USE OF SILICA SOL IN SELECTIVE SULPHIDE MINERAL FLOTATION

by

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This thesis is dedicated to my brother, B. Easwaran.

ABSTRACT

Micro - and batch flotation tests were conducted to explore the use of silica sol to control metal ions to reduce accidental activation and misplacement of minerals. As a comparison other 'metal control reagents', ethylenediaminetetraacetic acid (EDTA) and polyphosphate were also tested. X-ray photoelectron spectroscopy (XPS) was used to probe the silica sol - mineral interaction mechanism.

Micro flotation was performed on single mineral samples over a pH range 7 to 11. It was found that silica sol depressed all Cu minerals, Cu and Pb activated pyrite and Pb activated sphalerite but did not depress Cu activated sphalerite. XPS analysis revealed that silica sol adsorbed on all Cu minerals and Cu and Pb activated pyrite. Silica sol partially removed Pb from Pb activated sphalerite and had no apparent interaction with Cu activated sphalerite. The depressant action, therefore, appeared to be primarily adsorption of silica sol to form hydrophilic sites.

In the batch tests, generally, silica sol, polyphosphate and EDTA increased the rate of flotation in the Cu stage and in the Zn stage. This is attributed to removal of hydrophilic metal hydroxy species, i.e., surface 'cleaning'. Polyphosphate, and to a lesser extent EDTA, improved selectivity in the Zn stage for Les Mines Selbaie and Mine Louvicourt and arguably for Hudson Bay Mining and Smelting. This selectivity was not identified in the trials at Brunswick Mine directly on Zn stage flotation feed. The varying effect of polyphosphate on selectivity is attributed to the level of 'excess Cu' used in Zn activation: the higher the excess, the greater the effect of polyphosphate.

In conclusion, silica sol has some metal ion control capability but seems less attractive in this role than say polyphosphate.

RÉSUMÉ

Des essais de flottation à l'échelle laboratoire ainsi qu'en lot ont été effectués pour investiguer l'utilisation du sol de silice pour contrôler la réduction accidentelle de l'activation et l'égarement des minéraux par les ions métalliques. À fin de comparaison, d'autres « réactifs de contrôle des métaux », l'acide éhylènediaminetétraacétique (EDTA) ainsi que le polyphosphate ont aussi été testés. La spectroscopie photoelectronique à rayons-X (XPS) a été utilisée pour étudier le mécanisme d'interaction entre le sol de silice et les minéraux.

La flottation à l'échelle laboratoire a été faite sur des échantillons contenant 1 seul minéral dans une fenêtre de pH variant entre 7 à 11. Il a été trouvé que le sol de silice déprime tous les minéraux de cuivre, la pyrite activée au cuivre et au plomb ainsi que la sphalérite activée au plomb mais ne déprime pas la sphalérite activée au cuivre. Les résultats XPS ont révélé que le sol de silice s'adsorbe sur tous les minéraux de Cu ainsi que sur la pyrite activée au Cu et au Pb. Le sol de silice enlève partiellement le Pb de la sphalérite activée au Pb et semble n 'avoir aucune interaction avec la sphalérite activée au Cu. L'action déprimante, par conséquent, semble être principalement l 'adsorption du sol de silice pour former des sites hydrophiliques.

Dans les essais de lots, le sol de silice, le polyphosphate ainsi que l'EDTA augmentent généralement le taux de flottation du circuit de Cu ainsi que celui du circuit de Zn. Ceci est attribué à l'enlèvement des hydroxydes métalliques hydrophiliques, c'est à dire un nettoyage de surface. Le polyphosphate et à moindre importance l' EDTA, améliorent la sélectivité dans le circuit de Zn des Mines Selbaie et de la Mine Louvicourt et de façon controversée

pour les mines Hudson Bay Mining and Smelting. Cette sélectivité ne fut pas observée lors des essais fait directement à l'entrée du circuit de flottation de Zn des mines Brunswick. L'effet varié du polyphosphate sur la sélectivité est attribuée à la quantité d'excès de Cu utilisée lors de l'activation du Zn : plus l'excès est important, plus l'effet du polyphosphate est important.

En conclusion, le sol de silice semble avoir une certaine capacité de contrôler les ions métalliques mais semble être moins efficace que le polyphosphate dans ce rôle.

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TABLE OF CONTENTS

CHAPTER 1

Chapter 2

CHAPTER 3

CHAPTER 5

CHAPTER 6

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

1.1 Background

Froth flotation is undoubtedly the most important and versatile mineral separation technique, and applications continue to expand to treat greater tonnages and more complex ores and to new areas such as soil remediation and de-inking of recycled paper (Wills, 1997). It came into prominence early in the last century eventually replacing gravity methods as the single most important mineral concentration process. The reason for this was diminishing ore grades and the need to grind to finer liberation sizes (Harris, 1976).

Flotation utilizes the differences in physico-chemical surface properties of minerals. After treatment with chemical reagents known as collectors, differences in surface properties between the minerals in a slurry (or pulp) become magnified and an air bubble is able to attach to a selected particle and lift (float) it to the water surface. The air bubble adheres to a particle if it can displace water from the surface, i.e., the mineral surface is to some extent water repellent or hydrophobic. Having reached the surface of the slurry, the air bubble can only continue to support the mineral particle if a stable froth forms, otherwise the bubbles will burst and drop their load. To achieve this condition it is necessary to add a reagent referred to as a frother, which retards bubble coalescence. The variety of chemical reagents employed are collectively referred as flotation reagents (Crozier, 1992). These include apart from collectors and frothers, modifying agents (activators, depressants) and pH regulators.

The flotation process can only be applied to relatively fine particles - if they are too large the force of adhesion between the particle and the bubble will be less than the particle weight and the particle will detach. Typically this means particles less than 500 μm (Wills, 1997). The valuable mineral is usually the one floated, leaving the non-valuable minerals (gangue) in the pulp. This is direct flotation as opposed to reverse flotation, in which gangue is separated into the float fraction.

1.2 Formulation of research topic: use of silica sol

The misplacement of minerals to the wrong product is a common problem in flotation. This misplacement may be caused by inadequate liberation, mechanical entrainment in the water, entrapment among other floatable particles or true flotation due to the properties inherent in the mineral or induced by contaminant species. One source of contamination in processing sulphides ores is the release of metal ions (e.g., Cu and Pb) from minerals by oxidation, often enhanced by galvanic interaction, which then migrate to other mineral surfaces. Contamination of the mineral surface arising from metal ion transfer may change the floatability of minerals and affect selectivity.

One approach to this problem is to remove the metal ion from surfaces by appropriate reagent addition. We might call these reagents 'metal ion control' reagents. One possibility is activated silica sol. This reagent has a high adsorptive capacity for metal ions and poses less environmental challenge than is the case with other metal ion control reagents such as inorganic and organic complexing agents. Figure 1.1 depicts the structure of silica sol.

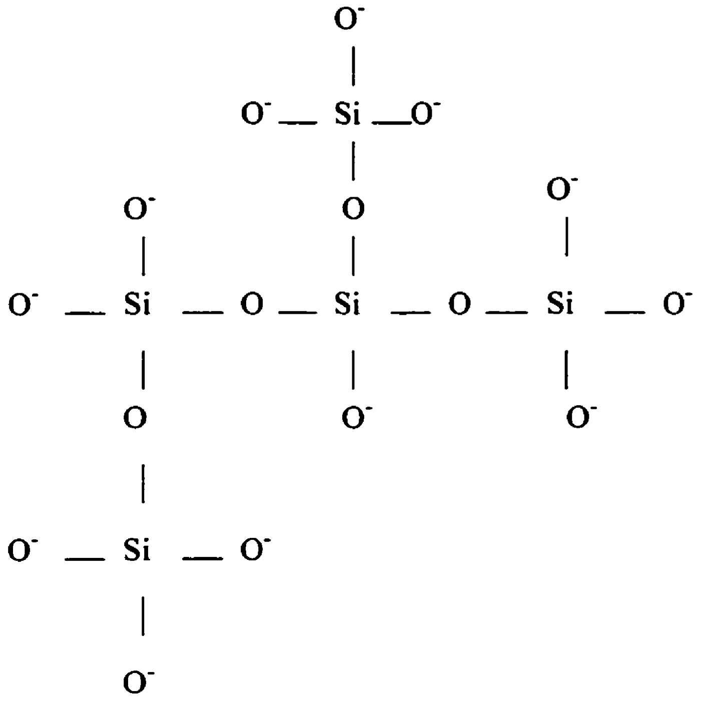

Fig. 1.1 Structure of silica sol

The most common practical application of activated silica sol is as a flocculant, added as 1-2 ppm, for removal of fine suspended solids from public water supplies. El-Ammouri (2000) used activated silica sol to adsorb heavy metals such as Cu, Ni from effluents. This process is an alternative to the universal method of effluent treatment by lime to precipitate metal hydroxides. Similar to the adsorption of metal ions on quartz and soluble silicates, the adsorption onto the surface of silica sol can be represented by (Dugger et al., 1964; Scindler et al., 1976),

$$M^{n+} + m\,(-\underset{|}{\overset{|}{\mathrm{Si}}}\,\mathrm{OH}) \Leftrightarrow M\,(\mathrm{O}\,\underset{|}{\overset{|}{\mathrm{Si}}}\,-)_m^{(n-m)} + m\,H^+ \qquad (1\text{-}1)$$

1.3 Objectives

The general objective is to evaluate silica sol to control contaminant metal ions which cause misplacement of sphalerite to copper / lead concentrates and pyrite to zinc concentrate. The specific objectives are:

1. Determine the effect of silica sol on flotation of Cu, Zn and Fe sulphide minerals with and without copper and lead contaminant ions.
2. Determine silica sol / mineral / contaminant ion interaction mechanism(s).
3. Determine the effect of silica sol on the Cu / Pb and Zn stages in processing Cu - Pb - Zn sulphide ores.
4. Compare silica sol with other 'metal ion control' reagents, ethylenediaminetetraacetic acid (EDTA) and polyphosphate.

1.4 Thesis outline

The thesis contains six chapters. Chapter one gives background and research objectives. Chapter two reviews sphalerite, pyrite and chalcopyrite mineral flotation chemistry and the processing of their ores.

Chapter three describes the mineral samples, ores and experimental procedures.

Chapters four and five present the results and discussion, respectively, for micro flotation, X-ray photoelectron spectroscopy (XPS) and batch flotation.

Finally, in chapter six conclusions are drawn with recommendations for future work.

CHAPTER 2

LITERATURE REVIEW

2.1 Factors influencing sphalerite flotation

2.1.1 Introduction

Sphalerite ((Zn,Fe)S) is the principal source of the world's supply of zinc. Natural sphalerite usually contains significant concentrations of cationic impurities. Iron is the most common minor element present and when concentration by weight is 13 % or above the mineral may be termed marmatite (Thrush, 1968). Sphalerite always occurs in association with other sulphide minerals. Flotation is largely concerned with the problem of separating sphalerite from copper sulphides, galena and iron sulphides (together forming what are commonly referred to as complex sulphide ores). The standard approach is to selectively float the copper and lead sulphide minerals while depressing sphalerite with reagents such as sodium cyanide or zinc sulphate, then activate the sphalerite with copper sulphate and float selectively from iron sulphide and gangue usually through pH control. Efficient collection of the zinc bearing minerals into the zinc concentrate, therefore, depends on the ability to control the floatabilty of sphalerite at a low level in the Cu stage and a high level in the Zn stage.

In practice this separation sequence often proves difficult and the production of clean zinc concentrate at good yield can pose a challenge for some ores. On occasion, sphalerites are found to float to a significant extent into lead and copper concentrates (e.g., Basilio et al., 1996). This floatability has been widely ascribed to natural or inadvertent activation of the sphalerite by heavy metal cations (Gaudin, 1957).

Early on it was established that sphalerite cannot be readily floated using short chain (e.g., ethyl) xanthates (Gaudin, 1930) and it is necessary to employ an activator, usually cupric ions, or use a long chain xanthate (Gaudin, 1957; Finkelstein and Allison, 1976; Fuerstenau, 1982). The amount of ethyl xanthate adsorbed on the surface is insignificant, reaching levels of 15 % with respect to the statistical monolayer and being easily washed off by water (Allison et al. 1972; Pomianowski et al., 1975). With this general background some specific topics are considered next.

2.1.2 Collectorless flotation

Sphalerite is generally considered not to float in the absence of collector (Steward and Finkelstein, 1973; Trahar, 1984; Shannon and Trahar, 1986; Rashchi, 2000). Some flotation without collector has been observed in weakly acidic media, attributed to self activation of sphalerite by cations such as iron (Fig. 2.1) present in the lattice (Popov and Vucinic, 1990). Rey and Formanek (1960) observed that sphalerite ground in a porcelain mill showed a degree of natural floatability that was not found if the sample was ground in an iron mill.

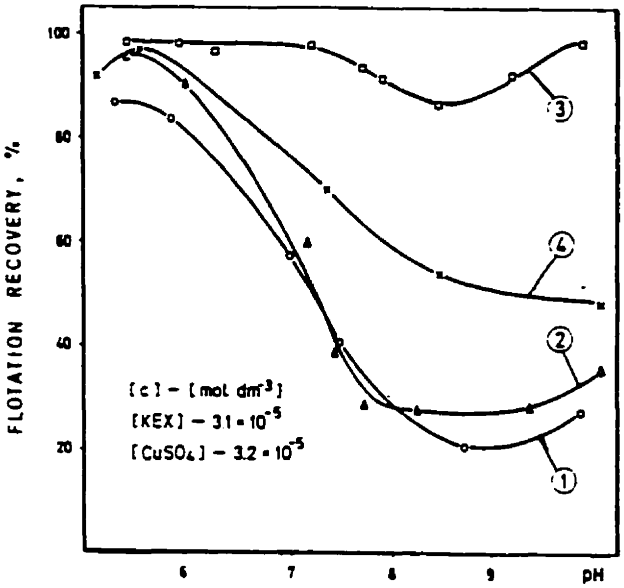

Fig. 2.1 Flotation recovery of sphalerite as a function of pH: 1= No reagents; 2 = $CuSO_4$; 3 = $CuSO_4$ + KEX; 4 = KEX (after: Popov and Vucinic, 1990).

Steward and Finkelstein (1973) investigating natural floatability of a variety of sphalerite samples from different sources, found that while some samples did show a certain degree of natural floatability after grinding and surface cleaning, all showed remarkably improved floatability after copper activation. Steward and Finkelstein (1973) and Lascalles et al. (2001) reported increased natural floatability if the Cu activated sphalerite is allowed to age.

There was some evidence of copper ion promoting collectorless flotation at acid pH in the work of Popov and Vucinic (1990). Increasing copper concentration had no any significant effect on the collectorless flotation of sphalerite in alkaline media. Increasing Cu concentration provoked a decline in flotation recovery of sphalerite in the presence of a constant potassium ethyl xanthate (KEX) addition, when the $CuSO_4$ solution was not decanted (Fig. 2.2). This suggests loss of xanthate through side reaction with Cu ions and / or depression due to excess $Cu(OH)_2$ on the surface. Nearly complete flotation of sphalerite was obtained in the presence of copper concentrations from 3 x10^{-5} to 2.5 x 10^{-4} mol dm^{-3}, when $CuSO_4$ solution was decanted.

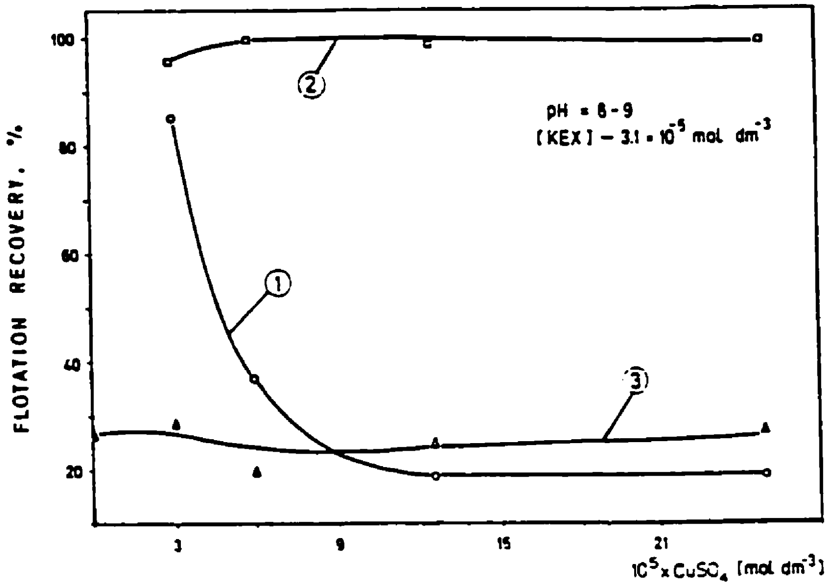

Fig. 2.2 Flotation recovery of sphalerite as a function of $CuSO_4$: 1= $CuSO_4$ (without decantation) + KEX; 2 = $CuSO_4$ (decantation) + KEX; 3 = $CuSO_4$ (after: Popov and Vucinic, 1990).

2.1.3 Flotation with collector but without activation

Clifford (1971) showed that at pH 3.5 about 7 x 10^{-2} M ethyl xanthate was required before an appreciable recovery of sphalerite was obtained. Girczys and Laskowski (1982) observed good flotation of sphalerite with 10^{-4} M ethyl xanthate in acidic solution. They explained this phenomenon by the presence of iron in the sample (1.7%) which dissolved to give ferric ion in solution which oxidized the xanthate to dixanthogen, which was responsible for the sphalerite flotation. The flotation of sphalerite from a medium concentrated solution of ethyl xanthate was observed by Mielczarski (1986), attributed to self activation by the Pb (1.5 %) contained in the mineral sample. It was found that lead concentrated on the surface of the sphalerite sample, the concentration exceeding 12 times the average lead concentration in the bulk sample. Sphalerite does float if KEX concentration is high enough (Fig. 2.3) (Popov et al., 1989).

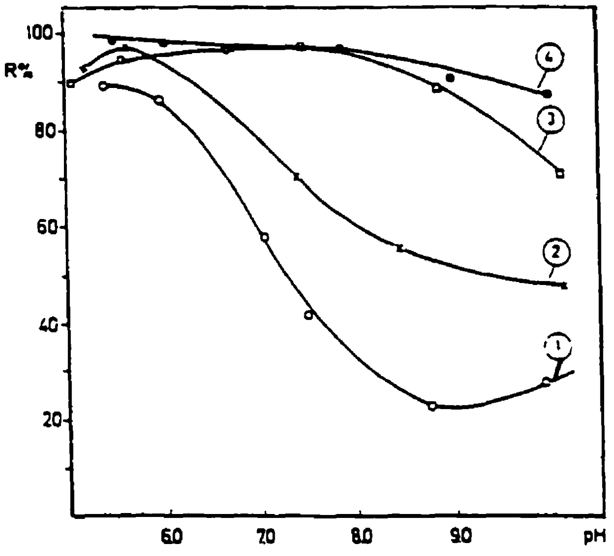

Fig. 2.3 Flotation recovery of sphalerite as a function of pH: 1= without reagents; 2 = 3.1×10^{-5}; 3 = 6.2×10^{-5}; 4 = 1.5×10^{-4} mol dm^{-3} KEX (after: Popov et al., 1989).

2.1.4 Oxidation of Sphalerite

Sulphide minerals are susceptible to reaction with water and dissolved oxygen. These reactions govern the state of the surface and interaction with flotation reagents. Oxidation of the sphalerite surface is slow in air under ambient conditions (Markwell and Pratt, 1984). Buckley et al. (1989), using X-ray Photoelectron Spectroscopy (XPS), observed that a sphalerite surface, after exposure to air for three weeks, was similar to a fresh specimen. Also sphalerite treated with an air saturated solution of pH 9.2 for one hour did not show additional oxidation products. Their results show that the sphalerite surface reacts only slowly with oxygen.

2.1.5 Cu Activation

Depending on the pH, different 'activation' reactions occur on the surface of sphalerite.

(i) Weakly acidic pH

The generally accepted mechanism (Finkelstein and Allison, 1976) is a 1:1 exchange of Cu for Zn and the subsequent reduction to Cu(I) as the Cu(II) sulphide is not stable. The reaction may be written as,

$$2ZnS + 2Cu^{++} \Leftrightarrow 2CuS + 2Zn^{++} \Rightarrow Cu_2S + S^0 + 2Zn^{++} \qquad (2\text{-}1)$$

Cooke (1950) found the atomic ratio of zinc released into solution to the quantity of copper taken up to be unity at distilled water pH. Gaudin (1959) found it to be 0.7 and 0.96 in two separate experiments at distilled water pH. Pomianowski et al. (1975) found it to be between 0.8 and 1 at pH 7, unless the sample was heavily oxidized, when it was somewhat higher than

1. Ralston and Healy (1980 a) determined the ratio to be unity over the pH range 4 to 6.4. Sui et al. (1999) determined the exchange ratio was close to 1 at pH 3 and 9.2 and at pH 6, the ratio was initially >1 for first 20 min and reached 1 after 1 hour.

(ii) Alkaline pH

The mechanism in (i) is extended to alkaline conditions by considering that copper hydroxy species ($CuOH^+$ for weakly alkaline conditions or $Cu(OH)_2$ at higher pH) absorb and act as a source of Cu(II) ions which slowly react with sphalerite releasing Zn. This can be represented (Jain and Fuerstenau, 1985; Laskowski et al., 1997) by,

$$ZnS + Cu(OH)_x^{(2-x)} \Rightarrow CuS + Zn(OH)_{(2-x)x} \qquad (2\text{-}2)$$

2.1.6 Factors affecting Cu uptake by sphalerite

Bushell et al. (1961) and Pomianowski et al. (1975) found that the higher the iron content of a range of sphalerites, the lower the amount of copper exchanged with zinc and subsequent uptake of collector. In contrast Nefedov et al. (1980) observed a greater concentration of copper at the surface of a sphalerite containing high iron compared to one with a low iron content. Mukai and Nakahiro (1970) found maximum copper adsorption to occur at about pH 6.5. Pomianowski et al. (1975), on the other hand, found no correlation between copper adsorption and pH. Solecki et al. (1979), found that adsorption of Cu (II) did not depend on the pH of the activating solution when testing oxidized synthetic sphalerites with iron content from 0 to 40 %. With a non-oxidized sample, a decrease in cupric ion adsorption with increasing pH was observed (with the exception of a sample with 5 % Fe, when the maximum occurred at pH 6 to 8 and then decreased with pH). Sui et al. (1999) reported that oxidation of sphalerite decreased the adsorption of Cu and Pb ions and consequently xanthate uptake. The decrease in adsorption was more significant for Cu than for Pb. These results (with increasing iron content of sphalerite, Cu adsorption decreases) agree with common flotation experience that the darker, iron bearing sphalerites float less readily than do the lighter coloured sphalerites (Finkelstein and Allison, 1976).

2.1.7 Pb activation

Lead activation is of great practical interest with any galena containing ore, as one of the consistent properties of the pulp is the supply of galena oxidation products equivalent to lead contents ranging up to 2000 ppm (Trahar et al., 1997). Lead activation of sphalerite in the presence of galena becomes more evident when the ore is finely ground with a long retention time in flotation. In acidic solutions, the specie is the lead ion and in weakly alkaline to alkaline conditions, $Pb(OH)^+$ and $Pb(OH)_2$, respectively. Depending on the pH, different 'activation' reactions occur on the surface of sphalerite.

(i) Weakly acidic pH

Popov et al. (1989) based on the zeta potential becoming more positive after Pb treatment, Houot and Raveneau (1992) from observing that sphalerite contacted with galena gave increased surface concentration ratios Pb/S and Pb/Zn and Trahar et al. (1997) noting that EDTA (a strong complexing agent) addition did not affect flotation response proposed a 1:1 exchange of Pb for Zn in the lattice, the reaction being written as,

$$ZnS + Pb^{++} \Leftrightarrow PbS + Zn^{++} \qquad (2\text{-}3)$$

Ralston and Healy (1980 a) noting that band gap of Pb activated sphalerite was reduced, also proposed an exchange reaction, expressed as,

$$ZnS + Pb^{++} \Leftrightarrow (Zn,Pb)S + Zn^{++} \qquad (2\text{-}4)$$

Sui et al. (1999) observing that adsorption of Pb ions was similar to that on silica and Pb atoms were much larger than Zn atoms than is the case for Cu atoms gave the adsorption as,

$$ZnS\,|\, + Pb^{++} \Leftrightarrow ZnS\,|\,Pb^{++} \qquad (2\text{-}5)$$

Pattrick et al. (1998) noting band energies equivalent to Pb-O using X-ray absorption spectroscopy (XAS) and observing that substitution energy would be high for Pb ion exchange with Zn in the lattice, suggested Pb adsorption took place through the development of Pb-O bonds, the oxygen coming from the oxidation reactions.

(ii) Weakly alkaline pH

Ralston and Healy (1980 b) observing the zeta potential became less negative, and Popov et al. (1989) noting high intensity infrared (IR) bands associated with, - C - O - C - Pb - ethyl xanthate when Pb conditioning time was increased from 3 to 40 min, proposed a two step reaction. The first step is a rapid precipitation of $Pb(OH)_2$ on sphalerite followed by a second, slow exchange step. The reactions may be written as,

$$Pb^{++} + 2OH^{-} \Leftrightarrow Pb\,(OH)_2 \qquad (2\text{-}6)$$

$$ZnS + Pb(OH)_2 \overset{slow}{\Leftrightarrow} (Zn,Pb)S + Zn(OH)_2 \qquad (2\text{-}7)$$

Sui et al. (1999) extended the simple adsorption in the double layer model and expressed the reaction as,

$$ZnS\,|\ + Pb(OH)_x^{(2-x)} \Leftrightarrow Zn\,|\,Pb(OH)_x^{(2-x)} \qquad (2\text{-}8)$$

Bessiere and Bernasconi (1983) considered the surface to be hydrated and suggested that the following type of reaction could accompany lead adsorption giving a result similar to Pattrick et al.,

$$ZnS\,|\,Zn\text{-}OH + Pb(OH)^+ \Leftrightarrow ZnS\,|\,Zn\text{-}0\text{-}Pb^+ + H_2O \qquad (2\text{-}9)$$

There is disagreement as to the mechanism for Pb adsorption onto the sphalerite. Table 2.1 gives a summary of proposed mechanisms and the evidence presented by the different researchers.

For reaction of Pb with sphalerite an exchange ratio of about unity was reported for pH values up to 7.7 (Allison, 1982; Wang et al., 1989 d). Ralston and Healy (1980 a) determined the exchange ratio to be from 0.7 to 1.3 at pH 5.5 and determined the ratio to be above 1 at pH 7.5 (Ralston and Healy, 1980 b). Sui et al. (1999) found that the exchange ratio of Pb to Zn was much greater than 1 at pH 3, 6 and 9.

Table 2.1: Pb exchange mechanism

Authors	pH	Mechanism	Evidence
Fuerstenau and Metzger (1960)		$Pb^{++} + ZnS \Leftrightarrow PbS + Zn^{++}$	Assumption
Ralston and Healy (1980 a)	5.5	$Pb^{++} + ZnS \Leftrightarrow (Zn,Pb)S + Zn^{++}$	Band gap was reduced
Ralston and Healy (1980 b)	7.5	$Pb(OH)_2 + ZnS \Leftrightarrow (Zn,Pb)S + Zn(OH)_2$	Zeta potential became less negative
Bessiere and Bernasconi (1983)	Alkaline	$ZnS \vert Zn\text{-}OH + PbOH^{+} \Leftrightarrow ZnS \vert Zn\text{-}O\text{-}Pb^{+} + H_2O$	Assumption
Popov et al. (1989)	5 - 6	$Pb^{++} + ZnS \Leftrightarrow PbS + Zn^{++}$	Zeta potential became higher positive
Popov et al. (1989)	Above 7.5	$Pb(OH)_2 + ZnS \Leftrightarrow (Zn,Pb)S + Zn(OH)_2$	High intensity IR bands when more conditioning time with Pb
Houot and Raveneau (1992)	Natural pH	$Pb^{++} + ZnS \Leftrightarrow PbS + Zn^{++}$	Pb/S and Pb/Zn ratios increased when contact with galena
Pattrick et al. (1998)	5.5	Through Zn-O-Pb bonds	XAS detected Pb-O bonds. Pb substitution energetically unfavorable.
Trahar et al. (1997)	4	$Pb^{++} + ZnS \Leftrightarrow PbS + Zn$	EDTA did not affect the recovery
Trahar et al. (1997)	9	No exchange	EDTA affected the recovery
Sui et al. (1999)	3 - 6	$Pb^{++} + ZnS \vert \Leftrightarrow ZnS \vert Pb$	Pb atoms larger than Zn atoms. Pb adsorption similar to adsorption of metal ions to silica.
Sui et al. (1999)	9	$Pb(OH)_x^{(2-x)} + ZnS \vert \Leftrightarrow ZnS \vert Pb(OH)_x^{(2-x)}$	-do-

Trahar et al. (1997) and Rashchi (2000) demonstrated that lead activated sphalerite can be floated by ethyl xanthate up to pH 9 and that complexing agents (EDTA and polyphosphate, respectively) eliminated the activation. Popov et al. (1989) found the addition of lead ion with xanthate caused a marked increase in sphalerite floatability compared with flotation without lead ion (Fig. 2.4). A long activation time, 40 minutes, was necessary to reach a near equilibrium condition in an alkaline medium compared with a few minutes (ca. 15 min) for activation in a weakly acidic media.

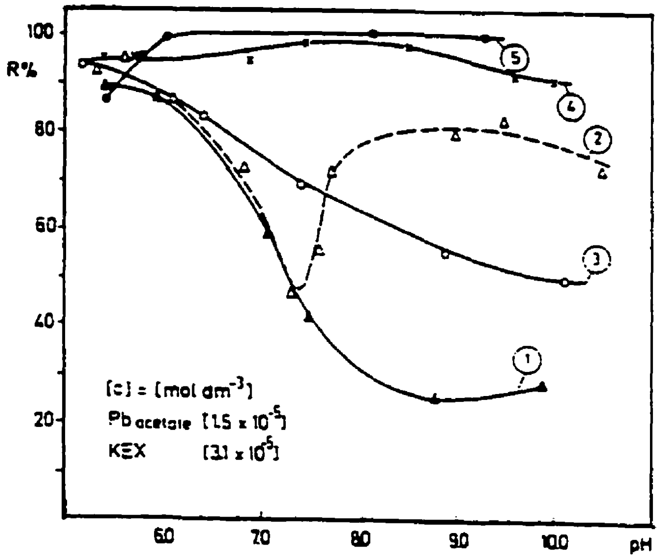

Fig. 2.4 Flotation recovery of sphalerite as a function of pH: 1= no reagents; 2 = Pb acetate; 3 = KEX; 4 = Pb acetate (pH 5 - 6) and KEX; 5 = Pb acetate and KEX, 8 < pH activation = pH flotation < 9 (after: Popov et al., 1989).

2.1.8 Comparison of Cu and Pb activators

In an adsorption study in the presence of both cations, Sui et al. (1999) showed copper adsorption on sphalerite was rapid during the first minute then slowed. The amount of copper adsorbed varied with pH. Over the first minute adsorption was lower in alkaline conditions (pH 9.2) than in acidic conditions (pH 3). Adsorption of lead was also rapid during the first minute and slow over the next 60 minutes. The amount of lead adsorbed increased with pH, opposite to the case with Cu. The amount of Pb adsorbed was greater than that of Cu when sphalerite was treated with the ions individually in near neutral (pH 6) and alkaline (pH 9.2) conditions. In the presence of both ions at the same concentration, Cu adsorption was enhanced and Pb adsorption was suppressed, i.e., Cu was preferentially adsorbed over Pb.

In the only flotation study employing this combination, Laskowski et al. (1997) found that in an acidic environment (pH 5.5), sphalerite floated better with lead than with copper when treated with the ions individually but when both copper and lead ions were present, the flotation was worse than that with copper alone. In an alkaline environment (pH 10.5), Cu activated sphalerite floated better than Pb activated sphalerite individually. In the presence of both ions at pH 10.5 the flotation results were worse than those with lead only.

2.1.9 Kinetics of Cu and Pb activation

Finkelstein and Allison (1976), Healy and Ralston (1980 a and b), Jain and Fuerstenau (1985), Wang et al. (1989 a) and Sui et al. (1999) reported that Cu activation was a two step process. The first step was fast and followed a logarithmic equation and the second was slow.

Jain and Fuerstenau, Wang et al. and Sui et al. found that second step followed a parabolic equation whereas Healy and Ralston found a logarithmic equation.

Fuerstenau and Metzger (1960) and Healy and Ralston (1980 a and b) found Pb adsorption was a two step process; a fast first step and second slow step. Fuerstenau and Metzger reported that lead adsorption followed an exponential equation for both stages whereas Healy and Ralston showed that first step followed a logarithmic equation and second followed no well defined equation. Sui et al. (1999) found adsorption was a three step process; a fast first step, following a logarithmic law, a second step with no well defined equation and a third, slow stage following a logarithmic law.

2.1.10 Deactivators

Deactivation is a process whereby an activating agent is removed from the surface of a mineral, thereby rendering it less able to react with a collector.

2.1.10.1 Deactivators for Cu activated sphalerite

Gaudin et al. (1959) found the following deactivators for Cu activated sphalerite (Fig. 2.5) (In this case $CuSO_4$ and deactivating agents were added simultaneously at pH 7).

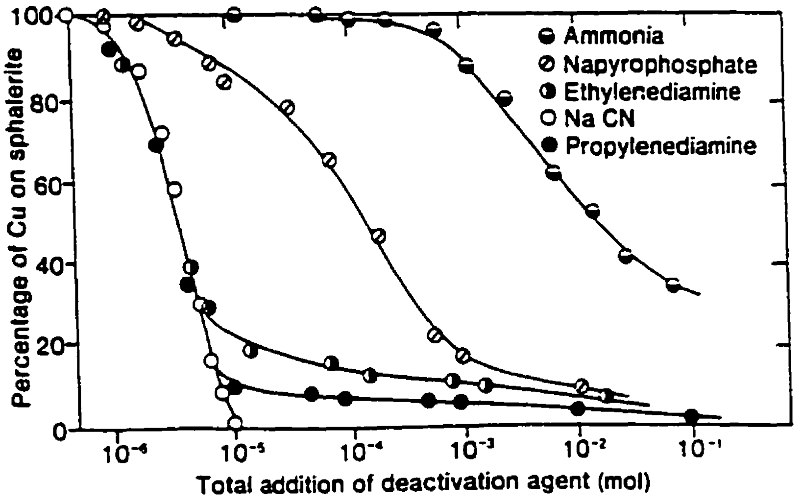

Fig. 2.5 Partition of copper between solution and sphalerite as a function of the addition of deactivating agent (after: Gaudin et al., 1959).

(i) Sodium cyanide

This is the most widely used deactivator for sphalerite. Copper activated sphalerite can be deactivated by removing the copper from the surface through dissolution of copper as cyano complexes.

(ii) Ethylenediamine and Propylenediamine

Both ethylenediamine (ED) and propylenediamine (PD) form very stable cupric chelate complexes but are significantly less effective than cyanide in removing the copper from the sphalerite surface.

(iii) Sodium pyrophosphate (diphosphate)

Pyrophosphate forms several complexes with cupric copper. Apparently the principal complex is the dipyrophosphatocuprate ion ($Cu(P_2O_7)_2$). It is a less strong deactivator than ethylenediamine and propylenediamine.

(iv) Aqueous ammonia

Ammonia does not complex Cu (II) as tightly as cyanide and, in addition, the stabilities of the Cu (II) and Zn (II) complexes do not differ greatly. Schwarzenbach (1952) found that five different copper - ammonia complexes ($Cu(NH_3)_n$, n from 1 to 5) exist but none is dominant. It is less strong a complexant than sodium pyrophosphate.

2.1.10.2 Deactivators for Pb activated sphalerite

Diethylenetriamine, sodium bicarbonate, silica sol, sodium phosphate and sodium polyphosphate were the deactivators tested for Pb activated sphalerite by Rashchi (2000) at pH 9. The strongest deactivator was sodium polyphosphate.

2.1.11 Depressants

Reagents that are most commonly used in the depression of sphalerite are mixtures of zinc sulphate with alkalis such as Na_2CO_3 and lime (Finkelstein and Allison, 1976). Zinc sulphate is used to keep sphalerite depressed during lead flotation. Its mode of action is considered to be one of deposition of a layer of hydrophilic zinc hydroxide or carbonate on the sphalerite surface.

2.2 Pyrite flotation

Pyrite (FeS_2) is the most widely occurring sulphide mineral. It occurs in association with other base metal sulphide minerals as well as coal. In most cases, pyrite is a gangue mineral and needs be removed from the associated sulphides (or coal) to reduce contamination of the concentrate. Excess pyrite leads to SO_2 emissions in smelting operations for Cu and Pb and electrolyte contamination with Fe in Zn hydro metallurgy. In flotation the rejection of pyrite is usually achieved by depression. Pyrite is recovered by flotation when it contains precious metals such as gold, and for acid making as a source of sulphur. To understand depression, first, the flotation of pyrite is reviewed.

Pyrite can be floated using many types of collectors, ranging from xanthates, dithiophosphates and dithiocarbamates to fatty acids and amines. Of these the xanthates are the most widely used (Ball and Richard, 1976). Flotation of pyrite is possible below pH 11 with short chain xanthates, but is depressed above about pH 11. This behaviour is clearly shown in Fig. 2.6 (Fuerstenau et al., 1968). The figure shows that with small additions of ethyl xanthate, there are two regions of flotation while at high levels of xanthate, flotation occurred from about pH 3 to pH 9. Zhang et al. (1997) reported that pyrite can be activated by Cu (II), Fe (II) and intriguingly Ca (II). Wang et al. (1989 b) and Leppinen et al. (1995) found that the adsorption of Cu and Pb on pyrite did not involve exchange with lattice cations.

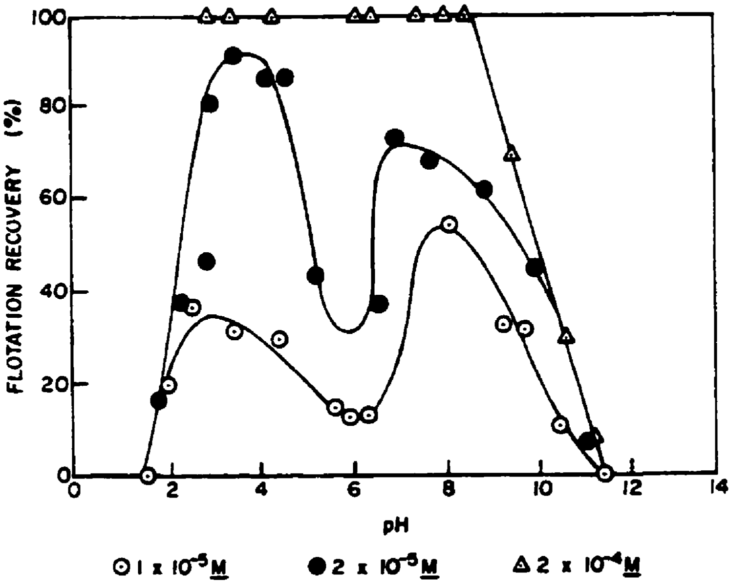

Fig. 2.6 Recovery of pyrite as a function of flotation pH with various additions of potassium ethyl xanthate (after: Fuerstenau et al., 1968).

2.2.1 The role of dixanthogen in pyrite flotation

The iso electric point of pyrite is about 6.5 (depending on the level of oxidation) and this probably means that physical adsorption of xanthate is ruled out above this pH where pyrite floats well (Gaudin and Sun, 1946). Gaudin and Wilkinson (1933) detected no ferric xanthate in a benzene leach of a pyrite sample but did extract undetemined oils and elemental sulphur. The evidence suggested that ferric xanthate was not formed unlike analogous salts in other systems, such as lead and copper. Gaudin et al.(1956), using a radiometric technique, found dixanthogen on a pyrite surface. Fuerstenau et al. (1968), from the infrared spectrum after amyl xanthate treatment, found principal adsorption bands of diamyl dixanthogen (1028 and 1258 cm^{-1}) (Fig 2.7). Leppinen (1990), using the Fourier Transform Infrared Attenuated

Total Reflectance (FTIR - ATR) technique, found that the xanthate species on pyrite occurred at approximately the same position as those of bulk dixanthogen with the main peaks at 1288, 1262, 1239, 1107 and 1021 cm^{-1}. Vreugdenhil et al. (1997 and 1999), using HeadSpace Analysis Gas - Phase Infrared Spectroscopy (HAGIS) to study the thermal decomposition products of adsorbed xanthate, found dixanthogen on a pyrite surface as evidenced by the small COS peak compared to decomposition of metal xanthate which gives large peaks for COS, CS_2 and alcohol. It is assumed that adsorption of xanthate in acidic media is through formation of ferric xanthate and that in alkaline media it is through formation of dixanthogen (Hanson and Fuerstenau, 1993).

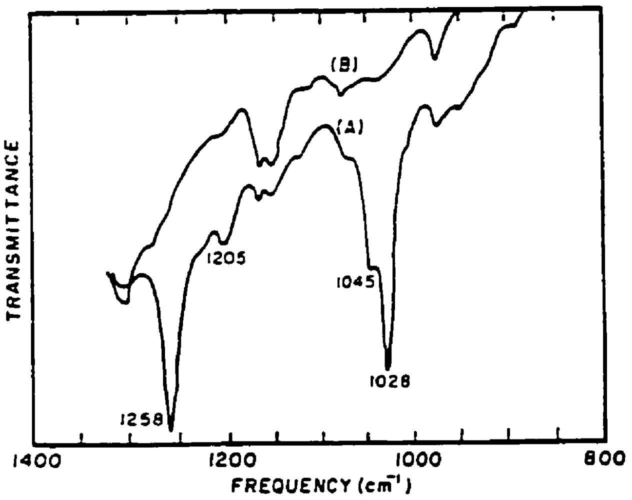

Fig. 2.7 Infrared spectra of pyrite conditioned in the absence of (curve B) and presence of (curve A) of potassium amyl xanthate (after: Fuerstenau et al., 1968).

2.2.3 Depressants

(i) Cyanide

The formation of the surface ferric ferrocyanide is considered responsible for pyrite depression (Ball and Richard, 1976) which can be represented by,

$$7\ Fe^{++} + 18\ HCN \Rightarrow Fe_4(Fe(CN)_6)_3 + 18H^+ + 4e \qquad (3\text{-}10)$$

(ii) Hydroxide

Complete depression can occur whether CaO, KOH, NaOH or K_2CO_3 were used above pH 11 (Ball and Rickard, 1976).

(iii) Sulphide

Flotation tests indicated that sodium sulphide depressed pyrite above pH 6 (Hoyack and Raghavan, 1987). The depression is attributed to formation of a hydrophilic product, $Fe_2(SO_4)_2.Fe(OH)_3$.

(iv) Quebracho and other tannic acid derivatives (organic polymers) have been used as depressants for pyrite (as well as sphalerite and galena) (Bulatovic, 1999). The depressive effect of quebracho occurs between pH 4 to 9.

(v) Miscellaneous depression

Ferrous and ferric salts can act as depressants in the pyrite - xanthate system. Many other ions have been suggested as depressants. Two of the most effective are dichromate and permanganate (Sutherland and Wark, 1955).

2.3 Chalcopyrite flotation

Chalcopyrite ($CuFeS_2$) is the most abundant copper bearing mineral and the major commercial source of copper. Like other sulphides, chalcopyrite is recovered by flotation, responding exceptionally well to xanthate collector. In the presence of $1x10^{-5}$ M ethyl xanthate, complete flotation was reported from pH 3 to 12, the range being extended when $5 x10^{-5}$ M ethyl xanthate was used (Fuerstenau and Rowse, 1978) (Fig. 2.8). It can be assumed that both oxidation of xanthate to dixanthogen as well as chemisorption of xanthate on chalcopyrite are responsible for the flotation (Kuhn, 1963; Allison et al., 1972; Vreugdenhil et al., 1999). New collectors with a high specificity for copper minerals are being developed. Two are thionocarbamate and thiourea (Serakova et al., 1975; Bogdanor et al., 1976).

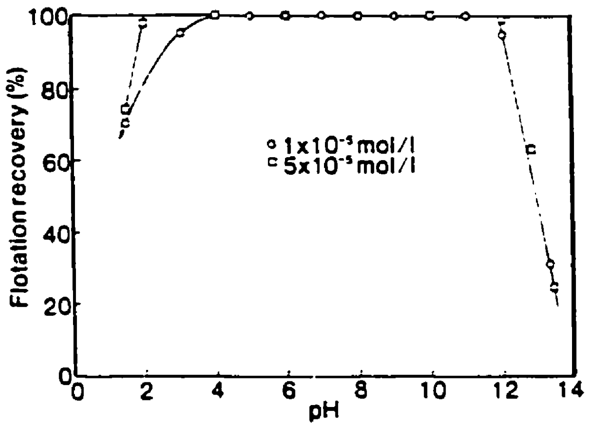

Fig. 2.8 Flotation recovery of chalcopyrite as a function of pH and ethyl xanthate concentration (after: Fuerstenau and Rowse, 1978).

2.3.1 Collectorless flotation

Yoon (1981) reported that chalcopyrite (as well as sphalerite) can be floated without a collector when the slurry was treated with sodium sulphide. The sulphide ions are thought to displace the hydrophilic surface oxidation products such as SO_4^{2-}, $S_2O_3^{2-}$ thereby restoring a fresh, unoxidized sulphide surface. Electron spectroscopy for chemical analysis (ESCA) spectrum of four year old samples of chalcopyrite showed the sulphate peak disappeared after sodium sulphide treatment, demonstrating that sodium sulphide was effective in displacing these hydrophilic oxidation products (Gerald et al., 1984). Fuerstenau and Sacky (1981) reported that freshly fractured chalcopyrite floated well without a collector in an essentially oxygen free atmosphere. Heyes and Trahar (1977), Trahar (1984) and Leroux et al. (1989) found that collectorless flotation of chalcopyrite was possible in an oxidizing environment; elemental sulphur formed as an oxidation product was considered the hydrophobic species responsible (Garner and Woods, 1979, Trahar, 1983). Gerald et al. (1984) showed that collectorless flotation of chalcopyrite required not only an oxidizing environment but also a surface relatively free of hydrophilic oxidation products.

2.3.3 Depressants

(i) Hydroxide

Hydroxyl ion can function effectively as a depressant for chalcopyrite at high pH, often in excess of pH 13 (King, 1982).

(ii) Thioglycolic acid (TGA)

TGA exhibits multilayer coverage on a chalcopyrite surface (Poling and Liu, 1986). The presence of oxygen enhanced adsorption and hence the depressive action of TGA. Strongest depressive effect was observed above pH 9.

(iii) Cyanide

Cyanide is used as a depressant for chalcopyrite (King, 1982).

(iv) Sulphide

In the case of sulphide ion as a depressant, copper sites on the chalcopyrite surface are involved (King, 1982). That is, due to the stability of copper sulphide, chemisorption of sulphide ion on that site will occur.

2.4 Processing of complex ores

As generally agreed, the term complex sulphide ore refers to an association of chalcopyrite, galena, sphalerite and pyrite, and sometimes pyrrhotite, in a gangue that is usually but not always siliceous. The features common to such ores have been summarized by Barbery et al. (1980) in the following terms:

(i) they have complex textures and associations

(ii) the pyrite content may be high

(iii) minor minerals containing precious metals and environmentally challenging elements are usually present

(iv) the non sulphides may include naturally floatable minerals such as talc and some of the sulphides may contain carbonaceous materials.

Wills (1997) described the methods of processing of complex ores as follows:

2.4.1 Flotation of lead - zinc ores

Lead (galena) flotation is usually performed at a pH between 9 and 11 with lime, being cheap, used to control alkalinity. Lime, or more specially Ca^{2+} also acts as a depressant for pyrite, but it can also depress galena if overdosed. Soda ash is sometimes preferred because it does not have this consequence, especially when the pyrite content is relatively low. In most cases, depressants are added to depress sphalerite, the most widely used being sodium cyanide and zinc sulphate, either alone or in combination. These reagents are either added to the grinding circuit or to the lead float. Although cyanides are widely used due to their high degree of selectivity, they do have certain disadvantages. They are toxic and expensive and dissolve some of the gold and silver often present in economic amounts. For this reason, zinc sulphate is used in many plants to supplement cyanide. Heavy metal ions are often present in the slurry water, due to the ease with which sulphide minerals oxidize. The addition of lime or soda ash to the slurry can precipitate them as relatively insoluble basic salts, thus deactivating the sphalerite to some extent. The alkalis are usually added to the grinding mill as well as to the lead float conditioner. After flotation of the galena, the tailings are treated with copper sulphate, which activates zinc minerals allowing them to be floated. Lime is used to depress pyrite and flotation is conducted ca. pH 10 - 12.

2.4.2 Flotation of copper - zinc and copper - lead - zinc ores

In the flotation of copper - zinc ores where lead is absent or not present in economic quantities, lime is almost universally used to control alkalinity at pH 8 - 12 and to deactivate the zinc minerals by precipitation of heavy metal ions. In a few cases, the addition of lime is sufficient to prevent the flotation of zinc minerals, but in most cases supplementary depressants are required. Sodium cyanide is often added in small quantities to the grinding mills and flotation cleaner banks. Zinc sulphite (or bisulphite) or sulphur dioxide depressants are also used. Copper flotation tailings are activated by copper sulphate and zinc minerals are floated as described in the previous section.

The method most widely used to treat ores containing economic amounts of lead, copper and zinc is to initially float a bulk lead - copper concentrate, while depressing the zinc and iron minerals. The bulk float is performed in an alkaline circuit usually pH 7.5 - 9.5 using lime in conjunction with sphalerite / pyrite depressants such as cyanide and zinc sulphate, being added to the mills and flotation cells. Depression of zinc and iron sulphides is sometimes supplemented by the addition of a small amount of sodium bisulphite or sulphur dioxide to the cleaning stages, although these reagents should be used sparingly as they can also depress galena. The bulk concentrate is treated by depression of either the copper or lead minerals to produce separate concentrates. Tailings from bulk concentrate is activated by copper sulphate and the zinc mineral is separated from pyrite as described previously.

The choice of method for separating the copper from lead minerals in the bulk concentrate depends on the response of the minerals and the relative abundance of the copper and lead minerals. It is preferable to float the mineral present in the least abundance and galena depression is usually performed when the ratio of lead to copper in the bulk concentrate is greater than unity. Lead depression is also undertaken if economic amounts of chalcocite or covellite are present as these do not respond to depression by cyanide which is used to depress chalcopyrite or if the galena is oxidized or tarnished and does not float readily.

Depression of galena is achieved using sodium dichromate, sulphur dioxide and starch in various combinations. In some plants, galena depression is aided by heating the slurry to about 40^{0} C.

CHAPTER 3

EXPERIMENTAL METHOD

3.1 Micro flotation

3.1.1 Mineral samples

Minerals samples, chalcopyrite, sphalerite, pyrite and chalcocite, were obtained from Ward's Natural Science Establishment Ltd., and synthetic covellite was obtained from Sigma - Aldrich. The minerals were prepared by crushing in a jaw crusher and visible impurities hand sorted. They were then pulverized and wet sieved to obtain the size fraction - 200 + 400 mesh (74 - 37 μm). For chalcopyrite and chalcocite this size fraction was further upgraded using a Mozley table to remove low density gangue, mainly silicates. Finally, the samples were acid washed (HCl, at pH 2) to remove soluble oxidation products and stored in acetone under air tight conditions. The covellite (99 % purity) sample was - 100 mesh and was also screened to 74 - 37 μm.

Chemical analysis was performed by Atomic Absorption Spectroscopy (AA) (Table 3.1). The relative standard deviation was about 5 %. The amount of Si in these minerals was below the detection limit of the instrument, 10 ppm.

Table 3. 1: Chemical composition of minerals

Minerals	Cu (%)	Fe (%)	Zn (%)	Pb (%)	Purity (%)
Pyrite	0.03	43.36	0.10	0.01	93
Sphalerite	0.09	0.27	61.11	< 0.002 % *	91
Chalcopyrite	30.60	26.92	3.23	0.19	88
Chalcocite	70.93	2.79	0.04	< 0.002 % *	89

* detection limit of Pb

3.1.2 Reagents

The following reagents were used: Commercial grade potassium ethyl xanthate (CH_3CHOCS_2K) (KEX) and sodium isopropyl xanthate ($(CH_3)_2CHOCS_2Na$) (SIPX) from Prospec Chemicals; reagent grade copper sulphate ($CuSO_4.5H_2O$) and lead nitrate ($PbNO_3$) from Fisher Scientific and Anachemia Chemicals, respectively; and, analytical grade hydrochloric acid and sodium hydroxide from Fisher Scientific.

The xanthate samples were purified by dissolving in acetone and precipitating with petroleum ether (Rao, 1971). The purified collectors were stored in ether. The other chemicals were used as received.

3.1.3 Silica sol preparation

Sodium silicate from National Silicates (SiO_2 / Na_2O = 3.22) was used to prepare the silica sol. A 1 % stock solution (pH 11.15) was made (by weight, water: sodium silicate ratio 1: 1) to reduce the viscosity and improve ease of handling. From this, 10 ml was added to 79.5 ml of distilled water. While stirring, 8.65 ml of 10 % (by weight) H_2SO_4 was added drop wise. This mixture was kept for 3.5 minutes (gelling time) until it turned a light blue colour. Finally the mixture was added to 98 ml distilled and stirred thoroughly for one minute. This formed the activated silica sol (SiO_2 / Na_2O = 2.04, pH was 8.2). Once every three days activated silica sol was freshly prepared. The stock 1% solution and 10 % H_2SO_4 solutions were prepared every month.

3.1.4 Micro flotation procedure

Tests were conducted on 1.5 gram samples using a Partridge - Smith type cell (Partridge and Smith, 1971). Samples were conditioned in a beaker for 10 minutes with and without activators, the solution was decanted followed by silica sol conditioning for 10 minutes at 250 rpm on an orbital shaker. The feed was added to the cell using a funnel. After flotation, the float and non float products were collected and dried. Recovery was calculated by the mass ratios. Figure 3.1 illustrates the experimental set-up

The reagent concentrations used were potassium ethyl xanthate (KEX) 5×10^{-5} M, Cu 2.5×10^{-5} M and Pb 5×10^{-4} M, unless otherwise stated. Flotation time was 2 min except for pyrite (3.25 min) and air flow rate was 12.5 ml / min.

In one test an 'oxidized' pyrite sample was used. This was prepared by keeping the sample in water for two days followed by drying in air.

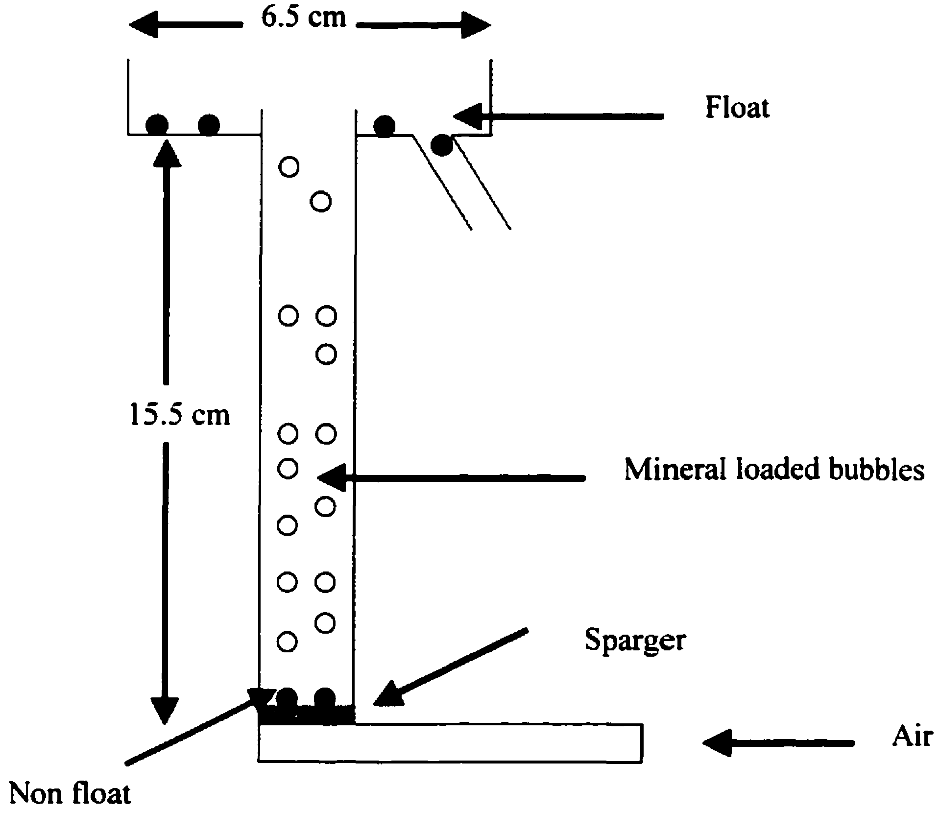

Fig. 3.1 Micro flotation set-up

3.2 X-ray Photoelectron Spectroscopy (XPS)

This analysis performed, at INRS-Energy and Materials, Varennes, Quebec, was used to detect elements on the mineral surface to help probe the mechanism of mineral - silica sol interaction. Mineral samples were prepared by conditioning at pH 8 and 9 with 1000 ppm of silica sol in the presence and absence of activating cations (same as in the flotation procedure). The solution was decanted, the minerals filtered and dried. The dried sample, was then pressed into a pellet of ca. 1.3 cm diameter and 3 mm thickness by a hydraulic press for XPS analysis.

The surface concentration of an element in atomic % is calculated as,

$$C_x = \frac{NPA_x}{(NPA_x + NPA_y + NPA_z)} * 100 \qquad (3\text{-}1)$$

where C_x is the concentration of element x (%) in a matrix of elements x, y and z (in this example) and NPA is the normalized peak area given by,

$$NPA = \frac{PA}{SF.KE^{0.6}} \qquad (3\text{-}2)$$

where, PA is the peak area, SF an empirical sensitivity factor, and KE is the kinetic energy of the core - level electrons.

Errors arise from the method of background subtraction used for the calculation of peak area intensity and from the non homogeneous surface distribution of a particular element or elements within the analysis area.

3.3 Batch flotation

3.3.1 Ores

In the case of Les Mines Selbaie and Mine Louvicourt testing was done on-site. Samples of rod mill feed were cut and split into approximately 1kg sub-samples using a riffle. For the Hudson Bay Mining and Smelting case, two rod mill feed samples (A and B) were sent to McGill University where they were crushed by jaw and cone crusher and split into approximately 1kg sub-samples using a riffle. The head assays are given in Table 3.2.

Table 3.2: Chemical composition of ores

Ore	Cu (%)	Pb (%)	Zn (%)	Fe (%)
Les Mines Selbaie	0.26	0.05	1.32	3.50
Mine Louvicourt	2.90	-	1.40	19.14
Hudson Bay Mining and Smelting-sample A	2.80	0.06	3.10	20.30
Hudson Bay Mining and Smelting-sample B	3.00	0.06	3.60	21.20

In the case of Brunswick Mine, tests were done on-site using Cu / Pb rougher tails, i.e., Zn feed, taken from the circuit. The slurry was used as collected, being approximately 45 w/w % solids, 80% - 45 μm grind size and composition 8 % Zn, 0.11% Cu, 0.6 % Pb and 30 % Fe.

3.3.2 Reagents: Silica sol, polyphosphate and ethylenediaminetetraacetic acid (EDTA)

Dosages of 0.5, 1, 1.5 and 3 g/kg of silica sol (from the stock solution of activated silica sol, 50, 100, 150 and 300ml, respectively) were used. For sodium polyphosphate ($(NaPO_3)_n$, n~17, supplied by Aldrich Chemical Company, Inc.) a stock solution (using tap water) of 20 g/l was prepared. Dosages of 0.1, 0.5 and 1 g/kg (from the stock solution, 5, 25 and 50 ml of 20 g/l, respectively) were used. The ethylenediaminetetraacetic acid (EDTA) (supplied by Aldrich Chemical Company, Inc.) concentration was 0.1 g/kg (added as 0.1g in 50 ml tap water). This EDTA concentration is equivalent to 0.5 g/kg of polyphosphate and 0.5 g/kg of silica sol on a molar basis (see Appendix 1 for calculation).

3.3.3 Procedure

3.3.3.1 Les Mines Selbaie

The 1kg sample was mixed with 840 ml process water (chemical analysis: Fe 0.25, Ca 253.7, Mg 7.6, Zn 9.9, Pb < 0.01 and Cu < 0.01 ppm) (ca. 55 w/w % solids), ground in a laboratory stainless steel rod mill with stainless steel rods for 5 min to ca. 80 % - 120 μm and transferred to a Denver 3L flotation cell. Baseline test conditions for the Cu and Zn stages are given in Table 3.3. Two baseline procedures were compared, one with NaCN in grinding and one without. The three reagents, silica sol, polyphosphate and EDTA, were applied (individually) to the Cu float after adjustment of pH to 9 - 9.5 using lime and conditioned for 15 minutes. To test in the Zn stage, after floating the Cu concentrate according to the baseline procedure, the three reagents were introduced after the addition of $CuSO_4$ and pH adjustment to 11 - 11.5 using lime and conditioned for 10 minutes. The flotation cell was operated at 1500 rpm for both Cu and Zn stages, and flotation conducted in timed increments.

Table 3.3: Standard (baseline) batch flotation procedure: Les Mines Selbaie

Stage	Time	pH	NaCN (g/t)	$ZnSO_4$ (g/t)	Sp129 [*] (g/t)	MIBC (g/t)	$CuSO_4$ (g/t)	SIPX (g/t)
Grind	5 min	-	10	300	-	-		-
Cu Float								
Condition	3 min	9 - 9.5	-	-	3	36		
Conc- 1	20s							
Conc-2	30s	9 - 9.5			1	18		
Conc-3	30s	9 - 9.5			1	18		
Zn Float								
Condition	1 min						150	
	1 min	11 - 11.5						
	3 min					18		5
Conc-1	30s							
Conc-2	30s							
Conc-3	2min	11 - 11.5				18		3
Conc-4	2min	11 - 11.5				18		2

---

[*] Sodium dialkyl dithiophosphate

3.3.3.2 Mine Louvicourt

The 1kg sample was mixed with 665 ml tap water (ca. 60 w/w % solids), ground for 20 minutes in a laboratory mild steel rod mill with mild steel rods to ca. 90 % - 75 μm and transferred to a 3L Denver cell. The baseline test conditions are given in Table 3.4. The same general approach to reagent testing as described for Les Mines Selbaie was used. The reagents were applied in the Cu stage after pH adjustment to 10.5 using lime and conditioned for 15 minutes. In the Zn float, after baseline flotation in the Cu stage, reagents were added after addition of $CuSO_4$ and pH adjustment to 10.1 (with lime) and conditioned for 10 minutes. Impeller speed was 1500 rpm and flotation was conducted in timed increments.

Table 3.4: Standard (baseline) batch flotation procedure: Mine Louvicourt

Stage	**Time**	**pH**	**$Ca(OH)_2$ (g/t)**	**3418 A* (g/t)**	**KAX (g/t)**	**MIBC (g/t)**	**$CuSO_4$ (g/t)**	**Flex 41 • (g/t)**
Grind	20min		1100	22				
Cu-Float								
Condition	3 min	10.5						
Conc-1	30sec					36		
Conc-2	30sec							
Conc-3	2 min	10.5			3	36		
Conc-4	1 min	10.5			1	36		
Zn- Float								
Condition	1 min	10.4						
	4 min	10.4					300	
	1min	10.1						6
Conc-1	30sec					54		
Conc-2	30sec							
Conc-3	1 min	10				54		3
Conc-4	1 min							

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[*] Sodium diisobutyldithiophosphinate

• Enhanced isobutyl xanthate

3.3.3.3 Hudson Bay Mining and Smelting - sample A

These were the first tests conducted and only polyphosphate was evaluated in the Cu stage and silica sol in the Zn stage (following the expected application of these two reagents, see later). The target grind size is ca. 80 % - 75 μm. The 1kg sample was mixed with 700 ml tap water (ca. 59 w/w % solids), ground in a laboratory stainless steel rod mill with a mixture of mild steel and stainless steel rods for 20 min to ca. 88 % - 75 μm (see Appendix 1 for the determination of grinding time) and transferred to a Denver 3L flotation cell. Baseline test conditions for the Cu and Zn stages are given in Table 3.5. Polyphosphate was applied to the Cu float after adjustment of pH to 7.5 using lime and conditioned for 15 minutes. In the Zn stage, after floating the Cu concentrate according to the baseline procedure at pH 9.5, silica sol was introduced after the addition of $CuSO_4$ and pH adjustment to 9 using lime and conditioned for 10 minutes. The flotation cell was operated at 1200 rpm for both Cu and Zn stages, and flotation was conducted in timed increments.

Table 3.5: Standard (baseline) batch flotation procedure: Hudson Bay Mining and Smelting; sample A

Stages	Time	pH	$CuSO_4$ (g/t)	KAX (g/t)	MIBC (g/t)
Grind	20 min	-	-	-	-
Cu Float					
Condition	2 min	7.5		200	18
Conc- 1	30s				
Conc-2	30s				
Condition	2 min			200	18
Conc-3	1 min				
Zn Float					
Condition	2min		130		
	2 min	9		400	36
Conc-1	30s				
Conc-2	30s				
Conc-3	1min				18
Conc-4	3min				18

3.3.3.4 Hudson Bay Mining and Smelting - sample B

In this case baseline flotation tests were conducted using the plant - specified conditions with the same approach to reagent testing as described for Les Mines Selbaie. The 1kg sample was mixed with 700 ml tap water (ca. 59 w/w % solids), ground in a laboratory stainless steel rod mill with a mixture of mild steel and stainless steel rods for 20 min to ca. 90% - 75 µm and transferred to a Denver 3L flotation cell. Baseline test conditions for the Cu and Zn stages are given in Table 3.6. The reagents were applied in the Cu stage after pH adjustment to 10 using lime and conditioned for 15 minutes. In the Zn float, after baseline flotation in the Cu stage, reagents were introduced after addition of $CuSO_4$ and pH adjustment to 12 (with lime) and conditioned for 10 minutes. The flotation cell was operated at 1200 rpm for both Cu and Zn stages, and flotation was conducted in timed increments.

Table 3.6: Standard (baseline) batch flotation procedure: Hudson Bay Mining and Smelting; sample B

Stages	**Time**	**pH**	**$CuSO_4$ (g/t)**	**KAX (g/t)**	**MIBC (g/t)**
Grind	20 min	-	-	-	-
Cu Float					
Condition	2 min	10		200	18
		10			
Conc- 1	30s				
Conc-2	30 s				
Condition	2 min			200	18
Conc-3	1 min				
Zn Float					
Condition	2min		130		
	2 min	12		400	36
Conc-1	30s				
Conc-2	30s				
Conc-3	1min				18
Conc-4	3min				18

3.3.3.5 Brunswick Mine

In this case only polyphosphate in the Zn stage was tested following the observations made on Les Mines Selbaie and Mine Louvicourt ores (see later). A factorial combination of $CuSO_4$ and polyphosphate dosages was tested, shown in Fig. 3.2. A slurry volume of ca. 2200 ml was taken from the Cu / Pb tails (Zn feed), the zinc grade was determined roughly by X-ray flourescence analysis (XRF) (on-line) and % solids by a Marcy density gauge. Reagent requirements were calculated based on the weight of dry solids and the Zn grade,

$$Weight\ of\ dry\ solids = \frac{volume\ of\ slurry * s.g}{(1 + s.g * (\frac{100}{\%Solids} - 1))} \tag{3.3}$$

where the solids specific gravity (s.g) is taken as 4.11. In the Zn stage, polyphosphate was introduced before and after addition of $CuSO_4$ and conditioned for 10 minutes after adjustment of pH to 10.5 using lime. Baseline test conditions are given in Table 3.7. The flotation cell was operated at 1500 rpm and flotation was conducted in timed increments.

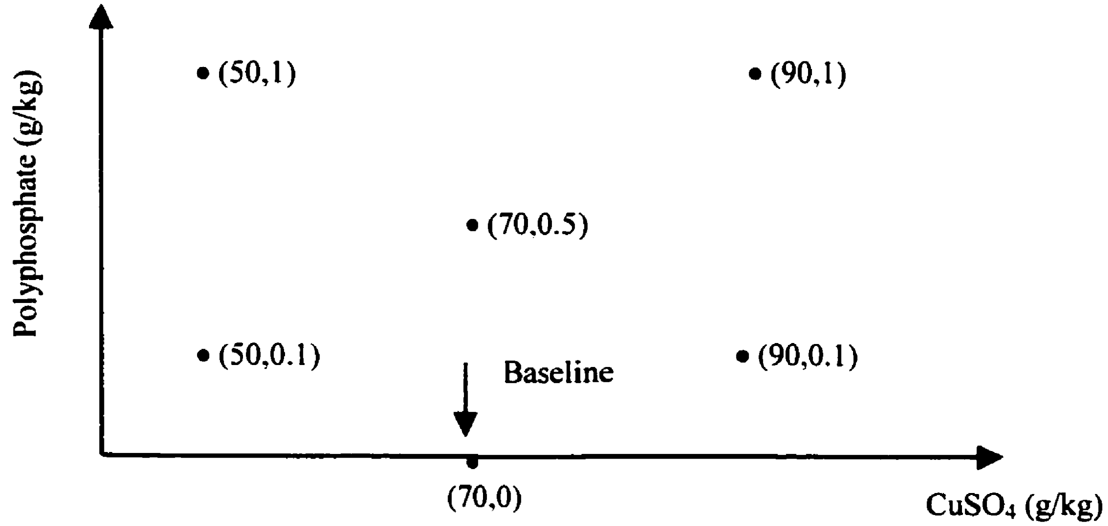

Fig. 3.2 Experimental design for Brunswick Mine tests.

Table 3.7: Standard (baseline) Zn batch flotation procedure: Brunswick Mine

Stages	Time	pH	$CuSO_4$ (g/t/% Zn)	SIPX/KAX (80:20) (g/t/%Zn)	MIBC (g/t)
Condition	5 min		70		
	-	10.5			
	2 min			6	2.5
Conc-1	30sec				
Conc-2	30sec				
Conc-3	1 min				
Conc-4	1 min				
Conc-5	2 min				
Conc-6	2 min				

CHAPTER 4

RESULTS

4.1 Micro flotation

4.1.1 Repeatability

Reprodubility was tested on three non activated oxidized pyrite samples using sodium isopropyl xanthate at pH 7 which gave recoveries of 50.4, 52.1 and 57.8 %, and at pH 9 for Cu activated sphalerite which gave recoveries of 91.8, 89.0 and 92.1 %. From these data, the standard deviation was estimated as ca. 4 % at 50 % recovery and ca. 2 % at 90 % recovery. The average standard deviation (σ) was taken as 3%.

4.1.2 Chalcopyrite

Figures 4.1 and 4.2 show the addition of silica sol reduced chalcopyrite recovery and the depressant effect was maintained over the pH range 7 to 11.

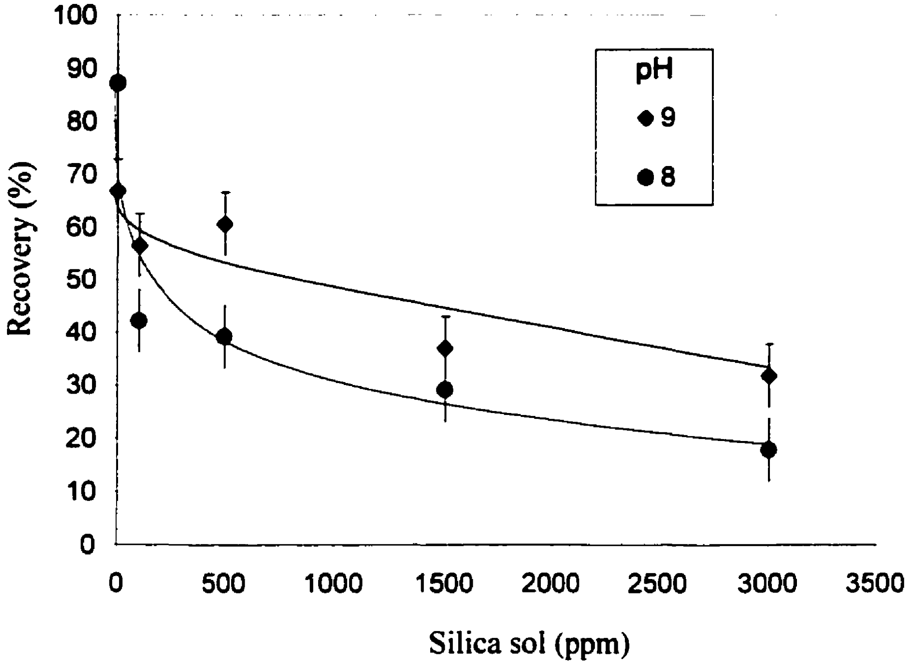

Fig. 4.1 Chalcopyrite recovery as a function of silica sol addition at pH 8 and 9. Note: Error bar is 2σ.

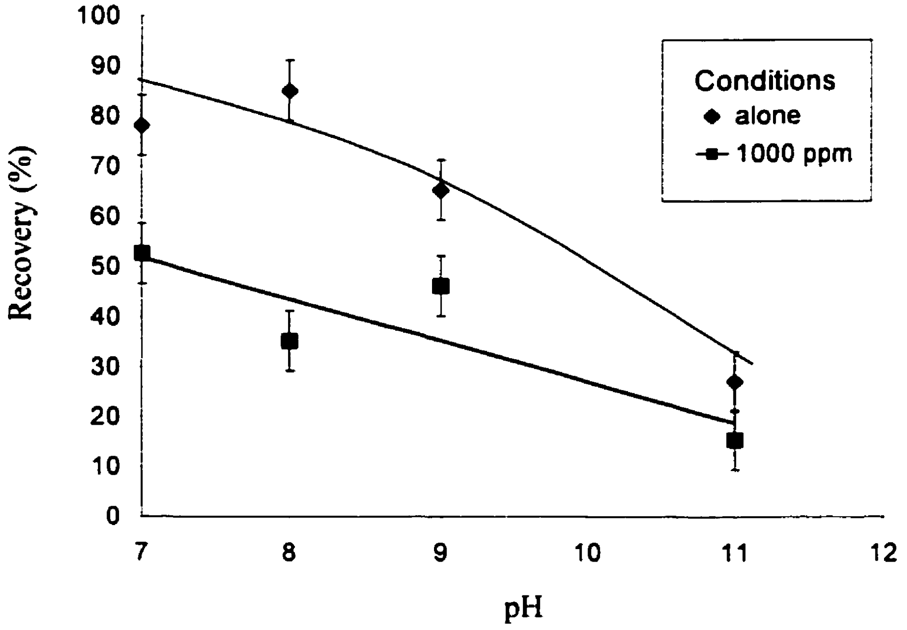

Fig. 4.2 Chalcopyrite recovery as a function of pH with and without 1000 ppm of silica sol. Note: Error bar is 2σ.

4.1.3 Sphalerite

Figure 4.3 shows at pH 9 that silica sol reduced recovery of sphalerite and Pb activated sphalerite but not Cu activated sphalerite. Figure 4.4 shows the trend was maintained over the pH range 7 to 11.

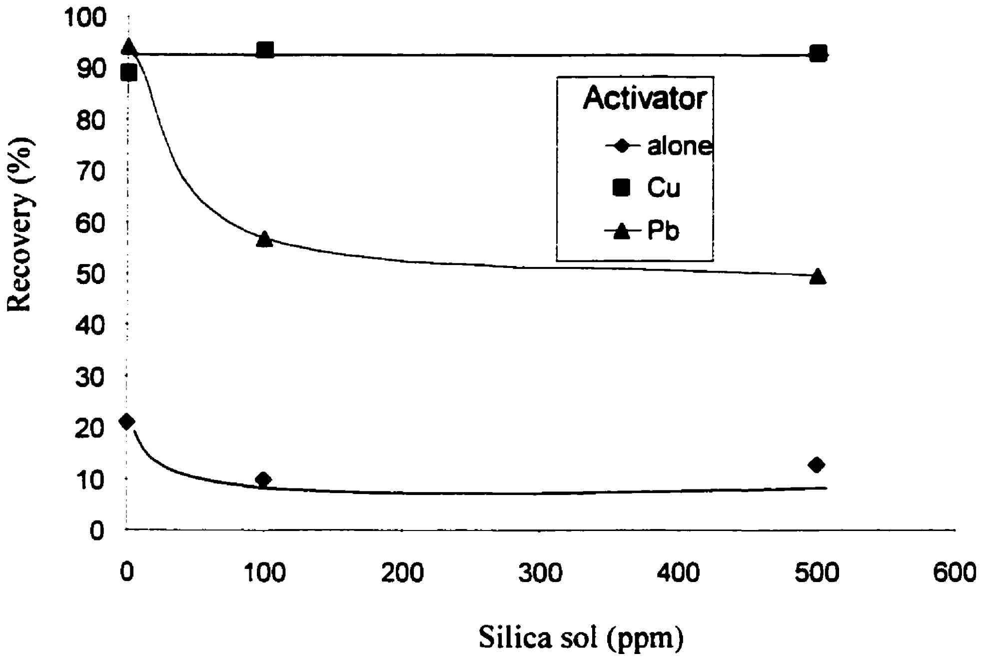

Fig. 4.3 Sphalerite recovery as function of silica sol addition at pH 9.

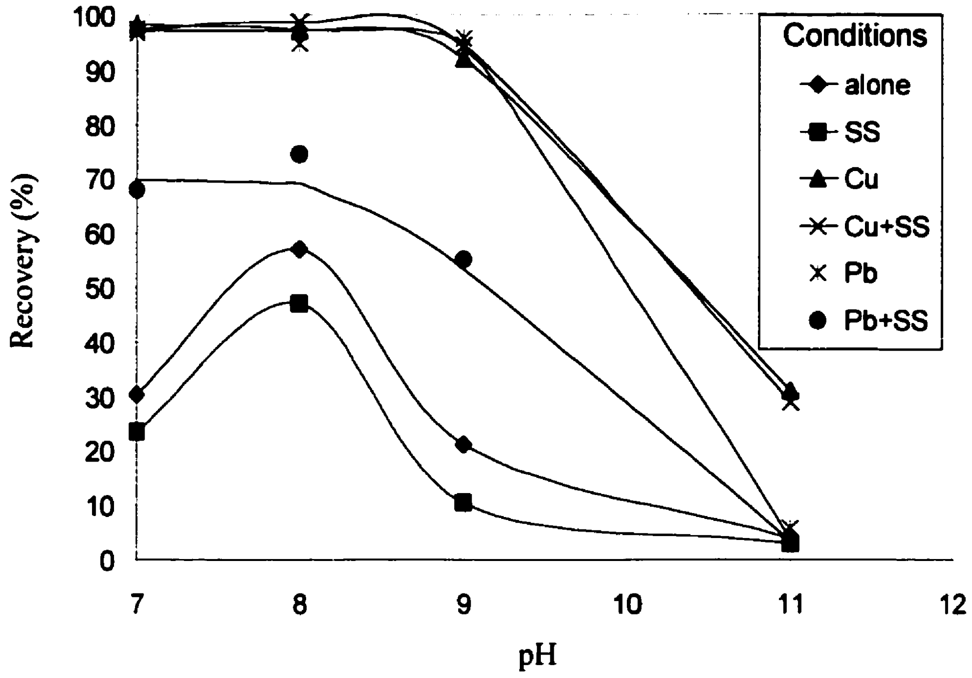

Fig. 4.4 Sphalerite recovery as a function of pH for various conditions. Note: SS = 1000 ppm silica sol.

4.1.4 Pyrite

Figure 4.5 shows at pH 9 that silica sol reduced recovery of Cu activated and Pb activated pyrite. Figure 4.6 shows the results for the oxidized pyrite sample as a function of pH using sodium isopropyl xanthate and higher concentrations of copper and lead. The presence of 1000 ppm of silica sol reduced the recovery in all cases over the pH range 7 to 11.

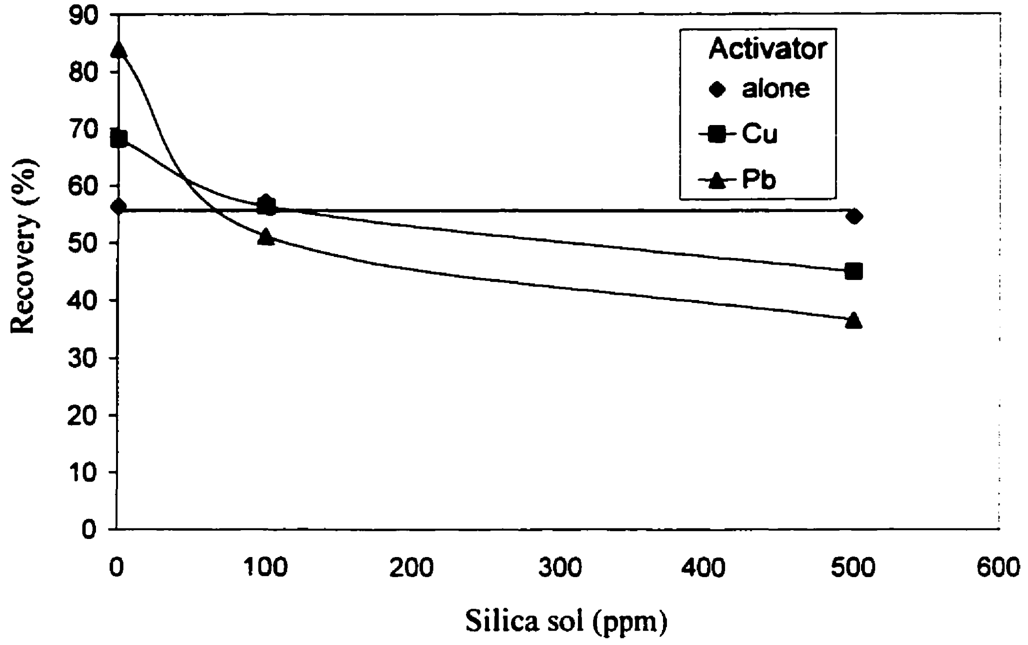

Fig. 4.5 Pyrite recovery as a function of silica sol addition at pH 9.

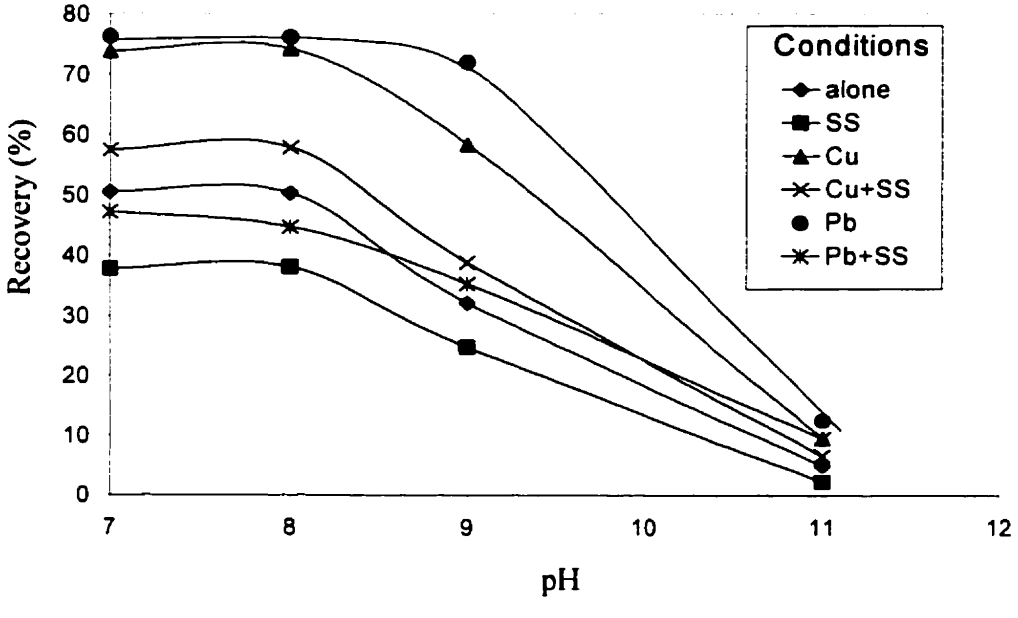

Fig. 4.6 Oxidized pyrite recovery as function of pH for various conditions.

NIPX 2.5 x 10^{-5}, Cu and Pb 2.5 x 10^{-4} and 2.5 x 10^{-3} M, respectively.

Note: SS = 1000 ppm silica sol.

4.1.5 Chalcocite and covellite

To help elucidate the mechanism of the action of silica sol, tests were conducted on chalcocite and covellite.

4.1.5.1 Chalcocite

Figure 4.7 shows chalcocite responded in a similar way to chalcopyrite; silica sol depressed the mineral over the pH range 7 to 11.

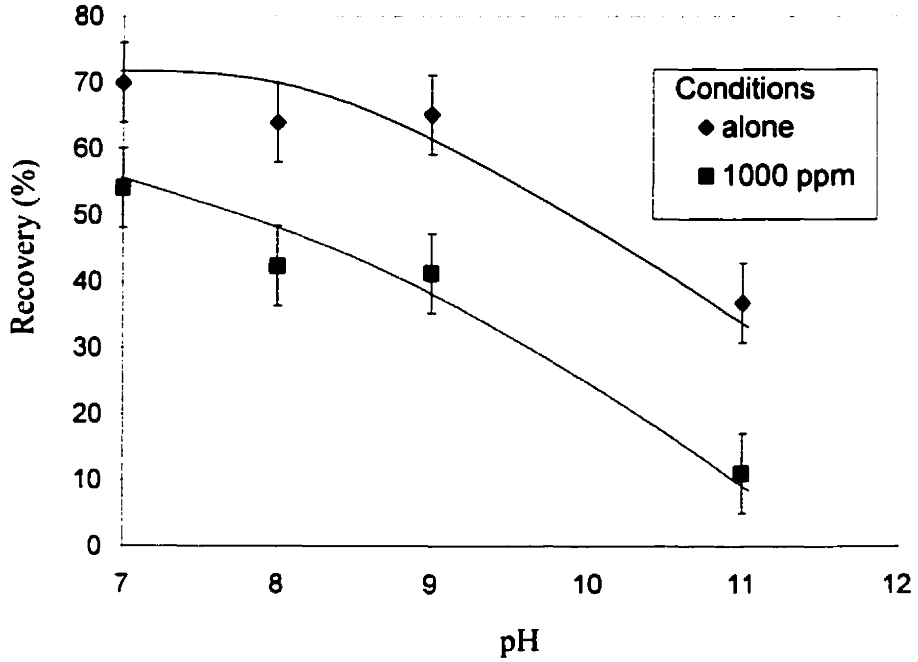

Fig. 4.7 Chalcocite recovery as a function of pH at 1000 ppm of silica sol.

Note: Error bar is 2σ.

4.1.5.2 Covellite

At pH 3, covellite was nearly completely depressed by 1000 ppm of silica sol (from ca. 52% to 4 % recovery using NIPX 2.5 x 10^{-5} M, flotation time 5 min). In the alkaline region covellite did not float.

4.1.6 Summary

From the micro flotation results it is clear that silica sol depressed all the copper minerals investigated as well as Cu and Pb activated pyrite and Pb activated sphalerite but did not depress Cu activated sphalerite. This suggests potential application in the Zn stage.

4.2 Mechanism of silica sol action – X-ray photoelectron spectroscopy (XPS)

4.2.1 Repeatability

Reprodubility of the XPS derived surface concentration was gauged from Cu activated sphalerite and Cu and Pb activated pyrite before and after silica sol addition as silica sol did not change the surface concentrations. The surface concentrations (in %) were 1.58 and 1.54 for Cu activated sphalerite, 1.25 and 1.3 for Cu activated and 0.62 and 0.68 for Pb activated pyrite. From this data, the relative standard deviation (standard deviation/mean) was estimated to be ca. 1.5 %, 2.3% and 6 % for Cu activated sphalerite and Cu and Pb activated pyrite, respectively. An average relative standard deviation of 3.3 % for a given set of conditions was used to estimate the standard deviation.

4.2.2 Chalcopyrite

Figure 4.8 shows the estimated surface concentration of Si on the chalcopyrite before and after silica sol addition. There was Si on the surface initially, presumably due to silicate mineral impurities. (Si was not detected by atomic absorption spectroscopy on the bulk samples but XPS has much greater sensitivity.) After silica sol addition, the Si concentration increased. This suggests silica sol was adsorbed.

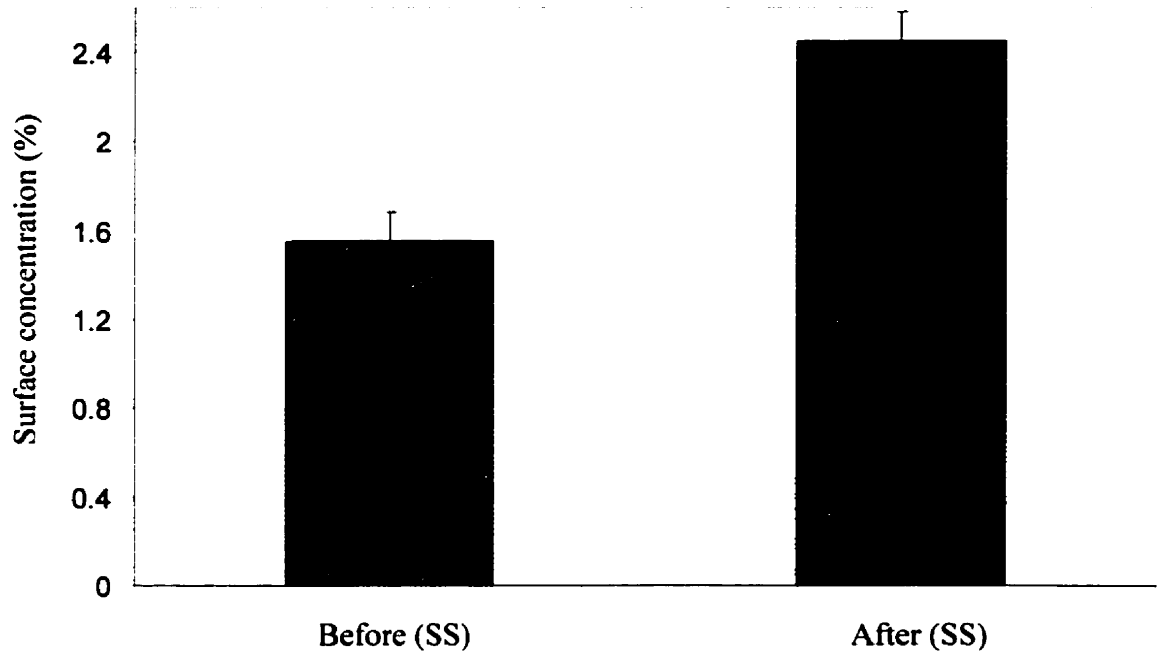

Fig. 4.8 Surface concentration of Si on chalcopyrite surface before and after silica sol (SS) addition at pH 8. Note: Error bar is 2σ.

4.2.3 Sphalerite

4.2.3.1 Cu activated sphalerite

Figure 4.9 shows surface concentration of Cu and Si on Cu activated sphalerite before and after silica sol addition. The Cu concentration remained unchanged and no Si was detected. This lack of change in surface concentration supports the lack of effect of silica sol on flotation of Cu activated sphalerite.

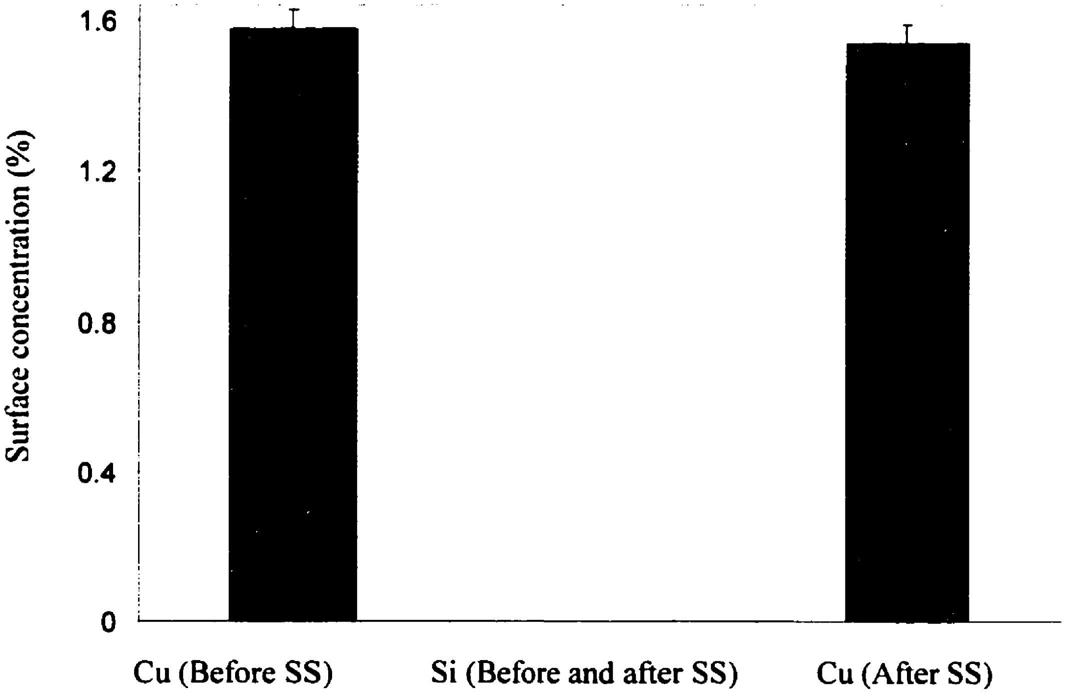

Fig. 4.9 Surface concentration of Cu on Cu activated sphalerite surface before and after silica sol (SS) addition at pH 9. Note: Error bar is 2 σ.

4.2.3.2 Pb activated sphalerite

Figure 4.10 shows surface concentration of Pb and Si on Pb activated sphalerite before and after silica sol addition. The Pb on the surface was partially removed and no Si was detected. The reduction in Pb concentration does not seem sufficient to account for the depression of Pb activated sphalerite.

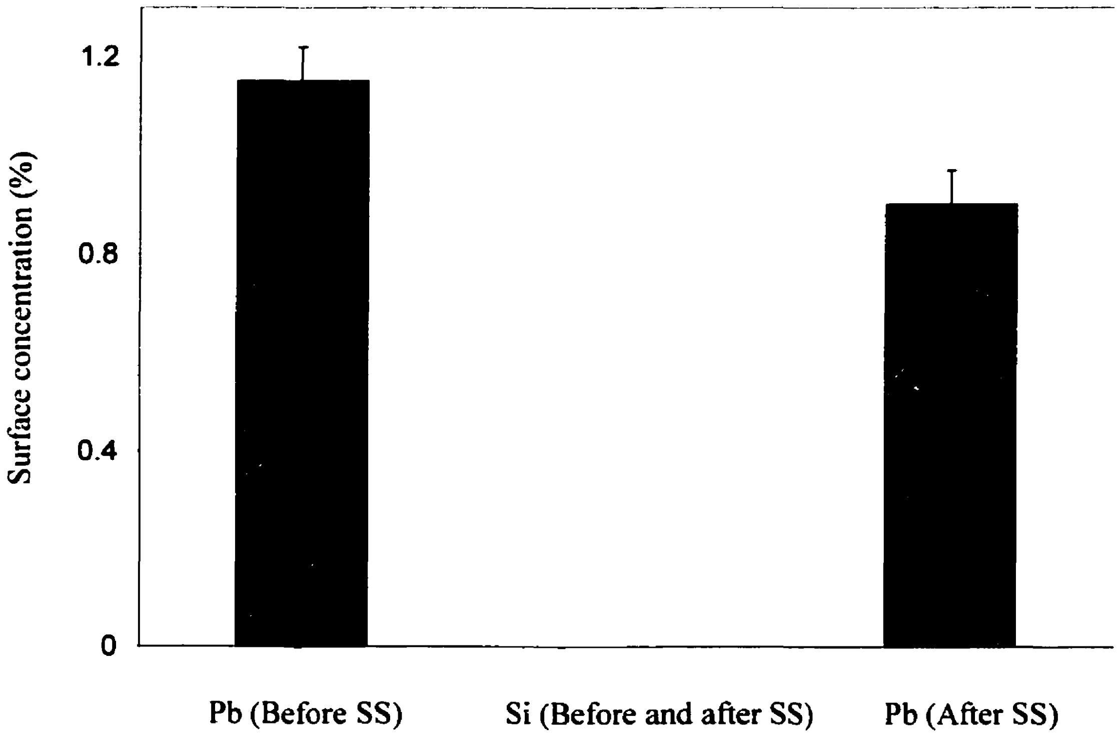

Fig. 4.10 Surface concentration of Pb on Pb activated sphalerite surface before and after silica sol (SS) addition at pH 9. Note: Error bar is 2σ.

4.2.4 Pyrite

4.2.4.1 Non activated pyrite

Figure 4. 11 shows surface concentration of Si on non activated pyrite showing silica sol was adsorbed.

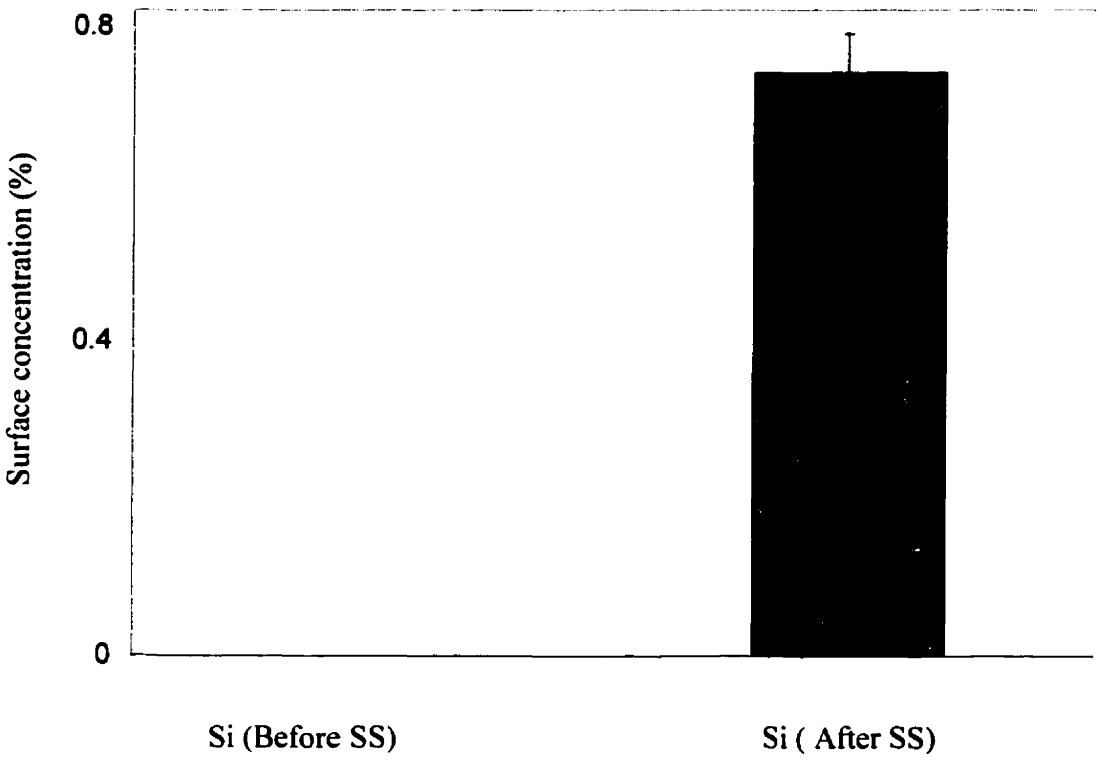

Fig. 4.11 Surface concentration of Si on non activated pyrite surface before and after silica sol (SS) addition at pH 9. Note: Error bar is 2σ.

4.2.4.2 Cu activated pyrite

Figure 4. 12 shows surface concentration of Cu and Si on Cu activated pyrite before and after silica sol. The Cu concentration was unchanged while the increase in Si on the surface indicated the adsorption of silica sol.

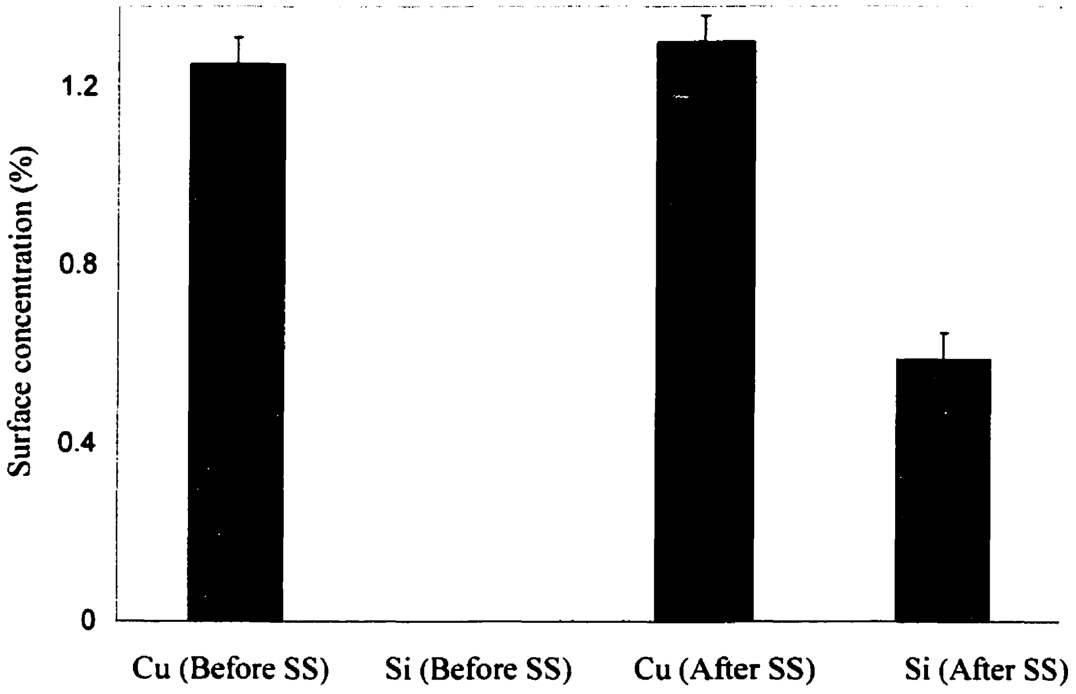

Fig. 4.12 Surface concentration of Cu and Si on Cu activated pyrite surface before and after silica sol (SS) addition at pH 9. Note: Error bar is 2σ.

4.2.4.3 Pb activated pyrite

Figure 4. 13 shows surface concentration of Pb and Si on Pb activated pyrite before and after silica sol. The Pb concentration was unchanged while the Si on the surface increased indicating adsorption of silica sol.

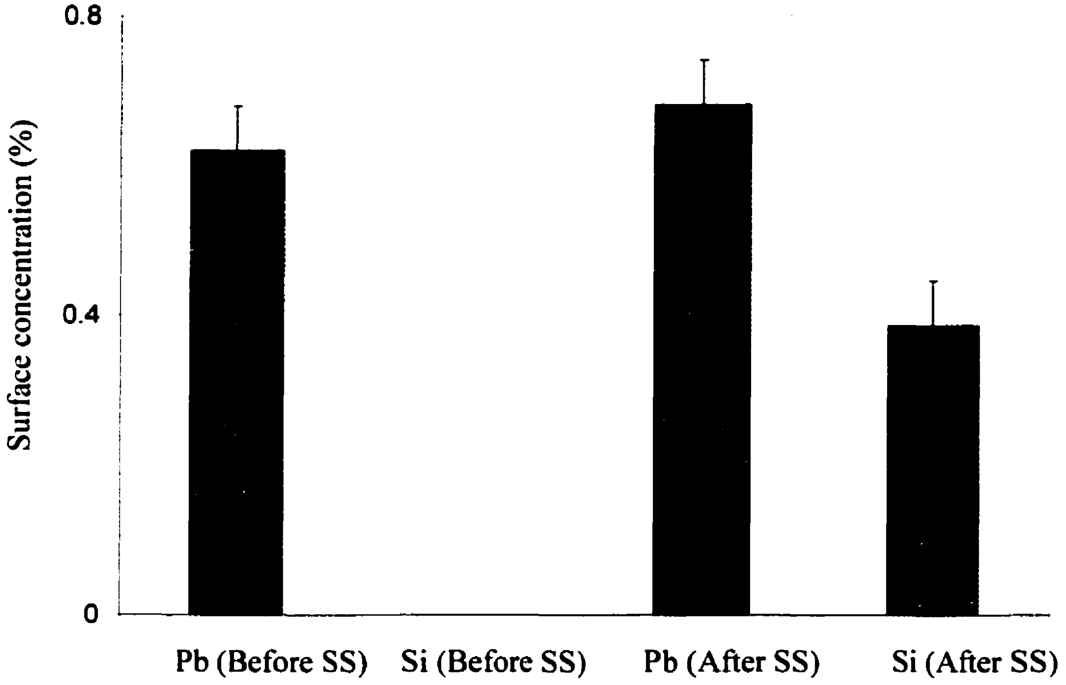

Fig. 4.13 Surface concentration of Pb and Si on Pb activated pyrite surface before and after silica sol (SS) addition at pH 9. Note: Error bar is 2σ.

4.2.5 Chalcocite

Figure 4.14 shows surface concentration of Si on chalcocite before and after silica sol addition. Like chalcopyrite, chalcocite initially had Si on its surface and after silica sol addition Si concentration went up, i.e., silica sol was adsorbed.

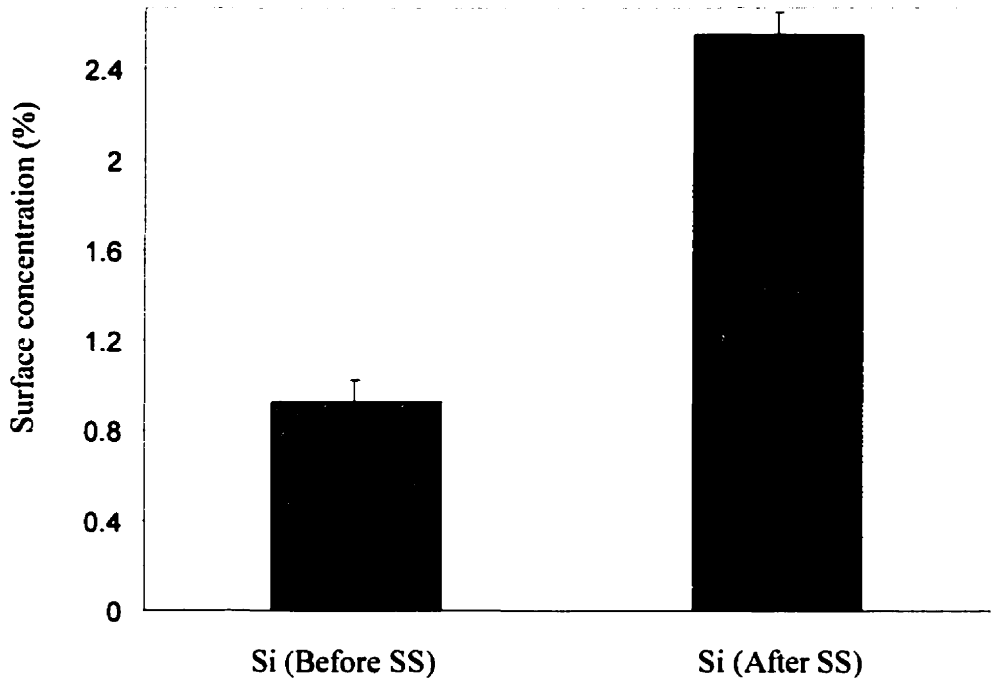

Fig. 4.14 Surface concentration of Si on chalcocite surface before and after silica sol (SS) addition at pH 9. Note: Error bar is 2σ.

4.2.6 Summary

The XPS results suggest that silica sol adsorbed on all copper minerals, non activated pyrite and Cu and Pb activated pyrite. In the case of sphalerite, silica sol showed no evidence of adsorption, limited removal of Pb and no removal of Cu.

4.3 Batch flotation

4.3.1 Determining repeatability

Baseline tests were repeated several times. An example of repeatability is given in Fig. 4.15a, cumulative Cu grade vs cumulative Cu recovery for Les Mines Selbaie (with NaCN). When more than 4 baseline tests were available a 95 % confidence interval (95% CI) band was generated. This was done as follows:

A given recovery was selected and the 95 % confidence interval on the corresponding grade was determined (see Appendix 1 for specimen calculations). By repeating this at several recoveries a 95 % confidence interval band was derived (Fig. 4.15b). This is reported on subsequent figures as a shaded area against which to assess the impact of the tested reagents. The same procedure was used for recovery vs recovery plots - the 95 % confidence interval on the y - axis was determined and a shaded area generated to represent the region of uncertainty. With fewer than 4 baseline tests, the same approach was followed but two times the standard deviation was determined rather than the 95 % CI.

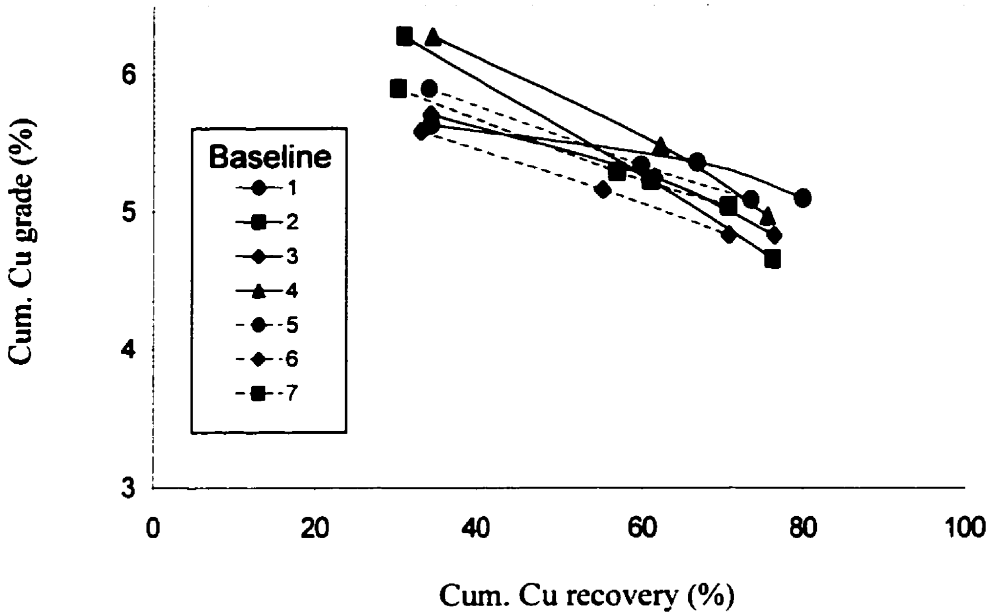

Fig. 4.15a Repeatability: Baseline cumulative Cu grade vs recovery test results - Les Mines Selbaie with NaCN added in grinding.

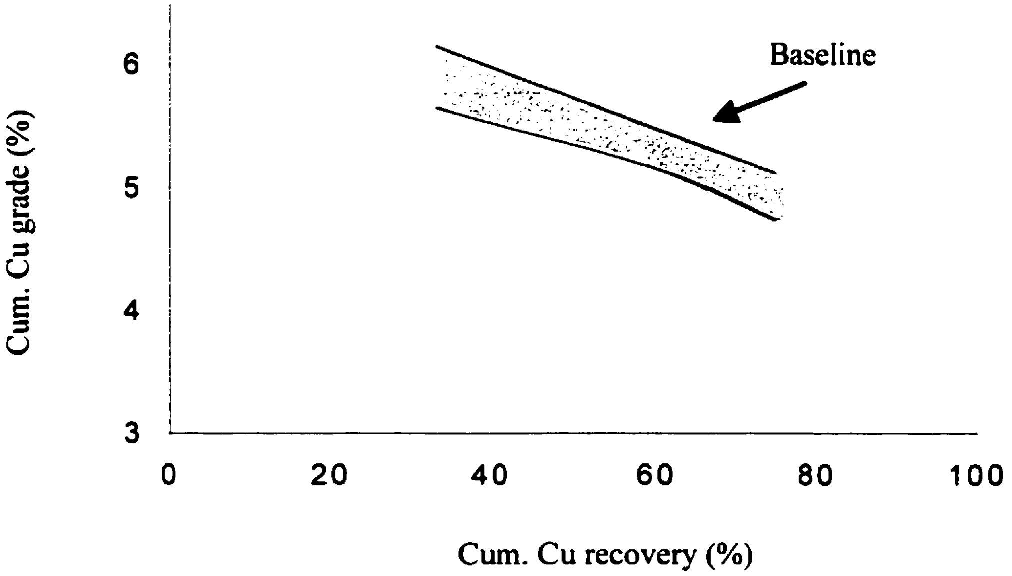

Fig. 4.15b 95 % confidence interval band derived from Fig. 4.15a.

4.3.2 Les Mines Selbaie

4.3.2.1 Cu stage: without NaCN

The results are shown in Fig. 4.16. Generally, the reagents degraded the Cu stage performance but tended to increase the flotation rate, i.e., points shifted to higher recovery for the same flotation time (0.1 g/kg EDTA being the exception).

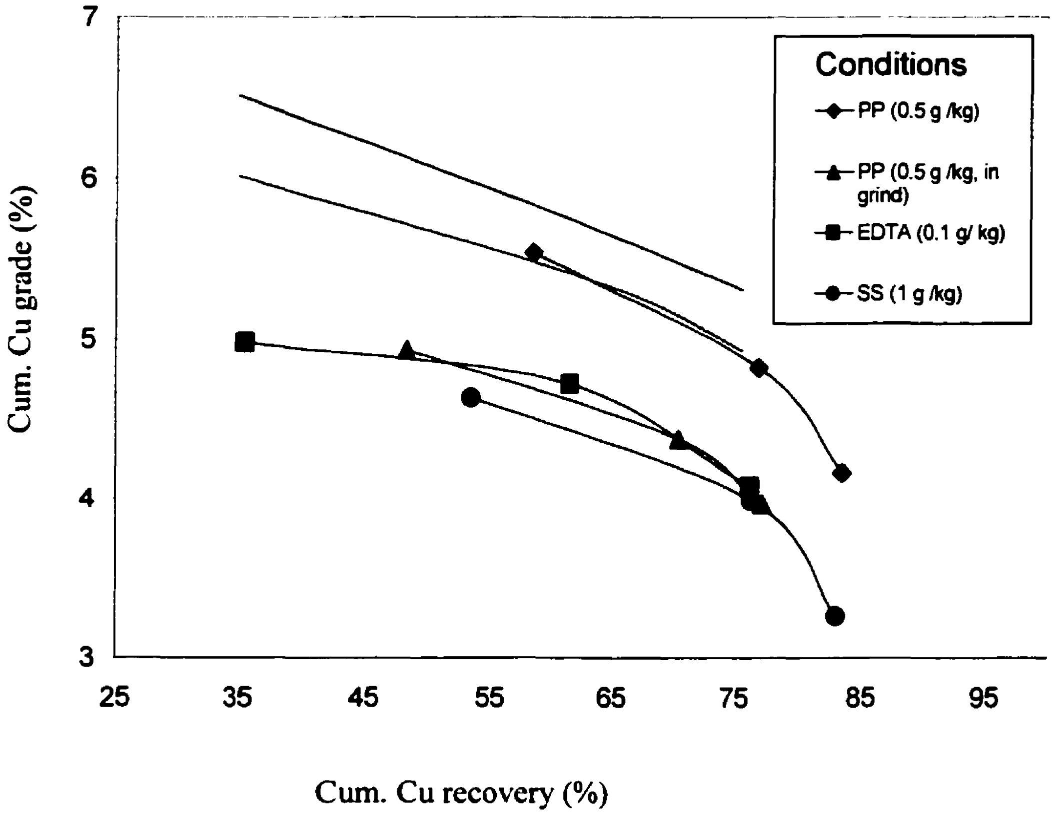

Fig. 4.16 Cumulative Cu recovery vs grade for various conditions: Les Mines Selbaie without NaCN.

The increased flotation rate is illustrated in Fig. 4.17 for the case of polyphosphate and silica sol. Both Cu (chalcopyrite) and Zn (sphalerite) flotation rate increased, i.e., there was no selective action. The high recovery of Zn, exceeding Cu recovery at 1.3 min, reflects the difficult processing of this ore type.

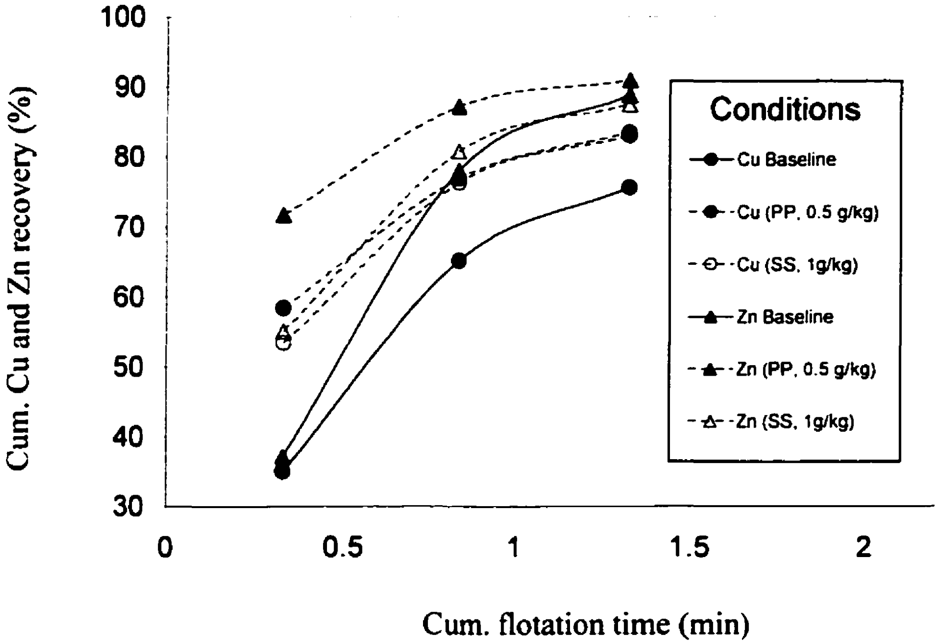

Fig. 4.17 Rate of flotation: Cumulative Cu and Zn recovery vs time with and without polyphosphate and silica sol.

4.3.2.2 Cu stage: with NaCN

In this case only polyphosphate at various concentrations was used (Fig. 4.18). The reagents increased flotation rates and marginally improved Cu stage selectivity.

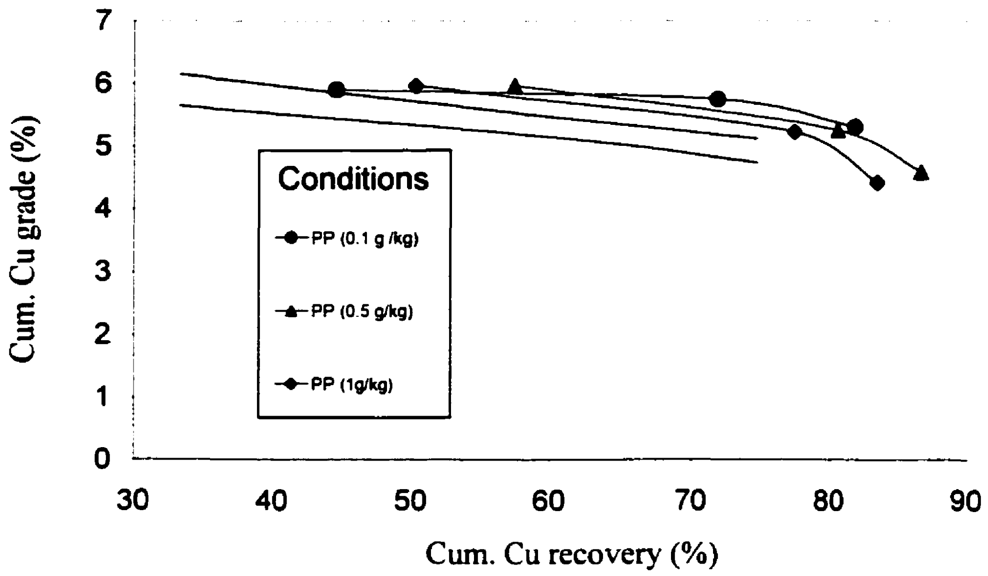

Fig. 4.18 Cumulative Cu grade vs recovery for various concentrations of polyphosphate with NaCN.

4.3.2.3 Zn stage

Zinc flotation followed baseline Cu flotation and recovery was calculated from the feed to the Zn stage. Figure 4.19 shows the grade - recovery results for all three reagents. The Zn grades are impractically low (partly reflecting the high Zn loss to the Cu concentrate (Fig.4.17)) but nevertheless this time an improvement was seen with EDTA, silica sol (1.5 g/kg), and especially, polyphosphate. As in the Cu stage, the flotation rate tended to increase (except for the lower SS dosages).

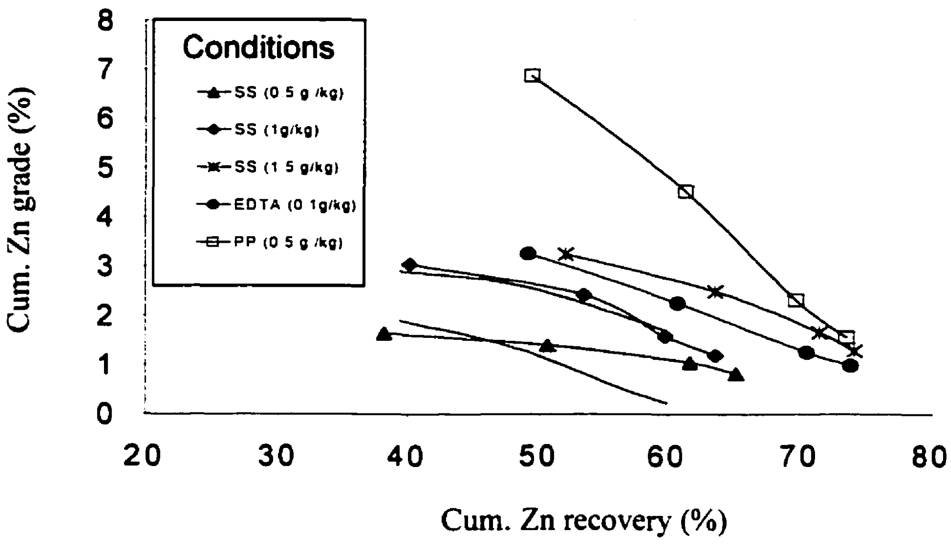

Fig. 4.19 Cumulative Zn grade vs recovery for various conditions (with NaCN in Cu stage).

The improvement in Zn grade was related to decreased pyrite recovery (Fig. 4.20); for example, with 0.5 g/kg polyphosphate, pyrite recovery decreased from ca. 35 % to ca. 5 % at ca. 55 % Zn recovery.

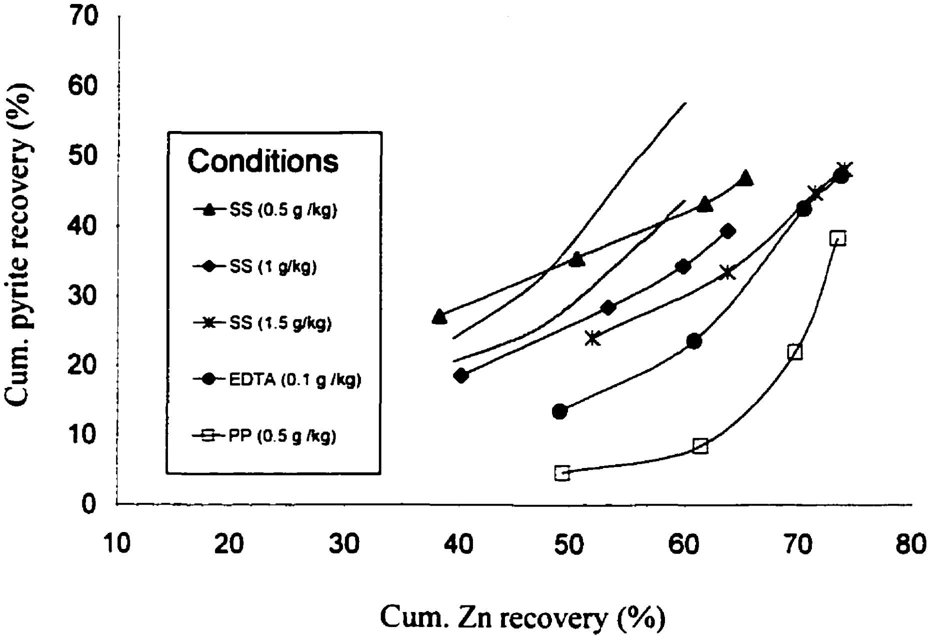

Fig. 4.20 Cumulative pyrite recovery vs Zn recovery for various conditions with NaCN in Cu stage). Note: Pyrite grade was computed from the metal assays allowing for Fe in chalcopyrite and 2 % Fe in sphalerite.

4.3.3 Mine Louvicourt

4.3.3.1 Cu stage

The reagents had little impact on the grade - recovery performance (Fig.4.21) but increased flotation rate.

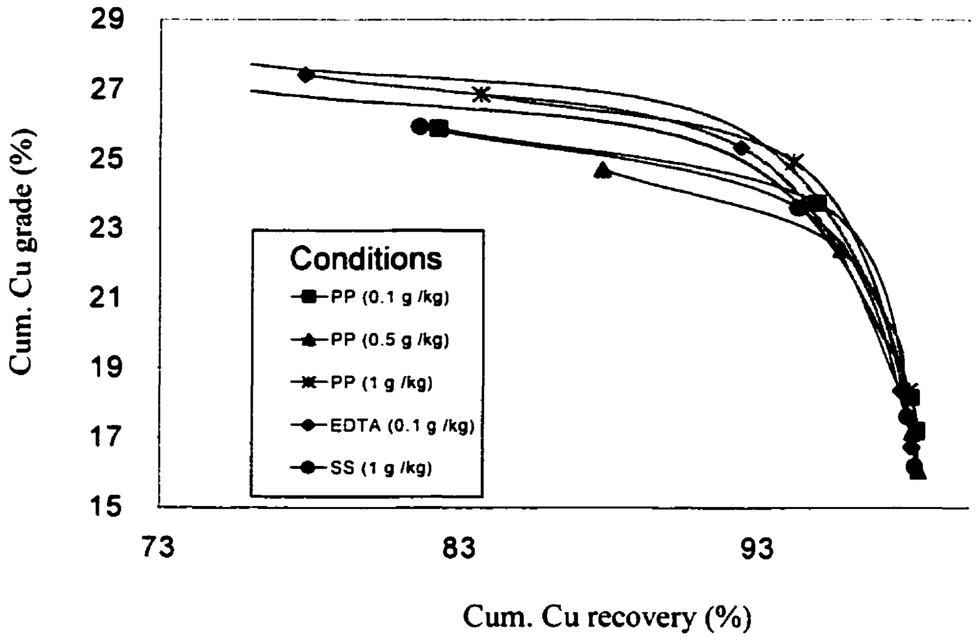

Fig. 4.21 Cumulative Cu grade vs recovery for various conditions.

The increased flotation rate is illustrated in Fig. 4.22 for the case of polyphosphate, silica sol and EDTA. Both Cu and Zn flotation rate increased, i.e., there was no selective action.

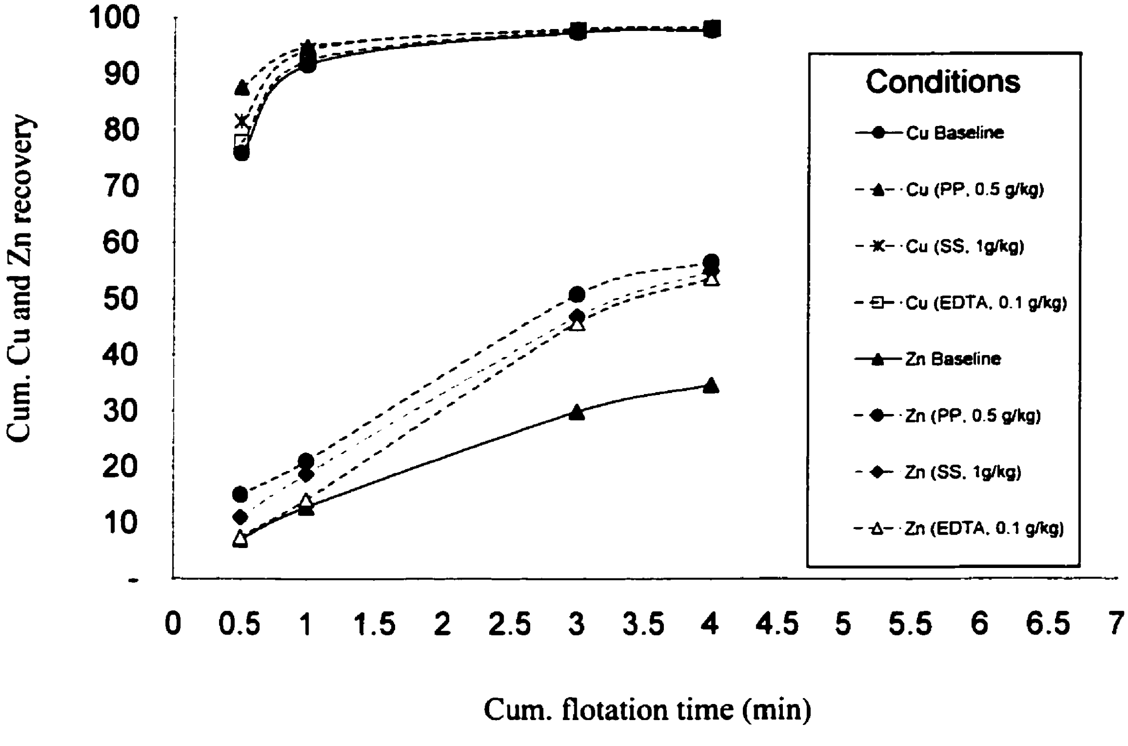

Fig. 4.22 Rate of flotation: Cumulative Cu and Zn recovery vs time with and without polyphosphate, silica sol and EDTA.

4.3.3.2 Zn stage

Zinc flotation followed baseline Cu flotation and recovery was calculated from the feed to the Zn stage. As in the Les Mines Selbaie case, polyphosphate notably improved the grade - recovery performance (Fig. 4.23). Unlike the previous situation, however, Zn grades are in the 'practical' range and the improvement, therefore, is more interesting.

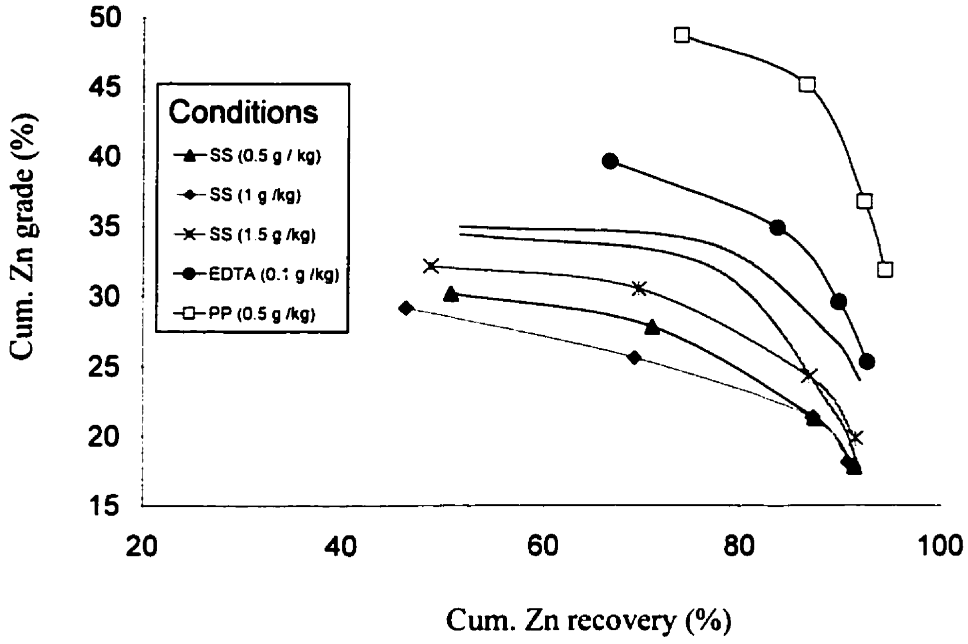

Fig. 4.23 Cumulative Zn grade vs recovery for various conditions.

The improvement in Zn grade is related to the reduction in pyrite recovery (Fig. 4.24) although pyrite recoveries are all low, less than 4%, making interpretation uncertain.

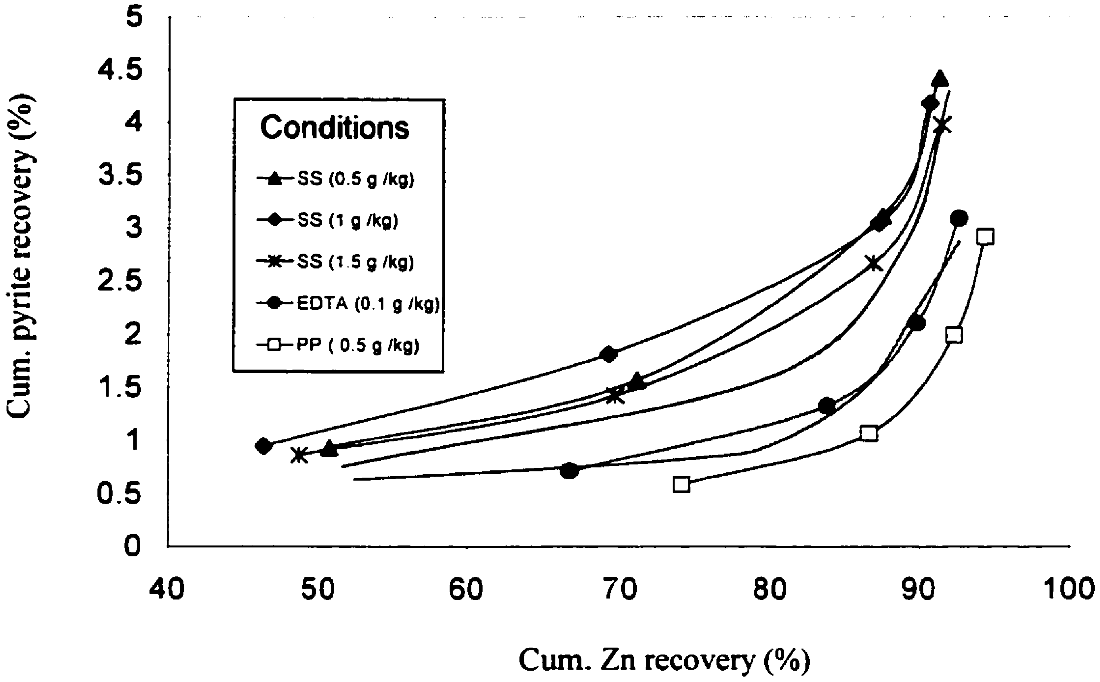

Fig. 4.24 Cumulative pyrite recovery vs Zn recovery for various conditions. Note: Pyrite grade was computed from the metal assays allowing for Fe in chalcopyrite and 6.6 % Fe in sphalerite.

4.3.4 Hudson Bay Mining and Smelting

4.3.4.1 Sample A

4.3.4.1.1 Cu stage

Two trials were completed: sample A represents the first scoping tests while sample B was tested after the experience gained at Les Mines Selbaie and Mine Louvicourt. For sample A one baseline test was conducted and only polyphosphate at three concentrations was tested. Polyphosphate degraded the Cu stage performance and did not increase flotation rates (Fig. 4.25).

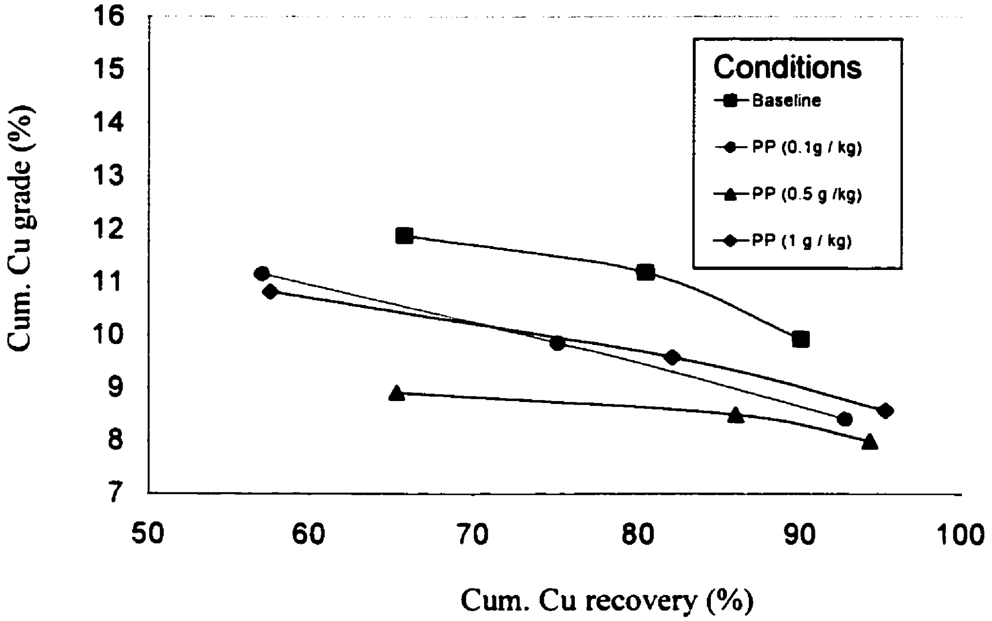

Fig. 4.25 Cumulative Cu grade vs recovery for various concentrations of polyphosphate.

4.3.4.1.2 Zn stage

Only silica sol was tested (Fig. 4.26). Flotation rate was increased and the final grade - recovery point was improved (but without repeats conclusions are tentative).

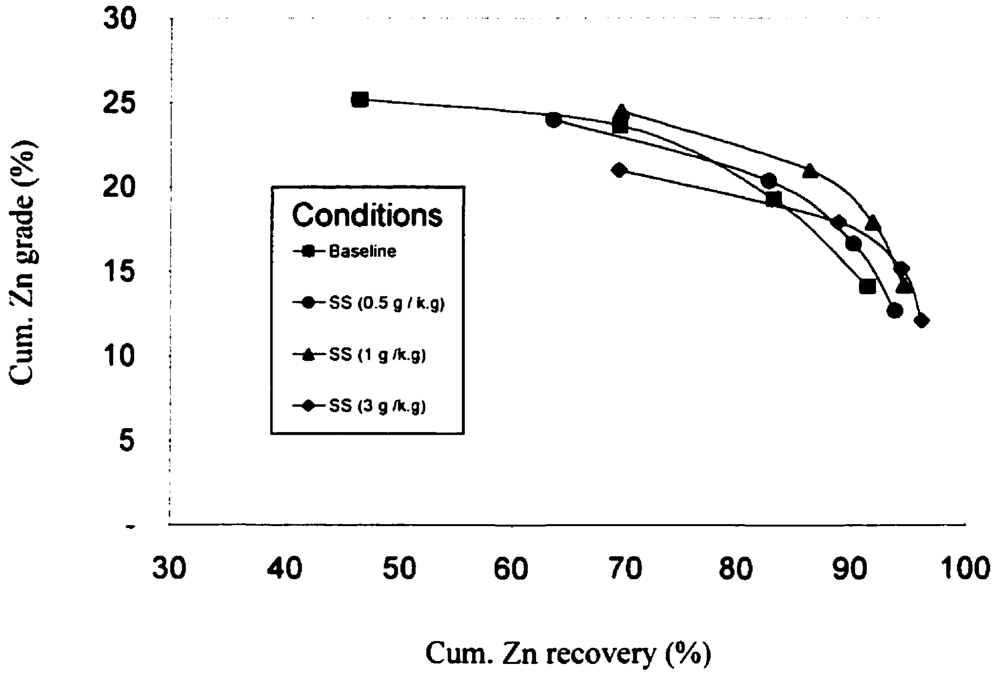

Fig. 4.26 Cumulative Zn grade vs recovery for various concentration of silica sol.

4.3.4.2 Sample B

4.3.4.2.1 Cu stage

The first observation (Fig. 4.27) is the unusual (but consistent) grade - recovery curve for the baseline tests obtained for sample B compared to sample A. This 'inverted' response (grade increases as recovery increases) sometimes indicates inadequate aeration (Johnson et al., 1982). (Chalcopyrite flotation is sensitive to pulp potential / dissolved oxygen levels (Leroux et al., 1989).) Leaving that aside, it is apparent that the reagents and / or reagent testing procedure (15 min of conditioning) had a significant impact, increasing the flotation rate and 'correcting' the grade - recovery relationship (although now narrowing the recovery range rendering the trend a little ambiguous).

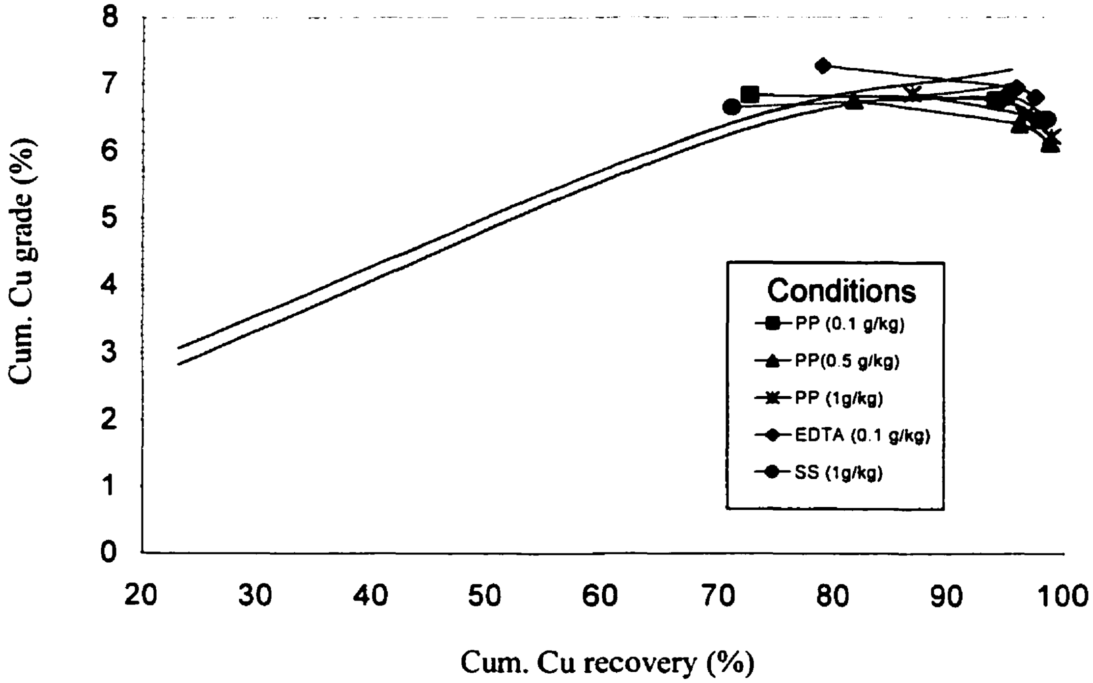

Fig. 4.27 Cumulative Cu recovery vs grade for various conditions.

4.3.4.2.2 Zn stage

Here a normal grade - recovery baseline response is obtained (Fig. 4.28). The results indicate an increase in flotation rate (less dramatic than in the Cu stage) with little impact on the separation. However, it is noted that the 'with reagent' results are concentrated on the high end of the 95 % CI, especially those for polyphosphate.

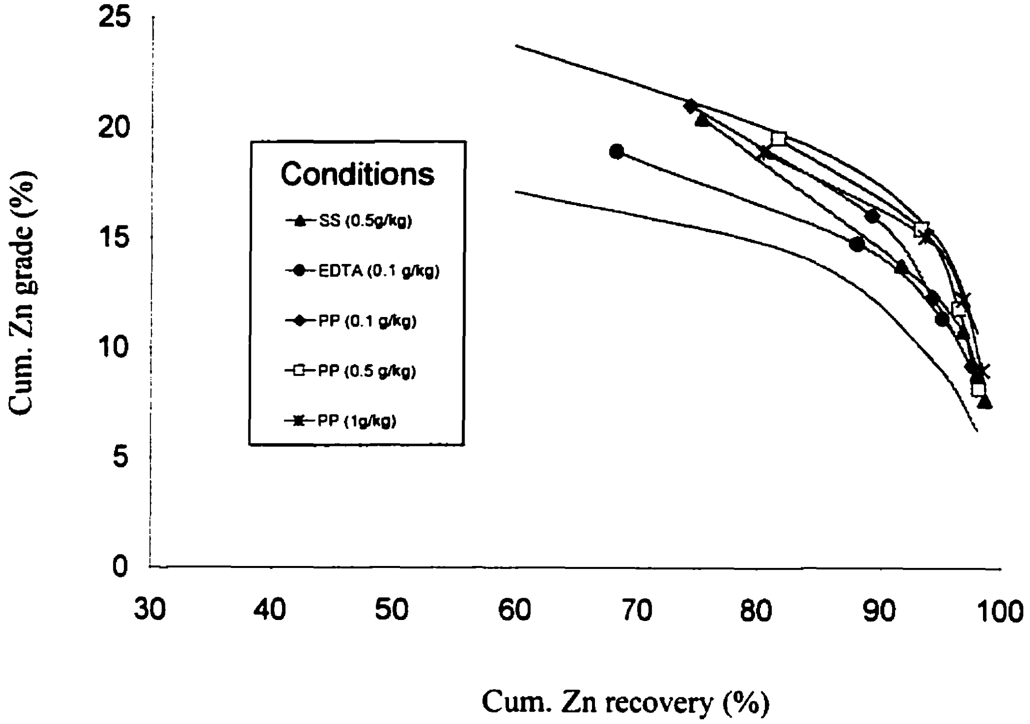

Fig. 4.28 Cumulative Zn grade vs recovery for various conditions.

The 95 % confidence band on the baseline was large compared to previous cases. Analysis of the four individual results (Fig. 4.29) indicate three were in a cluster and one (identified as baseline 1 on the figure) was outside.

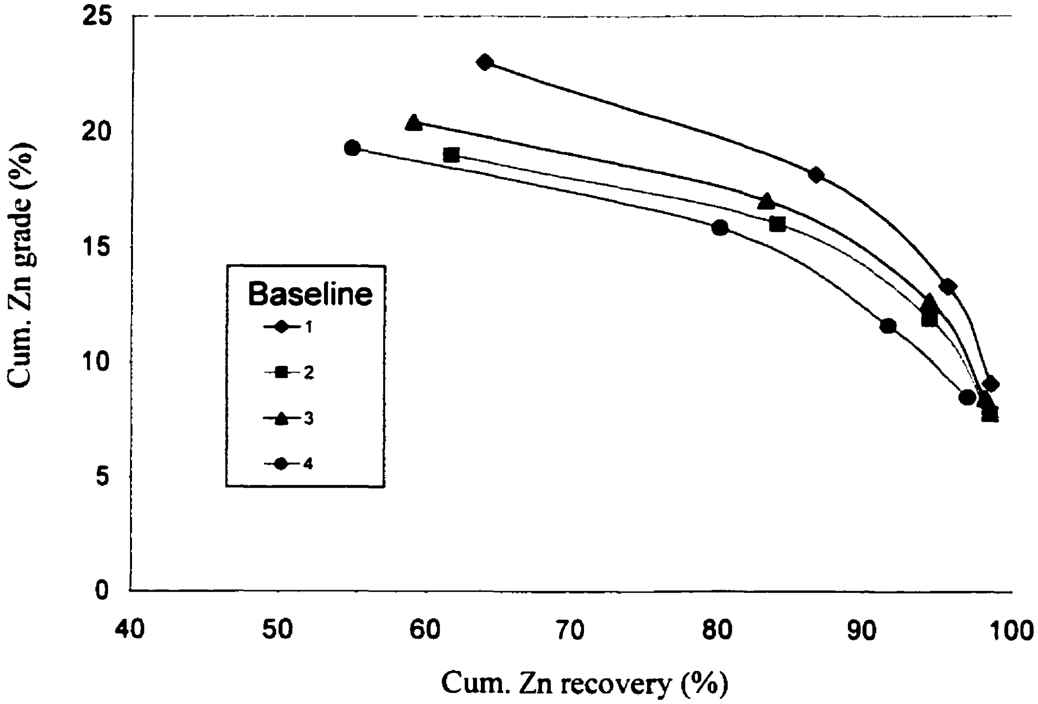

Fig. 4.29 Baseline cumulative Zn grade vs recovery.

The 95 % confidence interval band was recomputed based on the three clustered results and is represented in Fig. 4.30 compared against just the polyphosphate tests. While more contentious than the situation with Les Mines Selbaie and Mine Louvicourt, the polyphosphate seems to offer a benefit, giving a faster float than the baseline with grade - recovery on the upper side of the baseline 95 % CI band.

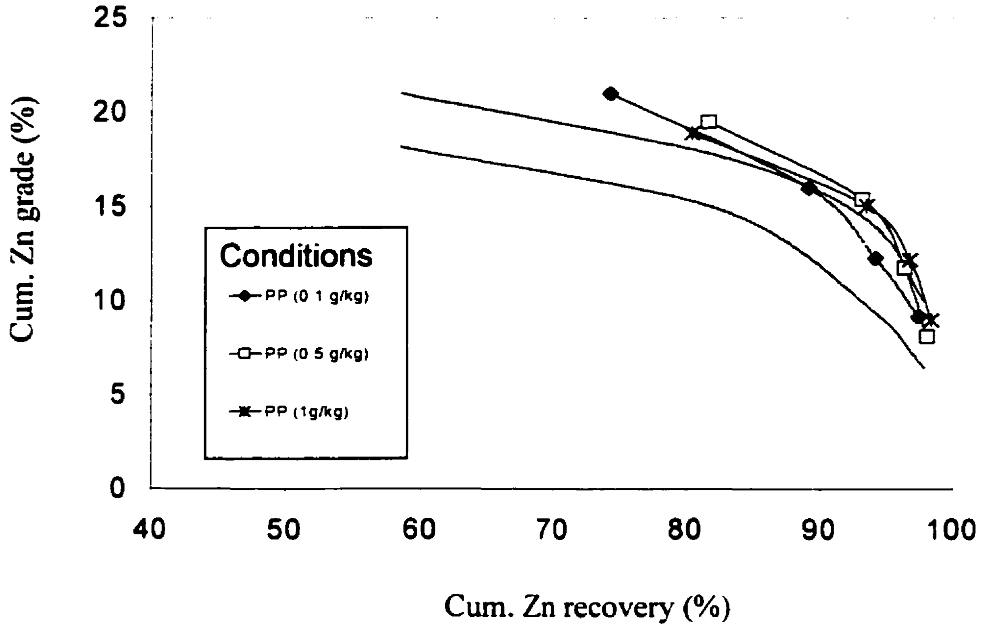

Fig. 4.30 Cumulative Zn grade vs recovery for various concentrations of polyphosphate with recomputed baseline 95 % CI band.

4.3.5 Brunswick Mine

4.3.5.1 Zn stage: polyphosphate addition before $CuSO_4$

In this case only polyphosphate in the Zn stage was tested following the observation on Les Mines Selbaie and Mine Louvicourt (Fig. 4.31). The baseline interval is derived from the 70 g/t of $CuSO_4$ tests. The reagent gave results to the low side of the baseline but all combinations gave a higher end recovery ca. 96% up from the ca. 92% for the baseline at the same Zn grade (ca. 27 %). Flotation rates were increased except for the lowest polyphosphate dosages.

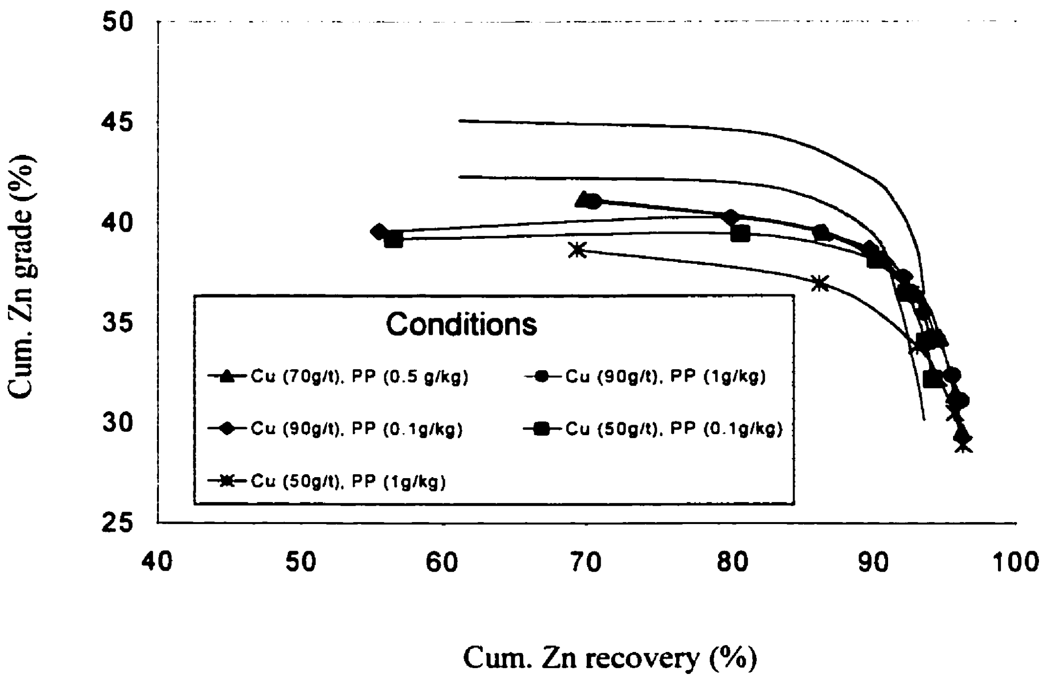

Fig. 4.31 Cumulative Zn grade vs recovery for various combinations of $CuSO_4$ and polyphosphate: PP added prior to $CuSO_4$.

4.3.5.2 Zn stage: polyphosphate addition after $CuSO_4$

The same combinations in Fig. 4.31 were employed but this time poyphosphate was added after the $CuSO_4$ (Fig. 4.32). Generally, the reagent degraded the Zn stage performance especially at the low $CuSO_4$ addition. Flotation rates were increased except for the lowest polyphosphate dosages.

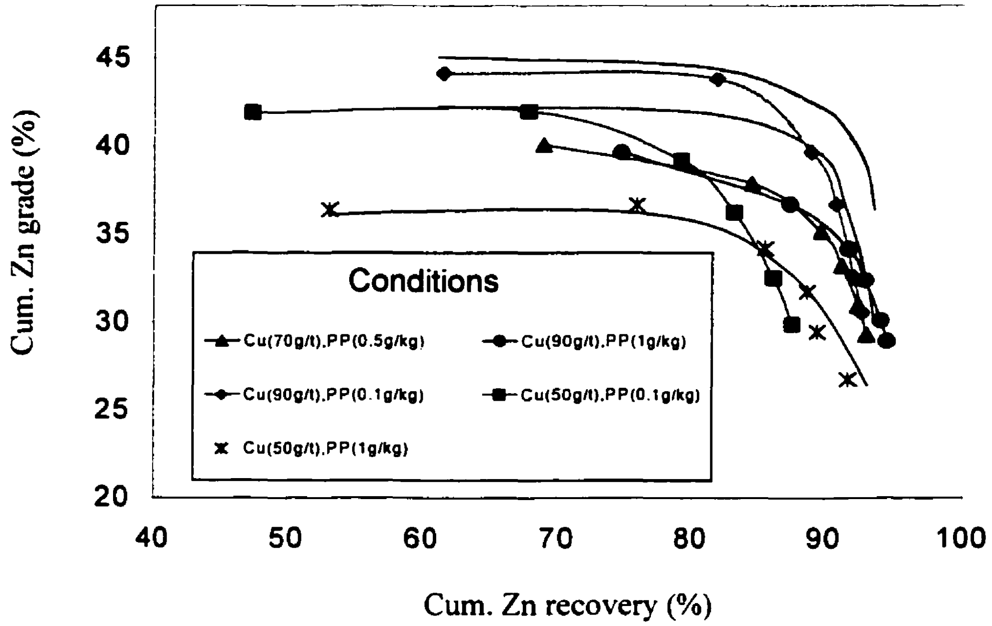

Fig. 4.32 Cumulative Zn grade vs recovery for various combinations of $CuSO_4$ and polyphosphate: PP added after $CuSO_4$.

4.3.6 Summary

Generally, all three reagents increased the rate of flotation in the Cu stage and Zn stages. Polyphosphate, in particular, improved selectivity in the Zn stage for Les Mines and Mine Louvicourt and arguably for Hudson Bay Mining and Smelting. This selectivity effect was not identified in the Brunswick Mine trials directly on Zn stage flotation feed.

CHAPTER 5

DISCUSSION

5.1 Silica sol as metal ion control reagent

5.1.1 Micro flotation and XPS results

The single mineral flotation studies showed that silica sol depressed all Cu minerals, Cu and Pb activated pyrite and Pb activated sphalerite but did not depress Cu activated sphalerite. The XPS results suggests that silica sol adsorbed on all Cu minerals. In the case of Cu and Pb activated pyrite, there was no evidence of Cu and Pb removal but evidence of silica sol adsorption. Silica sol arguably removed some Pb from Pb activated sphalerite (in alkaline media) and there was no evidence of adsorption. Overall, from the single mineral flotation and XPS tests, the depressant action of silica sol appears more related to adsorption rather than metal ion removal.

The observation is not as expected. While the removal of Cu from Cu activated sphalerite is not expected as Cu becomes incorporated in the lattice, Cu and Pb removal from pyrite and Pb removal from sphalerite was anticipated. It is worth reviewing the nature of the interaction of these ions with these minerals.

There is no evidence that Cu or Pb exchange with Fe in the pyrite lattice (Wang et al., 1989; Leppinen et al., 1995). The ions are held in the double layer as hydrated free ions and hydroxy species. In this regard they should be readily removed. The situation with Pb and sphalerite is more contentious. Table 2.1 (Chapter 2) is a summary of work on the mechanism of Pb activation of sphalerite. Ion exchange, Pb for Zn in the lattice, has been assumed in some cases (Fuerstenau and Metzger, 1960) and at acid pH Trahar et al. (1997) observed Pb could not be removed by EDTA implying incorporation in the lattice. At alkaline pH Pb is removed by EDTA (Trahar et al., 1997) and polyphosphate (Rashchi, 2000) implying simple retention in the double layer. The general observation that EDTA readily removes Pb but not Cu from sphalerite containing plant samples is strong evidence that a significant amount of Pb is not incorporated in the lattice (Kant et al., 1994).

The surface of sphalerite, like all sulphide minerals, retains products of reaction with water and dissolved oxygen. In the case of the Zn site the surface might be represented as Zn-O-H. Bessiere and Bernasconi (1983) and Pattrick et al. (1998) suggest Pb ions reacts with this hydroxy species to form $Zn\text{-}O\text{-}Pb^{+}$ and in this way Pb is held to the surface. If the strength of this bond varies with pH (e.g., decreasing at high pH) then the apparent pH dependence of Pb removal from sphalerite might be explained. It may be feasible that $Zn\text{-}O\text{-}Zn^{+}$ exists on the surface and an exchange with Pb^{2+} occurs giving to rise to an exchange ratio that is sometimes reported but is highly variable.

5.1.2 Batch flotation

The most prominent observation is that silica sol increased the rate of flotation but not selectivity. The increase in rate may be attributed to the original hypothesis, removal of metal hydroxy species. In the flotation of sulphide minerals, metal hydroxy species (e.g., of Pb, Ca and Mg) forming on the mineral surface above a certain pH tend to depress flotation. Their removal should increase flotation rates.

Shannon and Trahar (1986) and Trahar et al. (1994) reported that EDTA is capable of dissolving metal hydroxides and thereby restoring fresh mineral surfaces. Figure 5.1 (Shannon and Trahar, 1986) shows the results for Woodlawn (a complex sulphide ore). This figure shows the flotation rate of individual minerals (chalcopyrite, sphalerite and pyrite) with an increasing amount of EDTA. For additions up to 10 g/kg, there is little influence but above 13 g/kg, the rate of flotation increases quite substantially for all the sulphide minerals. They showed that metal hydroxides (e.g., Pb, Fe, Ca) were impartially removed by EDTA by solution analysis.

Similar findings were reported by Wang and Forssberg (1990) namely, that EDTA promoted flotation of pyrite and arsenopyrite by dissolving metal hydroxides from the mineral surfaces.

An inconsistency in the present work is that the XPS results showed little evidence of metal ion removal by silica sol. One resolution would be to perform solution analysis as a function of silica sol addition.

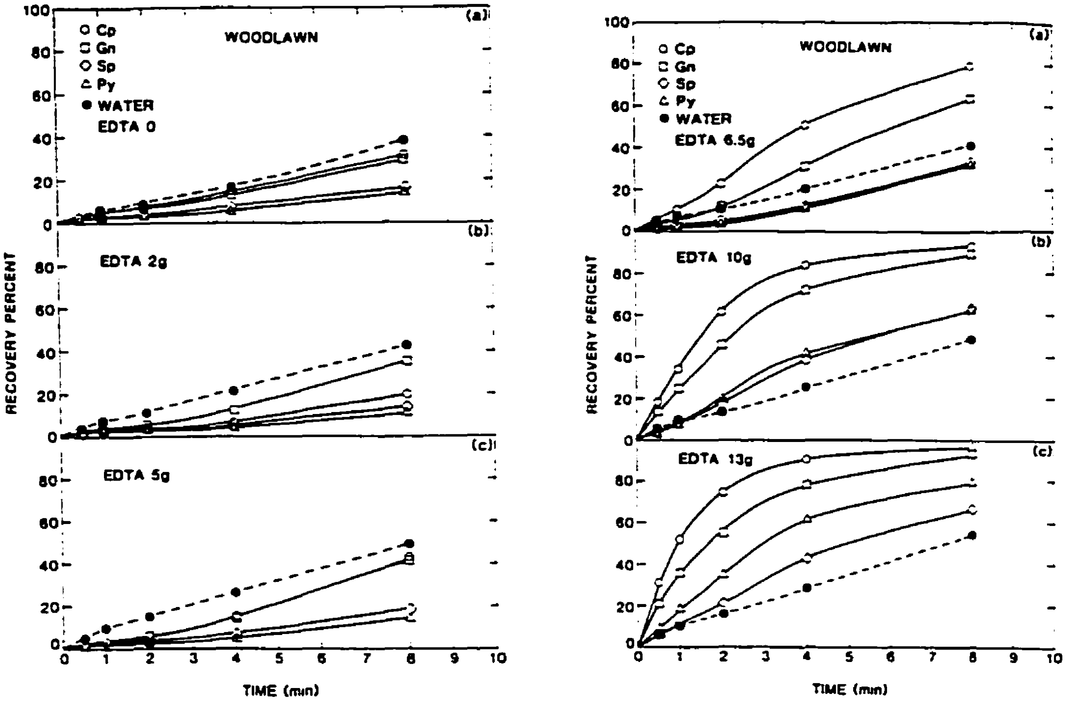

Fig. 5.1 Influence of EDTA on flotation of sulphides from Woodlawn ore (after: Shannon and Trahar, 1986).

5.2 Comparison of silica sol with other 'metal ion control' reagents

5.2.1 Rate of flotation

Generally, silica sol, polyphosphate and EDTA increased the flotation rate of all minerals without any change in selectivity (e.g., Fig. 4.22). This follows from their ability to remove hydrophilic hydroxy species as discussed above. While increased selectivity was the desired outcome, the increase in rate does offer some operational possibilities. These include:

(i) reducing flotation volume (i.e., number of cells in a stage)

(ii) reducing flotation time (i.e., increase capacity)

(iii) reducing collector dosage (i.e., return flotation rate to the original)

Items (i) and (ii) both offer a means to increase capacity per unit of installed flotation volume. The second, however adds an additional possibility, namely to increase pulp dilution. More dilute feeds generally translate to increased selectivity (Martin et al., 2000). For a given plant, taking advantage of this dilution effect may be limited by the installed capacity. Speeding up flotation by use of metal ion control reagents could restore this option. The last item, (iii), reducing collector dosage, not only offers a cost saving (to offset the cost of metal ion control reagent) but may yield increased selectivity.

The choice of reagent would depend on unit cost and the dosage, obviously, but could depend on the nature of the hydrophilic species to be removed. In some cases this could be dominated by Fe, in others Mg etc. and one metal ion control reagent may be more effective than other as a consequence. The amount of reagent required to increase the rate of flotation would be determined by the amount of metal to be complexed and the amount of precipitates to be dissolved. An over - riding concern in the choice of reagent today is any environmental liability. The use of metal ion control reagents to solubilize surface species may incur heavy metal contamination in discharge waters. The recent findings of Yeomans (2001), however, describing the use of EDTA to control effluent quality, suggest the bioavailability of heavy metals decreases when complexed. Thus the concern may not materialize. Indeed a metallurgical (increase in flotation rate) and environmental benefit may both accrue if the reagents are used in the process rather than just in water treatment.

5.2.2 Selectivity

The most prominent result - after the general increase in flotation rate - was the improved selectivity shown by polyphosphate in particular for the Les Mines Selbaie, Mine Louvicourt and, arguably, Hudson Bay Mining and Smelting cases. Since polyphosphate showed no evidence of increased selectivity in the Cu stage, the difference appears to be related to the addition of Cu in the Zn stage. As a hypothesis, perhaps the polyphosphate successfully counters inadvertent activation of pyrite (and / or non sulphide) by any Cu in excess of the demands of the sphalerite. This improved selectivity was not seen in the Brunswick Mine tests. The amount of 'excess Cu' may be different. Table 5.1 shows the Cu dosage converted to g/kg Zn and g/kg pyrite along with the grind size. It is evident that the order of Cu dosage per kg Zn is,

Mines Selbaie > Mine Louvicourt > Hudson Bay Mining and Smelting > Brunswick Mine

which corresponds to the order of effect of polyphosphate. Figure 5.2 illustrates the correlation showing the effect of polyphosphate on increasing Zn grade increases as Cu dosage increases.

Table 5.1: Cu dosages and grind sizes for different plants

Parameters	**Les Mine Selbaie**	**Mine Louvicourt**	**Hudson Bay Mining and Smelting**	**Brunswick Mine**
Cu dosage (g)	0.15	0.30	0.13	0.59 * 0.83 1.06
Mass of Zn to Zn stage (g)	1.7	9.45	13.53	118.8
Mass of pyrite to Zn stage (g)	34.83	142.75	62.68	424.6
Ratio = Cu dosage, g/Kg Zn	88.23	31.74	9.61	4.97 6.98 8.92
Ratio = Cu dosage, g/Kg pyrite	4.31	2.10	2.01	1.38 1.95 2.50
Grind size (μm)	80 % -120	90% -75	90% -75	80% -45

* $CuSO_4$ dosages for Brunswick Mine were derived from the 50, 70 and 90g / T / % Zn tests.

The average dry weight of slurry and Zn grade were 1.47 kg and 8.02 %, respectively.

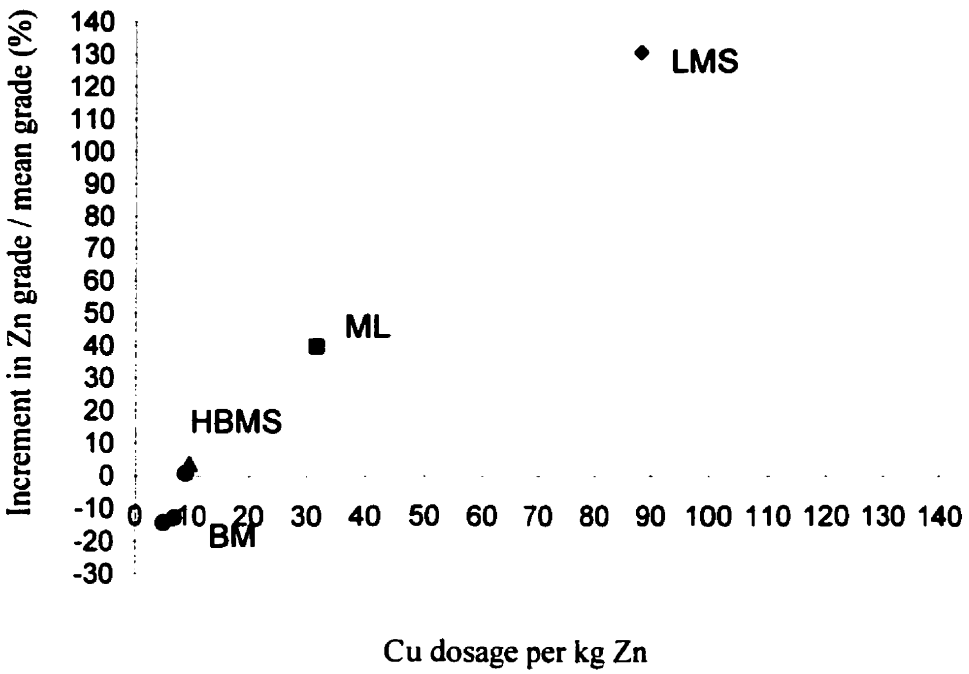

Fig. 5.2 Increment in Zn grade relative to mean grade vs Cu dosage per kg Zn for Les Mines Selbaie (LMS) ◆ (PP, 0.5 g/kg) at 60 % cum. Zn recovery, Mine Louvicourt (ML) ■ (PP, 0.5 g/kg) at 80 % cum. Zn recovery, Hudson Bay Mining and Smelting (HBMS) ▲ (0.5 g/kg) at 85 % cum. Zn recovery and Brunswick Mine (BM) ● (PP, 1, 0.5 and 0.1 g/kg for lowest to highest Cu dosages, respectively) at 80 % Cum. Zn recovery (different cum. Zn recoveries were chosen to avoid the extrapolation).

Particle size can also be expected to influence the definition of excess Cu. The finer the particles, the higher the specific surface area of sphalerite and the more Cu is required. In this regard, Brunswick Mine, having the finest grind, the high Cu dosage for the other cases emphasizes their 'excess'. The Cu dosage relative to kg pyrite, assuming pyrite is the main mineral activated (see next section), does not show any trend. From the three parameters considered, dosage per kg Zn is the most important to define 'excess Cu' dosage.

It should be added that the result here reflects the nature of the tests. The Cu added to the Zn stage in the batch tests for Les Mines Selbaie, Mine Louvicourt and Hudson Bay Mining and Smelting was done according to the recipe without prior knowledge of the Zn content in the ore or how much Zn reported to the Cu stage. Thus adding excess Cu was a possibility. This was not the case in the Brunswick Mine tests where Cu dosage was deliberately added according to the Zn content. Thus excess dosage, therefore, is an artifact of the test procedure and not an indication of plant practice. An interesting use of polyphosphate that emerges, however, is as a diagnostic of an excess Cu condition.

The conclusion is that the polyphosphate effect is related to excess Cu, the polyphosphate presumably complexing the Cu as a Cu-PP complex and removing it from the pyrite (or any other non Zn containing mineral). This action is the same as that proposed to explain the increase in rate but now the removal of Cu has a selective effect. Depending whether there is excess Cu and the reagent's ability to remove Cu (apparently it is highest for polyphosphate, then EDTA, and least for silica sol at the dosages tried) then depression of accidentally activated minerals can occur. The increase in flotation rate and selective depression appear to reflect the metal ion control capability of the reagents.

5.2.3 What mineral is depressed?

An increase in grade means one or more minerals have been depressed. The increase in grade was analyzed in the results section (Chapter 4) by considering depression of pyrite. The data are sufficient to determine the response of non sulphide gangue (NSG) (calculated by difference). The appropriate recovery vs recovery plots are shown for Les Mines Selbaie and Mine Louvicourt in Figs. 5.3 and 5.4, respectively. The rejection of pyrite is seen in both but there is also evidence for depression of non sulphide gangue.

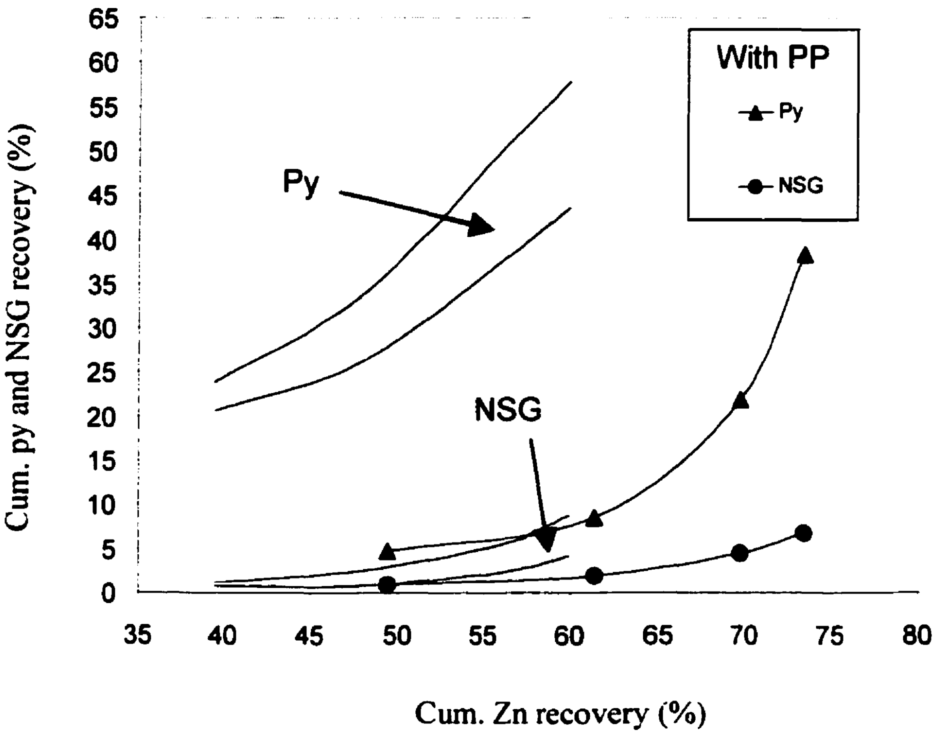

Fig. 5.3 Cumulative pyrite and non sulphide gangue recovery vs Zn recovery for Les Mines Selbaie (baseline - shaded area, and with 0.5 g /kg PP - symbols).

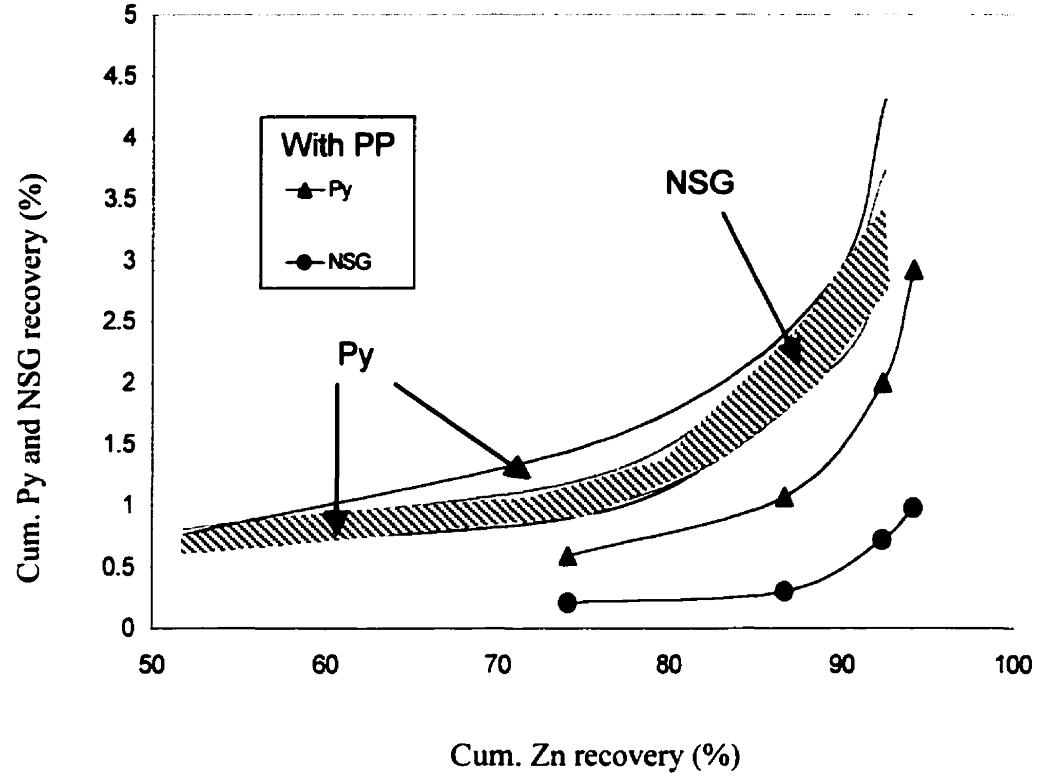

Fig. 5.4 Cumulative pyrite and non sulphide gangue recovery vs Zn recovery for Mine Louvicourt (baseline - shaded area, and with 0.5 g /kg PP - symbols).

Taking 60 and 80 % cum. Zn recovery for Les Mines Selbaie and Mine Louvicourt, respectively (to avoid extrapolation) as a basis for comparison, the reduction in pyrite and non sulphide gangue recovery upon adding polyphosphate relative to the mean baseline recovery is shown in Fig. 5.5. This shows polyphosphate depressed both minerals. This implies that polyphosphate counteracts the inadvertent activation of pyrite and non sulphide gangue by excess Cu.

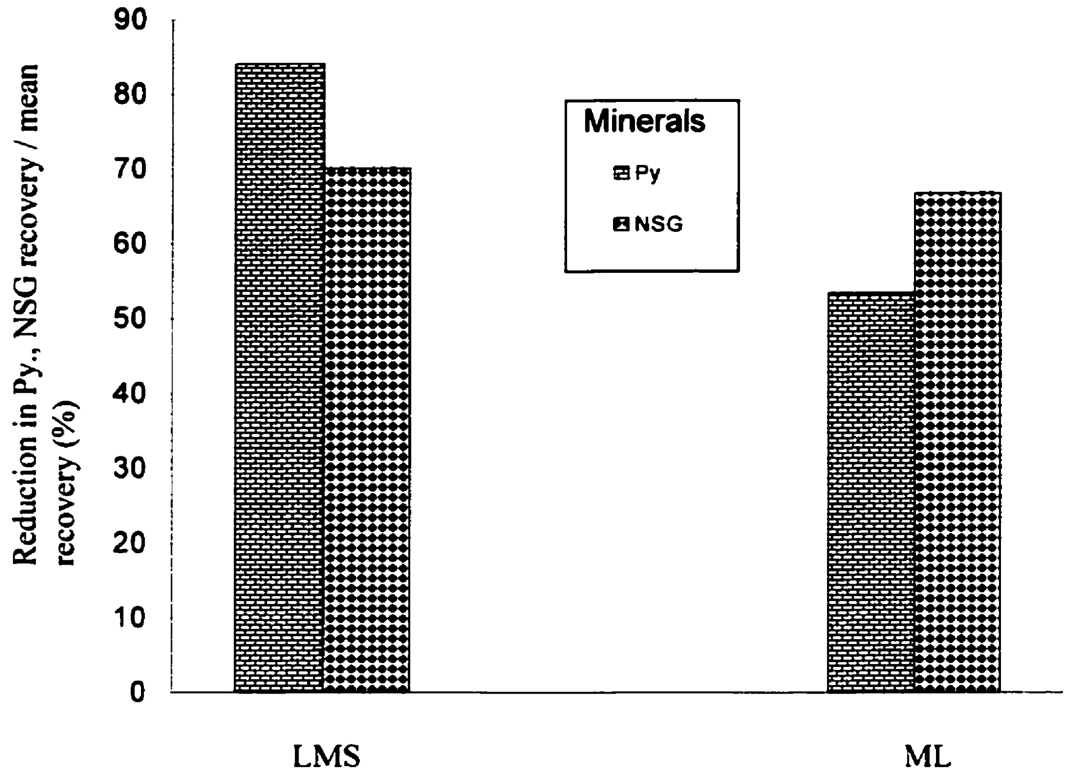

Fig. 5.5 Reduction in pyrite and non sulphide gangue recovey after polyphosphate (0.5 g/kg) addition relative to mean baseline recovery for Les Mines Selbaie (LMS) at 60 % cum. Zn recovery and Mine Louvicourt (ML) at 80 % cum. Zn recovery.

CHAPTER 6

CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

6.1 Conclusions

6.1.1 Micro flotation

1. Silica sol depressed all copper minerals, non activated and Pb activated sphalerite and non activated and Cu and Pb activated pyrite over the pH range 7 to 11.
2. Silica sol did not depress Cu activated sphalerite over the pH range 7 to 11.

6.1.2 X-ray Photoelectron Spectroscopy (XPS)

1. Silica sol adsorbed on the surface of all copper minerals and pyrite whether Pb or Cu activated or not.
2. Silica sol partially removed Pb from Pb activated sphalerite.
3. For Cu activated sphalerite, the Cu concentration remained unchanged and no silica sol adsorption was detected.

4. Silica sol appears to function as a depressant more by adsorbing on a mineral surface and providing competitive hydrophilic sites than as a deactivator. That is, it does not appear to function as a 'metal ion control' reagent.

6.1.3 Batch flotation

6.1.3.1 Cu stage

1. Generally, silica sol, polyphosphate and ethylenediaminetetraacetic acid (EDTA) increased the rate of flotation without any change in selectivity. This is attributed to impartial removal of hydrophilic metal hydroxides from surfaces.
2. In the case of silica sol, the inconsistency between the XPS results - silica sol does not clean surfaces - and the explanation offered for its effect on flotation rate in the batch tests - where 'cleaning' is claimed - needs to be reconciled.

6.1.3.2 Zn stage

1. Again, silica sol increased the rate of flotation without any change in selectivity.
2. EDTA improved the selectivity slightly for the Les Mines Selbaie and Mine Louvicourt cases.
3. Polyphosphate improved the selectivity for the Les Mines Selbaie, Mine Louvicourt and arguably for Hudson Bay Mining and Smelting but not for the Brunswick Mine case. The polyphosphate effect was related to 'excess Cu' (i.e., in excess of the equivalent to activate sphalerite).

6.2 Suggestions for future work

1. Study of effect of conditioning time on baseline.

For the three reagents tested 15 and 10 min conditioning times were used for Cu and Zn stages, respectively, but no conditioning time was used for the baseline tests. Therefore, any effect of conditioning time on the baseline tests needs to be explored.

2. Study of solution composition before and after reagent addition.

Solution analyses should be performed before and after reagent addition for elements such as Ca, Mg, Cu, Pb to determine the reagent's ability to clean the mineral surfaces.

3. Study of reagents without and with low collector dosages in the Cu stage.

Study the effect of reagents at reduced collector dosages to determine if selectivity is improved.

4. Test hypothesis that polyphosphate removes Cu from pyrite and non sulphide gangue.

5. Determination of minimum Cu concentration for sphalerite activation.

The minimum Cu concentration required for sphalerite activation needs to be explored based on Cu dosage per kg Zn and per unit area basis.

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Appendix 1

(1) Calculation of EDTA concentration

From El-Emmouri (2000),

At pH 7, 1 g of silica sol adsorbs 5 x 10^{-4} mole of Cu

At pH 10, 1 g of silica sol adsorbs 5 x 10^{-5} mole of Cu

2 mole EDTA reacts with 1 mole of Cu

1 mole EDTA gives 372.24 g

2.5 x 10^{-4} mole of Cu (pH 7) reacts with 0.186 g EDTA

2.5 x 10^{-5} mole of Cu (pH 10) reacts with 0.0186 g EDTA

1.4 x 10^{-4} mole of Cu (average, pH 7 and pH 10) reacts with 0.1 g (average) EDTA

Hence 0.5 g silica sol equivalent to 0.10 g EDTA on a molar basis

(2) Grinding time determination for Hudson Bay Mining and Smelting ore

Grinding time (min)	-75 µm (%)
10	57
15	72
20	88

(3) Determining repeatability: 95 % confidence limit

Specimen calculation

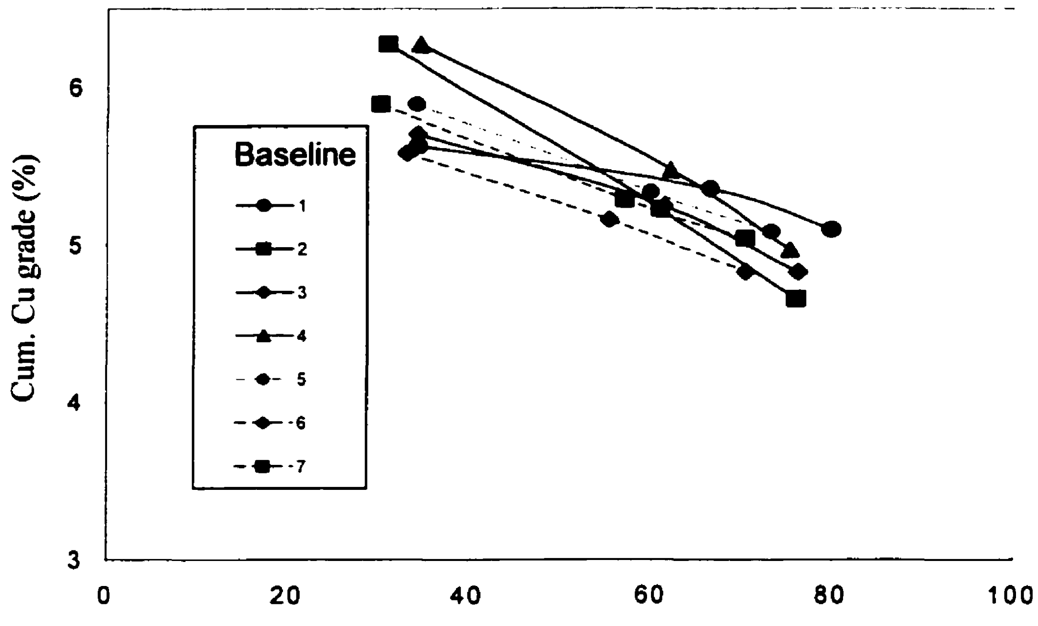

Fig. 4.15a Repeatability: Baseline cumulative Cu grade vs recovery test results - Les Mines selbaie with NaCN added in grinding.

At 38 % cumulative recovery, corresponding cumulative grades (X_i) are, 5.51, 5.64, 5.68, 5.75, 5.87, 6.08 and 6.27 %.

Mean, $\overline{X} = \Sigma X_i / n$ and Standard deviation = $(\text{Variance})^{1/2}$

Mean = 5.83 %

Variance, $S^2_x = \Sigma\,(X_i - \overline{X}\,)^2 / n\text{-}1$

$= 0.07\ \%$

Standard error, $S_x\ = (S^2_x / n)^{1/2}\ = 0.101\ \%$

95 % confidence coefficient ($1\text{-}\alpha = 0.95$: $\alpha / 2 = 0.025$, degree of freedom, $n\text{-}1 = 6$) and for a symmetric interval, we find $t_{0.975} = 2.447$ from the t - distribution table.

95 % confidence interval = ± 0.25 %

Appendix 2

(1) Micro flotation

Silica sol (ppm)	Chalcopyrite recovery (%) pH 9	Chalcopyrite recovery (%) pH 8
0	66.83	87.24
100	56.53	42.18
500	60.62	39.25
1500	37.05	29.16
3000	31.82	17.91

pH	Chalcopyrite recovery (%)	Chalcopyrite recovery (%) with 1000 ppm SS
7	78.19	52.61
8	85.15	35.23
9	65.25	46.1
11	27.08	15.38

Silica sol (ppm)	Sphalerite recovery (%) pH 9 (no activation)	Sphalerite recovery (%) pH 9 (Cu)	Sphalerite recovery (%) pH 9 (Pb)
0	21.17	89.01	94.23
100	9.92	93.456	56.85
500	12.8	92.82	49.65

pH	Sphalerite recovery (%) (no activation)	Sphalerite recovery (%) (no activation + 1000 ppm SS)	Sphalerite recovery (%) (Cu)	Sphalerite recovery (%) (Cu + 1000 ppm SS)	Sphalerite recovery % (Pb)	Sphalerite recovery % (Pb + 1000 ppm SS)
7	30.422	23.445	98.229	97.36	96.89	67.89
8	57.02	47.51	97.29	98.64	94.78	74.66
9	20.67	10.56	92.13	94.43	95.63	55.1
11	3.82	3.07	30.95	28.75	5.77	3.59

Silica sol (ppm)	Pyrite recovery (%) pH 9 (no activation)	Pyrite recovery (%) pH 9 (Cu)	Pyrite recovery (%) pH 9 (Pb)
0	56.4	68.2	83.98
100	57.1	56.36	51.16
500	54.61	44.96	36.57

pH	Pyrite recovery (%) (no activation)	Pyrite recovery (%) (no activation + 1000 ppm SS)	Pyrite recovery (%) (Cu)	Pyrite recovery (%) (Cu + 1000 ppm SS)	Pyrite recovery % (Pb)	Pyrite recovery % (Pb + 1000 ppm SS)
7	50.49	37.74	73.83	57.44	76.3	47.17
8	50.22	38.05	74.16	57.83	76.15	44.66
9	32.13	24.72	58.34	38.79	72	35.28
11	4.89	2.2	9.45	6.54	12.46	9.45

pH	Chalcocite recovery (%)	Chalcocite recovery (%) with 1000 ppm SS
7	70	54.09
8	63.97	42.32
9	65.23	41.23
11	36.81	11.02

(2) X-ray photoelectron spectroscopy (XPS)

surface concentrations (%)

	Chalcopyrite	Sphalerite	Pyrite	Chalcocite
Si (no activation before SS)	1.55		-	0.92
Si (no activation after SS)	2.44		0.74	2.55
Si (Cu activation before SS)			-	
Si (Cu activation after SS)			0.58	
Si (Pb activation before SS)			-	
Si (Pb activation after SS)			0.38	
Cu (Cu activation before SS)		1.57	1.25	
Cu (Cu activation after SS)		1.54	1.3	

Pb (Pb act				
-ation be				
- fore SS)		1.15	0.62	
Pb (Pb act				
-ation af				
- ter SS)		0.9	0.68	

(3) Batch flotation

(a) Les Mines Selbaie

(i) With NaCN

Cu Baseline (1) and Zn Baseline (1)

	Cu1	Cu2	Cu3	Zn1	Zn2	Zn3	Zn4	Tail
Cu (%)	5.633	5.092	4.099	1.074	0.645	0.287	0.114	0.01
Zn (%)	32.56	33.59	13.74	2.19	0.94	0.39	0.21	0.07
Fe (%)	7.9	7.02	9.94	28.21	22.87	15.12	9.34	1.9
Mass (g)	15.93	16.44	8.45	24.75	10.47	26.35	21.57	883.82

Cu Baseline (2) and Zn Baseline (2)

	Cu1	Cu2	Cu3	Zn1	Zn2	Zn3	Zn4	Tail
Cu (%)	6.277	4.445	3.234	1.01	0.79	0.34	0.12	0.02
Zn (%)	34.65	32.05	14.38	2.61	1.39	0.45	0.21	0.07
Fe (%)	7.87	6.71	8.63	28.46	20.72	14.23	6.73	1.62
Mass (g)	13.52	18.38	12.8	24.07	11.01	33.28	34.4	849.15

Cu Baseline (3) and SS (0.5 g/kg) in Zn stage

	Cu1	Cu2	Cu3	Zn1	Zn2	Zn3	Zn4	Tail
Cu (%)	5.707	4.761	3.627	0.75	0.59	0.375	0.09	0.016
Zn (%)	35.44	34.26	11.96	1.64	0.97	0.49	0.17	0.06
Fe (%)	7.74	6.84	9.69	29.8	16.93	8.89	4.5	2.3
Mass (g)	16.54	15.57	11.25	33.89	18.66	32.95	30.14	843.2

Cu Baseline (4) and SS (1 g/kg) in Zn stage

	Cu1	Cu2	Cu3	Zn1	Zn2	Zn3	Zn4	Tail
Cu (%)	6.352	4.669	3.461	0.92	0.75	0.25	0.17	0.019
Zn (%)	35.9	34.51	17.04	3.04	1.49	0.41	0.25	0.08
Fe (%)	7.96	6.64	8.99	28.52	22.37	7.7	6.54	2.64
Mass (g)	14.27	15.44	10.01	24.99	16.83	29.48	29.44	858.65

Cu Baseline (5) and SS (1.5 g/kg) in Zn stage

	Cu1	Cu2	Cu3	Zn1	Zn2	Zn3	Zn4	Tail
Cu (%)	5.896	4.735	4.215	1.36	0.6	0.21	0.09	0.017
Zn (%)	32.75	35.09	23.68	3.24	1.24	0.43	0.18	0.06
Fe (%)	7.48	6.54	8.69	29.56	19.56	12.45	4.46	2.3
Mass (g)	15.57	14.53	8.61	24.34	19.08	47.46	29.52	840.79

Cu Baseline (6) and EDTA (0.1 g/kg) in Zn stage

	Cu1	Cu2	Cu3	Zn1	Zn2	Zn3	Zn4	Tail
Cu (%)	5.586	4.622	3.933	1.14	0.8	0.32	0.09	0.017
Zn (%)	37.95	33.55	20.98	3.25	0.98	0.33	0.18	0.05
Fe (%)	7.55	6.9	9.51	21.34	19.72	14.66	5.79	2.29
Mass (g)	16.01	12.82	10.54	31.58	18.85	34.68	28.64	850.22

Cu Baseline (7) and PP (0.5 g/kg) in Zn stage

	Cu1	Cu2	Cu3	Zn1	Zn2	Zn3	Zn4	Tail
Cu (%)	5.63	4.915	4.29	2.61	1.04	0.3	0.13	0.018
Zn (%)	37.69	35.09	23.67	6.87	1.87	0.5	0.22	0.06
Fe (%)	7.25	7.14	9.04	14.32	11.72	15.08	17.5	2.56
Mass (g)	13.9	15.24	8.76	14.11	12.62	33.65	33.61	867.36

PP (0.1 g / kg) in Cu stage

	Cu1	Cu2	Cu3	Zn1	Zn2	Zn3	Zn4	Tail
Cu (%)	5.63	4.915	4.29	2.61	1.04	0.3	0.13	0.018
Mass (g)	20.5	13.46	7.94	14.45	10.28	28.34	22.57	884.33

PP (0.5 g / kg) in Cu stage

	Cu1	Cu2	Cu3	Zn1	Zn2	Zn3	Zn4	Tail
Cu (%)	5.974	4.048	1.715	0.463	0.433	0.193	0.084	0.01
Mass (g)	24.67	14.7	9.08	28.95	13.4	23.88	20.88	864.41

PP (1 g / kg) in Cu stage

	Cu1	Cu2	Cu3	Zn1	Zn2	Zn3	Zn4	Tail
Cu (%)	5.965	4.246	1.506	0.49	0.48	0.3	0.13	0.02
Mass (g)	22.46	17	10.8	22.67	10.46	24.6	22.89	874.89

(ii) Without NaCN

Cu Baseline

	Cu1	Cu2	Cu3	Zn1	Zn2	Zn3	Zn4	Tail
Cu (%)	6.262	4.775	3.633	0.84	0.85	0.43	0.14	0.02
Mass (g)	14.95	16.88	7.68	26.63	11.06	29	24.13	876.15

PP (0.5 g/kg) in Cu stage

	Cu1	Cu2	Cu3	Zn1	Zn2	Zn3	Zn4	Tail
Cu (%)	5.54	3.42	1.593	0.62	0.51	0.239	0.113	0.01
Mass (g)	26.67	13.69	10.4	28.33	11.48	29.85	23.28	858.34

PP (0.5 g/kg) in grinding in Cu stage

	Cu1	Cu2	Cu3	Zn1	Zn2	Zn3	Zn4	Tail
Cu (%)	4.932	3.505	2.024	0.78	0.56	0.26	0.11	0.02
Mass (g)	26.96	17.35	9.21	34.34	13.5	33.67	25.65	839.76

EDTA (0.1 g /kg) in Cu stage

	Cu1	Cu2	Cu3	Zn1	Zn2	Zn3	Zn4	Tail
Cu (%)	4.932	4.403	2.611	1.15	0.59	0.15	0.08	0.02
Mass (g)	20	16.46	15.94	29.18	13.53	37.68	31.03	839.72

SS (0.5 g /kg) in Cu stage

	Cu1	Cu2	Cu3	Zn1	Zn2	Zn3	Zn4	Tail
Cu (%)	4.638	3.012	1.0509	0.52	0.35	0.116	0.08	0.017
Mass (g)	29.71	19.59	16.27	33.68	14.97	38.53	30.05	822.84

(b) Mine Louvicourt

Cu Baseline (1) and Zn Baseline (1)

	Cu1	Cu2	Cu3	Cu4	Zn1	Zn2	Zn3	Zn4	Tail
Cu (%)	26.95	17.2	3.1	0.73	0.198	0.181	0.167	0.198	0.063
Zn (%)	1.34	4	6.6	6.49	34.1	29.12	8.85	3.42	0.099
Fe (%)	31	31.8	29.8	27.2	11.1	13.3	15.5	19.2	17.5
Mass (g)	83.1	23.21	41.98	11.87	14.52	7.53	12.5	7.88	794.8

Cu Baseline (2) and Zn Baseline (2)

	Cu1	Cu2	Cu3	Cu4	Zn1	Zn2	Zn3	Zn4	Tail
Cu (%)	27.44	19.72	4.56	0.93	0.26	0.22	0.22	0.21	0.06
Zn (%)	1.25	3.25	5.67	5.34	34.73	30.18	9.55	3.81	0.08
Fe (%)	30.9	32.1	32.6	30.1	10.6	15.714	15.7	18.3	17.5
Mass (g)	80.5	24.3	43.3	12.2	13.7	8.6	12	8.1	803.8

Cu Baseline (3)

	Cu1	Cu2	Cu3	Cu4	Zn1	Zn2	Zn3	Zn4	Tail
Cu (%)	27.4	18.67	4.4	1.13	0.244	0.245	0.271	0.307	0.072
Mass (g)	81.25	23.22	36.68	8.65	11.57	8.2	5.97	4.73	812.1

Cu Baseline (4) and SS (0.5 g/kg) in Zn stage

	Cu1	Cu2	Cu3	Cu4	Zn1	Zn2	Zn3	Zn4	Tail
Cu (%)	28.09	21.05	4.48	1.13	0.273	0.265	0.208	0.264	0.067
Zn (%)	1.18	3.15	5.9	5.84	30.24	23.27	10.59	3.74	0.101
Fe (%)	30.6	31.3	31.7	29.8	11.8	13.7	16.5	20.2	17.1
Mass (g)	76.26	23.38	39.22	10.25	15.57	8.14	14.39	9.55	802.1

Cu Baseline (5) and SS (1 g/kg) in Zn stage

	Cu1	Cu2	Cu3	Cu4	Zn1	Zn2	Zn3	Zn4	Tail
Cu (%)	27.16	18.13	3.42	0.86	0.201	0.197	0.187	0.21	0.066
Zn (%)	1.37	3.87	6.23	5.64	29.19	20.55	13.15	3.68	0.105
Fe (%)	31.2	32.8	32	28	12.6	14.6	15.8	20.1	17.2
Mass (g)	81.77	21.36	41.42	11.92	14.19	9.99	12.29	8.31	798.6

Cu Baseline (6) and SS (1.5 g/kg) in Zn stage

	Cu1	Cu2	Cu3	Cu4	Zn1	Zn2	Zn3	Zn4	Tail
Cu (%)	27.98	19.17	4.44	1.04	0.242	0.275	0.215	0.24	0.067
Zn (%)	1.23	3.39	6.18	5.96	32.18	27.35	13.34	4.41	0.097
Fe (%)	31	32.3	31.5	29.3	12.3	14.3	16.5	20.3	17
Mass (g)	80.77	21.64	35.97	10.66	13.89	7.04	11.89	9.51	810.9

Cu Baseline (7) and PP (0.5 g/kg)

	Cu1	Cu2	Cu3	Cu4	Zn1	Zn2	Zn3	Zn4	Tail
Cu (%)	28.74	21.09	5.25	1.11	0.351	0.53	0.48	0.57	0.067
Zn (%)	1.13	2.96	5.78	5.83	48.74	31.63	9.58	4.05	0.074
Fe (%)	31.4	32	33.5	30.9	10.5	20.3	23.1	29.5	17
Mass (g)	73.8	28.3	40.7	12.1	15.6	4.1	6.1	4.6	819.1

Cu Baseline (8) and EDTA (0.1 g/kg) in Zn stage

	Cu1	Cu2	Cu3	Cu4	Zn1	Zn2	Zn3	Zn4	Tail
Cu (%)	27.17	18.48	4.12	0.88	0.232	0.278	0.28	0.36	0.065
Zn (%)	1.29	3.62	6	5.06	39.65	23.82	9.46	4.6	0.088
Fe (%)	31.5	33.3	33.9	29.6	10.2	14.9	18.7	23.3	16.5
Mass (g)	82.7	25.5	38.8	13.6	16.2	6.9	6.1	6	8118

PP (0.1 g/kg) in Cu stage

	Cu1	Cu2	Cu3	Cu4	Zn1	Zn2	Zn3	Zn4	Tail
Cu (%)	25.88	15.45	2.24	0.69	0.182	0.192	0.226	0.33	0.055
Mass (g)	91.93	23.77	40.47	8.9	9.37	5.57	6.61	4.75	804.8

PP (0.5 g/kg) in Cu stage

	Cu1	Cu2	Cu3	Cu4	Zn1	Zn2	Zn3	Zn4	Tail
Cu (%)	24.7	11.1	1.66	0.52	0.14	0.162	0.154	0.208	0.056
Mass (g)	103.4	21.08	42	11.78	9.35	7.38	5.52	6.2	793

PP (1 g/kg) in Cu stage

	Cu1	Cu2	Cu3	Cu4	Zn1	Zn2	Zn3	Zn4	Tail
Cu (%)	26.88	15.87	2.45	0.66	0.136	0.116	0.147	0.221	0.057
Mass (g)	90.33	19.27	45.46	10.92	13.12	9.35	8.06	8.47	793.7

EDTA (0.1 g/kg) in Cu stage

	Cu1	Cu2	Cu3	Cu4	Zn1	Zn2	Zn3	Zn4	Tail
Cu (%)	27.43	18.05	3.17	0.69	0.193	0.233	0.264	0.332	0.064
Mass (g)	84	23.9	49.7	15.8	12.7	6.7	5.2	4.8	801.4

SS (1 g/kg) in Cu stage

	Cu1	Cu2	Cu3	Cu4	Zn1	Zn2	Zn3	Zn4	Tail
Cu (%)	27.43	18.05	3.17	0.69	0.193	0.233	0.264	0.332	0.064
Mass (g)	84	23.9	49.7	15.8	12.7	6.7	5.2	4.8	801.4

(c) Hudson Bay Mining and Smelting

(i) Sample A

Cu stage Baseline (Zn stage pH 12)

	Cu1	Cu2	Cu3	Zn1	Zn2	Zn3	Zn4	Tail
Cu (%)	11.89	8.86	5.1	2.55	2.72	2.68	1.71	0.14
Mass (g)	166.08	49.51	56.4	23.03	17.92	20.68	26.56	653.8

PP (0.1 g/kg) in Cu stage

	Cu1	Cu2	Cu3	Zn1	Zn2	Zn3	Zn4	Tail
Cu (%)	11.17	7.2	5.18	2.62	1.89	1.26	1.12	0.09
Mass (g)	143.31	70.63	95.39	22.29	16.75	19.62	27.1	627

PP (0.5 g/kg) in Cu stage

	Cu1	Cu2	Cu3	Zn1	Zn2	Zn3	Zn4	Tail
Cu (%)	8.92	7.4	5.1	1.83	2.02	1.72	1.14	0.08
Mass (g)	209.13	79.72	47.82	23.55	11.88	12.54	14.13	636.3

PP (1 g/kg) in Cu stage

	Cu1	Cu2	Cu3	Zn1	Zn2	Zn3	Zn4	Tail
Cu (%)	10.83	7.55	5.21	1.63	1.62	1.46	1.01	0.08
Mass (g)	152.9	93.14	73.43	20.94	9.93	10.91	15.4	650.6

Zn Baseline (Cu stage pH 9.5)

	Cu1	Cu2	Cu3	Zn1	Zn2	Zn3	Zn4	Tail
Cu (%)	3.12	6.91	11.16	25.2	21	10.04	3.81	0.227
Mass (g)	120.79	71	44.61	32.86	19.63	24.58	38.66	674.27

SS (0.5 g/kg) in Zn stage

	Cu1	Cu2	Cu3	Zn1	Zn2	Zn3	Zn4	Tail
Cu (%)	3.68	6.95	10.75	24	13.6	5.45	1.79	0.166
Mass (g)	124.51	67.29	47.48	46.2	24.73	23.82	34.58	656.87

SS (1 g/kg) in Zn stage

	Cu1	Cu2	Cu3	Zn1	Zn2	Zn3	Zn4	Tail
Cu (%)	2.72	5.77	11.25	24.5	13.2	5.38	1.74	0.165
Mass (g)	124.08	72.82	49.37	56.22	25.28	20.23	30.49	658.39

SS (3g/kg) in Zn stage

	Cu1	Cu2	Cu3	Zn1	Zn2	Zn3	Zn4	Tail
Cu (%)	2.81	5.73	11	21	11.8	4.27	1	0.172
Mass (g)	118.78	80.7	58.2	63.29	31.85	24.5	32.75	632.23

(ii) Sample B

Cu Baseline (1) and Zn Baseline (1)

	Cu1	Cu2	Cu3	Zn1	Zn2	Zn3	Zn4	Tail
Cu (%)	2.03	15.75	12.47	1.31	0.85	0.61	0.33	0.042
Zn (%)	1.85	7.35	14.03	23.02	11.4	3.77	0.78	0.047
Mass (g)	242.66	94.31	75.49	40.01	28.95	34.84	52.9	444.85

Cu Baseline (2) and Zn Baseline (2)

	Cu1	Cu2	Cu3	Zn1	Zn2	Zn3	Zn4	Tail
Cu (%)	3.9	13.37	7.71	0.99	0.85	0.57	0.29	0.039
Zn (%)	2.18	7.52	15.1	19	11.2	3.92	0.84	0.045
Mass (g)	246.89	104.25	66.51	41.69	25.79	34.54	61.49	426.29

Cu Baseline (3) and Zn Baseline (3)

	Cu1	Cu2	Cu3	Zn1	Zn2	Zn3	Zn4	Tail
Cu (%)	2.01	15.19	12.65	1.21	0.89	0.62	0.28	0.039
Zn (%)	1.95	7.51	14.06	20.44	12.2	4.4	0.89	0.055
Mass (g)	240.25	95.86	77.09	39.18	27.11	34.81	56.66	447.65

Cu Baseline (4) and Zn Baseline (4)

	Cu1	Cu2	Cu3	Zn1	Zn2	Zn3	Zn4	Tail
Cu (%)	3.59	13.59	9.4	1.1	0.92	0.69	0.55	0.065
Zn (%)	1.97	7.6	17.3	19.3	11.4	4.1	1.51	0.083
Mass (g)	237.72	105.55	65.59	36.62	28.51	36.67	45.43	462.05

Cu Baseline (5) and SS (0.5 g/kg) in Zn stage

	Cu1	Cu2	Cu3	Zn1	Zn2	Zn3	Zn4	Tail
Cu (%)	2.95	14.06	12.6	1.16	0.88	0.63	0.26	0.034
Zn (%)	2.16	7.52	15.3	17.9	7.5	2.3	0.51	0.043
Mass (g)	238.17	103.76	60.26	59.65	30.94	31.31	52.96	441.19

Cu Baseline (6) and PP (0.1 g/kg) in Zn stage

	Cu1	Cu2	Cu3	Zn1	Zn2	Zn3	Zn4	Tail
Cu (%)	2.79	14.52	10.87	1.14	0.96	0.85	0.63	0.054
Zn (%)	1.96	7.18	15.22	21	7.3	2.4	1.11	0.075
Mass (g)	234.59	96.49	76.49	49.31	28.31	28.98	41.14	465.82

Cu Baseline (7) and PP (0.5 g/kg) in Zn stage

	Cu1	Cu2	Cu3	Zn1	Zn2	Zn3	Zn4	Tail
Cu (%)	3.56	14.03	9.7	0.88	0.88	0.58	0.24	0.035
Zn (%)	2.02	7.8	15.6	19.5	6.2	1.5	0.44	0.051
Mass (g)	239.58	103.13	66.78	51.67	22.97	26.31	47.93	455.65

Cu Baseline (8) and PP (1 g/kg)

	Cu1	Cu2	Cu3	Zn1	Zn2	Zn3	Zn4	Tail
Cu (%)	2.46	13.82	12.1	1.43	0.98	0.62	0.22	0.035
Zn (%)	1.96	7.46	14.4	18.9	6.7	1.9	0.54	0.047
Mass (g)	235.06	102.43	74.31	57.59	26.46	23.23	40.66	453.01

Cu Baseline (9) and EDTA (0.1 g/kg) in Zn stage

	Cu1	Cu2	Cu3	Zn1	Zn2	Zn3	Zn4	Tail
Cu (%)	3.26	14.46	11.55	1.23	0.96	0.68	0.46	0.051
Zn (%)	2.2	7.78	15.86	18.9	8.4	2.9	0.97	0.062
Mass (g)	239.02	98.09	65.29	50.7	33.52	33.76	43.99	446.65

PP (0.1 g/kg) in Cu stage

	Cu1	Cu2	Cu3	Zn1	Zn2	Zn3	Zn4	Tail
Cu (%)	6.84	6.54	3	0.66	0.59	0.43	0.18	0.033
Mass (g)	320.6	100.31	37.44	26.85	16.58	27.63	53.18	431.44

PP (0.5 g/kg) in Cu stage

	Cu1	Cu2	Cu3	Zn1	Zn2	Zn3	Zn4	Tail
Cu (%)	6.76	4.93	2.29	0.37	0.47	0.33	0.12	0.027
Mass (g)	361.89	88.02	33.48	20.85	13.14	21.72	43.17	438.62

PP (1 g/kg) in Cu stage

	Cu1	Cu2	Cu3	Zn1	Zn2	Zn3	Zn4	Tail
Cu (%)	6.86	4.62	2.03	0.33	0.44	0.31	0.11	0.027
Mass (g)	386.67	64.97	33.96	19.79	11.98	20.63	45.01	436.49

SS (1 g/kg) in Cu stage

	Cu1	Cu2	Cu3	Zn1	Zn2	Zn3	Zn4	Tail
Grade	6.66	7.29	2.78	0.43	0.47	0.32	0.13	0.031
Mass	330.53	102.62	38	28.96	16.79	23.02	46.35	431.96

EDTA (0.1 g/kg) in Cu stage

	Cu1	Cu2	Cu3	Zn1	Zn2	Zn3	Zn4	Tail
Grade	7.28	5.74	3.11	0.59	0.63	0.49	0.27	0.038
Mass	333.42	91.48	16.14	33.91	21.43	28.01	46.9	427.2

(d) Brunswick Mine

Baseline (1)

	Zn1	Zn2	Zn3	Zn4	Zn5	Zn6	Tail
Zn (%)	163.3	50.7	35.7	19.3	30.5	22.6	1108.3
Mass (g)	44.51	42.05	26.25	14.82	6.1	2.97	0.73

% Zn in Feed	8.17	Feed (g)	1430.4
% Zn in Feed (XRF)	7.98	Feed (g) (calculated)	1451.15
% Solids	44		

Baseline (2)

	Zn1	Zn2	Zn3	Zn4	Zn5	Zn6	Tail
Zn (%)	151.5	47.1	31.9	19.4	28.6	21.3	1120.1
Mass (g)	44.46	39.58	23.38	12.9	6.24	3.11	0.75

% Zn in Feed	7.52	Feed (g)	1419.9
% Zn in Feed (XRF)	7.55	Feed (g) (calculated)	1451.15
% Solids	44		

Baseline (3)

	Zn1	Zn2	Zn3	Zn4	Zn5	Zn6	Tail
Zn (%)	166.2	60.1	33.3	18.6	23.5	23.9	1161.8
Mass (g)	44.51	44.06	30.09	13.37	6.74	2.83	0.7

% Zn in Feed	8.29	Feed (g)	1487.4
% Zn in Feed (XRF)	7.77	Feed (g) (calculated)	1501.16
% Solids	45		

Baseline (4)

	Zn1	Zn2	Zn3	Zn4	Zn5	Zn6	Tail
Zn (%)	151.4	54.6	39.6	23	30.8	22.4	1059.2
Mass (g)	43.1	39.64	19.24	7.24	3.56	2.06	0.49

% Zn in Feed	7.45	Feed (g)	1381
% Zn in Feed (XRF)	6.98	Feed (g) (calculated)	1402.26
% Solids	43		

Baseline (5)

	Zn1	Zn2	Zn3	Zn4	Zn5	Zn6	Tail
Zn (%)	185.5	72.8	43.3	20.3	30.1	24.9	1184.5
Mass (g)	41.85	42.65	32.35	14.77	6.65	2.98	0.68

% Zn in Feed	8.74	Feed (g)	1561.4
% Zn in Feed (XRF)	8.88	Feed (g) (calculated)	1604.7
% Solids	47		

(a) Polyphosphate addition before CuSO4

Cu (70 g/t) and PP (0.5 g/kg) - (1)

	Zn1	Zn2	Zn3	Zn4	Zn5	Zn6	Tail
Zn (%)	182.2	53.6	37.1	26.1	35.9	30	1099.4
Mass (g)	42.33	33.11	14.04	6.17	3.26	1.81	0.41

% Zn in Feed	7.37	Feed (g)	1464.3
% Zn in Feed (XRF)	6.99	Feed (g) (calculated)	1501.12
% Solids	45		

Cu (70 g/t) and PP (0.5 g/kg) - (2)

	Zn1	Zn2	Zn3	Zn4	Zn5	Zn6	Tail
Zn (%)	186.5	46.6	37.3	23.6	40.5	23.8	1057.3
Mass (g)	40.91	31.41	12.65	6.1	2.55	1.67	0.34

% Zn in Feed	7.21	Feed (g)	1415.6
% Zn in Feed (XRF)	6.83	Feed (g) (calculated)	1501.12
% Solids	45		

Cu (70 g/t) and PP (0.5 g/kg) - (3)

	Zn1	Zn2	Zn3	Zn4	Zn5	Zn6	Tail
Zn (%)	223	74.8	57.1	21.5	22.3	18	1170.4
Mass (g)	40.37	35.98	26.18	11.89	7.58	4.36	0.45

% Zn in Feed	8.96	Feed (g)	1587.1
% Zn in Feed (XRF)	8.73	Feed (g) (calculated)	1769
% Solids	50		

Cu (50 g/t) and PP (0.1 g/kg)

	Zn1	Zn2	Zn3	Zn4	Zn5	Zn6	Tail
Zn (%)	213.9	88.7	48	24.6	32.1	26.4	1214.9
Mass (g)	39.19	39.94	29.9	13.02	6.12	2.87	0.72

% Zn in Feed	8.99	Feed (g)	1648.6
% Zn in Feed (XRF)	8.87	Feed (g) (calculated)	1713.2
% Solids	49		

Cu (90 g/t) and PP (0.1 g/kg)

	Zn1	Zn2	Zn3	Zn4	Zn5	Zn6	Tail
Zn (%)	208.5	87.7	49.9	22.7	24.1	16.3	1282.1
Mass (g)	39.57	41.1	29.37	15.71	8.55	4.46	0.7

% Zn in Feed	8.78	Feed (g)	1691.3
% Zn in Feed (XRF)	8.92	Feed (g) (calculated)	1658.3
% Solids	48		

Cu (90 g/t) and PP (1 g/kg)

	Zn1	Zn2	Zn3	Zn4	Zn5	Zn6	Tail
Zn (%)	241.9	66	49.8	32.2	26	19.5	1157.9
Mass (g)	41.06	33.67	18.07	8.24	5.75	4.34	0.47

% Zn in Feed	8.85	Feed (g)	1593.3
% Zn in Feed (XRF)	8.97	Feed (g) (calculated)	1658.3
% Solids	48		

Cu (50 g/t) and PP (1 g/kg)

	Zn1	Zn2	Zn3	Zn4	Zn5	Zn6	Tail
Zn (%)	267.9	80.1	62.6	27.5	30.2	29	1197.9
Mass (g)	38.65	31.26	16.53	8.12	5.74	3.15	0.46

% Zn in Feed	8.81	Feed (g)	1695.2
% Zn in Feed (XRF)	8.98	Feed (g) (calculated)	1741.18
% Solids	49.5		

(b) Polyphosphate addition after CuSO4

Cu (70 g/t) and PP (0.5 g/kg) - (1)

	Zn1	Zn2	Zn3	Zn4	Zn5	Zn6	Tail
Zn (%)	162.2	48	29.2	21.7	22	14.6	1040
Mass (g)	40.4	26.32	15.35	7.19	4.95	2.84	0.56

% Zn in Feed	6.84	Feed (g)	1337.7
% Zn in Feed (XRF)	6.62	Feed (g) (calculated)	1451.15
% Solids	44		

Cu (70 g/t) and PP (0.5 g/kg) - (2)

	Zn1	Zn2	Zn3	Zn4	Zn5	Zn6	Tail
Zn (%)	147.9	43.1	23.6	14	14	15.1	1010.6
Mass (g)	40.2	32.15	19.81	10.58	7.9	4.33	0.84

% Zn in Feed	7.07	Feed (g)	1268.3
% Zn in Feed (XRF)	6.53	Feed (g) (calculated)	1354.46
% Solids	42		

Cu (70 g/t) and PP (0.5 g/kg) - (3)

	Zn1	Zn2	Zn3	Zn4	Zn5	Zn6	Tail
Zn (%)	200.2	61.7	44	22.6	40.1	27.9	1137.5
Mass (g)	39.71	32.82	14.06	6.43	3.19	2	0.53

% Zn in Feed	7.51	Feed (g)	1534
% Zn in Feed (XRF)	7.38	Feed (g) (calculated)	1451.13
% Solids	44		

Cu (50 g/t) and PP (0.1 g/kg)

	Zn1	Zn2	Zn3	Zn4	Zn5	Zn6	Tail
Zn (%)	126	54.2	45.1	30.8	39.6	31.2	998.7
Mass (g)	41.92	42.21	28.01	14.69	8.42	4.84	1.39

% Zn in Feed	8.42	Feed (g)	1325.6
% Zn in Feed (XRF)	7.73	Feed (g) (calculated)	1344.62
% Solids	42		

Cu (90 g/t) and PP (0.1 g/kg)

	Zn1	Zn2	Zn3	Zn4	Zn5	Zn6	Tail
Zn (%)	155	53	41.8	25.7	39.7	22.4	989
Mass (g)	44.16	42.91	19	7.86	3.66	2.39	0.83

% Zn in Feed	8.39	Feed (g)	1326.6
% Zn in Feed (XRF)	7.58	Feed (g) (calculated)	1173.4
% Solids	38		

Cu (90 g/t) and PP (1 g/kg)

	Zn1	Zn2	Zn3	Zn4	Zn5	Zn6	Tail
Zn (%)	190.2	50.5	30.7	18.6	26	14.1	1099.4
Mass (g)	39.68	25.6	14.26	6.5	4.32	3.09	0.51

% Zn in Feed	7.08	Feed (g)	1429.5
% Zn in Feed (XRF)	6.86	Feed (g) (calculated)	1451.13
% Solids	44		

Cu (50 g/t) and PP (1 g/kg)

	Zn1	Zn2	Zn3	Zn4	Zn5	Zn6	Tail
Zn (%)	161.9	67.7	48.2	32.9	26.8	43.5	1005.5
Mass (g)	36.42	37.32	22.5	10.72	3.03	5.71	0.92

% Zn in Feed	8.02	Feed (g)	1386.5
% Zn in Feed (XRF)	7.4	Feed (g) (calculated)	1476.01
% Solids	44.5		