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Modulation of Selectivity between Copper and Zinc Minerals  
Using Electrochemical Potential of the Pulp

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Faculty of Graduate Studies and Research  
in partial fulfilment of the requirements for the degree of  
Doctor of Philosophy

Department of Mining and Metallurgical Engineering  
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## ABSTRACT

Electrochemical effects occurring in the processing of the A-1 zone copper-zinc-silver-pyrite ore from Les Mines Selbaie, Joutel, Québec, were investigated and correlated with the redox potentials measured in flotation pulps using a gold sensing electrode. On-line pulp potential measurements at the head of the copper flotation circuit were performed over a period of nearly one year. Windows of selectivity between the copper and zinc minerals were observed but the leading edge, and the width of the window were affected by the state of the sensor. Procedures for the verification of the state of the on-line sensor were established to ensure long term reliability of sensor. Sensitivity analysis of the pulp potential to modifiers, such as lime and sodium cyanide, suggested that these reagents could be controlled using the measured pulp potential to maintain the oxidation-reduction state of the pulp within the window of selectivity. A shorter study at the Kidd Creek concentrator indicated the presence of a window of selectivity between copper and zinc minerals but the leading edge and width of the window were different than that observed at Les Mines Selbaie. This suggests that the windows of selectivity are affected by ore and plant specific variables.

Laboratory investigations on feed pulp samples demonstrated that collectorless flotation of the copper minerals was a significant contributor to copper recovery in the A-1 zone circuit. Unfortunately, collectorless copper recovery was limited to around 60% and only a small proportion of the silver could be recovered in this fashion. The addition of collectors such as Aerophine 3418A (sodium di-isobutyl dithiophosphate) or sodium isopropyl xanthate (SIPX) was required to achieve high recoveries but the selectivity response of these two collectors was different. The selectivity obtained with SIPX could be manipulated by modulation of the pulp potential before or after introduction of the collector. However, Aerophine 3418A exhibited an irreversibility in that an oxidation of the pulp before its introduction usually lead to a decreased selectivity even if the pulp potential was reduced prior to flotation.

## RESUMÉ

Les effets électrochimiques associés au traitement du minerai cuivre-zinc-argent-pyrite de la zone A-1 de Les Mines Selbaie, Joutel, Québec, ont été étudiés et reliés au potentiel électrochimique de la pulpe de flottation mesuré avec une sonde en or. Le potentiel de pulpe a été mesuré en ligne à la tête du circuit de cuivre sur une période de près d'un an. Des fenêtres de sélectivité entre les minéraux de cuivre et de zinc ont été observées. Par contre, la largeur de la fenêtre, et son potentiel de départ étaient affectés par l'état de la sonde. Des procédures ont été établies pour la vérification de la sonde pour s'assurer de la validité des mesures. Une analyse de sensibilité du potentiel de la pulpe au taux d'addition d'agents modifiants tels que le cyanure de sodium et la chaux suggère que l'addition de ces réactifs pourraient être contrôlée par le potentiel de la pulpe. Une étude de plus courte durée au concentrateur de Kidd Creek a indiqué elle aussi la présence d'une fenêtre de sélectivité mais ses limites étaient différentes de celles observées à Les Mines Selbaie. Cela suggère que les fenêtres de sélectivité sont dépendent du type de minerai et d'opération de l'usine.

Des essais en laboratoire effectués à partir d'échantillons de pulpe de l'usine de Les Mines Selbaie ont démontré que la flottation sans collecteur contribue significativement à la récupération du cuivre dans le circuit de la zone A-1. Malheureusement, la récupération du cuivre sans collecteur était limité à 60%, et beaucoup moins pour l'argent. L'addition de collecteurs tels que l'Aerophine 3418A (Diisobutyl dithiophosphate de sodium) ou l'isopropyl xanthate de sodium (SIPX) était requise pour obtenir de hauts recouvrements mais la sélectivité obtenue était différente selon le collecteur utilisé. La sélectivité obtenue avec le SIPX pouvait être manipulée par la modulation du potentiel de la pulpe avant ou après l'introduction du collecteur. Par contre, l'Aerophine 3418A démontrait une irréversibilité: l'oxidation de la pulpe avant l'introduction du collecteur donnait une sélectivité moindre et ne pouvait pas être rétablie par la réduction du potentiel avant la flottation.

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## INTRODUCTION

Froth flotation is the most common separation process by which sulphide minerals are beneficiated from ores. The ore received from the mine is first crushed and ground to a size sufficiently fine to liberate most of the sulphide minerals from the gangue. The ground ore, combined with water to make up a pulp and conditioned with reagents, is fed to the flotation machine where the mineral particles collide with gas bubbles introduced into the pulp. The mineral particles that have been rendered hydrophobic attach to the bubbles during these collisions and rise to the froth phase floating on top of the pulp. It is this froth phase which forms the flotation concentrate. The hydrophilic particles remain in the pulp and make up the tailings.

Rare are the sulphide minerals which are inherently hydrophobic. The adsorption of a suitable collector is usually required for the mineral surface to reach this desirable state. Under certain circumstances the grinding conditions and the chemical speciation of the process water may be such that the mineral surface is induced into a hydrophobic state and no collector is required to achieve recovery.

A surface active agent, the frother, is necessary in all cases to prevent the coalescence of the gas bubbles while they are still in the slurry phase. Such coalescence reduces the surface available for attachment of the mineral particles and by consequence, the rate at which they can be recovered decreases.

Some ores have only one metal bearing sulphide mineral of value and a non-sulphide gangue, silicate and carbonate minerals being the most common (e.g. copper porphyry ores, gold bearing pyritic ores). However, most ores contain more than one metal of value and the gangue consists of barren iron sulphides (pyrite and pyrrhotite being the most common) in addition to the non-sulphide gangue. The use of suitable reagents, often referred to as modifiers, is required to selectively recover the valuable minerals into two or more marketable concentrates.

This is a simple description of the ideal flotation process. In practice, several factors jointly affect the overall efficiency of the process.

Firstly, the ore cannot be ground fine enough to fully liberate the different minerals. Until a comminution machine in which breakage of the ore preferentially occurs along the grain boundaries of the minerals is invented, there will always be a certain proportion of the particles consisting of two or more mineral phases locked together. Recent advances, notably on the use of high power electrical pulses (1), suggest that such equipment is not too far in the future. With conventional comminution equipment the proportion of locked mineral particles generally decreases with increasing fineness of comminution.

There are, unfortunately, ores for which the geological conditions leading to their formation resulted in the formation of intricate textures. Such textures often require size reduction to the order of a few micrometers so that the particles become either liberated or simple locked mineral phases.

Liberated and nearly liberated mineral particles are easier to recover than locked particles with a large proportion of gangue. Locked particles can be recovered given sufficient flotation time and an excess collector but the grade of the concentrate will suffer due to the gangue associated with them. At the extreme, an encapsulated valuable sulphide mineral grain will never be recovered by froth flotation if the surrounding gangue is a silicate mineral while there is a probability of recovery if the encapsulating gangue is also a sulphide mineral.

In practice, comminution to a size sufficient for surface exposure is performed in a primary grinding circuit for recovery in the rougher and scavenger flotation stages. Re-grinding of the scavenger concentrate, and sometimes of the rougher concentrate, to a size ensuring high liberation of the valuable minerals is performed prior to cleaning flotation to yield a final concentrate. In the case of complex sulphide ores, for example

copper-lead-zinc ores, the regrinding requirement is often that for liberation of the copper, lead, and zinc minerals from each other rather than from the gangue minerals.

Liberation is the primary condition that dictates comminution requirements but the efficiency of the flotation process is also dependent on the particle size.

The lower surface to weight ratio of coarse particles makes it difficult for such particles to remain attached to the gas bubbles during their rise to the surface of the pulp. Recovery is not possible above a certain size and the higher the specific gravity of the sulphide mineral, the smaller this limiting size.

On the other end of the size spectrum, the high surface to weight ratio of fine particles makes them extremely susceptible to hydrodynamic effects from the surrounding fluid phases. At extremely fine sizes (e.g. less than 5  $\mu\text{m}$ ), the surface state of a given particle has little bearing on its fate and it tends to follow the surrounding water; into the concentrate or into the tailing. For hydrophilic particles, this phenomenon is described as mechanical entrainment in the froth and is a contributor to concentrate dilution. For hydrophobic particles, this phenomenon leads to recovery limitation although no term has yet been defined as it has drawn little attention.

The addition of froth washing equipment to the flotation machine, whether it is a flotation column or mechanically agitated cell, reduces mechanical entrainment. Also, the design of flotation machines, which has continuously improved over the years, is stretching the lower and upper size limits for recovery of hydrophobic particles.

The type of frother used may assist the recovery of weakly hydrophobic valuable mineral particles because of their surface state or their size but at the cost of enhancing the recovery of gangue particles.

Finally, the way in which the minerals are conditioned for flotation has a great impact upon the selectivity of the process for complex sulphide ores. Most thiol based collectors require oxidising conditions to adsorb on the sulphide mineral surface; the oxidation reaction required being that of the collector or of the mineral. Many modifiers traditionally used in modulating the flotation response of the minerals affect the oxidation-reduction state of the pulp. In addition, the flotation gas which carries the mineral particle from the slurry phase to the froth phase is usually air and, as the flotation proceeds, oxidation of the sulphide minerals and the collector(s) occurs.

The mechanisms by which the xanthate family of collectors interact with sulphide minerals have been the subject of many studies simply because these collectors are the most commonly used. These investigations, and others linked to the observation of flotation without the requirement of a collector, have allowed the establishment of the governing principles of an electrochemical model for the flotation of sulphide minerals.

Other collector families, although generally more selective than the xanthates for nearly the same level of recovery, have been less thoroughly investigated. Generalization of the mechanisms demonstrated for the xanthate family can be made for such collector families but only to a certain degree as their higher selectivity results from a lower susceptibility to oxidation than the xanthates, and/or a different adsorption mechanism altogether.

The mechanism of action of many flotation modifiers is complex and poorly understood even to this day when an extensive array of surface analysis techniques is available for investigation. Furthermore, conflicting observations found in the literature do not help the practising mineral processor who has to continuously improve the efficiency of the plant in the face of ever diminishing metal prices and rising costs of manpower and supplies.

Given the plausible existence of a relationship between the flotation response of sulphide minerals and the oxidation-reduction state of the pulp, manipulation of this state via the use of reducing or oxidizing reagents, or via reduction or enrichment of the oxygen content of the flotation gas is appropriate. Such an approach, when used in the laboratory or pilot operation, yields unquestionable results. It is less practical for a concentrator. Nitrogen may be used as flotation gas when reducing conditions are necessary for the separation; the savings associated with the lowered consumption of the reducing reagent far outweighing the cost of generating, and recycling, nitrogen for flotation. However, this is the exception rather than the rule.

Another approach is to monitor the oxidation-reduction state of the pulp while the modifiers normally used to modulate the flotation response are introduced in the circuit. If a relationship can be defined and the modifier(s) most effective in altering the oxidation-reduction state of the pulp identified, then the search for the required modifier dosage(s) to maximize selectivity in the laboratory may be narrowed. Furthermore, if a similar relationship can be observed under the less controlled conditions of an operating plant, then this opens the possibility of using such measurements to appropriately manipulate the dosage of the modifiers.

## 1 Overview of the flotation process from an electrochemical viewpoint

The occurrence of oxidation-reduction phenomena in the flotation of sulphide minerals and their utilization to modulate the flotation selectivity between two or more minerals have been known for a long time. An early process, reported in the mid 1950's, described the separation of pyrite from pyrrhotite and arsenopyrite by selective oxidation of the latter minerals with potassium permanganate (2).

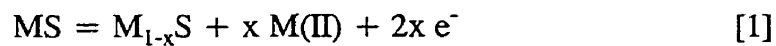
It is only since the early 1980's that advances in electrochemical and surface analysis techniques have provided the knowledge necessary to generalize ore and mineral specific observations into an electrochemical model for the flotation of sulphide minerals.

Although there are still gaps in the model, it has been found useful in explaining separation processes and operating challenges in mineral processing plants.

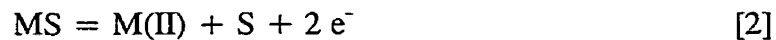
The hydrophobic character of a mineral may be induced by a fractional monolayer surface product, often covering less than 5% of the mineral surface (3). This is the case for collector dosages normally used in industry (4) and reflects a very fine balancing act between hydrophobic sites and the mainly hydrophilic mineral surface. The source of hydrophobicity representing less than a full surface on the mineral particles renders the study of electrochemical phenomena more difficult for flotation than for other systems where bulk compounds are produced.

Taking the xanthate family of collectors as an example, a sulphide mineral can be rendered hydrophobic via six distinct, but not necessarily incompatible, anodic oxidation (de-electronation) reactions:

i) Oxidation of the sulphide mineral to produce a metal deficient surface;



ii) Oxidation of the sulphide mineral to produce elemental sulphur on the surface;



iii) Oxidation and adsorption of the xanthate,  $X^-$  ( $R-O-CSS^-$ , where R is a hydrocarbon chain);



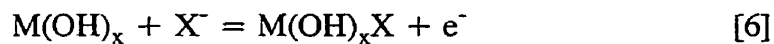
iv) Oxidation of the xanthate to its dimer, dixanthogen, and its adsorption on the surface;



v) Oxidation of the sulphide mineral and reaction of the semi-free cation with xanthate to metal xanthate;



vi) When a metal ion is precipitated from the solution, or as it leaves the mineral lattice, the formation of the metal hydroxyxanthate may occur;



The sulphide mineral serves as a source and sink of electrons for these reactions and the cathodic reduction of oxygen (electronation) (5, 6, 7):



The actual mechanisms are more complex (5, 6, 7) but the reactions in this simplified manner show the requirement of oxidizing conditions for the mineral surface to acquire a hydrophobic state via metal deficiency or elemental sulphur formation or the adsorption of the xanthate molecule. The dissolved oxygen content of the flotation pulp (air in the flotation gas) normally provides these conditions but other oxidation-reduction couples such as ferrous-ferric ions may act in this role as well.

As the minerals are liberated in the grinding mills, and sized by hydrocyclones, a certain amount of oxidation has occurred via reactions [1] and [2] even before the introduction of the collector in the system. The fate of the cations released during this

early oxidation depends on the pH of the pulp. If the pH is higher than that of stability in solution, these cations will precipitate as hydroxides nearly as fast as they are formed. This is generally the case for sulphide flotation.

Whereas the formation of a metal deficient surface or elemental sulphur increases the hydrophobicity of the surface, the precipitation of metal hydroxides increases its hydrophilicity. On the other hand, dry grinding may provide all the benefits of metal deficient/elemental sulphur formation without the noxious effects of the metal hydroxides leading to an easily observable flotation without collector (8).

Since chelating agents such as ethylene diamine tetra acetate (EDTA) can remove these metal hydroxides to leave a net hydrophobic surface, there have been some questions as to the exact role of collector sulphide flotation (9, 10). However, the adsorption of the collector might in fact be facilitated by the presence of these metal hydroxides, as the reacting sulphur atoms from the collector do not have to fight as intensely the repulsive forces from the sulphur atoms in the mineral surface with the hydroxides in between.

When the pH of the pulp is not elevated enough to precipitate all cations, then those that remain in solution may interact with other sulphide minerals and make them more susceptible for collector adsorption. Such inadvertent activation will lead to a reduced flotation selectivity. It can be controlled by the use of anions which can form complexes with these cations such as cyanide or its impact minimized by performing the flotation of the desired minerals at starvation collector levels.

The oxidation-reduction dependence of the adsorption of xanthate onto the sulphide minerals taken individually is relatively well understood (6). However, an ore contains more than one sulphide mineral and the indirect interaction through the ions released during their oxidation is rarely taken into account. In addition, wet grinding is performed with the grinding media being either the ore itself (autogenous and pebble



milling), or steel (rod and ball milling) (11). Hence, it may be expected that interactions between the minerals and the grinding media, as well as the minerals themselves will occur. These interactions are galvanic and each half-reaction occurs on a different mineral with the electron transfer occurring during contacts between the two.

The presence of a galvanic couple often yields reaction rates which are higher than if each of the two materials were separated. For example, sphalerite ( $ZnS$ ) is leached by acids at a faster rate when pyrite ( $FeS_2$ ) is present than when it is by itself (12, 13). This faster leaching rate occurs due to the combination of two factors. First, pyrite is one of the most electroactive sulphide minerals for oxygen reduction (14). Second, it is more noble than sphalerite (15). This combination forces pyrite to be the active surface for oxygen reduction while extracting the required electrons to sustain the reaction from sphalerite (zinc dissolution) during pyrite-sphalerite contacts.

The presence of galvanic interactions in flotation may be beneficial or detrimental depending on the minerals present. In some instances, the desired mineral is depressed because of the presence of the couple. Such is the case of galena when grinding is performed with a mild steel media (16). Sometimes, it is the flotation of the non-desired sulphide mineral which is enhanced, for example pyrrhotite in gold-bearing pyrite/pyrrhotite separation (17).

However, the usual ranking of sulphide minerals from most reactive to most noble by their increasing rest electrochemical potential in aerated solutions should not be assumed to be the same when a collector is present as demonstrated by Bozkurt et al. (18). In this particular study on the pentlandite/pyrrhotite/xanthate system, pyrrhotite became more noble than pentlandite upon the introduction of xanthate with the particular consequence that xanthate adsorption on pentlandite was enhanced while that on pyrrhotite was reduced. The net outcome was an increased selectivity over that predicted from single mineral studies.

Monitoring the electrochemical potential of a mineral slurry is a first step towards manipulation of the system to modulate flotation selectivity. Being able to monitor a process variable leads to its control. Essentially two means are available.

The first is to use a potentiostat, which is an electric device capable of literally "pumping" electrons through the system under investigation so that the desired potential is maintained. This is the preferred method for laboratory experiments (5, 6, 19, 20, 21) where it is relatively easy to obtain a good contact between the mineral particles and the current feeding electrode by compacting the particles around the electrode. Industrial electrochemical reactors based on the same principles have been investigated for hydrometallurgical processes and the challenge is to obtain high current efficiency due to the poor contact between the loosely moving particles and the electrode (22, 23, 24).

The other method relies on the use of oxidizing or reducing agents to move the electrochemical equilibrium in the desired direction. This is the acting principle behind selective oxidation of one of the minerals in the ore, for example, by potassium permanganate (2), or sodium peroxide (25). By using strong oxidizing or reducing agents, a modulation of the electrochemical potential nearly as large as that achievable by pumping electrons through the system can be obtained.

However, most flotation circuits, or laboratory flotation procedures, achieve a reasonable separation of the minerals. To improve on this separation, the required manipulation of the oxidation-reduction state of the slurry would not need to be as large as performed in fundamental studies. In a study on a copper-zinc-silver-pyrite ore sample from Les Mines Selbaie (26), it was observed that an indirect manipulation of the electrochemical potential of the pulp by the alkalinity of the pulp (roughly 50 mV/pH unit) was sufficient to modulate the flotation response of copper and zinc minerals enough to affect the overall observed selectivity. In a way, this is not much different than the control of the addition of sodium cyanide for gold leaching (27).

## 2 The electrochemical potential of the pulp; a dream or a reality?

Measurement of the electrochemical potential (also called oxidation-reduction potential or redox potential) of the flotation pulp is a first requirement for investigations into the establishment of a relationship between the oxidation-reduction state of the slurry and the flotation response. The measurement, and control, of the electrochemical potential of the system, during fundamental studies on single minerals or binary mineral mixtures is straight forward due to the experimental procedures and can be related to thermodynamic values.

Such is not the case with a flotation pulp, be it in the laboratory or in the plant. Woodcock and Jones (28, 29) were early investigators in the chemical characterization of plant flotation pulps. They measured a vast array of parameters, including the redox potential and they expressed some doubts into the value of such measurements due to an observed relationship between redox potential and pH.

Later, Johnson et al. (30) performed a similar characterization and expressed the following view on redox potentials in flotation systems in a footnote:

"The precise meaning of Eh in a complex sulphide pulp is obscure and the term is used solely for convenience. It is measured as the potential of a platinum electrode with respect to a saturated calomel electrode, both of which are inserted into the stirred pulp. This potential is then converted to the standard hydrogen electrode scale."

Given this, some investigators have avoided the issue of the complexity of the interpretation by using  $E_{Pt}$  (e.g. Guy and Trahar (19)) to represent the redox potential measured with a platinum electrode and converted to the hydrogen scale. Others have extensively examined the impact of oxidation in industrial flotation circuits, via extraction of hydroxides on the mineral surfaces, without performing a single electrochemical

measurement of the flotation pulp (31). Such correlations, although not easy to determine, can be made (32, 33, 34).

Other investigators have attempted to clarify the meaning and significance of electrochemical potentials in mineral slurries by using different sensing electrodes, including electrodes made from pure sulphide mineral pieces (26, 35, 36, 37, 38, 39, 40). The general conclusions reached in these studies were that the electrochemical potential of the pulp is a mixed potential; that the use of gold as material for the potential sensing electrode was preferable over platinum as its electrocatalytical activity for oxygen reduction is similar to that of the sulphide minerals and it generally exhibited potentials similar to mineral electrodes; and the shape of the sensing electrode should be conducive to intense contacts with the mineral particles present in the slurry. The underlying assumption in these conclusions was that the relevant electrochemical potential for flotation was that of the mineral-solution interface (20, 36, 37, 38, 39, 40).

Reflecting on the impossibility to directly relate the measured electrochemical potential of the pulp to thermodynamic quantities, the expression "pulp potential" to describe this measurement was proposed around 1990, for example Heimala et al. (41, 42), Hodgson and Agar (43), Labonté and co-workers (39, 44), Baker et al. (45), Gorken et al. (46), Trahar et al. (47). The term "pulp potential" appears to have been sufficiently accepted to appear in the title of a review by Cheng and Iwasaki (48). Its abbreviation to  $E_p$  has sometimes been used (33, 34, 44).

Some investigators prefer not to abbreviate the term (48, 49, 50), but to coin a new term like  $p_e$  (51) by analogy to pH, or to use the traditional Eh (45, 46, 47, 48). Both  $p_e$  and Eh implies that the potentials are related to the standard hydrogen scale, usually by conversion from the reference electrode actually used. The argument in favour of referring all pulp potentials to the hydrogen scale is an easier relation between the value obtained and the thermodynamic properties of the system. However, no practical reference electrodes are based on the standard hydrogen electrode, the silver/silver

chloride electrode (Ag/AgCl;  $E_h = 200$  mV at 25 °C) being the most frequent in commercial potential and pH sensors and the saturated calomel electrode (SCE;  $E_h = 245$  mV at 25 °C) commonly encountered in laboratory sensors.

What is often forgotten in performing the conversion is the temperature dependence of the practical reference electrodes at 0.65 mV/°C (52, 53). After all, this translates to only 13 mV for a concentrator operating in a nordic climate where the slurry temperature can be 10°C in the winter and 30°C in the summer. However, the potential range over which the hydrophobicity/hydrophilicity balance of the surface of a mineral tips from near zero to full floatability is often in the range of 10 to 15 mV (5, 6, 7, 9, 10, 19, 20, 21).

The reactions which cause the balance to tip from one surface state to the other are also affected by the temperature but the complexity of the system makes it impossible to predict for anything more than a single sulphide mineral. However, this is no reason not to include the temperature dependence of the reference electrode when converting from one scale to the other.

Given the acceptance of the concept of "pulp potential", the term will be used extensively in discussing the oxidation-reduction potentials obtained with a sensing electrode-reference pair immersed in a mineral slurry. To lighten the text, the abbreviation  $E_p$  will be used when the general term is meant with a notification of the sensing electrode and reference used. Abbreviations such as  $E_{Au}$ ,  $E_{Pt}$ ,  $E_{Cp}$ , etc. will be used when discussing pulp potentials obtained using sensing electrodes made from gold, platinum, chalcopyrite, etc. The temperature at which a given measurement was made will be reported if temperature related effects are expected.

All potential values will be quoted in the text, or on graphs, in the scale of the reference electrode used; either SCE for laboratory investigations or Ag/AgCl for plant studies. When appropriate, especially when some relation to thermodynamic properties

of the system are made, or when comparing potential regions from the laboratory to the plant, the potentials converted to the standard hydrogen scale (at a specified temperature) will also be given.

### 3 Statement of problem and objectives of project

The A-1 zone of Les Mines Selbaie, Joutel, Québec, is a complex zinc-silver-copper orebody which locally contains small amounts of lead. Soluble secondary copper minerals (e.g. chalcocite) are also present in variable amounts throughout the orebody. The copper/zinc selectivity is greatly reduced as the quantity of secondary copper minerals in the feed increases. In the extreme situation, no selective flotation is economically achievable.

The general objective was to investigate the possibility of reagent control using an on-line pulp potential sensor. Preventive maintenance procedures were developed to ensure the long term reliability of the on-line measurement. Plant surveys and laboratory flotation tests were performed to determine how the copper/zinc selectivity could be related to the pulp potential given different collectors, modifiers, and grinding environment used in the plant.

### 4 Method of attack

The task was approached concurrently with laboratory investigations on the effects of type of grinding media, flotation modifiers, and collector on the response of the A-1 zone ore from Les Mines Selbaie while developing the needed monitoring and preventive maintenance techniques for the on-line pulp potential sensor in the plant.

Attention was brought to the presence of five different ore types within the A-1 zone ore with possible distinct mineral characteristics. Microscopic examinations and microprobe analyses were performed for this purpose. However, the ore processed in the plant, or tested in the laboratory, was usually an unknown blend of all ore types.

As the grinding environment in the plant consisted of a semi-autogenous mill followed by a ball mill with rubber liners and a corrosion resistant ball charge, the possibility that the sulphide minerals were induced into a hydrophobic state as a result of this oxidizing environment was investigated. Possible negative impact on selectivity against sphalerite and pyrite, and/or in the recovery of silver to the copper concentrate was also to be examined. These tests also indicated the most appropriate location for the on-line pulp potential sensor.

Nitrogen as flotation gas, due to its minimization of oxidation via reduction of the dissolved oxygen content of the mineral slurry, was used in comparative tests to determine whether the inherent oxidation of the slurry when air is used as flotation gas affected selectivity between the copper and zinc minerals.

Finally, laboratory tests examining the impact of the composition of the grinding media, from stainless steel only, to a mixed mild steel/stainless steel charge, were performed to help interpret some of the observations made with plant samples. These tests examined both the copper and zinc flotation stages whereas most of the other flotation tests were concerned only with the copper stage.

The on-line sensor was installed early in the project, with only a partial indication of an optimal region of pulp potential for maximum copper/zinc selectivity. This ensured a sufficiently long period of continuous on-line monitoring (nearly a full year) to ascertain the long-term viability of the sensor and to determine if the approach has merit in the long term. Necessary procedures to ensure the reliability of the on-line pulp potential sensor were developed as monitoring progressed.

The opportunity presented to participate in a similar program at the Kidd Creek concentrator was seized. This provided the possibility to generalize observations made with the A-1 zone ore and flotation circuit of Les Mines Selbaie to other copper-zinc-pyrite ores.



## 1 ELECTROCHEMICAL EFFECTS IN SULPHIDE FLOTATION

### 1.1 Introduction

Investigation into electrochemical phenomena in the flotation of sulphide minerals has seen an explosive growth in the 1980's. The re-discovery of flotation in the absence of collector due to a chance observation by Lepetic (8) appears to have initiated this interest. This also coincided with advances in surface analysis techniques which allowed more precise quantitative determination of the composition of mineral surfaces rather than just inference from modelisation of the results from electrochemical investigations. The different analysis techniques were reviewed by Giesekke (54) with reference to in situ and ex situ capability, sensitivity, and target species.

Three techniques have been demonstrated for specific areas of investigation (54, 55). X-Ray Photoelectron Spectroscopy (XPS) primarily targets questions related to the valence state of the cations and sulphur on the mineral surface and is amenable to depth profiling (56, 57). Time of Flight Secondary Ion Mass Spectroscopy (TOF-SIMS) and Secondary Ion Mass Spectroscopy (SIMS) are highly versatile in that they can examine the surface for cations and anions (58), detect (59) and even map (60, 61) collector adsorbed on mineral grains, and pushed to the extreme, can assist in determining the type of bond by which the collector is adsorbed (62). Studies on metal ion activation of non-sulphide gangue have also been performed (63). Finally, Fourier Transform Infra Red (FT-IR) spectroscopy with its vast array of sampling techniques is especially suited for the determination of the chemical form in which the collector is adsorbed (64, 65, 66, 67). Recent developments allow in situ FT-IR analysis under electrochemical conditioning of the mineral surface (68, 69). In some cases, XPS and FT-IR analyses are used conjointly to obtain a more complete view of the resulting mineral surface that would otherwise only be possible with TOF-SIMS or SIMS, for example Laajalehto et al. (70) for a study on galena and Leppinen et al. (71) for pyrite.

A peak in electrochemical investigations for sulphide mineral flotation was reached late in the decade with the introduction of not only one, but three commercial process control equipment based on monitoring and manipulation of the electrochemical potential. These systems are OK-PCF (Outokumpu - Potential Controlled Flotation) which has been introduced in 1985 (41, 42, 72, 73, 74), PIRANA (Pulp Instrument for Regulation and ANALysis) promoted by Bureau de Recherches Géologiques et Minérales (BRGM; 75, 76, 77, 78, 79) and E-Con (Potential-Control) promoted by Control International and described in a review article (82).

Other research groups were also active in related areas for plant applications. For example, the US Bureau of Mines developed and tested multi- and single electrode on-line redox potential probes for flotation systems (37, 38, 80, 81) and Amdel appears to have been successful with the commercialization of its Controlled Potential Sulphidization (CPS) system (82, 83). Other investigations into the impact of the oxygen content of the flotation gas in pilot operation, for example Berglund and Forsberg (84), and selective collectorless flotation in an operating concentrator, for example Leroux et al. (85), were also performed.

There is certainly a need to review and discuss the basic principles behind this excitement with regard to achievement of a hydrophobic state on the mineral surface and the general role, from an electrochemical view point, of flotation modifiers. This review will focus particularly on the minerals, collectors, and reagents of relevance to Les Mines Selbaie and Kidd Creek Mine. It will also be aided by experiments whenever appropriate.

A sulphide mineral can be recovered through genuine froth flotation by three modes, the first two not involving the presence of a collector. How they arise and how they can be beneficial, or detrimental, to selectivity need to be discussed in more detail. For flotation with a collector, the distinguishing features of Aerophine 3418A (Diisobutyl dithiophosphate; Cytec), which was the main copper collector at both concentrators at the time of the study, have to be put in perspective of the electrochemical

model developed with xanthate, monothiocarbonate, and dithiophosphate collectors. With the presence of secondary copper minerals in the A-1 zone ore of Les Mines Selbaie, the possibility of in situ activation of sphalerite cannot be ignored and the mechanisms of copper activation, and how it can be prevented and/or overcome must be addressed. Finally, galvanic interactions that may have a beneficial or detrimental impact on selectivity between copper and zinc minerals cannot be ignored.

## 1.2 Natural floatability

Flotation without a collector can occur due to an inherently hydrophobic character of the mineral surface or by conditions imparted by the environment during comminution and conditioning. These two modes can be observed in the laboratory with a non-negligible fraction of the minerals being recovered after a few minutes of flotation with the addition of only a frother. As such they cannot be distinguished macroscopically except by a careful study of the grinding and chemical environment in terms of oxidation-reduction conditions.

The natural, or inherent, floatability of sulphide minerals has always been questioned. Early investigations using contact angle measurements showed that sulphide minerals were not inherently hydrophobic since any hydrophobicity without collector appeared to be induced by surface contamination (86). On the other hand, flotation in the absence of collectors was observed in industry. One example is a "self-float" bulk galena-sphalerite concentrate produced from a highly weathered copper-lead-zinc ore at the Tsumeb concentrator (87). Also, there was the chance observation of chalcopyrite flotation from a complex sulphide ore in the absence of collector occurring after dry autogenous grinding, such flotation being selective while the introduction of a collector lead to reduced selectivity and the requirement of modifiers (8).

The fine points between inherent floatability and induced floatability without collector have been extensively reviewed by Hayes et al. (88). Minor refinements to the

concepts have been made in the context of the implication of pulp potential in sulphide flotation by Cheng and Iwasaki (48). The key differentiating characteristic between the two phenomena was recognized fairly early; inherent floatability is not affected by maintaining a reducing environment prior to flotation (19, 20, 89, 90, 91). In most of the earlier investigations reporting "natural floatability" of a given sulphide mineral, for example sphalerite with respect to the grinding environment (92, 93), should be understood as being cases of self induced floatability.

There is one well known sulphide mineral which is inherently hydrophobic: molybdenite ( $\text{MoS}_2$ ) (48, 88, 94). The hydrophobic character originates from the crystal structure of the mineral and its preferred cleavage plane. The crystal lattice consists of layers of molybdenum atoms stacked between layers of sulphur atoms. The weakest bond is the S-S bond and the crystal will cleave between two sulphur layers upon impact during comminution leaving both surfaces created hydrophobic. Molybdenite can however be depressed in the presence of iron and aluminum hydroxides (95), but the mechanism involved is the adsorption of the hydroxides within the electrical double layer of the particles in water. Other sulphide minerals reported to be inherently hydrophobic are orpiment ( $\text{As}_2\text{S}_3$ ), realgar ( $\text{AsS}$ ), and stibinite ( $\text{Sb}_2\text{S}_3$ ) (48, 88).

Most sulphide minerals expose sulphur atoms upon cleavage and Fuerstenau and Sabacky (98) have shown that flotation under reducing conditions is possible if oxygen has been completely excluded from the system. The delicate balance between the hydrophobic sites from the sulphur atoms and the hydrophilic sites from the metal atoms could be tipped in favour of a hydrophilic character by the formation of hydroxides following exposure to any oxygen in an aqueous environment. However, these results have not been reproduced and an investigation of oleophilicity/hydrophobicity of galena and pyrite by Kocabag et al. (96, 97) suggests otherwise. Both minerals, when in a pristine surface state, were found to be oleophilic in a mineral/oil/water system but hydrophilic in a mineral/nitrogen gas/water system. The oleophilic character was dependent on the redox potential and pH of the system and decreased with rising

oxidation and alkalinity. The mechanisms proposed to explain the observed variation of the oleophilic character were similar to those suggested for collectorless flotation.

Although one could presume that inherently hydrophobic minerals cannot be selectively recovered, there are indications that selectivity may be achieved by fine control of the air-solution surface tension (99). The practical implication of this observation is that the type of frother may play a greater role than generally thought.

### 1.3 Collectorless flotation

In general terms, collectorless flotation refers to the hydrophobicity acquired by electrochemical interaction with the environment. This can be induced through simple oxidation occurring during grinding (8, 19) or by sodium sulphide/aeration conditioning of the ore (100). Most sulphide minerals are individually amenable to collectorless flotation with a varying degree of difficulty (88, 91) and this can be related to the rest potential of the minerals in water as shown in Table 1.1 (88).

One major exception to the rule of increasing difficulty at achieving collectorless flotation with increasing (more noble) rest potential is chalcopyrite for reasons still unclear. Most studies have been performed on simple ores or copper-lead-zinc-pyrite ores although there have been reports that chalcopyrite from copper-nickel-pyrrhotite ores (101, 102) and similarly pentlandite (102, 103) could be amenable to collectorless flotation. Collectorless flotation of pentlandite has been shown to be capable of yielding higher concentrate grades than that obtained by conventional flotation, at least in the laboratory (103). Recent studies, for example Fairthorne et al. (104), have re-confirmed the dissolution of iron and copper from chalcopyrite to leave a hydrophobic metal-deficient, sulphur rich surface. However, their re-adsorption as ferric and cupric hydroxide species was suggested as being likely and actually controlling the net degree of hydrophobicity of the surface.

Table 1.1 Approximate order of collectorless flotation of sulphide minerals (descending order) (88)

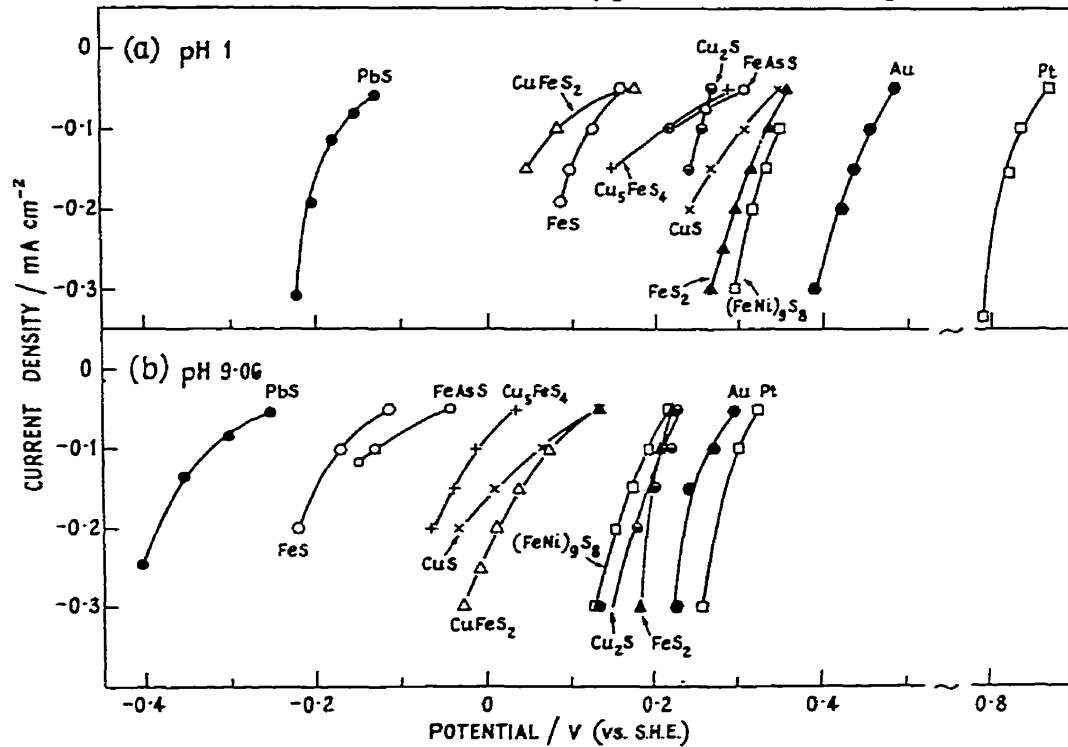
Mineral	Formulation	Rest Potential (pH 4; V vs SHE) (105)
Molybdenite	MoS <sub>2</sub>	0.11
Stibinite	Sb <sub>2</sub> S <sub>3</sub>	0.12
Argentite	Ag <sub>2</sub> S	0.28
Galena	PbS	0.40
Bornite	Cu <sub>5</sub> FeS <sub>4</sub>	0.42
Covellite	CuS	0.45
Sphalerite	ZnS	0.46
Chalcopyrite	CuFeS <sub>2</sub>	0.56
Marcasite	Fe{Zn}S	0.63
Pyrite	FeS	0.66

Although the ranking of sulphide minerals in the galvanic series as shown in Table 1.1 was proposed by Majima (15), the experimental data was obtained by Rachenberg (105). Some inconsistencies were observed when comparing rest potentials from different sources. Notably Chizhikov and Kovylna (106) had indicated rest potentials of -0.283 V (vs. SHE) for cast FeS, -0.242 V for sphalerite, 0.284 V for galena, and 0.442 V for Cu<sub>2</sub>S in 100 g/l sulphuric acid aqueous solution.

Mineral samples from varied orebodies may give rise to different rest potentials. Determination of rest potentials for the sulphide minerals in the A-1 zone ore of Les Mines Selbaie have been determined (26) to be 0.14 V (vs. SHE) for galena, 0.19 V for chalcopyrite, and 0.28 V for pyrite at pH 7.0. The rest potential of sphalerite could not be measured due to its high resistivity related to the large band gap of the mineral ( $\approx 3.6$  eV) (107). Although the rest potentials obtained at pH 7.0 are lower than those at pH 4.0 shown in Table 1.1, the general ranking remains the same ( $E_{Ga} < E_{Cp} < E_{Py}$ ).

There is generally a good agreement between the ranking of rest potentials determined by Majima (15) and the activity of the minerals for oxygen reduction determined by Rand (14) shown in Figure 1.1; the more noble the mineral, the lower the activation energy required for oxygen reduction on its surface.

Figure 1.1 Activation controlled current for oxygen reduction on sulphides (14)



The ranking shown in Table 1.1 is for an acidic pH corresponding to the formation of elemental sulphur. Although the rest potentials are more negative at alkaline pH where a metal-deficient surface is the primary cause for the collectorless flotation, this general ranking is still applicable. Some recent investigations have indicated rest potentials (e.g. 17, 18) and oxygen reduction current (e.g. 108, 109, 110), but these involved only selected sulphide minerals.

The terminology "self-induced floatability" has been appropriately coined, for example Shannon and Trahar (9) and Ahn and Gebhardt (111), to distinguish between

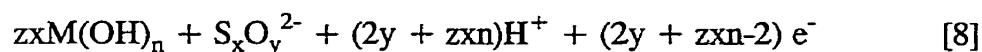
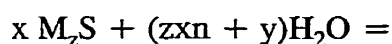
hydrophobicity arising from interaction between the mineral and the grinding and conditioning environments from that arising from "inherent floatability". Also, it contrasts with "collector induced floatability" describing the hydrophobic character arising from the adsorption of a collector. However, "collectorless" and "conventional" are terms often used and they are more than appropriate when no inherently hydrophobic minerals are present.

In a strict sense, the use of sodium sulphide to induce hydrophobicity in chalcopyrite and sphalerite ores (100), and further examined by other workers (20, 112, 113, 114, 115), cannot be described as collectorless flotation. The introduction of sulphide ions causes two effects. First there is the removal of surface oxidation products from the mineral surfaces (by sulphidization). Second, there is the formation of polysulphides (via first adsorption of sulphide ions) and a small amount of elemental sulphur on the surface of the minerals in alkaline pulps and the hydrophobic character is strongly related to the presence of the polysulphides (114). Hence, the externally added sulphide ions act in a similar fashion to thiol based organic collectors and should be considered as a collector. Nevertheless, there is a similarity with self-induced floatability since oxidizing conditions are required after sodium sulphide conditioning for flotation to occur with the minimum electrochemical potential for flotation being 0 mV vs. SHE (Pt sensing electrode) (20, 112, 113).

In most cases, hydrophobicity following oxidation results from the formation of a metal deficient surface or elemental sulphur, i.e. reactions [1] and [2] described previously. It has been shown that a metal deficient surface occurs predominantly in alkaline solutions (115) while elemental sulphur occurs in acidic solutions (116).

Reactions [1] and [2] apply to a system with limited oxidation. Under prolonged oxidation, the process may lead to the formation of oxy-sulphur species according to (7, 19, 104):





Reaction [8] is of particular importance to concentrators using a process water with a high proportion of water reclaimed from the tailings area. The oxy-sulphur species, also called thio-salts, arising from oxidation of the minerals during comminution and flotation, are present in high concentrations in the flotation tailings. The extent of degradation of the thio-salts in the tailings basin depends on several factors such as temperature, biological activity and retention time. With an incomplete degradation, a certain amount of thio-salts will be present in the reclaimed process water. This would limit the extent of oxidation reactions such as reaction [8], and in a cascading effect, the precursor reactions [1] and [2].

Electrochemical investigations are usually performed in pH buffered solutions prepared from distilled water (5, 6, 7) and this represents the case of only a "fresh" water being used. Recognizing the importance of thio-salts, some investigators have performed electrochemical investigations in solutions containing a population of thio-salts mimicking the process water, for example Hodgson and Agar (43, 117) and Kelebek and Huls (101), or at least with a sulphate bearing solution, for example Ahn and Gebhardt (111) and Tolley et al. (118).

The released metal ion in reactions [1] and [2] usually goes into solution and its fate depends on the chemistry of the system. It may remain in solution, be complexed, or be precipitated as a hydroxide when the pulp is alkaline. The latter case has some bearing on the flotation with a collector (9, 10).

The first two cases are two sides of the same coin; the formation of metal complexes being purposely performed if the presence of the metal cation is found to be

detrimental. The most noxious cations are those that can exist in two valence states in solution like:



Ions with multiple valence states are known to be catalysts for electrochemical reactions. For example, the cupric ion (reaction [9]) can act as a catalyst during the oxidation of pyrite leading to the formation of elemental sulphur rather than that of sulphate (119). Cupric ions can be sequestered by thio-salts and catalyze the transformation of sulphite ( $\text{SO}_3^{-2}$ ) to dithionite ( $\text{S}_2\text{O}_6^{-2}$ ) (120). Also, sphalerite usually requires copper activation to be recovered by a collector (121). But under some circumstances, it is possible to float sphalerite without copper activation when small amounts of ferrous ions are present, especially at pH above 10 (122, 123). Even in this case, oxidation is required for flotation as maintaining a nitrogen blanket does not allow flotation to occur (123).

Except when purposely desired, collectorless floatability occurs due to the galvanic interactions present during grinding. These interactions are between the sulphides and the media and between the sulphide minerals themselves from locking (lack of liberation of the minerals) and particle collisions. In the case of a copper-zinc-pyrite ore there would be benefits in achieving adequate copper recovery with a lower quantity of collector. On the other hand, if a portion of the sphalerite is promoted to collectorless flotation, or even was activated in situ as a result, selectivity will be reduced.

Sphalerite will exhibit collectorless recoveries over 90% if ground in a ceramic mill (92) and this observation can be easily confused with "natural floatability" (93) and in-situ activation of the sphalerite. Both causes of flotation can be repressed by the use of cyanide and ferrous ions (93), i.e. reducing conditions which can also be provided by grinding with a mild steel mill/media (92), or adding iron, zinc, or magnesium metal to a ceramic or a stainless steel mill (92).

By analogy, an autogenous or semi-autogenous mill in combination with a pebble mill may give rise to collectorless flotation while a conventional rod/ball mill grinding circuit may not. This generalization could be misleading as the "self-float" recovery observed at the Tsumeb concentrator was following rod/ball mill grinding (87). The predominance of chalcocite ( $\text{Cu}_2\text{S}$ ) for the copper minerals might have been a determining factor for this ore. Also, the major gangue mineral, carbonate or silica, may alter the expected flotation behaviour in relation to the grinding environment (124, 125).

Reducing conditions can be induced in grinding by nitrogen flushing of the mills. This would lead to the inhibition of collectorless flotation for an autogenous mill while grinding media consumption (by corrosion) would be reduced in conventional rod/ball mill circuits (126). This could lead to an appreciable reduction in operating cost for a concentrator since corrosion induced by the sulphide minerals represents about 40% of the grinding media consumption (127). Furthermore, high chrome grinding media has a lower wear component due to corrosion than other media (128).

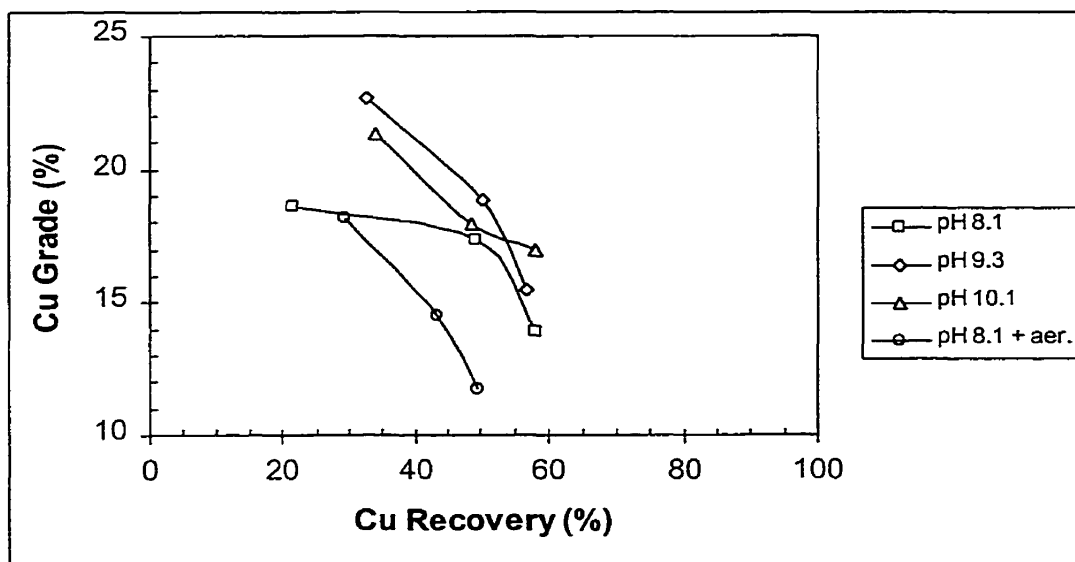
#### 1.4 Occurrence of collectorless flotation in the A-1 zone circuit of Les Mines Selbaie

The grinding circuit for the A-1 zone ore consists of a semi-autogenous mill followed by a rubber lined ball mill with a corrosion resistant ball charge (129). From the above discussion, such grinding environment might be oxidizing enough to induce some of the minerals present in the ore, hopefully not sphalerite or pyrite, into collectorless floatability.

In order to verify if this was the case, a series of four flotation tests were performed on a sample taken from the cyclone overflow feeding the copper rougher flotation cells. These tests were performed at the as-collected pH of 8.1, with some additional lime (pH 9.3 or 10.1), and at the as-collected pH with a 10 minute aeration prior to flotation. Only frother (Methyl Isobutyl Carbinol; MIBC) was added and flotation was carried with incremental concentrate collection after 1, 3, and 6 minutes of flotation. The results obtained in these tests are summarized in Figures 1.2 to 1.7.

First is the copper grade-recovery curve for the cumulative concentrate collected (Figure 1.2). Not surprisingly, up to 60% of the copper could be recovered without any collector present at a concentrate grade of 15% Cu. A higher pH yields higher initial concentrate grades but ultimately, the curve tends towards the same grade-recovery point at the completion of flotation. The additional 10 minute aeration appears to have been detrimental to both concentrate grade and recovery.

Figure 1.2 Copper grade-recovery curves under collectorless flotation



The selectivity was excellent as indicated by plots of chalcopyrite recovery against recovery of sphalerite (Figure 1.3) and pyrite (Figure 1.4). On such plots, a measure of the selectivity can be obtained by how far the curve for a given set of conditions deviates from bulk flotation behaviour (a straight line).

Figure 1.3 Chalcopyrite-sphalerite selectivity curves under collectorless flotation

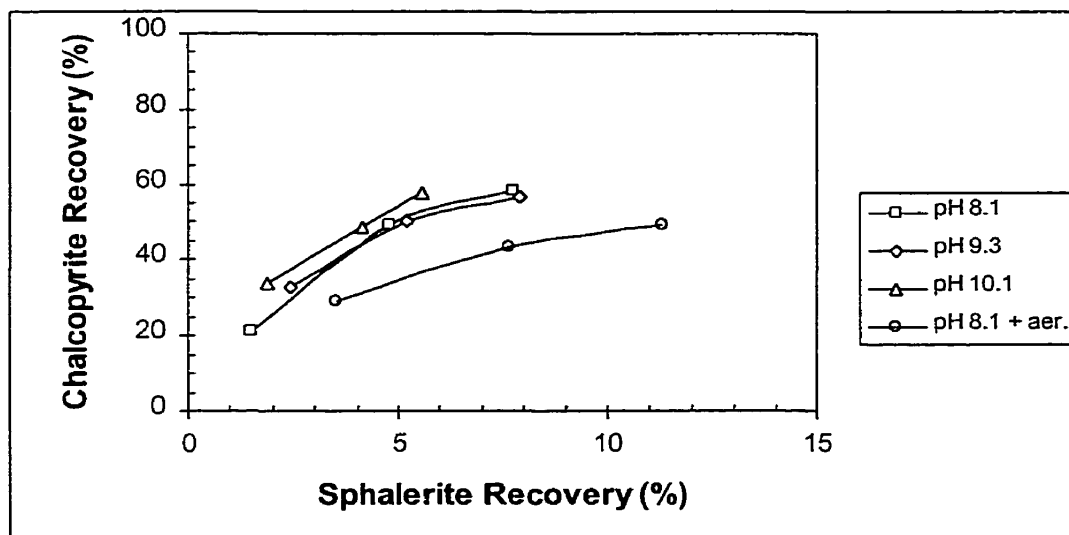
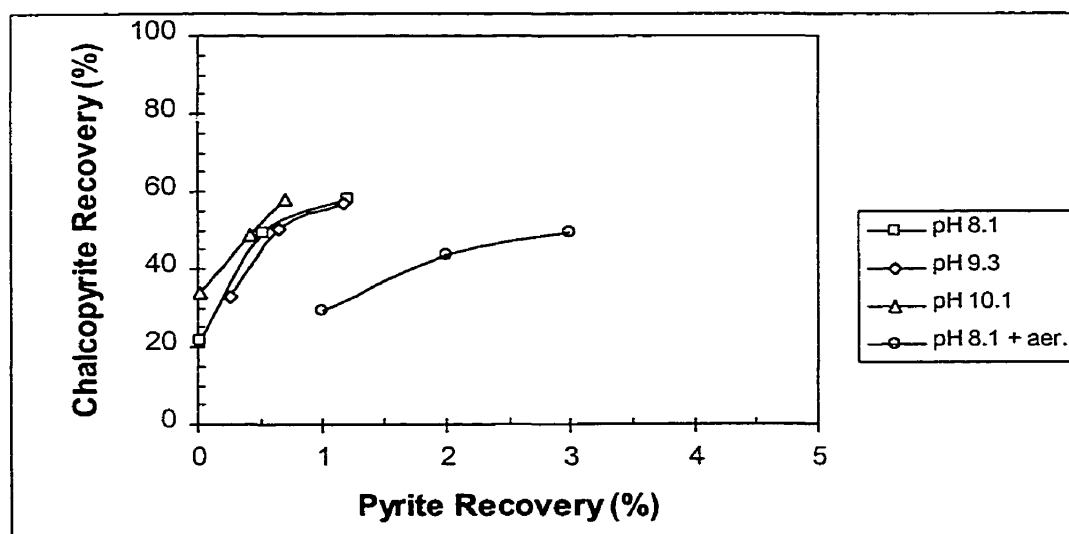


Figure 1.4 Chalcopyrite-pyrite selectivity curves under collectorless flotation



At the 60% chalcopyrite recovery level, less than 7.5% of the sphalerite (Figure 1.3) and around 1% of the pyrite (Figure 1.4) are recovered. Aeration is detrimental to selectivity against both sphalerite and pyrite with a combination of reduced chalcopyrite recovery and increased sphalerite and pyrite recoveries.

As an indication of the kinetics of flotation, plots of recovery against a given process variable (e.g. pH or pulp potential) at a given cumulative flotation time are frequently used (e.g. Trahar (130)). The flotation times usually selected are 1 minute (indication of flotation rate) and total time (indication of ultimate flotation recovery). Such plots have been made for pH (Figure 1.5) and pulp potential (Figure 1.6) using the recoveries obtained after one minute while the ultimate recoveries obtained after six minutes of flotation are shown in Figure 1.7. It is noted that for clarity the results of the single test performed with aeration (at pH 8.1) are not shown in Figure 1.5. In the case of the pulp potential, the value indicated in Figures 1.6 and 1.7 is the one at the start of flotation on the basis that the potential at that time would be the best indicator of the oxidation-reduction state of the pulp prior to introduction of air for flotation.

Figure 1.5 Mineral recoveries after 1 minute flotation (collectorless) as a function of pH

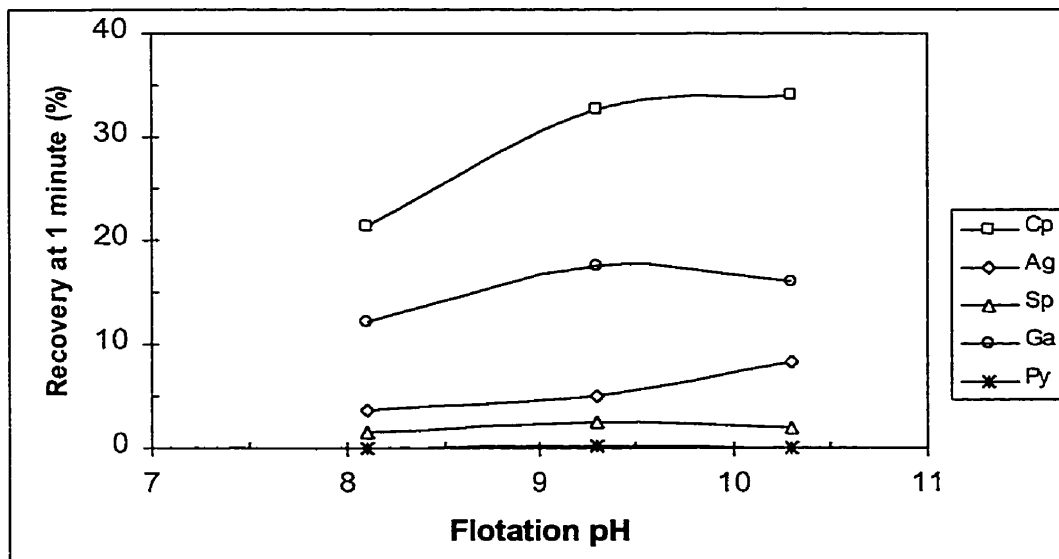
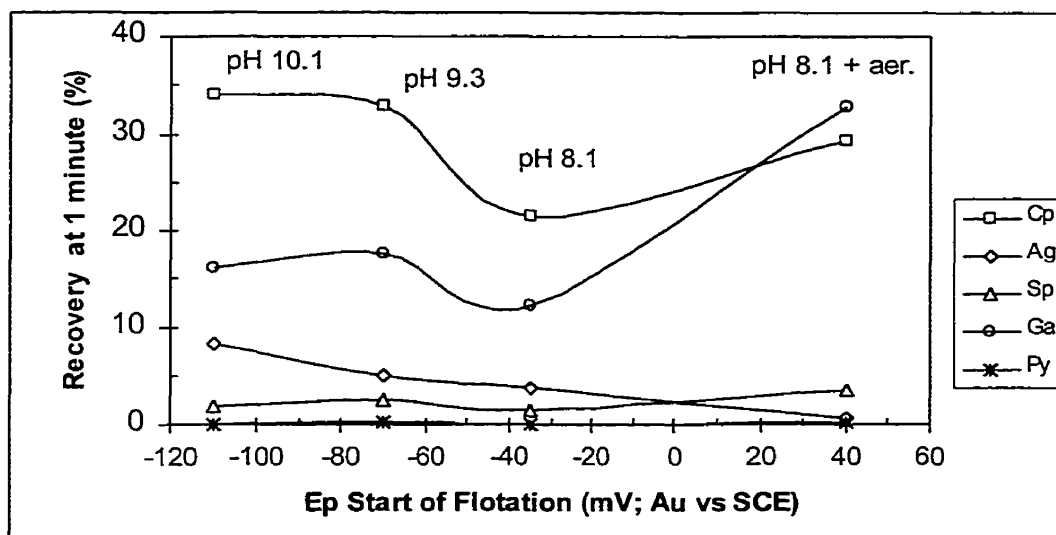
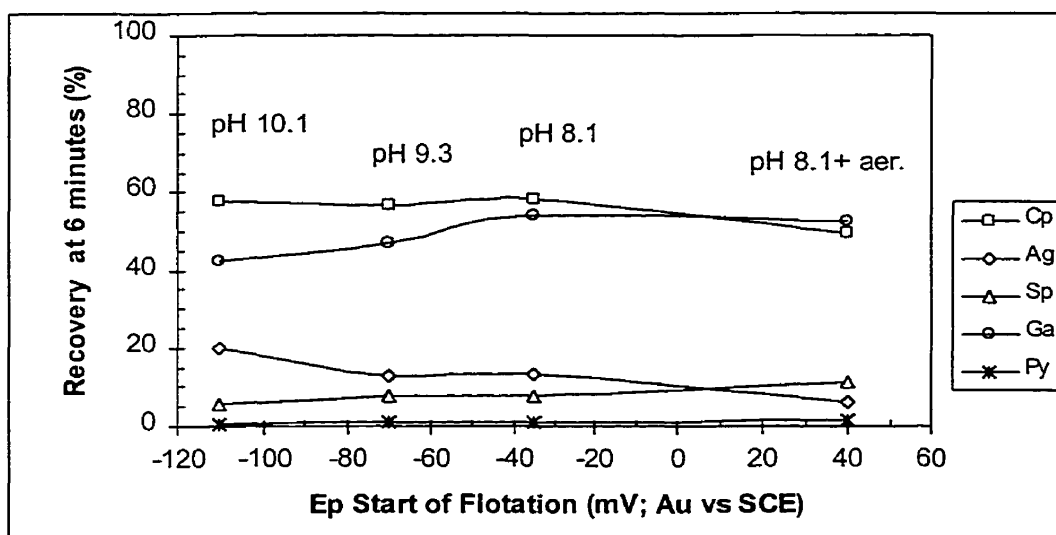


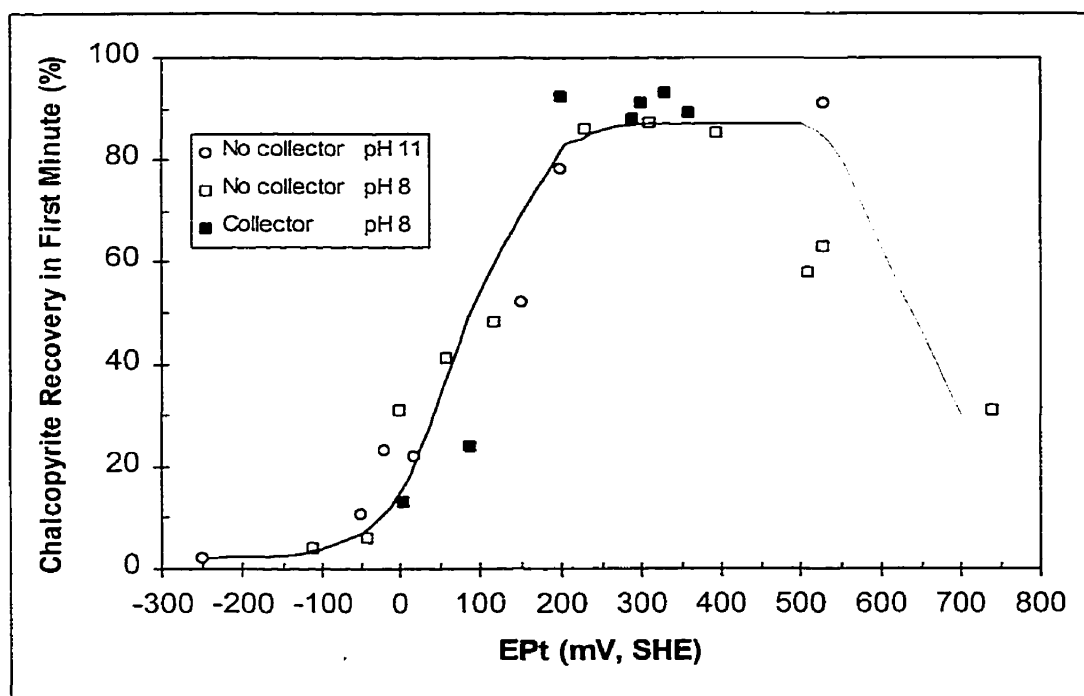
Figure 1.6 Mineral recoveries after 1 minute (collectorless) as a function of  $E_p$ Figure 1.7 Mineral recoveries after 6 minutes (collectorless) as a function of  $E_p$ 

Plotting the results in this fashion indicates that increasing the pulp pH from its as-sampled pH of 8.1, which translates to a reduction in  $E_p$  from its as-sampled value of -35 mV (Au vs. SCE), results in higher chalcopyrite, galena and silver recoveries after one minute of flotation. The aeration stage, which increased  $E_p$  to +40 mV, while not

affecting pulp pH, yielded higher recoveries of chalcopyrite and galena, lower recovery of silver, and had only a small impact (increase) on sphalerite and pyrite recoveries.

The chalcopyrite recovery vs. potential curve shown in Figure 1.6 differs in shape to those typically obtained in investigations on the impact of potential on collectorless and conventional flotation of chalcopyrite as shown in Figure 1.8 from Trahar (130). In the tests performed on the A-1 zone ore, the lowest pulp potential achieved was -115 mV (Au vs. SCE), corresponding to an Eh of around 130 mV ( $Eh \approx E_p + 245$  mV for conversion from SCE to SHE). The highest  $E_p$  was 40 mV, corresponding to an Eh of 285 mV. At these two extremes in potential, chalcopyrite recovery was 30 to 35% (Figure 1.6).

Figure 1.8 Self-induced and collector induced recovery of chalcopyrite (130).





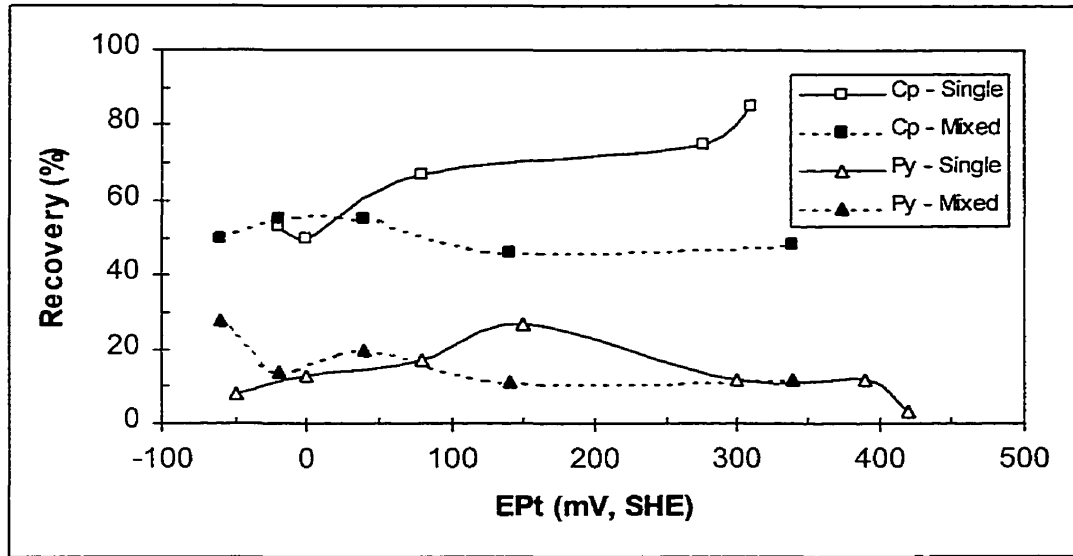
A collectorless chalcopyrite recovery of 90 to 95% at an Eh above 250 mV vs SHE (but below 500 mV) is indicated in Figure 1.8 while a recovery around 55% would be obtained at an Eh of 130 mV. Although the collectorless chalcopyrite recovery from the A-1 zone ore at an Eh of 130 mV is comparable to that obtained by Hayes et al., it is far from the 90 to 95% level indicated at an Eh of greater than 250 mV.

The observed difference at an Eh greater than 250 mV could be due to the pH modulation for the tests performed on the A-1 zone ore. However, the collectorless chalcopyrite recovery plateau in Figure 1.8 is the same at pH 8 and pH 11. Thus, even by accounting for the effect of pH on the potential, the variation in alkalinity level for the tests on the A-1 zone ore does not explain the difference.

It is also possible that use of a copper ore for the investigation of the phenomenon yields a much better floatability than that from a complex copper-zinc-pyrite ore. However, Kelebek and Huls (101) have observed collectorless chalcopyrite flotation from a copper-nickel-pyrrhotite ore with a floatability-potential curve overlapping that obtained by Trahar (130).

An investigation of collectorless flotation by Ekmekçi and Demirel (131, 132) on Murgul copper-pyrite ore suggested that the shape of the floatability-potential curves differ when chalcopyrite and pyrite are investigated as single minerals or as a mixtures of minerals as shown in Figure 1.9. Namely, the presence of pyrite reduces the collectorless floatability of chalcopyrite. Furthermore, there is an indication that collectorless chalcopyrite recovery is lower in the neutral pH region (pH 6 to 8) than under acidic or alkaline conditions (132).

Figure 1.9 Single and mixed minerals collectorless floatability of chalcopyrite and pyrite at pH 9.2 (131)



A plausible explanation for the different collectorless floatability-potential relationship with ore types possibly resides in the respective ranking of the sulphide minerals on a galvanic scale. In a copper-nickel-pyrrhotite ore, chalcopyrite lies between pentlandite and pyrrhotite (Figure 1.1) and may experience a similar oxidation-reduction environment as if it was alone. During contacts between chalcopyrite and the other minerals, its superficial oxidation is driven by oxygen reduction on pentlandite while it acts as the driver for superficial oxidation of pyrrhotite. On the other hand, in a copper-pyrite ore, chalcopyrite lies below pyrite (Table 1.1 and Figure 1.1) and is subjected to superficial oxidation driven by oxygen reduction on pyrite.

This would explain why the results of Kelebek and Huls (101) for the copper-nickel-pyrrhotite ore closely match those of Trahar (130) for chalcopyrite on its own and those by Ekmekçi and Demirel (131, 132) for a copper-pyrite ore do not. In the case of the A-1 zone ore, the small quantity of galena present (0.1% in the feed) would not affect the galvanic interaction between chalcopyrite and pyrite. The presence of sphalerite would likely have an impact. However, the impossibility of measuring the rest potential of sphalerite for the A-1 zone ore (26) makes it difficult to assess if it is less noble than

chalcopyrite as indicated in Table 1.1, or more noble; which is possible given its very low iron content (26).

These laboratory tests demonstrated that collectorless flotation is a reality for the A-1 zone flotation circuit. The achievable grade of the concentrate is high but the copper recovery appears to be limited to 60%. In addition, silver recovery to the copper concentrate is low and although there is no doubt that it could be recovered into the subsequent zinc flotation which is performed with a collector, the realized value for silver into a zinc concentrate is much less than that into a copper concentrate.

### 1.5 Conventional flotation

The third mode of flotation has been known since the discovery of the xanthate family of collectors. Flotation is induced by the adsorption of a collector onto the mineral surface. Even this, however, may be challenged eventually since the addition of chelating agents (non-surfactants) gives a flotation response similar to that induced by the addition of collectors (9, 10).

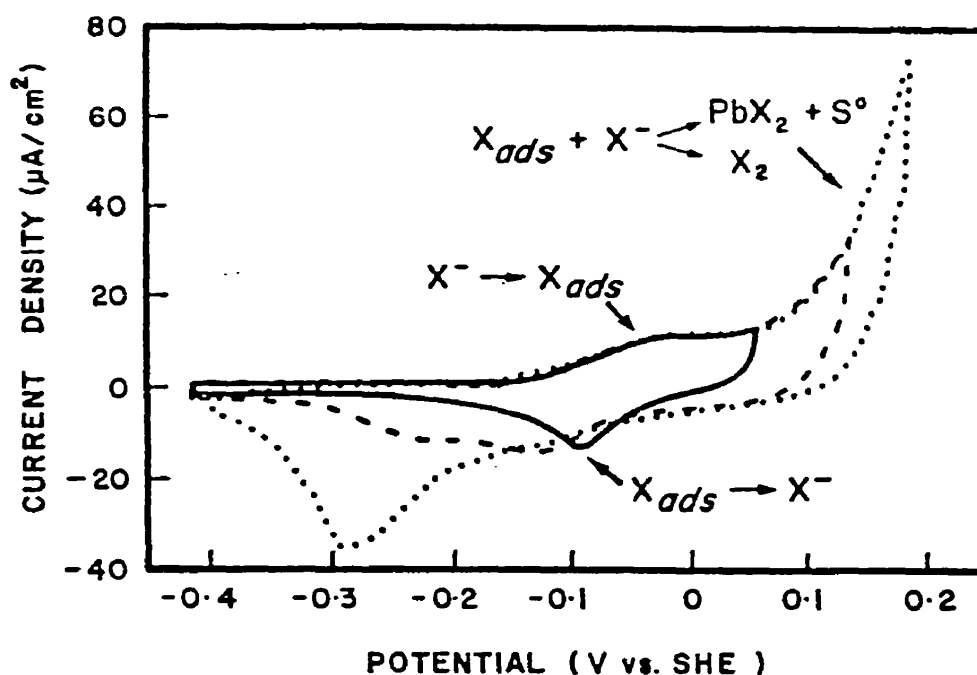
Woods (5, 6, 133) and Chander and co-workers (134, 135, 136) in their reviews of electrochemical phenomena behind sulphide mineral-collector interactions have been refining the concepts involved in collector-mineral interactions over the years. Some of these elements are worth extracting as they are relevant to this study.

#### A simple case - galena

The usual means of electrochemical investigation is cyclic voltammetry where the mineral under investigation (working electrode) is forced to enter electrochemical reactions via current pumped to/from an inert electrode (counter electrode, usually platinum) as the applied potential against a reference electrode (usually SCE) is swept between two pre-defined limits. An example of the outcome of such experiments is

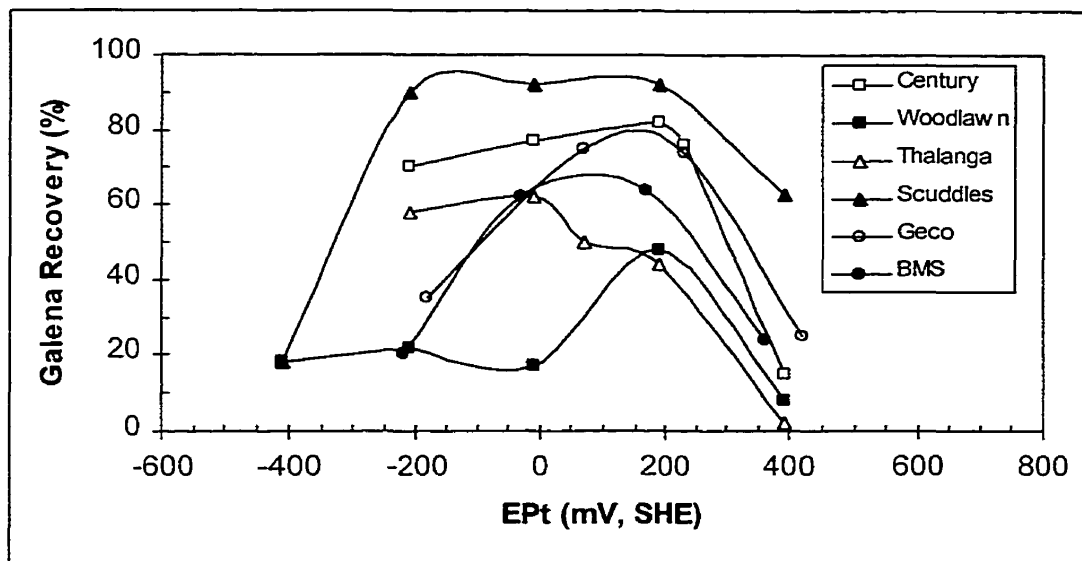
shown in Figure 1.10 for the case of galena at pH 9.2 (sodium tetraborate buffer) in the presence of  $10^{-2}$  M ethyl xanthate and a sweep rate of 5 mV/s (133). The current peaks corresponding to the adsorption of xanthate ( $-0.05$  V vs SHE), the formation of lead xanthate plus elemental sulphur and the formation of dixanthogen can be observed. It is noted that only xanthate adsorption is fully reversible in this case (symmetrical anodic and cathodic current peaks around a central, or reversible, potential).

Figure 1.10 Cyclic voltammogram for galena at pH 9.2 (sodium tetraborate) with  $10^{-2}$  M ethyl xanthate with upper limit for scan of 0.5 V (solid curve), 1.5 V (dashed curve) and 2.0 V (dotted curve) (133)



A challenge is the transformation of the results from cyclic voltammetry experiments into an interpretation of the floatability of galena as a function of pulp potential for different ores such as shown in Figure 1.11 which is a sample of curves reported by Ralston (137). These curves were among the outcome of comparative study of several lead-zinc and copper-lead-zinc ores. From Figure 1.11, it is noted that the flotation of galena, although generally occurring over a potential range of  $-200$  to  $+200$  mV vs. SHE, varies greatly between various ores from Australia (Century, Woodlawn, Thalanga and Scuddles) and Canada (Geco and Brunswick Mining and Smelting).

Figure 1.11 Potential dependence of galena flotation for several ores (137)



The results shown in Figure 1.11 indicate that there is a dependence of galena flotation on the electrochemical potential of the system for real ores. Unfortunately, the method used to vary the potential in the laboratory was not indicated. In addition, the main conditions used in the laboratory tests (flotation feed size, collectors, frothers, pH modifiers and depressants) were reported to be those of the respective plants but no in-plant measurements were given. Such information would have been highly valuable in demonstrating the pertinence of the electrochemical model for the flotation of sulphide minerals for industrial processes.

The only constant between the ores in Figure 1.11 is that galena flotation reaches its maximum recovery at around 200 mV vs. SHE. This potential is higher than that required for the formation of dixanthogen and/or lead xanthate plus elemental sulphur on the surface of galena (150 mV in Figure 1.10) meaning that these products would be expected to be found on the surfaces as a xanthaie type collector was used for all ores.

For some ores (e.g. Scuddles), it was possible to obtain high galena coveries under reducing conditions to -200 mV, while for others (e.g. Century, Geco, BMS),

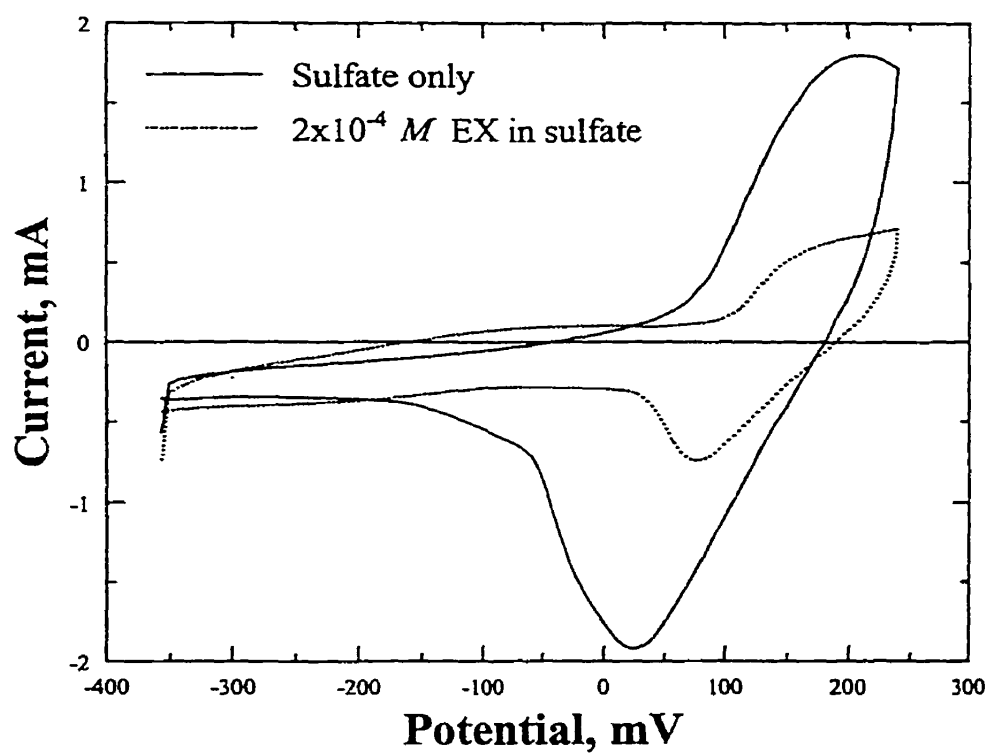
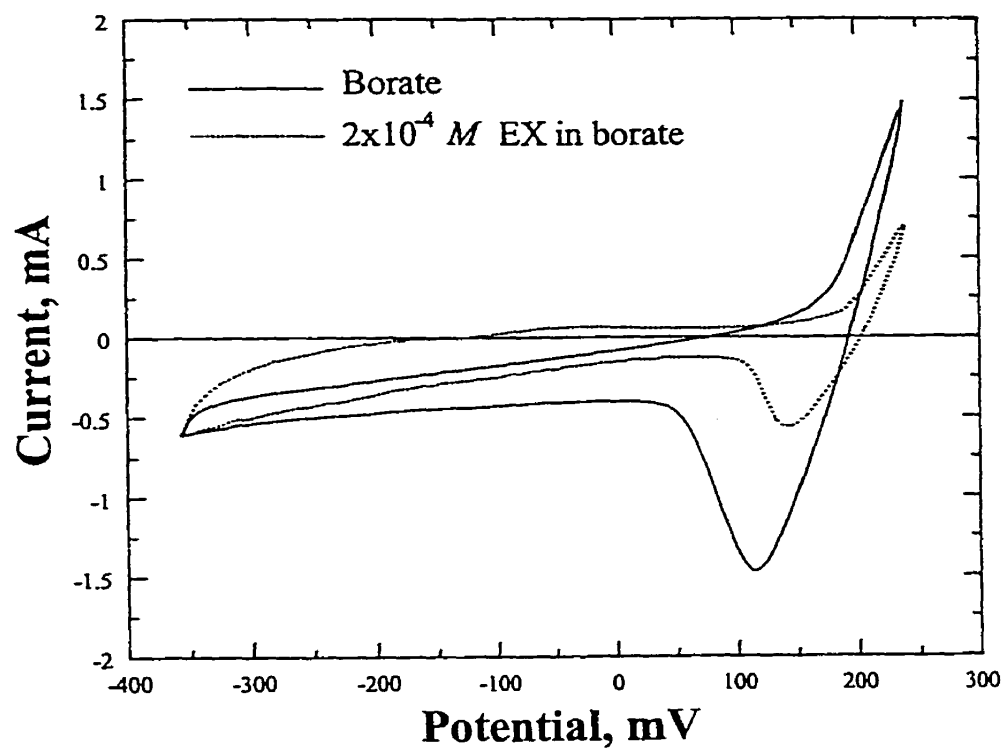
galena recovery decreased rapidly as the environment became more reducing. It is possible that for the ores exhibiting high galena floatability under reducing conditions, the laboratory conditions were such that the adsorption of xanthate (-50 mV in Figure 1.10) could occur.

Fineness of grind, degree of liberation and selection of reagents are likely to be factors affecting galena recovery but cannot account for the much lower galena recoveries for certain ores or how the recovery is affected by the potential.

#### Presence of thio-salts in the solution

One variable not generally included in fundamental investigations is the impact of the solution on the observed reactions. In their investigation on chalcocite, Tolley et al. (118) have indicated that the voltammogram obtained in the traditional borate solution is different than that obtained in a sulphate solution. Figure 1.12 shows examples of both, with and without ethyl xanthate. A small peak beginning at approximately -150 mV in the anodic (upper) sweep of the scan in the borate solution is attributable to xanthate adsorption. In the sulphate solution, the peak is broader and has a maximum near -100 mV. The voltammograms in borate solutions indicates lower current and narrower peaks than in sulphate solutions suggesting passivation of chalcocite by the borate ion but passivation occurs in sulphate solution solutions for chalcopyrite (118). This suggest that observations for one mineral cannot be generalized to others.

Figure 1.12 Voltammograms for freshly crushed chalcocite in aerated 0.05 M borate or 0.05 M sulphate solution with and without  $2 \times 10^{-4}$  M ethyl xanthate (118)



## Collecting power and selectivity of collectors

It is generally acknowledged that amyl xanthate is a more powerful and less selective collector than ethyl xanthate. Also, dithiophosphate collectors are more selective, with nearly similar recoveries as xanthates. Thus, there appear to be two parameters defining the selectivity and strength of a collector; its functional group by which it interacts with the mineral and the length of the hydrocarbon chain. Up to now, the different collectors have been described only by their respective names and it is only fitting to present their respective structure (Table 1.2) and the length of the hydrocarbon chain (Table 1.3).

Table 1.2 Structure of some thiol-based collectors (R is a hydrocarbon chain,  $M^+$  is either  $K^+$  or  $Na^+$ )

Collector Family	Structure
Xanthate (dithiocarbonate)	$R-O-\overset{\overset{S}{\parallel}}{C}-S^- M^+$
Monothiocarbonate	$R-O-\overset{\overset{O}{\parallel}}{C}-S^- M^+$
Dithiocarbamate	$\begin{array}{c} R \\ \diagdown \\ N-C-S^- M^+ \\ \diagup \\ R \end{array} \overset{\overset{S}{\parallel}}{\quad}$
Thionocarbamate	$R-O-\overset{\overset{S}{\parallel}}{C}-\overset{\overset{H}{\mid}}{N}-R$
Dithiophosphate	$\begin{array}{c} R-O \\ \diagdown \\ P \\ \diagup \\ R-O \end{array} \overset{\overset{S}{\parallel}}{\quad} S^- M^+$
Dithiophosphinate	$\begin{array}{c} R \\ \diagdown \\ P \\ \diagup \\ R \end{array} \overset{\overset{S}{\parallel}}{\quad} S^- M^+$
Mercaptan	R-SH



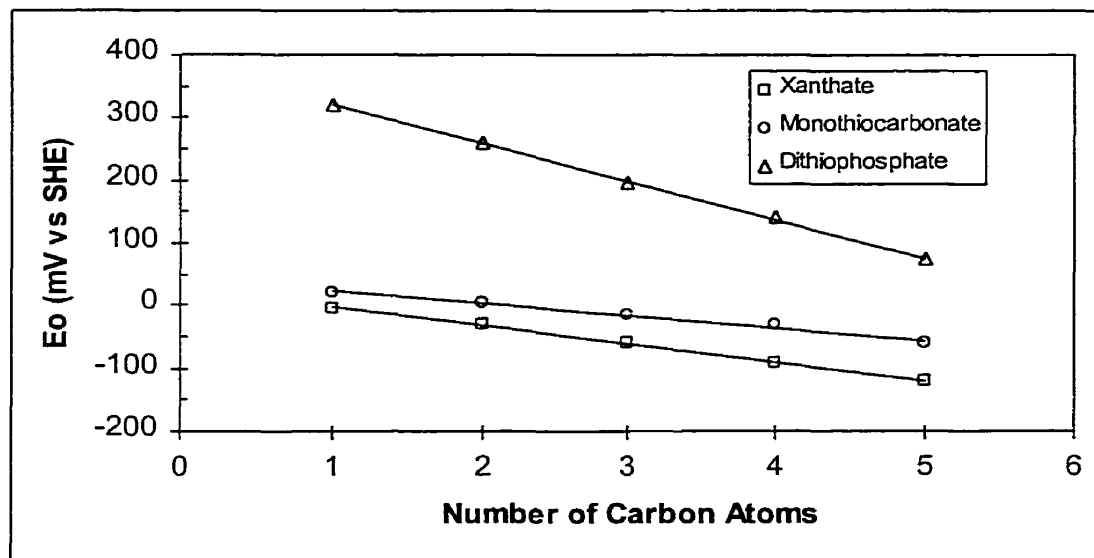
Table 1.3 Common hydrocarbon chains for thiol-based collectors

Collector	Structure
Methyl	$\text{CH}_3-$
Ethyl	$\text{CH}_3-\text{CH}_2-$
Propyl	$\text{CH}_3-\text{CH}_2-\text{CH}_2-$
Isopropyl	$\begin{array}{c} \text{CH}_3-\text{CH}- \\   \\ \text{CH}_3 \end{array}$
Butyl	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-$
Isobutyl	$\begin{array}{c} \text{CH}_3-\text{CH}-\text{CH}_2- \\   \\ \text{CH}_3 \end{array}$
Amyl	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-$

Both parameters can be condensed to one single parameter, namely the standard potential of the mono-thiolate/di-thiolate redox couple. Figure 1.13 shows the standard potentials of three collector families as a function of the number of carbon atoms on the hydrocarbon chain.

It is noted in Figure 1.13 that the dithiophosphate family has a higher standard potential than the xanthate and monothiocarbonate families. Also, the standard potential decreases with increasing number of carbon atoms on the hydrocarbon chain.

Figure 1.13 Standard potentials for homologous series of thiol collectors (134)



The practical implications of the decrease in standard potential of the dithiolate formation with increasing length of the hydrocarbon chain are that a collector becomes more powerful, due to the greater hydrophobicity imparted by the longer hydrocarbon chain at a given adsorption density (i.e. a given amount of reaction), and less selective in its interaction due to a lowering of its standard potential of the dithiolate formation, namely allowing formation of the dithiolate (e.g. dixanthogen) at pulp potentials over which it would not do so with the shorter homologue.

The impact of the hydrocarbon chain is not pronounced for the xanthate and monothiocarbonate, i.e. a 0.1 V decrease in standard potential from 1 to 5 carbon atoms on the chain. However, it is more noticeable for the dithiophosphates with a 0.25 V decrease from 1 to 5 carbon atoms.

An example of the impact of the increasing collecting power as the hydrocarbon chain is lengthened is that of sphalerite and marmatite at pH 3.5 and xanthate (138). Due to the acidic conditions, zinc dissolution was occurring giving rise to significant formation of zinc-xanthate on the surface of sphalerite. However, the xanthate concentration

required to achieve full recovery of sphalerite with a hexyl xanthate (6 carbons) xanthate was one hundredth that of ethyl xanthate (2 carbons).

#### Models for mineral-collector interaction

Several models have been proposed on why the mono-thiolate form of a collector is found on a given mineral while the di-thiolate (e.g. dixanthogen) form is found on another. Correlation with rest potential measurements (139), activity for oxygen reduction (117, 140), or the semi-conducting properties of the minerals (141, 142) have been proposed. Table 1.4 attempts to summarize the various correlations and fills in some of the gaps. It follows the format suggested by Allison et al. (139) and Ackerman et al. (141). For the form of xanthate found on the surface, the results for the propyl xanthate are used because it is about mid-way in terms of collecting power between the ethyl and the hexyl xanthate and the surface characterization gave a lower number of no positive identification (NPI in Table 1.4).

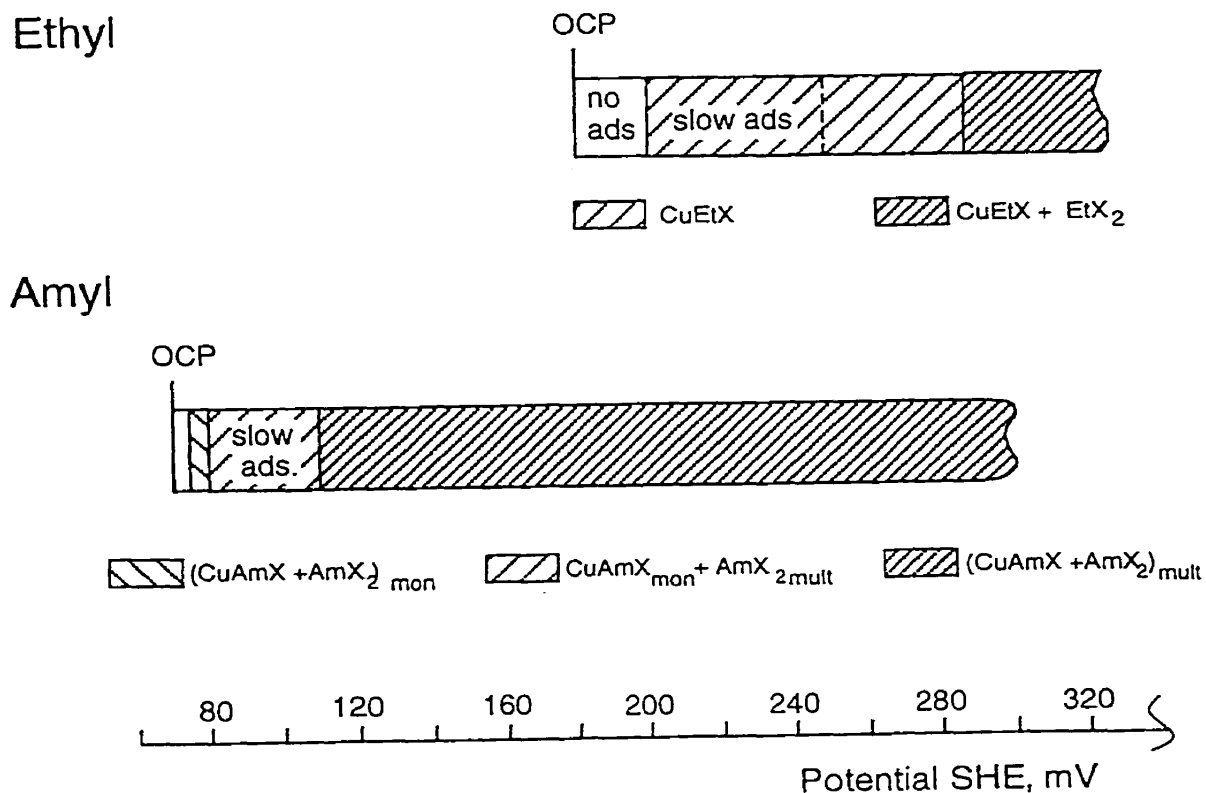
It is noted in Table 1.4 that propyl xanthate is generally found adsorbed as metal xanthate on p-type minerals and as dixanthogen on n-type minerals. Minerals for which no positive identifications could be made were either those which are inherently hydrophobic or that are poorly conducting (e.g. sphalerite). It is also noted that there is no direct correlation between the rest potential of a sulphide mineral in aerated solution and that in the presence of xanthate; those obtained in propyl xanthate solutions being between 0.14 and 0.22 V (vs. SHE) for dixanthogen found on their surface and around 0.05 V for metal xanthate. The minerals for which there is no positive identification of xanthate on their surface have rest potentials in xanthate solution below -0.09 V; namely below the standard potential for propyl xanthate-dixanthogen couple (Figure 1.13).

Table 1.4 Correlation between propyl xanthate found, semi-conducting properties and rest potential in ethyl xanthate and aerated solutions (138, 141)

Mineral	Propyl-xanthate form found (139)	Semi-conductor type (107)	Rest Potential (V vs SHE)	
			pH 7 Ethyl Xanthate (139)	pH 4 (105)
Orpiment	NPI	No data	-0.10	-0.10
Realgar	NPI	No data	-0.12	No data
Cinnabar	NPI	N	-0.05	No data
Antimonite	MX	No data	-0.09	No data
Molybdenite	X <sub>2</sub> +?	n and p	0.21	0.11
Stibinite	NPI	Poor conductor	-0.125	0.12
Argentite	No data	No data	No data	0.28
Pyrrhotite	X <sub>2</sub>	p	0.21	No data
	X <sub>2</sub> (Isobutyl; 18)	p (141)	0.29 (pH 9.2, Isobutyl; 18)	0.31 (pH 9.2; 18)
Galena	MX	n and p	0.06	0.40
Bornite	MX	p	0.06	0.42
Covellite	MX+X <sub>2</sub> MX (141)	p	0.05	0.45
Sphalerite	NPI	Poor conductor	-0.15	0.46
Chalcopyrite	X <sub>2</sub>	p	0.14	0.56
Arsenopyrite	X <sub>2</sub>	p	0.22	No
Alabandite	X <sub>2</sub>	No data	0.15	No data
Pentlandite	X <sub>2</sub> (Isobutyl; 18)	No data	0.19 (pH 9.2, Isobutyl; 18)	0.35 (pH 9.2; 18)
Marcasite	No data	No data	No data	0.63
Pyrite	X <sub>2</sub>	n and p	0.22	0.66

For chalcopyrite, the two extremes of the xanthate family have been investigated by Mielczarski et al. (143) using potentiometric conditioning and FT-IR spectroscopy. Their main results are shown in Figure 1.14. An observation is the presence of a region of slow adsorption as copper xanthate just above the open circuit (rest) potential of chalcopyrite in the respective xanthate solution. The lower rest potential of chalcopyrite in the amyl xanthate solution than in the ethyl xanthate solution is consistent with the impact of the length of the hydrocarbon chain on the standard potential of the xanthate-dixanthogen couple (Figure 1.14). There is also a compression of the potential region above the rest potential over which no adsorption occurs with amyl xanthate compared to ethyl xanthate. Similarly, the region of slow adsorption is also compressed with the longer hydrocarbon chain.

Figure 1.14 Potential regions of the formation of ethyl and amyl xanthate on chalcopyrite at pH 10 (143)



Rand (140) and Hodgson and Agar (43, 117) have related hydrophobicity in the presence of xanthates with the rate at which oxygen reduction occurs on the minerals. The observations made by Mielczarski et al. (143) for xanthate homologues tend in the same direction.

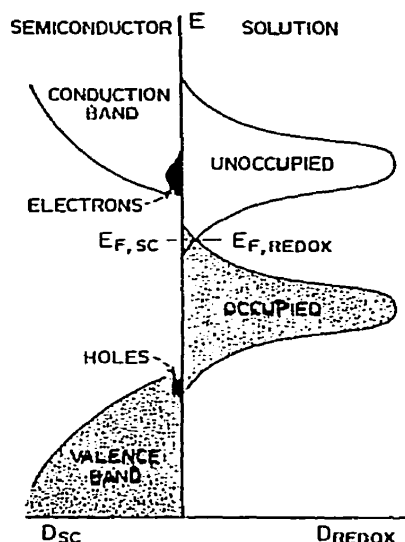
The investigation by Biegler (144) of oxygen reduction on pyrite indicated that n-type pyrite exhibits faster kinetics for oxygen reduction than n-type metallic and p-type pyrite. Using the semi-conducting properties of galena, Richardson and Maust (145) have developed a framework for the role of oxygen in xanthate adsorption on galena. This followed a similar investigation (146) for activation of sphalerite based on a semi-conducting surface-doping viewpoint.

#### Sulphide minerals as semi-conductors

It thus appears that an area which is worth exploring, but briefly, is the consideration of sulphide minerals as semi-conductors when they interact with their environment; especially collectors. This is an uncharted territory for mineral processors and rather than examining the differences between the electrochemistry of metals and semiconductors (e.g. 147), or reviewing the electrochemical phenomena occurring at sulphide mineral-solution interface (e.g. 148), the focus will be on how it impacts on the behaviour of the minerals.

Contrary to a metal where the valence and conduction bands overlap and exhibit an equilibrium energy, the Fermi level, these bands are separated in a semi-conductor; n-type implying conduction via the motion of electrons in the conduction band and p-type implying conduction via holes through the valence band. Figure 1.15 shows the relative distribution of energy states for a semiconductor in contact with an electrolyte solution containing a "reducing" redox couple (149).

Figure 1.15 Relative distribution of energy states for a semiconductor in an electrolyte solution with a reducing couple (149)

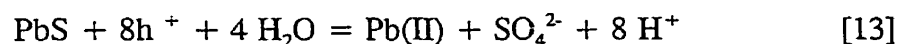


The presence of the redox couple causes a bending of the energy levels of the two bands over the "space charge" region. The space charge region is to the semi-conductor what the electrical double layer is to the solution. With this bending of the bands, and the overlap of the energy state in the solution, a hole (or a electron) can jump from the semi-conductor, through the electrolyte, and vice-versa.

When examined from a semi-conductor view point, many of the reactions familiar in the electrochemical model for sulphide mineral flotation can be re-written in steps involving either electrons or holes. For example, Mishra and Osseo-Asare (150) have investigated the corrosion of galena and pyrite in the presence and absence of water. Using the semi-conducting approach, the dissolution of galena can be represented as:

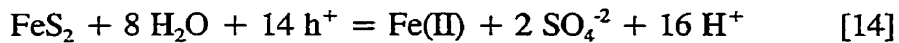


or



were  $h^+$  are holes.

while that of pyrite can only be represented as



Pyrite does not react via a reaction equivalent to [12] due to its valence band being represented by the iron "d" states contrary to galena where the valence band is represented by the sulphur "p" states, which is lower in energy. The implication of this model, which has been experimentally verified using aqueous and non-aqueous solutions (150), is that galena corrodes in the absence of water (reaction [12]) while pyrite does not.

Another example involves the examination of the oxide/hydroxide layers forming on chalcopyrite during oxidation using photo-electrochemical techniques (151). The band gap energy of a semi-conductor may fall in a region of energy where photons can induce or enhance reactions. Using this approach, Dean and Kelsall (151) have indicated that the initial layer formed on p-chalcopyrite over the potential range of -0.2 to 0.4 V (vs. SCE) was a thin oxide film of variable composition overlying an iron-depleted bulk chalcopyrite. At potentials higher than 0.4 V, the film decomposed to a compound producing photo-current, n-type  $\text{Fe}_2\text{O}_3$  being suggested, and  $\text{CuO/Cu(OH)}_2$ . The latter produced photo-current when reduced to p-type  $\text{Cu}_2\text{O}$  during the reverse potential scan. From this example, it can be ascertained that photo-electrochemical techniques complement the suite of experimental procedures available to elucidate the nature of the sulphide mineral-solution interface.

Although a mineral slurry will never lack water, it may be virtually free of dissolved oxygen, especially if flotation is carried out with nitrogen as flotation gas. From a fundamental view point, investigations on chalcopyrite in oxygen free and oxygen saturated solutions in the presence and absence of xanthate have indicated the formation of different surface layers; chalcopyrite actually forming hydroxide layers even in the absence of oxygen (7). From a practical view point, the implementation of nitrogen as



flotation gas for the pentlandite flotation stages at Norlisk (152) and the reverse flotation of pyrite from a sphalerite concentrate (153) could well be related to the semi-conducting properties of sulphide minerals.

Finally, consideration of the semi-conducting properties of sulphide minerals may help close the gap between the electrochemical model for their flotation and the adsorption of collectors due to surface charges. Fuerstenau and co-workers (154, 155) have investigated xanthate adsorption on galena, pyrite and sphalerite in the virtual absence and presence of oxygen. Their interpretation of the flotation results was aided by the determination of the Zeta potential (i.e. the surface charge determined from electrophoretic measurements) of the minerals in solutions with and without xanthate. A correlation was found between the adsorption density (measured by the determination of residual xanthate in solution) and the Zeta potential in the virtual absence of oxygen. For galena, the xanthate adsorption density (and the Zeta potential) were independent of pH. However, for pyrite and sphalerite, the xanthate adsorption density increased with decreasing pH and this corresponded to the Zeta potential (i.e. the surface charge) becoming more negative.

There is a striking similarity between the observed behaviour of galena, which corrodes in the absence of water while pyrite does not (150) and the constant adsorption of xanthate on galena irrespective of pH in the virtual absence of oxygen while there is a dependence on pH for pyrite (154).

#### Dithiophosphate collectors

The information available on dithiophosphate is sparse. There are trade papers (156, 157) and fundamental investigations (61, 158). SIMS imaging of dialkyl dithiophosphate adsorption on galena suggested a non-uniform adsorption (61) and this would be similar to that observed by Plaksin (3) for xanthate. There are also indications that the flotation response of Aerophine 3418A is strongly dependent on the pulp potential

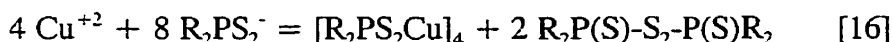
with mildly oxidizing conditions being required for selective flotation of galena and chalcopyrite (46). Galena flotation is best at potentials greater than -50 mV (Au vs. Ag/AgCl; Eh of 150 mV) while that of chalcopyrite is best at potentials greater than 0 mV (Au vs. Ag/AgCl; Eh = 200 mV) (46).

In many ways, the behaviour of the dithiophosphinate family of collector ( $R^-$ ,  $R'^-$ -PSS $\cdot M^+$ ) is expected to be similar to that of the dithiophosphate family ( $R-O^-$ ,  $R''-O^-$ -PSS $\cdot M^+$ ). The mechanism of adsorption has been studied mostly for gold, silver, and gold-silver alloys (158) but unfortunately not for sulphides.

The sulphide collector Aerophine 3418A is homologous to the metal extractant Cyanex 301 (bis(2,4,4-trimethylpentyl) dithiophosphinic acid; Cytec). There are two differences: first, Cyanex 301 has a longer hydrocarbon radical to minimize its solubility in aqueous solutions; second, it is in the acid form to ease release of the extracted metals by acidification.

Cyanex 301 is difficult to oxidize to form the di-thiolate (159). The extractant capability of Cyanex 301 for iron(III) has led to the development of analytical procedures for its determination at trace levels in biological samples and food-stuff (161). It has been suggested for purification of heavy metal bearing waste waters (162). It is known to form complexes with Zn(II) (163), with both Cu(I) and Cu(II) (163, 164).

The last two require some explanation:



Namely, complex formation with Cu(II) involves a reduction to Cu(I) and incidentally an oxidation of the dithiophosphine group to its dimer.

In general, this is not much different than other collectors. However, the copper complex is so stable in comparison of that with the other transition metals that it cannot be extracted even by strong acidification (Jean-Jacques Perraud, Communication, December 1998).

Translating these observations from the solvent-extraction field to mineral processing indicates two areas of concern with Aerophine 3418A. Firstly, there is the possibility that the complex with copper is so stable that it cannot be reversed, e.g. deactivation of sphalerite by sodium cyanide would be impeded if the collector is adsorbed before the introduction of cyanide. Secondly, there is the possibility of formation of complexes with zinc and this may lead to a direct adsorption on sphalerite given appropriate conditions.

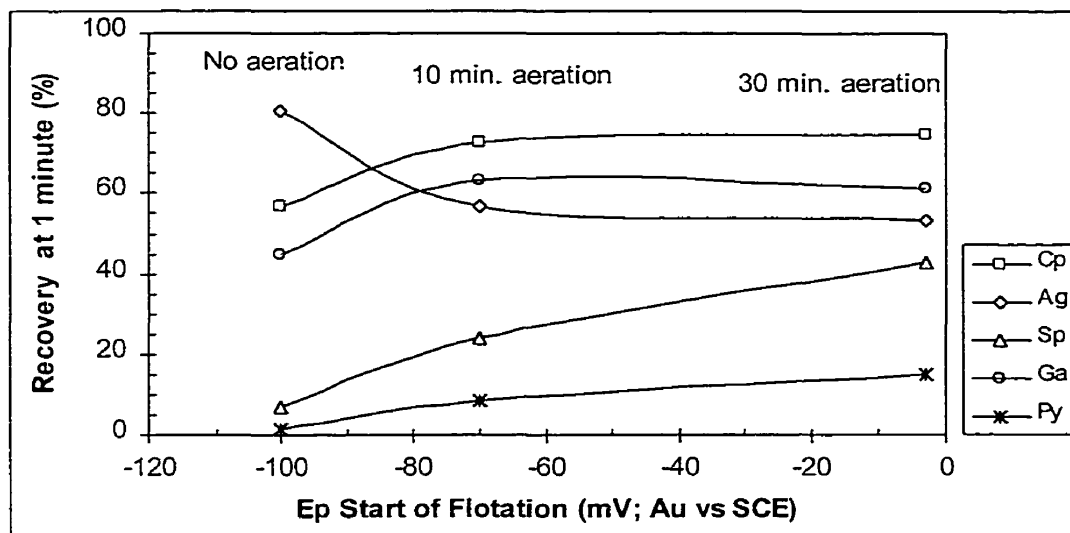
#### 1.6 Determination of impact of $E_p$ on conventional flotation of the A-1 zone ore

A series of three flotation tests were performed on a sample taken from the cyclone overflow feeding the copper rougher flotation cells to investigate the impact of aeration time (0, 10, or 30 minutes) prior to the addition of collector on the flotation response of the ore. These tests were performed at pH 8.0 and with a total of 30 g/t of Aerophine 3418A added in three increments of 10 g/t; one before each concentrate collection. Three concentrate increments were taken at 1, 2, and 3 minutes of flotation with nitrogen as carrier gas to prevent oxidation of the sulphides beyond what had occurred during the aeration. A fourth increment, of 6 minutes duration, was taken with air as flotation gas. The results of these tests are summarized in Figures 1.16 to 1.17.

Figure 1.16 presents the variation of the mineral recoveries after 1 minute of flotation as a function of the pulp potential. Without aeration, the pulp potential at the start of flotation was -100 mV vs. SCE and increased to -75 mV after 10 minutes and eventually to -5 mV after 30 minutes of aeration. It is noted that the recoveries of all

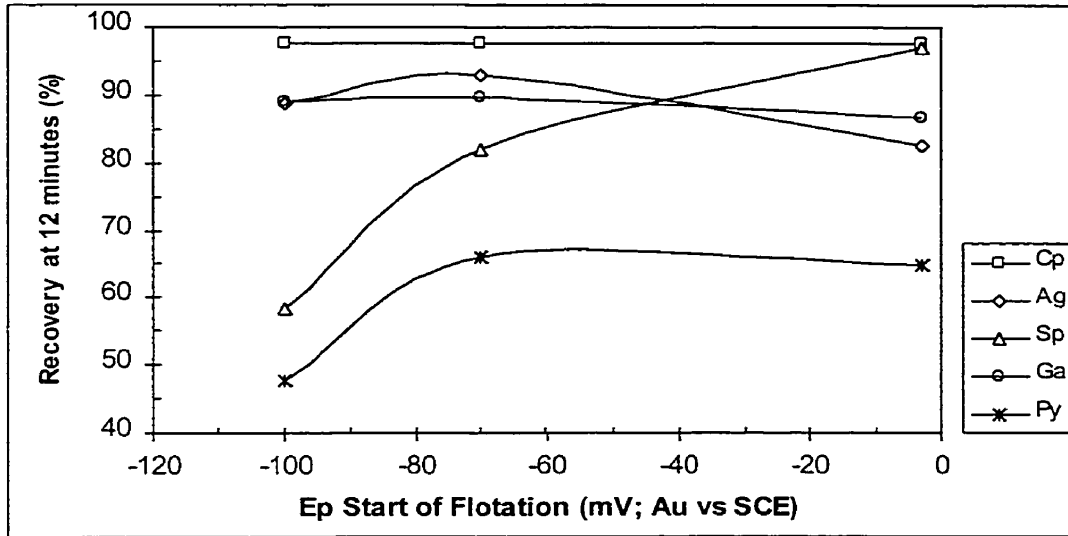
minerals, with the exception of the silver bearing ones, increase with increasing pulp potential. However, the impact is very minimal for chalcopyrite recovery past 10 minutes of aeration.

Figure 1.16 Impact of pulp potential (aeration) on conventional flotation of A-1 zone ore



The ultimate recoveries obtained (12 minutes of flotation) are presented as function of the initial pulp potential in Figure 1.17. There is essentially no impact of the pulp potential on the ultimate chalcopyrite recovery (98%). However, the higher the pulp potential, the higher the recovery of sphalerite to the point that bulk flotation is achieved when the starting Ep is -5 mV vs. SCE. Pyrite recovery is higher at -75 mV than at -100 but does not increase beyond that point. The recovery of both galena and the silver bearing minerals is lower when the starting Ep is -5 mV than at either -100 or -75 mV.

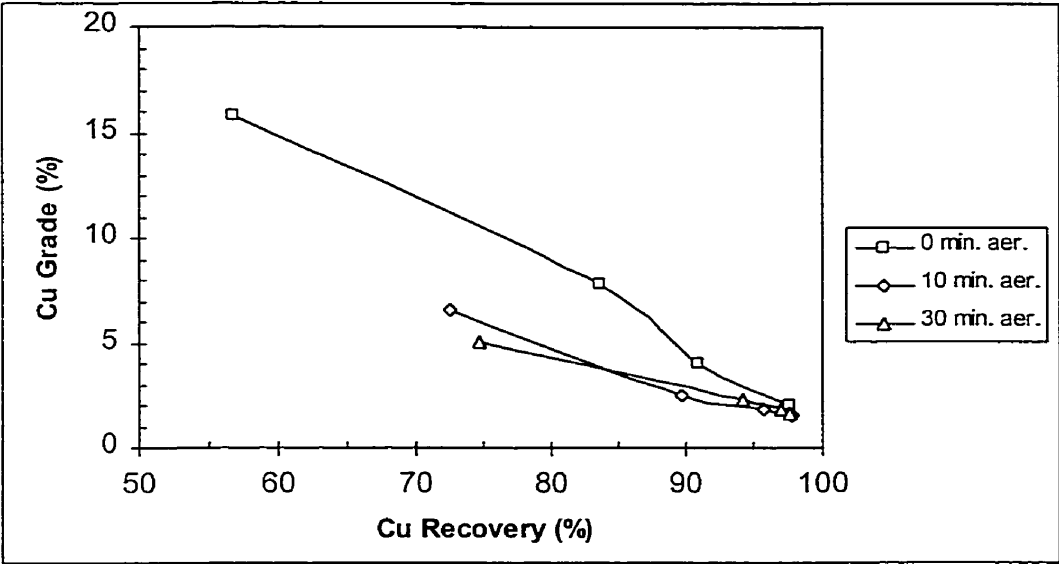
Figure 1.17 Impact of pulp potential on ultimate recoveries of A-1 zone ore



The curves for mineral recoveries as function of potential visually define what can be termed as windows of selectivity. For the curves presented in Figure 1.17, a window for selectivity between the chalcopyrite and sphalerite can be defined as starting to close at an  $E_p$  of  $-75$  mV and is entirely closed at  $-5$  mV. Similarly for chalcopyrite-pyrite selectivity, with a fully opened window for an  $E_p$  below  $-75$  mV and a half-closed window between  $-75$  and  $-5$  mV.

The net impact of the flotation response of the sulphide minerals to the pulp potential can be observed in the copper grade-recovery curves (Figure 1.18). As the pulp potential rises (aeration time increases), the grade of the first concentrate increment decreases. However, the curves all tend towards the same grade-recovery point where the fourth concentrate increment was floated with air.

Figure 1.18 Copper grade-recovery curve for aeration prior to flotation using collector



The main reason for the decrease in concentrate grade with aeration time is the increasing sphalerite recovery. Namely, chalcopyrite-sphalerite selectivity is reduced as a result of aeration (Figure 1.19). With respect to chalcopyrite-pyrite selectivity (Figure 1.20), past the initial large increase in pyrite recovery with 10 minutes of aeration, there is only a marginal impact on the selectivity with 30 minutes of aeration.

Figure 1.19 Chalcopyrite-sphalerite selectivity curves

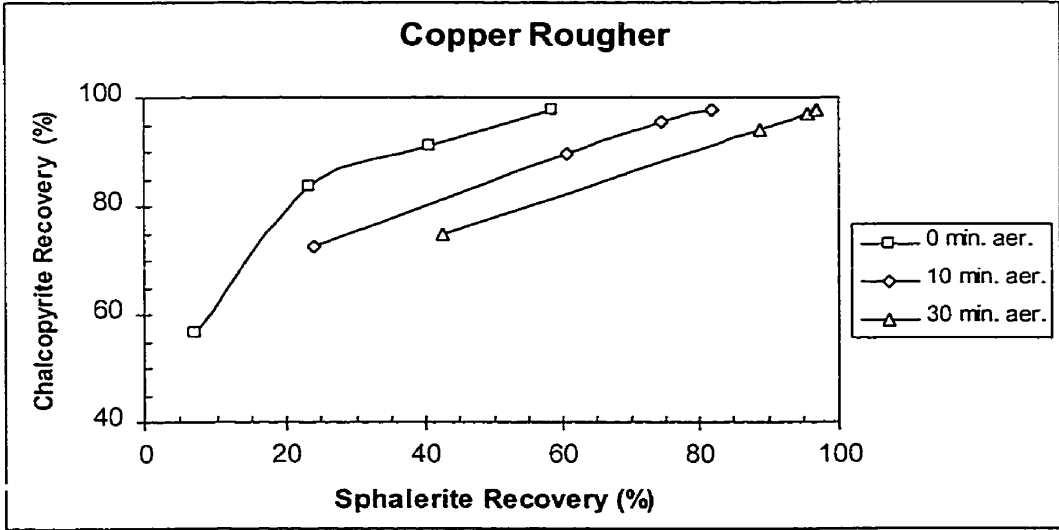
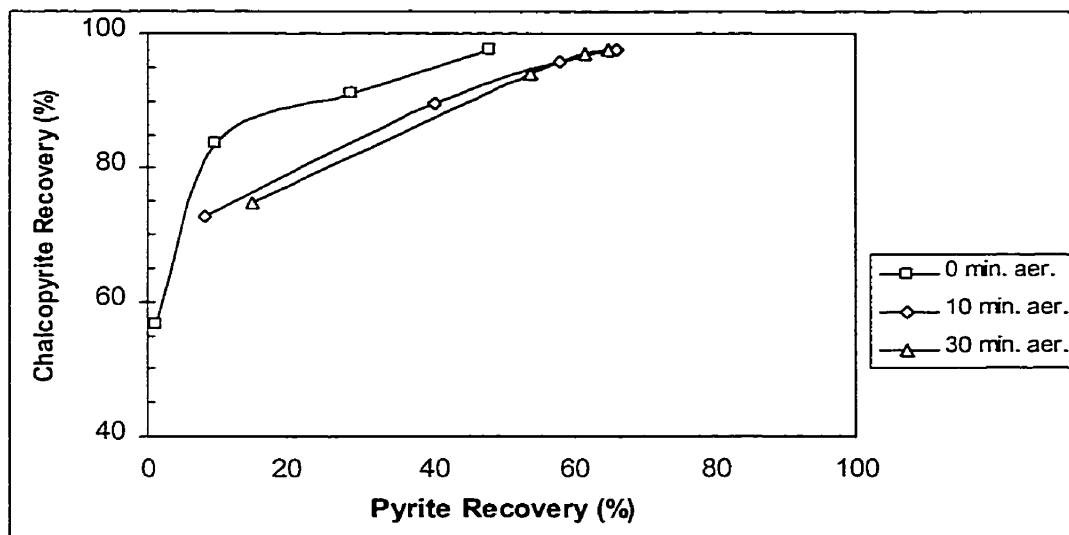


Figure 1.20 Chalcopyrite-pyrite selectivity curves



These test results suggested that aeration of the ore prior to the addition of the collector was detrimental to chalcopyrite-sphalerite and chalcopyrite-pyrite selectivities. The modification to the state of the pulp imparted by aeration could be monitored using the pulp potential. The increase in pyrite recovery between -100 and -75 mV vs SCE. could be due to a direct mineral-collector interaction. Raising the pulp potential decreases chalcopyrite-sphalerite selectivity to the point that at -5 mV a bulk chalcopyrite-sphalerite flotation is achieved. This could be due to the release of copper ions in solution from secondary minerals (e.g. chalcocite) present in the ore during the aeration and the fourth flotation stage with air. Such ions would then in turn activate the sphalerite.

In many ways, the results obtained are not too dissimilar with those obtained by Yuan and co-workers (165, 166) when investigating the impact of grinding environment and oxygen content of the gas introduced during a pre-conditioning stage and used for flotation on a copper-zinc-pyrite ore. Ultimate chalcopyrite recovery was relatively insensitive to the conditions imparted to the system when the ore was ground in an oxidizing environment (stainless steel mill and charge) and this would correspond to the semi-autogenous grinding environment of the A-1 zone circuit. Both sphalerite and pyrite

recoveries were affected by the conditions but a complete loss of chalcopyrite-sphalerite selectivity was not observed. This could be due to the presence of secondary copper minerals in the A-1 zone ore.

### 1.7 Activation and deactivation of sphalerite

Normally, sphalerite flotation requires activation with a heavy-metal cation which is usually Cu(II). Even though the overall reaction may be considered as an ion exchange, there seems to be experimental evidence that the activation of sphalerite proceeds through one or more electrochemical steps (119, 120). Similarly, deactivation may proceed through electrochemical steps (120). The processes involved in the activation of sphalerite have been generalized to other sulphide minerals (167).

One study of the activation of pyrite, pyrrhotite and galena by Cu(II) ions showed that the mechanism of activation involves electrochemical reactions as intermediate steps (119). Other investigations, especially on the activation of sphalerite, show similar findings with more complex systems: variable pH of the solution, activating ion (Cu(II), Cd(II), Pb(II)) and activation with UV irradiation (168, 169, 170).

An interesting development in the study of the electrochemistry of sphalerite during copper activation is the use of carbon paste electrodes (171, 172). A similar technique has been used for investigations on ilmenite (173), galena (174), low and high iron sphalerite (175) and chalcopyrite (176). Only in the latter case was a verification of the experimental results obtained with the carbon paste electrode using a massive mineral electrode was reported. All the known current peaks were present and at the expected potentials. The fabrication vary from a carbon matrix composite (CMC) electrode (171, 172) to a renewable carbon paste with a non-conductive binder (176).



The debate regarding the final form in which Cu(II) is present on the surface of sphalerite after activation is still not resolved, especially for short activation times. Early investigations indicated covellite (CuS; (120)) while others were suggesting chalcocite (Cu<sub>2</sub>S; (177, 178), an intermediate form between CuS and Cu<sub>2</sub>S (171, 172), a geerite-type structure (Cu<sub>1.6</sub>S (179), or a copper doped surface (146, 168, 169, 170, 178).

Industrial experience with sulphur dioxide (180) for sphalerite depression in the presence of small amounts of covellite appears to rule out CuS as the activating layer; sulphur dioxide caused the dissolution of covellite releasing copper ions into solution which then caused further activation of the sphalerite. It would be difficult to explain this behaviour if the activation layer was covellite, for it too would be attacked by sulphur dioxide. However, de-activation of sphalerite is more difficult to achieve than prevention of activation (120, 181, 182) and requires oxidizing conditions to be the most effective and the copper extracted must be prevented from re-activating the sphalerite usually by the use of a complexing agent such as sodium cyanide (120, 182), or amines (181).

However, it is generally accepted that the copper activation proceeds in two stages (165, 183): a fast first step involving the adsorption of copper ion on the surface of sphalerite and a slow second step involving the incorporation of copper within the lattice.

### 1.8 Generation of a separation process from fundamental studies

Generation of a separation scheme from the electrochemical behaviour of the minerals present in an ore appears to have been rarely attempted. However, a greater pressure to minimize pollution has caused a number of fundamental (184, 185, 186) and applied (187) investigations on the flotation behaviour of enargite (Cu<sub>3</sub>AsS<sub>4</sub>) and chalcopyrite (CuFeS<sub>2</sub>) to be initiated. The collector-mineral interactions of other impurity containing minerals like tetrahedrite (Cu<sub>12</sub>Sb<sub>4</sub>S<sub>13</sub>) and tennantite (Cu<sub>12</sub>As<sub>4</sub>S<sub>13</sub>) have recently been initiated (188).

Manufacturers of flotation collectors and speciality depressants can muster greater resources than mineral processors in plants and industrial research laboratories by the mere nature of their business. Definite advantages are an intimate knowledge of the reagents, which is rarely published for competitive reasons, and the possibility to investigate several different ores to generalize their observations.

Many flotation reagents are chance discovery, for example diethylene triamine as pyrrhotite depressant was discovered during an investigation on what might be the impact of epoxy compounds for rock bolts (189). However, some recent collector families, such as the F-series based on chelation chemistry, and S-series based on oxidation-reduction chemistry promoted by Mineral Reagents International (190) have been generated from a concerted understanding of the electrochemical model of the flotation of sulphide minerals.

## 1.9 Conclusions

The interpretation of flotation from an electrochemical view point showed that flotation, in the presence or absence of a collector, is possible only if the oxidation-reduction potential of the system is within limits which are dependent on the mineral present and the history of the mineral prior to flotation.

For a given mineral to be induced into being hydrophobic, the pulp potential must be higher than that of the reaction causing the hydrophobicity; metal deficient surface/ elemental sulphur for collectorless flotation or adsorption of a collector on the surface. In the case of collector adsorption, there are indications that the semi-conducting properties impact the form in which it can do so, namely as an adsorbed collector, a metal-collector compound, or adsorption of the dimer of collector.

There is limited information available on the interaction between dithiophosphinate based collectors and sulphide minerals but it appears that such collectors will generally behave similarly to the common xanthate and dithiophosphate families. A possible irreversibility of the reaction with copper, and a capability to complex zinc may give rise to difficulties for selective flotation of a copper-zinc ore.

The grinding environment of the A-1 zone circuit is conducive to selective collectorless flotation of the copper minerals. Unfortunately, the silver minerals cannot be recovered without a collector. A low pulp potential is required when the collector (Aerophine 3418A) is added to prevent in-situ activation of sphalerite during subsequent flotation with air as flotation gas. An aeration stage performed prior to collector addition does not improve recovery of the copper minerals and is detrimental to selectivity.

## 2 THE ELECTROCHEMICAL POTENTIAL OF THE PULP

### 2.1 Introduction

In a review paper addressed mainly towards mineral processors involved in the design of new concentrators or in the sustained improvement of old ones, Suttill (82) in 1990 provided astounding statements about the status of flotation control technology as the industry entered the last decade of the century. While challenging why mill metallurgists would be content with ninety percent recovery, he suggested that the most interesting developments which might help increase recoveries were concerning the use of electrochemical variables in flotation control. This coincided with the dissemination of the general concepts underlying the electrochemical model for the flotation of sulphide minerals within the industry.

Suttill however pointed out the lack of commercial applications for flotation control and attributed this to two factors. Firstly, the translation of laboratory defined conditions to the plant was difficult due to the complexity of the interactions occurring during grinding notably the degree of steel abrasion and oxygen uptake. Secondly, the selection of suitable electrodes to measure redox potentials in flotation pulps was still in flux. The traditional noble metal electrodes were deemed less suitable than mineral electrodes, because of dissimilar reaction kinetics to the sulphide minerals in the pulp and their poisoning over long periods of use.

In a more technically oriented review, Jones (83), who has been one of the pioneers in the measurements of chemical variables of flotation pulps (28, 29) described the state of the art of measurement and control techniques for xanthate, perxanthate, sulphide, and redox potential. With respect to redox potential, he noted the multitude of materials which have been used for the sensing electrode (platinum, platinum black, gold, sulphide minerals, glassy carbon), the general confusion as to the reference for the voltage scale when results are reported (saturated calomel electrode or standard hydrogen

electrode), the lack of consensus in terms of terminology (redox potential, pulp potential, Eh,  $E_{Pt}$ , pe), and the uncertain cause and meaning of such measurement.

Contrary to Suttill, Jones claimed that noble metal electrodes for redox measurements are rugged and relatively maintenance free and that determining the best location(s) for measurement and control in an operating plant would be the most challenging task. In addition, he indicated that only poorly maintained installations would require the use of electrode verification procedures which were starting to appear in the literature.

Both authors agreed there was a relationship between the floatability of sulphide minerals and the oxidation-reduction state of the pulp, as indicated by a redox sensing electrode pair. They unfortunately expressed nearly opposing views for one of the key factors in the translation of the laboratory practices into an effective plant monitoring and control: explainable and reliable on-line measurement of the electrochemical potential of the pulp.

The opposing camps were, and still are, noble metal electrodes against mineral electrodes. In addition, when it comes to noble metal electrodes, platinum is often selected over gold because of its traditional use in hydrometallurgical systems although there is evidence that it should not be so for flotation systems (26, 35, 36, 37, 38, 40, 44). Further complicating the issues are other inert sensing materials like glassy-carbon (83, 191). The fine points of measuring electrochemical potentials in mineral slurries need to be addressed and the timing appears appropriate.

## 2.2 Fundamental aspects

### 2.2.1 Solutions

## Simple solutions

The oxidizing or reducing conditions in a solution can be represented by an oxidation-reduction potential. Short-hand notations for the oxidation-reduction potential are ORP, redox and EMF (electromotive force; rarely encountered in recent publications). Synonyms to the oxidation-potential are rest potential ( $E^r$ ) and open circuit potential ( $E_{oc}$ ) and are often used when the electrode can actually interact with the solution (e.g. a mineral electrode) rather than just sensing it. When the potential is referenced to SHE then the notation Eh is preferred. A short-hand notation which has become common in mineral processing, particularly in Australia and in Europe is  $E_{Pt}$ , i.e. the potential measured using a platinum electrode and referenced to SHE (20, 30).

When the system is at equilibrium, and is reversible, the potential measured by inserting the inert indicator electrode and a reference electrode into the system is the rest potential of the reaction. From the knowledge of the concentrations and activity coefficients of the ions, the standard potential of the reaction can be determined. The equation linking the redox potential,  $E$ , to the standard potential,  $E^\circ$ , is the Nernst equation which is usually written as:

$$E = E^\circ - \frac{RT}{nF} \ln \left[ \frac{\alpha_{\text{Reduced}}}{\alpha_{\text{Oxidized}}} \right] \quad [17]$$

where  $n$  = number of electrons involved

$R$  = gas constant (joules/gmoles\*K)

$T$  = temperature (K)

$F$  = Faraday constant (96500 coulombs/gmoles)

$\alpha$  = activity = activity coefficient \* concentration

The Nernst equation is the electrochemical equivalent of the Gibbs free energy change equation for chemical reactions.  $E$  and  $\Delta G$ , the free energy change, are linked by

$$E = - \Delta G / nF \quad [18]$$

Hence,  $E^\circ$ , being a thermodynamic quantity, is dependent on the temperature and the values for redox electrode reactions are usually tabulated for a temperature of 25 °C (192).

For a given couple involving  $n$  electrons,  $E$  will depend on:

- i) The ratio of the activities (or concentrations) of the oxidized and reduced forms of the couple
- ii) The temperature  $T$  from  $E^\circ$  and the coefficient of the logarithmic term

It is desired to measure the open circuit potential, i.e. no current flow between the sensing and reference electrodes but in practice no voltage measuring device has an infinite impedance. The input impedance of the voltmeter (or the analogue to digital converter) must be at least 1000 times greater than the solution resistance and a value of  $10^{11}$  to  $10^{13}$  ohms is recommended (52).

The common reference electrode, SHE, has a potential of 0.0 V at 25 °C and this potential is independent of temperature by convention. This arbitrarily defined reference stems from the impossibility of measuring the absolute potential of a single electrode process (193) although attempts to calculate it are performed from basic principles (194).

The redox potential has a similar meaning to the change of free energy of a reaction but applied to reactions involving electron transfer. The redox potential indicates the capability of the solution to oxidize (or reduce) a given metal, a mineral, or another ion. Solutions with more positive  $E_h$  will oxidize metals, minerals, or ions with less positive electrode potentials and vice versa.

However, as with any thermodynamic quantity, no indication on how fast the reaction will proceed can be obtained from the redox potential. The greater the potential difference between the two electrode reactions, the greater the driving force for the overall reaction.

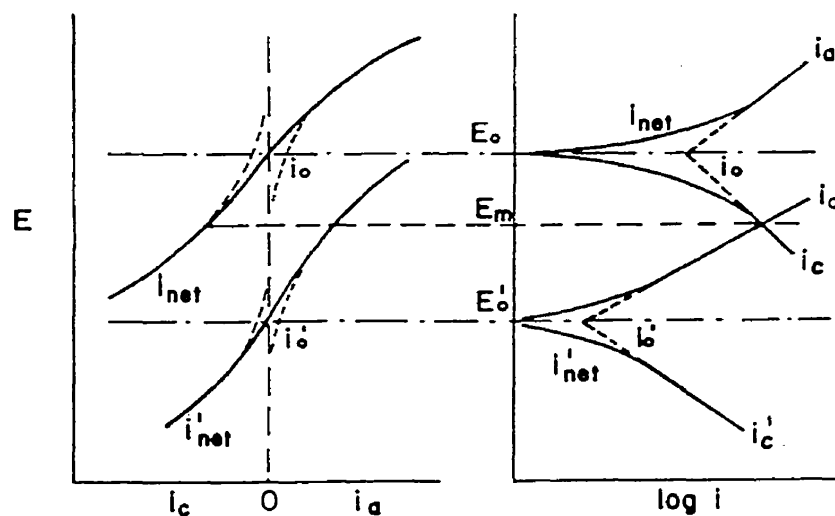
### Mixed potential model for complex solutions

When there are a number of couples present in equilibrium in the solution, the concept of the redox potential still holds. Namely, all the couples exhibit the same potential i.e. for two couples Ox1/Red1 and Ox2/Red2:

$$E_h(\text{Ox1/Red1}) = E_h(\text{Ox2/Red2}) \quad [19]$$

The two couples cannot be any more considered independently since the electron exchange can proceed internally to each couple and between the couples (Figure 2.1). The measured potential will reach a value which lies between the reversible potentials of the two couples, where the component anodic and cathodic processes proceed at equal and opposite rates (zero net electron flow).

Figure 2.1 Mixed potential model (left: linear scale; right log scale) (195).





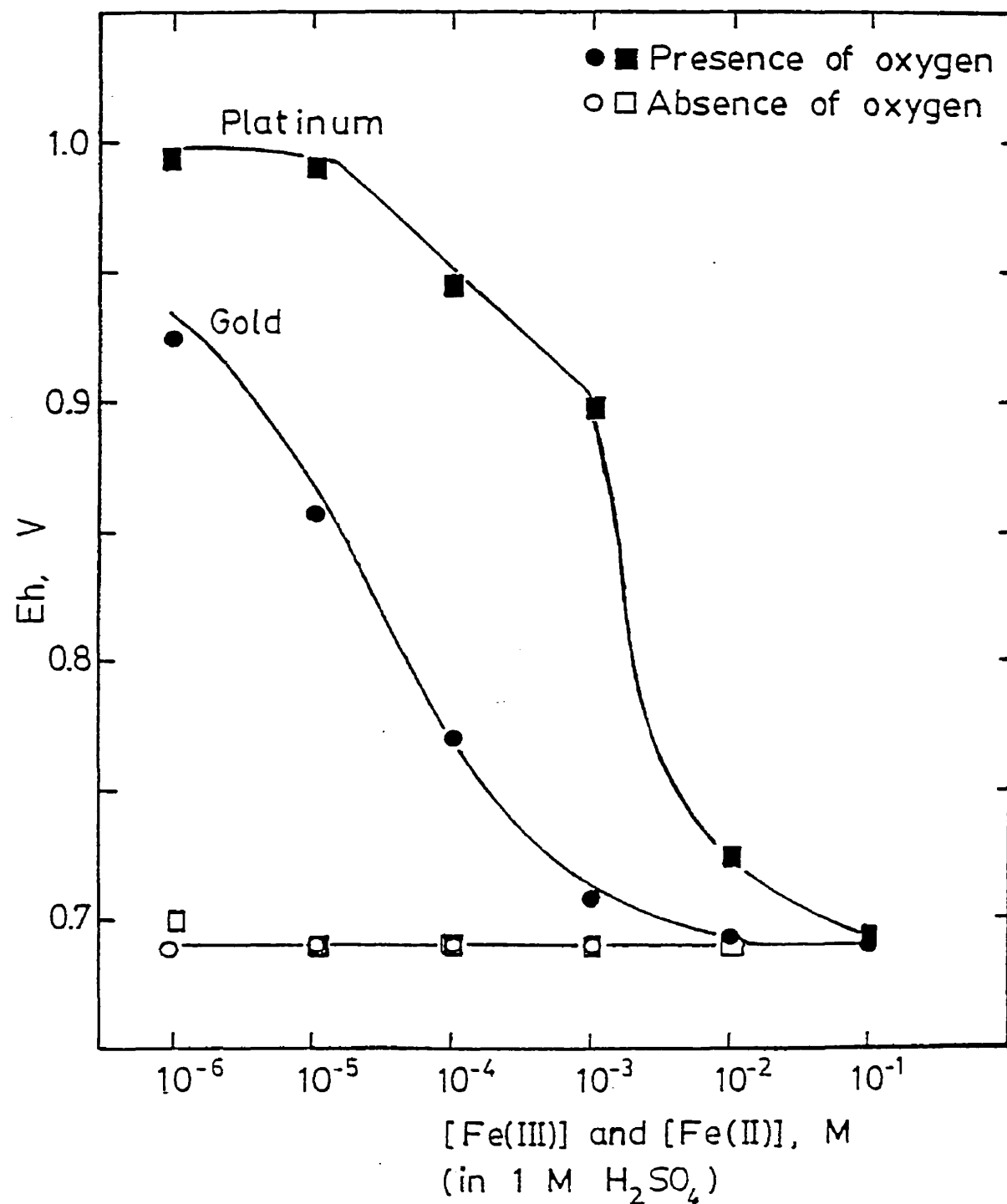
The mixed potential provides an explanation for the apparent "reactivity" of the platinum electrode (195) and the difference between platinum and gold electrodes when measuring the redox potential of the Fe(III)/Fe(II)-O<sub>2</sub>/H<sub>2</sub>O system in 1 M H<sub>2</sub>SO<sub>4</sub> (36, 195).

In the absence of oxygen, the experimental potentials are near the reversible potential (0.69 V) when equal concentrations of Fe(III) and Fe(II) are present as their sulphates, this for all level of concentrations (open symbols, Figure 2.2). The experimental results obtained by Natarajan and Iwasaki (195) are similar to that reported by Rand and Woods (36) shown in Figure 2.2. In the presence of oxygen, the experimental potentials differ from the reversible potential of Fe(III)/Fe(II) and the departure is more pronounced at low iron concentrations and greater for platinum than gold. Platinum being catalytically more active than gold for oxygen reduction senses this reaction more than that of Fe(III)/Fe(II) at low iron concentrations (36). A similar difference in response has been observed between platinum and glassy-carbon electrodes in aerated and de-oxygenated solutions (191).

The lines on Figure 2.2 are the theoretical values predicted by the mixed potential model. They were calculated from an Evans diagram (36) which presents potential-current curves similar to those shown in Figure 2.1, but for the individual couples and for the different concentration levels. A system consisting of two couples, as shown in Figure 2.1, is simple to analyze. If the reaction rate of Ox1/Red1 is determined by activation (i.e. independent of mixing or concentration like the reduction of oxygen) while the reaction rate of the couple Ox2/Red2 is diffusion controlled (like the reduction of ferric to ferrous), then varying the intensity of mixing, or the total concentration will change the reaction rate of Ox2/Red2, and consequently the measured mixed potential.

The situation is more complex when more than two couples are present in the solution. In general, the couple which will dominate the measured potential will be the one which is kinetically favoured. Often, this is the one in greatest concentration.

Figure 2.2 Redox potential measurements for the Fe(III)/Fe(II) system in the presence and absence of oxygen (36).



pe

Pålsson and coworkers (191, 196, 197) have introduced the concept of "pe" by analogy with the work of Du Rietz (198) who used extensively Bjerrum-diagrams where flotation conditions are defined from the concentrations of metal ions (pMe) and hydrogen ions (pH). pe is related to the redox potential of the solution through

$$pe = Eh / g \quad [19]$$

where  $g = RT / F \ln(10) = 59.16 \text{ mV}$  at  $25^\circ\text{C}$  and 1 atm.

The term is somewhat confusing in that the point of reference is still the standard hydrogen scale although not explicitly stated as in Eh. In addition, the prefix "p", by analogy with pH and pMe, implies a logarithmic scale. Although the activity ratio in the Nernst equation is logarithmic, the standard potential of the reaction is not. With pH, a unit means a ten fold change in concentration of the hydrogen ion. Does a pe unit mean a ten fold change in the oxidation power of the solution? Unfortunately not, it only implies that the measurement of this oxidation power has changed by 59.16 mV. Although the idea of having a concept capable of expressing relative changes in oxidation-reduction state is welcomed, by its definition, pe does not appear to be as clear as desired for the expression of such a concept.

#### Poise and flexibility

Two other terms related to the oxidation-reduction potential, but rarely used in recent literature are the poise and its inverse the flexibility. These concepts reflect the inertia of the systems to changes in its equilibrium point when potential modifying reagents are added, or due to the effect of mixing (199). As such, the poise is a good indicator of the ease of measuring redox potentials in complex solution and is expressed mathematically in a form similar to the Nernst equation (199):

$$\text{Poise} = \frac{dy}{dEh} = \frac{nF}{RT} \frac{y(B-y)}{B} \quad [20]$$

where  $y$  is the concentration of the oxidized form of the redox couple and  $B$  is the total concentration of the oxidized plus reduced forms.

Unfortunately, the concept of poise in electrochemical systems is too easily confused with the unit of poise for the viscosity of fluids. Nevertheless, it expresses a similar idea. That of a resistance to change.

The practical implication of poise is that  $Eh$  responds but weakly to small changes in  $y$  when the oxidized and reduced forms are present in equal amounts. The greater the poise, the easier it is to measure the redox potential. This is the case of  $Eh$  buffers such as ZoBell solutions (Fe(III)/Fe(II) as their cyanides) (200). And conversely, the greater the poise of a system, the more difficult it will be to modulate its oxidation-reduction state by introduction of oxidizing or reducing agents.

Having a well poised system was the main reason why Rand and Woods used a unity concentration ratio of iron species (36). In a multi-component system, the redox couple with the largest poise in relation to the others will dominate the perceived oxidation-reduction state (199).

#### Other considerations

The reference electrode for redox measurements can be any of the following: Standard Hydrogen Electrode (SHE), Saturated Calomel Electrode (SCE) or silver/silver chloride (Ag/AgCl). These are non-polarizable electrodes as their potential does not change with current being passed through them or ionic concentrations.

The reference electrode is connected to the solution via a porous junction which allows exchange of ions (and electrons) between the electrolyte of the reference and the solution. Under most circumstances, the small potential gradient across the junction is minimal and can be ignored unless one attempts to determine the standard potential of a reaction. However, if the junction becomes blocked due to precipitation of products of reaction between the ions of the electrolyte and those of the solution, then the potential gradient will rise and cannot be considered negligible for redox potential measurements. Ion selective electrode pairs, and pH sensors can always be calibrated with respect to concentration vs. measured potential; redox electrode pairs cannot.

Another complication is to identify the type of reference electrode in the pair because the values given above are with respect to the SHE (standard hydrogen electrode which is by definition, temperature independent). This can be tricky for combination electrodes.

Table 2.1 presents the potentials of the two most common reference electrodes as functions of temperature. The potentials given include the junction potential present at medium pH values.

Table 2.1 Reference electrode potentials as function of temperature (52, 53)

T (°C)	E SCE (mV vs. SHE) (53)	E Ag/AgCl (mV vs. SHE)	
		3M KCl (53)	4 M KCl (52)
5	+257.3	+222.4	+212
10	+254.1	+218.9	+209
15	+251.0	+215.3	+206
20	+247.7	+211.5	+203
25	+244.4	+207.6	+200
30	+241.1	+203.6	+196

The conversion to use is given by

$$E = E (\text{SHE}) - E (\text{R}) \quad [21]$$

### 2.2.2 Mineral slurries

The measurement of oxidation-reduction potentials in mineral slurries is further complicated by the presence of sulphide particles which collide with the sensing electrode.

It may be hypothesized that the sensing electrode monitors each contact with a mineral particle in addition to the mixed potential of the solution.

#### Impact of electrode material and shape

During each contact between the electrode and a mineral particle, there is an exchange of electrons so that they tend towards a single potential, similar to the concept of a galvanic potential. Because the particle has a much smaller surface area than the sensing electrode, it will limit the rate of the oxidation-reduction reaction required for the exchange of electrons. To some extent, the perceived oxidation-reduction state of the system will still depend on the material of the sensing electrode.

This partially explains the results obtained by Rand and Woods (36), Labonté and Finch (39, 40, 201), Neuharth et al. (37), and Ekmekçi and Demirel (131) when noble metal electrodes and mineral electrodes are used in the same slurry. In particular, a platinum black electrode (high surface area for exchange with solution compared to surface area available for contact with particles due to deposition of porous platinum on platinum) will sense exclusively the solution potential rather than the pulp potential (26, 36, 39). Since platinum black electrodes have been found to consistently exhibit a potential 200 to 300 mV higher than that of a smooth platinum electrode (26, 36, 39) and

were often insensitive to the introduction of oxidizing or reducing agents (26), it is plausible that they nominally sense only the potential of the oxygen reduction.

The relative behaviour of smooth platinum and gold electrodes compared to mineral electrodes when immersed in a galena slurry (36), a chalcopyrite-molybdenite-pyrite slurry (37), a chalcopyrite-galena-sphalerite-pyrite slurry (26, 36, 39, 201), or a chalcopyrite-pyrite slurry (131) is a combination of their affinity for the oxygen reduction reaction as discussed previously and the probability of contact with the particles in the slurry. Platinum electrodes have been found to consistently exhibit more positive potentials than gold and mineral electrodes in slurries. In addition, electrodes shaped to give a high probability of contact with the mineral particles (e.g. open spiral) exhibit potentials closer to the mineral electrodes than electrodes shaped to give a low probability of contact (e.g. foil) (26, 39, 201).

Commercially available redox electrodes for laboratory and process plants tend to fall within the guidelines of the ASTM standard (52), namely an electrode surface of 1 cm<sup>2</sup>. The most economical way to obtain such a surface area is a plate (rectangular or circular) or a ring and both shapes are not conducive to a high probability of contact with mineral particles. Less frequently used shapes are wires (e.g. 1 mm diameter and 1 cm long; laboratory) and a slug (e.g. 0.5 cm diameter and 1 cm long; industrial).

On the basis of the potential of the mineral-solution interface being the one that matters for flotation, and the closer correspondence between the potential exhibited by gold electrodes and mineral electrodes, it has been suggested that gold would be more suited for mineral flotation systems than platinum (26, 36, 39, 199, 201).

Some investigators have been using gold electrodes for mineral slurries with or without mentioning the reasons (43, 37, 38). But for the most part, this suggestion has remained relatively un-remarked (83, 103, 182) while others have suggested glassy-carbon electrodes instead of platinum (191, 196, 197).

Given these uncertainties, some investigators have been very cautious (e.g. Ekmekçi and Demirel (131)) and mineral electrodes are monitored in addition to the platinum one. The measurements made with the platinum electrode are used to establish the relationship between mineral floatability and potential and the mineral potentials are an aid in the interpretation. Others, for example Hintikka and Leppinen (202, 203), use only mineral electrodes of the main sulphides of the ore being investigated. However, they do not specify if a set of electrodes was prepared for each ore, or the same set used for all ores. In addition, the mineral electrode used to establish the mineral floatability potential relationship is rarely clearly specified.

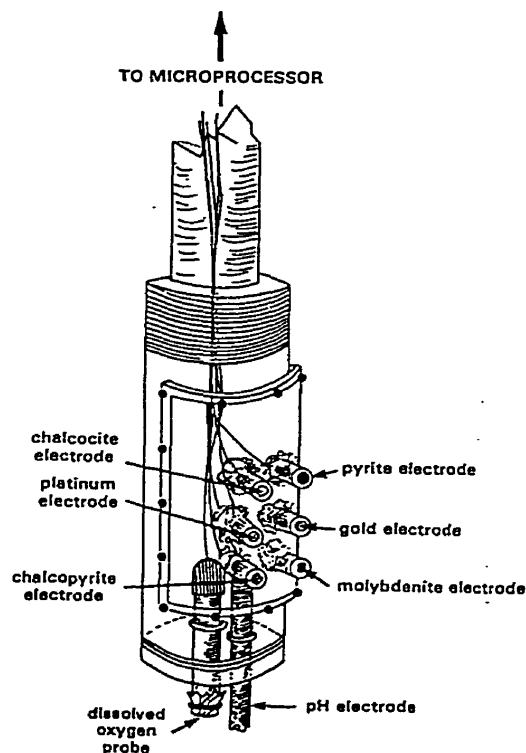
#### Solution or mineral potential

The uncertainty related to the physical significance of the measurement with noble electrodes in a mineral slurry may be avoided by measuring the potential of either the solution or the main sulphide mineral in the slurry. An examination of commercial flotation process control systems based on electrochemical principles indicate that both approaches have been taken.

Researchers at USBM developed a multi-electrode pulp potential sensor consisting of noble metals (gold and platinum) and mineral electrodes of the sulphides present in the pulp (37). A schematic of the probe is shown in Figure 2.1. The basis for mineral electrodes was that this was felt to be the potential to measure to sense the reactions at the mineral surfaces and noble metal electrodes were included as well because of their traditional use. However, practical considerations, namely the deposition of scale on the electrodes over days of continuous immersion in the mineral slurry rendered mineral electrodes impractical. The sensor was later simplified to a single gold electrode and included an automated electrochemical cleaning technique based on potentiostatic conditioning. It has been tested in a copper-molybdenum concentrator (80, 81). The dismantlement of the research and development function of USBM soon afterwards (204) has prevented further refinements to the system.



Figure 2.3 Multi electrode probe (37)



The OK-PCF system promoted by Outokumpu involved a "custom designed" sensing electrode which was later described as being a mineral electrode (41, 42, 72, 73, 74). The PIRANA system promoted by BRGM uses the redox potential of a micro-filtrate sample continuously obtained from the flotation pulp (75). Both systems are shown schematically in Figures 2.4 and 2.5 respectively. The choice of the redox measuring technique appears to have been dictated by the quality of the sample needed for the xanthate concentration monitor which is an integral part of the equipment. The xanthate concentration monitor proposed by Outokumpu is based on potentiometric titration which can be performed in the flotation pulp while BRGM uses a UV spectrometer requiring a sample free from solid particles.

Figure 2.4 OK-PCF electrode system (72)

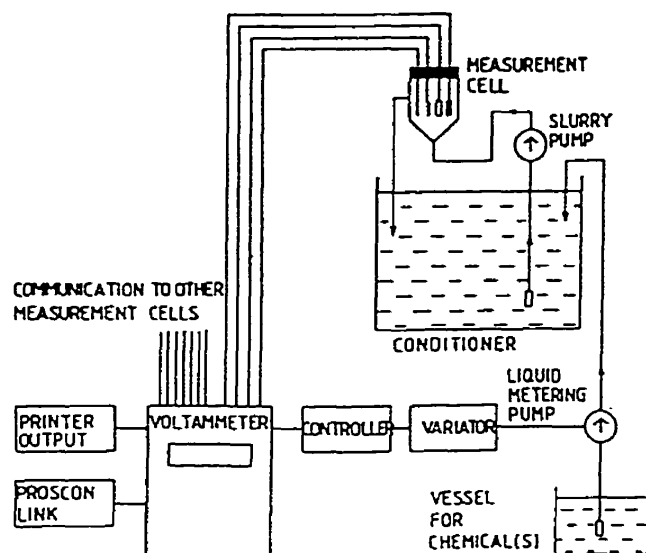
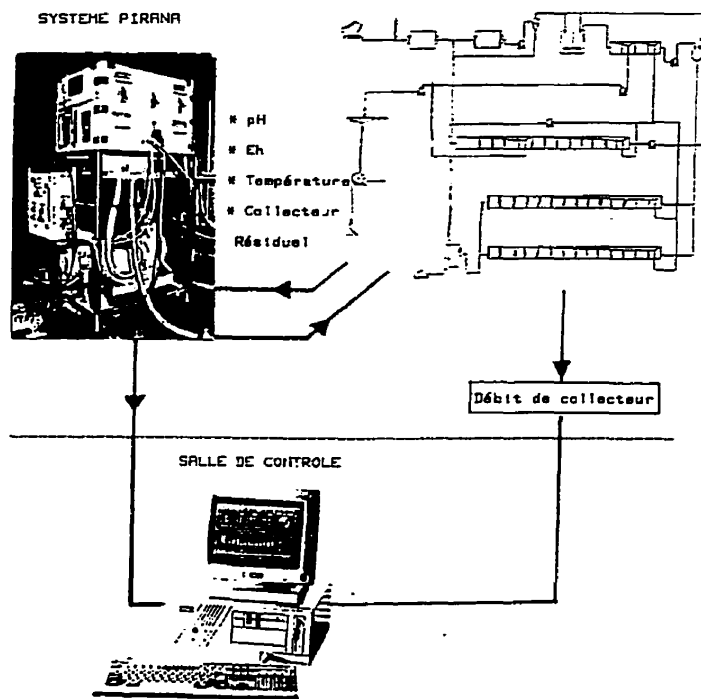


Figure 2.5 PIRANA system (75)



The E-Con system promoted by Control International (82) is also based on the use of mineral electrodes. However, the information available is insufficient to compare this system with OK-PCF or PIRANA.

The OK-PCF system does not appear to have been installed in concentrators outside of the Outokumpu group. Neither the PIRANA nor the E-Con system appears to have passed the stage of pilot plant test. Given the research and development might that these organizations have, one may have doubts as to the real promise of modulation of selectivity using the electrochemical potential of the system.

There are strong arguments in favour of using mineral electrodes over measuring only the pure solution potential. Although mineral electrodes have been used for investigative purposes, it is not desired to have a mineral electrode for on-line monitoring of the pulp potential. A gold electrode appears preferable especially when considering some practical factors.

For one thing, obtaining pure mineral pieces can be quite challenging. Literally mountains of broken ore had to be moved and examined to obtain the five raw electrodes of each mineral for the previous study on the A-1 zone ore of Les Mines Selbaie due to the disseminated nature of the copper and lead minerals (26). Obtaining pure chalcopyrite from Kidd Creek ore was easy in comparison. However, would the Kidd Creek chalcopyrite interact with the slurry at Les Mines Selbaie the same way as a chalcopyrite from Selbaie? Intuitively the answer would be no.

Slight differences in composition (e.g. sulphur rich vs. sulphur poor) and/or the presence of varied level of impurities (e.g. nickel in solid solution in pyrrhotite) are likely to affect the manner in which the surface of sulphide minerals from different sources interact with the solution. The impact will be more on the rates of reaction than on the equilibrium as indicated by Biegler (144) in an investigation of the relationship between activity and semi-conducting properties of pyrite electrodes. Since the measured potential

is a mixed potential, and thus dependent on reaction kinetics, there is a strong basis to ascertain that mineral electrodes from varied sources will yield different potentials.

Another matter is the selection of which sulphide mineral should be used for sensing the potential. The results by Labonté and Finch (39, 40, 201), Neuharth et al. (37), and Ekmekçi and Demirel (131) when noble metal electrodes and mineral electrodes are used in the same slurry clearly indicate that the potential sensed by one mineral is different than that of another mineral.

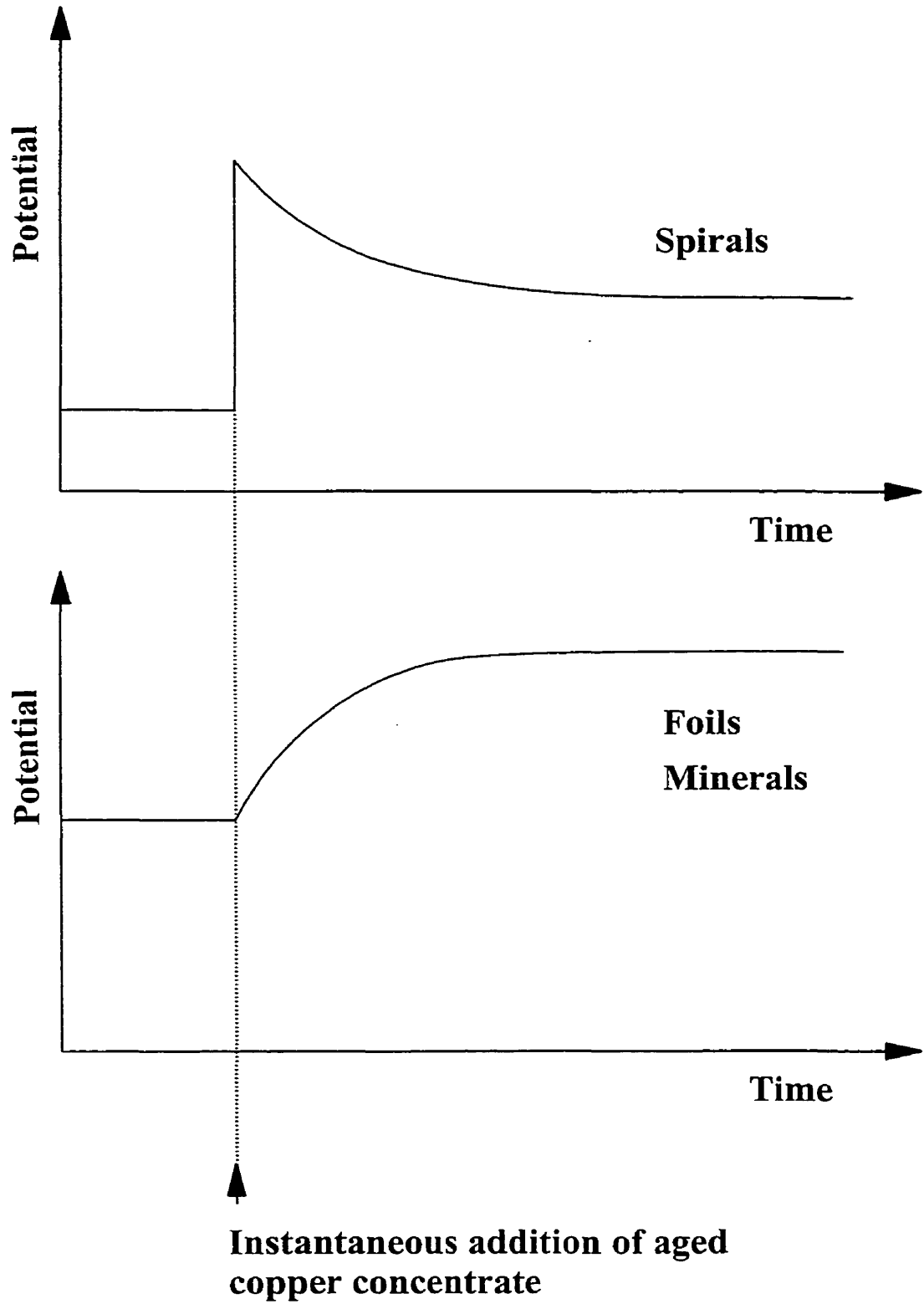
The use of multiple mineral electrodes during investigations of the impact of the electrochemical potential on the flotation response is beneficial in understanding the behavior of the minerals. However, the potential of only one sulphide mineral can be used to develop a process control scheme based on such measurement. This selection is not an obvious matter for most situations. For example, would a galena electrode be more appropriate than a chalcopyrite electrode for a bulk Cu-Pb rougher stage for a Cu-Pb-Zn ore? Such question cannot be answered without extensive studies.

Finally, while it is easy to implement a laboratory procedure involving polishing of the mineral electrodes prior to every test, it is another matter to implement a regular cleaning scheme when the mineral electrode is continuously immersed in the slurry. The use of dilute acid to remove scale, a common practice with pH sensors in plants, will attack the surface of a mineral electrode over time and lead to inaccurate measurements. A gold electrode would not be affected by such regular cleaning.

### 2.2.2 Modelling of pulp potential measured using a noble metal electrode

A previous investigation on the impact of shape of noble metal electrodes on the measured potential when sulphide particles were added to the solution resulted in potential-time profiles often looking like those shown in Figure 2.6 (26). Such profiles are similar to that for the response of a resistance-capacity circuit to a change in potential.

Figure 2.6 Typical potential-time profiles during addition of mineral particles to a solution (26)



Kastening and co-workers (205, 206, 207, 208, 209, 210, 211) have examined the charge transfer during the contact between a graphite or an activated carbon particle and a noble metal electrode. A model has been developed considering the surface of the electrode and that of the surface of the particle as capacitors and the electrolyte present between the two double layers as a resistance connecting one end of each capacitor. When a contact is made, represented by closure of a switch between the ends of the capacitors, current can flow to equilibrate the two potentials.

They examined the contact from the view point of potential conditioning of either the particle or the electrode and derived the following equation for the electrode potential  $E_m(t)$  during contact (208):

$$E_m(t) = E_\infty - [E_\infty - E_m(t_c)] \exp(-(t-t_c)/RC_e) \quad [22]$$

where  $E_\infty$  is the electrode potential at rest,  $E_m(t_c)$  is the potential at the end of the contact,  $t - t_c$  the time elapsed since the end of the contact,  $R$  the sum of the external measuring and the effective electrolyte resistance, and  $C_e$  the electrode capacity.

Using an oscilloscope, they examined the current passing between single particles contacting the electrode and various electrode and particle sizes were investigated. In the order of 8000 to 12000 contacts were evaluated per system using an automated data processing program. Particle electrode contacts were typically between 6 and 12  $\mu$ s in duration. However, the model was fitting well only contacts for activated carbon particles. Current pulses exchanged between graphite particles and the electrode were widely distributed to the point that only 10% of the contacts observed were fitting the model described.

Examples of current pulse distribution during contacts are shown in Figure 2.7 (activated carbon) and Figure 2.8 (graphite).

Figure 2.7 Current pulse distribution during particle-electrode contacts (activated carbon; 550  $\mu\text{m}$  particles, 50  $\mu\text{m}$  electrode) (208)

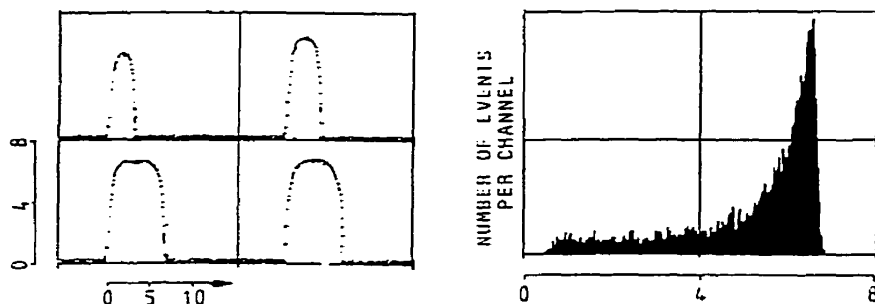
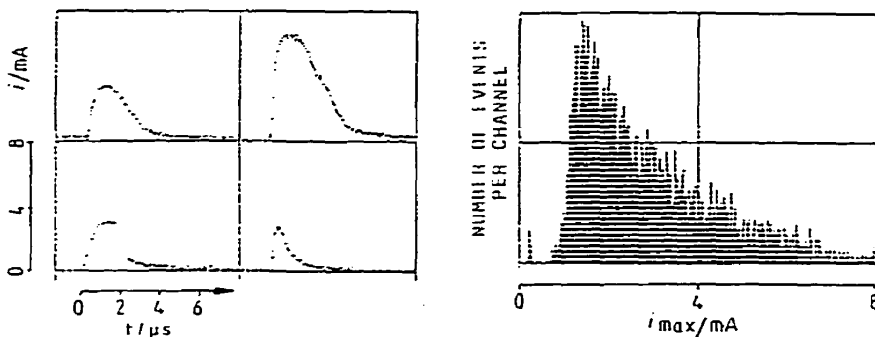


Figure 2.8 Current pulse distribution during particle-electrode contacts (graphite; 100  $\mu\text{m}$  particles, 50  $\mu\text{m}$  electrode) (208)



It is noted in Figures 2.7 and 2.8 that higher currents are exchanged when the diameter of the particles is much larger than that of the electrode. Another difference is the large surface area per unit volume of the activated carbon particles due to the internal pores compared to the graphite particles. This difference in surface areas translates into a larger capacitance for activated carbon particles than for graphite particles.

The current pulses in Figure 2.7 exhibit a shape close to an ideal square pulse and this reflects the much larger capacitance of the 550  $\mu\text{m}$  activated carbon particles in relation to the 50  $\mu\text{m}$  electrode. On the other hand, there is an exponential tail in the current pulses for the contacts between 100  $\mu\text{m}$  graphite particles and a 50  $\mu\text{m}$  electrode

which reflects the smaller difference in capacitance between the particles and the electrode.

The system is more complex than the idealized capacitor-resistance-switch model suggested (B. Kastening, Personal Communication, February 1990) with the conducting properties of the particles playing an important role. Later investigations (209, 210, 211) have suggested that the observed currents with activated carbon particles were due to the semi-conducting properties of the material with a band gap of 0.034 eV (210).

Most of the other investigations in the area of particle-electrode contact or interaction are related to electrochemical reactions, for example fluidised bed electrodes (212, 213, 214) or interference of the mass transfer to the electrode with inert particles (214, 216, 217). Hence, it would be difficult to obtain additional information of relevance to particle-electrode contact for monitoring the pulp potential.

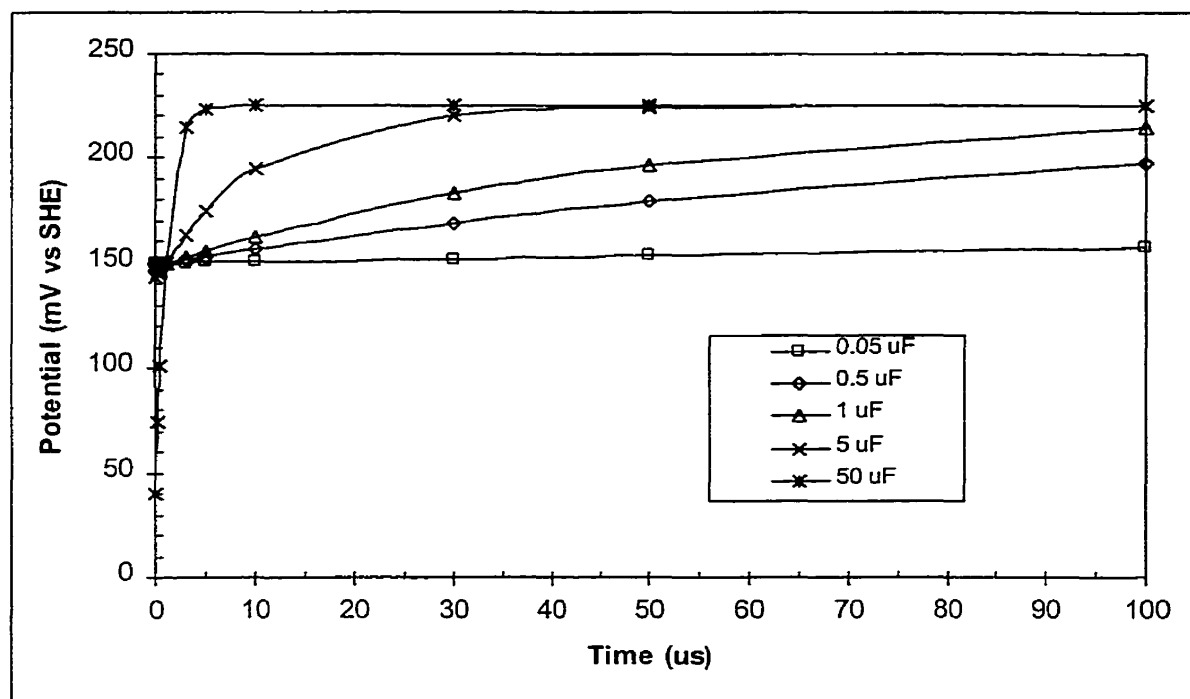
An experiment similar to that performed by Kastening and co-workers (208) could be devised from a view point of potential monitoring. However, successful modelling for sulphide mineral-sensing electrode contacts would require determination of the band gap of the mineral, the surface capacitance of the mineral particles and of the electrode, and the resistance of the electrolyte. In addition, an oscilloscope would be required and thousand of events examined.

Reversing the concepts expressed in Equation [22] to a monitoring electrode rather than a current feeding electrode yielded potential-time profiles shown in Figure 2.9. For the simulation, values were taken as 50 ohm for the electrolyte resistance, a rest potential of 225 mV for the solution and an end of contact potential of 150 mV due to the particle. The capacitance of the measuring electrode is as noted in the legend. The general indication of the curves shown in Figure 2.9 are that the larger the surface capacitance, the less it will be affected by single particle contacts. A large surface capacitance is appropriate for a black platinum electrode due to its high surface area. This is another



fashion to look at the relative insensitivity of a black platinum electrode to the presence of mineral particles.

Figure 2.9 Simulation of measured potential between an electrode and a particle



A difficult decision had to be made. A vast amount of evidence had been acquired during investigations with various electrode materials in mineral slurry to indicate that the approach is valid. It would have been nice to experimentally confirm the model. However, other challenges, especially how to maintain the pulp potential sensors in a reliable state were encountered. It was felt sufficient to note that between contacts with the mineral particles in the slurry, a noble metal electrode would be free to interact with the solution as it would if there were no particles. With an activity for oxygen reduction similar to that of the sulphide minerals, a gold electrode would deviate much less from the potential of the mineral particles between contacts than a platinum electrode and hence be more suitable.

### 2.3 Conclusions

The suggestion that gold electrodes are more appropriate for the measurement of the pulp potential than platinum ones has not been remarked despite a vast experimental evidence supporting this suggestion. This suggestion is largely based on the similarity in activity for oxygen reduction between gold and the sulphide minerals, while the activity of platinum is much higher, and the application of the mixed potential model for solutions containing more than one redox couple. Between contacts with mineral particles, a gold electrode exhibits a potential not much different than that of the minerals themselves while a platinum electrode tends to exhibit the potential of the oxygen reduction reaction.

Nevertheless, the relationships discussed previously between mineral floatability and redox potential should not be dis-credited on the basis that the electrode used to monitor the potential might not be the best one. Only the potentials defining the range of flotation for a single sulphide mineral, and the window(s) of selectivity for an ore would be dependent on the electrode used.

This would not be a problem for a concentrator since it is unlikely that the type of pulp potential sensor would be changed during the course of an investigation. However, comparison of measurements between different laboratories and plants is not aided by the lack of a recognized standard sensing electrode for mineral slurries.

Finally, the response of a potential sensing electrode to the presence of particles might be modelled using the surface capacitance of the electrode and the particles, an estimation of the duration of particle-electrode contact (degree of agitation) and the resistance of the solution.

### 3 DESCRIPTION OF ORES AND PLANTS

#### 3.1 Introduction

The nature of the ores and features of the plants of Les Mines Selbaie and Kidd Creek Division of Falconbridge Limited are discussed in some detail prior to presenting the experimental results. There are many similarities, as expected since both mills process copper-zinc ores. However, the nature of the ore at each mine has led to unique flowsheets to produce copper and zinc concentrates.

Emphasis will be placed on the A1-zone ore and circuit of Les Mines Selbaie as this was extensively investigated in the laboratory and plant during the course of the project. Publication of some of the results obtained at Les Mines Selbaie prompted an interest from the technical staff of Kidd Creek. This interest provided an opportunity to generalize the findings related to on-line monitoring of the pulp potential. Thus, the ore and circuit of the Kidd Creek operation are also discussed.

#### 3.2 Les Mines Selbaie

The discovery of mineralization in the Brouillan Township north of Joutel, Québec, and its development into a mine and mill site has been described in a special session at the 1989 CIM Annual Meeting (218) which led to a collection of papers in an issue of the CIM Bulletin (219). Some of the key points are recalled here.

An airborne electromagnetic survey performed with the Mark VI INPUT ® system by Questor Surveys Limited uncovered aerial anomalies in 1971. These anomalies were followed up by ground exploration and drilling programs in 1974-75 (220, 221).

The presence of anomalies had been revealed during an earlier airborne electromagnetic survey in 1958. Only with later advances in exploration expertise related to the gathering and interpretation of such anomalies was the potential of economic mineralizations at that location realized. It would appear that even from the start, the story of Les Mines Selbaie has been one of persistence.

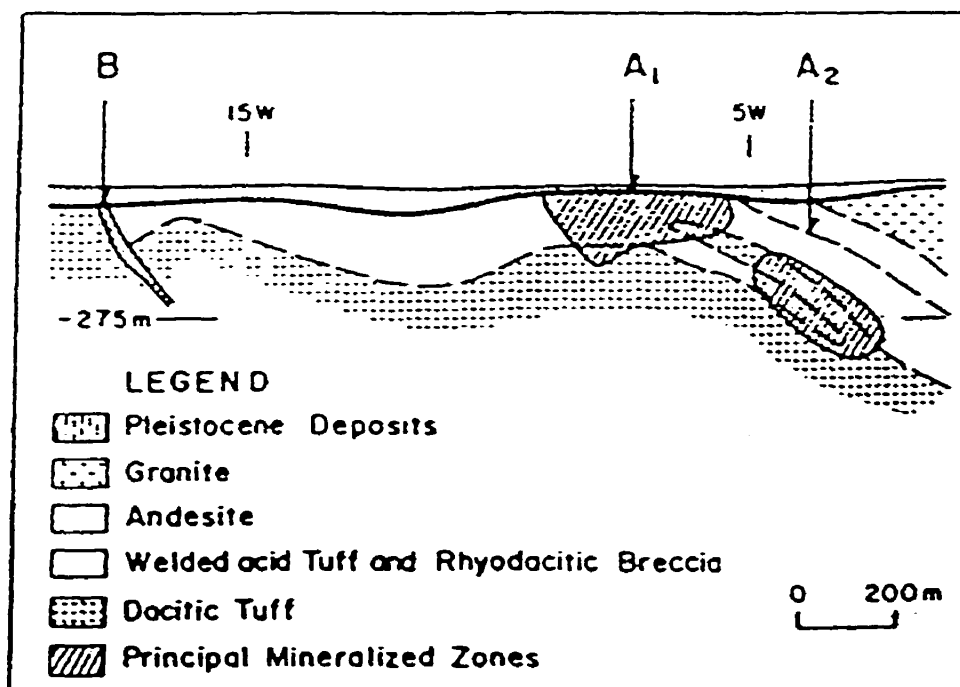
### 3.2.1 Ore zones and mine development

Three zones were defined during the 1974-75 drilling program (221) and their spatial relationship is shown in Figure 3.1:

1. The A-1 zone, amenable to open pit mining with an estimated resource of 20 million tonnes grading 0.8% Cu, 2.2% Zn, 31 g/t Ag and 0.5 g/t Au.
2. The A-2 zone, being an underground extension of the lower copper-rich veining of the A-1 zone, with an estimated resource between 2 and 5 million tonnes grading 2.2% Cu, 0.7% Zn, 30 g/t Ag, and 1.2 g/t Au.
3. The B zone, 1 km west of the A-1 zone with an estimated resource of 3.5 million tonnes grading 3.3% Cu, 0.3% Zn, 30 g/t Ag, and 1.0 g/t Au. Unfortunately, the zinc present in the B zone could not be economically recovered due to particular ore characteristics.

Underground exploration and metallurgical testwork lead to the decision to develop the B zone at a throughput of 1500 tonnes per day in 1978 and the mine and mill were commissioned in September 1981. Discovery of additional ore lenses allowed the throughput to be increased to 1650 tonnes per day in 1985. This mini-expansion permitted the operation to survive through the bottom of the price cycle for copper occurring at that time.

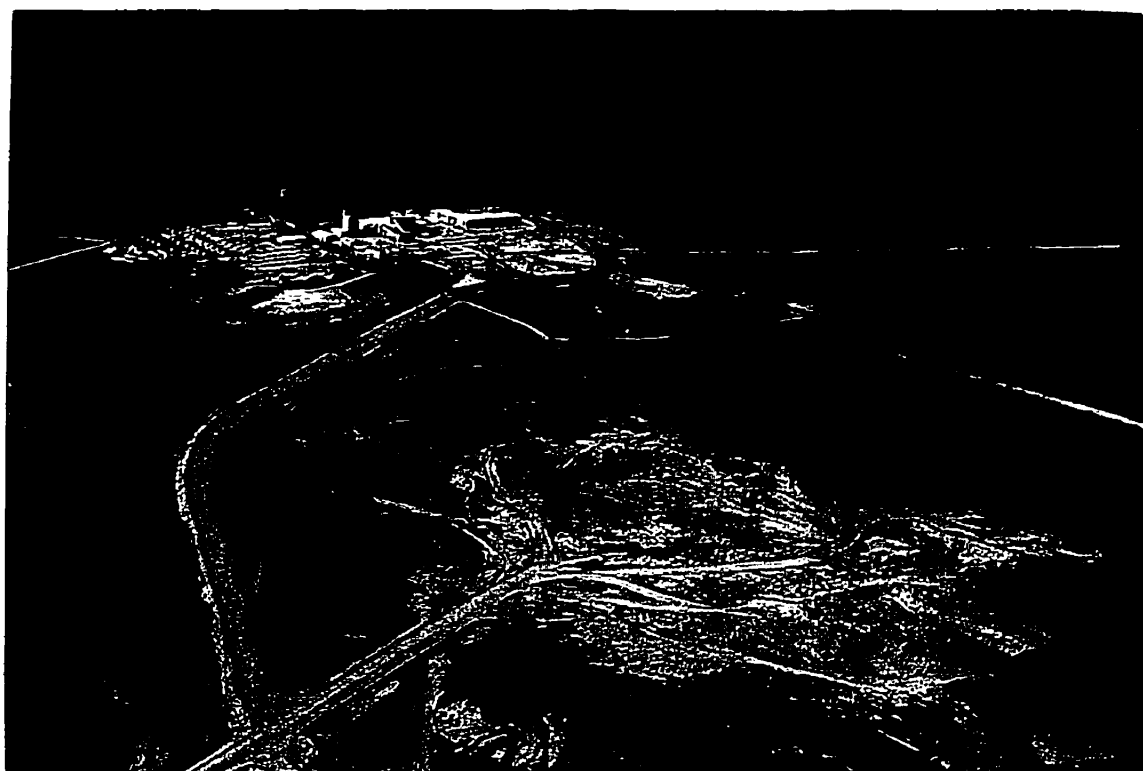
Figure 3.1 Simplified section of the ore zones; looking north (221)



Further exploration and metallurgical testwork lead to the decision to develop the A-1 zone late in 1984. Although market conditions were not promising over the short term, the economy of scale and other factors made a joint A-1 and B zones operation more viable than just the B zone on its own.

The A-1 zone open pit mine and mill circuit were inaugurated on November 15<sup>th</sup>, 1986. Initial throughput was 5000 tonnes per day (tpd) but this soon rose to 5500 tpd and eventually reached 6300. Figure 3.2 shows the mine site being readied for production with stripping of the open-pit in the foreground and the mill, maintenance, office, and camp buildings in the background.

Figure 3.2 Les Mines Selbaie site during the summer of 1986 (courtesy of Les Mines Selbaie)



Improvements in market conditions and diminishing reserves of the B zone ore lead to the development of the A-2 zone in 1988 and modification to the B circuit to process this ore. Production from A-2 lasted until the end of 1993 (222). With mine production exclusively from the lower grade A-1 zone, the throughput was raised to 8000 tpd with re-allocation of the A-2 circuit (crushing, rod and ball mill, and copper flotation cells) to the processing of A-1 zone ore. The reserves are capable of supporting the operation at this throughput well into the year 2004.

An earlier research project covered the period of commissioning the A-1 zone circuit up to the summer of 1987 (26). This project picked up from that point in time and carried out through the summer of 1990.

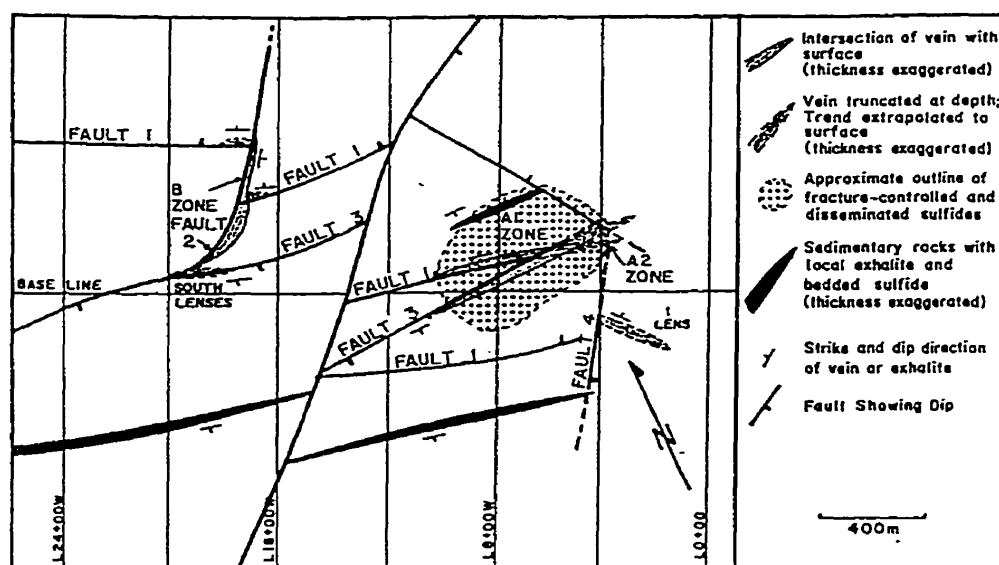
### 3.2.2 A-1 zone ore

The geology of the three ore zones has been described (223, 224, 225). Follow-up geological investigations have also been reported (226, 227, 228).

The close proximity of the ore zones to the surface and the presence of a number of faults resulted in a challenge to selective flotation. The B zone, which is right along a main fault (Figure 3.3), has experienced severe supergene alteration of the copper minerals as ground water percolated through this fault. The occurrence of chalcocite, digenite, and native copper allowed for high copper concentrate grades but was detrimental to selective copper-zinc flotation (26, 218).

The presence of secondary copper minerals in an ore and its detrimental impact on copper-zinc separation is not unique to Selbaie. The Rio Tinto Mines, Huelva, Spain (229) is a well documented mineralogical example. The Goldstream deposit is a case where a conventional depressant like sulphur dioxide resulted in as many problems as it solved (180).

Figure 3.3 Plan view of the ore zones and main faults (227)



In some deposits, copper-zinc separation could only be achieved by reverse flotation of the sphalerite out of the copper rougher concentrate, examples being in Zaire (125) and Australia (230).

Although faults exist within the A-1 zone, they do not have metallurgical consequences as severe as for the B zone. The main reason is that the faults span only a small volume of the overall mineralization. Nevertheless, at their western entry into the mineralized zone, the faults are the site of intense supergene alteration of the copper minerals. The impact of these faults on the ore (particularly the rust coloured rock) in that area of the open pit was always clearly visible as can be seen in Figure 3.4.

Figure 3.4 Visible effect of a fault on a mining bench





The main valuable sulphide minerals consist of sphalerite, chalcopyrite and galena while pyrite is the main iron sulphide gangue. In one area of the A-1 zone, pyrite is massive. As discussed above, there are local occurrences of chalcocite, very often as rims around chalcopyrite, bornite, covellite, digenite and tennantite. Gold occurs most often as electrum (gold-silver alloy) while silver occurs as acanthite (orthorhombic  $\text{Ag}_2\text{S}$ ; normally stable below  $175^\circ\text{C}$ ), argentite (isometric  $\text{Ag}_2\text{S}$ ; normally stable above  $175^\circ\text{C}$ ), and native silver (223). Nomenclature for the  $\text{Ag}_2\text{S}$  phase has been inconsistent with either acanthite (225) or argentite/acanthite (223) used by different authors.

One unique mineralogical characteristic of the chalcopyrite from the Les Mines Selbaie is that rapidly tarnishing grains (taking a deep orange colour within hours) can be found alongside normal grains (maintaining their greenish colour for days) in the same polished section (223). Detailed analyses did not revealed significant compositional differences between the two types of chalcopyrite (223).

### 3.2.3 Ore types

There are two main rock types hosting the mineralization in the A-1 zone: a rhyodacite breccia and felsic tuffs (225). The rhyodacite breccia consists of a subhorizontal bed which covers the felsic tuffs in the open pit area. Broad open folds can be observed with East-West subhorizontal axes. The felsic tuffs consist of dacitic tuffs (DT) with and without quartz phenocrysts, welded acid tuffs (WAT) which are mineralized and lapilli tuffs (DTL). In the absence of a marker horizon, the subhorizontal attitude as well as the stratigraphic succession of the tuffs is uncertain but all indications suggest a stratigraphic topmost layer to the south. All the tuffs, but most intensely the dacitic tuffs, are chloritized (altered).

Two quartz porphyry intrusions are found towards the south near the stratigraphic top of the tuffs. This rock type, along with other criteria, was sufficient to derive four main ore types along with an altered ore type. On any given day, the mill feed consists of mixtures of the five ores types.

Table 3.1 shows head grades of ore type samples and composite ore samples obtained for the purpose of this study. The ABCD composite sample was a blend of all ore types in the weight proportions representative of the overall resources in the A-1 zone. Although some preliminary tests were performed on the individual ore types, most of the flotation testwork was performed on samples obtained from the cyclone overflow of the mill, or on fresh ore.

Table 3.1 Assays of the A-1 zone ore samples

Ore	Description	Assays in % (g/t for Ag)				
		Cu	Zn	Pb	Fe	Ag
A	Rhyodacite breccia	0.13	3.56	0.06	11.4	23
B	Welded acid tuff	0.47	1.86	0.03	5.9	16
C	Silicified	4.44	6.35	0.62	9.0	480
D	Massive pyrite	0.60	3.06	0.24	15.9	180
E	Altered ore	0.40	5.40	0.22	15.0	130
ABCD Compo	Composite A:B:C:D = 3:5:1:1	0.78	2.88	0.11	8.9	94
Fresh Ore	Mill feed - 1987	0.21	3.10	0.17	8.2	160

### 3.2.4 Microscopic examination of the sulphide minerals

There are two distinct features of the copper and zinc minerals present in the A-1 zone which merit further attention for microscopic examination. The first feature briefly touched upon earlier is the rapid tarnishing of the chalcopyrite and typical examples are shown in Figures 3.5 and 3.6. The particular particle shown in Figure 3.6 contains both types of chalcopyrite with definite grain boundaries between the two.

Although no significant compositional differences have been indicated (89), such a dramatic response to atmospheric exposure for chalcopyrite can only be related to supergene alteration. For example, the chalcopyrite grains observed in B zone ore and concentrate samples mostly exhibited an orange tint (26). Mineralogical investigations of rapidly tarnishing chalcopyrite (232, 233, 234, 235, 236) and sphalerite (235) are linked to diffusion of silver and formation of a silver sulphide film. It is a possibility given the silver minerals present in the A-1 zone ore but it does not explain why some grains would tarnish rapidly and others not in the same mount or even the same particle.

This rapid tarnishing of a number of the chalcopyrite grains is indicative of a high susceptibility to oxidation. It is quite possible that under certain flotation conditions the tarnishing and non-tarnishing chalcopyrite grains will report to different concentrates and an examination of polished sections of these concentrates might provide an indirect form of surface analysis.

Figure 3.5 Example of tarnished and untarnished chalcopyrite grains

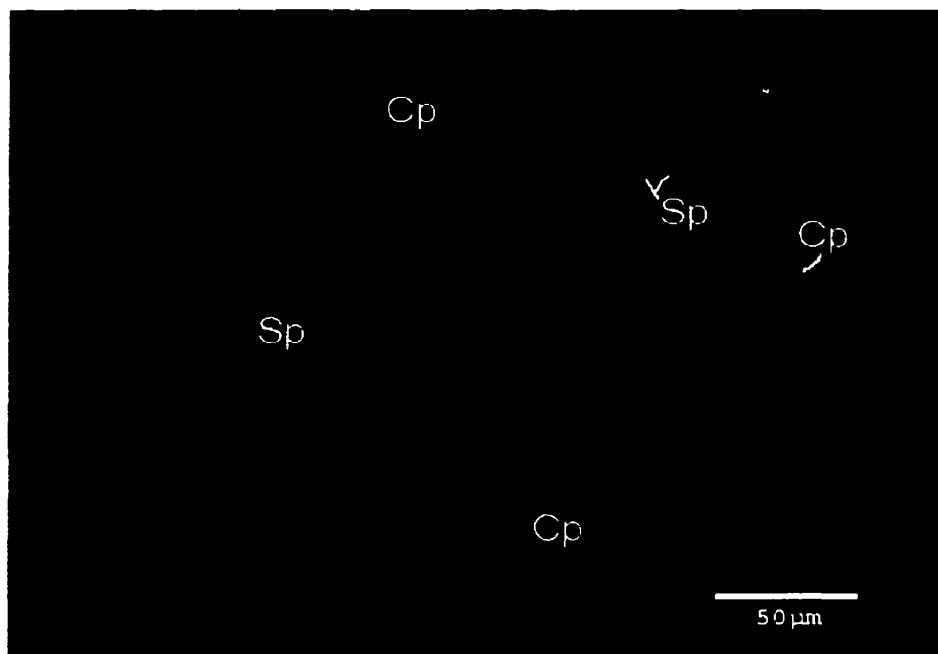
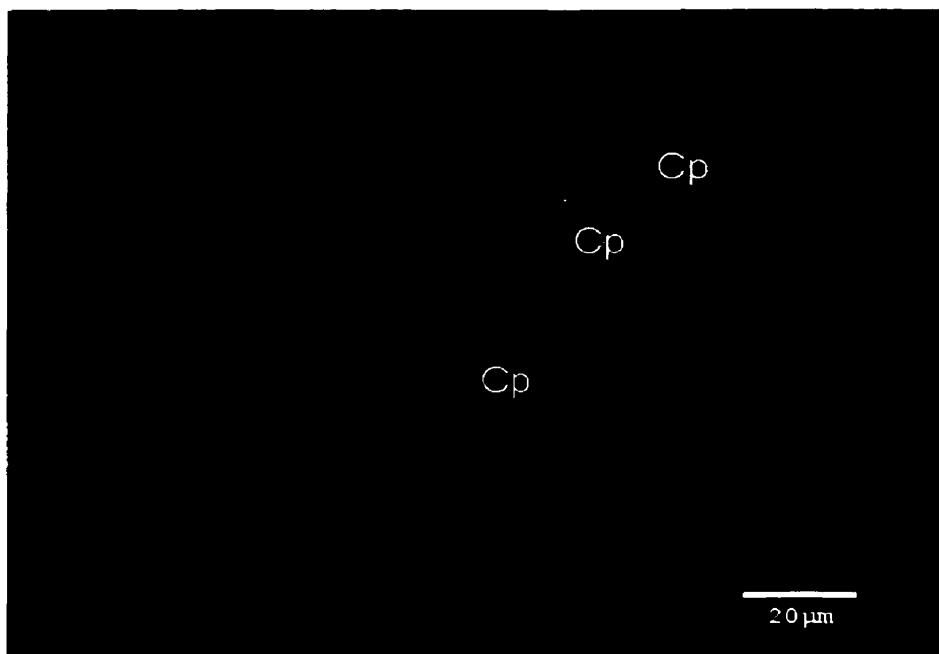


Figure 3.6 Example of tarnished and untarnished chalcopyrite complex grain



The second feature is the presence of chalcopyrite and pyrite exolutions in sphalerite. This feature is not unique to Les Mines Selbaie and in fact it has been encountered sufficiently frequently to be called "chalcopyrite disease" (237). It occurs mostly for the A, D, and E ore types as seen in Figures 3.7, 3.8 and 3.9 and does not affect all sphalerite grains. The inclusions vary in size from less than a few microns to more than 10  $\mu\text{m}$ . The sphalerite grain shown in Figure 3.9 contains coarse (50-75  $\mu\text{m}$ ) pyrite inclusions and fine (1-5  $\mu\text{m}$ ) chalcopyrite inclusions barely noticeable at the magnification used.

On the other hand, the sphalerite of the B, C ore types and fresh sample rarely exhibit inclusions as observed in Figure 3.10. This does not imply that there is no locking between sphalerite and chalcopyrite/pyrite in B and C ore types and the fresh ore sample.

An interesting feature of sphalerite samples from the B and C ore types is the presence of grains which are barely distinguishable in color from the epoxy matrix and appear to have a convex surface rather than a flat one. Since the sections were prepared from nearly pure sphalerite pieces it is unlikely that there was as much non-sulphide gangue as indicated in Figure 3.10. Examination under polarized light indicated the presence of internal reflections in these grains and this suggests that they are likely sphalerite. The fact that no non-sulphide gangue particles have been encountered while performing the microprobe analysis on similar sections confirms this indication. Unfortunately, such grains would be difficult to differentiate from non-sulphide gangue in a casual examination of test products.

Figure 3.7 Typical sphalerite particles: A, D, and E ore types



Figure 3.8 Typical sphalerite particles: A, D, and E ore types

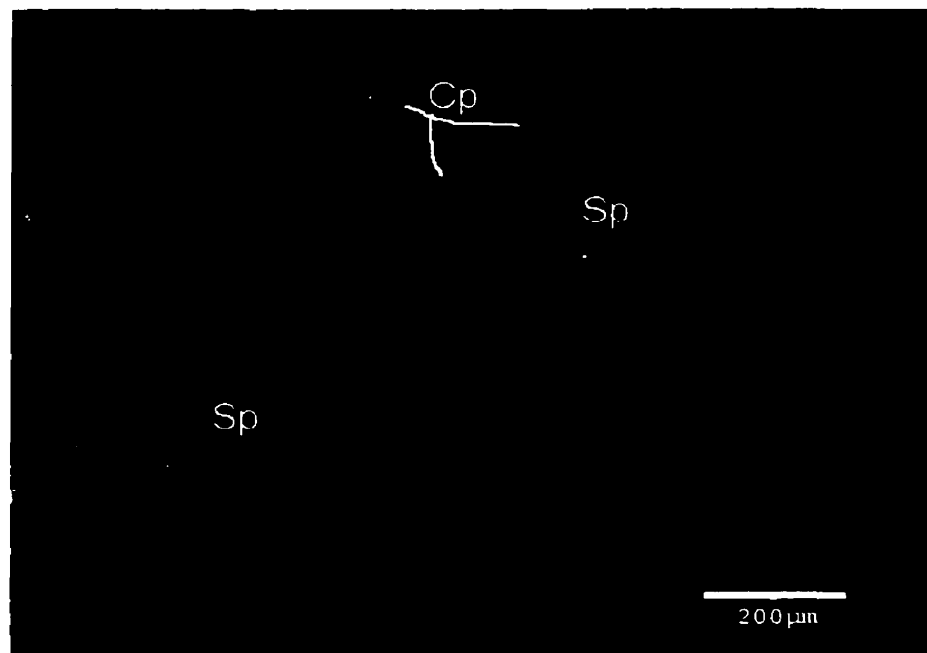


Figure 3.9 Typical sphalerite particle: A, D, and E ore types

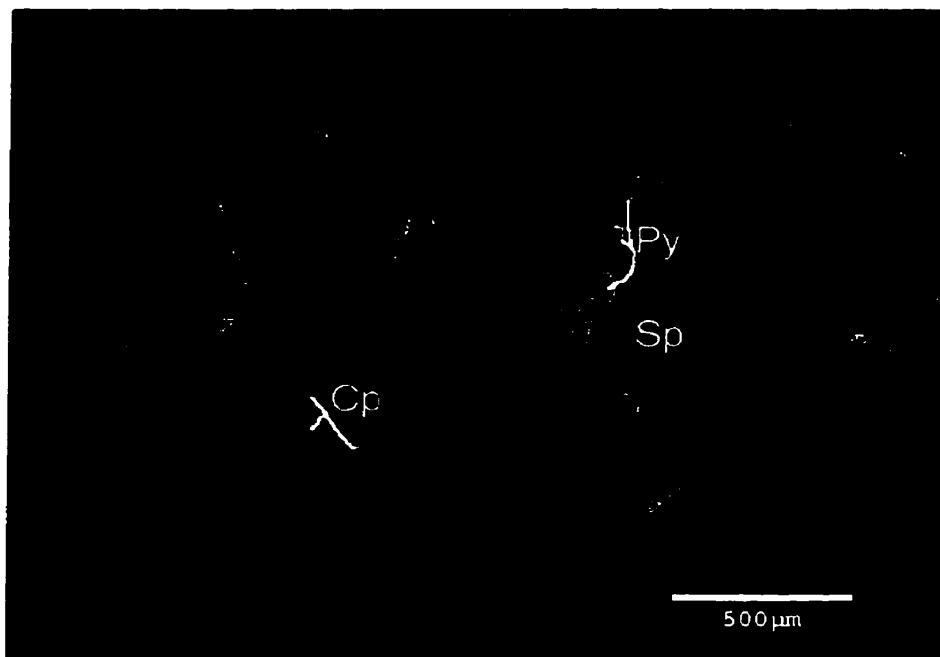
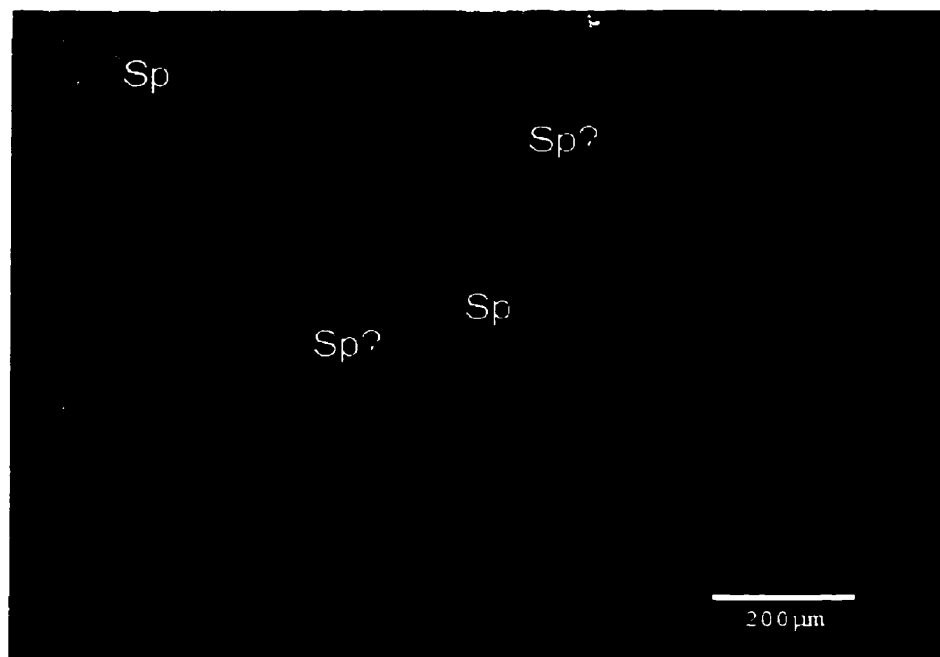
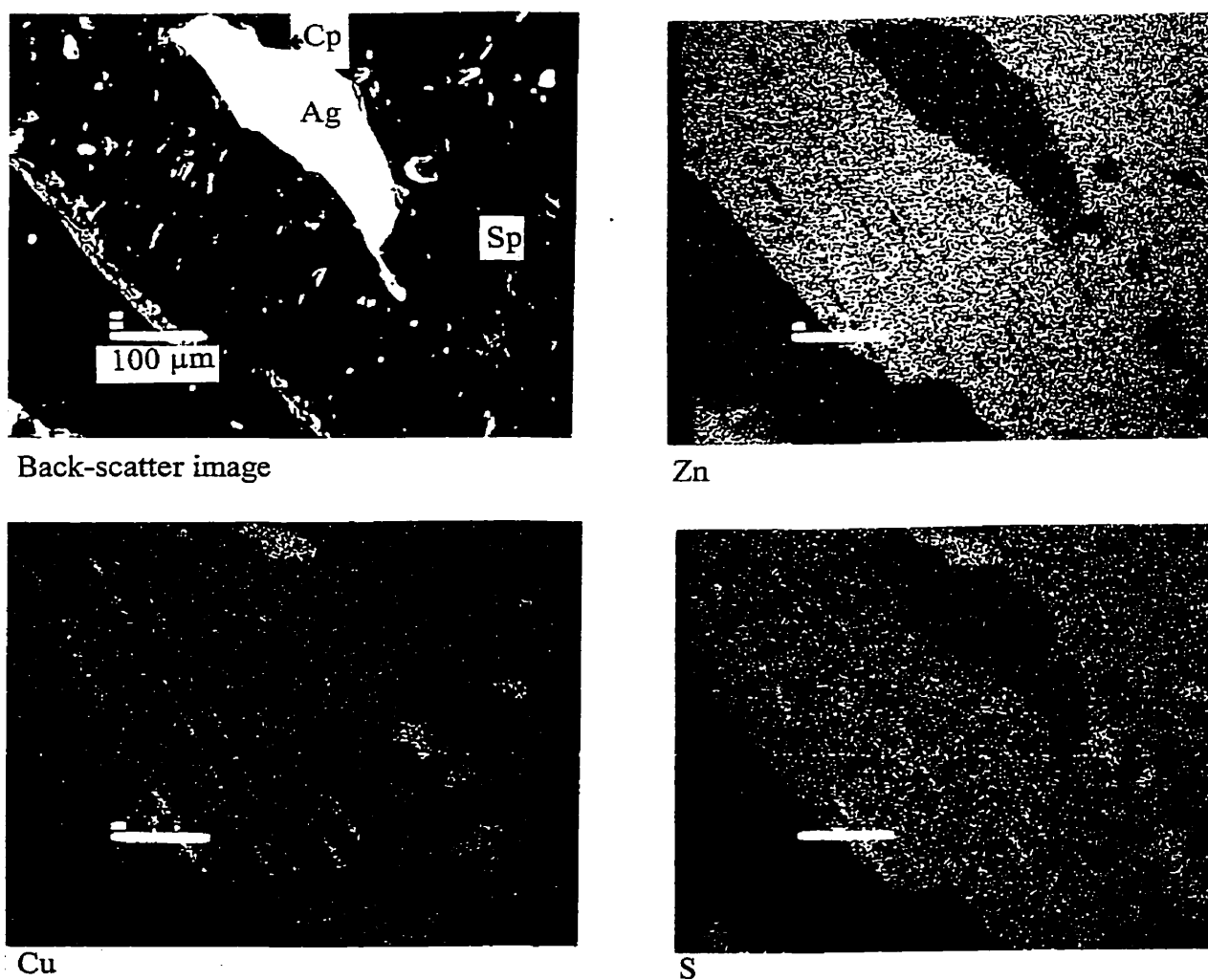


Figure 3.10 Typical sphalerite particles: B and C ore types and fresh ore



To verify that the presence of these chalcopyrite inclusions, and that supergene alteration did not yield higher levels of copper within the sphalerite lattice X-Ray mapping of sphalerite grains was performed. As it can be seen from an example shown in Figure 3.11, the amount of copper outside of the chalcopyrite grains is minimal. X-Ray mapping reveals the occurrence of chalcopyrite as large and nearly round grains as well as elongated grains (lamellae) which are barely noticeable in the back-scatter electron image. The sphalerite grain shown in Figure 3.11 exhibit a rare feature not often encountered during the mineralogical examination: the presence of a large native silver grain!

Figure 3.11 X-Ray mapping of sphalerite presenting chalcopyrite disease (E ore type)





Typical examples of the other sulphide minerals present in the A-1 zone ore are shown in Figures 3.12 to 3.15. Free chalcopyrite is easily found in a section only for the "C" ore type (Figure 3.12). On the other hand, the distinctive colour of chalcocite makes it difficult to miss for the "E" ore type (Figure 3.13). The presence of pyrite-oxidized sulphide particles in the fresh ore sample as shown in Figure 3.14 suggests that the designation "fresh" is relative to the early ore samples obtained for the pilot plant program and not an indication that the ore sample is free from altered sulphides.

The presence of chalcopyrite inclusions in the sphalerite severely limits the achievable separation between the copper and zinc minerals. Sphalerite grains exposing a large proportion of chalcopyrite inclusions on their surfaces will report to the copper concentrate if the flotation conditions aim at high copper recovery. On the other hand, sphalerite grains exposing a small proportion of chalcopyrite inclusions on their surfaces will report to the zinc concentrate as they would likely be depressed during the copper flotation. Regrinding for complete liberation of these inclusions is impractical due to their size (typically 1 to 5  $\mu\text{m}$ ).

There is an important implication to having chalcopyrite and pyrite inclusions in sphalerite with respect to the electrochemical model of the flotation of sulphide minerals. There will be a sustained galvanic interaction between the exposed inclusions and the sphalerite surface and the interaction will be more intense than that occurring via particle-particle collisions during grinding and flotation.

One additional note should be made here; although the sphalerite particles appear grey on the polished sections, the colour of large pieces and particles show a wider range: cream, "bottle brown", and dark grey. The colour of sphalerite is an indication of the iron content in solid solution, the lighter the sphalerite, the less iron it contains (107, 238).

Figure 3.12 Typical sulphides: A and D ore types

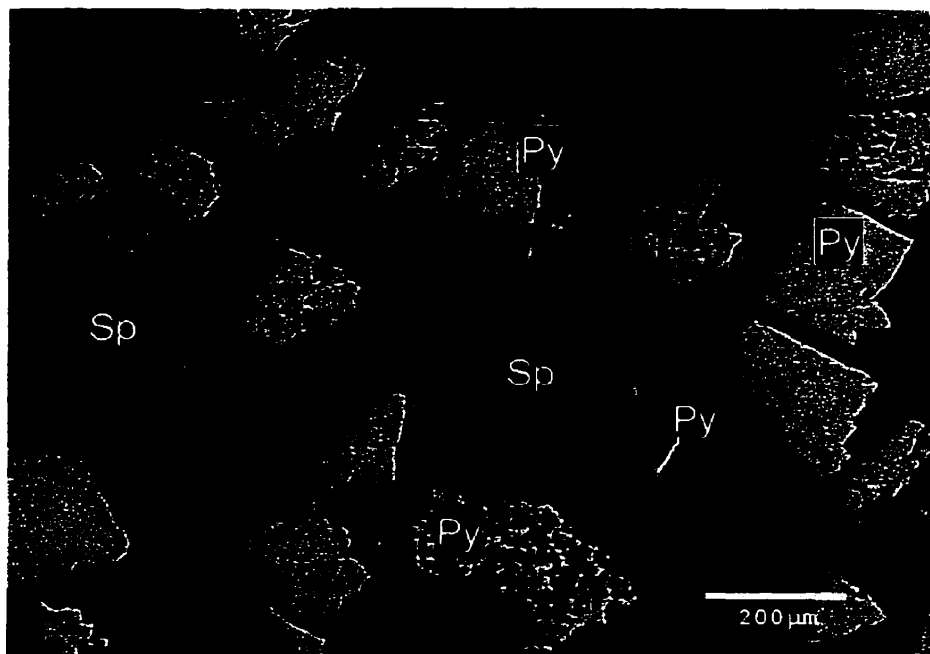


Figure 3.13 Typical sulphides: C ore type

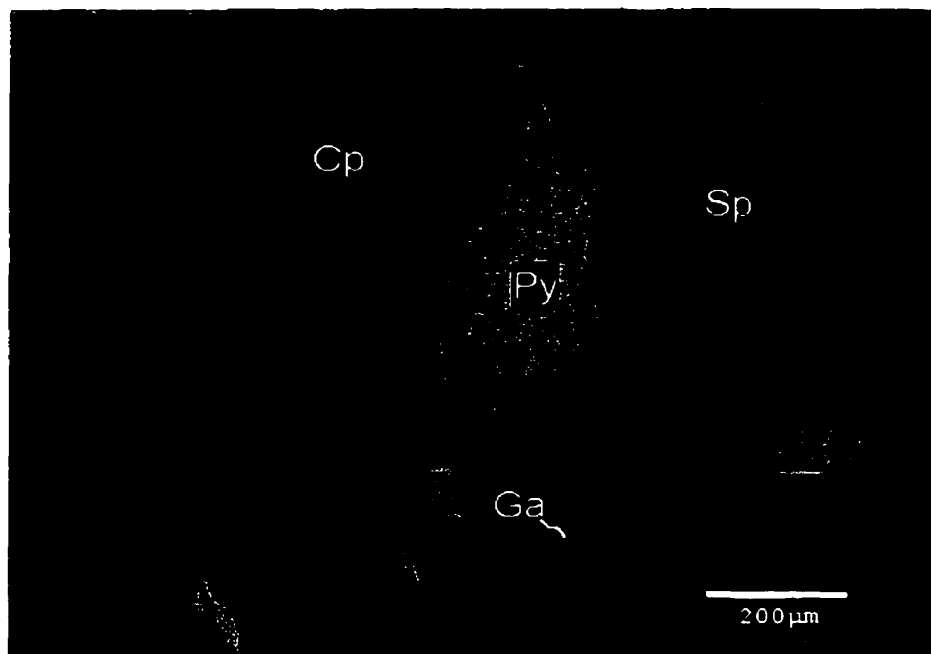


Figure 3.14 Typical sulphides: E ore type

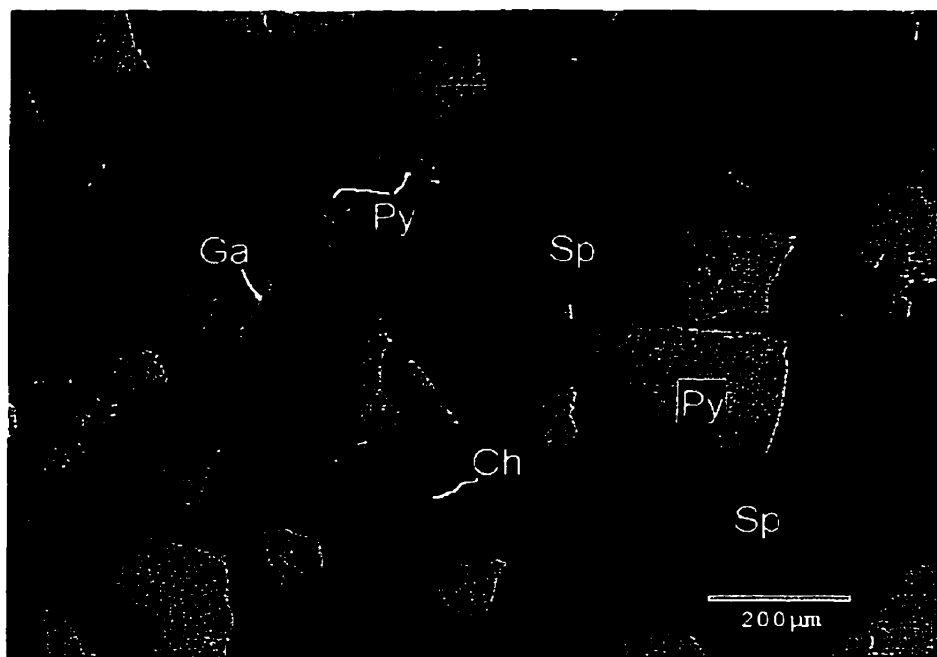
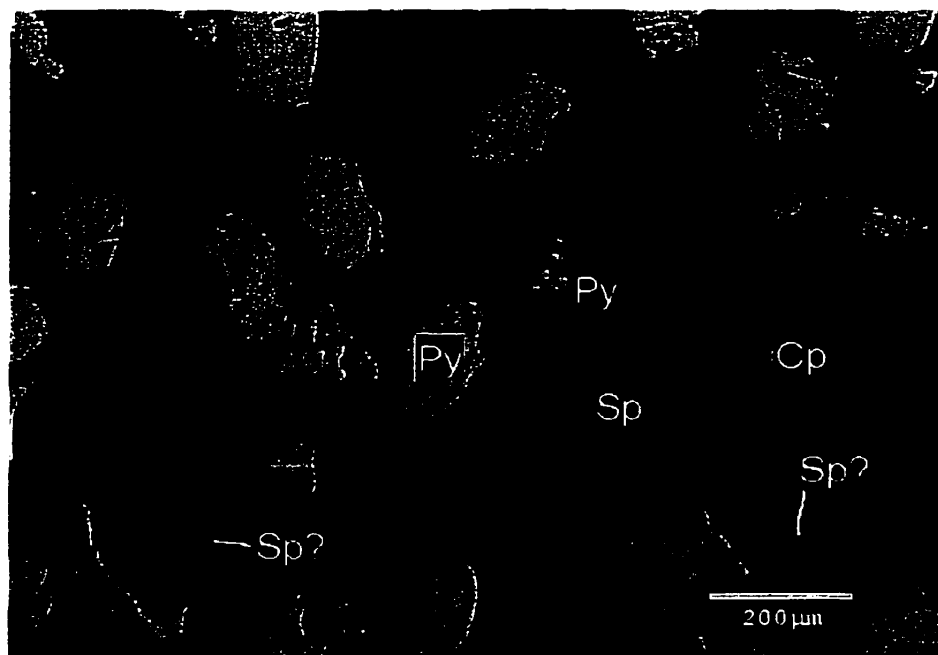


Figure 3.15 Typical sulphides: Fresh ore sample



From the literature regarding the composition of sphalerite and its response to activation by heavy metal ions, it is expected that there will be a range of flotation response. Actually, a frequent observation made by the author during laboratory flotation tests was first the appearance of the grey sphalerite during zinc rougher flotation, then the bottle brown, and finally the cream sphalerite. A similar gradual change in froth colour also occurred during the zinc cleaning stages but the boundaries between the different froth tints were not as clearly defined as for the rougher stage.

Finally, no microscopic examination would be complete without some general indication of grinding requirements for liberation. This was investigated quite thoroughly as part of the feasibility study (239) and the results were generally confirmed by the observations made here.

As a whole, the sulphide minerals are liberated from the silicate gangue (quartz, chlorite, muscovite and ankerite) at 100  $\mu\text{m}$ . Sphalerite is generally 50 to 70% liberated at 200  $\mu\text{m}$ . Most of the remaining sphalerite is liberated at 50 to 150  $\mu\text{m}$  depending on the ore type. Approximately 15% of the sphalerite is present as 20  $\mu\text{m}$  inclusions in pyrite while trace amounts occur as 10 to 15  $\mu\text{m}$  inclusions in chalcopyrite. Between 40 and 50% of the copper minerals are liberated at 150  $\mu\text{m}$  while an additional 35% are liberated at 30  $\mu\text{m}$ . The remaining copper minerals (mostly chalcopyrite) are present as less than 10  $\mu\text{m}$  inclusions in sphalerite and pyrite. Galena occurs as discrete 50 to 250  $\mu\text{m}$  grains, as 20 to 30  $\mu\text{m}$  inclusions in sphalerite, and as rims on chalcopyrite and pyrite. Pyrite occurs in a variety of sizes from discrete 300  $\mu\text{m}$  grains down to 20  $\mu\text{m}$  inclusions in chalcopyrite.

### 3.2.5 Mineral compositions

To assist in the interpretation of the metallurgical results, the chemical assays have been converted to mineral assays. This is important to follow the flotation response of pyrite. An experienced mineral processor can obtain a qualitative indication of the pyrite level in concentrates by the relative abundance of copper, zinc, and iron. Unfortunately, such information is not accurate enough to discriminate minor changes in the flotation response of pyrite.

The variation in iron content of sphalerite, along with a corresponding variation in colour, is well known. For example, there have been studies on Mississippi Valley type Pb-Zn deposits such as Pine Point (238). In the case of A-1 zone ore, the observed range of iron contents (near 0% to 4% Fe) is larger than usually encountered. Samples were analyzed using an electron microprobe to obtain the actual composition of the sphalerite in the A-1 zone ore. The average results are given in Table 3.2 along with an overall normalized average which was used for conversion of zinc assays into sphalerite assays.

Table 3.2 Microprobe analysis of sphalerite particles, A-1 zone ore, Les Mines Selbaie

Sample	No. of points/ particles	Average Assays (%)			
		Cu	Fe	Zn	S
A	14	0.03	2.45	63.61	33.21
B	12	0.01	2.71	63.40	33.16
C	9	0.03	1.58	64.20	33.29
D	4	0.02	3.17	62.96	33.16
E	12	0.04	4.14	60.78	33.00
Fresh Ore	15	0.02	2.68	62.52	32.93
Average	66	0.0256	2.787	62.911	33.125
Normalized	N.A.	0.0260	2.819	63.644	33.511

Since there were no strong indications that the composition of chalcopyrite, galena, and pyrite would dramatically vary with ore type, no microprobe analyses were performed for these minerals. The stoichiometric compositions of these minerals were taken for conversion of the element assays to mineral assays.

The mineral compositions were calculated as follows:

$$\text{Sphalerite (Sp, \%)} = \text{Zn (\%)} / 0.63644 \quad [23]$$

$$\text{Chalcopyrite (Cp, \%)} = [\text{Cu (\%)} - \text{Sp} \times 0.026] / 0.3463 \quad [24]$$

$$\text{Galena (Ga, \%)} = \text{Pb (\%)} / 0.8660 \quad [25]$$

$$\text{Pyrite (Py, \%)} = [\text{Fe (\%)} - \text{Cp} \times 0.3043 - \text{Sp} \times 0.02787] / 0.3655 \quad [26]$$

or when sulphur assays were available

$$\text{Pyrite (Py, \%)} = [\text{S (\%)} - \text{Cp} \times 0.3493 - \text{Sp} \times 0.33511 - \text{Ga} \times 0.1340] / 0.5345 \quad [27]$$

The absence of other iron bearing phases (e.g. magnetite and silicate minerals) allowed the iron assay to be used for the calculation of the pyrite content with reasonable accuracy. Comparison of the pyrite content calculated using iron and sulphur assays were usually within 5% relative from each other. This was deemed acceptable considering all the other sources of experimental errors which are inherent to flotation testing.

The small, and variable, quantity of chalcocite ( $\text{Cu}_2\text{S}$ ) which is present in the ore was ignored for the purpose of mineral calculations. The proportion of E ore type in the mill feed was maintained below 10% due to the detrimental impact on copper-zinc selectivity of this ore type. Typically, less than half of the copper present in the E ore type is present as chalcocite rather than chalcopyrite, meaning that at the most 5% of the

copper in the mill feed being might be present in this form and would not be accounted for by just a chalcopyrite calculation. Again, given all the other sources of experimental errors in flotation testing, this was deemed acceptable.

### 3.2.6 A-1 zone flotation circuit

The flowsheets and control schemes for processing the three ore zones have been described (129, 240, 241). For present purposes, it is necessary to review the key equipment for comminution and flotation, the arrangement of the flotation circuit, and the reagents used for the A-1 zone ore.

The process selection and design philosophy was to use state of the art technology proven in one or more previous installation (240). One key point was maximization of water recycling.

The electrochemical-based research supported in this thesis was a departure from this philosophy. Since the project aimed at an incremental improvement in copper-zinc selectivity rather than replacement of current strategies, however, it was deemed an acceptable risk.

The flowsheet and reagents described below are as they were during the plant studies. Comminution of run-of-mine ore is performed in three stages: a gyratory crusher, a variable speed semi-autogenous (SAG) mill operated in closed circuit with a screen, and a ball mill operated in closed circuit with cyclones. There is an ore stockpile between the gyratory crusher and the SAG mill to buffer the mine production and to allow some ore mixing.

Several combinations of mill liners and ball charges were used. However, from 1987 through 1990, the SAG mill was rubber lined with steel lifters while the ball mill was completely rubber lined. The ball charge was high chrome steel.

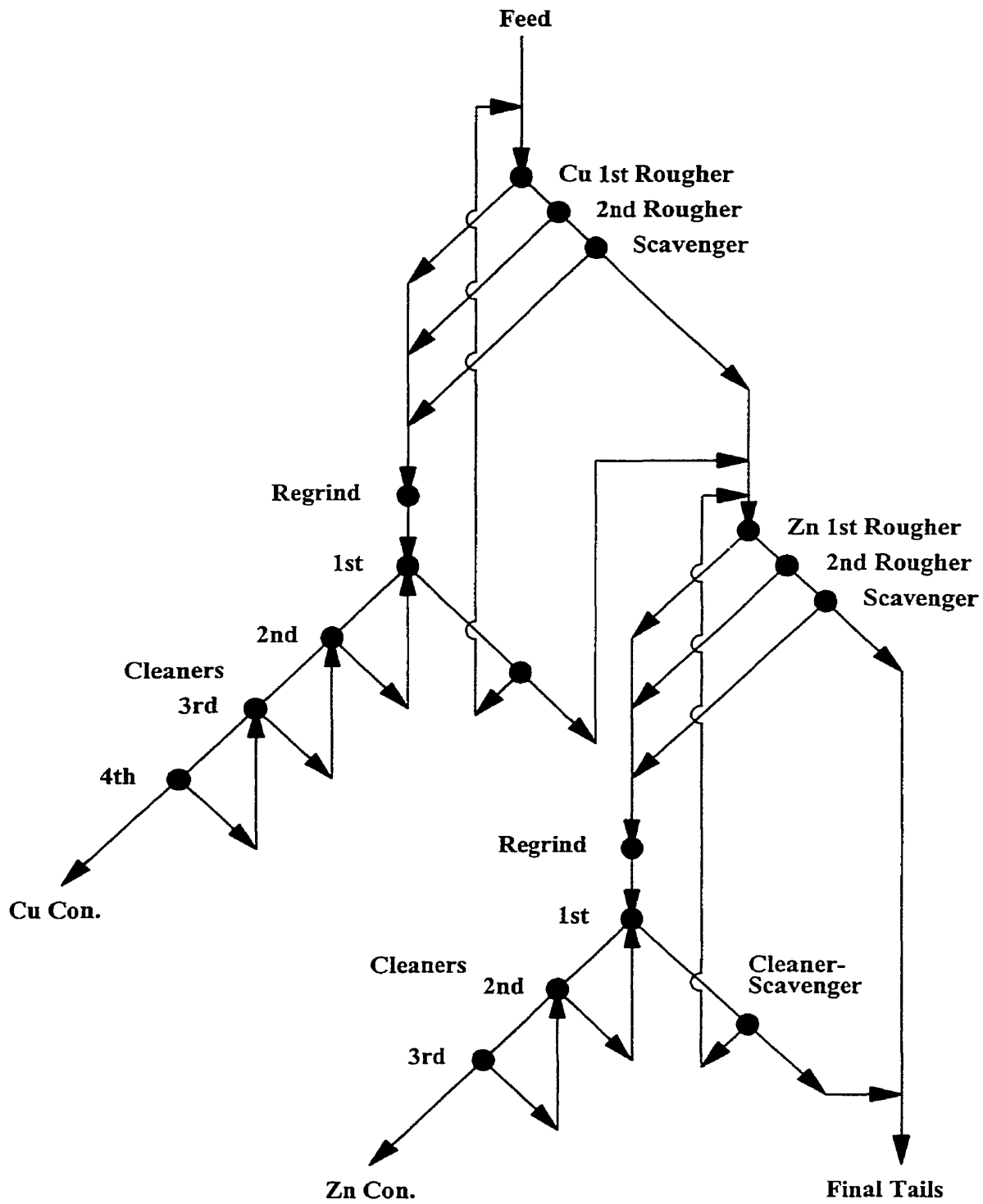
The flowsheet for the A-1 zone ore as it was in 1990 is shown in Figure 3.16 using the network symbolism (242). Flotation stages are shown as nodes (points), concentrates as left diagonals while tailings are as right diagonals. Feeds and recirculating streams are vertical or horizontal lines. This symbolism permits complex flowsheets to be presented in a compact format.

Separation of the minerals is performed by selective sequential flotation (129). The copper minerals are floated first (along with any galena present) in three banks of roughing and scavenging cells, and is cleaned in four counter-current stages. The copper scavenger tails, after copper activation and alkalinity adjustment, constitutes the feed to the zinc circuit. Roughing and scavenging are performed in three banks, the zinc rougher-scavenger concentrate being cleaned three times in counter-current stages. Both the copper rougher and zinc rougher concentrates are reground prior to being fed to the cleaning stages.

The collectors are Aerophine 3418A (Cytec) for copper flotation and sodium isopropyl xanthate (SIPX) for zinc. A small addition of potassium amyl xanthate (PAX) was used as secondary copper collector but in diminishing use from 6.0 g/t in 1987 to 1.5 g/t in 1988 and was eliminated in June 1989 (243). The frothers are methyl isobutyl carbinol (MIBC) for the copper circuit and Dowfroth 1012 (polypropylene glycol ether; Dow Chemicals) for the zinc circuit. Modifiers are lime, sodium cyanide, zinc sulphate (copper roughing), sulphur dioxide and dextrin (copper cleaning), and copper sulphate and lime (zinc).



Figure 3.16 A-1 zone flotation circuit



As discussed previously, the role of sodium cyanide is that of sphalerite de-activation and activation prevention during copper flotation while zinc sulphate is the actual depressant. Sulphur dioxide in the copper cleaning stages provide joint de-activation and depression of the sphalerite and pyrite. Dextrin is mostly used to depress galena; lead is an undesirable impurity in a copper concentrate and there is not enough lead in the deposit to justify the production of a separate lead concentrate.

Copper sulphate activates sphalerite in the zinc flotation circuit while alkalinity control during the conditioning stages prevents accidental promotion of pyrite flotation.

There is a sensitive balance between sodium cyanide added to the copper circuit and copper sulphate requirement for the zinc circuit. A mill feed with a higher content of secondary copper minerals requires higher sodium cyanide additions. However, excess cyanide at the end of the copper rougher-scavenger flotation will consume some of the copper ions introduced during the zinc conditioning stage. The general process control strategy is to maintain sodium cyanide dosage within set limits, even if it means a semi-bulk flotation in the copper rougher, and to complement the depression of sphalerite during the copper cleaning stages.

A Baily Network 90 distributed control system is used for process control (241). Fine tuning of several of the control strategies has occurred (243). The flowsheet and operating strategies have evolved after the project and now include less mixing of the ore types, especially when high copper or high zinc ores are encountered (243).

One major change to the reagent suite has been the replacement of Aerophine 3418A by SP-129 (Huntsman Chemicals). SP-129 is a blend of dithiophosphate and mercaptobenzothiazole plus a diamine modifier and it was extensively tried in the plant during 1991 and early 1992 (244). However, difficulties in maintaining copper recoveries have prompted the establishment of SIPX as secondary copper collector (243).

Other changes to the reagent suite have been the addition of sodium sulphide or sodium meta-bisulphite (ore type dependent) to enhance sphalerite depression in the copper circuit and carboxyl methyl cellulose (CMC) for talc depression during copper flotation (with sustained depression during zinc flotation).

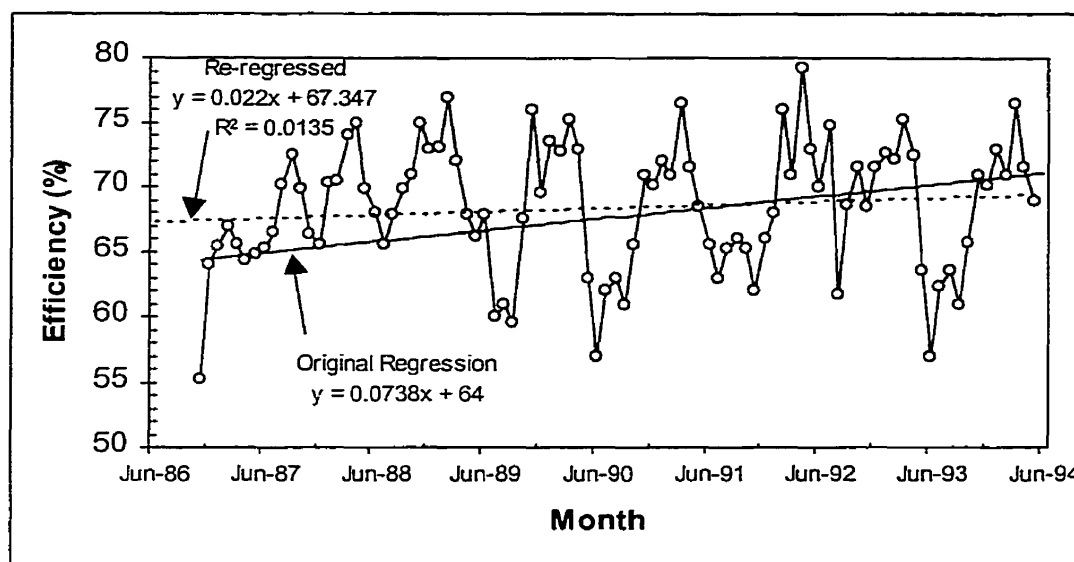
Equipment changes have been the installation of flotation columns for the cleaning stages, first in the zinc circuit, and finally in the copper circuit (243, 245). This followed an extensive series of plant tests initiated in 1989 (243).

Sponsored fundamental research has also continued, especially in the area of surface analysis of sphalerite reporting to the two concentrates and the tailings (246), reagent control (247), and grinding control (248, 249, 250). Co-operative test programs with reagent suppliers, for example Flex 31 for the zinc circuit (251) have been pursued and is still being investigated (G. Chevalier, Per. Com. Feb. 1999).

The evolution of process efficiency (on the basis of net smelter return) from commissioning to the summer of 1994 is shown in Figure 3.17 (243). The most noticeable feature in Figure 3.17 is that the process efficiency exhibits a cyclic behavior with higher efficiencies in the winter than in the summer. Such seasonal variation in metallurgical performance is common for mills operating in a nordic climate with a high proportion of water reclaimed from the tailings pond. Long-term ore type variation is also another factor which introduces fluctuations in process efficiency.

Gains in process efficiency have been sustained over the years and are shown by regression lines in Figure 3.17. A 1%/year sustained gain was claimed (243). However, the original regression supporting this claim tends to under-estimate the process efficiency in the early years and over-estimate it in the later years. The data was re-regressed without fixing the intercept and a sustained gain of 0.022%/month (0.3%/year) has been obtained. Although a 0.3%/year sustained gain does not appear to be as impressive as a 1%/year gain, it is still appreciable.

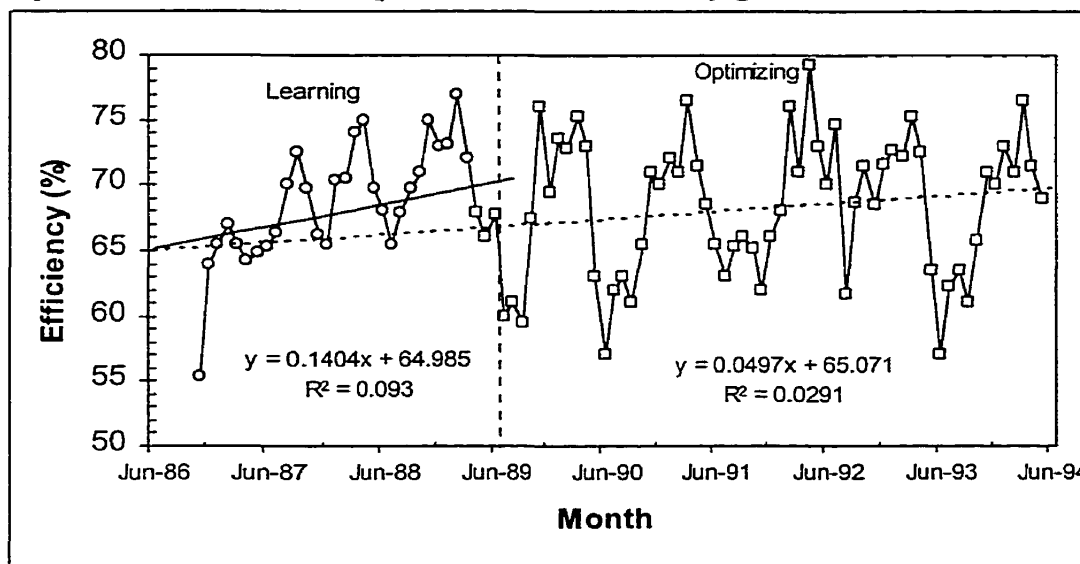
Figure 3.17 Efficiency gains at Les Mines Selbaie (243)



Interpretation of plant data always involve some subjective judgement and is never easy. Given that the mill was commissioned in the fall of 1986, attempting to assign an overall yearly efficiency gain over the whole period from 1986 to 1994 is mis-leading in some way as this ignores the steep learning curve experience by operating and technical staff during the early years. Given the apparent periodicity of the process efficiency data, the selection of starting and ending points for the determination of a time dependent trend is crucial.

A possible interpretation of the efficiency gains at Les Mines Selbaie is suggested in Figure 3.18. The data has been broken up into two time periods corresponding to a learning phase (September 1986 to August 1989) and an optimizing phase (April 1989 to May 1994). The overlap of the two phases (April to August 1989) was technically required to have the starting and ending points of each phase at the same position relative to the yearly cycle.

Figure 3.18 Possible interpretation of the efficiency gains at Les Mines Selbaie



The two regression lines in Figure 3.18 appear to better fit the data than a single line as in Figure 3.17 from a qualitative (visually) and quantitative (higher correlation coefficients;  $R^2$ ) assessments. The efficiency gain during the learning phase (0.1404%/month or 1.7%/year) is high but not-unreasonable. The sustained efficiency gain in the optimizing phase (0.0497%/month or 0.6%/year) is reasonable and corresponds to the reported flowsheet modifications and fine-tuning of the process control strategies over that time period (243). It is noted that on-line monitoring of the pulp potential was performed in 1989-1990 and would be, according to the interpretation suggested in Figure 3.18, at the start of the optimizing phase.

Although the monitoring of the pulp potential as part of the process control strategy has not been maintained beyond the duration of this project, many of the laboratory and plant observations made during the project have in fact lead to further testwork by the technical staff of Les Mines Selbaie and are still relevant to the on-going operation. The current challenge is balancing the flotation response of the A-1 ore ground in the conventional rod/ball mill circuit (former B/A-2 zone circuit) and that in the semi-autogenous/ball mill circuit (G. Chevalier, Per. Com., Feb. 1999).

### 3.3 Kidd Creek Division of Falconbridge Limited

The ores and flowsheets of the Kidd Creek concentrator have been described (252, 253, 254). The test program at Kidd Creek focused on the "A" ore, the main copper-zinc ore processed in three parallel lines; A, B, and C. The other ore, the "C" ore, is a copper-lead zinc ore with high silver values which is treated in its own line, D. Each line has a throughput of around 3000 tpd for a total of 12000 tpd for the concentrator.

As a note, the process water not only consists of water reclaimed from the tailings pond but also cooling water from the copper smelter. Although the type of process water can have a strong impact on the mill performance, consideration of this is outside the scope of the thesis. One concern is that cooling water from the copper smelter may bring copper ions which would lead to un-wanted activation of the sphalerite and this would be similar to the occurrence of supergene copper minerals in the ore.

#### 3.3.1 Ore zones

The Kidd Creek ore body is separated into two distinct zones, the North Orebody and the South Orebody. Two ore types occur within the North Orebody: a siliceous copper ore containing stringers of chalcopyrite in a cherty breccia with occurrences of massive chalcopyrite, and a massive sphalerite-pyrite ore containing native silver and galena. The South Orebody is characterized by a mixed ore containing massive sphalerite and chalcopyrite with notably lower silver, pyrite, and galena contents.

The North and South ore bodies present separate metallurgical challenges. In the North Orebody, the chalcopyrite present as stringers with minor associated pyrite and pyrrhotite forms an irregular network through the siliceous rhyolite host. This ore requires fine grinding but copper recovery in high-grade concentrates is achieved without undue difficulty. The massive sulphide ore in the North Orebody is the most difficult to treat because of the intimate association of the values with pyrite. The metallurgy is

further complicated by periodic occurrence of graphite and pyrrhotite. In the South Orebody, the copper and zinc minerals are in intimate association. As a result, zinc depression during copper flotation is difficult even with fine grinding.

What the concentrator treats as the "A" ore is actually a blend of the South Orebody and the siliceous copper ore from the North Orebody. The "C" ore is the massive sphalerite-pyrite component of the North Orebody and has not been present in sufficient quantities to justify running the D division since 1995; custom milling has been used to replace the "C" ore (254).

### 3.3.2 Flowsheet

The use of a conventional rod and ball mill circuit for comminution and medium capacity cells for flotation reflects the 1960's era during which the mill was built.

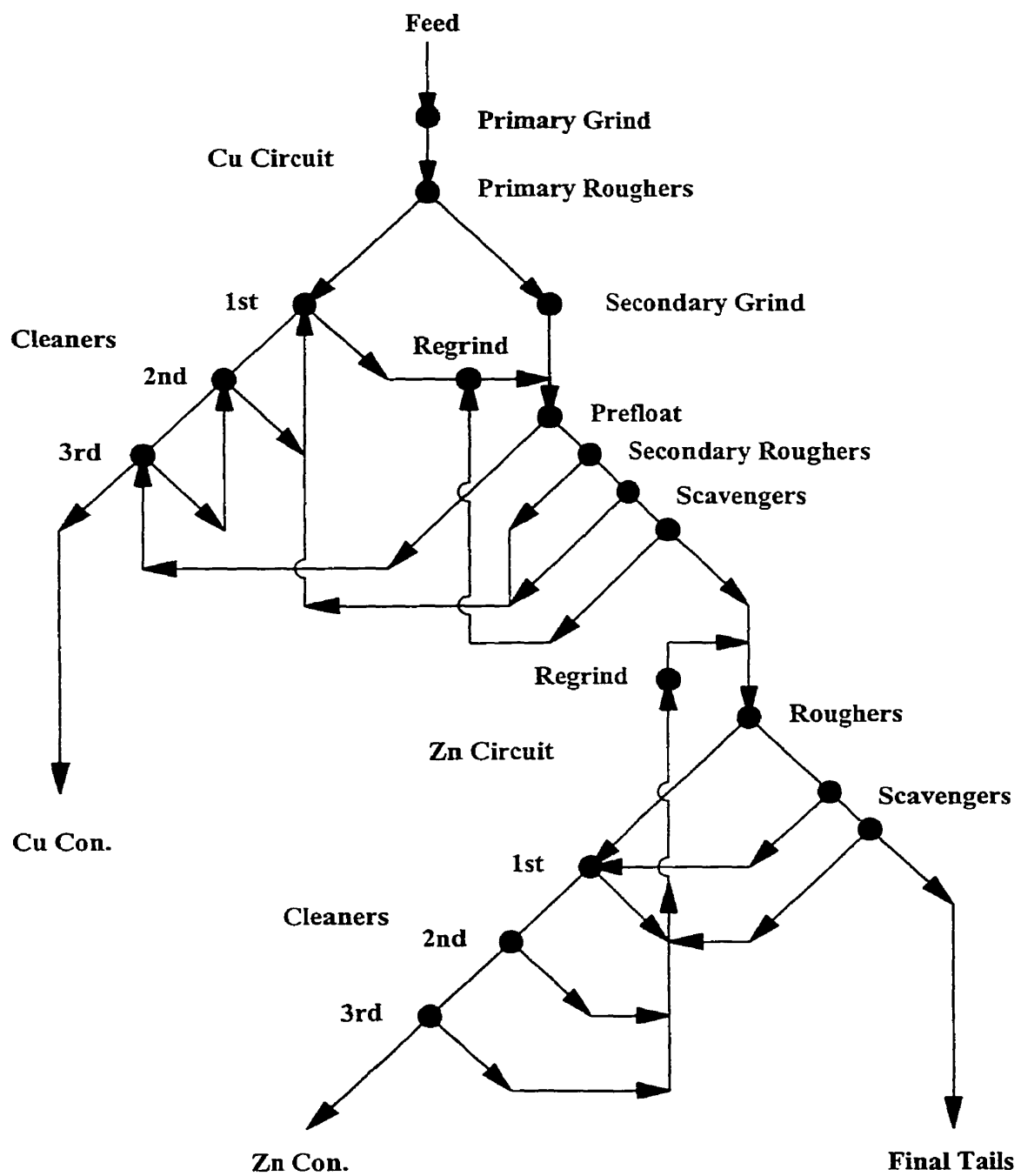
The rod mills have Ni-hard wave liners with Domite chrome-moly end liners. All ball mills are rubber lined. The grinding media are high carbon steel.

The flotation circuit as it was in 1990 is shown in Figure 3.19, also in network notation. Only one of the three parallel lines treating the "A" ore is shown.

The ore ground to 50% -45  $\mu\text{m}$  is conditioned with lime (pH 6.8), Aerophine 3418A, R208 (sodium diethyl and sodium di-secondary butyl dithiophosphate), and MIBC as frother. Sodium cyanide and sulphur dioxide are also added.

The conditioned ground ore is fed to primary rougher flotation. The tailings from this primary stage are further ground to 78% -45 $\mu\text{m}$ . A prefloat concentrate is first taken, and after further conditioning (A3418A and MIBC), secondary rougher flotation is performed.

Figure 3.19 Kidd Creek flotation circuit for the "A" ore





Scavenger flotation follows with another addition of 3418A and sodium isobutyl xanthate (SIBX).

The primary and secondary flotation concentrates are combined with the secondary cleaner tails as feed to the first cleaning stage. The prefloat concentrate, combined with the second cleaner concentrate form the feed to the third cleaning stage.

The first cleaner tails and the scavenger concentrate are combined and reground prior to joining with the main material to the prefloat stage. The third cleaner stage is operated in a counter-current fashion with recycling of its tailings to the preceding stage.

Copper flotation tails are conditioned with copper sulphate and lime (pH 10.0), SIBX, and Dowfroth 250 (frother). Roughing is followed by scavenging and the two concentrates are conditioned with lime before three stages of open circuit cleaning at a pH of 10.5 to 11.0. The scavenger concentrate and all cleaner tails are combined and reground. Following further addition of copper sulphate, SIBX, and DF250, this material is recycled mid-way down the rougher flotation stage.

The plant is well instrumented and process control strategies are firmly established. A major change in the reagent suite has been the replacement of Aerophine 3418A by a dithiophosphate based collector for the copper circuit (T. Cormode, Per. Com., Feb. 1999).

### 3.4 Similarities and differences

The ores processed differ in one key area; the presence of supergene copper minerals at Les Mines Selbaie makes it more difficult to achieve selective copper-zinc flotation.

Both mills use a relatively fine primary grind ( $\approx 80\%$   $-45\ \mu\text{m}$ ) to liberate the sulphide minerals with regrinding being performed for both the copper and zinc flotation circuits. A SAG/ball mill circuit is used at Les Mines Selbaie, while a rod mill/ball mill, plus a secondary ball mill mid-way in the rougher flotation is used at Kidd Creek.

The ball mills are rubber lined in both cases. However, the use of high chrome balls at Les Mines Selbaie (along with the SAG mill) is conducive to a greater oxidation of the sulphide minerals than the high carbon steel grinding media at Kidd Creek.

Both mills are using sodium cyanide for de-activation of the sphalerite. Zinc sulphate (rougher) and sulphur dioxide (cleaner) are used for sphalerite depression at Les Mines Selbaie while only sulphur dioxide (rougher) is used at Kidd Creek. Aerophine 3418A is used as the main copper collector although PAX is used as secondary collector at Les Mines Selbaie while SIBX and A208 are used in the same function at Kidd Creek.

The zinc circuits are similar (open circuit operation of the cleaning stages) and xanthate collectors are used in both cases, isopropyl at Les Mines Selbaie and isobutyl at Kidd Creek. The side branching of the hydrocarbon chain is expected to give a higher selectivity than a straight chain and the isobutyl has inherently less collecting power than isopropyl due to its shorter main chain.

Finally, both mills use a process water in which there is a high component reclaimed from the tailings pond.

## 4 PRACTICAL ASPECTS OF MONITORING THE PULP POTENTIAL

### 4.1 Introduction

There have been many pilot plant and plant investigations involving on-line monitoring of the electrochemical potential of the pulp. Outokumpu (41, 42, 73, 74), BRGM (75, 76, 77, 78, 79), USBM (37, 38, 80, 81), Amdel and Control International (82) have performed long term studies spanning periods from days to years, of continuous use of the sensing electrodes in mineral slurries. Unfortunately, even with such long term on-line use of electrochemical sensors, the preventive and curative maintenance requirements for the electrodes have been rarely discussed. In particular, the Controlled Potential Sulphidization (CPS) from Amdel and E-Con (Potential Control) from Control International appear to have been only succinctly described in trade reviews addressing more the expected benefits than the working principle (82).

The Outokumpu system, OK-PCF (Potential Controlled Flotation), has been reported to be in continuous use first in 1984 at the Hitura nickel concentrator following a successful pilot plant campaign and its installation at the Vammala nickel concentrator followed soon after (41). The system was eventually installed at the Vihanti copper-lead-zinc concentrator (42). There are no reports of use of the OK-PCF outside the Outokumpu group of mines.

The system is claimed to be effective and there is no reason to presume it would be otherwise from the discussion of the electrochemical model for the flotation of sulphide minerals. However, very few details about the functioning of the system are given with the exception of the use of mineral electrodes for the redox sensors and a voltammetric technique for the determination of xanthate concentrations. The published literature does not indicate major problems with the sensing electrodes although, in private discussions (Lauri Karhu, Per. Com., Feb. 1989), the location of the electrodes in the conditioner or flotation cell can be critical for accurate measurements. A good agitation must be

imparted for particle-electrode contact and to keep the electrodes relatively free from surface deposits such as the commonly observed scale.

The system promoted by BRGM, PIRANA (Pulp Instrument for Regulation and ANALysis) was in a plant trial for five months at the Salsigne mill, France (77). There does not appear to be other reports of the system in the mineral processing industry. The only indicated maintenance requirement for the system is a weekly replacement of the micro-filtration cloth (78). Preventive maintenance for the sensing elements (Eh, pH, UV spectrophotometer) does not appear to be required. However, a five month trial is still a fairly short test program if extensive support from BRGM technical staff was provided and is not an indicator of operating reliability in a real industrial situation.

Researchers at the USBM developed a multi-electrode redox sensor and performed extended trials at the Chino concentrator (37). The system was used in a slurry of chalcocite, chalcopyrite, pyrite, magnetite and sulphate minerals. The multi-electrode probe consisted of noble metals (gold and platinum) and the sulphide minerals present in the pulp. After only nine days of continuous immersion, the entire probe, including the surface of the electrodes, was covered with a highly resistive scale consisting mainly of calcite with magnetite as a minor fraction (37). This situation was similar to that experienced with pH electrodes at Chino and this led to the same solution: use of weakly acidic solutions to clean the electrodes on a regular basis.

The redox probe was later simplified to a single gold electrode and included an automated electrochemical cleaning technique based on potentiostatic conditioning and was tested in a copper-molybdenum concentrator (80, 81). The termination of the research and development function of the USBM soon afterwards (204) has prevented further refinement to the system.

Unfortunately, much of the information on maintenance of redox sensors in mineral slurries was published after the installation, in May 1989, of the on-line sensor at

Les Mines Selbaie. The best that could be done was to apply the knowledge gained from experience with pH sensors and discovered as the project progressed. As the commissioning of the A-1 zone circuit had only been completed in late 1986, this meant that there was just two and a half years of experience with pH sensors in a similar duty. With the challenges related to the operation of a new plant, the instrumentation group was just beginning to shift from a curative oriented approach to the development of preventive maintenance programs. Much remained to do to support the latter, including the monitoring of pH electrode life and the reason(s) for break-down.

In the case of Kidd Creek, the on-line sensor was installed in February 1990. The nearly twenty five years of operating experience with pH sensors and knowledge of some of the difficulties had produced well developed operating practices and preventive maintenance programs. These were simply "translated" to the on-line electrochemical sensors.

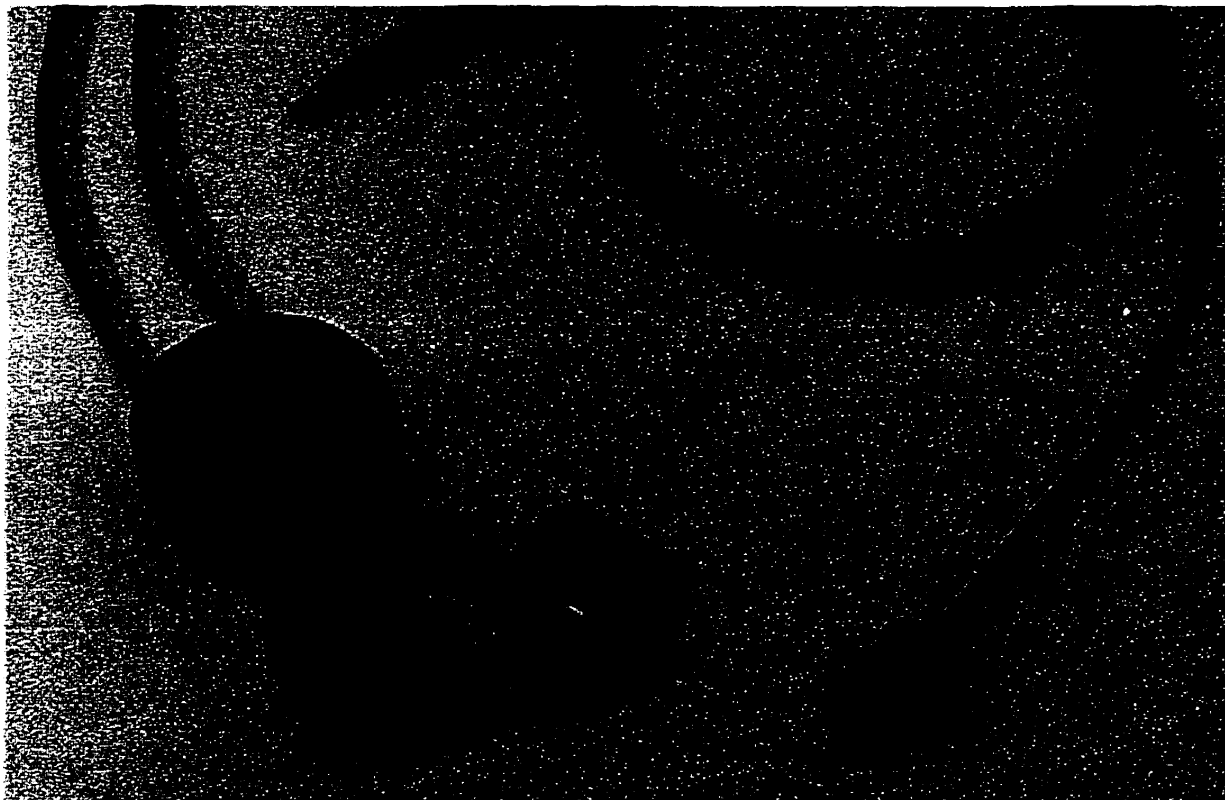
Mistakes were made during the early period of on-line monitoring at both plants. Mentioning these is by no way a dis-respect to the instrumentation and technical support staffs of both plant. Their experience in this endeavour was not much more than my own and the learning curve was steep for all.

#### 4.2 Description of laboratory redox sensing electrodes

It is appropriate at this point to describe the different redox sensing electrodes which have been especially made during the course of this study. These electrodes consisted of noble metal foils or spirals, black platinum wires, and mineral electrodes.

The noble metal foil electrodes are shown in Figure 4.1. The first two are 1 cm<sup>2</sup> foils (1 mm thick) of gold and platinum with only one face exposed. The third electrode is a 0.25 cm<sup>2</sup> gold foil mounted so that both faces are exposed. Contact between the noble metal and the copper wire was made with a solder.

Figure 4.1 Noble metal foil electrodes (gold, platinum and modified gold foil)

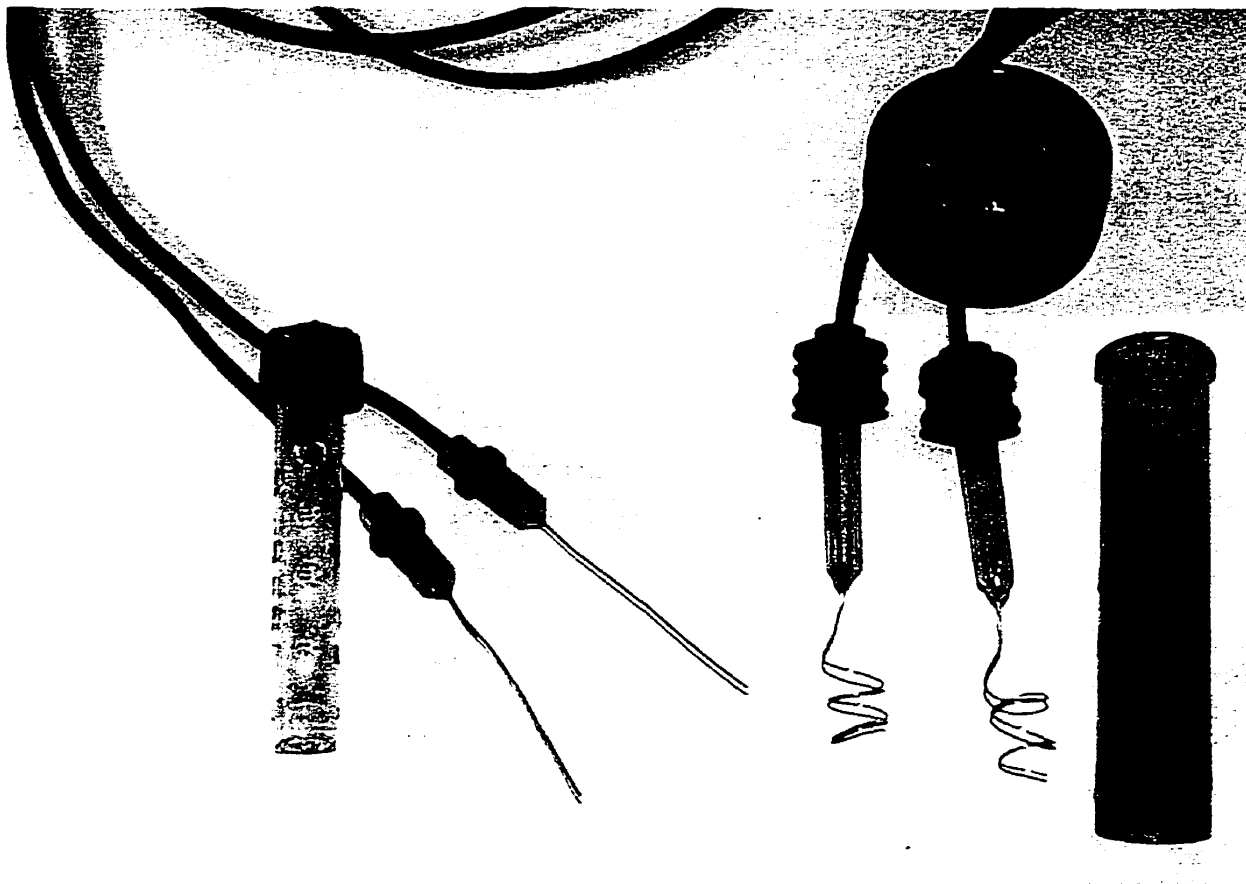


The black platinum electrodes and the gold and platinum spirals are shown in Figure 4.2 as well as the shrouds eventually made to protect these electrodes during measurements. The cables for all noble metal electrodes were shielded cables recovered from scrap combination pH electrodes as these were of high quality and were inferred, by their previous use, not to give rise to undesirable effects on the measurements.

The black platinum electrodes, which were rarely used during this study, were made by platinizing, at 20 mA for 3 minutes, 5 cm long by 0.5 mm diameter platinum wires. Two electrodes had to be made since the platinizing process requires a pair of similar electrodes. Although the black platinum deposit was fragile and tended to be removed after a long period of immersion in a slurry, it had the advantage that if poisoning was suspected, the deposit could be removed by mechanical polishing and a new one re-platinized. This

contrasts with the black platinum electrode (fuel cell element) used by Rand and Woods (36, 255) which must be replaced if poisoning occurs.

Figure 4.2 Black platinum, gold and platinum spiral electrodes and protective shrouds



In an early design, as shown in Figure 4.2, each spiral consisted of a 10 cm long wire coiled three times. However, even with the shroud installed, loss of the spiral was frequent. To minimize the cost of replacement material, a shorter version of the spiral (with a 5 cm long wire) was used for most measurements made during surveys of the copper and zinc circuits in the concentrator. Gold and platinum tip electrodes, remains from loss of the respective spirals, were retained for possible use and are shown in Figure 4.3. With only the tip showing, distinguishing between the gold and platinum electrodes becomes difficult and a ring of red epoxy was put around the gold tip.

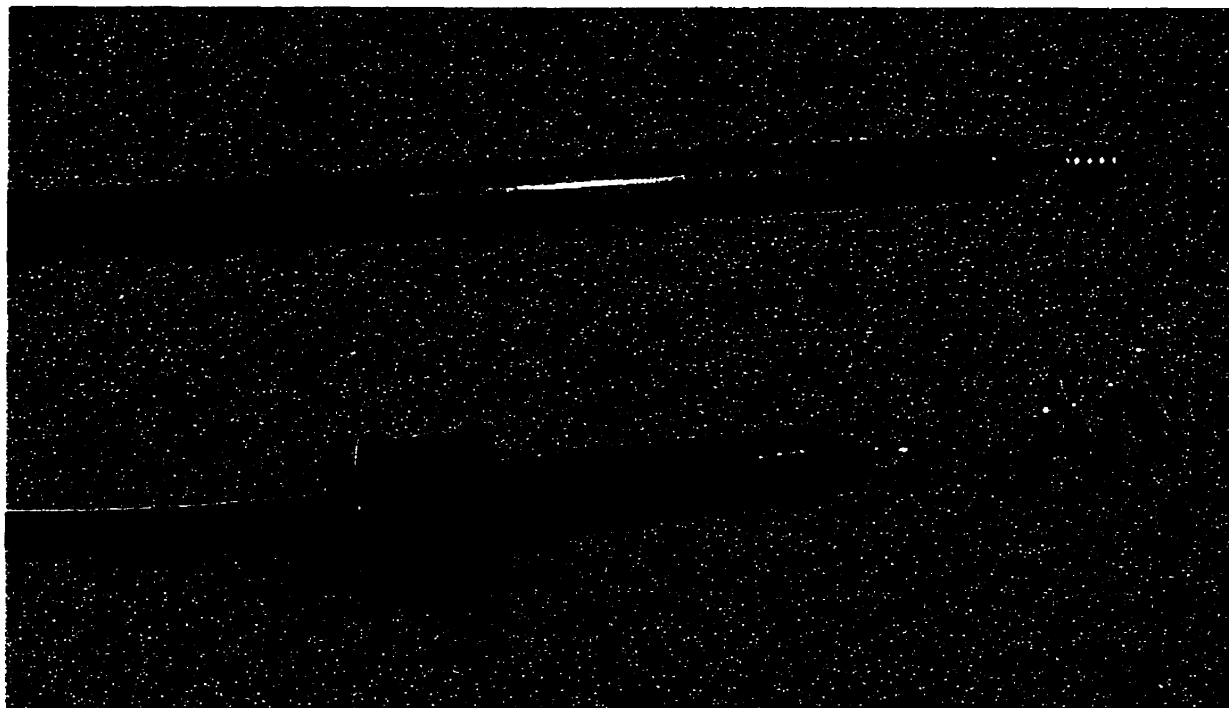
Figure 4.3 Gold (top with red epoxy) and platinum (bottom) tip electrodes



The fragility of the gold spiral electrode as designed for this study contrasts with the sturdiness of an electrode like those used within Inco's laboratory (43) or by Huntsman Chemicals (244) as seen in Figure 4.4. Both designs nevertheless provide a high turbulence around the electrode, and hence a high probability of contact with the mineral particles in the slurry.



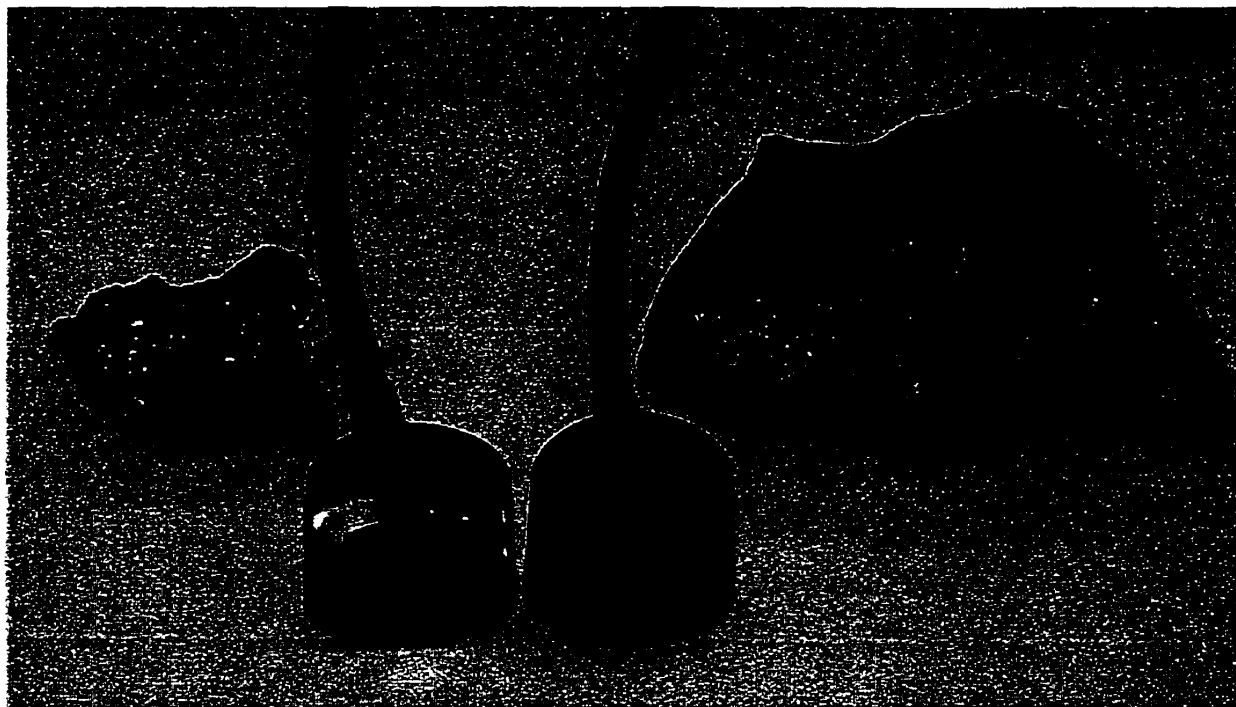
Figure 4.4 Sturdy gold spiral (top) (43, 244) and McGill gold spiral (bottom) electrodes



The mineral pieces utilized to fabricate the mineral electrodes were obtained by hand-sorting pure minerals from ore samples. The galena pieces obtained from the ore always contained inclusions of some kind (e.g. sphalerite, pyrite). Pure galena pieces from Kansas, obtained through Wards Scientific, were also used for comparison purposes.

The first mineral electrodes were fabricated in a manner which differed very slightly from usual practices (256, 257, 258). Large pieces which could fit within the selected epoxy mould (25 mm diameter) were broken away from mineral specimens. After obtaining two parallel surfaces by hand grinding, the mineral pieces were cast into epoxy resin. Once the resin had set, it was drilled so that a shielded copper wire could be inserted and contacted with the mineral piece by a drop of mercury. The finished electrode was sealed with epoxy resin and silicone. Figure 4.5 shows specimens of galena (from Les Mines Selbaie) and chalcopyrite (from Kidd Creek) and the resulting mineral electrodes.

Figure 4.5 Galena (left) and chalcopyrite (right) specimens and finished mineral electrodes



Difficulties were experienced in making sphalerite electrodes due to the high band gap of this mineral, 3.6 eV which in its pure, low iron form, is at the boundary between semi-conducting and dielectric minerals (107). Consequently, the resistivity of massive sphalerite pieces,  $8 \times 10^5$  ohm-m (107), is too great to permit passage of electrons between the exposed surface of the mineral and the mercury contact. Finely ground mixtures of sphalerite and graphite (ZnS:C ratio of 2:1) were pressed at 35.2 MPa (50 000 psi) and "mineral" electrodes made from these pellets. It was then possible to obtain measurements and these will be discussed later.

Mineral electrodes are not without long term problems. Corrosion of the copper wire and contamination of the mercury contact (Figure 4.6) and interfacial oxidation of the mineral within the epoxy cast, especially with chalcopyrite electrodes (Figure 4.7) were observed. Had the mount been anything else than clear epoxy, such developing faults would not have been noticed and erroneous measurements unwittingly recorded.

Figure 4.6 Corrosion of the copper wire and contamination of the mercury contact (galena at left, pyrite at right)

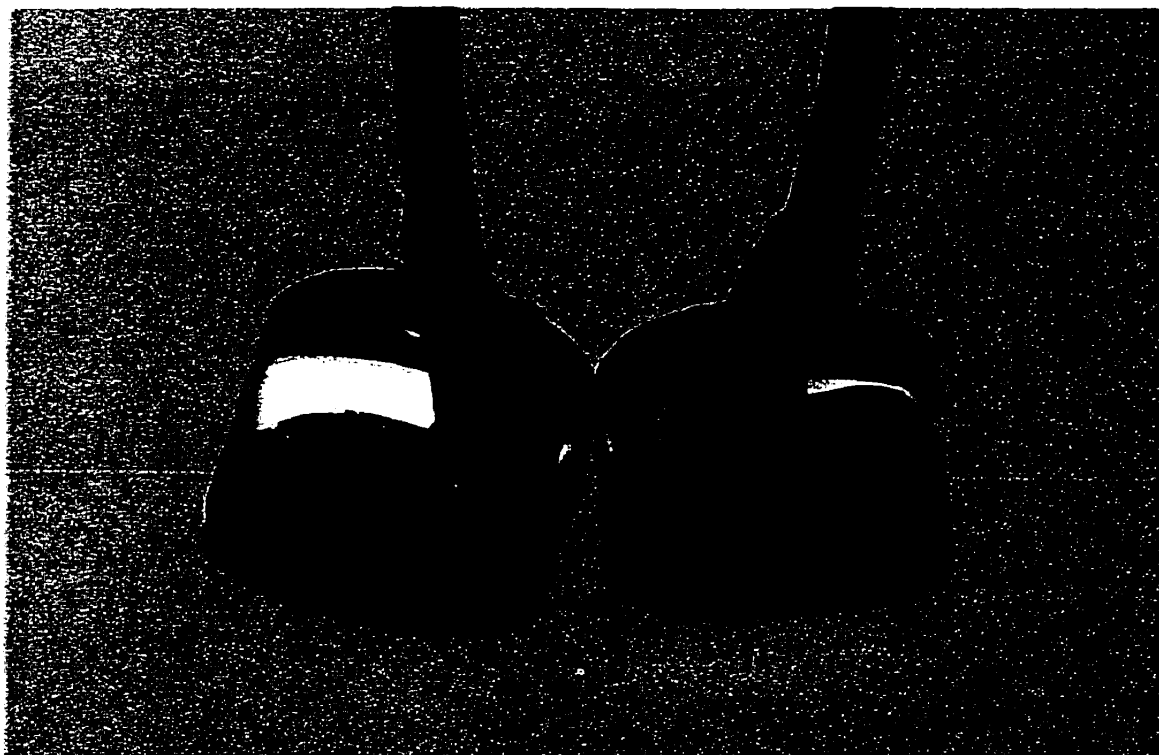


Figure 4.7 Interfacial oxidation of chalcopyrite within the epoxy cast



Late in the project, it was discovered that small diamond coring bits (12.5 and 6 mm diameter) could be used to obtain cylindrical mineral pieces which could be mounted into electrodes. Figure 4.8 shows 12.5 mm diameter mineral electrodes in various states of the fabrication process (left is galena, right is pyrite) while Figure 4.9 shows 6 mm diameter pyrite cores along with two 6 mm holding base for carbon paste electrodes. The mineral "cores" can be sawed neatly using a water cooled diamond blade to yield nearly flat faces. A conductive graphite based epoxy paint was used to make the contact between the wire and the electrode. There is one advantage with this approach. If the electrodes are used for fundamental electrochemistry experiments, the measured current can be directly compared between the minerals as the electrodes have the same surface areas.

Figure 4.8 Mineral electrodes in fabrication (12.5 mm diameter)

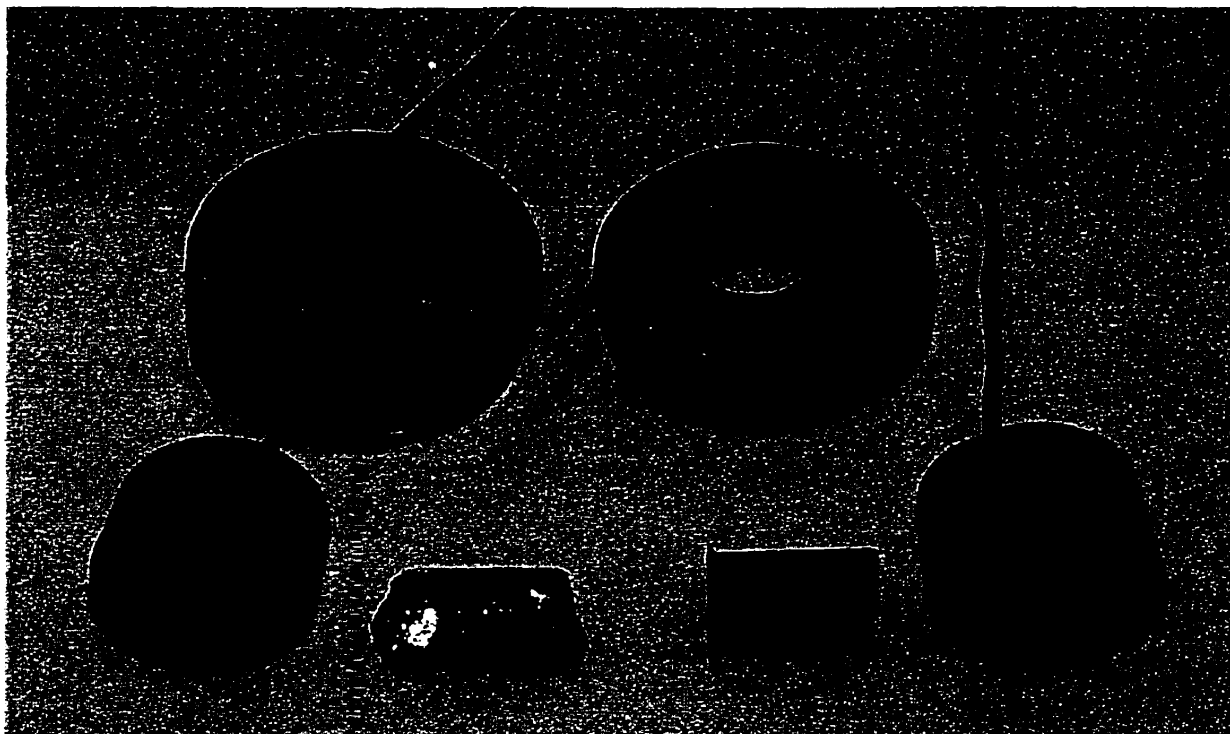


Figure 4.9 Carbon paste electrode bases and pyrite cores (6 mm diameter)



### 4.3 Known problem: electrode poisoning

Electrode poisoning is a special case of the mixed potential model. Namely a "poison" is formed, or adsorbed onto the electrode surface causing the mixed potential of the poison and the solution to be measured. Poisoning occurs over time and the measured potential drifts further away from the electrochemical potential of the solution (or slurry) as more of the poisoning species is formed, or adsorbed onto the electrode surface. Drifting will however be limited to the reversible potential of the poison itself.

Electrode poisoning is not limited to noble metal electrodes although the traditional use of platinum and gold as electrode materials has provided a greater opportunity for observation of its occurrence (259, 260, 261). It can be readily identified when measuring a series of sample solutions with an electrode pair. Lack of reproducibility when changing the order in which the samples are analyzed, potential drift, and a long period to stabilize are all signs that the sensing electrode is probably not in a perfect state (259).

It is unfortunately more difficult to observe poisoning with an on-line electrode. One clear sign will be a very sluggish response when large step changes are made to the dosage of potential modifying agents and/or pH modifiers.

A satisfactory method to regenerate laboratory electrodes is by mechanical polishing (259). As mechanical polishing generates surface distortions, some time should be allowed between the polishing step and the first measurement made so that the surface can relax to its natural energy state as demonstrated for platinum (262). The importance of surface state of the electrode resulting from preparation for experimentation is not limited to the measurement of the electrochemical potential.

Gerth and Lapique (263) evaluated coarse and fine emery paper for electrode surface preparation in the study of the  $\text{Cu(II)/Cu}^0$  reaction in sulphate solutions. In their

case, polarization of the electrode for a few minutes was required to obtain reproducible reaction rate determinations, irrespective of the type of emery paper.

Mechanically polishing on-line electrodes is impractical except on first use or during regular preventive maintenance inspections. The abrasiveness of mineral slurry yields some mechanical cleaning of the electrode between inspections although extreme pulp agitation (and resulting abrasion) are to be avoided if the electrode material is to last longer than a few days.

Electrochemical cleaning, or conditioning, is an approach which is still in the early development stages and would be quite attractive for on-line electrodes. In this technique, the electrode pair is taken off the measuring mode and the sensing electrode is subjected to a cycle of applied potentials (against the reference electrode) via a voltage supply and ancillary counter electrode. The first step of the cycle is usually a potential high enough to de-sorb the poison or oxidize it while the last step is a potential low enough to restore the surface of the electrode in a relaxed state (80, 260, 261). Like mechanical polishing, electrochemical cleaning may leave the electrode surface in a high energy state resulting in a long relaxation time prior to measurement.

The scheme developed at USBM targets mainly the removal of scale in-situ and involves polarisation of the gold electrode at +1.5 V vs. Ag/AgCl (+1.7 V vs. SHE) for 10 minutes (80). This polarisation is followed by six cycles of a triangular wave with limits of -0.6 and +0.8 mV vs. Ag/AgCl (-0.4 and +1.0 V vs. SHE) at 400 mV/s to decrease the electrode recovery time from 30 minutes to 1 minute (80).

One additional challenge with the electrochemical cleaning approach is the selection of the frequency of the potential reversal. Topographic changes (faceting and roughening) of silver and gold electrodes resulting from prolonged application of potential reversal have been observed (264). The main observation was that the topographic changes became more intense as the frequency of the potential reversal decreases. The

400 mV/s sweep rate for the post-cleaning polarisation empirically determined for the USBM system is high when compared to cyclic voltammetry conditions and may reflect an undesirable modification of the surface of the gold electrode at lower sweep rates.

A similar electrochemical cleaning of the gold electrode used in laboratory flotation tests is routinely performed at Inco (265). This particular scheme involves polarizing the gold electrode at +2.5 V and -1.5 V vs. SCE (+2.75 and -1.25 V vs. SHE) for 15 seconds at each potential in 0.1 M HCl. Zhou and Chander (260, 261) have demonstrated that polarizing a gold electrode at 1.0 V vs. SHE is an effective cleaning scheme for one of the most difficult poisons - the sulphide ion. Indirectly, the electrolytic cleaning scheme tested by the USBM for scale removal from redox sensors (80, 81) would also de-poison the electrode if the positive cycle of the conditioning is sufficient to de-sorb and/or oxidize the poisoning species.

Although the tell-tale signs of a poisoned electrode are readily identified, and means to restore the electrode to a pristine state exist, it is worth reviewing specific cases of electrode poisoning. Identifying the poisoning species is half the battle in eliminating the problem, especially for an electrochemical cleaning scheme. Knowledge of the poison is crucial for the definition of the potential cycle required to eliminate it while not irreversibly modifying the surface state of the electrode. Finally, a given compound recognized as a poison in hydrometallurgical systems may not be one for flotation systems due to different regimes of redox potentials and pH.

The possibility of poisoning of platinum electrodes by reagents present in flotation pulps has been investigated by Natarajan and Iwasaki (259, 266). They found that sulphide and cyanide ions can react and/or adsorb on the platinum surface impeding charge transfer with the other ions present in the solution. Collectors (e.g. xanthate and dithiophosphate) can adsorb on the platinum surface and establish redox couples of their own which are then the only ones sensed by the electrode. Also, the electrocatalytic properties of platinum can be greatly reduced in the presence of alcohols since these



adsorb on the active sites of the surface (267). As most of the flotation frothers have an alcohol group, they may cause poisoning.

#### 4.3.1 Sulphide ion

The approach taken by Natarajan and Iwasaki (259, 260) for sulphide ion poisoning was different than that by Zhou and Chander (260, 261). The former were attempting the measurement of the electrochemical potential of a solution after exposure of the sensing electrode to the sulphide solution while the latter were attempting to use the electrochemical potential of the sulphide solution to determine the hydrosulphide concentration.

It could be asked why one would want to use the electrochemical potential of the system as an indicator of hydrosulphide concentration while ion selective electrodes for such a measurement exist (268, 269, 270). Ion selective electrodes, which are based on electrochemical reactions across a membrane, have a typical response time of ten minutes for 98% of the end point value upon immersion in the system or on step change in concentration (271). Noble metal electrodes respond faster to change in hydrosulphide concentration (less than 1 minute) and are twice as sensitive as ion selective electrodes with calibration slopes of the order of 60 mV/M  $H_2S$  (260, 261), characteristics which are highly desirable for a control system.

The effects of a pre-immersion of the platinum electrode in a  $H_2S$  solution on the potential measured in a ZoBell solution (437 mV vs. SCE) are shown in Figure 4.10 as a function of pre-immersion time and in Figure 4.11 as a function of pH of the  $H_2S$  solution.

Even a 10 minute immersion in  $H_2S$  solutions affects the measurement made in the ZoBell solution. The increase in potential discrepancy is almost a linear function of time up to around 40 minutes after which point, the measured potential tends towards a

limiting value. From Figure 4.11, the impact of pre-immersion in saturated  $H_2S$  solutions is strongest when they are acidic.

Figure 4.10 Effect of pre-immersion of electrodes in  $H_2S$  solution (259)

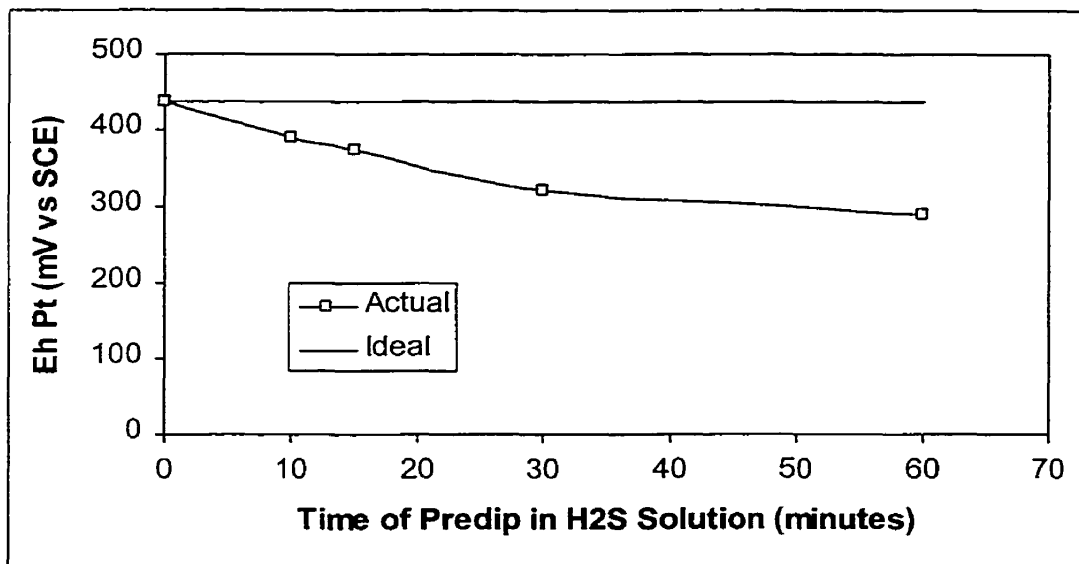
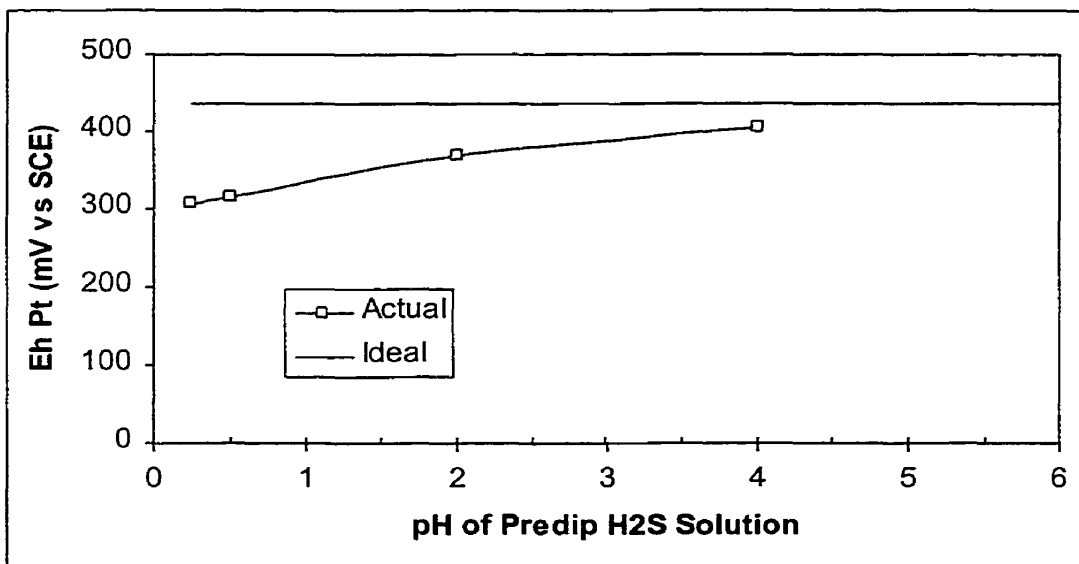
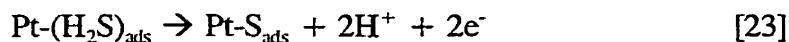


Figure 4.11 Effect of pH of  $H_2S$  solution (259)



The poisoning effect by H<sub>2</sub>S was attributed to its adsorption and subsequent oxidation to sulphur forming a resistant coating at the electrode surface:



The occurrence of the adsorption process is credible, and the trend exhibited in Figure 4.10 is very similar to that of a titration curve with the inflexion point corresponding to the completion of a mono-layer coverage. The observation of persistent poisoning under acidic conditions is consistent with the stability of H<sub>2</sub>S at pH less than 7 and its dissociation into H<sup>+</sup> and HS<sup>-</sup> at pH greater than 7 (272, 273).

The thermodynamic E-pH diagram for the sulphur-oxygen-water system indicates the formation of elemental sulphur at potentials slightly higher than those for the stability field of H<sub>2</sub>S. On the other hand, meta-stable E-pH diagrams suggest that this formation extends into the alkaline region (272). How far this extension goes depends on the presence of other species such as sulphite ion in the system (272).

The poisoning capability of sulphide ions is quite worrisome for hydrometallurgical processes because these are usually carried out in highly acidic environments (e.g. metal precipitation from pH 0-1 solutions using H<sub>2</sub>S). However, it is a lesser concern for flotation simply because alkaline environments are encountered more often than acidic ones. It is also one plausible reason why controlled potential sulphidization (82, 83) has been successfully implemented without major problems with the electrodes.

#### 4.3.2 Cations

One would normally not think of cations, especially heavy metal ions, as possible poisons for redox sensing electrodes. However, heavy metal ions can deposit a fraction of a monolayer at a potential significantly lower than the reversible potential of their

reduction reaction (274). There is some controversy as to whether the fractional monolayer should be described as adsorbed or deposited. Nevertheless, the phenomenon occurs on gold and platinum electrodes (275, 276, 277).

As with poisoning by the sulphide ion, a given cation may give rise to electrode poisoning if the pH of the system is less than that of its precipitation as hydroxide. In alkaline slurries, common in most flotation processes, metal ions should not be a problem.

#### 4.3.3 Collectors and frothers

Natarajan and Iwasaki investigated the poisoning effect of Aerofloat (Cytec, potassium diethyl dithiophosphate) on platinum (259). Extreme conditions were used for the demonstration with a collector concentration of  $8 \times 10^{-3}$  M (10 to 100 times that used generally for flotation) and a platinum electrode with an exposed surface of only  $1 \text{ mm}^2$  compared to the  $\text{m}^2/\text{g}$  of sulphide minerals in flotation slurry.

The results indicated that the collector adsorbed on the platinum electrode and affected the measurement of redox potential in the ZoBell solution. In practice, one would not observe an impact as dramatic as that presented by Natarajan and Iwasaki simply because the surface area of the sensing electrode is much less than that of the mineral particles in the slurry. Over an extended period of time, however, an on-line noble metal electrode will develop an adsorbed layer of collector.

This layer should be considered as a real poison if the form in which the collector adsorbs on the noble metal electrode (e.g. dixanthogen) is different than that for the sulphide mineral(s) being floated (e.g. metal xanthate). Nevertheless, the build-up of multiple layers of collector on the surface of the electrode will lead to a strong departure of the ideal ohmic contact upon collision with the sulphide mineral particles.

The possibility of electrode poisoning by frothers, which are generally alcohol based organic molecules, can be extrapolated from studies of the impact of alcohols on the reaction rates occurring at gold and platinum electrodes (277, 278, 279). The oxidation of alcohols is one possible reaction considered for fuel cells and any poison present reduces the efficiency of the energy producing device.

The poisoning action of alcohols on platinum is via surface blocking by strongly adsorbed intermediate species. Gold is less affected and tends to show higher activity for the reaction under alkaline conditions (277). The oxidation of alcohols requires high potentials (greater than 1.1 V vs. SHE) which are not usually encountered in sulphide flotation processes. Since it is the intermediate species which are responsible for poisoning, frothers by themselves are not cause for concern. However, this possibility should not be ignored under highly oxidative conditions.

#### 4.3.4 Oxygen, hydrogen peroxide, and oxide/oxy-hydroxide

There is one last phenomenon observed with platinum electrodes when measuring the redox potential in solutions or slurries containing oxygen dissolved in the solution phase or from gas bubbles. The potential-pH line for oxygen/OH<sup>-</sup> should intercept a potential of 1.229 V for an oxygen saturated solution at pH 0 with a pH dependence of -0.0591 V/pH (73). In practice, the line is found experimentally to be (280):

$$E_h = 0.9 - 0.059 \text{ pH.} \quad [24]$$

This experimental line was explained using the mixed potential model and assuming a Pt-O/Pt couple formed on the electrode surface. It was stated (280) that oxygen can be associated with a platinum surface either as adsorbed oxygen or as oxide. The exact nature of Pt-O was not established at that time and might be an oxide or adsorbed oxygen but was described as a poison.

Sato (256) found a similar experimental line for air saturated mine waters. However, his explanation was based on the reduction of oxygen via the formation of hydrogen peroxide. Again, this leads to a mixed potential which does not allow the observation of the 1.229 V oxygen reduction potential at pH 0. The presence of hydrogen peroxide as an intermediate product in the reduction of oxygen also occurs with other materials. For example, pyrite catalyses the reaction via the intermediate  $H_2O_2$  (108, 281) and galena also favours a similar reaction path (108, 109). Since perxanthates are often found in flotation slurries as a result of reaction between xanthate and hydrogen peroxide (83), it is likely that the hydrogen peroxide originated from oxygen reduction on the minerals.

These difficulties with oxygen reduction are not limited to sensing its potential but also are related to a degree of irreversibility of the reaction. Namely, the exchange current density is so low ( $10^{-9}$  A/cm<sup>2</sup>) that even traces of impurities can successfully compete with it. Thus, the equilibrium oxygen reduction potential could not be successfully observed until all impurities had been rigorously excluded (282, 283, 284). On the other hand, the oxide/oxy-hydroxide compounds usually found on platinum electrodes are important for the reduction of oxygen as they are stable (283) and serve as active sites for the formation of the hydrogen peroxide intermediate (282, 284, 285).

For our purposes, it is not necessary to resolve the debate between the theoretical 1.229 and experimental 0.9 V potential for oxygen reduction (283) as no flotation system is pushed into a 1.0 V vs. SHE (0.75 V vs. SCE) or greater oxidation regime for which the distinction between the two would be critical. Furthermore, with a reaction path for oxygen reduction on sulphide minerals being via the intermediate hydrogen peroxide (108, 156, 280), the experimental 0.9 V potential for oxygen reduction represents the "reality" for the system and is not an expression of a poison on the surface of the electrode. The implication for using potential-pH diagrams to interpret the flotation response is that it is the experimental oxygen reduction line which should be shown rather than the theoretical one. It is common practice to show both lines as guidelines.

#### 4.3.5 Summary

Electrode poisoning is a possibility for mineral slurries but under most flotation conditions would not be a major concern. The use of sulphide ions or the presence of metal ions in solution in a flotation process performed under acidic conditions may lead to electrode poisoning and should be investigated as such. The use of a high collector dosage could also lead to deterioration of the quality of the measurement.

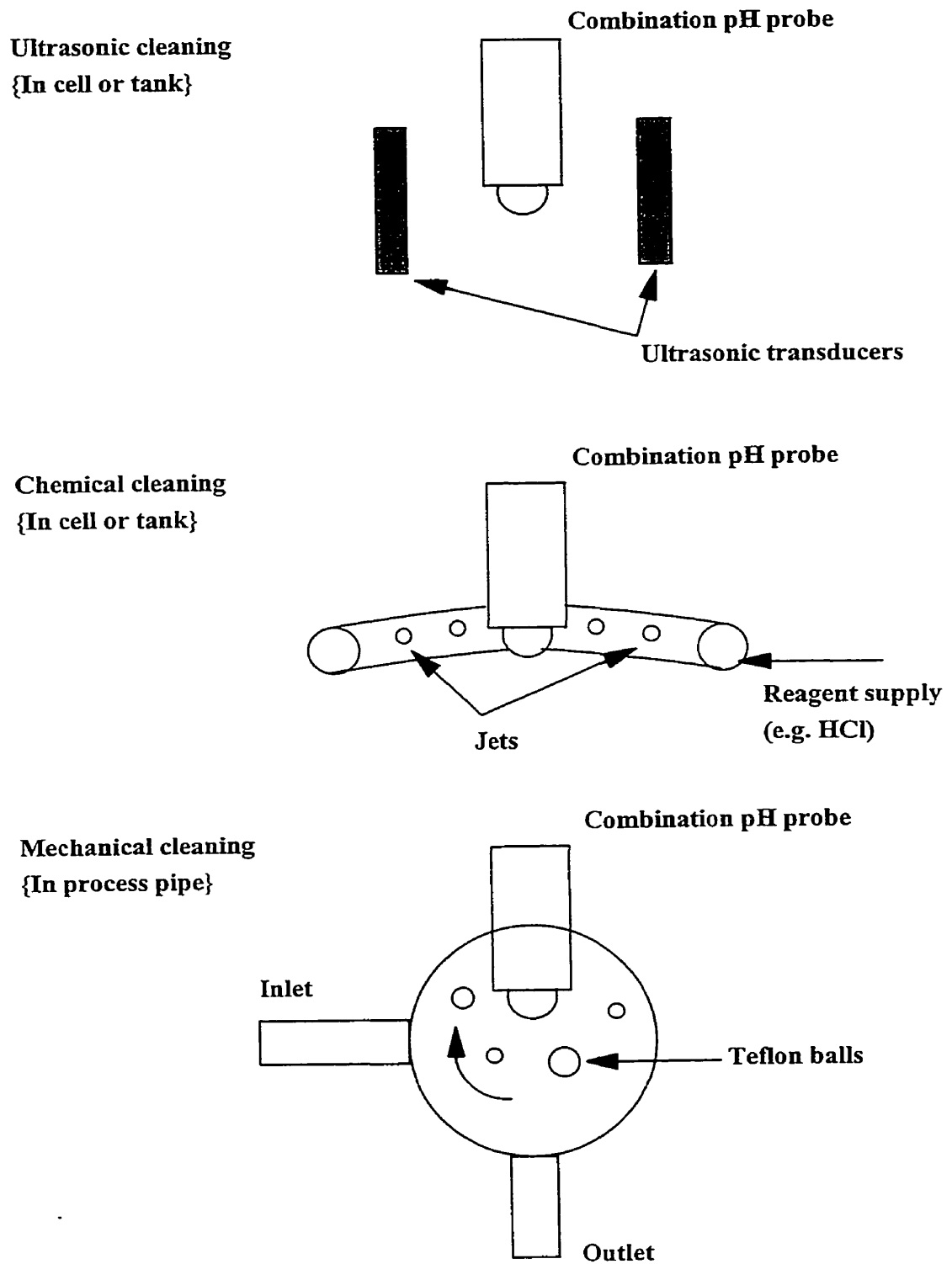
The experimental 0.9 V potential for oxygen reduction reflects the reality of the system, be it due to hydrogen peroxide or oxide/oxy-hydroxide species on the surface of the electrode, and should not be considered the expression of a poison in flotation pulps.

If electrode poisoning does occur, several methods are available for overcoming its impact on the measurement. Of these, electrochemical conditioning appears to be promising for noble metal electrodes used on-line in a flotation process although the exact conditions must be established experimentally for the system. Mineral electrodes, because of the possibility of irreversible surface changes during potential cycling, are less amenable to electrochemical conditioning for de-poisoning and mechanical polishing, imposed during electrode inspection, or inherent during use in the mineral slurry, is the most practical remedy.

#### 4.4 Expected electrode life in industry

At the time the on-line sensor was installed in the A-1 zone flotation circuit, no literature related to maintenance and/or the life of pH sensors had been found. Eventually, technical literature related to pH electrode maintenance was found but mostly originating from equipment manufacturers (286, 287, 288). In one particular paper, some of the electrode cleaning techniques already discussed with the instrumentation groups of Les Mines Selbaie and Kidd Creek were described (287). Figure 4.12 shows how one could implement ultrasonic cleaning, chemical cleaning, and mechanical cleaning.

Figure 4.12 Possible on-line electrode cleaning techniques: ultrasonic, chemical, and mechanical (287)





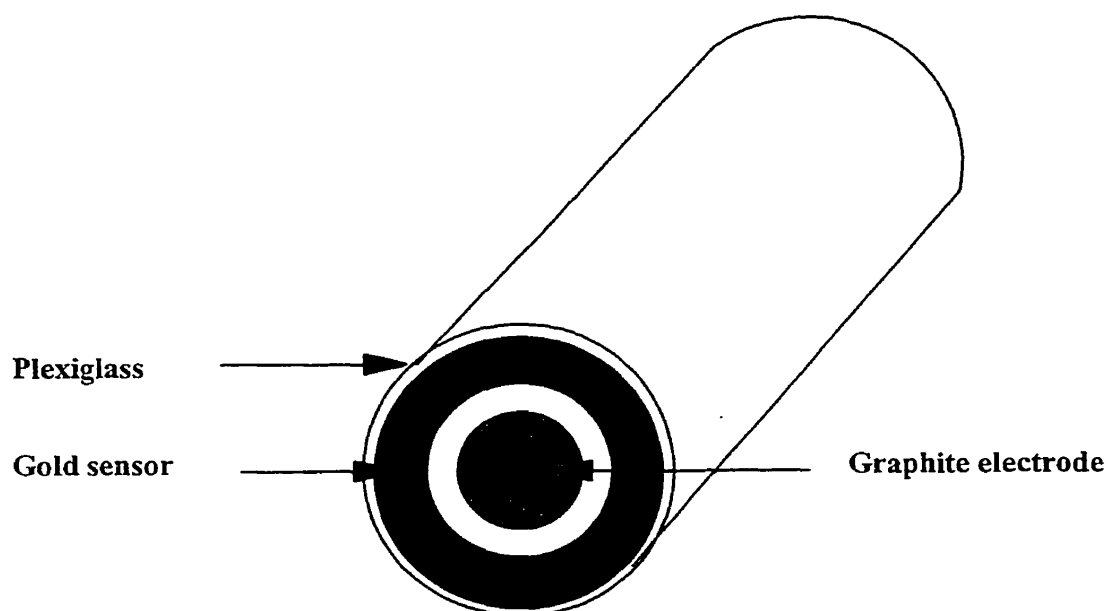
In the first scheme shown in Figure 4.12, two ultrasonic transducers are positioned to surround the combination pH probe. Regular energization of the transducers for a certain amount of time removes the deposited scale by vibration (287). The intensity, frequency, and duration of the ultrasonic cleaning are determined empirically for the particular application keeping in mind that wear of the sensor will increase with increasing cleaning intensity. This scheme is applicable to a pH sensor immersed in a conditioning tank or a flotation cell.

An example of implementation of a chemical cleaning scheme is also shown in Figure 4.12. In this scheme, a cleaning reagent (usually dilute HCl) is sprayed at regular intervals on the tip of the combination pH probe (287). Again, the frequency and duration of the treatment is application dependent. The pressure of the cleaning reagent supply must be high enough for the reagent to reach the probe tip against the velocity of the fluid or slurry surrounding the sensor but not so high as to form a jet which would cause erosion of the tip and reduced sensor life. As for ultrasonic cleaning, chemical cleaning is applicable to a pH sensor immersed in a conditioning tank or a flotation cell.

The last scheme shown in Figure 4.12 is applicable only to pH sensors installed in process pipes. By the installation of the sensor in a turbulent cavity in the pipe (usually an elbow), the insertion of teflon balls in this cavity, and the use of a mesh in the inlet and outlet to keep the balls in the cavity, the fluid flow causes the balls to move around and impact on the sensor tip. Again, a balance between cleaning efficiency and sensor life is desirable and too much agitation or too large balls will cause the sensor to fail prematurely.

Figure 4.13 shows schematically the gold redox probe developed by the USBM, which is an implementation in the same body of a gold sensor and the counter electrode (graphite) required for electrochemical cleaning and conditioning (38, 39). This system is an automation of the technique described by Zhou and Chander (260, 261) and that used for years within Inco in the laboratory (265).

Figure 4.13 Self-cleaning gold redox probe (38, 39)



To assist in the evaluation of electrode life, a survey was conducted on the more common pH electrodes among Canadian mining operations. A report summarizing the findings of the survey was made available to all participants (289). The most significant points for on-line measurement of the electrochemical potential of the flotation pulp and the possible implementation of control schemes based on such measurements are discussed below.

#### 4.4.1 Methodology

The mines selected were base metals and precious metals operations which use froth flotation as their main or secondary separation process.

In June 1988, 45 questionnaires were sent. Of these, 5 were returned completed (11.1%) and another 5 were returned due to closure of the operations (11.1%). In May 1989 another 45 questionnaires were sent targeting the 35 mines which did not respond in

1988 and another 10 which had started (or re-opened) in the interval. This time, 12 were returned completed (26.7%) and one (2.2%) was refused by the addressee.

The complete statistics are 17 responses for 90 questionnaires, or 19% response rate. This response rate is low and somewhat discouraging. Although the information gathered is valuable, it is not possible with this low response to accurately determine if a given complex sulphide ore and/or a given reagent system (e.g. SO<sub>2</sub> for copper/lead and copper/zinc separations) provide conditions that reduce the life of industrial pH electrodes.

#### 4.4.2 Respondents

The distribution of the responses among complex ore families is shown in Table 4.1. Operations with copper based ores were the most responsive and represented 88.2% of the total respondents. Operations with lead/zinc and nickel/copper ores were the least responsive.

Table 4.1 Distribution of respondents among complex ore families

Ore Family	Responses	%
Cu and Cu-Mo	4	23.5
Cu-Zn-Fe	3	17.7
Pb-Zn-Fe	1	5.9
Cu-Pb-Zn-Fe	4	23.5
Cu-Au-Fe and Au-Fe	4	5.9
Ni-Cu-Fe	1	5.9
Total	17	100.0

Whereas the advantages of control systems in mineral processing are well publicized it is surprising to find that only 52.9% of the responding operations use pH control with on-line monitoring (Table 4.2). Another 23.5% of the operations use pH measurements but only on a manual basis. Finally, pH does not appear to be a necessary process parameter for 23.5% of the operations.

Table 4.2 pH monitoring system

pH Monitoring System	Responses	%
On-line	9	52.9
Off-line	4	23.5
None	4	23.5
Total	17	100.0

The most frequent use of pH monitoring and control is for alkaline flotation circuits (41.2% of the operations; Table 4.3). Only one operation has an acidic only circuit while another 5 use both alkaline and acidic conditions in their flotation process.

Table 4.3 Selective flotation circuit

Type of Circuit	Responses	%
Alkaline	7	41.2
Acidic	1	5.9
Alkaline and acidic	5	29.4
Not specified	4	23.5
Total	17	100.0

### 4.4.3 pH electrodes

Only the responses from the operations monitoring pH in their flotation circuit will be discussed (13 operations). To make the most of the responses obtained no attempt is made to discriminate between the operations using on-line pH monitoring and control from those with off-line pH monitoring.

Most operations (84.6%) use combination pH probes (84.6%) i.e., both pH and reference electrodes in the same body. This type of electrode is preferred due to its ease of installation and maintenance. In only 3 operations (23.1%) the preamplifier is integral to the combination pH probe. This configuration permits a longer distance between the probe and the transmitter. On the other hand, it requires a water-proof electrode body and/or installation.

Tables 4.4a and 4.4b indicate the most common types of reference electrode, either a separate electrode or within the pH combination probe. The maintenance free gel and solid electrolyte reference electrodes are clearly favoured (80% of responses) over the solution electrolytes which need refilling at regular intervals. Figure 4.5 shows the different types of industrial reference electrodes currently in used.

Table 4.4a Type of junction for reference electrode

Junction	Responses	%
Double	3	21.4
Single	5	35.7
Not specified	7	50.0
Total	14	100.0

(Note: One mill uses the two types of references)

Table 4.4b Type of electrolyte for reference electrode

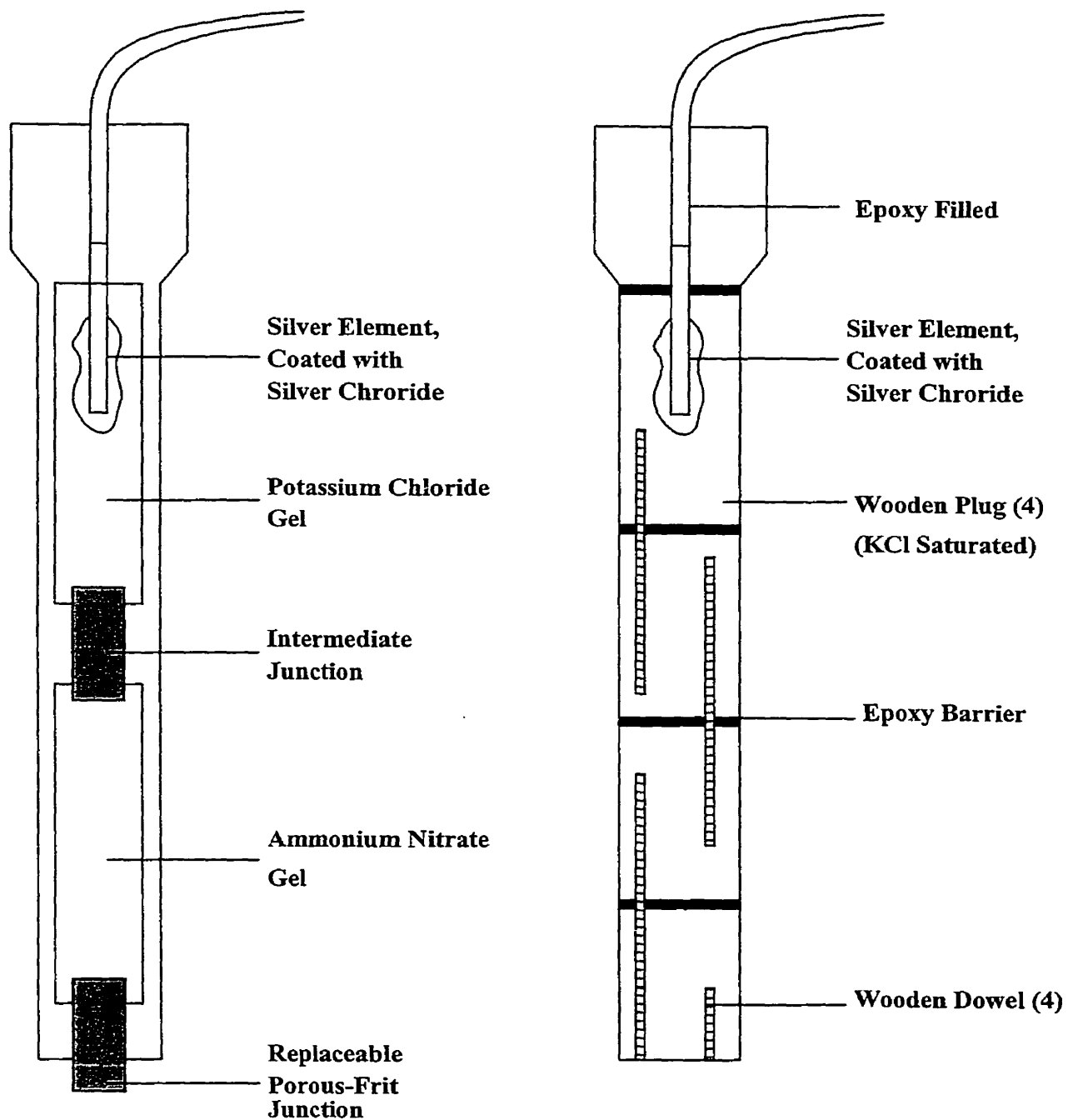
Reference Electrolyte	Responses	%
Solution	3	20.0
Gel	9	60.0
Solid	3	20.0
Total	15	100.0

(Note: Two mills use two types of references)

Half of the respondents did not specify the type of junction for the reference electrode (Table 4.4a). The double junction reference electrode is reported for 3 operations and exclusively in flotation circuits where  $\text{SO}_2$  is used for the separation process. These 3 concentrators do not, however, account for all of the ones reporting the use of  $\text{SO}_2$  and the requirement for double junction references may be ore specific.

The main reason why a double junction is preferable when sulphur dioxide is used in the process is the diffusion of free sulphite ions (as reaction product of water and sulphur dioxide) into the porous junction. These ions react with the silver ions from the electrolyte and precipitates within the pores of the junction. The consequence of this precipitation is two-fold. First, there is a depletion of silver ions in the reference electrolyte and this shifts the potential of the electrode. Second, the precipitate reduces the porosity of the junction and this increases the potential difference across the junction. Although both phenomena introduce a drifting response, the second eventually leads to electrode failure as a complete blockage renders the reference electrode isolated from the system. A disadvantage of a double junction reference electrode is a slightly reduced response time as the ions must diffuse through two porous junctions.

Figure 4.14 Industrial reference electrodes (double junction and solid electrolyte)



Almost all concentrators performing pH monitoring on either an on-line or off-line basis have a preventive maintenance schedule (Table 4.5). This schedule is most often on a weekly basis (38.4% of the responses).

On the other hand there is a large spread in calibration schedule from an "as needed basis" to once every year (Table 4.6). However, in nearly half the concentrators, there appears to be no regular probe calibration schedule or if there is one, it was not given.

Table 4.5 Preventive maintenance schedule

Maintenance Basis	Responses	%
Shift	2	15.4
Daily	3	23.1
Weekly	5	38.4
Monthly	2	15.4
Not given/applicable	1	7.7
Total	13	100.0

Table 4.6 Calibration schedule

Calibration Basis	Responses	%
As needed	2	15.4
Regular - 1 month	1	7.7
- 3 months	1	7.7
- 6 months	1	7.7
-12 months	1	7.7
Not given/applicable	7	53.8
Total	13	100.0



Where the pH probes are verified on a regular basis (Table 4.7, verification is daily for 23.1% of the respondents and weekly for another 38.4%. The verification procedure usually consists of process verification (using a portable pH-meter). This process verification is sometimes supplemented by measurement using pH buffers.

Table 4.7 Verification schedule

Verification Basis	Responses	%
Shift	2	15.4
Daily	3	23.1
Weekly	5	38.4
Monthly	1	7.7
Not given	2	15.4
Total	13	100.0

The observed life of industrial pH electrodes varies from 2-3 months up to 2 years (Table 4.8). Most concentrators reported a life between 6 and 12 months (53.8%). The low number of respondents does not allow to determine if the observed life of the electrodes is related to ores and/or processes.

Table 4.8 Observed electrode life

Electrode life	Responses	%
2-3 months	1	7.7
4-5 months	1	7.7
6-12 months	7	53.8
2 years	1	7.7
Not given	3	23.1
Total	13	100.0

The answers to the questions related to the overall pH monitoring and control system indicated that the most common weak points were equally breakage of the glass bulb and loss of sensitivity to pH change. One operation even indicated that, although all the equipment required for automatic pH control was present, manual control was still performed due to problems with the overall system!

#### 4.4.4 Summary

Industrial pH electrodes have a life of 6-12 months. Shorter lives indicate that the type of probe (mostly the reference electrode) is not suited for the specific application. Concentrators using SO<sub>2</sub> preferentially employ pH combination probes with a double junction reference electrode due to short a life with the single junction type.

The most common application for pH monitoring and control is for alkaline flotation circuits. The next most common application is for dual alkaline/acidic flotation circuits for complex sulphide ores.

About half of the concentrators responding use on-line pH monitoring and control while a quarter use off-line monitoring and manual control while another quarter do not use pH modification in their flotation process. The reported weakest points in the on-line pH monitoring and control system appear to be related to the probe itself (contamination, breakage and abrasion).

The most common electrode verification and preventive maintenance schedule is on a weekly basis. Daily and shift schedules seem to be required for certain applications and this might be ore/process specific.

Because of the similarity between on-line pH sensors and on-line pulp potential sensors, it is expected that operating difficulties experienced with the latter sensors will be

along the same lines determined for on-line pH sensors and that such difficulties should not be reason to give-up on the technology.

#### 4.5 Assessment of the state of the electrode pair

Procedures for the verification of the state of the electrodes exist but usually they do not indicate which electrode of the pair is at fault (52, 259, 291). The general tendency is to ascribe any measurement problem to the sensing electrode, notably electrode poisoning in the case of platinum electrodes (259). Some of these procedures were developed during the course of this project (201).

These procedures are discussed in two parts. First, the verification of the state of the reference electrode is addressed. Second, means of verification of the sensing electrode (material and shape) for industrial applications are presented.

##### 4.5.1 Verification of the reference electrode

The Standard Hydrogen Electrode (SHE) is inherently rugged due to the replenishment of the redox couple in the electrode compartment as ultra-pure hydrogen is bubbled in the electrolyte contacting the platinum contact wire. Unfortunately, the requirement of ultra-pure hydrogen and the danger associated with hydrogen gas makes the SHE somewhat impractical for industrial use unless one used a design similar to that proposed by Will (290) for a miniature, portable SHE.

As indicated previously when discussing electrode poisoning, the usual procedure for the verification of an electrode pair consists of the immersion of the pair in a buffer of known potential. This buffer may be a ferrous-/ferri-cyanide solution (ZoBell solution) (259), a ferrous-/ferric ammonium sulphate solution (52), or a saturated quinhydrone solution (52, 291). A discrepancy between the measured potential and the theoretical value for the buffer indicates a fault.

### Traditional verification

The traditional means of verification with a redox buffer assumes that the noble metal electrode is in a perfect state and that nothing else affects the electrochemical potential. Easily forgotten is the temperature dependency of the reference electrode and the redox buffer. The SHE, which is by definition temperature invariant, is often used as scale to present the temperature dependency of the redox buffer independently of the reference.

The temperature dependence of electrochemical systems can be circumvented with a constant temperature water bath at 25°C as for example, Natarajan and Iwasaki (259) in their study of electrode poisoning and Rand and Woods (36) in their study of the mixed potential of the ferrous-/ferric and oxygen system. Unfortunately, Canadian mineral processing plants are certainly not at a tempered environment like a laboratory and the temperature dependence of the buffer and the reference electrode must be considered for the verification.

Furthermore, the redox potential of the quinhydrone buffer is pH dependent and some equipment manufacturers are more explicit on these (291) than the ASTM standard (52). Within the pH region over which neither the ferrous nor the ferric ion precipitates, redox buffers based on the ferrous-/ferric couple are pH independent.

The combined temperature and pH dependency of the quinhydrone buffer is given by (291):

$$E_{\text{Qui.}} = E^{\circ}(t) - 0.1984 \times (273.16 + t) \times \text{pH} \quad [25]$$

where  $E^{\circ}(t)$  is obtained from Table 4.9 for the temperature range normally encountered in mineral processing processes (in step of 5°C). The standard potential can be interpolated with reasonable accuracy for a temperature within the range covered in Table 4.9.

Table 4.9 Temperature dependence of the standard potential of quinhydrone (291)

T (°C)	E°(t) (mV vs. SHE)
5	+714.3
10	+710.7
15	+707.0
20	+703.4
25	+699.7
30	+696.0

A complication when performing the verification of a given electrode is the proper identification of the type of reference electrode in the pair. This can be tricky for combination electrodes but once the identification is made, the value can be quickly converted at the temperature of the measurement (Table 2.1)

With a saturated quinhydrone buffer, prepared by dissolving analytical grade quinhydrone until an excess solid is present, in a pH buffer of pH 4 or pH 7, the potentials of platinum or gold electrodes in perfect condition at 20 °C are given as shown in Table 4.10. It should be noted that an excess quinhydrone must be present, particularly for the platinum electrode as otherwise, the electrode pair would sense mainly the oxygen reduction potential due to the dissolved oxygen present in the buffer solution. The quinhydrone buffers are should be used within 8 hours from making them (52).

Table 4.10 Theoretical values for quinhydrone buffers (53, 291)

t (°C)	pH	E mV vs. SHE	E mV vs. SCE	E mV vs. Ag/AgCl/4M KCl
20	4.0	471	232	268
	7.0	296	49	92
25	4.0	462	223	263
	7.0	285	46	86

The weak point in the traditional procedure is that it addresses only drifting of the reference electrode due to contamination of the internal electrolyte by foreign ions. It does not consider blockage of the porous junction by fine particles or precipitates due to the high concentration of ions present initially in the pH buffer, and the redox couple. As mentioned earlier, the silver/silver chloride reference commonly found in industrial pH and Redox sensors is prone to junction blockage because of the low solubility of most silver compounds. Furthermore, quinhydrone buffers allow only verification at pH 4 and pH 7.

#### Proposed verification procedure

An old reference electrode could be verified against a new one by measuring the difference in potential across the two electrodes when they are immersed in a solution. This difference should be zero (for reference electrodes of the same type). If the potential measured is significantly different from zero (say 5 mV or more), then the old reference is probably faulty.

The proposed verification is a variant of the simple test just described. It involves several test solutions ranging from buffers (concentrated solutions) to complex weak solutions. It is also applicable to the verification of a large number of reference electrodes with minimal experimental effort. A "new" reference electrode is not absolutely necessary but is nevertheless strongly recommended for completeness of the verification.

The experimental requirements are an Eh-pH meter, a noble metal sensing electrode (gold or platinum), and test solutions. The test solutions include pH buffers, dilute redox solutions (such as  $K_2Cr_2O_7$  or  $Na_2SO_3$  at a concentration of 10 g/l equivalent to 0.034 M and 0.079 M respectively), and a solution with several species, but at very low concentration. For convenience, this latter solution may be potable water. A prepared solution, however, may yield more consistent results over time.

The reference electrodes to be verified are cleaned and prepared in the usual manner suggested by the manufacturer; usually a wash in dilute HCl followed by rinsing and overnight soaking in distilled water. The test solutions are prepared and the sensing electrode mechanically polished using 600 grit emery paper. The reference electrodes and the sensing electrodes are immersed in each test solution and the measured potential against the sensing electrode is recorded for each reference. The test solution is stirred while the measurements are taken. The electrodes are thoroughly rinsed between each test solution.

Only references which are in a good state will give results which are within 5 to 10 mV of each other for all solutions. Agreement between references is much easier to achieve with buffer solutions than with dilute or complex solutions, hence the need to include the latter in the testing.

### Experimental

Five combination pH electrodes were used for the demonstration of the procedure (see Table 4.11). Three of them were industrial electrodes which had been removed from the circuit (copper cleaning section) due to difficulties in calibration. Electrode No. 4 was brand new while electrode No. 5 was a currently used electrode of the double junction type.

Table 4.11 Electrodes used for the development of verification procedure

Reference	Type	Material	Electrolyte
1	Industrial	Ag/AgCl	Gel
2	Industrial	Ag/AgCl	Gel
3	Industrial	Ag/AgCl	Gel
4	Laboratory	Ag/AgCl	Gel
5	Laboratory	Ag/AgCl:KCl Sat.	Solution

A gold electrode (foil, 1 cm<sup>2</sup> exposed area) was used to verify the state of the reference electrodes. The Eh/pH meter was a portable unit with digital read-out (Orion Research Model 230).

The test solutions consisted of pH buffers (from Fisher Scientific) and solutions of known composition (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, CaS/Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub>, and Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub> all at a concentration of 10 g/l). Potable water from the laboratory was used as the complex, weak test solution.

## Results and discussion

The results are shown in Table 4.12. It is noted that the two laboratory electrodes (Nos. 4 and 5) agree within 10 mV for all solutions.

Electrodes 1 and 3 show significant discrepancies with respect to electrodes 4 and 5 for the pH buffers and are certainly in an unacceptable state.

For the pH buffers, electrode 2 exhibits insignificant (< 10 mV) differences with respect to electrodes 4 and 5. However, this is not the case for the other test solutions (differences of the order of 50 to 60 mV). This combination pH electrode, could not be calibrated in the process even though calibration using pH buffers was always correct. This verification procedure determined that the fault was due to the reference electrode which probably has a partially blocked junction, a fault which is very difficult to determine by visual inspection.

The repeated measurements on potable water did not reproduce well for any of the five references; there is a hysteresis, or memory effect from the previous solution (see Table 4.12). When the solution preceding the measurement in potable water was oxidizing, (i.e. K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>), the measured value is higher than the one obtained previously. Similarly a lower value is obtained when the preceding solution was reducing



(CaS/Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub>). This is related to a poisoning of the gold electrode. This effect does not reduce the validity of the verification of the reference electrodes.

The results indicate that two of the industrial electrodes (Nos. 1 and 3) have probably contaminated electrolytes while one of them (No. 2) possibly has a partially blocked junction. Electrodes 1 and 3 are no longer useable for either pH or redox measurements. Electrode 2 could possibly be used for pH measurements. The high mobility of the hydrogen ion does not appear to be greatly impeded by a partially blocked junction but the reference element would not be useable for redox potential measurements.

Table 4.12 Verification of reference electrodes

Solution	Potential, mV (Au Foil)				
	Ref. 1	Ref. 2	Ref. 3	Ref. 4	Ref. 5
Buffer, pH 4.0	345	304	268	312	317
Buffer, pH 10.0	232	202	160	202	200
Buffer, pH 7.0	268	234	186	225	232
Potable water	285	273	192	214	211
K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	387	355	311	338	342
CaS, Na <sub>2</sub> S <sub>2</sub> O <sub>5</sub>	35	10	-35	-10	-8
Potable water	142	140	58	83	82
Na <sub>2</sub> S <sub>2</sub> O <sub>5</sub>	112	87	41	74	75
K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	325	299	255	289	293
Potable water	245	235	153	187	185

The observations made by applying this procedure confirmed that the three industrial combination pH electrodes which had been removed from the process were done so with just cause. It also provided some clues as to why they had to be removed, a first step in the selection of long life electrodes.

#### Ruggedness under stress

The best test of a procedure is to determine what may happen if short-cuts are taken. The most likely short-cuts here are using only a 437 mV vs. SCE ferrous-/ferric chloride redox buffer, pH buffers and potable water and not cleaning or preparing the electrodes prior to the verification.

Five Saturated Calomel Electrodes (SCE) were gathered from a flotation laboratory along with one gold spiral electrode routinely used for flotation tests. The first two references were from one manufacturer while the other three were from another. Buffers were taken from the shelf and used as-is. The measuring instrument was a Corning Eh/pHmeter Model 130 and a simple electrode switch box was used to select the electrode pair to measure; the "reference" electrode of the pair being kept the same for all measurements. In the first series of measurements, the "reference" was the gold spiral electrode while in the second series the "reference" was one of the SCEs. The sequencing of the solutions measured was potable water, pH 4, 7, and 10, and the sequence was repeated once. With a gold spiral electrode, a final measurement was made with the 437 mV redox buffer before and after cleaning the gold electrode. The gold electrode was cleaned using a potential square wave of 15 seconds period first at 2.5 V (vs. SCE) then at -1.0 with the electrodes immersed in 0.1 M HCl aqueous solution (265).

The results obtained with the gold spiral as the common reference are shown in Table 4.13 while those with electrode 4 as common reference are shown in Table 4.14. It is noted that the polarity of the potentials recorded in Table 4.13 is reverse of that

indicated by the meter due to the experimental set-up (gold spiral as common "reference" for all electrodes).

Table 4.13 Short-cut verification of reference electrodes with a sensing electrode

Solution	Potential, mV (Au Spiral)				
	Ref. 1	Ref. 2	Ref. 3 *	Ref. 4	Ref. 5
Potable water	465.5	455.0	600	460.0	456.6
Buffer, pH 4.00	485.6	461.6	700	474.0	472.0
Buffer, pH 7.00	447.3	432.6	400	440.8	439.6
Buffer, pH 10.00	275.7	261.0	250	266.5	265.8
Potable water	318.0	320.4	350	320.2	321.9
Buffer, pH 4.00	364.6	347.5	360	348.3	347.5
Buffer, pH 7.00	348.8	331.5	350	330.6	331.6
Buffer, pH 10.00	294.4	266.3	300	264.7	266.3
Fe(II)/Fe(III) As-is Au	435.2	423.6	500	450.9	451.2
Fe(II)/Fe(III) Cleaned Au	450.2	438.1	600	461.2	460.7

(\*: +/- 200 mV)

The results show that electrode 3 is in very poor shape with drastically different potentials and unstable readings. The electrodes 1 and 2 give potentials which are consistently different than electrodes 4 and 5 although electrode 2 is further away than electrode 1. With the gold spiral electrode taken as-is (Table 4.13), only one electrode pair (electrode 1) yields the 437 mV +/- 5 mV vs. SCE value of the redox buffer. After cleaning, still only one exhibits this potential but a different one though (electrode 2).

Table 4.14 Short-cut verification of reference electrodes without a sensing electrode

Solution	Potential, mV (against Ref. 4)				
	Ref. 1	Ref. 2	Ref. 3 *	Ref. 4	Ref. 5
Potable water	-3.1	20.4	50	N.A.	0.3
Buffer, pH 4	13.1	29.2	25	N.A.	-1.7
Buffer, pH 7	12.9	28.9	100	N.A.	-1.5
Buffer, pH 10	6.5	23.1	-100	N.A.	0.5
Potable water	2.9	16.4	-300	N.A.	1.0
Buffer, pH 4	10.7	28.1	-100	N.A.	-1.0
Buffer, pH 7	11.9	29.9	-100	N.A.	-0.8
Buffer, pH 10	5.5	25.5	0	N.A.	1.0

(\*: +/-50 mV)

The results shown in Table 4.14 (one SCE as common reference) are somewhat easier to interpret than those in Table 4.13 (gold spiral as common reference). For one thing, the apparent lack of reproducibility due to poisoning of the gold spiral is completely eliminated if one of the reference is taken as common comparison electrode. It is noted that electrode 5 gives virtually the same potential as that of electrode 4 ( $\approx 0$  mV difference). On the other hand, a near zero voltage difference between two reference electrodes do not imply that they are functioning properly as demonstrated with the 437 mV redox buffer (Table 4.13).

Electrodes 1 and 2 yield discrepancies which are reproducible for a given buffer, but are not constant across the solutions. Interestingly, in the pH 10 buffer or in potable water, electrode 1 gives only a small ( $< 5$  mV) voltage difference from electrode 4. This voltage difference rises to 13 mV at pH 4 and 7. Electrode 2 follows a similar trend in being closer at pH 10 and in potable water but further off at the other pH values; roughly 20 mV offset. The pH of the potable water sample was 8.6.

Electrodes 1 and 2 differ from electrodes 3, 4, and 5 in that they have replaceable porous junctions. Such junctions may become loose enough that they pop out from the electrode during handling. This is what happened with electrode 2 and unfortunately the lost junction could not be recovered; a brand new junction had to be used and a fresh electrolyte poured into the electrode! This chance event has the indirect consequence that electrode 2 can be considered like a brand new electrode.

There does not appear to be any consistency in the voltage discrepancies between electrodes 1 and 2 on one side and electrodes 4 and 5 on the other. With the gold spiral electrode, electrode 2 is very close to electrodes 4 and 5 for the pH buffers and potable water but not for the ferrous-/ferric redox buffer (Table 4.13) while a definite bias is observed for electrode against electrode measurements (Table 4.14).

This observation is at first surprising but is related to the state of the porous junction for all electrodes; equally dirty (actually black) for electrodes 4 and 5 and somewhat dirty for electrode 1. Electrode 2 had a brand new junction. The potentials reported in Table 4.14 are in fact the potential differences due to the porous junctions themselves. There is a close correspondence between the potential discrepancies observed with the redox buffer (as-is or cleaned gold electrode) and the potential differences between the reference electrodes.

One may entertain what would have been the interpretation of the results had electrode 3 been used as common reference, a likely situation if the measurements had been made without having performed a first series of measurements with the gold spiral. In this the case, changing the common reference to any of the other electrodes would have provided stable readings, except for that particular electrode. In a worst case scenario none of the reference electrodes could have been used as a stable common comparative point, then it might be time to replace all the electrodes!

These observations suggest that although the verification procedure is rugged enough to survive short-cuts, there are two elements which should be maintained: first to use a brand new, or near new electrode as part of the verification, and second to clean the gold electrode prior to performing the verification. Otherwise, the results obtained may lead to selecting the wrong electrodes as being in good condition!

#### 4.5.2 Sensing electrode

The aim of the proposed procedure is the determination of the best sensing electrode for the electrochemical modulation of the flotation of sulphide minerals. This requires a perfect contact between the mineral particles and the noble metal. In particle bed electrodes used for electrochemical conditioning of minerals prior to micro-flotation, this can be achieved by compacting the bed (21). In industrial flotation, however, the mineral particles cannot be physically compacted onto the noble metal electrode; mineral particle-electrode contacts will occur in a random manner and will not be continuous. Hence, the potential sensed by the noble metal electrode will be between the potential of the sulphide minerals (assuming the noble metal acts only as a contact) and the potential of the solution (noble metal acting as a redox sensing electrode).

The reported discrepancies and inconsistencies between a platinum electrode and mineral electrodes immersed in the same system (26, 36, 38, 39) makes it necessary to look for an electrode material which consistently exhibits the potential of the sulphide minerals in the flotation pulp. In theory, a mineral electrode of the same mineral being floated (or depressed) should be selected. However, it is not always possible to obtain a mineral electrode. For example, it is rare that natural sphalerite is conductive enough to obtain a reading (26); a fact limiting electrochemical investigations on sphalerite (15, 26, 201, 257).

Gold has been shown to be a better material for sensing the potential than platinum in certain mineral pulps (26, 36). Questions still to be resolved are the validity

of this statement for all ores, and the possible influence of sulphide gangue minerals such as pyrite on the measured potential. Also, does the agreement between the mineral electrode and the gold electrode hold for all types of pulps; from the final tailings to the final concentrate and to which extent is this agreement dependent on the shape of the gold electrode (26, 39)?

#### Proposed verification procedure

The proposed procedure consists in taking potential measurements in the flotation pulps of concentrator using a mineral electrode of the sulphide mineral being recovered and the noble metal electrodes contemplated as on-line sensing electrodes. The general degree of agreement between the mineral electrode and the noble metal electrode will be an indicator of the overall performance to be expected from a sensing electrode. Severe disagreement may force the use of a mineral electrode as the on-line sensing electrode.

The measurements should be taken in flotation cells (using a portable Eh-pH meter) rather than in grab samples taken from the cells. In this manner it is certain that the oxygen already present in the pulp has not been consumed prior to the measurement or that air has not been entrained into the pulp during mixing, possibilities that exist with grab samples.

#### Experimental

The reference electrode was a porous sleeve calomel electrode (Fisher). This reference electrode was initially verified using the procedure described in 4.5.1.1. The sensing electrodes were the following: gold foils 1 cm<sup>2</sup> (one face exposed), and 0.5 cm<sup>2</sup> (both faces exposed), gold spiral (5 cm long wire of 0.5 mm diameter, coiled and protected by a perforated plastic tubing), platinum wire (5 cm long, 1 mm diameter, from Fisher). The two mineral electrodes were a chalcopyrite and a sphalerite/graphite

composite electrode. The electrode assemblies were cast in epoxy resin to ensure electrical insulation of the contacts and for ease of handling.

Prior to each verification, all electrodes were mechanically polished on 600 grit emery paper to prepare a fresh, un-oxidised surface. The electrodes were immersed in the pulp of the first flotation cell surveyed for a few minutes till a stable reading was reached; stability of readings for the mineral electrodes takes more time than for noble metal electrodes. Measurements in the other flotation cells were taken after obtaining stable values for all electrodes. This was usually achieved within 1 minute of immersion.

Scanning the potential range experienced in the flotation circuit was performed by immersing the electrodes in flotation cells of the circuit. Portable Eh/pH meters (Orion Research model 230 and Canlab) were used for the measurements.

## Results and discussion

The results for three studies are shown in Figures 4.15 to 4.19; Figures 4.15, 4.17, 4.19 are for the copper circuit, while Figures 4.16 and 4.18 are for the zinc circuit.

For the copper circuit, the results indicate that in the cleaner section there is not an appreciable difference between the gold foil and the platinum wire (Figure 4.15), the smaller gold foil and the protected gold spiral (Figure 4.17), and the protected gold spiral and the platinum wire (Figure 4.19) with respect to the chalcopyrite electrode. The interpretation is that the concentration of chalcopyrite (number of chalcopyrite particles per unit volume of the pulp) is high enough so that the noble metal electrodes behave as a contact between the chalcopyrite particles in the pulp and the instrument.



Figure 4.15 Comparison of electrodes in the copper circuit (I)

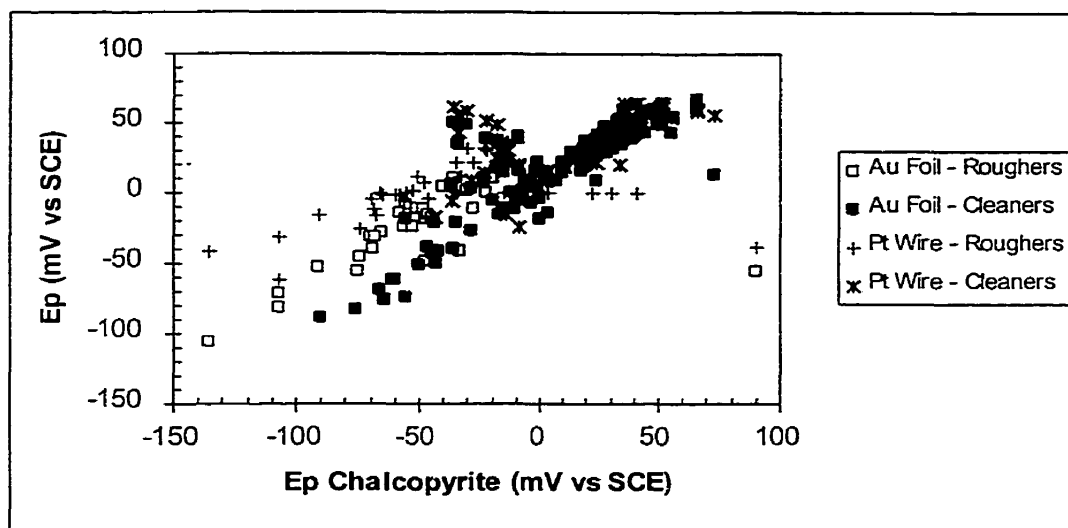
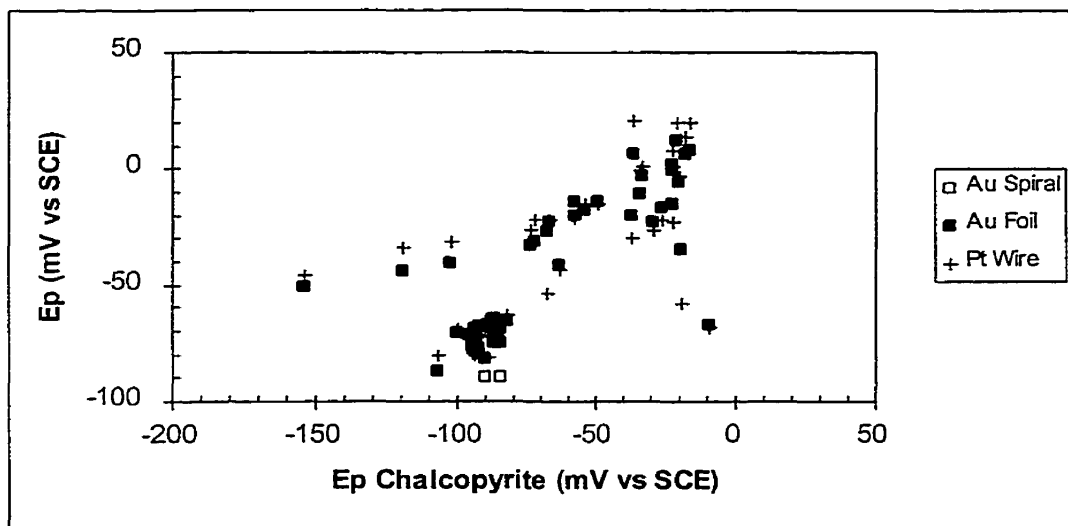


Figure 4.16 Comparison of electrodes in the zinc circuit (I)



This is not the case for the roughing section and the cleaner-scavenger bank of the copper circuit. There are noticeable discrepancies between the noble metal electrodes and the chalcopyrite electrode. In the first case, the gold foil is closer to the chalcopyrite electrode than the platinum wire (Figure 4.15). In the second case, the protected gold spiral is closer to the chalcopyrite electrode than the smaller gold foil or the platinum wire

(Figures 4.17 and 4.19). Different chemical conditions or ore types may be the cause of the change from more positive values for the noble metal electrodes compared with the chalcopyrite electrode in Figures 4.15 and 4.19 to the more negative values with the noble metal electrodes in Figure 4.17.

Figure 4.17 Comparison of electrodes in the copper circuit (II)

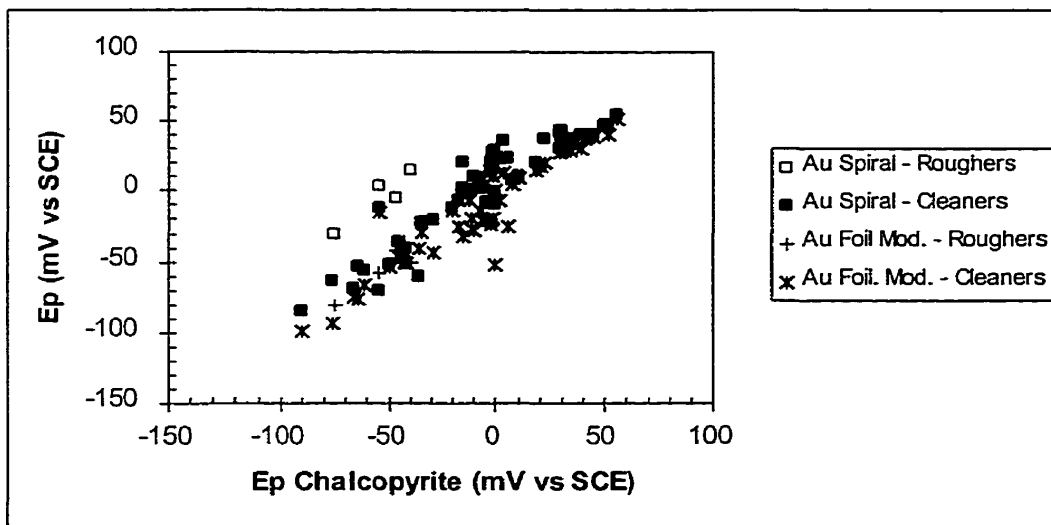


Figure 4.18 Comparison of electrodes in the zinc circuit (II)

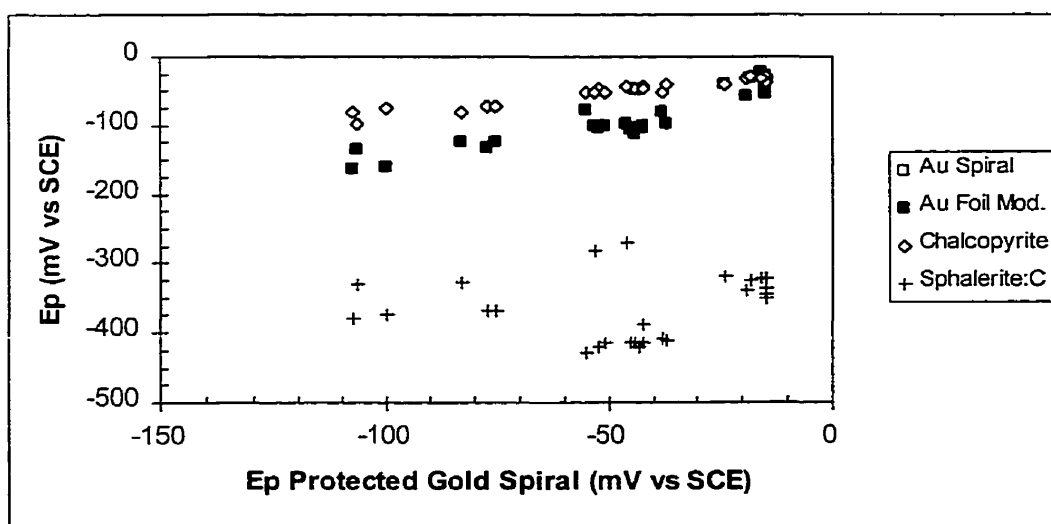
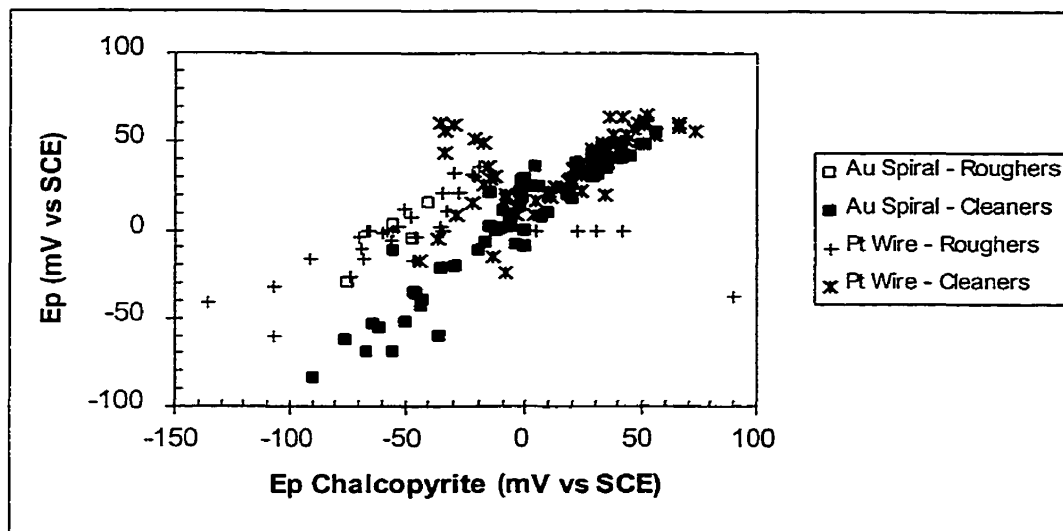


Figure 4.19 Comparison of electrodes in the copper circuit (III)



In the zinc circuit the sulphide minerals present are mostly sphalerite and pyrite. Hence, the noble metal electrodes exhibit potentials different from the chalcopyrite electrode in both the roughing and cleaning sections. Also, the points for the noble metal electrodes are more scattered for the zinc circuit (Figures 4.16 and 4.18) than for the copper circuit (Figures 4.15, 4.17, and 4.19).

It is premature to conclude that the noble metal electrodes respond in a manner similar to sphalerite particles in the zinc circuit. The information provided by the composite sphalerite/graphite electrode is not reliable although it complements that obtained from the other electrodes. Results obtained by other workers using sphalerite (15) and ZnS precipitates (257) indicate potentials for sphalerite of the same order as that of the other sulphide minerals. However, other investigators (172, 183) have found that composite sphalerite electrodes yield much lower rest potentials than generally encountered for sulphide minerals. In the latter case, the composite electrodes were used for cyclic voltammetry experiments and such a bias in potential was not deemed to affect the reaction occurring on the surface, especially after copper activation (172, 183).

In this investigation, the composite sphalerite/graphite electrode yielded potentials much more reducing (by about 350 mV) than those obtained with the chalcopyrite or the gold electrodes. This is an indication that the potential measured was more related to carbon than sphalerite (26).

It is intuitive to use an electrode which senses the potential of the sphalerite particles in the zinc circuit. In view of the difficulties in preparing a sphalerite electrode it might be advantageous to monitor the potential of the pyrite particles, the main sulphide gangue to be depressed in the zinc circuit for the A1 zone of Les Mines Selbaie. The use of a pyrrhotite electrode to control the  $\text{CuSO}_4$  dosage for zinc flotation has been reported for a complex sulphide ore where pyrrhotite is the major iron sulphide mineral (41).

Even in the case of the copper circuit, where an acceptable correlation between the chalcopyrite and the noble metal electrodes is achieved in the cleaners, there is quite a large experimental scatter. As some scatter is reported for pulps containing only one sulphide mineral (26, 36) it is to be expected here. An even larger discrepancy may occur with complex ores consisting of several sulphide minerals. If high enough potentials are achieved in an acidic pulp, there is always the possibility that a mineral electrode will passivate (15, 38). This could render more difficult the monitoring of pulp potential for certain types of separation processes.

#### 4.5.3 Summary of verification procedures

A relatively simple procedure has been proposed for the verification of the state of reference electrodes. It provides clues as to the possible cause of the deterioration of the state of the reference. Also, it indicates whether the electrode should be discarded, or could still be used in situations where the reliability of the measurement is not critical.

The suitability of a given sensing electrode to monitor the pulp potential in flotation circuits can also be verified. For copper flotation (or the copper circuit of a

complex sulphide concentrator) noble metal electrodes (regardless of material or shape) behave similarly to a chalcopyrite electrode in the cleaning section. However, a gold electrode (preferably shaped as a spiral) follows more closely the potential of the chalcopyrite electrode in the rougher section than an electrode of the other tested shapes or materials. The difference between cleaning and roughing appears to be related to the concentration of chalcopyrite particles in the pulp and the probability of collision with the electrode.

More investigations are required for the monitoring of the pulp potential in a zinc circuit. The high resistivity of sphalerite does not permit its use as a mineral electrode. Utilisation of a conductive material in a composite electrode appears to distort the measurements. Monitoring the potential of pyrite, the main mineral to be depressed in zinc flotation, may provide a viable alternative as suggested by the reported success with the OK-PCF method (41).

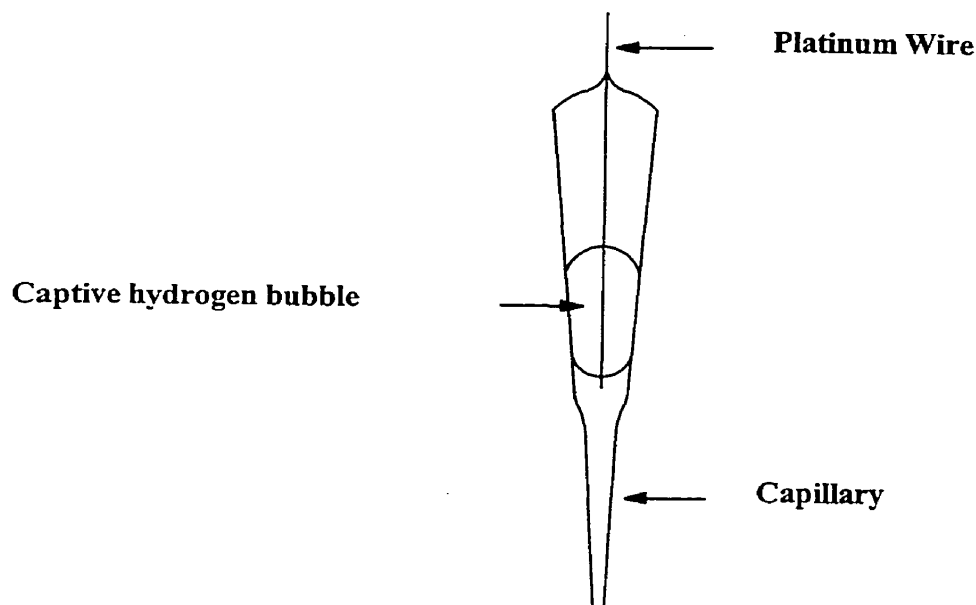
#### 4.6 Improvement to sensors - reference

An improvement to the redox sensor would be a more rugged reference electrode. Also, if such an electrode could be based on the hydrogen electrode, then much of the confusion as to which potential is referred to (SHE, SCE, Ag/AgCl) would be avoided.

Will (290) designed a self-contained miniature hydrogen reference electrode which is described as convenient to use as the more usual saturated calomel and silver/silver chloride electrode. This self-contained hydrogen electrode is based on a partially immersed platinized platinum electrode with its emerging part in contact with a hermetically sealed hydrogen bubble. The emerging part of the partially immersed electrode is covered with a meniscus and thin film of electrolyte. Such a thin electrolyte film allows dissolved hydrogen to diffuse faster to the electrode surface than the boundary layer electrolyte created by hydrogen bubbles dispersed in bulk electrolyte.

In practice the electrode (shown schematically in Figure 4.20) consists of a platinized platinum wire of 1 mm diameter sealed into a long glass capillary whose opening can function as a Luggin capillary (with proper bending of the tip) or as normal interface.

Figure 4.20 Schematic of shelf-contained miniature hydrogen reference electrode (290)



The electrode is prepared for operation by filling the glass capillary with electrolyte under vacuum, followed by electrolytic generation of hydrogen gas on the platinum wire. Any inert auxiliary electrode can be used as the oxygen-evolving anode which is then removed after use. The hydrogen formed on the platinum wire displaces electrolyte at the top end of the glass capillary. Electrolysis is continued until 1/4 to 3/4 of the platinum wire is surrounded by hydrogen gas. A current of 0.04 A produces a hydrogen bubble of 2 cm length in a glass tube of 0.4 cm inner diameter in approximately 1 minute.

The useful life of this electrode depends on the rate of hydrogen loss, unless gradual poisoning of the platinum black catalyst occurs earlier. If the platinum wire is sealed properly, the rate of hydrogen loss is determined by diffusion into the bulk electrolyte. For a lower capillary portion of 2 cm length and 0.1 cm diameter, hydrogen out-diffusion is reported to occur in approximately five years. The rate of catalyst poisoning depends on the purity of the electrolyte, more specifically, the concentration of organic impurities, carbon monoxide, and metal ions reducible at the hydrogen potential. The in-situ electrolytical generation of hydrogen reduces the risk of poisoning from gaseous contaminants.

Electrode to electrode reproducibility is better than 0.5 mV against one another. Long-term stability is also  $\pm 0.5$  mV against a conventional hydrogen electrode.

#### 4.7 Observations during long term monitoring

The investigation at two different concentrators, each one with its own particular ore and reagent practice, permitted to establish some general principles for the application of the electrochemical model of sulphide flotation to copper/zinc separation. Some problems, particularly with the sensing electrodes, were encountered.

The gold spiral electrodes used in the laboratory were deemed too fragile for extensive use in a plant environment. Hence, industrial gold potential sensing electrodes have been used. The choice of the electrode was mainly based on the shape of the sensing element which had to protrude into the pulp to ensure a good contact with the mineral particles of the pulp. Figure 4.21 shows an example of the industrial electrode used.

The initial electrodes used at Les Mines Selbaie and at Kidd Creek were protruding gold cylinders for their potential sensing elements. The reference electrode was in both cases a silver/silver chloride electrode.

Figure 4.21 Industrial electrode installed (Les Mines Selbaie)



#### 4.7.1 Location of on-line electrodes

The work by Gebhardt et al. (21) on chalcocite and pyrite and laboratory tests performed (Sections 1.4 and 1.5) showed that the potential at which the collector is introduced into the flotation pulp has a greater impact upon selectivity than that at which flotation is performed. This observation was used to select the most appropriate location of the pulp potential sensors.

At Les Mines Selbaie, the first collector addition point is at the feed box of the rougher flotation bank. Hence, the most logical and practical choice was to locate the on-line potential sensor in the first flotation cell of the rougher bank.



At the Kidd Creek Concentrator, the first collector addition point is in the feed box to the sulphur dioxide conditioner. Testing with hand-held electrodes showed that the short term variability of the pulp potential measurement in the sulphur dioxide conditioner was too large to be useable. The on-line sensor was located in the feed box to the primary rougher bank which proved the most easily accessible location.

#### 4.7.2 Electrode maintenance

For each plant the initial preventive maintenance program for the pulp potential sensing electrodes was modelled on the program which was used for the on-line pH electrodes in similar service. This was complemented with redox buffer verifications as recommended by the manufacturers. Over time, however, this proved un-satisfactory and improved procedures for the verification of electrodes were defined (201). In addition, the on-line electrode in the process was compared to freshly cleaned gold and mineral (chalcopyrite) electrodes on a routine basis.

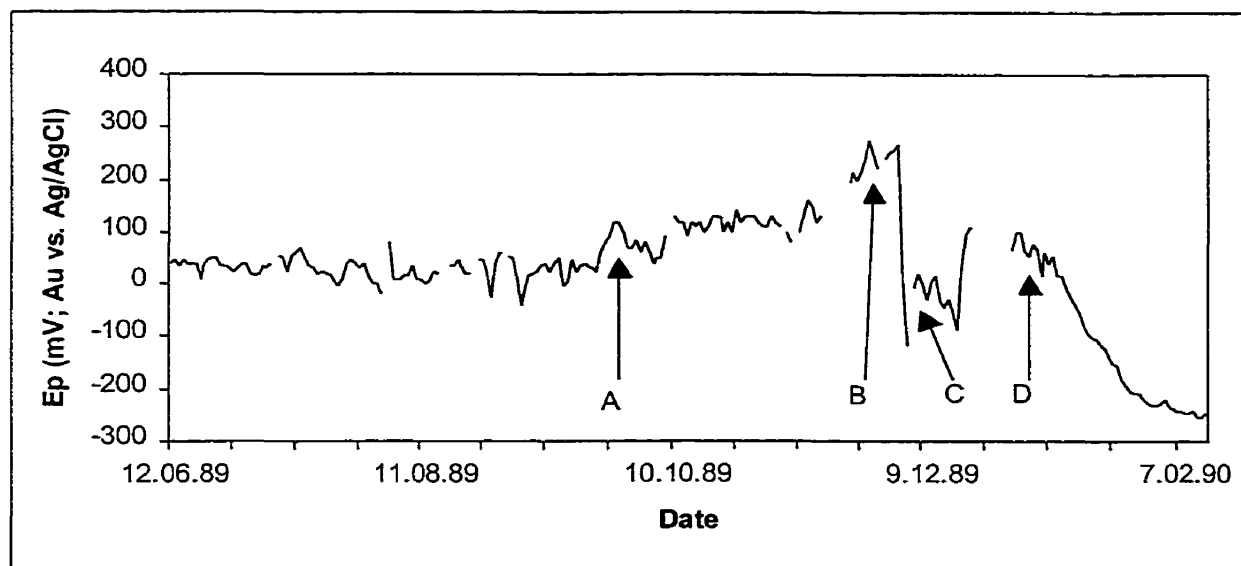
There was a notable observation. For one electrode, the "gold" sensing element was actually gold plating on platinum. Needless to say that as soon as the gold plating was worn away, "erroneous" measurements were observed.

#### 4.7.3 Observations at Les Mines Selbaie

Ore type variability is an obvious cause for observed variation in the optimum value of any process variable such as the pulp potential in this case. However, there were some doubts as to the reliability of the measurements.

In Figure 4.22, the daily average pulp potential is plotted for the period reviewed (June 12 1989 to February 14 1990). The behaviour of the daily average is not similar throughout the investigated period. There appears to be five distinct intervals and the divisions between these intervals are indicated by the letters A, B, C, and D.

Figure 4.22 Long-term Ep trend at Les Mines Selbaie



The daily average pulp potential appears to vary in a random fashion between June 12 and point A. The 2-3 days peaks and troughs could well represent short periods of different ore types.

Between points A and B, the average daily pulp potential steadily increases. This increase was initially thought to be related to the arrival of winter. However, tests (at B), when the sensor reading appeared to be consistently in a 200-250 mV vs. Ag/AgCl range compared to 100-150 mV in the two weeks before, showed that the electrode was not responding properly (contamination of the reference electrode). As no rigorous verification of the sensor was performed between points A and B, the exact time at which the contamination of the reference electrode started cannot be ascertained. Conservatively, the period of time between the initial installation of the pulp potential sensor (mid-May) until point A (early-October) is nearly five months and this compares well with the pH electrode immersed in the same location (four to six months).

Replacing the pulp potential electrode (point C) apparently corrected the problem. However, this was for a very short time (C to D; three weeks). Examination of the

electrode (D) showed that the seal between the porous junction and the body of the electrode was impaired and the reference electrode was again contaminated. Unfortunately, there was no spare electrode on hand and the electrode was re-installed as it was.

It is interesting to note that from D to the end of the acquisition program (February 14), the daily average pulp potential shows limited or no day to day variation. The contamination of the reference electrode was more severe than the previous one and had the on-line sensor been used in a process control scheme, the observed drift would have caused the control loop to fail. As discussed in Section 4.4, failure of the sensor is the main cause of poor process control.

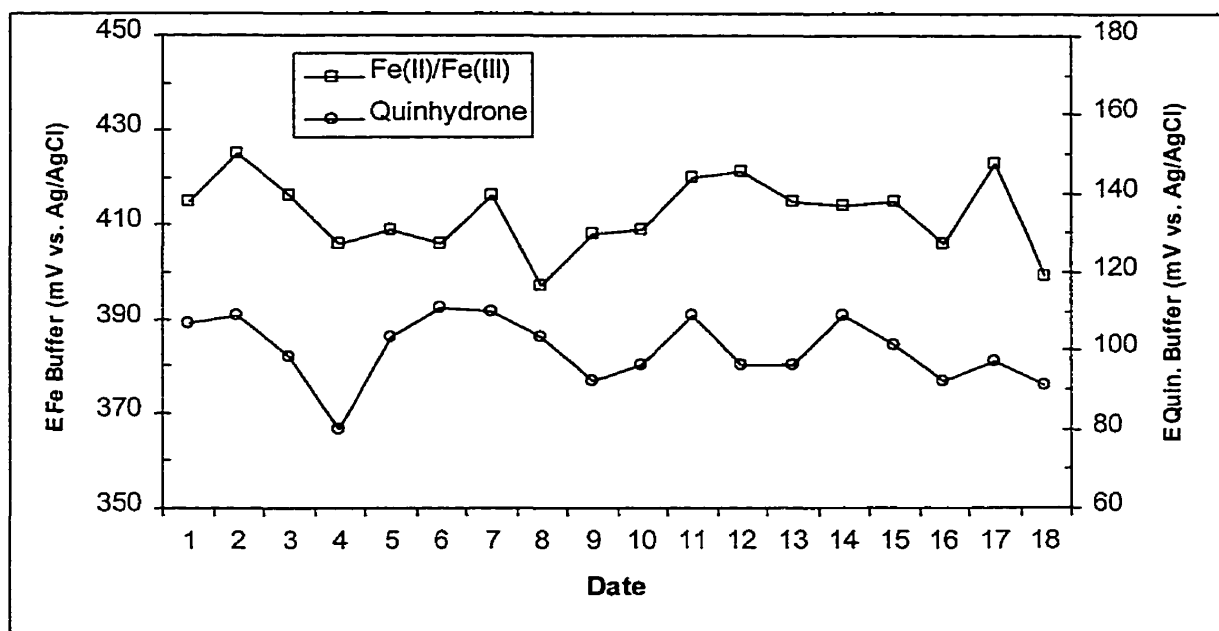
The two failures of the on-line pulp potential probe have a detrimental impact on the establishment of relationships between the copper-zinc selectivity and the pulp potential. This will be further discussed in Chapter 6.

#### 4.7.4 Observations at Kidd Creek

Difficulties with the sensing electrodes were already known. Hence, one of the first steps was to ensure that the state of the sensing electrode was correctly assessed at any point in time. This was, however, not easily achieved. It appeared sufficient to perform periodic verifications of the on-line industrial electrode using a clean, well preserved, electrode similar to the on-line one.

The "verification" electrode was verified on a daily basis using redox buffers. Figure 4.23 shows the potentials measured in the two redox buffers (Fe(III)/Fe(II) and quinhydrone). The electrode gives higher values than expected for the quinhydrone buffer (100 mV average vs 86 mV theoretical). However, the electrode gives lower values than expected for the ferric/ferrous buffer (412 mV vs 437 theoretical). For both buffers, the magnitude of the measurement error is 24 to 25 mV.

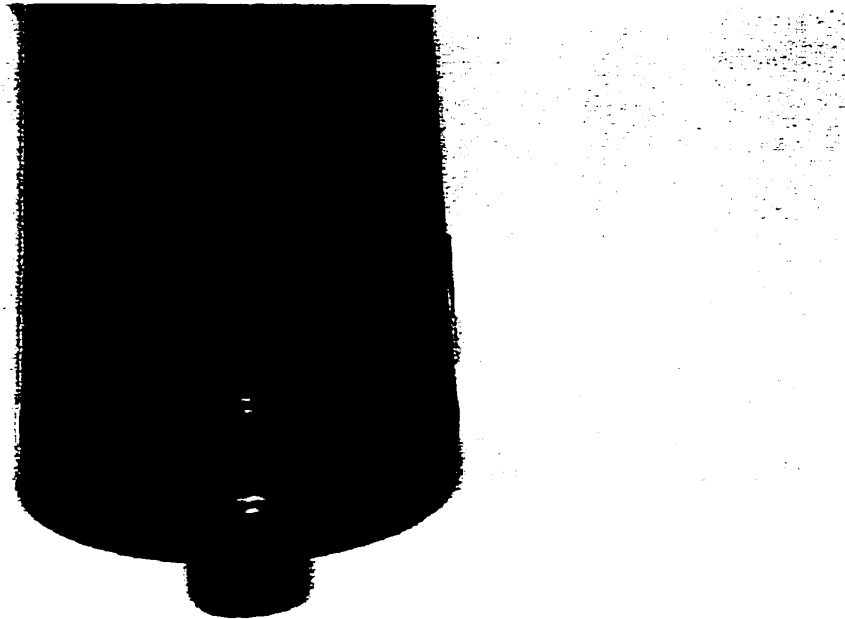
Figure 4.23 Buffer verification trend



This was considered a minor problem in comparison to the apparent trend in the daily measurements. The measurements were typically higher on Mondays and Tuesdays than on Thursdays and Fridays. It was found that the probe was allowed to "dry" over the weekend as it was not immersed in an aqueous solution. The probe could recover during the week as it was immersed in solutions or flotation pulps for most of the time.

Some problems were experienced with the first on-line pulp potential sensor installed. It is shown in Figure 4.24 as taken out of the process after three weeks of use. Firstly, the pressure on the acid wash/water rinse jets to prevent the deposition of scale on the sensor was too high. These jets pierced a hole through the glass tip of the electrode effectively destroying the sensor. Secondly, the gold ring was actually a gold plating on a platinum ring and abrasion from the solids in the slurry was high enough that the plating had been removed for the most part (some gold remains on the edges of the ring).

Figure 4.24 Post-mortem examination of first sensor installed at Kidd Creek



Following this post-mortem evaluation of the first sensor, the pressure on the cleaning jets was considerably reduced. Also, another manufacturer which could supply electrodes with solid gold, rather than a plating on another substrate, was found and awarded the task of providing replacement sensors.

#### 4.8 Proposed techniques for the preventive maintenance of on-line pulp potential sensor

Experience has indicated that the first element to fail in a combination pH or potential electrode is often the reference element due to contamination of the electrolyte or blockage of the porous junction. In the case of redox sensors, the sensing element is quite robust in comparison to the reference element. Having the possibility to replace the sensing component independently of the reference, while maintaining the convenience of

the single body of a combination electrode will certainly diminish maintenance costs associated with the installation of several redox sensors in a concentrator.

The electrochemical conditioning/cleaning schemes mentioned earlier have been developed on an *ad hoc* basis. It would help the cause if turn-key systems consisting of the sensor and electrochemical conditioning/cleaning circuitry were available commercially. Although the necessary conditions for the potential cycle would be site specific, there is no reason why a generic package could not be made.

#### 4.9 Overcoming unexpected problems for control loops based on the pulp potential

Although on-line pH electrodes have been used for the past thirty years in mineral processing plants, failure of the sensor is still the main cause of break-down of the process control loops based on pH.

Experience gained at Les Mines Selbaie and at Kidd Creek indicates that a similar situation will exist for control loops based on pulp potential measurements, no matter how well prepared the technical and instrumentation personnel are. As the electrode potential is measured directly, the response of the instrument cannot be calibrated as for a pH meter/controller. The implication is that preventive maintenance of on-line pulp potential sensors will be more crucial than for pH.

With only one pulp potential sensor installed, the only way to cope with a drifting sensor if it cannot be immediately replaced is to arithmetically shift the measured value by the observed drift between the on-line sensor and the off-line verification sensor. This assumes that the drift observed during the verification is of the same order of magnitude as the one occurring in the process; a valid assumption if the final stage of the verification involves immersing the verification sensor in the process pulp in addition to immersing the on-line sensor in buffers.

Such an approach may allow the on-line sensor to remain in operation for a longer period of time once drifting has become unacceptable. It may also keep the control scheme in operation while a spare sensor is ordered if one is not on hand. In this fashion, the measured pulp potential values seen by the operators will be the sum of the actual value and the drift correction (which could be called on-line standardization) and this may maintain confidence in the measurements.

The presence of a drift will be determined only as a result of a verification of the sensor. Such verifications are usually performed at regular intervals as part of a preventive maintenance program. From the survey on pH electrodes in industry, the pH electrodes are most often verified using buffer solutions on a weekly basis (Table 4.7) and unless there is a suspicion that a fault is present, a given sensor may be drifting unwittingly between two scheduled verifications.

#### 4.9.1 Redundancy in the pulp potential measurements

Increasing the reliability of the system by redundant measuring points is a way to cope with the situation. Having two sensors for the same process point is one way to implement a redundant measuring system but this approach relies on an accurate and timely identification of which one of the two sensors is at fault.

It is not uncommon that pH measurement and control in a mineral processing plant is made at the rougher stage and at each and every cleaner stage. When the entire pH control system is working perfectly, there is a pH progression from the rougher to the final cleaner stage. When one pH sensor and/or control loop is mal-functioning, it stands out dramatically from the progression and draws immediate attention to it.

Potential-pH surveys of flotation circuits generally show a progression from one process point to the next. Figures 4.25 and 4.26 summarize several potential-pH surveys of the copper and zinc circuits at Les Mines Selbaie.

Figure 4.25 Summary of potential-pH surveys for the A-1 zone copper circuit

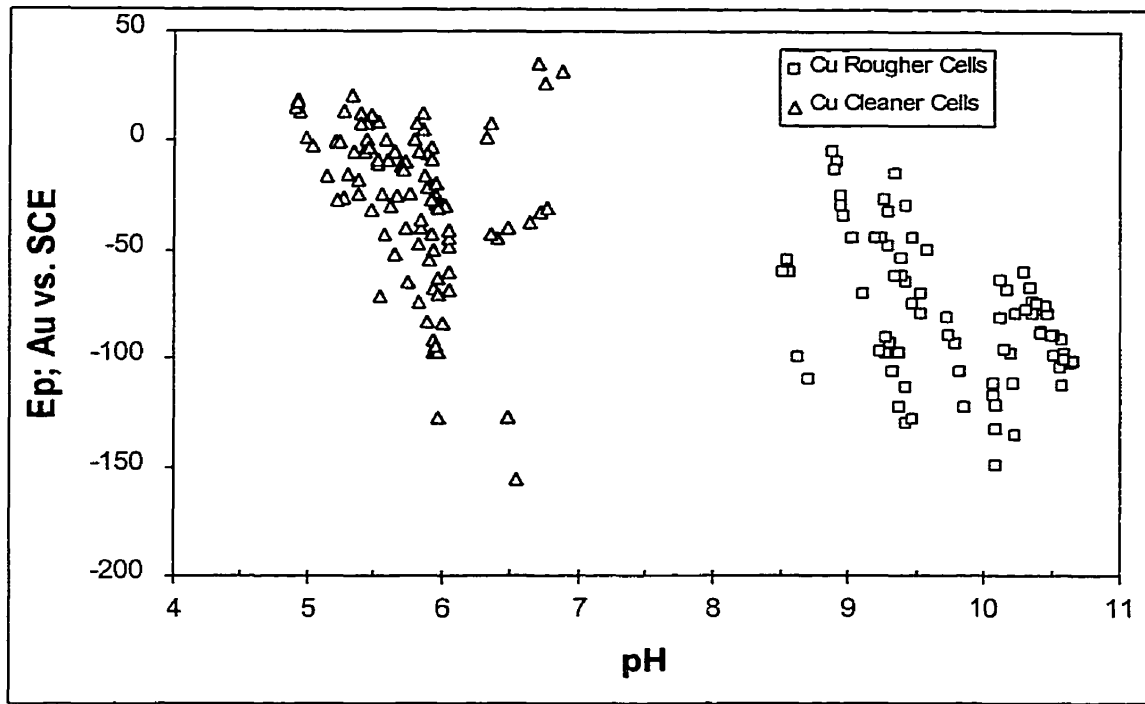
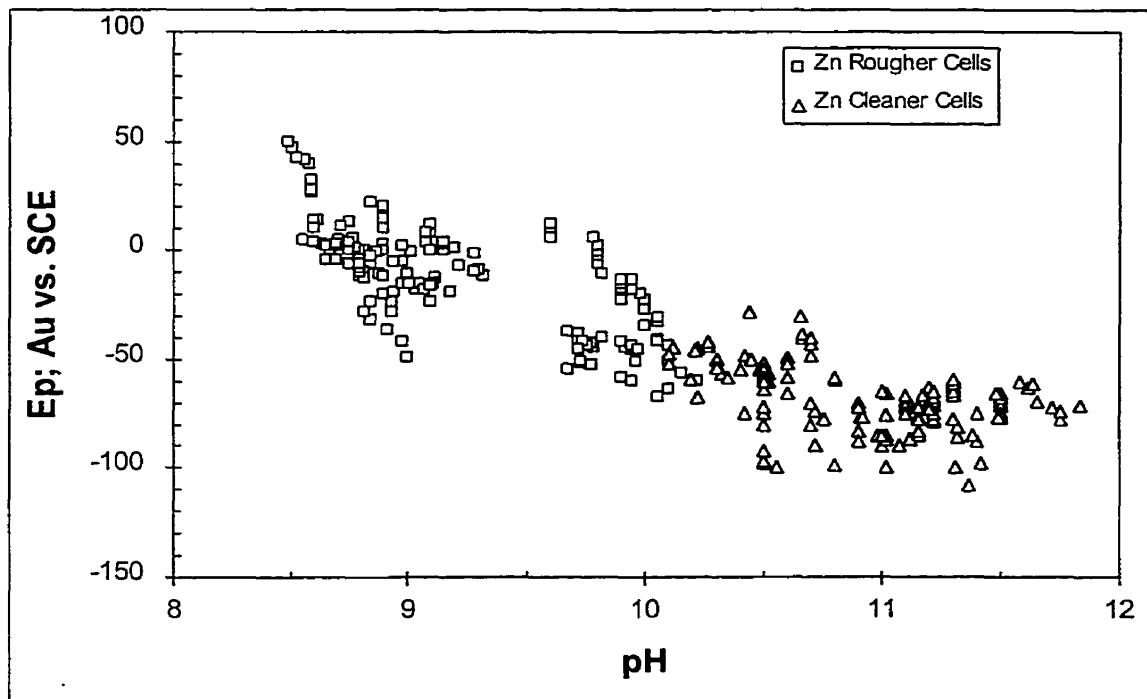


Figure 4.26 Summary of potential-pH surveys for the A-1 zone zinc circuit





For both the copper and zinc circuits, the  $E_p$ -pH data points are clustered depending on their origin; rougher or cleaner cells. For the copper circuit (Figure 4.25), the addition of sulphur dioxide to depress sphalerite in the copper cleaning stages results in a much lower pulp pH than for the copper rougher stages. For the zinc circuit (Figure 4.26), the addition of lime to depress pyrite in the cleaning stages results in a higher pulp pH than for the rougher stages.

The data points appear to follow bands of decreasing potential with increasing pH, partly due to a pH dependence of the electrochemical reactions involved, but also due to the simple fact that the flotation air introduced causes oxidation of the sulphides and yield an increasing pulp potential and decreasing pH down a flotation bank.

The lowest potentials are obtained in the first flotation cell (e.g. first rougher cell) and the highest potentials are obtained in the last cell (e.g. last scavenger cell). Due to the adjustments to the pulp pH in the cleaning stages (e.g. pH 10.5 for the zinc first cleaner, 11.0 for the second cleaner, and 11.5 for the third cleaner), the pulp potentials in the flotation cells of the last cleaning stage are not necessarily higher than those in the first cleaning stage.

The presence of regular patterns in the data shown in Figures 4.25 and 4.26 suggests that it is conceivable to use multiple pulp potential sensors in the flotation circuit to use obtain an indirect redundancy in the pulp potential measurements similarly to current practices for pH measurement and control. A faulty sensor would stand out from the progression indicated by the other sensors. A minimal implementation of redundancy would be two sensors although four would allow a sturdier system.

Another way to achieve redundancy is to have two sensors; one before the addition of the reagent manipulated by pulp potential and one after. By it-self, the second sensor provides a limited degree of redundancy. However, the degree of redundancy drastically increases if the reagent and ore flowrates are considered. As an example, if

every 10% speed increase on the metering pump for the reagent yields a 15 mV potential drop between the before and after electrodes for an average throughput, then anything outside this norm, e.g. 50% speed for a 5 mV potential drop, will automatically attract attention. Such exceptional situations may be due to ore type changes and/or sensor drift in either location.

One weakness of all the methods suggested above is that the flotation operator and/or control room operator must observe the pulp potential measurements and act upon suspicious values. This may not always be possible and including some "intelligence" into the process control system may prevent overlooking suspicious measurements.

Redundancy in measurements allow the application of methods resulting from advances in process control theory such as the parity space technique (292) to detect and locate gross errors in instruments and Kalman filtering (293) which determines maximum likelihood estimates of measured and unmeasured process states by combining information from a mathematical model of the process with actual measurements.

The level of mathematics involved in these approaches makes them unlikely to be easily implemented, and maintained, in a concentrator except as a turn-key system. Interestingly, a model predictive control system (using the combination of model based predictions with actual measurements) has recently been implemented with success at the Brunswick Mining concentrator (294). The hope expressed by the authors is that with a friendlier user interface, the system will have a higher probability of remaining in use than the previous two advanced control systems that had been almost completely abandoned even though its underlying principles are more complex than minimum variance based controllers or knowledge based expert system.

#### 4.9.2 Redundancy with other process measurements

The pulp potential of the mineral slurry is one of several process variables for modulating the flotation response. An experienced flotation operator has often a sixth sense in terms of what is right, or wrong, with a snap shot picture of the process obtained through instrumentation and visual inspection of the mineralized froth.

Neural nets, which mimic the learning process of the brain, are one way to try to account for the complexity of a system without having to generate a full mathematical model. Recent developments in the technology and its application to mineral processing operations (295, 296) are encouraging. In particular, the possibility for on-line determination of the ore type being processed (297) could yield an adaptation of the pulp potential set-point if laboratory and plant investigations have demonstrated that such adaptation is required for the different ore types.

Knowledge-based interpretation of sensor patterns (298) is another way to introduce a degree of intelligence into the control system. This intelligence may allow the control system to weigh a situation, as indicated by several process variables, and recommend appropriate actions. These actions could vary from the verification of sensors which appear to give anomalous measurements to set-point changes.

Finally, machine vision for qualitative and quantitative evaluation of the mineralized froth (299, 300, 301, 302, 303) may prove to be the ultimate in instrumentation and control redundancy. The technology is still in its infancy but given time and further development will greatly assist the operation of flotation circuits.

### 4.9.3 Differential pulp potential set-point

Using a differential pulp potential set-point rather than an absolute one may prevent the control loop from failing due to a large drift of a single pulp potential sensor.

It would involve a smart control system to manipulate the set-point independently for a process optimization. An inherent advantage of this approach would be the capability to adjust to different ore types being processed. If the ideal pulp potential for selectivity for ore type A is say  $-75$  mV and the one for ore type B is  $-25$  mV, then by trying out moving the pulp potential by increments up to  $\pm 50$  mV from the initial value, it may be possible to self-adjust the control loop during variation of ore types.

Compensation of a state with an erroneous sensor may mean a smart (expert-system like) control scheme which adjusts the potential set-point from its current measured value.

## 5 LABORATORY DETERMINATION OF THE IMPACT OF $E_p$

### 5.1 Introduction

Over one hundred flotation tests have been performed during the course of this study. Plant pulps, usually the cyclone overflow which feed the copper circuit, were used as test material in many of these tests. This was a bonus for the tests related to the investigation of selective collectorless flotation from the A-1 zone ore as using the plant feed eliminated any doubts as to whether collectorless flotation was an artefact from the laboratory procedure or was indeed a possibility arising from the grinding environment in the plant. Laboratory flotation tests performed with a crushed ore sample being ground in the laboratory prior to flotation were performed last; mostly to better understand the action of the collectors and modifiers with a constant feed but also to determine how the type of grinding media was affecting the collectors and modifiers.

It was initially intended to use the test results to screen for conditions to be further investigated by fundamental studies involving potentiostatic conditioning and surface analysis of the flotation products using XPS. Arrangements had been made with the mineral processing group at the BP Research Centre, Sunbury-on-Thames, U.K. to use the laboratory facilities, including the XPS instrument available there, for this phase of the project. When BP announced the deal made with RTZ for the sale of all wholly owned mines and milling assets world wide, these arrangements were unfortunately cancelled. BP Selco, the majority owner of Les Mines Selbaie at that time, was not included in this deal and the commitments made to the project were continued. The downside of all this was that instead of actual surface analysis, the results of other investigators will be used in the task of interpreting from a fundamental viewpoint what happened during the tests.

Only the flotation tests pertinent to the hypothesis pursued, namely that there is a relationship between the pulp potential and the observed flotation response, will be discussed.

## 5.2 Rest potentials of grinding media and minerals

The rest potentials of the grinding media used in the laboratory and in the plant, along with the sulphide minerals have been determined to provide a point of reference for the conditions evaluated in the flotation tests. In the case of the media, electrodes were made out of pieces cut from either the balls or the rods. Due to the high hardness of the material, this proved challenging. The mineral electrodes were those normally used to sense the pulp potential in plant surveys and laboratory tests.

The system used was an aqueous solution of 250 ppm calcium sulphate with the pH adjusted to 9.5 using lime. This was to provide an approximation of the process water used in the plant. For the minerals, additional measurements were taken with 50 ppm of SIPX and 50 ppm of Aerophine 3418A. The collectors were always added to a fresh solution. The measurements are shown in Table 5.1 for the grinding media and Table 5.2 for the minerals.

For the grinding media (Table 5.1), two electrodes of each type were used and all electrodes were mechanically polished on 600 grit emery paper prior to the measurements. It is noted that the measured potentials with the two electrodes for each grinding medium are usually within 5 mV of each other. Also, the conversion to SHE has been performed so that the results could be directly comparable with those published in the literature. In a study on the impact of grinding media on galena flotation, Learmont and Iwasaki (16) have obtained rest potentials for mild steel of -17 mV (SHE) with oxygen flushing of the solution, -41 mV with air flushing, and -481 mV with nitrogen flushing.

The results presented in Table 5.1 indicate generally lower potentials, likely because the measurements were taken under natural diffusion of oxygen from the air into the solution. The measurements made rank between the air flushing and the nitrogen flushing conditions of Learmont and Iwasaki (16).

Table 5.1 Rest potentials of grinding media in pH 9.5 calcium sulphate water

Media	E vs. SCE (mV)	E vs. SHE (mV)
Rod, mild steel	-560	-315
Rod, mild steel	-540	-295
Rod, stainless steel	-335	-90
Rod, stainless steel	-340	-95
Ball, mild steel	-500	-255
Ball, mild steel	-495	-250
Ball, high chromium	-430	-185
Ball, high chromium	-435	-190

The most noble of the grinding media is the stainless steel of the laboratory rods (-90 mV SHE), then the high chromium steel (-190 mV), followed by the mild steel ball (-250 mV) and finally by the mild steel laboratory rod (-310 mV). For laboratory grinding, the mild steel rods will give a slightly more reducing environment than that of the mild steel media in the plant. However, the stainless steel rods will yield a more oxidizing environment than that of the high chromium steel media. Thus, in order to simulate the plant grinding environment in the laboratory, it would appear that a mixed rod charge would be required.

The rest potentials of gold and sulphide minerals (Table 5.2) indicate that SIPX does not change dramatically the potentials (slight decrease), with the exception of the gold electrode but that of Aerophine 3418A increases all the potentials by around 30 mV

for the copper bearing minerals, 20 mV for galena, and 10 mV for pyrite. The potentials observed with Aerophine 3418A appear, at first, to be odd. However, the gold electrode was electrochemically cleaned prior to the measurements while the mineral electrodes were mechanically polished on 600 grit emery paper and the electrodes were allowed to recover to the same state (approximately the same potential) as measured in the calcium sulphate solution prior to adding the collector.

Table 5.2 Rest potentials of minerals in pH 9.5 calcium sulphate solutions

Minerals	E vs. SCE (mV)		
	CaSO <sub>4</sub> Only	SIPX (50 ppm)	Aerophine 3418A (50 ppm)
Gold	26	-40	35
Pyrite	0	-4	10
Chalcocite (B zone)	130	125	150
Chalcopyrite (A-1 zone)	-61	-70	-30
Chalcopyrite (Kidd Creek)	-99	-100	-65
Galena (A-1 zone)	-90	-100	-70
Galena (Ward's)	-76	-80	-60

It is noted that the chalcocite electrode from B zone ore contained a large proportion of pyrite and thus the potentials measured have to be taken as galvanic potentials rather than true rest potentials. This would indicate that Aerophine 3418A is more reactive (adsorption?) than SIPX under the conditions investigated and that it "oxidizes" the minerals. Without more studies, e.g. cyclic voltammetry, it cannot be assessed if the increase in mineral rest potentials resulting from the addition of Aerophine



3418A are due to an actual oxidation of the surface by the collector (unlikely) or chelation with the metal atoms which would prevent the formation of hydroxides impeding the rate of oxygen reduction.

The ranking of the sulphide minerals, with the exception of the chalcocite electrode, generally follows the usual order from less to more noble minerals: galena, chalcopyrite, pyrite, gold. It is noted that the chalcopyrite from Kidd Creek gives lower potentials than that from the A-1 zone. Similarly for the galena from Ward's compared to that from the A-1 zone. Differences due to the origin of the minerals were expected but not of that magnitude.

### 5.3 Experimental conditions

All flotation tests were performed with a Denver D12 flotation machine fitted with the D1 impellor and either the 500 g (rougher) or 250 g (cleaner) flotation cell. Nominal impellor speed was 1500 rpm for the rougher stage and 1200 rpm for the cleaner stage. The flotation air flowrate was not measured but the air valve was usually fully open during flotation corresponding to roughly 3 l/min for the rougher stage and 2 l/min for the cleaner stage; the froth rarely exhibiting a tendency for flooding over the froth lip which would have required the air flow to be brought under control. An interesting challenge was the proper setting of the nitrogen pressure controller to obtain the same overall froth characteristics as with air as flotation gas. Once this setting had been determined, it was locked in place.

When grinding was performed, it was with 10 l polypropylene rod mill, with three lifters inside the shell (Pascall Engineering) rotated on a roller drive (60 rpm or 80% critical speed). The grinding charge (25 kg) was graded in size with 25, 12.5, and 6.5 mm rods. Rods in stainless steel (type 440) and mild steel were available in sufficient quantity to provide a full stainless steel charge, a full mild steel charge, or any weighted proportion in between.

All reagent solutions were prepared daily. All reagent dosages were recorded with the exception of the pH modifiers.

The two collectors investigated, Aerophine 3418A added neat and Sodium Isopropyl Xanthate (SIPX) added as a 1 wt% solution, were taken from the mill supply. No attempt was made to purify the collectors. The frothers, MIBC for copper flotation and Dowfroth 1012 for zinc flotation, were added neat using a syringe with a #18 needle. Each drop corresponded to 5 g/t frother for a 1000 g feed.

Quick lime (CaO) was used for pH adjustment when needed. When sulphur dioxide was used in a test, it was added as a saturated aqueous solution obtained by overnight bubbling of sulphur dioxide gas into distilled water. The inorganic reagents (sodium cyanide, zinc sulphate, copper sulphate, potassium permanganate, ferrous sulphate) were prepared as 10 wt% aqueous solutions.

The pulp potential was monitored using a gold spiral electrode paired with a porous sleeve SCE (Fisher) while pH was monitored using an Orion combination pH electrode and the recording instruments were portable Eh/pH meters (Orion Model 230). The state of the electrodes was verified prior to each series of tests. The dissolved oxygen (DO) content of the slurry was measured sporadically with a YSI DO probe and meter.

#### 5.4 Experimental results

The results of selected tests will be discussed using selectivity curves and floatability-potential curves for paired set of conditions, e.g. air vs. nitrogen as flotation gas, SIPX vs. Aerophine 3418A as collector, etc. Determination of the flotation rate parameters would have allowed an evaluation of whether the observed impact was due to an acceleration (or retardation) of flotation or change in overall hydrophobic character (ultimate recovery). Also, this would have provided some means of distinguishing between mechanical entrainment and genuine flotation when low recoveries were

observed. However, as the first concentrate increment in the flotation tests was taken after one minute of flotation, there would be no way to be certain that the kinetic parameters were affected or not. Such determination requires the collection of concentrate increments very early in the test, for example Dowling et al. (304) and Agar et al. (305).

#### 5.4.1 Combination of collectorless and conventional flotation

##### Impact of nitrogenation time and pH

Combining the possibility of selective collectorless flotation with the need to increase copper and silver recoveries required adding a collector. The tests results discussed in Sections 1.4 and 1.6 indicated that pulp pH had some impact on copper and silver recoveries under collectorless flotation and that aeration would be detrimental to selectivity when the collector would be introduced. Using nitrogen as flotation gas would limit the inherent oxidation that would occur when using air as flotation gas during the collectorless stage. Furthermore, performing a conditioning stage while introducing nitrogen into the pulp (nitrogenation) would allow a manipulation of the pulp potential prior to flotation.

A series of flotation tests was performed to investigate the possibilities offered. Figures 5.1 and 5.2 show the selectivities obtained with 5 or 10 minutes of nitrogenation prior to flotation at pH 8 or 10. The first three concentrate increments were collected after 1, 2, and 3 minutes of flotation respectively (total time of 6 minutes) using nitrogen as flotation gas with the first concentrate increment being without collector and the second and third with 10 g/t of Aerophine 3418A each. Two additional concentrate increments (3 minutes each) were collected with air as flotation gas.

The nitrogenation stage was effective in reducing the pulp potential but the observed impact was inconsistent with a drop of 25 mV for 10 minutes of nitrogenation and 55 mV for 5 minutes from a starting potential typically around -55 mV (Au vs.

SCE). The only consistency was a slight increase in pulp pH from 7.8 at the beginning of the nitrogenation stage to 8.0 at the end for all four tests. The lime addition required to obtain pH 10.0 caused the pulp potential to be reduced to around  $-150$  mV (Au vs. SCE) irrespective of the duration of the nitrogenation stage. Hence, the pulp potentials prior to flotation were  $-150$  mV (Au vs. SCE) for the two tests at pH 10.0,  $-80$  mV and  $-130$  mV for the long and short nitrogenation stages at pH 8.0.

Figure 5.1 Impact of nitrogenation time and pH on Cp/Sp selectivity (Aerophine 3418A)

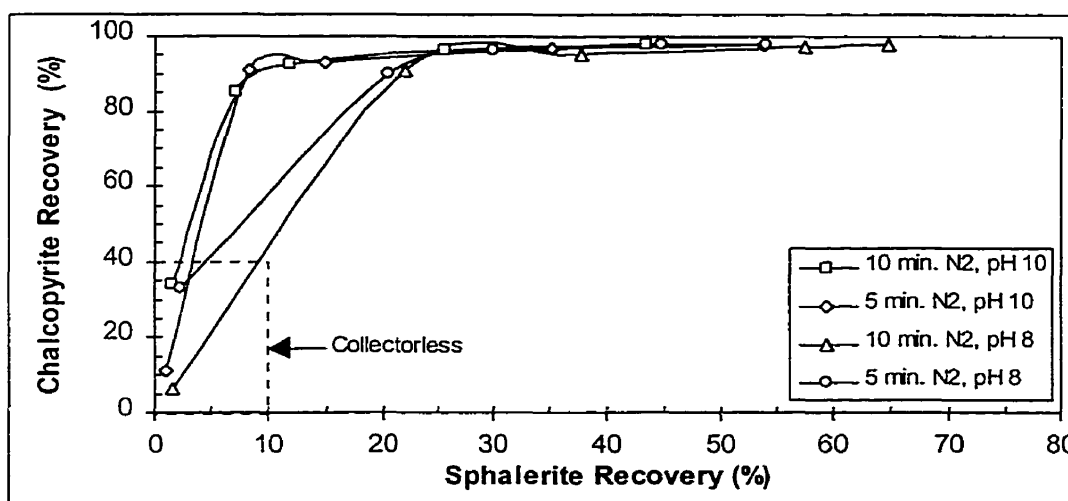
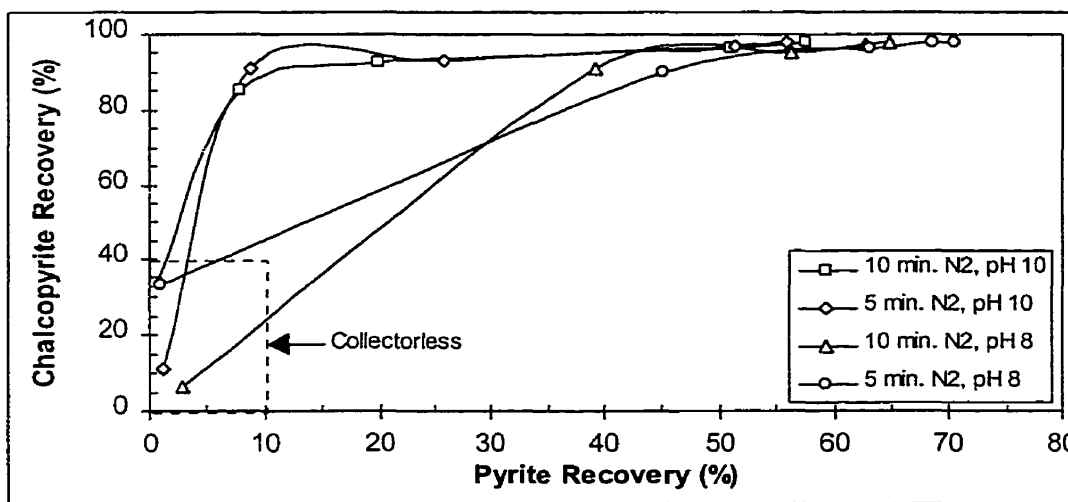


Figure 5.2 Impact of nitrogenation time and pH on Cp/Py selectivity (Aerophine 3418A)



It is noted in Figures 5.1 and 5.2 that the collectorless flotation increment, which was for 1 minute flotation, yields two vastly different levels of chalcopyrite recovery (around 35% and around 7%) for very similar sphalerite and pyrite recoveries. Both levels were expected from the initial collectorless flotation tests discussed earlier (Figure 1.6) with chalcopyrite recovery increasing as the pH increases (and pulp potential decreases). The nitrogenation stage, however, appears to affect this relationship and a higher flotation pH does not always yield a higher collectorless recovery of chalcopyrite.

The selectivities between chalcopyrite and sphalerite and pyrite are, with the addition of Aerophine 3418A, more dependent on pH (better selectivity at higher pH) than on the duration of the conditioning stage with nitrogen. Furthermore, the last two concentrate increments (air as flotation gas) contribute very little to the total chalcopyrite recovery but significantly to sphalerite and pyrite recovery. It is worth noting that the ultimate silver recovery at pH 10.0 was around 85% compared to only 55% at pH 8.0.

With a chalcopyrite recovery around 90% after the second concentrate increment, it would appear that the 10 g/t Aerophine 3418A addition for that increment was higher than necessary and consequently the total dosage of 20 g/t was likely to be excessive.

Impact of sodium cyanide and reduced collector dosage.

On the presumption that in-situ activation of the sphalerite was occurring, an addition of 10 g/t of sodium cyanide was performed prior to the two collectorless flotation stages and another 10 g/t prior to the addition of the collector (5 g/t). These sodium cyanide additions were supplementing the amount already present in the feed pulp collected from the cyclone overflow (around 15 g/t). The lower collector dosage was expected to reduce recovery of sphalerite and pyrite. The impact of the addition of the sodium cyanide was a lowering of the pulp potential prior to collectorless flotation from -25 mV to -100 mV. The selectivity curves can be found in Figures 5.3 and 5.4.

It is noted in Figure 5.3 that the addition of sodium cyanide does not prevent an increase in sphalerite recovery when air is used as flotation gas rather than nitrogen (8% sphalerite recovery with nitrogen, 28 to 65% sphalerite recovery with air). Also, the use of cyanide did not decrease appreciably the level of sphalerite recovery. Nevertheless, the levels of pyrite recovery in Figure 5.4 are lower than that obtained without cyanide (2-5% vs. 10-70% in Figure 5.2).

Figure 5.3 Impact of flotation gas and pH on Cp/Sp selectivity (NaCN and Aerophine 3418A)

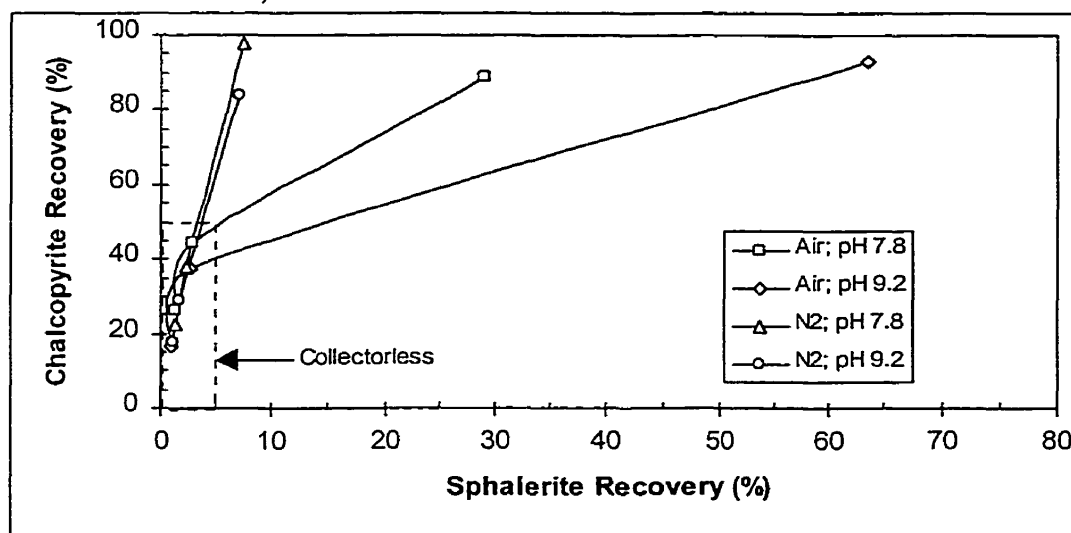
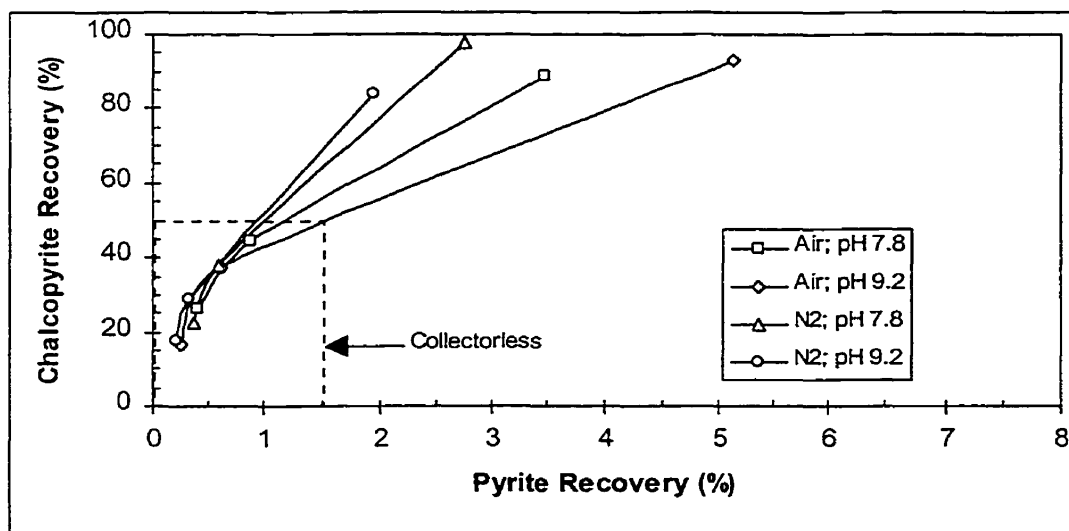
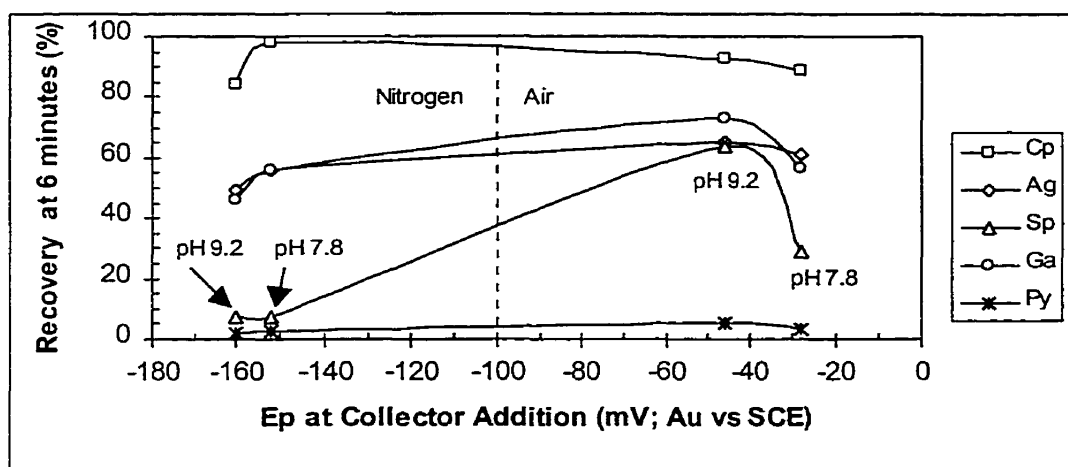


Figure 5.4 Impact of flotation gas and pH on Cp/Py selectivity (NaCN and Aerophine 3418A)



The introduction of sodium cyanide, prior and during flotation, appears to have reduced the impact of pH on sphalerite and pyrite recoveries with nitrogen as flotation gas. However, a higher pH yields higher sphalerite and pyrite recoveries with air as flotation gas. This difference is more visible when the ultimate recoveries are plotted as function of the pulp potential at the time the collector was added as shown in Figure 5.5.

Figure 5.5 Ultimate recoveries as function of pulp potential (NaCN and Aerophine 3418A)

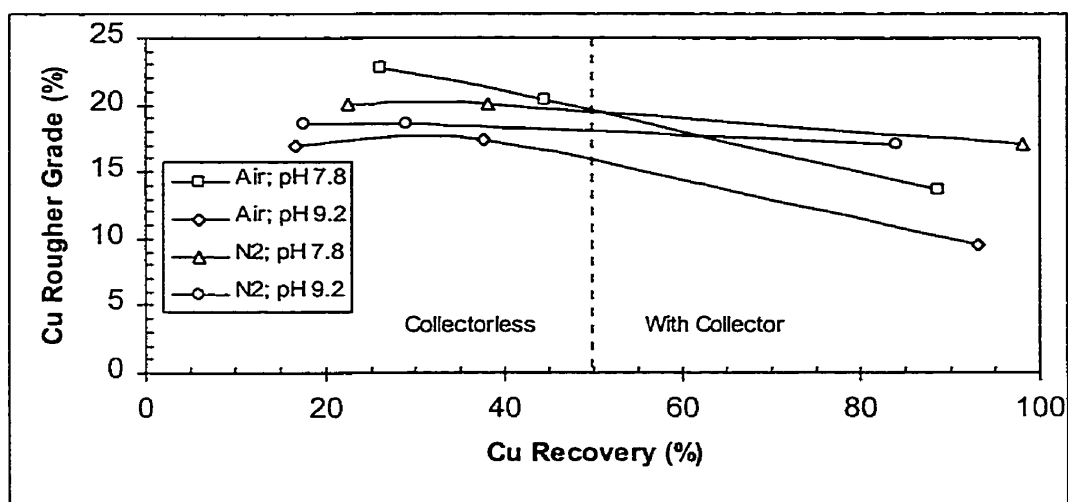


The relationship between ultimate sphalerite recovery and the pulp potential at the time of the collector addition has been condensed into one curve since only four experimental points were available. However, the pH dependence of sphalerite recovery with air as flotation gas suggests that pH specific curves would be more appropriate.

It is worth noting in Figure 5.5 that, with the addition of Aerophine 3418A, the third concentrate increment recovered between 40 and 50% of the silver and accounts for most of the ultimate silver recoveries shown as only 5 to 10% of the silver was recovered in the two collectorless concentrate increments. These recovery levels (after collector addition) were comparable to those achieved by performing the copper rougher flotation only after the introduction of a collector.

As a matter of interest, the copper grade-recovery curves obtained for this test series are shown in Figure 5.6. It is noted that the collectorless flotation stages yield high grade rougher concentrates (above 15% copper). However, the addition of the collector required to get the copper recovery above 80% reduces the overall concentrate grade, especially with air as flotation gas.

Figure 5.6 Copper grade-recovery curves for the rougher stage (NaCN and Aerophine 3418A)



#### Mineralogical examination of test products

The test products from the tests just described were mounted for mineralogical examination. As a long delay had passed between the initial mounting and the examination, the sulphide minerals were tarnished. However, it was observed that the chalcopyrite in the first concentrate increment (Figure 5.7) was more tarnished than those in the third concentrate increment (Figure 5.8).



Figure 5.7 First flotation concentrate (air, pH 7.8; without re-polishing)

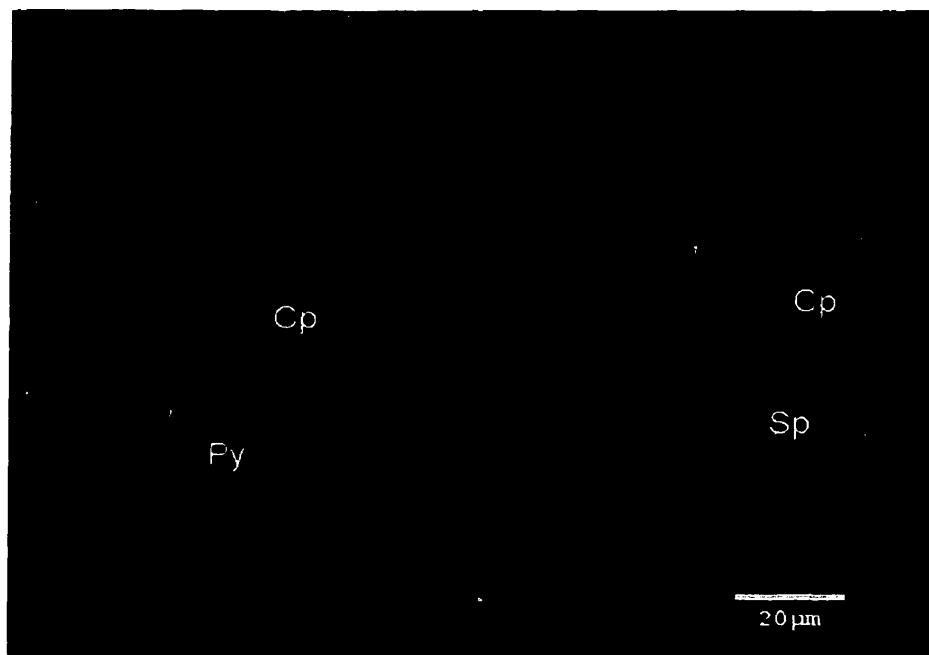
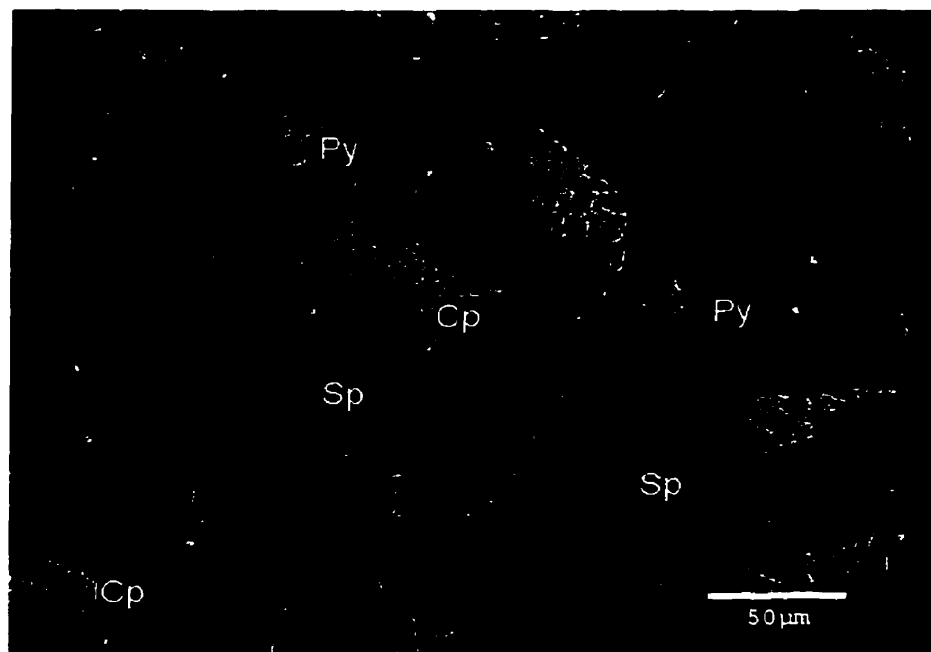


Figure 5.8 Third flotation concentrate (air, pH 7.8; without re-polishing)



The presence of highly tarnished chalcopyrite grains in the initial concentrate, and the lack thereof in the third concentrate, is contrary to the general mineralogical observation that silver migration is a key element in the formation of the tarnish (231, 232, 233, 234, 235, 236). It was the third concentrate which contained most of the silver.

Besides the highly tarnished sulphides in Figure 5.7, the most striking differences between the initial concentrate and the last one was the average particle size. The particles were generally larger in the last concentrate than in the first one. This is not entirely surprising since coarse particles are more difficult to float than medium sized ones.

The mounts were re-polished and re-examined after a 24 hour storage. All three concentrates were examined and typical fields of view are shown in Figures 5.9 to 5.11. Even with only 24 hour of storage, the chalcopyrite grains in the first two concentrates (Figures 5.9 and 5.10) are already exhibiting a tarnish while those in the third concentrate do not (Figure 5.11)

Figure 5.9 First flotation concentrate (air, pH 7.8; 24 hour re-polish)

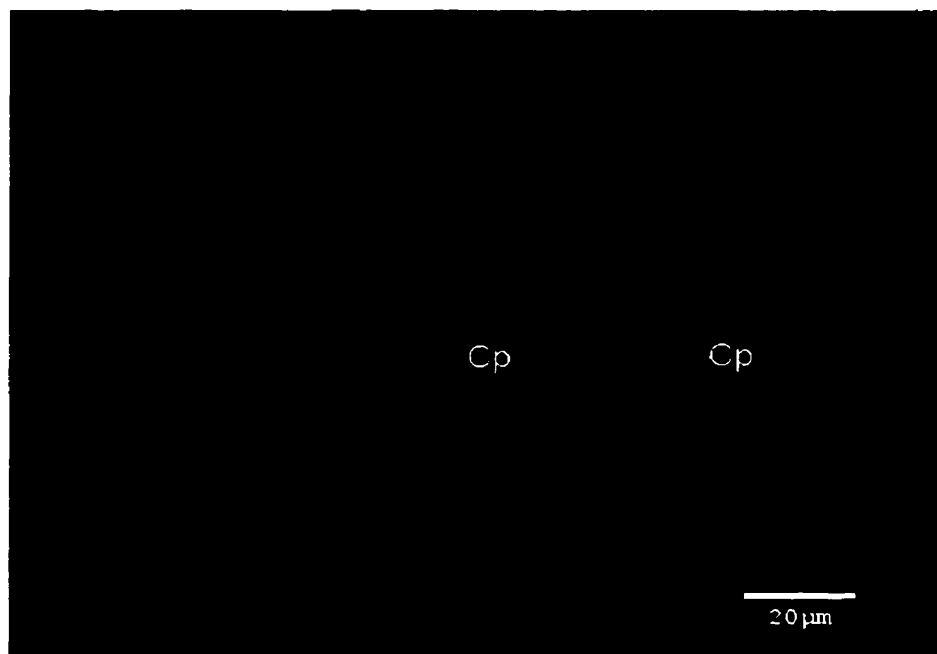


Figure 5.10 Second flotation concentrate (air, pH 7.8; 24 hour re-polish)

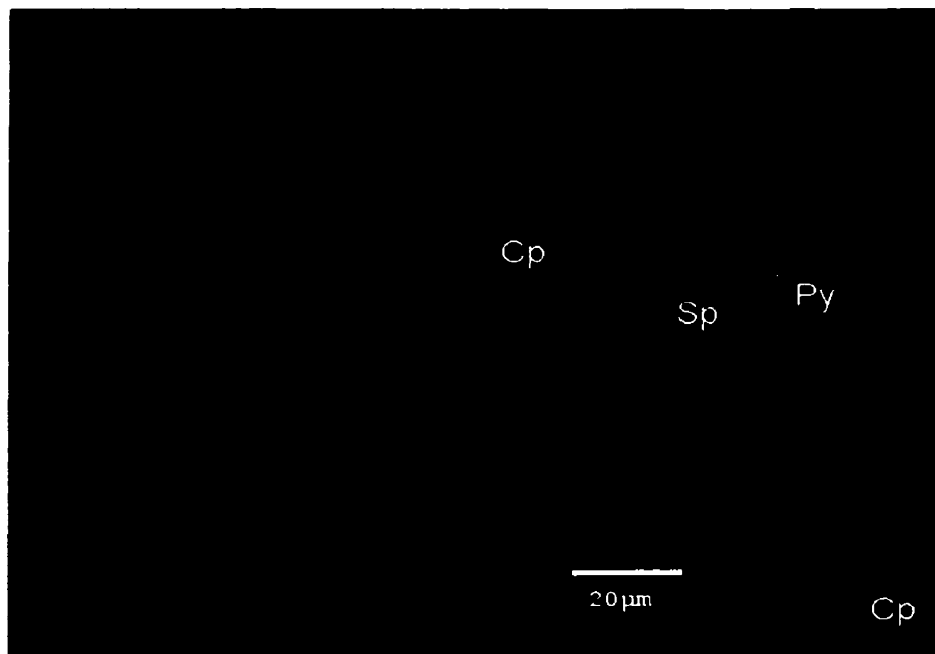
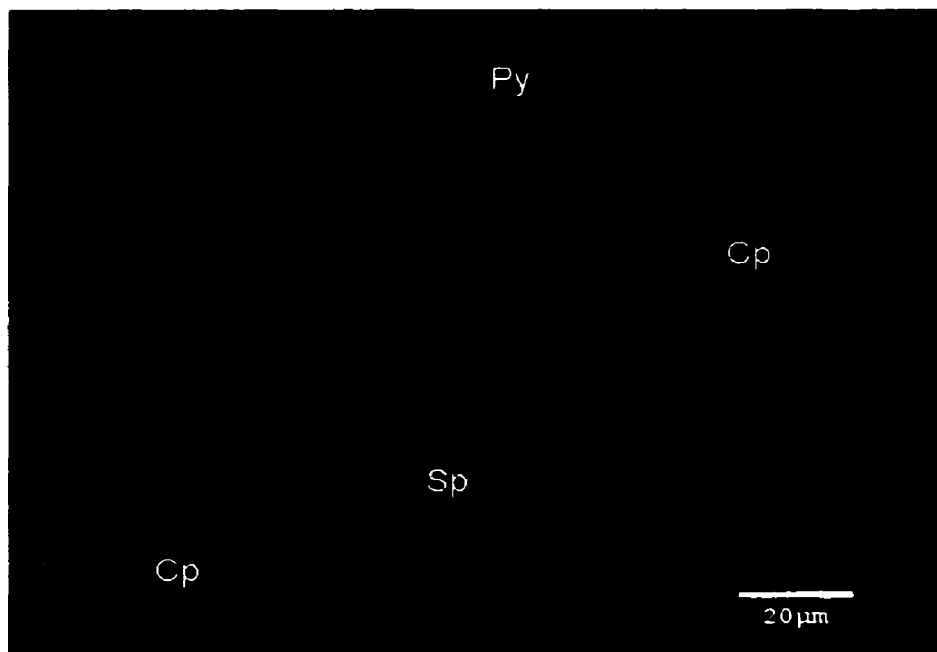


Figure 5.11 Third flotation concentrate (air, pH 7.8; 24 hour re-polish)



The concentrates from the test performed at pH 9.2 were also examined, without re-polishing, in the chance event that the observations made earlier were abnormal. Examining Figures 5.12 to 5.14, it can be noted that the particle size is generally larger in the third increment (Figure 5.14) than in the other two concentrates. Also, while chalcopyrite is heavily tarnished in the first two concentrates, it is almost pristine in the third concentrate.

The only plausible explanation is that the chalcopyrite grains recovered collectorlessly do not have a stoichiometric composition. Given their presence in collectorless concentrates, they are likely to be metal deficient.

Figure 5.12 First flotation concentrate (air, pH 9.2; without re-polishing)

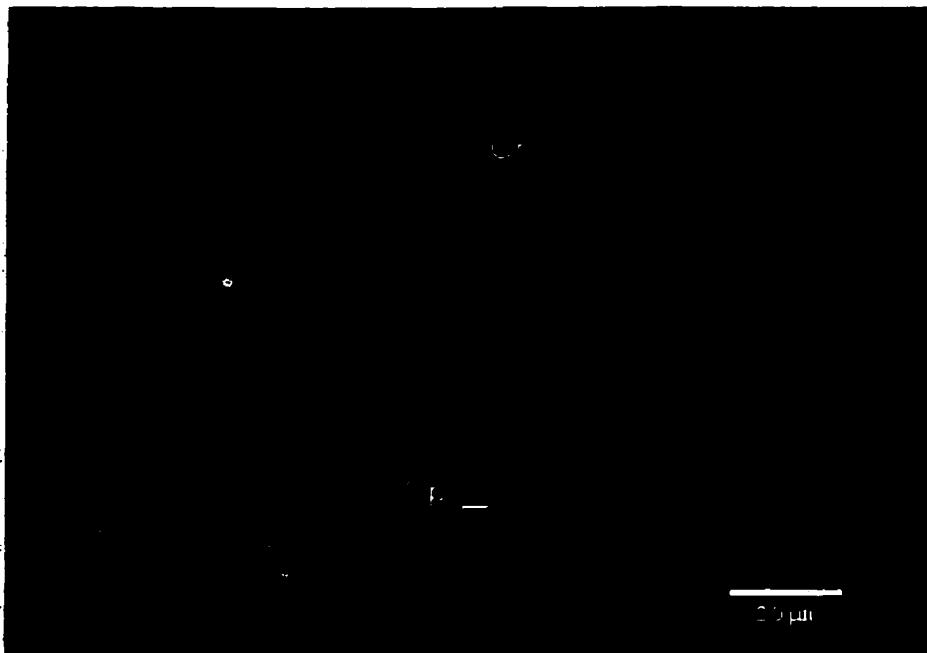


Figure 5.13 Second flotation concentrate (air, pH 9.2; without re-polishing)

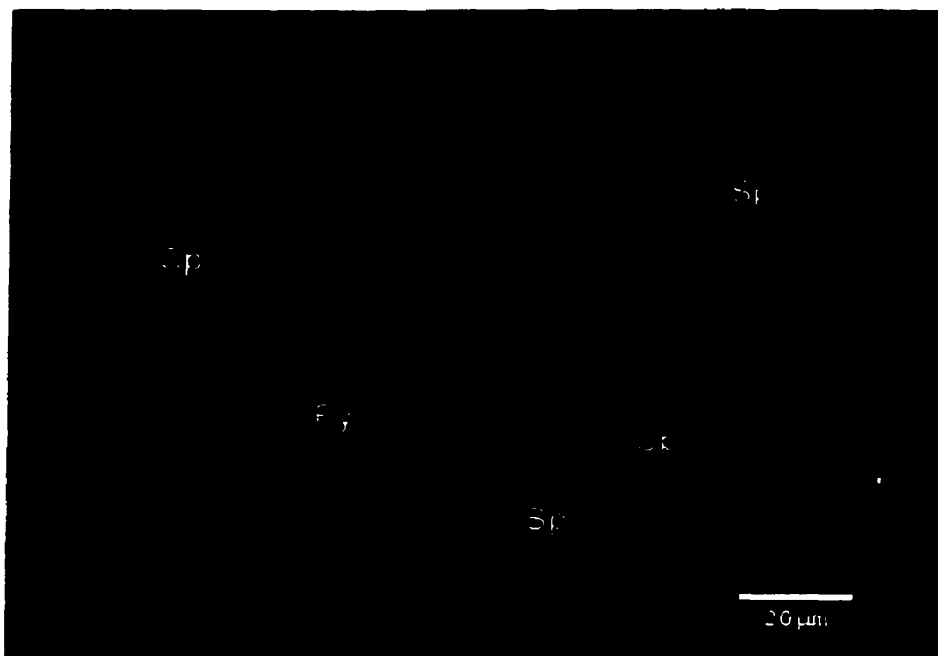
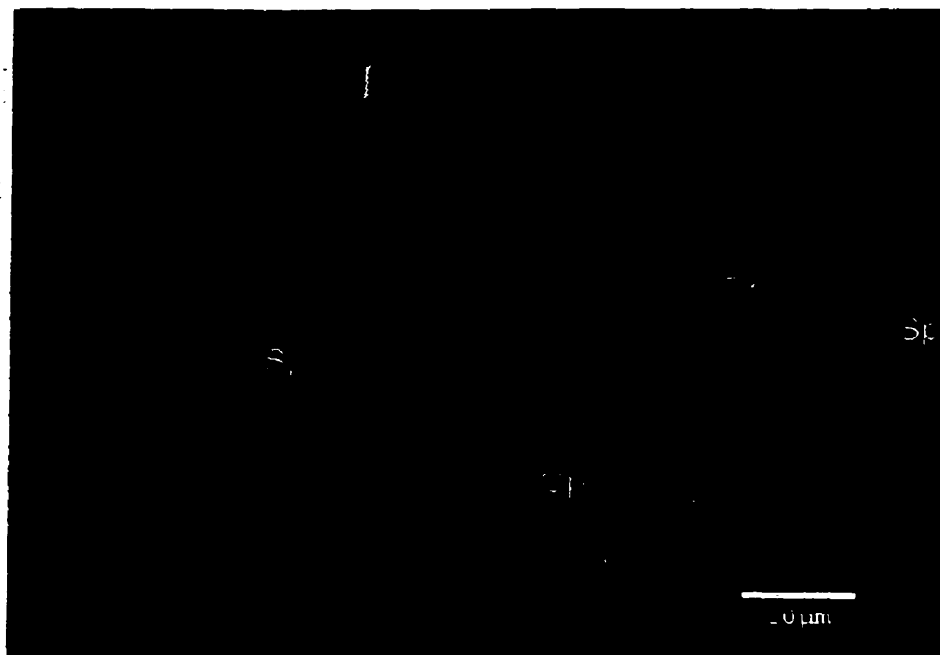


Figure 5.14 Third flotation concentrate (air, pH 9.2; without re-polishing)



### Impact of flotation gas and collector

An investigation was made to evaluate combinations of flotation gas for the collectorless and conventional flotation stages (air or nitrogen) and the collector used in the latter stage (Aerophine 3418A or SIPX). In these tests, the pH was 9.2 and an addition of 10 g/t sodium cyanide was made. The dosage of Aerophine 3418A was 5 g/t while that of SIPX was 10 g/t.

The chalcopyrite/sphalerite selectivity curves obtained with Aerophine 3418A are shown in Figure 5.15 and those with SIPX in Figure 5.16. The legends show the combination of gas used in the format “collectorless : conventional” referring to the two stages of flotation performed. The most noticeable differences between the selectivity curves presented are that the sphalerite recoveries obtained with SIPX (5 to 7% recovery) are lower than those obtained with Aerophine 3418A (10 to 15% recovery).

Figure 5.15 Impact of flotation gas and collector (Aerophine 3418A) on Cp/Sp selectivity

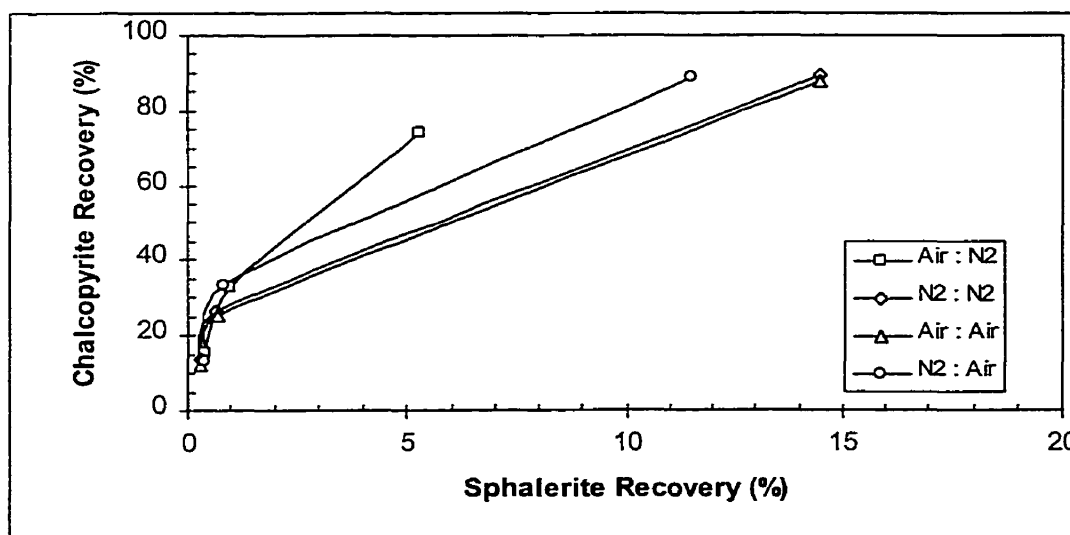
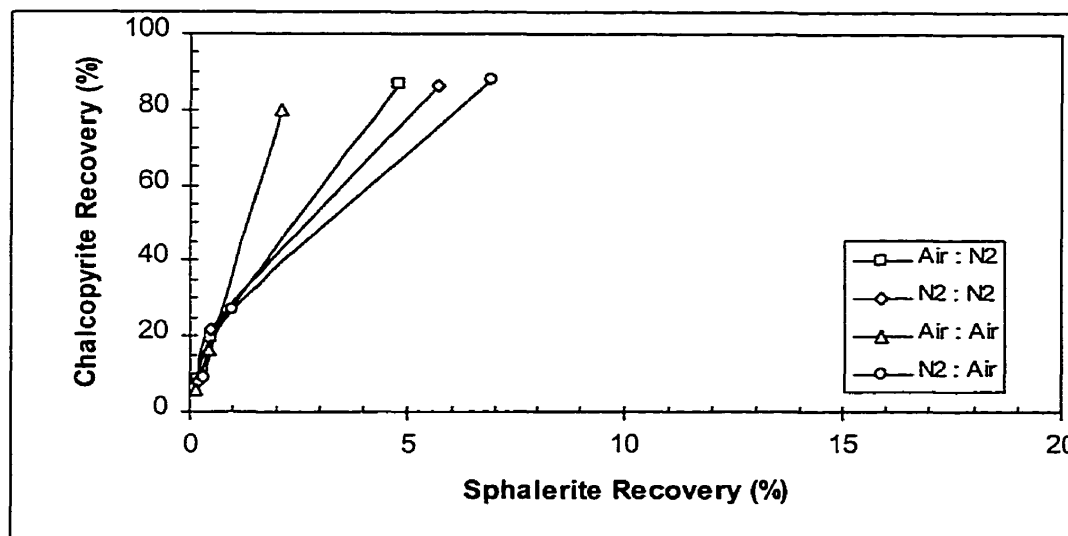


Figure 5.16 Impact of flotation gas and collector (SIPX) on Cp/Sp selectivity



For these tests, and contrary to the expectation from the response observed previously, the use of nitrogen as flotation gas in any of the flotation stages is detrimental to chalcopyrite/sphalerite selectivity with SIPX as collector (last increment in Figure 5.16). On the other hand, Aerophine 3418A gave worst selectivities when the same flotation gas was used for the collectorless and conventional flotation stages (i.e. air : air or nitrogen : nitrogen; Figure 5.15). From Figure 5.16, it is noted that with SIPX as collector, performing the collectorless flotation stage with nitrogen gave worst overall selectivities than performing it with air although the collectorless flotation stages gave essentially the same results.

The difference between the expected response to the type of flotation gas from the previous flotation tests and these tests is likely to be related to the characteristics of the feed sample. Variable feed characteristics is always a difficulty when performing investigations on plant material. However, it did not appear that using different types of flotation gas would allow the manipulation of the flotation response in a controllable manner.

### Impact of oxidizing or reducing agents

A series of four tests was performed to evaluate the impact of oxidizing or reducing agents such as potassium permanganate ( $\text{KMnO}_4$ ) and ferrous sulphate ( $\text{FeSO}_4$ ) respectively on the copper rougher flotation. The main conditions were an addition of 10 g/t of sodium cyanide ( $E_p$  after addition of  $-80$  mV vs. SCE) and the addition of either 10 g/t of  $\text{KMnO}_4$  ( $\Delta E_p$  of  $+20$  mV) or 40 g/t of  $\text{FeSO}_4$  ( $\Delta E_p$  of  $-15$  mV). The first two concentrate increments were collected without the addition of collector while the third increment was collected after the addition of either 5 g/t of Aerophine 3418A or 10 g/t of SIPX. The flotation gas was nitrogen.

The selectivities between chalcopyrite and sphalerite are shown in Figure 5.17 while that between chalcopyrite and pyrite are shown in Figure 5.18. It can be noted in Figures 5.17 and 5.18 that the collectorless flotation stages (first two concentrate increments) gave essentially the same results for all four tests. Only with the third concentrate increment, where the collector was added, that the selectivity curves show visible differences.

Figure 5.17 Impact of potential modifying agent and collector on Cp/Sp selectivity

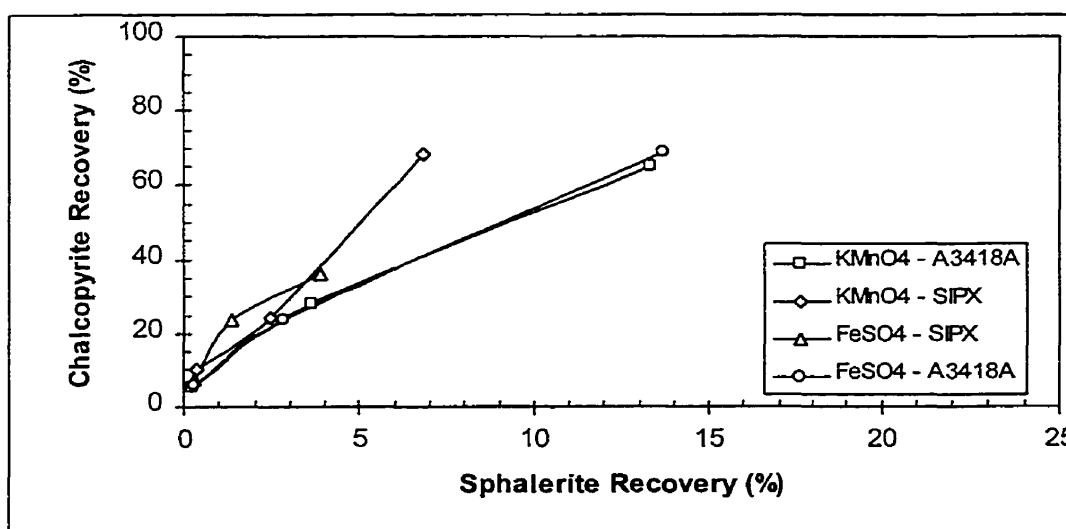
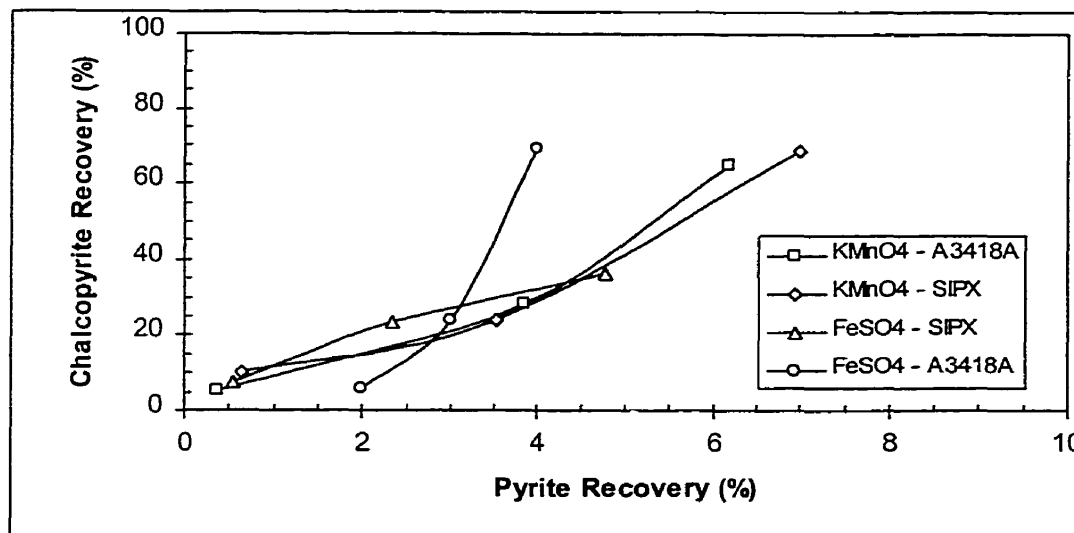




Figure 5.18 Impact of potential modifying agent and collector on Cp/Py selectivity



The main observation is that Aerophine 3418A yields essentially the same recoveries irrespective of the potential modifying agent added while chalcopyrite recovery with SIPX is drastically reduced when ferrous sulphate is present (reducing conditions). The apparent lack of response of Aerophine 3418A to the introduction of oxidizing or reducing agents could be related to a collector-mineral interaction mostly based on chelation rather than on oxidation-reduction reactions. The results obtained confirm that Aerophine 3418A is less selective than SIPX under the conditions investigated.

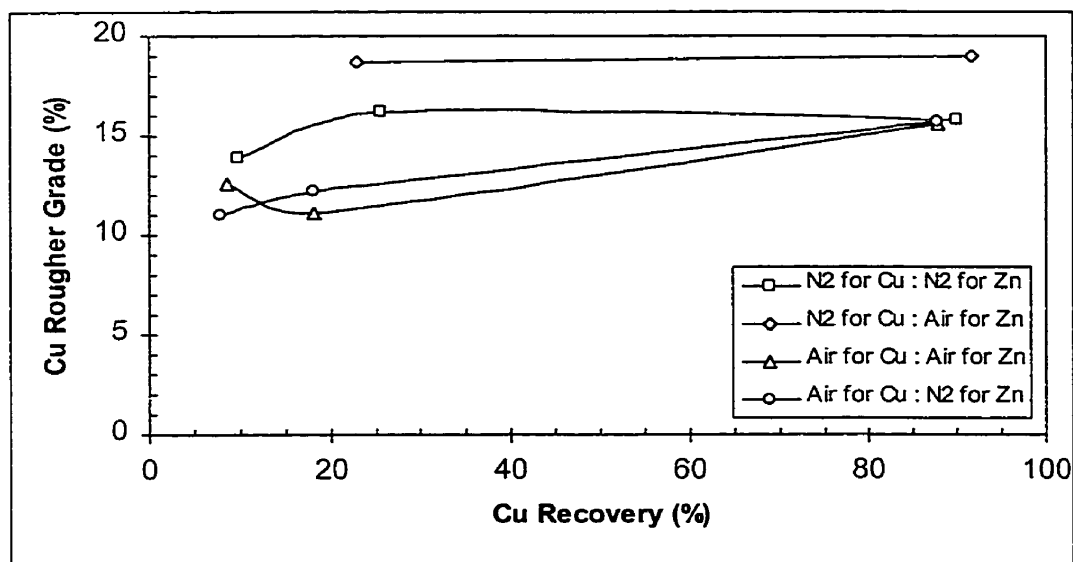
An impact of the addition of oxidizing or reducing agents was expected for SIPX from the discussion of the electrochemical model for the flotation of sulphide minerals although the magnitude of the reduction in chalcopyrite recovery with ferrous sulphate (from 70% to less than 40%) is large in relation to the small observed drop in pulp potential prior to flotation (15 mV). This is due to the use of nitrogen as flotation gas which prevented the oxidation of the ferrous ions to ferric ones normally occurring with air. Chalcopyrite flotation can be delayed by the introduction of ferrous ions but is not depressed when air is the flotation gas.

## Impact of flotation gas on copper and zinc flotation

As a final investigation on the combination of collectorless and conventional flotation for copper rougher flotation with either air or nitrogen as flotation gas, the subsequent impact on the zinc rougher flotation was examined. The conditions were 10 g/t sodium cyanide prior to copper collectorless flotation (two concentrate increments for 1 and 2 minutes of flotation) and a 5/t of Aerophine 3418A addition for the collection of a third increment (3 minutes of flotation). The zinc rougher was performed following copper sulphate activation (200 g/t) and three concentrate increments for 1, 2, and 3 minutes of flotation, each one with the addition of 5 g/t SIPX. Air or nitrogen was used as flotation gas. The pulp pH was raised to 10.0 using lime prior to the introduction of sodium cyanide, from the as collected pH of 9.0, to correspond to the plant copper rougher pH at that time.

The copper grade-recovery curves are shown in Figure 5.19 while the zinc grade-recovery curves are shown in Figure 5.20. The legends refer to the flotation gas used respectively for the copper and zinc flotation stages.

Figure 5.19 Copper grade-recovery curves (combined collectorless and conventional flotation; Aerophine 3418A and air or nitrogen as flotation gas)



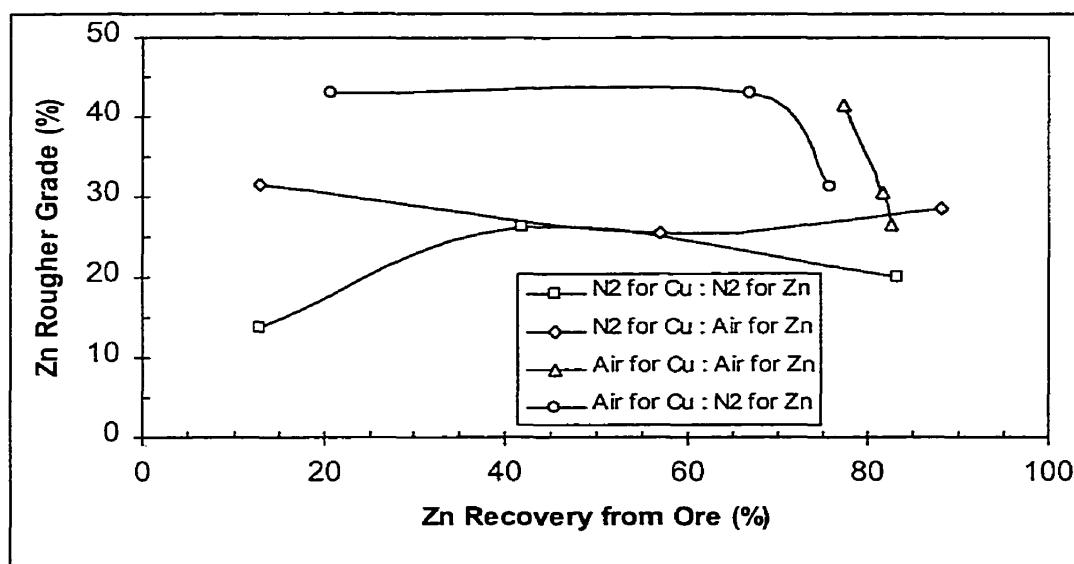
The copper grade-recovery curves (Figure 5.19) follow the ranking established earlier (Figure 5.6) in that the collectorless concentrate collected with nitrogen as flotation gas (first two increments in Figure 5.19 with the exception of one test where both increments had to be combined for assaying) have higher copper grades and recoveries than those collected with air as flotation gas.

The experimental design indirectly provided two copper rougher results with nitrogen as flotation gas and two with air. It can be observed in Figure 5.19 that the reproducibility of the copper rougher with air as flotation gas was excellent while it was less than desirable with nitrogen. This appears to be related to the order in which the tests were performed. The pulp potential was  $-103$  mV vs. SCE in the first test which was with nitrogen as flotation gas for the copper rougher ( $\square$  in Figure 5.19) and  $-60$  mV in the second one ( $\diamond$ ) also with nitrogen. The corresponding values were  $-40$  mV for the third test ( $\Delta$ ) and  $-19$  mV for the fourth one ( $\circ$ ) which were performed with air. The jump in pulp potential is larger between the first and second tests in the series than between the second and third, and the third and fourth. The progression towards higher pulp potentials as a test series progresses is linked to diffusion of oxygen from atmospheric air into the feed pulp over time and represents a challenge for test reproducibility. Nevertheless, the pulp potential at the time of the collector addition (third increment) was  $-130$  mV vs. SCE with nitrogen for copper flotation and  $-20$  mV with air, irrespective of the actual initial potential.

With air as flotation gas, there is an apparent delayed chalcopyrite flotation during the collectorless stages compared to nitrogen and the collectorless concentrate increments have lower grades than the combined concentrate. This appears to be related to the presence of a higher proportion of galena in the feed sample than encountered earlier and the collectorless increments contained around 2% Pb with air as flotation gas compared to 1.0% Pb with nitrogen.

The zinc grade-recovery curves (Figure 5.20) can be grouped according to which gas was used for the copper rougher flotation stage. In the two tests where air was used for the copper rougher stage, the first zinc rougher concentrate graded above 40% zinc but lower zinc recoveries were obtained when nitrogen was used for the zinc flotation stage. In the two tests where nitrogen was used for the copper rougher stage, the first zinc rougher concentrate graded less than 30% zinc or less, with the worst grade achieved when nitrogen was also used for the zinc rougher stage. Pyrite was the main mineral initially recovered in this case.

Figure 5.20 Zinc grade-recovery curves (combined collectorless and conventional copper flotation and air or nitrogen as flotation gas)



The results obtained with nitrogen as flotation gas are not surprising since that it has been demonstrated that nitrogen can lead to a preferential flotation of pyrite over that of sphalerite (153). This makes the use of nitrogen less than desirable in this case. With air as flotation gas for the zinc flotation, the grade of the zinc rougher concentrate eventually recovers, when nitrogen was used for the preceding copper flotation, but the shape of the grade-recovery curve is not the most inviting.

Interestingly, all four tests yielded essentially the same 4–5% zinc losses to the tailings. The apparent higher zinc recovery into the zinc rougher concentrate observed for some of the tests in Figure 5.20 essentially arises from the lower amount of zinc recovered into the corresponding copper rougher concentrate.

It unfortunately appears that the conditions which are best for the copper rougher flotation stage are not necessarily ideal for the zinc rougher flotation stage. Moreover, in a plant, a good portion of the zinc reporting to the copper rougher concentrate would be depressed in the copper cleaning stages and would thus report to the zinc circuit. The challenge, often based on economic criteria, is one of balancing selectivity in one part of the circuit with that in another part. It thus appears that performing a combination of collectorless and conventional flotation for the copper rougher stage with the assistance of nitrogen as flotation gas, although technically feasible and promising, is not practical when considering the subsequent zinc rougher flotation stage.

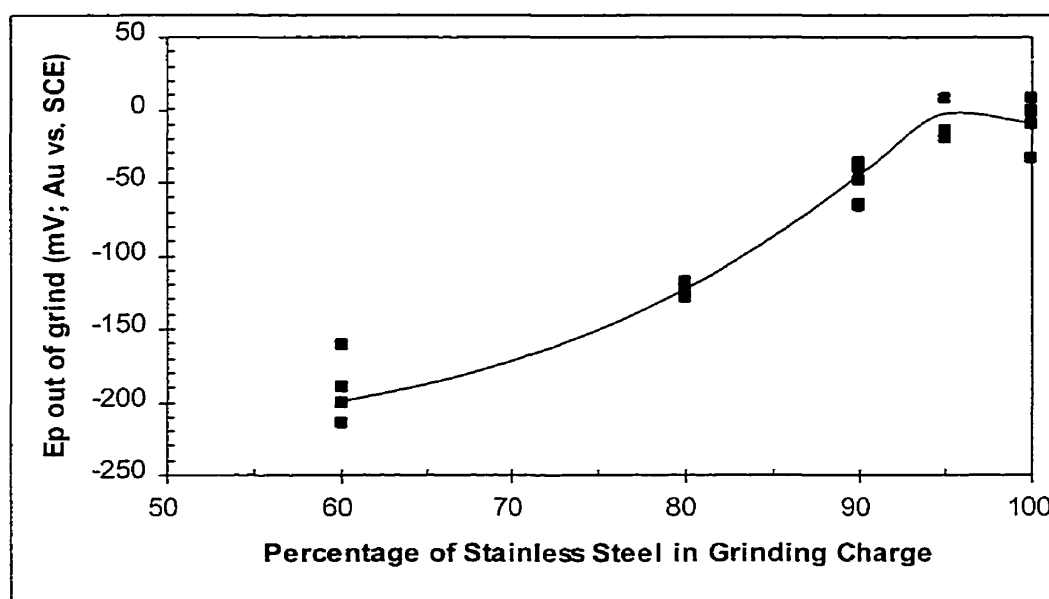
#### 5.4.2 Impact of grinding environment

A series of tests was performed by using a crushed plant feed and performing the grinding in the laboratory. The composition of the grinding media was varied between 60 and 100 wt% stainless steel to better understand the impact of the grinding media on flotation selectivity. The copper collector used was Aerophine 3418A at a total dosage of 15 g/t with equal increments to the three flotation stages. However, in some of these tests, the first collector increment was added to the grind rather than to the flotation stage.

Also, tests involving one cleaning stage as well as the rougher stage were performed with sulphur dioxide (to pH 6) being the main depressant in the copper cleaning stage. The conventional reagent suite of sodium cyanide (50 g/t), zinc sulphate (250 g/t) and lime (250 g/t to the grinding stage plus what was needed to obtain pH 9.5 for the copper flotation) was used. Both copper and zinc flotation stages were performed but only the results obtained for the copper stages will be discussed here.

The relationship between the pulp potential measured after grinding and the proportion of stainless steel in the grinding charge is shown in Figure 5.21. Reproducibility of the pulp potential measurement from test to test with the same composition of grinding media was generally within 25 mV. It is noted in Figure 5.21 that the pulp potentials obtained with a full stainless steel charge do not appear to be an extrapolation of those obtained with the mixed charges.

Figure 5.21 Impact of composition of grinding media on pulp potential after grinding



#### Copper rougher response

The observed mineral recovery relationships are shown in Figures 5.22 through 5.24 for the tests where all the collector was added to the flotation stage and in Figures 5.25 through 5.27 for the tests where one third of the collector was added to the grinding stage.

The most striking feature of the plots is an apparent discontinuity of the curves between 95 and 100% stainless steel especially in Figures 5.22 and 5.25 where the

relationships are shown as a function of the composition of the grinding charge. It would appear that the response obtained at 100% stainless steel cannot be projected by an extrapolation of the curves to 100% stainless steel, similarly to what was observed for the pulp potential after grinding (Figure 5.21). Recalling that galvanic interactions play a major role as to the outcome of the flotation process, the conditions imparted by a 100% stainless steel charge are that of the sulphides being oxidized whereas at lower proportion of stainless steel, it is the grinding media which is oxidized.

The rest potentials shown in Table 5.1 indicate a 200 mV difference between the mild steel and the stainless steel rods. The range in initial pulp potentials observed in these tests, between 60% and 100% stainless steel in the grinding media is around 150 mV. This would indicate that even at 60% stainless steel in the grinding media, the grinding environment is dominated by mild steel.

Figure 5.22 Initial floatabilities as a function of grinding media composition (all collector to flotation)

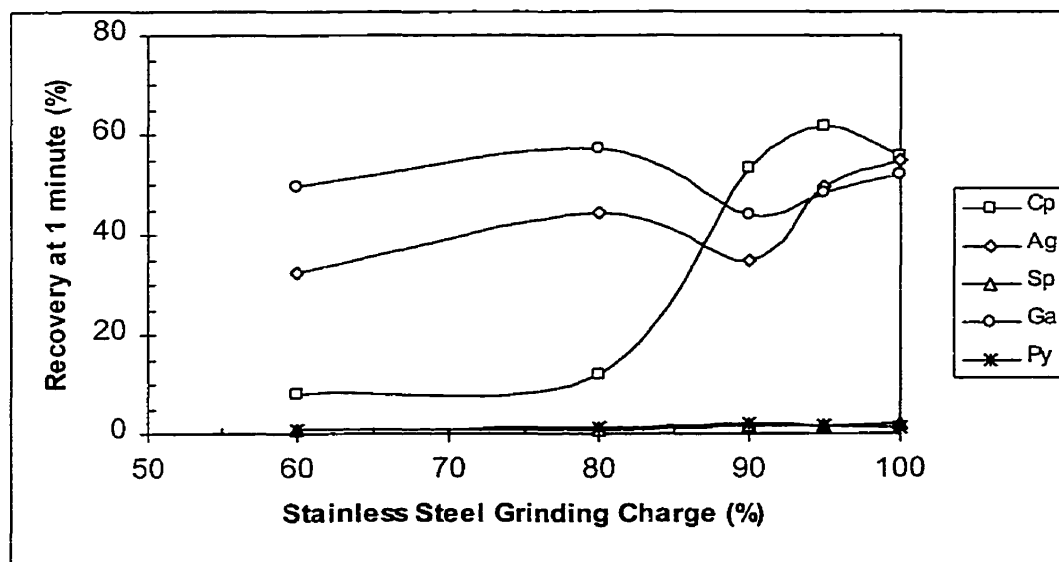
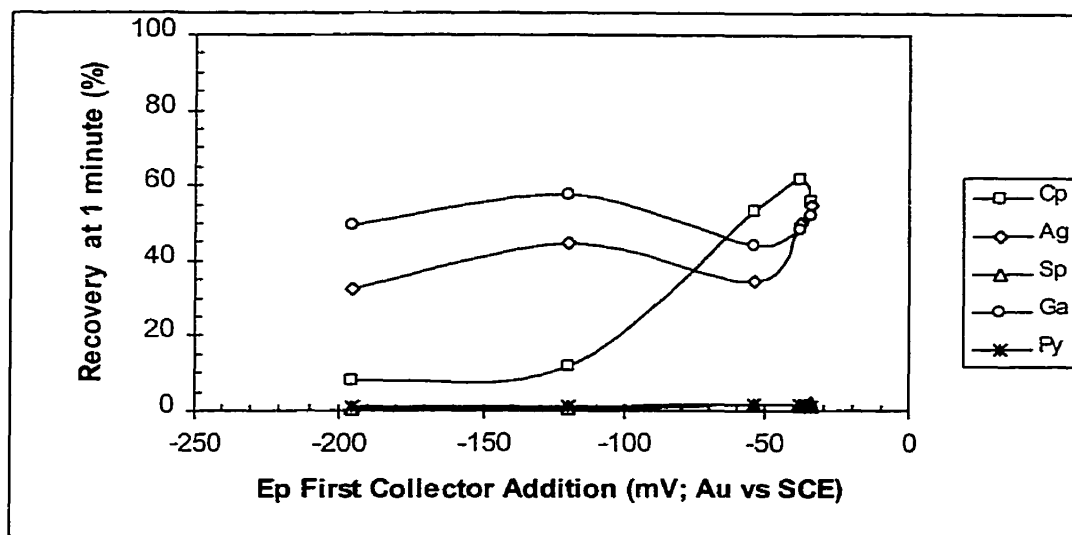
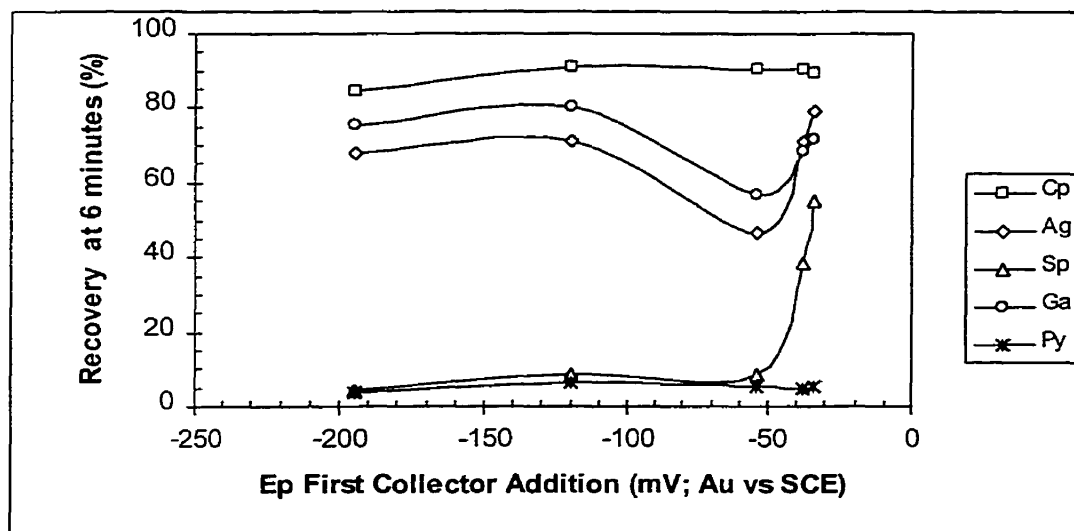


Figure 5.23 Initial floatabilities as a function of  $E_p$  (all collector to flotation)Figure 5.24 Ultimate floatabilities as a function of  $E_p$  (all collector to flotation)

With all the collector added to the flotation stages (Figures 5.22 through 5.24), the initial and ultimate floatabilities are strongly dependent on the composition of the grinding media (and hence the initial pulp potential). Notably, the ultimate sphalerite recovery increases noticeably for pulp potentials higher than  $-50$  mV vs. SCE (Figure 5.24) corresponding to a composition of 90% stainless steel or higher (Figure 5.22).



However, when one third of the collector is added to the grinding mill (Figures 5.25 through 5.28), the impact is lessened. In fact, for the ultimate floatabilities with one third of the collector added to the grinding mill (Figure 5.27), there would be no impact of the composition of the grinding charge (and thus the initial pulp potential) up to 95% stainless steel (Figure 5.27) corresponding to  $-25$  mV vs. SCE (Figure 5.27).

Figure 5.25 Initial floatabilities as a function of grinding media composition (1/3 of collector to grind)

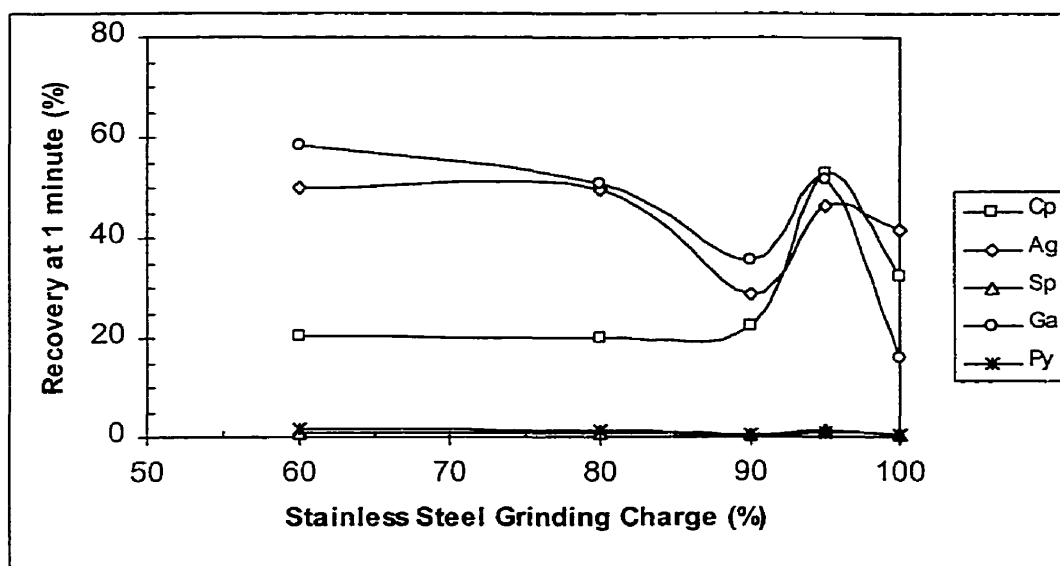


Figure 5.26 Initial floatabilities as a function of  $E_p$  (1/3 of collector to grind)

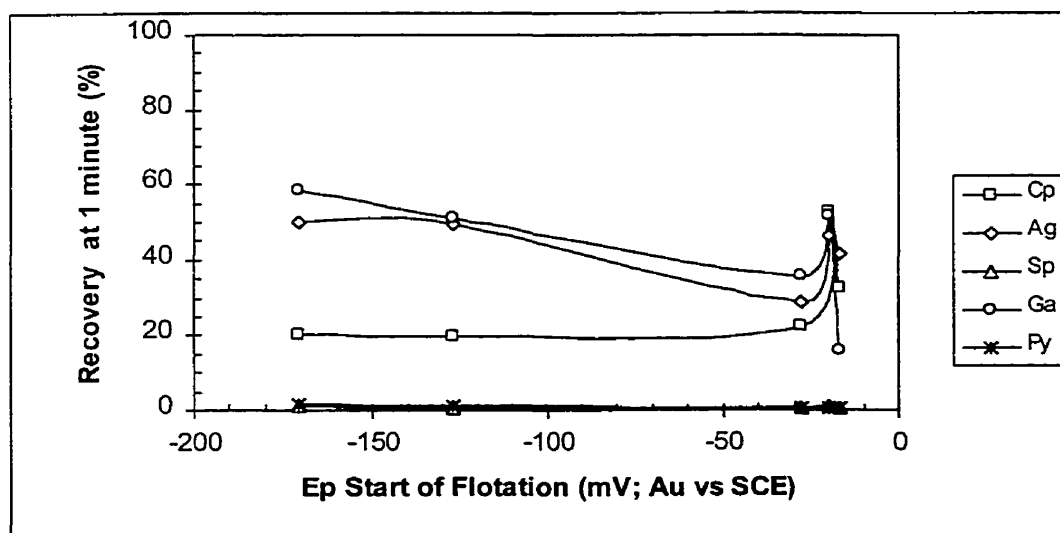
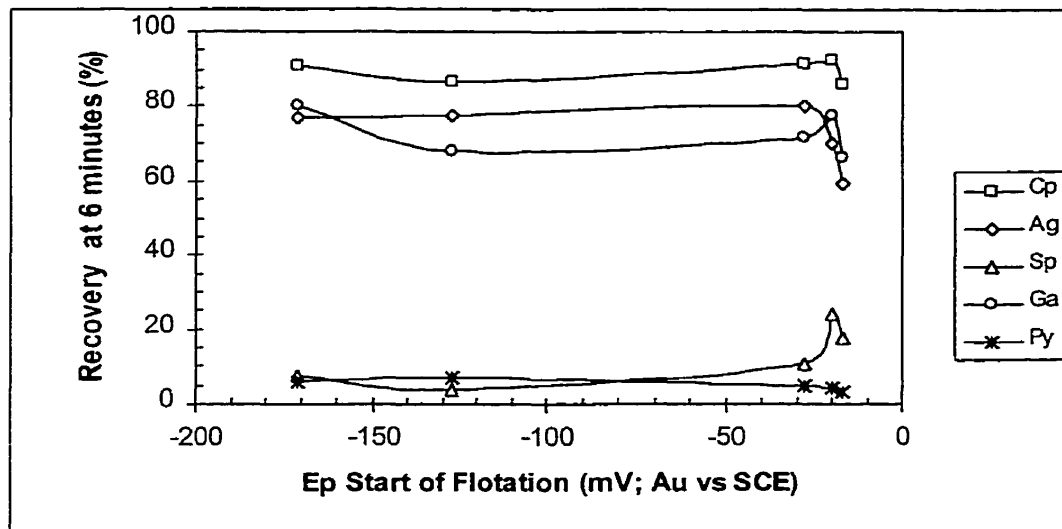


Figure 5.27 Ultimate floatabilities as a function of  $E_p$  (1/3 of collector to grind)

It would appear that by adding the collector to the grinding mill, the sulphides are protected from galvanic interactions. Furthermore, when the collector is added in the grinding circuit, as performed at many concentrators, the probability of being capable of defining a relationship between selectivity and the measured potential at the head of the flotation circuit is small; the collector having performed its function at the lowest possible degree of oxidation for the pulp.

#### Copper cleaner response

Similar relationships can be observed when examining the ultimate cleaner floatabilities as a function of pulp potential with all the collector added to the rougher flotation stage (Figure 5.28) and one third of the collector added to the grinding stage for the rougher (Figure 5.29).

The ultimate copper and silver recoveries from the cleaner stage are relatively independent of the pulp potential at the rougher stage although there is a small trend of increasing recovery at the higher potentials. Also, sphalerite recovery is minimal when

the pulp potential in the rougher stage was lower than  $-50$  mV vs. SCE. This is more noticeable when all the collector was added to the flotation in the rougher (Figure 5.28) than when one third of the collector was added to the grind (Figure 5.29). Galena recovery is variable and this could be related to the use of sulphur dioxide in the cleaning stage. Finally, very little pyrite is recovered from the copper cleaner.

Figure 5.28 Ultimate cleaner floatabilities as a function of  $E_p$  (all collector to flotation in the rougher)

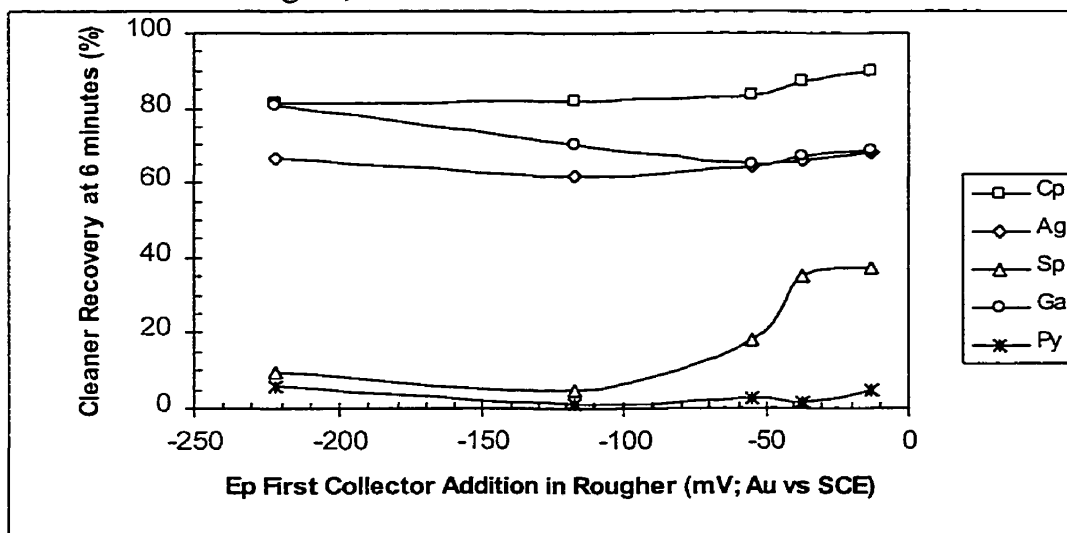
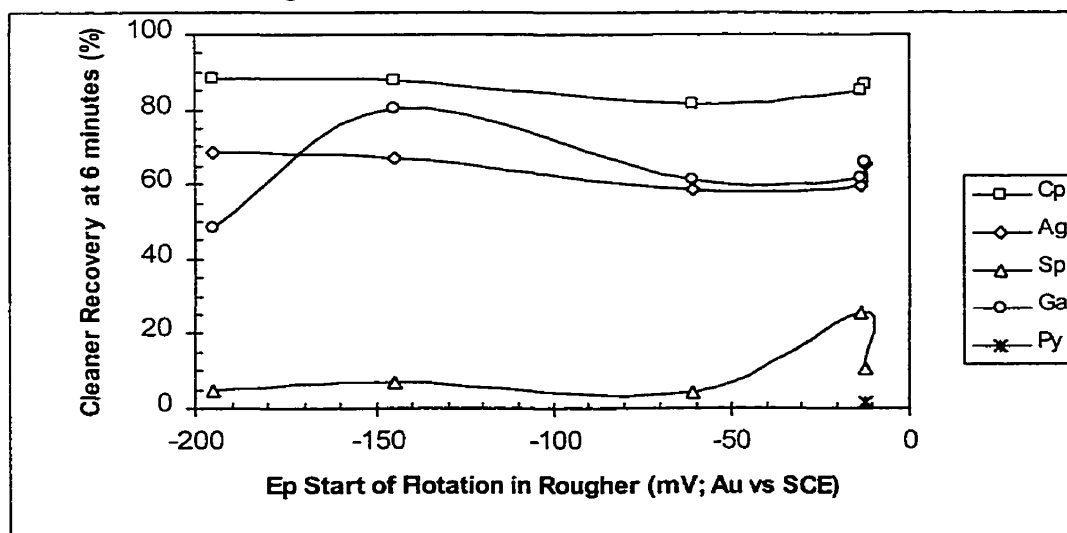


Figure 5.29 Ultimate cleaner floatabilities as a function of  $E_p$  (1/3 of collector to grind in the rougher)



## 5.5 Conclusions

The rest potentials of sulphide minerals are higher in the presence of Aerophine 3418A than in its absence, especially for the copper minerals. This could be due to chelation of the metal atoms from the surface of the minerals when adsorption occurs.

Addition of Aerophine 3418A following collectorless flotation leads to a lowered selectivity between the copper minerals and sphalerite. Use of nitrogen as flotation gas prevents oxidation which in the case of the A-1 zone ore may lead to in-situ activation of the sphalerite and thus restores selectivity while achieving high copper and silver recoveries. Pulp pH has a major impact on selectivity.

When sodium cyanide is used to prevent sphalerite activation, conflicting results are obtained as to the impact of the flotation gas on selectivity. Feed sample variation could be an origin for the conflicting results. SIPX was generally more selective than Aerophine 3418A, irrespective of the flotation gas, and its selectivity could be modulated by addition of oxidizing or reducing agents contrary to Aerophine 3418A.

There appears to be a correlation between rapidly tarnishing chalcopyrite grains and their presence in collectorless flotation concentrates. Chalcopyrite grains in the concentrates recovered with a collector remained relatively pristine.

The flotation response obtained with a 100% stainless steel grinding charge cannot be extrapolated from the response established as the proportion of stainless steel increases. Adding a portion of the collector to the grinding stage minimizes the detrimental impact of the oxidation-reduction environment during grinding on the flotation response at the rougher and subsequent cleaning stages. Finally, chalcopyrite/sphalerite selectivity was best if the pulp potential when the collector was first introduced, or copper flotation was initiated, was  $-50$  mV (Au vs. SCE) or lower.

## 6 PLANT DETERMINATION OF THE IMPACT OF PULP POTENTIAL

### 6.1 Selection of location for on-line electrodes

The work by Gebhardt et al. (83) on chalcocite and pyrite and laboratory tests (Sections 1.5, 1.6 and 5.4) showed that the potential at which the collector is introduced into the flotation pulp has a greater impact upon selectivity than that at which flotation is performed. This observation was used to select the most appropriate location of the pulp potential sensors.

At Les Mines Selbaie, the first collector addition point is at the feed box of the rougher flotation bank. Hence, the most logical and practical choice was to locate the on-line potential sensor in the first flotation cell of the rougher bank.

At the Kidd Creek Concentrator, the first collector addition point is in the feed box to the sulphur dioxide conditioner. Testing with hand-held electrodes showed that the short term variability of the pulp potential measurement in the sulphur dioxide conditioner was too large to be useable. The on-line sensor was located in the feed box to the primary rougher bank which was the most easily accessible alternative location.

### 6.2 Les Mines Selbaie

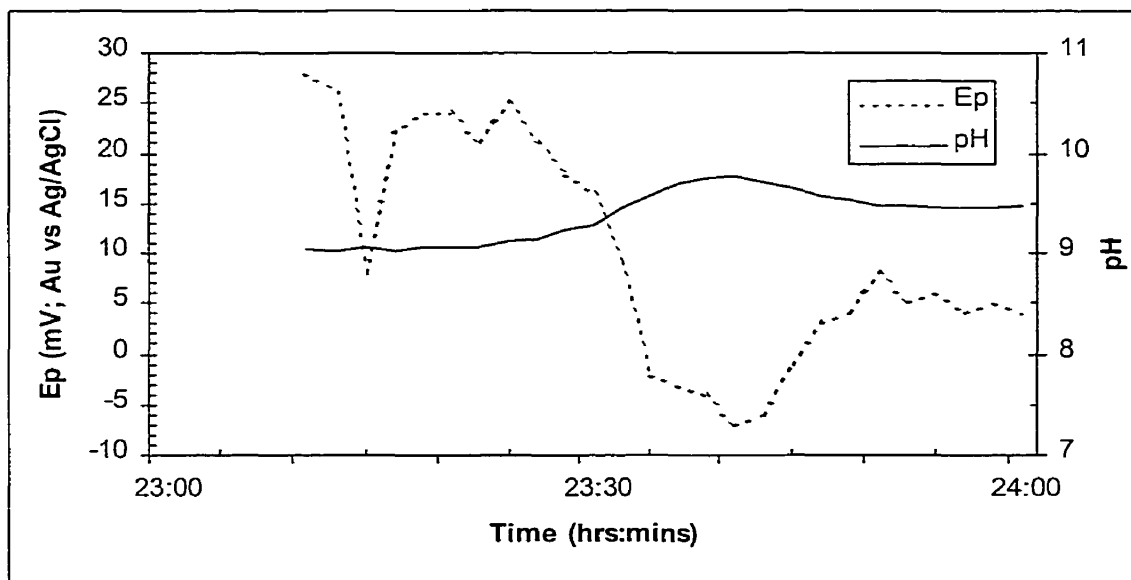
#### 6.2.1 Sensitivity to pH level and sodium cyanide dosage

The traditional practice to modulate copper/zinc selectivity is to vary the flotation pH and sodium cyanide dosage. The collector dosage is also used but the permissible variation is limited by the minimum level required to sustain copper recovery. The zinc sulphate dosage has a very limited impact on the selectivity. However, there are only a few copper/zinc concentrators which can achieve selectivity without the addition of zinc sulphate.

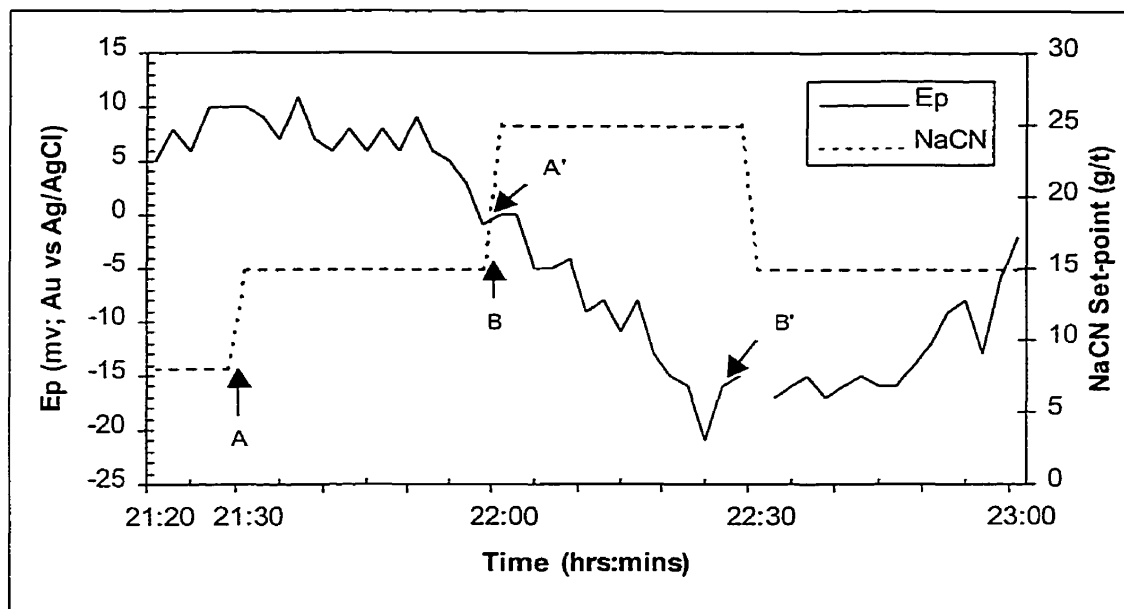
Step changes in the pH (lime addition) set-point and sodium cyanide dosage were performed to determine the sensitivity of the pulp potential,  $E_p$ , to these process variables in the plant. Figures 6.1 and 6.2 show examples of the results obtained.

An increase in pH from 9.0 to 9.5 (Figure 6.1) introduces a drop in  $E_p$  from about 25 to 5 mV. The pulp potential would decrease by about 40 mV per pH unit increase in the alkalinity of the pulp. The effect of pH on  $E_p$  is relatively rapid. The lime addition point used to automatically maintain the pH in the copper rougher is in the copper rougher conditioner where the fresh feed and recycled copper cleaner-scavenger concentrate are mixed together.

Figure 6.1 Sensitivity of  $E_p$  to a step change in pH set-point from 9.0 to 9.5



The pulp potential is also sensitive to the sodium cyanide dosage (Figure 6.2). However, there is a significant lag (about 25 minutes from A to A' and B to B') between a step-change in NaCN dosage and the resulting  $E_p$  response. This lag reflects the residence time in the grinding circuit where the reagent is added. Increasing the dosage from 8 to 25 g/t NaCN causes the  $E_p$  to drop from about 8 to -15 mV. This would give a drop of 1.4 mV in potential per g/t NaCN increase.

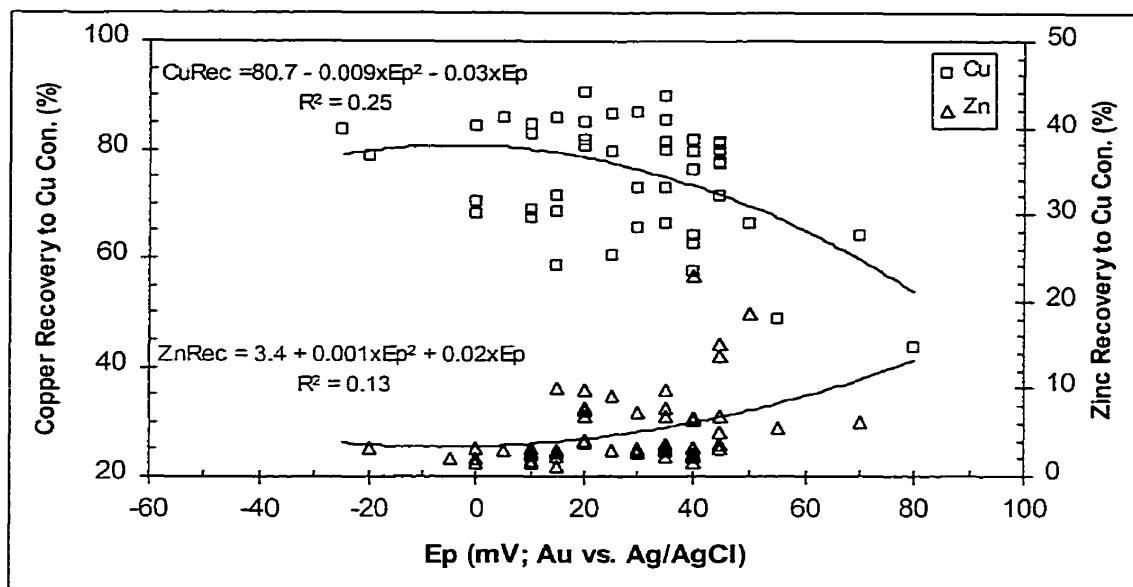
Figure 6.2 Sensitivity of  $E_p$  to changes in NaCN dosage set-point

### 6.2.2 Window of selectivity

The sensitivity of the pulp potential to the chemical conditions of the pulp indicates that it might be possible to use this approach to optimize the reagent dosages for copper/zinc selectivity. Hence, plotting the copper and zinc recoveries against the pulp potential might indicate a region, or a window, over which selectivity is achieved and consequently what might be set-points for these reagents. This is similar to what was performed for the interpretation of the laboratory flotation test results although no attempt was made in the plant to manipulate the pulp potential as was done in the laboratory. Such a plot is shown in Figure 6.3.

In Figure 6.3, the daily averages for the copper and zinc recoveries to the final copper concentrate from June through August 1989 are plotted against the daily average of the pulp potential. This time period was selected because it was certain that the on-line pulp potential sensor was giving good measurements (Figure 4.22). The regressions, as well as the correlation coefficients, for the two observed trends are shown as well.

Figure 6.3 Window of copper/zinc selectivity at Les Mines Selbaie: June-August 1989



The data in Figure 6.3 exhibit a high scatter, which is typical for plant results even after removing the data points representing start-up/shut-down conditions. Nevertheless, relationships between copper and zinc recoveries to the copper concentrate and the pulp potential can easily be observed even though their quantitative determination is not unequivocal as suggested by the low correlation coefficients obtained. The copper/zinc selectivity is highest (highest copper recovery and lowest zinc recovery) for pulp potentials below 10 mV (Au vs. Ag/AgCl). This limit corresponds well to the value of  $-50$  mV vs. SCE ( $-10$  mV vs. Ag/AgCl) determined in the laboratory flotation tests.

The relationship between zinc recovery to the copper concentrate and the pulp potential is one of increasing recovery with potential as seen in the laboratory testwork (e.g. Figure 1.17). However, the relationship for copper recovery is one of decreasing recovery with increasing potential contrary to the laboratory results which generally indicated a plateau over a similar range of pulp potentials.

The decreasing copper recovery with increasing pulp potential, and indirectly the scatter in the data, arise from the operating constraints experienced in the plant compared



to the laboratory conditions. In the laboratory, the feed characteristics (grades and ore type) remain constant during a test series and the flotation response is allowed to yield its ultimate concentrate quality. In the plant, the ore characteristics vary on a daily basis, and the concentrates must meet minimum quality standards to be accepted by the smelting and refining facilities.

There are five ore types with average assays varying between 0.13% Cu and 3.56% Zn and 4.44% Cu and 6.35% Zn at Les Mines Selbaie (Table 3.1). The assays of the mill feed at a particular moment is determined by the mining schedule and the degree of blending performed. It is difficult to track the proportion of each ore type, particularly the "E" type containing the secondary copper minerals. However, it is relatively easy to examine the impact of the feed assays on the metallurgical response. Figures 6.4 through 6.6 present trends determined over the duration of the on-line monitoring of the pulp potential.

The impact of the copper content of the mill feed on the copper recovery to the final copper concentrate is shown in Figure 6.4. A trend of increasing copper recovery to the concentrate with increasing feed copper assay can easily be observed in Figure 6.4 even though there are a few outlying points. The lower copper recovery at the lower feed copper assay reflects the greater difficulty in concentrating the valuable minerals as they become more disseminated in the gangue.

The zinc content of the mill feed is somewhat related to the copper content as seen in Figure 6.5. The observed trend is not one of a nearly constant zinc to copper assay ratio, which would reflect how concentrated the mineralization was in the ore, but one of increasing zinc to copper assay ratio as the copper content in the ore decreases. This is due to the presence of different ore types in the mine.

Figure 6.4 Relationship between copper recovery and copper feed assay: June 1989-February 1990

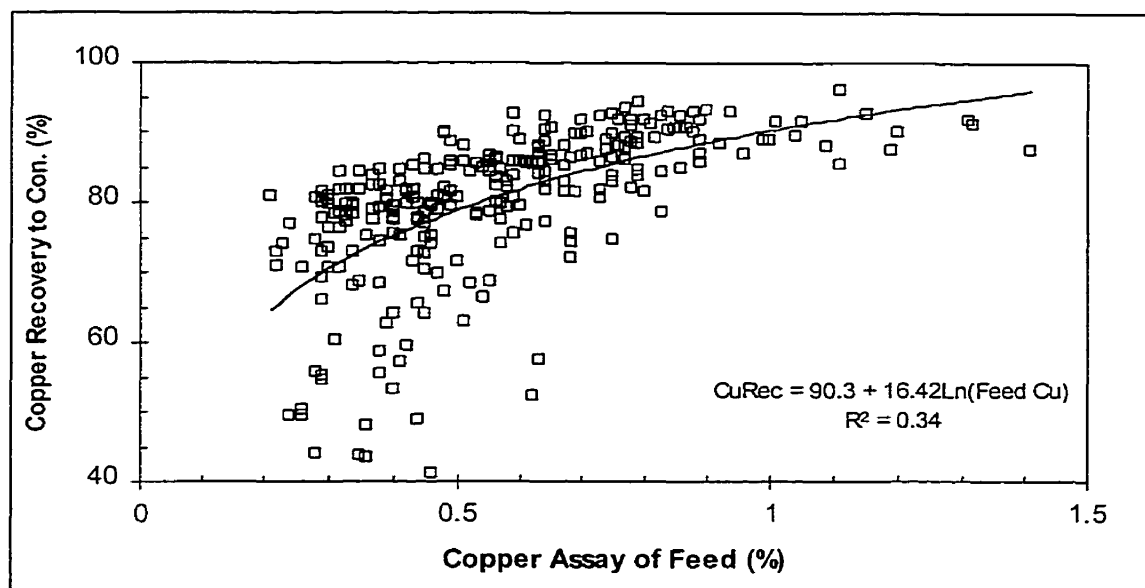
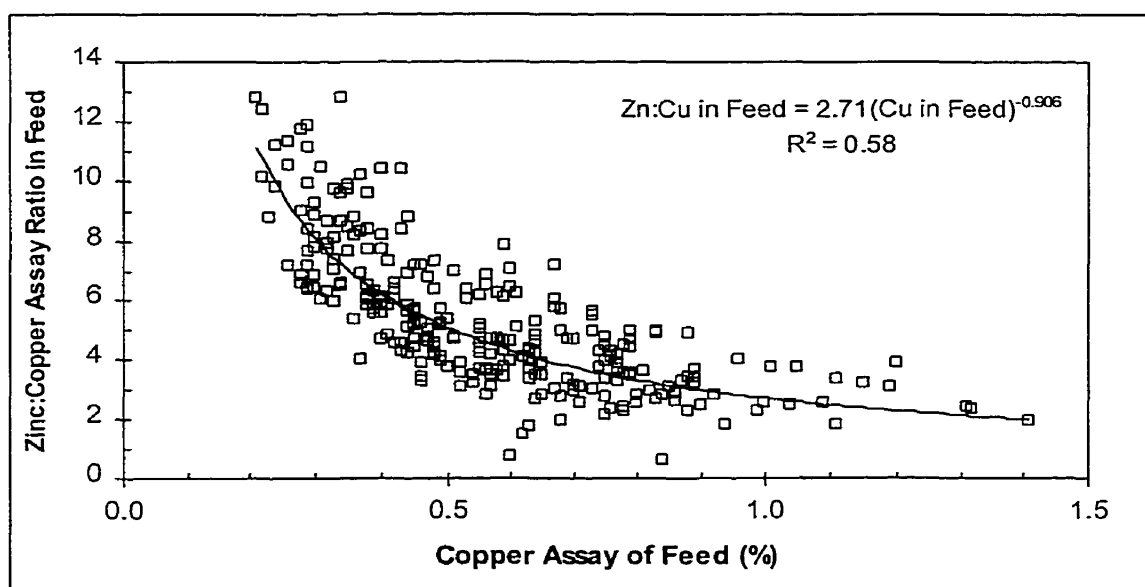


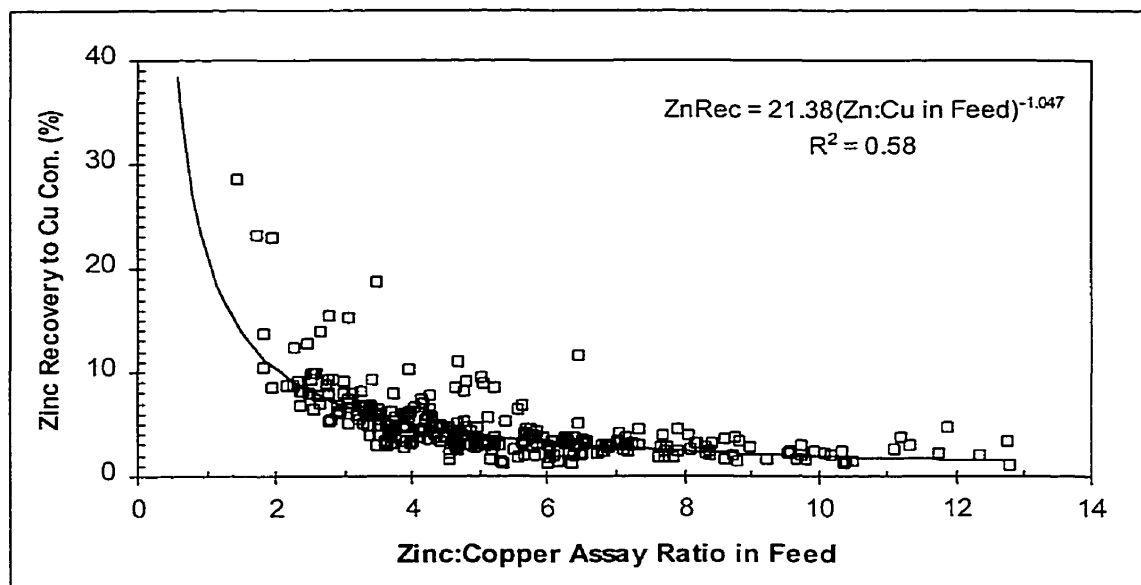
Figure 6.5 Relationship between copper and zinc contents of the mill feed: June 1989-February 1990



There are two implications of a rising zinc to copper assay ratio with decreasing copper feed assay. The first one is a decreasing copper recovery to the copper concentrate as the zinc to copper assay ratio in the feed increases. This can be inferred from the relationship between copper recovery and copper feed assay (Figure 6.4).

The second one arises from the need to maintain the quality of the final copper concentrate irrespective of the quality of the mill feed. Essentially, the zinc recovery to the copper concentrate must decrease as the zinc to copper assay ratio in the feed increases to obtain a similar quality of the copper concentrate. The trend observed over the duration of the on-line monitoring of the pulp potential at Les Mines Selbaie is shown in Figure 6.6.

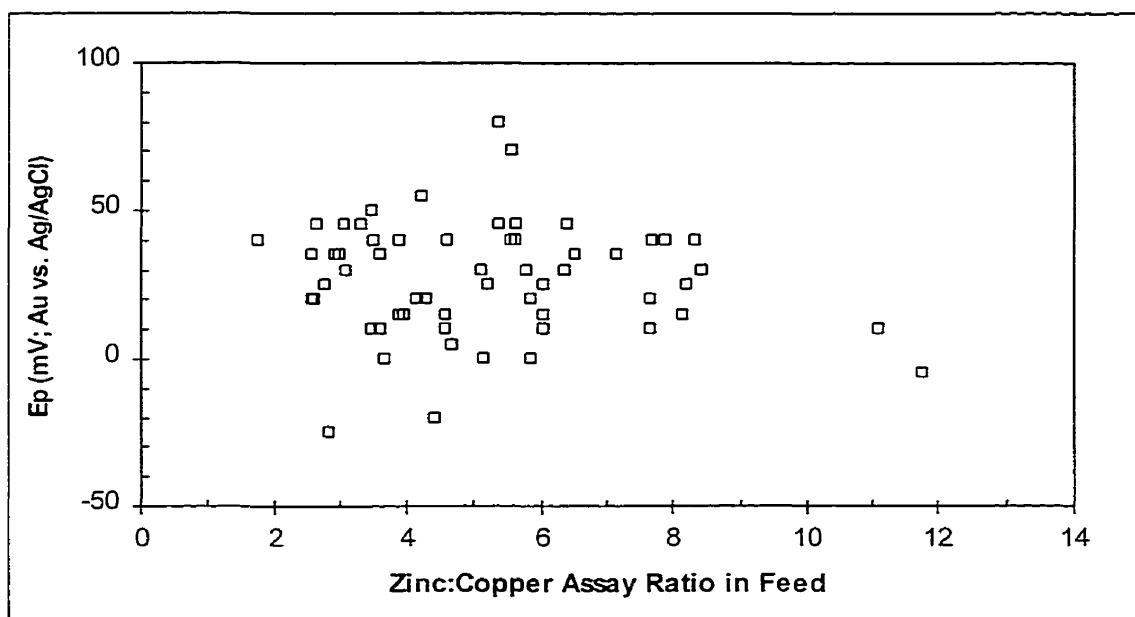
Figure 6.6 Relationship between the zinc recovery to the copper concentrate and the zinc to copper assay ratio in the mill feed: June 1989-February 1990



Given these relationships, one might expect to observe a trend between the measured pulp potential and the zinc to copper assay ratio in the mill feed as the operators would manipulate the flotation pH (better selectivity at higher pH) and the sodium cyanide dosage set-point accordingly to maintain the quality of the copper concentrate. A plot of

the measured pulp potential as a function of the zinc to copper assay ratio in the feed for the period of June to August 1989 is presented in Figure 6.7. This period corresponds to the window of selectivity presented in Figure 6.3. Unfortunately, no clear trend is visible in the data.

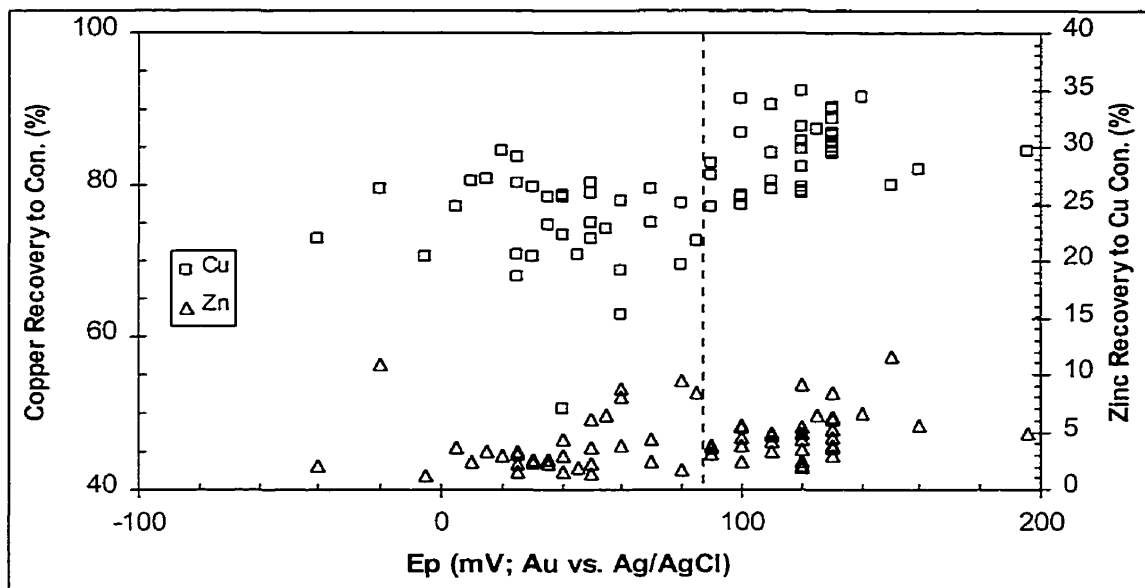
Figure 6.7 Relationship between the pulp potential and the zinc to copper assay ratio in the feed: June-August 1989



The copper and zinc recoveries to the copper concentrate as a function of the pulp potential over the period from September through November 1989 are shown in Figure 6.8. This time period corresponds to an upward trend in the measured pulp potential (Figure 4.22). The arrival of winter and contamination of the reference electrode of the pulp potential sensor were suggested as two possible causes for this upward trend.

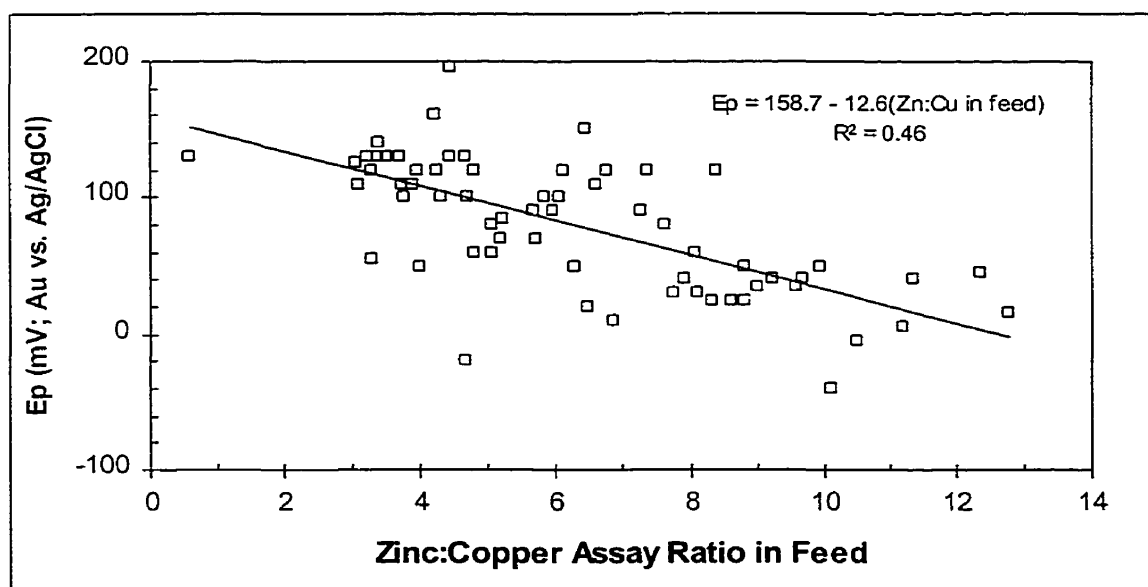
No clear window of copper/zinc selectivity can be observed in Figure 6.8. However, the data can be divided into two groups along a pulp potential of 85 mV (Au vs. Ag/AgCl). Below this value, trends similar to that observed earlier for the period from June through August 1989 (Figure 6.3) can be seen. Above this value, the only definite trend is one of increasing zinc recovery with increasing pulp potential.

Figure 6.8 Window of copper/zinc selectivity at Les Mines Selbaie: September - November 1989



All the factors discussed previously apply with one exception. For this time period, there is a clear trend between the measured pulp potential and the zinc to copper assay ratio in the feed as suggested by the data presented in Figure 6.9.

Figure 6.9 Relationship between the pulp potential and the zinc to copper assay ratio in the feed: September - November 1989

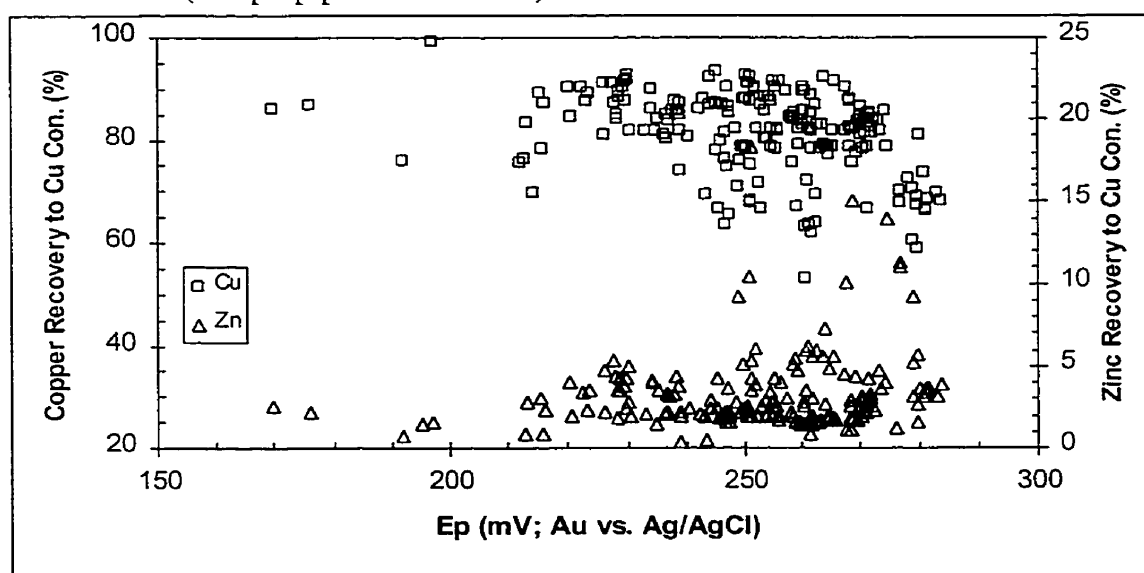


The higher pulp potentials in Figure 6.8 correspond to days for which the zinc to copper assay ratio in the feed was low and the process requirements for depression of sphalerite could be relaxed. Hence, there is a third plausible reason for the upward pulp potential trend from September through November in Figure 4.22. This one is simply related to the process itself.

From December 1989 through February 1990, the pulp potential measurements and the recoveries were available as hourly averages from the process control system. Three time periods of interest were selected and the corresponding windows of copper/zinc selectivity are shown in Figures 6.10 through 6.12. The data will not be analysed as extensively as for Figures 6.3 and 6.8. The aim here is to provide a flavour of the challenges facing the implementation of the technology in an operating plant.

In Figure 6.11, the time period covered is the week prior the pulp potential sensor was tested and determined not to respond properly (point B in Figure 4.22). It is noted that the copper and zinc recoveries to the copper concentrate follow similar trends as that already determined earlier for the period of June through August 1989 (Figure 6.3).

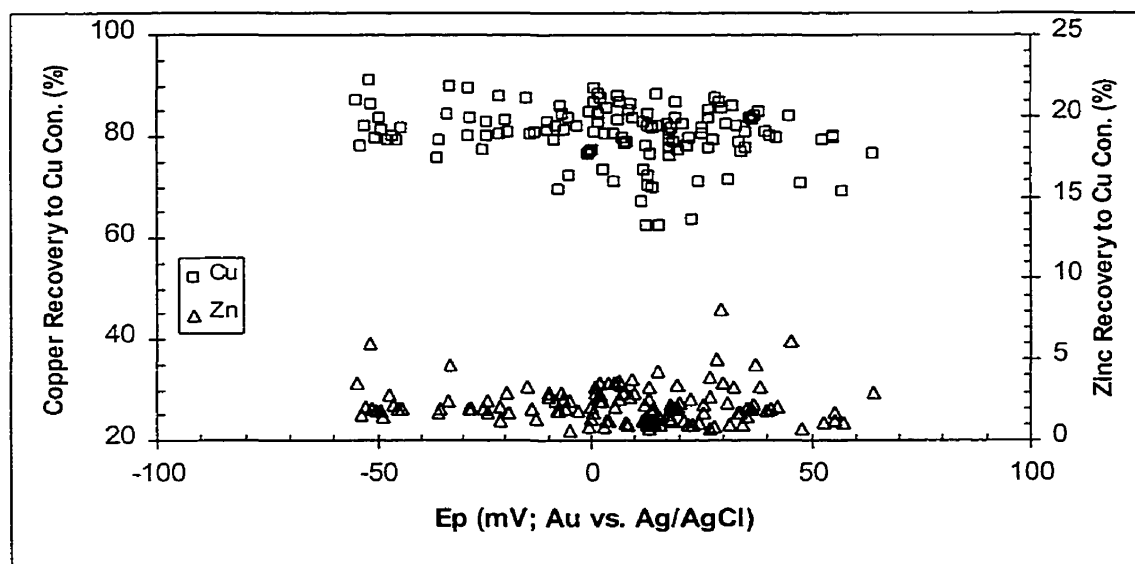
Figure 6.11 Window of copper/zinc selectivity at Les Mines Selbaie: December 1989 (bad pulp potential sensor)



However, the pulp potential at which copper recovery decreases rapidly, while zinc recovery starts to rise significantly, is now around 250 mV vs. Ag/AgCl rather than the 10 mV value determined previously (Figure 6.3). Hence, although the sensor was indicating an erroneous measurement (bias) due to a contamination of the reference electrode, relationships between copper and zinc recoveries and the pulp potential can still be observed.

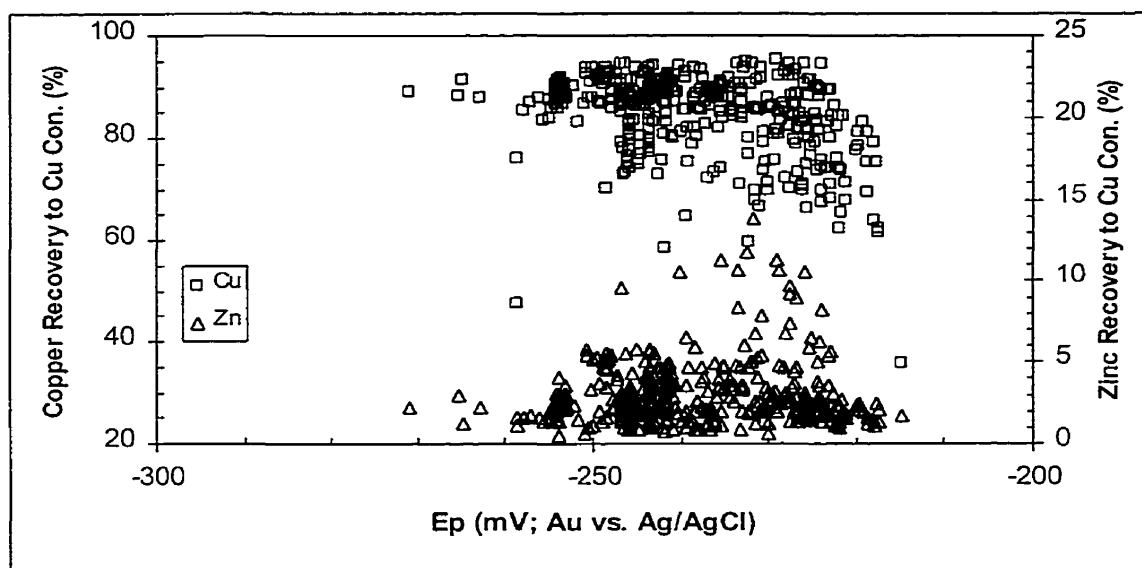
The window of copper/zinc selectivity after replacement of the on-line pulp potential sensor (point C in Figure 4.22) is shown in Figure 6.11. The copper recovery to the copper concentrate tends to decrease as the pulp potential rises above 0 mV vs. Ag/AgCl. Also, the zinc recovery tends to be more scattered, and slightly increasing as the pulp potential rises above 0 mV. These trends are however not as convincing as those observed earlier in Figure 6.3 but exhibit a similar limiting pulp potential for the highest copper/zinc selectivity. A thorough analysis (e.g. pulp potential vs. zinc to copper assay ratio in the feed as performed in Figure 6.9) might indicate the existence of other process factors affecting the window of selectivity.

Figure 6.11 Window of copper/zinc selectivity at Les Mines Selbaie: December 1989 (new pulp potential sensor)



Finally, the results for February 1990 are shown in Figure 6.12. During that time period, the on-line pulp potential had a contaminated reference electrode but no spare sensor was available for replacement. Relationships between copper and zinc recoveries and pulp potential can be observed and these are similar to those in Figures 6.3 and 6.11. However, the "optimum" pulp potential would appear to be around  $-250$  mV vs. Ag/AgCl rather than the initially observed  $10$  mV in Figure 6.3 and  $0$  mV in Figure 6.11. The situation is the same as that observed in Figure 6.10 with strong trends between recoveries and pulp potential but erroneous measurements due to a faulty sensor.

Figure 6.12 Window of copper/zinc selectivity at Les Mines Selbaie: February 1990



These results obtained over nearly a full year of on-line monitoring of the pulp potential indicate that gains in selectivity could be achieved if the pulp potential was maintained below the limiting value at which copper recovery starts to drop. Depending on the feed characteristics, zinc recovery to the copper concentrate may or may not increase when the pulp potential exceeds this threshold level.



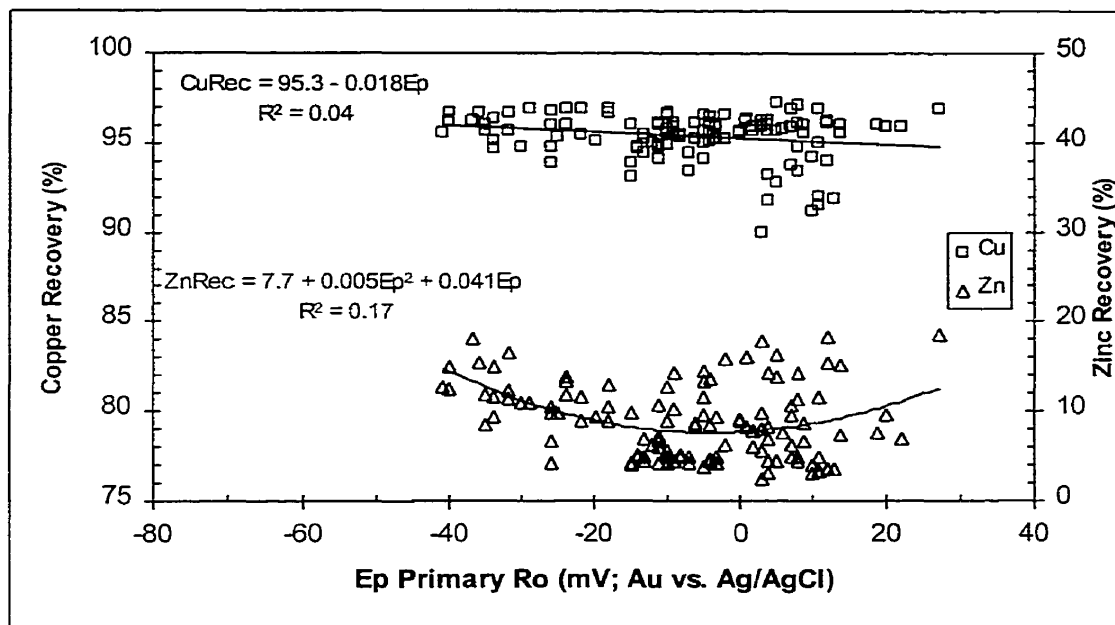
Maintaining the pulp potential below the threshold level could be achieved by modulating the dosages of reagents which are currently used for the process (e.g. lime and sodium cyanide). The success of such an approach would nevertheless be highly dependent on the quality of the on-line pulp potential probe and the establishment of an efficient preventive maintenance program for this electrode. Also, as with any other process variables in flotation, the impact of ore variability will be significant.

### 6.3 Kidd Creek

Figures 6.13 and 6.14 present different attempts to correlate the copper and zinc recoveries to the copper concentrate with the pulp potential measured in different locations of the circuit. These measurements were made daily over a period of one month.

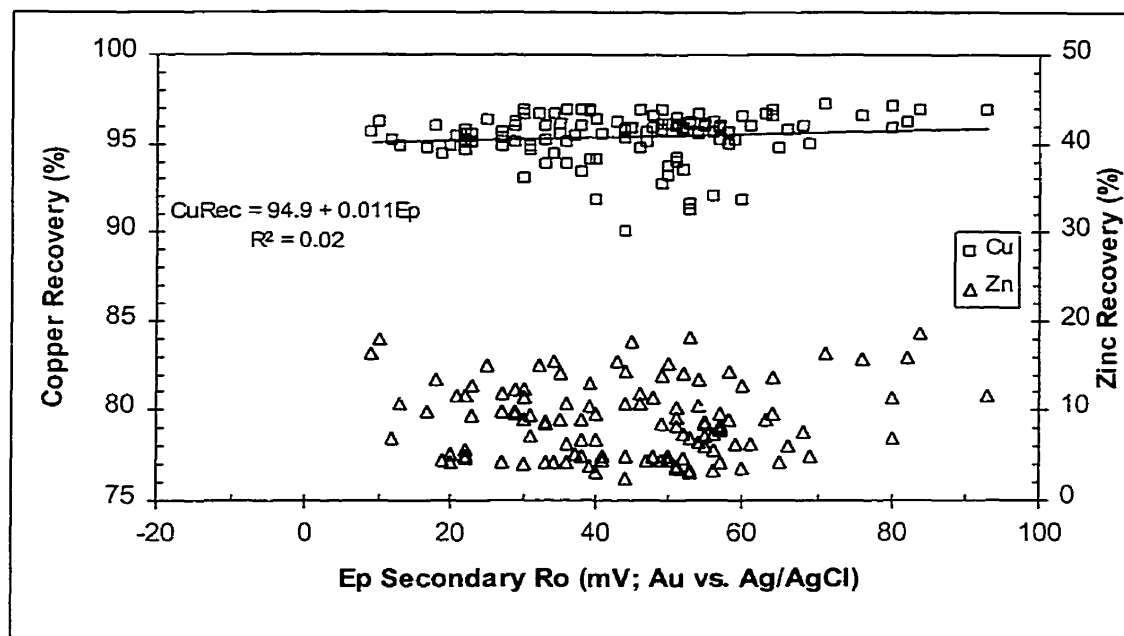
In Figure 6.13, the monitoring point was the feed box of the primary copper rougher. The average of the three parallel banks is reported. The relationship between copper recovery and the pulp potential is similar in general nature to the one observed at Les Mines Selbaie as the recovery to the copper concentrate drops if the pulp potential becomes higher than 0 mV vs. Ag/AgCl. The extent of at which copper recovery drops as the pulp potential increases is, however, not as marked as that observed at Les Mines Selbaie.

On the other hand, the apparent relationship between zinc recovery to the copper concentrate and the pulp potential differs from that observed previously. Zinc recovery appears to increase if the pulp potential decreases below -20 mV vs. Ag/AgCl, or increases if the pulp potential rises above 10 mV. However, the scatter in the data somewhat dampens any excitement which could be generated from this observation.

Figure 6.13 Window of selectivity at Kidd Creek using the  $E_p$  at the primary rougher

A different picture is observed when the pulp potential at the feed box of the secondary copper rougher (Figure 6.14). Namely, it would appear that the copper recovery increases with increasing pulp potential. However, this trend is very weak in comparison of the scatter in the data. No visible trend could be observed between zinc recovery to the copper concentrate and the pulp potential at the secondary copper rougher.

The potentials at the secondary copper roughers are significantly higher (5 to 95 mV vs. Ag/AgCl) than those at the primary copper roughers (-40 to 20 mV vs. Ag/AgCl) although the observed ranges tend to overlap. The higher potentials are due to the presence of a flotation stage, the Prefloat stage, between the secondary grind and the secondary roughers (Figure 3.19).

Figure 6.14 Window of selectivity at Kidd Creek using the  $E_p$  at the secondary rougher

The results in Figures 6.13 and 6.14 confirm that the best location for the on-line sensor is at the primary copper rougher with respect to copper recovery. On the other hand, the apparent relationship between zinc recovery to the copper concentrate and the pulp potential differs from that observed previously in that zinc recovery increases as the pulp potential moves on either side of a central value. This central value, around 0 mV vs. Ag/AgCl, corresponds to the pulp potential at which copper recovery tends to drop more rapidly with increasing potential.

In the absence of significant amounts of secondary copper minerals in the Kidd Creek ore, in-situ activation of sphalerite would not be the mechanism by which impedes copper/zinc selectivity in this case contrary to Les Mines Selbaie. It is possible that the observed relationship between the zinc recovery to the copper concentrate and the pulp potential at the primary rougher flotation stage is genuine. Only with an examination of other process variables such as ore characteristics and reagent dosages could this relationship be confirmed.

## 6.4 Conclusions

The use of the pulp potential is not the miracle solution to a selectivity problem in a copper-zinc concentrator.

The copper recovery to the final concentrate appears to drop with increasing pulp potential at the beginning of flotation. Limiting potentials of 10 mV vs Ag/AgCl and 0 mV have been observed at the A1 zone circuit of Les Mines Selbaie and the Kidd Creek Concentrator respectively. The similarity between these values is surprising considering the much higher copper feed assay at Kidd Creek (3.5% Cu) compared to Les Mines Selbaie (0.9% Cu).

It appears that a definite relationship between the zinc recovery to the final copper concentrate and the pulp potential exists only if in-situ activation of the sphalerite is the main mechanism for poor copper/zinc selectivity. When this relationship exists, it tends to indicate limiting pulp potentials for low zinc recovery which are nearly equal to those inferred for optimum copper recovery.

A conservative approach would be to maintain the pulp potential below the limiting value at which the copper recovery starts to drop. This could be achieved by modulating the dosages of reagents which are currently used for the process (e.g. lime and sodium cyanide).

The success of such a conservative approach would nevertheless be highly dependent on the quality of the on-line pulp potential probe and the establishment of an efficient preventive maintenance program for this electrode. Also, as with any other process variables in flotation, the impact of ore type variability will be significant.

## 7 CONCLUSIONS, RECOMMENDATIONS AND CONTRIBUTIONS TO KNOWLEDGE

### 7.1 Conclusions

#### 7.1.1 Significance of the pulp potential, $E_p$

Investigation of the behaviour of noble metal and mineral electrodes in mineral slurries and the determination of relationships between mineral floatability and measured potential, under various conditions of conditioning and flotation, have indicated that:

- i) The electrochemical potentials monitored in flotation slurries are mixed potentials involving the oxidation-reduction couples in the solution and those of the mineral particles when contacting the sensing electrode. As such, they cannot be readily related to thermodynamic quantities of the system (such as the standard potentials of reaction) unless the kinetics of all oxidation-reduction reactions occurring in the system are known.
- ii) The response of a potential sensing electrode immersed in a mineral slurry appears to be amenable to a model considering the relative capacitances of the surface of the electrode and the mineral particles. This model is however incomplete and does not account for all the responses observed.
- iii) The oxidation-reduction state of the mineral pulp, as indicated by the pulp potential measured using a suitable sensing-reference electrode pair, is conducive to flotation of a given mineral if this state is more oxidizing than that required for (i) induction of metal-deficient/elemental sulphur surface, (ii) adsorption of the collector on the mineral in galvanic contact with the other sulphide minerals in the system.
- iv) The sulphide minerals can be ranked in galvanic series by measuring the rest potentials of mineral electrodes immersed in a solution of the same pH as the flotation system. Rest potentials under aeration of the solution are indicative of the ranking for

collectorless flotation while those under aeration and collector addition are indicative of the ranking for conventional flotation. Those minerals with the lowest rest potentials will see their reactions and resulting floatability enhanced by galvanic contact with minerals with higher rest potentials.

v) Selective flotation of one mineral is generally achieved if the measured pulp potential is higher than that of its rest potential for the system considered but lower than that for the gangue sulphides. However, oxidation products such as metal ions can lead to a reduced selectivity if they can act as activators for the other sulphide minerals, for example copper ions and sphalerite.

vi) The use of gold as a suitable general material for laboratory and on-line pulp potential measurement has been confirmed. There are also practical advantages of gold electrodes over the ideally preferable mineral electrodes.

#### 7.1.2 Application of $E_p$ for modulation of flotation response of sulphide minerals

The laboratory and plant investigations performed demonstrated the possibility of modulating the flotation response indirectly by manipulation of the pulp potential via the addition rate of modifiers normally used in the process. A simple monitoring of the pulp potential while the process is manipulated allows for the determination of windows of selective flotation and which modifier is most effective in varying the pulp potential. Implementation of a control strategy would simply require a changeover for a rate based control loop (e.g. grams reagent per tonne of ore) to one involving a pulp potential set-point. Some limitations to this approach were observed:

- i) The on-line pulp potential sensor should be immersed in the process at or before the first point of addition of the collector. It is the oxidation-reduction state of the pulp at the instant of introduction of the collector which has the greatest impact on the selectivity of adsorption and resulting flotation.
  
- ii) The window of selectivity between two sulphide minerals is likely to be specific to a given ore and a given concentrator. Notably the leading edge, and width, of the windows were different between the A-1 zone ore of Les Mines Selbaie and the copper-zinc ore of the Kidd Creek Division of Falconbridge Limited.
  
- iii) Maintaining the on-line pulp potential sensor in good condition is crucial to the success of the approach.
  
- iv) Varying the proportion of mild steel grinding media in a mixed charge may be a practical way to manipulate the pulp potential for laboratory investigations. However, the pulp potentials and flotation response with a stainless steel charge are not an extrapolation of those obtained with mixed charges to zero percent mild steel.

### 7.1.3 Preventive maintenance for on-line pulp potential sensors

A survey of Canadian mining operations regarding the similar combination pH sensors, and experience gained during plant monitoring campaigns have indicated that contamination of the electrolyte and/or blockage of the porous junction of the reference electrode is the most frequent cause of failure of the on-line sensor. This was unexpected since from the literature, the main challenges indicated were poisoning of the potential sensing material and build-up of scale.

Consequently, sound procedures, capable of surviving short cuts often taken in an industrial environment were developed to test if the on-line sensor is in a state leading to give reliable measurements. Furthermore, the procedures are able to indicate which element of the electrode pair, the reference or the potential sensing electrode, is at fault when a poor state is observed.

If electrode poisoning and build-up of scale is problematic, schemes such as timed acid wash/water rinse and electrochemical conditioning of the sensor can be implemented. However, such schemes are not usually available from suppliers of sensors and have to be devised on a custom basis. The repeated attack of the surface of the potential sensing electrode by the acid or the strong oxidizing conditions required for electrochemical conditioning means that sulphide mineral electrodes could not be used for these applications.

## 7.2 Recommendations for future work

The present study has highlighted areas for further investigations. Some of these are of fundamental nature while the others are more related to the practical use in mineral processing laboratories and plants.

### 7.2.1 Fundamental work

i) With the exception of the xanthate and dithiophosphate collectors, there is very little information relating to the standard potential of more selective collectors and how it is affected by the length of the hydrocarbon chain such as the dithiophosphate collectors (e.g. Aerophine 3418A). Although thermodynamic calculations can be used to generate this information, there is a need for its experimental determination.



ii) The generation of galvanic series of the sulphide minerals in collector solutions would prove useful in screening suitable selective collectors (family and/or length of hydrocarbon chain).

iii) The semi-conducting properties of sulphide minerals are rarely investigated. There are indications that the form in which a collector is found on a mineral surface (either thiolate or di-thiolate) is related to the mode of conduction (n- or p-type, or degenerated to metallic). Also, when a sulphide mineral may exhibit n- or p-type conduction due to impurities in its lattice, this may impact the reaction rates. Particularly of relevance to the flotation system is the rate of oxygen reduction as it plays a significant role in single mineral and multi-mineral systems.

iv) Further investigations into the nature of charge/electron transfer during particle-electrode contacts, and how they affect the measured potential, would allow us to refine the suggested model based on the relative capacities of the electrode and particle surfaces.

### 7.2.2 Development of reagent control schemes

Although on-line pH electrodes have been used for the past thirty years in mineral processing plants, failure of the sensor is still the main cause of break-down of the process control loops based on pH. The experience gained at Les Mines Selbaie and Kidd Creek indicates that a similar situation will exist for pulp potential sensors no matter how well prepared the technical and instrumentation personal are.

On the positive side, even though an on-line sensor may drift badly over a period of time due to several reasons, there will still be a relationship between the flotation selectivity and the measured value. It is just that the measured value will be at an offset from the "true" value.

Redundancy of the measurements, either with one or more additional pulp potential sensors along the flotation circuit or with other process measurements, would increase the reliability of a reagent control schemes based on manipulation of the pulp potential. If for some reasons the critical sensor, that at the point of introduction of the collector, develops a fault, then its odd behaviour will become apparent before misleading the control loop.

### 7.2.3 Process control strategies

Using a differential pulp potential set-point rather than an absolute one may prevent the control loop from failing due to a large drift of a single pulp potential sensor. It would involve a smart control system to manipulate the set-point for a process optimization. An inherent advantage of this approach would be the capability to adjust to different ore types being processed. If the ideal pulp potential for selectivity for ore type A is say  $-75$  mV and the one for ore type B is  $-25$  mV, then by trying out moving the pulp potential by increments up to  $\pm 50$  mV from the initial value, it may be possible to self-adjust the control loop during variation of ore types. Compensation of a state with an erroneous sensor is required and this may mean a smart (expert-system like) control scheme which adjusts the potential set-point from its current measured value.

Inclusion of pulp potential measurements into advanced control systems involving neural networks, expert systems, along with other information such as machine vision for quantification of the froth character may provide a total control solution.

### 7.3 Contributions to knowledge

- i) Development of verification procedures applicable to on-line pulp potential sensors.
  
- ii) Confirmation of crucial process monitoring point, namely that the first introduction of the collector in the slurry for the establishment of mineral recovery vs. potential relationships.
  
- iii) Confirmation of gold as a suitable electrode material for pulp potential measurements.
  
- iv) Collectors which involve chelation during their adsorption process, such as the dithiophosphinates, may not be amenable to modulation of their selectivity via manipulation of the pulp potential after they have been introduced into the slurry.
  
- v) Varying the proportion of mild steel grinding media in a mixed charge may be a practical way to manipulate the pulp potential for laboratory investigations. However, the pulp potentials with a stainless steel charge are not an extrapolation of those obtained with mixed charges to zero percent mild steel.
  
- vi) Suggestion of capacitance-resistance model for charge/electron exchange during contacts between the mineral particles and the sensing electrode.

## REFERENCES

- 1 Rudashevsky, N.S., Burakov, B.E., Lupal, S.D., Thalhammer, O.A.R., Saini-Eidukat, B. Liberation of accessory minerals from various rock types by electric-pulse disintegration - method and application. *Trans. Instn Min. Metall.* Vol. 104, January-April 1995, pp C25-C29.
- 2 Sutherland, K.L., and Wark, I.W. *Principles of Flotation*, AusIMM, 1955, p. 232.
- 3 Plaskin et al. As quoted by Leja, J. in *Surface Chemistry of Froth Flotation*, Plenum, 1982, p. 501.
- 4 Ref. 2 p. 109.
- 5 Woods, R. Electrochemistry of sulphide flotation. Chap. 10 in *Flotation - A.M. Gaudin Memorial Volume*. (Ed. M.C. Fuerstenau). AIME, 1976, pp 298-333.
- 6 Woods, R. Electrochemistry of sulphide flotation. *Principles of Mineral Flotation. The Wark Symposium*, (Eds. M.H. Jones and J.T. Woodcock). AusIMM, 1984, pp 91-115.
- 7 Pang, J, and Chander, S. Oxidation and wetting behavior of chalcopyrite in the absence and presence of xanthates. *Minerals & Metal. Process.*, August 1990, pp 149-155.
- 8 Lepetic, V.M. Flotation of chalcopyrite without collector after dry, autogenous grinding. *CIM Bull.*, June 1974, pp 71-77.
- 9 Shannon, L.K. and Trahar, W.J. The role of collector in sulphide ore flotation. *Advances in Mineral Processing* (P. Somansundaran, Ed.), SME/AIME, New York, pp 408-425.
- 10 Senior, G.D. and Trahar, W.J. The influence of metal hydroxides and collector on the flotation of chalcopyrite. *Int. J. Miner. Process.* 33(1991):321-341.
- 11 MacPherson, A.R. and Turner, R.R. Autogenous grinding from test work to purchase of a commercial unit. Chap. 13 in *Mineral Processing Plant Design*. (A.L. Mular and R.B. Bhappu, Eds.). SME-AIME, 1978, p. 286.
- 12 Lo, W.W., Surges, L.J., Hancock, H.A. The preferential aqueous oxidation of sphalerite in a mixed sulphide tailing using manganese dioxide. *Complex Sulphides: Processing of Ores, Concentrates and By-Products*. TMS-AIME, 1985, pp 907-923.
- 13 Mizoguchi, T. and Habashi, F. Aqueous oxidation of zinc sulphide, pyrite and their mixtures in hydrochloric acid. *Trans. Instn Min. Metal.* 92(1983):C14-C19.

- 14 Rand, D.A.J. Oxygen reduction on sulphide minerals. Part III. Comparison of activity of various copper, iron, lead and nickel mineral electrodes. *J. Electroanal. Chem.* 83(1977):19-32.
- 15 Majima, H. How oxidation affects selective flotation of complex sulphide ores. *Can. Metall. Quart.* 78(1969):269-273.
- 16 Learmont, M.E., and Iwasaki, I. The effect of grinding media on flotation of galena. Preprint 84-84, *AIIME Annual Meeting*, Los Angeles, 1984.
- 17 Nakazawa, H., and Iwasaki, I. Effect of pyrite-pyrrhotite contact on their floatabilities. *Min. and Met. Proc.*, 2(1985):206-211.
- 18 Bozkurt, V., Xu, Z., Finch, J.A. Pentlandite/pyrrhotite interaction and xanthate adsorption. *Int. J. Miner. Process.* 52(1998):203-214.
- 19 Guy, P.J. and Trahar, W.J. The effects of oxidation and mineral interaction on sulphide flotation. *Flotation of Sulphide Minerals*. (Ed. K.S.E. Forssberg). Elsevier, 1985, pp 91-110.
- 20 Trahar, W.J. A laboratory study of the influence of sodium sulphide and oxygen on the collectorless flotation of chalcopyrite. *Int. J. Miner. Process.* 11(1983):57-74.
- 21 Gebhardt, J.E., Dewsnap, N.F., Richardson, P.E. Electrochemical conditioning of a mineral particle bed electrode for flotation. *U.S. Bureau of Mines*, RI-8951, 1985.
- 22 Robinson, D. and Walsh, F.C. The performance of a 500 Amp rotating cylinder electrode reactor. Part 1: Current-potential data and single pass studies. *Hydrometallurgy*, 26(1991):93-114.
- 23 Robinson, D. and Walsh, F.C. The performance of a 500 Amp rotating cylinder electrode reactor. Part 2: Batch recirculation studies and overall mass transport. *Hydrometallurgy*, 26(1991):115-131.
- 24 Vatistas, N.M., Batrolozzi, B.M. A three-dimensional current feeder for fluidized bed electrodes. *J. of Applied Electrochem.* 20(1990):951-954.
- 25 Casudo, A.S., and Casudo, C.S. Flotación selectiva de sulfuros por oxidación diferencial. *II Congreso Latino-americano de Flotación*, Universidad de Concepción, 19-23 Agosto, 1985, pp Lu 5.1-5.29.
- 26 Labonté, G. *Electrochemical Potentials in Flotation Systems: Measurement, Interpretation and Applications*. M.Eng. Thesis, McGill University, 1987, 174 p.
- 27 Dufresne, C., Deschêne, G., Cimon, D., Corrigan, J. Technical Note - Control of cyanidation at Yvan Vézina plant. *Min. Eng.* Vol. 7, No. 11, 1994, pp 1427-1434.

- 28 Woodcock, J.T. and Jones, M.H. Chemical environment in Australian lead-zinc flotation plant pulps: I. pH, redox potentials, and oxygen concentrations. *Proc. AusIMM* 235(1970):45-60.
- 29 Woodcock, J.T. and Jones, M.H. Chemical environment in Australian lead-zinc flotation plant pulps: II. Collector residuals, metals in solution, and other parameters. *Proc. AusIMM* 235(1970):147-183.
- 30 Johnson, N.W., Jowett, A., Heyes, G.W. Oxidation-reduction effects in galena flotation: observations on Pb-Zn-Fe sulphides separation. *Trans. Instn Min. Metal.* 91(1982):C32-C37.
- 31 Rumball, J.A. and Richmond, G.D. Measurement of oxidation in a base metal flotation circuit by selective leaching with EDTA. *Int. J. Miner. Process.* 48(1996):1-20.
- 32 Grano, S.R., Wong, P.L.M., Skinner, W., Johnson, N.W., Ralsont, J. The effect of autogenous and ball mill grinding on the chemical environment and flotation of the copper ore of Mount Isa Mines Limited, Australia. *A. Sutulov Memorial Volume, Vol. II Flotation* (S.Castro and J. Alvarez, Eds.), Universidad de Concepción, Concepción, Chile, 1994, pp 351-388.
- 33 Kant, C., Rao, S.R., Finch, J.A. Distribution of surface metal ions among the products of chalcopyrite flotation. *Minerals Engineering*, Vol. 7, No. 7,(1994):905-916.
- 34 Kant, C. The Effect of Pulp Potential and Surface Products on Copper Mineral Flotation. M.Eng. Thesis, McGill, 1997, 98 p.
- 35 Natarajan, K.A. and Iwasaki, I. Practical implications of Eh measurements in sulphide flotation circuits. *Trans. SME-AIME*, 254(1973):323-328.
- 36 Rand, D.A.J. and Woods, R. Eh measurement in sulphide mineral slurries. *Int. J. Min. Process.* 13(1984):29-42.
- 37 Neuharth, C.R., O'Dell, C.S., Walker, G.W. Development of an in-situ probe for monitoring redox conditions in commercial processing plants. *Mathematical Modelling of Materials Processing Operations* (J. Szekely, L.B. Hales, H. Henein, N. Jarrett, K. Rajamani, I. Samarsekera, Eds.), The Metallurgical Society, Inc, 1987, pp 247-256.
- 38 Richardson, P.E., Gebhardt, J.E., Rice, D.A., Yoon, R.H. Electrochemical control of sulphide flotation circuits. Ch. 32 in *Emerging Computer Techniques for the Minerals Industry*, (B.J. Scheiner, D.A. Stanley, and C.L. Karr, Eds.), 1993, SME, pp 307-317.
- 39 Labonté, G. and Finch, J.A. Measurement of electrochemical potentials in flotation systems. *CIM Bull.*, December 1988, pp 78-83.
- 40 Labonté, G. and Finch, J.A. Behavior of redox electrodes during flotation and relationship to mineral floatabilities. *Min. and Met. Process.* May 1990, pp 106-109.

- 41 Heimala, S., Jounela, S., Rantapuska, S., Saari, M. New potential controlled flotation method developed by Outokumpu Oy. XVth IMPC, Cannes 1985, pp 88-95.
- 42 Heimala, S., Himmi, M., Jounela, S., Sarri, M. The potential controlled flotation (OK-PCF) method in Outokumpu nickel concentrate production. Paper presented at the 25th Annual Conference of Metallurgists, CIM, Toronto, August 1986.
- 43 Hodgson, M., and Agar, G.E. The INCO-voltammetric cell: A new approach to flotation modelling. *Int. J. Mineral. Proc.* 24(1988):27-47.
- 44 Labonté, G., Lacombe, P., Ratnayake, S., Finch, J.A. Relating copper-zinc selectivity to the pulp potential. *Copper-91. Vol. II, Mineral Processing and Process Control* (G.S. Dobby, S.A. Argyropoulos, S.R.Rao, Eds.). Pergamon Press, 1991, pp 245-258.
- 45 Baker, M.W., Pietrobon, M.C., Ralston, J., Smart, R. St. C. Pulp potentials and flotation performance: Australian base metal sulphides. *Fourth Mill Operators' Conference, Aust. IMM*, 1991, pp 109-119.
- 46 Gorken, A., Nagaraj, D.R., Riccio, P.J. The influence of pulp redox potentials and modifiers in the flotation separation of complex sulfide ores with dithiophosphinate. *Electrochemistry in Mineral and Metal Processing III* (R. Woods, and P.E. Richardson, Eds.). The Electrochemical Society, 1992, pp 95-107.
- 47 Trahar, W.J., Senior, G.D., Shannon, L.K. Interactions between sulphide minerals - the collectorless flotation of pyrite. *Inter. J. Miner. Process.* 40(1994):287-321.
- 48 Cheng, X, and Iwasaki, I. Pulp potential and its implications to sulphide flotation. *Miner. Process. and Extract. Review*, 1992, Vol. 11, pp 187-210.
- 49 Leppinen, J.O., Hintikka, V.V., Kalapudas, R.P. Effect of electrochemical control on selective flotation of copper and zinc from complex ores. *Minerals Engineering*, Vol. 11, No. 1, 1998, pp 39-51.
- 50 Hintikka, V.V. and Leppinen, J.O. Potential control in the flotation of sulphide minerals and precious metals. *Minerals Engineering*, Vol. 8, No. 10, 1995, pp 1151-1158.
- 51 Pålsson, B.I. and Persson, H. Redox control in a pilot flotation column. *Minerals Engineering*, Vol. 9, No. 1, 1996, pp 73-83.
- 52 Standard Practice for Oxidation-Reduction Potential of Water, ASTM Standard D1498-93, ASTM Volume 11.01, 1993, pp 261-267 {Now available via Internet; pages refer to 1984 edition of Volume 11.01}
- 53 Instruction for use, E 512 pH-meter, Metrohm Ag, Switzerland.
- 54 Giesekke, E.W. A review of spectroscopic techniques applied to the study of interactions between minerals and reagent in flotation systems. *Int. J. Miner. Process.* 11(1983):19-56.

- 55 Marabini, A.M., Contini, G., Cozza, C. Surface spectroscopic techniques applied to the study of mineral processing. *Int. J. Miner. Process.* 38(1991):1-20.
- 56 Kartio, I., Laajalehto, K., Suoninen, E. Application of electron spectroscopy to characterization of mineral surfaces in flotation studies. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 93(1994):149-158.
- 57 Buckley, A.N. A survey of the application of X-ray photoelectron spectroscopy to flotation research. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 93(1994):159-172.
- 58 Chryssoulis, S.L., Stowe, K.G., Reich, F. Characterization of composition of mineral surfaces by laser-probe microanalysis. *Trans. Instn Min. Metall.*, Vol. 101, 1992, pp C1-C6.
- 59 Chryssoulis, S.L., Stowe, K.G., Niehuis, E., Cramer, H.G., Bendel, C. Detection of collectors on mineral grains by TOF-SIMS. 27th CMP, 1995, pp 186-201.
- 60 Stowe, K.G., Chryssoulis, S.L., Kim, J.Y. Mapping of composition of mineral surfaces by TOF-SIMS. *Minerals Engineering*, Vol. 8, No. 4/5, 1995:421-430.
- 61 Brinen, J.S., Greenhouse, S., Nagaraj, D.R., Lee, J. SIMS and SIMS imaging studies of adsorbed dialkyl dithiophosphinates on PbS crystal surfaces. *Int. J. Miner. Process.* 38(1993):93-109.
- 62 Nagaraj, D.R. and Brinen, J. SIMS study of adsorbed collector species on mineral surfaces. *SME Preprint #96-181*, 8 p.
- 63 Nagaraj, D.R. and Brinen, J. SIMS study of metal ion activation in gangue flotation. *XIX IMPC, SME*, 1995, pp 253-257.
- 64 Leppinen, J.O. FTIR and flotation investigation of the adsorption of ethyl xanthate on activated and non-activated sulfide minerals. *Int. J. Mineral Process.* 30(1990):245-263.
- 65 Persson, I., Persson, P., Valli, M., Fözö, S., Malmensten, B. Reactions on sulfide mineral surfaces in connection with xanthate flotation studied by diffuse reflectance FTIR spectroscopy, atomic absorption spectrophotometry and calorimetry. *Int. J. Mineral Process.* 33(1991):67-81.
- 66 Xu, Z., and Finch, J.A. Direct method for studying collector adsorption on minerals in mixed-mineral system. *Trans. Instn Min. Metall.*, 105, 1996:C197-199.
- 67 Kellar, J.J., Cross, W.M., Yalamanchili, M.R., Yong, C.A., Miller, J.D. Surface phase transitions of adsorbed collector molecules as revealed by in-situ FT-IR/IRS spectroscopy. *SME Preprint #92-88*, 10 p.



- 68 Leppinen, J.O, Basilio, C.I. Yoon, R.H. In situ FT-IR study of ethyl xanthate adsorption on sulphide minerals under conditions of controlled potential. *Int. J. Miner. Process.* 26(1989):259-274.
- 69 Bozkurt, V. , Brienne, S.H.R., Xu, Z., Rao, S.R., Butler, I.S., Finch, J.A. Technical Note - Development of in situ external reflection spectroscopy technique for adsorbed films. *Minerals Engineering*, Vol. 9, No. 3, 1996:351-355.
- 70 Laajalehto, K., Nowak, P., Suoninen, E. On the XPS and IR identification of the products of xanthate sorption at the surface of galena. *Inter. J. Miner. Process.* 37(1993):123-147.
- 71 Leppinen, J., Laajalehto, K., Kartio, I. Suoninen, E., FTIR and XPS studies of surface chemistry of pyrite in flotation. XIXth IMPC, SME, 1995, pp 35-38.
- 72 Heimala, S., Jounela, S., Saari, M. Flotation control with mineral electrodes. XVI IMPC (E. Forssberg, Ed.), Elsevier, 1988, pp 1713-1718.
- 73 Heimala, S., Pulkkinen, K., Jounela, S., Saari, M. Use of electrochemistry to control the flotation of metal sulphides. *Electrochemistry in Minerals and Metals Processing - II* (P.E. Richardson and R. Woods, Eds.), The Electrochemical Society, 1988, pp 170-182.
- 74 Lähteenmäki, S., Mustikkamäki, U-P., Laurial, H., Heimala, S., Jounela, S., Salminen, K. The use of the OK-PCF method to increase recoveries and grades of concentrates in flotation processes. Preprints - XVIIth IMPC, Volume I - Comminution and Classification - Modelling and Process Control, 1991, pp 345-356.
- 75 Barbery, G. and Cécile, J.L. Instrumentation for reagent control in flotation: present status and recent developments. *Advances in Mineral Processing.* (Ed. P. Somasundaram). SME, 1986, pp 726-739.
- 76 Anonymous. Notice de présentation du système PIRANA. BRGM document, 20 p.
- 77 Anonymous. Le système PIRANA dans l'usine de flottation de Salsigne. BRGM Report, 1988, 9 p.
- 78 Cécile, J.-L., Villeneuve, J., Belpaume, P. Exploitation d'un nouveau système de mesure et de contrôle des paramètres physico-chimiques des pulpes. *Industrie Minérale - Mines et Carrières - Les Techniques.* Mars-Avril 1988, pp 3-7.
- 79 Cécile, J.-L. and Villeneuve, J. Correlation between physico-chemical parameters and results in a flotation plant of sulphides: A new approach for the control of the process. *Int. J. Miner. Process.* 33(1991):185-191.
- 80 Tolley, W.K., Rice, D.A. Electrolytic cleaning and conditioning of gold redox probes in flotation circuits. SME Preprint 94-153, 6 p .

- 81 Tolley, W.K., Hall, R.R., Rice, D.A. Redox measurement in flotation. EPD Congress 1995, (G.W. Warren, Ed.), The Minerals, Metals & Materials Society, 1995, pp 411-420.
- 82 Suttill, K.R. Why are we content with ninety percent? Eng. & Mining J., November 1990, pp 26-29.
- 83 Jones, M.H. Some recent developments in the measurement and control of xanthate, perxanthate, sulphide, and redox potential in flotation. Int. J. Miner. Process. 31(1991):193-205.
- 84 Berglund, G. and Forssberg, E. Influence of different gases in flotation of sulphide minerals. Advances in Coal and Mineral Processing Using Flotation (S. Chander and R.R. Klimpel, Eds.), SME, 1989, pp 71-76.
- 85 Leroux, M., Rao, S.R., Finch, J.A., Gervais, V., Labonté, G. Collectorless flotation in the processing of complex sulphide ores. Advances in Coal and Mineral Processing Using Flotation (S. Chander and R.R. Klimpel, Eds.), SME, 1989, pp 65-71.
- 86 Ref. 2, p. 103.
- 87 Boyce, J.H., Wessel, J.V., Adam, J. Beneficiation practice at the Tsumeb concentrator. Lead & Zinc, Vol. 1. (D.O. Raush and B.C. Mariocher, Eds.). AIME, 1970, pp 542-570.
- 88 Hayes, R.A., Price, D.M., Ralston, J., Smith, R.W. Collectorless flotation of sulphide minerals. Mineral Process. and Extrac. Metal. Review, 2(1987):1-20.
- 89 Heyes, G.W. Trahar, W.J., The natural floatability of chalcopyrite. Int. J. Miner. Process.. 4(1977):317-344.
- 90 Trahar, W.J. The influence of pulp potential in sulphide flotation. Principles of Mineral Flotation - The Wark Symposium (M.H. Jones and J.T. Woodcock, Eds.), Aust. IMM, 1984, pp 117-135.
- 91 Hayes, R.A. and Ralston, J. The collectorless flotation and separation of sulphide minerals by Eh control. Int. J. Miner. Process. 23(1988):55-84.
- 92 Kocabag, D. and Smith, M.R. The effect of grinding media and galvanic interactions upon the flotation of sulphide minerals. Complex Sulphides: Processing of Ores, Concentrates and By-Products. TMS-AIME, 1985, pp 55-81.
- 93 Draskic, P., Gifing, M., Pavlica, J. Cyanide depression of naturally floating sphalerite in the presence of ferrous ions. Complex Sulphide Ores. (M.J. Jones, Ed.). Instn Min. Metal., 1980, pp 113-117.

- 94 El-Shall, H., Zucker, G., Lafftus, K. Electrochemical surface properties of molybdenite. *Electrochemistry in Minerals and Metal Processing*. (P.E. Richardson, S. Srinivasan, R. Woods, Eds.). The Electrochemical Society, 1984, pp 96-111.
- 95 Hoover, M.R. Water chemistry effects in the flotation of sulphide ores- a review and discussion for molybdenite. *Complex Sulphide Ores*. (M.J. Jones, Ed.). *Instn Min. Metal.*, 1980, pp 100-112.
- 96 Kocabag, D., Kelsall, G.H., Shergold, H.L. Natural oleophilicity/hydrophobicity of sulphide minerals, I. Galena. *Inter. J. Miner. Process.* 29(1990):195-210.
- 97 Kocabag, D., Kelsall, G.H., Shergold, H.L. Natural oleophilicity/hydrophobicity of sulphide minerals, II. Pyrite. *Inter. J. Miner. Process.* 29(1990):211-219.
- 98 Fuerstenau, M.C. and Sabacky, B.J. On the natural floatability of sulfides. *Int. J. Min. Process.*, 8(1981):79-84.
- 99 Kelebek, S. and Smith, G.W. Selective flotation of inherently hydrophobic minerals by controlling the air/solution interfacial tension. *Inter. J. Miner. Process.* 14(1985):275-289.
- 100 Yoon, R.H. Collectorless flotation of chalcopyrite and sphalerite ores using sodium sulfide. *Int. J. Miner. Process.* 8(1981):31-48.
- 101 Kelebek, S. and Huls, B.J. Collectorless flotation behaviour of chalcopyrite in the nickel-copper ores from Sudbury basin. *Copper-91*. Vol. II, *Mineral Processing and Process Control* (G.S. Dobby, S.A. Argyropoulos, S.R.Rao, Eds.). Pergamon Press, 1991, pp 171-186.
- 102 Heiskanen, K., Kirjavainen, V., Laapas, H. Possibilities of collectorless flotation in the treatment of pentlandite ores. *Int. J. Miner. Process.* 33(1991):263-274.
- 103 Senior, G.D. Trahar, W.J., Guy, P.J. The selective flotation of pentlandite from a nickel ore. *Int. J. Miner. Process.* 43(1995):209-234.
- 104 Fairthorne, G., Fornasiero, D., Ralston, J. Effect of oxidation on the collectorless flotation of chalcopyrite. *Int. J. Miner. Process.* 49(1997):31-48.
- 105 Rachenberg, H. *Neues Jahrb. Mineral., Monatsh.*, 1951, p. 88. As quoted by Majima (Ref. 15).
- 106 Chizhikov, D.M., and Kovylina, V.N. *Trudy Chetvertogo Soveshaniaya po Elektrokhemii*. Moscow, 1956 (Pub. 1959), p. 715. As quoted by Majima (Ref. 15).
- 107 Shuey, R.T. *Semiconducting Minerals*. Elsevier, 1975, p. 319.
- 108 Ahlberg, E. and Broo, A.E. Oxygen reduction at sulphide minerals. 1. A rotating ring disc electrode (RRDE) study at galena and pyrite. *Int. J. Miner. Process.* 46(1996):73-89.

- 109 Ahlberg, E. and Broo, A.E. Oxygen reduction at sulphide minerals. 2. A rotating ring disc electrode (RRDE) study at galena and pyrite in the presence of xanthate. *Int. J. Miner. Process.* 47(1996):33-47.
- 110 Ahlberg, E. and Broo, A.E. Oxygen reduction at sulphide minerals. 3. The effect of surface pre-treatment on the oxygen reduction at pyrite. *Int. J. Miner. Process.* 47(1996):49-60.
- 111 Ahn, J.H. and Gebhardt, J.E. Effect of grinding media-chalcopyrite interaction on the self-induced flotation of chalcopyrite. *Inter. J. Miner. Process.* 33(1991):243-262.
- 112 Luttrell, G.H. and Yoon, R.H. The collectorless flotation of chalcopyrite ores using sodium sulfide. *Int J. Min. Process.* 13(1986):271-283.
- 113 Craynon, J. Collectorless flotation of sphalerite ores. M.Sc. Thesis, Virginia Polytechnic Institute and State University. 1983.
- 114 Luttrell, G.H. and Yoon, R.H. Surface studies of the collectorless flotation of chalcopyrite. *Colloids and Surfaces*, 12(1984):239-254.
- 115 Gardner, J.R. and Woods, R. An electrochemical investigation of the natural floatability of chalcopyrite. *Int. J. Min. Process.*, 6(1979):6-16.
- 116 Buckley, A.N., Hamilton, I.C., Woods, R. Investigation of the surface oxidation of sulphide minerals by linear potential sweep voltammetry and X-ray photoelectron spectroscopy. *Flotation of Sulphide Minerals*. (K.S.E. Forssberg, Ed.). Elsevier, 1985, pp 41-60.
- 117 Hodgson, M., and Agar, G.E. Electrochemical investigations into the Inco lime aeration process for copper-nickel separation. *XVI IMPC* (E.Forssberg, Ed.), 1988, pp 637-649.
- 118 Tolley, W., Kotlyar, D., Van Wagoner, R. Fundamental electrochemical studies of sulfide mineral flotation. *Minerals Engineering*, 1996, pp 603-637.
- 119 Nicol, M.J. An electrochemical study of the interaction of copper(II) ions with sulphide minerals. *Electrochemistry in Mineral and Metal Processing*. (P.E. Richardson, S. Srinivasan, R. Woods, Eds.). The Electrochemical Society, 1984, pp 152-168.
- 120 Katagiri, A., Arai, H., Takehara, Z. Mechanism of the electro-oxidation of sulphite catalyzed by copper ion. *J. Electrochem. Soc.*, Vol. 142, No. 9, September 1995, pp 2899-2905.
- 121 Finkelstein, N.P. and Allison, S.A. The chemistry of activation, deactivation and depression in the flotation of zinc sulphide: a review. Chap. 14 in *Flotation-A.M. Gaudin Memorial Volume* (M.C. Fuerstenau, Ed.). *AIME*, 1976, Vol. 1, pp 417-457.
- 122 Leroux, M., Rao, S.R., Finch, J.A. Selective flotation of sphalerite from Pb-Zn ores without copper activation. Paper presented at the 25th CMP meeting, 1987.

- 123 Zhang, Q., Xu, Z., Brienne, S.H.R., Butler, I.S., Finch, J.A. The effect of iron ions on the flotation of sphalerite and pyrite. *Zinc & Lead '95*, pp 167-176.
- 124 Thorton, E. The effect of grinding media on flotation selectivity. *Proceedings, 10th CMP meeting, 1972*, pp 223-239.
- 125 Rey, M. *Memoirs of milling and process metallurgy: 2-flotation of sulphide ores.* *Trans. Instn Min. Met.*, 89(1980):C1-C6.
- 126 Presentation by Air Liquide, McGill University, March 1986.
- 127 Dodd, J., Dunn, D.J., Huiott, J.L. Norman, T.E. Relative importance of abrasion and corrosion in metal loss in ball mills. *Min. and Metal. Proc.* Nov. 1983, pp 212-216.
- 128 Natarajan, K.A. Ball wear and its control in the grinding of a lead-zinc sulphide ore. *Inter. J. Mineral. Process.* 34(1992)161-175.
- 129 Wood, K.R., and Duval, Luc. Mill expansion at Les Mines Selbaie. Paper presented at the 25th CMP Meeting, Jan. 1987.
- 130 Trahar, W.J. The influence of pulp potential in sulphide flotation. *Principles of Mineral Flotation - The Wark Symposium.* (M.H. Jones and J.T. Woodcock, Eds.). AusIMM, 1984, pp 117-135
- 131 Ekmekçi, Z. and Demirel, H. Collectorless flotation of chalcopyrite pyrite: influence of pulp potential, pH and galvanic contact. *XX IMPC*, (H. Hoberg, Ed.), Vol. 3: Flotation and other Physical-Chemical Processes, GMDB, 1997, pp 77-85.
- 132 Ekmekçi, Z. and Demirel, H. Collectorless flotation of Murgul (Turkey) copper ore. *Trans. Instn Min. and Metall.* Vol. 107, May-August 1998, pp C76-C81.
- 133 Woods, R. Flotation of Sulfide Minerals. *Reagents in Mineral Technology* (P. Somasundaran and B.M. Moudgil, Eds.). Marcel Dekker, Inc., 1988, pp 39-78.
- 134 Aplan, F. and Chander, S. Collectors for sulfide mineral flotation. *Reagents in Mineral Technology* (P. Somasundaran and B.M. Moudgil, Eds.). Marcel Dekker, Inc., 1988, p 335-370.
- 135 Chander, S. Inorganic depressants for sulfide minerals. *Reagents in Mineral Technology* (P. Somasundaran and B.M. Moudgil, Eds.). Marcel Dekker, Inc., 1988, pp 429-470.
- 136 Chander, S. and Gebhardt, J.E. Application of electrochemical techniques in sulfide mineral flotation. *Challenges in Mineral Processing* (K.V.S. Sastry and M.C. Fuerstenau, Eds.), SME, 1989, pp 90-108.
- 137 Ralston, J. The chemistry of galena flotation: principles & practice. *Minerals Engineering*, Vol. 7, Nos 5/6, 1994, pp 715-735.

- 138 Fuerstenau, M.C., Clifford, K.L., Kuhn, M.C. The role of zinc-xanthate precipitation in sphalerite flotation. *Inter. J. Miner. Process.*, 1(1974):307-318.
- 139 Allison, S.A., Goold, L.A., Nicol, M.J., Granville, A. A determination of the products of reaction between various sulfide minerals and aqueous xanthate solutions and a correlation of the products with electrode rest potentials. *Met. Trans.* 3(1972):2613-2618.
- 140 Rand, D.A.J. Oxygen reduction on sulphide minerals, Part III: Comparison of activities of various copper, iron, lead and nickel electrodes. *J. Electroanal. Chem.* 83(1977):19-32.
- 141 Ackerman, P.K., Harris, G.H., Klimpel, R.R., and Aplan, F.F. Evaluation of flotation collectors for copper sulfides and pyrite, I. Common sulfhydryl collectors. *Inter. J. Miner. Process.* 21(1987):105-127.
- 142 Ackerman, P.K., Harris, G.H., Klimpel, R.R., and Aplan, F.F. Evaluation of flotation collectors for copper sulfides and pyrite, III. Effect of xanthate chain length and branching. *Inter. J. Miner. Process.* 21(1987):105-127.
- 143 Mielczarski, J.A., Mielczarski, E., Cases, J.M. Influence of chain length of adsorption of xanthates on chalcopyrite. *Inter. J. Miner. Process.* 52(1998):215-231.
- 144 Biegler, T. Oxygen reduction at sulphide minerals. Part II. Relation between activity and semi-conducting properties of pyrite electrodes.
- 145 Richardson, P.E. and Maust, E.E, Jr., 1976. Surface stoichiometry of galena in aqueous electrolytes and its effect on xanthate interactions. In: M.C. Fuerstenau (Ed.), *Flotation. A.M. Gaudin Memorial Volume, AIME, New York*, pp 364-392.
- 146 Maust, E.E. and Richardson, P.E. Electrophysical consideration of the activation of sphalerite for flotation. U.S. Bureau of Mines. RI-8108, 1976, 22 p.
- 147 Vijh, A.K. *Electrochemistry of Metals and Semiconductors.* Marcel Dekker, Inc., N.Y., 1973.
- 148 Koch, D.F.A. *Electrochemistry of sulfide minerals. Modern Aspects of Electrochemistry (J.O'M Bockris and B.E. Conway, Eds.), Plenum Press, 1975*, pp 211-237.
- 149 Gertacher, H. *Z. Physik. Chem. N.F.*, 26, 223, 325(1960); 27, 48(1961). As quoted in Ref. 147.
- 150 Mishra, K.K. and Osseo-Asare, K. Aspects of the interfacial electrochemistry of semiconductor pyrite (FeS<sub>2</sub>). *J. Electrochem. Soc.*, Vol. 135, No. 10, October 1988, pp 2502-2509.

- 151 Dean, F.W.H. and Kelsall, G.H. Photoelectrochemical behaviour of chalcopyrite ( $\text{CuFeS}_2$ ) in alkaline solutions. *Electrochemistry in Mineral and Metal Processing III* (R. Woods, and P.E. Richardson, Eds.). The Electrochemical Society, 1992, pp 297-317
- 152 Rybas, V., Volkov, V., Ivanov, V., Mantsevich, M., Pnomarov, G. Ecological outlook for the new technology of the copper-nickel ore beneficiation based on the flotation with nitrogen. XVIIIth IMPC, Aust. IMM, 1993, pp 997-998.
- 153 Xu, M., Finch, J.A., Rao, S.R., Lin, D. Reverse flotation of pyrite from a zinc-concentrate using nitrogen. *Minerals Engineering*, Vol. 8, No. 10 1995, pp 1159-1173.
- 154 Fuerstenau, M.C., Natalie, C.A., Rowe, R.M. Xanthate adsorption on selected sulfides in the virtual absence and presence of oxygen. Part 1. *Inter. J. Miner. Process.* 29(1990):89-98.
- 155 Fuerstenau, M.C., Misra, M., Palmer, B.R. Xanthate adsorption on selected sulfides in the virtual absence and presence of oxygen. Part 2. *Inter. J. Miner. Process.* 29(1990):89-98.
- 156 Wang, S.S. and Avotins, P.V. The use of dialkyldithiophosphinates in sulfide flotation. Paper presented at the 111th AIME Meeting, Feb. 14-18, 1982, Dallas, Texas, 8 p.
- 157 Mingione, P.A. Use of Aerophine 3418A promoter for sulphide minerals flotation. *Proceedings 22nd CMP*, 1990, pp 485-507.
- 158 Basilio, C.I., Kim, D.S., Yoon, R.H. Interaction of thiophosphinate collectors with precious metals. *SME Preprint 92-174*, 7 p.
- 159 Almela, A., Elizalds, M. P. Interactions of metal extractant reagents Part VIII. Comparative aggregation equilibria of Cyanex 302 and Cyanex 301 in heptane. *Analytical Proceedings Including Analytical Communications*, Vol. 32, April 1995, pp 145-147.
- 160 Argekar, A.P, Shetty, A.K. Extraction and spectrophotometric determination of iron(III) with Cyanex 301. *Indian Journal of Chemistry*, Vol. 35A, September 1996, pp 806-808.
- 161 Pareau, D., Stambouli, M., Durand, G. Procédé novateur d'épuration d'effluents liquides industriels - exemples de l'élimination de métaux toxiques. *Récents Prog. Génie Procédés*, 1995, 9(143) *Boues Industrielles: Traitement Valorisation*. pp 111-116.
- 162 Calligaris, M., Nardin, G., Ripamonti, A. Crystal and molecular structure of Zinc(II) and cobalt(II) diethyldithiophosphinates. *J. Chem. Soc.* Vol. 5, (A), 1970, pp 714-722.
- 163 Kuchen, W. and Hertel, H. Metal complexes of thiophosphinic and selenophosphinic acids. *Angewandte Chemie (International Edition)* Vol. 8, No. 2, February 1969, pp 89-156.

- 164 Yordanov, N.D. A spectroscopic study of the self-redox reaction of sulphur-containing copper(II) complexes. *Transition Met. Chem.* 22, 1997, pp 200-207.
- 165 Yuan, X.-M., Pålsson, B.I., Forsberg, K.S.E. Flotation of a complex sulphide ore I. Cu/Zn selectivity control by adjusting pulp potential with different gases. *Int. J. Miner. Process.* 46(1996):155-179.
- 166 Yuan, X.-M., Pålsson, B.I., Forsberg, K.S.E. Flotation of a complex sulphide ore II. Influence of grinding environments on Cu/Fe sulphide selectivity and pulp chemistry. *Int. J. Miner. Process.* 46(1996):181-204.
- 167 Finkelstein, N.P. The activation of sulphide minerals for flotation: a review. *Inter. J. Miner. Process.* 52(1997):81-120.
- 168 Ralston, J., and Healy, T.W. Activation of zinc sulphide with Cu(II), Cd(II) and Pb(II): I Activation in weakly acidic media. *Int. J. Min. Process.*, 7(1980):175-201.
- 169 Ralston, J., and Healy, T.W. Activation of zinc sulphide with Cu(II), Cd(II), and Pb(II): II Activation in neutral and weakly alkaline media. *Int. J. Miner. Process.*, 7(1981):203-217.
- 170 Ralston, J., Alabaster, P., Healy, J.A. Activation of zinc sulphide with Cu(II), Cd(II) and Pb(II): III The mass-spectrometric determination of elemental sulphur. *Int. J. Miner. Process.* 7(1981):279-310.
- 171 Richardson, P.E., Hu, Q., Finkelstein, N.P. Yoon, R.-H. An electrochemical study of the flotation chemistry of sphalerite. *Int. J. Miner. Process.* 41(1994):71-76.
- 172 Yoon, R.-H. and Chen, Z. Electrochemical aspects of copper-activation of sphalerite. *Electrochemistry in Mineral and Metal Processing IV* (R. Woods, F.M. Doyle, P. Richardson, Eds.). The Electrochemical Society, 1996, pp 38-47.
- 173 Marinovich, Y., Bailey, S., Avraamides, J., Jayasekera, S. An electrochemical study of reduced ilmenite carbon paste electrodes. *J. Applied Electrochem.* 25(1995):823-832.
- 174 Ahlberg, E. and Åsbojörnsson, J. Carbon paste electrodes in mineral processing: an electrochemistry study of galena. *Hydromet.* 34(1993):171-185.
- 175 Ahlberg, E. and Åsbojörnsson, J. Carbon paste electrodes in mineral processing: an electrochemistry study of sphalerite. *Hydromet.* 36(1994):19-37.
- 176 Lázaro, I., Martínez-Medina, N., Rodríguez, I., Arce, E, González, I. The use of carbon paste electrodes with non-conducting binder for the study of minerals: Chalcopyrite. *Hydromet.* 38(1995):277-287.
- 177 Perry, D.L., Tsao, L., Tayler, J.A. Surface studies of the interactions of copper ions with metal sulphide minerals. *Electrochemistry in Mineral and Metal Processing.* (P.E. Richardson, S. Srinivasan, R. Woods, Eds.). The Electrochem. Soc., 1984, pp 169-184.



- 178 Baldwin, D.A, Menton, M.R., Pratt, J.M., Storey, M.J. Studies on the flotation of sulphides. I. The effect of Cu(II) ions on the flotation of zinc sulphides. *Int. J. Min. Process.*, 6(1979):173-192.
- 179 Goble, R.J., Whiteside, L.S., Ghazi, A.M. Geerite-type structures and the flotation of sphalerite. Submitted for publication to CIM, 1985.
- 180 Konigsmann, K.W. Flotation techniques for complex ores. *Complex Sulphides: Processing of Ores, Concentrates and By-products*. TMS-AIME, pp 10-18.
- 181 Bessière, J. and Bernasconi, P. Electrochemical study of sphalerite activation and deactivation in a complexing medium: role of potential. *Reagents in the Mineral Industry*. (M.J. Jones and R. Oblati, Eds.). *Instn Min. Metal.*, 1984, pp 291-294.
- 182 Prestidge, C.A., Ralston, J., St. C. Smart, R. The actions of cyanide in the flotation separation of base-metal sulphides. *Innovations in Mineral Processing* (Y. Tugut, Ed.), 1994, pp 67-97.
- 183 Yoon, R.H., Chen, Z., Finkelstein, N.P., Richardson, P.E. An electrochemical study of sphalerite activation by copper in acid solution. *XIXth IMPC*, Vol. 3, 1995, pp 297-301.
- 184 Pauporté, Th. and Schuhmann, D. An electrochemical study of natural enargite under conditions relating to those used in flotation of sulphide minerals. *Colloids and Surfaces*, 111(1996):1-19.
- 185 Schuhmann, D., Ndzebet, E., Pauporté, Th., Vanel, P. Impedance measurements with minerals under conditions similar to those in flotation, comparison of galena and enargite. *Electrochemistry in Mineral and Metal Processing III* (R. Woods, F.M. Doyle, P.E. Richardson, Eds.). *The Electrochem. Soc.*, 1996, pp 215-226.
- 186 Córdova, R., Gómez, H., Real, S.G., Schrebler, R., Vilche, J.R. Characterization of natural enargite/aqueous solution systems by electrochemical techniques. *J. Electrochem. Soc.*, Vol. 144, No. 8, August 1997, *The Electrochem. Soc.*, pp 2628-2636.
- 187 Tajadod, J. and Yen, W.T. A comparison of surface properties and flotation characteristics of enargite and chalcopyrite. *Proceedings XXth IMPC* (H. Hoberg, and H. von Blotnitz, Eds.), *GmDB Besellschaft für Bergbau, Metallurgie, Rohstoff-und Umwelttechnik*, Clausthal-Zellerfeld, Germany, 1997, pp 409-418.
- 188 Mielczarski, J.A., Mielczarski, E., Cases, J.M. Infrared evaluation of composition and structure of ethyl xanthate monolayers produced on chalcopyrite, tetrahedrite, tennantite at controlled potentials. *J. of Colloids and Interf. Science*, Vol. 188, 1997:150-161.
- 189 Marticorena, M.A., Hill, G., Kerr, A.N., Liechti, D., Pelland, D.A. INCO develops new pyrrhotite depressant. *Innovations in Mineral Processing* (Y. Turgut, Ed.), 1994, pp 15-33.

- 190 Klimpel, R.R., Hansen, R.D., Fee, B.S. Recent advances in new frother and collector chemistry for sulfide mineral flotation. In "Developments in Mineral Processing", Vol. 10B, K.S.E. Forssberg, Ed., Elsevier, Amsterdam, 1988, pp 1173-1184.
- 191 Pålsson, B.I. and Persson, H. Redox control in a pilot flotation column. Minerals Engineering, Vol. 9, No. 1, 1996:73-83.
- 192 Handbook of Chemistry and Physics, 60th edition, CRC Press, 1979, pp D155-D160.
- 193 Bockris, J.O'M. and Reddy, A.K.N. Modern Electrochemistry. Vol. 2, Plenum, p. 649.
- 194 Trasatti, S. The absolute electrode potential: an explanatory note. Pure & Appl. Chem. 58(1986):957-966.
- 195 Natarajan, K.A. and Iwasaki, I. Significance of Mixed Potentials in Eh measurements with platinum electrodes. Trans. SME-AIME, 255(1974):82-86.
- 196 Pålsson, B.I. and Forssberg, K.S.E. Computer-assisted calculations of thermodynamic equilibria in the galena-ethyl xanthate system. Int. J. Miner. Process., 23(1988):93-121.
- 197 Pålsson, B.I. and Forssberg, K.S.E. Computer-assisted calculations of thermodynamic equilibria in sphalerite-xanthate system. Int. J. Miner. Process., 26(1989):223-258.
- 198 Du Rietz, C., Chemisorption of collectors in flotation. 11th IMPC, Università di Cagliari, Cagliari, 1975, pp 375-403.
- 199 Michealis, L. as quoted in Ref. 65, pp 36-37.
- 200 Natarajan, K.A. and Iwasaki, I. Behaviour of platinum electrodes as Redox potential indicators in systems of metallurgical interest. Trans. SME-AIME, 247(1970):317-324.
- 201 Finch, J.A. and Labonté, G. Technical Note - Verification of electrodes for pulp potential measurement. Minerals Engineering, 2(1989):557-564.
- 202 Hintikka, V.V. and Leppinen, J.O. Potential control in the flotation of sulphide minerals and precious metals. Minerals Engineering, Vol. 8, No. 10, 1995:1151-1159.
- 203 Leppinen, J.O., Hintikka, V.V. and Kalapudas, R.P. Effect of electrochemical control on selective flotation of copper and zinc from complex ores. Minerals Engineering, Vol. 11, No. 1, 1998:39-51.
- 204 Saperstein, L.W. Fundamental research: Meeting the need in the minerals industry. Mining Engineer, Jan. 1997, pp 51-54.
- 205 Kastening, B. Properties of slurry electrodes from activated carbon powder. Ber. Bunsenges, Phys. Chem. 92(1988):1390-1402.

- 206 Kastening, B., Schiel, W., Henschel, M. Electrochemical polarization of activated carbon and graphite powder suspensions. Part I. Capacity of suspensions and polarization dynamics. *J. Electroanal. Chem.* 191(1985):311-328.
- 207 Kastening, B. and Spinzinger, S. Electrochemical polarization of activated carbon and graphite powder suspensions. Part II. Exchange of ions between electrolyte and pores. *J. Electroanal. Chem.* 214(1986):295-302.
- 208 Kastening, B., Busscher, N., Asskamp, U. Electrochemical polarization of activated carbon and graphite powder suspensions. Part III. Charge transfer during single collisions and contact resistance. *J. Electroanal. Chem.* 265(1989):77-101.
- 209 Muller, M., Kastening, B. The double layer of activated carbon electrodes. Part 1. The contribution of ions in the pores. *J. Electroanal. Chem.*, 374(1-2), 1994, pp 149-158.
- 210 Kastening, B., Hahn, M., Kremeskoetter, J. The double layer of activated carbon electrodes. Part 2. Charge carriers in the solid material. *J. Electroanal. Chem.* 374(1-2), 1994, pp 159-166
- 211 Kastening, B., Hahn, M., Rabanus, B., Heins, M., zum Felde, U. Electronic properties and double layer of activated carbon. *Electrochimica Acta*, Vol. 42, No. 18, 1997, pp 2789-2800.
- 212 Fleischmann, M., and Oldfield, J.W. Fluidised bed electrodes. Part I. Polarisation predicted by simplified models. *J. Electroanal. Chem.*, 29(1971):211-230.
- 213 Fleischmann, M., and Oldfield, J.W. Fluidised bed electrodes. Part II. The effective resistivity of the discontinuous metal phase. *J. Electroanal. Chem.*, 29(1971):231-240.
- 214 Fleischmann, M., Oldfield, J.W., Porter, D.F. Fluidised bed electrodes. Part III. The cathodic reduction of oxygen on silver in a fluidised bed electrode. *J. Electroanal. Chem.*, 29(1971):241-253.
- 215 de Ficquelmont-Loizos, M.M., Tamisier, L., Caprani, A. Mass transfer in laminar flow at a rotating disk electrode in suspensions of inert particles. I. Experimental investigation on the influence of the electrode, the medium, and the particle. *J. Electrochem. Soc.* Vol. 135, No. 3, March 1988, pp 626-634.
- 216 Caprani, A., de Ficquelmont-Loizos, M.M., Tamisier, L., Peronneau, P. Mass transfer in laminar flow at a rotating disk electrode in suspensions of inert particles. II. Theoretical evaluation of experimental results. *J. Electrochem. Soc.* Vol. 135, No. 3, March 1988, pp 635-642.
- 217 Fransaer, J., Bouet, V., Celis, J.-P., Gabrielli, C., Huet, F., Maurin, G. Perturbation of the flow of current to a disk electrode by an insulating sphere. *J. Electrochem. Soc.*, Vol. 142, No. 12, Dec. 1995, pp 4181-4189.
- 218 Preprint of Les Mines Selbaie at the 1989 CIM Annual General Meeting, Québec.

- 219 CIM Bulletin Issue on Les Mines Selbaie, May 1990.
- 220 Reed, L.E. The airborne electromagnetic discovery of the Detour zinc-copper-silver deposit, northwestern Québec. *Geophysics*, Vol. 46, No. 9, Sept. 1981, pp 1278-1290.
- 221 Bryce, R.C. Introduction. Ref. 218, 14 p.
- 222 Selbaie shifting to open pit operation. *The Northern Miner.*, January 25, 1993.
- 223 Sinclair, I.G.L and Gasparini, C. Textural relationship between hypogene and supergene ore minerals in the Detour deposit, Province of Quebec. *Econ. Geol.* Vol. 75, 1980, pp 470-477.
- 224 Deptuck, R., Wierzbicki, V., Squair, H. Geology of the Detour zinc-copper deposit-Brouillan Township, Quebec. *Precambrian Sulphide Memorial Volume, G.A.C. special paper no. 25, 1982, pp 319-342.*
- 225 Bouillon, J.J. Geology. Ref. 218, 9 p.
- 226 Barrie, C.T., Ludden, J.N., Green, T.H. Geochemistry of volcanic rocks associated with Cu-Zn and Ni-Cu deposits in the Abitibi subprovince. *Econ. Geol.*, Vol. 88, 1993, pp 1341-1358.
- 227 Larson, J.E. and Hutchinson, R.W. The Selbaie Zn-Cu-Ag deposits, Quebec, Canada: An example of evolution from subaqueous to subaerial volcanism and mineralization in an Archean caldera environment. *Econ. Geol.*, Vol. 88, 1993, pp 1460-1482.
- 228 Barrie, C.T. and Krogh, T.E. U-Pb zircon geochronology of the Selbaie Cu-Zn-Ag-Au mine, Abitibi subprovince, Canada. *Econ. Geol.* Vol. 91, 1996, pp 563-575.
- 229 Garcia, G.G. The Río Tinto Mines, Huelva, Spain. *The Miner. Record*, Vol. 27, July-August, 1996, pp 275-285.
- 230 Wong, K.Y., Breen, A.M., Doherty, R.J., Phelan, J.M. Flotation treatment of supergene complex sulphide ores at Thalanga. *Fourth Mill Operators' Conference, Aust. IMM, 1991, pp 205-211.*
- 231 Merlina, F.E. Phase analysis of enrichment ores for copper compounds. *Industrial Laboratories* Vol. 40, No. 3, 1974:314-316.
- 232 Cabri, L.J. and Harris, D.C. Comments on "silver-bearing chalcopyrite" from Garpengerg Norra. - *N. Jb. Miner. Mh.*, 1984, H. 8., pp 383-384.
- 233 Redmond, G., Holloway, P.H., Hovland, C.T., Olson, R.R. Bulk and surface silver diffusion related to tarnishing of sulfides. *Scanning Electron Microscopy, 1982, III, pp 995-1011.*

- 234 Redmond, G., Holloway, P.H., Kosakevitch, A., Ruzakowski, P., Packwood, R.H., Taylor, J.A. X-Ray Spectrometry, electron spectroscopies and optical microreflectometry applied to the study of ZnS tarnishing in polished sulfide ore specimens. *Scanning Electron Microscopy*, 1985, IV, pp 1305-1326.
- 235 Chen, T.T., Dutrizac, J.E., Owens, D.R., Laflamme, J.H.G. Accelerated tarnishing of some chalcopyrite and tennantite specimens. *Canadian Mineralogist*, Vol. 18, 1980, pp 173-180.
- 236 Jeppson, M. Photochemically accelerated surface-diffusion of silver on chalcopyrite, isocubanite and pyrrhotite. *Canadian Mineralogist*, Vol. 26, 1988, pp 973-978.
- 237 Craig, J.R., and Vaughan, D.J. Compositional and textural variations of the major iron and base-metal sulphide minerals. Sulphide deposits - their origin and processing. P.M.M. Gray, G.J. Bowyer, J.F. Castle, D.J. Vaughan and N.A. Warner, Eds. IMM, 1990, pp 1-16.
- 238 Hill, G.S., Rowlands, N., Finch, J. Correlation between colour and iron content in Pine Point sphalerites. *Econ. Geol.* Vol. 80, 1985, pp 2035-2037.
- 239 Les Mines Selbaie, A-1 Zone - Definitive Feasibility Study (Concentrator) Appendix IV, Book 1, April 1984, pp 1-4.
- 240 Wood, K. and Duval, L. Concentrator. Ref. 218, 30 p.
- 241 Lauder, J. and Swift, L. Automation at Selbaie's mill. Paper presented at the 89th Annual General Meeting of CIM, 1987.
- 242 Jowett, A. and Sutherland, D.N. Some theoretical aspects of optimizing complex mineral separation systems. *Int. J. Min. Process.*, 14(1985):85-109.
- 243 Wright, A. Flotation at Les Mines Selbaie. *Proceedings of the 27th CMP*, 1995, pp 119-135.
- 244 Auger, S., McDonald, S., Ward, K. Uniflot SP129 - Copper Sulphide Collector. *Proceeding of the 24th CMP*, 1992, Paper 20, 17 p.
- 245 del Villar, R., Soto, H., Lacombe, P. Column flotation circuit design at Les Mines Selbaie. *Column '91* (G.E. Agar, B. J. Huls, D.B. Huma, Eds.), CIM, 1991, pp 149-163.
- 246 Negery, T., Wilson, J., Chevalier, G. Investigation of Les Mines Selbaie sphalerite flotation characteristics by surface and solution analysis techniques. *Proceedings of the 29th CMP*, 1997, Paper 11, pp 117-145.
- 247 Basin, C. and Perry, R. Mass flow prediction for reagent control at Les Mines Selbaie. *Proceedings of the 25th CMP*, 1993, Paper 31, 15 p.

- 248 McIvor, R.E., "Technoeconomic Analysis of Plant Grinding Operations, Ph.D. Thesis, McGill University, 1988.
- 249 McIvor, R.E., Lavallée, M.L., Wood, K.R., Blythe, P.M., Finch, J.A. Functional performance, characteristics of ball milling. *Mining Engineering*, March 1990, pp 269-276.
- 250 Perry, R., and Hall, M. Les Mines Selbaie semi-autogenous grinding circuit expert system. *Proceedings of the 26th CMP*, 1994, Paper 19, 24 p.
- 251 Cousins, B.G. and Macphail, R.S. Improvement of recoveries from copper bearing and copper-activated mineral ores using FLEX 31. *Minerals Engineering*, Vol. 9, No 5, (1996):509-518.
- 252 Thompson, B.A., Amsden, M.P., Chapman, C. Texasgulf Canada Ltd. - Kidd Creek Concentrator. *Milling Practice in Canada. CIM Special Volume 16 (D.E. Pickett, W.S. Hall, G.W. Smith, Eds.)*. CIM, 1978, pp 194-200.
- 253 The Kidd Concentrator, Orientation Manual, June 1988, 33 p.
- 254 Kidd's 30th Anniversary 1966-1996 - 106 Million tonnes and Counting! Supplement to the June 1996 Issue of *Canadian Mining Journal*. Patrick Whiteway, Ed. Pp 13-15 for geology, pp 50-53 for mill.
- 255 Constable, D.C. High-stability cathodes for fuel batteries. *J. Electrochem. Soc.*, 18(1971):1391-1393.
- 256 Sato, M. Oxidation of sulphide ore bodies, I. Geochemical environments in terms of Eh and pH. *Econ. Geol.* 55(1960):1202-1231.
- 257 Sato, M. Oxidation of sulphide ore bodies, II. Oxidation mechanism of sulphide minerals at 25 oC. *Econ. Geol.* 55(1960):1202-1231.
- 258 Hansuld, J.A. Oxidation potential of pyrite, Ph. D. Thesis, Geological Sciences, McGill University, Nov. 1961, 152 p.
- 259 Natarajan, K.A. and Iwasaki, I. Effect of poisoning of platinum electrode on Eh measurements. *Trans. SME-AIME*, 254(1973):323-328
- 260 Zhou, R. and Chander, S. Effect of pretreatment on Eh response of a gold electrode. *Advances in Coal and Mineral Processing using flotation*. (Eds., S. Chander and R.R. Klimpel), SME, 1989, pp 57-64.
- 261 Zhou, R. and Chander, S. A comparison of gold, platinum and sulphide ion selective electrodes as sensors for Eh measurement in sulphide solutions. *SME*, 1990, Preprint 90-156.

- 262 Molodkina, E.B., Tsirlina, G.A., Danilov, A.I., Plukarov, Y.M., Kazrinov, V.E. Relaxation phenomena in the surface layers of platinum electrodes. *Soviet Electrochem.*, 1990, pp 473-477.
- 263 Gerth, L., Lopicque, F. Importance of surface preparation in electrochemical investigations of the copper system in dilute copper sulphate solutions. *J. Electrochem. Soc.*, Vol. 143, No. 12, Dec. 1996, pp 3910-3917.
- 264 Carro, P., Hernández Creus, A., Schilardi, P., González, S., Salvarezza, R.C., Arvia, A.J. Topographic changes of polycrystalline Ag and Cu electrodes in acid aqueous solutions resulting from a prolonged application of the potential reversal technique. *J. Electrochem. Soc.* Vol. 143, No. 7, July 1996, pp 2294-2305.
- 265 Agar, G.E. *Electrochemistry of Flotation - Professional Development Seminar - Department of Mining and Metallurgical Engineering - McGill University, May 18-19, 1990.*
- 266 Natarajan, K.A. and Iwasaki, I. Behaviour of platinum electrodes as Redox potential indicators in systems of metallurgical interest. *Trans. SME-AIME*, 247(1970):317-324.
- 267 de Ficquelmont, A.M. and de Ficquelmont-Loizos, M.M. Influence of dissolved molecular oxygen on the time dependence of blockage in the methanol/electrolyte/rotating disk electrode system. *J. Electrochem. Soc.* 131(1986):2880-2887.
- 268 Jones, M.H. and Woodcock, J.T. Optimization and control of laboratory sulphidization of oxidized copper ores with an ion selective electrode. *Proc. AusIMM*, 266(1978):11-19.
- 269 Hecker, C.C., Castro, S.F., Sepúlveda, J.V. Comportamiento del electrodo específico de Ag/Ag<sub>2</sub>S en pulpas de flotación. *II Congreso Latinoamericano de Flotación*, 1985, pp Mi5.1-5.13.
- 270 Jones, M.H. and Woodcock, J.T. Applications of pulp chemistry to regulation of chemical environment in sulphide mineral flotation. *Principles of Mineral Flotation. The Wark Symposium.* (Eds. M.H. Jones and J.T. Woodcock). *AusIMM*, 1982, pp 147-183.
- 271 Buck, R.P. *Electrochemistry of ion-selective electrodes. Sensors and Actuators*, 1(1981):197-260.
- 272 Kelsall, G.H. and Thompson, I. Redox chemistry of H<sub>2</sub>S oxidation in the British Gas Stretford Process - Part I: Thermodynamics of sulphur-water systems at 298 K. *J. Applied Electrochem.* 23(1993):279-286.
- 273 Kelsall, G.H. and Thompson, I. Redox chemistry of H<sub>2</sub>S oxidation in the British Gas Stretford Process - Part II: Electrochemical behaviour of aqueous hydrosulphide (HS<sup>-</sup>) solutions. *J. Applied Electrochem.* 23(1993):287-295.

- 274 Breiter, M.W. Electrochemical formation and dissolution of different types of copper layers on platinum. *J. Electrochem. Soc.*, Vol. 113, No. 11, Nov. 1967, pp 1125-1129.
- 275 Azarchenko, T.L., Maskimov, Yu.M., Schönfb, D., Podlovchenko, B.I., Müller, L. Effect of copper adatoms on process of hydrogen evolution at platinum electrodes. *Russian Journal of Electrochemistry*, Vol. 29, No. 9, 1993, pp 949-951.
- 276 Mikhailova, A.A., Osetrova, N.V., Vasil'ev, Yu.B. Comparison of the influence of tin and lead adatoms on different electrochemical reactions at Platinum. *Russian Journal of Electrochemistry*, Vol. 25, No. 12, 1989, pp 1445-1449.
- 277 Beltowskae-Brzezinska, M., Luczak, T., Holze, R. Electrocatalytic oxidation of mono- and polyhydric alcohols on gold and platinum. *J. of Applied Electrochem.* 27(1997):999-1011.
- 278 Richard, K.M., and Gewirth, A.A. Observation of electrode poisoning during the electro-oxidation of aromatic alcohols on (111)Au. *J. Electrochem. Soc.* Vol 143, No. 7, July 1996, pp 2088-2092.
- 279 Tripković, A.V., Marinković, N., Popović, K.Dj., Adžić, R.R. Oxidation of methanol on single crystal platinum electrodes in alkaline solution. *Russian J. of Electrochem.* Vol. 31, No.,10, 1995, pp 993-1003.
- 280 Natarajan, K.A. and Iwasaki, I. Significance of Mixed Potentials in Eh measurements with platinum electrodes. *Trans. SME-AIME*, 255(1974):82-86.
- 281 Biegler, T., Rand, D.A.J., Woods, R. Oxygen reduction on sulphide minerals Part I. Kinetics and mechanisms at rotated pyrite electrodes, *J. Electroanal. Chem. Interfacial Electrochem.*, 60(1975):151-162.
- 282 Burke, L.D. and O'sullivan, J.F. The stability of hydrous oxide films on platinum. *J. of Applied Electrochem.* 21(1991):151-157.
- 283 Damjanovic, A. Mechanistic analysis of oxygen electrode reactions. *Modern Aspects of Electrochemistry*, No. 5 (J.O'M. Bockris and B.E. Conway, Eds.), Plenum Press, New York, 1969, pp 369-483.
- 284 Schuldiner, S., Warner, T.B., Piersma, B.J. Potentiostatic current-potential measurements on a platinum electrode in a high-purity closed system. *J. Electrochem. Soc.*, Vol. 114, No. 4, April 1967, pp 343-349.
- 285 Birss, V.I. and Damjanovic, A. Oxygen evolution at platinum electrodes in alkaline solutions I. Dependence on solution pH and oxide film thickness. *J. Electrochem. Soc.*, Vol. 134, No. 1, January 1987, pp 113-117.
- 286 Sharratt, M. Robustness of pH probes in process usage. Use and abuse of modern measuring equipment, *North Western Branch Papers 1991 No. 2*, Institution of Chemical Engineers, pp 6.1-6.15.



- 287 Nichols, M.L. Improve the performance of pH measuring loops. *Chemical Engineering Progress*, Dec. 1994, pp 64-67.
- 288 Stevens, J.L. pH electrode maintenance and care. *American Laboratory*, Vol. 29, No. 17, Aug. 1997, pp 16-18.
- 289 Labonté, G. Industrial pH Electrodes - A report on a survey - May 30, 1990, 10 p.
- 290 Will, F.G. A self-contained miniature hydrogen reference electrode. *J. Electrochem. Society*, Vol. 133, No 2, 1986, pp 454-455.
- 291 Checking the condition of platinum or gold electrodes used for redox-potential measurements. *Metrohm. Application-Bulletin No. 48e*, August 26, 1966 (Revised October 1977).
- 292 Ragot, J., Aitouche, A., Kratz, F., Maquin, D. Detection and location of gross errors in instruments using parity space technique. *Int. J. Miner. Process.* 31(1991)281-299.
- 293 Myers, M.A. and Luecke, R.H. Short Note - Process control applications of an extended Kalman filter algorithm. *Computers Chem. Engng*, Vol. 15, No. 12, (1991):853-857.
- 294 Suichies, M., Leroux, D., Dechert, C., Trusiak, A. Model predictive control of the flotation process. *Proceedings of the 31st CMP, 1999*, pp 425-441.
- 295 Van Der Walt, T.J., Van Deventer, J.S.J., Barnard, E. Neural nets for the simulation of mineral processing operations: Part I. Theoretical Principles. *Minerals Engineering*, Vol. 6, No. 11, (1993):1127-1134.
- 296 Van Der Walt, T.J., Van Deventer, J.S.J., Barnard, E. Neural nets for the simulation of mineral processing operations: Part II. Applications. *Minerals Engineering*, Vol. 6, No. 11, (1993):1135-1153.
- 297 Laine, S., Lappalainen, H., Jämsä-Jounela, S.-L. On-line determination of ore type using cluster analysis and neural networks. *Minerals Engineering*, Vol. 8, No. 6, 1995:637-648.
- 298 Whitely, J.R, and Davis, J.F. Knowledge-based interpretation of sensor patterns. *Computers chem. Engng.* Vol. 16, No. 4, 1992, pp 329-346.
- 299 Moolnan, D.W., Aldrich, C., van Deventer, J.S.J., Stange, W.W. Digital image processing as a tool for on-line monitoring of froth in flotation plants. *Minerals Engineering*, Vol. 7, No. 9, 1994:1149-1162.
- 300 Moolman, D.W., Eksteen, J.J., Aldrich, C., van Deventer, J.S.J. The significance of flotation froth appearance for machine vision control. *Int. J. Miner. Process.* 48(1996):135-158.

- 301 Hargrave, J.M., Miles, N.J., Hall, S.T. The use of grey level measurement in predicting coal flotation performance. *Minerals Engineering*, Vol. 9, No. 6, 1996:667-674.
- 302 Moolman, D.W., Alldirch, C., Schmitz, G.P.J., van Deventer, J.S.J. The interrelationship between surface froth characteristics and industrial flotation performance. *Minerals Engineering*, Vol. 9, No. 8, 1996:837-854.
- 303 Moolman, D.W., Eksteen, J.J., Aldrich, C., van Deventer, J.S.J. The significance of flotation froth appearance for machine vision control. *Int. J. Miner. Process.* 48(1996):135-158.
- 304 Dowling, E.C., Klimpel, R.R., Aplan, F.F. Model discrimination in the flotation of a porphyry copper ore. *SME Preprint #84-144*, 64 p.
- 305 Agar, G.E, Stratton-Crawley, R., Bruce, T.J. Optimizing the design of flotation circuits. *CIM Bulletin*, Vol. 73, No. 824, 1980:173-191.