The Role of Copper Ions in Sphalerite and Pyrite Flotation Selectivity

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To my father and the rest of my family for their love,
encouragement and support in everything I do.
This thesis, like all my other achievements, is a tribute to them.

ABSTRACT

Microflotation, laboratory batch, and continuous in-plant minicell tests were conducted to determine if copper ions not only activate sphalerite but also depress pyrite when the minerals are together.

Microflotation was performed on mineral samples over a pH range of 3.5-11. It was found that pyrite recovery increased with addition of copper ions when alone, but decreased by more than 25% (absolute) when sphalerite was also present for the pH range 6-9.5.

Bench flotation tests were performed on Louvicourt Mine ore and Red Dog Mine ore. The results for Red Dog showed that upon addition of copper, pyrite recovery decreased significantly. Pyrite recovery decreased from ca. 70% (no copper) to ca. 10% (4.5 g Cu/kg Zn) at a sphalerite recovery of ca. 70%.

Continuous in-plant minicell tests at Louvicourt Mine also showed that pyrite recovery decreased with addition of copper and further indicated that with excess copper (20 g Cu/kg Zn) pyrite recovery can increase.

The mechanism responsible for the depression of pyrite seems to be competition first for copper then xanthate that favours sphalerite over pyrite. To take advantage of this competition it may be necessary to control the sequence and rate of copper, collector, and lime addition.

RESUME

Des tests de microflotation, des essais de flotation en laboratoire ainsi que des tests continuels au plant utilisant des mini-cellules furent effectués afin de déterminer si les ions de cuivre non seulement activent la sphalérite mais dépressent aussi la pyrite lorsque les deus minéraux sont ensemble.

La microflotation a été performée sur des échantillons de minéraux pour le champ de pH 3.5 à 11. Il fut noté que la récupération de la pyrite augmenta avec l'addition d'ions de cuivre lorsque seul mais baissa par plus de 25% (absolu) lorsque la sphalérite était présente pour le champ de pH 6 à 9.5.

Les essais de flotation en laboratoire ont été éffectués sur du minérai provenant de la Mine Louvicourt et de la Mine Red Dog. Les résultats pour Red Dog ont démontré qu'avec l'addition de cuivre, le taux de récupération de la pyrite diminuait significativement. La récupération de la pyrite diminuait d'environ 70% (sans cuivre) à environ 10% (4.5g Cu/kg Zn) moyennant une récupération de la sphalérite d'environ 70%.

Les essais continuels au plant avec mini-cellules effectués à Louvicourt ont aussi démontrés que la récupération de la pyrite diminuait avec l'addition de cuivre et démontra aussi qu'avec un excess de cuivre (20g Cu/kg Zn) la récupération de la pyrite peut augmenter.

Le mechanisme responsible pour la dépression de la pyrite semble être une compétition entre les deux minéraux pour les ions de cuivre en premier lieu suivi par le xanthate ou la sphalérite est favorisée. Afin de prendre avantage de cette compétition, il serait probablement nécessaire de controler la séquence et le taux d'addition du cuivre, du collecteur, et de la chaux.

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TABLE OF CONTENTS

CHAPTER ONE

CHAPTER TWO

CHAPTER THREE

CHAPTER FOUR

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

1.1 Background

Flotation, in common with all physical separations, is an imperfect process that results in misplacement of minerals. One source of this imperfection is accidental activation by contaminating metal ions. An important practical example is the misplacement of pyrite to zinc concentrates. Flotation of zinc sulphide minerals generally requires activation by copper ions, added as copper sulphate. Copper ions are also used to activate pyrite [Voigt et al., 1994] hence there is the suspicion that accidental activation contributes to the recovery of pyrite (Py) to the zinc concentrate. However, recent literature has shown that copper ions may make Py less floatable if Sp is also present. Xu et al. [1992] conducted continuous minicell tests in-plant at Kidd Creek Operations (division of Falconbridge Ltd.) and showed that while the addition of copper sulphate improved zinc/iron selectivity, it did so as much by reducing the recovery of pyrite as increasing zinc recovery.

In a follow-up fundamental study, Zhang et al. [1997] conducted microflotation tests on pyrite (Py) singly and sharing solution with sphalerite (Sp). It was observed that Py alone was activated by copper ions, but Py recovery was significantly decreased when Sp was present. These results suggest that Py activation by copper is moderated by the presence of Sp. They concluded that xanthate adsorption on pyrite was retarded when copper-activated sphalerite was present due to competition for the collector. It is also the case that the Sp surface is more energetically favourable for copper uptake as copper can exchange for zinc in the Sp lattice whereas there is no evidence for exchange with iron in Py. In a mixed mineral system, this would favour Sp activation rather than Py.

Another possible form of competition is through galvanic coupling. Sphalerite has a low conductivity and is generally regarded as electrochemically inert yet galvanic coupling with Py will occur [Woods, 1976 and 1984; Rao and Finch, 1988]. The addition of copper may enhance the galvanic couple since copper-activated Sp is more conductive and theoretically more electrochemically active and a stronger galvanic couple may form with Py. Pyrite has a higher rest potential than copper-activated Sp therefore oxygen reduction to hydroxide ions occurs on its surface. These hydrophilic hydroxide ions may depress the Py [Woods, 1986; Xu et al., 1995]. Thus not only does competition tend to starve the Py of xanthate (i.e., indirect depression), this galvanic mechanism also provides a direct depression action. However, Chen and Yoon [1997] reported that the rest potential of Sp increased to that of covellite (CuS) when activated by copper ions. The difference between the rest potential of copper-activated Sp and Py is thus smaller than without copper activation which suggests that the galvanic coupling between the minerals would not be as strong. The role of galvanic coupling and the effect that copper activation has on Sp-Py mineral competition remains unclear.

A study by Heyes [1999] on Sp and Py selectivity proposed that formation of copper-hydroxide complexes on the Py surface depressed the mineral upon addition of copper ions at alkaline pH. Furthermore, Boulton et al. [1999] demonstrated that more copper-hydroxide species were present on Py than on Sp. These results suggest that copper-hydroxide species occur preferentially on Py and act as depressants thus enhancing Sp selectivity against Py.

1.2 Objectives

In the present study, the action of copper ions is examined through microflotation, laboratory batch, and continuous minicell in-plant tests. Given the increasing demand to reduce iron levels in zinc concentrates there is a need to better understand the mechanism of Sp-Py separation. The objectives were to:

1. Determine if copper ions not only activate Sp but also depress Py when the minerals are together.
2. Determine if this also occurs under plant conditions.
3. Probe the mechanism whereby Py floatability is reduced.

1.3 Thesis Outline

The thesis consists of six chapters. Chapter one gives the justification for this study as well as the objectives of the project.

Chapter two reviews sphalerite and pyrite flotation chemistry, focussing in particular on the role of copper ions and pulp potential.

In chapter three the material selection and preparation are given and the experimental apparatus and procedure are described in detail.

Chapters four and five present the results and discussion respectively for the microflotation tests, bench flotation tests, and continuous in-plant minicell tests. The effects of pH, reagent scheme (in particular copper dosage), and pulp potential are investigated.

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

CHAPTER 2

LITERATURE REVIEW

2.1 Sphalerite Flotation

Sphalerite is the most important mineral source of zinc. Sphalerite is nominally ZnS but is always associated with some iron in the lattice leading to the more general formula (Zn,Fe)S. When the mineral contains a high amount of iron it is referred to as marmatitie, or Zn_xFe_yS (where the ratio of zinc to iron is 9:1). Sphalerite is generally associated with other sulphide minerals such as galena, chalcopyrite, pyrite, and pyrrhotite. Flotation technology has therefore focussed on the separation of these sulphide minerals.

The flotation characteristics of zinc sulphide minerals are distinct from most other sulphides in that they do not respond well to short-chain thiol collectors (such as xanthates), but can be activated for flotation with these collectors by heavy metal salts. Copper sulphate is the most commonly used activator for sphalerite. However, there are cases where sphalerite floats to a significant extent without an activator which can result in zinc misreporting to lead or copper concentrates. This results in a loss of zinc units and a lower lead or copper concentrate grade. The misreporting of zinc is often attributed to accidental activation by heavy metal ions but the mechanism is not well understood.

There are several cases in the literature that show that the interaction between zinc sulphides and xanthate is weak [Gaudin, 1957; Rogers, 1962; Sutherland and Wark, 1955]. The relative weakness of xanthate adsorption onto sphalerite has been ascribed by Dixon et al.[1975] to sphalerite's high band gap which renders it relatively inert to the adsorption of anions. Sphalerite's low conductivity makes it unable to sustain the electron transfer necessary for the adsorption of xanthate. It is also possible that the adsorption involves a competition between the xanthate and another anion present at the surface of the mineral such that the collector uptake is retarded. Another contributing factor is that zinc xanthate is relatively soluble as compared to other metal xanthates [Finkelstein and Allison, 1976].

2.1.1 Effect of Copper Ions

Various heavy metal cations are effective sphalerite activators but cupric ions are the most commonly used due to their low cost relative to other cations such as Ag^+. The overall reaction for sphalerite activation is an ion exchange. It is generally accepted that the following chemical reaction is the driving force for copper adsorption on sphalerite [Jain and Fuerstenau, 1985]:

$$ZnS + Cu^{2+} \rightarrow CuS + Zn^{2+} \qquad (1)$$

where $G = -62.82$ kJ/mole Cu^{2+}

and $K = [Zn^{2+}] / [Cu^{2+}] = 10^{11}$

Reaction 1 implies a 1:1 exchange of copper and zinc which the literature supports. Thermodynamically, copper ions should continue to replace zinc ions in the sphalerite lattice until the zinc to copper ion ratio is 10^{11}. Gaudin et al. [1959] found a ratio of 0.80 and 0.96 in two separate tests while Pomianowski [1975] found the ratio ranged from 0.8-1.0, being greater than one if the sample was heavily oxidized. Pomianowski also observed that the amount of copper uptake decreased as the iron content of the sphalerite sample increased. Bushell [1961] suggested that the iron in the lattice formed $Fe(OH)_3$ which inhibited adsorption of copper.

Reaction 1 occurs in two stages whereby a rapid first stage is followed by a second, much slower stage. Stage I of the ion exchange, reaction (1), can occur either by adsorption followed by ion exchange and desorption or by dissolution followed by surface-nucleated precipitation. The adsorption - ion exchange - desorption mechanism is as follows:

$$ZnS_{(s)} + Cu^{2+} \rightarrow ZnS_{(s)}\,Cu^{2+} \rightarrow CuS_{(s)} + Zn^{2+} \qquad (2)$$

The reaction for the dissolution and precipitation is as follows:

$$ZnS_{(s)} + Cu^{2+} \rightarrow ZnS_{(s)} + Zn^{2+} + S^{2-} + Cu^{2+} \rightarrow ZnS{\cdot}CuS_{(s)} + Zn^{2+} \qquad (3)$$

Reaction (2) is a simple lattice replacement reaction and reaction (3) is a dissolution/precipitation reaction followed by a lattice rearrangement. Stage II of reaction (1) is a slower oxidation/reduction reaction given by:

$$2Cu^{2+}{}_{(surface)} + 2S^{2-}{}_{(surface)} \rightarrow Cu_2{}^{+}\,(S_2)^{2-}{}_{(surface)} \qquad (4)$$

Stage II of the overall reaction is slower since the process of exchange is inhibited by the accumulation of product on the surface. It was proposed that the rate-limiting-step was the diffusion of zinc ions outwards as the copper ions diffused inwards [Gaudin et al., 1959; Sui et al., 1999]. After three monolayers, the reaction is controlled by the parabolic rate law for solid-state diffusion which is clearly indicated in Figure 2.1.

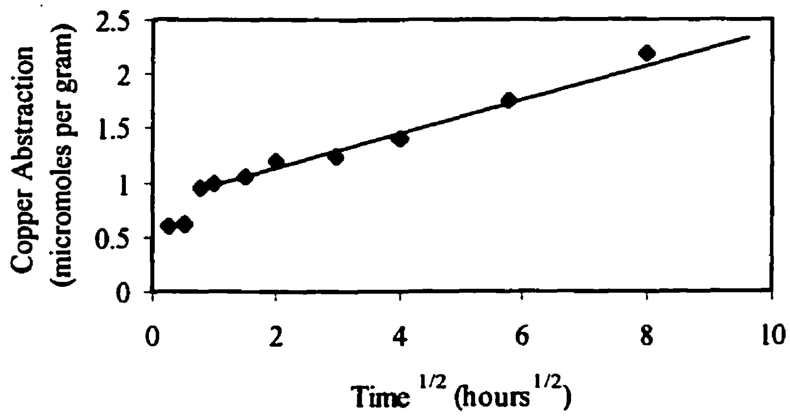

Figure 2.1: The copper abstraction of sphalerite as a function of the square root of the activation time (after Gaudin et al., 1959).

The amount of copper ions needed to form a monolayer can be determined through knowledge of the crystal structure of sphalerite. A crushed sphalerite surface exposes mainly dodecahedral cleavage faces (110) with two cationic sites available for every unit area. Gaudin et al. [1959] assumed that two surface zinc atoms were replaced by two copper atoms. If this assumption is true then about 0.3 micromoles of copper ions are needed to form one monolayer on one unit area (0.42 nm^2, or 41.6 A^2) of sphalerite. However, Gaudin et al. [1959] determined experimentally that 0.58 micromoles of copper uptake occurred rapidly in the first stage of the reaction which implies that two monolayers formed almost immediately. This can be explained by the uptake of copper immediately at the surface zinc sites labeled 1 in Figure 2.2, followed rapidly by copper uptake by the partially buried zinc atoms labeled 2.

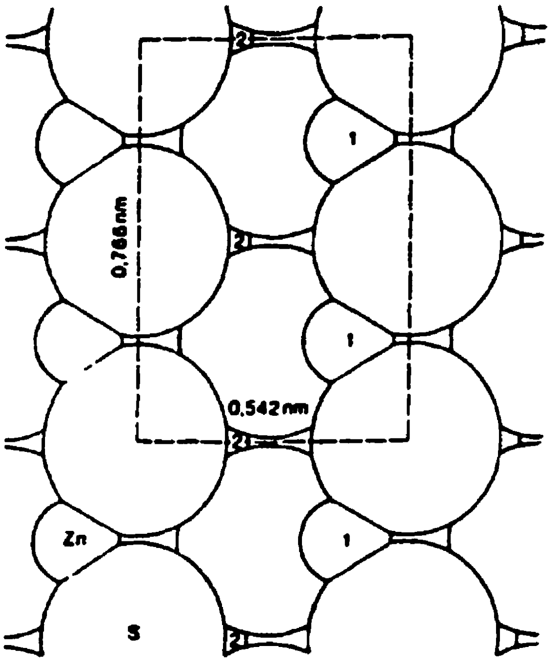

Figure 2.2: The (110) plane of sphalerite. Unit area, 41.6 A^2. Zinc ions in the surface are designated by numeral 1 and zinc ions in the next lower layer by numeral 2 (after Gaudin et al., 1959).

Sui et al. [1999] also showed that copper adsorption on Sp was rapid initially and then slowed after about five minutes. The presence of calcium ions at pH 9.2 resulted in a decrease in copper adsorption, most likely due to the adsorbed calcium hydroxide species "blocking" copper adsorption sites.

Laskowski et al. [1997] conducted an electrokinetic and flotation study of sphalerite activation and found that the copper ion activation mechanism of sphalerite is pH dependant. At acidic pH the surface is activated readily by an ion exchange between copper and zinc in the lattice and long conditioning times are not required. Neutral conditions result in the formation of copper hydroxide complexes that adsorb onto the sphalerite surface. This surface layer is "flotation-inactive" thus longer conditioning times are required before the flotation kinetics improve. Alkaline conditions yield an ion exchange between copper (originating from copper hydroxide species) and zinc as well as a precipitation/coagulation layer of copper hydroxide on the sphalerite surface [Jain and Fuerstenau, 1985]. This surface is already "flotation-active" therefore long conditioning times are not necessary.

The form of copper on the surface of sphalerite after copper activation has not yet been clearly identified. Finkelstein and Allison [1976] and Cooke [1950] concluded that the surface product is covellite, CuS, while Buckley et al. [1989] and Popov and Vucinic [1990] claimed that the resultant surface species was not a true copper sulphide phase.

Popov and Vucinic [1990] noted that while copper ions are good sphalerite activators, too high a concentration, $[Cu^{2+}] > 2.5\text{x}10^{-4}M$, led to an apparent depressing affect. This could be explained by the tendency of the copper species in solution to use up the available ethyl xanthate ions to form copper-xanthate complexes.

Prestige et al. [1996] proposed that the mechanism for copper ion activation is copper hydroxide precipitation followed by a copper-zinc exchange. This results in a surface layer of copper substituted sphalerite. The thickness of the $Cu(OH)_2$ precipitation layer increased as the copper ion concentration increased.

In summary, the literature proposes that sphalerite activation by copper ions is effectively an ion exchange between copper and zinc which takes place in two stages, a fast initial stage followed by a slower, continuous stage.

2.1.2 Role of Electrochemical Potential

Sulphide minerals are electrical semi-conductors therefore they can act as a source or sink for electrons and thus can support redox reactions at their surface. The reaction of minerals with flotation reagents often involves a charge transfer, therefore cyclic voltammetry can be used to study the interaction of sulphide minerals with metal ion activators and collectors. This electrochemical technique has been implemented successfully by several researchers. Minerals have a potential where equilibrium is established, referred to as a rest potential since no current has been imposed externally. In general, an increase in this potential would drive anodic reactions, such as the formation of dixanthogen, while a decrease in potential drives cathodic reactions.

Studies have shown that the interaction of activator and collector with sphalerite is electrochemical in nature. Cyclic voltammetry can thus be used to study copper activation of sphalerite [Richardson et al., 1993]. Yoon et al. [1993, 1994] showed that longer activation times increased copper uptake on sphalerite and the absence of oxygen (removed by nitrogen sparging) enhanced copper uptake. Furthermore, copper activated sphalerite was deactivated at potentials just slightly anodic of the rest potential, perhaps due to oxidative leaching of copper. Copper activation of sphalerite was favoured at low pH (pH 6.8 versus pH 9.2).

Electrochemical studies were conducted on copper activated sphalerite at pH 9.2 by Chen and Yoon [1997]. It was found that a decrease in potential from 0.275V (rest potential) to 0.195V increased copper uptake. The potential yielding maximum copper uptake was not determined.

2.2 Pyrite Flotation

Pyrite, a common iron sulphide mineral, is almost always associated with sulphide minerals such as galena, sphalerite and chalcopyrite. The flotation behaviour of pyrite is reasonably well understood and by controlling reagent additions it can generally be separated from other sulphide minerals. The usual practice is to depress the pyrite.

It has been shown through electrochemical measurements that pyrite has the highest rest potential of the common sulphide minerals, i.e., it is the most noble [Ball and Rickard, 1976]. The rest potential of pyrite is higher than the redox potential of the xanthate/dixanthogen couple therefore the form of xanthate on the surface is dixanthogen. Pyrite floats with xanthate collectors due to this formation of dixanthogen. A redox couple is established on the pyrite surface: xanthate oxidation to dixanthogen coupled with oxygen reduction. The oxidation (anodic) and reduction (cathodic) reactions according to Fuerstenau [1982] are as follows:

Anodic: $2X^- \rightarrow X_2 + 2e^-$

Cathodic: $\frac{1}{2} O_{2(ads)} + H_2O + 2e^- \rightarrow 2OH^-$

The overall reaction is:

$$2X^- + \tfrac{1}{2} O_{2(ads)} + H_2O \rightarrow X_2 + 2OH^-$$

The overall reaction is only possible at less than pH 11 partly because dixanthogen is unstable at higher pH, and partly since an increase in pH lowers the rest potential. Depression of pyrite by elevating the pH is the common practice. Figure 2.3 illustrates this depression at high pH. The figure also shows two maxima, one at ca. pH 4 and a second at ca. pH 8. The high recovery at acidic pH may be due to the formation of ferric xanthate while the basic maxima is due to dixanthogen. The intermediate region of depression at ca. pH 6 may be caused by formation of insoluble ferric hydroxy xanthates which are only slightly hydrophobic thereby reducing pyrite floatablilty [Wang et al., 1989; Wang and Forrsberg, 1991; Hanson and Fuerstenau, 1993].

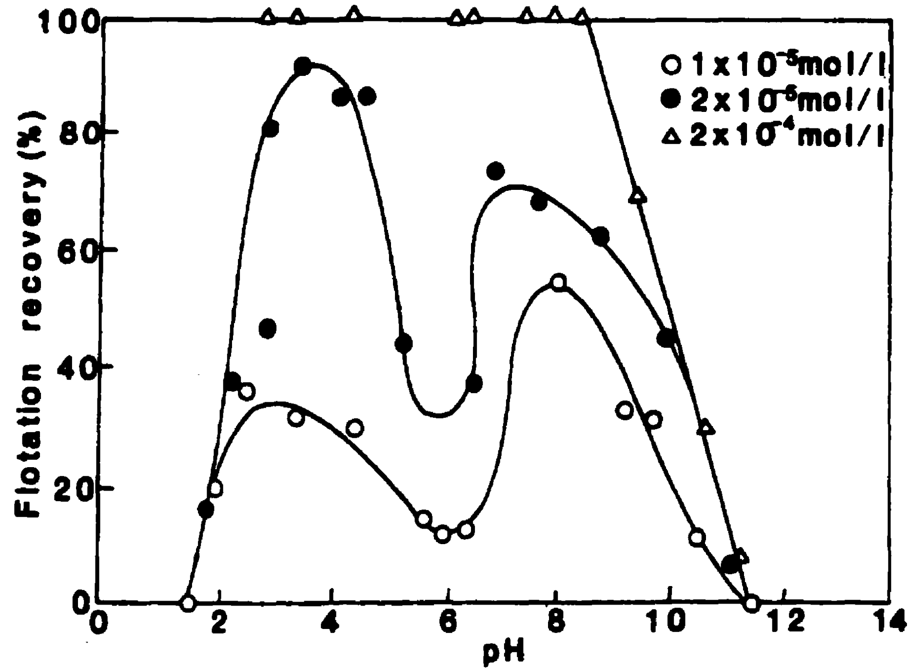

Figure 2.3: Recovery of pyrite as a function of flotation pH with various additions of potassium ethyl xanthate (after Fuerstenau et al., 1968).

Apart from elevated pH, a commercial route to depress pyrite is through addition of sodium cyanide. Ball and Rickard [1976] proposed that cyanide addition leads to the formation of surface ferric ferrocyanide which is responsible for the depression of pyrite. The overall reaction is as follows:

$7Fe^{++} + 18HCN \rightarrow Fe_4[Fe(CN)_6]_3 + 18H^+ + 4e^-$

The pyrite produces ferric ions in solution which react with cyanide ions to produce ferrocyanide, $Fe(CN)_6^{4-}$, which further react at the pyrite surface to form ferric ferrocyanide.

2.2.1 Effect of Copper Ions

Copper is known to alter the flotation response of pyrite-bearing ores significantly. Voigt and Szargan [1994] studied the interaction of Cu(II) ions with pyrite and its influence on ethyl xanthate adsorption. It was determined that copper ions activate pyrite and that the uptake of copper dictated the extent to which xanthate was adsorbed. Copper ions are adsorbed onto the pyrite forming a $Cu^+S_2^-$ surface species but at alkaline pH copper was deposited via a hydrolysis mechanism such that $FeOH \cdot Cu(OH)^+$ and $FeOH \cdot Cu(OH)_2$ were formed.

2.2.2 Role of Electrochemical Potential

Like sphalerite, cyclic voltammetry can be used to study pyrite-reagent interactions. The activation of pyrite with copper ions was investigated by Yoon et al. [1995]. It was found that the most sensitive parameter governing copper uptake by pyrite was the redox potential of the activating solution. Aggressive reduction caused a significant decrease in copper uptake, possibly due to a loss of sulphur resulting in fewer bonding sites for copper. At very high potentials flotation recovery of pyrite decreased, most likely due to oxidation of the mineral surface [Woods and Richardson, 1986]. Sparging with pure oxygen increased the open-circuit potential to +0.15V and copper uptake was completely inhibited. A decrease in potential of 50 mV (0V to -0.05 V vs. SCE) tripled copper uptake on pyrite [Yoon et al., 1995]. Figure 2.4 shows the effect of redox potential on copper activation of pyrite.

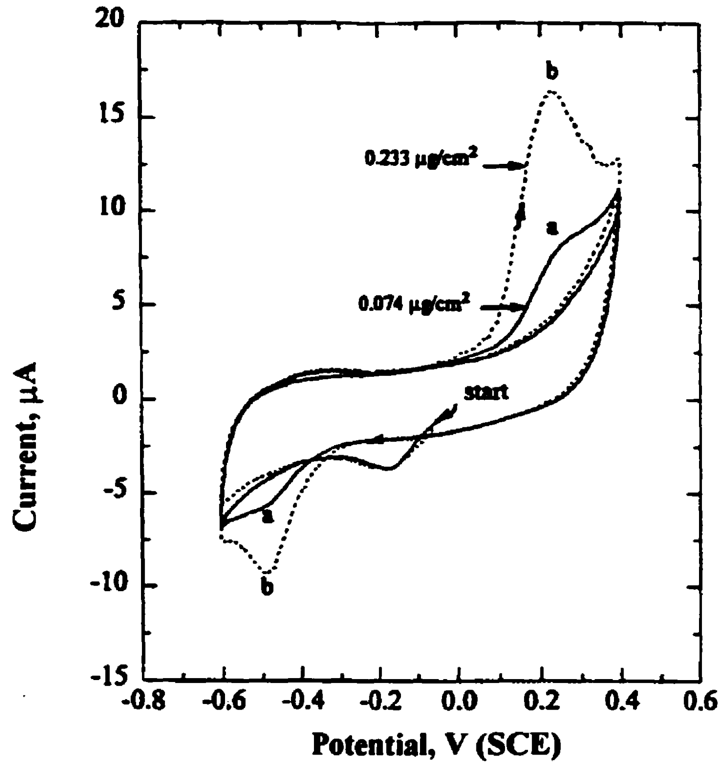

Figure 2.4: Voltammograms for pyrite electrode in pH 4.6 buffer with 10^{-4}M $CuSO_4$ solution at 0V (curve a) and –0.05V (curve b), (after Yoon et al., 1995).

Tolley et al. [1996] observed that pyrite flotation was enhanced under reducing conditions. Oxidizing conditions (+1.2V) also gave good recovery since bulk flotation of all sulphides was favoured.

The presence of other metal ions in solution can affect copper activation of pyrite. Ferric and calcium ions decreased copper uptake on pyrite [Yoon et al., 1995]. Galvanic coupling between iron (from mild steel grinding media) and pyrite caused a significant increase in copper uptake. Oxidizing conditions are required for galvanic coupling to occur thus the galvanic effect could be suppressed by lowering the potential. These results suggest that calcium or ferric ions combined with control of the redox potential during activation could be effective in depressing pyrite.

2.3 Sphalerite-Pyrite System

2.3.1 Effect of Copper Ions

Literature has shown that single mineral studies can be misleading [Trahar et al., 1994]. This research project concerns sphalerite and pyrite selectivity thus it is useful to understand the role of copper ions when sphalerite and pyrite are present together. Shen et al. [1996] investigated the effect of metal ions and their hydrolysis products on the activation and depression of pyrite and sphalerite flotation. It was found that pyrite was activated by copper and lead ions but that stronger activation occurred with copper ions. Pyrite activation could be inhibited by the addition of zinc, magnesium, or calcium ions which can be used as metal depressants. Figure 2.5 illustrates these observations. This figure indicates that the recovery of pyrite decreased due to the addition of copper ions, and that when zinc was also present the recovery of pyrite was even more depressed (although statistically this is debatable). No mechanism was proposed to explain why pyrite flotation was inhibited by copper ions and the effect of zinc ions on pyrite flotation was not discussed.

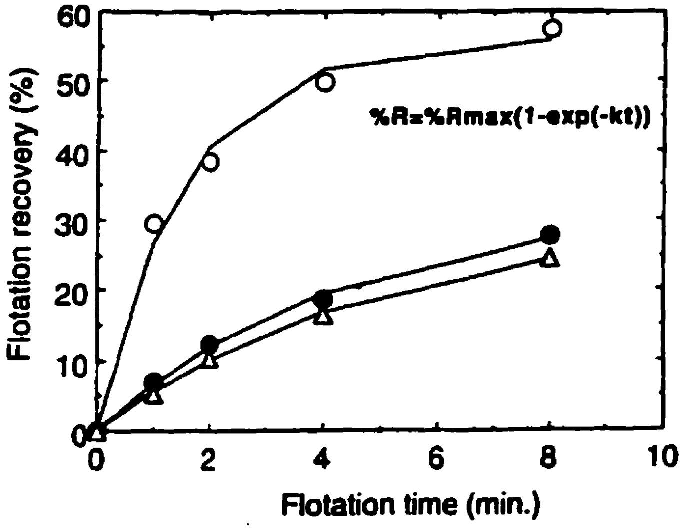

Figure 2.5: Pyrite recovery as a function of time and in the presence of (o) KEX; (•) Cu(II) and KEX; (Δ) Cu(II), KEX, and Zn (after Shen et al.,1996).

Furthermore, Shen et al. observed that too high a copper ion concentration led to sphalerite depression. The exchange of copper with zinc results in a higher amount of zinc ions in solution. These zinc ions may depress the sphalerite by forming a zinc hydroxide which re-adsorbs onto the mineral surface to form a layer that blocks collector uptake. The depressant effect of zinc ions on pyrite flotation may also be explained by this mechanism.

Steininger [1968] investigated the depression of sphalerite and pyrite and stated that both sphalerite and pyrite were depressed at neutral pH in the presence of copper due to the formation of basic copper collector complexes. Copper ions undergo hydrolysis followed by the formation of a copper-xanthate species. Steininger concluded that the formation of metal-xanthate species was detrimental to mineral flotation since they adsorbed on the surface and made the mineral unresponsive to other flotation chemicals.

Xu et al. [1992] conducted in-plant tests on sphalerite flotation and showed that while the addition of copper sulphate improved zinc/iron selectivity, it did so as much by reducing the recovery of iron as increasing sphalerite recovery (Figure 2.6).

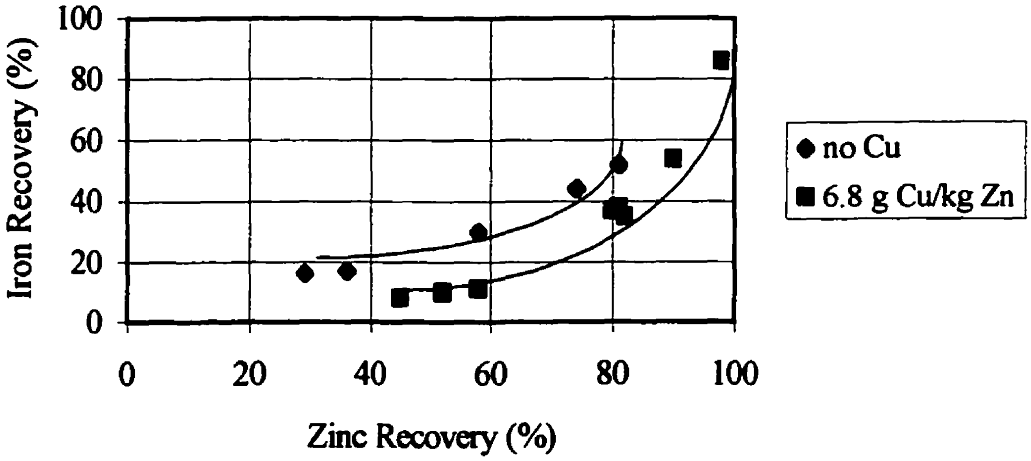

Figure 2.6: Iron Recovery as a Function of Zinc Recovery (adapted from Xu et al., 1992).

Trahar et al. [1994] studied how interactions among sulphide minerals affected the collectorless flotation of pyrite. It was observed that pyrite did not exhibit collectorless flotation when in the presence of sphalerite but that it floated without collector if galena or chalcopyrite were present. This may imply that lead and copper ions promote collectorless flotation but that zinc ions do not. However, the mechanism proposed was not based on metal ion activation but rather a transfer of sulphur, produced by galvanically driven oxidation of the less noble galena and chalcopyrite. No explanation was offered to clarify why pyrite did not display collectorless flotation when sphalerite was present. A possibility is that since sphalerite is less electrochemically active than galena, pyrite, and chalcopyrite, sulphur production is lower.

Zhang et al. [1997] conducted a study which showed that pyrite was activated by copper ions and floated with xanthate when alone but was depressed when sphalerite was also present. This was attributed to competition either for the copper ions or for the xanthate collector. The flotation behaviour of pyrite without copper did not change when sphalerite was present. However, when sphalerite was copper-activated it consumed most of the available xanthate therefore the recovery of pyrite was reduced.

Zhang et al. performed infrared spectroscopy to determine the surface species present on both minerals. The spectra showed that xanthate was absent from pyrite when sphalerite was also present in the copper activated system thereby supporting the competition hypothesis. If the competition mechanism holds, then once the sphalerite has floated the pyrite should be free to consume the remaining copper and become activated. This could lead to pyrite recovery “down-the-bank” in a zinc flotation process since there would no longer be as much competition from the sphalerite towards the end of the bank.

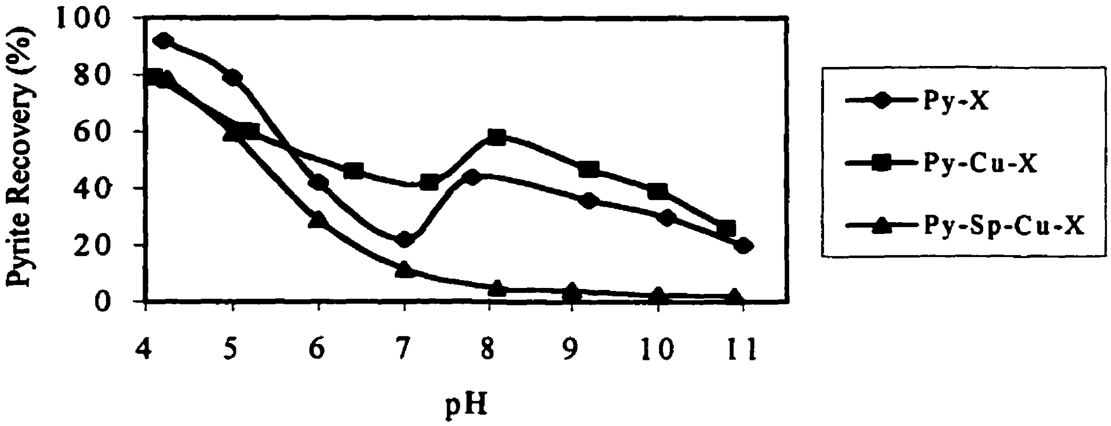

Figure 2.7: The effect of 10^{-5}M copper ions on pyrite flotation with 10^{-5}M isobutyl xanthate as a function of pH (adapted from Zhang et al., 1997).

The recent literature therefore suggests that pyrite activation by copper may not be an issue when sphalerite is also present. Accidental activation of pyrite can still occur when the stream is low in sphalerite content since it has been shown that pyrite is activated by copper ions when alone. An understanding of the competition mechanism may enable mineral processors to improve sphalerite/pyrite selectivity.

2.3.2 Role of Electrochemical Potential

Galvanic coupling occurs when two minerals with different rest potentials are in contact. The mineral with the higher rest potential acts as the cathode while the less noble mineral acts as the anode. The order of rest potential of common sulphide minerals at pH 9.2 [Sui, 1996] was given as:

pyrite > pyrrhotite > chalcopyrite > galena > sphalerite

This ranking indicates that pyrite would act as the cathode with respect to both galena and sphalerite. Figure 2.8 shows how galvanic interactions between pyrite and sphalerite can be represented. The mixed system adopts a potential where anodic and cathodic currents are equal, referred to as a mixed potential.

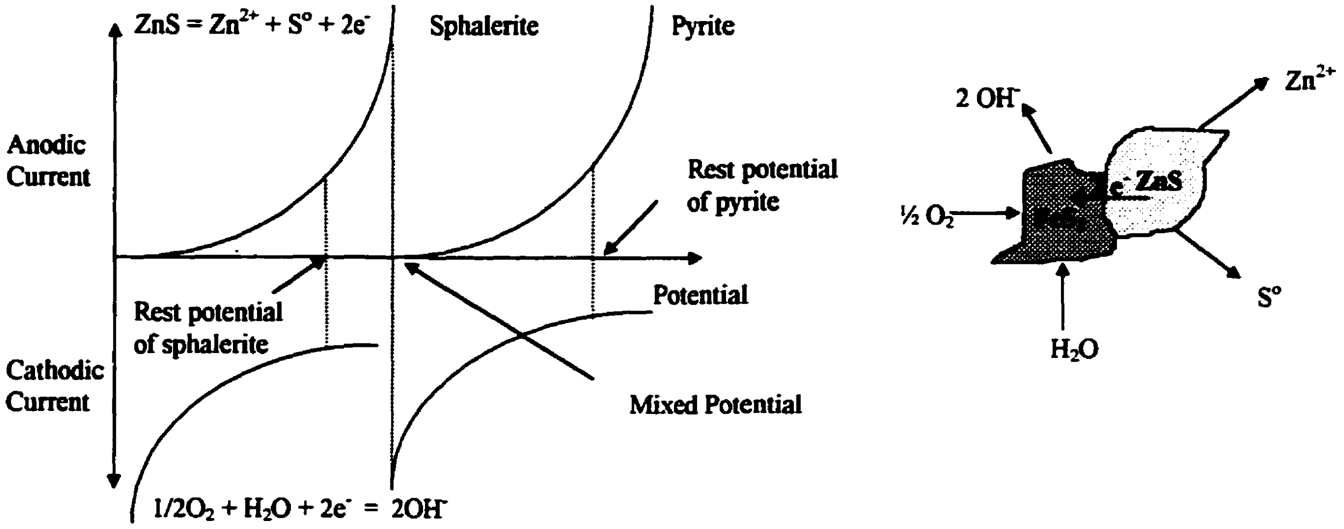

Figure 2.8: Galvanic Coupling Theory Applied to Sphalerite and Pyrite (adapted from Sui, 1996)

The rest potential of Py is higher than Sp therefore it is expected that the mixed potential of Sp and Py would fall between that of the individual minerals. However, when trying to measure this Bozkurt [1996] noted that the Sp-Py mixture increased the oxygen demand of the pulp (as compared to the minerals alone) therefore decreasing the dissolved oxygen content and the mixed potential was then below the rest potential of Sp. By analogy, a change in Sp:Py ratio can therefore be expected to influence pulp potential.

The idea that the interaction of minerals with flotation reagents could be explained by electrochemical mechanisms has led to the development of strategies for selective flotation of minerals based on control of pulp potential. An illustration of the impact of potential can be seen in the work of Xu et al. [1995] on reverse flotation of pyrite from a zinc concentrate. It was speculated that pyrite was depressed in the presence of sphalerite due to galvanic coupling. Pyrite, being the more noble sulphide mineral, was the site for oxygen reduction producing hydrophilic OH^- ions which depress the pyrite. When flotation was performed under nitrogen the redox reaction was suppressed, galvanic coupling was inhibited and pyrite recovery improved as hydroxide ions were no longer produced on the surface. Figure 2.9 shows how pyrite flotation is enhanced by nitrogen.

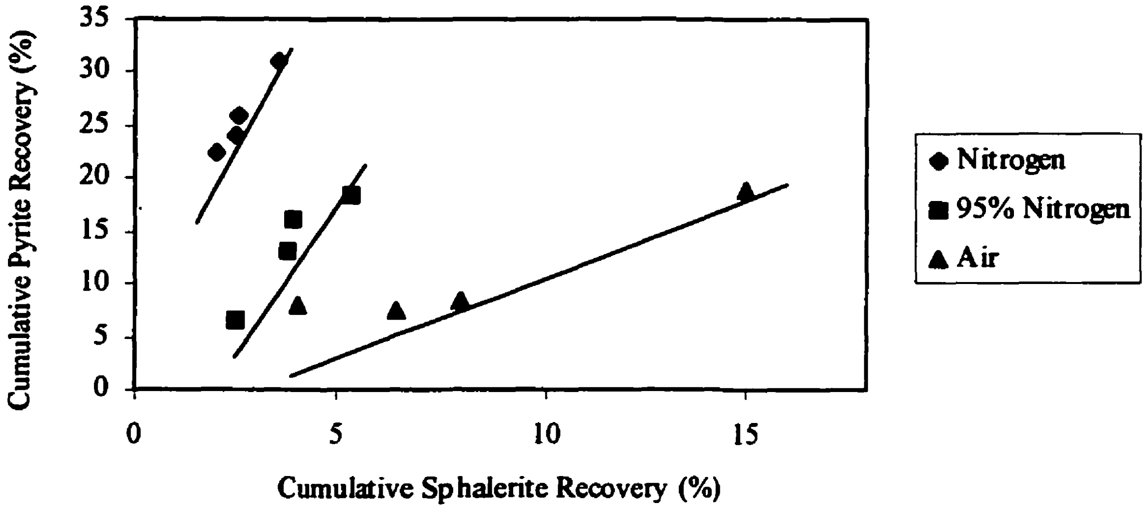

Figure 2.9: Cumulative pyrite versus sphalerite recovery to pyrite concentrate at pH 7 and 60°C (adapted from Xu et al., 1995).

2.4 Summary

The major findings of this survey indicate there remain several controversies regarding sphalerite and pyrite flotation. These controversies include the mechanism responsible for the misreporting of zinc to lead and copper concentrates which is a common problem. It has been established that the interaction between zinc sulphides and xanthate is weak but a dominant single reason for this remains elusive.

The samples of sphalerite and pyrite used in experimental work should be well characterized since the presence of copper or lead in the sample can change the flotation behaviour. Several technical papers fail to mention the zinc to iron ratio. The source of water used for experiments should also be recorded since dissolved metal ions (and other species) may lead to inadvertent activation/depression. The type of mill and grinding media used is important since mild steel acts as an anode with respect to most minerals promoting galvanic interactions. Furthermore, erosion of the grinding media is a source of iron ions which may influence flotation.

The efficient operation of a flotation process is largely dependant on the pH and the potential of the pulp. Literature shows that oxidizing conditions inhibit copper uptake while reducing potentials enhance copper activation of pyrite and sphalerite. The optimal conditions for copper distribution to favour sphalerite over pyrite have not been determined. A combination of calcium and ferric ions could be used to minimize copper uptake by pyrite while maximizing copper activation of sphalerite. The effect of other metal ions and the role of pH should also be studied in greater detail.

Dissolved oxygen levels and temperature should be monitored since these factors affect the pulp potential. Industrial flotation is generally carried out under alkaline conditions since iron sulphides are depressed and most collectors are stable at high pH. However, the literature showed research is often done under conditions that are not relevant to industrial practice. Several papers have been published where test work was performed at acidic or neutral pH.

Some of the discrepancies found in the literature may be ascribed to the high band gap and corresponding low conductivity of sphalerite. It is therefore expected that lattice defects, impurities, and even radiation would have a greater impact on sphalerite than on other sulphides. Sensitivity to small changes in composition may explain some of the contradictory findings for sphalerite. Furthermore, test work done on sphalerite alone could differ greatly from experiments done in association with other minerals. The role that copper ions play in sphalerite or pyrite flotation when the minerals are alone has been studied for several decades and is well documented and understood. Several studies have shown that single mineral test results are misleading but such research is still often done. For this reason, this masters project will investigate the effect of copper ions on flotation response when sphalerite and pyrite are both present.

CHAPTER 3

EXPERIMENTAL METHOD

3.1 Microflotation

3.1.1 Materials

Mineral specimens were obtained from Ward's Scientific Establishment Ltd., New York. Samples were crushed and hand-picked to eliminate visible impurities. Two size fractions were prepared, sphalerite (Sp) at +37-74 μm and pyrite (Py) at -37 μm, so that after flotation the mineral mixtures could be separated by screening. The minerals were acid washed (HCl solution at pH 2) to remove soluble impurities such as oxidation products, then stored under acetone. The composition of the minerals is given in Table 3.1.

Table 3.1: Mineral Composition

Sample	% Copper	% Zinc	% Iron	% Lead
Pyrite	0.14	0.42	40.8	0.24
Sphalerite	0.063	64.0	1.80	0.007

Reagent grade copper sulphate ($CuSO_4 \cdot 5H_2O$) from Fisher Scientific was used as the source of copper ions. Reagent grade sodium isopropyl xanthate, or SIPX ($[CH_3]_2CHOCS_2Na$), from Prospec Chemicals was selected since it is a common collector for sulphide minerals. The SIPX was purified using standard procedures and stored under petroleum ether [Rao, 1971]. Hydrochloric acid and sodium hydroxide were used as pH modifiers. Disodium ethylenediamine tetraacetate (EDTA) was used to extract metal ions from mineral surfaces.

3.1.2 Procedure

Tests were conducted on one gram samples. The samples were conditioned in a glass beaker with two compartments such that the minerals could (1) share the same solution or (2) be in contact. Figure 3.1 shows the setup used for conditioning for case (1) where the minerals share solution. For the contact experiments, both minerals were in the outer compartment.

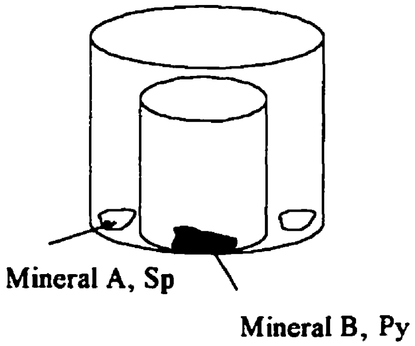

Figure 3.1: Microflotation Conditioning Setup

Conditioning of minerals for case (1) was done with one gram of each mineral in each compartment. After conditioning the minerals were floated individually. Conditioning of minerals in contact, case (2), was done with 0.5 grams of each mineral, preserving the ratio between the minerals at 1:1 and the total mass for flotation at 1 gram. The minerals were conditioned on an orbital shaker at 200 RPM for 10 minutes with copper sulphate. The solution was then decanted and the minerals conditioned for 10 minutes with SIPX at the set pH. Blank tests (no $CuSO_4$) involved conditioning for 10 minutes in distilled water prior to conditioning with SIPX.

Figure 3.2 illustrates the experimental set-up for microflotation. Feed was added to the cell column using a funnel. The air flow rate was 37 mL/min (0.16 cm/s) and the flotation time 5 minutes. After flotation, the float and non-float products were collected and dried, and screened for the case (2) procedure. Recovery was determined by the mass ratios. Two test series were performed:

a) Series A: Flotation was conducted at 5×10^{-5} M SIPX and 0 or 10^{-5} M $CuSO_4$ over the pH range 3.5-11 for pyrite and 8-11 for sphalerite.

b) Series B: Different reagent schemes were tested to further investigate "competition" between minerals. Four experiments were run at pH 8 with the minerals in contact (case (2)) using a two level factorial design for $CuSO_4$ and SIPX concentrations (refer to Table 3.2).

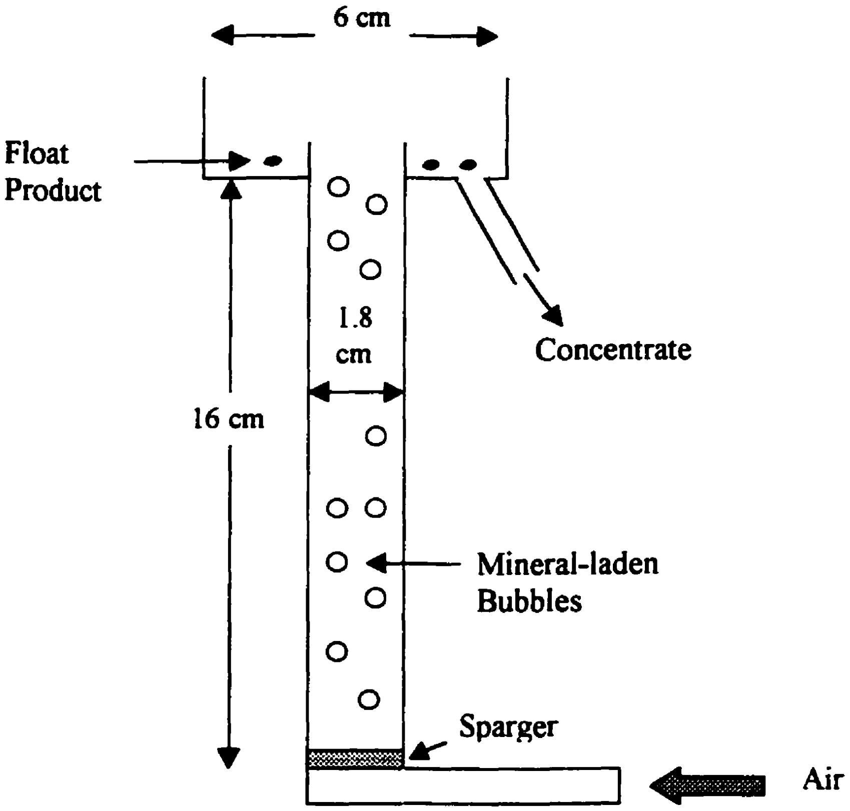

Figure 3.2: Microflotation Setup

Table 3.2: Test Series B Reagent Scheme

Reagent	Concentration
low [SIPX]	1 x 10^{-5} M
high [SIPX]	5 x 10^{-5} M
low [$CuSO_4$]	1 x 10^{-5} M
high [$CuSO_4$]	5 x 10^{-4} M

3.1.3 EDTA Extraction Tests

EDTA extraction tests were performed to quantify the amount of soluble copper species on the mineral surface. The same mineral conditioning set-up was used as for microflotation. After conditioning in copper sulphate solution at pH 8, the minerals were filtered and treated with 30 mL of a 0.05M EDTA solution for 20 minutes.

Tests were conducted to study the effect of contact time on migration of copper between pyrite and sphalerite. The minerals were conditioned with copper, filtered, conditioned in distilled water (pH 8) for a known length of time, then filtered and treated with 30 mL of 0.05M EDTA.

3.1.4 XPS Tests

X-ray photoelectron spectroscopy (XPS), performed at INRS-Energie et Materiaux in Varennes, Quebec, was used to detect the presence of copper on the mineral. After copper conditioning at pH 8, the minerals were screened, filtered, dried, and analysed. Tests were performed with the minerals individually, sharing solution, and in contact. XPS data was converted to percent surface coverage using Windows XPSpeak software.

3.2 Bench Flotation Tests

3.2.1 Materials

3.2.1.1 Louvicourt Mine

Louvicourt Mine is a copper-zinc operation located in Val d'Or, Quebec. A sample of rod mill feed was crushed to 100% passing 1.7 mm and split into 1 kilogram charges. The head assay was 4.0% copper, 1.2% zinc, and 25.2% iron. Hydrated lime ($Ca(OH)_2$) was used to regulate pH. Methyl isobutyl carbinol (MIBC) was the frother and copper sulphate ($CuSO_4$) was the source of copper ions for sphalerite activation. Aerophine collector, 3418A, and potassium amyl xanthate (PAX) were used in the copper rougher and Flex 31 (a xanthate collector with a surfactant) was used for the zinc rougher float. All collectors were obtained from Cytec Ltd and used as received.

3.2.1.2 Red Dog Mine

Red Dog Mine is a lead-zinc operation located in Alaska. A sample of ore from stockpile 132 was crushed and then split into 1 kilogram charges and stored in a freezer until used. The feed sample contained 4.7% lead, 18.3% zinc, 7.1% iron, and 44% silica. Table 3.3 shows the composition of the simulated Red Dog water used as the make-up water.

Table 3.3: Simulated Red Dog Water Composition

Impurity	Concentration (mg/L)
Aluminum	0.7
Calcium	680
Iron	0.05
Magnesium	32
Manganese	0.06
Sodium	27
Lead	0.06
Zinc	0.91

Zinc sulphate ($ZnSO_4$), sodium metabisulphate (NaMBS), and sodium cyanide (NaCN) were used as depressants. Methyl isobutyl carbinol (MIBC) was the frother and copper sulphate ($CuSO_4$) was the sphalerite activator. Potassium ethyl xanthate (KEX) from Cytec Ltd. was the collector for the lead rougher float and potassium amyl xanthate (PAX) from Cytec Ltd. was the collector for the zinc rougher float. The collectors were used as received.

3.2.2 Procedure

3.2.2.1 Louvicourt Mine

A 1 kilogram sample was ground at 60% solids with Montreal tap water in a rubber-lined mill using mild steel rods to an 80% passing size of 50 μm. Flotation was performed in a 2.2 L Denver flotation cell at an impeller speed of 1100 rpm. Tests were conducted in the pH range 9-11. Table 3.4 shows the baseline flotation conditions.

Table 3.4: Louvicourt Mine – Baseline Flotation Procedure (reagent dosages in grams per tonne).

Flotation Stage	3418A	Lime	PAX	MIBC	$CuSO_4$	Flex 31	Time (mins)	pH
Grind	18	1000					20	
Cu Conditioning							3	10.5
Cu Rougher				15			0	10.5
Cu Rougher			4				1	10.5
Cu Rougher			2				3	10.5
Zn Conditioning							1	11
Zn Conditioning					250		3	11
Zn Conditioning						4	1	11
Zn Rougher				30			0	11
Zn Rougher						2	1	11

The flotation slurry was conditioned for three minutes at pH 10.5 prior to the four minute bulk copper rougher float. PAX was added after one and three minutes of flotation and pH was maintained at 10.5 throughout the copper float. Zinc conditioning was performed in three stages. The pH was adjusted then the slurry was conditioned with $CuSO_4$ for three minutes, followed by one minute conditioning with Flex 31. Zinc flotation was conducted at pH 11 for eight minutes with incremental cuts at thirty seconds, one, two, four, and eight minutes. Flex 31 was added after one minute of flotation. Potential was measured using gold against a $Ag/AgCl_2$ electrode and ranged from 200-250 mV (versus standard hydrogen electrode, SHE) for all tests. All tests were performed in duplicate with the average reported. Standard deviation was approximately +/- 2% absolute.

Different reagent schemes were tested to further explore the microflotation results. A two level reagent concentration experimental design was used for $CuSO_4$ and Flex 31 (refer to Table 3.5).

Table 3.5: Louvicourt Bench Test Reagent Scheme

	First Flex 31 Addition (g/t)	**Second Flex 31 Addition (g/t)**	**$CuSO_4$ (g/t)**	**Cu (g Cu/kg Zn)**	**pH**
Low Dosage	2	1	125	4	9.7
High Dosage	4	2	250	8	9.1

Tests were also performed at pH 8 with high copper and high xanthate concentrations. The pH was adjusted using a dilute HCl solution.

3.2.2.2 Red Dog Mine

One kilogram of ore was ground at 67% solids with simulated Red Dog water in a rubber-lined mill to 80% passing 58 µm. High chrome balls were used as the grinding media. Flotation was performed in a 4.5 L Wemco cell running at 900 rpm with an Agitair impeller mechanism. Tests were conducted at the natural pulp pH of about 6.5. Table 3.6 describes the baseline flotation procedure.

Table 3.6: Red Dog Mine – Baseline Flotation Procedure

Flotation Stage	$ZnSO_4$	NaMBS	NaCN	KEX	MIBC	$CuSO_4$	PAX	Time (mins)
Grind	100	65						18.5
Pre-Float					10			5
Pb Conditioning	30		45					1
Pb Conditioning				80				1
Pb Rougher					5			10
Zn Conditioning						900		1
Zn Conditioning							300	1
Zn Rougher								8

A 5 minute pre-float was performed to remove organics (mainly carbonaceous material), followed by a 10 minute lead rougher. Zinc flotation was conducted at time increments of 1, 2, 4, and 8 minutes. All tests were performed in duplicate with the average reported. Standard deviation was approximately +/- 2% absolute. Three test series were carried out. Potentials were measured using gold against a $Ag/AgCl_2$ electrode and reported with respect to the standard hydrogen electrode (SHE).

a) Effect of Copper Concentration: Tests were conducted with no copper activation (pH 6.7, Eh 450 mV), 450g/t $CuSO_4$ (pH 6.6, Eh 480 mV), 900g/t $CuSO_4$ (baseline, pH 6.3, Eh 565 mV), 1800g/t $CuSO_4$ (pH 6, Eh 610 mV), and 8500g/t $CuSO_4$ (pH 4.6, Eh 650 mV). Copper dosages expressed as g Cu/kg Zn were 0, 1.12, 2.25, 4.5, and 21.2 respectively.

b) Staged Addition of Copper: Copper activation was performed in two stages. Primary activation with 900g/t $CuSO_4$ (or 2.25 g Cu/kg Zn) was done for all tests, followed by an additional 225g/t $CuSO_4$ after 2 minutes (2.6 g Cu/kg Zn) or 4 minutes (5.3 g Cu/kg Zn) of zinc flotation.

c) Effect of Copper Conditioning Potential: The conditioning potential was lowered by nitrogen bubbling, or raised with the addition of hydrogen peroxide (H_2O_2) prior to copper addition. Potentials studied were 400 mV, 440 mV, 470 mV, and 500 mV (with a range of +/- 15 mV) with reference to SHE. Flotation was performed in air without controlled potential.

3.3 Continuous In-plant Minicell Tests

3.3.1 Experimental Set-up

One or two continuous minicells (Figure 3.3) were used to conduct on-line flotation tests at Louvicourt Mine in Val d'Or, Quebec.

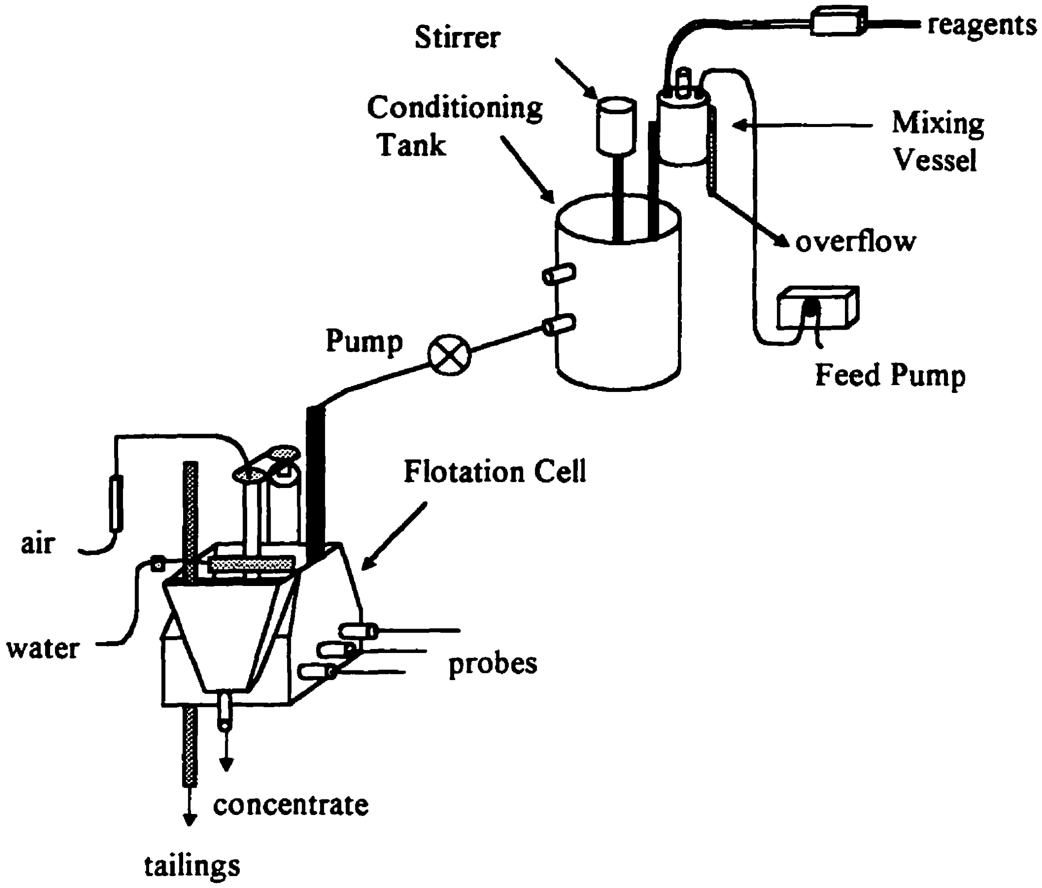

Figure 3.3: Set-up for one minicell; with two minicells tailings from cell 1 was pumped to cell 2

Feed and reagents were pumped into a small mixing vessel then to the conditioning tank. The overflow outlet on the conditioning tank provides level control with the volume in the tank maintained at 30 liters. The slurry was pumped to the 5 L flotation cell to control the retention time. Air was introduced through the impeller shaft and a flow meter controlled the air flow. The froth depth could be adjusted by raising or lowering the tailings pipe. The froth overflowed into a launder where it was periodically washed down with an intermittent water spray controlled by a solenoid. Flow rates were monitored to estimate conditioning and flotation times.

3.3.2 Flotation Feed

The sample was taken from the feed line to the zinc circuit prior to reagent addition. The composition was approximately 0.12% copper, 2.7% zinc, and 24% iron for plant trial I and about 0.11% copper, 1.0% zinc, and 17.5% iron for plant trial II. Copper sulphate was used as the sphalerite activator, Flex 31 as the collector in the zinc circuit, and SC frother as the frothing agent. The frother was added using an intravenous drip bag. The pH was adjusted using slaked lime and reagents were prepared daily from stock solutions.

Table 3.7: Louvicourt Continuous In-plant Minicell Test reagent Scheme

	$CuSO_4$ (g/t)	Cu (g Cu/kg Zn)	Flex 31 (g/t)	SC Frother (g/t)
Plant Trial I	0, 460	0, 6.8	8	7.5
Plant Trial II	0, 125, 250, 500	0, 5, 10, 20	4	4

3.3.3 Procedure

Each flotation test was run for 10 minutes and the concentrate samples were collected for the duration of the test while feed and tailings samples were collected at two minute intervals. Plant trial I had probes for pH, potential, and temperature connected to a control system, OPTO22, and this control board was connected to a computer. The potential was measured using gold against a Ag/AgCl electrode. The signals were recorded online and the pump speeds were controlled through the computer interface. Potential and pH were monitored and recorded manually for plant trial II. Mineral content in the samples was determined from the elemental assays.

Plant trial I employed two minicells and studied the effect of copper ions by conducting tests with and without copper sulphate addition. The copper off tests were performed shortly after the copper on tests to try to obtain similar feed samples. Tests were run at the plant operating pH ca. 11-11.2 with potential range of ca. 150-180 mV vs. SHE. Plant trial II studied the effect of different copper concentration at a slightly lower pH range 9.7-9.9 with potential of ca. 180-220 mV vs. SHE. The copper sulphate concentrations used were 0, 125, 250, and 500 g/t $CuSO_4$ (or 0, 5, 10, and 20 g Cu/kg Zn). One minicell was used and flotation retention time was constant at 1 minute. Conditioning time was 5 minutes for both plant trials.

CHAPTER 4

RESULTS

4.1 Microflotation

Test Series A

The effect of copper ions and the presence of sphalerite on pyrite flotation recovery can be seen in Figure 4.1. This work involves a repeat of the conditions used by Zhang et al. [3] where minerals shared solution (case (1)), and an extension to include minerals in direct contact (case (2)).

The addition of copper increased pyrite recovery when the mineral was alone (Py-Cu-X vs. Py-X), particularly in the moderately alkaline pH range, 7-10. However, when Sp was also present Py recovery decreased. This effect was stronger when the two minerals were in contact (case (2)) as compared to when the minerals shared the same solution (case (1)). The effect of Sp on Py recovery was greatest over the pH range 6-9.5; for example, at pH 8 Py recovery decreased by about 45% when Sp was present. At ca. pH 11 there was no significant difference in Py recovery for all test conditions.

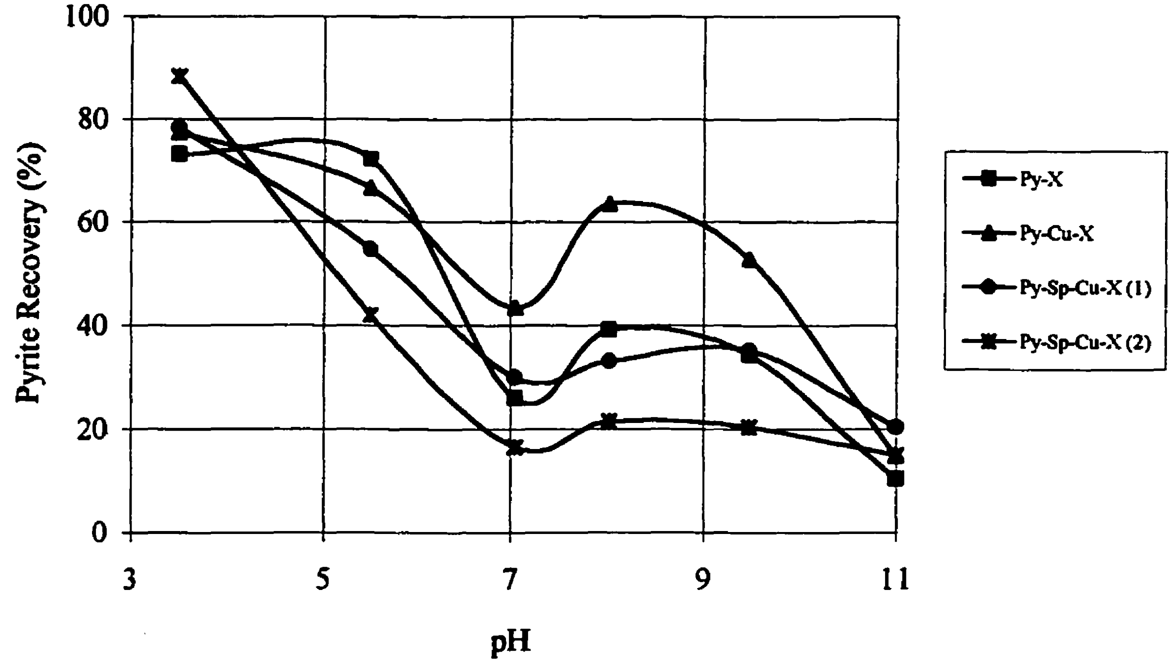

Figure 4.1: Pyrite Microflotation: Test Series A

Sphalerite flotation response is shown in Figure 4.2.

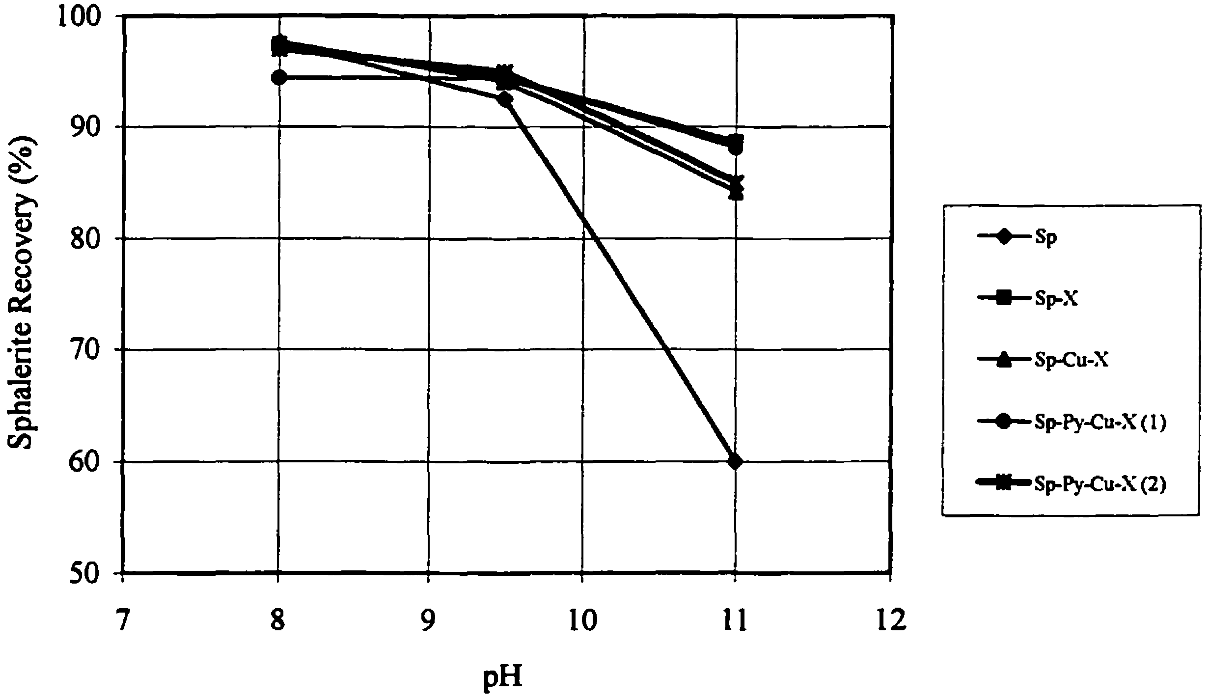

Figure 4.2: Sphalerite Microflotation: Test Series A

The results show that there was no significant difference between the test series except for sphalerite alone at pH 11. The main conclusion relevant to the present topic is that the presence of pyrite had no significant influence on sphalerite recovery.

Test Series B

The strongest competition was at ca. pH 8 (Figure 4.1) therefore test series B was conducted at this pH. Different reagent schemes were selected to determine whether the minerals compete for the copper or the collector. Figure 4.3 shows the pyrite recovery for the four reagent schemes.

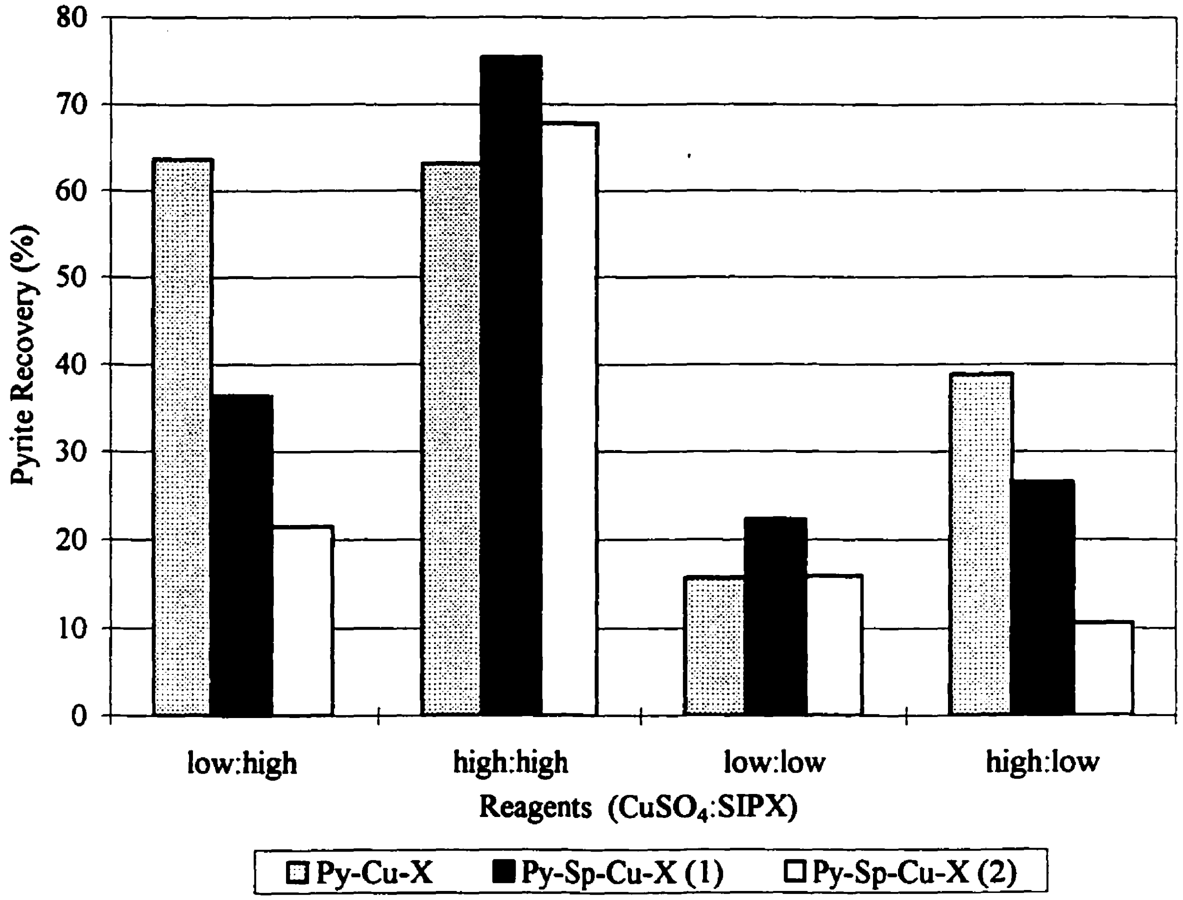

Figure 4.3: Pyrite Microflotation: Test Series B

The low copper:high xanthate test, equivalent to test series A, showed a marked decrease in pyrite recovery in the presence of sphalerite. The high copper:high xanthate test showed that the pyrite recovery remained high in the presence of sphalerite. The low copper:low xanthate test refers to a shortage of both reagents where pyrite recovery remained low and no effect from the presence of sphalerite could be detected. The high copper:low xanthate test showed a decrease in pyrite recovery in the presence of sphalerite.

EDTA Extraction Tests

Figure 4.4 shows the amount of copper extracted from the pyrite surface decreased in the following order; pyrite alone, sharing solution with sphalerite (case (1)), and in contact with sphalerite (case (2)).

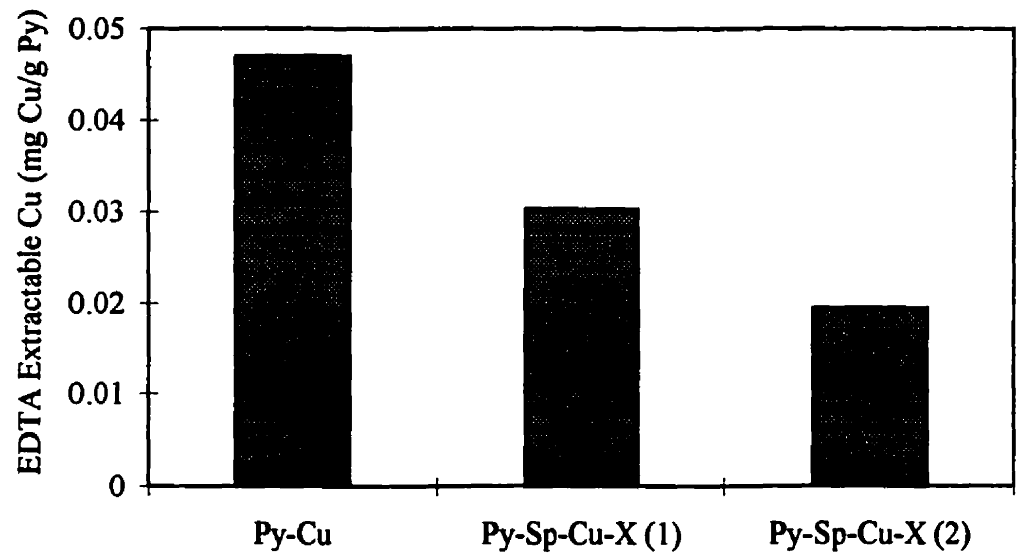

Figure 4.4: EDTA-Extractable Copper on Pyrite Surface

The result indicates that pyrite did not take up as much copper when in competition with sphalerite although there was copper present. It was hypothesized that, given time, this copper would migrate to the sphalerite surface.

Experiments were then conducted to test the hypothesis. Figure 4.5 shows the amount of EDTA-extractable copper on the pyrite surface decreased by nearly 50% after thirty minutes of contact.

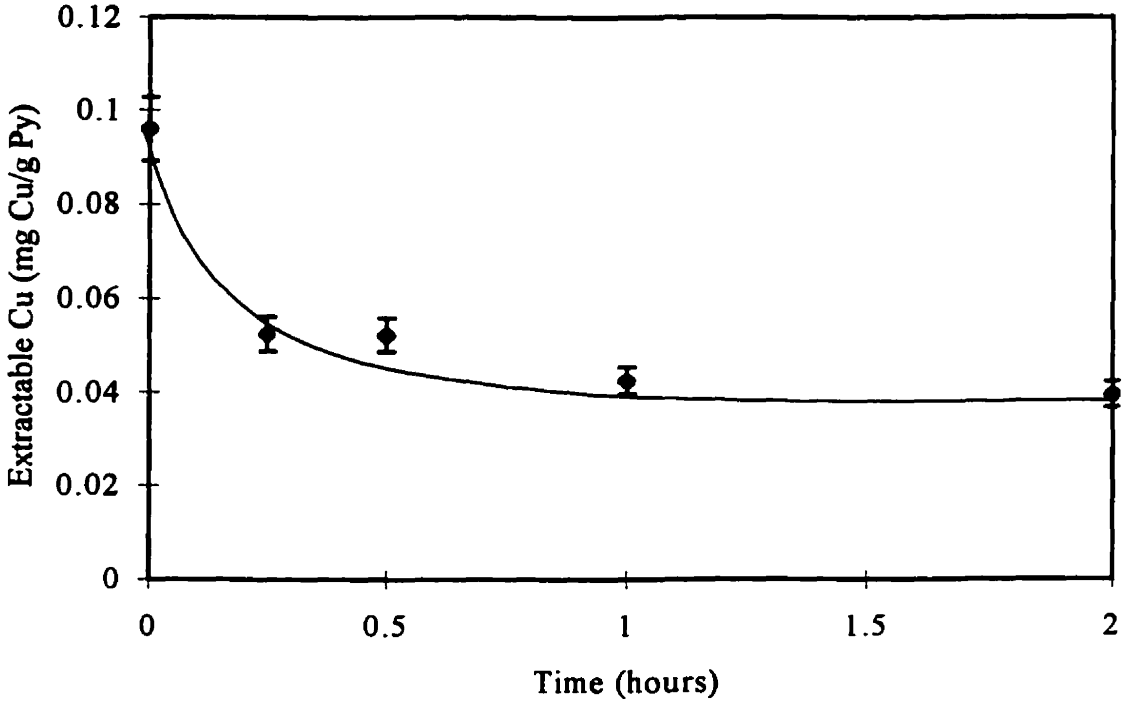

Figure 4.5: EDTA-Extractable Copper on Py Surface as a Function of Contact Time with Sp

XPS Tests

Figure 4.6 shows the percentage of pyrite surface covered by copper, determined by X-ray photoelectron spectroscopy (XPS). It can be seen that the amount of copper on the surface decreased in the presence of sphalerite for case (1), and decreased even further for case (2) (i.e., when in contact with sphalerite). The result is not as conclusive as in Figure 4.4, but confirms the trend.

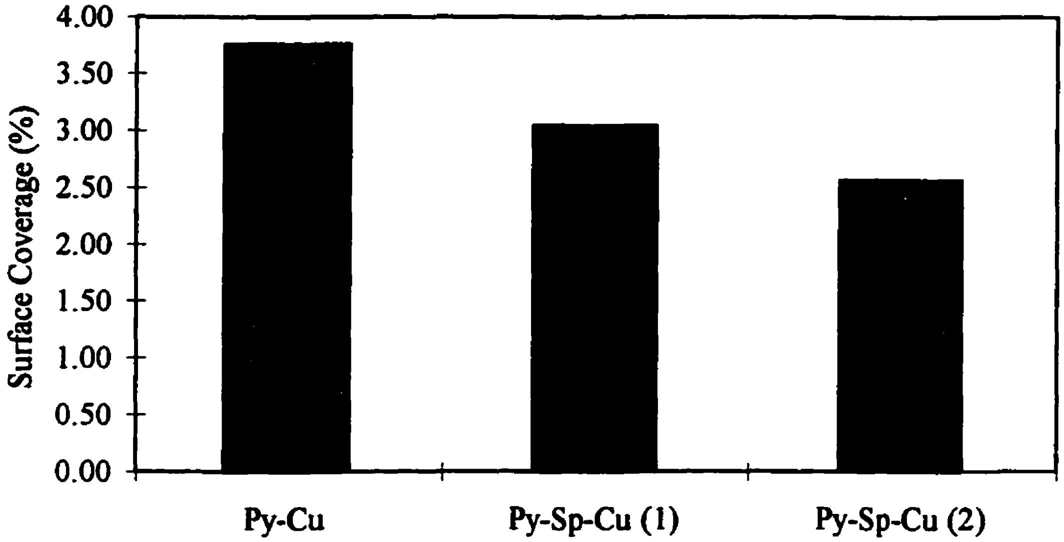

Figure 4.6: Percentage of Surface Coverage by Copper on Pyrite Determined by XPS.

Figure 4.7 shows the percentage of surface coverage by copper on sphalerite.

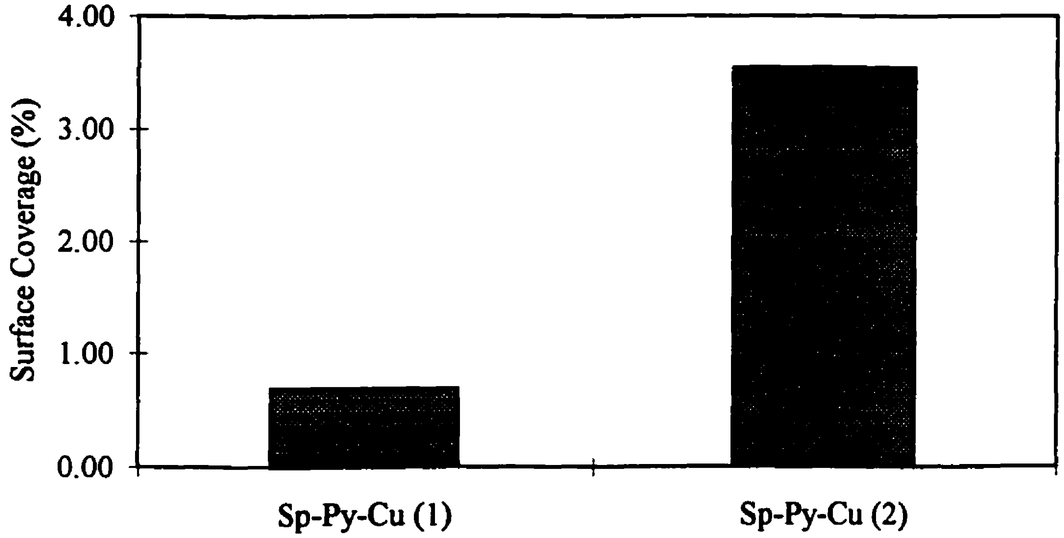

Figure 4.7: Percentage of Surface Coverage by Copper on Sphalerite Determined by XPS.

The amount of copper increased substantially when in contact with pyrite. Together, Figures 4.6 and 4.7 support the hypothesis that the copper is preferentially adsorbed on sphalerite when the minerals are together.

4.2 Bench Flotation Tests

4.2.1 Louvicourt Mine Ore

Figure 4.8 gives the pyrite-sphalerite selectivity curves for bench tests on Louvicourt rod mill feed for different reagent schemes.

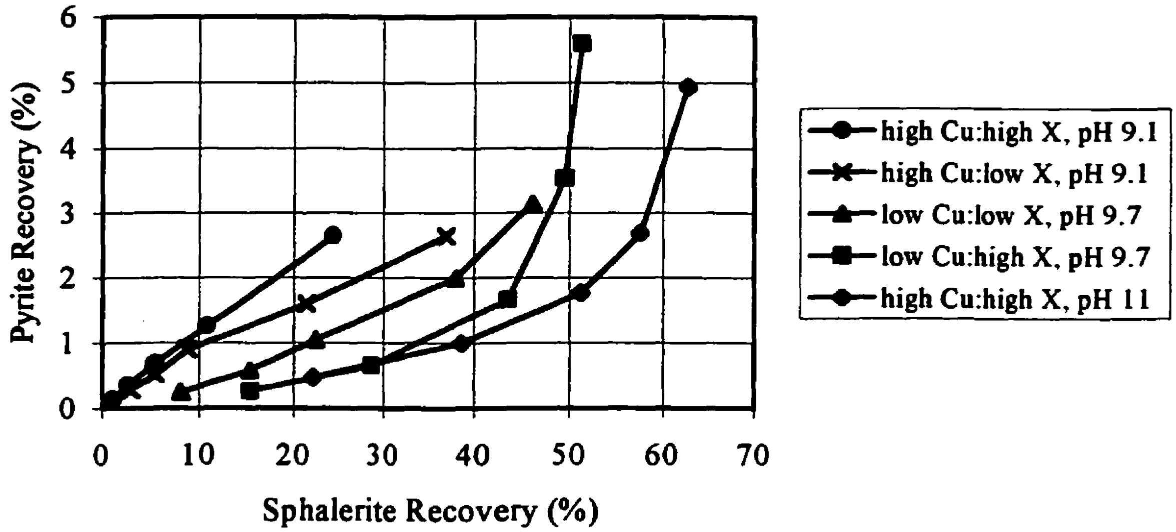

Figure 4.8: Effect of Reagent Dosage and pH on Py-Sp Selectivity for Louvicourt Ore

The results show that the baseline conditions (6 g/t Flex 31, 8 g Cu/kg Zn, pH 11) yielded the highest sphalerite recovery and the best selectivity against pyrite. An increase in copper concentration resulted in a decrease in flotation pH. At high copper concentration, Sp recovery is lower than the low copper test for the same xanthate concentration. However, it is not possible to determine if this decrease in Sp recovery is an effect of the copper dosage or the change in pH. The effect of pH can be seen more clearly for the high copper and high xanthate tests where sphalerite recovery is much lower at pH 9.1 than at pH 11.

4.2.2 Red Dog Mine Ore

a) Effect of Copper Concentration

Figure 4.9 shows that sphalerite and pyrite recovery reached approximately 70% without copper activation. The addition of copper sulphate dramatically improved mineral selectivity, primarily by reducing Py recovery.

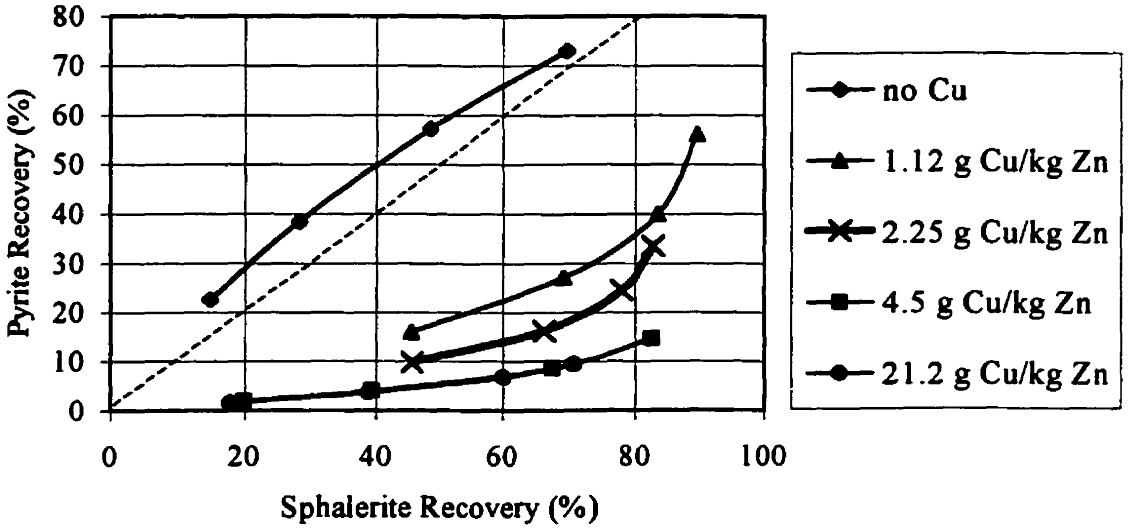

Figure 4.9: Effect of Copper Dosage at pH 6-6.7 on Py-Sp Selectivity for Red Dog Ore. Note: the dashed line represents the "no separation" line.

At low copper (1.12 g Cu/kg Zn) the maximum sphalerite recovery attained increased by about 20% with a corresponding pyrite recovery decrease of approximately 20% as compared to tests without copper addition. The middle copper dosage (2.25 g Cu/kg Zn) yielded a further decrease in Py recovery with no significant change in Sp recovery. At high copper (4.5 and 21.2 g Cu/kg Zn) pyrite recovery decreased further, yielding the best selectivity with an overall Py recovery of less than 15% and a Sp recovery greater than 80%.

Figures 4.10 and 4.11 show the grade versus recovery curves for sphalerite and pyrite, respectively.

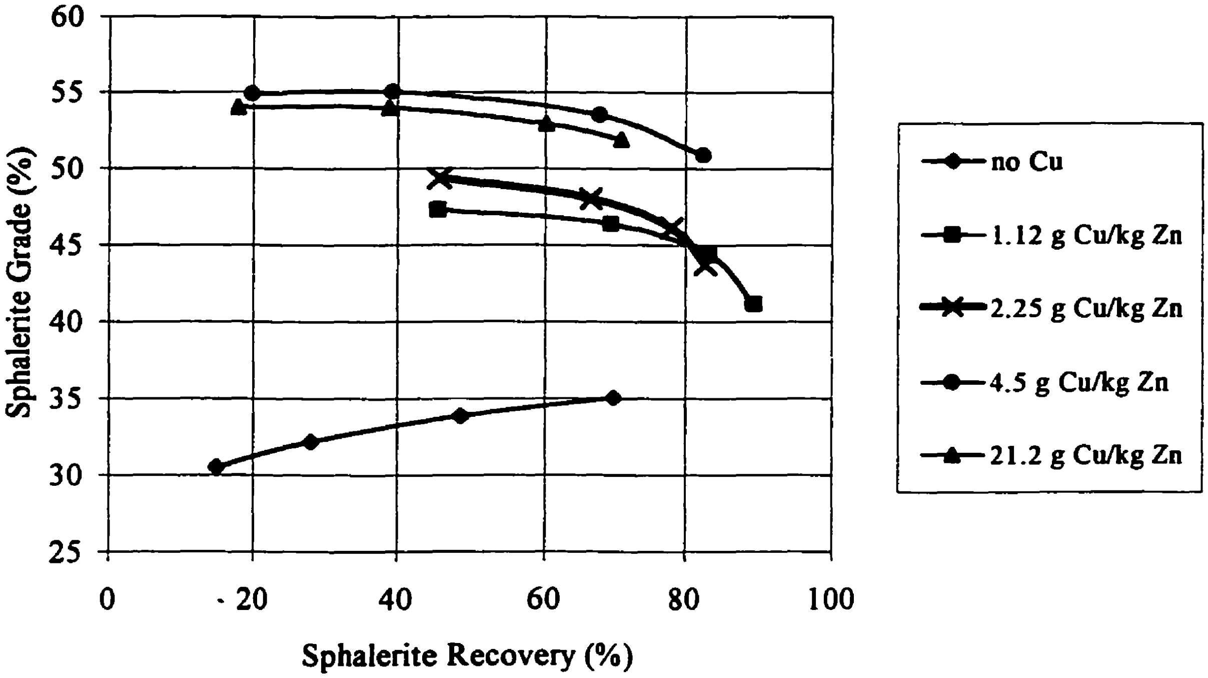

Figure 4.10: Sphalerite Grade vs. Recovery Curves for Different Copper Dosages at pH 6-6.7 for Red Dog Ore

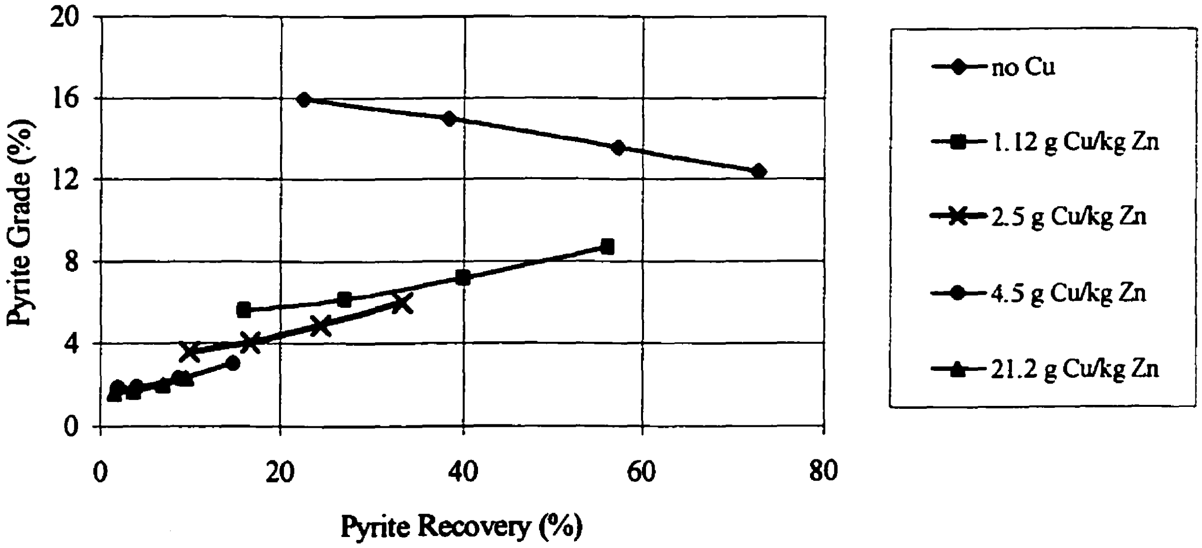

Figure 4.11: Pyrite Grade vs. Recovery Curves for Different Copper Dosages at pH 6-6.7 for Red Dog Ore

The results in Figures 4.10 and 4.11 show that the addition of copper ions improved sphalerite grade and decreased pyrite grade. At high copper dosage the Sp grade increased to 55% as compared to 35% for the no copper test. Pyrite grade was highest when no copper was added (cumulative grade ca. 13%). Pyrite grade decreased to less than 4% with the addition of 4.5 g Cu/kg Zn.

For interest, Figure 4.12 shows the effect of copper ions on sphalerite-galena selectivity. The figure shows that the addition of copper ions also improved flotation selectivity against galena. At 70% Sp recovery, the galena recovery decreased progressively with increased copper dosage from ca. 26% to ca. 12%.

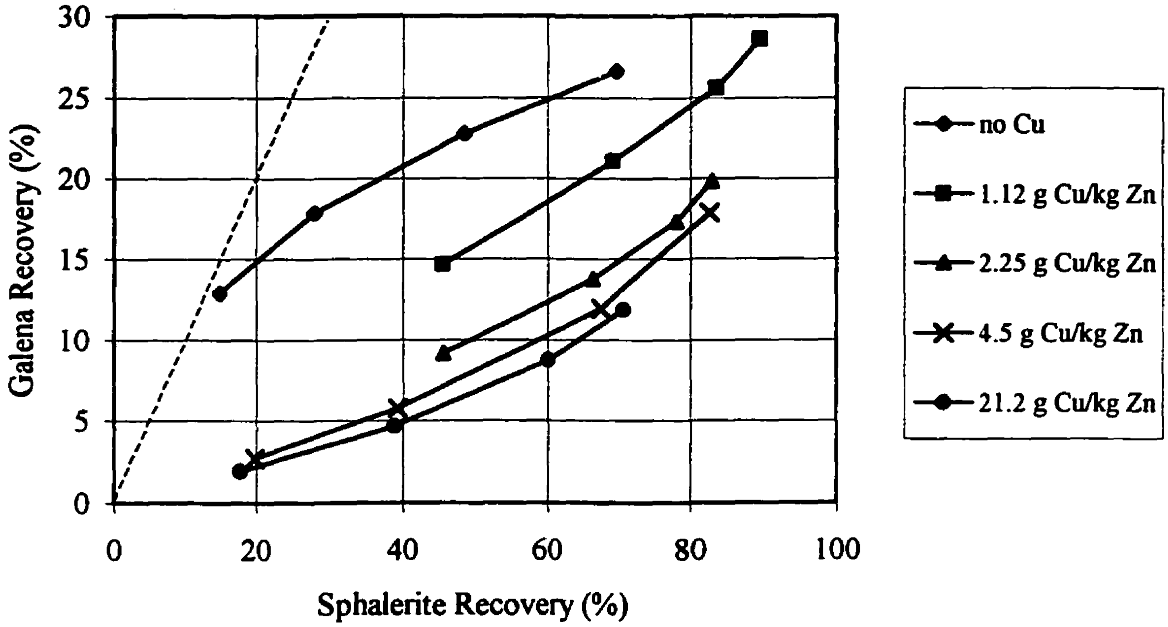

Figure 4.12: Effect of Copper Dosage on Sphalerite-Galena Selectivity at pH 6-6.7 for Red Dog Ore. Note: the dashed line represents the "no separation" line.

b) Staged Addition of Copper

Tests with staged addition of copper were performed to investigate flotation behaviour when the ratio of sphalerite to pyrite was low. At the start of the float, the sphalerite to pyrite ratio was about 3:1 while towards the end of the float the ratio approached 1:2. Figure 4.13 shows the results for the baseline test (2.25 g Cu/kg Zn) and for the staged addition of copper after 2 minutes (2.25 + 2.6 g Cu/kg Zn) and 4 minutes (2.25 + 5.3 g Cu/kg Zn) of flotation.

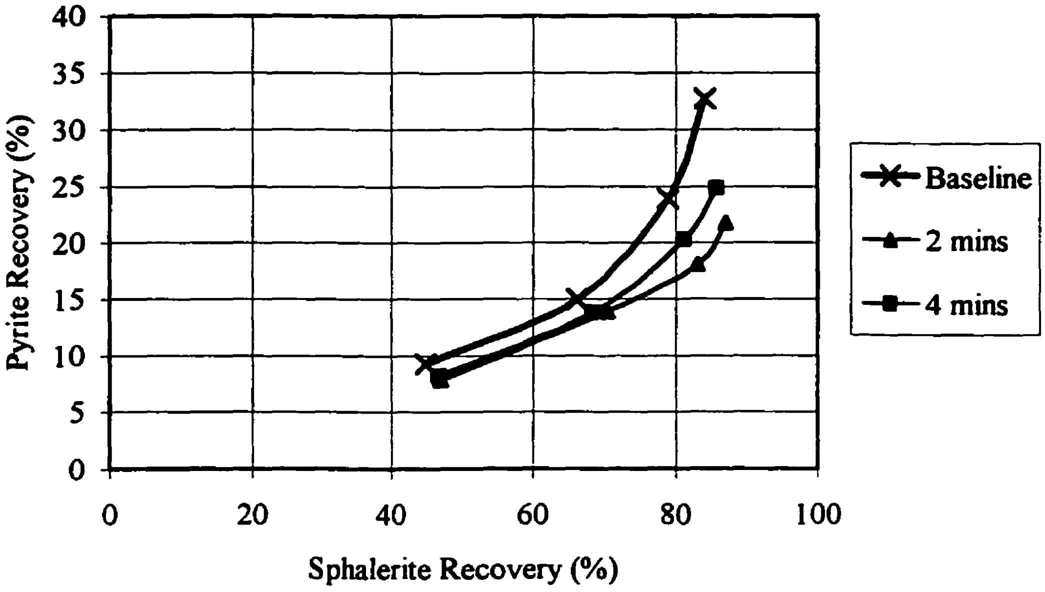

Figure 4.13: Effect of Staged Addition of Copper Sulphate on Py-Sp Selectivity at pH 6.7 for Red Dog Ore

The stage addition of copper resulted in a further decrease in pyrite recovery and enhanced pyrite-sphalerite selectivity.

Figure 4.14 shows the sphalerite grade versus recovery curves for the staged addition of copper.

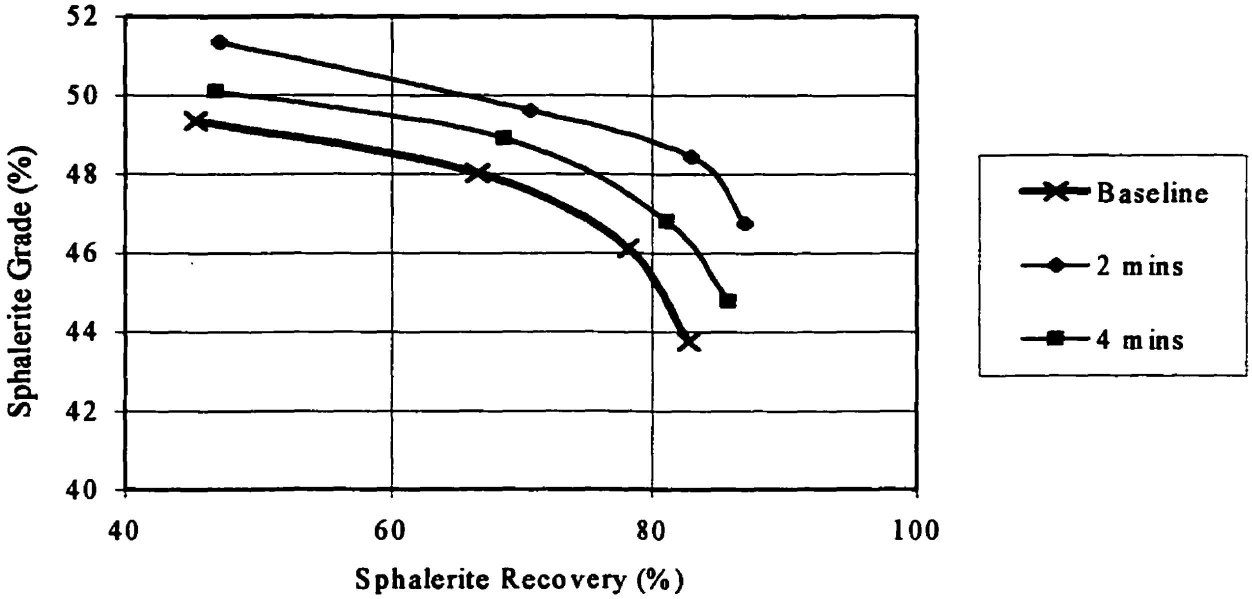

Figure 4.14: Sp Grade vs. Recovery Curves for Staged Addition of Cu at pH 6.7 for Red Dog Ore

Figure 4.15 shows that pyrite grade versus recovery curves for staged addition of copper.

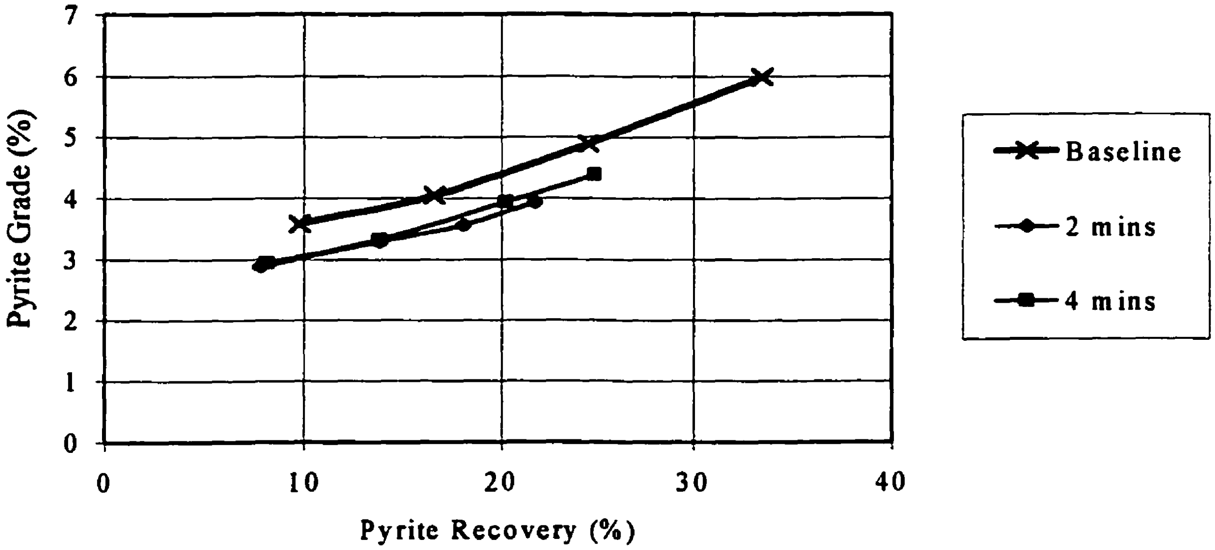

Figure 4.15: Pyrite Grade vs. Recovery Curves for Staged Addition of Cu at pH 6.7 for Red Dog Ore

Figures 4.14 and 4.15 show that staged addition of copper later in the zinc rougher float resulted in an increase in Sp grade and a decrease in Py grade.

c) Effect of Copper Conditioning Potential

Figure 4.16 shows the flotation results obtained for different copper conditioning potentials. Activation at potentials lower than the baseline resulted in a decrease in Py recovery, while an increase in potential to 300 mV resulted in improved selectivity.

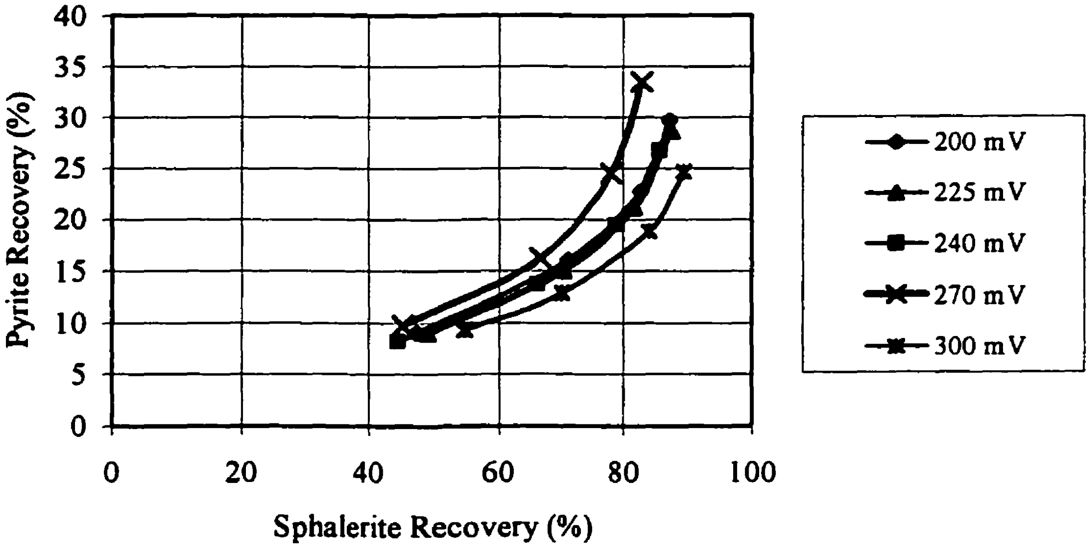

Figure 4.16: Effect of Conditioning Potential on Py-Sp Selectivity at pH 6.7 for Red Dog Ore

4.3 Continuous In-plant Minicell Tests

4.3.1 Plant Trial I

Figure 4.17 shows the cumulative pyrite recovery as a function of cumulative sphalerite recovery. Each point represents an independent test performed for different flotation retention times.

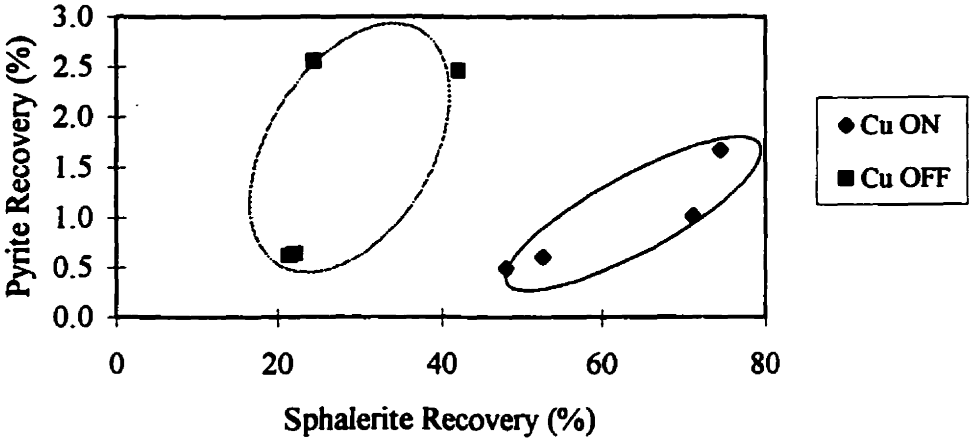

Figure 4.17: Effect of Cu Addition (6.8 g Cu/kg Zn) on Py-Sp Selectivity in Minicell Tests, Plant Trial I, Louvicourt Mine

The sphalerite-pyrite selectivity curve in Figure 4.17 shows that mineral separation is improved by the addition of copper sulphate. The increase in sphalerite recovery is evident but any decrease in pyrite recovery is not conclusive.

Figures 4.18 and 4.19 show the grade versus recovery curves for sphalerite and pyrite respectively.

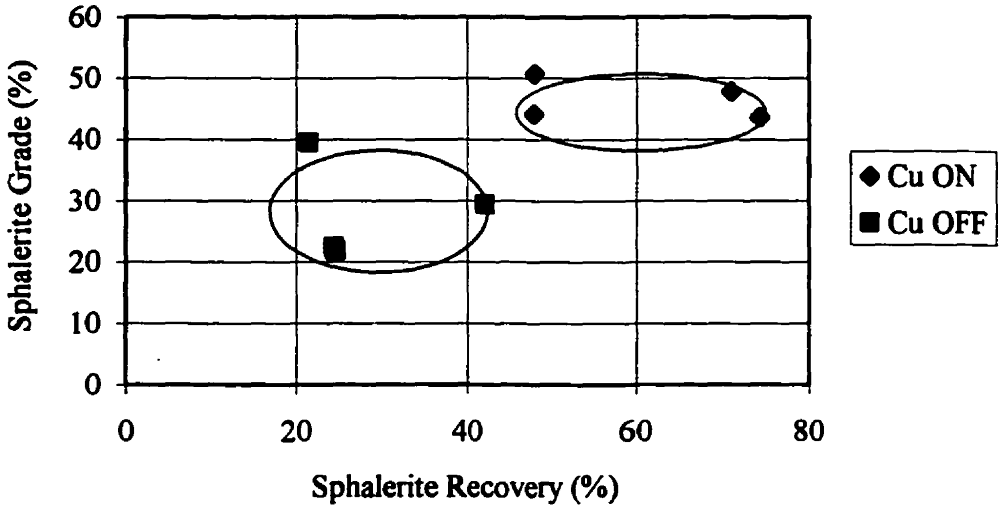

Figure 4.18: Sphalerite Grade vs. Recovery Curves for Copper On/Off Tests in Continuous Minicell Tests, Plant Trial I, Louvicourt Mine

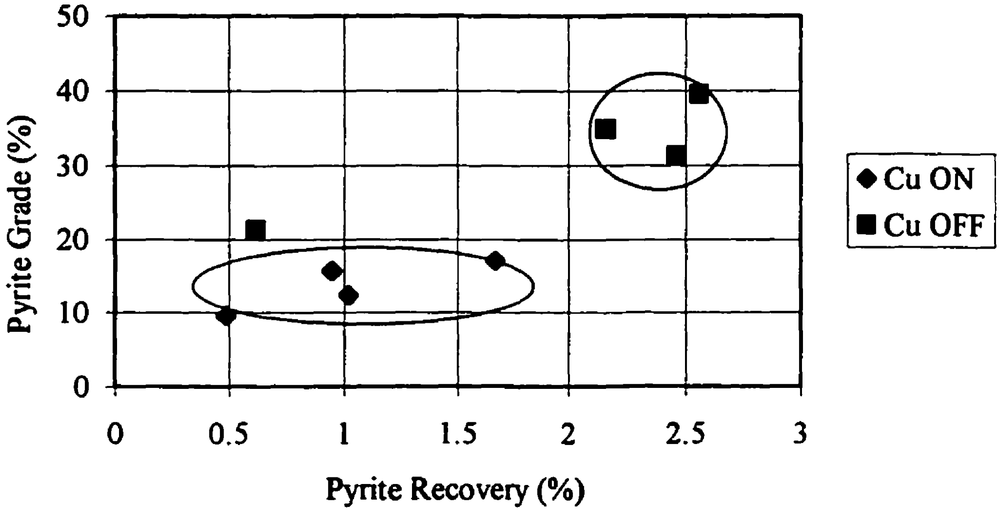

Figure 4.19: Pyrite Grade vs. Recovery Curves for Copper On/Off Tests in Continuous Minicell Tests, Plant Trial I, Louvicourt Mine

Figures 4.18 and 4.19 indicate that the addition of copper ions resulted in an increase in Sp grade and a decrease in Py grade, respectively. The pyrite recoveries were low with or without copper sulphate most likely due to the high operating pH.

4.3.2 Plant Trial II

Tests for the second plant trial were run at lower pH (9.7-9.9) than typical plant conditions (pH 11) in order that the effect of the copper ions would not be masked by the depressant effect of high pH (see Figure 4.1). Different copper sulphate concentrations were investigated with the results given in Figure 4.20.

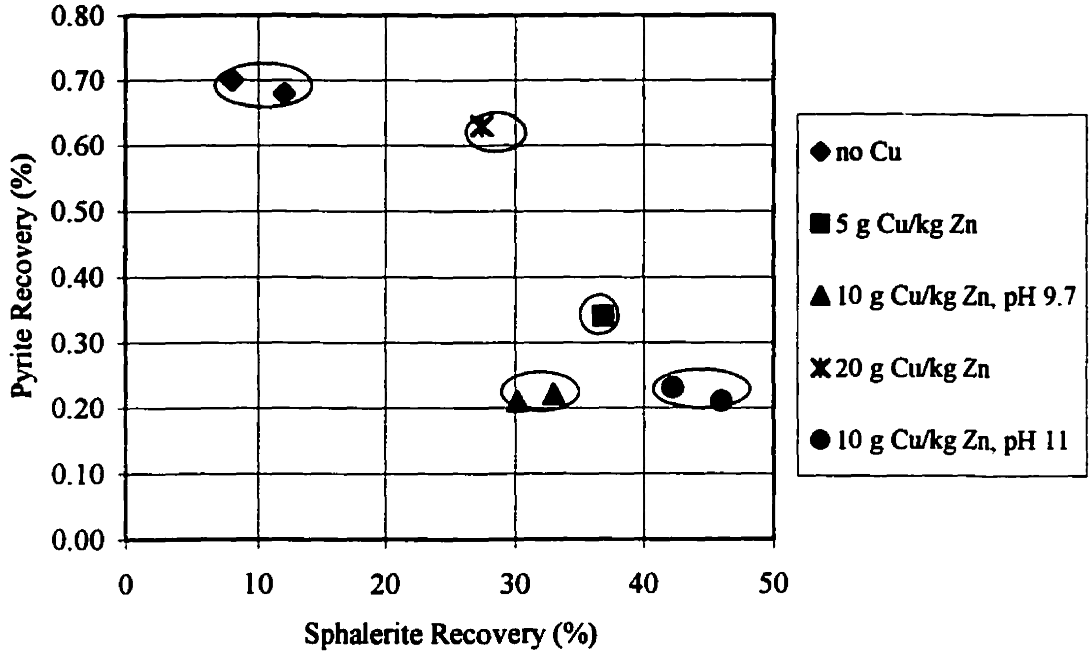

Figure 4.20: Effect of Copper Dosage at pH 9.7-9.9 on Py-Sp Selectivity in Continuous Minicell Tests, Plant Trial II, Louvicourt Mine

The figure shows that the addition of copper sulphate improved mineral selectivity by a combination of increased Sp recovery and decreased Py recovery. At low copper addition (5 g Cu/kg Zn) Py recovery decreased by about half as compared to tests run without copper addition. The middle copper dosage (10 g Cu/kg Zn) yielded a further decrease in Py recovery while high copper (20 g Cu/kg Zn) resulted in an increase in Py recovery. Plant conditions (10 g Cu/kg Zn and pH 11) were also tested. The results show that Py recovery did not change as compared to the 10 g Cu/kg Zn test (pH 9.7). However high pH did improve Sp recovery significantly in accordance with the batch test results, Figure 4.8.

Figures 4.21 and 4.22 show the grade versus recovery curves for plant trial II for sphalerite and pyrite, respectively. The Sp grade (Figure 4.21) increased with the addition of copper up to 25 g Cu/t Zn. An excess of copper (20 g Cu/kg Zn) resulted in a decrease in Sp grade as compared to results for 5 g/t and 10 g Cu/kg Zn. Plant conditions (10 g Cu/kg Zn, pH 11) yielded the best grade-recovery curve, although results for low and mid copper dosages (5 g/t Cu and 10 g Cu/kg Zn, pH 9.7) were comparable. Figure 4.22 shows that the addition of copper resulted in a decrease in Py grade. Plant conditions yielded the same result as the mid copper test at pH 9.7. These results suggest that high pH may not be required for the depression of Py at Louvicourt Mine.

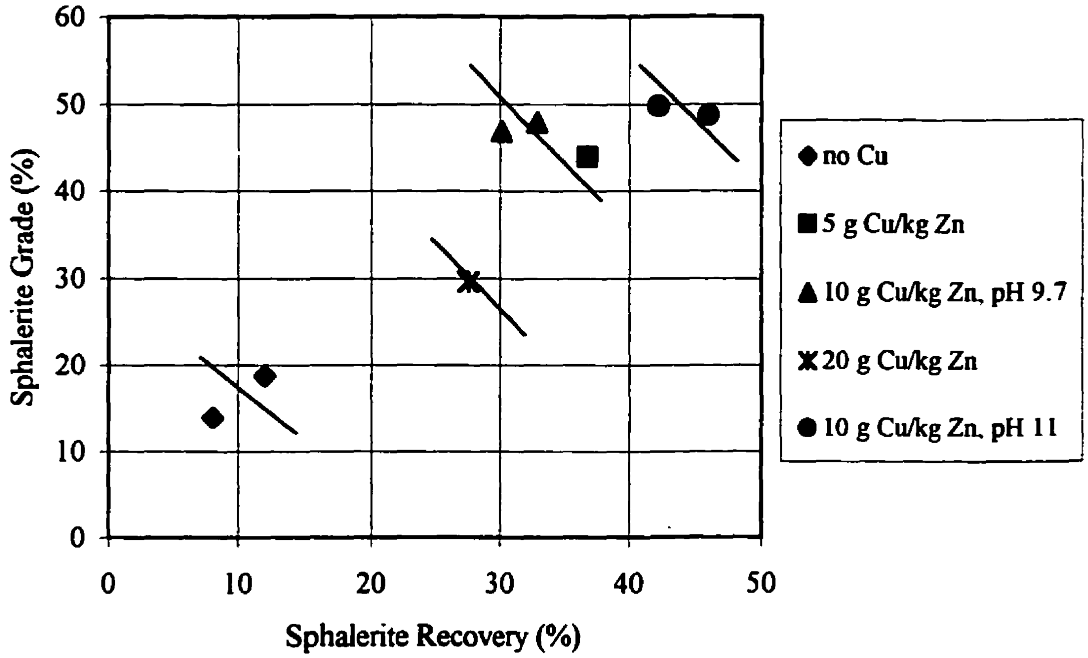

Figure 4.21: Effect of Copper Dosage at pH 9.7-9.9 on Sphalerite Grade vs. Recovery in Continuous Minicell Tests, Plant Trial II, Louvicourt Mine

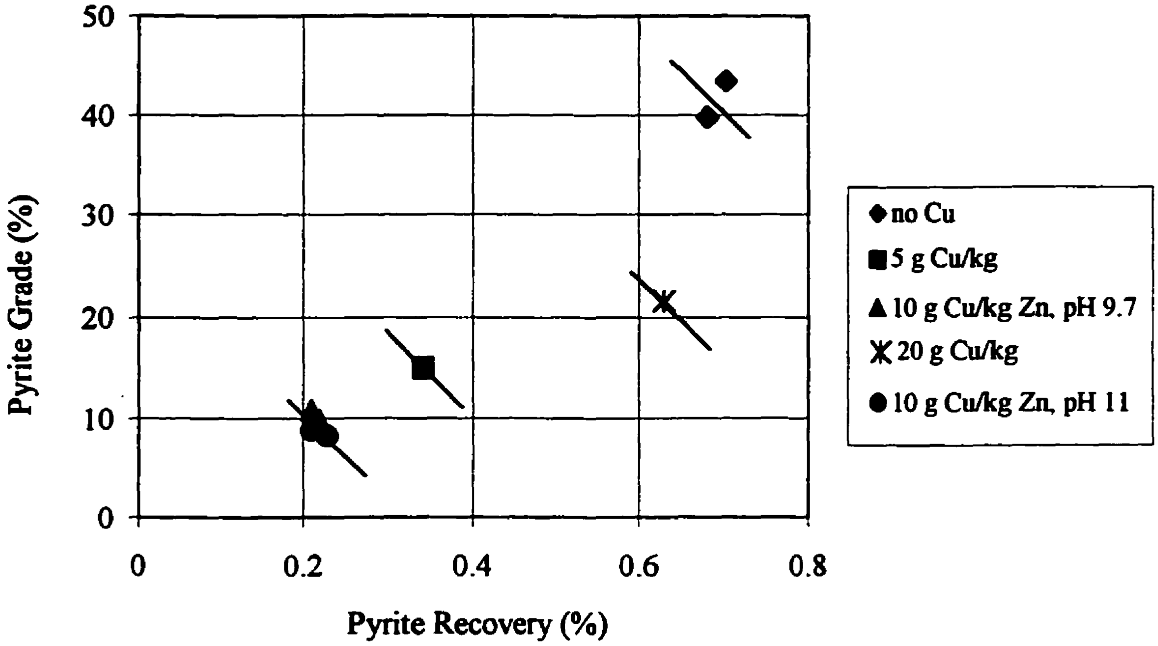

Figure 4.22: Effect of Copper Dosage at pH 9.7-9.9 on Pyrite Grade vs. Recovery in Continuous Minicell Tests, Plant Trial II, Louvicourt Mine

CHAPTER 5

DISCUSSION

Microflotation, laboratory batch, and in-plant continuous minicell tests were performed to compare the effect of copper ions on sphalerite and pyrite flotation. From the literature and the results presented here, the evidence shows that copper ions make the Py less likely to float when Sp is also present. Microflotation tests (Figure 4.1) show that pyrite recovery increased with addition of copper ions in the pH range of 5-10 when alone, but decreased when sphalerite was also present. The batch flotation results on Red Dog ore (Figure 4.9) support this Py depression effect. The second series of continuous tests at Louvicourt Mine (Figure 4.20) show the same trend and indicate that with excess copper pyrite recovery can increase. The continuous test results are less emphatic since Py recoveries are very low.

There appear to be three main mechanisms for the combined action of copper ions and sphalerite in depressing pyrite. Firstly, there is competition for xanthate which shifts in favour of Sp over Py upon addition of copper ions, which preferentially adsorb on Sp. Secondly, at alkaline pH there may be copper-hydroxide species forming on the Py surface which renders it hydrophilic. Thirdly, galvanic interactions between Sp and Py, possibly enhanced by the addition of copper ions, favour oxygen reduction on the Py surface and formation of hydrophilic hydroxide species while xanthate adsorption, the oxidation reaction in the couple, would be favoured on the Sp surface. The competition mechanism is considered to be a significant cause of reduced Py floatability.

5.1 Microflotation

The effect of copper ions and the presence of sphalerite on pyrite flotation recovery can be seen in Figure 4.1. This work extends that of Zhang et al. [1997] in that the minerals were in physical contact as well as simply sharing solution. The literature shows that fundamental studies on single sulphide minerals can be misleading since effects such as galvanic coupling between contacting minerals are excluded. In order for galvanic interactions to occur the minerals must be in physical contact. Galvanic coupling between a noble (e.g. Py) and a less noble sulphide mineral can result in a significant decrease in the floatability of the noble mineral. The interactions enhance the formation of a hydrophilic metal hydroxide film on the noble mineral thus decreasing its floatability [Nakazawa and Iwasaki, 1986; Yelloji et al., 1989]. These results emphasize that it is important to study mixed sulphide systems with the minerals in direct contact.

The addition of copper increased pyrite recovery when the mineral was alone, particularly in the moderately alkaline pH range, 7-10. When sphalerite was also present, however, pyrite recovery decreased over this pH range. At pH 11 the presence of copper ions and Sp had no significant effect. These results are essentially the same as those reported by Zhang et al. [1994]. It is likely that at high pH the pyrite is already strongly depressed thus making it difficult to observe any additional "depressant" effect of copper ions. It should also be noted that there was a region of depression at ca. pH 7 which is characteristic of Py. This dip in recovery, as noted, may be due to the formation of hydroxyl ferric xanthates which render the mineral only slightly hydrophobic [Wang et al., 1989; Hanson and Fuerstenau, 1993].

The effect of copper ions on Sp flotation in the presence of Py was also studied. Sphalerite recovery as a function of pH for the mineral alone, sharing solution, and in direct contact with Py is shown in Figure 4.2. The sphalerite sample clearly shows evidence of strong collectorless flotation. This may be related to oxidation of the lattice sulphide which could lead to the formation of a metal-deficient layer, polysulphides, or even elemental sulphur on the surface which renders the mineral hydrophobic [Buckley et al., 1986; Kartio et al., 1996]. Collectorless floatability is also enhanced by the presence of copper or iron in the Sp lattice [Hayes and Ralston, 1988]. The main conclusion from Figure 4.1 relevant to the present work was that the presence of pyrite had no significant influence on sphalerite recovery.

The results so far show that there is competition between the minerals for copper ions and/or collector. It is possible that the minerals may compete first for copper ions, then once the more competitive mineral is copper-activated xanthate would preferentially adsorb on this mineral surface. In the case of sphalerite and pyrite, Figures 4.1 and 4.2 reveal that Sp is the more competitive mineral.

A two-level reagent experimental design was used to try to elucidate whether the minerals compete for the copper and/or the collector. Figure 4.3 shows the Py recovery for the four reagent schemes. The low copper:high xanthate test showed a marked decrease in pyrite recovery in the presence of Sp. This result implies competition for copper ions. The high copper:high xanthate test showed that the Py recovery remained high in the presence of Sp. Competition between the minerals was not observed, perhaps because there was sufficient copper and xanthate available to activate and float the Py after Sp uptake needs were satisfied. The high copper:low xanthate test showed a decrease in Py recovery in the presence of Sp. This result suggests that the minerals also compete for the xanthate collector. The low copper:low xanthate test yielded low pyrite recovery and no detectable effect from the presence of sphalerite. It appears that this competition favours sphalerite when there is a shortage of either copper ions or collector, and this competition is not evident when both reagents are restricted or in excess.

Metal ion extraction using EDTA was performed as a direct test of whether the presence of sphalerite influenced the amount of copper on pyrite. Figure 4.4 showed the amount of copper extracted from the pyrite surface decreased when in contact with sphalerite, but that there was still some copper on the pyrite surface. It was hypothesized that even this copper would migrate to the sphalerite given enough time. Figure 4.5 shows that an increase in contact time did further decrease the amount of extractable copper from the pyrite. This result supports the notion of copper migration from pyrite to sphalerite. This fits a model of physical adsorption of copper on Py where EDTA can readily solubilize it, while on sphalerite the copper exchanges with zinc in the lattice and is no longer available to the EDTA. In this sense the sphalerite acts as a "copper sink": contact between the minerals results in a net transfer of copper from the pyrite to the sphalerite surface. This observation corresponds to results found from EDTA extraction surveys on plant sphalerite-containing streams which indicate that EDTA-extractable copper is very low [Kant et al., 1994; Shannon and Trahar, 1994]. Some copper remained EDTA-extractable which could indicate that sphalerite sites are filled before the supply of copper from pyrite is exhausted, or that there is a certain amount of EDTA-extractable copper available resulting from the copper detected in the pyrite lattice.

X-ray photoelectron spectroscopy (XPS) was employed to try to confirm if copper preferentially adsorbed on Sp when it was present with Py. Figures 4.6 and 4.7 showed the percentage of surface coverage by copper for pyrite and sphalerite, respectively. The amount of copper decreased on the pyrite surface and conversely increased substantially on the sphalerite surface when the minerals were in contact as compared to the minerals sharing solution. These results support the migration hypothesis and show that the copper is preferentially adsorbed on sphalerite when the minerals are in contact.

5.2 Bench Flotation Tests

To this point the experiments have been micro scale tests on mineral samples. Bench scale flotation tests on Louvicourt and Red Dog ore were conducted next to determine if the depressant action of copper on Py could also be detected for a real ore.

Louvicourt Ore

Batch tests on Louvicourt ore showed that plant operating conditions yielded the best selectivity against pyrite. A two-level reagent design was used with the pH allowed to drift.An increase in copper concentration resulted in a subsequent decrease in pH. The results (Figure 4.8) show that tests run with low copper concentration (pH 9.7) resulted in better pyrite-sphalerite selectivity than the high copper tests (pH 9.1). This contradicts previous findings which showed enhanced selectivity with addition of copper ions. However, the improved selectivity at low copper concentration may be linked to the higher operating pH. High pH appears to affect Sp flotation rate, a known effect at this operation [Cayouette, 2000].

Red Dog Ore

The effect of copper on Py and Sp flotation was much more significant for Red Dog ore than for Louvicourt ore. In the absence of copper, Figure 4.9 showed that the mineral recovery relationship is approximately 1:1 with sphalerite and pyrite recovery reaching about 70%. (In the case of Sp this also corresponds to the high recovery observed without copper activation in the microflotation tests.) This result is of the order observed for Kidd Creek [Xu et al., 1992, Figure 2.6]. This high recovery may be related to superficial sphalerite oxidation leading to the formation of a metal-deficient surface, elemental sulphur, or polysulphides all of which are hydrophobic, or it could reflect accidental activation by lead ions or other special local circumstances.

Sutherland and Wark [1955] showed that high Sp recoveries could be obtained at ca. pH 6.5 with the use of amyl xanthate collectors. The collector used for the zinc rougher float at Red Dog is potassium amyl xanthate (PAX) and flotation pH is about 6.5-7. Furthermore, Sp recovery without copper activation is highest in the pH range 4-8 [Fuerstenau et al., 1974]. Good sphalerite floatability without the addition of copper, notably in the case of lead-zinc ores, is sometimes observed and is usually attributed to accidental activation by heavy metal cations (lead in particular) [Ralston and Healy, 1980; Kim et al., 1995]. Lead-activated Sp will float with ethyl xanthate between pH of 4-9 [Trahar et al., 1997]. Popov et al. [1989] showed that lead ions enhanced the natural floatability of Sp and improved its flotation with xanthate addition as compared to flotation without lead activation.

The presence of iron ions, either from the grinding media, in the Sp lattice, or from the ore itself (pyrite and pyrrhotite) may also have an effect. Sphalerite samples with high iron content showed higher floatability than samples with low iron content at pH 3-7 [Mukherjee and Sen, 1976]. Batch tests suggested that ferrous ions could be responsible for Sp flotation in the absence of copper ions over a limited pH range of 8-10 [Leroux et al., 1987].

The addition of copper significantly altered the result for Red Dog ore, there being a modest increase in maximum sphalerite recovery but a marked decrease in pyrite recovery as copper dosage is increased. The selectivity at 2.25 g Cu/kg Zn (the standard baseline addition rate), 4.5 g Cu/kg Zn, and 21.2 g Cu/kg Zn is excellent as compared to the no copper test. The grade versus recovery curves for sphalerite and pyrite showed an increase in Sp grade and a decrease in Py grade with the addition of copper ions. The improvement in Sp grade may also be linked to a decrease in galena recovery (Figure 4.12).

The Py-Sp selectivity curve shows a significant decrease in Py recovery and only a modest increase in Sp recovery upon addition of copper ions. This result indicates that the depressant effect on Py is not simply a competitive mechanism, otherwise the decrease in Py recovery would naturally be associated with an increase in Sp recovery. It suggests that the competitive effect may be combined with a direct depression of Py. Galvanic coupling may be enhancing the competition between Py and Sp in favour of Sp and directly depressing Py through the formation of hydrophilic hydroxides.

These results suggest competition for copper ions and xanthate occurs at Red Dog. Pyrite recovery is high when copper ions are not present since pyrite and non-activated sphalerite compete equally well for the xanthate collector. However, once Sp is activated, xanthate preferentially adsorbs onto sphalerite which has the effect of depressing the pyrite.

Staged addition experiments were performed to test the competitive effect at a point in the flotation process where there would be more Py present than Sp. If the competitive mechanism is valid, then at the start of the zinc rougher float (Sp:Py ratio ca. 3:1) the addition of copper ions will result in lower Py floatability. Towards the end of the float the Sp:Py ratio is about 1:2 therefore the addition of copper at this stage could result in activation of Py assuming the Sp copper consumption needs have been satisfied.

Figure 4.13 shows that staged addition of copper resulted in a further decrease in Py recovery contrary to what was expected. However, there may still be sufficient sphalerite present to consume the copper activator and retard Py flotation. Sphalerite continues to "win" the competition and even staged addition of copper makes the Py less likely to float. Staged addition after 4 minutes of flotation resulted in a slight increase in Py recovery as compared to staged addition after 2 minutes. This result may indicate that the Py is becoming more floatable after further Sp has been removed. It is also possible that the copper dosages were not sufficient to satisfy Sp needs and have enough residual copper to activate the Py. Microflotation tests also showed that even with a high copper dosage, a shortage of xanthate would still result in reduced pyrite recovery in the presence of sphalerite (Figure 4.3). There is a need to define a critical copper dosage for Py activation as a function of sphalerite to pyrite ratio, and a critical collector dosage.

Literature has shown that the conditioning potential can have a significant effect on copper uptake on sphalerite and pyrite. Single mineral studies have indicated that conditioning under mildly reducing potentials led to enhanced copper uptake on Sp and Py while oxidizing conditions inhibited copper adsorption [Yoon et al., 1995; Woods and Richardson, 1986].

Different conditioning potentials were studied to try to determine which maximized sphalerite-pyrite selectivity for the Red Dog ore. Figure 4.16 shows activation at potentials lower than the baseline resulted in a decrease in Py recovery. It may be possible that reducing conditions favour copper activation of sphalerite when in the presence of pyrite. Thus at lower potentials there is preferential adsorption of copper on Sp such that Sp flotation is enhanced and Py recovery decreased. However, this is speculative at the moment.

Figure 4.16 also shows that an increase in potential to 300 mV resulted in improved selectivity. Activation at 300 mV yielded a significant decrease in Py recovery, most likely due to the formation of hydrophilic hydroxide species on the Py surface. Oxidizing conditions drive the galvanic interaction between the minerals such that the reduction of oxygen to hydroxide ions is enhanced when the conditioning is performed at anodic potentials with respect to the open circuit potential. In these experiments, the potential was only controlled during the copper activation stage. Flotation should also be performed at controlled potential in order to observe galvanic effects during the float.

5.3 Continuous In-plant Minicell Tests

The batch flotation, particularly the Red Dog results, confirm the microflotation findings and clearly show that the addition of copper ions improves mineral selectivity not only by increasing sphalerite recovery but also by decreasing pyrite recovery. The next step involved continuous, in-plant test work to determine if similar results could be obtained when under plant operating conditions.

The results from the first plant trial showed an improvement in mineral separation upon addition of copper sulphate. The increase in sphalerite recovery was significant while the decrease in pyrite recovery was modest (ca. 1.5%) thus mineral selectivity improved mainly due to a higher sphalerite recovery. The pyrite recoveries were low with or without copper sulphate, initially attributed to the high operating pH. However, after reviewing all the results it appears that differences in the type of Py in the ore may lead to substantial variations in response. The plant trials at Louvicourt Mine (Figures 4.17 and 4.20) yielded low Py recoveries (less than 1%) while bench tests on Red Dog ore (Figure 4.9) and literature results from a plant trial at Kidd Creek (Figure 2.6) showed significant Py recoveries (greater than 50%), implying that Py from different ores can exhibit various flotation responses. A significant portion of the iron sulphide from the Red Dog ore is marcasitic, which oxidizes to elemental sulphur and is likely more floatable than pyrite [Fairweather, 2000]. Other factors such as liberation, degree of oxidation and types of impurities may also contribute to this variable response.

To avoid the overall depressant effect on Py at high pH, the second plant trial was conducted at lower pH (9.7-9.9) than typical plant conditions (pH 11). Plant trial 2 investigated several copper addition rates. The results (Figure 4.20) showed that a moderate addition of copper decreased Py recovery. These results indicate that mineral competition for copper ions and xanthate occurs in a plant environment. High copper dosage resulted in approximately the same Py recovery as the no copper test. This suggests that an excess of copper, after satisfying the Sp demand, can also activate Py.

The test performed at mid copper dosage and pH 11 (plant conditions) yielded the same pyrite recovery as the test performed at mid copper dosage and pH 9.7. This result suggests that high pH is not required for the depression of Py at Louvicourt Mine. However high pH did improve Sp recovery significantly (effectively due to an increase in flotation rate as retention time was fixed), an effect known at this operation and alluded to in the discussion of batch flotation work (Figure 4.12).

5.4 Implications for Flotation

Results from the three levels of flotation testing (micro, batch and continuous) confirm the depression of Py in the presence of Sp after copper activation. Zhang et al. (1997) considered this was due to competition for xanthate favouring Sp and essentially starving the Py of collector. The evidence here supports this. In addition, evidence is provided for competition for copper ions also favouring Sp thus reducing the potential for accidental Py activation.

Zhang et al. also speculated on galvanic effects but did not pursue this idea since the minerals were not in direct contact. Sphalerite is electrochemically more active after copper activation. In galvanic contact with Py, which has a higher rest potential than copper-activated sphalerite [Rand, 1977], xanthate adsorption (i.e., the anodic or oxidation reaction in the electrochemical couple) is promoted on the copper activated Sp while the cathodic reaction, oxygen reduction to hydroxide ions, shifts to the Py surface. This mechanism not only provides for reduced xanthate adsorption on the Py – in common with the notion of competition as discussed above – but also provides for creation of hydrophilic OH^- sites on the Py, i.e., a direct form of depression.

Another form of direct depression of Py could be the formation of hydrophilic copper hydroxide species on the Py surface when copper activation is done at alkaline pH [Heyes, 1999].

Understanding the mechanism should lead to its exploitation in flotation practice. Some implications are already worth considering. The decrease in Py recovery upon addition of copper ions raises a question regarding the role of pH as a Py depressant. Lime addition to increase pH could be done "down the bank" rather than at the head. After most of the Sp has been removed, it is possible that competition is reduced sufficiently such that residual copper and xanthate will promote Py flotation. Raising the pH to compensate for this when required, rather than at the head of the bank where it is not initially needed, may be beneficial. Separating in space and time the copper and pH functions may increase selectivity and achieve overall reagent savings (copper sulphate, xanthate, and lime).

The notion that excess copper can activate Py was tested. An effect was apparently detected at Louvicourt Mine (Figure 4.20) but was not observed in the case of Red Dog ore (Figure 4.9). The experiments were designed to have a similar copper dosage on a per kilogram of zinc basis (ca. 20 g Cu/kg Zn) but in the case of Red Dog ore an excess copper condition was not met. The microflotation data from the reagent combination tests (Figure 4.3) suggests that excess copper is not enough to activate Py when there is a shortage of collector. Therefore it is possible to have a high copper dosage and still not recover the Py when the collector conditions are close to the minimum required for Sp flotation. A further consideration is the impact of particle size. A more scientific estimate of "excess copper" would be on a per unit area of Sp basis. At this juncture there is insufficient data to compute this quantity.

The results here have shown that while the copper depression effect is common, the extent of pyrite flotation response is highly variable. In the case of Kidd Creek and Red Dog the Py was quite floatable, but at Louvicourt Py recovery was very low. The difference would be worth investigating. The origins may be in the type of Py (e.g., the nature of its impurities, liberation, degree of oxidation, surface contaminants such as copper and lead derived from the environment), and the reagents being used.

CHAPTER 6

CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

6.1 Conclusions

6.1.1 Microflotation and Surface Analysis

1. Pyrite recovery increased upon addition of copper ions when alone, but decreased when sphalerite was also present over the pH range 6-9.5. This effect was stronger when the two minerals were in direct contact as compared to sharing solution. The depressant effect was strongest at pH 8 while at pH 11 it did not appear to be significant.

2. Competition between the minerals appeared to take place when there was a shortage of either copper activator or xanthate collector. This competition was not evident when both reagents were in excess.

3. Surface analysis showed that the amount of copper on the pyrite surface decreased in the presence of sphalerite (EDTA extraction) and that the amount of copper on sphalerite increased when in contact with pyrite (XPS). These results support the hypothesis that copper is preferentially adsorbed on sphalerite when the minerals are together.

6.1.2 Bench Flotation Tests

1. Sphalerite recovery increased and pyrite recovery decreased with increased pH (Louvicourt ore).

2. The addition of copper sulphate dramatically improved mineral selectivity, primarily by reducing pyrite recovery (Red Dog ore). The stage addition of copper also resulted in a further decrease in pyrite recovery and enhanced selectivity.

3. Copper conditioning at oxidizing potential yielded the best selectivity against pyrite.

6.1.3 Continuous In-plant Minicell Tests

1. Plant Trial I (Louvicourt Mine) showed that mineral separation was improved by the addition of copper sulphate. The increase in sphalerite recovery was clear, but any decrease in pyrite recovery was debatable, possibly due to the high flotation pH of 11.

2. Plant Trial II (Louvicourt Mine) indicated that the addition of copper sulphate at pH 9.7-9.9 improved mineral selectivity by a combination of increased sphalerite recovery and decreased pyrite recovery. High pH (11 vs. 9.7) improved sphalerite recovery significantly in accordance with the bench test results.

6.2 Suggestions for Future Work

1. There is a need to understand the mechanism that is responsible for the mineral competition that has been observed here. It is possible that galvanic coupling drives this competitive effect. Tests should be done to determine if galvanic interactions are contributing to the reduced recovery of pyrite in the presence of copper and sphalerite. Electrochemical techniques such as the manipulation of pulp potential during flotation (by nitrogen bubbling or addition of oxidizing agents such as peroxide) or cyclic voltammetry can be used to examine this, and possibly find means to control the mineral competition and improve selectivity.

2. Understanding the mechanism should lead to its exploitation in flotation practice. It may be possible to take advantage of the natural competition and rely on the high Sp:Py ratio at the head of the bank of a zinc flotation process to promote Py depression, and only raise the pH further down the bank where the Sp content is low. In-plant tests should be done "down-the-bank" to investigate this hypothesis.

3. A more scientific estimate of "excess" copper dosage needs to be defined not only in terms of grams per tonne, but also on a per unit area basis. Sphalerite to pyrite ratio may also influence excess copper conditions.

4. An investigation should be done to study the highly variable pyrite flotation response of the Kidd Creek and Red Dog ores versus Louvicourt ore. It may be caused by factors such as the type of lattice impurities in pyrite, surface contaminants, liberation, degree of oxidation, process water, or the reagent scheme being used.

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