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Some aspects of the electrochemistry of the flotation of pyrrhotite

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Abstract

The iron sulfide mineral, pyrrhotite ($Fe_{(1-x)}S$), has long been known to be more difficult to recover by flotation from alkaline slurries than many other base metal sulfide minerals. This paper summarizes the results of an electrochemical study of the surface reactions that occur during the flotation of nickeliferous pyrrhotite in the recovery of nickel and the platinum group metals. Mixed potential measurements conducted with natural pyrrhotite electrodes in various stages of an operating flotation plant showed that the mineral potential is positive to the equilibrium potential of the xanthate/dixanthogen couple. Similar results were obtained during batch flotation experiments and in synthetic solutions in the laboratory. Cyclic voltammetric and potentiostatic current/time transient experiments were used to investigate the oxidation of pyrrhotite under various conditions. In addition, the reduction of oxygen, the reaction of copper ions and the oxidation of xanthate ions at the mineral surface were investigated. The formation of dixanthogen on pyrrhotite surfaces is thermodynamically favourable in plant flotation slurries. However the interaction with xanthate at pH values above 7 is inhibited by a surface species formed during the conditioning prior to xanthate addition. In acidic solutions copper ions react readily with pyrrhotite to form a species, possibly CuS that can be oxidized at potentials above 0.4 V. At pH 9 this species does not form and there is no electrochemical reaction between pyrrhotite and copper ions. The beneficial effects of copper ions to flotation performance appear to be related to an enhancement of the oxidation of xanthate.

1. Introduction

There are a number of industrial operations where the recovery of nickel (and cobalt) and the platinum group metals by flotation is important. A specific example of this is the Bushveld igneous complex in South Africa which is exploited on a large scale for these metals. These deposits typically have a combined sulfide grade of less than 1% making efficient beneficiation of the ore to a flotation concentrate a prerequisite. Chalcopyrite, pyrite, pentlandite and pyrrhotite are the major sulfide minerals, which are recovered. Pyrrhotite is recognised as the most difficult to efficiently float especially as fine particles and is generally termed 'slow floating'.

Xanthate compounds are widely used as collectors in flotation. Their function is to render the mineral surface hydrophobic and thus facilitate bubble attachment. The adsorption of xanthates onto sulfide minerals occurs via an electrochemical mechanism involving the reduction of oxygen and the anodic adsorption of xanthate [1]. In a process termed 'copper activation', copper ions are added in order to promote the adsorption of xanthate onto some minerals such as sphalerite and pyrrhotite. The mineral particles are extensively exposed to aqueous environments prior to reaction with reagents and as such oxidation of the mineral surface will occur. The nature and extent of the surface oxidation plays an important role in understanding the subsequent reaction with reagents.

The oxidation of pyrrhotite in alkaline media is considered to result in a sulfur rich surface covered with ferric hydroxide [2, 3]. It has been difficult to identify the exact form of the sulfur on the surface of the oxidized mineral. In acidic conditions, the formation of sulfate is less favoured than in alkaline conditions, with the result that surfaces are likely to be more sulfur rich under acidic conditions.

Pyrrhotite is a poor catalyst for oxygen reduction as compared to other sulfide minerals [4]. This may, in part, explain the slow floating characteristics of this mineral. Attempts to correlate the oxygen reduction kinetics of sulfide minerals with their semiconducting properties have not been successful [5, 6]. Nevertheless, it is possible that the stoichiometry and level of impurities within the mineral plays an important role in defining the kinetics of oxygen reduction.

The dominant surface product on pyrrhotite from interaction with xanthate at pH 9 has been identified as dixanthogen [8–10]. There are, however, reports of metal xanthate being detected in addition to dixanthogen depending on conditions [7, 11]. Although a certain degree of oxidation appears necessary for xanthate adsorption, it is clear that heavily oxidized particles are not readily floated due to the hydrophilic nature of the iron oxide surfaces.

The role and effectiveness of copper ions for the activation of pyrrhotite under alkaline conditions is not fully understood. Fundamental work appears to indicate that copper activation is not possible at pH 9 [12]. The explanation for this may be that copper ions are essentially insoluble at pH values above about 8 and thus may not be available for reaction with the surface of the mineral. Furthermore, pyrrhotite particles are likely to be well oxidized and covered with iron hydroxides, which may inhibit any reaction with the underlying mineral surface. However, recent studies [13–15], have shown that pyrrhotite recoveries are significantly improved when copper ions are present. Copper has been detected on concentrate particles from actual flotation circuits operating at pH 9 [11, 16], thus suggesting that pyrrhotite was effectively activated.

The aim of this study was to develop an understanding of the flotation of pyrrhotite by using electrochemical techniques to investigate surface composition and reactions. The reactions of dissolved copper sulfate and sodium isobutylxanthate with the mineral were studied because of their specific industrial use in the platinum industry for the flotation of sulfides.

2. Experimental details

Table 1 details the natural pyrrhotite samples used in this study. Unfortunately, relatively pure, massive samples cannot be obtained from the Bushveld mining operations. No significant electrochemical differences between the samples were observed. X-ray diffraction analysis showed the presence of peaks which could only be attributed to hexagonal pyrrhotite.

Roughly cubic mineral pieces were cut from the massive samples. Stationary electrodes were made by plating copper onto one end of the mineral piece, soldering a lead to the copper plating and encasing the piece in epoxy resin within a plastic tube. To measure the rest potentials of these electrodes in the plant, these tubes were sealed into specially designed PVC pipes of about 2 m in length. A platinum and silver chloride reference probe were also similarly fabricated. Rotating electrodes were made by encasing the copper-plated mineral piece in a specially shaped PTFE cylinder. Sodium isobutylxanthate was supplied by Sentrachem, South Africa and was used as received. All other reagents were analytical grade. All solutions were made up in distilled water. Potentials were measured using a silver|silver chloride reference electrode and are reported against the standard hydrogen electrode. A potentiostat and sweep generator manufactured by Mintek, South Africa, were used to perform the cyclic voltammetry in a standard three-electrode cell. The current–potential output was recorded on an X–Y recorder. A rotating shaft controlled by a stepping motor was used to perform the rotating disc experiments.

Linear sweep voltammetric experiments were conducted at 25 °C. Solutions were deoxygenated by sparging with high purity nitrogen. In certain experiments oxygen was sparged into solutions. Experiments were conducted in 0.1 M Na_2SO_4 or 0.05 M $Na_2B_4O_7$ solutions. Sodium sulfate solutions were used as they more closely resemble the composition of plant solutions and the pH was adjusted through small additions of concentrated sodium hydroxide or sulfuric acid. Sweeps were commenced from the rest potential unless otherwise indicated. For experiments in which the effects of copper ions were investigated, the electrodes were exposed to copper ions in separate solutions and then transferred to copper free solutions for the voltammetry. This was done to avoid reaction of the copper ions with the mineral during the cathodic sweeps.

Electrode surfaces were ground on 200 grit emery paper and washed with distilled water prior to being immersed into the laboratory solutions or plant slurries. In the case of measurements conducted during a series of laboratory batch flotation experiments one electrode was resurfaced at the beginning of the experiment and then left in the slurry for the entire experiment, while the surface of another electrode was renewed after each stage of the flotation experiment. All measurements were made at ambient temperature. The potential was allowed to stabilise for approximately one minute before recording.

3. Results

3.1. *Rest potentials*

Table 2 presents the results of rest potential measurements made using both pyrrhotite and platinum electrodes in plant slurries at various points throughout a flotation circuit at a South African platinum concentrator, a simplified diagram of which is shown in Figure 1.

Rest potential measurements conducted during laboratory batch flotation experiments are presented in

Table 1. Pyrrhotite samples (elemental composition by SEM/EDAX spot analysis)

Code	Description	Origin	Source	Major elements	Trace elements
A	Pure pyrrhotite (massive)	Unknown	Ward's Natural Science	Fe, S	Al, Si, P, K, Ni, Cu
B	Pyrrhotite (massive)	Unknown	RSA mineral dealer	Fe, S	Not measured

Table 2. Potentials of pyrrhotite and platinum electrodes measured at various point in a flotation plant operating at pH 9. At the time of measurement, copper sulfate was added in the surge tank while SIBX, Saskol 95, Acrol IMP4 and Senfroth were added in conditioning tank 1

Electrode	Potential/ V						
	Cyc. O/F	Surge	Cond. 1	Cond. 2	Bank 1	Bank 2	Bank 3
Pyrrhotite	0.223	0.194	0.160	0.147	0.156	0.156	0.150
Platinum	0.293	0.284	0.207	0.267	0.200	- - - -	0.229

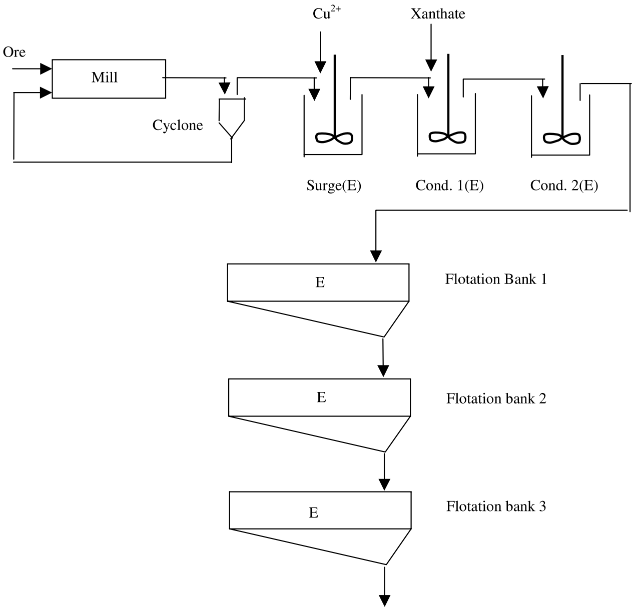

Fig. 1. Configuration of the flotation plant at which potential measurements were taken at the points designated E.

Figure 2. The potential of the electrode whose surface was reground at each stage addition is about 0.05 V lower than that of the electrode that remained in the slurry for xanthate addition.

The equilibrium potential of the xanthate/dixanthogen couple was measured by partially oxidizing dissolved xanthate to dixanthogen on a platinum electrode and then open circuiting the platinum electrode. The potential stabilized within a minute after open circuiting. The standard equilibrium potential was calculated from this data using the Nernst equation and the value of −0.128 V was obtained which is the same as reported by Winter and Woods [17].

3.2. *Cyclic voltammetry*

3.2.1. *Oxidation of the mineral*

The oxidation of pyrrhotite in the absence of collector or activator was investigated in an attempt to establish the nature of the mineral surface prior to reaction with flotation reagents.

Figure 3 shows the cyclic voltammogram for a pyrrhotite electrode in a deaerated borate solution. There are no obvious peaks associated with cathodic reactions on the first sweep in a negative-going direction from the rest potential. On the return positive-going sweep there is a small anodic current plateau from 0.2 to 0.5 V (a_1). Above 0.5 V the anodic current increases reaching a plateau at 0.7 V (a_2). Subsequent cycling results in cathodic reactions at about −0.4 V (c_1) and at −0.55 V (c_2), and anodic reactions at −0.05 V (a_3) and 0.1 V (a_4). Peaks c_2 and a_4 increase with additional cycling and

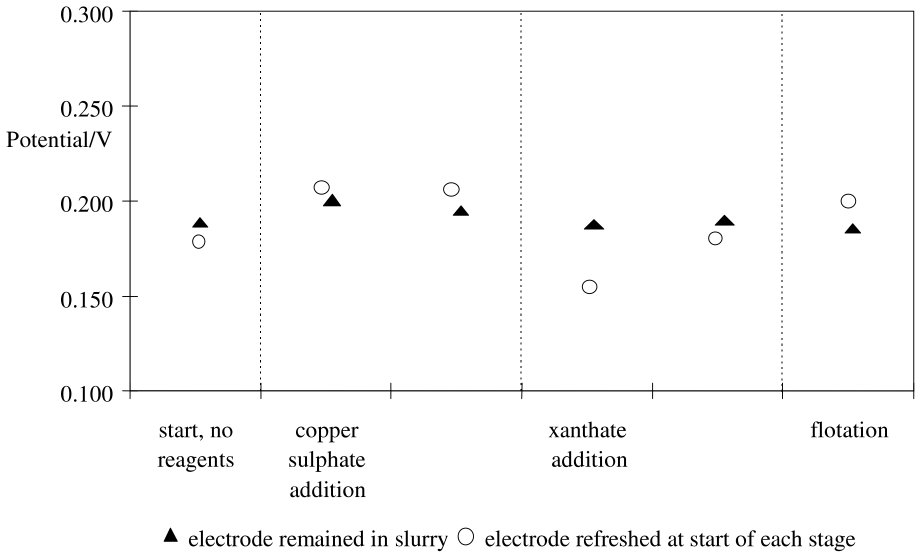

Fig. 2. Pyrrhotite mixed potentials measured during a batch flotation experiment conducted with an electrode that was kept in the slurry throughout the experiment and with an electrode that was resurfaced before each reagent addition (copper sulfate and sodium isobutylxanthate).

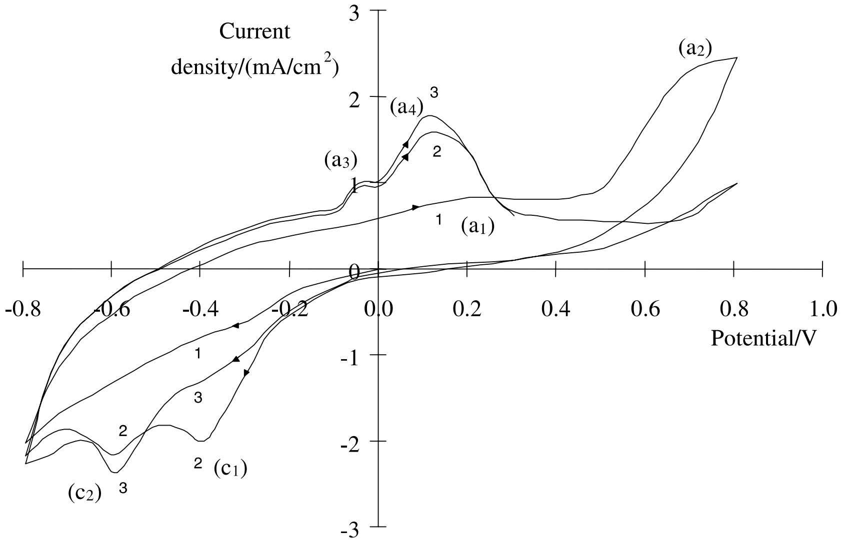

Fig. 3. Cyclic voltammogram for a stationary pyrrhotite electrode in deoxygenated 0.05 M $Na_2B_4O_7$ (pH 9.3) with a sweep rate of 20 mV s^{-1} (numbers represent sweep number and letters in parenthesis identify reactions).

appear to be the reverse of each other. Peak a_2 was significantly smaller on subsequent cycling. Rotating electrodes gave the same results as stationary electrodes indicating that all products are insoluble or are electrochemically inactive within the potential range investigated.

Figure 4 shows the corresponding cyclic voltammogram generated in sodium sulfate solutions. Unlike the case of borate solutions shown in Figure 3, peak a_2 was not significantly diminished on subsequent cycling. The cathodic peak c_1 occurs at more negative potentials while there is no anodic reaction at −0.05 V (reaction a_3 in Figure 3).

Potential measurements of pyrrhotite electrodes carried out in plant slurries indicated that the mineral is exposed to potentials in the region of 0.2 to 0.3 V prior to flotation. A freshly polished electrode was held at a potential of 0.3 V for 2 min in a borate solution after which the potential was scanned in the negative direction. The reactivity of the electrode was considerably reduced and a small cathodic peak observed at −0.3 V and it is considered that this may be due to reaction c_1. A similar response was observed for an electrode which had been held for 5 min under open circuit (~0.26 V) in an oxygen saturated borate solution. Therefore potentials similar to those measured in plant slurries result in an oxidation product that can be reduced during the negative-going sweep.

3.2.2. *Reaction with copper ions*

Voltammograms obtained after exposure to copper ions in sodium sulfate solutions at varying pH are shown in Figure 5. An anodic peak (a_5) occurs at 0.5 V and a smaller cathodic peak (c_3) at 0.3 V. It should be noted

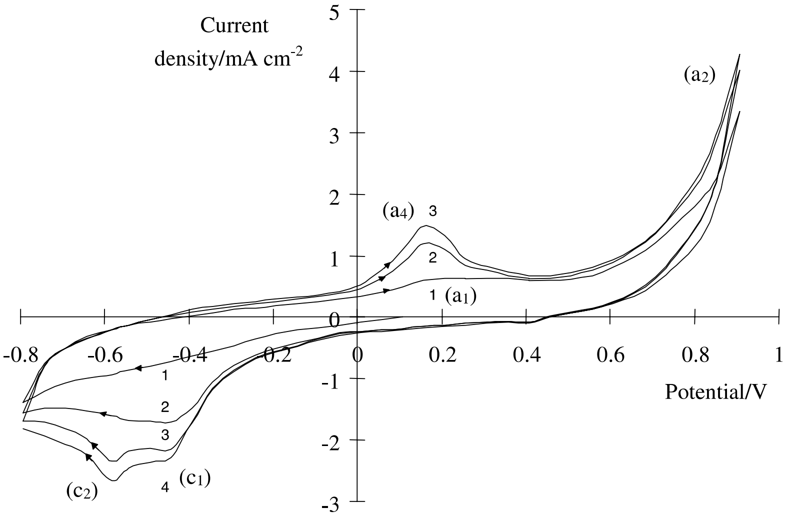

Fig. 4. Cyclic voltammogram for a rotating (500 rpm) pyrrhotite electrode in deoxygenated 0.1 M Na_2SO_4 (pH 9.2) with a sweep rate of 20 mV s^{-1}.

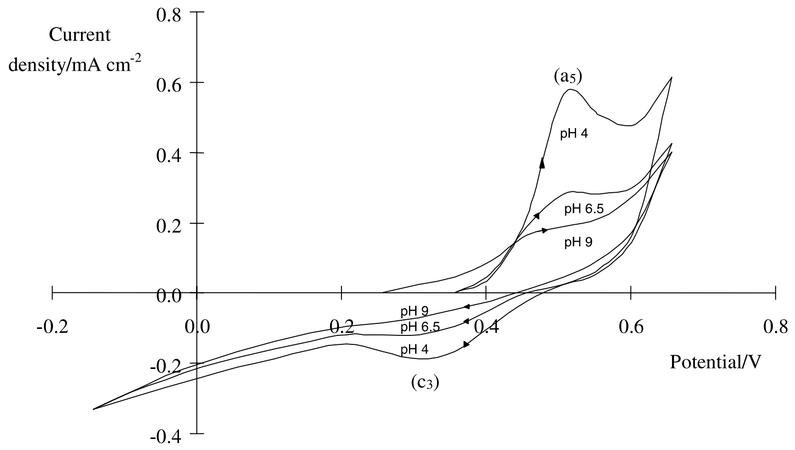

Fig. 5. Current–potential curves for stationary pyrrhotite electrode conditioned for 5 min in 0.1 M Na_2SO_4 (pH 4, 6.5 and 9) at open circuit, followed by the addition of 10^{-4} M Cu^{2+} and 5 min conditioning, with a sweep rate of 10 mV s^{-1}.

that the pH indicated was the pH before the addition of copper ions to the solution. On addition of copper ions the pH decreased and, especially in the case of the solution of pH 9, the actual pH was probably lower than 7. On cycling of a stationary electrode after exposure to copper ions both peaks a_5 and c_3 are significantly reduced in size in the second and subsequent cycles. In all cases, Reaction c_3 has considerably less charge associated with it than Reaction a_5 which is consistent with Reaction a_5 producing soluble products which diffuse away from the electrode surface thus diminishing the reaction c_3. This was confirmed by holding the potential positive whilst stirring the solution. The stirring would ensure that all soluble products from Reaction a_5 are removed from the electrode surface into the bulk solution and this was observed by the disappearance of peak c_3 in the subsequent sweep. The anodic peak at 0.5 V is therefore characteristic of a reaction between pyrrhotite and copper ions and this reaction was not observed in buffered alkaline solutions. The characteristic peak at 0.5 V was, however, observed if the electrode was exposed to copper ions in acidic solutions and subsequently transferred to buffered alkaline solutions for voltammetry.

3.2.3. *Reduction of oxygen*

The reduction of oxygen on the mineral surface is an important step in the adsorption of xanthate. Since copper ions are used extensively to enhance the flotation of pyrrhotite the effect of exposing pyrrhotite to copper ions in acidic solutions on oxygen reduction in alkaline solutions was investigated. Due to the fact that cyclic voltammograms obtained in the presence and absence of copper ions showed very little difference when dissolved oxygen was present it was decided to make pseudo steady-state measurements of the currents due to oxygen reduction before and after addition of copper ions. Table 3 summarizes the results of these experiments. Exposure to copper ions did not significantly affect the kinetics of oxygen reduction.

Table 3. Currents due to oxygen reduction on a pyrrhotite electrode in a solution of 0.05 M $Na_2B_4O_7$

Potential \V	No exposure to Cu^{2+}		Exposure to Cu^{2+}	
	Mean current density /μA cm^{-2}	Std dev /%	Mean current density /μA cm^{-2}	Std dev /%
0.107	42.7	11	38.0	14
0.157	20.3	9	20.3	5

3.2.4. *Oxidation of xanthate*

The presence of isobutylxanthate during positive-going sweeps resulted in enhanced anodic currents (a_6) above ~0.1 V in both sodium sulfate and borate solutions (Figure 6). The enhanced anodic currents were less visible at a higher sweep rate of 10 mV s^{-1}. At lower concentrations of xanthate than that used in Figure 6 no obvious enhanced anodic currents were detected. No anodic reactions due to xanthate were detected below 0.1 V that could correspond to the chemisorption of xanthate. Experiments were conducted in which the potential sweep was reversed after a positive potential limit of 0.4 V. However no cathodic reaction associated with the enhanced anodic currents was observed.

The affect of anodic conditioning at 0.5 V for 10 min in the absence of xanthate prior to sweeping the potential positive in xanthate solutions showed that the anodic current associated with the oxidation of xanthate is considerably reduced indicating that the anodic treatment does partially inhibit the reaction with xanthate. One of the problems associated with studying the reaction of xanthate with pyrrhotite is that pyrrhotite oxidizes at the potentials where the anodic adsorption of xanthate is expected. In the experiments shown in Figure 7, the electrode was conditioned at various potentials prior to adding xanthate to the solutions. This allowed the anodic currents due to pyrrhotite oxidation to stabilise so that any increase in anodic current on xanthate addition could be attributed to the anodic

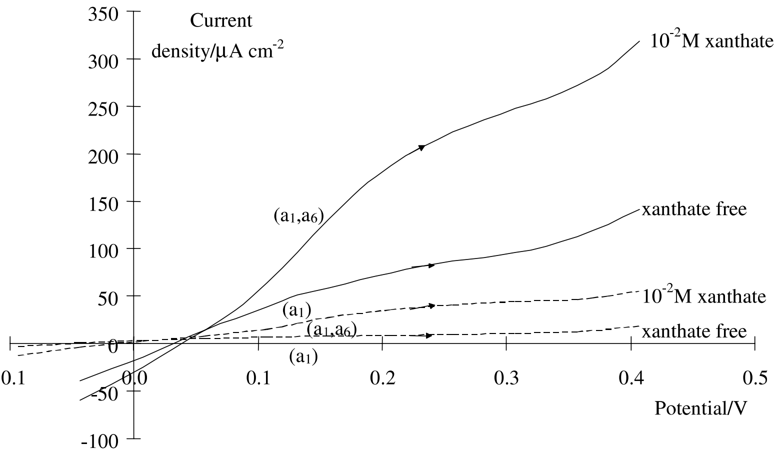

Fig. 6. Anodic current–potential curves for a rotating (500 rpm) pyrrhotite electrode in deoxygenated 0.1 M Na_2SO_4 (—) (pH 9.2) and 0.05 M $Na_2B_4O_7$ (···) (pH 9.3) with and without 10^{-2} M sodium isobutylxanthate with a sweep rate of 2 mV s^{-1}.

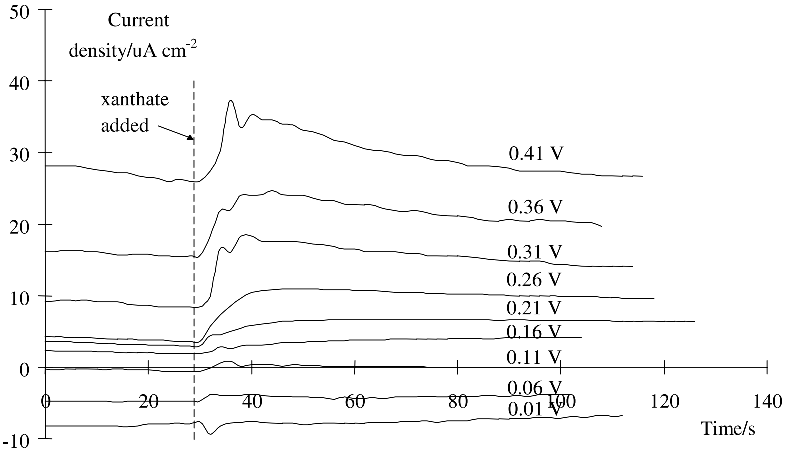

Fig. 7. Current transients for rotating (500 rpm) pyrrhotite electrode held at various potentials in deoxygenated 0.05 M $Na_2B_4O_7$ (pH 9.3) with sodium isobutylxanthate added (xanthate concentration after addition was 10^{-3} M) after anodic currents due to pyrrhotite oxidation stabilized.

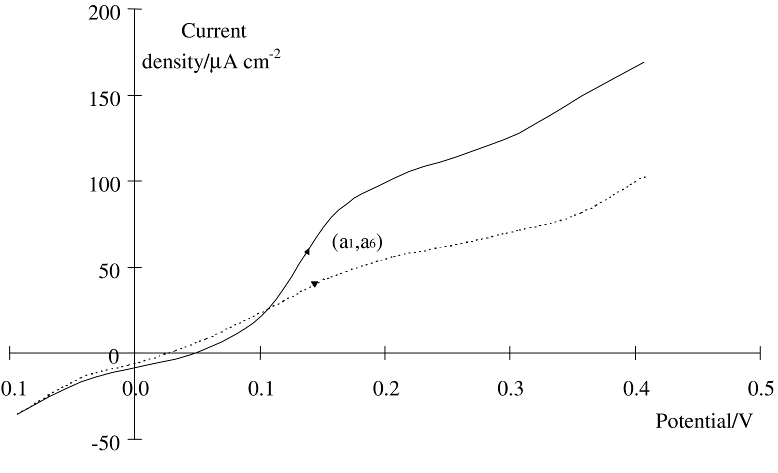

Fig. 8. Anodic current–potential curves for rotating (500 rpm) pyrrhotite electrode, with (—) and without (···) prior exposure at open circuit to 0.1 M Na_2SO_4 (pH 3.4) and 2×10^{-3} M Cu^{2+} for 5 min, in deoxygenated 0.1 M Na_2SO_4 (pH 9.2) and 10^{-2} M sodium isobutylxanthate with a sweep rate of 1 mV s^{-1}.

reaction of the xanthate with the pyrrhotite surface. Above 0.05 V small increases in anodic current were observed with the magnitude of the increase in current increasing up to 0.3 V. Prior exposure to copper ions enhanced the anodic currents in the presence of xanthate as shown in Figure 8.

4. Discussion

The range of values measured in the plant and in the batch flotation experiment is shown in relation to the Eh–pH diagram for the pyrrhotite system in Figure 9. Also indicated is the equilibrium line for the xanthate/dixanthogen couple for a concentration of 10^{-4} M xanthate and assuming unit activity for the dixanthogen.

The voltammograms of pyrrhotite are similar to those reported by Hamilton and Woods [2]. The oxidation of pyrrhotite must involve the formation of an iron oxide/hydroxide and/or a sulfur species. On positive-going sweeps two anodic processes occur at a_1 and a_2. In buffered solutions reaction a_2 is passivated on subsequent sweeps. This may be due to local pH effects at the surface of the electrode especially if a_2 involves the formation of protons. Reaction c_2 was only visible after Reaction a_2. Correspondingly reaction a_4 only occurs after Reaction c_2. It is possible that Reaction a_1 is the formation of ferric hydroxide leaving a sulfur rich sublattice, where $Fe_{(1-x)}S$ represents pyrrhotite and $Fe_{(1-(x+y))}S$ represents an even more iron deficient pyrrhotite.

$$Fe_{(1-x)}S + 3yOH^- \rightarrow Fe_{(1-(x+y))}S + yFe(OH)_3 + 3ye^- \qquad (a_1)$$

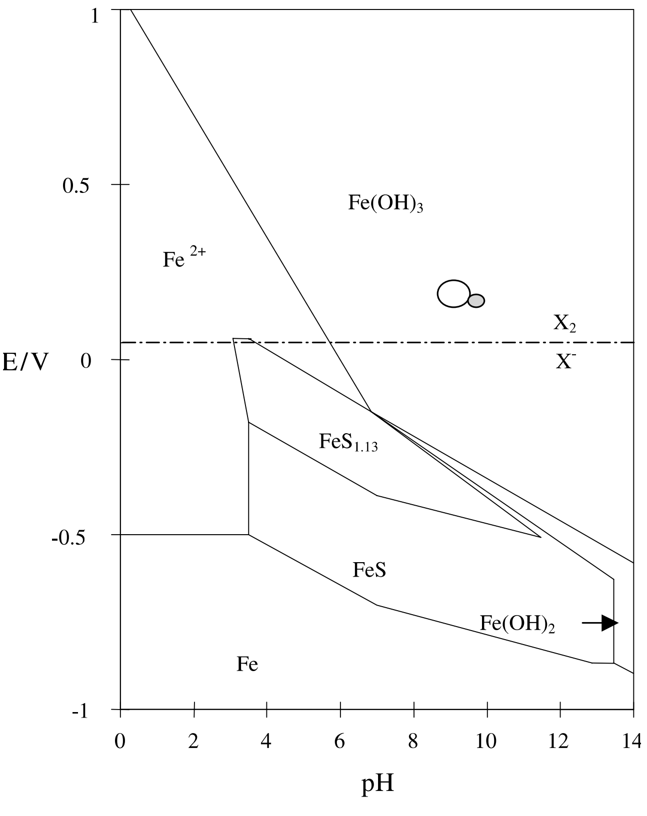

Fig. 9. Eh–pH diagram for pyrrhotite system (25 °C and 10^{-3} M dissolved species, (adapted from Hamilton and Woods [2]) with 10^{-4} M xanthate/dixanthogen equilibrium line (– · –) and the range of pyrrhotite mixed potential measurements made in a plant circuit (○) and during batch flotation tests (●).

On negative-going sweeps after Reaction a_1 only ferric hydroxide is available for reduction to ferrous hydroxide via Reaction $c_{1,a}$. The equilibrium potential for Reaction $c_{1,a}$ at pH 9 is −0.250 V.

$$Fe(OH)_3 + e^- + H^+ \leftrightarrow Fe(OH)_2 + H_2O \qquad (c_{1,a})$$

As pointed out by Hamilton and Woods [2] the oxidation of pyrrhotite does not likely occur via the formation of pyrite as an intermediate and as such Reaction a_1 probably does not proceed beyond initial coverage of the mineral surface with ferric hydroxide. This is confirmed by an estimate of the charge involved in peak a_1 which is less than 0.5 mC cm^{-2}.

At potentials above 0.5 V the oxidation may proceed via Reactions $a_{2,a}$ and $a_{2,b}$ given by Hamilton and Woods [2].

$$FeS_{1.13} + 3\,OH^- \rightarrow Fe(OH)_3 + 1.13\,S + 3e^- \qquad (a_{2,a})$$

$$FeS_{1.13} + 4.52\,H_2O \rightarrow Fe(OH)_3 + 1.13\,SO_4^{2-} + 9.04\,H^+ + 9.78\,e^- \qquad (a_{2,b})$$

The formation of protons in Reaction $a_{2,b}$ may explain why in nonbuffered solutions Reaction a_2 does not appear to be passivated on subsequent sweeps. The availability of sulfur on the surface of the mineral during cathodic sweeps after Reaction $a_{2,a}$ may result in additional cathodic reactions, namely the reduction of sulfur ($c_{1,b}$) and the possible formation of an iron sulfide (c_2).

$$S + 2\,e^- + H^+ \rightarrow HS^- \qquad (c_{1,b})$$

$$S + Fe(OH)_2 + 2\,e^- \rightarrow FeS + 2\,OH^- \qquad (c_2)$$

The equilibrium potential for Reaction $c_{1,b}$ at pH 9 is −0.328 V. The fact that the potentials of Reactions $c_{1,a}$ and $c_{1,b}$ are so close may explain why two distinct reaction peaks were not observed in the voltammograms. FeS formed by Reaction c_2 may be oxidized at a_4. The reaction at a_3 is considered to be the reverse of Reaction $c_{1,a}$. It is not clear why Reaction a_3 is absent from voltammograms performed in nonbuffered solutions. However ferrous hydroxide is considerably more soluble than ferric hydroxide, which may result in ferrous hydroxide moving away from the surface of the electrode into the bulk solution or the acid generated in Reaction $a_{2,b}$ could have inhibited the reverse of Reaction $c_{1,a}$.

Mixed potential measurements conducted in plant circuits and during batch flotation experiments indicate the potential that pyrrhotite particles experience in flotation environments. The potentials correspond to the region where Reaction a_1 was observed during anodic sweeps with freshly exposed electrodes. During cathodic sweeps after conditioning at these potentials a cathodic reaction was observed, which following from the previous discussion, is considered to be the reduction of ferric hydroxide to ferrous hydroxide. In terms of flotation performance, it may be beneficial to maintain a potential below that at which reaction a_1 occurs, thus minimising ferric hydroxide formation, up until xanthate is added, and then to allow oxidative conditions to promote the anodic adsorption of xanthate onto the mineral surface.

It is considered that the reaction between pyrrhotite and copper ions in acidic solutions results in CuS. The reaction may occur via [14] the following:

$$Fe_9S_{10} + 9\,Cu^{2+} \rightarrow 9\,Fe^{2+} + 9\,CuS + S \qquad (1)$$

The CuS formed through Reaction 1 can be oxidized above 0.4 V by a_5 for which the standard equilibrium potential is 0.548 V:

$$CuS \leftrightarrow Cu^{2+} + S + 2\,e^- \qquad (a_5)$$

The basis for proposing reaction a_5 was that soluble species were formed when the activation product was oxidized. The area of the anodic peak a_5 can be used to gauge the extent of activation in terms of the surface coverage of CuS. As the pH of the solutions was increased the coverage of CuS decreased and in borate solutions no evidence for CuS was detected. This may be partly due to the low solubility of copper ions and to the formation of a surface product on pyrrhotite that inhibits the activation reaction. In either case it would appear that activation of pyrrhotite to form a copper sulfide species does not occur in alkaline solutions.

Enhanced anodic currents were observed on anodic sweeps in relatively high concentrations of sodium isobutylxanthate (10^{-2} M). At concentrations of relevance to plant conditions (10^{-4} M) no enhanced currents were detected, although it is considered that this was due to the magnitude of the currents associated with xanthate oxidation being too low to detect above the baseline current due to pyrrhotite oxidation. No anodic reactions representing chemisorption of xanthate were detected supporting the view that the initial adsorption of xanthate occurs via physisorption. Current transients clearly indicated the anodic reaction of xanthate with the mineral surface. It is considered that the anodic currents represent the oxidation of xanthate to dixanthogen. The potential that this reaction occurs was slightly higher than, but consistent with, that expected from the equilibrium potential of the xanthate/dixanthogen couple as measured on a platinum electrode. No cathodic reactions associated with dixanthogen reduction were detected and it is not clear whether this is an indication that dixanthogen desorbed from the mineral surface before it could be reduced or whether the current measurements were not sensitive enough to detect this reaction above the background current.

Although it has been shown that an oxidation product does form on the surface of pyrrhotite at potentials applicable to flotation pulps, this product appears to only partially inhibit the reaction of xanthate with the mineral. Even after 10 min under closed circuit at 0.5 V the reaction of xanthate with the mineral surface was still detected although the reaction was enhanced with freshly exposed electrodes. In terms of flotation this may mean that the extent of dixanthogen surface coverage, and hence the hydrophobicity of the mineral particles, is affected by the extent of surface oxidation occurring prior to reagent addition.

The reaction of xanthate with the pyrrhotite was enhanced by activation of the mineral surface with copper ions in acidic solutions. As no evidence for the formation of CuS in alkaline conditions was found the effect of exposing pyrrhotite to copper ions in alkaline solutions prior to reaction with xanthate was not investigated. However, this would be relevant as flotation test work and plant practise suggests that there is a significant improvement in the flotation of pyrrhotite when copper ions are present. It is considered that this cannot be due to the formation of copper sulfide on the surface of the mineral since no evidence for the formation of such a species in alkaline solutions was found. It may involve, for instance, the formation of a copper hydroxide species on the surface of the mineral. Such a species may react with xanthate more favourably than an iron hydroxide species.

5. Conclusions

The potential that pyrrhotite particles experience was gauged by potential measurements made with a pyrrhotite electrode. It was shown that, at these potentials, oxidation of the surface occurs with the formation of a product that could be reduced on cathodic sweeps. It is considered that this product is ferric hydroxide. At higher potentials the oxidation of the mineral involves the formation of sulfur and sulfate, in addition to ferric hydroxide. Activation of pyrrhotite by copper ions in alkaline solutions to form a copper sulfide species does not occur. However, due to the reported results of pyrrhotite flotation activation may occur via a different mechanism, for instance involving a copper hydroxide species. Such a species may be more favourable for xanthate adsorption. The anodic reaction of xanthate with pyrrhotite was observed. Oxidation of the mineral surface only partly inhibited the reaction of xanthate with pyrrhotite. The flotation of pyrrhotite may be enhanced by minimizing the effects of oxidation through rapid addition of collector reagents and/or by imposing reducing conditions on the pulps up until reagent addition. The mechanism whereby copper ions enhance the flotation of pyrrhotite under alkaline conditions requires further investigation.

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