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EFFECT OF ELECTROCHEMICAL ENVIRONMENT ON COLLECTORLESS FLOTATION OF SULPHIDE MINERALS

Marcel Kalemba Matabishi

UNIVERSITY OF JOHANNESBURG
EFFECT OF ELECTROCHEMICAL ENVIRONMENT ON COLLECTORLESS FLOTATION OF SULPHIDE MINERALS

By

Marcel Kalemba Matabishi

THESIS

Submitted in compliance with the requirements for

MASTER'S DEGREE IN TECHNOLOGY

In the Department of

METALLURGY

At the

TECHNIKON WITWATERSRAND

SUPERVISORS: Dr. R.V.R. HANDFIELD-JONES

Dr. G. AKDOGAN

SEPTEMBER 2000
ABSTRACT

The present study aims to investigate the influence of the pulp chemistry on the collectorless flotation of chalcopyrite and galena. Experimental findings revealed that chalcopyrite exhibited significant collectorless flotation at pH 10 and pulp potentials between +100mV and +120mV. Raman spectroscopy confirmed the formation of the mixed metal polysulphides on the surface of chalcopyrite floated with no additions. This might contribute to the importance of these species in the collectorless flotation of chalcopyrite. The chalcopyrite flotation was significantly depressed due to sodium metabisulphite addition. This might be due to the decrease in pulp potential which took place upon the introduction of sodium metabisulphite. The same type of depression has been observed in the presence of ferric nitrate, which increased the pulp potential to about 250mV.

Galena showed good floatability at pH 8 and pulp potentials between +190mV and +230mV. At this pH, addition of ferric nitrate as an oxidising agent depressed the flotation of galena. Sodium metabisulphite introduced in the pulp could not improve galena self-induced flotability because of a decrease of pulp potential, which leads to more reducing conditions.

The use of ethylene diamine tetra-acetic acid as a complexing agent did not improve the self-induced flotation of galena, however, polypropylene glycol
satisfactorily increased the flotation recovery of both chalcopyrite and galena, depending upon the pH, conditioning time and concentration.
DECLARATION

I hereby declare that the thesis, which I herewith submit for the research qualification of Master of Technology in Extractive Metallurgy to the Technikon Witwatersrand is, apart from the recognised assistance, my own work and has not previously been submitted by me to another institution to obtain a research degree.

Marcel Kalembe Matabishi.

_________________ Day of _____________. ___________.

v
ACKNOWLEDGEMENTS

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The support of Richard Ward Endowment Fund is gratefully acknowledged. I am also indebted to the School of Process and Materials Engineering, University of the Witwatersrand, for all facilities that have been made available to me during the realisation of the present research work.
DEDICATION

To all of you

who have been supporting me

with patience and love while,

with sacrifice,

I was working

so that

this goal becomes today reality.
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1. INTRODUCTION

The production of separate concentrates from complex ores containing economic amounts of copper, lead and zinc is complicated and selective flotation seems to be the only viable method. The main reason for this is the complex mineralogy of many of these ores which consist of finely disseminated and intimately associated sulphide minerals in a gangue comprising iron sulphides, quartz and carbonates. Such massive sulphide ores are a valuable source of silver and gold. Platinum group metals are also associated with massive sulphides. In most cases, concentrates are produced at relatively poor grades and recoveries.

Smelting charges become excessive with contaminated concentrates and penalties are often imposed for the presence of zinc and lead in copper concentrates as well as the presence of iron in zinc concentrates. The concentration of nickel sulphide ores by flotation and the effective separation of iron sulphides are becoming increasingly necessary since iron sulphide raises sulphur dioxide emission during smelting. With the imposition of stringent limits on these emissions, cost effective and more efficient methods of removing copper, lead, zinc, nickel sulphides from iron sulphide minerals have attracted much attention over the last ten years.
Among those, collectorless flotation of sulphide minerals from their gangues through electrochemical control is gaining importance as a cost effective and environmental friendly method. Electrochemical control has direct application to the separation of naturally hydrophobic minerals from other minerals.
2. AIMS

Although the relationship between flotation recovery, pH and pulp potential ($E_p$) for single minerals in the absence of other sulphide minerals has been investigated, there is no proposed mechanism to explain the effects of different electrochemical environments on the floatability of sulphides. Moreover, the greatest difficulties in application and understanding are encountered for real ores, which have complex mineralogy.

It is therefore believed that a fundamental systematic investigation of collectorless flotation responses of selected individual sulphide minerals in the presence of reducing and/or oxidising agents is desirable. Aeration conditions are also a prerequisite so as to determine the effect of the electrochemical environment on the collectorless floatability of sulphide minerals. Understanding of sulphide minerals collectorless flotation should, for instance, take into consideration pre-flotation steps such as milling, since this may affect the flotation responses of mineral ores due to the transformation of mineral surface. The effect of grinding media on self-induced flotation will be investigated by introducing ferric ions into the pulp and determined by measuring the pulp potential.

The present investigation was undertaken to shed some light on the influence of the pulp chemistry on the collectorless flotation of sulphide minerals. It can
3. LITERATURE SURVEY

3.1 COLLECTORLESS FLOTATION OF SULPHIDE MINERALS

Since the early days of flotation one of the controversial issues of flotation chemistry has been whether sulphide minerals are naturally floatable (Gaudin, 1932; Ravitz and Porter, 1933). Some sulphides, such as molybdenite, are naturally floatable under most conditions whereas others are considered to have hydrophobic character in the absence of oxidation (Ravitz and Porter, 1933; Fuerstenau and Sabacky, 1981).

The basis for native floatability lies on the assumption that sulphide lattice ions are expected to be weakly hydrated and do not interact strongly with water molecules. Miller (1988) stated that sulphide minerals are thermodynamically unstable and sufficient oxygen remains in the system to cause oxidation, presumably leading to the formation of elemental sulphur. This hypothesis was originally proposed by Wark (1938).

Several researchers have suggested that sulphide minerals could be floated under mild to modest oxidising conditions (Heyes and Trahar, 1977; Tollet et al., 1996). Plaksin (1938) stated that adsorbed oxygen decreases surface hydration, thereby, rendering hydrophobicity to the mineral.
nature of the mineral and the activities of different species present in the aqueous phase and at the mineral surface.

Another consideration is that, if the sulphide minerals make contact with each other or with other conducting surfaces, an electrochemical cell will form. The mineral or conductor with the higher oxidation potential will act, as a cathode while the anode will be the mineral or material with the lower oxidation potential. For instance, when a sulphide mineral like chalcopyrite, which has a low oxidation potential (0.56V), is in galvanic contact with pyrite with its high oxidation potential (0.66V), oxidation of chalcopyrite and other sulphide minerals will take place. Majima (1969) confirmed that, at pH 2, the formation of elemental sulphur (S^0) on chalcopyrite, galena and sphalerite by oxidation was accelerated in the presence of pyrite. During selective flotation of these base sulphide minerals, the formation of elemental sulphur (S^0) on their surface may promote their floatability but at the same time it may prevent their selective flotation (Tollet et al., 1996; Rey and Formanek, 1960; Kocabag and Smith, ).

From Figure 3.1 below, which illustrates the Pourbaix diagram in the form of E_r-pH diagram for galena (Barry, 1992), possible oxidation and reduction states of this sulphide mineral are presented. It can be said that, according to the conditions in the Pourbaix diagram, some hydrophilic surface oxidation products such as S_2O_3^{2-}, HPbO_2^- and Pb(OH)_2 can exist in oxidising
conditions and, if not removed from mineral surface, the restoration of collectorless flotation of the concerned sulphide mineral may be impossible. Their removal depends, not only on their solubility product but also upon the stirring rate. In oxidising conditions, depending on the pH and pulp potential, Pb will dissolve or form oxidised metal species on the galena surface.

![Eh-pH diagram](image)

**Figure 3.1** E$_h$-pH diagram for galena (equilibrium lines correspond to dissolved species at 10$^{-4}$M). (Barry, 1992)

It is not excluded that the formation of elemental sulphur might derive from the initial oxidation of sulphide minerals (Barry, 1992) in both, acid (1) and alkaline (2) solution. The equations (1) and (2) related to those conditions are:
MS → M^{2+} + S^0 + 2e^- \quad (1)

MS + 2H_2O → M(OH)_2 + S^0 + 2H^+ + 2e^- \quad (2)

The presence of elemental sulphur (S^0) at the mineral surface can lead to hydrophobicity, and collectorless or natural flotation of sulphide minerals may be promoted (Tollet et al., 1996). By the use of cyclic voltammograms, it has been demonstrated that the cathodic reduction of galena produces Pb and H_2S in accordance with Figure 3.1. Any variation of pH, temperature, presence or absence of other substances than that were used to establish this pH-E_n diagram will considerably change the regions of sulphide mineral ores stability and consequently their collectorless flotation. For each mineral, there is a correspondent Pourbaix diagram, which may not have the same regions of stability for different species present in the system studied. The diagram changes according to the electrochemical environment in the media (system) where all species are involved (Pourbaix, 1966). The more species involved in the establishment of this diagram, the more sophisticated is the E_n-pH diagram. This diagram E_n-pH is helpful for the theoretical study of stability regions where different species involved in collectorless flotation of sulphide minerals exist.

The above electrochemical phase diagram for galena (PbS) shows that negative potentials will result when the galena surface is converted to metallic
lead, the sulphide ion passing into solution. Depending on the pH, anodic oxidation of galena in acidic solution will lead to the dissolution of lead (Pb) or formation of oxidised metal species on the mineral surface. The potential range in which galena is thermodynamically stable depends on pH. The following chemical equations from this Pourbaix diagram are:

\[ \text{PbS} \rightarrow \text{Pb}^{2+} + \text{S}^0 + 2\text{e}^- \quad (3) \]

\[ \text{PbS} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{Pb} + \text{H}_2\text{S} \quad (4) \]

\[ 2\text{PbS} + 3\text{H}_2\text{O} \rightarrow \text{PbS}_2\text{O}_3 + \text{Pb}^{2+} + 6\text{H}^+ + 8\text{e}^- \quad (5) \]

Equation (3), involving the formation of elemental sulphur, is assumed to be responsible of collectorless flotation of galena (Barry, 1992).

An illustration of electrochemical diagram of stability (Pourbaix diagram) for Cu-Fe-S-H₂O is given below.
Figure 3.2 $E_h$-pH stability diagram for the Cu-Fe-S-H$_2$O system (Fairthorne et al., 1997).

This diagram depicts the effect of oxidation on the collectorless flotation of chalcopyrite. Empty and filled circles represent the experimental pulp potential ($E_p$) and pH values for chalcopyrite conditioned in nitrogen (o) and oxygen (●), respectively. Inspection of this $E_h$-pH stability diagram for the Cu-Fe-S-H$_2$O system reveals the formation of insoluble ferric oxide/hydroxide, which is thermodynamically predicted at natural and basic pH values but also in acidic conditions at high $E_h$ values (Fairthorne et al., 1997).
The presence of these ferric oxides and/or hydroxide have a negative effect on the self-induced flotation of sulphide mineral ores if their removal from the mineral-solution interface is not achieved.

3.2 COLLECTORLESS FLOTATION OF CHALCOPYRITE

A number of research works state that chalcopyrite is naturally floatable under circumstances where an ideal chemical environment has been achieved through kinetics of the transformation (Heyes and Trahar, 1977; Gardner and Woods, 1979; Grano et al., 1997; Labonté et al. 1989; Fairthme et al., 1997 and Barry, 1992). For example, Heyes and Trahar (1977) observed that modest oxidation is required for collectorless flotation of chalcopyrite. This was attributed to the formation of sulphur by oxidation.

Gardner and Woods (1979) and Trahar (1983) proposed that the elemental sulphur formed as an oxidation product was the hydrophobic species responsible for flotation and suggested that, at pH 11, the start of collectorless flotation corresponded to the potential where anodic oxidation of chalcopyrite occurred according to the following reactions in alkaline solution:

\[
\text{CuFeS}_2 + 3 \text{H}_2\text{O} \rightarrow \text{CuS} + \text{Fe(OH)}_3 + \text{S}^0 + 3 \text{H}^+ + 3 \text{e}^- \quad (6)
\]
And for acidic solutions, (7)

$$\text{CuFeS}_2 \rightarrow \text{CuS} + S^0 + \text{Fe}^{2+} + 2 e^- \quad (7)$$

In equations (6) and (7), the formation of elemental sulphur is believed to be the mechanism responsible for collectorless flotation. X-ray photoelectron spectroscopic (XPS) evidence suggested the formation of an iron-deficient chalcopyrite lattice (Equation 8) rather than the existence of free elemental sulphur (Equation 3). The formation of a hydrated iron oxy-hydroxide layer in air-saturated alkaline solutions was confirmed by Buckley and Wood (1984) as well as Zachwieja et al., (1989):

$$\text{CuFeS}_2 + 3/4 \times \text{O}_2 + 3/2 \times \text{H}_2\text{O} \rightarrow \text{CuFe}_{1-x}\text{S}_2 + x \text{Fe(OH)}_3 \quad (8)$$

The collectorless flotation of chalcopyrite seems to be controlled by the balance between the formation of the iron-deficient chalcopyrite via reaction (8), removal of iron oxy-hydroxide either by dissolution or dispersion, and decomposition of the iron deficient chalcopyrite. By XPS examination of chalcopyrite conditioned at pH 6, Grano et al. (1997), found that chalcopyrite exhibited a great floatability due to the increased surface coverage of hydrophobic iron-deficient chalcopyrite, evidence for both iron deficient chalcopyrite and an iron oxy-hydroxide.
On the natural floatability of chalcopyrite, Trahar et al. (1977) established that freshly ground chalcopyrite displayed natural floatability in an oxidising environment and non-floatability in a reducing environment. A strongly reducing environment, not favourable for flotation, could be changed to create favourable flotation conditions by raising the pulp potential, either by aeration or by the addition of an oxidant. These authors found out that collectorless flotation of chalcopyrite was affected by the particle size; the response of coarse particles was not fully restored by aeration after grinding in an iron mill since the behaviour of the coarse particles is critical in terms of ultimate recovery and selectivity obtained (Trahar, 1976). The impact of grinding in an iron mill, which has not been fully recognised, might impose a limit to flotation performance. Although Rey et al. (1960) and Rao et al. (1977) were more interested in the influence of the grinding environment on subsequent floatability, the role of the pulp potential ($E_p$) of the grinding system has rarely been considered.

Although it has been also observed that the type and addition of frother had a profound effect on the natural floatability of chalcopyrite, there is no evidence of its impact on the hydrophobicity. The flotation of a mixture of chalcopyrite in real ore samples does not necessarily show the same flotation behaviour as in the case of flotation of single pure mineral.
Investigation of flotation of chalcopyrite without collector after dry, autogenous grinding (Lepetic, 1974) led to the conclusion that chalcopyrite was successfully floated using a small amount of polypropylene glycol methyl ether 200, which provided the highest cumulative copper recovery (90.0%) among all frothers tested, as the only reagent. Chalcopyrite showed a lower flotation rates than pyrrhotite, pyrite and arsenopyrite. Lack of selectivity that has been encountered in conventional method was improved when frother alone was used. According to Lepetic's work, this process is cheaper because of low reagent consumption than conventional, which consists of using modifier-collector-frother.

Leroux et al. (1989) have conducted some tests on the impact of pH, pulp potential, presence of oxygen as a flotation gas, and zinc sulphate on collectorless flotation of chalcopyrite. The following points were found in their investigations:

- At pH 7.8 chalcopyrite floated better than galena when zinc sulphate (ZnSO₄) was used as depressant. The flotation of chalcopyrite is affected by the size of fraction of mineral.
- The depressive effect of sulphur dioxide (SO₂) on chalcopyrite and galena was more greatest when the pH is less than 8, however when the pH was set between 9-10 during aeration, the depressive effect of sulphur dioxide (SO₂) was reduced due to an increase of pulp potential.
- Selective flotation of chalcopyrite and galena, by using sodium cyanide, showed that chalcopyrite was depressed than galena. This was due to the fact that cyanide ions react with Cu$^{2+}$ ions to form an hydrophilic complex on the mineral surface which competes with the hydrophobic sites created by oxidation of sulphide ion. This mechanism is not yet well understood.
- The results of tests conducted in the presence of oxygen, nitrogen or a mixture of oxygen and nitrogen showed that the collectorless flotation of chalcopyrite occurs after the pulp potential was raised to about 0mV (Standard calomel electrode). Both gas composition and conditioning time influence the collectorless flotation of chalcopyrite. If the oxygen content or the conditioning time is increased, the recovery of chalcopyrite reaches maximum at a pulp potential of $E_p = 70$mV after which the chalcopyrite recovery starts decreasing. This reduction could be attributed to the formation of hydrophilic sulphoxyl species (e.g., $\text{SO}_3^{2-}$) at high pulp potentials.

Grano et al. (1997) studied the effect of surface modification of the chalcopyrite-sulphite ion system on the collectorless flotation of chalcopyrite and point out that:
- Sulphite, like sodium metabisulphite ($\text{Na}_2\text{S}_2\text{O}_5$) and sodium sulphite ($\text{Na}_2\text{SO}_3$), strongly depresses the flotation of chalcopyrite because of the decomposition of a sulphur rich surface species by sulphite.
- Sulphite increases the collectorless flotation of chalcopyrite if the adsorbed iron oxy-hydroxide is removed from the chalcopyrite surface, therefore exposing a sulphur rich sub-layer.
- The mechanism involves reduction of the adsorbed ferric oxy-hydroxide to the more soluble ferrous species.

Misra et al. (1985) found that sulphur dioxide (SO₂) solution removed hydrophilic ferric oxy-hydroxide, exposing iron-deficient chalcopyrite and activating collectorless flotation of the mineral. This mechanism has been confirmed by Grano et al. (1997). In their studies it was found that the effect of sulphite or metabisulphite ions was apparently dependent on the pulp potential, the oxygen concentration, implying the redox process which controls the surface cleaning mechanism Ross et al.'s work[27] led to the same deduction. Broman et al. (1985) also ascertained that restoration of chalcopyrite mineral surface damaged by cement was possible at low pH (<7.5) and in reducing conditions. He observed that, in the absence of sulphite, the collectorless flotation of chalcopyrite in a nitrogen atmosphere was greater at pH 6 than at pH 9.5. This was thought to occur due to superficial oxidation resulting in the formation of elemental sulphur (S⁰), polysulphide or an iron-deficient chalcopyrite.

From the study of the dissolution of chalcopyrite using zeta potential and XPS done by Fairthorne et al. (1997) during their investigation on the effect of
oxidation on the collectorless flotation of chalcopyrite, a mechanism of dissolution of iron and copper from the chalcopyrite leaving a hydrophobic metal-deficient, sulphur-rich surface followed by their readsoption as ferric and cupric species has been proposed to explain the flotation results of chalcopyrite during oxidation. It was postulated that the kinetics of formation and precipitation of these metal hydroxide species might control the hydrophobicity of the sulphide mineral surface and therefore their collectorless flotation.

The collectorless flotation of Murgul (Turkey) copper ore (containing principally chalcopyrite and pyrite) was investigated by Ekmekçi and Demirel (1997, 1998). Their results confirmed also that the collectorless flotation of chalcopyrite depends upon the pH, pulp potential (Eₚ), chemical environment. They found that chalcopyrite recovery increased when the pH was set up between 9 and 10. A series of tests conducted in a neutral pH solution using sodium sulphide as pulp potential (Eₚ) regulator and nitrogen as flotation gas to exclude the effect of oxygen revealed that slight selectivity could be obtained only at a potential of 450mV. The flotation behaviour of chalcopyrite and pyrite were similar at potentials lower than 200mV, and their recovery decreased dramatically down to 20% at reducing potentials (<0mV). Ekmekçi et al. (1997, 1998) believed that the depression of both minerals at reducing potential was due to the formation of soluble sulphide species, such as H₂S and /or HS⁻, depending on the pulp potential. The pulp potential and the
oxygen concentration, which are not independent, are the major determining factors in the flotation of both chalcopyrite and pyrite.

Good selectivity between chalcopyrite and pyrite could be obtained in the presence of a moderate concentration of ethylene diamine tetra-acetic acid (EDTA) by the formation of Cu-EDTA compounds, which prevent the activation of pyrite by Cu ions. Equations (9) and (10) have been proposed to express the action of EDTA on selective flotation of chalcopyrite and pyrite present in real ores. Excess of EDTA was found to increase the floatability of pyrite by removal of hydrophilic ferric hydroxide layers from its surface (equation 9), thereby exposing a sulphur-rich surface (Ekmekçi et al., 1997, 1998).

\[
Cu(OH)_2 + EDTA^{4-} \rightarrow Cu(OH)EDTA^- + OH^- \quad (9)
\]

\[
Cu + EDTA^{4-} \rightarrow CuEDTA^{2-} + 2e^- \quad (10)
\]

This increase of pyrite floatability is principally responsible for decreasing selective flotation of pyrite in the presence of chalcopyrite.
3.3 COLLECTORLESS FLOTATION OF GALENA.

Leroux et al. (1989) also investigated collectorless flotation in the processing of complex sulphide ores and found that, among major minerals, galena showed the greatest response to collectorless flotation after chalcopyrite. They also stated that the collectorless flotation was influenced by pulp potential ($E_p$) and pH. Using SO$_2$, as a depressant, at different pH, they concluded that this reagent depresses both galena and chalcopyrite when the pH was less than 8.0, but this effect was not noticeable for chalcopyrite when the pH was above 9.5. Sodium cyanide (NaCN) did not depress galena.

The collectorless flotation was promoted when the pulp potential was greater than about 0mV (SCE). Although there exists of some controversy among investigators, Ralston and Hayes (1988) have proposed that oxidising atmosphere is essential for collectorless flotation. The values of the pulp potential required to create an oxidising environment seem to be a function of the system.

The particle size of galena is one of the major factors that may affect its collectorless flotation. Galena was recovered in the intermediate size range (average size 53 µm). Trahar (1981) found that the less the mineral, the more difficult the coarser size fraction to float. This is one more proof that galena
becomes less hydrophobic than chalcopyrite. Tests done in the same conditions confirmed that the collectorless flotation of chalcopyrite was always greater than that of galena.

Guy and Trahar (1979) found that galena is floatable without the addition of a collector and ascribed this behaviour to oxidation producing sulphur rich compounds on the mineral surface. According to Woods and Trahar's investigations (1996), the highest rates of collectorless flotation of sulphide mineral ores are a result of their degree of oxidation and formation of elemental sulphur on the surface. Hamilton et al. (1981), on the basis of XPS and electrochemical results, have shown that in most situations the surface sulphur species which are responsible for collectorless flotation are metal-deficient sulphides rather than elemental sulphur alone.

Wang & Forssberg (1989) studied the collectorless flotation of pure sulphide minerals (sphalerite, pyrite, arsenopyrite, glaucodot and galena) and found that the floatability of galena in ethylene diamine tetra-acetic acid (EDTA) solution was strongly dependent on the pH value and EDTA concentration. Galena exhibited good flotation in the pH range 6-10, while flotation was low or absent up to pH 5 and above 11. In those tests EDTA concentration was $5 \times 10^{-4}$ M. They explained that the absence of floatability of galena, pyrite, and arsenopyrite and depression of glaucodot in acidic EDTA solutions was due to the adsorption of EDTA on the sulphide surface and the inability of EDTA
to remove the metal hydroxides. At pH 8.5, the floatability of these minerals initially increases with increasing EDTA concentration. However, further increase in EDTA concentration above $10^{-3}$ M significantly decreases the flotation. The flotation was completely depressed by EDTA concentrations greater than to $10^{-2}$ M. This is in contradiction with Shannon and Trahar’s results (1986). They found good floatability of chalcopyrite, galena and sphalerite in EDTA concentration above $6.45 \times 10^{-3}$ M, no depression even for EDTA concentrations above $10^{-2}$ M was observed. The discrepancy was attributed to the sample preparation or the quality of the minerals that were used in those tests. Forssberg attributed good floatability of sulphide minerals in the pH range 6-10 to removal of the hydrophilic metal oxide layer by EDTA, thus exposing a hydrophobic sulphur rich surface to water.

It is well known that the grinding media also affects the collectorless flotation of sulphide mineral ores (Leppinen et al., 1998). The general conclusion about this consideration is that steel grinding media have a depressive action on the flotation of sulphide minerals due to the electrochemical effect of iron. The reducing conditions at a sulphide mineral surface created by oxidation of steel in a galvanic interaction can hinder the adsorption of collector, whether it takes place by ion exchange or through an electrochemical reaction. For example, the separation of sphalerite from other sulphide minerals can be promoted through the prevention of oxidation of the mineral and formation of sulphur during grinding which would induce natural or collectorless flotation.
However, with complex sulphide ores, the overall result of galvanic reactions depends upon the properties of the minerals and ions present in the pulp.

Wark and Cox (1934) found that galena was activated by copper sulphate. This activation makes galena more like chalcopyrite in its response to sodium dithiophosphate.

Mitrofanov and Kushnikova (1964) showed that adsorption of copper onto galena increases sharply with increasing concentration of copper ions and pH, and Shimizuaka et al. (1976) found that the activation of galena with copper proceeds according to the exchange reaction:

$$\text{PbS} + \text{Cu}^{2+} \rightarrow \text{CuS} + \text{Pb}^{2+} \quad (11)$$

and is not controlled by linear law but a parabolic law. They found that this leads to an increase in the floatability of galena, and speculated that this increase might have been caused, not by increased uptake of the collector, but by increased native floatability of galena.

In aqueous alkaline solution and oxidising conditions, Pb$^{2+}$ will form Pb(OH)$^+$ and Pb(OH)$_2$ that may adsorb at the galena surface forming a hydrophilic lead hydroxide layer by the equation:
\[(n-1)\text{PbS} + \text{Pb}^{2+} + 2 \text{OH}^- \rightarrow \text{(PbS)}_{(n-1)}\text{Pb(OH)}_2 \quad (12)\]

Grano et al., (1991) presumed that the reduction of collectorless flotation of galena might be due to the formation of hydrophilic lead hydroxide overlayer on galena.

In the present discussion, the collectorless flotation of sulphide minerals, in particular chalcopyrite and galena is examined from theoretical considerations and according to previous researches done on collectorless flotation of sulphide minerals. Some of the important highlights are made in the following points. However, the existence of some controversies between researchers tends to muddy the waters of what mechanisms exist in collectorless flotation.

-The mechanism of collectorless flotation of sulphide minerals may be due to: the presence of hydrophobic substances, like elemental sulphur and polysulphides adsorbed onto the surface of sulphide minerals or, the dissolution of metal from the lattice of sulphide minerals leaving a hydrophobic lattice sulphur rich at the mineral surface.
- Oxidation and reducing conditions (the electrochemical environment) govern the transformation at the mineral surface and hence the collectorless flotation.

- The presence of some complexing agent like ethylene diamine tetra-acetic acid (EDTA) in a reasonable quantity may selectively restore the collectorless flotation of sulphide minerals. Its excess may depress selective flotation.
4. EXPERIMENTAL

4.1 MATERIALS

4.1.1 Minerals

During this investigation, the flotation behaviour of high purity chalcopyrite and galena were studied using a microflotation unit. These chalcopyrite and galena samples, which originated from Mexico and USA respectively, were obtained from Wards Natural Science Museum. Their composition is given in the table below.

Table 1. Chemical analyses of minerals

<table>
<thead>
<tr>
<th>Minerals</th>
<th>Elements</th>
<th>Cu</th>
<th>Pb</th>
<th>Fe</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chalcopyrite (CuFeS$_2$)</td>
<td></td>
<td>35.9</td>
<td>-</td>
<td>21.0</td>
<td>36.23</td>
</tr>
<tr>
<td>Galena (PbS)</td>
<td></td>
<td>-</td>
<td>84.42</td>
<td>-</td>
<td>13.7</td>
</tr>
</tbody>
</table>

4.1.2 Flotation reagents

Some chemical reagents of analytical grade have been used during this investigation such as:
Diluted hydrochloric acid and sodium hydroxide (NaOH) made respectively from concentrated solution of HCl (32%, 1.16 kg/l) and sodium hydroxide pellets (98%) have been used to monitor the pH in the tests where the pH was kept constant. Changes in floatability that can be attributed to pH changes may reflect variations in pulp potential (E_p), since pH and (E_p) are not normally independent variables.

Ethylene diamine tetra-acetic acid (EDTA, 98.5%) has been also used to study the effect of complexing agent on collectorless flotation of chalcopyrite and galena. The presence of complexing agents, which can be useful for collectorless flotation of sulphide minerals, are expected to form, with the metal present in the slurry, hydrophobic compounds on the surface of the mineral particles. Complexing agents may also form insoluble salts that will precipitate in the solution by removing hydrophilic compounds from the desirable mineral surface.

Polypropylene glycol of average molecular weight 400 (P.P.G 400) has been chosen as frother because of its power of producing a stable gas-water interface and thus bubbles by which the hydrophobic sulphides are removed.

Sodium metabisulphite (Na_2S_2O_3) of analytical grade 98% minimum and ferric nitrate (Fe(NO_3)_3.9H_2O) at 97% purity were introduced as reducing agents
whereas oxygen is oxidising. Ferric nitrate has been also used in the test to simulate the effect of grinding in the iron mill on collectorless flotation of sulphide minerals.

Nitrogen and oxygen, both, of high purity have been used as flotation gas in all laboratory tests. The first gas to lower the pulp potential or to create an inert environment and the second to increase the pulp potential to oxidising values so that the oxidation effect on collectorless flotation of sulphide minerals (chalcopyrite and galena) can be examined. All of them were purged separately in the micro-flotation cell at constant flow rate of about 50 ml per minute. This value has been selected from the literature according to previous researches done on collectorless flotation of some sulphide minerals such as chalcopyrite, galena and pyrite.

All these chemical reagents mentioned above affect the flotation of chalcopyrite and galena. Their concentration might be playing an important role on the self-induced floatability of these sulphide minerals. Thus they should be taken in consideration.
4.2 MICROFLotation SET UP

4.2.1 Introduction

Once the microflotation unit was set up, preliminary tests were carried out on pure sulphide minerals (chalcopyrite and galena) for reproducibility tests of flotation.

4.2.2 Apparatus

The microflotation unit comprises two components namely the microflotation cell where all experimental tests are run and the bubble sizing system to control the gas flow rate and mean bubble size before starting each test.

The microflotation cell consists of a micro-column flotation with peristaltic pump connected to its conical base for slurry recirculation.

The bubble sizing system consists of four main parts, namely the optical detectors, the detector electronics, the microprocessor system and a personal computer (PC). The signals, obtained as a bubble travelling up the capillary tube passes the two phototransistors, are amplified, and squared by the detector electronics. These signals are used to produce two pulses for each bubble, from which the velocity and the volume can be calculated. The
function of the microprocessor system is to time these pulses, store the result in the memory together with the real time of the event, and transmit this data to the PC at the end of the measurement cycle. A program on the PC receives this data and stores it in the disc file. Additional software operates on this file and performs the data analyses.

In order to measure the total volume of bubbles they are collected in a gas burette, individual bubble volumes are determined as a fraction of total volume.

After the required gas flow rate is obtained from repetitive tests, the mineral conditioning started as it is explained in the following paragraph.

In the figures 4.1 and 4.2 below are shown the microflotation unit. (Goodal, 1990)
Figure 4.1 Bubble size system (Goodal, 1990)
Figure 4.2 Microflotation system (Goodal, 1990)
4.3 PROCEDURE OF MINERAL CONDITIONING AND FLOTATION TESTS

4.3.1 Procedure of mineral conditioning

Each sample weighing 3 grams was ground in a ceramic mortar and pestle until the whole sample was below 75 μm. The minus 75 μm was screened through 38 μm screen. Grinding and screening were performed in distilled water. After screening, the mineral was ultrasonically dispersed, following by sedimentation and decantation to remove the fine particles. The ~75+38 μm fraction (~2g) was transferred to conditioning cell which was continuously purged with pure nitrogen (99.99%), passing through successive distilled water for saturation during 30 minutes prior to each flotation tests.

The pulp potential was continuously measured throughout the test by using a platinum electrode against a silver-silver chloride (Ag/AgCl) inserted into the micro-flotation cell. Changes in the recorded potential reflect the transformations that are taking place in the system.

4.3.2 Procedure of flotation test

Sodium metabisulphite (Na₂S₂O₃) and Ferric nitrate Fe(NO₃)₃.9H₂O were used for the experiments to observe the reproducibility in pulps where
sulphur-oxy and ferric species influenced the floatability. Dilute HCl and NaOH solutions made up from analytical grade reagents were used for pH control.

During pH adjustments, 20 minutes preconditioning was allowed, and further 5 minutes conditioning period for sulphur and further more other 5 minutes for ferric reagents prior to flotation.

At the completion of conditioning period, the microflotation cell was filled to the appropriate level with distilled water and the flotation test was started. The flotation cell was purged with nitrogen as a flotation gas, unless otherwise stated, at a constant rate of 50ml/minute; this rate was controlled by flow meter. Concentrate samples were collected at 0.5, 2, 4 minutes. Four minutes was found as an optimum time. The pulp volume was maintained automatically at a pre-set level by addition of fresh water of the same pH as the pulp.

After the flotation test, the concentrates and tails were filtered, dried, and weighted and the flotation recovery determined by calculation.

In the following paragraphs, which consists of two main parts, the results of collectorless flotation for chalcopryite and galena are presented separately and some of them are followed by comments. The discussion is focused on
the effect of each parameter of the flotation response and the relationships between the pH, pulp potential ($E_p$), flotation time and recovery.

After these results on pH and the impacts of the above parameters on the electrochemical environments of self-induced flotation for these two pure sulphide minerals (chalcopyrite and galena), a comparison is made between their collectorless flotation in the last section.
5. RESULTS AND DISCUSSIONS

5.1 INTRODUCTION

In this section which is subdivided into three parts, all results on the collectorless flotation of sulphide minerals (chalcopyrite and galena) are represented in flotation recovery versus flotation time graphs, unless otherwise stated, since pure minerals have been used. The influences of other variables, such as type of chemicals, pH, frother and potential of the pulp, on the flotation behaviour are also examined. The impact of the frother, polypropylene glycol 400, on the collectorless flotation of chalcopyrite and galena has also been investigated in order to examine its influence on self-induced flotation. The first part deals with the effects of different parameters such as pH, sodium metabisulphite, ferric nitrate, EDTA and polypropylene glycol 400 on the collectorless flotation of chalcopyrite. The second part of the section is about the collectorless flotation of galena in line with the same parameters mentioned above. In the third part of this section, the comparison between chalcopyrite and galena self-induced flotation investigated in this work has been analysed. The reproducibility of the results on chalcopyrite and galena is respectively illustrated in appendices A and B.
5.2 RESULTS ON COLLECTORLESS FLOTATION OF CHALCOPYRITE

5.2.1 Effect of pH and pulp potential on chalcopyrite floatability, without addition of ferric nitrate nor sodium metabisulphite

The Figure 5.1 shows the variation of collectorless flotation behaviour of chalcopyrite with respect to pH of the pulp in nitrogen bubbling.

![Graph showing the effect of pH on chalcopyrite flotation](image.png)

Figure 5.1 Effect of pH on chalcopyrite flotation

In the Figure 5.2, the recovery of chalcopyrite and the pulp potential are presented as function of pH.
Figure 5.2 Effect of pH and pulp potential on chalcopyrite

As seen on those Figures 5.1 and 5.2, in the absence of chemical reagents, the collectorless flotation is greatest at pH 10.

The collectorless flotation is thought to occur due to surface oxidation resulting in the formation of a sulphur rich phase such as sulphur, polysulphide or an iron-deficient chalcopyrite (Gardner and Wood, 1979; Heyes and Trahar, 1977 and Luttrell and Yoon, 1984). In the present investigation, Raman spectroscopy was also used to determine surface products on floated chalcopyrite samples in the tests with no additions of chemical reagents (Appendix C). In these spectra there are two characteristic peaks. One of the peaks is between 290 and 300 cm\(^{-1}\), which is in line with the
experimentally observed Raman frequency for chalcopyrite (Mernagh and Trudu, 1993). The other peak was between 450 to 470 cm\(^{-1}\) and can be attributed to the mixed metal polysulphides on the basis of previous Raman spectroscopy studies (Mycroft et al., 1990). However, it was not possible to identify positively the specific polysulphides formed. The bands for mixed polysulphides tended to increase in intensity as the pH changed from 4 to 10. These polysulphides, which formed due to the oxidation of the surface, might be playing an important role in the collectorless flotation of chalcopyrite.

5.2.2 Effect of Na-metabisulphite on chalcopyrite floatability

![Graph showing the effect of Na-metabisulphite on chalcopyrite floatability.]

Figure 5.3 Effect of sodium metabisulphite (0.005M) on chalcopyrite collectorless flotation in nitrogen at various pH values
Figure 5.3 illustrates the influence of Na-metabisulphite ($\text{Na}_2\text{S}_2\text{O}_5$) on self-induced flotation of Chalcopyrite at various pH levels. It is clear that metabisulphite ions caused depression of chalcopyrite and was more pronounced in alkaline conditions. The average degree of depression was as follows: 2% pH 4, 6% pH 8 and 14% pH 10. Grano et al. (1997) also pointed out that sodium metabisulphite ($\text{Na}_2\text{S}_2\text{O}_5$) depressed the collectorless flotation of chalcopyrite because of the decomposition of a sulphur rich surface by adsorbed sulphite.

![Graph showing the effect of pH on Chalcopyrite recovery and pulp potential](image)

Figure 5.4 Effect of sodium metabisulphite (0.005M) on chalcopyrite collectorless flotation and pulp potential in nitrogen at various pH levels
Figure 5.4 depicts the variation of mass percent floated and pulp potential according to pH. As seen addition of sulphite decreased the pulp potential for all pH values. At pH 10 initially $E_p$ was around 112mV and as this value decreased to around 30mV floatability dropped 14%. At pH 8, although drop in the pulp potential was almost 100mV, the depression effect was found to be 6%. Similarly at pH 4, the pulp potential was 266mV and after metabisulphite introduction this value came down to 160mV. However the mass percent decrease was only 2%. This indicates that pH influence is more pronounced than that of pulp potential in metabisulphite depression.

Fairthorne et al. (1997) performed a series of experiments on chalcopyrite at pH 9.5 (75mV) in nitrogen as well as in oxygen (210mV). They reported that the degree of floatability for both conditions was almost same. The results of the present investigation might be interpreted as follows: at pulp potentials between $+20$mV to $+300$mV, pH of the pulp has a stronger impact on the floatability and depression of chalcopyrite. In plant practice, where complex ores are treated, chalcopyrite floatability will be adversely affected when metabisulphite is used to depress the other sulphides such as galena, sphalerite, and pyrite.
5.2.3 Effect of Ferric Nitrate on chalcopyrite floatability

Figure 5.5 Effect of ferric nitrate (0.005M) on chalcopyrite collectorless flotation at different pH

Figure 5.5 shows that the introduction of ferric nitrate strongly depressed the collectorless floatation of chalcopyrite. However, the effect of ferric ions on the floatability appears to be stronger than that of metabisulphite.

On the other hand, this finding can be utilised in operations of a pre-flotation separation where flotation of naturally hydrophobic gangue component is
needed before sulphide flotation. For example, sodium metabisulphite addition during milling may significantly decrease chalcopyrite flotation during pre-flotation of talc (Grano, 1997).

![Graph showing the comparison of chalcopyrite recovery with and without metabisulphite and ferric nitrate at pH 6.]

**Figure 5.6** Comparison of the effects of ferric nitrate and sodium metabisulphite on collectorless flotation at pH 6

Figure 5.6 depicts the comparative floatabilities in the presence of metabisulphite and ferric nitrate. It indicates that the relative depression power of the ferric ions is higher than that of metabisulphite. It is also apparent that the pulp potential plays important role in the collectorless floatability of chalcopyrite. An increase in pulp potential from 126.9 mV (with
sodium metabisulphite) to 249.6mV (with ferric nitrate) decreases the chalcopyrite recovery considerably, which is more than 20%.

Figure 5.7 Comparison of the effects of ferric nitrate and sodium metabisulphite on chalcopyrite collectorless flotation
Figure 5.8 Comparison of the effects of ferric nitrate and sodium metabisulphite on chalcopyrite collectorless flotation at pH 8

Grano et al. (1997) also studied the effect of ferric ions on chalcopyrite collectorless flotation. They reported that ferric nitrate depressed the flotation strongly at pH 6. They proposed that adsorption or precipitation of iron oxyhydroxide species as an overlayer on the iron deficient chalcopyrite. They argued that at pH 6 the precipitated Fe(OH)$_3$(s) might have a positive surface judging from the point of zero charge (pzc) of Fe$_2$O$_3$, which is around pH 7.2 to 8.5. They suggested that Fe(OH)$_3$(s) could potentially adsorb on a negatively charged chalcopyrite surface at pH 6 by taking the pzc point of unoxidised chalcopyrite as pH 2.2.
This findings corroborates the conclusion of Fairthorne et al. (1997) investigation. They found that freshly ground chalcopyrite conditioned in nitrogen at pH 5 and pH 9.5 has negative surface charge from pH 3 to pH 10. They also reported that freshly ground chalcopyrite conditioned in oxygen at pH 9.5 has a negative surface in the same pH range. On the other hand, aged chalcopyrite has a pzc around pH 6.

This finding is also very important in interpreting the present results. In our investigation, chalcopyrite flotation was found to be depressed to around 30% mass floated at pH values 6, 8 and 10 suggesting that the above mechanism might be valid in the present case as well. Similar depression mechanisms involving lead and zinc were suggested in chalcopyrite flotation in the literature (Senior et al., 1991).

The effect of pH of the pulp and pulp potential is illustrated in Figure 5.9 for chalcopyrite. As seen at pH 10 without any addition to the pulp chalcopyrite is floatable at pulp potentials just above 100mV and becomes depressed around 200mV at pH levels between 8 and 10.
Figure 5.9 Effect of variation in pulp potential on chalcopyrite collectorless flotation in the presence of various chemicals

5.2.4 Effect of oxygen gas purging

Figure 5.10 shows the influence of gas type on the chalcopyrite collectorless floatability at pH 10. In the presence of nitrogen, flotation recovery is about 73 percent. When oxygen was purged into the pulp at the same gas flow rate it was found that flotation recovery decreased to about 56 percent. The pulp potential was around 175mV in the presence of oxygen and around 100 mV in the presence of nitrogen. This finding is very much in agreement with the previous research work (Ekmekçi and Demirel, 1998; Fairthorne et al., 1997 and Grano et al., 1997).
Figure 5.10 Effects of oxygen and nitrogen on chalcopyrite collectorless flotation at pH 10

Fairthorne et al. (1997) found that, at pH 9.5, chalcopyrite collectorless flotation recovery was reduced about 20 percent when the flotation gas was changed to oxygen. The corresponding pulp potential values were 70mV in nitrogen and 210mV in oxygen gas. Grano et al. (1997) also experienced similar trends. They reported about 20 percent decrease in collectorless chalcopyrite flotation recovery when they used oxygen as flotation gas at pH 6. Ekmekci and Demirel (1998) reported that during flotation of chalcopyrite from a mixed sulphide ore at pH 9, recovery decreased from 70 percent to about 45 percent when the dissolved oxygen of the pulp was increased to 18 parts per million (ppm) levels. These results indicate that highly oxidising
conditions are not desirable during chalcopyrite flotation. During the present investigation, mild oxidising conditions from about 90 to around 150mV promoted the chalcopyrite floatability. Pulp potentials above 220mV considerably reduced the chalcopyrite floatability because of formation of hydrophilic species on its surface.

5.2.5 Effect of polypropylene glycol 400 (PPG 400) as a frother on chalcopyrite floatability

The effect of PPG 400 has been investigated at different pH in order to improve the collectorless flotation of chalcopyrite. The concentrations of PPG 400 have been considered. In the figure thereafter, the flotation recovery of chalcopyrite has been presented as a function of flotation time. The Figure 5.11 shows that the self-induced flotation of chalcopyrite is increased by the introduction of few drops of polypropylene glycol 400 of concentration 5 mg/ml. It is noted that an increase of chalcopyrite recovery of 14%. Trahar et al. (1997) reported some cases where the collectorless flotation of chalcopyrite was improved by the addition of this type of frother. At the same pH, the presence of frother moves the pulp potential to more oxidising condition. According to those researchers the increase of the chalcopyrite recovery was attributed to the collecting properties that polypropylene glycol 400 could have. However, they did not verify this phenomenon.
Figure 5.11 Effect of polypropylene glycol 400 on chalcopyrite flotation recovery at pH 8

Figure 5.12 Effect of pH on the collectorless flotation of chalcopyrite in the presence of 5 mg/ml of polypropylene glycol 400
As it can be seen in the Figure 5.12 that the collectorless flotation of chalcopryrite is pH dependent. Some tests were conducted in the presence of frother, polypropylene glycol 400, so that the optimum pH should be retained for the following investigations. At pH 8 the self-induced flotation of chalcopryrite is higher than at pH 10. This could be attributed to more oxidising conditions that exist in the system. It can be seen that the values of pulp potential change from 189mV to 218.75mV when the pH is decreased from 10 to 8.
5.3 RESULTS ON COLLECTORLESS FLOTATION OF GALENA

5.3.1 Effect of pH on galena floatability

![Graph showing galena recovery vs time for pH 5, 8, and 10](image)

Figure 5.13 Effect of pH on the collectorless flotation of galena, no addition

The collectorless flotation of galena is also influenced by pH changes in the pulp. It increased from about 60% at pH 6 to 72% at pH 8. After pH 8, further increases in pH of the pulp to 10 decreased the recovery to about 66 percent. It seems that pH 8 is very suitable for galena collectorless floatability. If this result is compared with chalcopyrite one could easily say that chalcopyrite
and selective separation might be possible in the absence of chemical reagents.

6.3.2 Effect of Na-metabisulphite on galena floatability

Addition of Na-metabisulphite to the flotation pulp decreased the flotation recovery of galena about 20 percent at pH 10. This value is very similar to the depression degree obtained in chalcopryite collectorless flotation where the recovery dropped from 73 percent to 59 percent. These results suggest that metabisulphite depresses galena more strongly than chalcopryite.

![Graph showing the effect of Na-metabisulphite addition on galena collectorless flotation at pH 10](image)

Figure 5.14 Effect of Na-metabisulphite addition on galena collectorless flotation at pH 10
6.3.3 Effect of Ferric Nitrate on galena floatability

As it can be seen from Figure 5.15 that galena depression reaches greater levels of about 65-70 percent at pH values between 8 and 10. This phenomenon indicates very strong adsorption or precipitation of oxy-hydroxide species on galena surface. These depression figures are higher than those of chalcopyrite flotation in the presence of ferric nitrate.

![Graph showing galena recovery over time with various additions of ferric nitrate at different pH values.](image)

**Figure 5.15** Galena collectorless flotation with ferric nitrate

Figure 5.16 shows that variations in the pulp potential affects the flotation recovery. A small increase in the pulp potential of 56mV to 94mV in the
presence of Na-metabisulphite increased the recovery about 3 percent at pH 10, which again highlights the influence of potential of the pulp in galena collectorless flotation.

![Graph showing galena recovery percentage](image)

**Figure 5.16** Effect of variation in pulp potential on galena collectorless flotation in the presence of Na-metabisulphite

An increase in the pulp potential from 75mV in the presence of Na-metabisulphite to about 105mV in the absence of reducing and oxidising reagents promotes the self-induced flotation of galena from 50 percent to 68 percent at pH 10 (Figure 5.14). These results suggest that initial oxidation of the galena surface above 50mV leads to development of a metal deficient sulphide layer or elemental sulphur, which are responsible for the self-
induced floatability in alkaline conditions. Buckley and Woods (1984) and Buckley et al., (1985) discussed this point. Further increase in pulp potential decreases the floatability. This could be due to the formation of hydrophilic species at pulp potentials above 125mV. Labonté et al. (1989) also reported that when the pulp potential increased from 56mV to 60mV their lead recovery from a complex sulphide ore also increased about 15 percent.

Figure 5.17 Effect of various chemical reagents and corresponding pulp potentials on galena collectorless flotation at pH 10
5.3.4 Effect of Ethylene Diamine Tetra-acetic Acetic (EDTA) on galena floatability

5.3.4.1 Effect of pH on galena floatability in the presence of Ethylene Diamine Tetra-acetic Acetic

EDTA, as a complexing agent, has been used to determine its influence on the collectorless flotation of galena.

![Graph showing the effect of pH on galena floatability](image)

Figure 5.18 Effect of pH on galena collectorless flotation in the presence of 0.0005M EDTA
Wang and Forssberg (1989) argued that at pH 8.5 the collectorless floatability of galena first increased with increasing EDTA concentrations. Above $10^{-3}$M the floatability was decreased significantly about 35 percent. They also stated that no flotation was observed in the absence of EDTA and reported no reason for this anomaly. This is quite contradictory to the experimental observations in the present case in which galena self-induced floatability was about 60 to 65 percent in the pH range between 6 to 10. In the presence 0.0005M EDTA (Figure 5.18), collectorless floatability decreased to about 35 percent as the pH of the pulp increased from 6 to 10.

![Graph showing the effect of ferric nitrate and EDTA on galena flotation at pH 8.](image)

Figure 5.19 Effect of ferric nitrate and EDTA on galena flotation at pH 8.
Neither ferric nitrate nor ethylene diamine tetra-acetic acid at the same concentration in the pulp activates collectorless flotation of galena. At the pH of investigation, both, depressed galena flotation. The collectorless flotation of galena is more dependent upon the pulp potential, which somehow reflects the surface transformation. The nature of chemical reagents could also have a major impact on the process. Leroux\textsuperscript{[16]} attributed the decrease of self-induced floatability to the formation of hydrophilic species on the mineral surface at high potential as it can be seen on the Pourbaix diagram for galena (Figure 3.1).

![Graph showing the effect of ferric nitrate, sodium metabisulphite and EDTA on galena collectorless flotation at pH 10](image)

Figure 5.20 Effect of ferric nitrate, sodium metabisulphite and EDTA on galena collectorless flotation at pH 10
Figure 5.20 illustrates the comparative influences of various chemical reagents on galena collectorless flotation. It clearly indicates the adverse effects of metabisulphite, EDTA and ferric nitrate on the floatability. Ferric nitrate depresses galena more effectively than chalcopyrite. This is almost a complete depression to mechanical entrapment level that is less than 5 percent.

5.3.4.2 Effect of EDTA concentration on galena collectorless flotation

The effect of ethylene diamine tetra-acetic acid (EDTA) concentration as a complexing agent have been also investigated because according to previous results found by others researchers, there are controversies among them as so far as the concentration of this reagent is concerned. In the following figures, the flotation recovery has been presented versus flotation time for different pH and EDTA concentration.
Figure 5.21 Effect of EDTA concentration on galena flotation at pH 8

Figure 5.22 Effect of EDTA concentration on galena flotation at pH 10.
Figure 5.23 Effect of pH on galena flotation in the presence of [EDTA] = 0.0005 M.

The previous three Figures 21 and 22 show the effect of EDTA concentration on the self-induced flotation of galena. In these figures, at both pH 8 and 10, the increase of the EDTA concentration from 0.0005M to 0.005M has an undesirable impact on the collectorless flotation response of galena. The present results have confirmed those obtained by Forssberg and Wang (1989) who stated that an increase of EDTA concentration above 0.001M decreased the self-induced floatability of galena. However an attempt to increase the concentration of this chemical above 0.001M resulted in more depression of galena at all pH's investigated. Their optimum flotation recovery for galena was 80%. The discrepancy could be due to the purity of the minerals used during their investigation, the sample preparation prior to
flotation tests or to the chemical reagents. Another point that could explain the discrepancies between Forssberg et al.'s results (1989) and the results of the present work could be the type and concentration of frothers used in these investigations. They used methyl isobuyl carbinol (MIBC) instead of polypropylene glycol 400 that has been used in the present work. The decrease of pulp potential could be also considered as one of the causes to this decrease of galena flotation recovery. At the same concentration of EDTA in the presence of nitrogen, an increase of pH decreases the galena recovery. So the collectorless flotation of galena in the presence of EDTA as a complexant agent depends upon the pH and also the pulp potential that exists in the system as it can be seen from the Figures 5.21, 5.22 and 5.23.

5.3.5 Effect of gas purging on galena floatability in the presence of EDTA

In the course of this work, tests have been carried out to investigate the impacts of flotation gas, oxygen and nitrogen, on galena collectorless flotation in the presence of ethylene diamine tetra-acetic acid as a complexing agent. Oxygen has been also used as oxidising agent while nitrogen was used to exclude the effect of oxygen by creating reducing environment.
Figure 5.24 Effect of 0.0005 M of EDTA on Galena flotation at pH 8 in the presence of oxygen and nitrogen.

From the results represented in Figure 5.24, it can be said that the type of gas used in the flotation process also seems to play an important role for the galena. In the presence of EDTA as a complexing agent, galena floats better by using oxygen than nitrogen.
Figure 5.25 Effect of pH on Galena flotation in the presence of 0.0005 M of EDTA and oxygen

In the presence of EDTA, the self-induced floatability of galena, by using oxygen as a flotation gas, is increased by increasing the pH while the concentration of EDTA is kept constant in all tests. Those results have been found by Forssberg et al. (1989) who asserted that between pH 6 and 10 the collectorless flotation of galena in oxygen was dependent upon the pH and the concentration of EDTA. At the same concentration of EDTA in the pulp, the collectorless flotation of galena increased with increasing pH. It was found that galena floatability increased as the pulp potential increased.
5.3.6 Effect of polypropylene glycol 400 (PPG 400) on galena self-induced flotation.

Polypropylene glycol of average molecular weight 400 has been used in the flotation of sulphide minerals in alkaline conditions. Trahar et al., (1977) used this type of frother in their study on the natural floatability of chalcopyrite. They found out that, at pH 11, the collectorless flotation of chalcopyrite was improved by the presence of polypropylene glycol 400 in the slurry. Among a number of frothers tested by Lepetic (1974), polypropylene glycol methyl ether 200 was found to be the most powerful in increasing the recovery of sulphide minerals, such as chalcopyrite, than other frothers like pine oil and cresylic acid. No explanation for this effect was given. It is possible that this frother decreases the attachment time between bubble and sulphide minerals giving rise to higher floatability.

5.4.6.1 Effect of pH on galena collectorless flotation in the presence of polypropylene concentration

From Figures 26 and 29, it can be seen that polypropylene glycol really improves the collectorless flotation of galena at pH 8 and 10. In both cases, an increase in flotation recovery of about more than 10% was obtained after four minutes of flotation. The conditioning time was fixed at 20 minutes.
Figure 5.26 Galena flotation in the presence of 5mg/ml polypropylene glycol 400 at pH 8

Figure 5.27 Galena flotation in the presence of 5mg/ml polypropylene glycol 400 at pH 10
Figure 5.28 Galena flotation in the presence of 10mg/ml polypropylene glycol 400 at pH 8

Figure 5.29 Galena flotation in the presence of 10mg/ml of polypropylene glycol 400 at pH 10
5.4.6.2 Effect of polypropylene concentration on galena collectorless flotation

In the following figures, the galena flotation recovery has been expressed as a function of flotation time at different concentrations of polypropylene glycol 400. For all the tests done in the presence of frother, the conditioning time has been fixed at 20 minutes before starting flotation tests, except where the effect of conditioning time has been investigated.

Figure 5.30 Effect of PPG 400 concentration on Galena flotation at pH 8
Figure 5.31 Effect of PPG 400 concentration on Galena flotation at pH 10

The collectorless flotation of galena increases by increasing the concentration of frother, PPG 400. This may be due to a decrease of bubble size by the polypropylene glycol, which is lowering the surface tension and the induction time.

5.4.6.3 Effect of conditioning time on the galena flotation in the presence of frother.

In order to determine the effect of conditioning time on the collectorless flotation of Galena, some tests were conducted in the presence of polypropylene glycol 400 (PPG 400) as a frother at different pH and time.
Figure 5.32 Effect of conditioning time on Galena flotation in the presence of 5 mg/ml of PPG 400 at pH 8

From the Figures 30 to 32, it is clear that both the concentration of PPG 400 and the conditioning time have an impact on the floatability of the galena. The galena self-induced flotation response to an increase of PPG 400 concentration was favourable below 10mg/ml of PPG400 depending upon the conditioning time. This means that neither the frother concentration nor the conditioning time could be increased indefinitely without the recovery being affected negatively. More frother means, changing the hydrodynamics in the flotation cell and therefore the overflow. Lepetic (1974) investigated the impact of various types of frothers (pine oil, cresylic acid, methyl amyl alcohol) on the collectorless flotation of chalcopyrite and the test results
demonstrated that polypropylene glycol methyl ether with average molecular weights of 200 provided the highest cumulative copper recovery (90.0%) of all frothers tested. Pine oil and cresilic acid, which are considered having some collecting properties, could not produce copper recovery higher than 80.7% and 76.5% respectively. As far as chalcopyrite is concerned Lepetic’s results are much higher than what has been found in this work. At pH 8, for example chalcopyrite recovery was around 80 % as compared to 88 % from this investigation.

Results from the present investigation have shown that polypropylene glycol with an average molecular weight of 400 improves considerably the collectorless flotation of galena to about 87%, which is approximately in the same range as that obtained by Lepetic for chalcopyrite.

The galena flotation recovery depends on the concentration of the frother but also the time for conditioning the mineral before flotation takes place. More time may result in mechanical entrapment.

A maximum conditioning time of ten minutes for the frother with the concentration of 5mg/ml would be reasonable instead of increasing the concentration of this reagent in order to reach high galena flotation recovery.
The Figure 5.32 shows that after twenty minutes of conditioning with 5mg/ml of polypropylene glycol 400, galena flotability decreases.
5.4 COMPARISON OF THE COLLECTORLESS FLOTATION OF CHALCOPYRITE AND GALENA

This section deals with the collectorless flotation of individual selected mineral such as chalcopyrite and galena at different pH and in the presence of oxidising and reducing agents. Collectorless flotation results of these two sulphide minerals have been compared from Figure 5.33 to 5.40.

![Graph comparing flotation recovery of chalcopyrite and galena at pH 8, no addition](image)

Figure 5.33 Comparison of flotation recovery of chalcopyrite and galena at pH 8, no addition

At pH 8, galena shows better floatability than chalcopyrite. The difference of pulp potential is considerable and this could explain the difference in self-induced flotation that has been observed.
A review of Figure 3.1 relating to the Pourbaix diagram for galena reveals that galena is thermodynamically stable in a wide range of pH and pulp potential depending upon the activities of different species involved in the flotation process. The pH, activities of species present in the medium and pulp potentials are not independent. If the concentrations of different species dissolved in the pulp are kept constant at $10^{-4}$ M, an increase of pH implies a decrease of pulp potential so that the working conditions should be set in the galena stability region. Nevertheless, mild oxidising conditions leading to the formation of hydrophobic substances on galena surface should be more favourable for its collectorless flotation.

![Graph](image)

Figure 5.34 Comparison of flotation recovery of chalcopyrite and galena at pH 10, no addition
For chalcopyrite, the situation is quite complex because of the formation of insoluble and hydrophilic copper or iron oxide compounds, which can hinder its collectorless flotation if these are not removed from the mineral surface.

Figure 5.35 Comparison of the flotation recovery of chalcopyrite and galena in the presence of ferric nitrate at pH 8

Figure 5.35 shows that, at pH 8, galena is more depressed by ferric nitrate than chalcopyrite although the difference of pulp potential is almost 24mV. At this pH, 40% of chalcopyrite has been recovered compare to 5% for galena.
Figure 5.36. Comparison of flotation recovery of chalcopyrite and galena in the presence of ferric nitrate at pH 10.

Figure 5.36 highlights that galena is more depressed than chalcopyrite at pH 10 when in the presence of ferric nitrate (0.0005M). The pulp potential is nearly the same at this pH. This is important because it seems that the pulp potential plays an important role in the separation of the two minerals. However, the physico-chemical behaviours of each mineral and the interactions between them should be taken into account for better selective separation.
Figure 5.37 Comparison of flotation recovery of chalcopyrite and galena in the presence of sodium metabisulphite (0.005M) at pH 10.

From Figure 5.37, it can be seen that although chalcopyrite recovery is slightly higher than that of galena, the depressant effect of sodium metabisulphite is on both minerals and is not selective enough to effect a separation. Ralston and Prestidge (1996) investigating on the contact angle of particulate sulphide minerals by using different chemical reagents found also that sodium metabisulphite and iron oxide depressed galena by reducing the hydrophobicity significantly. The effect of iron oxide is more marked at pH 4 rather than at pH 10.
Figure 5.38 Comparison of the collectorless flotation of chalcopyrite and galena in the presence of 5 mg/ml of PPG 400 at pH 8.

From Figure 5.38, it can be said that the collectorless flotation of sulphide minerals in the presence of frother like PPG 400 depends upon the mineral and the pulp potential. At pH 8, galena floats better at low pulp potential than chalcopyrite. The introduction of polypropylene glycol 400 (frother) in the microflotation cell increases chalcopyrite flotation recovery from 66% to 80%. Galena floatability is improved from 73% to 88% by the presence of polypropylene glycol 400.
Figure 5.39 Effect of ferric nitrate on chalcopyrite and galena collectorless flotation at pH 8

Figure 5.39 depicts the effect of ferric nitrate on both galena and chalcopyrite collectorless flotation behaviour. At pH 8 with the addition of ferric ions to the system, galena become totally depressed while chalcopyrite remains floatable up to 40 percent. This effect seems to be usable in the flotation of galena-chalcopyrite mixtures that by decreasing ferric concentrations chalcopyrite floatability can be increased up to 60 percent while at the same time galena floatability will stay around the mechanical entrapment levels of 6 to 10 percent. This feature can be effectively used in selective flotation.
Figure C8 in the Appendix C shows that the selective amounts of these sulphide substances increase as the pH increases.
circuits where chalcopyrite galena separations are crucial without resorting to cyanide depression.

Figure 5.40 Effect of pulp pH and potential on chalcopyrite and galena collectorless flotation

The Figure 5.40 summarises the effect of pH and pulp potential on the self-induced floatation of chalcopyrite and galena. It is clear that both, pH and pulp potential affect the flotation response of chalcopyrite and galena due to the modification of the chemical environment in which the process takes place. This modification might reflect the transformation that happened on the mineral surface. The Raman spectroscopy for chalcopyrite has confirmed the presence of metallic sulphide compounds on its surface at pH 8 and 10. The
6. GENERAL CONCLUSIONS

The present experimental work on collectorless flotation of chalcopyrite and galena revealed the following points:

Chalcopyrite exhibited significant collectorless flotation at pH values between 8 and 10. At pH 10 and pulp potentials between +100mV and +120mV, floatability reached highest level around 73 percent. Raman spectroscopy used to determine surface products on floated chalcopyrite has revealed, in addition to the presence of chalcopyrite on the first peak (290cm⁻¹ - 300cm⁻¹), mixed metal polysulphides on the second peak situated between 450cm⁻¹ and 470cm⁻¹ (Appendix C). These polysulphides, which formed due to the oxidation of the surface, might be playing an important role in the collectorless flotation of chalcopyrite. The use of an oxidising agent such as ferric nitrate, which increases the pulp potential and a reducing agent, sodium metabisulphite which decreases the pulp potential to more reducing values, depressed the flotation significantly. The flotation recovery of chalcopyrite was 73 % when nitrogen was purged as compared to 66 % recovery obtained with Oxygen purging. Polypropylene glycol introduced in the flotation process as a frother improved the collectorless flotation of chalcopyrite. An increase of flotation recovery of chalcopyrite of 14% has been observed during this investigation.
Galena showed good floatability about 72 percent at pH 8 and pulp potentials between +190mV and +230mV. At pH 8, addition of ferric nitrate depressed the flotation of galena to around 3 percent. Galena was found to be more sensitive to pulp potential and pH modifications by the use of chemical reagents. At both pH 8 and 10 the variation of EDTA concentration from 0.0005M to 0.005M caused depression of galena. The self-induced floatability of galena has been satisfactorily improved by the introduction of polypropylene glycol 400. In both cases, an increase in flotation recovery of about more than 10% was obtained after four minutes of flotation.

According to the pH of the pulp, the collectorless flotation of chalcopyrite was favourable at pH 10 while galena exhibits good floatability at pH 8.

From above findings, it can be concluded that ferric and metabisulphite ions may be utilised for pulp modifications to separate chalcopyrite and galena from each other selectively. This option is safer than the use of cyanide which is dangerous when the pH is lower than 10.5 because of evolution of hydrocyanic acid (HCN). These results are also applicable to pre-flotation separations where value bearing sulphide minerals are depressed prior to their selective separations from talc.
7. REFERENCES


Goodal, C.M., 1990, Bubble sizing system, Mintek, Randburg, South-Africa.


APPENDICES

In the following, some reproducibility results for chalcopyrite and galena and Raman Spectra of oxidation products of the chalcopyrite from flotation experiments are presented.

Appendix A. Tests of reproducibility of chalcopyrite collectorless flotation.

In this section, some of the figures have been re-plotted in order to illustrate the reproducibility of the experiments during the investigation.

![Graph showing reproducibility of flotation recovery of chalcopyrite at pH 4, no addition.](image)

Figure A1 Reproducibility of flotation recovery of chalcopyrite at pH 4, no addition.
Figure A2 Reproducibility of flotation recovery of chalcopryite at pH 8, no addition.

Figure A3 Reproducibility of flotation recovery of chalcopryite at pH 10, no addition.
Figure A4 Reproducibility of self-induced flotation of chalcopyrite at pH 10 in the presence of oxygen.

Figure A5 Reproducibility of flotation recovery of chalcopyrite in the presence of sodium metabisulphite at pH 4.
Figure A6 Reproducibility of flotation recovery of chalcopyrite in the presence of ferric nitrate at pH=8.
Appendix B. Tests of reproducibility of galena collectorless flotation.

Figure B1 Reproducibility flotation recovery of galena at pH 6, no addition.

Figure B2 Reproducibility of flotation recovery of galena at pH 8, no addition.
Figure B3 Reproducibility of flotation recovery of galena in the presence of ethylene diamine tetra-acetic acid (EDTA) at pH 6.

Figure B4 Reproducibility of flotation recovery of galena in the presence of ethylene diamine tetra-acetic acid (EDTA) at pH 8.
As indicated from the Figures A1 to B4 above, a number of charts have been plotted to illustrate the reproducibility of flotation tests. During this work, each test was run at least three times and only close results have been considered. The reproducibility of these results is satisfactory since the limit of error estimated by statistical methods was less than 5%.

Appendix C. Raman Spectra of oxidation products of the chalcopyrite from flotation experiments

![Graph of Raman Spectra](image)

C1 Raman spectra of unfloated chalcopyrite at pH 8.

The peak around 290-300 cm\(^{-1}\) correspond to pure chalcopyrite
C2 Raman spectra of pure chalcopyrite ground in water

C3 Raman spectra of floated chalcopyrite at pH 6, after 8 minutes of flotation
C4 Raman spectra of floated chalcopyrite after 8 minutes flotation at pH 8

C5 Raman spectra of floated chalcopyrite at pH 10 after 8 minutes of flotation.

The peak around 450-470cm⁻¹ reveals the presence of polysulphide
The first peak corresponds to chalcopyrite while the second reveals the presence of polysulphide on the mineral surface.

C8 Raman spectra of floated chalcopyrite at different pH after 8 minutes of flotation.

The intensity of the peaks goes up as the pH increases.