide precipitate particles is shown in Fig. 4-3-17.

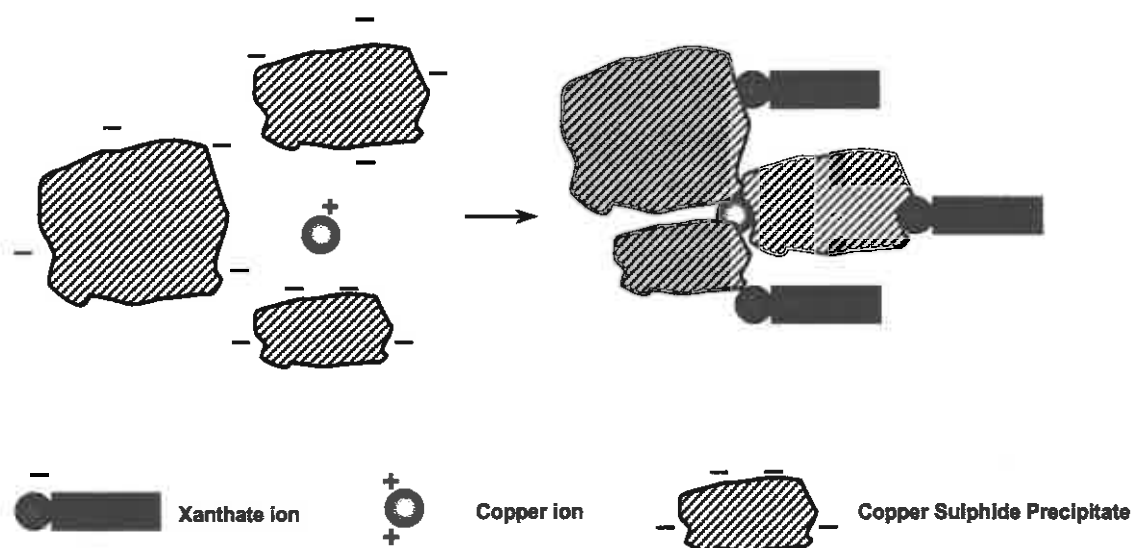


Fig. 4-3-17 Schematic representation of surplus copper ion combining the copper sulphide precipitate particles

The surplus copper ion can also decrease the “thickness” of the double layer of the copper sulphide precipitate, reduce the potential energy between the precipitate and xanthate ion, improve the adsorption of xanthate ion onto the sulphide precipitate surface and hence increase the flotation recovery. This has been discussed in more detail in Section 1.

It is well known that the oxidation of sulphide mineral surface is very important for thiol collectors attaching to the mineral surface. In an alternative possible mechanism, the surplus copper might be reduced from  $\text{Cu}^{2+}$  to  $\text{Cu}^+$  and react with  $\text{CuS}$  forming  $\text{Cu}_2\text{S}$ . The equivalent and simultaneous anodic oxidation reactions involving the xanthate ion at the copper precipitate surface may also occurred and thus lead to flotation. The electrochemical reactions will be discussed in the next part (section 3.2).

When  $\text{pH} < 2.5$  and  $[\text{S}^{2-}]:[\text{Cu}^{2+}]_{\text{ini}} = 1:1$  (the  $[\text{Na}_2\text{S}]$  is slightly excessive), the copper sulphide precipitate can be floated by using xanthate as collector (see Fig. 4-3-3). It may be assumed that with such an acid solution, the  $[\text{H}_2\text{S}_{(\text{aq})}]$  concentration is high enough to

form  $\text{H}_2\text{S}$  gas (refer to Fig. 4-3-12). As the  $\text{H}_2\text{S}$  gas escapes into the air, the copper ion in the solution becomes surplus thus making the flotation possible. In fact, during the tests, when the pH was lower than approximately 5.0,  $\text{H}_2\text{S}$  gas could be smelled, particularly when pH was lower than 2.5, the  $\text{H}_2\text{S}$  smell was remarkably stronger. When  $\text{pH} < 5.0$  ( $[\text{S}^{2-}]:[\text{Cu}^{2+}]_{\text{ini}} = 0.8:1$ ), the flotation recovery is only about 75% (not 80%, see Fig. 4-3-8), presumably because of the escape of  $\text{H}_2\text{S}$  gas. However, when  $\text{pH} > 7$ , the copper flotation recovery can reach more than 90%, this is because a copper sulphide and copper hydroxide precipitate mixture was formed (see Fig. 4-3-14) and part of the copper hydroxide accompanying the sulphide precipitate was floated.

The copper recovery to the initial copper concentration ( $[\text{Cu}^{2+}]_{\text{ini}}$ ) is approximately 105-110% without a change in the added copper ion concentration, in the range of 20-200% (see Fig. 4-3-10). It is assumed therefore that the amount of surplus copper ions adsorbing (Fig. 4-3-16 model) and/or combining (Fig. 4-3-17 model) with the copper sulphide precipitate is about 10%.

### 3.1.3 Brief Summary

Calculations showed that copper sulphide precipitation is significantly more efficient than copper hydroxide precipitation. With a slight surplus concentration of sulphide precipitant, the total remaining copper concentration can decrease to lower than  $3.2\text{--}3.6 \times 10^{-25}$  M. However, the particle size of copper sulphide precipitate is very fine. When the sulphide precipitant is in surplus, copper sulphide precipitate cannot be floated using xanthate as collector.

When the copper ion concentration exceeds the sulphide precipitant concentration, or when extraneous copper ion is added, the copper sulphide precipitate can be efficiently floated using xanthate as collector in a wide pH range of 2.5-11.5. It is possible that in this process the surplus copper ions adsorb onto the copper sulphide precipitate surface decreasing its negative surface charge, and/or combining the sulphide precipitate particles, thereby improving the flotation.

## **3.2 The influence of stirring time and oxidation on copper sulphide precipitate flotation**

A current theory regarding sulphide mineral flotation holds that the mechanism of the xanthate attaching to the sulphide mineral surfaces is an electrochemical process. It has been established that the sulphide mineral surface is not joined to the thiol collector without being previously oxidized (Jay, 1993). In this work, the influence of oxidation on copper sulphide precipitate has been investigated and the mechanisms involved are discussed below.

### **3.2.1 Results**

#### ***3.2.1.1 Influence of stirring time on copper sulphide precipitate flotation***

It has been found in this work that surplus copper ion in a solution is required to bring about copper sulphide precipitate flotation, using xanthate as collector. Sulphide ion and its precipitate in solution are thermodynamically unstable in the presence of oxygen. Oxygen from the air is involved in the precipitation process when the sulphide precipitate solution is stirred under normal atmospheric conditions.

Tests have been carried out to investigate the influence of stirring time, under normal atmospheric conditions, on the copper sulphide precipitate flotation, using xanthate as collector and the results have been presented in Fig. 4-3-18 (line 1).

It was found that some very fine particles floated on top of the solution after sulphide precipitation with prolonged stirring, before the xanthate collector was added. In view of previous studies (Yoon, 1981; Trahar, 1983; Bannearland, & Quast, 1993; Trahar, Senior, & Shannon, 1994) on the hydrophobicity of metal sulphide and collectorless flotation of sulphide minerals, flotation tests without additional xanthate ion (with frother only) were carried out and the results are shown in Fig. 4-3-18 (line 2).

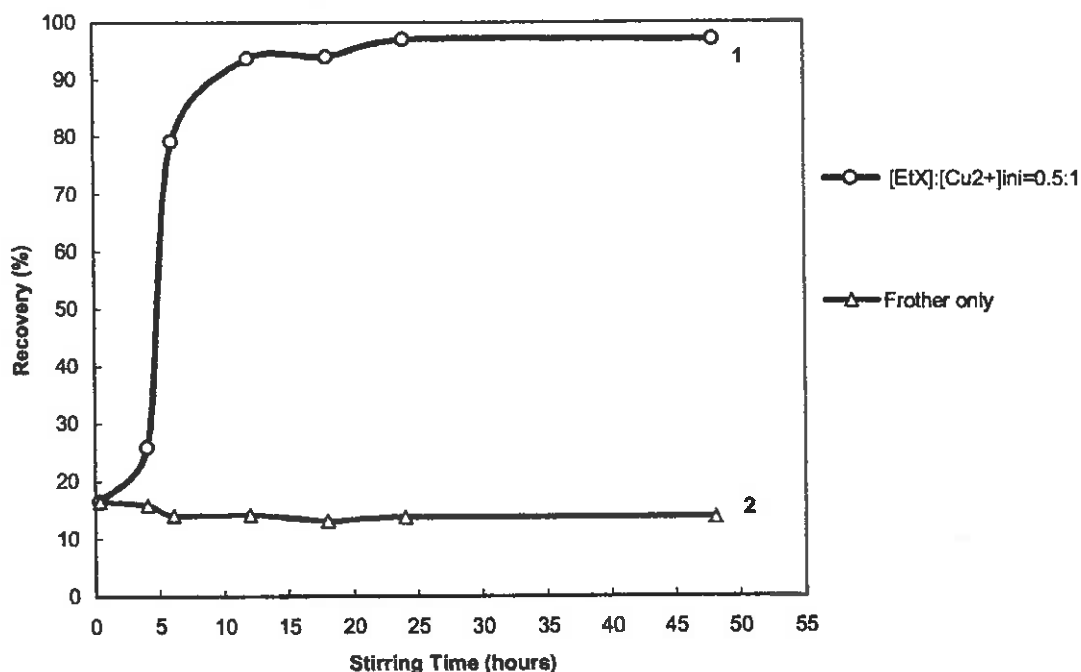


Fig. 4-3-18 The influence of stirring time on the copper sulphide precipitate flotation using xanthate as collector ( $[Cu^{2+}]_{ini}$  50ppm,  $[S^{2-}]:[Cu^{2+}]_{ini}=1:1$ , MAA 9.25ppm, pH  $6.0 \pm 0.5$ )  
 1--- $[EtX]:[Cu^{2+}]_{ini}=0.5:1$ ; 2 ---  $[EtX]:[Cu^{2+}]_{ini}=0$

Stirring time significantly influences the copper sulphide precipitate flotation, using xanthate as collector (see Fig. 4-3-18 line 1). It is known that when  $[S^{2-}]:[Cu^{2+}]_{ini}=1:1$ , the copper sulphide precipitate cannot be floated using xanthate as collector. However, increased stirring time markedly increases the copper flotation recovery. Six hours of stirring increases the flotation recovery from 16% (in normal flotation conditions, i.e., stirring for 20 minutes) to 80%. When the stirring time is in the range of 12 to 48 hours, the flotation recoveries remain above 95%.

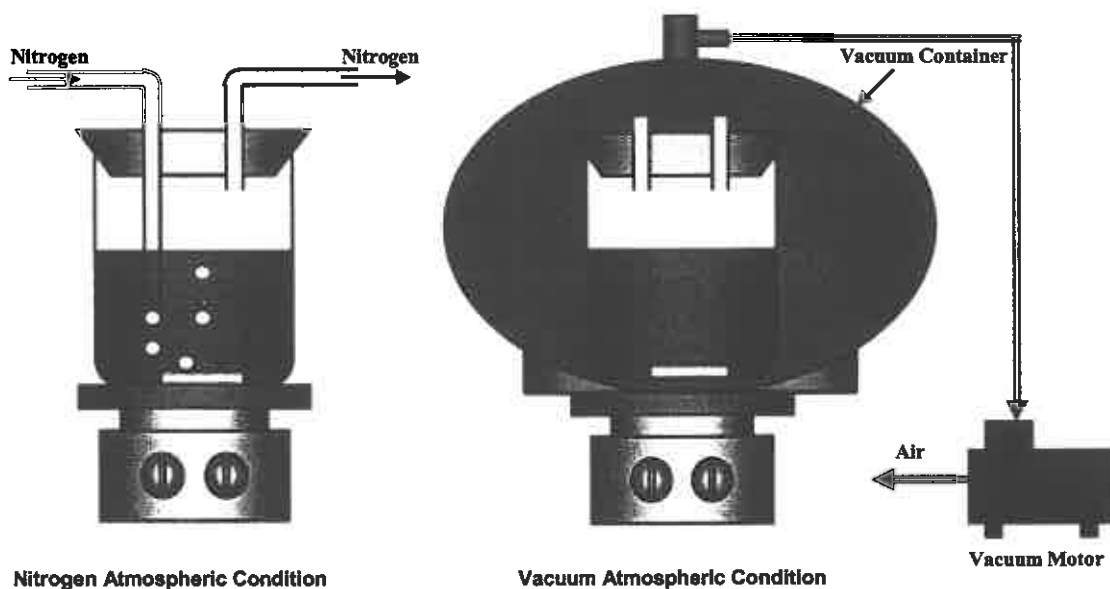
In spite of some visible evidence of hydrophobic particles in the system when copper precipitate is stirred for a long time, the flotation results do not confirm the existence of hydrophobicity. With increased stirring time and without additional xanthate, the flotation recovery is constantly approximate 15% (see Fig. 4-3-18 line 2). However, no conclusion can be drawn regarding the hydrophobicity, as the bubble size produced from the flotation column is too large to collect these very fine copper sulphide precipitate particles. For a

further investigation of these phenomena, new test methods and equipment would need to be carefully prepared and designed. This is beyond the scope of this thesis.

### *3.2.1.2 Effect of atmospheric conditions related to the stirring time on copper sulphide precipitate flotation*

It is assumed that oxygen in the air will oxidize the copper sulphide precipitate after prolonged stirring and enhance the flotation recovery, using xanthate as collector. Accordingly when stirring under nitrogen or vacuum conditions, copper sulphide precipitate flotation recovery should not increase, as oxygen should be absent from the stirring system.

Tests were carried out to investigate the effects of different stirring atmospheric conditions on copper sulphide precipitate flotation. Stirring apparatus for the tests are shown schematically in Fig. 4-3-19. The vacuum was kept at  $-92$  Kpa, for flotation results see Fig. 4-3-20.



*Fig. 4-3-19 Schematic presentation of the equipment used for testing the effects of nitrogen and vacuum atmospheric conditions on the copper sulphide precipitate flotation.*

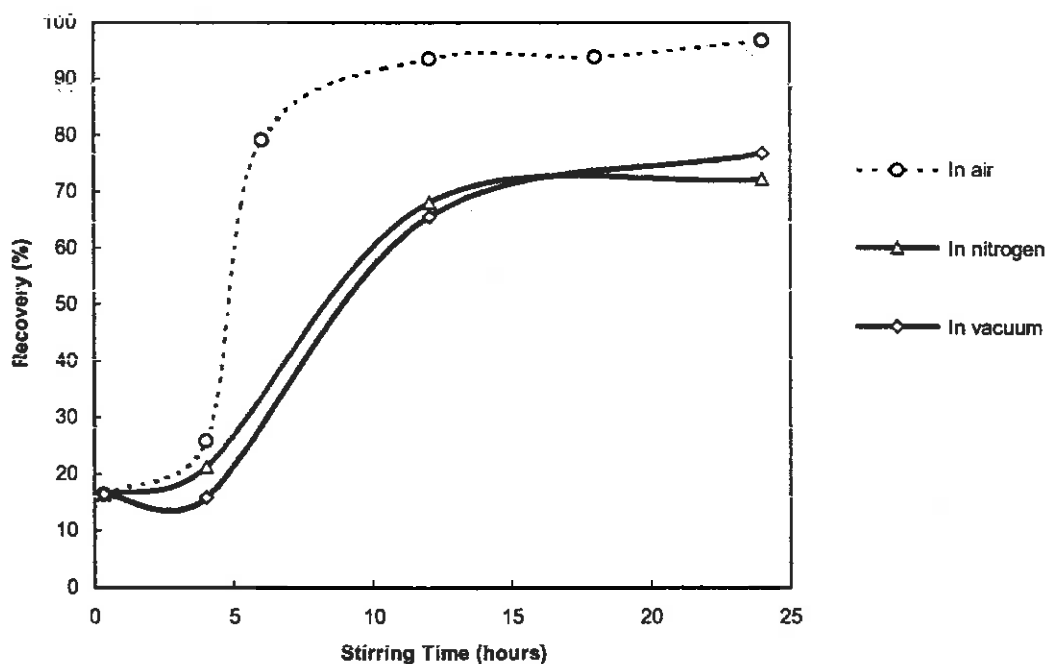


Fig. 4-3-20 The influence of nitrogen and vacuum atmospheres on copper sulphide precipitate flotation in relation to stirring time ( $[Cu^{2+}]_{ini}$  50ppm,  $[EtX]:[Cu^{2+}]_{ini}=0.5:1$ ,  $[S^{2-}]:[Cu^{2+}]_{ini}=1:1$ , MAA 9.25ppm, pH  $6.0 \pm 0.5$ )

Contrary to predictions, the flotation recoveries of copper sulphide precipitate increase after 12 hours of stirring under both nitrogen and vacuum atmospheric conditions, using xanthate as collector. The flotation recoveries of copper sulphide precipitate in both nitrogen and vacuum atmospheric conditions after 12 hours or more stirring were similar (approximately 70%), and slightly lower than in normal air condition (see Fig. 4-3-20).

The copper sulphide precipitate was observed to change from dark red to dark green in the tests. This is possibly due to the fact that a very small amount of oxygen might remain in both nitrogen and vacuum systems and oxidize the copper sulphide precipitate. However, as copper and sulphide species are multivalent, it is also possible that the electrochemical oxidation has occurred in the copper sulphide precipitate itself. Details will be discussed later.

### 3.2.1.3 Effect of $H_2O_2$ on copper sulphide precipitate flotation

The copper sulphide precipitate can be floated after prolonged stirring, even in a nitrogen atmosphere or under vacuum condition, using xanthate as collector. It was necessary to explore the effect of added oxidant on the copper sulphide precipitate flotation.  $H_2O_2$  was selected as an oxidant for this test, because it acts only as an oxidant without introducing any other extraneous ions into the sulphide precipitation and flotation system.

Analytical grade  $H_2O_2$  was diluted to 1% for the tests. The normal flotation process was used for these tests: the sulphide was precipitated for 20 minutes, an amount of  $H_2O_2$  was then added, followed by a further 10 minutes stirring; xanthate and frother were added stirred for 10 minutes and finally floated for 5 minutes. The effect  $H_2O_2$  on the copper sulphide precipitate flotation is shown in Fig. 4-3-21.

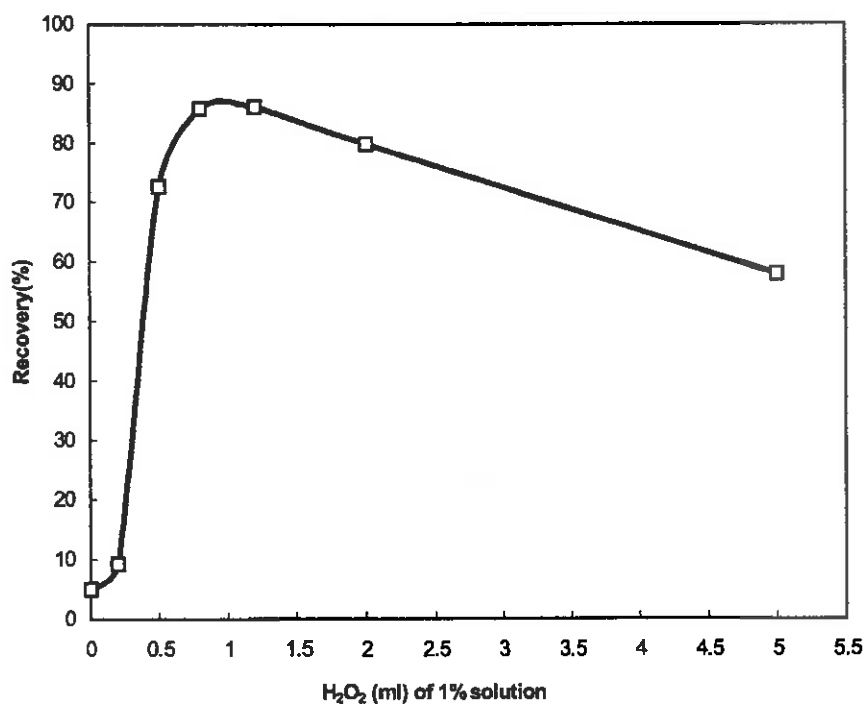


Fig. 4-3-21 The effect of  $H_2O_2$  consumption on copper sulphide precipitate flotation ( $[Cu^{2+}]_{ini}$  50ppm,  $[EtX]:[Cu^{2+}]_{ini}=0.5:1$ ,  $[S^{2-}]:[Cu^{2+}]_{ini}=1:1$ , MAA 9.25ppm, pH  $6.0 \pm 0.5$ )

Clearly, with a suitable amount of  $H_2O_2$  (0.8-1.2ml of 1% solution), the flotation recovery of copper sulphide precipitate can reach more than 85% (refer to Fig. 4-3-21). Oxidation therefore plays a major role in the improvement of copper sulphide precipitate flotation when using xanthate as collector. When the consumption of  $H_2O_2$  is more than 1.5 ml, the flotation recovery decreases, which indicates that only partial oxidation is required for flotation.

### 3.2.1.4 Effect of ferric ion on copper sulphide precipitate flotation

Ferric ion is commonly present with heavy metal ions in industrial wastewater. As it is an oxidant and potential co-precipitant, it was important to investigate its effect on copper sulphide precipitate flotation by using xanthate as collector. The flotation results are presented in Fig. 4-3-22.

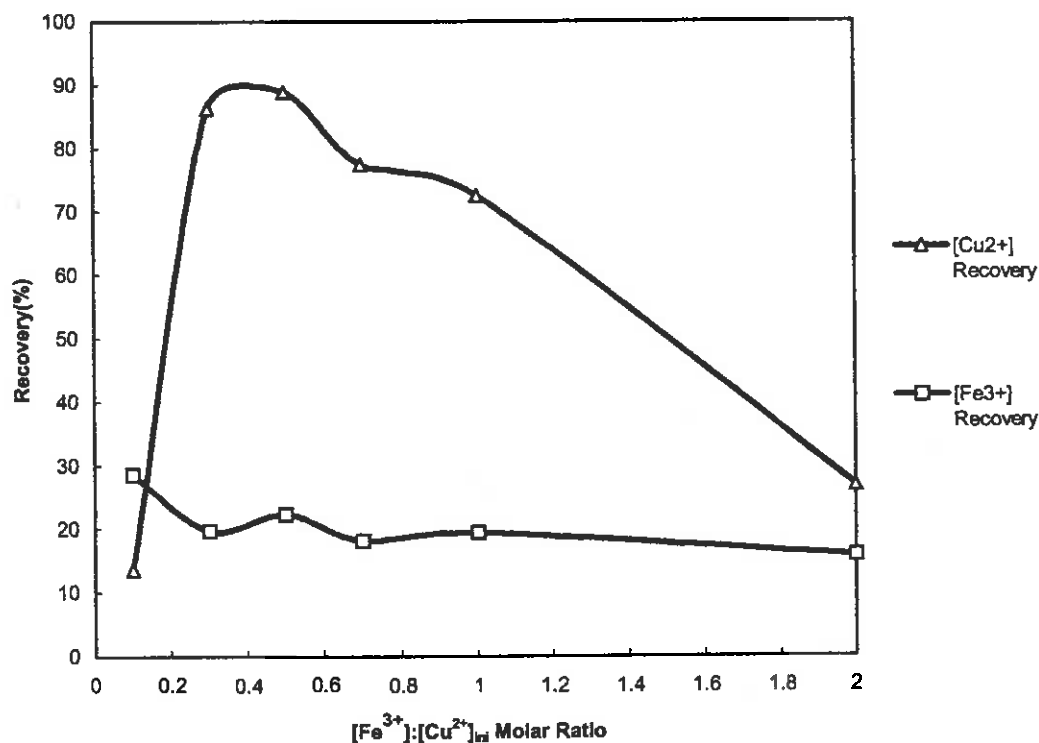


Fig. 4-3-22 The effect of  $[Fe^{3+}]$  concentration on the copper sulphide precipitate flotation using xanthate as collector ( $[Cu^{2+}]_{ini}$  50ppm,  $[EtX]:[Cu^{2+}]_{ini}=0.5:1$ ,  $[S^{2-}]:[Cu^{2+}]_{ini}=1:1$ , MAA 9.25ppm, pH  $6.0\pm0.5$ )



As shown (Fig. 4-3-22), when the  $[\text{Fe}^{3+}]:[\text{Cu}^{2+}]$  mole ratio is in the range of 0.3-0.5, the flotation recovery of copper sulphide precipitate increases to approximately 90%. When this mole ratio is more than 0.5, the flotation recovery decreases. The recovery of  $[\text{Fe}^{3+}]$  itself seems to remain constant and low with the change in the  $[\text{Fe}^{3+}]$  concentration. This probably means that the increase in the copper sulphide precipitate recovery is not because of the adsorption of ferric hydroxide colloid, but because of the oxidation by ferric ion of the copper sulphide precipitate.

In order to fully investigate the effect of ferric ion on the flotation recovery of copper sulphide precipitate, four detailed flowsheets have been developed as shown in Fig. 4-3-23.

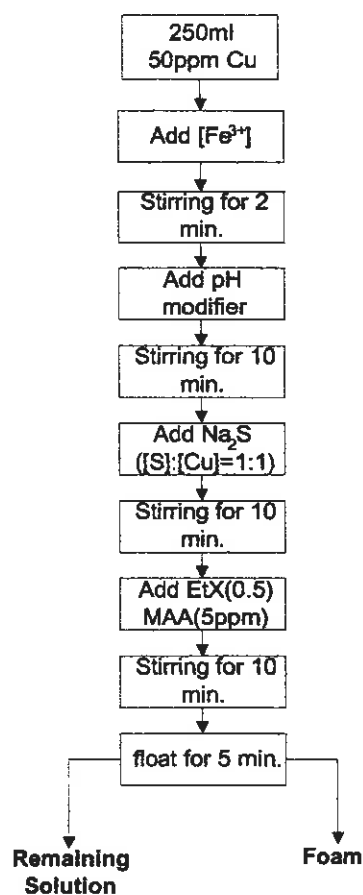


Fig. 4-3-23A

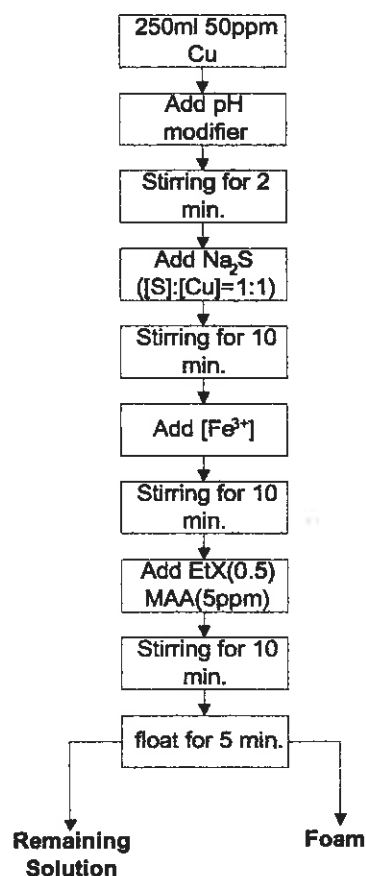


Fig. 4-3-23B

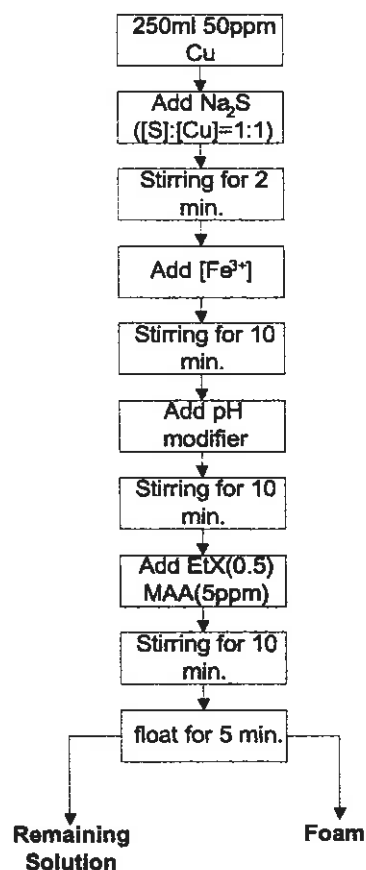


Fig. 4-3-23C

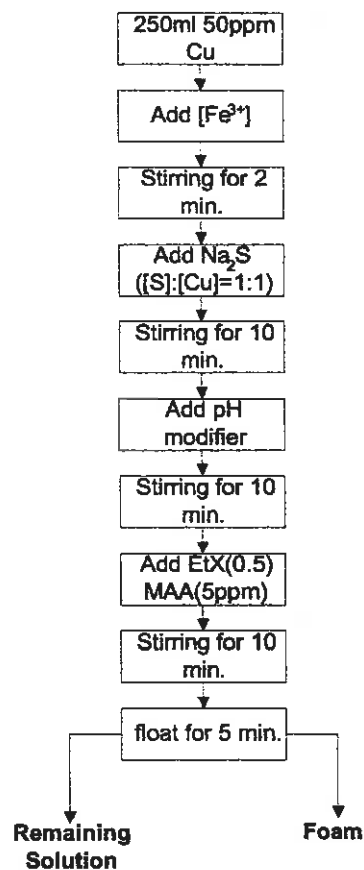


Fig. 4-3-23D

Fig. 4-3-23 The flowsheets illustrate the effect variation of sequence of  $[S^2-]$ , pH modifier and  $[Fe^{3+}]$  on copper flotation recovery

Flowsheet Fig. 4-3-23A indicates that the ferric ion was added to the solution prior to the pH modifier. After 10 minutes stirring, sodium sulphide was added to form sulphide precipitate and then xanthate was used as collector for flotation. Flowsheet Fig. 4-3-23B shows that the pH modifier and sodium sulphide were added prior to the ferric ion addition. Flowsheet Fig. 4-3-23C demonstrates that the sodium sulphide was added to form the copper sulphide precipitate first, followed by adding ferric ion and then a pH modifier. In flowsheet Fig. 4-3-23D, the ferric ion and sodium sulphide were added to the solution first; after 10 minutes stirring the pH was adjusted using the pH modifier, then this was followed by flotation by using xanthate as collector.

The flotation results for the above flowsheets Fig. 4-3-23A-D are shown in Fig. 4-3-24, Fig. 4-3-25, Fig. 4-3-26 and Fig. 4-3-27 respectively.

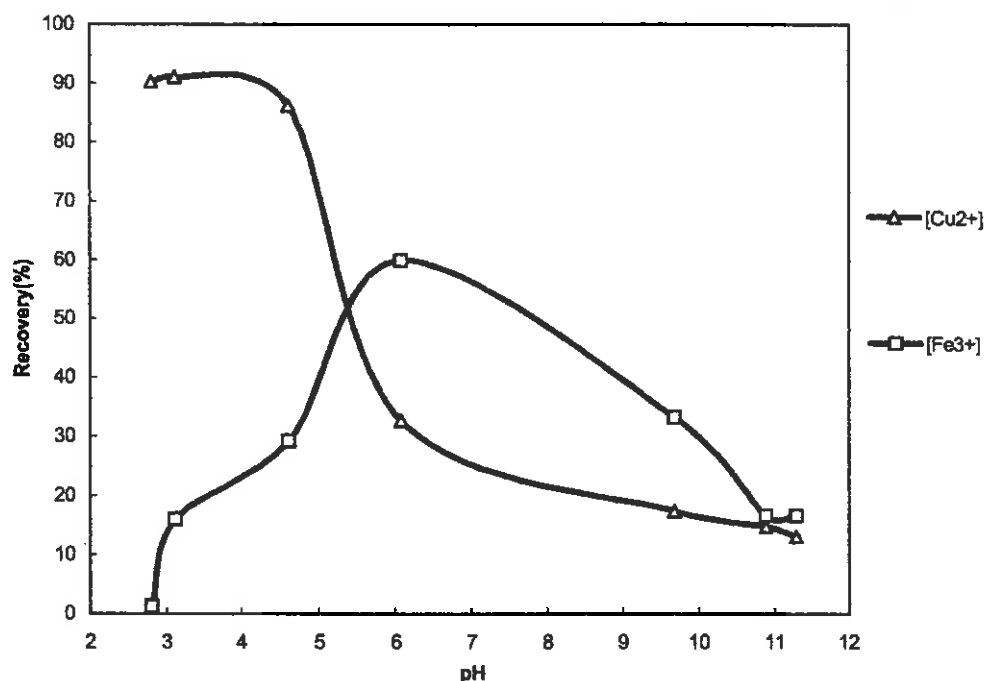


Fig. 4-3-24 The effect  $[Fe^{3+}]$  has on copper sulphide precipitate flotation as a function of pH ( $[Cu^{2+}]_{ini}$  50ppm,  $[Fe^{3+}]:[Cu^{2+}]_{ini}=0.3:1$ ,  $[EtX]:[Cu^{2+}]_{ini}=0.5:1$ ,  $[S^{2-}]:[Cu^{2+}]_{ini}=1:1$ , MAA 9.25ppm) – according to the flowsheet shown in Fig. 4-3-23A

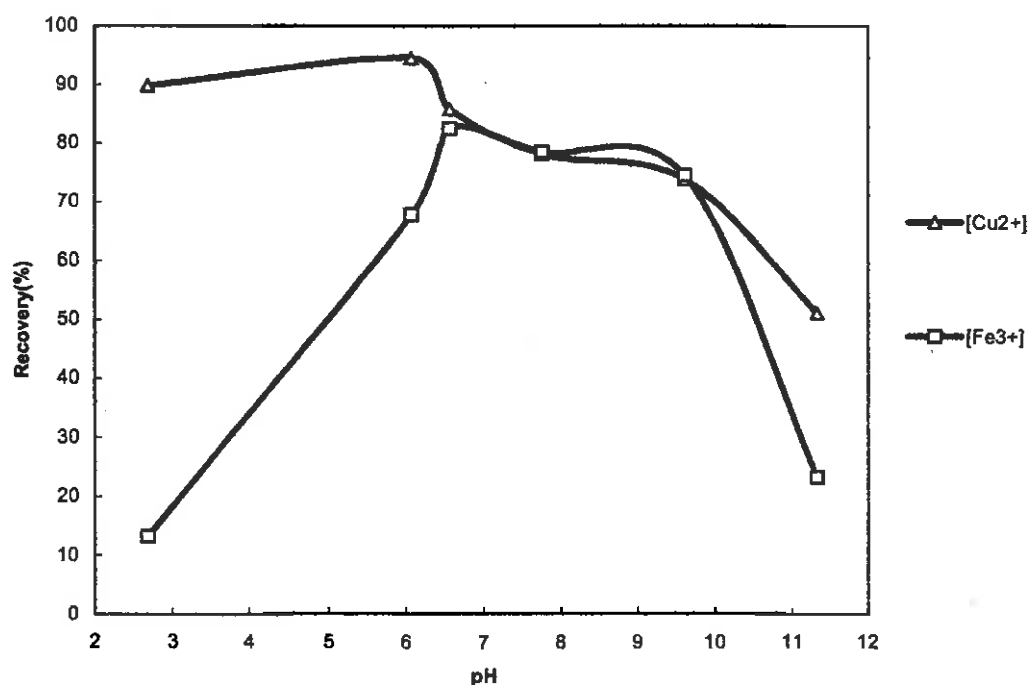


Fig. 4-3-25 The effect  $[Fe^{3+}]$  has on copper sulphide precipitate flotation as a function of pH ( $[Cu^{2+}]_{ini}$  50ppm,  $[Fe^{3+}]:[Cu^{2+}]_{ini}=0.3:1$ ,  $[EtX]:[Cu^{2+}]_{ini}=0.5:1$ ,  $[S^{2-}]:[Cu^{2+}]_{ini}=1:1$ , MAA 9.25ppm) – according to the flowsheet shown in Fig. 4-3-23B

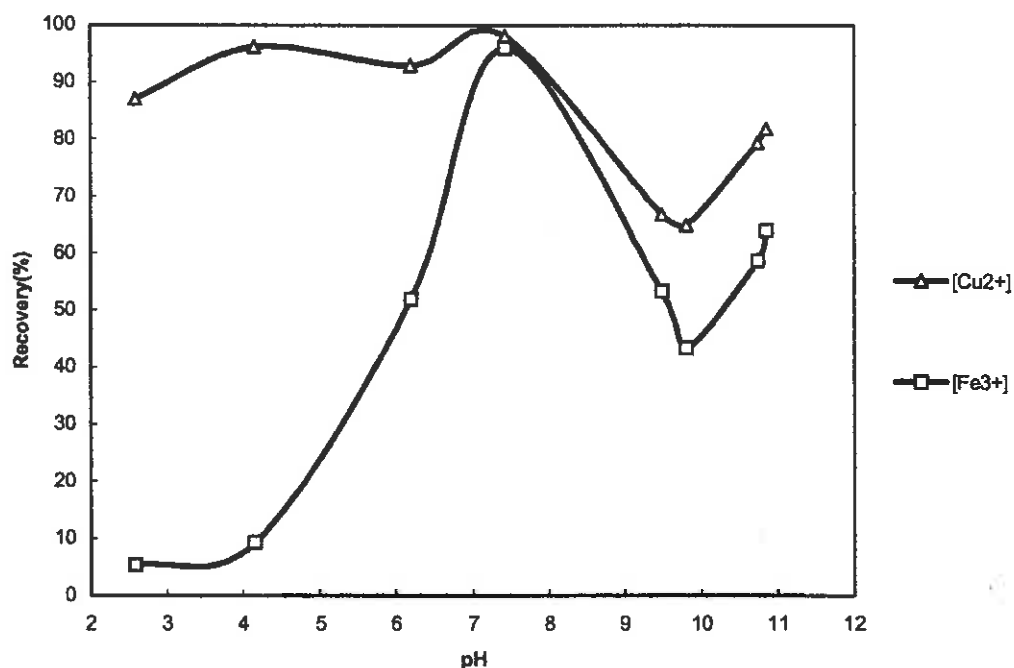


Fig. 4-3-26 The effect  $[Fe^{3+}]$  has on copper sulphide precipitate flotation as a function of pH ( $[Cu^{2+}]_{ini}$  50ppm,  $[Fe^{3+}]:[Cu^{2+}]_{ini}=0.3:1$ ,  $[EtX]:[Cu^{2+}]_{ini}=0.5:1$ ,  $[S^{2-}]:[Cu^{2+}]_{ini}=1:1$ , MAA 9.25ppm) – according to the flowsheet shown in Fig. 4-3-23C

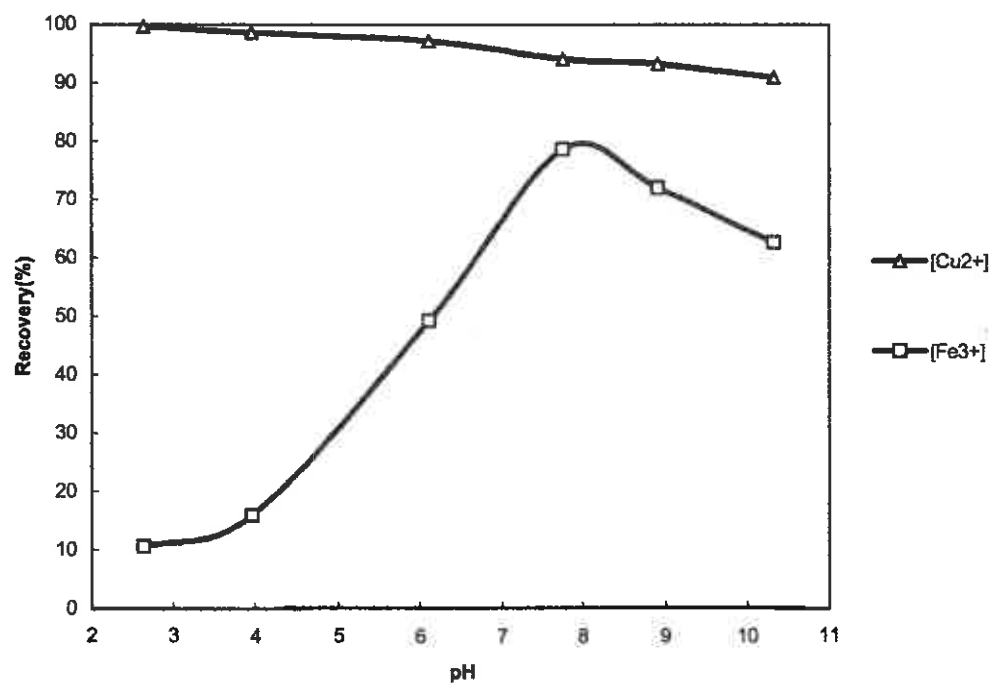


Fig. 4-3-27 The effect  $[Fe^{3+}]$  has on copper sulphide precipitate flotation as a function of pH ( $[Cu^{2+}]_{ini}$  50ppm,  $[Fe^{3+}]:[Cu^{2+}]_{ini}=0.3:1$ ,  $[EtX]:[Cu^{2+}]_{ini}=0.5:1$ ,  $[S^{2-}]:[Cu^{2+}]_{ini}=1:1$ , MAA 9.25ppm) – according to the flowsheet shown in Fig. 4-3-23D

The results shown in Fig. 4-3-24 were derived from the Fig. 4-3-23A flowsheet according to which the copper and ferric ions together in the solution were treated with a pH modifier (normally sodium hydroxide to form hydroxide precipitate) and then with sodium sulphide, followed by xanthate flotation. The flotation results show that when the pH value is higher than pH=4.5, the flotation recovery of copper sulphide precipitate decreases. When the pH is lower than pH=4.5, the flotation is good and the recovery is approximately 90%. When the pH is higher than 3, the flotation recovery of ferric increases. When the pH is in the range of 6-7, the highest ferric recovery can be obtained. Briefly, the results indicate that when copper and ferric ions are present together in a solution, the ferric ion can improve the copper sulphide precipitate flotation. However, when ferric ion has formed as ferric hydroxide precipitate, the flotability of copper sulphide precipitate decreases and part of the ferric hydroxide may be entrained into the foam.

The results shown in Fig. 4-3-25 and Fig. 4-3-26 were obtained from the flowsheets presented in Fig. 4-3-23B and Fig. 4-3-23C, according to which the ferric ion was added after sodium sulphide precipitant (and/or pH modifier) had been added to form copper sulphide precipitate. It is clear from Fig. 4-3-25 that the flotation recovery of copper can reach more than 75% in the pH range of 2.5 to 10. When pH>6.2, the recovery of both copper and ferric becomes the same. As is shown in Fig. 4-3-25, 90% of copper recovery can be obtained when the pH is in the range of 2.5 to 7.2. When pH>7.2, the copper flotation recovery decreases. However, the recovery of ferric becomes almost the same as that of copper while pH>7.2.

The results according to the Fig. 4-3-23D flowsheet process are shown in Fig. 4-3-25. This flowsheet shows that the copper and ferric ions together in the solution were precipitated using sodium sulphide. The copper sulphide precipitate in the solution was oxidized by ferric ion, and then the pH modifier was added followed by xanthate flotation. The flotation results show that the copper recovery was more than 90% in a wide pH range of 2.5 to 10.5. These results support the hypothesis of oxidation at the copper sulphide precipitate surface.

### 3.2.2 Discussion

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### 3.2.2.1 Possible causes for the effect of prolonged stirring and oxidation on copper sulphide precipitate flotation

It has been established in this investigation that prolonged stirring and suitable oxidation can improve the flotation recovery of copper sulphide precipitate, using xanthate as collector. The results obtained appear to support Gardner and Woods (1979) findings in relation to collectorless flotation of sulphide minerals, namely that slight surface oxidation is required for forming elemental sulfur to obtain the hydrophobic surface. The copper sulphide precipitate is thermodynamically unstable in solution in the presence of oxygen, and the precipitate surface can be oxidized depending upon the Eh-pH conditions. Fig. 4-3-28 shows the Eh-pH diagram of the Cu-S-H<sub>2</sub>O system at [Cu]  $7.87 \times 10^{-4}$  (50ppm) and  $[S]_T 7.98 \times 10^{-4} M$  ( $[S]_T:[Cu]_{ini}$ , simplified as 1:1).

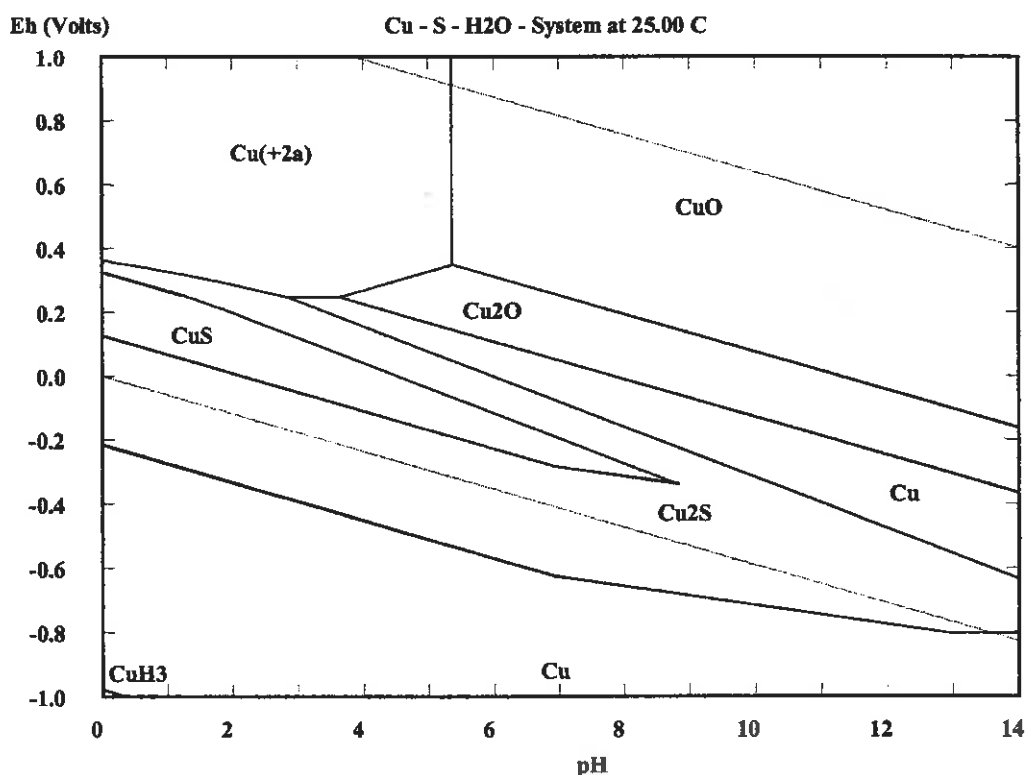


Fig. 4-3-28 Eh-pH diagram of Cu-S-H<sub>2</sub>O system at 25°C at [Cu]  $7.87 \times 10^{-4}$  (50ppm) and  $[S]_T 7.98 \times 10^{-4} M$  ( $[S]_T:[Cu]_{ini}$ , simplified as 1:1)\*\*

\*\* Eh-pH diagram was drawn using Outokumpu HSC Chemistry® for Windows software Version 3.0.

Fig. 4-3-28 shows that CuS may convert to Cu<sub>2</sub>S under slight atmospheric oxidation or reduction conditions:

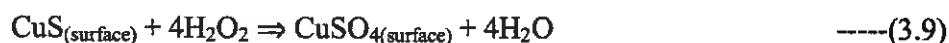


The mechanism of the effect of prolonged stirring and oxidation on copper sulphide precipitate flotation, using xanthate as collector, can be explained by using the chemisorption theory. Chemisorption takes place when adsorbate species become bonded to sites on the copper sulphide precipitate surface. According to this theory, the adsorption of xanthate ion on the copper sulphide precipitate surface occurs as follows:

- (a) Oxidation of surface sulphide to sulphate or thiosulphate by dissolved oxygen from air or added oxidant:

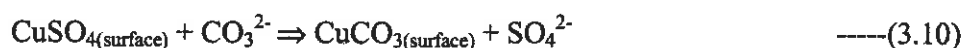


And/or,

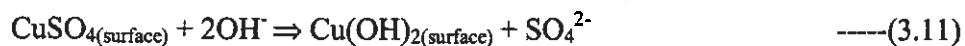


At equilibrium for (3.8), a partial oxygen pressure of approximately  $10^{-53.3}$  atm would be required. This is well exceeded when the partial pressure of oxygen in the air is in the order of 0.2 atm. Even under nitrogen and vacuum atmospheric conditions, it is still possible for enough oxygen to remain in the systems necessary for oxidation.

- (b) Ion-exchange replacement of surface sulphate ion by carbonate ion or hydroxyl ion:



and/or (when pH is high enough),



<sup>††</sup> K was calculated using Outokumpu HSC Chemistry® for Windows software Version 3.0.

It is known that both carbonate and bicarbonate ions may be present in the aerated solution. However, the reaction cannot occur in nitrogen or vacuum conditions.

(c) Ion-exchange replacement of surface sulphate, carbonate and hydroxyl ions by xanthate ion:



Thus, copper xanthates have been formed at the surface of copper sulphide precipitate and subsequently been floated.

The above chemisorption theory explains the phenomena of oxidation (prolonged stirring) on the copper sulphide precipitate flotation. However, more and more evidence indicates that the mechanism of collection is an electrochemical process (Usul and Tolun, 1973; Nicol, 1984; Woods et al., 1990). The following discussion is from an electrochemical point of view to explore the mechanism of the process.

The process rendering the surface hydrophobic is an anodic reaction that transfers electrons from sulphide and collector ions to the precipitate. These electrons are transferred to  $\text{Cu}^{2+}$  ion in copper sulphide precipitate surface or returned to the solution phase by a cathodic reaction such as the reduction of oxygen,

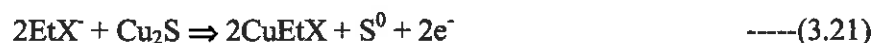
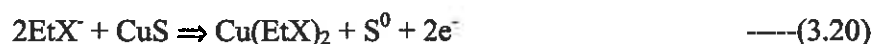


The anodic oxidation reaction in the solution or precipitate surface is probably as follows,





When xanthate is added to the solution, a number of different products may result from anodic oxidation reactions at the precipitate surface,



It can be seen that elemental sulphur can be formed on the copper sulphide precipitate surface or in the solution with the presence or absence of xanthate collector. Elemental sulphur was observed in the copper flotation product from XRD results (refer to Fig. 4-5-6, page 205).

With continued oxidation, sulphide may be further oxidized and result in the formation of oxy-sulphur ions, such as  $\text{S}_2\text{O}_3^{2-}$  and  $\text{SO}_4^{2-}$  ions. When the copper sulphide precipitate is oxidized too much, the sulphide forms soluble oxy-sulphur ions and causes the copper ion to re-dissolve into the solution, hence, the flotation recovery decreases. This is the reason why when the consumption of  $\text{H}_2\text{O}_2$  is more than 1.5 ml, the flotation recovery decreases (see Fig. 4.3.21).

### *3.2.2.2 Possible causes for the effect of ferric ion on copper sulphide precipitate flotation*

It is clear from above test results and discussions that oxidation is very important to copper sulphide precipitate flotation using xanthate as collector. As ferric ion can reduce its valance to ferrous ion, it acts as an oxidant in the solution,



When the concentration of ferric ion in the solution is high, too much oxidation causes the copper sulphide flotation recovery to decrease (see Fig. 4-3-22). For copper sulphide precipitate flotation using xanthate as collector, best results can be obtained when the  $[\text{Fe}^{3+}]:[\text{Cu}^{2+}]$  mole ratio is in the range of 0.3-0.5; when the  $[\text{Fe}^{3+}]:[\text{Cu}^{2+}]$  mole ratio is over 1, the flotation recovery decreases. It is expected that more sulphide ion may be required when  $[\text{Fe}^{3+}]:[\text{Cu}^{2+}] > 1:1$  to obtain good copper flotation recovery.

It was also found that the sequence of addition of the ferric ion in solution significantly affects the flotation recovery of copper sulphide precipitate. If ferric ion is added after copper sulphide precipitate has formed (Fig. 4-3-25 and Fig. 4-3-26), the flotation recovery of copper sulphide precipitate can be improved in the pH range of 2.5 to 10. However, if ferric ion is added before copper sulphide precipitate has formed,  $\text{Fe}^{3+}$  forms  $\text{Fe}(\text{OH})_3$  precipitate ( $\text{pH} > 3$ ) and the flotation recovery of copper sulphide precipitate decreases (see Fig. 4-3-24).

The effect of ferric ion on copper sulphide precipitate flotation may be very complicated due to the fact that the ferric ion may react with copper and sulphide ions and form copper iron sulphide complexes, such as  $\text{CuFeS}_2$ ,  $\text{Cu}_5\text{FeS}_4$  etc., depending upon the Eh in solution and the kinetics of the reactions. No further investigation has been done in this work. However, it is strongly suggested that more research works would have to be done in the future to examine the mechanism involved in the process by using some existing techniques which have been successfully used in studies of sulphide minerals, such as Eh measurements (Rand and Woods, 1984), X-ray photoelectron spectroscopy (XPS) (Buckley and Woods, 1984), in-situ FTIR (Leppinen et al., 1989), etc.

### 3.2.3 Brief Summary

Using xanthate as collector, the flotability of copper sulphide precipitate (with a slight surplus of sulphide ion) is normally very poor. However, with prolonged stirring under air, nitrogen or vacuum atmospheric conditions, it can be significantly improved. Suitable oxidation using an oxidant such as  $\text{H}_2\text{O}_2$  can achieve similar results.

Chemisorption theory and electrochemical reactions were used to hypothesize the mechanism involved in the flotation process. It is suggested that oxidation is the main

reason for the improved effect of prolonged stirring on the copper sulphide precipitate flotation using xanthate as collector.

The presence of a specific amount of ferric ion in the solution can improve the copper sulphide precipitate flotation by using xanthate as collector. However, if the  $[\text{Fe}^{3+}]:[\text{Cu}^{2+}]$  mole ratio is over 1, the flotation recovery decreases. The effects of varying the additional sequences of ferric ion on the copper precipitate flotation were tested.

### 3.3 The effect of extraneous ions on copper sulphide precipitate flotation

Copper is always accompanied by some other ions existing in the waste solution. These ions may influence the copper precipitate flotation behavior. This section considers the influence of some common metal ions on copper sulphide precipitate flotation as well as the mechanism involved in the process. The same flowsheet as shown in Fig. 4-3-23D, designed to illustrate the process of metal ions accompanying copper ion in the solution and its treatment with sulphide precipitant, applies to all the tests in this part.

#### 3.3.1 Results and Discussion

##### 3.3.1.1 *Effect of ferrous ion on copper sulphide precipitate flotation*

With the presence of a specific amount of ferric ion in a solution, it has been shown in this work that the copper sulphide precipitate flotation can be improved. The mechanism involved was considered to be due to the oxidising effect of the ferric ion on the copper sulphide precipitate surface.

Unlike ferric ion, ferrous ion does not have strong oxidation ability. For a better understanding of the influence of iron ions on the copper sulphide precipitate flotation, the effects of ferrous ion at different concentrations ( $[\text{Fe}^{2+}]:[\text{Cu}^{2+}]_{\text{ini}}=0.3:1$  and  $[\text{Fe}^{2+}]:[\text{Cu}^{2+}]_{\text{ini}}=0.7:1$ ) on copper sulphide precipitate flotation were carried out and the results are shown in Fig. 4-3-29 and Fig. 4-3-30.

The flotation recovery of copper sulphide precipitate can be improved with the presence of ferrous ion in the solution when the  $\text{pH}<6$  (Fig. 4-3-29 and Fig. 4-3-30). When the  $\text{pH}<6$ , the flotation recovery of copper sulphide precipitate at  $[\text{Fe}^{2+}]:[\text{Cu}^{2+}]_{\text{ini}}=0.3:1$  is higher than in the case of  $[\text{Fe}^{2+}]:[\text{Cu}^{2+}]_{\text{ini}}=0.7:1$ . However, when the  $\text{pH}>6$ , the flotation recoveries of copper sulphide precipitate at both  $[\text{Fe}^{2+}]:[\text{Cu}^{2+}]_{\text{ini}}=0.3:1$  and  $[\text{Fe}^{2+}]:[\text{Cu}^{2+}]_{\text{ini}}=0.7:1$  conditions decrease rapidly. With  $\text{Fe}^{3+}$  ion (Fig. 4-3-25), the flotation recovery of copper sulphide precipitate is more than 90% in a wide pH range of 2.5 to 10.5. This indicates that the oxidation ability of  $\text{Fe}^{3+}$  ion is the main reason for improving the copper sulphide precipitate flotation.

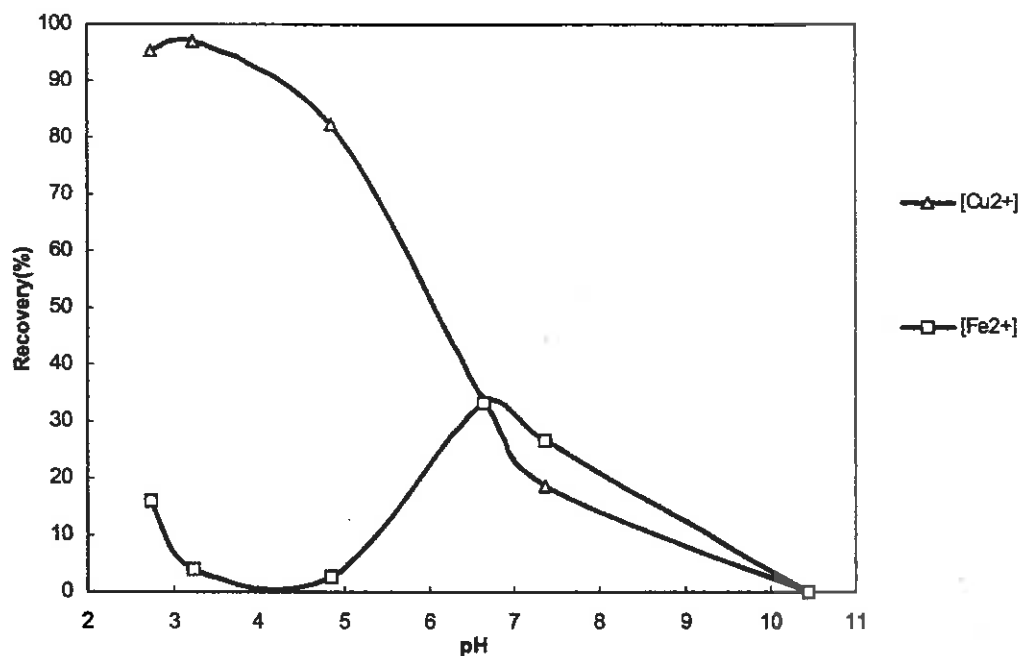


Fig. 4-3-29 The effect of ferrous ion on copper sulphide precipitate flotation as a function of pH ( $[Cu^{2+}]_{ini}$  50ppm,  $[Fe^{2+}]:[Cu^{2+}]_{ini}=0.3:1$ ,  $[EtX]:[Cu^{2+}]_{ini}=0.5:1$ ,  $[S^{2-}]:[Cu^{2+}]_{ini}=1:1$ , MAA 9.25ppm)

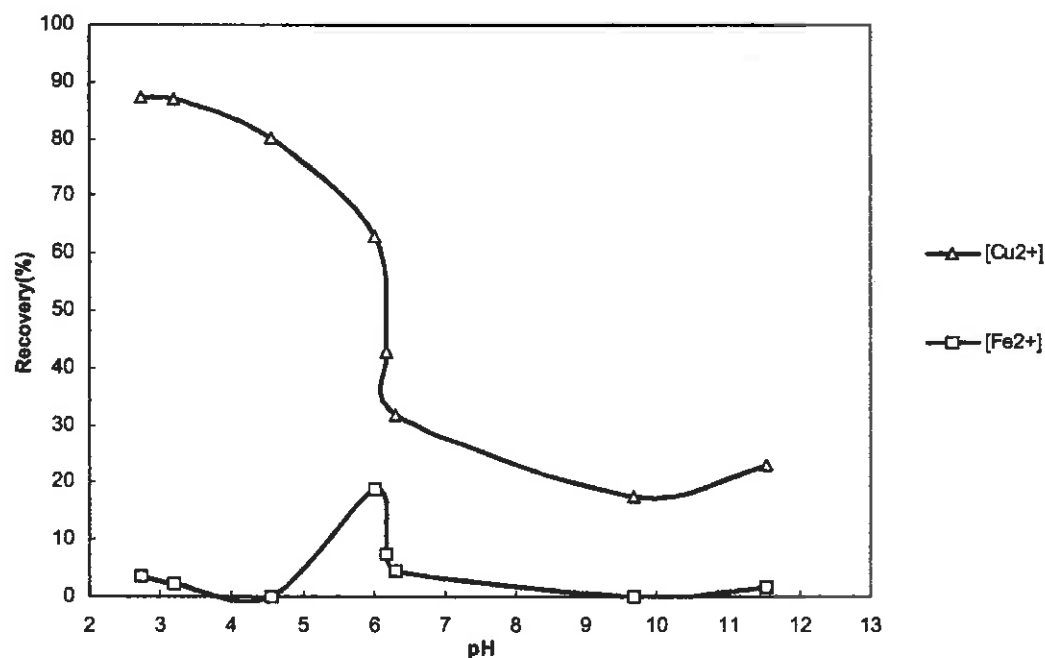


Fig. 4-3-30 The effect of ferrous ion on copper sulphide precipitate flotation as a function of pH ( $[Cu^{2+}]_{ini}$  50ppm,  $[Fe^{2+}]:[Cu^{2+}]_{ini}=0.7:1$ ,  $[EtX]:[Cu^{2+}]_{ini}=0.5:1$ ,  $[S^{2-}]:[Cu^{2+}]_{ini}=1:1$ , MAA 9.25ppm)

The calculated ferrous hydroxide precipitate pH starting point is pH=8 (see Fig. 4-3-31). This is much higher than the flotation decreasing pH point (pH=6) where ferrous ion is present in the solution as shown in Fig. 4-3-29 and Fig. 4-3-30. Thus, the presence of ferrous hydroxide precipitate may not be the reason why the copper sulphide precipitate flotation recovery is reduced.

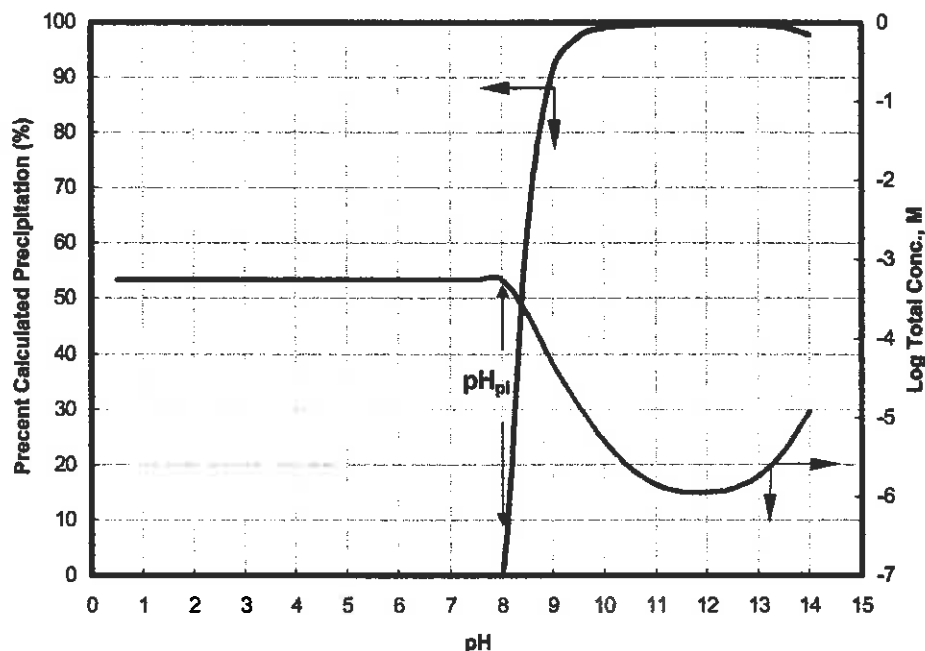


Fig. 4-3-31 Calculated ferrous percentage precipitation and total soluble ferrous species concentration as a function of pH ( $[Fe^{2+}] 5.51 \times 10^{-4} M$ )

Fig. 4-3-32 shows the distribution of soluble ferrous species versus pH in aqueous solution. It shows that:

- When the pH=6, the distribution of  $Fe^{2+}$  ion decreases sharply; when the pH<7.8, the major ferrous hydroxo complex is  $Fe^{2+}$ ;
- $7.8 < pH < 10.5$ , the major complex is  $FeOH^+$ ;
- $10.5 < pH < 13$ , the major complex is  $Fe(OH)_2(aq)$ ;
- pH>13, the major complex is  $Fe(OH)_3^-$ , and amount of the  $Fe(OH)_4^{2-}$  increases.

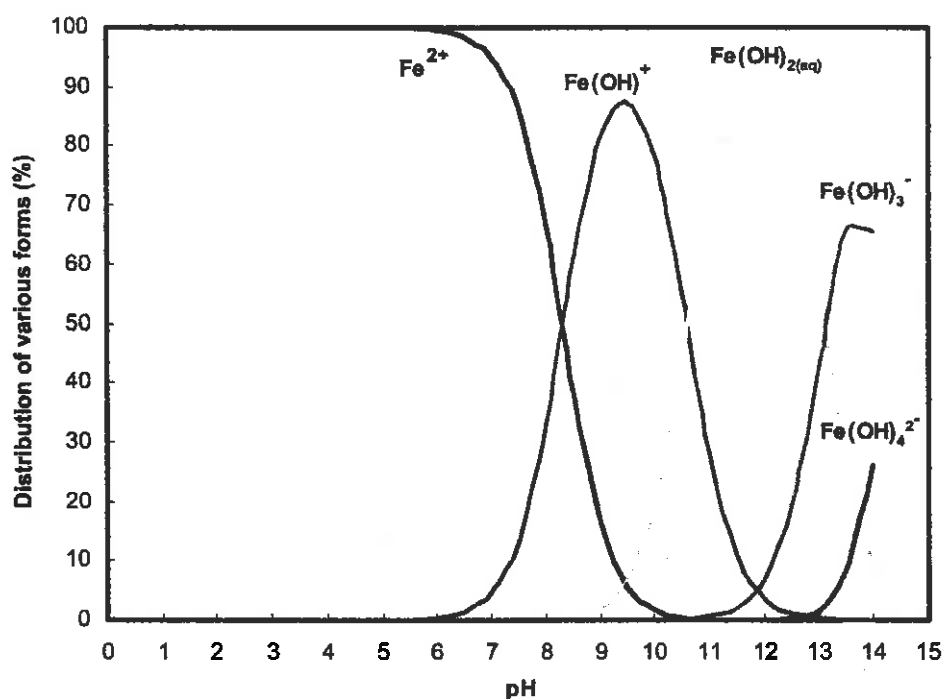


Fig. 4-3-32 The distribution of soluble ferrous species versus pH in aqueous solution

Compared with the flotation results shown in Fig. 4-3-29 and Fig. 4-3-30, the flotation decreasing pH value corresponds well with the distribution of  $[\text{Fe}^{2+}]$  ion in the solution. It is suggested that the  $[\text{Fe}^{2+}]$  species, rather than the  $\text{FeOH}^+$ ,  $\text{Fe}(\text{OH})_{2(\text{aq})}$  or other species, is the main reason for the improved the flotation recovery of copper sulphide precipitate by using xanthate as collector.

### 3.3.1.2 Effect of calcium, magnesium and barium ions on copper sulphide precipitate flotation

Calcium and magnesium ions are the most common extraneous ions existing in copper waste solutions. Understanding the influence of these two ions on the copper sulphide precipitate flotation is very important for subsequent studies of industrial waste flotation and separation. Tests on the effects these two ions have on copper sulphide precipitate flotation, using xanthate as collector, were carried out and the results of these tests have been graphically presented in Fig. 4-3-33 and Fig. 4-3-34.

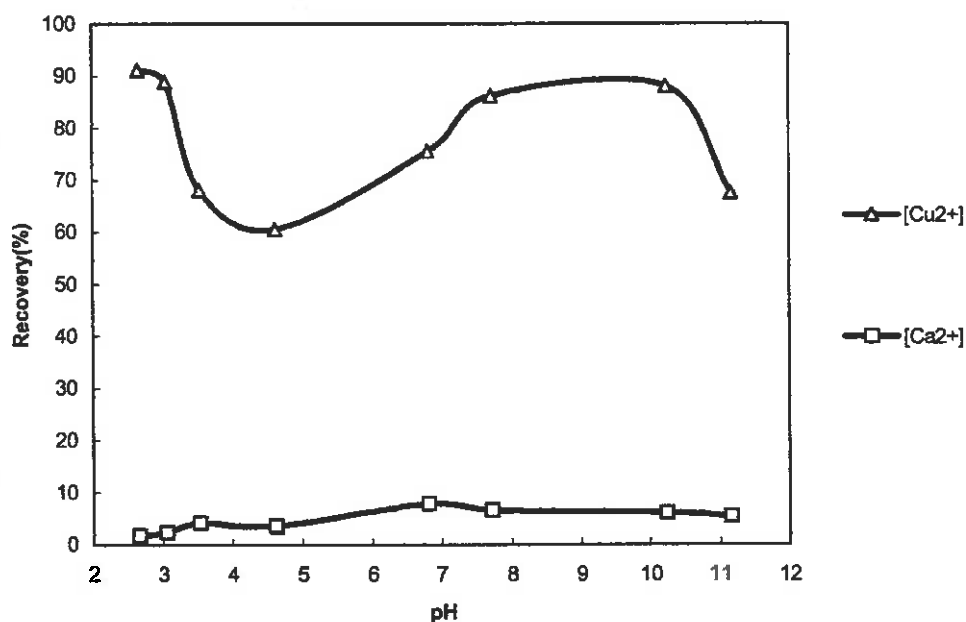


Fig. 4-3-33 The influence of calcium ion on copper sulphide precipitate flotation as a function of pH ( $[Cu^{2+}]_{ini}$  50ppm,  $[Ca^{2+}]:[Cu^{2+}]_{ini}=0.7:1$ ,  $[EtX]:[Cu^{2+}]_{ini}=0.5:1$ ,  $[S^{2-}]:[Cu^{2+}]_{ini}=1:1$ , MAA 9.25ppm)

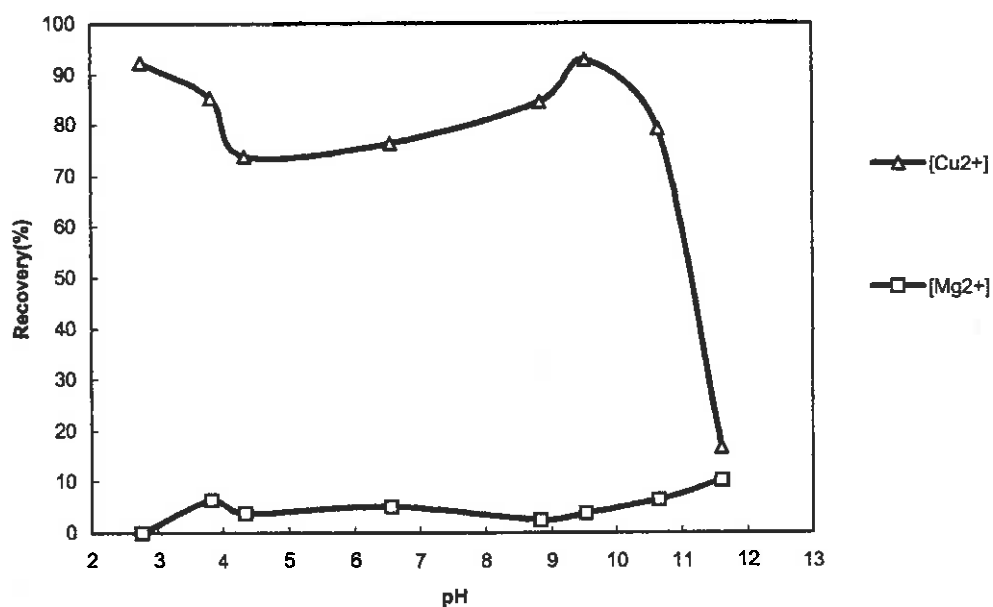


Fig. 4-3-34 The influence of magnesium on copper sulphide precipitate flotation as a function of pH ( $[Cu^{2+}]_{ini}$  50ppm,  $[Mg^{2+}]:[Cu^{2+}]_{ini}=0.7:1$ ,  $[EtX]:[Cu^{2+}]_{ini}=0.5:1$ ,  $[S^{2-}]:[Cu^{2+}]_{ini}=1:1$ , MAA 9.25ppm)



When calcium ion is present in the solution, the flotation recovery of copper sulphide precipitate is significantly improved in a wide pH range (Fig. 4-3-33). The calcium recovery in the solution remains at a very low level with the variation of pH. When the  $\text{pH} > 10.5$ , the flotation recovery of copper begins to decrease. (Note: copper sulphide precipitate flotation without extraneous ions is shown in Fig. 4-3-3)

The effect of magnesium ion is similar to that of calcium ion. The flotation recovery of the copper sulphide precipitate is quite high when magnesium ion is present in a pH range of 2.5 to 10.5 (Fig. 4-3-34). However, When the  $\text{pH} > 9.8$ , the flotation recovery of copper begins to decrease. The recovery of magnesium remains at a very low level in the pH range of 2.5 to 10.5. The effects of calcium or magnesium concentration on the copper sulphide precipitate flotation are shown in Fig. 4-3-35.

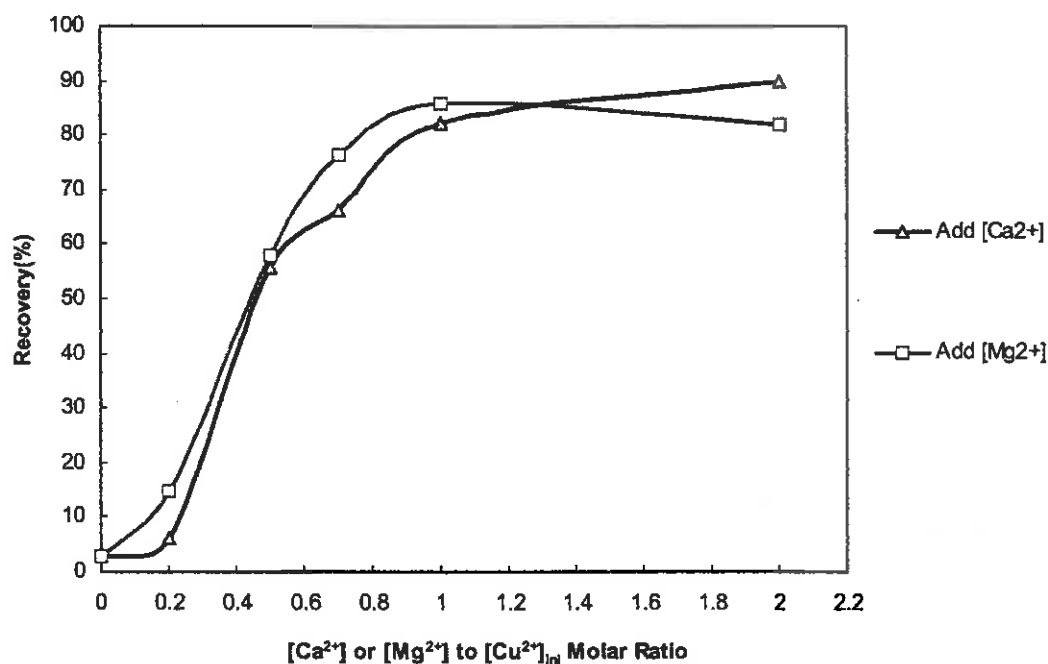


Fig. 4-3-35 The influence of calcium or magnesium concentration on the copper sulphide precipitate flotation using xanthate as collector ( $[\text{Cu}^{2+}]_{\text{ini}} 50\text{ppm}$ ,  $[\text{EtX}]:[\text{Cu}^{2+}]_{\text{ini}}=0.5:1$ ,  $[\text{S}^{2-}]:[\text{Cu}^{2+}]_{\text{ini}}=1:1$ , MAA 9.25ppm,  $\text{pH } 6.0 \pm 0.5$ )

The flotation recovery of copper increases with an increase of calcium or magnesium concentration when the calcium or magnesium to  $[\text{Cu}^{2+}]_{\text{ini}}$  mole ratio is in the range of 0

to 1 (Fig. 4-3-35). When the calcium or magnesium to  $[\text{Cu}^{2+}]_{\text{ini}}$  mole ratio is greater than 1, the flotation recovery of copper remains constant at about 80%.

Fig. 4-3-36 and Fig. 4-3-37 show the distribution percentage of soluble calcium or magnesium species versus pH in an aqueous solution.

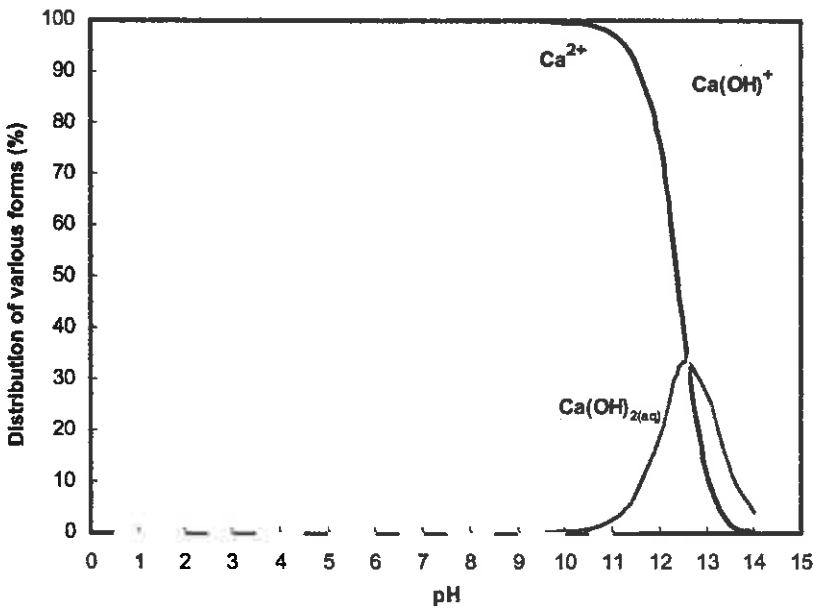


Fig. 4-3-36 The distribution of soluble calcium species versus pH in an aqueous solution

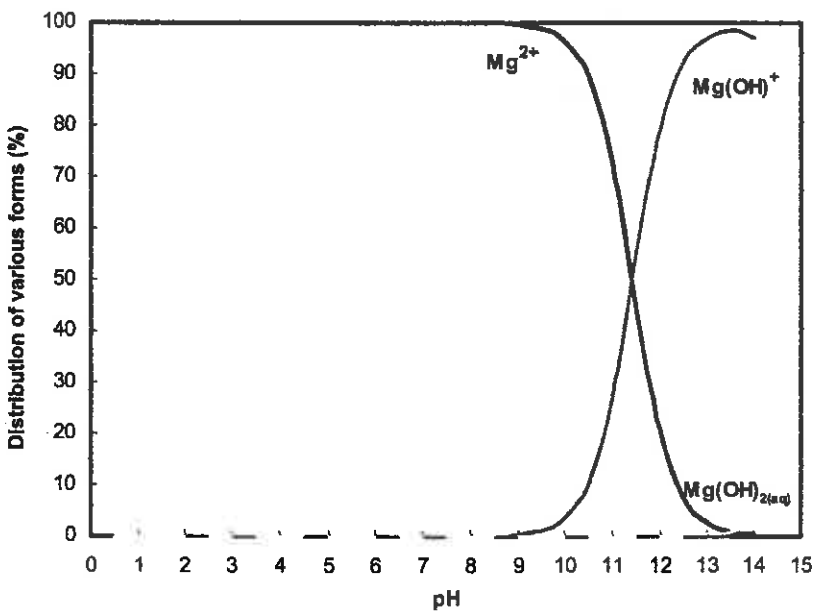


Fig. 4-3-37 The distribution of soluble magnesium species versus pH in an aqueous solution

Fig. 4-3-36 shows that:

- When the pH=10.5, the distribution of  $\text{Ca}^{2+}$  ion decreases sharply; pH<12.5, the major calcium hydroxo complex is  $\text{Ca}^{2+}$ ;
- pH>12.5, the major complex is  $\text{CaOH}^+$ ;
- 10.5<pH<12.5,  $\text{Ca(OH)}_{2(\text{aq})}$  increases; the maximum distribution percentage is approximate 32%; when pH>12.5,  $\text{Ca(OH)}_{2(\text{aq})}$  decreases.

Fig. 4-3-37 shows that:

- When pH=9.5, the distribution of  $\text{Mg}^{2+}$  ion decreases sharply; pH<11.3, the major magnesium hydroxo complex is  $\text{Mg}^{2+}$ ;
- pH>11.3, the major complex is  $\text{MgOH}^+$ ;
- pH>14,  $\text{Mg(OH)}_{2(\text{aq})}$  begins to increase, however the distribution percentage is very small.

When we compare the distribution percentages of calcium and magnesium shown in Fig. 4-3-36 and Fig. 4-3-37 with the flotation results shown in Fig. 4-3-33 and Fig. 4-3-34, it is clear that the decreasing pH points of the  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  species correspond well with the pH point where the copper flotation recovery begins to decrease. The conclusion drawn from these results is the same as from the effect of ferrous shown in Fig. 4-3-29 and Fig. 4-3-30, that is, the presence of divalent metal species may be the main reason for improvement in the copper sulphide precipitate flotation.

### ***3.3.1.3 Effect of zinc ion on copper sulphide precipitate flotation***

One of the main objectives of this thesis is to study the separation of copper and zinc ions from waste solution. An investigation on the effect of zinc ion on the copper sulphide precipitate flotation is in this context of considerable importance.

The effect of zinc ion on the copper sulphide precipitate flotation as a function of pH is shown in Fig. 4-3-38.

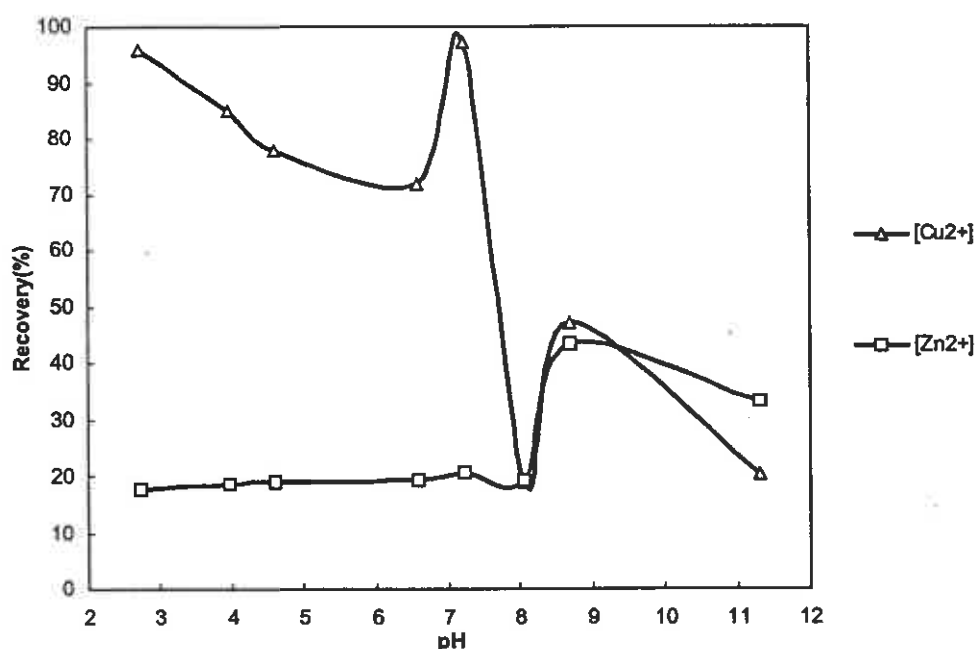


Fig. 4-3-38 The effect of zinc ion on copper sulphide precipitate flotation as a function of pH ( $[Cu^{2+}]_{ini}$  50ppm,  $[Zn^{2+}]:[Cu^{2+}]_{ini}=0.7:1$ ,  $[EtX]:[Cu^{2+}]_{ini}=0.5:1$ ,  $[S^{2-}]:[Cu^{2+}]_{ini}=1:1$ , MAA 9.25ppm)

When zinc ion is present in the solution, the flotation recovery of copper sulphide can be improved provided the pH is in the range of 2.5 to 7 (see Fig. 4-3-38). However, when the  $pH > 7$ , the recovery of copper decreases significantly. A closer look at the distribution of the zinc hydroxo species in the aqueous solution (refer to Fig. 4-1-12) shows that the pH point at which the copper recovery decreases corresponds to that at which the divalent zinc species ( $[Zn^{2+}]$  ion) decreases. When the pH is about 9, the flotation recoveries of both copper and zinc are approximately 45%. It is assumed that at this pH, the zinc hydroxide precipitate was formed and un-selectively aggregated with the copper sulphide precipitate.

The effect of zinc concentration on the copper sulphide precipitate flotation is shown in Fig. 4-3-39.

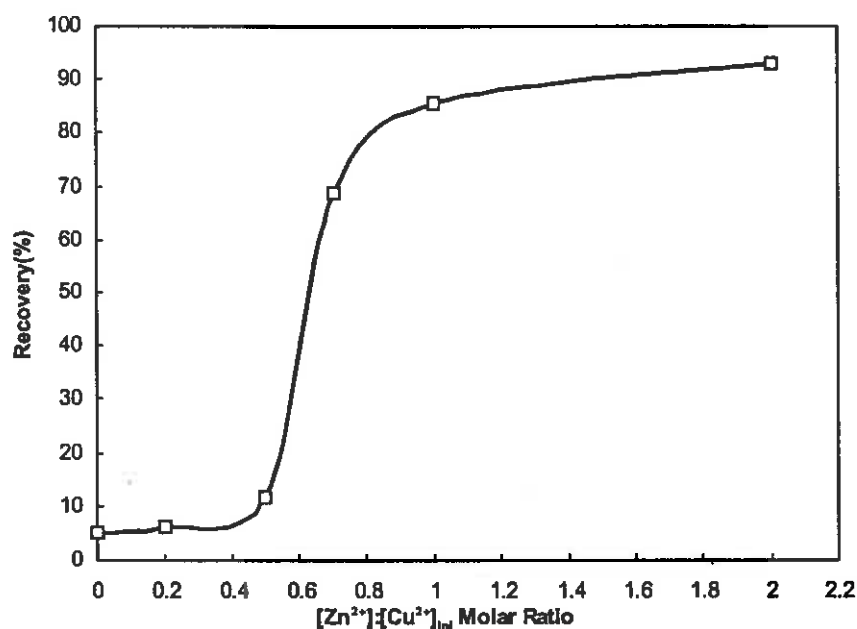


Fig. 4-3-39 The influence of zinc concentration on the copper sulphide precipitate flotation using xanthate as collector ( $[Cu^{2+}]_{in}$  50ppm,  $[EtX]:[Cu^{2+}]_{in}=0.5:1$ ,  $[S^{2-}]:[Cu^{2+}]_{in}=1:1$ , MAA 9.25ppm, pH  $6.0\pm0.5$ )

When the zinc to copper mole ratio is lower than 0.5 in the solution, the flotation recovery of copper remains very low; however, when the mole ratio is higher than 0.5, the flotation recovery increases sharply. At a zinc to copper mole ratio of 2, the flotation recovery of copper reaches approximately 95%.

The above findings are based on the assumption that the molar concentration of copper in the solution is close to that of zinc. However, in some cases such as that of the tailing wastewater from a mineral processing plant, of the Woodlawn Mines (N.S.W., Australia), the molar concentration of zinc in the waste solution is approximately twenty times higher than that the copper molar concentration. The Woodlawn tailing wastewater was chosen for the final separation tests (see Chapter III), hence variable copper to zinc ratios need to be considered.

Tests in which the zinc to copper mole ratio was 20 were carried out and the results are graphically presented in Fig. 4-3-40.

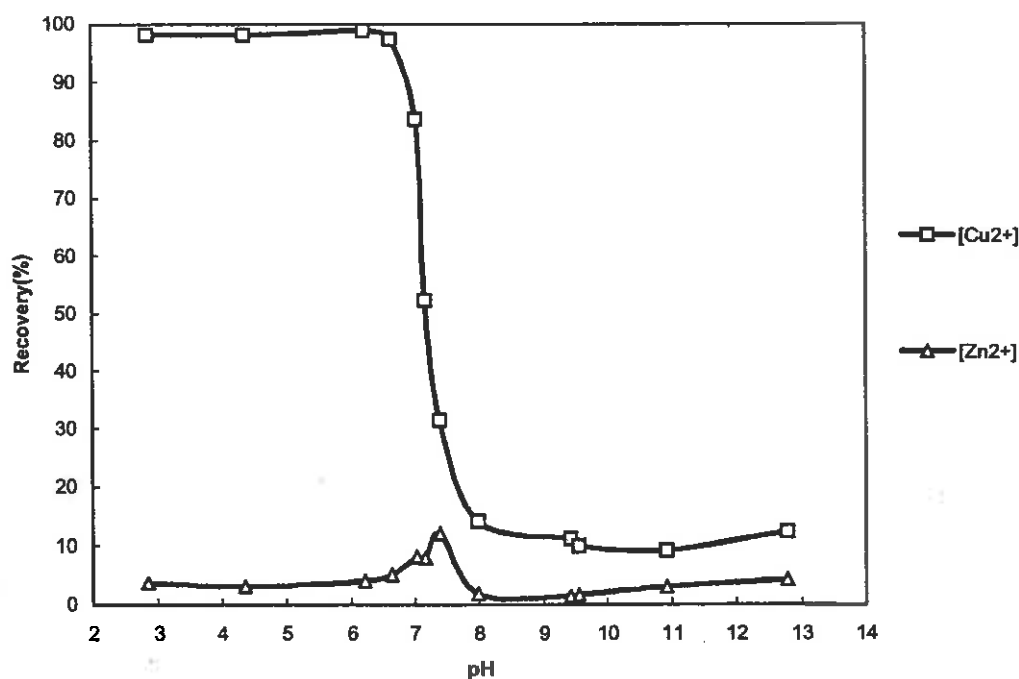


Fig. 4-3-40 The influence of zinc ion on copper sulphide precipitate flotation as a function of pH ( $[Cu^{2+}]_{ini}$  50ppm,  $[Zn^{2+}]:[Cu^{2+}]_{ini}=20:1$ ,  $[EtX]:[Cu^{2+}]_{ini}=0.5:1$ ,  $[S^{2-}]:[Cu^{2+}]_{ini}=1:1$ , MAA 9.25ppm)

When  $[Zn^{2+}]:[Cu^{2+}]_{ini}$  is 20:1, the tendency of the copper flotation recovery (see Fig. 4-3-40) is very similar to the case when  $[Zn^{2+}]:[Cu^{2+}]_{ini}$  is 0.7:1 (refer to Fig. 4-3-38). More than 98% of copper flotation recovery can be obtained in the pH range of 2.5 to 7 when  $[Zn^{2+}]:[Cu^{2+}]_{ini}$  is 20:1, this is a better and more stable recovery than in the case when  $[Zn^{2+}]:[Cu^{2+}]_{ini}$  is 0.7:1 (refer to Fig. 4-3-38). Zinc flotation recovery remains at a very low level. However, when the  $pH > 7$ , the copper flotation recovery decreases rapidly, which is also the pH point at which the divalent zinc species ( $[Zn^{2+}]$  ion) decreases. Thus, the flotation separation of copper and zinc ions in the solution is possible by using sulphide precipitant and xanthate as collector.

The influence of sulphide precipitant consumption on the copper flotation recovery when  $[Zn^{2+}]:[Cu^{2+}]_{ini}$  is 20:1 has been graphically presented in Fig. 4-3-41.

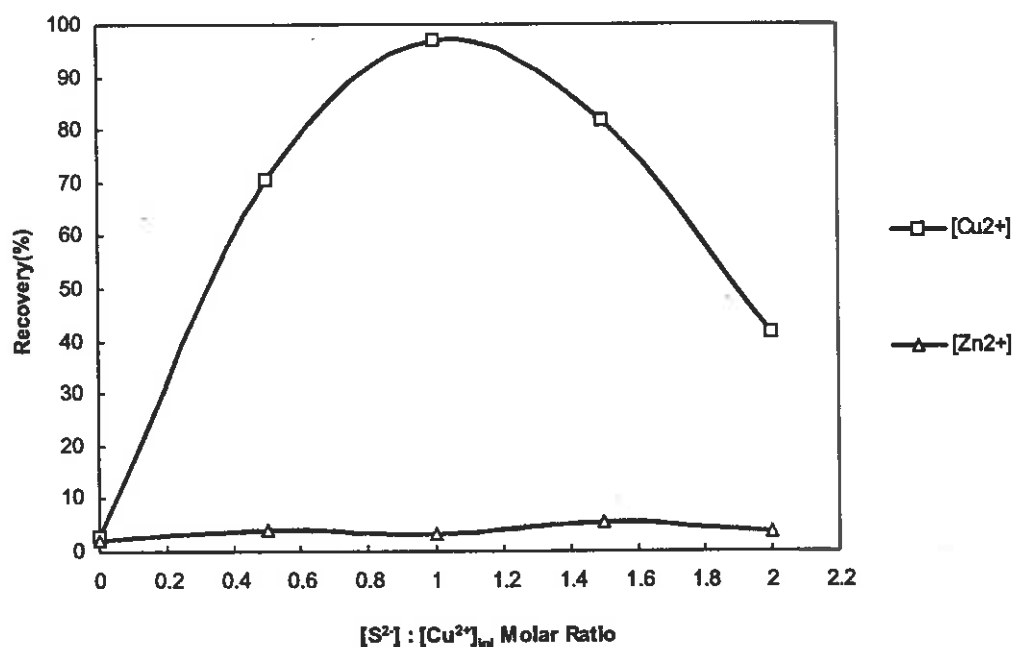


Fig. 4-3-41 The influence of sulphide precipitant concentration on the copper flotation recovery using xanthate as collector ( $[Cu^{2+}]_{ini}$  50ppm,  $[Zn^{2+}]:[Cu^{2+}]_{ini}=20:1$ ,  $[EtX]:[Cu^{2+}]_{ini}=0.5:1$ , MAA 9.25ppm, pH  $6.0 \pm 0.5$ )

The highest copper flotation recovery was obtained when the molar amount of the sulphide precipitant is the same as that of the copper ion (see Fig. 4-3-41). Yet, when  $[Zn^{2+}]:[Cu^{2+}]_{ini}=20:1$  (at pH= $6.0 \pm 0.5$ ), there should have been plenty of divalent zinc species in the solution, however when  $[S^{2-}]:[Cu^{2+}]>1$ , the copper flotation recovery decreased (Fig. 4-3-40). It is assumed that the surplus sulphide ion reacted with zinc ion and form zinc sulphide precipitate covering the surface of the copper sulphide precipitate; the ethyl xanthate not being a good collector for zinc sulphide, hence causing the decrease in copper flotation recovery. According to this assumption, the addition of some copper ion to replace the zinc ion on the precipitate surface, should increase the copper flotation recovery. Tests demonstrating the effect of additional copper ion on the copper sulphide precipitate flotation at  $[S^{2-}]:[Cu^{2+}]_{ini}=2:1$  and  $[Zn^{2+}]:[Cu^{2+}]_{ini}=20:1$  were carried out. The results are graphically presented in Fig. 4-3-42.

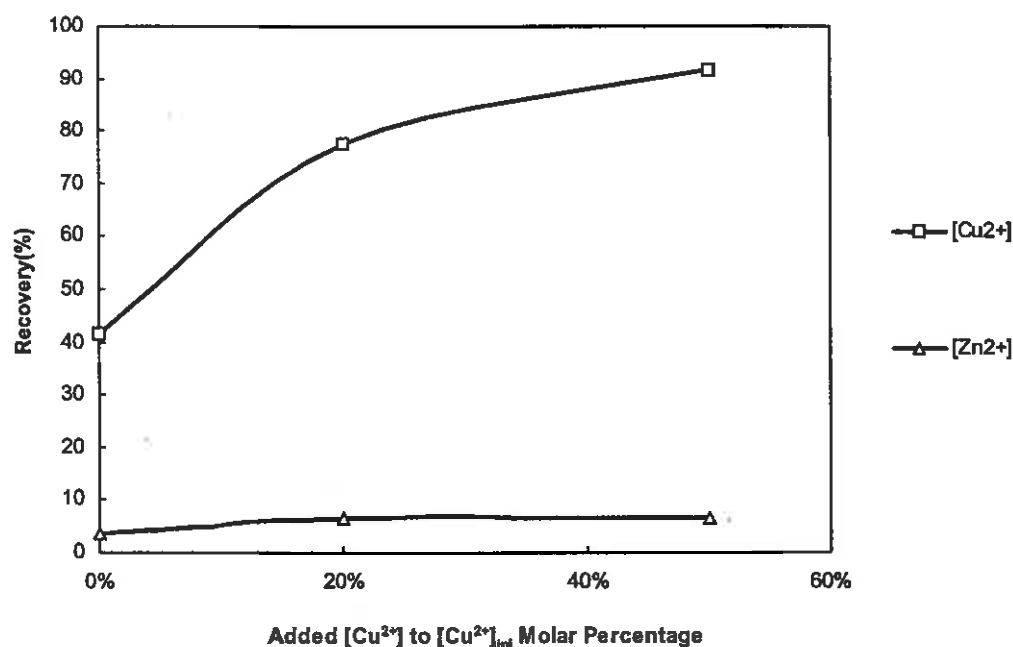


Fig. 4-3-42 The effect of additional copper ion on the copper flotation recovery using xanthate as collector ( $[Cu^{2+}]_{ini}$  50ppm,  $[Zn^{2+}]:[Cu^{2+}]_{ini}=20:1$ ,  $[EtX]:[Cu^{2+}]_{ini}=0.5:1$ ,  $[S^{2-}]:[Cu^{2+}]_{ini}=2:1$ , MAA 9.25ppm, pH  $6.0 \pm 0.5$ )

As was assumed, the copper flotation recovery increased with an additional copper concentration at  $[S^{2-}]:[Cu^{2+}]_{ini}=2:1$  and  $[Zn^{2+}]:[Cu^{2+}]_{ini}=20:1$ . When copper ion is added to  $[Cu^{2+}]_{ini}$  with a 50% molar percentage, the copper flotation recovery can exceed 90% (see Fig. 4-3-42).

### 3.3.1.4 Model of the effect of divalent ion on copper sulphide precipitate flotation

The divalent metal ions in the solution are considered to act as a catalyst, assisting the negatively charged xanthate ion to overcome the repulsive energy from the highly negatively charged copper sulphide surface. The xanthate ion can then attach itself onto the copper sulphide precipitate surface and lead to flotation.

The mechanism of adsorption of xanthate ion on the copper sulphide precipitate surface, with the association of divalent ions, takes place in the following steps:



(a) The free divalent metal ion in the solution combines with xanthate ion and forms the positive charged species:

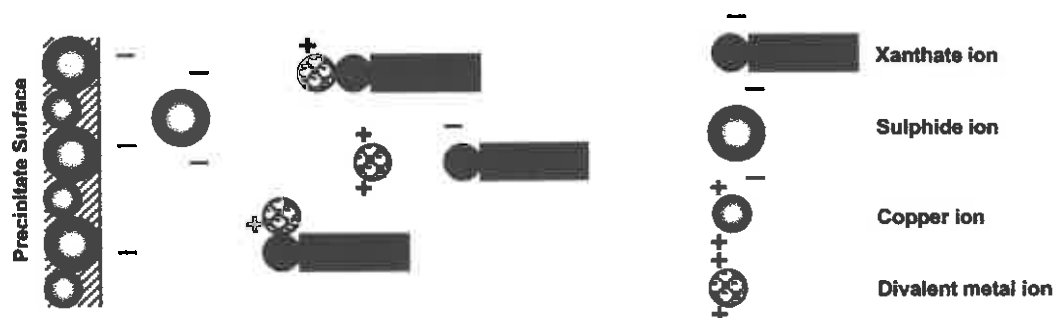


Fig. 4-3-43a Schematic representation of the divalent metal ions improving the copper sulphide precipitate flotation: the divalent metal ion and xanthate ions forming the positively charged species

(b) The positively charged species attach onto the highly negatively charged copper sulphide precipitate surface. The xanthate ion then bonds with the copper ion on the sulphide precipitate surface and the divalent metal ion returns to the solution:

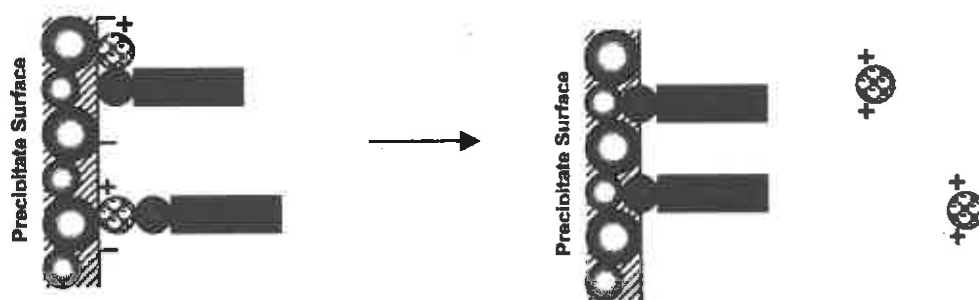
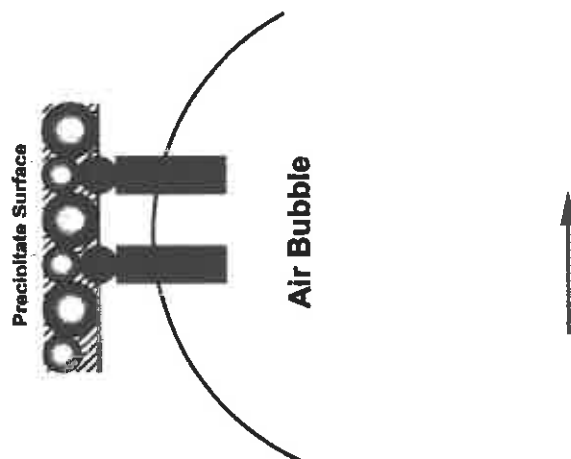


Fig. 4-3-43b Schematic representation of the divalent metal ions improving the copper sulphide precipitate flotation: the positively charged species (with xanthate ions) attaching to the copper sulphide precipitate surface and the divalent metal ion returns to the solution

(c) The copper sulphide precipitates with xanthate adsorbed on the surface, attach to the air bubble and is subsequently floated:



*Fig. 4-3-43c Schematic representation of the divalent metal ions improving the copper sulphide precipitate flotation: copper sulphide precipitate with adsorbed xanthate attaching the air bubble and able to be taken into the froth.*

The above schematic description demonstrates how the divalent metal ions improve the copper sulphide precipitate flotation. When the concentration of divalent metal ions in the solution begins decrease and hydroxyl metal complexes such as univalent metal hydroxyl ( $\text{MeOH}^+$ ) increase, the xanthate ion may still form other species with metal hydroxyl. However, as it is neutral it does not easily attach itself to the highly negatively charged copper sulphide precipitate surface. Hence, the copper flotation recovery decreases.

### 3.3.2 Brief Summary

Some extraneous ions, such as  $\text{Fe}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Zn}^{2+}$ , present in the solution can improve the flotation recoveries of copper sulphide precipitate at specific pH values, depending on the distribution of the divalent metal ions in the solution.

The divalent metal ion in the solution appears to be the main reason for improved copper flotation recovery. It is suggested that the divalent metal ions act as a catalyst assisting the

xanthate ion to overcome the repulsive energy from the highly negatively charged copper sulphide surface.

When the zinc concentration in the solution is 20 times higher than that of the copper, flotation results show that copper can be readily floated using sodium sulphide as precipitant and xanthate as collector in a pH range of 2.5 to 7. The zinc recovery remains very low. The flotation separation can then be achieved.

### 3.4 Zinc sulphide precipitate flotation using xanthate as collector

In mineral flotation, zinc sulphide (sphalerite) cannot normally be easily floated using short chain xanthates such as sodium ethyl xanthate. In this part, the zinc sulphide precipitate flotation behavior is reported.

#### 3.4.1 Results and Discussion

##### 3.4.1.1 Zinc sulphide precipitate flotation behavior using ethyl xanthate as collector

Ethyl xanthate has never been a good collector for zinc sulphide minerals, neither is it therefore a good collector for zinc sulphide precipitate. The flotation results (see Fig. 4-3-44) show that the zinc sulphide precipitate cannot be floated over a wide pH range of 3 to 11 by using sodium ethyl xanthate as collector, under these conditions.

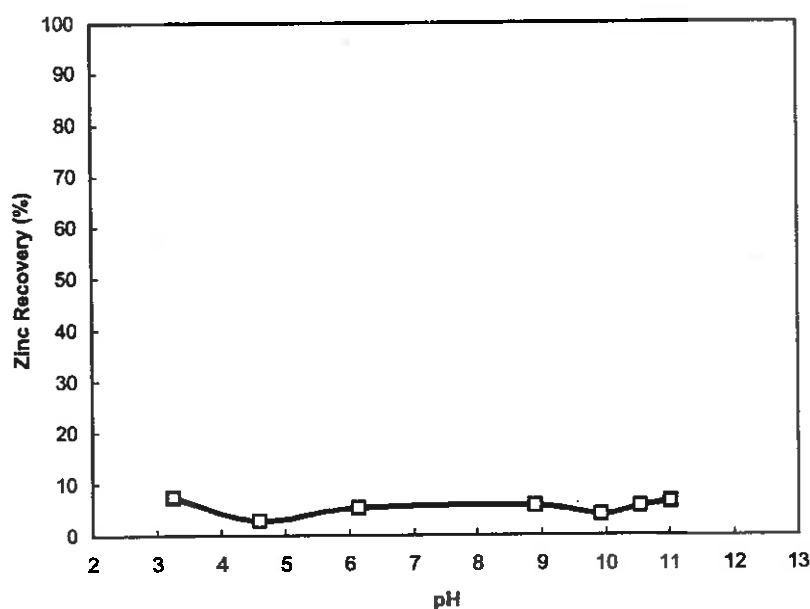


Fig. 4-3-44 Effect of pH on the zinc sulphide precipitate flotation using sodium ethyl xanthate as collector ( $[Zn^{2+}]_{ini}$  50ppm,  $[S^{2-}]:[Zn^{2+}]_{ini}=1:1$ ,  $[EtX]:[Zn^{2+}]_{ini}=0.5:1$ , MAA 9.25ppm)

When the ethyl xanthate concentration is increased, the flotation recovery of zinc sulphide precipitate remains very low (see Fig. 4-3-45). Even when the molar concentration of  $[\text{EtX}]$  is twice that of the zinc ion, the zinc flotation recovery remains less than 10%.

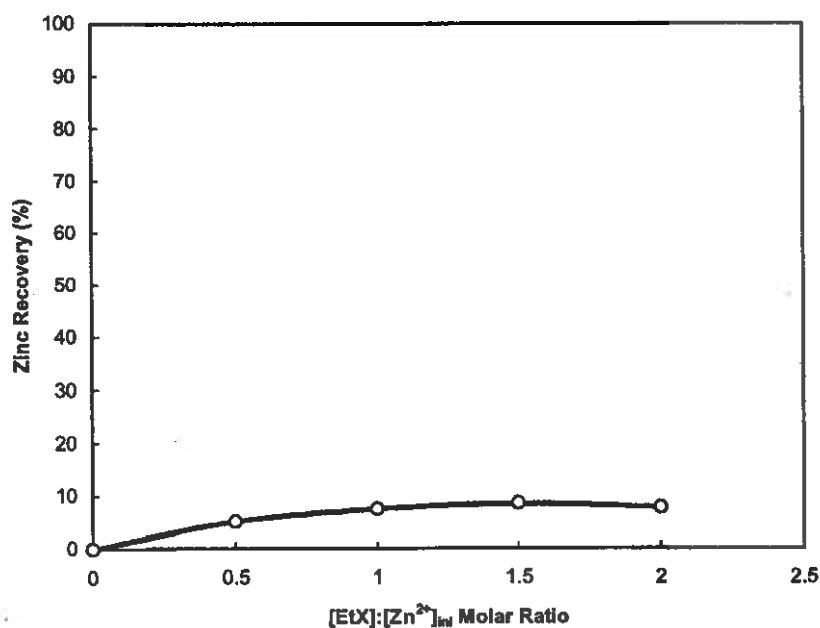


Fig. 4-3-45 Effect of concentration of sodium ethyl xanthate on the zinc sulphide precipitate flotation ( $[\text{Zn}^{2+}]_{\text{ini}} 50\text{ppm}$ ,  $[\text{S}^{2-}]:[\text{Zn}^{2+}]_{\text{ini}}=1:1$ , MAA 9.25ppm, pH  $6.5 \pm 0.2$ )

### 3.4.1.2 Zinc sulphide precipitate flotation using $\text{Cu}^{2+}$ as activator

In zinc sulphide mineral flotation, copper sulphate is widely used as an activator for sphalerite (zinc sulphide). The copper ions alter the sphalerite surface into a copper sulphide surface. The activated zinc sulphide becomes coated with a very thin film of  $\text{CuS}$ , which can be floated with simple short chained collectors such as ethyl xanthate.

Flotation tests were carried out to investigate whether zinc sulphide precipitate can be activated by copper sulphate and then be floated with ethyl xanthate. Precipitation tests using centrifugal method on the zinc precipitation, in which the copper concentration was varied, were also carried out. The results are shown in Fig. 4-3-46.

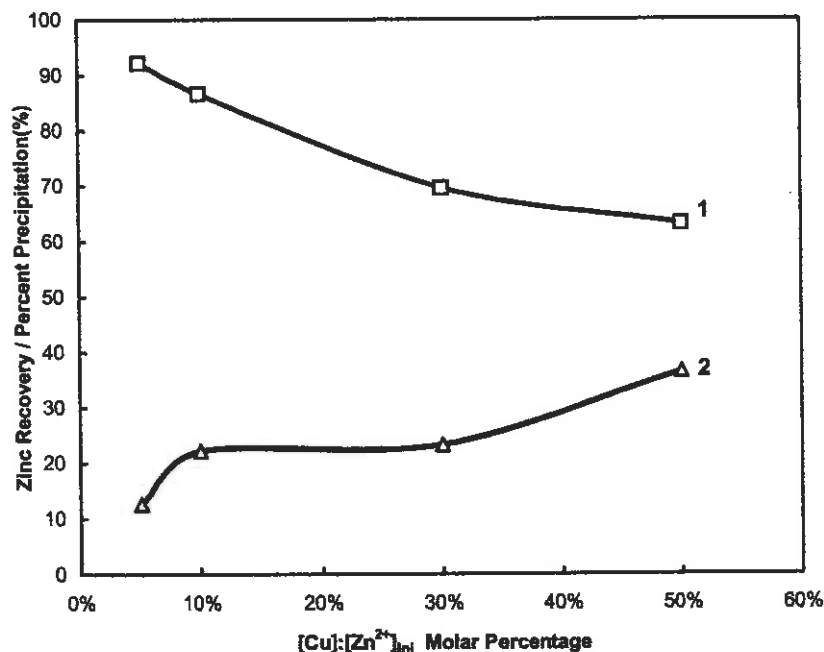


Fig. 4-3-46 Effect of added  $[Cu^{2+}]$  concentration on zinc sulphide precipitate precipitation and flotation ( $[Zn^{2+}]_{ini}$  50ppm,  $[S^{2-}]:[Zn^{2+}]_{ini}=1:1$ , pH  $6.2\pm0.2$ )

1--- Percent Precipitation, centrifugal separation 4000rpm 20 min without xanthate and frother  
 2--- Flotation recovery,  $[EtX]:[Zn^{2+}]_{ini}=0.5:1$ , MAA 9.25 ppm.

The above results show that when the concentration of the added copper activator is increased, there is a limited increase in the flotation recovery of the zinc sulphide precipitate (see Fig. 4-3-46 line 2). Even when the copper concentration is increased to 50% (by mole) of the zinc, the flotation recovery of the zinc sulphide precipitate remains less than 40%. The reason can be explained from the results of the precipitation tests. The percentage precipitation of the zinc sulphide decreases when the copper activator concentration increases (see Fig. 4-3-46 line 1). When the copper concentration is 50% of zinc, the percentage precipitation of the zinc sulphide precipitate is down to approximately 65%. This means that, as the particle size of zinc sulphide precipitate is very fine, most of the copper ions simply replaced the zinc ion from the zinc sulphide precipitate and formed individual particles of the copper sulphide precipitate, rather than coating onto the zinc sulphide precipitate surface. The replaced zinc ions were re-dissolved into the solution. From Fig. 4-3-46 it appears that the zinc flotation recovery

cannot be significantly improved using copper ion as activator and short-chained xanthate as collector for activating the flotation of zinc sulphide precipitate cannot be applied.

In the flotation of oxidized non-ferrous metal ores, sodium sulphide is commonly used as activator to coat the mineral surface and copper sulphate then added to form copper sulphide on the mineral surface followed by flotation using xanthate as collector. A further trial was carried out to investigate whether this method can also be used for zinc sulphide precipitate flotation.

The solution containing 50ppm zinc ion was treated with sodium hydroxide to form zinc hydroxide precipitate; then 20% mole ratio of sodium sulphide to zinc ion was added to sulphidize the zinc hydroxide precipitate surface, followed by addition of copper activator, and finally using xanthate to float. The flotation results are presented in Fig. 4-3-47.

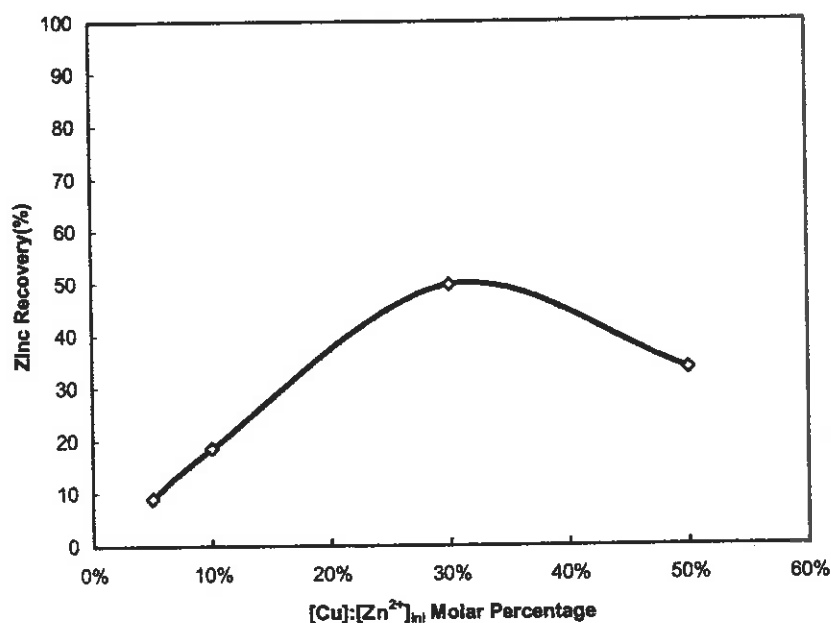


Fig. 4-3-47 Effect of added  $[Cu^{2+}]$  on the flotation recovery of zinc hydroxide precipitate activated by sodium sulphide and using ethyl xanthate as collector ( $[Zn^{2+}]_{ini}$  50ppm,  $[S^{2-}]:[Zn^{2+}]_{ini} = 0.2:1$ ,  $[EtX]:[Zn^{2+}]_{ini} = 0.5:1$ , MAA 9.25 ppm, pH  $7.8 \pm 0.5$ )

Maximum zinc flotation recovery was only approximately 50% when the added copper ion to zinc molar concentration was 30% (see Fig. 4-3-47). Clearly, this is also not an effective method for zinc precipitate flotation.

### 3.4.2 Brief Summary

Ethyl xanthate is not a good collector for zinc sulphide precipitate in a wide pH range of 3 to 11. In spite of increased ethyl xanthate concentration, the flotation recovery of the zinc sulphide precipitate remains very low.

No reasonable flotation recovery could be obtained by using copper ion as activator and ethyl xanthate as collector to float zinc sulphide or hydroxide precipitate with sulphide as activator. The main reason being the particle size of zinc sulphide precipitate which is so fine that individual particles of copper sulphide precipitate are formed rather than the copper coating the zinc sulphide precipitate surface.



### **3.5 Selective separation of copper and zinc ions from a synthetic waste solution by sulphide precipitate flotation using xanthate as collector**

The above findings (Section 3.1-3.4) indicate that flotation separation of copper and zinc ions from waste solution is possible, using sodium sulphide as precipitant and sodium ethyl xanthate as collector. However, the findings are based on a simple aqueous system, in which the flotation of copper or zinc ions in pure water system or in the presence of other single ions were investigated. Industrial waste solutions are normally very complex, i.e., a number of ions are present in one solution. This will probably influence the flotation separation.

A synthetic waste solution, containing different ions, similar to the tailing wastewater from the Woodlawn Mines Pty. (Australia), was used for the flotation separation tests. Sodium sulphide was used as precipitant and sodium ethyl xanthate was the collector. A trial, using sodium IsoButyl Xanthate (denoted hereafter as IBXt) as collector to float zinc sulphide together with copper and cadmium sulphide precipitate, was also carried out.

#### **3.5.1 Synthetic Waste Solution and the Flotation Process**

In accordance with the outcome of the chemical analyses of the tailing wastewater from the Woodlawn Mines (Australia), a synthetic waste solution was prepared from specific chemical reagents (refer to Chapter III, page 39). To keep the flotation tests stable, ten liters of synthetic waste solution were prepared in a container for all the tests.

The flotation process is presented in the flowsheet shown in Fig. 4-3-48: the synthetic solution was precipitated using a sulphide precipitant first, followed by addition of xanthate and the frother, and finally the solution was moved to the flotation column for five minutes flotation. The ion concentrations remaining in the solution were analyzed for the recovery calculation. This is the same as the normal flotation process adopted in the above tests.

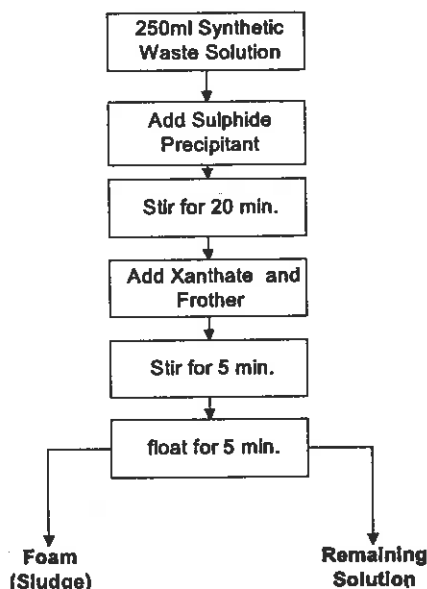


Fig. 4-3-48 Flowsheet of flotation process for synthetic waste solution

### 3.5.2 Results and Discussion

#### 3.5.2.1 Selective precipitation and flotation separation of copper ion from the synthetic solution by using ethyl xanthate as collector

The selective flotation results of copper ion from the synthetic solution using sodium sulphide as precipitant and sodium ethyl xanthate as collector, as a function of the sulphide precipitant concentration, are listed in Table 4-3-1 and are graphically presented in Fig. 4-3-49.

The best copper flotation recovery (more than 90%) can be obtained when the  $[S^{2-}]$  to  $[Cu^{2+}]$  mole ratio is in the range of 1.5 to 1.75, using ethyl xanthate as collector (Table 4-3-1 and Fig. 4-3-49). It is assumed that the reason why the mole ratio is higher than that required in Fig. 4-3-41 (page 158), is because of the presence of the ferric ions (150ppm) in the synthetic solution. The ferric ions oxidized the sulphide ions resulting in formation of oxy-sulphur ions, such as  $S_2O_3^{2-}$  and  $SO_4^{2-}$  ions (refer to section 3.2). Therefore, in order to precipitate all the copper ions from the synthetic solution in the presence of the ferric ions, more sulphide precipitant was required.

Table 4-3-1 Selective flotation of copper ion from the synthetic solution by using sulphide as precipitant and ethyl xanthate as collector\*

Test No.	pH	$[S^{2-}]:[Cu^{2+}]$ Mole ratio	Metal Ion Conc. in the Solution after Flotation (ppm)			Flotation Recovery (%)		
			Cu	Zn	Cd	Cu	Zn	Cd
1	2.86	0.75:1	90.24	1969	10.23	9.76	1.55	0
2	2.87	1:1	67.44	1997	10.11	32.56	0.15	0
3	2.91	1.25:1	38.49	1954	10.08	61.51	2.30	0
4	3.02	1.5:1	9.26	1967	9.84	90.74	1.65	2.6
5	3.04	1.75:1	6.58	1975	8.76	93.42	1.25	12.4
6	3.42	5:1	88.3	1832	10.07	11.7	8.40	0

\*  $[Cu^{2+}]_{ini}$  100ppm,  $[Zn^{2+}]_{ini}$  2000ppm,  $[Cd^{2+}]_{ini}$  10ppm,  $pH_{ini}$  2.7,  $[EtX]:[Cu^{2+}]_{ini}$  mole ratio 0.4:1, MAA 6ppm

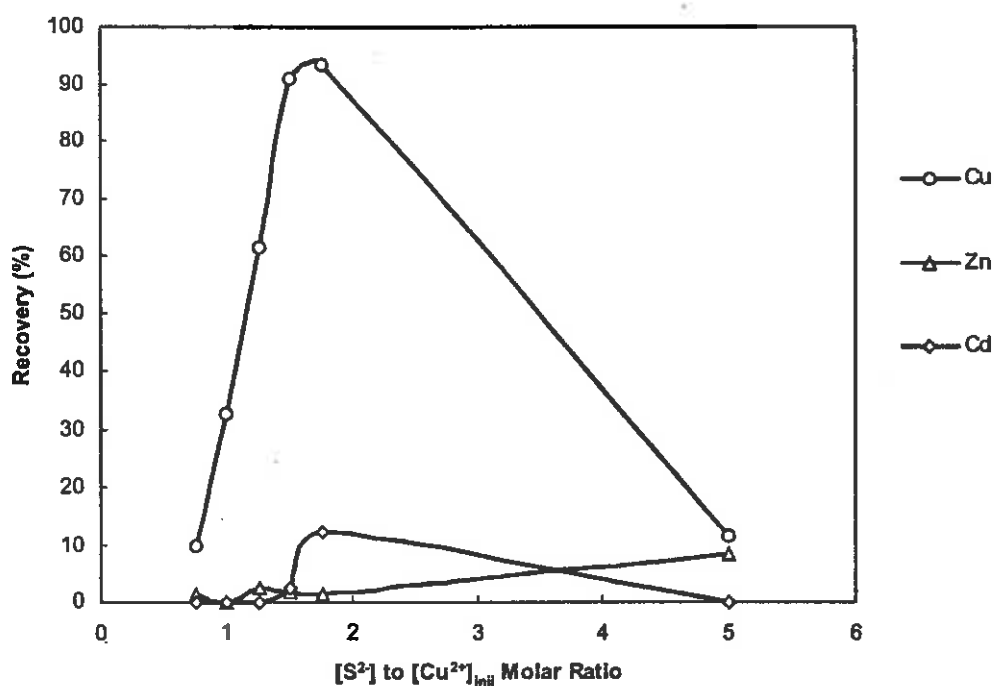


Fig. 4-3-49 Effect of sulphide concentration on copper flotation recovery from the synthetic solution by using sulphide as precipitant and ethyl xanthate as collector ( $[Cu^{2+}]_{ini}$  100ppm,  $[Zn^{2+}]_{ini}$  2000ppm,  $[Cd^{2+}]_{ini}$  10ppm,  $pH_{ini}$  2.7,  $[EtX]:[Cu^{2+}]_{ini}$  mole ratio 0.4:1, MAA 6ppm)

When the  $[S^{2-}]$  to  $[Cu^{2+}]$  mole ratio is more than 1.75, the copper flotation recovery decreases. It is considered that this occurred because the zinc sulphide precipitate was formed and it covered the surface of the copper sulphide precipitate (refer to section 3.2).

The zinc flotation recovery remained very low during the flotation process. Therefore, copper ion can be selectively floated ion from the synthetic solution, with the zinc ions remaining in the solution.

#### ***3.5.2.2 Zinc, copper and cadmium sulphide precipitate flotation from the synthetic solution by using isobutyl xanthate as collector***

Sodium isobutyl xanthate has a stronger capability for collecting zinc sulphide than ethyl xanthate. Due to the limited scope of this research project, it was not included in this work. However, a trial, using sodium isobutyl xanthate as collector to float together zinc, copper and cadmium sulphide precipitates from the synthetic solution, was carried out and the flotation results are presented in Table 4-3-2. The best flotation results of these tests are graphically presented in Fig. 4-3-50.

As copper and cadmium ions can react with sulphide ions more strongly than zinc ions, using sulphide precipitant, the formation of copper and cadmium sulphide precipitate precedes the formation of zinc sulphide precipitate. To precipitate zinc ions from the solution, the concentration of copper and cadmium ions must therefore be taken into account. Hereafter,  $[M]_T$  will be used to represent the total concentration of the zinc, copper and cadmium ions in the synthetic solution. The concentrations of the sulphide precipitant and isobutyl xanthate collector will be compared with this  $[M]_T$ .

Zinc, copper and cadmium sulphide precipitate can easily be floated from the synthetic solution by using isobutyl xanthate as collector (Table 4-3-2). When the concentration of sulphide precipitant is slightly greater than the  $[M]_T$  and the  $[IBXt]$  to  $[M]_T$  mole ratio is 0.1:1, flotation recoveries of 98.58% copper, 93.88% zinc, and 96.52% cadmium can be obtained (see Fig. 4-3-50).

Table 4-3-2 Flotation results of zinc, copper and cadmium sulphide precipitates from the synthetic solution by using sodium isobutyl xanthate as collector\*

Test No.	Flotation Conditions	Metal Ion Conc. in the Solution after Flotation (ppm)			Flotation Recovery (%)		
		Cu	Zn	Cd	Cu	Zn	Cd
1	$[\text{IBXt}]:[\text{M}]_{\text{T}}^{**}=0.02:1$ $[\text{S}^{2-}]:[\text{M}]_{\text{T}}=1.05:1$ $\text{pH}=4.31$	32.31	953.75	4.911	67.69	52.31	50.89
2	$[\text{IBXt}]:[\text{M}]_{\text{T}}=0.05:1$ $[\text{S}^{2-}]:[\text{M}]_{\text{T}}=1.05:1$ $\text{pH}=4.35$	4.34	213.25	0.742	95.66	89.34	92.58
3	$[\text{IBXt}]:[\text{M}]_{\text{T}}=0.1:1$ $[\text{S}^{2-}]:[\text{M}]_{\text{T}}=1.05:1$ $\text{pH}=4.21$	1.42	122.5	0.348	98.58	93.88	96.52
4	$[\text{IBXt}]:[\text{M}]_{\text{T}}=0.1:1$ $[\text{S}^{2-}]:[\text{M}]_{\text{T}}=1:1$ $\text{pH}=4.13$	4.44	228.75	0.682	95.56	88.56	93.18
5	$[\text{IBXt}]:[\text{M}]_{\text{T}}=0.1:1$ $[\text{S}^{2-}]:[\text{M}]_{\text{T}}=0.9:1$ $\text{pH}=4.01$	4.88	352.5	0.838	95.12	82.38	91.62
6	$[\text{IBXt}]:[\text{M}]_{\text{T}}=0.1:1$ $[\text{S}^{2-}]:[\text{M}]_{\text{T}}=0.7:1$ $\text{pH}=4.03$	11.1	697.5	1.77	88.9	65.13	82.3

\*  $[\text{Cu}^{2+}]_{\text{ini}} 100\text{ppm}$ ,  $[\text{Zn}^{2+}]_{\text{ini}} 2000\text{ppm}$ ,  $[\text{Cd}^{2+}]_{\text{ini}} 10\text{ppm}$ ,  $\text{pH}_{\text{ini}} 2.7$ ,  $\text{MAA } 6\text{ppm}$ \*\*  $[\text{M}]_{\text{T}}$  is the total concentration of zinc, copper and cadmium ions in the solution

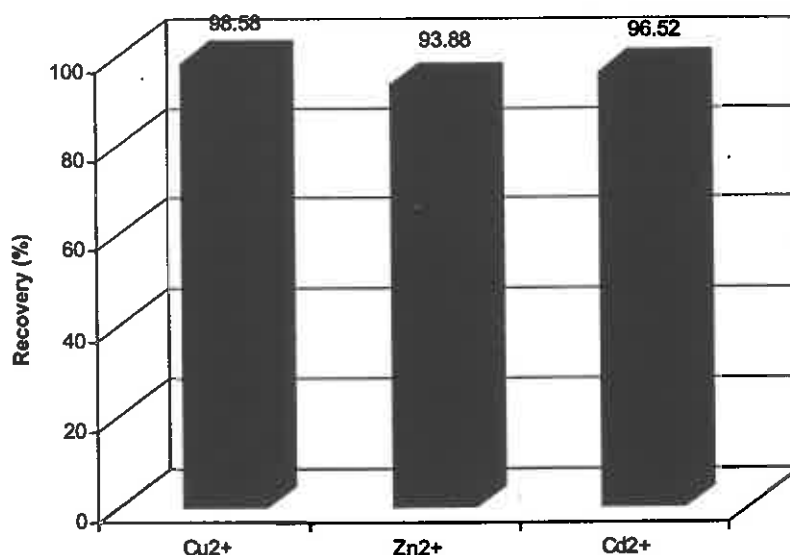


Fig. 4-3-50 The best flotation results of zinc, copper and cadmium sulphide precipitates from the synthetic solution by using isobutyl xanthate as collector (refer to Table 4-3-2 test 3,  $[Cu^{2+}]_{ini}$  100ppm,  $[Zn^{2+}]_{ini}$  2000ppm,  $[Cd^{2+}]_{ini}$  10ppm,  $pH_{ini}$  2.7,  $[IBXt]:[M]_T=0.1:1$ ,  $[S^{2-}]:[M]_T=1.05:1$ , MAA 6ppm, pH 4.21)

The isobutyl xanthate shows a good ability to float zinc sulphide precipitate in suitable conditions. In accordance with the limited scope of this research project, the matter has not been further investigated. The potential usage of isobutyl (or other carbon chain) xanthate for flotation of zinc sulphide precipitate has been established however.

### 3.5.3 Brief Summary

It has been demonstrated that copper ion can be selectively floated from the synthetic solution by using sodium sulphide as precipitant and sodium ethyl xanthate as collector, with the zinc ions remaining in the solution. A  $[S^{2-}]$  to  $[Cu^{2+}]$  mole ratio over the range of 1.5 to 1.75 is required to obtain the maximum recovery because of oxidation of copper sulphide precipitate surface caused by the reduction of ferric ions in the solution.

A trial, using sodium isobutyl xanthate as collector to float zinc, copper and cadmium sulphide precipitate together from the synthetic solution, has brought to light a good potential for sodium isobutyl xanthate to float out zinc sulphide precipitate.

### 3.6 Section Conclusion

- Copper sulphide precipitation was found to be significantly more efficient than copper hydroxide precipitation. However, the particle size of the copper sulphide precipitate is so fine that a slight surplus of sulphide precipitant prevents the copper sulphide precipitate from being floated when xanthate is used as collector.
- The copper sulphide precipitate can be efficiently floated when using xanthate as collector over wide pH range of 2.5-11.5 with a surplus of copper ion. It is thought that in the process the surplus copper ion adsorbs onto the copper sulphide precipitate surface, decreasing its negative surface charge, and/or combining with the sulphide precipitate particles, thereby improving the flotation.
- The flotability of copper sulphide precipitate (with a slight surplus of sulphide ion) can be significantly improved over a prolonged stirring (more than 12 hours) in air, nitrogen or vacuum atmospheres. Suitable oxidation using an oxidant such as  $H_2O_2$  can achieve similar results.
- Oxidation of the copper sulphide precipitate surface is considered to be the main reason for the improvement of the copper sulphide precipitate flotation. Chemisorption and electrochemical reactions were used to explain the mechanism involved in the flotation process.
- Excessive oxidation of the copper sulphide precipitate causes the copper ion to re-dissolve into the solution, and the flotation recovery decreases.
- A specific amount of ferrous ion in the solution can improve the copper sulphide precipitate flotation. Too much ferrous ion in solution will cause the flotation recovery to decrease. It is suggested that this mechanism is the result of over-oxidation.

- Extraneous ions, such as  $\text{Fe}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Zn}^{2+}$  ions, can improve the copper sulphide precipitate flotation in a specific pH range, depending on the distribution of the divalent metal ions in the solution.
- The divalent metal ion species in the solution is considered to be the main reason for improved copper flotation recovery. It is suggested that the divalent metal ions act as a catalyst assisting the xanthate ion to overcome the repulsive energy from the highly negatively charged copper sulphide surface.
- When the zinc concentration is much higher than that of copper in the solution, copper ion can easily be floated using sodium sulphide as precipitant and xanthate as collector in pH range of 2.5 to 7. The zinc recovery remains very low. The flotation separation can thus be achieved.
- Ethyl xanthate is not a good collector for zinc sulphide precipitate in a wide pH range of 3 to 11. As the particle size of zinc sulphide precipitate is very fine, using copper ion as activator and ethyl xanthate as collector to float zinc sulphide or hydroxide (with sulphide as activator) precipitate no reasonable flotation recovery could be obtained.
- Copper ions can be selectively floated from the synthetic solution by using sodium sulphide as precipitant and sodium ethyl xanthate as collector, with the zinc ions remaining in the solution. A  $[\text{S}^{2-}]$  to  $[\text{Cu}^{2+}]$  mole ratio over the range of 1.5 to 1.75 is required to obtain the maximum recovery.
- Sodium isobutyl xanthate shows good potential for floating zinc sulphide precipitate from the synthetic solution.



## Section 4 Copper And Zinc Sulphide Precipitate Flotation Using Non-Thiol Collectors

Metal sulphide precipitates are normally negatively or positively charged in an aqueous solution depending upon the pH. In a specific pH range, the precipitate can be collected by using the oppositely charged surfactant as collector, e.g. Sodium Dodecyl Sulfate (denoted hereafter as SDS) or Sodium DodecylBenzeneSulphonate (denoted hereafter as SDBS) for the positively charged precipitates and Dodecylammonium Acetate (denoted hereafter as DAA) for the negatively charged precipitates.

In this section, copper and zinc sulphide precipitate flotation behaviour, using non-thiol collectors, are discussed.

### 4.1 Copper and zinc sulphide precipitate flotation using non-thiol collectors

#### 4.1.1 Copper and zinc sulphide precipitate flotation behavior using anionic collectors

The copper and zinc sulphide precipitate flotation behavior as a function of pH, using the non-thiol anionic collectors SDBS or SDS, are shown in Fig. 4-4-1. It can be seen that copper sulphide precipitate cannot be floated over a wide pH range of 2.5 to 11.5, using either SDBS or SDS as collector. This indicates that the surface charge of the copper sulphide precipitate is highly negative over a wide pH range, which corresponds with the conclusion drawn in the previous section (Section 3).

Zinc sulphide precipitate cannot be floated over a pH range of 5.5 to 11.5 using SDBS as collector. However, when the pH is approximately 3.8, the zinc flotation recovery can be as high as 95%. The pH range for obtaining good zinc flotation is very narrow. When the  $\text{pH} < 3.5$ , the flotation recovery decreases sharply. The reason would seem to be that some  $\text{H}_2\text{S}$  gas escaped at the very low pH value and could therefore not form enough zinc sulphide precipitate.

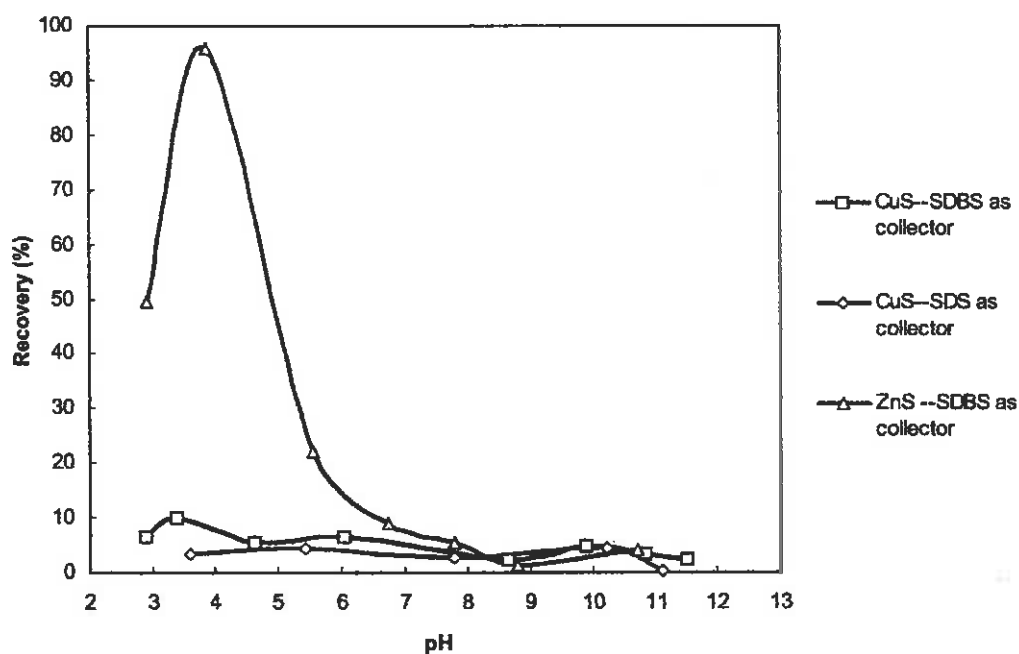


Fig. 4-4-1 The copper and zinc sulphide precipitate flotation behaviour as a function of pH using SDBS or SDS as collector ( $[Cu^{2+}]_{ini}$  or  $[Zn^{2+}]_{ini}$  50ppm;  $[SDBS]$  or  $[SDS]$  to  $[Cu^{2+}]_{ini}$  or  $[Zn^{2+}]_{ini}$  mole ratio 0.2:1,  $[S^{2-}]$  to  $[Cu^{2+}]_{ini}$  or  $[Zn^{2+}]_{ini}$  mole ratio 1:1)

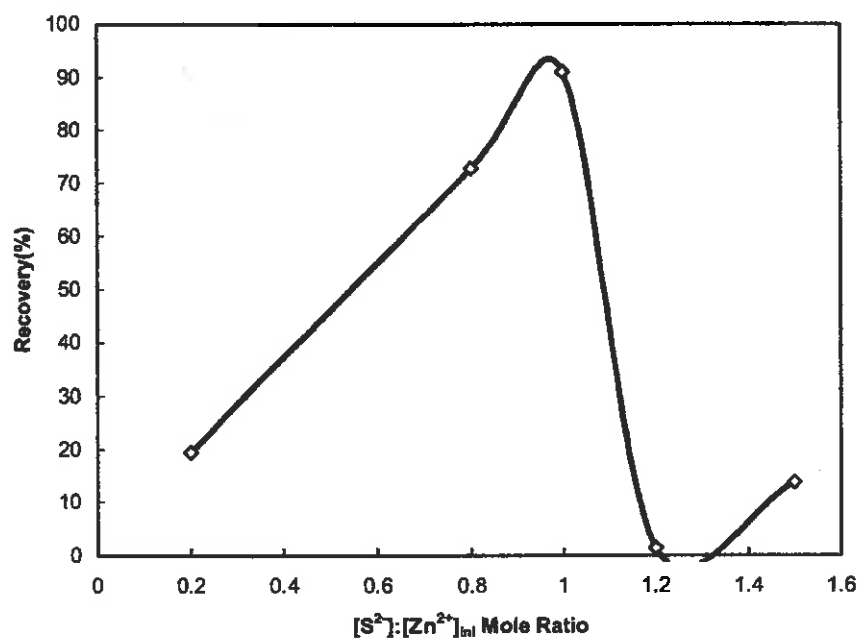


Fig. 4-4-2 Effect of the sodium sulphide concentration on the zinc sulphide precipitate flotation ( $[Zn^{2+}]_{ini}$  50ppm,  $[SDBS]:[Zn^{2+}]_{ini}=0.2:1$ )

The effect of the sodium sulphide concentration on zinc precipitate flotation is shown in Fig. 4-4-2. A small amount of surplus sulphide ion can cause the zinc flotation recovery to sharply decrease. A specific amount of the sulphide concentration at a 1:1 mole ratio to total zinc concentration is required. Any amount greater or less than this would cause the zinc flotation recovery to be significantly reduced because it is not tolerant to a variation in sulphide precipitant concentration. Over all, the non-thiol anionic collector is an inefficient collector for zinc sulphide precipitate flotation.

#### **4.1.2 Copper and zinc sulphide precipitate flotation using a cationic collector**

The above results indicate that the copper sulphide precipitate is negatively charged over a wide pH range, which indicates that it may be floated by using positively charged collectors. Dodecylammonium Acetate (denoted hereafter as DAA) is the most commonly used cationic collector in the mineral flotation industry. It was selected and used in the flotation tests which are reported below.

##### ***4.1.2.1 Copper and zinc sulphide precipitate flotation behaviour using DAA as collector***

Copper and zinc sulphide precipitate flotation behaviour as a function of pH have been presented in Fig. 4-4-3. The copper sulphide precipitate can be well floated by using DAA in the pH range of 1.5 to 8.5. When the  $\text{pH} > 9$ , the flotation recovery of the copper sulphide precipitate sharply decreases. The increase of the copper recovery at the  $\text{pH} > 10$  is due to the excessive bubble formation at high pH and is therefore a non-chemical effect.

High flotation recovery of zinc sulphide precipitate can be obtained, using DAA as collector, over a pH range of 4.5 to 9.5 (Fig. 4-4-3). However when the  $\text{pH} > 9.5$  or  $\text{pH} < 4.5$ , the zinc flotation recovery decreases. A comparison of the results presented in Fig. 4-4-3 and Fig. 4-4-1, shows that the Isoelectric Point (IEP) of the zinc sulphide precipitate is approximately at pH 4.2, which means that when the  $\text{pH} < 4.2$ , the surface charge of zinc sulphide precipitate is positive and when the  $\text{pH} > 4.2$ , it becomes negative. The surface charge of the copper sulphide precipitate appeared to be negative over all the tested pH ranges.

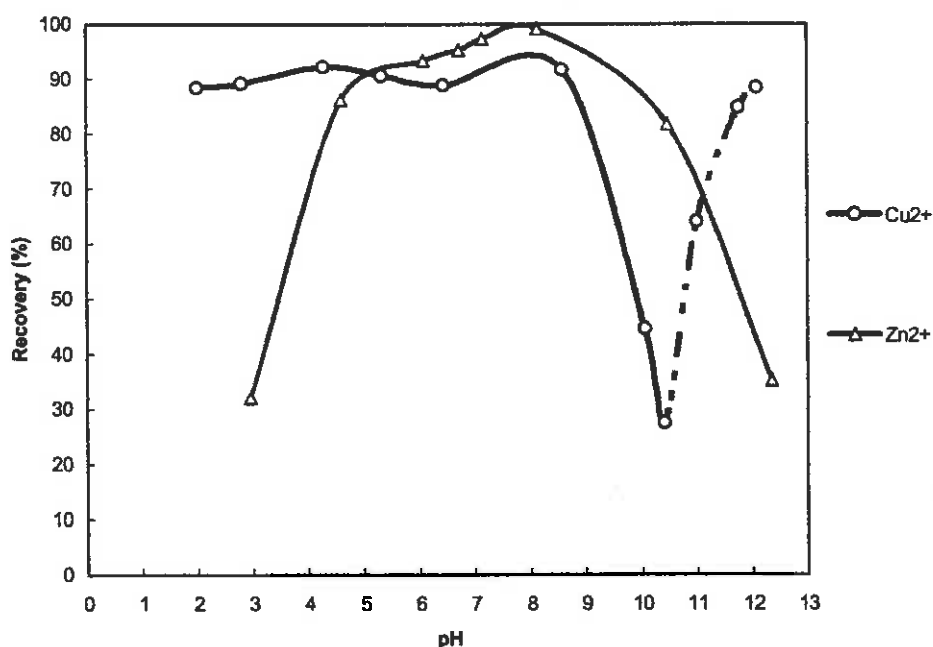
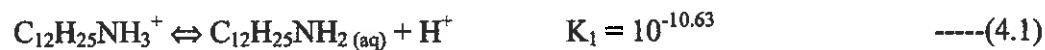


Fig. 4-4-3 The copper and zinc sulphide precipitate flotation behaviour as a function of pH using DAA as collector ( $[Cu^{2+}]_{ini}$  or  $[Zn^{2+}]_{ini}$  50ppm;  $[DAA]$  to  $[Cu^{2+}]_{ini}$  or  $[Zn^{2+}]_{ini}$  mole ratio 0.2:1,  $[S^{2-}]$  to  $[Cu^{2+}]_{ini}$  or  $[Zn^{2+}]_{ini}$  mole ratio 1:1)

The decrease in copper and zinc sulphide precipitate flotation recovery when the pH > 9-9.5, would seem to have been caused by the variation of the distribution of Dodecylammonium species as a function of pH. The DAA in an aqueous solution can produce the following reactions (Wang and Hu, 1988):



The total initial concentration of the added Dodecylammonium species in the solution is  $1.57 \times 10^{-4} M$  ( $[DAA]:[Cu^{2+}]_{ini} = 0.2:1$ ), which represents before the formation of  $C_{12}H_{25}NH_2(s)$  precipitate:

$$[C_{12}H_{25}NH_3^+] + [C_{12}H_{25}NH_2(aq)] = 1.57 \times 10^{-4} M \quad \text{----(4.3)}$$

From Eq.(4.1), Eq. (4.2) and Eq. (4.3), the log concentration of each Dodecylammonium species in the solution varying with the pH change can be calculated, the results are graphically presented below.

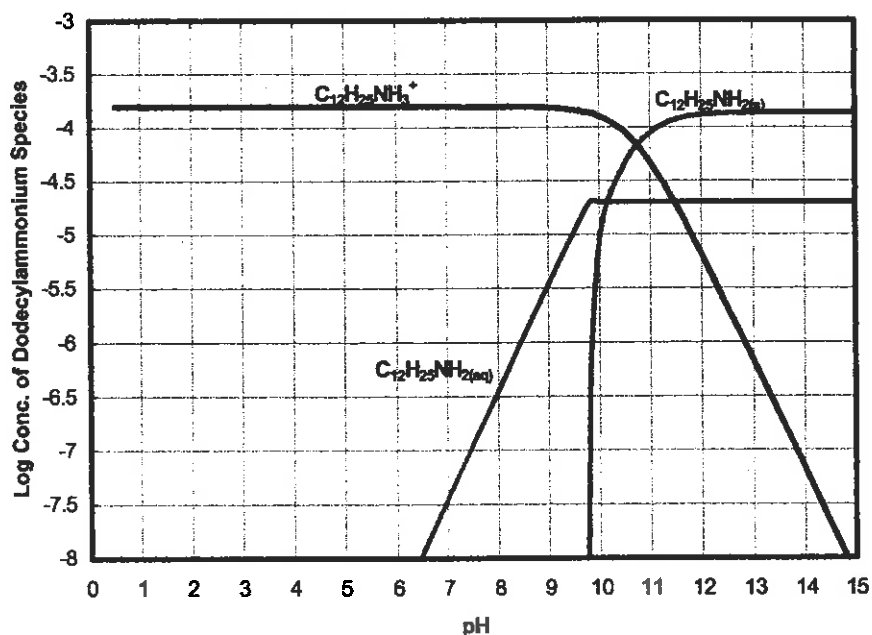


Fig. 4-4-4 Log concentration of Dodecylammonium species in the aqueous solution varies with the pH change ( $[DAA]_{ini} 1.57 \times 10^{-4} M$ )

When the  $pH > 9.5$ , the concentration of positively charged  $C_{12}H_{25}NH_3^+$  ions decreases and the concentration of non-charged  $C_{12}H_{25}NH_2(aq)$  ions increases (Fig. 4-4-4). When the  $pH > 9.8$ , the  $C_{12}H_{25}NH_2(s)$  precipitate is formed which is known to be unsuitable as a flotation collector. This may be the reason why when the  $pH > 9-9.5$ , the flotation recoveries of the copper and zinc sulphide precipitate decrease.

The effects of the sodium sulphide precipitant concentration on the copper or zinc sulphide precipitate flotation were tested. For the results see Fig. 4-4-5. With a slight surplus of sulphide ion concentration, the highest copper or zinc flotation recovery can be obtained. However, too much surplus of sulphide ion in the solution will also cause the copper or zinc flotation recovery to decrease. The effects of the DAA concentration on the copper or zinc sulphide precipitate flotation show that when the mole ratio of DAA

concentration to copper or zinc is 0.2 or more, high flotation recovery can be obtained (see Fig. 4-4-6).

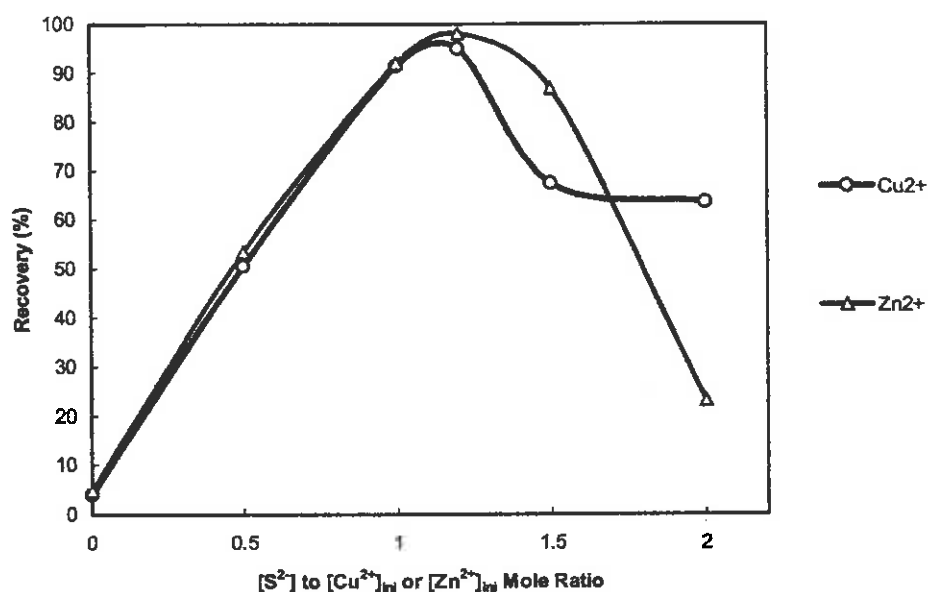


Fig. 4-4-5 Effects of the sodium sulphide concentration on the copper and zinc sulphide precipitate flotation ( $[Cu^{2+}]_{ini}$  or  $[Zn^{2+}]_{ini}$  50ppm,  $[DAA]$  to  $[Cu^{2+}]_{ini}$  or  $[Zn^{2+}]_{ini}$  0.2:1)

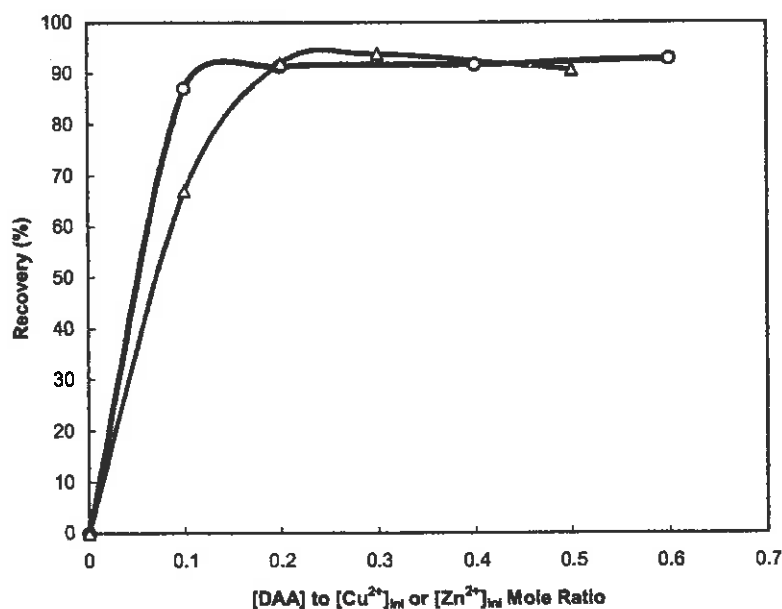


Fig. 4-4-6 Effects of the DAA concentration on the copper and zinc sulphide precipitate flotation ( $[Cu^{2+}]_{ini}$  or  $[Zn^{2+}]_{ini}$  50ppm,  $[S^{2-}]$  to  $[Cu^{2+}]_{ini}$  or  $[Zn^{2+}]_{ini}$  1:1)

Thus, it is clear that when the cationic collector DAA is used for copper and zinc sulphide precipitates flotation, high flotation recovery can be obtained. It shows good tolerance to the changes of the pH and the sulphide precipitant concentration as well as the DAA concentration.

#### 4.1.2.2 Mutual effects of copper and zinc on the sulphide precipitate flotation using DAA as collector

To fully understand the separation of copper and zinc from waste solution by using DAA as collector, it is important to investigate the mutual effects of copper and zinc on the precipitate flotation. A mixed solution with 50ppm  $[Cu^{2+}]_{ini}$  and 1000ppm  $[Zn^{2+}]_{ini}$  was used for the tests. This mixture of zinc and copper was similar to the Woodlawn Mines Ltd tailing wastewater composition. The flotation results as a function of sulphide precipitate concentration are shown in Fig. 4-4-7 and Fig. 4-4-8.

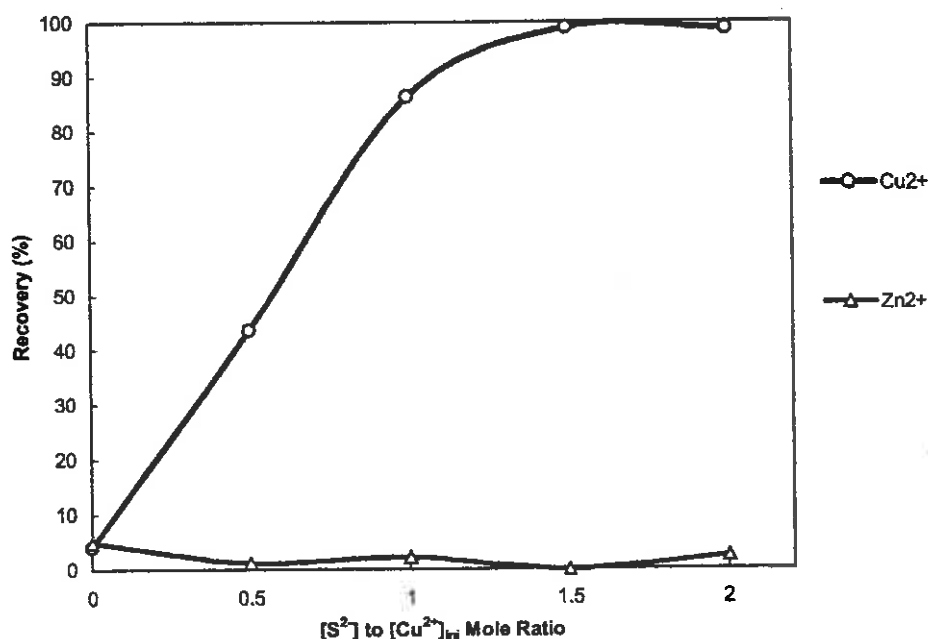


Fig. 4-4-7 The effect of zinc ion on copper sulphide precipitate flotation as a function of sulphide precipitant concentration using DAA as collector ( $[Cu^{2+}]_{ini}$  50ppm,  $[Zn^{2+}]:[Cu^{2+}]_{ini}=20:1$ ,  $[DAA]$  to  $[Cu^{2+}]_{ini}$  0.2:1, pH 6.0 $\pm$ 0.5)

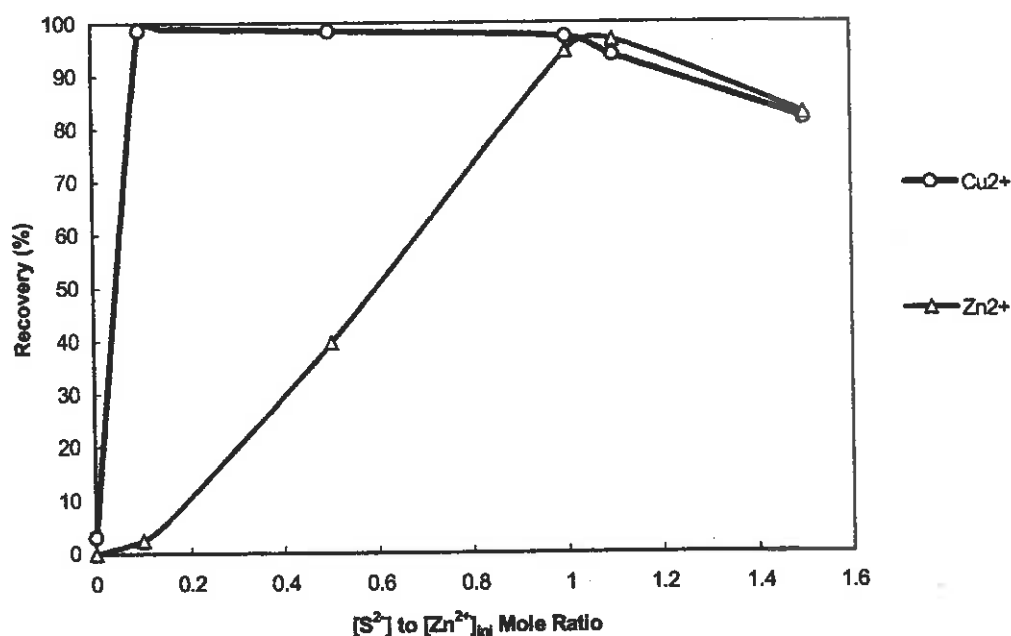


Fig. 4-4-8 The mutual effect of copper and zinc ions on the sulphide precipitate flotation as a function of sulphide precipitant concentration using DAA as collector ( $[Cu^{2+}]_{ini}$  50ppm,  $[Zn^{2+}]:[Cu^{2+}]_{ini}=20:1$ ,  $[DAA]$  to  $[Cu^{2+}]_{ini}$  0.2:1, pH  $6.0\pm0.5$ )

Copper ion can more easily be precipitated as a sulphide and floated using DAA as collector than zinc ion (see Fig. 4-4-7). When the mole ratio of sulphide concentration to copper ion is 1.5 to 2, nearly 100% copper ion can be floated with the zinc ion remaining in the solution.

Zinc ion can however also be floated well at a slight surplus mole ratio of sulphide concentration to zinc ion (see Fig. 4-4-8). When the mole ratio of sulphide concentration to zinc is 1.1, approximately 97% flotation recovery can be obtained. Copper sulphide precipitate can be floated together with formed zinc sulphide precipitate. However, the copper sulphide precipitate is able to be floated at high recovery when  $[S^{2-}]$  to  $[Zn^{2+}]_{ini} = 0.1:1$  at which ratio the zinc recovery is very low.

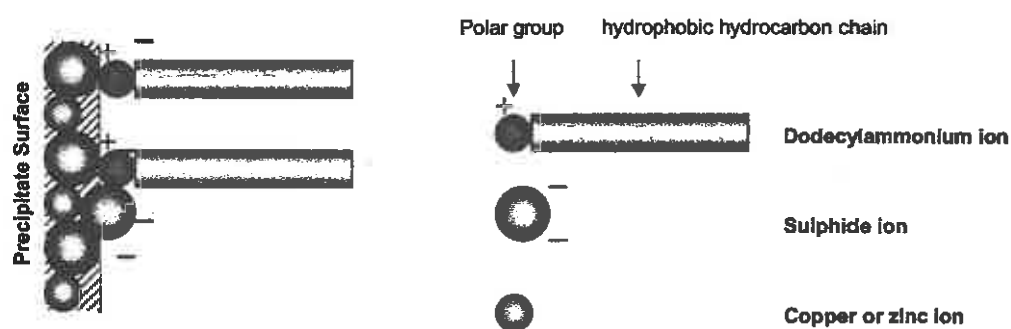
Thus, copper and zinc ions may be selectively precipitated and separately floated from the waste solution using sulphide as precipitant and DAA as collector.

#### 4.1.3 Mechanism of adsorption of non-thiol collectors on the sulphide precipitate



Non-thiol collectors are known to collect onto minerals by electrostatic type attraction. It is assumed that the SDS, SDBS and DAA attaching onto the copper or zinc precipitate surface is also by electrostatic type attraction.

Dodecylammonium Acetate (DAA) has a positively charged polar group (amine) associated with the hydrophobic hydrocarbon chain (dodecyl) when it is dissolved in the solution. How the dodecylammonium ion attaches to the negatively charged copper or zinc sulphide precipitate surface is shown schematically in Fig. 4-4-9.



*Fig. 4-4-9 Schematic representation of dodecylammonium ion attaching to the negatively charged copper or zinc sulphide precipitate surface*

#### 4.1.4 Brief Summary

The non-thiol anionic collectors SDS and SDBS cannot float the negatively charged copper sulphide precipitate over a wide pH range of 2.5 to 11.5. They may be used to float the zinc sulphide precipitate at a very narrow range of approximately 3.8. As they lack tolerance to the variation of pH and the sulphide precipitant concentration, they are not considered as efficient collectors for zinc sulphide precipitate flotation.

Copper and zinc sulphide precipitates can be floated well by using the cationic collector DAA over a wide pH range. The flotation exhibits good tolerance to changes of the pH and the sulphide precipitant concentration as well as the DAA concentration.

Copper ion can more easily be precipitated as sulphide and floated using DAA as collector than zinc ion in a copper and zinc mixed solution. Copper and zinc ions may be selectively precipitated and separately floated from the waste solution using sulphide as precipitant and DAA as collector.

It is assumed that the non-thiol collectors (SDS, SDBS and DAA) attaching onto the copper or zinc precipitate surface is by electrostatic type attraction.

## **4.2 Selective separation of copper and zinc ions from a synthetic waste solution by sulphide precipitate flotation using DAA as collector**

The results in Section 4.1 show that the copper and zinc sulphide precipitates can be easily floated by using the cationic collector DAA over a wide pH range. In a copper and zinc mixed solution, the copper ions can be selectively precipitated and floated, by using DAA as collector prior to zinc ions. This part of the work deals with the selective separation of copper and zinc ions from a synthetic waste solution by sulphide precipitate flotation, using DAA as collector.

The synthetic waste solution and flotation process have been described in Chapter III and Chapter IV Section 3.5 (page 168).

### **4.2.1 Results and Discussion**

Although DAA is a good collector for both copper and zinc sulphide precipitates, the flotation separation of copper and zinc sulphides can be effected because it is a selective precipitation process.

According to previous results, when the mole ratio of sulphide concentration to copper ion is 1.5 - 2 in a copper and zinc mixed solution, good copper flotation recovery can be obtained, with the zinc ion remaining in the solution (refer to Fig. 4-4-7). For the selective flotation results of copper ion from a synthetic solution when sodium sulphide was used as precipitant and DAA as collector, and a variation of sulphide precipitant concentrations were applied, see Table 4-4-1 and the graphic presentation in Fig. 4-4-10.

As predicted, copper ion can be selectively floated from the synthetic solution, by using sulphide as precipitant and DAA as collector. When the mole ratio of sulphide to copper ion is 2.0 - 2.5, above 90% of copper flotation recovery can be obtained (see Table 4-4-1 and Fig. 4-4-10). This mole ratio range is higher than what was required for the mixed solution containing copper and zinc (refer to Fig. 4-4-7). In this case, it was assumed that some of the sulphide ions were oxidized because of the presence of  $\text{Fe}^{3+}$  ions in the synthetic solution.

The flotation behavior of cadmium shows a similarity to that of the copper. However, the flotation recovery of cadmium ion was lower than that of copper ion. As cadmium flotation is not an objective of this thesis, no further special investigation on cadmium flotation behavior was undertaken.

Table 4-4-1 Selective flotation of copper ion from the synthetic solution using sulphide as precipitant and DAA as collector\*

Test No.	pH	$[S^{2-}]:[Cu^{2+}]$ Mole ratio	Metal Ion Conc. in the Solution after Flotation (ppm)			Flotation Recovery (%)		
			Cu	Zn	Cd	Cu	Zn	Cd
1	2.91	1:1	72.48	2008	10.12	27.52	0	0
2	3.02	1.5:1	23.88	1934	6.76	76.12	3.3	32.4
3	2.94	2:1	9.57	1909	4.84	90.43	4.55	51.6
4	2.99	2.5:1	5.82	1917	4.46	94.18	4.15	55.4
5	3.07	3:1	19.42	1877	4.76	80.58	6.15	52.4

\* See Table 3-1-2,  $pH_{ini}$  2.7,  $[DAA]:[Cu^{2+}]_{ini}$  mole ratio 0.1:1

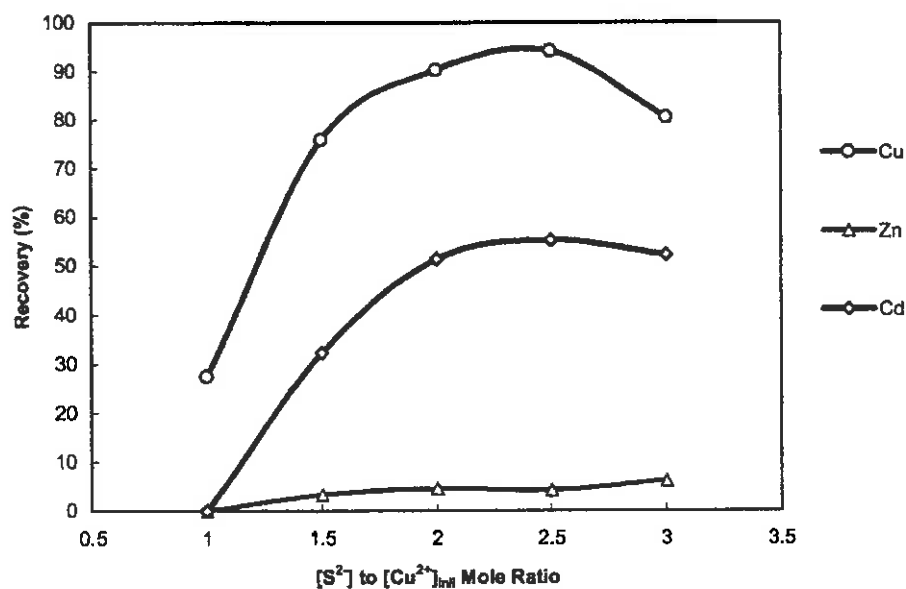


Fig. 4-4-10 Selective flotation of copper ion from the synthetic solution by using sulphide as precipitant and DAA as collector ( $[Cu^{2+}]_{ini}$  100ppm,  $[Zn^{2+}]_{ini}$  2000ppm,  $[Cd^{2+}]_{ini}$  10ppm,  $pH_{ini}$  2.7,  $[DAA]:[Cu^{2+}]_{ini}$  mole ratio 0.1:1,  $pH=3.0\pm0.1$ )

Compared with the zinc concentration in the synthetic solution, the amount of sulphide precipitant is very small. The zinc ion remains in the solution during copper sulphide precipitate flotation. Therefore, the copper ion can be selectively precipitated and floated prior to the zinc flotation, using sodium sulphide as precipitant and DAA as collector.

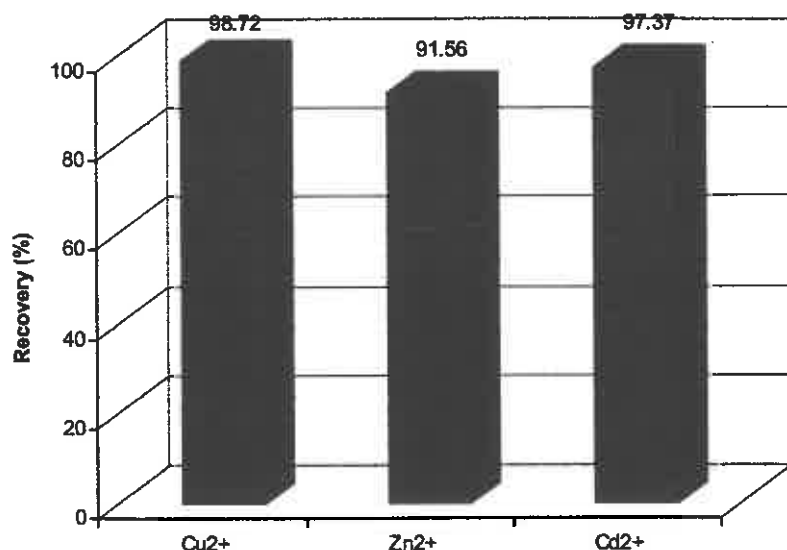
Zinc sulphide precipitate was easily floated in a copper and zinc mixed solution. However, the zinc ion concentration was much higher than that of copper and cadmium ions in the synthetic solution ( $[\text{Zn}^{2+}]:[\text{Cu}^{2+}]\approx 20:1$ ). To investigate the flotation of zinc sulphide precipitate in the synthetic solution by using DAA as collector, the bulk flotation of zinc, copper and cadmium sulphide precipitates, was tested and some of the results are listed in Table 4-4-2, for the best flotation results see Fig. 4-4-11.

*Table 4-4-2 Bulk flotation results of combined zinc, copper and cadmium sulphide precipitates, from the synthetic solution by using DAA as collector<sup>s</sup>*

Test No.	Flotation Conditions	Metal Ion Conc. in the Solution after Flotation (ppm)			Flotation Recovery (%)		
		Cu	Zn	Cd	Cu	Zn	Cd
1	[DAA]:[M] <sub>T</sub> <sup>*</sup> =0.013:1 [S <sup>2-</sup> ]:[M] <sub>T</sub> =1.2:1 pH=4.20	5.31	162.5	0.783	94.69	91.88	92.17
2	[DAA]:[M] <sub>T</sub> =0.026:1 [S <sup>2-</sup> ]:[M] <sub>T</sub> =1.05:1 pH=3.76	2.28	208.8	0.39	97.72	89.56	96.1
3	[DAA]:[M] <sub>T</sub> =0.013:1 [S <sup>2-</sup> ]:[M] <sub>T</sub> =1.2:1 pH=4.36	1.28	168.75	0.263	98.72	91.56	97.37

<sup>s</sup> See Table 3-1-2,  $pH_{\text{ini}}$  2.7

<sup>\*</sup> [M]<sub>T</sub> is the total concentration of zinc, copper and cadmium ions in the solution



*Fig. 4-4-11 The best bulk flotation results of zinc, copper and cadmium sulphide precipitates from the synthetic solution by using DAA as collector (refer to Table 4-4-2 test 3, chemical containing see Table 3-1-2,  $pH_{ini}$  2.7,  $[DAA]:[M]_T$  0.013:1,  $[S^{2-}]:[M]_T$  1.2:1, pH 4.36)*

Zinc, copper and cadmium sulphide precipitate were easily floated from the synthetic solution, DAA being used as collector (Table 4-4-2). When the concentration of sulphide precipitant was 1.2 times that of the total concentration of zinc, copper and cadmium ions and the  $[DAA]$  to  $[M]_T$  mole ratio was 0.013:1, the best flotation recoveries of 98.72% Cu, 91.56% Zn, and 97.37% Cd were obtained (see Fig. 4-4-11).

Hence, copper and zinc were selectively separated and recovered from the synthetic solution by sulphide precipitate flotation at a very low pH range, using DAA as collector. As the chemical contents of the synthetic solution were very close to those of the industrial waste solution (the tailing wastewater from the Woodlawn Mines), it might be possible to use this process to separately recover the copper and zinc ions from this industrial waste solution.

#### 4.2.2 Brief Summary

The cationic collector DAA is a good collector for both copper and zinc sulphide precipitate flotation. Copper ion can be selectively precipitated and floated from a synthetic solution by using sodium sulphide as precipitant and DAA as collector. A multiple of about two times the amount (to  $[\text{Cu}^{2+}]$  mole ratio) of sulphide precipitant is required to obtain the maximum recovery.

Good bulk flotation recoveries of zinc, copper and cadmium sulphide precipitates can also be obtained from a synthetic solution. Therefore, it is possible to use this process for the industrial waste solution to achieve flotation separation of copper and zinc ions.

### 4.3 Section Conclusion

- The anionic collectors SDS and SDBS are inefficient collectors for copper and zinc sulphide precipitate flotation. The cationic collector DAA can collect copper and zinc sulphide precipitate over a wide pH range with good tolerance to the pH, the sulphide precipitant concentration and changes in DAA concentration .
- The copper ion can be selectively precipitated and floated prior to the zinc ion by using sodium sulphide as precipitant and DAA as collector in a copper and zinc mixed solution. The selective precipitation and flotation separation of copper and zinc ions from a synthetic solution has been achieved by using sulphide as precipitant and DAA as collector. Therefore, it might be possible to use this process for the industrial waste solution to achieve flotation separation of copper and zinc ions.
- The attachment of the non-thiol collectors (SDS, SDBS and DAA) onto the copper or zinc precipitate surfaces is considered as by the electrostatic type attraction.



## Section 5 Selective Flotation of Copper and Zinc Ions from Industrial Waste Solution

### 5.1 Introduction

Woodlawn Mines is situated 70km northeast of Canberra, A.C.T., and 50 km south of Goulburn, N.S.W., Australia. As the plant is located in a rural area away from other industrial activities, the environmental requirements are very strict (Gauci and Cameron, 1980). The tailing from the mineral processing plant is stored in a conventional water-storage type dam. After almost 20 years, the tailing water (wastewater) in the dam has become very acidic (pH value is about 2.8) and harmful heavy metal ions such as zinc (~2000ppm), copper (~100ppm) and cadmium (~10ppm) are concentrated in the water. This dangerous solution should have been treated before the mining company terminated its activities and vacated the mine.

The most widely used method of treatment of wastewater containing heavy metals is by precipitation and sedimentation, normally hydroxide precipitation. This treatment method may, when operating at peak efficiency, give a solution which contains heavy metal ions at concentrations allowed for discharge. Under normal operation conditions often the remaining liquid exceeds the limitation for sewer disposal set by the MMBW Trade Waste By-law (Mainwaring, 1989). Another disadvantage of this method is that the large amount of precipitation product can not be reused, secondary treatment, such as packing and deep burial is therefore required, giving rise to secondary pollution. Clearly, a more reliable and effective method of treating wastewater containing heavy metal ions is needed.

Based on the findings of this study with regard to precipitate flotation and separation, a process has been developed for flotation separation of the zinc, copper and cadmium ions from the Woodlawn Mines tailing wastewater (hereafter denoted as Woodlawn wastewater). These heavy metal flotation products can be reused in subsequent smelting or hydrometallurgy processes or directly for some other industrial purposes. The process

may be "waste-free" and may well be able to meet requirements of effectiveness and cost competitiveness.

## 5.2 Woodlawn Wastewater and Flotation Process

The Woodlawn wastewater was obtained from the Woodlawn Mines' Evaporation Dam No.1. A typical analysis supplied by Denehurst Analytical Services Pty. Ltd., showed that it contained 2440ppm zinc, 115ppm copper and 13ppm cadmium at pH 2.85. For more detailed analysis, see Chapter III page 38. Analyses carried out in this study on the actual wastewater supplied resulted in 1935ppm zinc, 122ppm copper and 12ppm cadmium. The copper and zinc are very close to the supplied analysis, but the zinc concentration differed somewhat. Because the precipitation and flotation tests showed that 1935ppm zinc more closely approximated the sulphide precipitant consumption, the calculations of the flotation recovery in this study have been based on our own analysis. As the solubility product of the cadmium sulphide precipitate is within the range of that of the copper sulphide and zinc sulphide, the cadmium concentration was also analyzed in the tests.

Compared with the zinc ions (1935ppm) in the Woodlawn wastewater, the copper (122ppm) and cadmium (12ppm) ions in the solution are much less significant. Only the zinc ion is potentially valuable. From the metallurgical point of view, recovering such a small amount of copper and cadmium ions together with the zinc sulphide precipitate flotation product would not significantly influence the grade of the zinc product. Furthermore, the copper and cadmium ions may be separated and recovered at the next smelting or hydrometallurgy stage. Therefore, for metallurgical purposes, recovering copper and cadmium ions together with the zinc ion may be an economical process.

However, if high purity of the zinc precipitate flotation product recovered from the wastewater is required for some other industrial purposes, such as ceramic and chemical industries, the selective separation of the copper and cadmium ions from the zinc ion may become important. Be this as it may, from the technological and environmental point of view, the flotation separation of heavy metal ions from industrial wastewater is of unquestionable importance for the "waste-free" process to achieve its maximum potential.

In this study, both the bulk flotation of zinc, copper and cadmium and the flotation of copper and cadmium ions separately from zinc ion, have been investigated.

For the bulk flotation of zinc, copper and cadmium sulphide precipitates, DAA was used as collector. This bulk flotation process is shown in Fig. 4-5-1

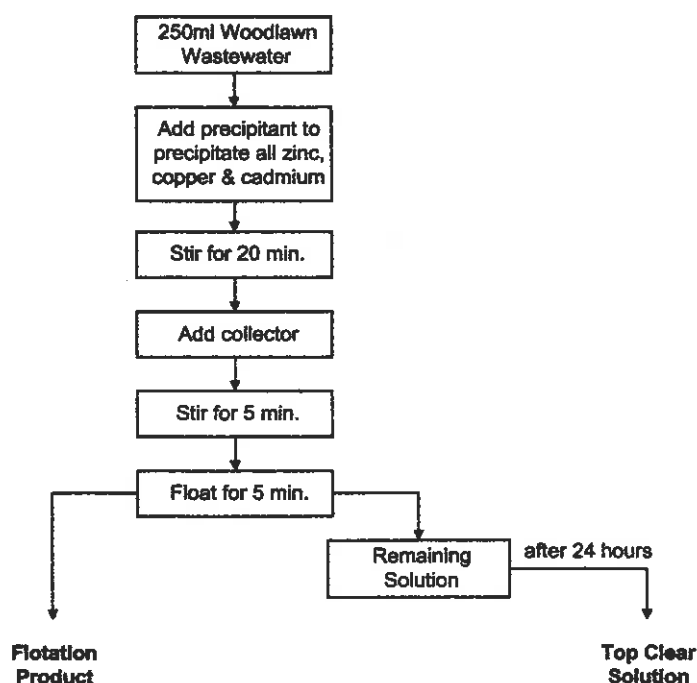


Fig. 4-5-1 Bulk flotation process for recovering zinc, copper and cadmium from the Woodlawn wastewater

An analysis of the remaining solution was carried out to evaluate the flotation efficiency. A further analysis of the top clear solution made it possible to establish the degree of precipitation, as some of the unfloated/uncollected precipitate remained in the solution after flotation.

For flotation separation of copper and cadmium ions with zinc ion, a two-stage flotation process was required. Firstly, the copper and cadmium ions were selectively precipitated and floated from the wastewater by using sodium sulphide as precipitant and sodium ethyl xanthate or DAA as collector. Secondly, after this first stage flotation, zinc ion was

precipitated and floated from the solution, by using sodium sulphide as precipitant and DAA as collector.

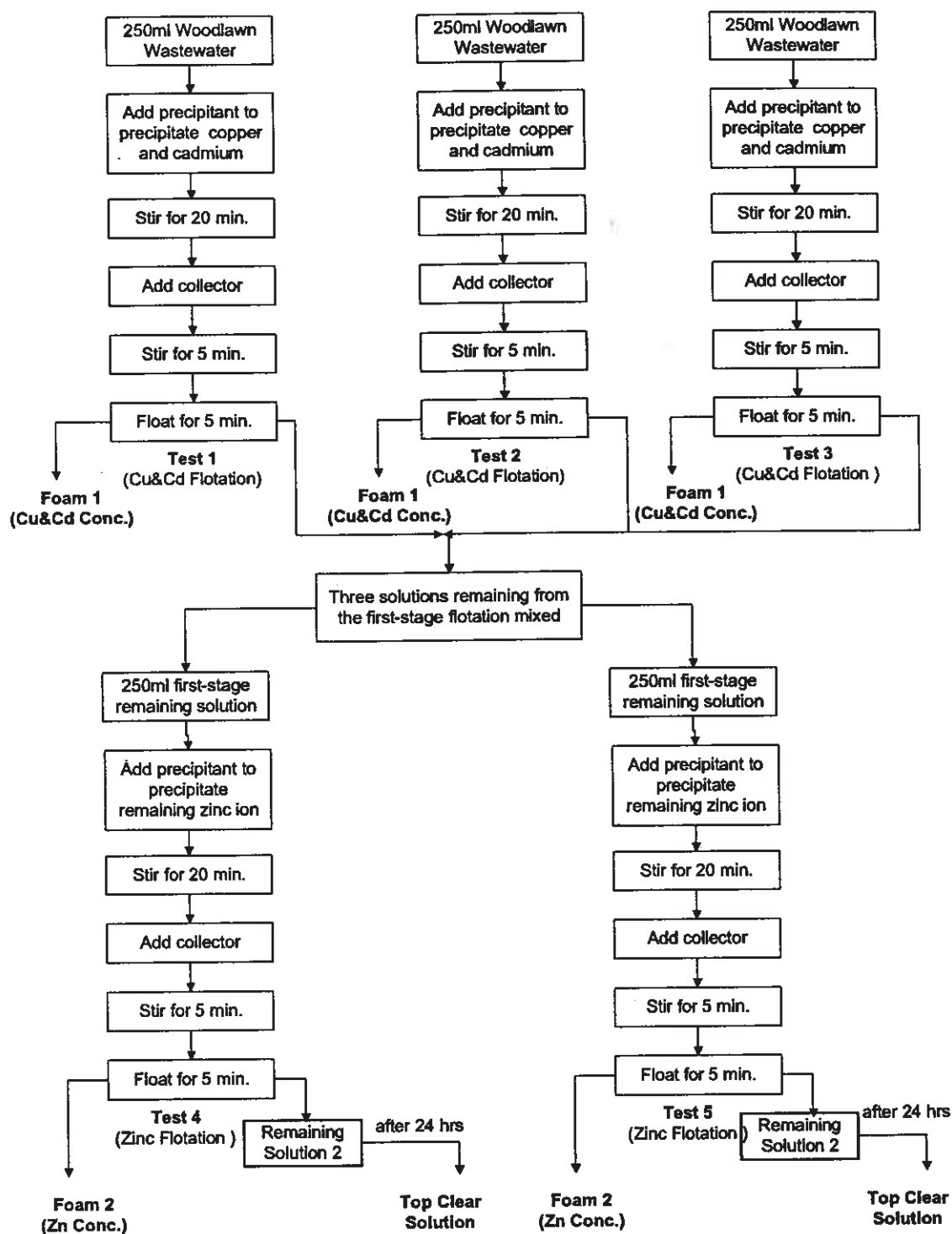


Fig. 4-5-2 Two-stage flotation process for selectively flotation of copper and cadmium ions with zinc ion from the Woodlawn wastewater by using sodium sulphide as precipitant

The volume of wastewater after the first-stage flotation is less than 250ml, depending upon the results of the flotation. This is not enough for the second-stage zinc sulphide precipitate flotation. The uncertain volume remaining from the first-stage would cause the second-stage zinc precipitation difficult. Therefore, the two-stage flotation process was adjusted to suit our purpose as shown in Fig. 4-5-2. In this process, three first-stage flotation processes under the same conditions were carried out. The remaining flotation solutions were mixed and two 250ml portions were prepared from this for the second-stage flotation. This allowed for more stable conditions for the second-stage flotation process.

Previous experiments have demonstrated that both sodium ethyl xanthate and DAA are good collectors for copper sulphide precipitate. In this study, both of these collectors have been tried in the first-stage copper and cadmium sulphide precipitate flotation. In the second-stage flotation process of Fig. 4-5-2 and the bulk flotation process of Fig. 4-5-1, only DAA was used as collector.

### 5.3 Results and discussion

#### 5.3.1 A trial on hydroxide precipitate flotation

Although the outcome of this study does not favor the use of hydroxide precipitation and flotation, nevertheless, it is the most popular process in wastewater treatment for removal of heavy metal ions from solution. For this reason, a trial of hydroxide flotation was carried out on the Woodlawn wastewater.

When the pH of the Woodlawn wastewater was adjusted to 9-9.5, which is the best pH range for most metal hydroxide precipitates as well as copper and zinc ions, the whole solution became gelatinous and the precipitates failed to settle. After an additional 4ml 0.2M SDBS collector ( $[SDBS]:[M]_T^* \approx 0.05:1$ ) and 10 minutes flotation, the whole of the solution changed into bubbles and only approximately 80ml (initially 250ml) was left in the flotation column after flotation. Most of the water had passed into the flotation foam. The analyzed results of the remaining solution are shown in Table 4-5-1.

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\*  $[M]_T$  is the total concentration of zinc, copper and cadmium ions in the solution

Table 4-5-1 The results of hydroxide precipitate flotation for Woodlawn wastewater using SDBS as collector

Test No.	Flotation Conditions	Metal Ion Conc. in the Solution after Flotation (ppm)			Flotation Recovery (%)		
		Cu	Zn	Cd	Cu	Zn	Cd
1	[SDBS]:[M] <sub>T</sub> ≈ 0.05:1 pH = 9.5 ± 0.2	23.2	517.5	3.79	80.98	73.26	68.42

It should be noted that, as significant volumes of water (above two-thirds of the solution) were recovered into the flotation foam, the flotation recoveries of metal ions were meaningless. In addition, the concentrations of metal ions in the remaining solution were still very high (Table 4-5-1). Clearly, hydroxide precipitation and flotation would not be suitable for the Woodlawn wastewater treatment.

### 5.3.2 Bulk flotation process for recovering zinc, copper and cadmium from the Woodlawn wastewater

In accordance with the conditions applied in the synthetic flotation, bulk flotation tests for recovering zinc ion together with copper and cadmium ions from the Woodlawn wastewater by using sodium sulphide as precipitant and DAA as collector were carried out. The flotation results are listed in Table 4-5-2. The best results have been graphically presented in Fig. 4-5-3.

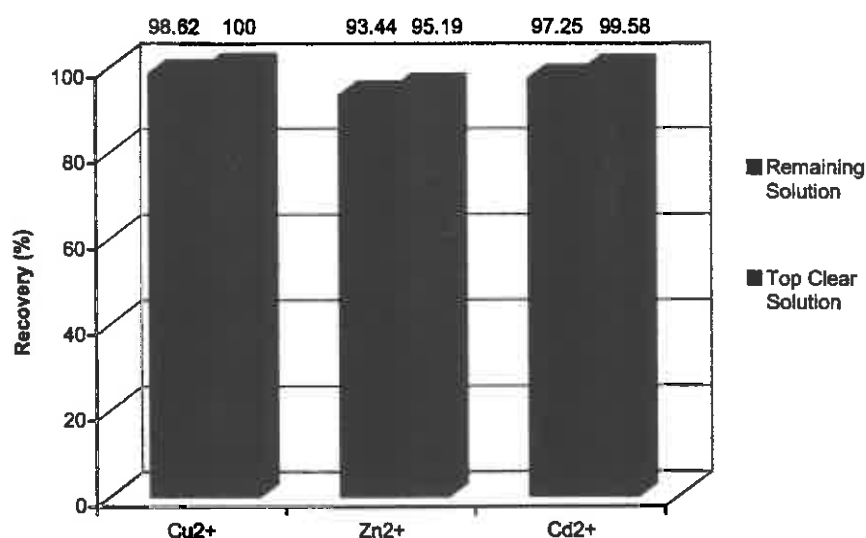
A very simple bulk flotation process (refer to Fig. 4-5-1), using DAA as collector, allowed for very high recoveries (see Table 4-5-2) of zinc, copper and cadmium sulphide precipitates to be obtained from the Woodlawn wastewater. When the quantity of sulphide precipitant 10ml of 1M Na<sub>2</sub>S ([S<sup>2-</sup>]:[M]<sub>T</sub> ≈ 1.25:1) and 5ml of 0.02M DAA ([DAA]:[M]<sub>T</sub> ≈ 0.01:1) was used, the best flotation recoveries of 98.62% Cu, 93.44% Zn and 97.25% Cd were achieved. After 24 hours settling, the concentrations of copper and cadmium ions in the top clear solution were even lower than the analytical detection limits (Table 4-5-2).

Table 4-5-2 Bulk flotation results of zinc, copper and cadmium sulphide precipitates, from the Woodlawn wastewater, DAA having been used as collector

No	Flotation Conditions	Solution Name	Metal Ion Conc. in the Solution after Flotation (ppm)			Flotation Recovery (%) <sup>*</sup>		
			Cu	Zn	Cd	Cu	Zn	Cd
1	1M NaS 8ml <sup>†</sup> 0.02M DAA 5ml <sup>#</sup> pH=3.93	Remaining Solution	2.88	433.8	0.47	97.64	77.58	96.08
		Top Clear Solution	-	-	-	-	-	-
2	1M NaS 8ml 0.02M DAA 5ml 4M NaOH 2ml pH=4.31	Remaining Solution	0.79	285	0.15	99.35	85.27	98.75
		Top Clear Solution	>0.01	160	0.07	100	91.73	99.42
3	1M NaS 10ml 0.02M DAA 5ml pH=4.17	Remaining Solution	1.69	127	0.33	98.62	93.44	97.25
		Top Clear Solution	>0.01	93	0.05	100	95.19	99.58
4	1M NaS 10ml 0.02M DAA 5ml 4M NaOH 2ml pH=4.23	Remaining Solution	2.31	97	0.32	98.11	94.99	97.33
		Top Clear Solution	0.30	38	0.08	99.75	98.04	99.33
5	1M NaS 12ml 0.02M DAA 5ml pH=4.45	Remaining Solution	19.66	366	1.99	83.89	81.08	83.42
		Top Clear Solution	0.10	45	0.06	99.92	97.68	99.50
6	1M NaS 12ml 0.02M DAA 5ml 4M NaOH 2ml pH=4.58	Remaining Solution	17.89	349	1.91	85.34	81.96	84.08
		Top Clear Solution	0.04	53	0.06	99.97	97.26	99.50

<sup>\*</sup> All flotation recoveries were calculated with the initial metal concentration

<sup>†</sup> 1M NaS 8ml is approximately  $[S^{2-}]:[M]_T \approx 1.05:1$ ; <sup>#</sup> 0.02M DAA 5ml is  $[DAA]:[M]_T \approx 0.01:1$



*Fig. 4-5-3 The best bulk flotation results of zinc, copper and cadmium sulphide precipitates, from the Woodlawn wastewater; DAA having been used as collector (refer to Table 4-5-2 test 3, 1M NaS 10ml, 0.02M DAA 5ml, pH 4.17)*

The zinc concentration in the remaining solution after flotation is still about 100ppm, which is probably higher than the discharge requirement. However, according to previous results obtained in this study, very low zinc concentrations may be achieved by thorough control of the precipitant consumption and further precipitate flotation.

### 5.3.3 Selective flotation of copper and cadmium ions from zinc ions in the Woodlawn wastewater by using sodium ethyl xanthate as the first-stage collector

According to previous studies, ethyl xanthate can be used as a good collector for selective flotation of copper sulphide from zinc ions in the synthetic solution. Tests of selective flotation of copper and cadmium ions from zinc ions from the Woodlawn wastewater, by using sodium sulphide as precipitant and sodium ethyl xanthate as the first-stage flotation collector and DAA as the second-stage flotation collector, were carried out. The results have been listed in Table 4-5-3. For the graphical best results, see Fig. 4-5-4.



Table 4-5-4 The results of flotation separation of copper with zinc ions from the Woodlawn wastewater by using sodium sulphide as precipitant, sodium ethyl xanthate as the first-stage flotation collector and DAA as the second-stage flotation collector

Stage	Flotation Conditions	Name	Metal Ion Conc. in the Solution after Flotation (ppm)			Flotation Recovery (%) <sup>*</sup>		
			Cu	Zn	Cd	Cu	Zn	Cd
First-stage flotation	1M NaS 0.8ml <sup>†</sup> 0.1M EtX 2ml <sup>**</sup> pH 2.9±0.1	Test 1 Solution	19.42	1933 <sup>‡</sup>	4.20	84.08	0.1	38.00
		Test 2 Solution	16.38		4.76	86.57		25.67
		Test 3 Solution	21.24		4.50	82.59		29.00
		Average	19.03	1933	4.49	84.40	0.1	30.32
Second-stage flotation	1M NaS 8.5ml <sup>§</sup> 0.02M DAA 5ml pH 3.98	Remaining Solution	1.44	119	0.58	98.82	93.85	95.17
		Top Clear Solution	>0.01	56	0.06	100	97.11	99.50
	1M NaS 9ml 0.02M DAA 5ml pH 4.17	Remaining Solution	1.69	89	0.59	98.61	95.40	95.08
		Top Clear Solution	>0.01	26	0.05	100	98.66	99.58

\* All flotation recoveries have been calculated with the initial metal concentration

<sup>†</sup> 1M NaS 0.8ml is approximately  $[S^{2-}]:[Cu^{2+}]_T \approx 2:1$ ; 0.1M EtX 2ml is  $[EtX]:[Cu^{2+}]_T \approx 0.4:1$

<sup>‡</sup> Note: this is the combined feed analysis

<sup>§</sup> 1M NaS 8.5ml is approximately  $[S^{2-}]:[Zn]_T \approx 1.15:1$ ; 0.02M DAA 5ml is  $[DAA]:[Zn]_T \approx 0.01:1$

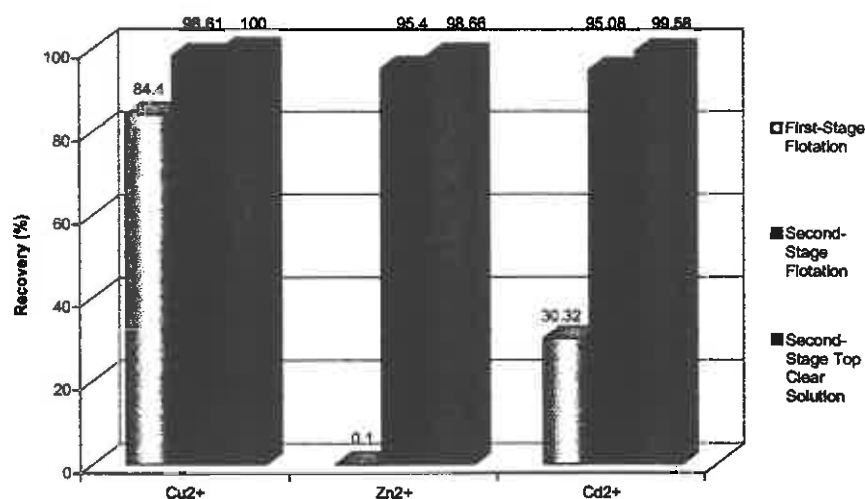


Fig. 4-5-4 The best flotation separation results of copper and zinc ions from the Woodlawn wastewater by using sodium sulphide as precipitant, sodium ethyl xanthate as the first-stage flotation collector and DAA as the second-stage flotation collector (refer to Table 4-5-3)

In the first-stage of the flotation process, 84.4% copper flotation recovery was obtained while almost all the zinc ions remained in the solution. In the second-stage of the flotation process, 95.4% zinc was recovered from the wastewater together with a small amount of the residual copper and cadmium ions from the first-stage of the flotation process. Hence, with this two-stage flotation process, copper and zinc were separately recovered successfully from the Woodlawn wastewater.

#### 5.3.4 Selective flotation of copper and cadmium ions from zinc ions in the Woodlawn wastewater by using DAA as the first-stage collector

The selective flotation of copper and cadmium ions from zinc ion in the Woodlawn wastewater, using sodium sulphide as precipitant and DAA as both the first-stage and the second-stage flotation collector, was carried out. The results of these flotation processes are listed in Table 4-5-4. The best results have been graphically presented in Fig. 4-5-5.

Table 4-5-4 The results of flotation separation of copper with zinc ions from the Woodlawn wastewater using sodium sulphide as precipitant and DAA as both the first-stage and the second-stage flotation collector

Stage	Flotation Conditions	Name	Metal Ion Conc. in the Solution after Flotation (ppm)			Flotation Recovery (%) <sup>*</sup>		
			Cu	Zn	Cd	Cu	Zn	Cd
First-stage flotation	1M NaS <sup>†</sup> 1ml 0.02M DAA 1ml pH 2.9±0.1	Test 1 Solution	3.22	1947 <sup>‡</sup>	7.44	97.36	0	65.00
		Test 2 Solution	3.74		8.92	96.93		60.33
		Test 3 Solution	3.80		8.52	96.88		62.50
		Average	3.59	1947	8.29	97.06	0	62.58
Second-stage flotation	1M NaS <sup>§</sup> 9ml 0.02M DAA 5ml pH 4.16	Remaining Solution	0.74	119	0.35	99.39	93.85	97.08
		Top Clear Solution	0.73	123	0.35	99.40	93.64	97.08
	1M NaS 10ml 0.02M DAA 5ml pH 4.28	Remaining Solution	0.63	34	0.19	99.48	98.24	98.42
		Top Clear Solution	0.51	33	0.19	99.58	98.29	98.42

<sup>\*</sup> All flotation recoveries have been calculated with the initial metal concentration

<sup>†</sup> 1M NaS 1ml is approximately  $[S^{2-}]:[Cu^{2+}]_T \approx 2.5:1$ ; 0.02M DAA 1ml is  $[DAA]:[Cu^{2+}]_T \approx 0.4:1$

<sup>‡</sup> Note: this is the combined feed analysis

<sup>§</sup> 1M NaS 8.5ml is approximately  $[S^{2-}]:[Zn]_T \approx 1.15:1$ ; 0.02M DAA 5ml is  $[DAA]:[Zn]_T \approx 0.01:1$

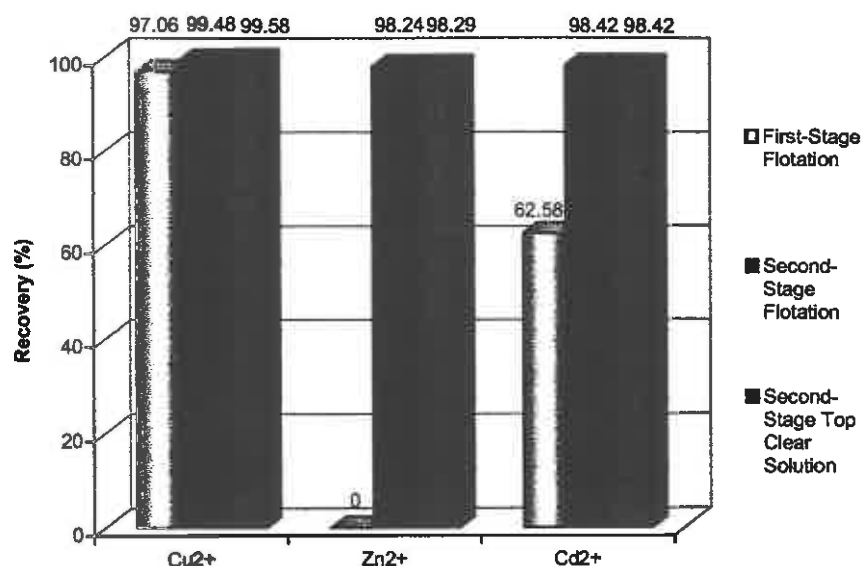


Fig. 4-5-5 The best flotation separation results of copper with zinc ions from the Woodlawn wastewater by using sodium sulphide as precipitant and DAA as both the first-stage and the second-stage flotation collector (refer to Table 4-5-4)

In the first-stage flotation process, using DAA as collector, the best flotation recoveries of 97.06% Cu and 62.58% Cd were obtained with almost 100% zinc ion remaining in the solution for the next stage flotation. In the second-stage flotation process, 98.24% of zinc ion was floated from the wastewater. These results are slightly better than when ethyl xanthate as the first-stage flotation collector was used (Table 4-5-3 and Fig. 4-5-4).

Both the one-stage and the two-stage flotation (using both ethyl xanthate and DAA as first-stage collectors) processes successfully floated zinc, copper and cadmium from the Woodlawn wastewater. The flotation processes were operated under the original pH conditions of the Woodlawn wastewater. Upon completion of the flotation process, the wastewater contained very low levels of heavy metal ions. The pH therefore needed only to be adjusted slightly to reach the lowest level of pH value allowed for discharge. This represents a significant advantage over current methods of heavy metal removal techniques which use caustic liquors and for which substantial acidification is required before effluent standards can be met. Furthermore, the flotation products (zinc sulphide concentrate and copper sulphide concentrate) can be reused for other industrial purposes. Clearly, the above flotation processes have significant industrial potential for recovery of heavy metal ions from industrial wastewater in the future.

### 5.3.5 Flotation products

The flotation products from the two-stage flotation process, using DAA as collector in both first and second-stage flotation processes, were investigated using X-ray diffraction (XRD) analysis. The XRD results for copper and zinc concentrates from the flotation processes are shown in Fig. 4-5-6 and Fig. 4-5-7.

The X-ray diffraction results indicate that the concentrate obtained from the first-stage flotation process is copper sulphide ( $\text{CuS}$ ) (see Fig. 4-5-6). No cadmium sulphide was identified from the XRD results, probably because the amount was too small to be recognized (only about 6% of the product).

Element sulphur was found in the concentrate obtained from the first-stage flotation process (Fig. 4-5-6), which strongly supports the outcome of the electrochemical reaction mechanism discussed in section 3.2.

The second-stage flotation product was identified as zinc sulphide ( $\text{ZnS}$ ) from the X-ray diffraction analysis results (Fig. 4-5-7). The zinc sulphide particle size was so fine that the XRD patterns were very wide. An approximate computer calculation indicated that the zinc sulphide precipitate particle size was around 25nm. No other crystalline substances were found in the zinc sulphide concentrate.

Scanning Electron Microscopy (SEM) was used to explore the structure and purity of the zinc sulphide concentrate. The particle size is too fine to be identified under the SEM (see Fig. 4-5-8). The chemical analysis results in the middle of the photo shown in Fig. 4-5-8 have been graphically presented in Fig. 4-5-9.

The analyses show that the second-stage flotation product was very pure and consisted mainly of zinc sulphide (Fig. 4-5-9A). Careful investigation found a trace amount of iron and aluminum. It may be assumed that a small amount of iron and aluminum ions in the wastewater were entrained with the zinc sulphide precipitate and entered into the concentrate. No copper and cadmium was found. Hence, the copper and zinc ions were well separated from the wastewater.

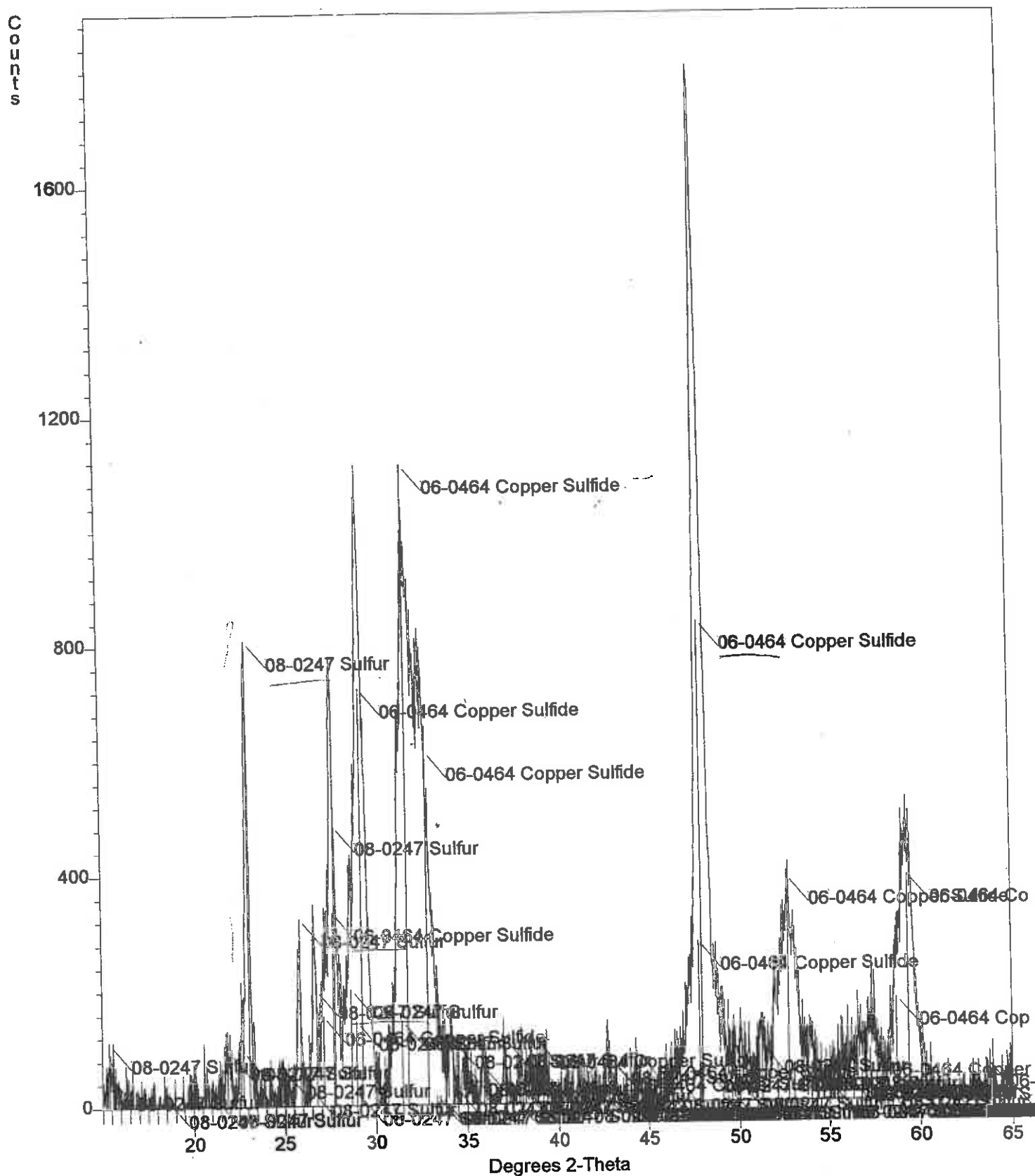


Fig. 4-5-6 The X-ray diffraction results of the first-stage flotation product (copper & cadmium sulphide) from section 5.3.4 Table 4-5-4

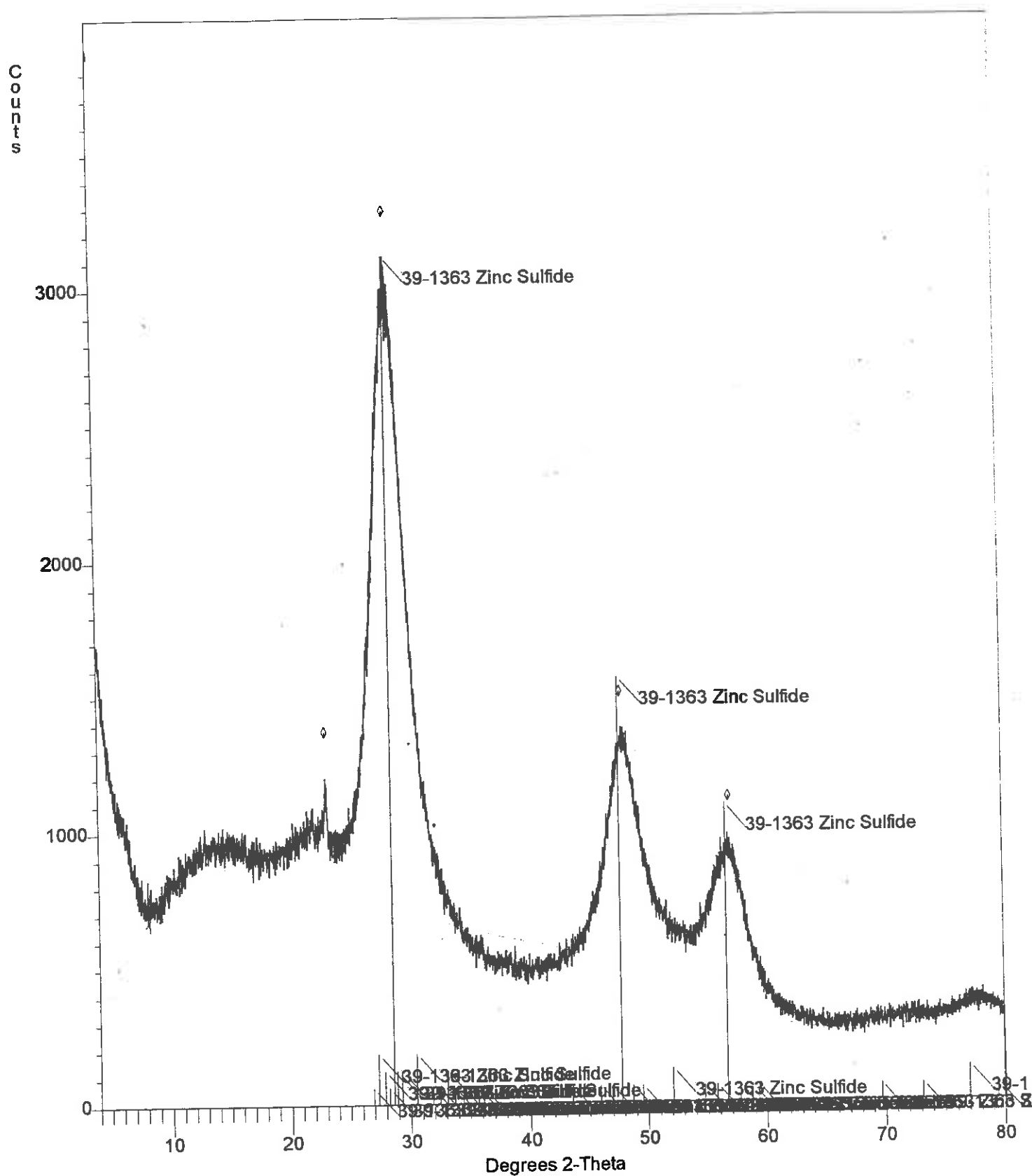
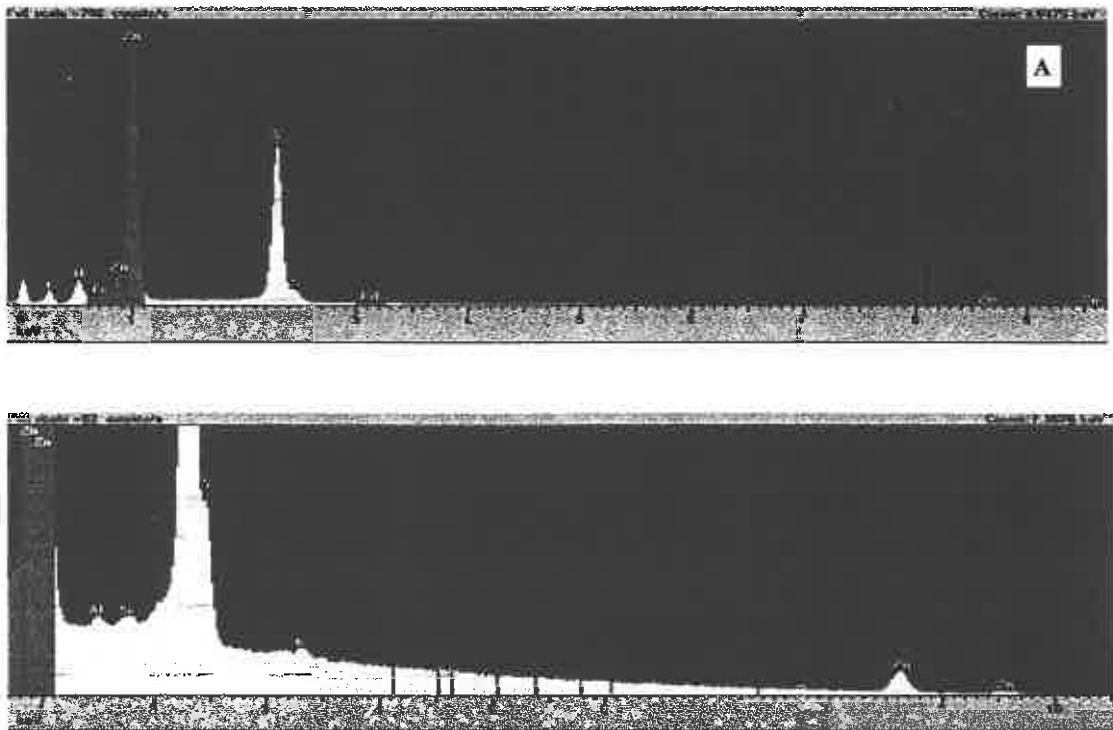


Fig. 4-5-7 The X-ray diffraction results of the second-stage flotation product (zinc sulphide) from section 5.3.4 Table 4-5-4



Fig. 4-5-8 The SEM photograph of the second-stage flotation product (zinc sulphide) ( $\times 9500$ )





## 5.4 Section Conclusion

- Copper and zinc ions could not be efficiently recovered (removed) from the Woodlawn wastewater using the hydroxide precipitate flotation method.
- Using sodium sulphide as precipitant and DAA as collector, with a very simple bulk flotation process, very high recoveries of zinc (93.44%), copper (98.62%) and cadmium (97.25%) were obtained from the Woodlawn wastewater. After 24 hours settling, the concentrations of copper and cadmium ions in the top clear solution were even lower than the analytical detection limits.
- With a two-stage sulphide precipitate flotation process, copper and zinc were efficiently separated and recovered from the Woodlawn wastewater without the need to adjust its original pH. In the first-stage flotation process, both sodium ethyl xanthate and DAA were tested as first-stage collector. In the first-stage, the best flotation recoveries of 97.06% Cu and 62.58% Cd were obtained with almost 100% zinc ion remaining in the solution for next stage flotation. In the second-stage flotation process, 98.24% of zinc ion was recovered from the wastewater.
- The XRD analyses indicated that the product obtained from the first-stage flotation process was copper sulphide (CuS) and that from the second-stage flotation process was zinc sulphide (ZnS). Elemental sulphur was found in the first-stage flotation product. The Scanning Electron Microscopy analyses showed that the second-stage flotation product was very pure and no copper and cadmium was found, however, trace amount of iron and aluminum elements were found.
- Both the bulk flotation process and the two-stage flotation process successfully floated zinc, copper and cadmium from the Woodlawn wastewater. The precipitate flotation processes have significant industrial potential for recovery of heavy metal ions from industrial wastewater in the future.

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## Chapter V Conclusions & Recommendations

### 5.1 Conclusions

1. Anionic collectors, such as SDBS and SDS, are efficient for both zinc and copper hydroxide precipitate flotation. The results of the precipitation and flotation of zinc and copper (as a function of pH) can clearly be explained by calculation of the hydrolysis reactions. A reasonable hydroxide precipitate flotation separation of copper and zinc ion from solution can be obtained at a pH of 6.1 in pure water. However, using hydroxide precipitation and flotation where ferric or aluminum ions are present in the solution, it is impossible to separate copper and zinc efficiently.
2. The zinc and copper hydroxide precipitate flocculation and flotation can be improved with electrolytes. The mechanisms of the influence of electrolytes on the hydroxide flocculation and flotation recovery can be adequately explained by using the classic DLVO theory calculation. The calculation results show that the "thickness" of the double layer and the total energy peak between two hydroxide precipitate particles drop significantly when the concentration of electrolytes is increased.
3. The self-carrier precipitate flotation (SCPF) process is a new process for the removal of heavy metal ion from solution. This process is less sensitive to changes in flotation conditions (pH and collector concentration) than conventional precipitate flotation. It would appear that the carrier precipitate behaves as a seed crystal to aid the aggregation and to combine the fine precipitate particles.
4. The particle size of the copper sulphide precipitate is so fine that a slight surplus of sulphide precipitant prevents the copper sulphide precipitate from being floated when ethyl xanthate is used as collector. However, with a surplus of copper ion in the solution, the copper sulphide precipitate can be efficiently floated by using ethyl xanthate as collector over the wide pH range of 2.5-11.5.
5. The floatability of copper sulphide precipitate (in the presence of a slight surplus of sulphide ion) can be significantly improved with prolonged stirring (more than 12

hours) in air, nitrogen or vacuum atmospheres. Suitable oxidation, using an oxidant such as  $\text{H}_2\text{O}_2$ , can achieve similar results. Oxidation of the copper sulphide precipitate surface is considered to be the main reason for the flotation improvement. However, excessive oxidation of the copper sulphide precipitate will cause the copper ion to redissolve into the solution, thereby decreasing the flotation recovery.

6. Extraneous ions, such as  $\text{Fe}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Zn}^{2+}$ , can improve the copper sulphide precipitate flotation in a specific pH range. The divalent metal ion species in the solution is considered to be the main reason for improved copper flotation recovery. It is suggested that the divalent metal ions act as a catalyzer assisting the xanthate ion to overcome the repulsive energy from the highly negatively charged copper sulphide surface. A specific amount of ferrous ion in the solution can improve the copper sulphide precipitate flotation. However, too many ferrous ions in the solution will cause the flotation to decrease. Ethyl xanthate is not a good collector for zinc sulphide precipitate in a wide pH range of 3 to 11. Hence, copper ions can be selectively floated from the synthetic solution by using sodium sulphide as precipitant and sodium ethyl xanthate as collector, the zinc ions remaining in the solution
7. The anionic collectors SDS and SDBS are inefficient collectors for copper and zinc sulphide precipitate flotation. The cationic collector DAA can collect copper and zinc sulphide precipitate over a wide pH range with adequate tolerance to the pH, the sulphide precipitant concentration and the changes in DAA concentration. The selective precipitation and flotation separation of copper and zinc ions from a synthetic solution has been achieved by using sulphide as precipitant and DAA as collector. The attachment of the non-thiol collectors (SDS, SDBS and DAA) onto the copper or zinc precipitate surfaces is considered to be the electrostatic type attraction.
8. The Woodlawn wastewater, containing harmful heavy metal ions such as zinc (~2000ppm), copper (~100ppm) and cadmium (~10ppm) at pH about 2.8, could not be efficiently floated using the hydroxide precipitate and flotation method. However, using sodium sulphide as precipitant and DAA as collector, with a very simple one-stage flotation process, very high recoveries of zinc (93.44%), copper (98.62%) and cadmium (97.25%) were obtained from the Woodlawn wastewater. After 24 hours

settling, the concentrations of copper and cadmium ions in the top clear solution proved to be even less than analytical detection limits.

9. In a two-stage sulphide precipitate flotation process, copper and zinc were separately floated and efficiently recovered from the Woodlawn wastewater without considerably changing the original pH. In the first-stage, the best flotation recoveries of 97.06% Cu and 62.58% Cd were obtained, while almost 100% zinc ion remained in the solution. In the second-stage flotation process, 98.24% of zinc ion was recovered.
10. The XRD analyses indicated that the product obtained from the first-stage flotation process was copper sulphide (CuS) and that obtained from the second-stage flotation process was zinc sulphide (ZnS). Elemental sulphur was found in the first-stage flotation product. Scanning Electron Microscopy analyses showed that the second-stage flotation product was almost pure ZnS and neither copper nor cadmium was found. However, a trace amount of iron and aluminum were found.

## 5.2 Recommendations

- Ethyl xanthate has been found to be an efficient collector for copper sulphide precipitate flotation over the wide pH range of 2.5-11.5 when a surplus of copper ion, as well as a slight oxidation on the sulphide precipitate surface was present in the solution. Thiol collectors show good potential for floating heavy metal sulphide precipitates from a solution. However, further studies need to be carried out towards a fuller understanding of the mechanism involved in the process.

In the flotation of sulphide minerals, the electrochemistry of the mineral surface and the reaction of xanthate have been extensively studied (Healy and Moignard, 1976; Janetski et al., 1977; Ahmed, 1978a, b; Bockris and Pillai, 1984). Investigations concerning the oxidation/reduction at the sulphide mineral surface have also been carried out (Castro et al., 1974a, b; Heyes and Trahar, 1979; Szczypa et al., 1980; Barzyk et al., 1981). Recent studies have used the rotating ring-disc electrode (RRDE) technique (Ahlberg and Broo, 1996a, b, c) to

investigate oxidation and reduction on the mineral surface. The nature of the interactions between sulphide minerals and xanthates has been thoroughly studied (Harris and Finkelstein, 1975; Mielczarski et al., 1995). Some surface analyses and in-situ techniques such as XPS, in-situ FTIR etc. (Buckley and Walker, 1988; Woods et al., 1990; Leppinen et al., 1989, 1995; Steudel et al., 1996) were used to study the surface chemistry.

Application of some of these techniques and instrumental analysis methods of sulphide mineral flotation in future studies, may well result in a better understanding of oxidation and the flotation of metal sulphide precipitate using xanthates as collector.

- The Self-Carrier Precipitate Flotation (SCPF) process can significantly improve the hydroxide precipitate flotation recoveries and make the flotation less sensitive to changes in flotation conditions. However, the SCPF process for sulphide precipitate flotation has not been tested. In future studies, a continuous flow flotation system for the SCPF process should be investigated.
- Heavy metal ions were efficiently separated and recovered from the Woodlawn Mines wastewater by using the sulphide precipitate flotation method. It is suggested that in future studies a continuous flow laboratory flotation system be established or alternatively a continuous dissolved-air flotation system to enable simulation of the plant flotation process. The future economic analyses can then be made.

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## Appendix 1 Solution Equilibrium Calculation

### 1. Anionic Ion Calculation

#### 1.1 Calculation method on the distribution of species for the anionic ion

##### 1.1.1 General Method

For anionic ion ( $A^{n-}$ ), the reactions in the water can be described like follows:

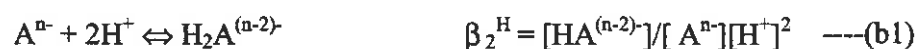
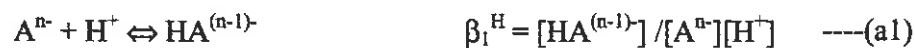


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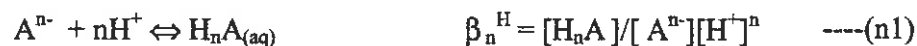


The above reactions can also be described as:



...

...



So,

$$\beta_1^H = K_1^H$$

$$\beta_2^H = [HA^{(n-2)-}] / [A^{n-}][H^+]^2 = [HA^{(n-2)-}][HA^{(n-1)-}] / [HA^{(n-1)-}][H^+][A^{n-}][H^+] = K_1^H K_2^H$$

...

$$\beta_n^H = \prod_{i=1}^n K_i^H \quad \text{----(1-1)}$$

From (a1) to (n1), the following results can be obtained:

$$[\text{HA}^{(n-1)-}] = \beta_1^H [\text{A}^{n-}] [\text{H}^+] \quad \text{---(a2)}$$

$$[\text{HA}^{(n-2)-}] = \beta_2^H [\text{A}^{n-}] [\text{H}^+]^2 \quad \text{---(b2)}$$

...

...

$$[\text{H}_n\text{A}_{(\text{aq})}] = \beta_n^H [\text{A}^{n-}] [\text{H}^+]^n \quad \text{---(n2)}$$

Set  $[\text{A}]_T$  as the total concentration of its complexes in the solution, from (a2) to (n2), it is:

$$\begin{aligned} [\text{A}]_T &= [\text{A}^{n-}] + [\text{HA}^{(n-1)-}] + [\text{HA}^{(n-2)-}] + \dots + [\text{H}_n\text{A}_{(\text{aq})}] \\ &= [\text{A}^{n-}] + \beta_1^H [\text{A}^{n-}] [\text{H}^+] + \beta_2^H [\text{A}^{n-}] [\text{H}^+]^2 + \dots + \beta_n^H [\text{A}^{n-}] [\text{H}^+]^n \\ &= [\text{A}^{n-}] \{ 1 + \beta_1^H [\text{H}^+] + \beta_2^H [\text{H}^+]^2 + \dots + \beta_n^H [\text{H}^+]^n \} \quad \text{---(1-2)} \end{aligned}$$

The fraction (distribution ratio) of each complexes in the solution, set as  $\Phi_n$ , can be calculated as follows:

$$\begin{aligned} \Phi_0 &= [\text{A}^{n-}] / [\text{A}]_T = [\text{A}^{n-}] / [\text{A}^{n-}] \{ 1 + \beta_1^H [\text{H}^+] + \beta_2^H [\text{H}^+]^2 + \dots + \beta_n^H [\text{H}^+]^n \} \\ &= 1 / \{ 1 + \beta_1^H [\text{H}^+] + \beta_2^H [\text{H}^+]^2 + \dots + \beta_n^H [\text{H}^+]^n \} \\ \Phi_1 &= [\text{HA}^{(n-1)-}] / [\text{A}]_T = \beta_1^H [\text{A}^{n-}] [\text{H}^+] / [\text{A}^{n-}] \{ 1 + \beta_1^H [\text{H}^+] + \beta_2^H [\text{H}^+]^2 + \dots + \beta_n^H [\text{H}^+]^n \} \\ &= \beta_1^H [\text{H}^+] \Phi_0 \\ &\dots \\ \Phi_n &= \beta_n^H [\text{H}^+]^n \Phi_0 \quad \text{---(1-3)} \end{aligned}$$

As  $\text{pH} = -\log[\text{H}^+]$ , so  $[\text{H}^+] = 10^{-\text{pH}}$ , formula (1-3) can also be changed as:

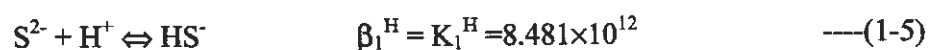
$$\begin{aligned} \Phi_0 &= 1 / \{ 1 + \beta_1^H 10^{-\text{pH}} + \beta_2^H 10^{-2\text{pH}} + \dots + \beta_n^H 10^{-n\text{pH}} \} \\ \Phi_1 &= \beta_1^H 10^{-\text{pH}} \Phi_0 \\ &\dots \\ \Phi_n &= \beta_n^H 10^{-n\text{pH}} \Phi_0 \quad \text{---(1-4)} \end{aligned}$$

From formula (1-4), it can be seen that the fraction of each complex is the function of the equilibrium constants and pH. At a certain temperature, the equilibrium constants for an anionic ion are constant, so pH is the only function of fraction of complexes at a given

temperature. Using formula (1-4), the diagram of distribution of species for an anionic ion vs pH can be drawn.

### 1.1.2 Example

Sodium sulphide ( $\text{Na}_2\text{S}$ ) is chosen as an example. The reaction of sodium sulphide in the water is as follows:



Using formula (1-4), the distribution of species  $\text{H}_2\text{S}_{(\text{aq})}$ ,  $\text{HS}^-$ , and  $\text{S}^{2-}$  can be calculated as follows:

$$\begin{aligned} \Phi_0 &= 1 / \{ 1 + 8.481 \times 10^{12} \times 10^{-\text{pH}} + 6.909 \times 10^{19} \times 10^{-2\text{pH}} + 7.977 \times 10^{20} \times 10^{-2\text{pH}} \} \quad (\text{S}^{2-} \text{ fraction}) \\ \Phi_1 &= 8.481 \times 10^{12} \times 10^{-\text{pH}} \times \Phi_0 \quad (\text{HS}^- \text{ fraction present}) \\ \Phi_2 &= 6.909 \times 10^{19} \times 10^{-2\text{pH}} \times \Phi_0 \quad (\text{H}_2\text{S}_{(\text{aq})} \text{ fraction present}) \\ &\quad \text{---(1-7)} \end{aligned}$$

The diagram is shown in Figure 1.

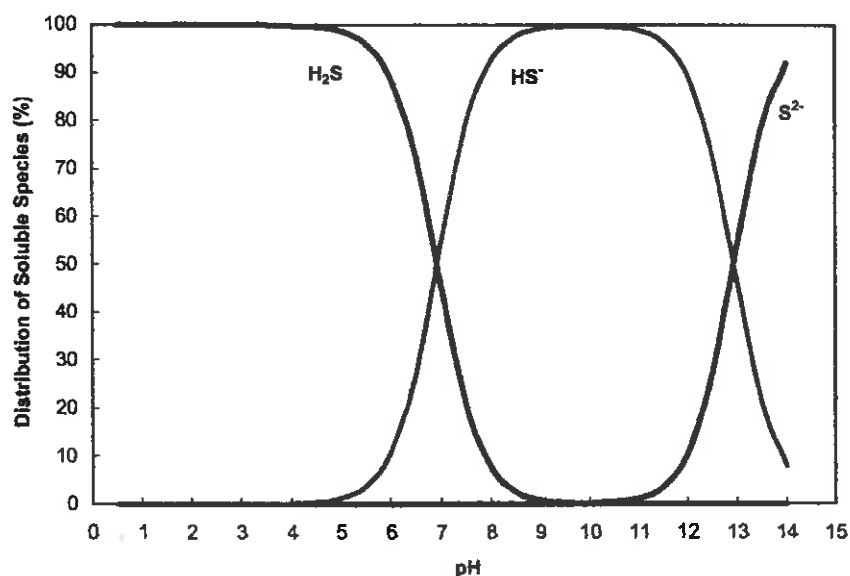


Figure 1. Distribution of species for sulphide ion vs pH

### 1.2 Calculation on the total concentration remaining in the water

When the concentration of  $H_nA_{(aq)}$  is high enough, it will form un-dissolvable species, like gas, precipitate or liquid phases. This will change the total concentration remaining in the water. The reaction can be as follows:



So, the concentration of  $[H_nA_{(aq)}]$  will be a constant, that is,

$$[H_nA_{(aq)}] = K \times [B_{(s, g, l)}]^x = C \quad \text{----(1-9)}$$

Normally, the concentration of  $[B_{(s, g, l)}]$  can be considered as 1, so the formula (1-9) will be:

$$[H_nA_{(aq)}] = K \quad \text{----(1-10)}$$

Note: when  $[B_{(s, g, l)}] \neq 1$ , the constant C needs to be determined and input into the calculation.

The formula (1-9) and (1-10) mean that the concentration of  $[H_nA_{(aq)}]$  cannot be more than  $K_{sp}$  (or  $C$ ).

If the concentration of  $[H_nA_{(aq)}]$  is high enough to produce the phase  $B_{(s, g, l)}$ , from Formula (n2), the concentration of  $[A^{n-}]$  can be calculated out as follows:

$$[A^{n-}] = [H_nA_{(aq)}] / \beta_n^H [H^+]^n = K / \beta_n^H [H^+]^n \quad \text{---(1-11)}$$

From formula (1-2), the total concentration of the complexes in the aqueous solution  $[A]_T$  will be:

$$\begin{aligned} [A]_T' &= [A^{n-}] \{ 1 + \beta_1^H [H^+] + \beta_2^H [H^+]^2 + \dots + \beta_n^H [H^+]^n \} \\ &= K \times \{ 1 + \beta_1^H [H^+] + \beta_2^H [H^+]^2 + \dots + \beta_n^H [H^+]^n \} / \beta_n^H [H^+]^n \quad \text{---(1-12)} \end{aligned}$$

It can be seen that the total concentration in the aqueous solution  $[A]_T'$  is only influenced by the equilibrium constants  $K$  and  $\beta$ . It is not a function of initial concentration  $C_T'$ , which means when equilibrium (1-8) occurs, the total concentration in the aqueous solution will become a constant, no matter how much the initial concentration  $C_T$  increases.

If the concentration of  $[H_nA_{(aq)}]$  is NOT high enough to produce the phase  $B_{(s, g, l)}$ , from Formula (n2), the total concentration in the aqueous solution will equals to the initial concentration  $C_T'$  (which is the user adds in), and at this condition the  $[A]_T$  (see the formula (1-2)) will equal to  $C_T'$ .

It is easy ascertain when the  $[H_nA_{(aq)}]$  will be high enough to produce the phase  $B_{(s, g, l)}$ , just compare  $[A]_T'$  and  $C_T'$ , if  $[A]_T' < C_T'$ , that means the equilibrium (1-8) is present and the phase  $B_{(s, g, l)}$  is produced. Otherwise, the equilibrium (1-8) has not been reacted.

So, the total concentration remaining in the aqueous solution  $C_T$  will be:

$$C_T = \text{MIN} ([A]_T', C_T') \quad \text{---(13)}$$

### 1.3 Calculation method on the concentration (or logarithm concentration) of each anionic species of as a function of pH

As we can calculate the total concentration remaining in the aqueous solution  $C_T$  using formula (1-13), and the fraction of each complexes varying with pH can be obtained from formula (1-4), so the concentration (or logarithm concentration) of each anionic species as a function of pH can be calculated as follows:

$$\begin{aligned}
 [A^{n-}] &= C_T \times \Phi_0 \\
 [HA^{(n-1)-}] &= C_T \times \Phi_1 \\
 &\dots \\
 [H_n A_{(aq)}] &= C_T \times \Phi_n
 \end{aligned}
 \tag{1-14}$$

And logarithm concentration is:

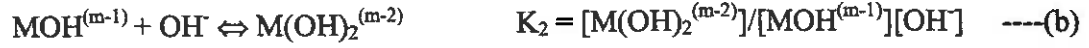
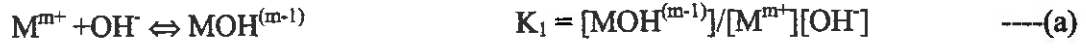
$$\begin{aligned}
 \text{Log}[A^{n-}] &= \text{Log}(C_T \times \Phi_0) \\
 \text{Log}[HA^{(n-1)-}] &= \text{Log}(C_T \times \Phi_1) \\
 &\dots \\
 \text{Log}[H_n A_{(aq)}] &= \text{Log}(C_T \times \Phi_n)
 \end{aligned}
 \tag{1-15}$$

As  $\Phi$  is a function of pH, so we can get the concentration (or logarithm concentration) of each species at various pH values.

## 2. Metal Ion Equilibrium Calculation

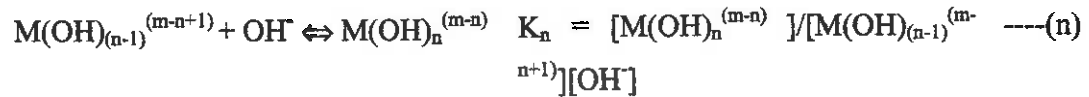
## 2.1 Calculation method on the distribution of species for the metal ion in aqueous solution

For metal ion ( $M^{m+}$ ), the reactions in the water can be described like follows:

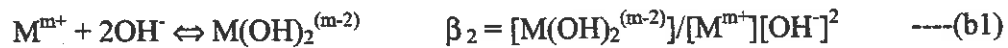
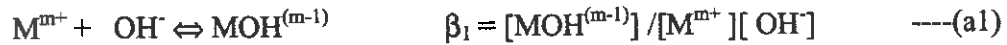


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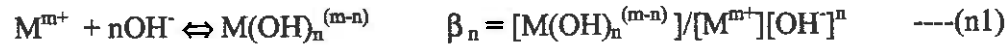


The above reactions can also be described as:



...

...



So,

$$\beta_1 = K_1$$

$$\beta_2 = K_1 K_2$$

...

$$\beta_n = \prod_{i=1}^n K_i \quad \text{---(2-1)}$$

From (a1) to (n1), the following results can be obtained:

$$[MOH^{(m-1)}] = \beta_1 [M^{m+}][OH^-] \quad \text{---(a2)}$$

$$[M(OH)_2^{(m-2)}] = \beta_2 [M^{m+}][OH^-]^2 \quad \text{---(b2)}$$

...

...

$$[M(OH)_n^{(m-n)}] = \beta_n^H [M^{m+}][OH^-]^n \quad \text{---(n2)}$$

Set  $[M]_T$  as the total concentration of its complexes in the solution, from (a2) to (n2), it is:

$$\begin{aligned} [M]_T &= [M^{m+}] + [MOH^{(m-1)}] + [M(OH)_2^{(m-2)}] + \dots + [M(OH)_n^{(m-n)}] \\ &= [M^{m+}] + \beta_1 [M^{m+}][OH^-] + \beta_2 [M^{m+}][OH^-]^2 + \dots + \beta_n [M^{m+}][OH^-]^n \\ &= [M^{m+}] \{ 1 + \beta_1 [OH^-] + \beta_2 [OH^-]^2 + \dots + \beta_n [OH^-]^n \} \end{aligned} \quad \text{---(2-2)}$$

The fraction (distribution ratio) of each complexes in the solution, set as  $\Phi_n$ , can be calculated as follows:

$$\begin{aligned} \Phi_0 &= [M^{m+}] / [M]_T = [M^{m+}] / [M^{m+}] \{ 1 + \beta_1 [OH^-] + \beta_2 [OH^-]^2 + \dots + \beta_n [OH^-]^n \} \\ &= 1 / \{ 1 + \beta_1 [OH^-] + \beta_2 [OH^-]^2 + \dots + \beta_n [OH^-]^n \} \\ \Phi_1 &= [MOH^{(m-1)}] / [M]_T = \beta_1 [M^{m+}][OH^-] / [M^{m+}] \{ 1 + \beta_1 [OH^-] + \beta_2 [OH^-]^2 + \dots + \beta_n [OH^-]^n \} \\ &= \beta_1 [OH^-] \Phi_0 \\ &\dots \\ \Phi_n &= \beta_n [OH^-]^n \Phi_0 \end{aligned} \quad \text{---(2-3)}$$

As  $pH = 14 + \log[OH^-]$ , so  $[OH^-] = 10^{(pH-14)}$ , formula (3) can also be changed as:

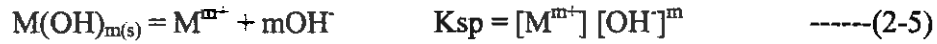
$$\begin{aligned} \Phi_0 &= 1 / \{ 1 + \beta_1 10^{(pH-14)} + \beta_2 10^{2(pH-14)} + \dots + \beta_n 10^{n(pH-14)} \} \\ \Phi_1 &= \beta_1 10^{(pH-14)} \Phi_0 \\ &\dots \\ \Phi_n &= \beta_n 10^{n \times (pH-14)} \Phi_0 \end{aligned} \quad \text{---(2-4)}$$

From formula (2-4), it can be seen that the fraction of each complex is a function of the equilibrium constants and pH. At a given temperature, the equilibrium constants for an anionic ion are constant, so pH is the only function of fraction of complexes at that temperature. Using formula (2-4), the diagram of distribution of species for an anionic ion vs pH can be drawn.

## 2.2 Calculation on the total metal ion remaining in the water



When the concentration of  $M(OH)_{m(aq)}$  is high enough, the  $M(OH)_{m(s)}$  precipitate will be produced. The equilibrium is shown as follows:



So, the concentration of  $[M^{m+}]$  will be:

$$[M^{m+}] = K_{sp} / [OH^-]^m = K_{sp} / 10^{m(pH-14)} \quad \text{-----(2-6)}$$

When the  $M(OH)_{m(s)}$  precipitate is produced in the aqueous solution, the total concentration of the complexes in the aqueous solution  $[M]_T'$  will be:

$$\begin{aligned} [M]_T' &= [M^{m+}] \{ 1 + \beta_1[OH^-] + \beta_2[OH^-]^2 + \dots + \beta_n[OH^-]^n \} \\ &= K_{sp} \times \{ 1 + \beta_1 \times 10^{(pH-14)} + \beta_2 \times 10^{2(pH-14)} + \dots + \beta_n 10^{n \times (pH-14)} \} / 10^{m(pH-14)} \quad \text{---(2-7)} \end{aligned}$$

It can be seen that the total concentration in the aqueous solution  $[M]_T'$  is only influenced by the equilibrium constants  $K$ ,  $\beta$  and  $pH$ . It is not a function of initial concentration  $C_{T0}$ .

As with the anionic ion calculation, the total concentration of metal ion complexes remaining in the aqueous can be determined by comparing  $[M]_T'$  with initial concentration  $C_{T0}$ . That is, the total concentration remaining in the aqueous solution  $C_T$  will be:

$$C_T = \text{MIN} ( [M]_T', C_{T0} ) \quad \text{-----(2-8)}$$

### 2.3 Calculation method on the concentration (or logarithm concentration) of each species of metal ion vary with pH

Using total concentration remaining in the aqueous solution  $C_T$  using formula (2-8), and the fraction of each complexes varying with  $pH$  obtained from formula (2-4), the concentration (or logarithm concentration) of each species of metal ion vary with  $pH$  can be calculated as follows:

$$\begin{aligned}
[M^{m+}] &= C_T \times \Phi_0 \\
[MOH^{(m-1)}] &= C_T \times \Phi_1 \\
&\dots \\
[M(OH)^{(m-n)}] &= C_T \times \Phi_n
\end{aligned}
\quad \text{---(2-9)}$$

And logarithm concentration is:

$$\begin{aligned}
\text{Log}[M^{m+}] &= \text{Log}(C_T \times \Phi_0) \\
\text{Log}[MOH^{(m-1)}] &= \text{Log}(C_T \times \Phi_1) \\
&\dots \\
\text{Log}[M(OH)^{(m-n)}] &= \text{Log}(C_T \times \Phi_n)
\end{aligned}
\quad \text{---(2-10)}$$

As  $\Phi$  is a function of pH, so we can get the concentration (or logarithm concentration) of each species at various pH values.

## 2.4 Saturated aqueous solution

For a saturated aqueous solution, precipitate exists, so the total concentration is according to the formula 2-7:

$$\begin{aligned}
C_T &= [M]_T \\
&= K_{sp} \times \{1 + \beta_1 \times 10^{(pH-14)} + \beta_2 \times 10^{2(pH-14)} + \dots + \beta_n 10^{n \times (pH-14)}\} / 10^{m(pH-14)}
\end{aligned}
\quad \text{---(2-11)}$$

the concentration of each species of metal ion vary with pH is:

$$\begin{aligned}
[M^{m+}] &= \Phi_0 \times K_{sp} \times \{1 + \beta_1 \times 10^{(pH-14)} + \beta_2 \times 10^{2(pH-14)} + \dots + \beta_n 10^{n \times (pH-14)}\} / 10^{m(pH-14)} \\
[MOH^{(m-1)}] &= \Phi_1 \times K_{sp} \times \{1 + \beta_1 \times 10^{(pH-14)} + \beta_2 \times 10^{2(pH-14)} + \dots + \beta_n 10^{n \times (pH-14)}\} / 10^{m(pH-14)} \\
&\dots \\
[M(OH)^{(m-n)}] &= \Phi_n \times K_{sp} \times \{1 + \beta_1 \times 10^{(pH-14)} + \beta_2 \times 10^{2(pH-14)} + \dots + \beta_n 10^{n \times (pH-14)}\} / 10^{m(pH-14)}
\end{aligned}
\quad \text{---(2-12)}$$

And logarithm concentration is:

$$\text{Log}[M^{m+}]$$

$$= \text{Log}(\Phi_0 \times K_{sp} \times \{1 + \beta_1 \times 10^{(pH-14)} + \beta_2 \times 10^{2(pH-14)} + \dots + \beta_n \times 10^{n \times (pH-14)}\} / 10^{m(pH-14)})$$

$$\text{Log}[\text{MOH}^{(m-1)}]$$

$$= \text{Log}(\Phi_1 \times K_{sp} \times \{1 + \beta_1 \times 10^{(pH-14)} + \beta_2 \times 10^{2(pH-14)} + \dots + \beta_n \times 10^{n \times (pH-14)}\} / 10^{m(pH-14)})$$

...

$$\text{Log}[M(\text{OH})^{(m-n)}]$$

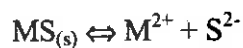
$$= \text{Log}(\Phi_n \times K_{sp} \times \{1 + \beta_1 \times 10^{(pH-14)} + \beta_2 \times 10^{2(pH-14)} + \dots + \beta_n \times 10^{n \times (pH-14)}\} / 10^{m(pH-14)})$$

---(2-13)

### 3. Divalent Metal Ion, Hydroxide and Sulphide Ion System Equilibrium Calculation

As shown above, the general calculation methods for the complexes of anionic ions and metal cationic ions have been discussed. In what follows, a more complicated system, the equilibrium of metal ion, hydroxide and an anionic ion mixed system, is discussed. In order to simplify the calculation, a divalent metal ion, hydroxide and sulphide ion system has been chosen. This is a common set of condition in waste water systems.

The concentration of sulphide species as a function of pH can be calculated using the method in part 1 and the equilibrium of divalent metal ion with hydroxide (pH) can be obtained from part 2. Here, we look at the equilibrium between metal ion and sulphide ion,



$$K_{sp(\text{MS})} = [\text{M}^{2+}][\text{S}^{2-}] \quad \text{----(3-1)}$$

Set:  $C_{T(M)}$  as the initial total metal ion concentration;  $C_{T(S)}$  as the initial total sulphide concentration;  $[M]_T$  as the total remaining metal ion concentration after reaction;  $[S]_T$  as the total remaining sulphide concentration after reaction.

Consider formula (1-14) and (2-9), at equilibrium we have:

$$K_{sp(MS)} = [M^{2+}][S^{2-}] = [M]_T \times \Phi_{0(M2+)} \times [S]_T \times \Phi_{0(S2-)} \quad \text{----(3-2)}$$

Assume that no  $H_2S$  gas escaped and no copper hydroxide or other copper precipitate (except  $CuS$ ) is formed. The following three cases are possible:

- When  $C_{T(S)} = C_{T(M)}$  :

As  $[M^{2+}] = [S^{2-}]$ , from Eq.(3-2):

$$[M]_T = \sqrt{K_{sp(MS)} / (\Phi_{0(M2+)} \times \Phi_{0(S2-)})} \quad \text{----(3-4)}$$

- When  $C_{T(S)} > C_{T(M)}$  :

This occurs when most of metal complexes have been precipitated, thus  $[S]_T \approx C_{T(S)} - C_{T(M)}$ , using this in Eq.(3-2), we get:

$$[M]_T = K_{sp(MS)} / (\Phi_{0(M2+)} \times \Phi_{0(S2-)} \times (C_{T(S)} - C_{T(M)})) \quad \text{----(3-5)}$$

- When  $C_{T(S)} < C_{T(M)}$  :

This occurs when most sulphide complexes have been precipitated, from Eq.(3-2):

$$[S]_T \approx \sqrt{K_{sp(MS)} / (\Phi_{0(M2+)} \times \Phi_{0(S2-)})}$$

Thus:

$$[M]_T = C_{T(M)} - C_{T(S)} + \sqrt{K_{sp(MS)} / (\Phi_{0(M2+)} \times \Phi_{0(S2-)})} \quad \text{----(3-6)}$$

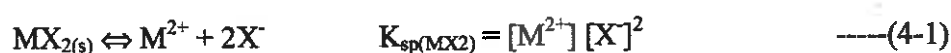
However, the above calculations only considered the sulphide as precipitant. With a change of pH, metal hydroxide precipitate may form as shown in 2.2, particularly when sulphide concentration is lower than total metal ion concentration. After consideration of both these two possibilities, the total concentration of metal ion remaining in solution after precipitation will be the minimum one of the two balances, that is:

$$C_T = \text{MIN} ([M]_T, C_{T(M(OH)_2)}) \quad \text{----(3-7)}$$

#### 4. Divalent Metal Ion, Hydroxide, Sulphide Ion and Univalent Collector System -- Equilibrium Calculation

For normal metal sulphide precipitate flotation system, there are not only divalent metal ion, hydroxide and sulphide ion in the aqueous solution, but also collector ion must to be considered. Normally anionic collectors like xanthate are monovalent, in order to simplify the calculation, here only monovalent collector has been considered.

Consider the reaction between metal ion and collector ion (set as  $X^-$ ),



From formula (1-14), it will be:

$$[M^{2+}] = K_{sp(MX_2)} / [X^-]^2 = K_{sp(MX_2)} / (C_{T(X)} \times \Phi_{0(X^-)})^2 \quad \text{---(4-2)}$$

Neglecting dissolved complexes of the metal ion with collector and assuming the total concentration of metal ion remaining in the aqueous solution is still considered as metal hydroxide complexes, using the formula (2-9), the total concentration of metal ion  $C_{T(MX_2)}$  in the presence of sulphide will be:

$$C_{T(MX_2)}' = [M^{2+}] / \Phi_{0(M^{2+})} = K_{sp(MX_2)} / [(C_{T(S)} \times \Phi_{0(X^-)})^2 \times \Phi_{0(M^{2+})}] \quad \text{---(4-3)}$$

Using  $C_{T(MX_2)}$  in formula (3-4), the total concentration of metal ion ( $C_T$ ) remaining in the solution will be:

$$C_T = \text{MIN} (C_{T(MS)}', C_{T(M(OH)_2)}, C_{T(MX_2)}')$$

## Appendix 2 Calculation of Aggregation and Dispersion of Fine Particles

A most important physical property of colloidal dispersions is the tendency of the particles to aggregate. Encounters between particles dispersed in liquid media occur frequently as the results of Brownian motion and the stability of a dispersion is determined by the interaction between the particles during these encounters.

In 1940s, Derjaguin and Landau (1941) and Verwey and Overbeek (1948) have independently developed a comprehensive theory of the interaction potential between colloidal particles. This so-called "DLVO theory" involves estimations of the energy of attraction (London-van der Waals forces,  $V_A$ ) and the energy of repulsion (overlapping of electric double layers,  $V_R$ ) in terms of inter-particle distance. According to the classical DLVO theory, the total energy ( $V_T$ ) between two particles can be described as:

$$V_T = V_A + V_R \quad (1.1)$$

The classical DLVO theory has successfully established the base of the colloid stability theory and clearly explained the phenomena of aggregation and dispersion of many electrostatic colloidal systems. Nevertheless, there are a large body of observations which do not fit into the DLVO scheme of colloid stability (Pashley, 1992). For example, when particles are highly hydrophobic and have the contact angles greater than  $45^\circ$ , it is necessary to consider an additional force, namely, the hydrophobic force (Churaev and Derjaguin, 1985). Direct force measurements showed that hydrophobic force at this condition are much larger than the dispersion forces (Rabinovich and Yoon, 1994).

In order to make the DLVO theory fit more complex colloidal systems, such as flotation or magnetic coating systems, it is necessary to consider all the main forces which act between the particles in the system. The extended DLVO formula with additional energy contributions is given as follows (Parsonage, 1988):

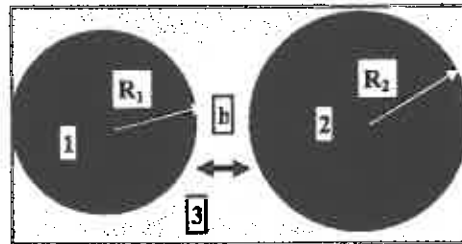
$$V_T = V_A + V_R + V_B + V_{HPB} + V_{ST} + V_{HDN} + V_{assoc} + V_M + V_{BR} \quad (1.2)$$

Where  $V_T$  is the total interaction energy;  $V_A$  is van der Waals forces;  $V_R$  is the electrical double layer interactions;  $V_B$  is the Born repulsion;  $V_{HPB}$  is the hydrophobic effects;  $V_{ST}$  is the steric interactions;  $V_{HDN}$  is the hydration forces;  $V_{assoc}$  is the hydrocarbon chain association;  $V_M$  is the magnetic interactions; and  $V_{BR}$  is the bridging forces.

Most of these interactions are amenable to modification by the use of reagents, such as surfactants and polymers, and it is by the judicious use of these that control over the selectivity of the coating process can be achieved. The various energies which may be involved in extending the DLVO calculation are briefly reviewed below.

### 1. Van der Waals forces ( $V_A$ )

These are attractive forces due to dipoles, induced dipoles and London forces. They may be modified by the presence of adsorbed layers. Fig.1 shows the interaction between two spheres.



The simplified expression (without considering the effects of retardation) for the van der Waals force ( $V_A$ ) between two identical colloid spheres (radius  $R_0$ ) is given as (Shaw,1970):

$$V_A = -\frac{AR_0}{12h} \quad (1.3)$$

where  $A$  is the Hamaker constant and  $h$  is the distance between the spheres.

The critical parameter determining the magnitude of van der Waals interaction is Hamaker constant. The expression of Hamaker constant is given as (Lu and Weng, 1992):

$$A = \pi^2 \rho^2 \frac{3\alpha_0^2 h_0 \nu}{4(4\pi\epsilon_0)^2} \quad (1.4)$$

where  $\rho$  is the density of the material;  $\alpha$  is the atomic polarizability;  $h_0$  is Plank's constant;  $\nu$  is the characteristic vibrational frequency of electrons and  $\epsilon_0$  is the permittivity of free space.

Eq. (1.4) expresses the Hamaker constant of isolated molecule or macroscopic bodies in a vacuum system. However, for dispersions of one phase in another, the effect of the medium must be taken into account. Set  $A_{11}$  as the Hamaker constant of particle of type 1 in a vacuum and  $A_{33}$  as the Hamaker constant of medium of type 3 in a vacuum, the Hamaker constant ( $A_{131}$ ) of two particles of type 1 separated by the medium of type 3 is:

$$A_{131} = A_{11} + A_{33} - 2A_{12} \approx (A_{11}^{1/2} - A_{33}^{1/2})^2 \quad (1.5)$$

For the particle of type 1 separated with particle of type 2 by the medium of type 3 (see Fig. 1), the Hamaker constant  $A_{132}$  is:

$$A_{132} \approx (A_{131} \times A_{232})^{1/2} \approx (A_{11}^{1/2} - A_{33}^{1/2}) (A_{22}^{1/2} - A_{33}^{1/2}) \quad (1.6)$$

What makes the result particularly interesting is that one of the factors in Eq. (1.6) can be positive and one negative, in which case the effective Hamaker constant itself becomes negative. This means that in this case, the van der Waals forces between the two particles are no longer as attraction interactions but rather repulsion forces.

The range of values of Hamaker constant for substances immersed in water can be summarized as follows (Hunter, 1987):

$$A = \underbrace{30 \quad 10}_{\text{metals}} \quad \underbrace{3 \quad 1}_{\text{oxides and halides}} \quad \underbrace{0.3}_{\text{hydrocarbons}} \times 10^{-20} J$$



These figures reflect the differences in the polarizabilities of various materials, on which  $A$  largely depends. For approximate calculations, the above information may be sufficiently accurate.

Values for various materials have been given by Gregory (1969), Visser (1972), Hunter (1987), and Lu and Weng (1992). A method for calculating the Hamaker constant from absorption data has been described by Hough and White (1980).

Schenkel and Kitchener (1960) gave a more accurate expression for the magnitude of the interaction by taking into account the effects of retardation.

For  $P_0 < 0.5$ :

$$V_A = -\frac{AR_1R_2}{6(R_1 + R_2)h} \left( \frac{1}{1 + 1.77P_0} \right) \quad (1.7)$$

For  $P_0 = 0.5$  to  $\infty$  and  $h \ll R_1$  or  $R_2$ :

$$V_A = -\frac{AR_1R_2}{6(R_1 + R_2)h} 12 \left[ -\frac{2.45}{60P_0} + \frac{2.17}{180P_0^2} - \frac{0.59}{420P_0^3} \right] \quad (1.8)$$

Where  $P_0 = 2\pi h/\lambda$

Further forms of the retarded van der Waals interaction in the presence of adsorbed layers have been described by Vincent (1973).

## 2. Electrical Double Layer Interactions ( $V_R$ )

Electrical double layer interactions arise due to the charges on the particles and the overlap of the ionic double layers. When two colloidal particles or two double-layer systems approach one another, the electrical interactions will occur. For same type particles, the forces will always be repulsive; for particles of difference types, the

interactive forces can be either repulsive or attractive, depending on the differences of the charges on the particle surfaces.

These forces are very important because they can be controlled by the changes of conditions or (and) the use of reagents, and subsequently control the aggregation or dispersion of the particles. The principal parameter determining their magnitude is the relevant potential at the particle surface and the Stern plane. The rather can, in many cases, be shown to be approximately equal to the potential measured by electrokinetic measurements, namely the  $\xi$ -potential.

The interaction between spherical particles has been given by Hogg et al. (1966) as:

*for constant potential interaction,*

$$V_R = \frac{\pi\epsilon_0\epsilon_r R_1 R_2 (\psi_1^2 + \psi_2^2)}{(R_1 + R_2)} \left\{ \frac{2\psi_1\psi_2}{(\psi_1^2 + \psi_2^2)} \ln \left[ \frac{1 + \exp(-\kappa h)}{1 - \exp(-\kappa h)} \right] + \ln[1 - \exp(-2\kappa h)] \right\} \quad (1.9)$$

*for constant charge interactions,*

$$V_R = \frac{\pi\epsilon_0\epsilon_r R_1 R_2 (\psi_1^2 + \psi_2^2)}{(R_1 + R_2)} \left\{ \frac{2\psi_1\psi_2}{(\psi_1^2 + \psi_2^2)} \ln \left[ \frac{1 + \exp(-\kappa h)}{1 - \exp(-\kappa h)} \right] - \ln[1 - \exp(-2\kappa h)] \right\} \quad (1.10)$$

Where  $\kappa$  is the Debye-Huckel parameter ( $\text{m}^{-1}$ );  $\epsilon_r$  is the relative permittivity;  $\psi_1$  and  $\psi_2$  are the zeta or Stern potential of particles 1 and 2.

The quantity of  $\kappa^{-1}$  is often called the "thickness" of the double layer. All distances within the double layer are judged large or small relative to this length. The  $\kappa$  can be calculated as (Hiemenz, 1986):

$$\kappa = \left( \frac{1000e^2 N_A}{\epsilon kT} \sum_i z_i^2 M_i \right)^{1/2} \quad (1.11)$$

Eq. (1.15) is of the same form as Eq.(1.3) and,  $K_{132}$  is the only parameter representing the magnitudes of the hydrophobic interaction.  $K_{132}$  can be determined using the hydrophobic force parameter for particle1-particle1 in the media 3 interaction ( $K_{131}$ ) and that for particle2-particle2 (or bubble-bubble) in the media 3 interaction ( $K_{232}$ ) using the combining rule (Yoon and Mao, 1996; Yoon et al., 1997; Mao and Yoon, 1997):

$$K_{132} = \sqrt{K_{131}K_{232}} \quad (1.16)$$

For the case of one hydrophobic surface approaching a hydrophilic surface, the interaction is intermediate to those between two hydrophobic surfaces and two hydrophilic surfaces (Claesson et al., 1987).

### 5. Steric interactions( $V_{ST}$ )

These forces are usually repulsive and arise due to interaction between adsorbed species on opposing surfaces as they approach.

High molecular weight polymers are often used in colloid and mineral systems. Consideration of these effects needs to be taken into account. Several theoretical approaches have been made to describe the steric effects and generally fall into two groups (Laskowski and Pugh, 1992): volume restriction effect (entropic theories) and interpenetration or osmotic pressure effect (osmotic theories). In entropic theories, the layers of adsorbed polymers do not penetrate on particles collisions but the compression effects cause a decrease in entropy. This results in an increase in Gibbs free energy causing interparticle repulsion. For the osmotic theories, the polymer chains can penetrate on collision causing an increase in Gibbs free energy due to the reduction of polymer chains in contact with the dispersion medium which increases the enthalpy. Also the configurational entropy of the adsorbed polymer is reduced.

For the conditions  $h > 2\delta$ , steric interactions are absent. When the particles approach such that  $h < 2\delta$  then either compression of the layer or mixing (interpenetration) of the chains take place.

For steric interactions due to compression effects, Jaeckel (1964) has given the following expression for identical spheres:

$$V_{ST} \approx \frac{E_y}{1.325} \left( \frac{2\delta_0 - h}{2} \right)^{5/2} (R_0 + \delta_0)^{1/2} \quad (1.17)$$

where  $E_y$  is the elastic modulus of the adsorption layer, which for cross-linked gelatin gels is in the order of  $10^5 \text{ Nm}^{-2}$ ;  $\delta_0$  is the adsorbed layer thickness in the uncompressed state.

Bagchi and Vold (1970) have given another expression of steric repulsion for two identical spheres:

$$V_{ST} = \left[ \frac{4\pi R_0 (l - h/2)}{Z(R_0 + l)} \right] \ln \frac{2l}{h} \quad (1.18)$$

where  $l$  is the length of the adsorbed polymer and  $Z$  is the occupation area for one polymer molecular.

For the interpenetration model, again for the condition that  $h < 2\delta$ , Ottewill (1977) has given the following expression:

$$V_{ST} = \frac{RT4\pi c_g^2}{3V_1 \rho_2^2} (\psi_{ent} - \chi_1) \left( \delta - \frac{h}{2} \right)^2 (3R_0 + 2\delta + h/2) \quad (1.19)$$

where  $c_g$  is the concentration,  $\text{kg/m}^3$ ;  $\psi_{ent}$  is the entropy parameter, ideally 0.5;  $\chi_1$  is the Flory interaction parameter characterising interaction of polymer with solvent;  $V_1$  is the molar volume of solvent molecules;  $\rho_2$  is the density of adsorbed material.

In fact, the volume restriction effect and interpenetration or osmotic pressure effect are always occurring at the same time and the total steric forces can be approximately regarded as the summarization of these two effects. From the view of numeral, the interpenetration effect is much important than the volume restriction effect.

## 6. Hydration forces( $V_{HDN}$ )

These effects arise through changes in the water structure and are induced by hydrated surfaces or by hydrated ions in the vicinity of the surface.

Generally, the repulsive hydration forces occur whenever the particles are strongly hydrated or water is strongly bound to hydrophilic groups such as  $-\text{OH}$ ,  $-\text{PO}_4^{3-}$ ,  $-\text{N}(\text{CH}_3)^{3+}$ , etc., and their strength depends on the energy needed to disrupt the ordered water structure and ultimately dehydrate the end groups of the adsorbed molecules.

Most authors express the hydration force as decaying exponentially with distance, for unequal spheres with layers of reagent of thickness  $\delta_1$  and  $\delta_2$ :

$$V_{HDN} = \frac{2\pi(R_1 + \delta_1)(R_2 + \delta_2)}{(R_1 + \delta_1) + (R_2 + \delta_2)} l_{HDN}^2 K_{HDN} \exp[-(h - (\delta_1 + \delta_2))/l_{HDN}] \quad (1.20)$$

The values of the hydration constant  $K_{HDN}$  are in the range  $8 \times 10^5 \sim 10^7 \text{ Nm}^{-2}$  for silicate minerals, with decay lengths  $l_{HDN}$  of the order of 1 nm (Israelachvili and Adams, 1978).

## 7. Hydrocarbon chain association

This effect is the attraction force due to association of hydrocarbon chains as the particles approach each other. Parsonage (1987) has given an expression for the magnitude of this interaction.

For identical spheres:

$$V_{assoc} = 2[CH_2^1] \times v_0 \phi K_f \quad (1.21)$$

where:

$$[CH_2^1] = \frac{3R_0^2 C_{surf} n_c}{[(R_0 + \delta)^3 - R_0^3]}$$

$$v_0 = \frac{2\pi}{3} \left( \delta - \frac{h}{2} \right)^2 \left( 3R_0 + 2\delta + \frac{h}{2} \right)$$

$$\phi = -0.8RT \text{ approx.}$$

$$K_f = 0 \text{ to } 1$$

### 8. Magnetic interactions( $V_M$ )

In magnetic fields, this interaction is probably very strong for some kinds of particles such as hematite. Pugh (1992) indicated that the hematite particles can flocculate in magnetic fields of about 0.1T for 1  $\mu\text{m}$  and about 3T for 10 $\mu\text{m}$ , where the particles have an electrostatic repulsive potential.

Watson (1976) has given the following equation for the magnetic interaction between two particles:

$$V_M = -\frac{4\pi^2 R_0^6 \chi_v^2 B_0^2}{(2R_0 + h)^3 \mu_0} \quad (1.22)$$

where  $\chi_v$  is the volume magnetic susceptibility;  $B_0$  is the magnetic flux density;  $\mu_0$  is the permeability of free space.

### 9. Polymer Bridging Forces( $V_{BR}$ )

These interactions due to bridging by long chain polymers are dependent on factors such as time and mixing regime. These influence the conformation of polymer at the particle surface and make equilibrium impossible.

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## Appendix 3 List of Publications Produced During PhD Study

1. Ren, X.; Brady, K.T.; and Schrieke, R.R.; 2000, Recovery and Separation of Zinc, Copper and Cadmium from Woodlawn Mines WasteWater Using Precipitate Flotation Method. (accepted by XXI IMPC, Rome, Italy, 2000)
  2. Zhang, J., Brady, K.T.; and Ren, X.; 1999, Removal and Recovery of Nickel from Electroplating Waste Solution by Precipitate Flotation. (Submitted for "6<sup>th</sup> Conference on Environmental Science & Technology (CEST)", Samos, Greece, Aug. 30-Sep. 2, 1999)
  3. Ren, X., Brady, K.T., Jay, W.H., & Schrieke, R.R. 1997, A Study of "Self-Carrier" Precipitate Flotation for the Removal of Heavy Metal Ions from Solution. In: H. Hoberg, & H. Blottnitz (Eds.), Proceedings of the XX IMPC (Volume 3) (pp. 693-704). Aachen, Germany: GDMB.
  4. Ren, X.; Brady, K.T.; McKee, I, 1996, Recycling of Surfactants in Ion Flotation, UB Postgraduate Conference 1996, Ballarat, Australia.
  5. Ren, X.; Li, Q.; Zhang, Y.; and Liu, D.; 1995, Development of SL-type centrifugal separator for the gravity concentration of fines and ultra-fines, Proceedings of the 19th International Mineral Processing Congress, October 23-27, San Francisco, USA,
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## **Appendix 4 A Copy of Main Publication**

***---- A Study of "Self-Carrier" Precipitate Flotation  
for the removal of Heavy Metal Ions from Solution***

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# A study of "self-carrier" precipitate flotation for the removal of heavy metal ions from solution

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## Abstract

*In this paper, a new process, named "self-carrier" precipitate flotation (SCPF) using an anionic surfactant as collector is described. Laboratory tests on the removal of zinc ion from pure water were carried out using this process. The results show that the recovery of zinc ion can be increased from 92% using conventional precipitate flotation to more than 97% for the SCPF process with the added benefit of more a controllable flotation process. The mechanism of the SCPF process is discussed in detail with reference to data collected from Optical Microscopy, Scanning Electron Microscopy and Zeta potential measurement.*

## 1 Introduction

The removal of heavy metal ions from waste water is one of the most urgent problems in mining and metal process industries. Hydroxide precipitation of heavy metals followed by settling of the precipitates is most often used to treat industrial wastewater [1,2]. An hydroxide precipitate process, which returns part of the precipitate slurry back to the precipitate reaction cell, has been briefly introduced [3] and it is claimed that good results have been obtained in copper and zinc industrial wastewater treatment in Japan.

Self-Carrier Precipitate Flotation (SCPF) is a new process in precipitate flotation for the removal of heavy metal ion from solution. In this process, the floated foam (heavy metal precipitate) was treated and returned to the flotation column and used as a self-carrier for adsorbing the heavy metal ions from the solution prior to re-flotation. The returned precipitate (self-carrier) can act as a seed crystal which adsorbs the ions precipitating on the surface, and also acts as a bridge to combine the fine "fresh" precipitates. Thus the collector consumption can be reduced.

Carrier flotation has been considered as one efficient way for recovering the fine minerals in mineral processing [4]. It has been noticed that autogenous or ramification carrier flotation [5,6], which used the same pre-conditioned coarse mineral particles instead of externally added minerals as a carrier, has achieved a higher recovery and better separation efficiency with the reagent consumption markedly reduced. The optimum size of carrier using this process is 25 to 36 microns[7]. This size range however is not applicable for the precipitate flotation process.

Precipitate flotation has been extensively reviewed by several authors [8,9,10,11] almost in every decade since this process was developed. Very few papers have been devoted to the actual precipitation process. This has inspired the authors to undertake the present study to develop the self-carrier precipitate flotation process for precipitate flotation and to clarify the mechanism occurring in this process. Zinc ion was used as an example of heavy metal ions in this paper.

## 2 Experimental

### 2.1 Reagents and solutions

Solutions containing zinc ions, obtained from analytically pure zinc sulfate (AJAX Chemicals), were used for this study in double distilled water. Analytical grade sodium hydroxide and nitric acid (AJAX Chemicals) were used to adjust pH. Sodium DodecylBenzeneSulphonate (SDBS) (Aldrich Chemical Company, Inc. USA) dissolved to  $2 \times 10^{-2}$  M concentration was used as collector.

### 2.2 Flotation

Flotation was carried out in a multibubble apparatus, which is similar to that described by Jurkiewicz [12,13]. The apparatus was a 320mm high and 250ml volume glass column with a G-3 sinter (15-40  $\mu$ m nominal porosity) at the base. The conventional precipitate flotation process is: a small volume of a concentrated aqueous solution of the modifiers ( $\text{HNO}_3$ , NaOH, etc.) was added to the zinc feed solution (250 ml). After it was stirred (magnetic stirring) for 20 min, the collector was added and stirred for a further 10 min. Then, the feed solution was transferred to the flotation column and floated for 5 min at a constant air flow rate of 70  $\text{cm}^3/\text{min}$ . The pH of feed solution was measured twice, before flotation (pH<sub>i</sub>) and after flotation (pH<sub>f</sub>). Ambient temperature conditions were used (20 $\pm$ 2°C).

The removal rates were determined by measuring the zinc ion residual concentrations in the treated solutions. These solutions were diluted and acidified ( $\text{HNO}_3$  2% by vol) in order to ensure complete solution of the zinc ion and precipitate. The removal rate was calculated as follows:

$$R(\%) = (1 - C/C_0) \times 100 \quad (1)$$

where, C is the total concentration of zinc ions in the treated solution (in the dissolved and precipitated state), and  $C_0$  is the initial concentration of zinc ion in the feed solution.

### 2.3 Measurements

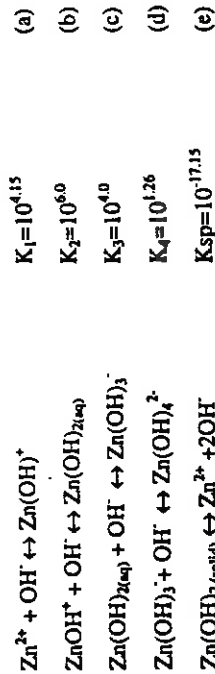
A 900P Microprocessor pH Meter (T.P.S. Pty Ltd, Australia) was used to measure the pH and temperature of solution, and a Varian SpectraAA-20 atomic absorption spectrophotometer was used to analyze for zinc ion. A Nikon Optical Microscope was used to measure the size of precipitates. Scanning Electron Microscopy was used to investigate the coagulation and dispersion of precipitates

(Jeol JSM-6300). A Coulter 440 Laser Zeta potential meter was used to measure the zeta potential of precipitates with the assistance of the staff at the University of Melbourne.

## 3 Results and discussion

### 3.1 Ionic equilibrium

Heavy metal ions remaining in the water will produce a series of complexes with hydroxyl ion. The reactions of zinc ion with hydroxyl ion have been shown to be as follows at 25°C [14]:



According to the above reactions, the ionic equilibrium diagram and the total ion concentration remaining in the solution varies with pH. A specific computer program which was developed by the authors was used to show the variation of the species with pH. Figure 1 and Figure 2 show that variation. A total zinc concentration of 50ppm (0.765mM) was considered.

Figure 1. illustrates the variation in molar percent of the various complexes of zinc ion in the solution as a function of pH. When  $\text{pH} > 9.5$ , the negative complex/s will be the dominant species. From Figure 2. it can be seen that when the pH is in the range of 8.5-10, the solubility of zinc hydroxide is the lowest, which means there is much more zinc hydroxide precipitate existing in this pH range.

### 3.2 Flotation behavior

The effect of pH on the flotation recoveries of zinc from three solutions of different initial zinc ion concentration is shown in Figure 3. The anionic collector Sodium DodecylBenzeneSulphonate (SDBS) was used in the flotation described in Figure 3.

It appears from Figure 3 that the maximum removal of zinc can be obtained in the pH range 8.5-9.5. Thus, with reference to Figure 2, it can be seen that the highest recovery can be obtained in the pH range at which the solubility of zinc hydroxide is the lowest. The initial concentration of zinc ion in solution is not influencing the recovery significantly.

### 3.3 Self-carrier precipitate flotation

Based on the concept of Self-Carrier Precipitate Flotation, four interesting flowsheets have been developed as shown in Figure 4.

Figure 4A shows that the foam from the first stage precipitate flotation was treated using sodium hydroxide and immediately added to the second flotation stage. Figure 4B shows that the first stage foam has been aged (without stirring) for 24 hours and then added to the second flotation stage without any sodium hydroxide pre-treatment. Figure 4C shows that the first stage foam has been aged for 24 hours and then was treated using half the amount of sodium hydroxide and added to the second flotation stage which was pre-treated using another half amount of sodium hydroxide.

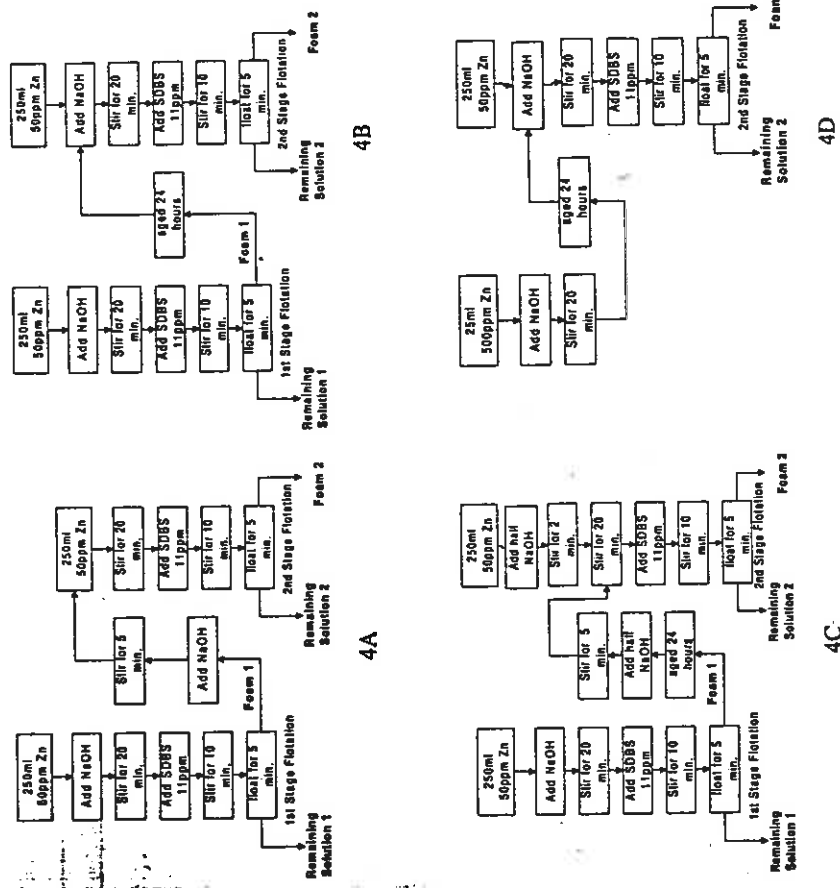


Figure 4: Self-carrier precipitate flotation flowsheets

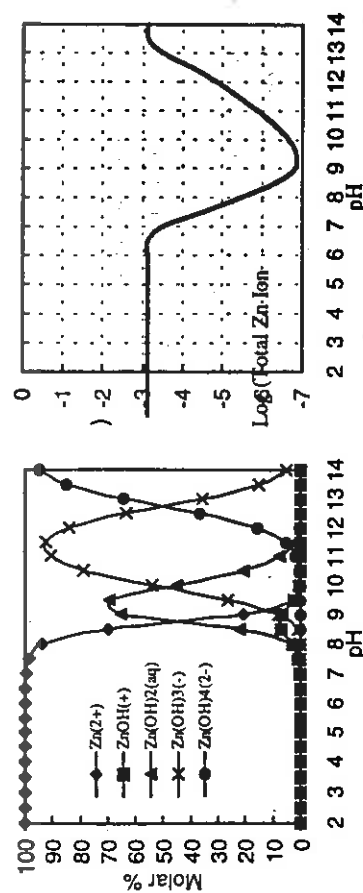


Figure 1: Zinc ionic equilibrium diagram for an initial concentration of 50 ppm.

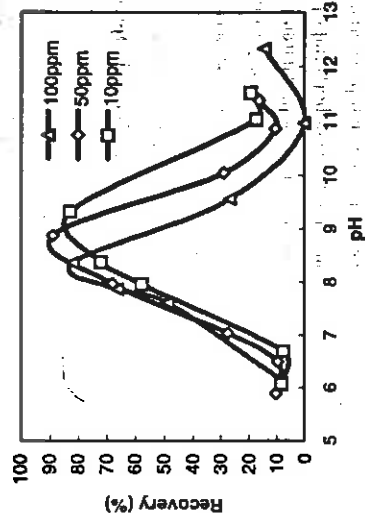


Figure 2: The effect of pH on the flotation recoveries of zinc from three solutions of different initial zinc ion concentration using SDBS as collector at 11ppm ( $3 \times 10^{-5}$  M).

However, when the pH is above 9.5, the recovery decreases although the solubility of zinc hydroxide is still very low at this pH (see Figure 2). The reason for this is considered to be as follows. When the pH > 9.5, the concentration of the negatively charged complexes ( $Zn(OH)_3^-$ ,  $Zn(OH)_4^{2-}$ ) are becoming more significant (see Figure 1), the zeta potential of precipitate is becoming more negative (See Figure 5) and this will impede the negatively charge anionic collector ions (SDBS) from adsorbing onto the surface of the precipitate. This explanation was also suggested by Rubin [15], Basak and Charewicz [16] and Jurkiewicz [13].

Figure 4D shows a flowsheet in which a high initial zinc concentration is used to make the  $Zn(OH)_2$  precipitate followed by 24 hrs of aging prior to its addition into the flotation process. In all these flowsheets, the flotation pH was controlled at  $8.8 \pm 0.2$ .

The self-carrier precipitate flotation (SCPF) results for the above flowsheets are shown in Table 1.

Table 1: Self-carrier precipitate flotation (SCPF) results (2nd Stage Flotation) compared with the conventional precipitate flotation results (1st Stage Flotation). SDBS 11ppm.

Flowsheet	Tests	Zn Conc. of Remaining Solution1(ppm)	Zn Conc. of Remaining Solution2(ppm)	Recovery (%) (1st Stage Flotation )	Recovery (%) (2nd Stage Flotation)
Figure 4A	1	5.014	2.300	89.97	95.40
Figure 4A	2	3.500	2.298	93.00	95.41
Average		4.257	2.299	91.49	95.40
Figure 4B	1	5.690	1.742	88.62	96.52
Figure 4B	2	3.016	1.452	93.97	97.10
Figure 4B	3	2.604	1.614	94.79	96.77
Figure 4B	4	5.112	2.526	89.78	94.95
Average		4.106	1.833	91.79	96.34
Figure 4C	1	4.600	1.526	90.80	96.95
Figure 4C	2	4.052	1.166	91.90	97.67
Figure 4C	3	3.656	1.426	92.69	97.15
Figure 4C	4	3.684	1.014	92.63	97.97
Average		3.998	1.283	92.00	97.44
Figure 4D	1		1.352		97.28
Figure 4D	2		1.428		97.14
Average			1.390		97.21

From Table 1 it can be seen that all four SCPF flowsheets have obtained much better recoveries than that of the conventional precipitate flotation. Comparing the four flowsheets, the best results can be obtained from Figure 4C.

Figure 5 shows the difference in zeta potential between the "fresh" (stirring 20 minutes) and aged (24 hours) zinc hydroxide precipitate. Compared with the "fresh" precipitate, the zeta potential of aged zinc hydroxide precipitate seems less positive and negative respectively in the pH range 7.5 to 11 than the "fresh" precipitate. For "fresh" precipitate, when  $pH < 8.7$ , it is positively charged and when  $pH > 8.7$ , it becomes negatively charged.

Considering flowsheet Figure 4C, when the self-carrier precipitate (aged 24 hours) was treated using half the amount of sodium hydroxide, the pH was raised to 11.5 and the zeta potential of the precipitate was about -27mV. At the same time, the bulk solution was treated using the other half of the sodium hydroxide, before the self-carrier precipitate was added. The pH of the solution was  $8 \pm 0.2$  and the zeta potential of the "fresh" zinc precipitate was about +8mV. When the carrier precipitate was added, the negatively charged carrier strongly adsorbed the positively charged "fresh" zinc precipitate and a better flotation recovery was achieved.

With the results of Figure 4B and Figure 4D, no evidence has been found that the reagent (collector) carried over from the concentrate foam (self-carrier) has improved the zinc recovery. This is probably because the influence of additional collector at an SDBS:Zn ratio above 0.04 is very small. (see Figure 6).

Since the results from flowsheet Figure 4D are similar to those from Figure 4C, the flowsheet Figure 4D was used to develop SCPF data for Figures 6, 7 and 8 as its conditions are controlled more easily than those of Figure 4C in the laboratory.

Figure 6 illustrates the effect of concentration of SDBS on the zinc recovery between the conventional precipitate flotation and SCPF. The effect of pH on the zinc recovery between the conventional precipitate flotation and SCPF is shown in Figure 7. Compared with conventional precipitate flotation, the SCPF process has a much wider adaptability to the change of pH and collector concentration, over which a high recovery is obtained and that a lower collector concentration can be used. When the SDBS:Zn molar ratio is 0.02 and 0.03, for the conventional precipitate flotation the precipitate is difficult to float, but using SCPF process it can obtain reasonable recoveries.

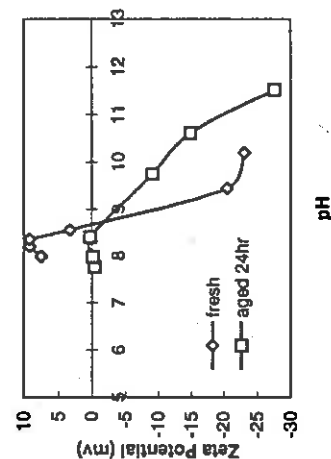


Figure 5: Zeta potential of the "fresh" (stirring 20 minutes) and aged (24 hours) zinc hydroxide precipitate.

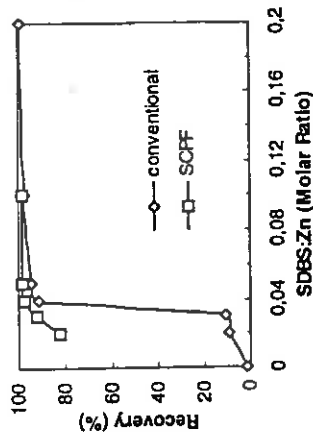


Figure 6: Effect of concentration of SDBS on the zinc recovery between the conventional precipitate flotation and SCPF.

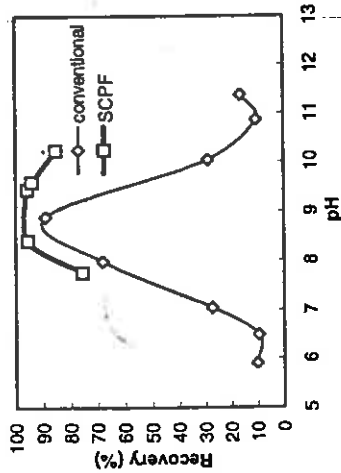


Figure 7: Effect of pH on the zinc recovery for the conventional precipitate flotation and SCPF (SDBS 11ppm).

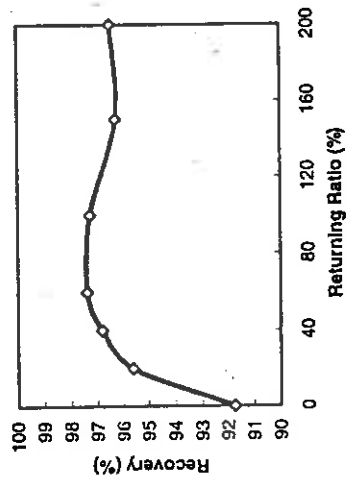


Figure 8: Effect of self-carrier returning ratio of SCPF on the zinc recovery (SDBS 11ppm).

The effect of self-carrier returning ratio on the zinc recovery using Figure 4D flowsheet has been tested and the results are shown in Figure 8.

The returning ratio is defined as the amount of zinc contained in the aged solution in Figure 4D (25 ml, 500ppm) compared with the amount of zinc in the flotation feed stream (250ml, 50ppm) in Fig 4D. This combination of concentrations and volumes gives a returning ratio of 100%. From Figure 8 it can be seen that good results can be obtained even when the returning ratio of the self-carrier to the target ion in the solution varies from 20-200%.

From Figures 6, 7 and 8, it can be seen that the SCPF process is tolerant to a wide range of flotation conditions. This provides the possibility for this process to be more readily accepted and more widely used in the future.

### 3.4 Microphotographs and discussion

In order to understand how the SCPF process works, Optical Microscopy and Scanning Electron Microscopy were used to investigate the precipitate changes during the process.

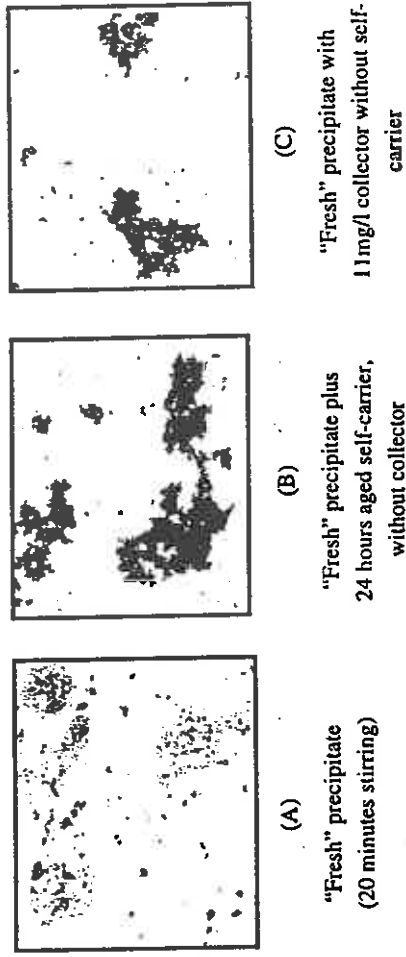


Figure 9: Optical microphotographs of precipitate in various conditions (pH=8.8±0.2).

Figure 9 shows the optical microphotographs of precipitate in various conditions. It can be seen that the "fresh" zinc hydroxide precipitate is very fine and only slightly agglomerated. (Figure 9A). When self-carrier precipitate (aged 24 hours) was added, the precipitates agglomerate and became larger aggregates (Figure 9B). This is very similar to the appearance of "fresh" precipitate with some collector (SDBS) added (Figure 9C). The fine structures of precipitates and aggregates were revealed by Scanning Electron Microscopy as shown in Figure 10.

Figure 10A illustrates that the "fresh" precipitate is amorphous with the particle size around 0.1-0.5 micron. After 24 hours aging, most of the precipitate (self-carrier) grows and becomes plate like crystals with the size around 5-10 microns although a small amount of amorphous precipitate



still can be found (Figure 10B). When 24 hour aged self-carrier precipitate was put into the "fresh" precipitate, it can be seen that the plate-shape crystals became larger and thicker and it also adsorbed (combined) a lot of small amorphous precipitates (Figure 10C), this increased the precipitate size and decreased the total precipitate surface area and subsequently reduced the consumption of collector. Figure 10D shows that the small amorphous precipitates were combined with the aid of collector, very few large plate-shaped crystals were found. This means that part of the function of the collector is to combine the fine precipitate.

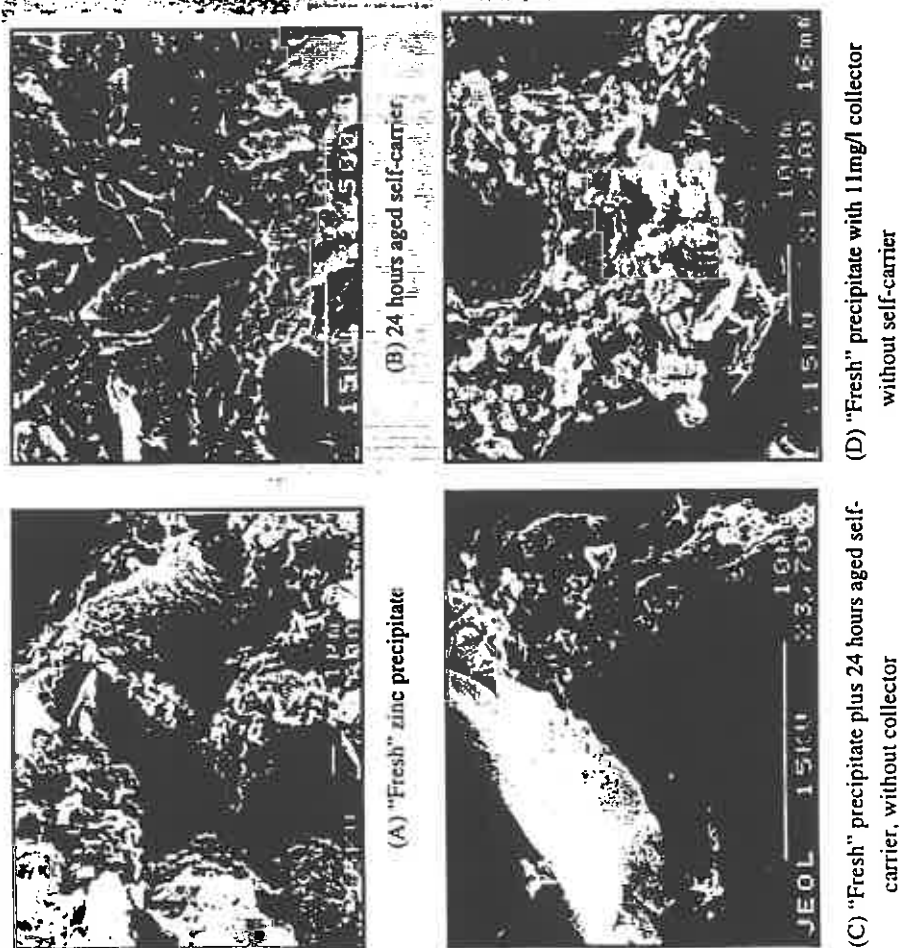


Figure 10: SEM microphotographs of precipitate in various conditions (pH=8.8±0.2).

Summarizing above evidence, the mechanism of self-carrier precipitate flotation is considered to be in the first instance, the new precipitate was produced on the surface of the carrier which acted like a seed crystal; secondly the carrier can adsorb (combine) the "fresh" precipitate that has already

existed in the solution and produce larger aggregates. This partly replaces the function of the collector and hence improves the flotation recovery.

## 4 Conclusions

The self-carrier precipitate flotation (SCPF) is a new process for removal heavy metal ion from the solution. The laboratory tests have shown that it can improve the zinc hydroxide precipitate flotation results.

The SCPF process is less sensitive to changes in flotation conditions than the conventional precipitate flotation.

The mechanism of self-carrier precipitate flotation is considered to be that the carrier precipitate behaves as a seed crystal to aid the aggregation and to combine the fine precipitate particles.

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# Flotation technology for high enrichment of rare metal production tails

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## Abstract

*There have been flotation processes developed in view to obtain lithium concentrates, potassium feldspar and all concomitant products on the conditions of complete water recycling from the rare metals processing tails - a poor off-grade material. The main technological problem has been solved by application of chosen minute doses of various chemical classes reagents for better selectivity in the flotation process permitting to sharply reduce the total consumption of flotation reagents.*

## 1 Introduction

The rare metal production tails presented by micas are rarely treated further on due to absence of reliable techniques permitting to recover the most valuable component - potassium feldspar at the ratio  $K_2O/Na_2O$  below 1.0. Any novel technology for thorough beneficiation of such material will create a powerful source for extra production without new deposits having to be developed, thus saving the environment at the same time.

## 2 Characteristics of the investigation subject

Integrated technology for the rare metal amazonite granites of the Etykin massive [1] permits to obtain Ta, Nb, Sn but it accumulates waste flotation tails totaling 90% of the rock mass coming for processing. The mineralogical composition of the tails, %: albite - 59.9, microcline - 20.1, quartz - 16.5, lithium micas - 3, other minerals (topaz, apatite, sulphides, etc.) - 0.5. The data on chemical composition of tails and major constituting minerals are given in Table 1.

It is characteristic of the minerals in the product to have lower contents of valuable components as well as their non-uniformity due to microinclusions. The micas are presented by lithium-containing isomorphous species series: zinnwaldite-cryophyllite-lepidolite. The composition of minerals permits to obtain high quality commercial products.

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