Electrochemical Potentials in Flotation Systems:
Measurement, Interpretation and Applications

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ABSTRACT

Electrochemical effects occuring in the processing of complex sulphide ores from the A-1 and B zones of Les Mines Selbaie, Joutel, Québec, were investigated and correlated with the redox potentials measured in flotation pulps, on a laboratory and plant scale. Observed discrepencies between different redox sensing electrodes (black platinum, platinum, gold, chalcopyrite and galena) and the different shapes for the noble metal electrodes (spiral, foil) were explained using the mixed potential model for electrochemical reactions, and a stochastic model to account for the particulate nature of a mineral slurry.

It was found that in the absence of flotation air, or in the presence of air and reducing agents (Na_2S, $FeSO_4$, NaCN), the potential exhibited by a gold spiral was the nearest (difference less than 10 mV) to that of a chalcopyrite electrode for mineral slurries. However, the use of oxidizing agents such as $KMnO_4$ or pH modifers (HCl, CaO) yielded discrepencies from 30 to 209 mV between the same two electrodes. Interpretation of the flotation response in terms of the redox potential was rendered more difficult by the effect of the grinding conditions and the complexity of the chemical systems created by the addition of the modifiers.

RESUME

Le traitement des minerais sulfurés des zones A-1 et B de Les Mines Selbaie, Joutel, Québec, a été étudié par une approche électrochimique de la flottation, tant en laboratoire qu'en usine. Les écarts observés, lorsque différentes électrodes de mesure du potentiel d'oxidation-réduction (platine poreux, platine, or, chalcopyrite, galène) étaient immergées simultanément dans les pulpes de flottation, sont expliqués à l'aide du modèle du potentiel mixte des réactions électrochimiques complexes et d'un modèle stochastique tenant compte de la nature particulaire d'une pulpe minéralisée.

Il a été observé qu'en l'absence d'air de flottation, ou qu'en la présence d'air et d'agents réducteurs (Na_2S, NaCN, $FeSO_4$), le potentiel mesuré à l'aide d'une spirale d'or était le plus près (écart moindre que 10 mV) de celui mesuré à l'aide d'une électrode de chalcopyrite. Par contre, l'utisation d'agents oxydants tels que le permanganate de potassium ou de modification du pH (HCl, CaO) engendrait un écart significatif, de 30 à 209 mV, entre ces deux mêmes électrodes. L'interprétation de la réponse métallurgique par une approche électrochimique est en plus compliquée par la présence d'effets induits par les conditions de broyage et par la complexité des conditions chimiques propres à la flottation.

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CONVENTIONS

The convention used for the description of the electrochemical couples and the standard electrode potentials is that of the International Union of Pure and Applied Chemistry (IUPAC). The convention defines the implicit charge-transfer reaction in the statement of a standard potential of an electrode reaction as a reduction (electronation).

Unfortunately, the American convention is used in most of the references cited. In the American convention, the implicit charge transfer reaction is an oxidation (de-electronation). In certain cases the explicit statement of the electrode reaction is an oxidation, but the standard potential of the electrode reaction is given according to the IUPAC convention.

The potential axis for the cyclic voltammograms described in the present thesis (Figs. 23 to 28) is the potential applied to the electrode; the potentiostat following the American convention. The sign of the applied potential must be inversed so that it can be related to the standard electrode potentials (IUPAC).

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INTRODUCTION

Froth flotation is the major separation process by which sulphide minerals are beneficiated from ores. The process consists in introducing gas bubbles into a pulp made of the finely ground ore and water, which has been previously conditioned with surfactants and modifiers. The mineral particles which have been rendered hydrophobic during the conditioning step attach to the rising gas bubbles and are recovered as a concentrate in the froth phase floating on top of the pulp. The hydrophilic particles remain in the pulp and make up the tailings. The concentrate recovered is usually of the desired mineral, but sometimes it is easier to perform a reverse flotation in which non-desired minerals are floated.

This is a simple description of the ideal flotation process. In practice, the ore cannot be ground fine enough to fully liberated the different minerals and this limits the quality of separation which can be ultimately achieved. Depending on the type of flotation machine, fine hydrophilic particles are mechanically entrained into the froth further decreasing the quality of the concentrate. Also, the type of frother (surfactant) used to stabilize the froth during the recovery process may influence the quality of separation.

Finally, the way in which the minerals are conditioned for flotation has a great impact upon the selectivity of the process. This is the aspect of the flotation process which is addressed in this thesis. Particularly, the oxidation-reduction phenonema occuring prior to, or during flotation are examined.

Oxidation-reduction effects in the flotation of sulphide minerals have been kwown since the 50's. For example, an early process describes the separation of pyrite from pyrrhotite and arsenopyrite by selective oxidation of the latter minerals with potassium permanganate (1). However, it is only recently that prototype commercial control equipment has become available to modulate the flotation response by methods based on oxidation-reduction potentials (2, 3, 4, 5). This time gap is due to the complexity of a general analysis of sulphide flotation from an electrochemical approach. Moreover, the absence of a reliable and accepted technique to measure the potential in a flotation pulp appears to have been a determining factor, especially for applications in mineral processing plants.

1. Overview of the flotation process from an electrochemical approach

The hydrophobic character of a mineral may be induced by a monolayer surface product, often covering less than 5% of the mineral surface (6). This is the case for collector dosages normally used in industry (7). Consequently, the study of electrochemical phenomena is more difficult for flotation than for other systems.

Until recently, the only reaction which was known to proceed by electrochemical steps was that of the adsorption of collectors of the xanthate family. The overall reaction can be viewed as a two step process, with the mineral serving as a source and sink of electrons (8):

Cathodic reduction of oxygen (electronation):

$$O_2 + 2\,H_2O + 4\,e^- = 4\,OH^- \qquad [1]$$

Anodic oxydation (de-electronation) and adsorption of the xanthate, X^-, ($R\text{-}O\text{-}CSS^-$, where R is a hydrocarbon chain):

$$X^- = X_{ads.} + e^- \qquad [2]$$

More complex mechanisms have been proposed (9) but the reactions just described show the requirement of oxidizing conditions for the collector to be adsorbed onto the mineral surface. The dissolved oxygen content of the flotation pulp (air in the flotation gas) normally provides these conditions.

The oxidation-reduction dependence of the adsorption of xanthate onto the sulphide minerals taken individually is relatively well understood (9). However, an ore contains more than one sulphide mineral. Also, wet grinding is performed with the grinding media being either the ore itself (autogenous and pebble milling), or steel (rod and ball milling) (10). Hence, it may be expected that interactions between the minerals and the grinding media, and the minerals themselves will occur. These interactions are galvanic and each half-reaction occurs on a different material with the electron transfer occuring during contacts between the two materials.

The presence of a galvanic couple often yields reaction rates which are higher than if each of the two materials where separated. For example, sphalerite (ZnS) is leached by acids at a faster rate when pyrite (FeS_2) is present then when it is by itself (11, 12).

The presence of galvanic interactions in flotation may be beneficial or detrimental depending on the minerals in presence. In some instances, the desired mineral is depressed because of the presence of the couple. Such is the case of galena which is depressed when grinding is performed with a mild steel media (13). Sometimes, it is the flotation of the non-desired sulphide mineral which is enhanced, for example pyrrhotite in pyrite/pyrrhotite separation (14).

Flotation in the absence of collectors may be induced by electrochemical reactions (15, 16, 17). It has been shown that if the ore is collectorlessly floatable, its flotation will be selective while the use of a collector will yield a non-selective flotation, and modifiers are required to regain the original selectivity (18).

When one of the two minerals in the couple is highly soluble it is possible that the ions introduced in the solution will affect the flotation behavior of the other mineral. One laboratory demonstration of this effect is in the flotation of mixtures of chalcocite (Cu_2S) and pyrite (FeS_2) where the presence of pyrite promotes the dissolution of the chalcocite which releases copper ions in solution causing the activation of pyrite (19).

On the positive side, the adverse effect of the mixture could be inhibited by electrochemical conditioning (application of an electric potential to the minerals) (19). This is an interesting and valuable application resulting from an understanding of the electrochemical processes occuring in flotation.

Two means are available for the application of a desired potential to a mineral system. The first one 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 (8, 9, 15, 17). 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 (1), or sodium peroxide (20).

For both modulation methods, the modification to the system must be well controlled. Hence, the need for a reliable method to measure the electrochemical potentials. Unfortunately, few investigations have been made in this area, particularly on the type of electrode to be used, and apparently conflicting techniques have been proposed (2, 5).

2. 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 as for the B-zone ore.

The general objective was to investigate the possibilities of reagent control by electrochemical methods. It was thus required to define oxidation-reduction conditions which would reduce the degree of in-situ activation of the sphalerite. The most important specific objective was to determine the proper method for monitoring the electrochemical potential in the flotation pulp.

3. Method of attack

The task was approached concurrently with investigations on the effects of the grinding media and flotation modifiers on the response of the ore while developing the needed monitoring techniques. Particular attention was brought to the presence of five different ore types within the A-1 zone ore with possible distinct mineral characterics. Microscopic examinations and microprobe analyses were performed for this purpose.

To study the extreme case of in-situ activation of sphalerite by soluble copper minerals, the B-zone material was also investigated. A better understanding of the activation mechanism of sphalerite was required so that it might be possible to inhibit in-situ activation, and perform deactivation of previously activated sphalerite.

In order to determine a reliable monitoring technique for electrochemical potentials in flotation pulps, noble metal and mineral electrodes were studied simultaneously. To investigate the sensitivity of the measurement to the shape of the noble metal electrode, foil, spiral, and black platinum electrodes were designed and tested. Comparison of the measurements permitted the selection of the proper electrode for investigations in flotation.

1. ELECTROCHEMICAL EFFECTS IN SULPHIDE FLOTATION

1.1 Introduction

Investigation into electrochemical phenomena in the flotation of sulphide minerals has seen an impressive growth in the recent years. It seems that the re-discovery of flotation in the absence of collector initiated the interest. As a result of these investigations, clarifification of old concepts and an introduction of new ones have been made. These concepts will be reviewed.

There appear to be three modes of genuine flotation for sulphide minerals. The first two occur in the absence of collector. Namely, the mineral is either inherently hydrophic or is induced into hydrophicity by its environment. These two modes can be observed in the laboratory with a non-negligeable fraction of the minerals being recovered after a few minutes of flotation with the addition of 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 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 (21).

1.2 Natural floatability

The inherent flotability of sulphide minerals has always been questioned. Contact angle studies in the 30s showed that sulphide minerals were not inherently hydrophobic since hydrophobicity without collector seemed to be induced by surface contamination (22).

However, 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 Cu-Pb-Zn ore at the Tsumeb concentrator (23). Also, it was later observed that flotation in the absence of collector occured after dry autogenous grinding (18).

Further studies showed that collectorless flotation occuring after comminution was only possible if the environment was mildly oxidizing (17). Hence, this could not be related to natural floatability as this property is expected to be independent of the conditions prevailing prior to flotation.

Actually there is one sulphide mineral which is inherently hydrophobic: molybdenite (MoS_2) (24). The hydrophobic character originates from the crystal structure of the mineral and its prefered 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 in comminution. The sulphur atoms, which are hydrophobic are then exposed on the surface. Molybdenite can be depressed in the presence of iron and aluminum hydroxides (25), but the mechanism involved is the adsorption of the hydroxides within the electrical double layer of the particles in water.

Even though it can be showed that the other sulphide minerals expose sulphur atoms upon cleavage, the observation of flotation under reducing conditions is possible only if oxygen has been completely excluded from the system (26). The mineral surfaces expose both sulphur and metal atoms so that only a mild hydrophobic character is imparted to the mineral. This delicate balance appears to be tipped in favor of a hydrophilic character by the formation of hydroxides following exposure to oxygen.

1.3 Collectorless flotation

Collectorless flotation refers to the hydrophobicity acquired by electrochemical interaction with the environment. This can be induced trough simple oxidation occuring during grinding (15, 18) or by sodium sulphide/aeration conditioning of the ore (16). Most sulphide minerals are individually amenable to collectorless flotation with varying degrees of difficulty (27).

The normal mechanism for collectorless flotation is that of the anodic oxidation of the sulphide mineral. Considering a metal sulphide,

$$MS = M(II) + S + 2e^- \qquad [3]$$

The M(II) ion usually goes into solution. Its fate depends on the chemistry of the system. It may remain in solution, be complexed, or be precipitated.

Reaction [3] involves the complete oxidation of sulphur atoms from sulphide through elemental sulphur. The hydrophobic character of the surface is attributed to the resulting elemental sulphur layer (or fraction of a layer) in acid solutions (28).

Further studies have shown that full oxidation does not occur in alkaline solutions, but rather a metal deficient surface is formed (29). This is a fundamental difference but the net result, namely an induced hydrophobicity following oxidation, is the same.

The complementary cathodic reaction depends on the particular system. In an aerated pulp it will be the cathodic reduction of oxygen (reaction [1]) and in a solution containing Fe(II) and Fe(III) ions,

$$\text{Fe(III)} + 1\ e^- = \text{Fe(II)} \qquad [4]$$

Other cathodic reactions may occur but the two described are possibly the most common in regard to the chemistry of flotation pulps.

There are at least two minerals for which the anodic reaction preferentially produces the sulphate ion instead of elemental sulphur: pyrite and arsenopyrite. These exceptions are still unexplained (G. Demopoulos, communication Jan. 1986). However, Nicol (30) showed that in the presence of cupric ions, elemental sulphur can be formed on pyrite. The cupric ion appears to act as a catalyst.

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 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, selectivity will be reduced.

Sphalerite usually requires copper activation to be recovered by a collector (31). In some circumstances, it is possible to float sphalerite without prior copper activation when small amounts of ferrous ions are present (32).

However, sphalerite when ground in ceramic mill will exibit collectorless recoveries over 90% (33). This can be easily confused with "natural floatability" (34) and in-situ activation of the sphalerite. Since these latter causes of flotation can be repressed by the use of cyanide and ferrous ions (34), i.e. reducing conditions, it is likely that most of the earlier work on sphalerite flotation would have to be critically reviewed with respect to the test conditions.

It can be noted that when sphalerite is ground in a mild steel mill, negligeable collectorless flotation is observed (33). The same occurs when iron, zinc, or magnesium metal is added to a ceramic or a stainless steel mill (33).

Some insight into what is occuring during grinding may be inferred from the rest potentials of the minerals and the grinding media in presence. Table 1 presents rest potentials for the minerals of the A-1 zone and steel media. It can be observed that pyrite has the highest rest potential while steel has the lowest.

Table 1. Rest potentials for A-1 zone minerals at pH 7 in water (section 3.2.3) and mild steel (13).

Mineral or system	Rest potential (mV vs SHE)
Pyrite	276 to 281
Chalcopyrite	189 to 195
Galena	142 to 195
Sphalerite	Could not be measured
Mild steel:	
oxygen flushing	-17
air flushing	-41
nitrogen flushing	-481

For a mineral taken on an individual basis, the lower the rest potential, the more readily it is oxidized. However, when a galvanic couple is formed by the contact of two different minerals (or materials), the one having the highest rest potential will permit the cathodic reduction of oxygen, while the other one will be oxidized (reaction [3]).

The situation is more difficult to rationalize for a complex Cu-Pb-Zn-Fe sulphide ore since all four minerals are present. The only certainty is that pyrite will not be oxidized while galena will experience the highest degree of oxidation (of the four minerals).

The influence of the grinding media on the presence or absence of collectorless flotation can be explained. In a ceramic or a stainless steel laboratory mill/media, the sulphide minerals are exposed to the oxygen from the air entrapped in the mill. Similarly, the same would occur on a plant scale autogenous or pebble mill. The conventional rod/ball milling circuit would yield reducing conditions similar to laboratory grinding with a mild steel media.

Hence, collectorless flotation would be expected when grinding is performed in an autogenous mill while grinding with the more conventional rod/ball milling circuit should not give rise to collectorless flotation.

This generalization could be misleading as the "self-float" recovery observed at the Tsumeb concentrator was following rod/ball mill grinding (23). The predomicance of chalcocite (Cu_2S) for the copper minerals might have been a determining factor for this ore. Also, the major gangue mineral, dolomite or silica, may alter the expected flotation behavior in relation to the grinding environment (35).

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 (36). 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 (37).

Sodium sulphide could be utilized instead of nitrogen but it may also induce collectorless flotation given the appropriate conditions (17, 38, 39) and is best discussed separately. Performing comminution under reducing conditions may be advantageous. However, if conventional or collectorless flotation is desired, the pulp will have to be oxidized to a value of the redox potential depending on the ore or mineral (15, 38).

1.4 Collectorless flotation in the presence of sodium sulphide.

Yoon investigated the use of sodium sulphide to induce collectorless flotation of chalcopyrite and sphalerite ores (16). Further work has been done among his research group (38, 39) and elsewhere (17).

As with the collectorless flotation induced during comminution, oxidizing conditions are required after the sodium sulphide conditioning for flotation to occur; the minimum potential for flotation being 0 mV vs SHE (Pt sensing electrode) (17, 38, 39).

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 on the surface of the minerals which induces the hydrophobic character in alkaline conditions (40). Elemental sulphur was also found on the surface but in too small an amount to account for the observed hydrophobicity at high pH.

From a practical view point, the importance of these findings does not lie in the different proposed mechanisms or hydrophic surface layers in alkaline pulps, but rather in the fact that in both cases flotation occurs only at potential equal or greater than 0.0 V vs SHE. Too high an oxidizing condition, e.g. a potential higher than 0.250 V vs SHE, leads to the suppression of flotation in the case of galena (17). Furthermore, an ion selective electrode might be better than a platinum electrode to control and optimize the sulphidization and subsequent oxidation process (41, 42).

1.5 Activation and deactivation of sphalerite

Normally, sphalerite flotation requires activation with a heavy-metal cation. This cation is usually Cu(II). Even though the overall reaction may be considered as an ion exchange, there seems to be experimental evidences that the activation of sphalerite proceeds through one or more electrochemical steps (31, 43). Similarly, deactivation may proceeds through electrochemical steps (31).

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 (30). 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 (43, 44, 45).

Considering a simplified mechanism for the formation of a copper sulphide surface layer on sphalerite:

$$ZnS = Zn(II) + S + 2\ e^- \qquad [5]$$

$$ZnS + 2\ Cu(II) + 2\ e^- = Zn(II) + Cu(I)_2S \qquad [6]$$

$$Cu(I)_2S + S + 2\ e^- = 2\ Cu(II)S \qquad [7]$$

Under alkaline conditions, both ions would be precipitated as their hydroxides, $Cu(OH)_2$ and $Zn(OH)_2$, onto the sphalerite surface. Depending on the occurence of reaction [7], the overall reaction might be:

$$2\ ZnS + 2\ Cu(II) = 2\ Zn(II) + Cu(I)_2S + S \qquad [8]$$

or

$$2\ ZnS + 2\ Cu(II) = 2\ Zn(II) + 2\ Cu(II)S \qquad [9]$$

Both overall reactions do not violate the 1:1 Zn:Cu molar ratio observed for the activation of sphalerite (31). The two proposed overall reactions stem from the controversy regarding the nature of the product layer: chalcocite, Cu_2S (46), cupric sulphide/covellite, CuS (31), or copper doped sphalerite, (Zn,Cu)S, (43, 44, 45, 47, 48). This last product would be more consistent with the semi-conducting properties of sphalerite (48, 49).

However, it is easier for mineral processors to deal with "mineral type" product layers rather than with a copper doped sphalerite surface.

Goble et al. (50) showed that the flotation behavior of copper-activated sphalerite is extremely similar to that of digenite ($Cu_{1.8}S$). The flotation behavior of the non-activated sphalerite is, on the other hand, similar to that of covellite. They further discussed that, from crystallography, the formation of a covellite layer is less likely than the formation of a geerite type ($Cu_{1.6}S$) layer.

Furthermore, if one considers some plant results, it would be unlikely that the activation layer is covellite (51). For the ore treated, SO_2 was used as a sphalerite depressant but about 0.1 by weight of covellite was also present. The SO_2 attacked the covellite hereby releasing copper ions into solution which then caused activation of the sphalerite. Is would be difficult to explain this behavior if the activating layer was covellite, for it too would be attacked by SO_2.

Activation may be prevented by complexing agents, e.g. cyanide (31). On the other hand, de-activation of sphalerite is more difficult to achieve than prevention of activation (31, 52).

Assuming chalcocite as activation product, copper must be oxidized to re-enter into solution (50):

$$Cu_2S \rightarrow Cu_{1.6}S + 0.4\ Cu(II) + 0.8\ e^- \qquad [10a]$$

$$Cu_{1.6}S \rightarrow CuS + 0.6\ Cu(II) + 1.2\ e^- \qquad [10b]$$

$$CuS = Cu(II) + S + 2\ e^- \qquad [11]$$

The Cu(II) ions must then be prevented from re-activating sphalerite. This is best achieved by complexing agents such as cyanide. For cyanide, the complexing reaction is (with excess cyanide):

$$Cu(II) + 3\ (CN)^- + 1\ e^- = Cu(CN)_3^{-2} \qquad [12]$$

However, the residual elemental sulphur on the sphalerite surface would give rise to collectorless flotation. This could be avoided by further oxidizing the sulphur to, for example, the soluble sulphate ion. This may or may not be feasible and appears to be the difficulty in achieving deactivation. A residual elemental sulphur layer on sphalerite may also explain the non-depressing action of SO_2 when covellite is present in the ore.

Experimental results seem to confirm the above speculations (52). In a study of the effects of complexing agents, ammonia, ethylene diamine (EN) and ethylene diamine tetra acetate (EDTA), on the flotation response of activated sphalerite, Bessières and Bernasconi showed that oxidizing conditions are required to inhibit flotation after deactivation (52). The results are shown in Table 2. It can be noted that the presence of complexing agents is not sufficient to reduce the floatability of the sphalerite to its natural level. Unfortunately, the nature of the "strong oxidizer" which gave the lowest recovery (7.2%) is not provided.

Table 2. Effect of oxidation on deactivation and on prevention of activation of sphalerite (52).

	pH	Conditioning	Recovery, %
Blank test			
ZnS activated by Cu^{2+}	12	pH 4.5, 20 min.	92.7
ZnS activated by Cu^{2+}	12	pH 4.5, 1 min	92.5
Activation prevention			
With NH_3	11.7	ZnS in 1 M NH_3 in presence of Cu^{2+} without O_2, 10 min	15.2
With EDTA	12	ZnS in 2×10^{-3} M EDTA with O_2, 10 min	4.3
With EN	12	ZnS in 10^{-3} M EN with O_2, 10 min	8.0
Deactivation			
With NH_3	11.7	(*a*) ZnS in 5×10^{-4} M $CuSO_4$, 20 min (activation) (*b*) Addition of 1 M NH_3 with O_2, 20 min.	18.5
With EDTA	12	(*a*) As above (*b*) pH 12, addition of 3×10^{-3} M EDTA with O_2, 20 min	25.5
With EN	12	(*a*) As above (*b*) As above but with 10^{-3} M EN	22.3
Deactivation in presence of EN and strong oxidising agent			
	12		7.2

1.6 Window of selectivity and potential-pH path

The main noticeable relationship between the redox potential and the flotation response is that flotation will occur at a potential greater than a minimum value which seems to be specific for a given ore.

Fig. 1 shows the flotation response of chalcopyrite in relation to the redox potential (Pt electrode) (53). The collector was potassium ethyl xanthate (KEX) and the frother a polypropylene glycol (PPG 400). It can be observed that significant flotation does not occur unless the potential is greater than 0.0 V vs SHE. Extreme oxidizing conditions ($E_{Pt} > 400$ mV) causes depression of the chalcopyrite. These limits define the flotation region, or range, for the flotation of chalcopyrite in the presence or absence of collector.

Fig. 2 shows a similar range for galena when ground in a steel mill/media and with KEX as collector and PPG 400 as frother (54). However, there is also a floatability region below 0.0 mV. On the other hand, the response of galena when ground in a ceramic or stainless steel mill (Fig. 3) shows a wide and uniform range for flotation (-400 to 400 mV). Also, the use of air (crossed symbols) as flotation gas does not appear to affect the relationship (Fig. 2).

Fig. 1. Floatability-potential curve for chalcopyrite in the presence and absence of collector (53).

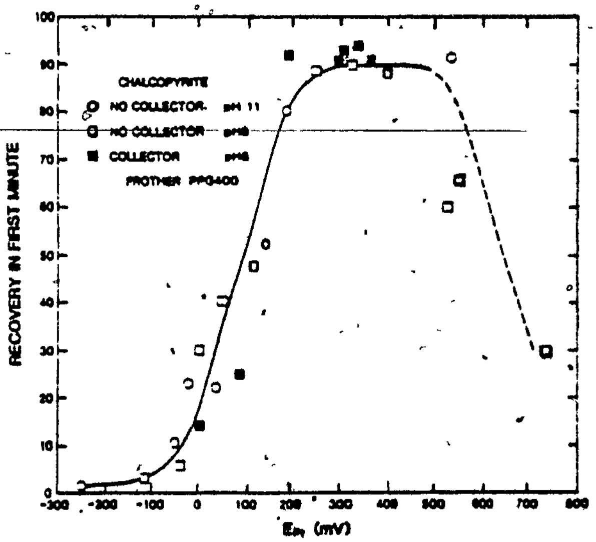


Fig. 2. Floatability-potential curve for galena in the presence of collector when ground in a steel mill (54).

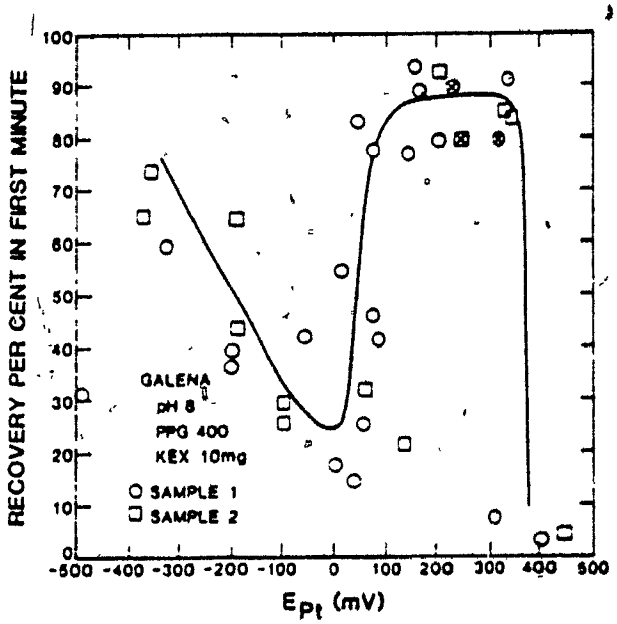
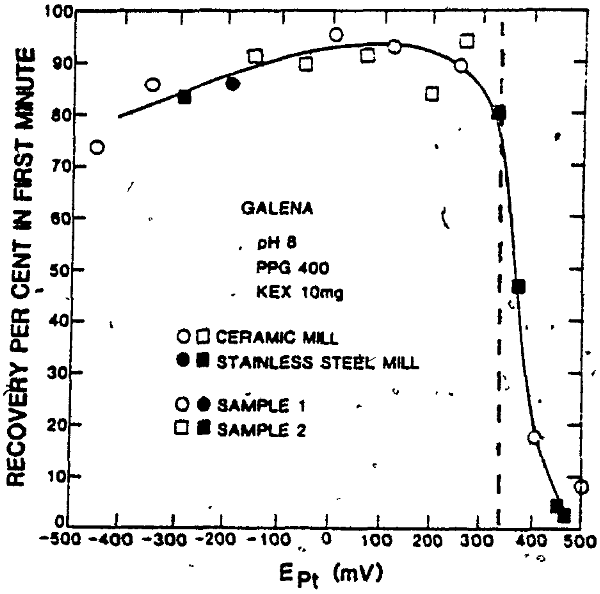


Fig. 3. Floatability-potential curve for galena when ground in a stainless or ceramic mill (54).



The depression of galena when ground with mild steel is due to the formation of iron hydroxides from the galvanic corrosion of the steel (13, 54). Of practical importance is the effect of the grinding media on laboratory results. But does the same occur in industrial plants?

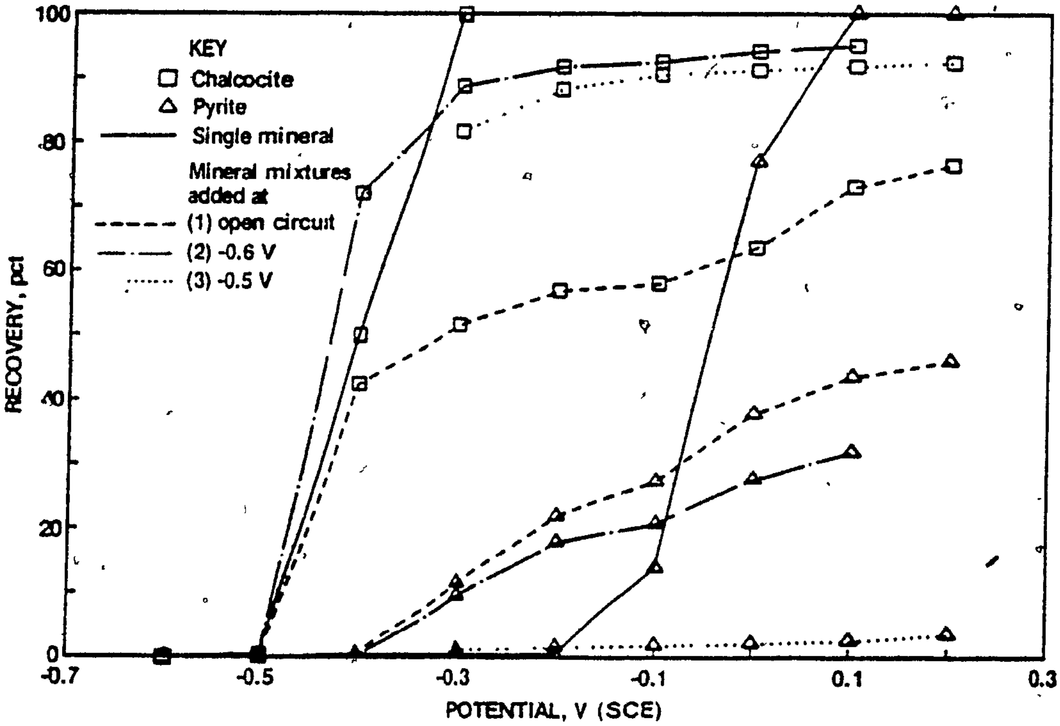
At Mount Isa Mines, Jonhson et al. (55) showed that the flotation of galena was impeded if the potential measured in the flotation pulp with a platinum electrode-reference pair was below 0.0 V vs SHE. No definite relationship could be determined between the potential measured in micro-filtrate samples of the pulp and the flotation response.

Woodcock and Jones (56, 57) were probably among the first workers to monitor pH, redox potentials, oxygen concentrations, residual collector concentrations, metals in solution, and other parameters in several lead-zinc circuits. They later disregarded the redox potential as a useful parameter to monitor (and eventually control) the chemical conditions of the pulp on the basis that all the plants appeared to achieve readily the potentials permitting flotation (58). However, the same may be said about the other variables which were monitored. This is not surprizing since the concentrators surveyed have been in operation for nearly a century with relatively stable processes (58).

On the other hand, laboratory investigations confirms the importance of electrochemical potentials upon the flotation response of complex mineral mixtures. For example, the flotation behavior of chalcocite and pyrite is different when they are in presence of each other than when they are by themselves (see Fig. 4) (19).

The results demonstrate the importance of conditioning the minerals prior to the addition of the collector (ethyl xanthate). Also, this shows some of the limitations inherent to pure mineral studies in determining the flotation conditions for the separation of two (or more) minerals. The range of potentials over which flotation will be selective, which can be viewed as a window of selectivity, will not necessarily be the range in which one of the mineral floats and the other one is depressed on an individual basis.

Fig. 4. Floatability-potential curves for chalcocite and pyrite, individually and as their mixture (19).



The flotation of the minerals individually (with nitrogen as flotation gas) gives rise to a wide window of selectivity (-0.3 to 0.2 V vs SCE on Fig. 4). However, when they are in the presence of each other the selectivity decreases and the window is reduced to -0.5 to -0.4 V vs SCE. Conditioning the mineral mixture (at -0.5 V) inhibits the interaction between chalcocite and pyrite, and results in a much better selectivity with a widening of the window to -0.45 to -0.2 V vs SCE.

A concern may be that poor results will be obtained if the oxidation-reduction potential of the flotation pulp is modified by chemical agents instead of a potentiostat. This does not seem to occur. In a study on selective depressants for Cu/Mo separation, Nagaraj et al. (59) showed that the depressing action of most inorganic modifiers on chalcopyrite could be related to the achieved electrochemical potential in the pulp. On the other hand, organic polymers did not appear to follow this general relationship. Furthermore, it has been recognized for a long time that an excessive addition of cyanide can depress chalcopyrite (60). The depressing action appears to be due to the potential achieved in the flotation pulp regardless of the quantity of sodium cyanide added (in the range of 0.15 to 0.45 kg/t) (61).

Finally, there is the possibility of (irreversible) passivation of minerals by the formation of insulating hydroxide surface layers (62). Once a passive state has been reached, the mineral does not participate anymore in redox reactions. This puts constraints on how intense a change can be imparted to the flotation pulp by electrochemical means. Practical importance of passivation of minerals would be in sequential selective flotation where one mineral is floated at a time. If one mineral has been passivated during depression, it may be extremely difficult, if not impossible, to induce it into flotation for a subsequent stage.

There is a strong influence of the "history" of the surface of the mineral on flotation. This indicates that some "paths" will lead to successful beneficiation while others will not. Since passivation is related to the alkalinity of the pulp (hydroxide layers), these paths might well be termed potential-pH paths.

The concept of window of selectivity can also be discussed with the aid of potential-pH diagrams showing the stability regions for the adsorption of the collector for the mineral mixture (4). Even though these diagrams may hint at certain possible potential-pH paths, probably the best way to determine the paths is by using floatability vs potential curves (for the mineral mixture).

1.7 Conclusions

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

For mixtures of minerals, e.g. natural ores, the ranges of flotation for the minerals taken on an individual basis cannot be used to infer the window of selectivity within which successful separation will occur. Also, for a sequential selective flotation, there would be sequences leading to efficient separation of the minerals while others will fail. The sequences may be described as potential-pH paths.

Finally, the presence of electrochemical steps in the activation and deactivation of sphalerite suggests that it would be possible to inhibit activation by reducing conditions, and promote deactivation by strongly oxidizing conditions with complexing agents to prevent reactivation. However, it is possible that this would leave a residual layer of elemental sulphur (or metal deficient zinc sulphide) which would give rise to collectorless flotation.

2. MEASUREMENT OF ELECTROCHEMICAL POTENTIALS

2.1 Introduction

The technique for measuring electrochemical potential in slurries is an adaptation of that used for solutions. The measurement consists of taking the potential difference between a sensing-reference electrode pair immersed in the slurry. The sensing electrode is usually platinum. The non-polarizable reference electrode can be any of the following: Standard Hydrogen Electrode (SHE), Standard Calomel Electrode (SCE) or silver/silver chloride (Ag/AgCl). Short-hand notations for the oxidation-reduction potential are ORP, redox, and EMF (electromotive force). When the potential measured is referenced to SHE then the notation Eh is preferred. A notation which has become common in mineral processing, particularly in Australia, is E_{Pt}, i.e. the potential measured using a platinum electrode and referenced to SHE (17, 55).

One of the earliest application of Eh measurements in mineral systems was the study of the genesis and transformation of orebodies (63, 64, 65). However, Eh measurements in mineral slurries are more difficult to interpret with the dependence of the measured value upon the material used for the sensing electrode (2, 3, 54, 66, 67). Also, the particulate nature of mineral slurries must be considered.

Attempts to resolve the discrepencies between the different electrode materials are rare (66, 68) but as more information is gathered, some definitive explanations may be obtained.

Furthermore, the prototype commercial control equipments based on the redox potential for flotation offer two different techniques. The first technique, proposed by Outokumpu, involves a "custom designed" sensing electrode immersed into the mineral slurry (2, 3, 4). The second one, originating from Bureau de Recherches Géologiques et Minières (BRGM), uses the redox potential of a micro-filtrate sample continuously obtained from the flotation pulp (5). 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.

There appears to be some confusion regarding redox potentials in flotation slurries. Clarification is needed for more consistent fundamental results and acceptance of the technique by industry.

2.2 Fundamental aspects

2.2.1 Solutions

Simple solutions

The oxidizing or reducing conditions in a solution can be represented by a redox potential. 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^{O}, is the Nernst equation which is usually written as:

$$E = E^{O} - \frac{RT}{nF} \ln \frac{a_{Reduced}}{a_{Oxidized}} \qquad [6]$$

where n = number of electrons involved

R = gas constant (joules/gmoles K)

T = temperature (K)

F = Faraday constant (96500 coulombs/gmoles)

a = activity = activity coefficient x concentration

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

$$E = - \Delta G / nF \qquad [7]$$

Hence, E^{o}, 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 (69).

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 (70).

The common reference electrode, SHE, has a potential of 0.0 V at 25 °C by convention. This arbitrarily defined reference stems from the impossibility of measuring the absolute potential of a single electrode process (71) although attempts to calculate it are performed from basic principles (72).

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 Eh 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:

$$Eh\ (Ox1/Red1) = Eh\ (Ox2/Red2) \qquad [8]$$

The two couples cannot be anymore considered independently since the electron exchange can proceed internally to each couple and between the couples (Fig 5). 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).

The mixed potential provides an explaination for the apparent "reactivity" of the platinum electrode (73) and the difference between platinum and gold electrodes when measuring the redox potential of the Fe(III)/Fe(II)-O_2/H_2O system in 1 M H_2SO_4 (66).

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, Fig 6). 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 (66).

Fig. 5. Mixed potential model.

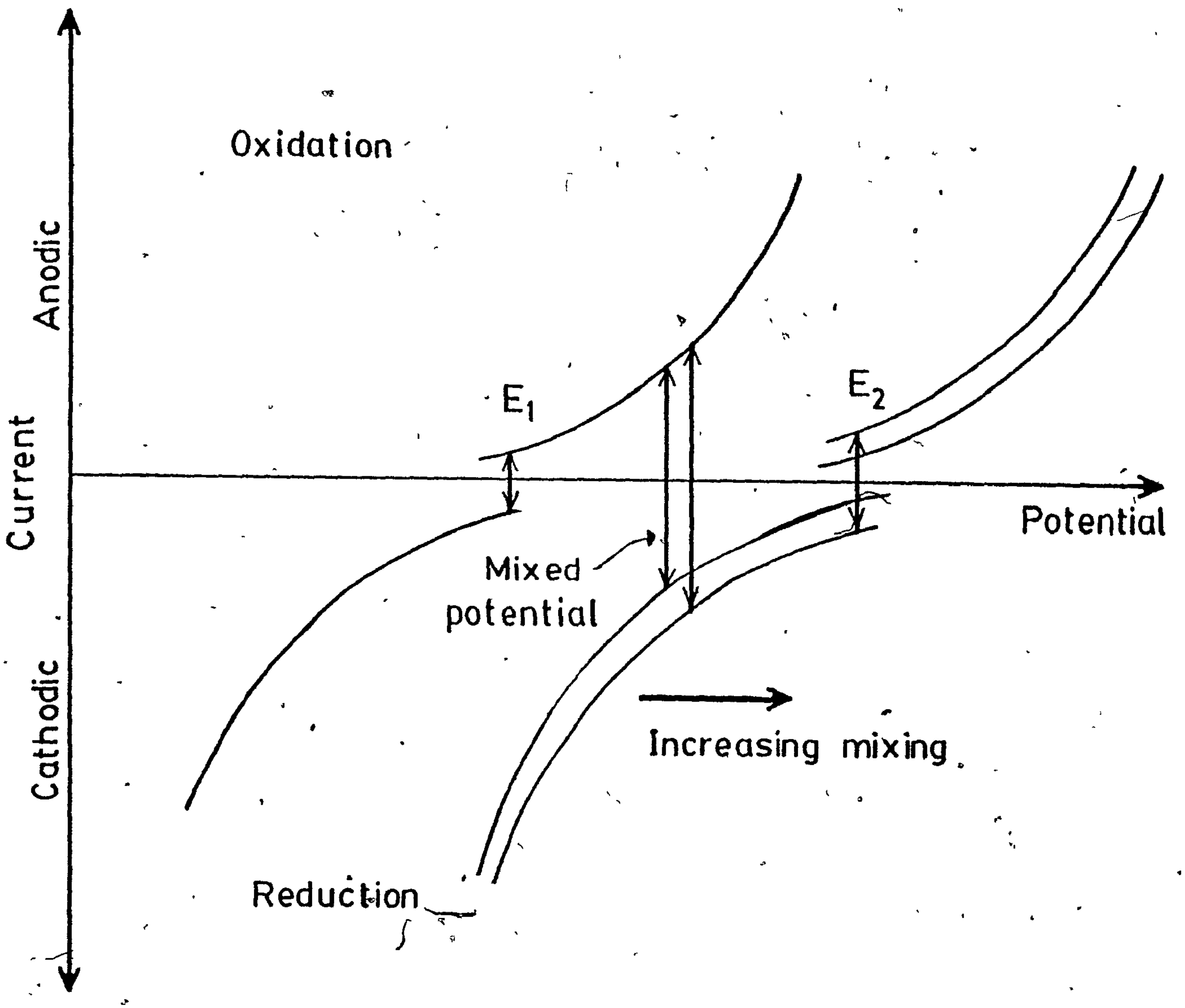
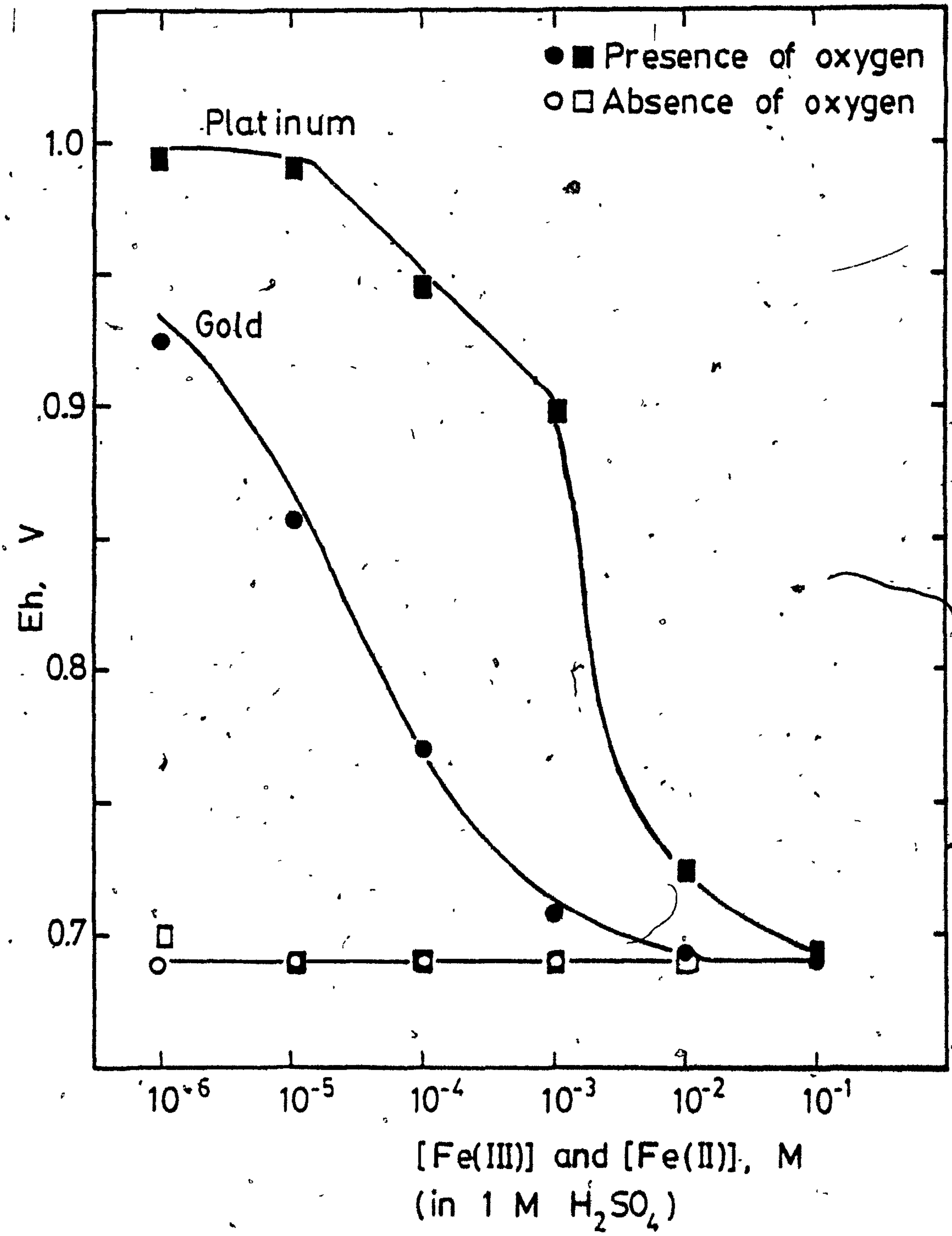


Fig. 6. Redox potential measurements for the Fe(III)/Fe(II) system in the presence and absence of oxygen (66).



The lines on Fig. 6 are the theoretical values predicted by the mixed potential model. They were calculated from an Evans diagram (66) which presented potential-current curves similar to those shown in Fig. 5, but for the individual couples and for the different concentration levels. A system consisting of two couples, as shown in Fig. 5, is simple to analyse. If the reaction rate of Ox1/Red1 is determined by activation (i.e. independent of mixing) while the reaction rate of the couple Ox2/Red2 is diffusion controlled, then varying the intensity of mixing, or the total concentration will change the reaction rate of Ox2/Red2, and consequently the measured mixed potential as seen in Fig. 5.

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 favored. Often, this is the one in greatest concentration.

The poise (and its inverse the flexibility) reflects the inertia of the systems to changes in its equilibrium point when potential modifying reagents are added, or due to the effect of mixing (74). 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 (74):

$$\text{Poise} = \frac{dy}{dEh} = \frac{nF}{RT}\,\frac{y(B - y)}{B} \qquad [9]$$

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.

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) (75).

Poisoning of sensing electrodes

Electrode poisoning is a special case of the mixed potential. Namely a "poison" is formed, or adsorbed onto the electrode surface, causing the mixed potential of the poison and the solution to be monitored.

The possibility of poisoning of platinum electrodes by reagents present in flotation pulps has been investigated by Natarajan and Iwasaki (75, 76). 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 solutions. Collectors (e.g. xanthate) 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 (77). Since most of the flotation frothers have an alcohol group, they may cause poisoning.

A poisoned platinum electrode can be identified by a lack of reproducibility, potential drift, and a long period to stabilize. The most satisfactory method to regenerate the electrode is by mechanical polishing (76).

There is one last phenomenon observed with platinum electrodes when measuring Eh in solutions or slurries containing oxygen. The line for oxygen reduction 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 (73):

$$Eh = 0.9 - 0.059\ pH \qquad [10]$$

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 (73) 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.

Sato (63) 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. The presence of hydrogen peroxide as an intermediate product in the reduction of oxygen appears to occur on other materials. For example, pyrite catalyses the reaction via the intermediate H_2O_2 (78).

2.2.2 Stochastic model of pulp potential

It has been observed that the presence of sulphide mineral particles in a flotation pulp gives rise to a different potential from that of the solution obtained by microfiltration (55). When the sensing electrode is immersed in an agitated mineral slurry, mineral particles collide with the sensing electrode. In a fashion, the sensing electrode acts as a contact between the connecting copper wire and the mineral particles similarily to the mercury drop or conductive paint used in the construction of massive sulphide electrodes. However, the contact is not anymore constant but occurs randomly and depends on the intensity of mixing.

Rand and Woods (66) explained the observed discrepency between the black platinum electrode and either the smooth gold or platinum electrodes, as being due to the high porosity of black platinum. These electrodes, obtained by pressing fine platinum powder, expose a much larger area for contact with the solution than the solid particles. As such, they followed less closely the galena potential than smooth platinum or gold when immersed in a galena slurry (66).

These observations suggest that the random nature of the contact between the sensing electrode and the particles must be considered. To better represent the system, a stochastic model would be needed in addition to the mixed potential model.

It was decided to verify the validity of the stochastic model, at least conceptually. Simple experiments were performed using the fast data acquisition capability of a potentiostat (EG&G PAR model 273). Fig. 7 presents the potential measured every 10 ms of a Fe(III)/Fe(II)-silica system while Fig. 8 presents the values obtained after the addition of iron powder to the system. The initial Fe(III) and Fe(II) concentrations, as their chlorides, were 2.5 M. The particle size of silica and iron was 75 µm and the slurry contained 75 g silica per 1 liter of solution. The mass of iron added was 50 g (per liter of solution).

Fig. 7. Redox potential of Fe(III)/Fe(II)-silica system, gold spiral electrode.

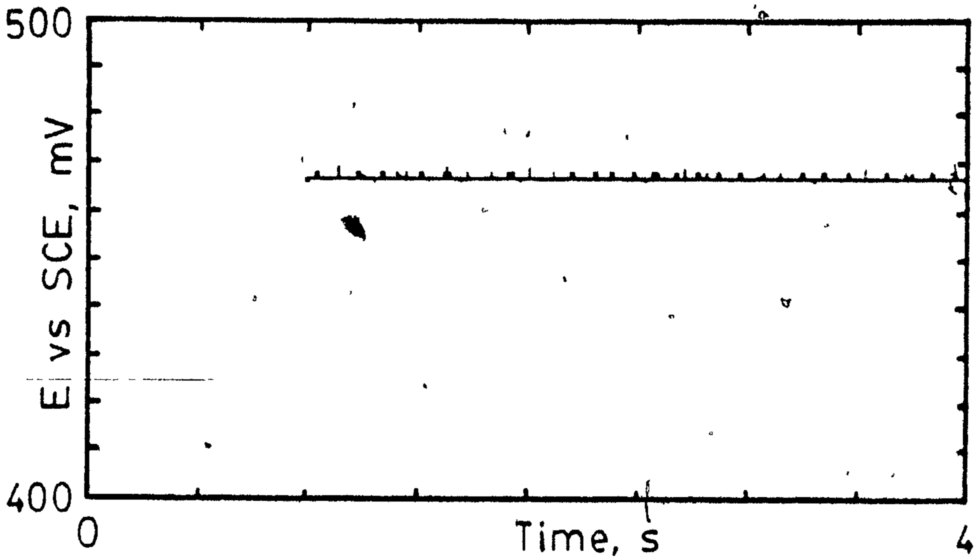
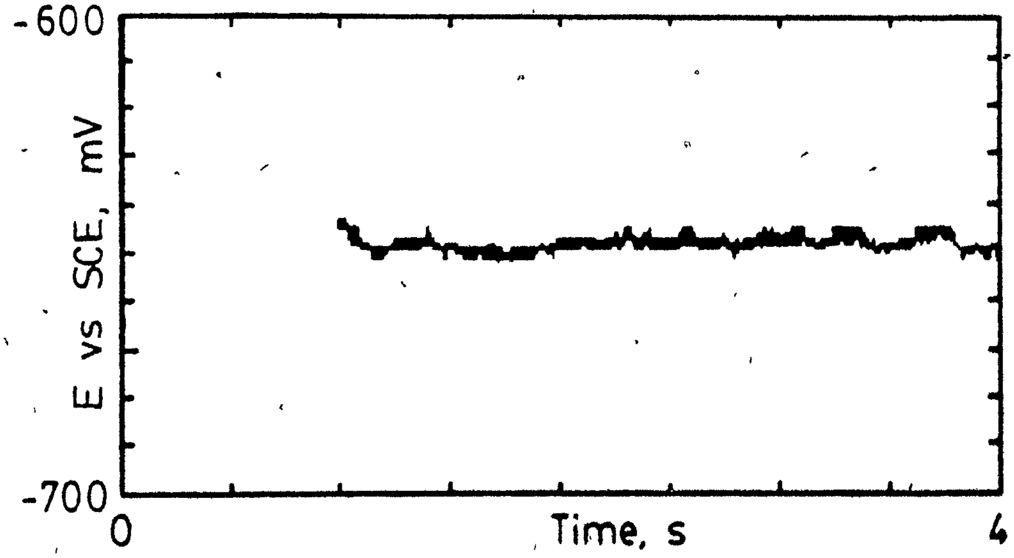


Fig. 8. Redox potential of Fe(III)/Fe(II)/Fe-silica system, gold spiral electrode.



The slurries were stirred during the measurements. The values obtained for the Fe(III)/Fe(II)-silica system (Fig. 7) are extremely stable except for small peaks occuring at almost regular time intervals. These peaks are highly reproducible and may be attributed to noise induced by the data acquisition system.

On the other hand, the values obtained for the Fe(III)/Fe(II)/Fe-silica system fluctuate widely. Reproducibility is poor since it is difficult to exactly duplicate the stirring conditions. The presence of these fluctuations appears to be related to the randomness of the contact between the gold spiral electrode and the iron particles. More oxidizing potentials are measured when fewer particles are touching the electrode. Conversely, lower potentials are observed when more iron particles are touching the electrode.

From these arguments, the conceptual stochastic model for the measurement of electrochemical potentials in mineral slurries appears to better represent the system. Such an approach has also been used with success for fluidized bed electrochemical reactors (79) and corrosion processes (80).

2.3 Minerals as pulp potential sensing electrodes.

In some instances mineral electrodes of the same mineral as that of the slurry are utilized. Reported examples in the literature are in the use of galena electrodes in galena slurries conditioned with sodium sulphide (54, 67) and with xanthate (66).

The rationale of using mineral electrodes is that the mineral potential may differ from the solution potential. This has been observed for the oxidation of pyrite over several days (84). This will be more important in flotation since the time span is, at the most, four to five hours between comminution of the ore and filtration of the final concentrate(s). Also, since flotation is based on the state of the surface of the mineral, this state is more important than that of the solution.

Ideally, there should be no problems since the mineral electrode is the same as the mineral particles in the slurry. However, the building up of oxidation products layers on the electrode surface would lead to poisoning similarily to noble metal electrodes (R. Woods, communication June 1986). The remedy is the same, mechanical polishing prior to the experiments.

Also, there are uncertainties introduced with mineral electrodes. The addition of modifiers (e.g. CaO, Na_2S) and collectors to the pulp introduces ions which are foreign to the natural equilibria of the minerals. Hence the potentials initially monitored are irreversible (64) causing drifts to be observed until a new equilibrium is reached. Also, the electrode surface has a different history than that of the mineral particles in the slurry. Again, drifts will be observed until an equivalent history is reached.

Discrepencies have been observed between galena and platinum electrodes simultaneously immersed in the slurry when sodium sulphide was added. The response of the galena electrode was characterized as erratic (54), or very close to that of the platinum electrode (67). In the latter case, the discrepency was found to be less than 10 mV for potentials between -400 to -100 mV (vs SCE), 20 mV or less between -100 to 0 mV, and greater than 20 mV for potentials higher than 0 mV (J. Leppinen, communication Nov. 1986). In both investitions, the analysis of the results was based on the potential exhibited by the platinum electrode.

From a comparative study of different electrodes, Rand and Woods (66) showed that a gold electrode followed more closely the potential exhibited by the galena electrode than a platinum one when immersed in a synthetic galena/silica slurry, in the presence and absence of collector (potassium ethyl xanthate).

Although other chemical systems have to be verified experimentally, this last result appears to confirm that a platinum electrode may not be the best redox sensing electrode for mineral slurry. However, what should be the criteria permitting to select the proper electrode, especially for flotation?

2.4 Criteria for the selection of monitoring electrodes for mineral slurries

From the basic principles reviewed, the following criteria can be used to select the appropriate sensing electrode:

i) The monitoring electrode must be chemically stable. If the electrode material degrades with time, measurement drifts will occur. This would diminish the long term reliability of a control scheme based on electrochemical potentials.

ii) The electrode must not exhibit strong electrocatalytic properties for redox couples present in the system. This would promote oxidation-reduction reactions on the electrode surface at a different potential from that of their occurence in the slurry.

iii) A smooth noble metal electrode must have a shape which favors contact with particles, even for dilute pulps or when mixing is poor.

iv) The electrode must be as much as possible insensitive to poisoning by the reagents present in the flotation pulp.

Based on i), noble metal electrodes (Au, Pt) would be the best choice since they are chemically inert. Based on ii), gold would be the preferred noble metal since platinum is catalytically more active than gold. However, a mineral electrode could be used since the pulp consists of mineral particles in a solution. Considering iii), wires or spirals would be preferred over foils or solid pieces, but this preference may have to be modified because the possibility of poisoning (iv) requires a shape which is amenable to mechanical polishing.

To some extent, the selection criteria are conflicting. No firm choice can be made. However, whichever the material or shape is choosen it must be remembered that the potential monitored in a mineral slurry is a mixed potential. Unless the chemical composition of the system and the kinetics of the reactions are known, it will be impossible to relate, without doubts, the measured potentials to the thermodynamic potentials of the electrode reactions.

Finally, the relationships discussed previously between mineral floatability and redox potential should not be discredited 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.

3. SELECTION OF MONITORING ELECTRODES

3.1 Description of the experimental apparatus

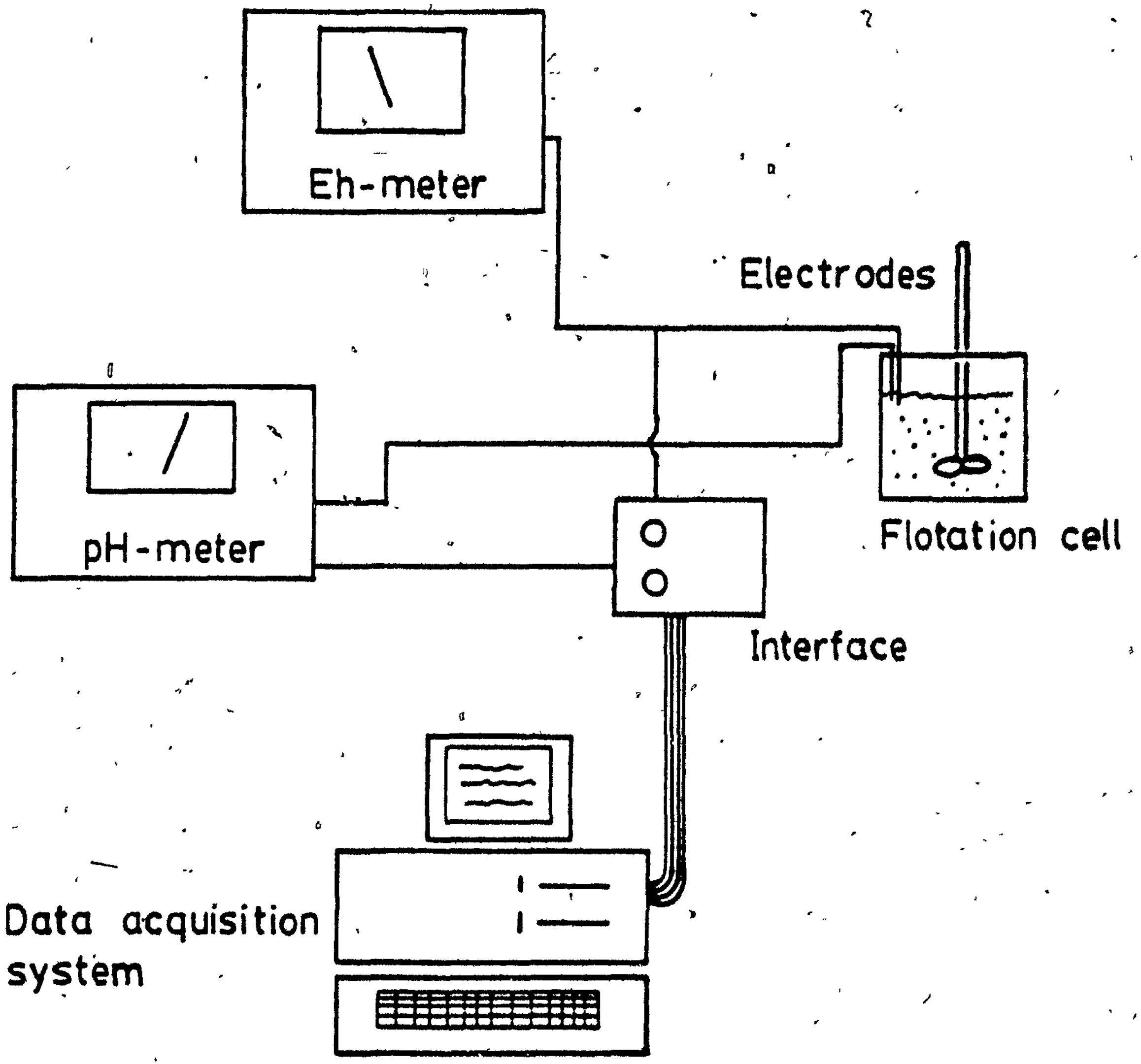
With the criteria for the selection of monitoring electrode(s) being defined, it is possible to assess the behavior of different electrodes under conditions encountered in flotation: dilute pulps, conditioning, and flotation with air.

The experimental apparatus has evolved through the course of the project and its final state, for monitoring of the potentials, is presented in Fig. 9. The apparatus can be divided into two parts: the flotation cell in which the system is investigated, and the data acquisition system (IBM-PC compatible fitted with a Data Translation DT2801 analogue to digital interface card).

Two types of flotation cell were used: a Denver D12 machine fitted with a 500 g stainless steel cell (1 liter of pulp) and an Agitair L-500 cell with a 500 g cell. Impellor speeds of 1500 rpm for rougher flotation, and 1200 rpm for cleaning and redox monitoring tests were used.

The data acquisition software was an integrated package developed at M.I.T under the name of Unkelscope. The program

Fig. 9. Experimental apparatus.



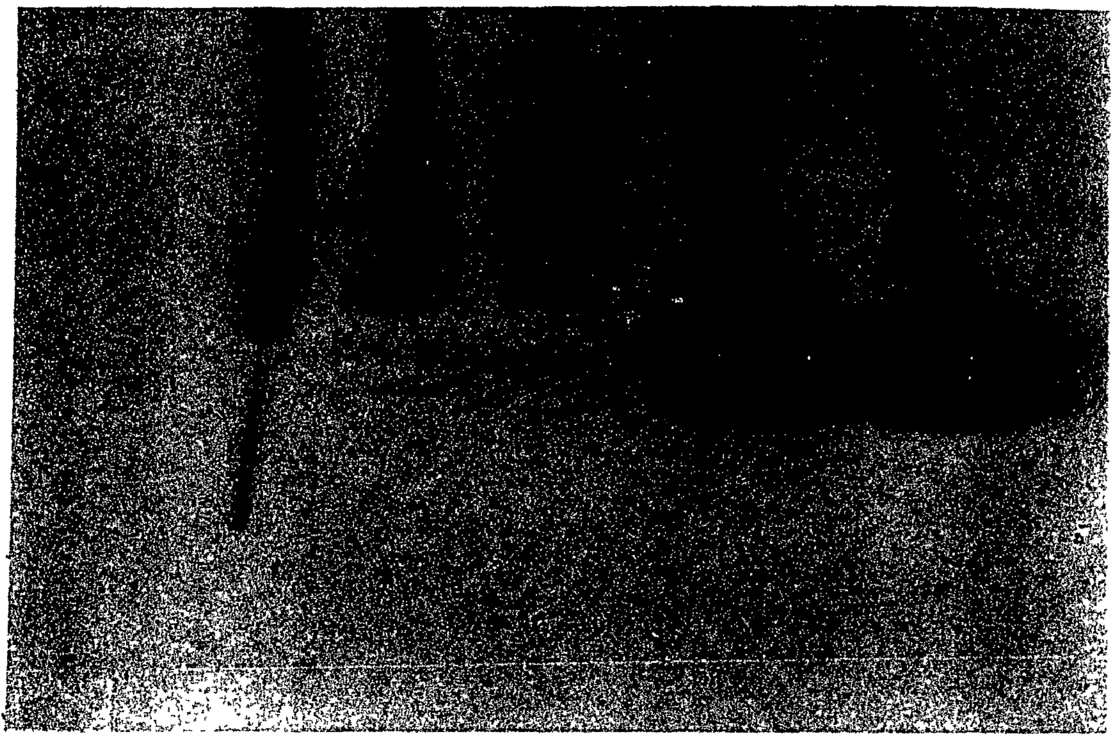
could perform data acquisition up to the limit of the hardware (5000 samples per sec) as well as plotting, digital filtering and other useful features. However, it was possible to monitor only up to four different input signals simultaneously.

To permit the monitoring of up to 8 different electrodes plus pH, temperature, and a timing signal for identification of flotation steps, a special amplifying interface has been designed (see Appendix A) and a simple data acquisition program was written to cope with the additional inputs. The amplifying unit can also be used for plant monitoring with standard 4 to 20 mA current outputs.

The noble metal electrodes which were investigated are shown in Fig. 10. They are presented in the following order: black platinum wire, Pt and Au spirals, and Pt and Au foils. The exposed area of each foil is 1 cm^2 while each spiral consists of a 10 cm long wire coiled three times.

The black platinum electrodes were obtained by platinizing, at 20 mA for 3 minutes, 5 cm long by 0.5 mm diameter platinum wires. The black platinum deposit is somewhat fragile and is easily detached from the wire by abrasion. However the electrode is easier to make than by utilizing pressed

Fig. 10. Noble metal electrodes.



black platinum (e.g. fuel cell elements) as used by Rand and Woods (66, R. Woods, communication Oct. 1986, 81). Also, if it is suspected that the electrode has been poisoned, the deposit can be removed by mechanical polishing and a new, fresh deposit re-platinized.

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, were also used for comparison purposes.

The mineral electrodes were fabricated in a manner which differed very slightly from usual practices (64, 84). 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 the shielded copper wire could be inserted and contacted with the mineral piece by a drop of mercury. The finished electrode was finally sealed with epoxy resin and silicone.

Fig. 11 shows some epoxy castings and one completed mineral electrode. On the top row there are two galena from the ore, one pure galena, a chalcopyrite, and a pyrite. On the bottom row there are the three types of sphalerite electrode tried during the investigations: pressed sphalerite/ graphite, pure sphalerite, and activated sphalerite.

The difficulties experienced with the sphalerite electrodes are due to the particular properties of the mineral. Sphalerite has the widest band gap, 3.6 eV, of all semi-conducting sulphide minerals and as such it is at the boundary between semi-conducting and dielectric minerals (49). Consequently, the resistivity of massive sphalerite pieces, 8 x 10^5 ohm•m (49), is too great to permit passage of electrons between the exposed surface of the mineral and the mercury contact.

Fig. 11. Mineral electrodes.

As sphalerite would appear to behave within the electrochemical model of collector adsorption once it is copper activated, sphalerite pieces were immersed for 36 hours in a 500 g/l solution of copper sulphate. Although the activation layer was thick enough to be visible, no measurement could be made. The resistivity was still too high.

Finally, since Sato (64) managed to perform electrochemical measurements on fine ZnS precipitates, 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.

Besides the difficulties with sphalerite, the mineral electrodes did not give major problems. Only the most frequently used mineral electrodes developed oxidation products within one year after fabrication. Surface oxidation of one chalcopyrite electrode occured at the interface between the mineral and the epoxy resin. The mercury contact of two electrodes (one galena and one pyrite) has been contaminated by a copper compound originating from the corrosion of the copper wire. The seal between the rubber envelope of the cable and the electrode body has degraded so that the solution could reach the mercury contact.

The reference electrodes for all monitoring performed with the data acquisition system were porous sleeve standard calomel electrodes (Fisher Scientific). For the manual monitoring during laboratory flotation, either a combination Pt-Ag/AgCl electrode (Cole-Palmer) or a platinum wire (Fisher) in conjunction with the reference electrode (Ag/AgCl) of a combination pH electrode (Radiometer) were utilized.

3.2 Selection of monitoring electrodes; pulp potential

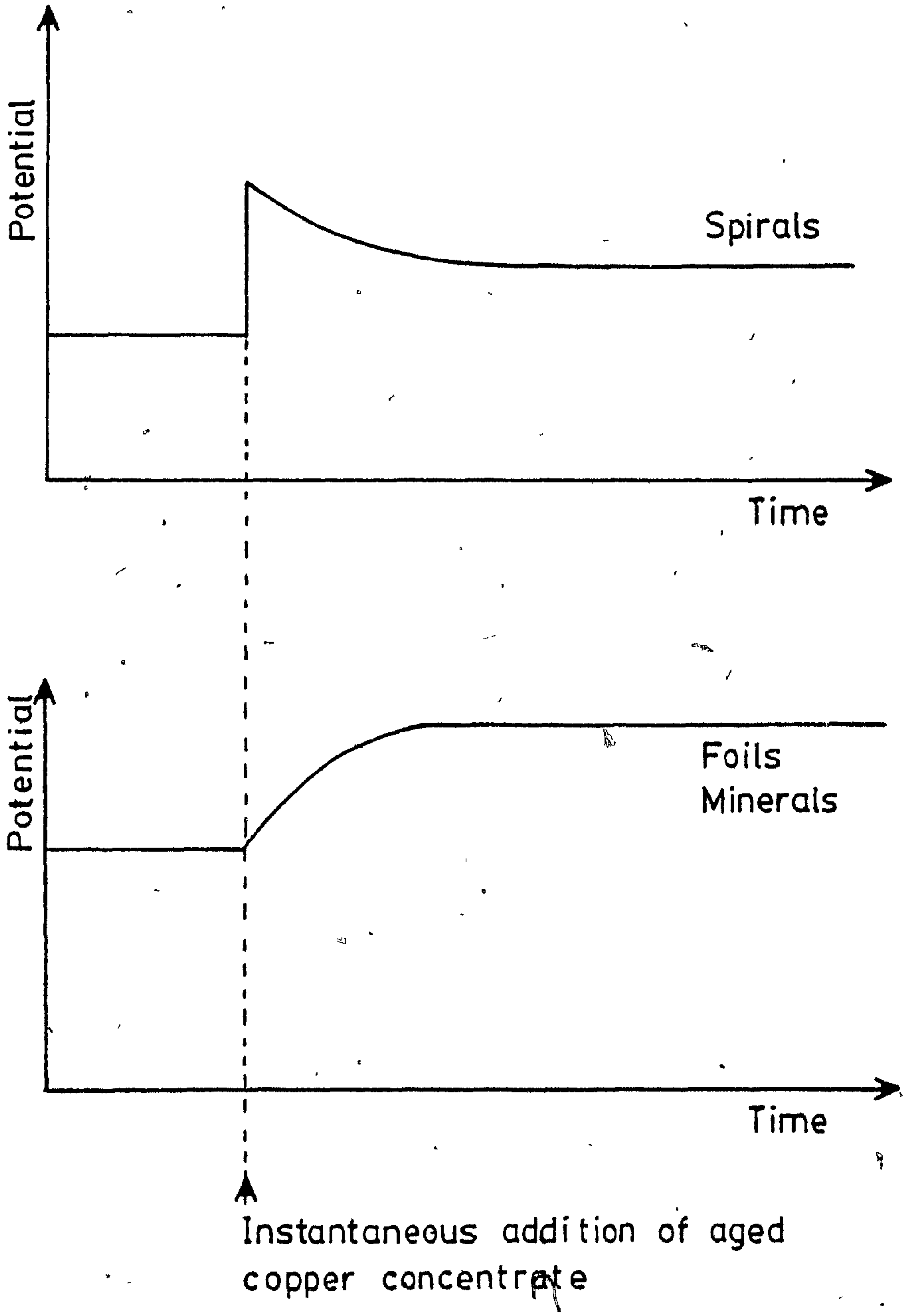
3.2.1 Conditioning

Initial experiments were conducted to compare the behavior of the electrodes upon the addition of a small amount of aged copper concentrate to a tap water or a silica slurry system. The objective was to determine the sensitivity of the electrodes to small quantities of sulphide minerals. Use of an aged copper concentrate practically eliminated potential drifts due to the diffusion of atmospheric oxygen into the system.

The procedure was essentially the same for the two series of experiments. The results are summarized in Tables 3 and 4. Starting with tap water, known masses of solids (silica or copper concentrate) were instantaneously added to the system. Prior to each series of experiments, the noble metal foils and mineral electrodes were mechanically polished on 600 grit paper.

Fig. 12 shows typical potential time profiles which were obtained for the first addition of copper concentrate. Some profiles are shown in Appendix B. It can be observed that noble metal spirals are more sensitive to the addition of sulphide particles than the foils or mineral electrodes.

Fig. 12. Potential-time profiles for an instantaneous addition of copper concentrate.



A similar trend can be observed in Table 3. As the mass of copper concentrate increases, the foil and spiral (of the same noble metal) appears to converge towards the same potential. It can also be noted that both types of platinum electrodes exhibit higher potentials than their respective gold counterparts.

Table 3. Comparison of noble metal foils and spirals.

Mass of solids in 1 l water	End potential, mV vs SCE Pt foil	Pt spiral	Au foil	Au spiral
0	172	92	123	4
0	161	92	121	6
100 g silica	168	82	101	24
300 " "	172	80	95	31
700 " "	177	83	128	25
" " " 1 g Cu. Con.	192	125	125	80
" " " 3 " "	200	143	121	103
" " " 7 " "	206	159	128	120

The gold electrodes exhibit a marked change upon the addition of silica. This is possibly due to a combination of removal of ions from the solution by adsorption onto the silica surface and abrasion by the particles. The relative importance of each effect would be dependent on the shape of the electrode. In comparison, the platinum foil was barely affected by the presence of silica while the platinum spiral showed only a slight change.

The great discrepency between the electrodes in water and in the silica slurry may be due to the small poise of tap water (dilute solution). The measurement would be strongly affected by the electrode material and the shape of the electrode.

Table 4 shows the comparison of the black platinum, chalcopyrite, gold foil and platinum foil electrodes. Again, the first addition of silica sand introduces changes in the measured potentials. It can be noted that although the chalcopyrite electrode was ground prior to the series of experiments, its potential decreases as the quantity of silica sand increases. This indicates that the chalcopyrite of the electrode is oxidized by the solution but the silica particles abrade any oxidation product layer at a faster rate than it can be formed.

The first addition of copper concentrate causes a large step increase in the measured potential for all four electrodes. Further additions enable the electrodes to be discriminated. The black platinum electrode does not exhibit potentials significantly different for the different copper concentrate contents. Similarly for the platinum foil.

Table 4. Comparison of noble metal foils with black platinum wire and chalcopyrite electrode.

Mass of solids in 1 l water	End potential, mV vs SCE			
	Black Pt	$CuFeS_2$	Au foil	Pt foil
0	227	43	83	175
250 g silica	204	17	63	177
500 " "	206	-10	59	194
" " " 15 g Cu.Con.	303	147	168	238
" " " 50 " "	309	170	188	237
" " " 100 " "	311	192	206	237
" " " 200 " "	303	202	212	237

The discrepency between the gold foil and the chalcopyrite electrode, which was roughly of 70 mV prior to the addition of the copper concentrate, was reduced to about 20 mV for the first addition and appeared to remain constant at about 10 mV ~~for the~~ further additions. However, both electrodes indicate changes in the same direction, towards more oxidizing potentials. This increase in potential would mean that the degree of oxidation of the system increases with respect to the content of mineral particles.

The nearly steady potentials exhibited by the black platinum and platinum foil electrodes could indicate a saturation of the solution in soluble oxidation product from the chalcopyrite particles.

Although the effect of electrode material upon the measurement of the solution potential was expected from the mixed potential model, the effect of the electrode shape may be at first surprising.

The importance of shape is seen in the trend in analytical electrochemistry to utilize micro-electrodes (5 µm dia.) for investigations in dilute solutions or for ultrafast cyclic voltammetry (1000 mV/s) (82). The rationale for this is that the diffusion layer around the electrode is quasi-spherical which limits distortion of the readings by iR drops accross the electrode/solution interface. A similar phenomenon may occur for the spirals.

It would be tempting to further assertain the behavior of the black platinum electrode as a solution redox sensor, in comparison with the pulp redox, by investigating the potentials in micro-filtrate samples obtained from the pulp. However, the measurement of the solution potential in the micro-filtrate sample would also be subjected to the complications arising from mixed potentials.

3.2.2 Flotation

The potential's exhibited by the different electrodes differ. However, which electrode gives a value which is closer to the reality of the system? Since the floatability of a sulphide mineral is dependent on the surface state, the mineral potential should be more important than the solution potential, if the two values differ due to the dynamic nature of flotation.

To permit the selection of the monitoring electrode for future investigations, it was required to study the behavior of different electrodes during flotation. However, the data acquisition system limited the investigation to only four electrodes.

Since the mineral to be floated selectively was chalcopyrite, a chalcopyrite electrode was an obvious choice. A gold spiral electrode was also choosen since it is inert and was found to exhibit a potential closer to that of the chalcopyrite electrode. Also choosen were a black platinum electrode to obtain some information on the solution potential, and a galena electrode to observe the action of the modifiers on other minerals. A sphalerite electrode would have been choosen since copper/zinc separation was sought but no reliable sphalerite electrode was available.

Detailed examination of the potential traces obtained during the flotation tests is quite involved but ultimately illuminating. With the flotation conditions investigated (section 5.6), the potential vs flotation time profiles can be grouped in two classes:

i) The introduction of air, as flotation gas, induces a significant change to the oxidation state of the pulp, as indicated by the monitored potentials.

ii) The introduction of air does not appear to change the state of the pulp.

Class i) is mainly observed when reducing agents are added to the pulp (Figs. 13 and 14). Class ii) is also observed for certain reducing agents such as $FeSO_4$ (Fig. 15) but is most often associated with oxidizing agents and pH modifiers (Fig. 16). A similar behavior is observed during roughing flotation (Appendix C).

As expected, the potential exhibited by the black platinum electrode is always significantly higher (70 to 350 mV) than the gold spiral (Au) and the two mineral electrodes (Cp, Ga). The black platinum deposit was more resistant than expected, and only in one test did the abrasion of the deposit caused an erratic response as shown in Fig. 17.

Fig. 13. Example of class i potential-time profiles in flotation, reducing agent.

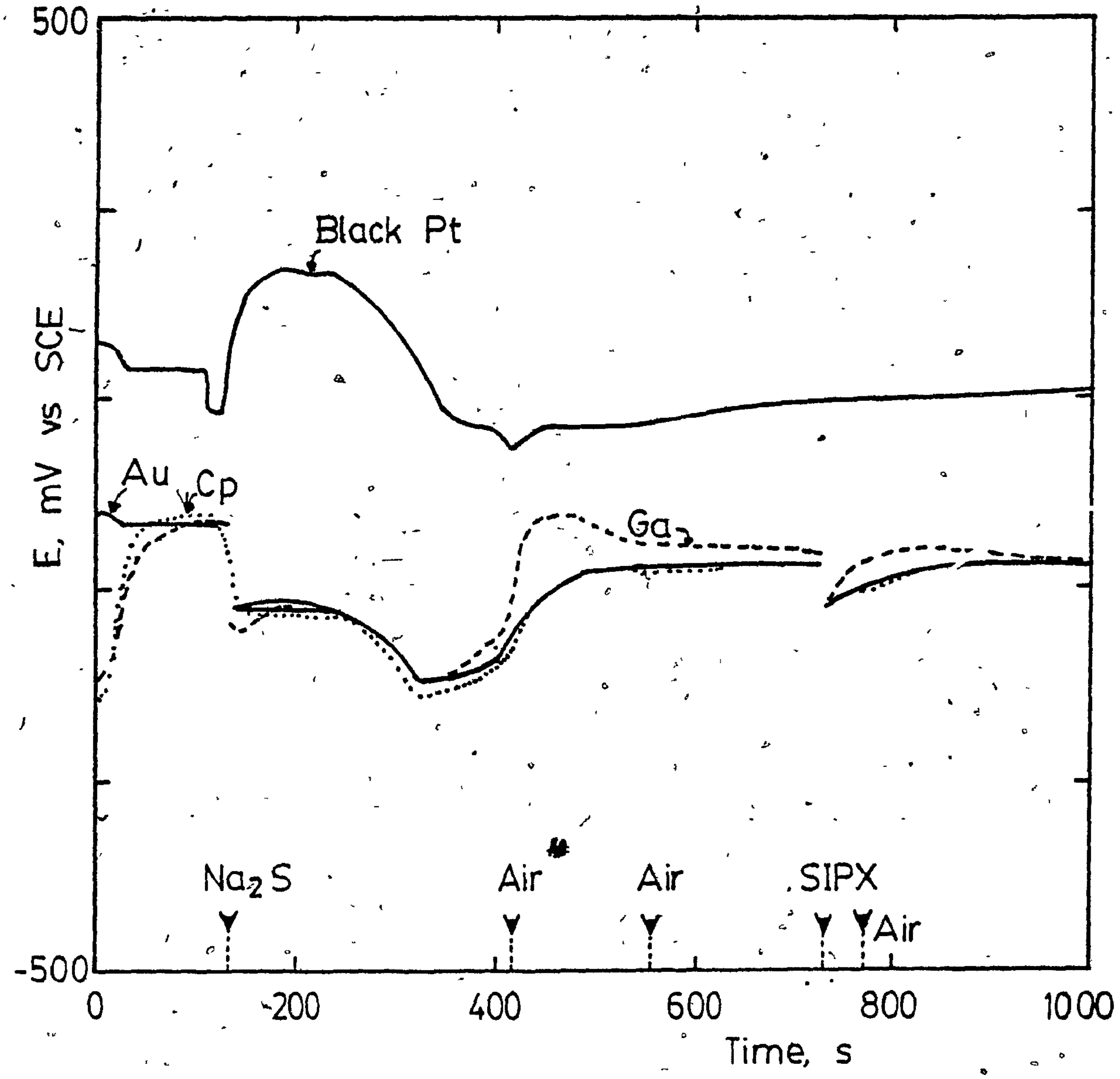


Fig. 14. Example of class i potential-time profiles in flotation, reducing agents.

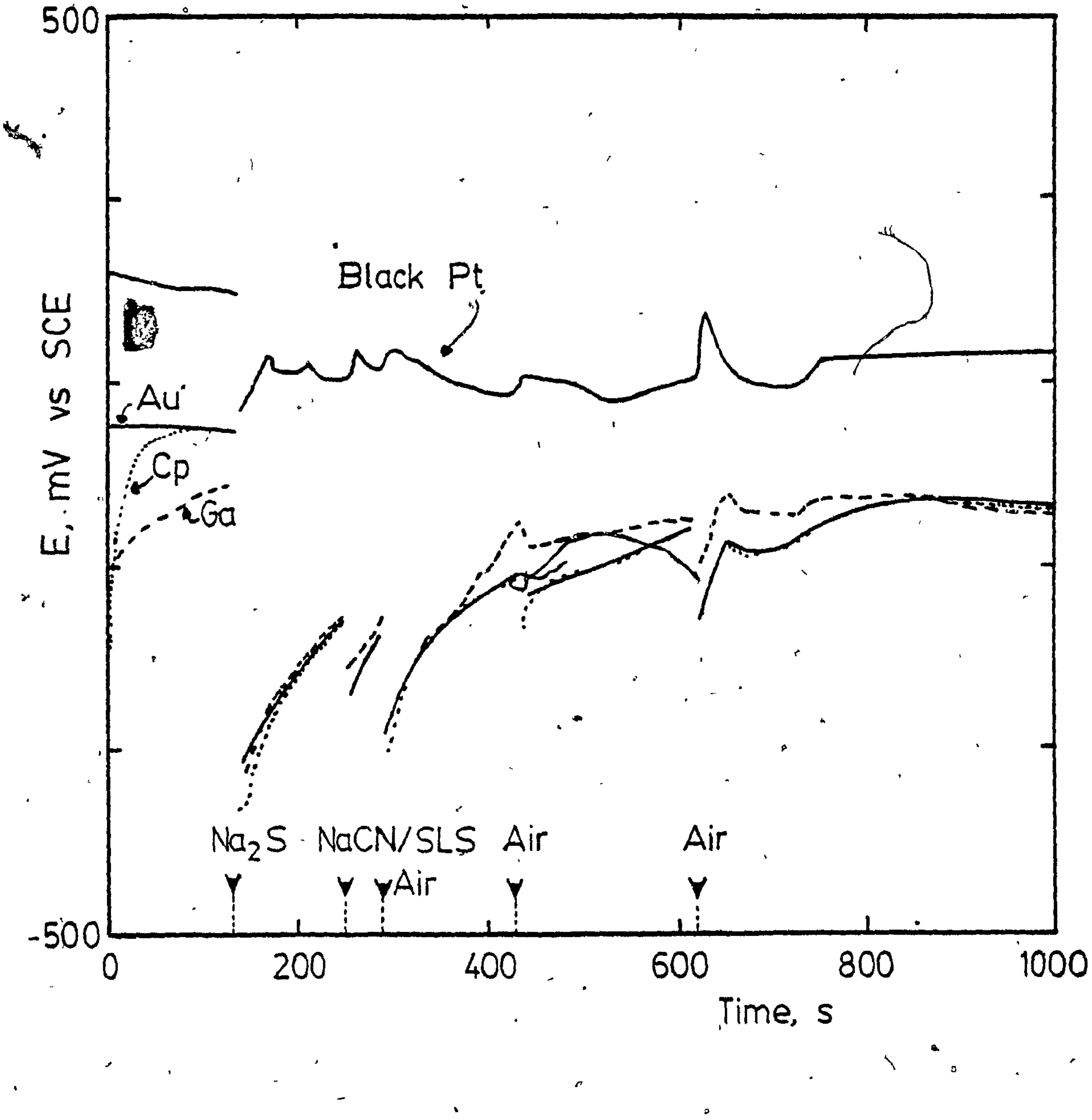


Fig. 15. Example of class ii potential-time profiles in flotation, reducing agent.

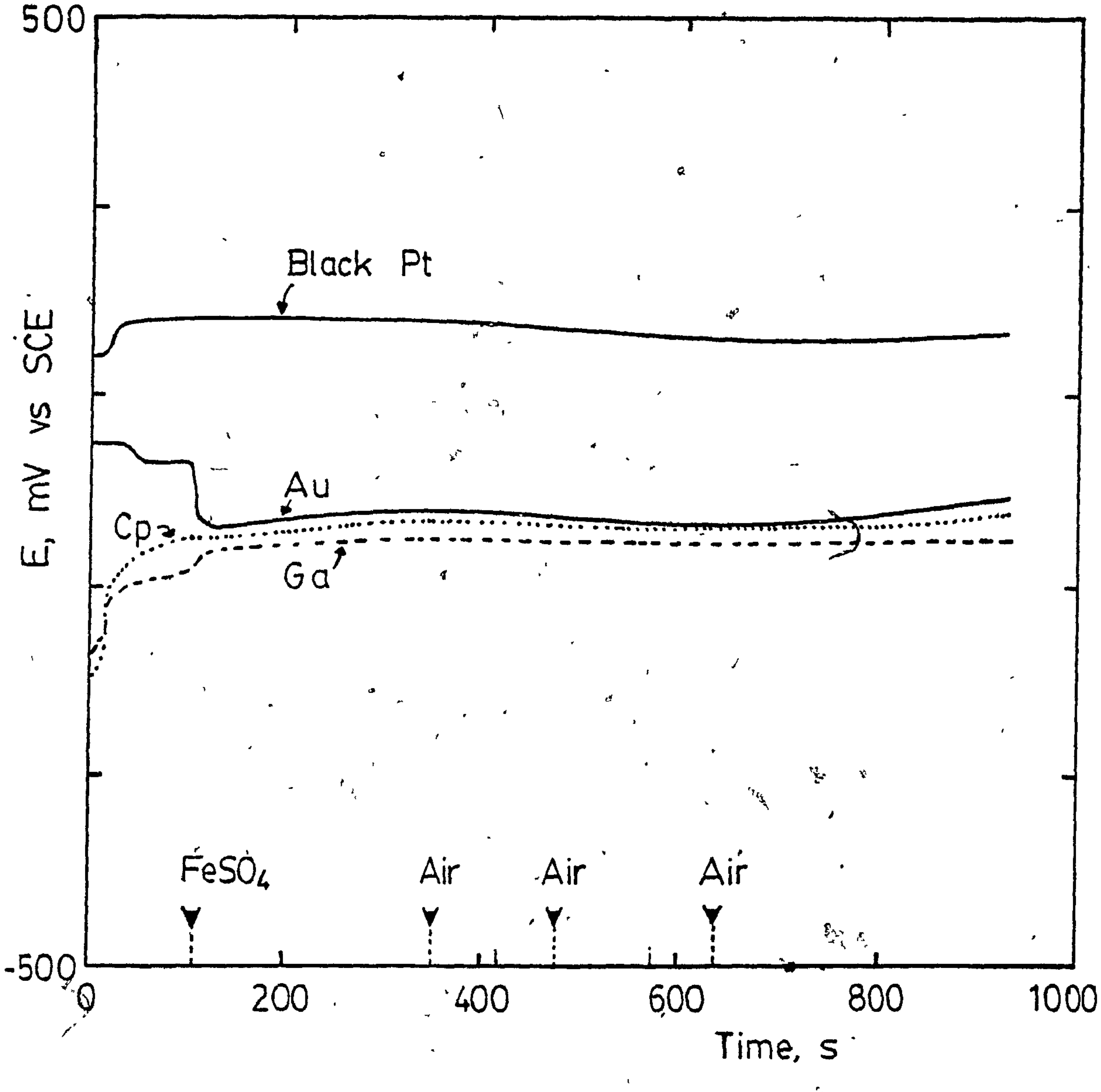


Fig. 16. Example of class ii potential-time profiles in flotation, oxidizing agent.

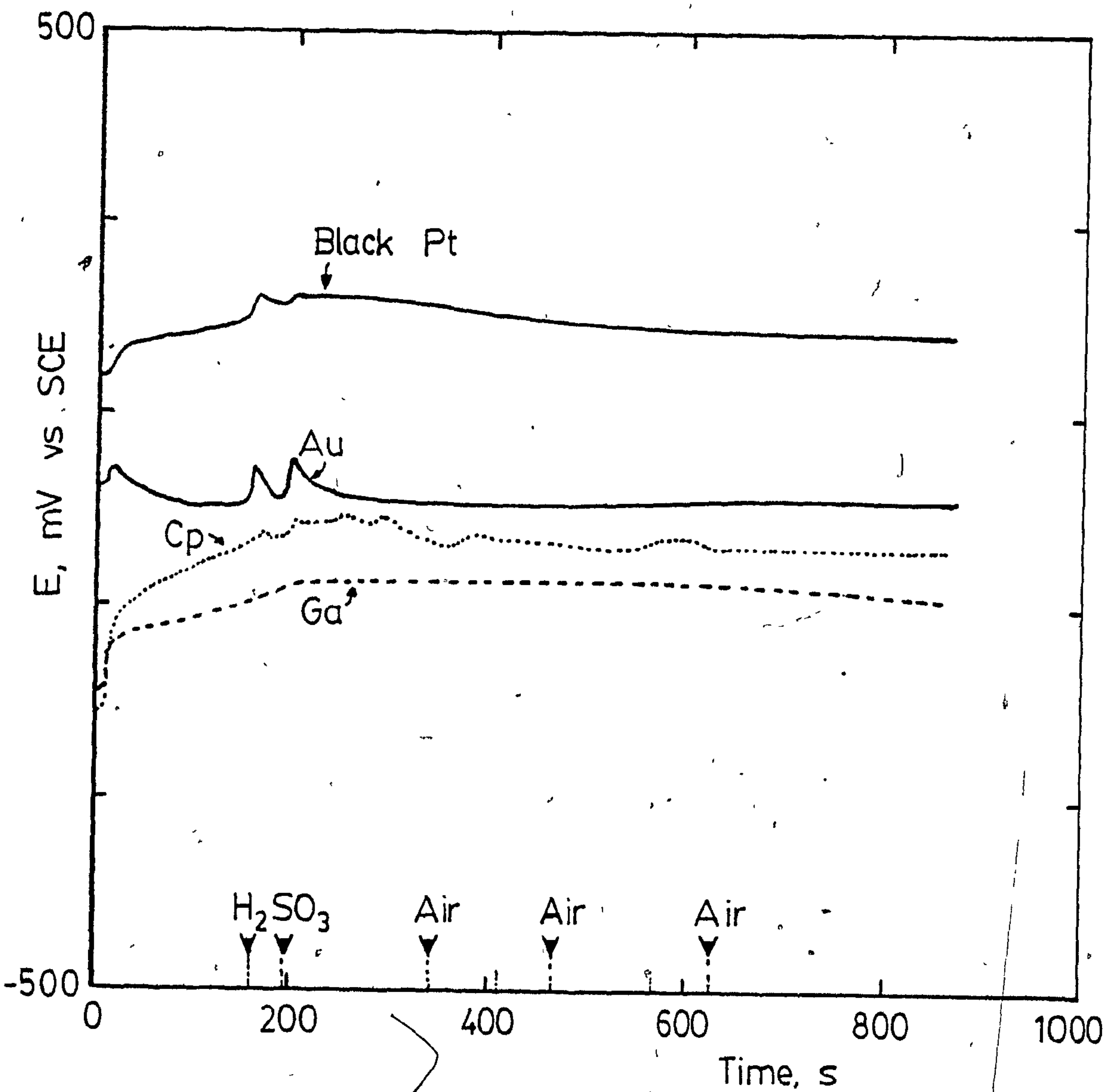
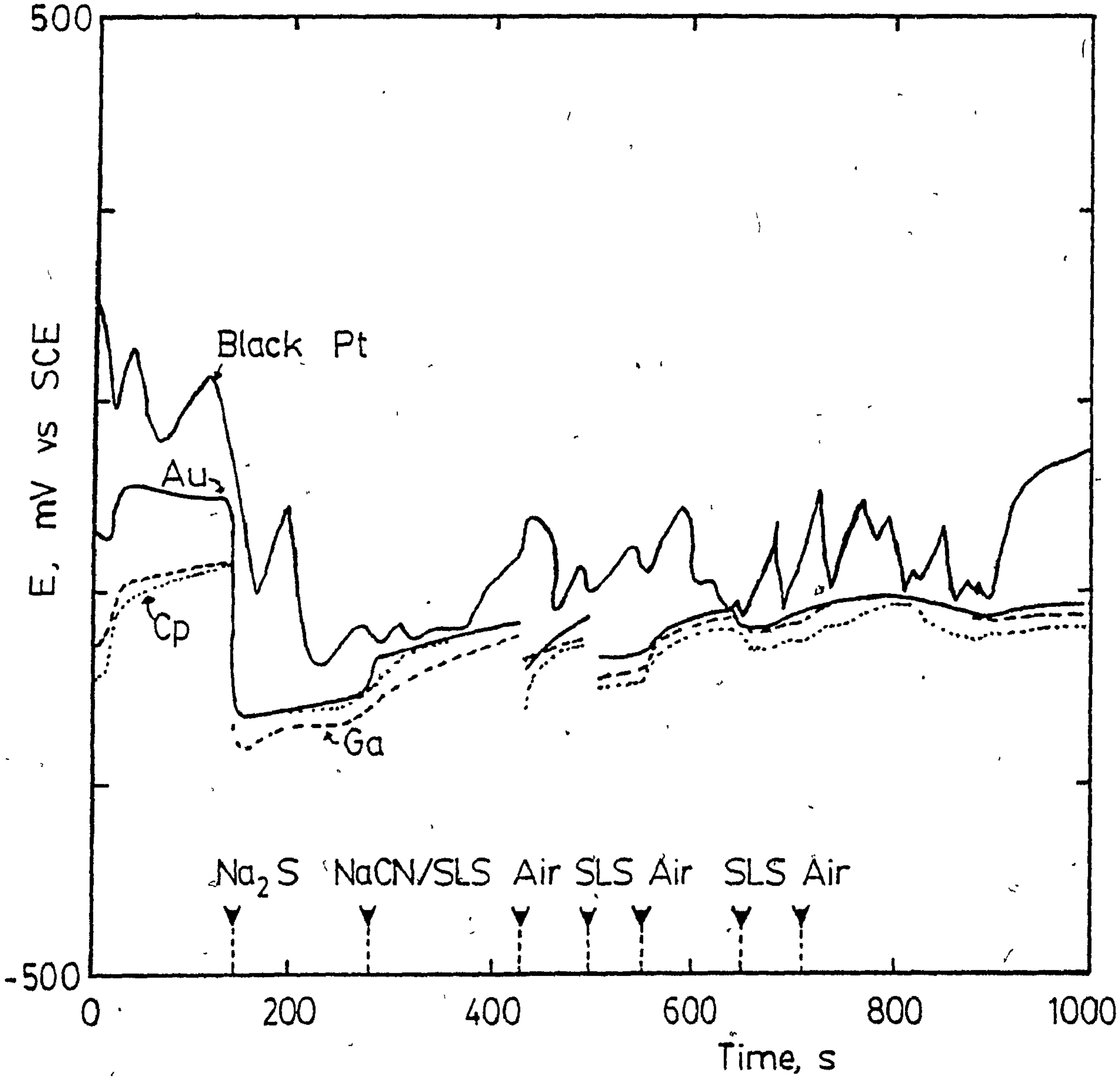


Fig. 17. Erratic response of the black platinum electrode due to the abrasion of the deposit.



During certain tests, the black platinum electrode sensed the reagent addition as a "mirror image" of the gold spiral and mineral electrodes (Figs. 13 and 14). In other tests, the black platinum electrode did not sense, or sensed marginally, the reagent addition (Figs. 15 and 16).

The "mirror image" behavior of the black platinum electrode was observed only when sodium sulphide, sodium cyanide, or potassium ferricyanide is added. On the other hand, the addition of alkaline reagents (lime, sodium carbonate) induced a reduction of the potential for the black platinum electrode in a similar fashion to the other electrodes.

This behavior of the black platinum electrode does not appear to be due to poisoning of the platinum deposit. Poisoning by sulphide and cyanide ions would lead the electrode to sense a potential lower than the true potential of the system (75, 76). In fact, an increase in potential is monitored during conditioning with sodium sulphide and potassium ferricyanide.

Hansuld (84) determined that during the oxidation of pyrite, the solution potential and the potential of pyrite may diverge over time. A similar phenomenon may be observed here, but for the reduction of minerals.

For certain modifiers, the galena electrode appears to reach "equilibrium" after the reagent addition faster than the chalcopyrite electrode (Figs. 13 to 15). However, for other modifiers, it is the chalcopyrite electrode which equilibrates faster than the galena electrode (Fig. 16).

In order to clarify the observed discrepencies between the different electrodes, the results have been tabulated (Table 5). The values reported are taken from a relatively flat portion of the profiles, usually during the last flotation step.

It appears that the greater discrepencies between the gold spiral and the chalcopyrite electrodes occur for alkaline and/or oxidizing conditions. This may suggest that the formation of hydroxide passive layers has occured. However, it is difficult to say whether the hydroxide was formed on the gold spiral or on the chalcopyrite electrode. Similar passivation phenomena have been previously observed but in the acid range (83). On the other hand, most of the significant discrepencies are observed for the A-1 sample. It is possible that the lower content of the A-1 sample in soluble secondary copper minerals may be of importance.

The discrepencies between the chalcopyrite and the galena electrodes are not readily rationalized. The magnitude of

Table 5. Summary of potential discrepencies during batch flotation.

Sample	Reagents	Average pH	E (mV vs SCE)		ΔE (mV)		Class
			Au	Bl. Pt	Au-Cp	Cp-Ga	
B (2)	SIPX	7.8	-30	130	-5	11	ii
B (2)	Na_2S/SIPX	10.0	-106	105	-2	-20	i
B (2)	Na_2S/SIPX	10.7	-110	47	-2	-43	i
B (2)	None	7.8	45	200	-3	24	ii
B (2)	Na_2S	10.8	-130	114	-5	13	ii
B (2)	Na_2S	10.6	-140	305	-2	-94	i
B (2)	$KClO_3$	7.8	1	157	-2	15	ii
B (2)	Na_2S/NaCN/ SLS	9.3	-23	99	-3	-46	i
B (2)	Na_2S/NaCN/ SLS	10.4	-80	62	-11	-8	i
B (2)	Na_2S/NaCN/ SLS	10.4	-110	56	-11	-9	i
B (3)	$K_3Fe(CN)_6$	8.4	15	129	2	40	ii
B (3)	$KMnO_4$ [1]	9.0	210	126	209	30	ii
B (3)	$KMnO_4$	8.2	36	116	39	20	ii
A	Na_2S	8.8	-130	148	-27	10	i
A	Na_2S/NaCN/ SLS [2]	9.0	-140	-96	-11	1	i
A	None	6.9	-9	221	-5	61	ii
A	CaO/NaCN	12.2	-120	-32	38	11	ii
A	CaO/Air/ NaCn/M2030	12.1	-88	0	47	0	ii
A	CaO/Air/ M2030	12.0	-62	27	59	8	ii
A	H_2SO_3	6.1	10	152	40	35	ii
A	$K_3Fe(CN)_6$	8.1	20	99	54	70	ii
A	$FeSO_4$	6.6	-34	157	1	19	ii
A	$KMnO_4$	7.3	140	202	39	67	ii
A	HCl	5.2	27	214	33	27	ii
A	H_2SO_3	5.8	13	189	50	39	ii
A	Na_2CO_3	9.7	-55	107	45	47	ii

SIPX: Sodium Isopropyl Xanthate
M2030: Minerec 2030 (thionocarbamate)
SLS: Sodium Lignin Sulfonate

[1]: Excess permanganate (pink color in slurry)
[2]: Abrasion of black platinum deposit (Fig. 17)

the discrepencies range from 1 to 94 mV. Also, a small gold-chalcopyrite discrepency does not necessarily imply a small chalcopyrite-galena difference. Furthermore, the discrepencies do not appear to be related to the galena content of the mineral slurry which is low for B zone (0.31% Pb) and high for A-1 zone (7.9% Pb). This is rather intriguing.

However, the introduction of modifiers to the pulp increases the complexity of the system. This does not permit to provide unequivocal conclusions regarding the best monitoring electrode. The gold spiral appears to be a good electrode, especially for the B-zone material, but further investigations would be required for the A-1 zone material.

3.2.3 Remarks on mineral electrodes as sensing electrodes for pulp potential.

With mineral electrodes, one may fear a lack of reproducibility from electrode to electrode since it is rare that the composition of sulphides is consistent throughout the orebody.

For fundamental work, i.e. the study of mineral reactions, the mineral pieces have to be screened either by visual inspection under the microscope for inclusions (64), or by rejecting electrodes which differ greatly from the average value.

These requirements might be waived for the use of the mineral pieces as pulp potential sensing electrodes. As previously observed, the contact with the mineral particles of the slurry is far more important than the electrode material, within the constraint that the electrode material does not exhibit reaction kinetics much greater than the other sulphide minerals.

The mineral electrodes which have been made were verified in water at pH 7.0 and in mineral slurries (copper concentrate). As expected, the different minerals gave different potentials, and the presence of inclusions gave rise to discrepencies between electrodes of the same type (see Table 6). However, when immersed in the same mineral slurry, the electrodes yielded potentials within 5 mV of each other (for the same mineral).

The chalcopyrite no. 1 electrode differs from the others after one year due to surface oxidation of the mineral piece. The pyrite no. 1 and galena no. 1 electrodes also differ from the others but this is due to the contamination of the mercury contact by copper products originating from the corrosion of the wire.

Table 6. Potential for mineral electrodes in water at pH 7.0 and in mineral slurries.

Mineral	Electrode	E (mV vs SCE)		
		In water	In a Cu con. slurry	
			Fresh	After 1 year
Chalcopyrite	1	-50	198	247
	2	-52	200	258
	3	-56	N.D.	261
(Inclusions)	4	-69	N.D.	257
Pyrite	1	33	170	224
	2	31	140	254
	3	35	N.D.	255
Galena	1	-101	184	211
	2	-71	180	243
(Pure)	3	99	N.D.	245
(Pure)	4	-103	N.D.	244
Sphalerite/ graphite (ZnS:C = 2:1)	1	-250	N.D.	223
	2	-240	N.D.	224
	3	-240	N.D.	220

The last comment is on the composite sphalerite/graphite electrode. According to the rest potentials given in literature (75), the sphalerite would give a rest potential not far of that of the other sulphides even though the measurement of a rest potential with sphalerite is always questionable. However, the composite carbon/sphalerite electrodes give potentials much lower than that of the other ones (-250 mV vs SCE or -5 mV vs SHE) and hence appear to give the rest potential of carbon instead of sphalerite. The rest potential of sphalerite is 210 mV vs SHE at pH 4, (75), or 76 mV vs SHE at pH 6.8 for ZnS precipitates (64).

As such, these electrodes are not reliable and improvements will have to be made.

3.3 Selection of the reference electrode.

The attention has been mainly on the sensing electrodes themselves. However, the potentials measured are against a reference electrode. The quality of this electrode is as important as the sensing electrode.

3.3.1 Temperature compensation

Contrary to pH measurements, redox measurements cannot be automatically compensated for the temperature of the solution or slurry. This is due to the presence of mixed potentials in complex systems and to the ignorance of the main redox reaction(s) present.

Strickly speaking, the temperature of the system in which the redox potential was measured must be stated, particularly when the temperature may vary by 10 °C or more between measurements. This is usually not a problem for laboratory investigations which are conducted at room temperature. For the present study, all measurements were carried out at 20 +/- 3 °C. However, this is certainly not the case for a concentrator where the temperature of the process water can vary appreciably according to the season, e.g. +5 to +25 °C.

A certain degree of temperature compensation of the redox potential will be needed for plant application. Even though it might be impossible to compensate the redox system in itself, it is possible to take into account the variation of the reference potential with respect to temperature. For example, the electrode potential of the calomel electrode decreases by 0.65 mV/°C between 10 and 30 °C while that of the Ag/AgCl electrode decreases by 1 mV/°C between 20 and 25 °C. (93).

These differences are small, 3.25 to 5 mV for a 5 °C temperature variation, but one equipment manufacturer claims that potential control of the flotation process can be performed within 5 mV of the potential set point (2, 3, 4). In such a case, a monitored change in potential may be due to a change in the temperature of the process rather than an actual modification in the chemical environment of the pulp. Fortunately, the effect of temperature variation will be observed over periods of months rather than days or hours.

3.3.2 Bias and memory effects due to the liquid junction

The presence of a liquid junction between the electrolyte of the reference electrode and the solution/slurry to be measured introduces a potential difference between these two solutions. The junction potential depends on the concentration and the velocity of migration of the ions contained in the two contiguous solutions. The magnitude of the junction potential is small (an average of + 5 mV for the SCE over the entire pH range) but can be calculated if the concentrations are known and extremely accurate results are desired (93).

However, contamination of the liquid junction (porous plug or sleeve) will lead to an actual junction potential which is greatly different from the expected one. Table 7 shows such effects for laboratory references electrodes.

The two SCE electrodes are in good agreement for the two systems. On the other hand, there is no agreement between the five different Ag/AgCl reference electrodes. This seems to be linked to the type of electrolyte utilized for these electrodes. Contrary to the saturated KCl electrolyte used for the porous sleeve electrodes, the gel electrolyte of the combination electrodes is never changed or refilled. Hence, long term contamination of the gel electrolyte is possible.

It can be observed that the difference between any of the Ag/AgCl reference is dependent on the sample. It is thus impossible to perform a simple arithmetic correction and a contaminated reference electrode should be discarded.

Table 7. Comparison of reference electrodes. ([Fe(III)] = [Fe(II)] = 2.5 M as their chlorides).

Reference	E Au foil vs Ref. (mV)	
	Water	Fe(III)/Fe(II)
A (SCE, porous sleeve)	43	452
B (SCE, porous sleeve)	41	461
C (Ag/AgCl, gel, combination pH)	63	449
D (Ag/AgCl, gel, combination pH)	74	492
E (Ag/AgCL, gel, combination ORP)	76	465
F (Ag/AgCl, gel, combination ORP)	98	503
G (Ag/AgCl, gel, combination ORP)	39	446

A contaminated reference electrode may also introduce memory effects from solution to solution, similar to a poisoned sensing electrode. These memory effects are more visible when performing the measurements in dilute systems such as process water in a concentrator since the measured value is relatively small.

3.4 Conclusions

The electrochemical potentials measured in flotation systems are mixed potentials, coupled with the randomness of the contact of the electrode and the mineral particles of the slurry. As such they cannot be directly related to fundamental quantities such as the rest potential unless the kinetics paramaters of the electrode reactions and the concentrations of ions in solution are known.

The significance of the redox potential measurements in mineral slurries during conditioning and flotation is similar to that of solution systems. The redox potential in the pulp indicates the driving force for oxidation or reduction of the minerals.

Smooth noble metal electrodes and mineral electrodes sense these conditions in a similar manner. However, a black platinum electrode exhibits a different pattern due to a large surface area for contact with the solution but a small projected area for contact with the minerals, and senses more the solution potential than the mineral potential. Unless the system has reached an equilibrium, the solution potential will differ from the mineral potential (or pulp potential).

A "general purpose" sensing electrode would be a gold spiral since it exhibits a potential near that of a chalcopyrite electrode for most of the conditions encountered during conditioning and flotation. On the other hand, large discrepencies (30 to 209 mV) were observed between the gold and chalcopyrite electrodes, mainly under alkaline and, or, oxidizing conditions. Hence, it is suggested that these discrepencies arise from the formation of passive layers (hydroxides ?) onto either the gold or the chalcopyrite surface.

Mineral sensing electrodes (chalcopyrite and galena) yielded slightly different responses during laboratory flotation, namely in the presence of modifiers which may depress either one of the two minerals. The difference appears to be linked to the kinetics of reaction of the individual minerals.

Finally, the reference electrode must not be neglected. The temperature at which measurements were taken should be stated particularly if the system being investigated is subject to important temperature variations. Also, the reference electrode should be verified for possible contamination of the porous junction or of the electrolyte.

4. DESCRIPTION OF ORE AND CONCENTRATE SAMPLES

Specific characteristics of ores and ore types have a great impact on the expected metallurgical response (86, 87). The following description highlights some of the responses obtained in the laboratory but is by no means exhaustive.

4.1 Origin of samples

The deposit of Les Mines Selbaie consists of three ore zones named "A-1", "A-2" and "B" (88, 89, 90). Production is presently carried out on the B and the A-1 ores. These two ores are metallurgically incompatible due to a high content of secondary copper minerals such as chalcocite, covellite and even native copper in the B zone (88). These secondary copper minerals were formed during supergene alteration of the massive sulphides (89, 90).

The A-1 zone has been divided in five ore types according to the geological formation, host rock, and metal contents. Table 8 presents the assays for these ore types as well as two other samples used in the experiments. With the low copper content of most of the samples, 0.13 to 0.78% Cu, one of the difficulties for metallurgical testing was to get sufficient copper rougher concentrate to investigate the response during cleaning. Hence a sample of the copper concentrate produced during the pilot plant run on the "Fresh ore" was used. In order to study the effect of a high quantity of secondary copper minerals, copper concentrate samples were obtained from the B-zone flotation circuit. Table 9 presents the assays of these concentrate samples.

Table 8. Assays of the A-1 ore samples.

Sample	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	Composite A:B:C:D: = 3:5:1:1	0.78	2.88	0.11	8.9	94
Fresh ore		0.21	3.10	0.17	8.2	160

Table. 9. Assays of the copper concentrate samples.

Sample	Assays in % (g/t for Ag)				
	Cu	Zn	Pb	Fe	Ag
A-1	17.2	21.1	7.9	18.9	8300
B zone (2)	30.0	4.66	0.31	23.7	260
B zone (3)	27.2	4.65	N.A.	25.0	300

4.2 Microscopic examinations

Head assay of ore and concentrate samples is often not sufficient to describe the sample. Primarily, it does not provide the mineralogical composition of the samples. Sometimes, microprobe analysis is used to obtain more detailled information on individual mineral assays, normally for mineral indentification.

4.2.1 Identification of the minerals.

No formal quantitative analysis was performed. The main problem lies with the textural occurence of the supergene minerals which often occur as rims around the other minerals (89). Any accurate determination of the mineral distribution would require image analysis, on an area basis (91).

Fig. 18 presents occurences of chalcocite as rims around chalcopyrite particles while Fig. 19 shows a "family portrait" of the secondary copper minerals: chalcocite veinlets, complex chalcocite/bornite, and native copper. These minerals and textures are typical of the B zone ore.

The occurence of secondary copper minerals in the A-1 zone ore is different. The chalcocite is mainly present as distinct particles instead of rims or veinlets (Fig. 20).

Fig. 18. Typical occurence of chalcocite (B-zone).

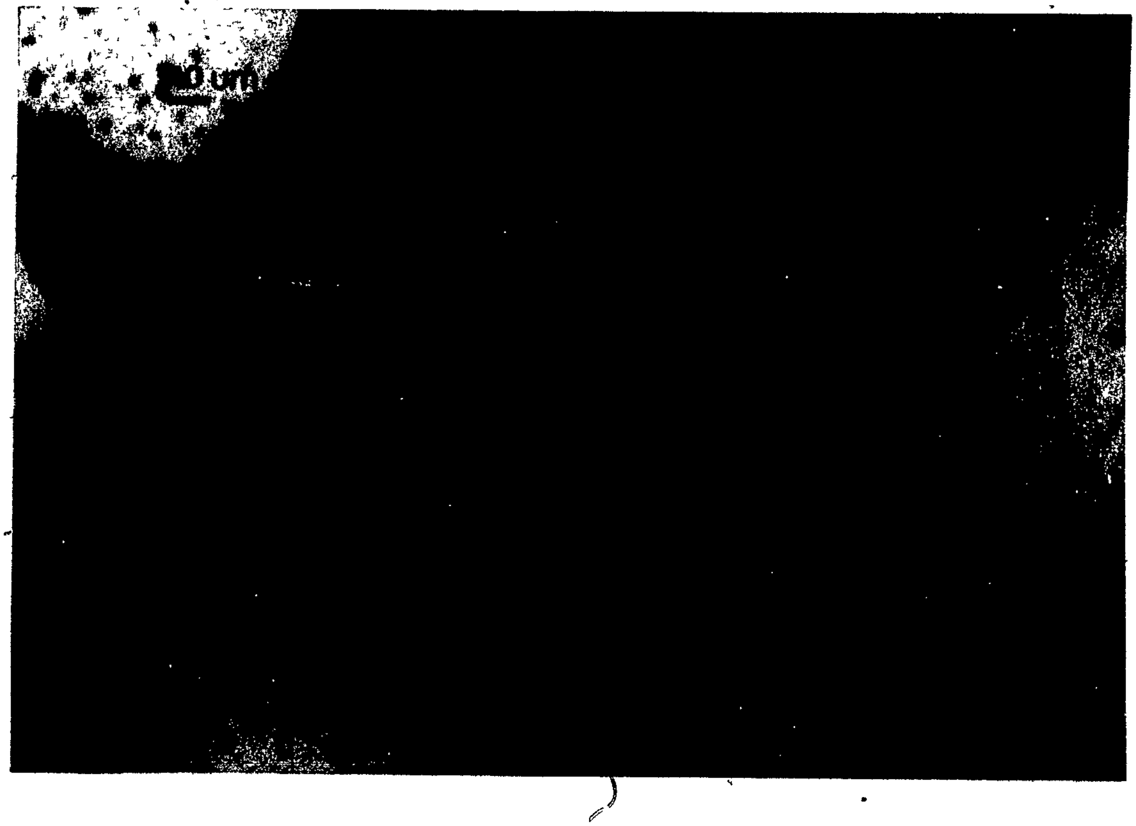


Fig. 19. "Family portrait" of secondary copper minerals (B-zone).

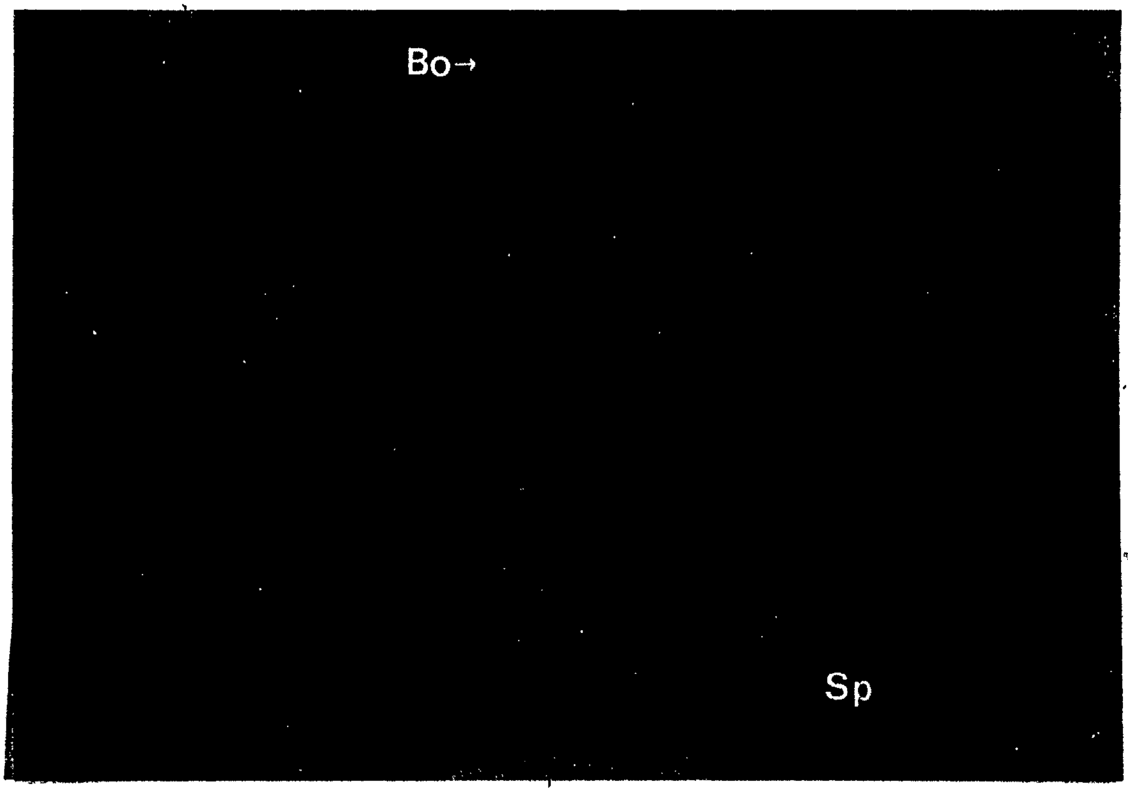
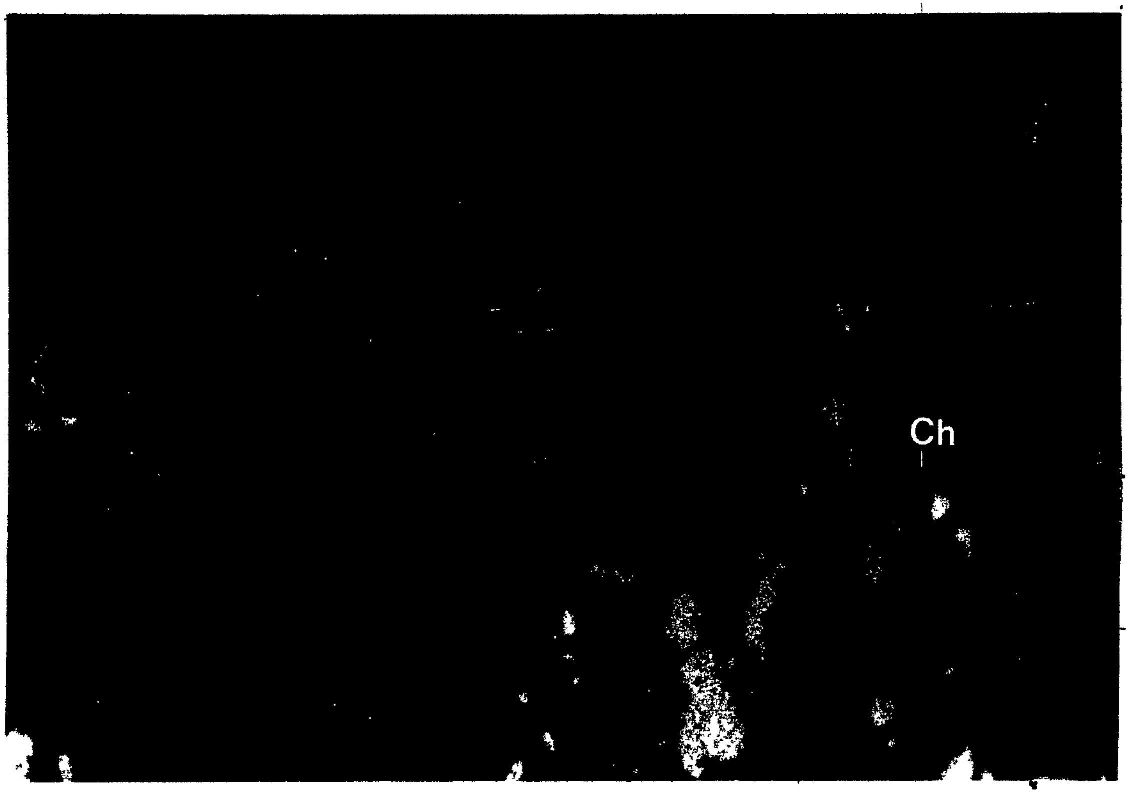


Fig. 20. Typical occurence of chalcocite (A-1 zone).



The secondary copper minerals present in the B-zone concentrate samples represented between 5 to 10 % of the total mineral surface of the sections. On the other hand, the secondary copper minerals present in the A-1 zone concentrate samples appeared to represent less than about 1% of the mineral area. The secondary copper minerals were more easily found in the concentrate samples than in high density fractions of ore samples from the A-1 zone.

Figs. 21 and 22 show typical sphalerite particles from the A-1 zone ore. Although the sphalerite particles appear grey on the polished sections, the color of large pieces and particles showed a wider range: cream, "bottle brown", and dark grey. The color of sphalerite is an indication of the iron content in solid solution, the lighter the sphalerite, the less iron it contains (49).

The sphalerite in the A, D, and E ore types frequently has inclusions of exolved pyrite and/or chalcopyrite as seen in Fig. 21. In some instances, the inclusions are quite large. On the other hand, the sphalerite of the B, C, and Fresh samples rarely exhibit inclusions as observed in Fig. 22.

The presence of chalcopyrite inclusions in sphalerite particles severely limits the achievable separation between copper and zinc. Sphalerite particles will report to the copper concentrate if they expose a large proportion of chalcopyrite inclusions on their surfaces. On the other hand, the sphalerite particles which contain less inclusions, and are successfully depressed during copper flotation, will cause an appreciable fraction of the copper to be recovered in the zinc concentrate. Since the size of the inclusions is typically from 1 to 5 µm, it would be impractical to grind the ore to this size range.

Fig. 21. Typical sphalerite particle: A, D, and E ore types.

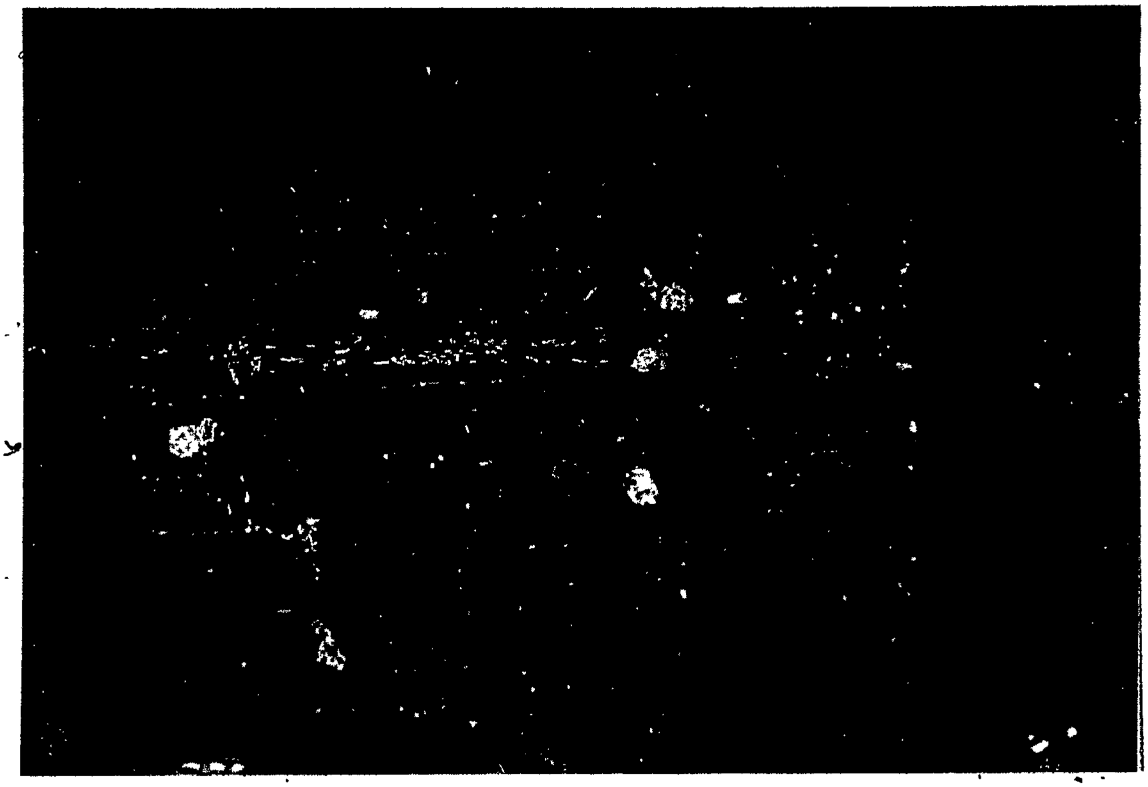


Fig. 22. Typical sphalerite particles: B and C ore types and Fresh ore.

4.2.2 Microprobe analyses of the sphalerite.

Further information on the composition of the sphalerite was obtained by microprobe analysis. This was to permit the classification of sphalerite by chemical composition rather than by the color of the pieces. This latter quality is subjective and is greatly affected by the lighting conditions. Table 10 shows the micro-assays for the different ore samples.

Table 10. Microprobe analysis of sphalerite particles.

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	15	0.02	2.68	62.52	32.93

The iron and copper contents of the sphalerite do not appear to be related to the presence or absence of inclusions. For example, the copper and iron assays for the A, and Fresh sphalerite are not greatly different even though the A sphalerite presents extensive inclusions while the Fresh one is almost free of them.

4.3 Macroscopic characterization of the ore types .

Microscopic examination is a time consuming procedure. Also, it is difficult to find and observe the trace sulphide minerals by light microscopy. There may be other techniques which could permit characterization of the ore/mineral at a macroscopic level.

4.3.1 Activity of the ore

The main ore samples originated from stock-piles which were left exposed to atmospheric conditions for a long time. It was felt necessary to determine the extent of activity due to the weathering of the ore. A test procedure has been designed similarly to that of a study on chromium dissolution from waste slag (92).

The procedure consists in letting a simulated acid rain solution percolate through a crushed sample of the ore (300 g). The sample is put into a 2.5 cm I.D tube fitted with a

500 µm nylon mesh at the bottom. The solution is recirculated for 6 hours using a peristaltic pump and a 4 cm head of solution is maintained above the solids.

The simulated acid rain is prepared from a stock solution of 30 ml sulphuric acid and 10 ml of nitric acid in 100 ml of distilled water. This provides a ratio of $H_2SO_4:HNO_3$ of 3:1 (92). The final acid rain solution is made by diluting 5 ml of the stock solution into 1 liter with distilled water. The pH of the solution is adjusted to 4.5 by adding sodium carbonate from the original pH of 1.5

After percolation through the sample, the final pH is measured and the recovered solution (about 60 ml) is filtered and analysed by atomic absorption for dissolved metals. Table 11 presents the results.

The procedure was repeated twice for the ABCD composite sample to ensure reproducibility of the test which appears to be good regarding the final pH and zinc content.

It can be observed that the final pH of the liquor is higher than the original one (4.5) for most of the samples. Only the D ore type (massive pyrite) appears to generate acid during the percolation (final pH of 4.0) and is the only one which yields a significant amount of dissolved iron.

Lead seems to be hardly soluble except for the Fresh ore (upper part of the A-1 zone orebody). This would be an indication that the ore is weathered but to a lesser degree than the E ore type (altered ore) which is the only one yielding a high level of dissolved copper (72 ppm). Such weathering is common in sulphide orebodies (63).

The high copper and zinc concentrations in solution may be due to the high assays of the ore type (4.44% Cu and 6.35% Zn). Nevertheless, the C ore type may be subjected to in-situ activation of the sphalerite although to a lesser degree than the E type.

Table 11. Ore activity (initial pH of 4.5).

Sample	Final pH	Metal concentrations in solution (ppm) Cu	Zn	Pb	Fe
ABCD	7.50	0	115	0	0
ABCD	7.50	0	132	0	0
Fresh	5.00	0.2	322	2.6	0
A	7.65	0	0.1	0.2	0
B	6.50	0.5	2.3	0.2	0
C	6.45	3.5	>1000	1.1	0
D	4.00	0.8	440	1.6	526
E	4.60	70.0	>1000	1.1	4

4.3.2 Response of sphalerite to copper activation

The sphalerite of the A and E ore types showed extensive chalcopyrite/pyrite inclusions while presenting a large difference in iron assays (2.45% Fe for A and 4.14% Fe for E). This difference in composition may lead to a distinct behavior upon copper activation and flotation of the sphalerite (31, 47).

Cyclic voltammetry was used to study the electrochemical behavior of un-activated and activated sphalerite. The experiments were performed in an electrochemical cell designed so that particulate bed mineral electrodes could be used, similarly to the cell described by Gebhardt et al. (19).

In view of the difficulties experienced in manufacturing sphalerite electrodes for monitoring the redox potentials in flotation pulps (section 3.2.3), it is not sure whether the applied potential was across the sphalerite/solution interface or across the sphalerite particle bed. The cyclic voltammograms (current vs applied potential curves) can be corrected for iR drop in the solid/solution interface although this may be difficult (82). However, no information could be found on correction techniques for iR drop across the solid phase.

The un-activated sphalerites presented flat cyclic voltammograms (Figs. 23 and 24). Hence, no electrochemical reaction is observed within the potential range studied. The effective potential applied to the sphalerite particles may have been too small, due to the high resistivity of sphalerite, to promote any electrochemical reaction at an observable rate (high current).

Copper activation was performed by inserting 0.25 g of solid $CuSO_4{:}5H_2O$ into the cell for the 1 g of -150 µm sphalerite already present. This is slighly more than 100 times the average amount used in the flotation tests (100 g/t for a 3.0% Zn head or 0.0022 g $CuSO_4{:}5H_2O$ for 1 g ZnS). The pH of the solution was not re-adjusted after the introduction of the copper salt. Cyclic voltammetry was performed after 2 min. of reaction, and the voltammograms can be seen in Figs. 25 and 26.

In comparison with the un-activated sphalerite, there is an appreciable current being recorded. Significant differences can be observed between the two types of sphalerite. First, the copper activated A type sphalerite experiences a greater current than the E type, about 4 times greater in the anodic region (positive potentials) and 7 times in the cathodic region. Second, the A type appears to enter a passive region at around -300 mV vs SCE. In this region, the

Fig. 23. Cyclic voltammogram for un-activated A type sphalerite at pH 10.5 (scan: 4 mV/s).

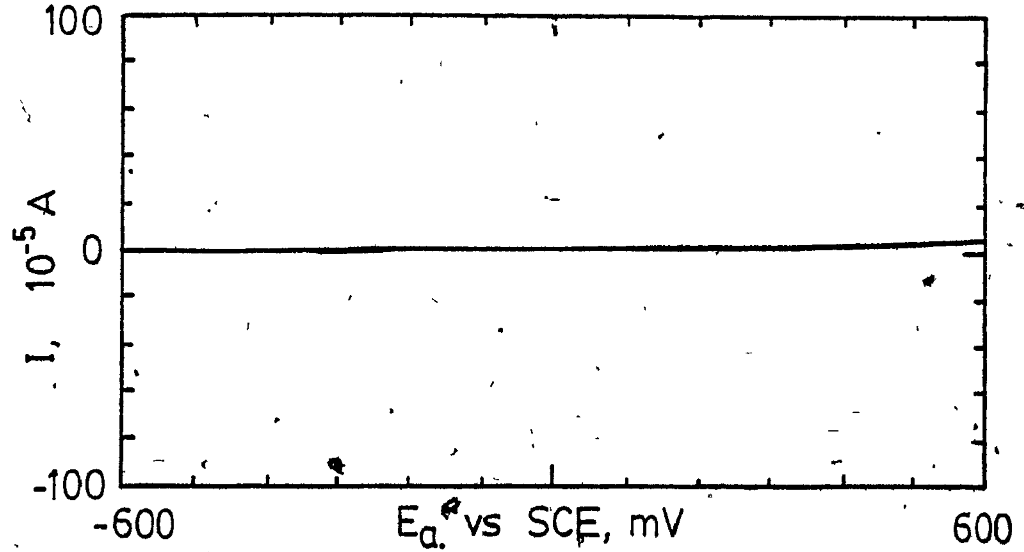


Fig. 24. Cyclic voltammogram for un-activated E type sphalerite at pH 10.5 (scan: 4 mV/s).

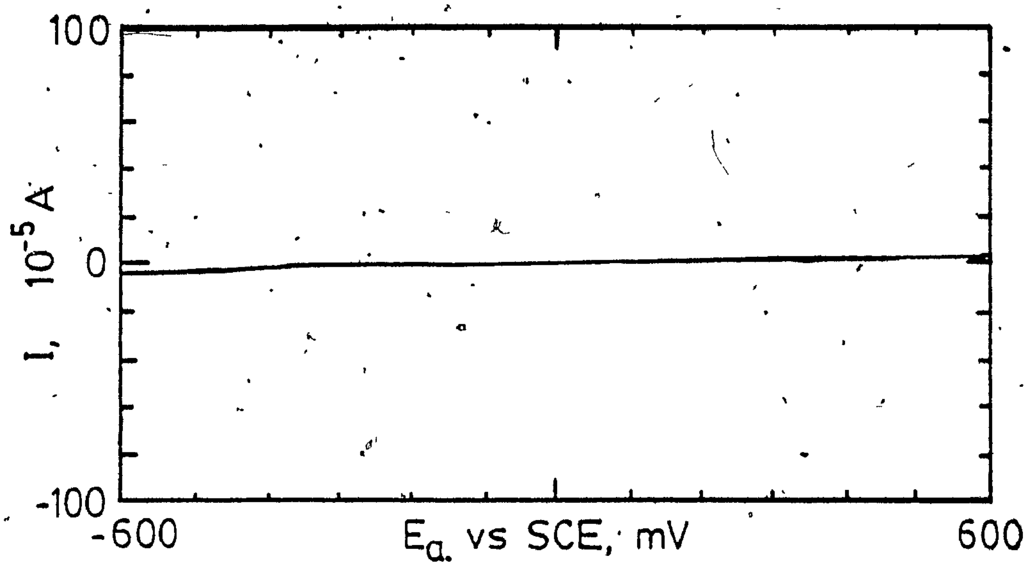


Fig. 25. Cyclic voltammogram for copper-activated A type sphalerite (scan: 4 mV/s).

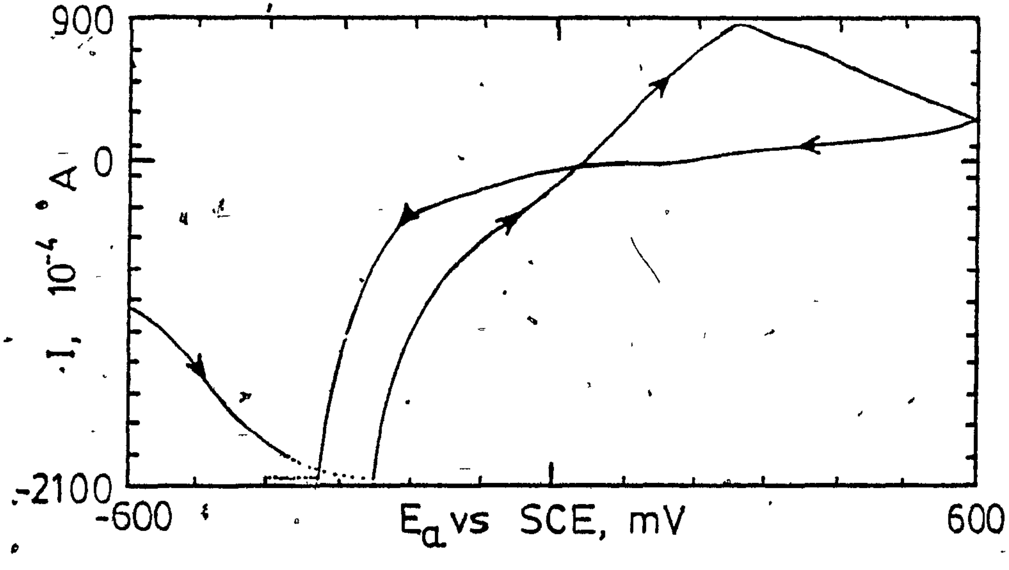
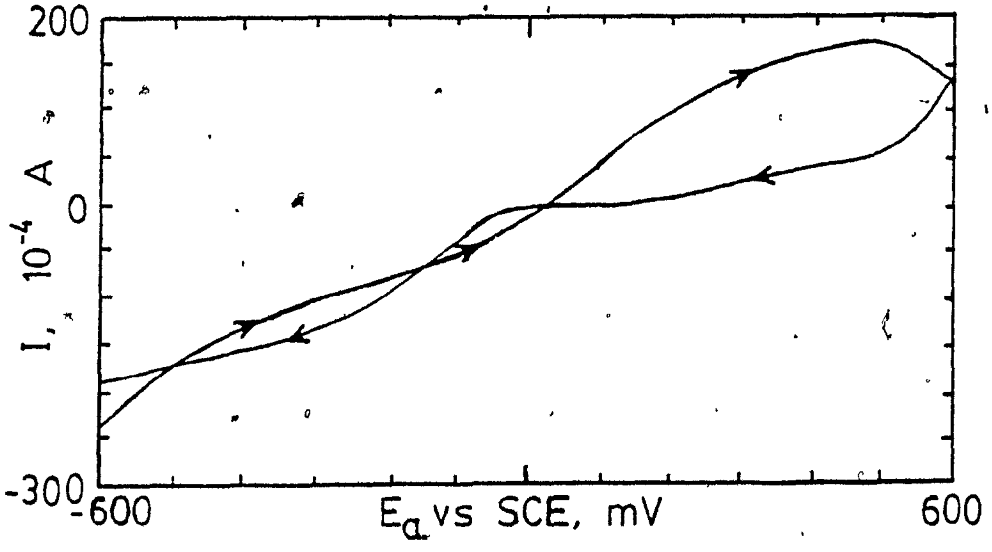


Fig. 26: Cyclic voltammogram for copper-activated E type sphalerite (scan: 4 mV/s).



potentiostat could not control anymore the applied potential, indicated by the steps in the measured current. This is not observed with the E type sphalerite.

Also, it can be observed that the reaction occuring is not fully reversible (cathodic current is not equal in magnitude the anodic current). This was expected as the electrochemical reactions involving electronation or de-electronation of the sulphur atom are rarely reversible (94). The "reversible" potential, $E^r = -E_a$, of the reaction appears to be between 0 and 50 mV vs SCE (245 to 295 mV vs SHE). Possible couples corresponding to the reaction are: SO_4^{-2}/H_2SO_3 (E^o = 200 mV vs SHE), and Cu(II)/Cu (E^o = 340 mV).

Without a knowledge of the activities of the ions present in the solution after copper activation, the assignation of a plausible electrode reaction requires blank tests with simple solutions. Comparison with a blank copper sulphate solution (Fig. 27) and blank copper oxide dissolved in hydrochloric acid (Fig. 28) shows that the sulphate/sulphite couple may be the main one observed in the anodic regions on Figs. 25 and 26. Also, copper plating onto the electrode the main reaction observed in the chloride solution, might occured simultaneously with other reactions for the negative potentials, particularly for the copper-activated A type sphalerite.

Fig. 27. Cyclic voltammogram for a blank solution of copper sulphate (scan: 4 mV/s).

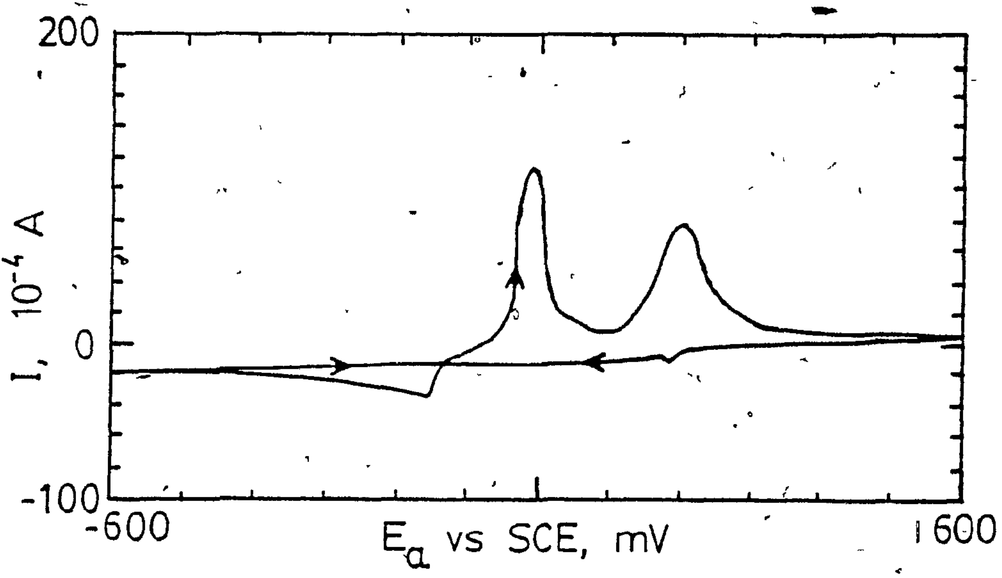
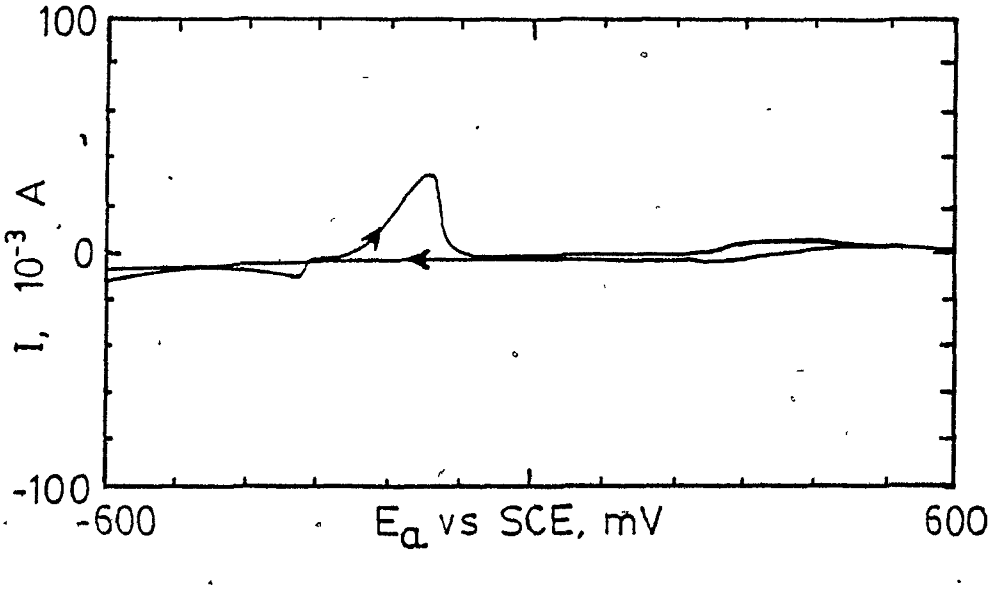


Fig. 28. Cyclic voltammogram for a blank solution of copper oxide in hydrochloric acid (scan: 4 mV/s).



4.4 Conclusions.

For the A-1 zone, simple light microscopy does not permit an accurate quantification of the level of secondary copper minerals (mainly chalcocite) associated with each ore type due to the trace amount observed.

Two classes of sphalerite have been identified. The first one exhibits a great quantity of chalcopyrite or pyrite inclusions (A, D, and E ore types) while the second one rarely shows inclusions (B and C ore types and Fresh ore). This will have a strong influence on the achievable Cu/Zn separation.

Microprobe analysis showed that the iron content in the sphalerite varies according to the ore type and was not related to the presence of chalcopyrite or pyrite inclusions. Cyclic voltammetry of un-activated and copper-activated A and E type sphalerite samples showed differences which may be attributed to the different iron contents of the sphalerite samples. On the other hand, the high resistivity of sphalerite does not allow the use of these results as a confirmation of an electrochemical mechanism for copper activation.

5. LABORATORY BATCH FLOTATION

5.1 Introduction

Investigation of the flotation response of the A-1 zone ore from an electrochemical approach is a task more complex than generally attempted. The possibility of collectorless flotation (16, 17, 18), the effect of the grinding environment (33, 35), and the presence of the highly soluble chalcocite mineral (19, 23, 87) had to be considered almost simultaneously. Also, variation in the floatability of sphalerite between the ore types was possible.

The experiments performed were directed along the following lines:

i) Effect of grinding environment and sodium sulphide on the flotation of the ore.

ii) Effect of the ore type upon the potential and pH achieved after laboratory grinding.

iii) Comparison of responses of the different ore types.

iv) Screening of modifiers (redox, pH) for selective flotation of bulk Cu-Zn-Pb concentrates.

5.2 Evaluation techniques

Traditionally, grade-recovery curves, where the concentrate grade is plotted versus the metal recovery into the concentrate, have been the most common graphical means for evaluation. Also, sometimes the metal recoveries are related to operating parameters such as pH, collector dosages, etc. More convenient and informative methods have been introduced and they will be briefly described.

The floatability-potential curves (see section 1.6) are probably the best method to evaluate the flotation of the mineral as a function of the electrochemical potential. However, flotation is only but one step in the mineral processing flowsheet. The separability curve introduced by Dell (95, 96) graphically presents the mineral recovery against the yield or the total mass recovered in the concentrate. When the laboratory procedure is extended to the limit that a quasi-perfect flotation is performed (release analysis (95)) then the separability curve obtained indicates the maximum separation which can be achieved due to the liberation of the minerals (95, 96).

The technical efficiency, E_t, of the flotation process can be evaluated from the separability curve. The technical efficiency as defined by Taggart (97) and Jowett (98) will be used:

$$E_t = \text{Amount separated / amount separable} \qquad [11]$$

The efficiency may also be expressed as

$$E_t = Rv - Rg \qquad [12]$$

where Rv and Rg are the recoveries of the valuable mineral and the gangue mineral respectively.

The latter equation is often used when the separation is performed between two minerals, e.g. a sulphide mineral and a non-sulphide gangue. However, when dealing with several minerals, the technical efficiency must be evaluated from the separability curve.

The construction of the separability curve requires the removal of concentrate increments from the ore, usually by means of longer flotation time for each increment. The experimental technique is as such the same as that required to determine the kinetic parameters for flotation models (99).

Separability curves have one limitation when investigating separation on complex sulphide ores. Ther is no indication about which non-desired sulphide mineral has been successfully depressed.

5.3 Laboratory procedures

The laboratory flotation procedures were designed around typical standard procedures for bench scale flotation tests (100, 101). All reagents were of commercial purity for the surfactants: Sodium Isopropyl Xanthate (SIPX), Minerec 2030 (a thionocarbamate), Methyl Isobutyl Carbinol (MIBC), and sodium lignin sulfonate (S.L.S.); the inorganic reagents were of laboratory grade.

Distilled water was used to prepare the solutions and the solution strengths were 0.1% by weight for the organic thiols and 5% for the inorganics. MIBC was added pure while quick lime (CaO) was added dry. All solutions were prepared daily. Potable water was used for pulp dilution in grinding and flotation.

Two kinds of laboratory rod mill were used. The first one was a polypropylene mill for the investigation of the effects of the grinding environment on the flotation response. A stainless steel mill with a mixed stainless/mild steel charge was used to study the response of the different ore types. The grinding charge was approximately 32 kg for the polypropylene mill, consisting of rods ranging between 5 and 25 mm in diameter. The charge used in the stainless steel mill was 20 kg of rods of 12.5 mm and 25 mm diameter.

Besides the grinding conditions, standard bench scale practices were followed for flotation, drying, weighing and sample preparation.

5.4 Effect of the grinding environment and sodium sulphide on the flotation response.

The effect of the grinding environment (stainless steel or mild steel) on the response during roughing was studied for the ABCD composite and the Fresh Ore. Sequencial selective flotation was attempted (Table 12). Following grinding and conditioning, three incremental copper rougher concentrates were recovered. Similarly, three zinc rougher concentrates were obtained after activation with copper sulphate. A second addition of copper sulphate was required prior to the third zinc rougher to increase the recovery of sphalerite for the mild steel grinding media.

The first relationship explored was that of the alkalinity level in the copper rougher. The total copper and zinc recoveries into the copper rougher concentrate are shown for the stainless steel (Fig. 29) and the mild steel (Fig. 30) grinding environment.

Table 12. Test conditions: effect of grinding environment and alkalinity level.

Stage	Time	Reagents (g/t)					
	(min.)	CaO	NaCN	$ZnSO_4$	$CuSO_4$	SIPX	MIBC
Grinding	20	250	50	250			
Conditioning	1	To pH	50	250			
Conditioning	1					10	5
Cu Ro 1	1						
Conditioning	0.5					10	
Cu Ro 2	2						
Conditioning	0.5					10	
Cu Ro 3	3						
Conditioning	1	To pH 10					
Conditioning	1	pH 10			50		
Conditioning	1					10	5
Zn Ro 1	1						
Conditioning	0.5					10	
Zn Ro 2	2						
Conditining	0.5				(50)	10	
Zn Ro 3	3				(Mild steel)		

For the stainless steel environment, the copper recovery shows a very slight increase with increasing alkalinity. However, the effect of pH on the zinc recovery is more dramatic, especially for the ABCD composite.

The test for the ore activity showed that the Fresh ore was more active (releases greater quantities of metal ions in solution) than the ABCD composite (Table 11). A greater oxidation of the copper minerals and the lower heads for the Fresh ore in comparison with the ABCD composite (0.22% vs

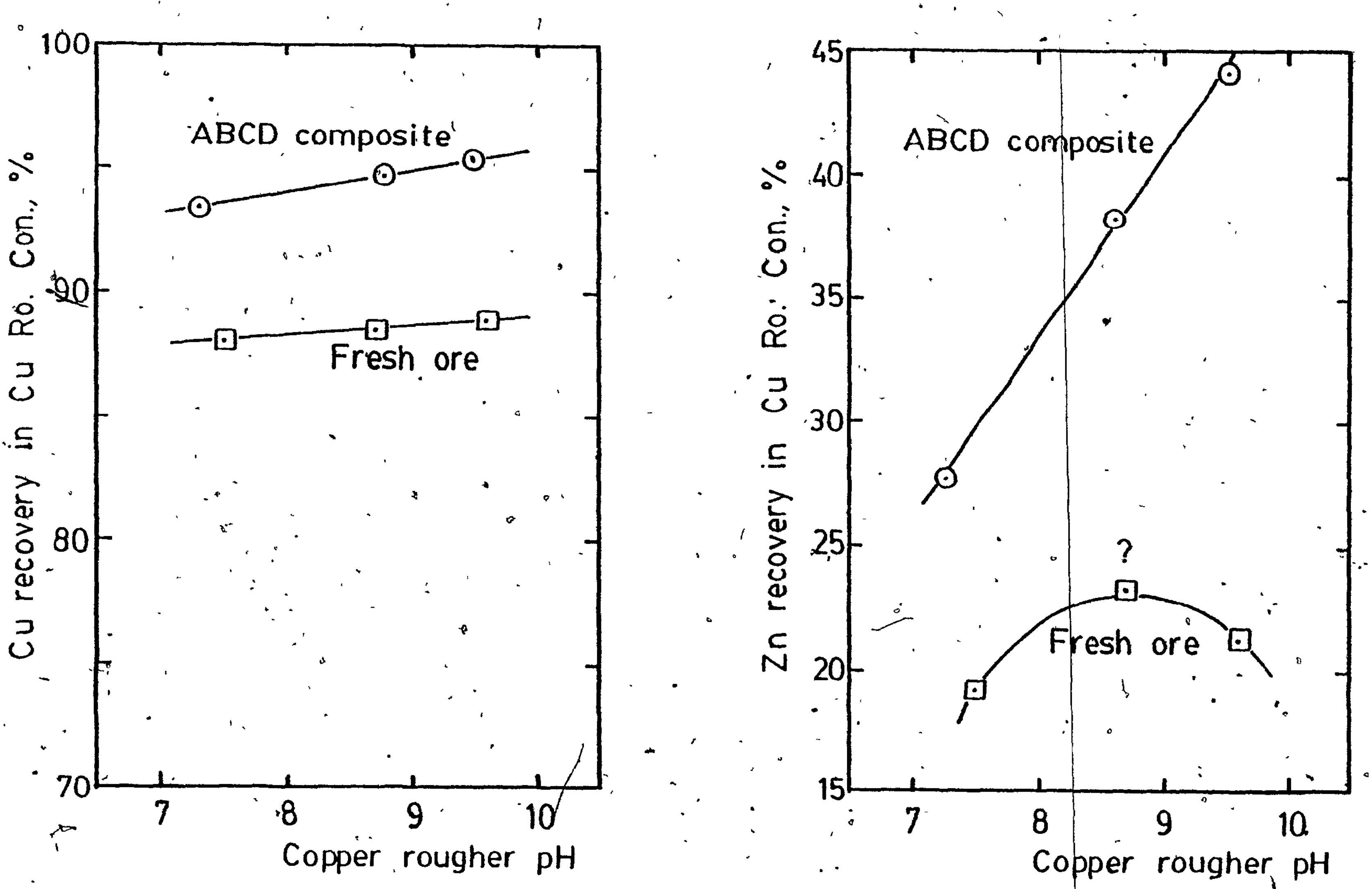


Fig. 29. Cu and Zn recoveries in the copper rougher concentrate vs pH: stainless steel grinding media.

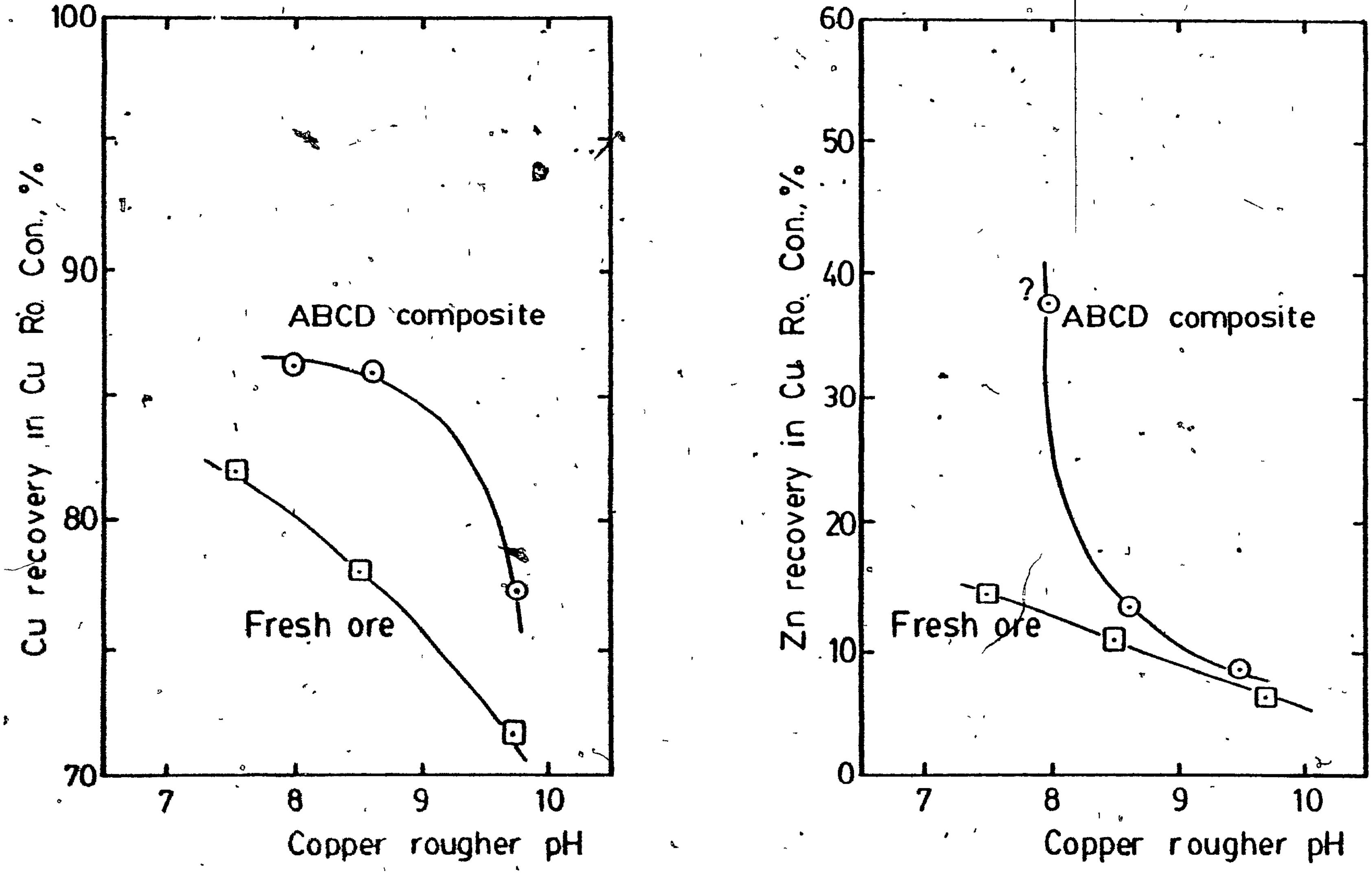


Fig. 30. Cu and Zn recoveries in the copper rougher concentrate vs pH: mild steel grinding media.

0.78% Cu) resulted in the lower copper recoveries achieved with the Fresh ore, for both the stainless and the mild steel media.

The zinc recoveries are greater for the ABCD composite for both the stainless steel (SS) and the mild steel (MS) environments (Fig. 30). The results of the ore activity test indicated that the Fresh ore was slightly more active than the ABCD composite (cf Table 11). Hence, higher zinc recoveries were expected for the Fresh ore. This is not the case and this implies that other factors must be considered.

Grinding with a MS charge yields a 10 to 20% lower copper recovery and a 10 to 40% lower zinc recovery in comparison ~~of the~~ SS charge. Also, the metal recoveries decrease as the alkalinity increases. It can be noted that the redox potential measured after grinding was around 80 mV vs SCE for SS and from -280 to -180 mV for MS, using a platinum sensing electrode. A platinum electrode was used so that the measured potentials would be comparable to those of other investigations reported in the literature.

Grinding in a mild steel environment introduces ferrous ions which impede flotation of the sulphides (87). Also, the reducing environment will reduce, if not eliminate, the occurence of collectorless flotation (33). On the other hand, these factors do not explain the dependence of the floatability upon the alkalinity level.

The decreasing copper recovery, for a constant xanthate addition, may be explained using Barsky's rule for the critical pH for flotation:

$$[OH^-] / [X^-] = K \qquad [13]$$

where the constant K is dependent on the mineral and the length of the hydrocarbon chain of the xanthate (102). For a constant collector dosage (and concentration), an increase in pH will lead to the depression of the mineral if the ratio of the concentrations becomes greater than K.

The behavior of sphalerite is more difficult to explain. The increasing zinc recovery with increasing pH for the stainless steel media is consistent with the findings of Leroux et al. (32) where appreciable zinc recovery is experienced without copper activation if the pH is between 9.5 and 11.0. However, their suggestion that this is due to the presence of iron ions (and $Fe(OH)_2$) in the pulp does not explain the present observations with the mild steel media.

Even though the Barsky rule may be applied to the flotation of sphalerite when grinding was performed with the mild steel media, floatability-potential curves for the copper rougher flotation appear to provide more insight. The recoveries achieved after the first minute of flotation are related to the potential prior to the addition of xanthate (Fig. 31). On the other hand, the total recoveries do not show clear relationships with the end potential (Fig. 32). This could be due to the much narrower potential range achieved at the end of copper roughing, -100 to 75 mV vs SCE instead of -400 to 75 mV.

The potential at which the collector is introduced in the mineral mixture is an important factor. This has been previously determined when nitrogen is used for flotation (19). However, floatability-potential relationships appear to be the same whether nitrogen or air is used as flotation gas (54). Thus the oxidation of the pulp during flotation, when air is used, should not distort the observed response.

There are differences between the ore types but it seems that the same general relationships apply to both samples (Fig. 31). First, zinc and iron recoveries are low as long as the potential is below 50 mV vs SCE. Second, the floatability of chalcopyrite is greatly reduced for potentials lower than -50 to -100 mV. Third, the floatability of galena,

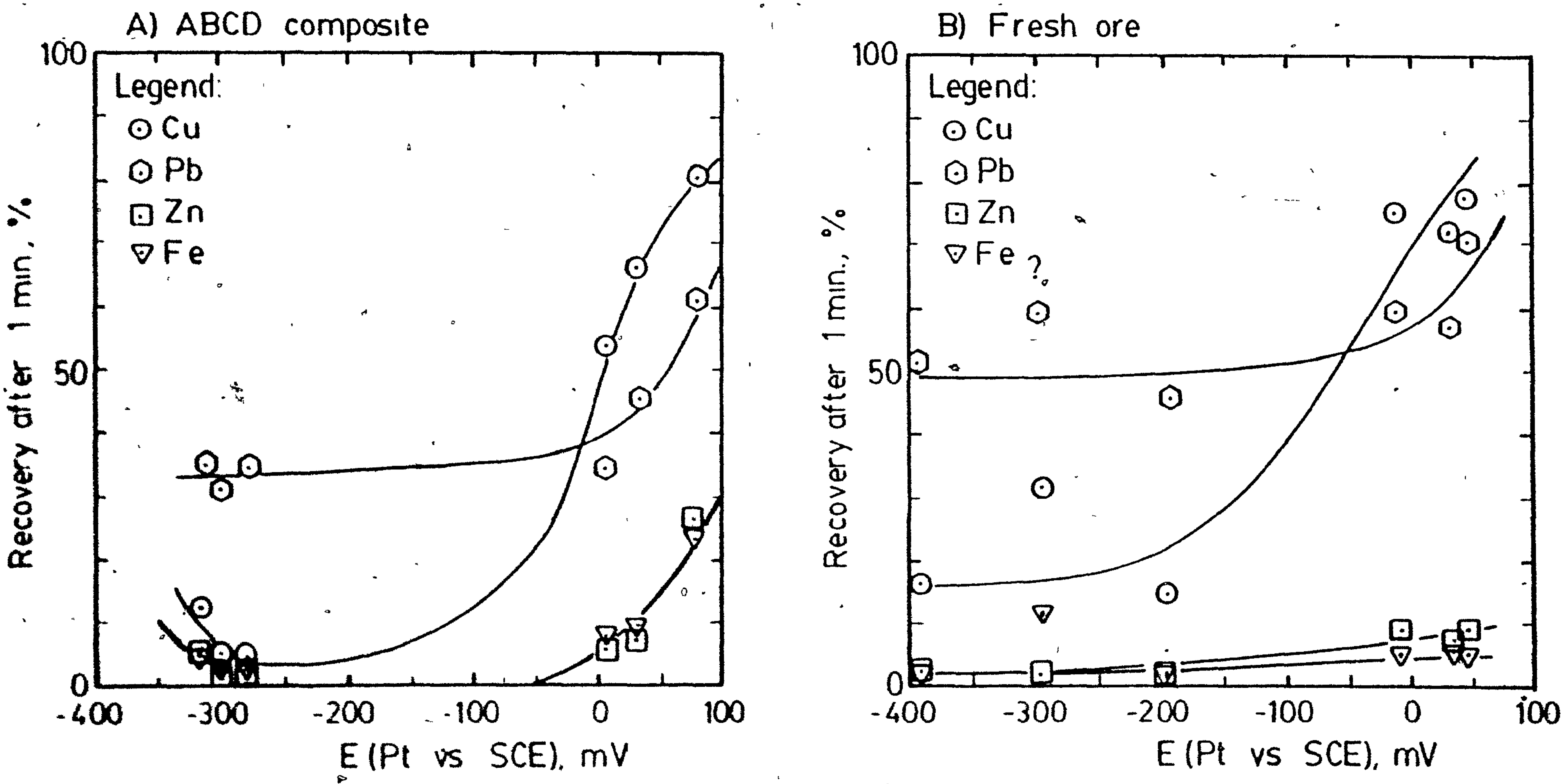


Fig. 31. Floatability-potential curves for copper rougher flotation: prior to the addition of xanthate.

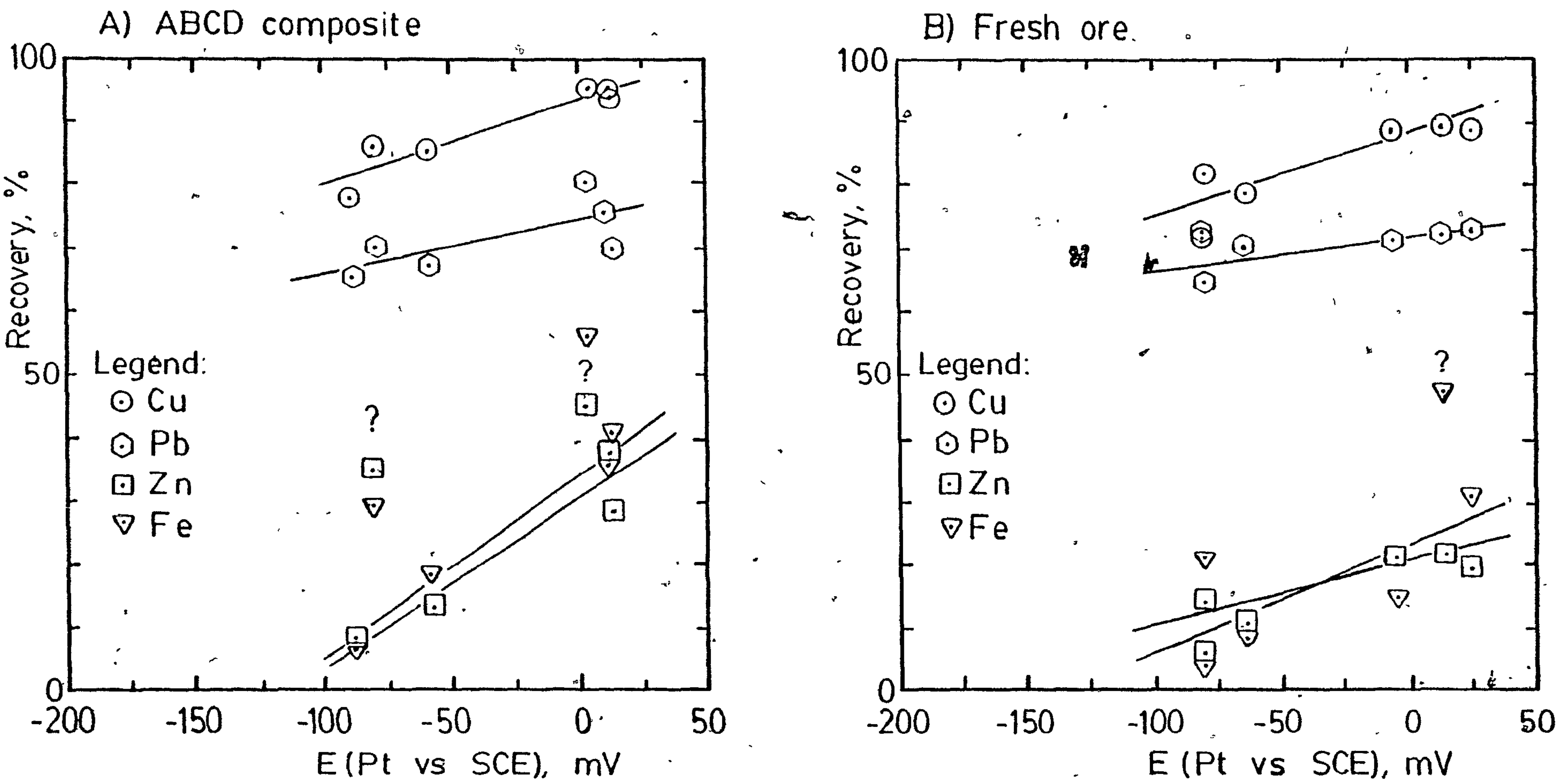


Fig. 32. Floatability-potential curves for copper rougher flotation: end-of-flotation.

although lower than for the positive potentials, appears to remain constant between 0 and -400 mV.

Hence, two windows of selectivity can be defined. The first one, from -400 to 0 mV, yields a preferential flotation of galena while the second one, from 0 to 50 mV, provides preferential flotation of chalcopyrite and galena over that of sphalerite and pyrite. The sustained floatability of galena under reducing conditions, when ground in a steel mill and when a collector of the xanthate family is used, has been observed previously (54). However, it was found to occur only when a strong frother (PPG 400) was utilized but not for an alcohol frother (54).

Floatability-potential curves were also obtained for zinc roughing (Fig. 33 and 34). To diminish distortion of the data due to poor selectivity during copper roughing, the recoveries are calculated with respect to the feed to the zinc rougher. Again, there are remarkable differences between the "initial" (Fig. 33) and "end-of-flotation" conditions (Fig. 34).

The ABCD composite appears to have a narrower potential range for zinc flotation than the Fresh ore. However, for both samples, it seems that the window of selectivity between sphalerite and pyrite is between -80 and -40 mV vs SCE.

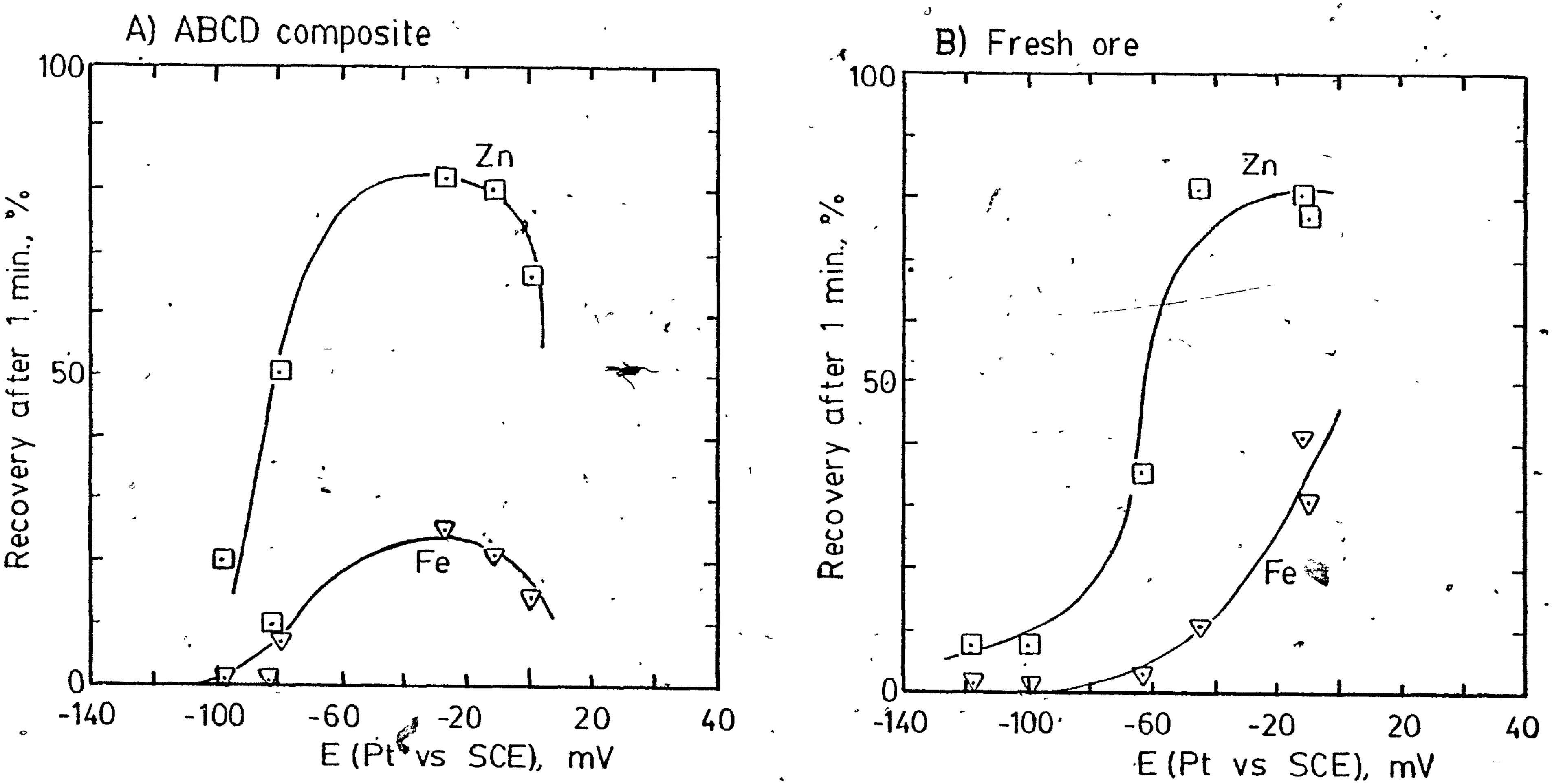


Fig. 33. Floatability-potential curves for zinc rougher flotation: prior to the addition of xanthate.

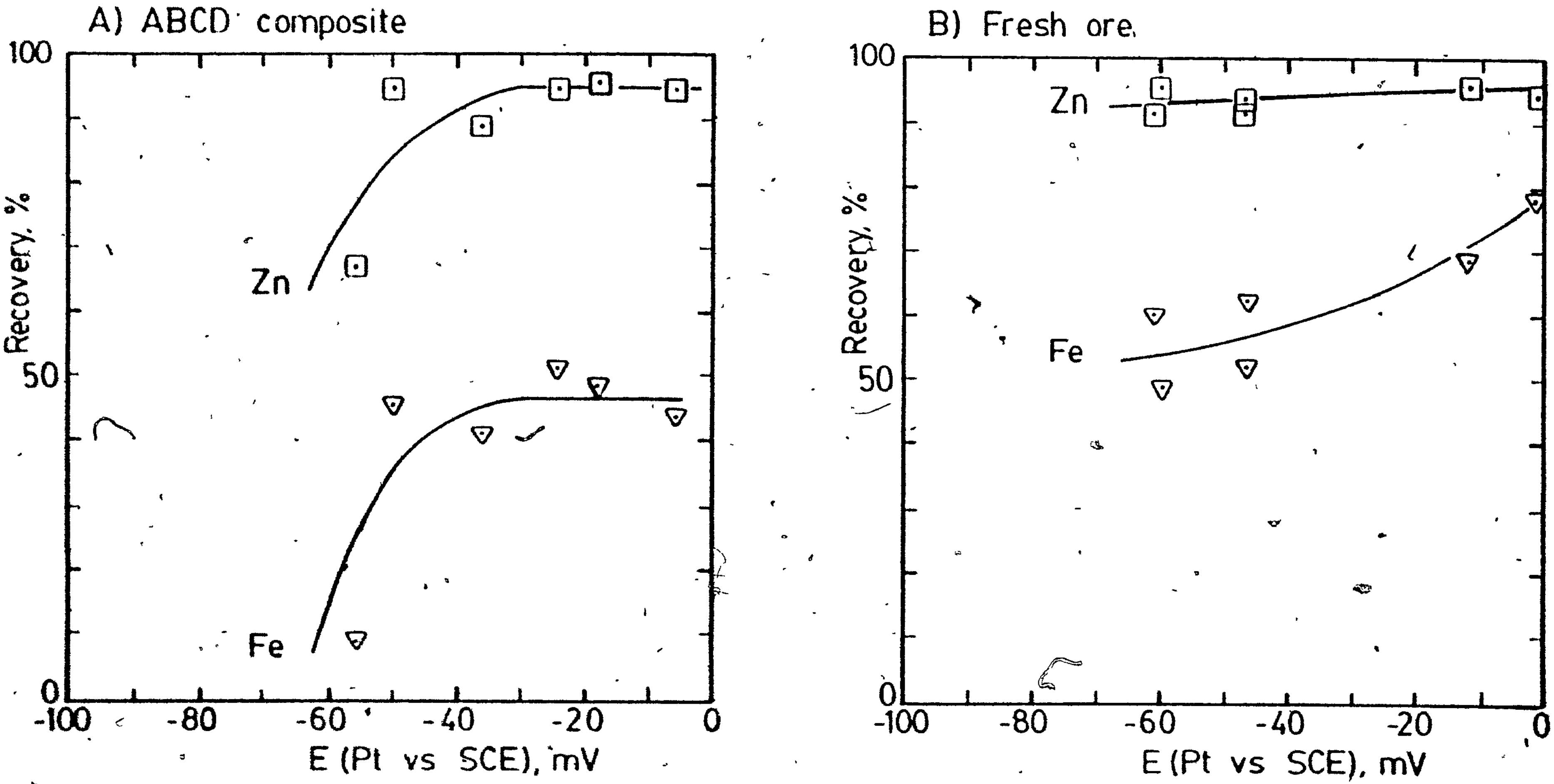


Fig. 34. Floatability-potential curves for zinc rougher flotation: end-of-flotation.

The end-of-flotation floatability-potential curves (Fig. 34) appear to confirm the upper limit of -40 mV for the window. On the other hand, it must be remembered that an additional copper sulphate addition was performed prior to the last zinc rougher in the tests at the lower potentials (mild steel media).

The addition of copper sulphate raised the potential from a value ranging from -80 to -100 mV, to a value between -60 and -40 mV. Did the additional quantity of copper sulphate provide a further activation of sphalerite or did it act as an oxidizing agent by increasing the potential? This cannot be clarified with the present data.

The collectorless flotation induced by the stainless steel charge cannot be ignored. Table 13 shows some results on the effect of the reducing environment in the mill (using magnesium metal) and sodium sulphide on the collectorless floatability of the ABCD composite.

The results with $CaO/NaCN/ZnSO_4$ are disturbing. With the exception of a lower copper recovery, the result are extremely similar to those obtained in the presence of SIPX after 1 min. of flotation (Fig. 31). This possibly indicates that the collector may have a marginal role on the selectivity. This has been suggested by Shannon and Trahar (21).

Table 13. Collectorless floatability after 3 min. of flotation for the ABCD composite ground with the stainless steel media.

Reagents (g/t)		Initial		Recoveries (%)		
Mill	Cond.	E vs SCE	pH	Cu	Zn	Pb
$CaO/NaCN/ZnSO_4$		28	7.6	30.7	17.3	57.4
Mg (500)	Na_2S (500)/ HCl/air	50	7.1	37.0	20.5	17.7
Mg (1000)	Na_2S (500)/ HCl/air	10	7.0	38.5	14.0	13.9
Mg (1000)	None	-80	10.3	61.6	15.6	26.0
None	Na_2S (500)/ HCl	+40	6.4	33.8	15.0	10.4
None	Na_2S (500)/ H_2SO_4	+35	6.2	30.3	16.3	9.7

Notes:
- $CaO/NaCN/ZnSO_4$ additions and grinding time are the same as in Table 12
- Grinding time of 30 minutes for the other tests
- Na_2S conditioning for 15 minutes
- Aeration, when performed, was for 5 minutes
- Platinum sensing electrode

The use of Na_2S gave the same result regardless of aeration, acid type, or the presence of magnesium (Mg) in the mill.

The potentials measured during Na_2S conditioning were between -500 to -400 mV vs SCE (-255 to -155 mV vs SHE). There are comparable to those obtained by Luttrell and Yoon (38), -210 to -50 mV vs SHE (platinum electrode) for different ores and a constant addition of 2.5 kg/t of Na_2S.

The potentials just prior to flotation were between 10 and 50 mV vs SCE (255 to 305 mV vs SHE). These potentials are within the individual ranges of flotation for chalcopyrite, 150 to 550 mV (53), and galena, 100 to 300 mV vs SHE, (54) in the presence of sodium sulphide.

Luttrel and Yoon (38) obtained values between 0 and 200 mV vs SHE after 5 minutes of flotation with air; the copper recoveries being greater at the higher potentials (e.g. 95% Cu recovery at 200 mV vs SHE). The potentials appeared to indicate the reactivity of the ore to the presence of Na_2S. Some ores required a longer conditioning time (at a fixed dosage) while others needed lower addition levels (for a fixed conditioning time) (38).

The relatively similar potentials monitored for the A-1 zone ore, with or without aeration after the sulphidization (10 to 50 mV vs SCE), would indicate a high reactivity of the ore with Na_2S. The utilization of a stainless steel media instead of a mild steel one (38, Yoon, communication Nov. 1986) may have been a factor. However, a ceramic charge has been used for some tests without any report on adverse or positive effects on the floatabilities obtained (38).

The use of magnesium into the grinding mill yielded the highest copper recovery, 61.6%, while giving the lowest redox potential prior to flotation, -80 mV vs SCE. The lower redox potential may be attributed to the higher alkalinity of the pulp without the addition of an acid (pH 10.3 against 6.2 to 7.6). However, collectorless floatability usually decreases with increasing pH (38).

The apparent depressing action of Na_2S for the collectorless flotation of the A-1 zone ore may be attributed to a high activity of the ore. Either the dosage of Na_2S was not high enough to remove the hydrophilic oxidation product layers formed during grinding, or a too long conditioning time was allowed providing a partial re-oxidation of the surfaces (38). On the other hand, it may be that the interpretation of Lepetic (18) may be extended to sulphidization. Namely, if the ore can be induced into collectorless flotation during grinding, its flotation will be selective while attempting to condition the ore will yield a poorer selectivity.

5.5 Metallurgical and potential responses of the different ore types.

The B, C, D and E ore types were tested. Grinding times were 10, 20, and 30 minutes with a mixed stainless steel/mild steel grinding charge. The reagent additions to the grinding mill were CaO (250 g/t), NaCN (50 g/t) and $ZnSO_4$ (200 g/t). Although this was initially to establish grind vs metallurgy relationships, interesting findings emerged regarding the potential and pH monitored just prior to conditioning for flotation.

Figs. 35a, b) present the pH and potentials vs the iron content of the ore as an indicator of the pyrite content of the ore. The pyrite content was deemed important from the review of collectorless flotation induced by galvanic interactions (section 1.3), and similar effects were expected for conventional flotation.

It can be observed that the potential and pH points for the E ore type lay outside the trends defined by the other ore types. This can be attributed to the altered nature of the E ore type where a great portion of the iron is as hydroxides, or limonites, instead of pyrite.

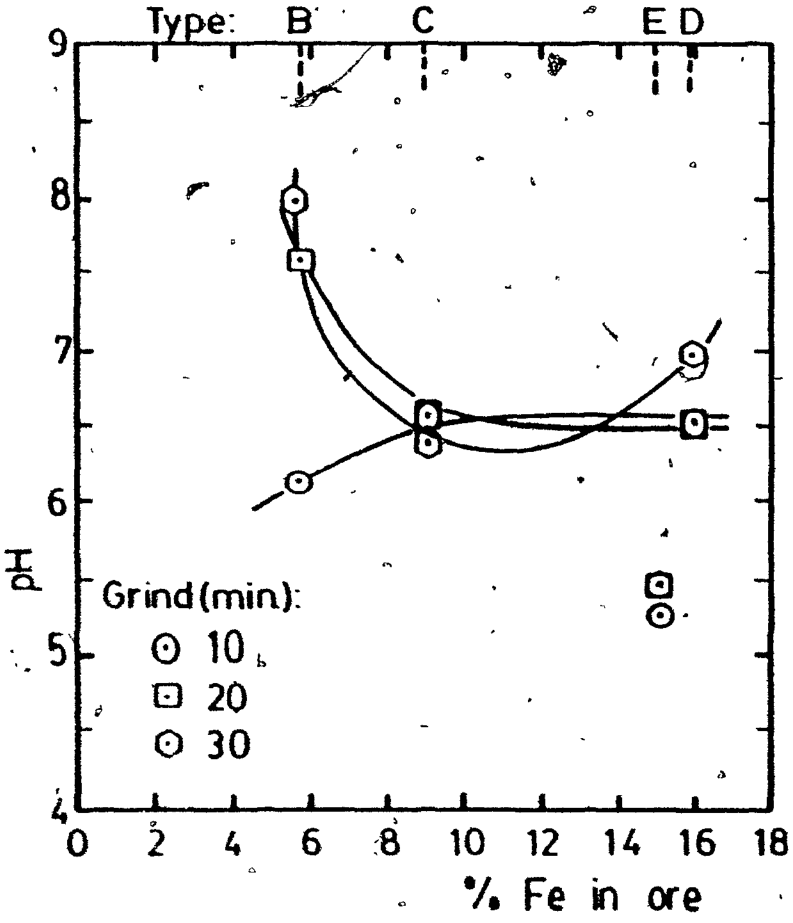


Fig. 35a. pH vs Fe content.

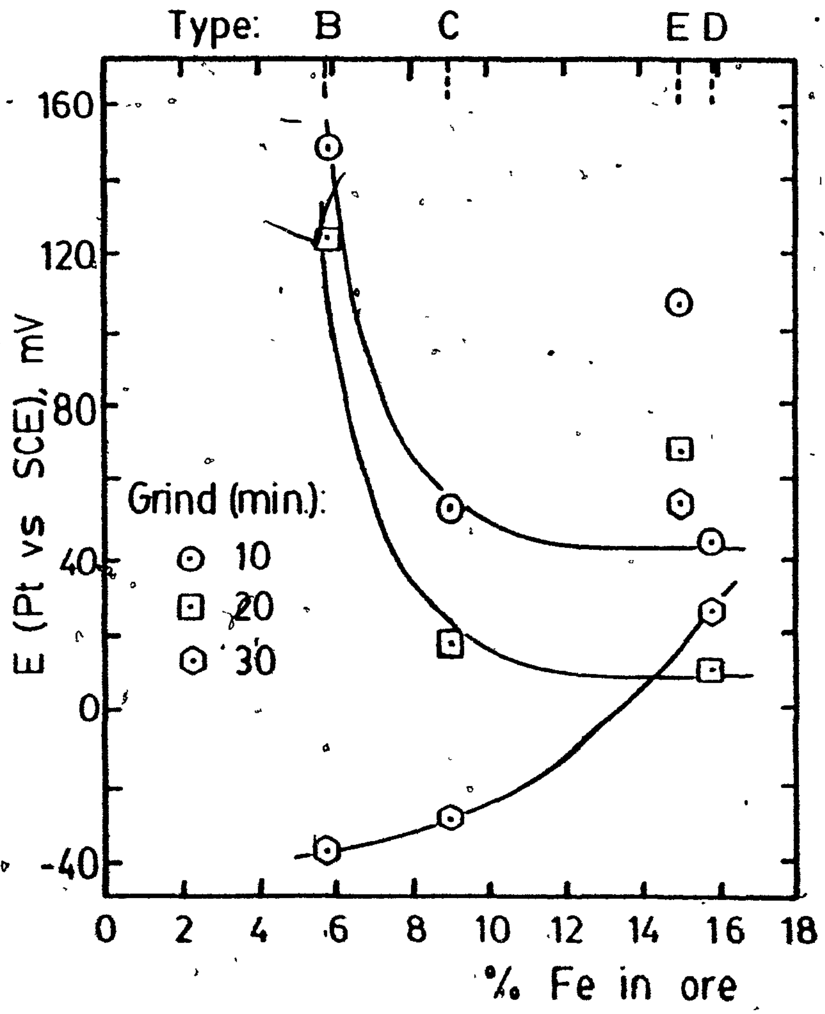


Fig. 35b. Potential vs Fe content.

It can be observed that an increase in the pyrite content in the ore, or an increase in grinding time leads to more reducing potentials (Fig. 35b). The lower potentials do not appear to be related to the pH of the pulp after grinding. The more reducing potentials obtained after the longer grinding times, or for the higher pyrite contents indicate the driving force for the ore to be oxidized. This would confirm the interpretation that the oxygen demand of the ore increases with increasing grinding time or pyrite/pyrrhotite content ~~(103).~~

The flotation response varies according to the ore type. Table 14 presents the metal recoveries obtained after 1 min. flotation (copper rougher, 20 min. grind). A further addition of CaO (to pH 10.0), NaCN (50 g/t), $ZnSO_4$ (200 g/t) was performed prior to the addition of the collector (SIPX, 20 g/t) and frother (MIBC, 10 g/t).

Table 14. Metallurgical responses after 1 min. flotation (20 min. grind).

Ore type	Concentrate grade (%)			Metal recovery (%)		
	Cu	Zn	Fe	Cu	Zn	Fe
B	5.75	5.85	15.30	14.9	3.4	2.6
C	29.60	1.85	27.00	41.7	2.1	18.5
D	9.66	5.00	33.30	24.6	2.3	2.8
E	1.42	22.60	27.50	53.4	64.4	28.7

As expected, the highly active E ore type yields the lowest selectivity against sphalerite and pyrite. The C ore type gives the highest initial copper concentrate grade (29.6%) as the feed grade is the highest of all types (4.44% Cu vs 0.47 to 0.60%). The much lower Cu:Zn and Cu:Fe ratios for the B and D types give an apparent lower selectivity in comparison with the C type.

Since increasing the grinding time increases the fineness of the solids, i.e. the liberation of the minerals is increased, it would be fallacious to compare the metallurgical results obtained with the different grinding times. Also, comparison of the metallurgical responses of the ore types in terms of the potential and pH achieved after grinding is not possible due to the large differences in feed grades. However, it may be inferred that the higher the pyrite content of the ore, the lower the redox potential achieved after grinding. On the other hand, will the same effect be observed in the flotation circuit?

5.6 Screening of conditions for re-cleaning of bulk Cu-Pb-Zn concentrates

The flotation response for the flotation tests discussed in section 3.3.2 are now re-examined to determine possible relationships between the potential and the flotation response. It must be remembered that since the materials used in these experiments were copper concentrates obtained from pilot or plant flotation, the metallurgical results are likely to be distorted due to superficial oxidation of the minerals.

The reagents tried were selected on the basis of possible redox phenomena demonstrated or inferred from literature. These were sodium sulphide, Na_2S (15, 16, 17), potassium permanganate, $KMnO_4$ (1), alkaline oxidation (103), potassium ferricyanide, $K_3Fe(CN)_6$ (87), ferrous sulphate, $FeSO_4$ (35, 87), and sulphur dioxide/oxygen, SO_2 (104). Sodium lignin sulfonate, SLS, was also used. Although it is not a redox modifying agent, it appears to inhibit the formation of solid sulphur layers on the surface of minerals during pressure leaching (105).

5.6.1 "Direct" vs "indirect" potential modifying agents.

The potential-pH points achieved during the flotation tests are presented in Table 15. The initial and final potentials achieved during conditioning are given whenever there is a large variation between these values. Potentials as low as -520 mV and as high as +210 mV vs SCE (gold sensing electrode) could be achieved by the addition of Na_2S and $KMnO_4$ respectively.

The addition of redox modifying agents (e.g. $KMnO_4$) also induces a modification of the pH of the pulp. Conversely, the addition of pH modifying agents (e.g. Na_2CO_3, HCl) induces a change in the pulp potential. However, a reagent addition resulting in an increase of the pH does not always induce a lowering of the pulp potential, and vice versa. This would imply that the action of pH modifiers on the potential is not just via solubilization of oxidation products, or precipitation of ions from the solution.

There are some unusal results which were not be predicted. For example HCl, which is not considered as an oxidizing agent, induces a more oxidizing potential than H_2SO_3 (6.3% SO_2 solution), for an equivalent pH. This could be due to the effect of the chlorine ion on surface product layers. It is observed that HCl is more effective than H_2SO_4 for the

Table 15. Summary of pH and potentials during batch flotation along with the achieved technical efficiency, E_t, and yield, Y, after 1 min. flotation.

Sample	Reagents	Average pH	E, Au vs SCE (mV)			E_t %	Y %
			Cond.	Init.	Flot.		
B (2)	SIPX	7.8	-32	-32	-30	-4	38.9
B (2)	Na_2S/SIPX	10.0	-200	-190	-106	-19	12.7
B (2)	Na_2S/SIPX	10.7	-520/-180	-160	-110	0	N.D
B (2)	None	7.8	67	50	45	-13	72.5
B (2)	Na_2S	10.8	-130	-107	-130	-12	N.D
B (2)	Na_2S	10.6	-240	-200	-140	-6	N.D
B (2)	$KClO_3$	7.8	60	40	1	-6	68.9
B (2)	Na_2S/NaCN/ SLS	9.3	-300/-112	-106	-23	-4	66.4
B (2)	Na_2S/NaCN/ SLS	10.4	-136	-78	-80	-13	2.2
B (2)	Na_2S/NaCN/ SLS	10.4	-100/-72	-74	-130	-12	4.0
B (3)	$K_3Fe(CN)_6$	8.4	35	18	15	-60	6.8
B (3)	$KMnO_4$ [1]	9.0	210	210	210	0	0
B (3)	$KMnO_4$	8.2	60	50	36	-23	48.6
A	Na_2S	8.8	-260/-200	-160	-110	11	14.5
A	Na_2S/NaCN/ SLS	9.0	-220/-126	-200	-140	19	10.6
A	None	6.9	11	3	-9	22	32.5
A	CaO/NaCN	12.2	-110	-140	-120	6	6.8
A	CaO/Air/ NaCN/M2030	12.1	-74	-110	-88	2	4.4
A	CaO/Air/ M2030	12.0	-67	-60	-62	10	6.8
A	H_2SO_3	6.1	18	4	10	39	44.6
A	$K_3Fe(CN)_6$	8.1	40/30	26	20	25	27.7
A	$FeSO_4$	6.6	-40/-22	-14	-34	24	37.0
A	$KMnO_4$	7.3	310/180	180	140	-11	14.4
A	HCl	5.2	100/46	46	27	30	30.0
A	H_2SO_3	5.8	22	22	13	25	49.4
A	Na_2CO_3	9.7	-68	-62	-55	27	43.9

SIPX: Sodium Isopropyl Xanthate
M2030: Minerec 2030 (thionocarbamate)
SLS: Sodium Lignin Sulfonate
N.D.: Not determined (not sufficient mass recovered)

[1]: Excess permanganate (pink color in slurry), total yield is 0.9% after 6 min. of flotation.

leaching of sphalerite and pyrite (12). Also, sulphur dioxide is an amphotere redox modifier (107). In aqueous acidic solutions, SO_2 is a strong oxidizer, but it is a reducing agent in alkaline solutions.

The action of potassium ferricyanide is rendered complex because the ferric ion is an oxidant, and the cyanide ion is a complexing agent. Also, it appears that cyanide acts as a reducing agent when complexing copper ions (31). For the B zone material, "B (3)", the action of potassium ferricyanide appears to lead to a reduction in the potential in comparison with the blank test, 35 mV against 67 mV vs SCE respectively. On the other hand, it appears to act as a mild oxidizer for the A-1 zone material, "A", yielding a potential of 22 mV vs SCE while the material with no modifiers gave 11 mV. Again, these observations seem to be related to the higher content in soluble secondary copper minerals of the B zone material in comparison with the A-1 zone.

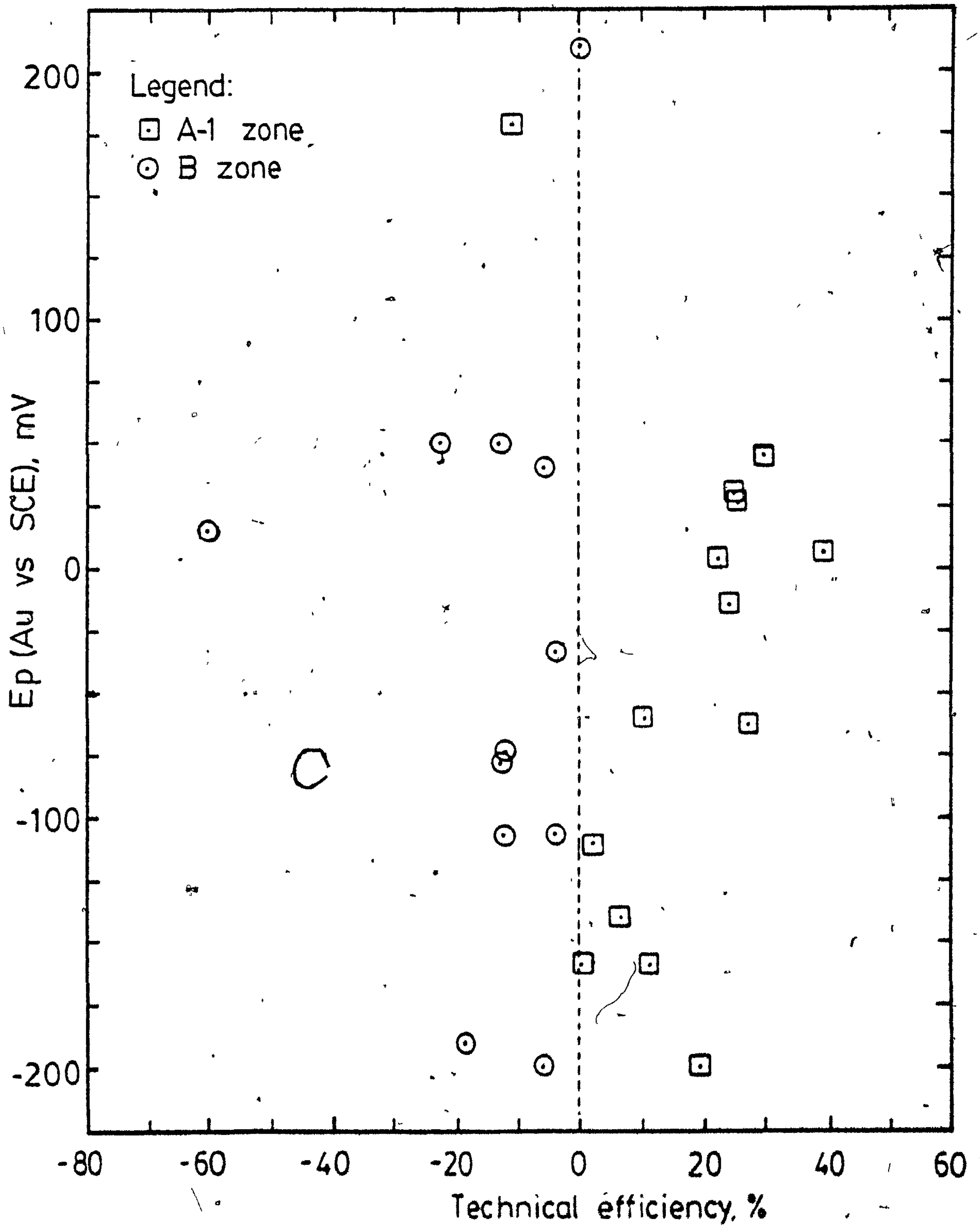
The addition of $KMnO_4$ which yielded the largest discrepency between the gold and chalcopyrite electrode (209 mV, cf section 3.2.2) was excessive. With no material recovered after 1 min. of flotation (0.9% after 6 min.), it is evident that flotation was completely suppressed, either by complete oxidation of the previously adsorbed collector, or by the formation of a passive hydroxide layer onto the mineral surfaces. This suggests that the large discrepency (209 mV) observed between the gold and chalcopyrite electrodes was more likely due to the presence of passive hydroxides on the chalcopyrite electrode rather than on the gold electrode.

5.6.2 Relationships between the flotation response and the pulp potential

The technical efficiency of the separation, E_t, is mapped onto the potential. There appear to be two distinct regions (Fig. 36). The potential exhibited by the gold spiral electrode was used as it appeared to be the most reliable.

For the B zone material, the natural tendency is for a reverse flotation of the sphalerite (indicated by a negative technical efficiency). Since a bulk concentrate was treated, and collector was already present, the effect on the dissolution of the secondary minerals would be less important than in rougher flotation. Nevertheless, going to oxidizing potentials increases the natural tendency for preferential flotation of sphalerite. The best technical efficiency (-60%, reverse flotation) is achieved with $K_3Fe(CN)_6$.

Fig. 36. Pulp potential vs technical efficiency: bulk Cu-Zn-Pb concentrates.

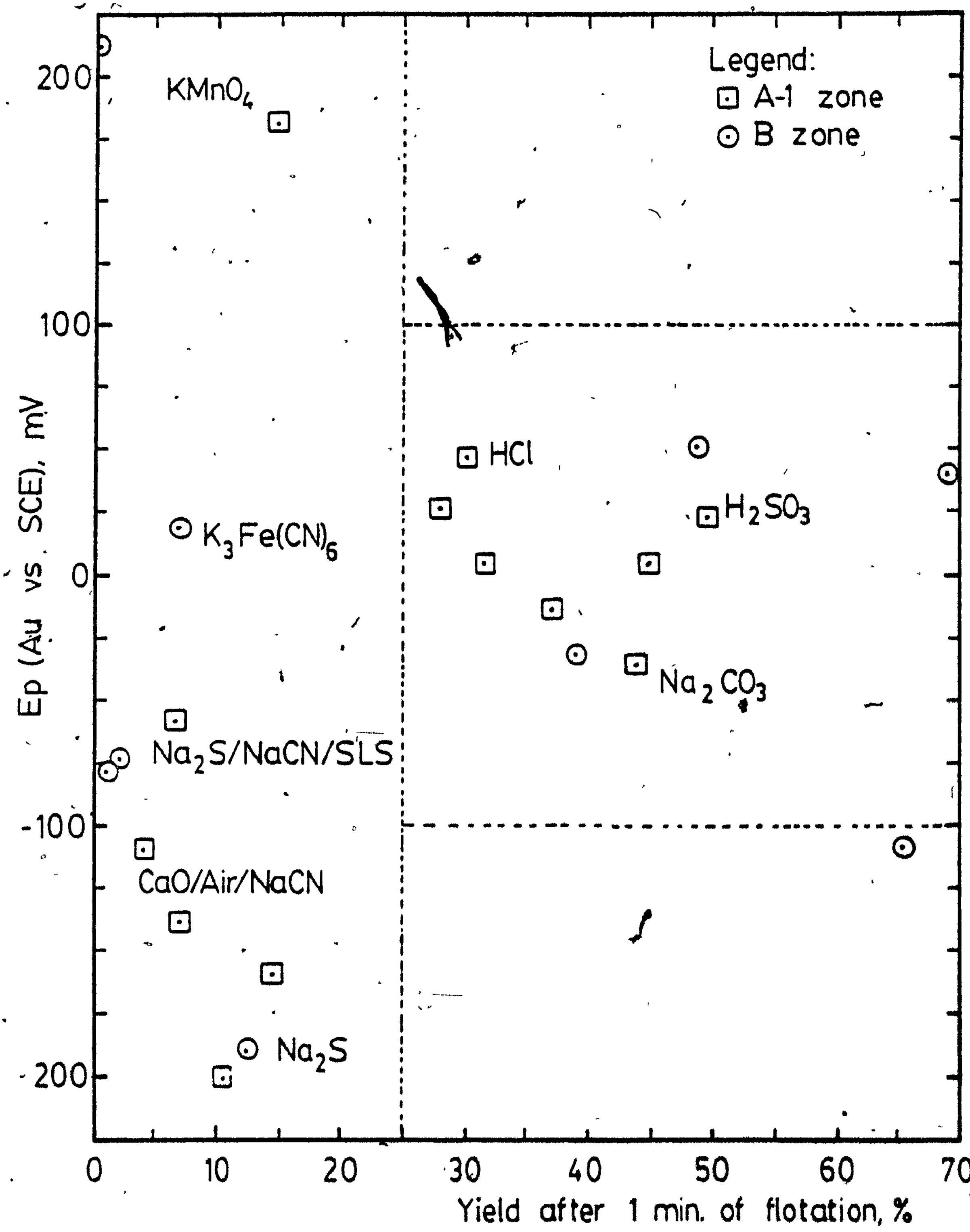


For the A-1 zone material, mildly oxidizing or reducing conditions yield a selective flotation of copper. Although the content of the A-1 zone material in secondary copper is less than that of the B zone, highly oxidizing conditions (180 mV vs SCE with $KMnO_4$), yielded a reverse flotation. On the other hand, highly reducing conditions are detrimental. Strangely, alkaline oxidation (aeration at pH 12.0) provided reducing conditions, but this could be due to the precipitation of ions as hydroxides.

The concentrate yield after 1 minute of flotation (Fig. 37) shows that most of the points fall within -100 mV and +100 mV vs SCE (145 and +345 mV vs SHE) for yields greater than 25%. This potential region is within the range found for the individual flotation of chalcopyrite (53) and galena (54) in the presence of xanthate collectors.

Besides the main floatability area, little correlation is observed between the potential and the yield. However, it seems that the high alkalinity induced by lime (CaO), and, or, the presence of sodium cyanide creates conditions which greatly inhibit the flotation of the sulphide minerals. It is plausible that adsorption of cyanide onto the mineral surfaces (60), and its consequent depressing action, cannot be monitored by the potential. The nature of the materials does not, however, warrant a firm interpretation.

Fig. 37. Pulp potential vs concentrate yield after 1 min. of flotation: bulk Cu-Zn-Pb concentrates.



5.7 Conclusions

The pulp potential achieved after grinding, or after an addition of a redox modifying agent such as Na_2S, appears to indicate the reactivity of the ore. The higher the pyrite content of the ore, the lower the potential achieved, until exhaustion of the oxygen entrapped in the laboratory mill, or present in the pulp during industrial milling. The A-1 zone material appears to be highly reactive with Na_2S and hence attempts at selective collectorless flotation in a manner similar to Yoon (16) failed. Optimization of the sulphidization process may yield better results, either by adding more Na_2S or by using shorter conditioning times.

The nature of the grinding media, stainless steel or mild steel, gives rise to different relationships between the floatabilities of the minerals and the alkalinity level during copper roughing. With mild steel media, the flotation vs pH appears to follow Barsky's rule. However, this was not observed with the stainless steel media. This would suggest that the manner in which flotation is approached (from an initially reduced or oxidized pulp) must be considered (potential-pH paths).

The floatabilies appear to be more related to the potential prior the addition of the collector yielding windows of selective flotation for copper and zinc roughing. Preferential flotation of galena occurs for potentials between -400 to 0 mV vs SCE (platinum electrode) while both chalcopyrite and galena are preferentially floated between 0 and 50 mV. Sphalerite flotation, without deliberate copper activation, would be significant at potentials greater than 50 mV vs SCE.

With copper activation, the selective flotation of sphalerite from pyrite appears to be possible for potentials between -80 and -40 mV (at pH 10.0). Contrary to copper roughing, the floatability-potential relationships for zinc roughing appear to be the same whether the potential prior to xanthate addition or the end-of-flotation potential is used.

Finally, the high content of secondary copper minerals in the B zone ore promotes a reverse flotation of the sphalerite during cleaning of the bulk concentrate. This tendency may be used to advantages by using potential modifying agents which induce oxidizing conditions. Potassium ferricyanide appears to be the best reagent. On the other hand, the A-1 zone ore, with a much lower content of secondary copper minerals, requires mild oxidation (using SO_2 or HCl), or mild reduction (using Na_2CO_3) for the selective flotation of copper. The altered E ore type may require reverse flotation of the sphalerite during cleaning to be economically processed.

6. POTENTIAL/pH SURVEYS OF THE A-1 ZONE FLOTATION CIRCUIT

Laboratory batch flotation possesses inherent limitations for investigations into electrochemical effects. One of them is the exposure of the ground pulp to air as the pulp is transfered from the grinding mill to the flotation cell. Also, there is a time lapse between the production of the rougher concentrate and its subsequent cleaning. Hence, the minerals are exposed to air for a much longer time than in an actual concentrator. This may distort the interpretation of the results obtained in the laboratory.

Potential/pH surveys of flotation circuits have been performed, but again, with conflicting potential measuring techniques. In some, the sensing electrode is immersed in the mineral slurry (55, 57, 73). In others, the sensing electrode is immersed in a micro-filtrate sample obtained from the slurry (55, 108). The results obtained in these surveys are mostly discussed in terms of the oxygen saturation of the pulp (55, 57, 73). It appears that in only one instance were the measurements correlated with Eh-pH diagrams for the system (109).

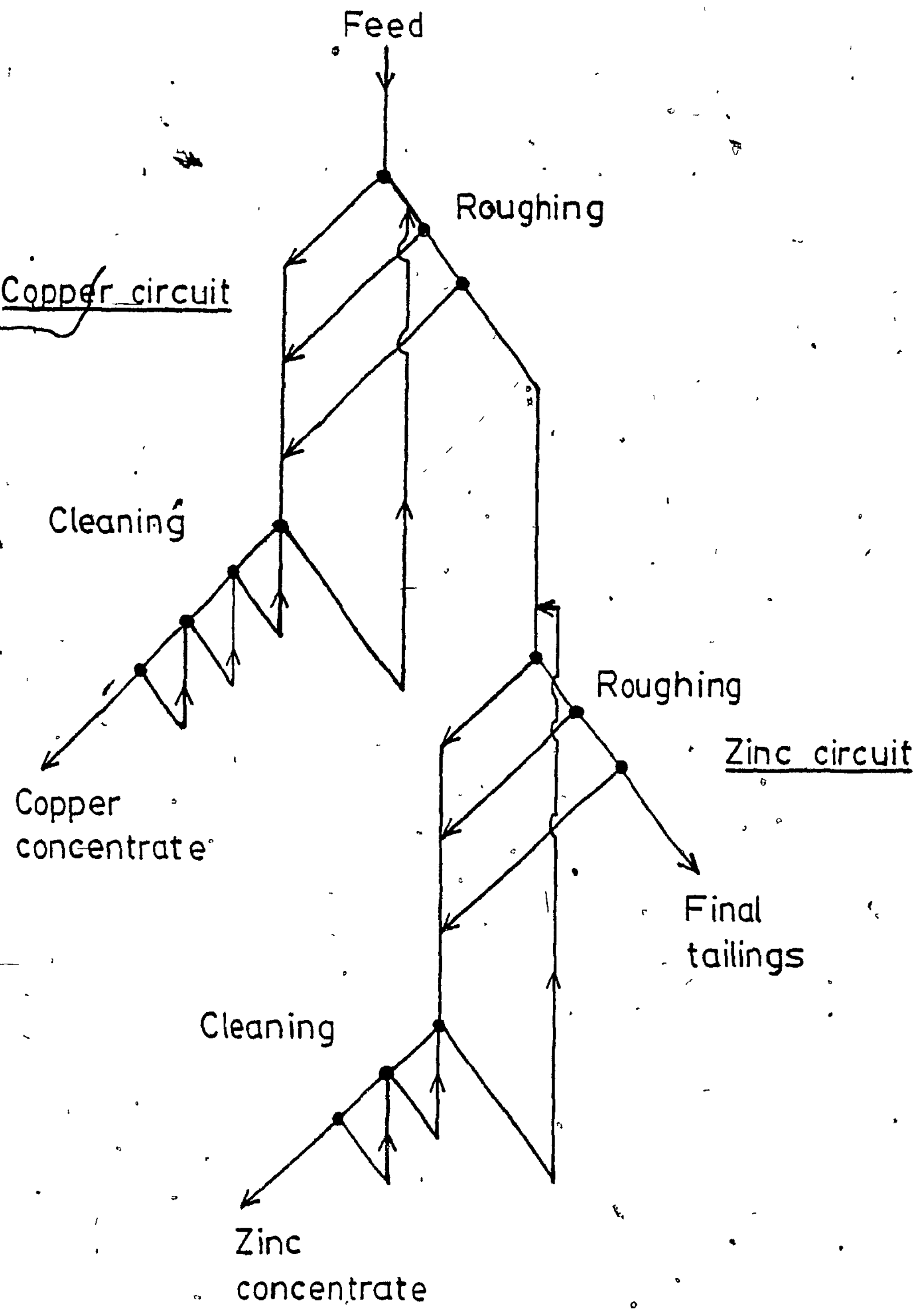
6.1 Description of the flotation circuit

The A-1 zone flotation circuit is shown in Fig. 38 using the "network" symbolism (98). Flotation stages are shown as nodes (points), concentrates as left diagonals while tailings are as right diagonals. Feeds and recirculating streams are vertical lines.

Separation of the minerals is performed by selective sequential flotation (88). Copper is first floated in three banks of roughing and scavenging cells, and is cleaned in four counter-current stages. The copper scavenger tails, after copper activation, comprises the feed to the zinc circuit. Roughing and scavenging are performed in three banks, the zinc rougher-scavenger concentrate being cleaned three times in a counter-current fashion.

The collectors are Aerophine 3418A (Cyanamid) for copper flotation and Sodium Isopropyl Xanthate for zinc. The frothers are Methyl Isobutyl Carbinol for the copper circuit and Dowfroth 1012C (polypropylene glycol ether) for the zinc circuit. Modifiers are lime, sodium cyanide and zinc sulphate (copper), and lime and copper sulphate (zinc). A Bailey Network 90 distributed control system is used for process control (111).

Fig. 38. A-1 zone flotation circuit.



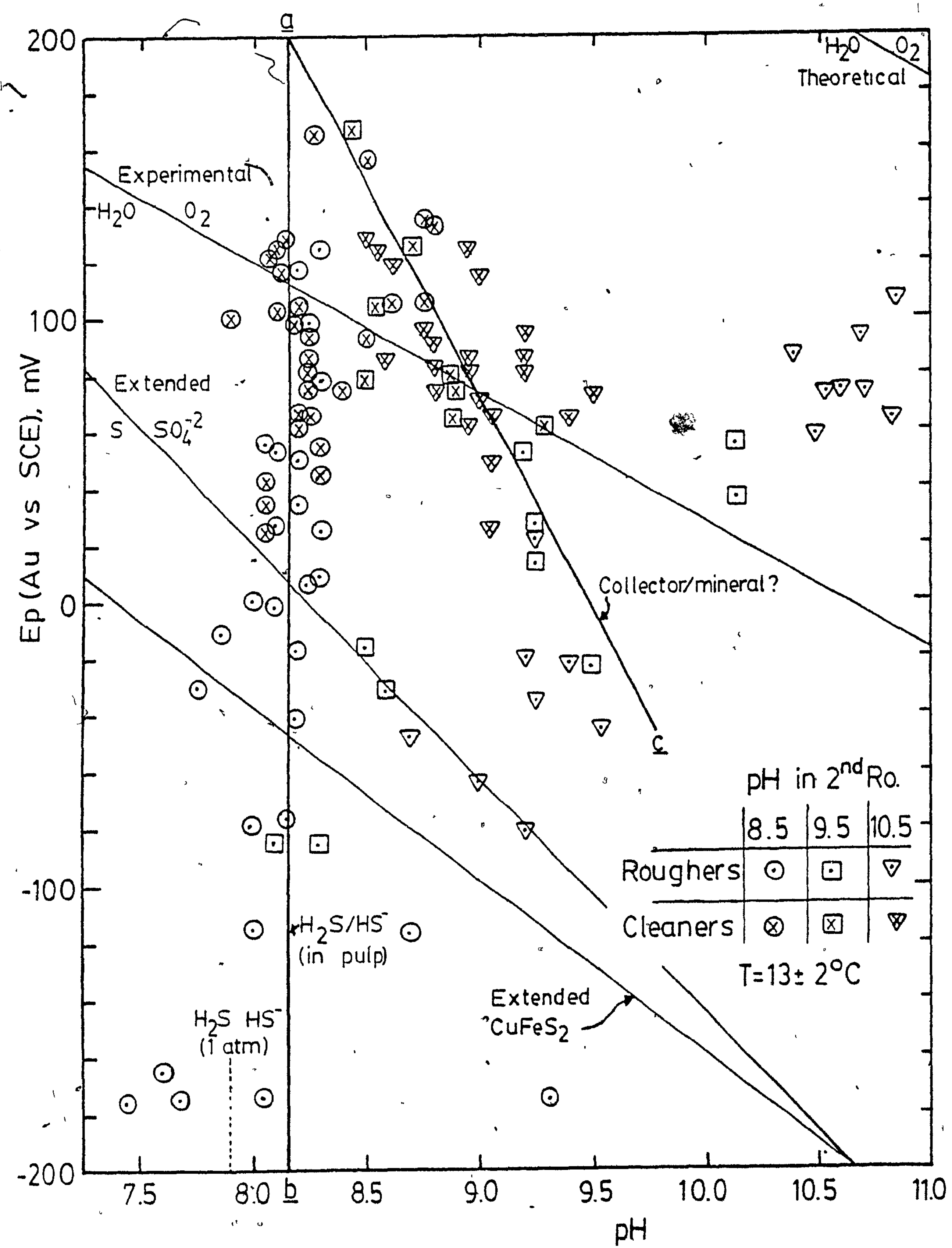
These surveys were performed in March 1987. Even though only fives months had elapsed since the start-tup of the circuit, the operation was stable enough to obtain reliable results. By surveying in March, water quality changes upon spring thaw were avoided.

6.2 Manual surveys

The surveys were performed using a gold foil electrode with a combination pH electrode. Samples were obtained from the process, either from the feed or the tail box of the flotation bank, and were brought to the instruments (two pH/Eh-meters). The samples were agitated with the electrodes during the measurements. The gold foil was polished on a 600 grit emery paper prior to each measurement. A gold foil electrode was used instead of gold spiral since the latter was too fragile to withstand these conditions.

The results of the surveys, which were performed over five consecutive operating days, are presented in the form of potential/pH graphs. For the copper circuit (Fig. 39), a clustering of points along the process nodes are observed. A similar clustering has been observed in other surveys including one where two qualities of process water (fresh and recycle) were investigated (108). No major difference between

Fig. 39. Potential-pH graph for the copper circuit.



the two types of process water were observed for the samples taken in the flotation circuit even though the Eh-pH point of the water samples differed. Also, the points along the circuit formed lines parallel to the O_2/H_2O line (108).

The A-1 zone copper circuit appears to operate along a vertical line when no lime is added during flotation (line "a-b" on Fig. 39). However, the addition of lime during the roughing stage causes the Ep/pH points to be shifted towards higher pH. Also, the cleaning section operates along a different line (line "a-c"). It can be noted that none of these lines are parallel to the experimental and theoretical lines for the reduction of oxygen (73).

For reference, some of the lines from a meta-stable Eh-pH diagram for chalcopyrite have been superimposed onto the graph. These lines were obtained by raising the energy change of the sulphur to sulphate reaction, i.e. introducing a kinetic barrier representing the observations in real systems (111). The barrier was 74 kJ/gmole. Peters (111) warns that this barrier may not be accurate for the alkaline range, pH > 9.0, and this must not be forgotten.

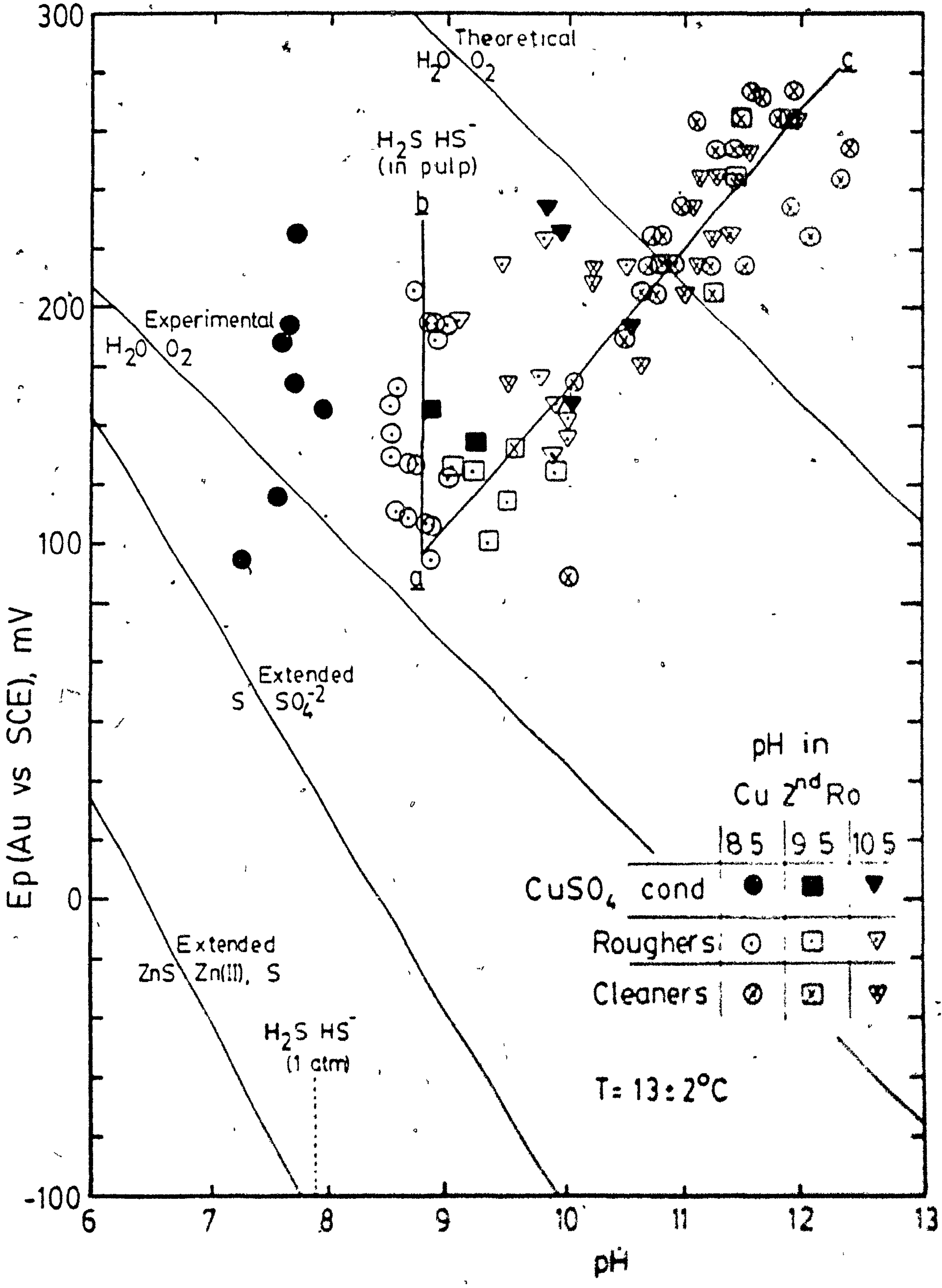
The line "a-b" is similar to the H_2S/HS^- equilibrium line (1 atm partial pressure). However, the line "a-c" does not correspond to any of the meta-stable lines for chalcopyrite even by considering the measured potential as a mixed potential. An observed line would be shifted towards more oxidizing values due to the presence of oxygen in the pulp, but would remain relatively parallel to the equilibrium line.

It may be speculated that the operating line for cleaning operation follows an equilibrium line for the reaction of the collector with chalcopyrite. However, little is known about the collector (Aerophine 3418A) except that it belongs to the dithiophosphine family (112). It is thus impossible to verify this speculation by thermodynamic calculations.

The potential-pH graph for the zinc circuit is presented in Fig. 40, with the meta-stable lines for the oxidation of sphalerite (111) and the experimental and theoretical lines for the reduction of oxygen (73).

Similarly to the copper circuit, the operating line for zinc roughing (line "a-b") is parallel to the H_2S/HS^- equilibrium line except when lime is added during copper roughing flotation. On the other hand, most of the points for the cleaning section of the zinc circuit are <u>above</u> the theoretical line for the reduction of oxygen.

Fig. 40. Potential-pH graph for the zinc circuit.



The apparent pH dependence of the potential for the cleaning operating line, "a-c", is intriguing. An Ep-pH relationship was expected, but an increasing potential with increasing pH is rare in the alkaline range (113).

Further surveys, with the electrodes immersed in the flotation pulp rather than in samples withdrawn from the process, would be required to ascertain that the line is not a consequence of the experimental technique used. Also, the high resistivity and band gap of sphalerite (49) may cause difficulties similar to those experienced with massive sphalerite electrodes and during cyclic voltammetry of unactivated and copper-activated sphalerite.

The extent to which the line would be related to the electrochemistry of copper activated sphalerite is difficult to determine. Certainly, it would be induced by the addition of lime as pH modifier. Determination of the concentrations of ions in solutions would help to resolve the question.

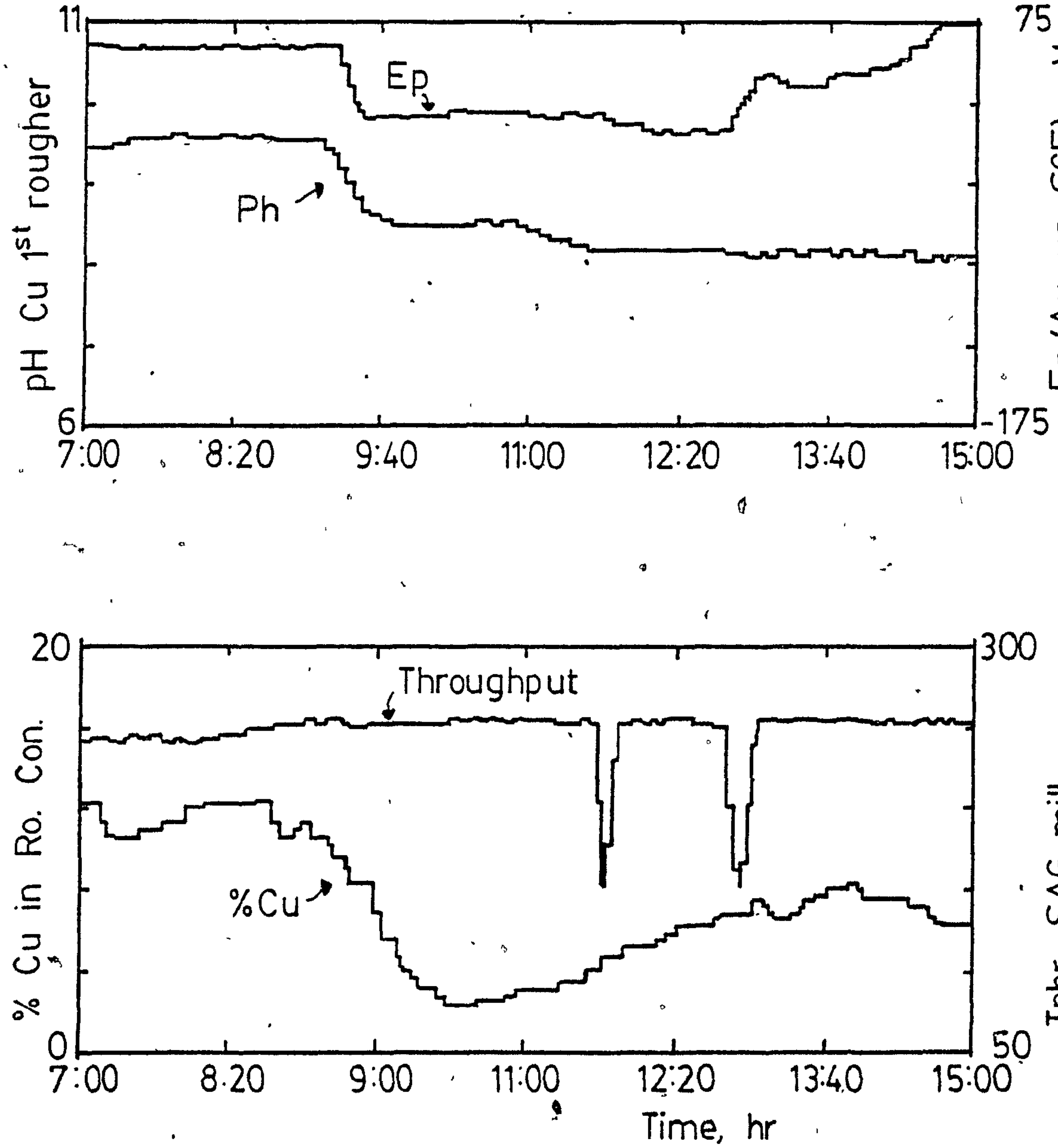
6.3 Continuous monitoring

Continous monitoring of the pulp potential requires judicious selection of the monitoring points and this cannot be decided before hand. The presence of recirculating streams, changes in ore type and reagent dosage introduces further complications (68). From the laboratory investigations it was determined that the potential-pH point achieved after grinding was related to the ore type. On a plant scale, it might be possible to identify specific ore types, on-line, and if required to adjust the control strategy as a consequence. This is an application which would be welcomed in industry.

Fig. 41 shows the interrelation between a change in ore type, the metallurgical response, and the pulp potential, Ep, and pH achieved in the first cell of the copper rougher.

At about 9:30, the flotation operator being warned that a change in ore type was occuring reacted by decreasing the rougher pH set-point from 9.5 to 8.5. A concurrent drop in potential was recorded. However, the operator action was not sufficient to avoid a catastrophic decrease of the copper rougher concentrate grade, from 15% to 4% Cu within 30 minutes of the change in ore type.

Fig. 41. Example of identification of ore type change.



A further decrease of the pH set-point to 8 at 11:00 stabilized the roughing circuit, and consequently, permitted control to be regained with the concentrate grade apparently stabilizing at around 9% Cu. During that time, the potential remained relatively constant until 13:00, when it started to rise. The feed to the circuit was reverting to that prior to the upset. The concentrate grade, after reaching a maximum of 10% Cu at 13:45, started to decrease again, the operating conditions no longer being suited to the ore.

This is only one example of "seeing" an ore type change with monitored variables. Strangely, the potential decreased with the pH. Although this is contrary to the normal observation in mineral-water systems (63, 64, 83, 108), such relationships have been observed when redox and pH modifiers are added during flotation (sections 3.3.2 and 5.6.1). Again, this may be due to different mineral proportions and reactivities.

The potential alone would not be sufficient to provide information on the ore type being treated, as observed in Fig. 41. From the laboratory investigation on the different ore types, it was found that the pH of the pulp and the iron assay would also be required to ascertain the ore type with an acceptable confidence. Thus, all three variables (Ep, pH, %Fe) would have to be considered.

The potentials recorded in the first copper rougher cell were between 0 and 75 mV vs SCE (gold electrode). The potential observed in the laboratory with the stainless steel charge and similar reagent additions was +28 mV vs SCE (platinum electrode) for collectorless flotation (section 5.2). Even though the potentials are not directly comparable due to the different sensing electrodes, the similar values permit to suggest that collectorless flotation contributed to the total recovery in the plant.

Finally, there are two possible problems associated with continuous surveys of redox potentials. The first one is that the measurements may be affected by electrical noise. This does not appear to be the case as seen in Fig. 41. The measurements do not seem to be affected by variations in the throughput, and consequently of the power input of the semi-autogenous mill.

The second possible problem is electrode poisoning. It seems that the agitation of the slurry is intense enough to perform a continuous "gentle" abrasion of the electrodes (68). Particularly, no scale deposit was found on the gold spiral electrodes immersed in the lime conditioner of the zinc circuit (68). On the other hand, this may cause a short service life for the electrodes.

6.4 Conclusions

Potential-pH surveys of the copper and zinc circuits revealed that operating conditions for given parts of a circuit may be mapped as lines on potential-pH graphs. For the copper circuit, the roughing operating line appears to follow a H_2S/HS^- equilibrium while the cleaning operating line appears to follow a line for the reaction of the collector with the mineral. The lines do not seem to be related to the reduction of oxygen, even if the presence of mixed potentials is considered.

For the zinc circuit, the roughing section appeared to operated in a similar fashion to the copper roughing section. However, the cleaning section showed a relationship where the potential increased with increasing pH. This is still to be confirmed and explained.

Continuous monitoring of the pulp potential along with pH and iron assay in the feed may provide a means of identifying ore-type changes on-line. This could ease the implementation of control strategies for complex sulphide separation.

7. CONCLUSIONS, RECOMMENDATIONS AND CONTRIBUTIONS TO KNOWLEDGE

7.1 Conclusions

7.1.1 Monitoring of electrochemical potentials in mineral slurries.

Reviewing the literature and investigating the behavior of noble metal and mineral electrodes in mineral slurries, with and without flotation reagents and, with and without flotation air demonstrated that:

i) The electrochemical potentials monitored in flotation slurries are mixed potentials coupled with random contacts between the sensing electrode and the mineral particles. They cannot be readily related to thermodynamic quantities of the system (e.g. the standard potentials) unless the kinetics of the redox reactions are known.

ii) The physical interpretation of the redox potential measured in a mineral slurry is the same as that of a simple solution. Namely, it indicates the tendency for oxidation or reduction. However, the dynamic nature of flotation may enforce situations where the pulp potential is a much different value from the solution potential.

iii) The preferred noble metal for measurement is gold. It follows closely the potential exhibited by a mineral electrode (chalcopyrite, galena) when immersed in a slurry consisting mainly of chalcopyrite, or a mixture of chalcopyrite, galena and sphalerite.

iv) The preferred shape for the electrode is a spiral since this shape appears to be the most sensitive to the presence of sulphide mineral particles, even for solid contents as low as 1 g solids per liter of pulp (about 0.1% by weight).

v) A significant discrepency, typically 30 mV, between a gold spiral and a chalcopyrite electrode was observed under alkaline and, or, oxidizing conditions. This appears to be due to the formation of passive hydroxide layers on the mineral electrode as indicated by the depression of the sulphide minerals under these conditions.

vi) Black platinum electrodes might prove an adequate alternative to monitor, in-situ, the solution potential of a mineral slurry. This may be more advantageous than continuous micro-filtration of the slurry.

vii) There appear to be advantages in using mineral electrodes for laboratory investigations. Indication of the reaction kinetics is given by the rapidity at which a given mineral re-equilibrates after a reagent addition. However, it is to be demonstrated whether the additional information is of practical relevance for industrial applications.

7.1.2 Promises and limitations of an electrochemical approach for modulation of the flotation response.

The investigations demonstrated the possibilities of modulating the flotation response by control, potentiostatic or chemical, of the redox potential of the pulp. Namely, the presence of windows of selective flotation in the processing of a complex sulphide ore would permit a more efficient separation to be performed if these windows are determined and utilized. However, some limitations linked to this promise were determined:

i) The presence of galvanic interactions between the sulphide minerals and the grinding media introduces conditions which do not permit to infer the window(s) of selective flotation of an ore from investigations on the minerals, each one being taken on an individual basis.

ii) Laboratory investigations must be carefully controlled with respect to the environment induced by the grinding step. The occurence of collectorless flotation may distort laboratory results. Also, the presence of soluble minerals, such as chalcocite, may induce in-situ activation of other minerals, e.g. sphalerite and pyrite.

iii) Each ore, or ~~ore~~ type, is unique and generalization of processing options in terms of pulp potential and pH may be misleading. This is a limitation for dissemination of knowledge. However the pulp potential, along with other variables, can be advantageously used for on-line sensing of ore type change in a concentrator.

iv) The potential achieved after the addition of a redox or a pH modifier appears to be an indication of the reactivity of the ore or minerals. Interpretation of laboratory or plant data in terms of surface products is rendered difficult by the presence of mixed potentials.

7.2 Recommendations for future work

The present study has highlighted areas for further investigation. Some of these are of fundamental nature while the others may find direct and economical application in industry.

7.2.1 Fundamental work

i) Measuring techniques have to be defined for electrochemical investigations of sphalerite since the large band gap of (3.6 eV) and resistivity (8×10^5 ohm·m) of the mineral renders the manufacture of massive sphalerite electrodes impossible. Investigations on particulate bed electrodes suffer also of the high resistivity of the mineral.

ii) Further investigations should be undertaken to study the electrode kinetics and surface products of the reactions of the sulphide minerals with common flotation modifiers such as lime and sulphur dioxide, and uncommon ones such as potassium ferricyanide.

iii) The electrochemical behavior of hydrochloric acid in mineral slurries should be clarified at to why it yields more oxidizing potentials than sulphur dioxide for an equivalent pH.

7.2.2 Development of reagent control schemes

The indication of the reactivity of the ore, upon conditioning with a modifier, by the pulp potential shows promise for application of electrochemical techniques in industry. The measurement may be used for on-line determination of the ore type which would permit the control strategy to be adapted to the particular ore being treated.

Conversely, the measurement may be used to control the addition of reagents, particularly of modifiers. The definition of the windows of selective flotation in a concentrator should permit a better control and consequently, an improvement in the technical and economic efficiencies of beneficiation may be expected.

7.3 Contributions to knowledge

i) A conceptual stochastic model for the measurement of electrochemical potential in mineral slurries has been proposed. This model complements the mixed potential model for complex electrochemical phenomena and aids the interpretation of redox potential measurements in slurries.

ii) A gold spiral has been determined to be a reliable general purpose sensing electrode for the measurement of the pulp potential under most of the conditions encountered in flotation.

iii) The presence of windows of selective flotation has been verified for a complex Cu-Zn-Pb sulphide ore.

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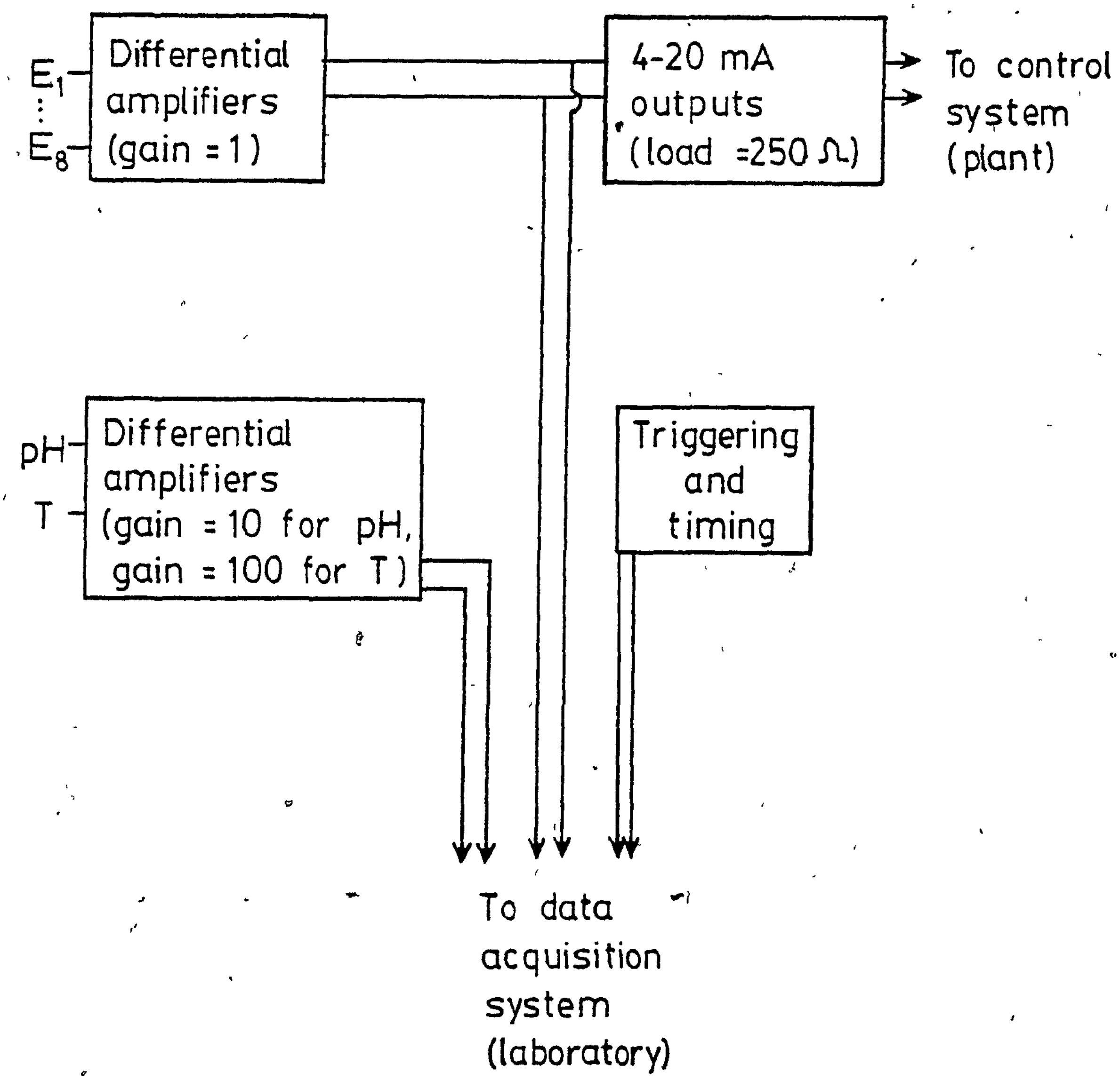
APPENDIX A: BLOCK DIAGRAM OF THE AMPLIFYING UNIT

Fig. A1 shows the block diagram of the interface unit. The diagram can be separated into three parts. First, there is the voltage generating circuit for timing and triggering of the data acquisition process. Second, the unity gain amplifiers for the electrochemical potentials and associated 4-20 mA current loops, Third, and last, high gain amplifiers for the pH (recorder output of pH-meter) and temperature (thermocouple).

The circuit configuration for the amplifiers is a differential input-single output amplifier (114, 115). The differential amplifier is preceeded by a voltage follower stage so that a high, symmetrical impedance is presented to the electrodes. The design of the circuit for the 4-20 mA current sources was based on adjustable high precision current sources (114, 115). The combination of differential inputs and 4-20 mA outputs offers the lowest senstivity to electrically induced noise, in the laboratory and especially in industrial plants.

For reliable operation, the circuits were kept as simple as possible.

Fig. A1. Block diagram of the amplifying unit.



APPENDIX B: Selected potential vs time profiles for the selection of the monitoring electrodes.

Only two sets of profiles are presented. In the first one, Fig. A2, an addition of 1 g of copper concentrate was made to a slurry containing 700 g of silica. The response of the electrodes can be described in terms of an impulse response (116). The platinum spiral appears to provide the highest sensitivity to the impulse addition. However, as the platinum foil, the spiral re-equilibrates rapidly to a value not much different from the original potential. On the other hand, the two gold electrodes show step increases, with very slow decays.

Fig. A3 shows an extreme case of impulse response. For the addition of copper concentrate (150 g), the spirals show oscillations prior to stabilization. The sampling interval was 0.1 s, which is ten times faster than that used for the flotation tests and transcient effects are more evident. The chalcopyrite electrode responded to the addition in a manner similar to the noble metal foils in Fig. A2.

Fig. A2. Transcient response of sensing electrodes during the addition of copper concentrate: spirals and foils.

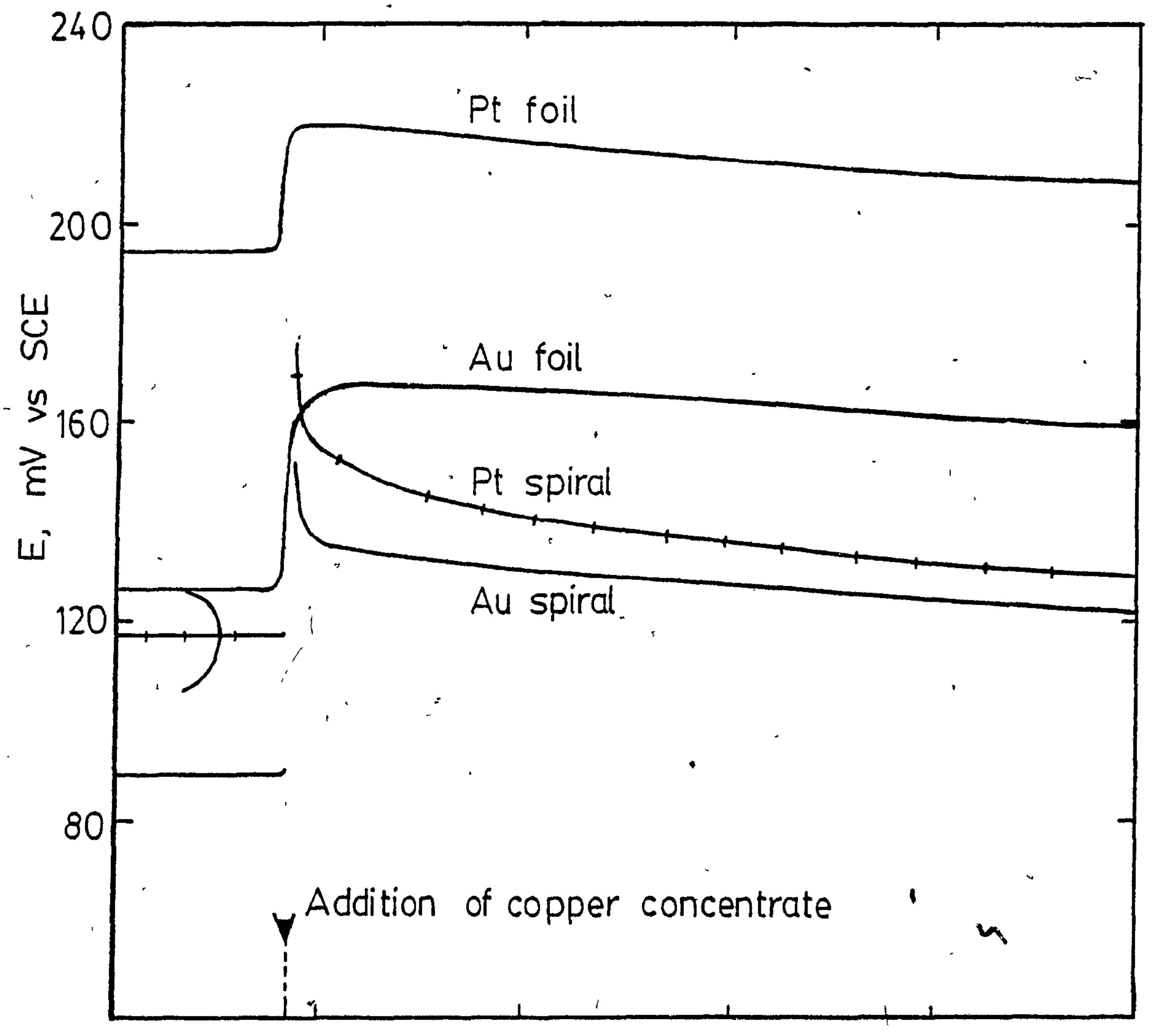
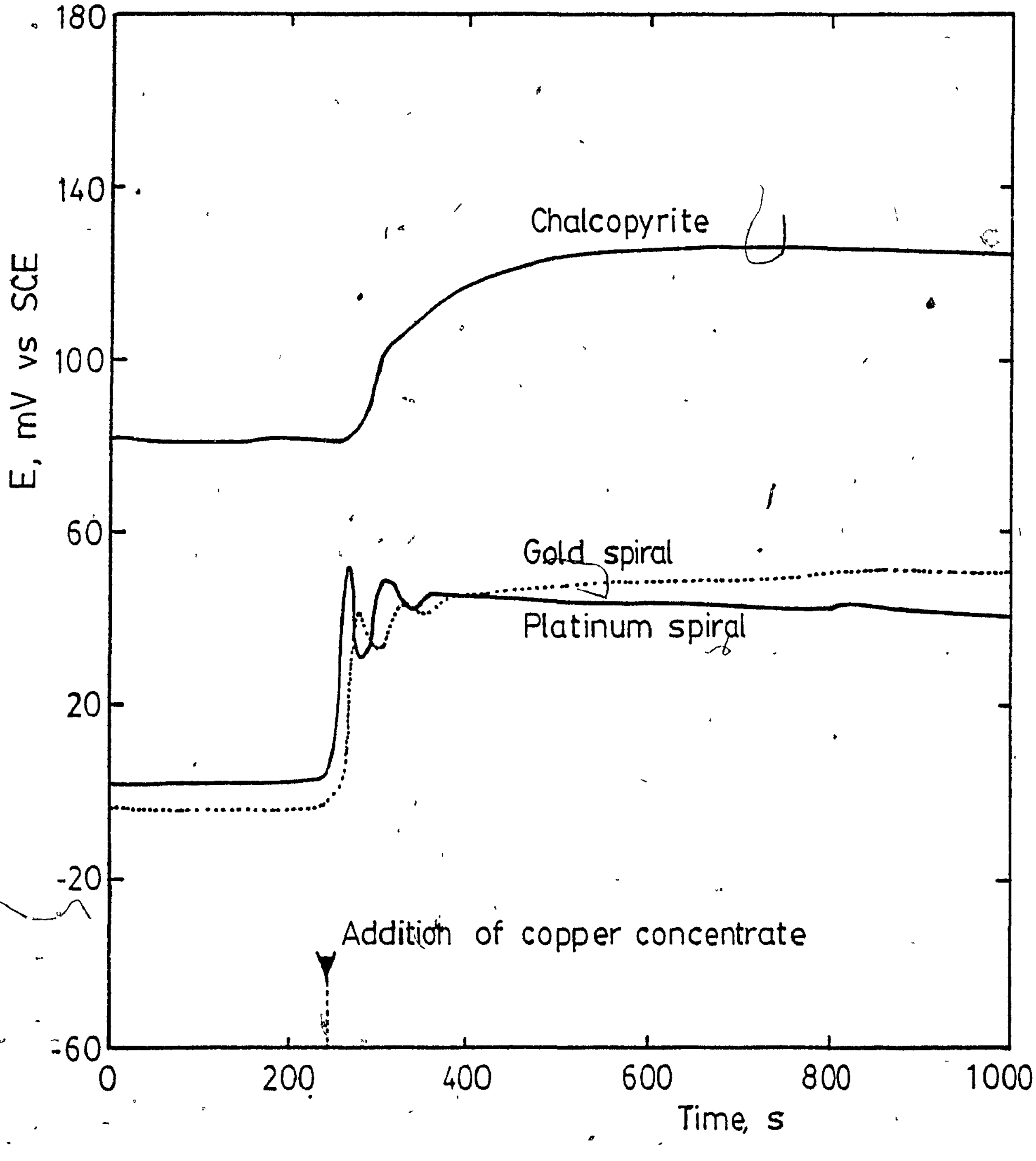


Fig. A3. Transcient response of sensing electrodes during the addition of copper concentrate: spirals and chalcopyrite.



APPENDIX C: Selected potential vs time profiles during roughing flotation.

Figs. A4 and A5 show potential vs time profiles obtained during rougher flotation of the B-zone ore. Again, class i is observed when the pulp is initially reduced (Fig. A4, mild steel media) while class ii is observed when the pulp is initially oxidized (Fig. A5, stainless steel media).

However, the difference between the two classes of profiles for roughing flotation is not as sharp as for cleaning flotation. In Fig. A4, the introduction of air has the greatest impact on the oxidation state of the pulp (as sensed by the electrodes) during the first roughing step.

In Fig. A5, the introduction of air appears mainly to compensate for the reduction caused by the addition of the xanthate (SIPX). For the last roughing step, however, the introduction of air does not seem to re-oxidize the pulp. This is probably due to an almost complete recovery of the sulphide minerals.

Fig. A4. Class i potential profiles during roughing. (mild steel media).

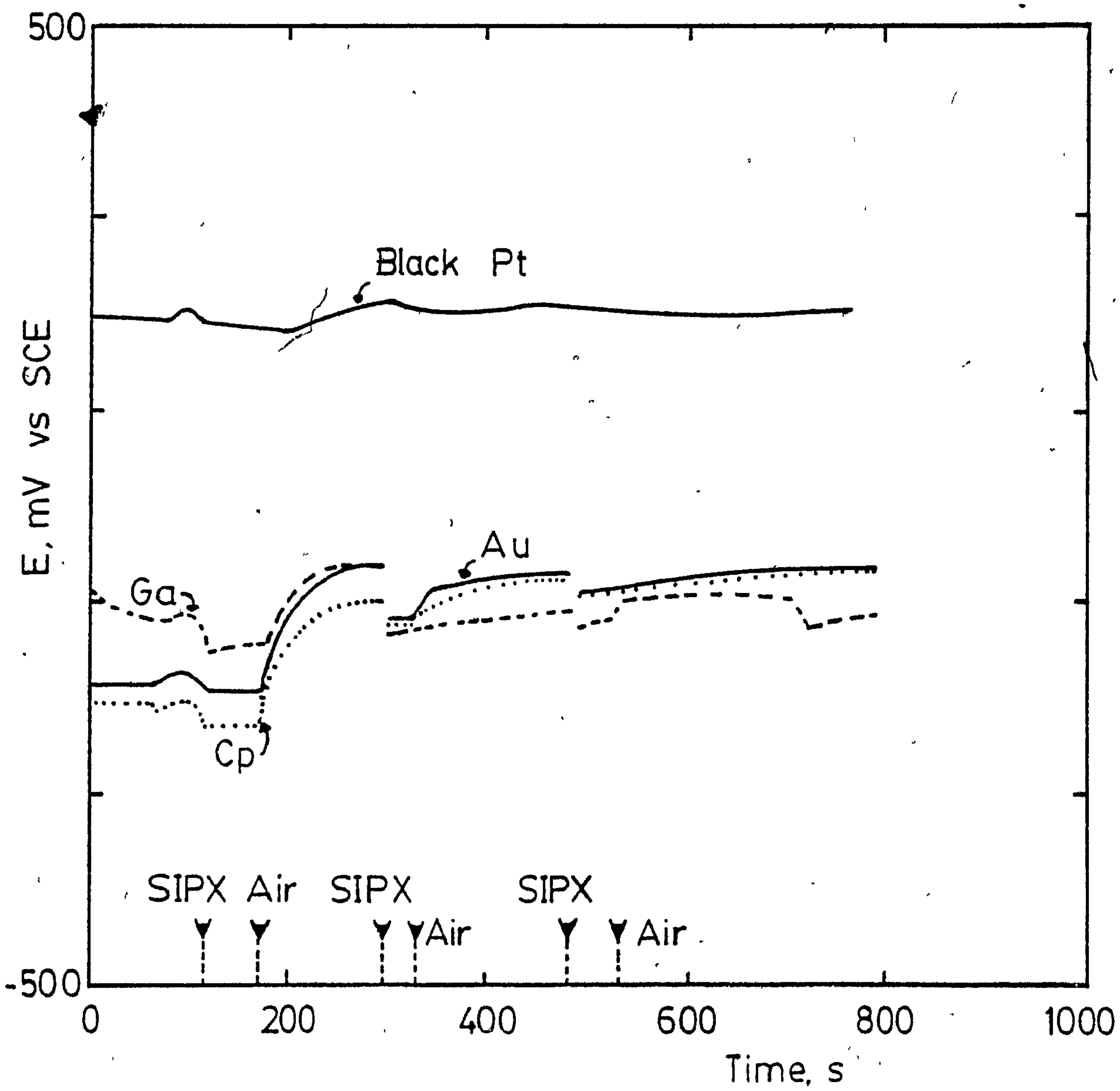


Fig. A5. Class ii potential profiles during roughing. (stainless steel grinding media).