

Linear potential sweep voltammetry in conjunction with small amplitude cyclic voltammetry study for chalcopyrite – xanthate electrochemical flotation system

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Abstract

The present study was undertaken to investigate the electrochemical aspects of reactions on platinum, copper, and chalcopyrite aqueous xanthate solution interfaces by the small amplitude cyclic voltammetry (SACV) technique. In the technique, the potential of an electrode is swept linearly with time within very narrow potential limits. Typically a 10 to 20 mV peak-to-peak triangular potential excitation has been used. Characteristic parameters of the observed current-potential response loop, like apparent polarization resistance, was used to analyze the surface reaction mechanism in the flotation of chalcopyrite minerals. The analysis of the electrochemical interaction between platinum, copper and xanthate ions has also been carried out by using linear potential sweep voltammetry (LPSV) techniques in different xanthate concentrations. The voltammograms obtained on platinum appear due to the possibility of the formation of dioxanthogen from the oxidation of xanthate ions, and the formation of copper-xanthate species from electrochemical reactions between xanthate ions and copper.

Keywords : *electrochemical, flotation, platinum, copper, dioxanthogen, chalcopyrite, small amplitude cyclic voltammetry, linear potential sweep voltammetry, micro-flotation cell.*

Sari

Studi voltametri penyapuan potensial linier dikaitkan dengan voltametri siklus amplitudo kecil untuk sistem flotasi elektrokimia kalkopirit-xantat

Penelitian ini memberikan gambaran reaksi elektrokimia pada antarmuka elektroda platina, tembaga, dan kalkopirit di dalam larutan encer xantat. Penelitian dilakukan dengan metode SACV (Small Amplitude Cyclic Voltammetry), dengan rentang eksitasi potensial segitiga yang sangat kecil, yaitu 10 mV sampai 20 mV eksitasi dipakai untuk menganalisis mekanisme reaksi flotasi mineral kalkopirit. Untuk mempertegas hasil SACV penelitian dilanjutkan dengan metode LPSV (Linear Potential Sweep Voltammetry). Voltammogram yang diperoleh menggambarkan terbentuknya dioxanthogen di permukaan elektroda platina, dan terbentuknya senyawa tembaga-xantat karena adanya reaksi permukaan antara ion xantat dengan tembaga.

Katakunci : *elektrokimia, flotasi, platina, tembaga, dioxanthogen, kalkopirit, small amplitude cyclic voltammetry, linear potential sweep voltammetry, sel flotasi mikro.*

1 Introduction

Potassium ethyl xanthate (KetX) is an organic substance commonly used as flotation collector. Although the basic objective of the addition of KetX is to alter the behavior of the particle surfaces from hydrophylic to hydrophobic, chemical and electrochemical reactions occur in the flotation pulp cannot be avoided. Progress in the flotation theory has been rapid and during recent years research on the chemistry of the interaction between sulfide minerals and KetX has been directed to the study of the electrochemical reactions taking place and the products formed that confer hydrophobicity.

In the present investigation, SACV (Small Amplitude Cyclic Voltammetry) measurements are carried out on

Cu-sulfide mineral chalcopyrite (CuFeS_2). Platinum and copper have been chosen as references to elucidate the formation of dioxanthogen and Cu-EtX species. The last part of experiments treats flotation test in a microflotation-electrochemical cell to analyze the influence of potential on the flotability. From a comparison between electrochemical data with flotation data the mechanism of collection is further elucidated.

This study was undertaken to further investigate the electrochemical aspects of reactions on platinum and copper electrodes dipped in aqueous xanthate solutions. It is anticipated that the observed cyclic current responses can be used to elucidate surface reaction mechanisms in the flotation of sulfide minerals. The

comparison of the interaction of xanthate ions with metal surfaces and with sulfide minerals is an indicated way of approaching to the problem.

2 Measurements of polarization resistance

In the SAVC-technique, the value of the polarization resistance can be calculated from the steady-state current-potential hysteresis loop which is obtained by applying a triangular potential wave. Typical SAVC curves obtained on an electrode are shown in Fig. 1 (Roos et. al, 1988).

The characteristic parameters of the hysteresis loop are calculated from the simulated curve (see Fig. 1). The term apparent polarization resistance (R_{app}) is used for the slope of the hysteresis loop determined by the tangent at the maximum potential (or maximum current). The diagonal resistance R_d is defined as the slope of the line joining the maximum and minimum points of the hysteresis loop with I_{max} = maximum current density, and I_{min} = minimum current density.

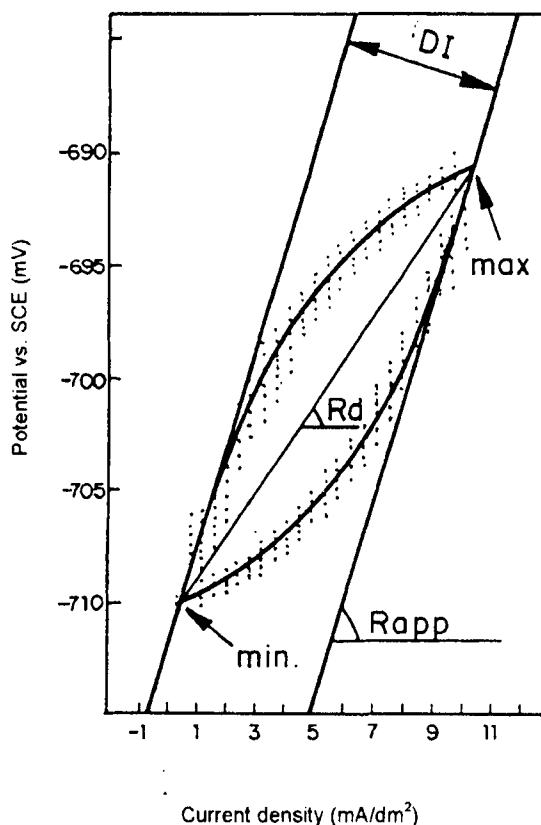


Figure 1 Typical SAVC current-potential hysteresis loop. Solid lines are obtained by curve fitting technique (Roos et. al, 1988)

3 Experimental procedures

Small amplitude cyclic voltammetry (SACV) were performed on copper wire and chalcopyrite. Sulfide electrodes of about 0.5 cm^2 area were hand-selected to be free as far as possible from inclusions, cracks and voids. Before each SACV-experiment a new surface was produced by wet grinding on 600 grade paper and the electrode was immediately transferred to the test cell.

Test solutions were prepared from $\text{Na}_2\text{B}_4\text{O}_7$ and distilled water. A 10 g/l borate solution was used as electrolyte, its natural pH was 9.2. Potassium ethyl xanthate (KETX) was prepared from a high purity ethyl alcohol, CS_2 and KOH.

The chemical composition of the chalcopyrite mineral was 32.22% Cu, 30.30% Fe, 35.11% S and 2.37% as others. A three-electrode system was used for the electrochemical measurements. The counter electrode was a platinum electrode. All potential values in this work were given with respect to a saturated calomel electrode (SCE).

For SACV test, a Princeton Applied Research Electrochemistry system and a Synthesizer/Function Generator HP 3325A were used for programming and controlling the electrode potentials. A triangular potential waveform of 20 mV peak-to-peak was applied to the working electrode. The waveform was then recorded on a Nicolet Instrument corporation model 206 oscilloscope. The data was then transferred to a MINC VT 105 computer for further treatment. The SACV-test was performed at different potentials from -1.2 V up to $+1 \text{ V}$ in successively intervals of $+50 \text{ mV}$.

For LPSV test, a Princeton Applied Research Electrochemistry system (Model 175 Universal Programmer, Model 173 Potentiostat/Galvanostat and Model 176 current follower) was used for programming and controlling the electrode potentials. The potential was swept linearly with time generally at a potential sweep rate of 10 mV/s .

The platinum and copper electrodes had diameters of 0.8 and 1.7 mm respectively and the length immersed in the solution was 45 mm. After a couple of experiments the electrolyte was replenished. Stock of xanthate solutions was prepared just before the experiment to ensure minimum decomposition.

A conventional three-electrode system was used for the electrochemical measurements. The electrodes were inserted into the solution through appropriate holes in a glass lid which covered a 1 liter glass vessel. All measurements had been carried out at room temperature without agitation of the solution. The counter electrode was a platinum electrode.

A Schematic representation of the microflotation-electrochemical cell is shown in Figure 2. A slightly different flotation set-up was used by Gardner and Woods (1973) and by Walker et. al (1984) and Richardson and Walker (1985).

- A. Fritted glass discs
- B. Platinum wire electrode
- C. Platinum counter electrode
- D. Calomet reference electrode tube
- E. Air inlet tube
- F. Fresh water tube
- G. Floted product receiver

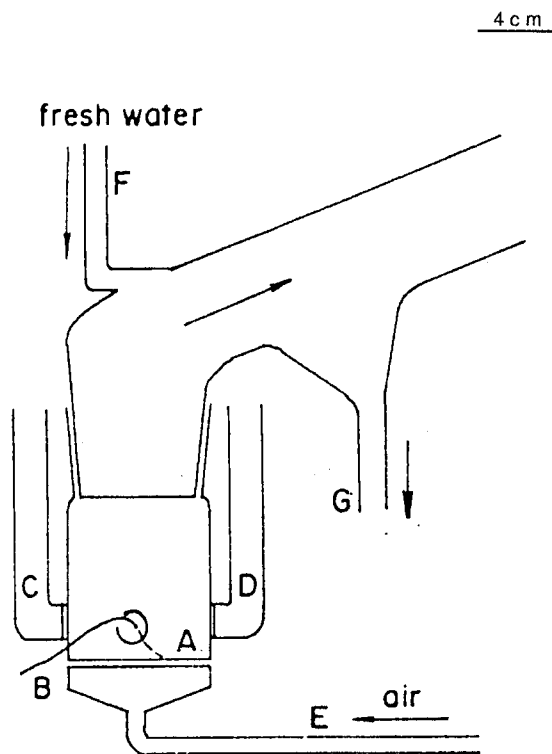


Figure 2 Schematic representation of microflotation-electrochemical cell (Sudarsono, 1988a)

Copper particles of $-160+45$ micrometers were used for flotation experiments. They were initially rinsed with a 5% HNO_3 solution for 10 min and then filtered several

times with distilled water to remove traces of contaminants. The size fraction used in the flotation of chalcopyrite was $-180+45$ micrometers.

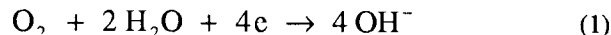
The micro-flotation cell was first loaded with 10 g particles and then filled with a xanthate containing borate solution. After sedimentation on a fritted glass disc of 15-40 micrometers porosity the particles were connected to a potentiostat through a coiled single platinum wire electrode of 4 cm^2 surface area. Finally the electrochemical preconditioning was performed by applying the desired potential for 10 minutes.

Air was fed to the cell at a constant rate of 1.6 liter/min through the base, and the flotation tests were carried out at room temperature for 1 to 2 minutes of flotation time.

No frother was used in any of the microflotation experiments. Froth was removed by the addition of distilled water through the head of the column.

4 Experimental results and discussion

Platinum electrode in xanthate - free borate solutions



The present experimental results (Fig. 3) indicated a possibility of the one-path oxygen reduction process since only one clear cathodic current peak in the xanthate-free solution is observed at ca. -250 mV .

As was suggested by Feldberg et. al. (1963), the oxidation of a platinum surface which is not necessarily the formation of oxides proceeds along two consecutive steps as indicated by reactions:

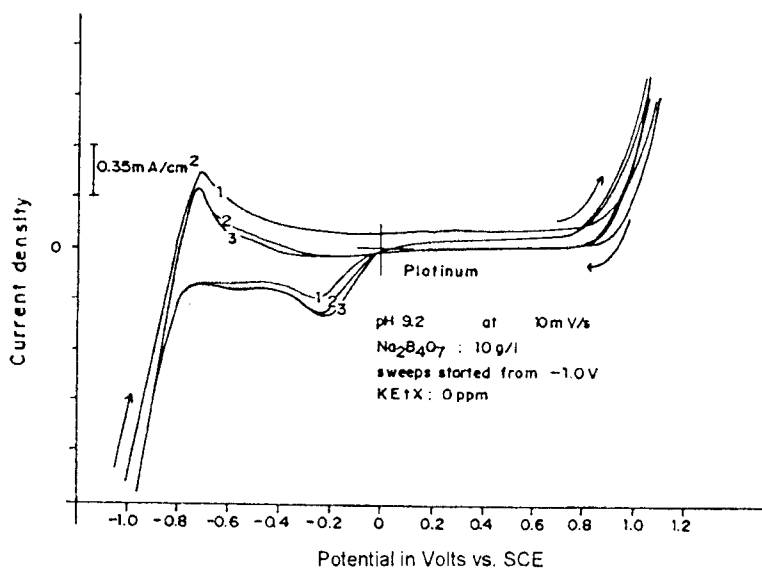
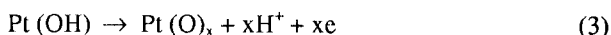
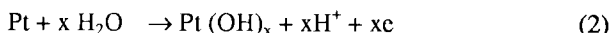


Figure 3 Voltammograms obtained on a platinum electrode dipped in xanthate-free borate solutions for a potential sweep rate of 10 mV/s

From the phenomenon shown in Fig 3, that is the appearance of positive potential plateau (from 0 to 800 mV), it seems that the LPSV test performed on platinum electrodes does not allow to distinguish between chemisorption of substances OH and O on the platinum surface.

Observation in the positive regions of Fig. 3 suggests that the oxygen evolution proceeds in one step, namely the reverse of reaction (1).

Since the reversible potential of reaction:



is -789 mV the hydrogen overvoltage at platinum is negligible, it is evident that at pH 9.2 hydrogen evolves at platinum electrodes at potentials more negative than -800 mV. As the potential is increased from -1000 mV, current begins to increase crossing the potential axis at -800 mV, which is close to the equilibrium potential of reaction (4).

5 Platinum electrode in aqueous xanthate borate solutions

The voltammograms presented in Fig. 4 which are obtained by sweeping the potential of the platinum electrode between -1000 mV and $+1200$ mV, indicate the decrease of the anodic oxidation peak at ca. -750 mV with increasing xanthate concentration. It seems thus that the hydrogen adsorption is inhibited in the presence of xanthate ions. The inhibition of hydrogen adsorption is probably due to the adsorption of xanthate ions without charge transfer.

Since the current density for the oxygen evolution decreases with increasing xanthate concentration, the oxygen desorption is inhibited in the presence of xanthate ions. This is probably due to the presence of dixanthogen on the surface of the platinum electrode,

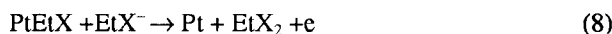
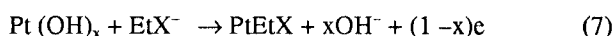
according to:



In Fig. 4 as a potential increases, the current begins to increase rapidly, giving rise to a very well defined at ca. $+750$ mV. This peak which is observed only in the presence of xanthate ions can be envisaged as a further possible reaction between xanthate ions and chemisorbed OH at the surface of platinum according to :



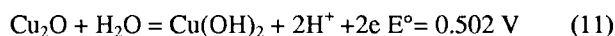
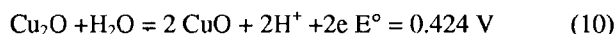
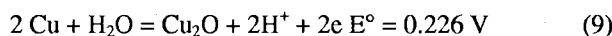
A similar behavior was reported by Sudarsono (1988b), studying the current reversal chronopotentiometric responses of electrochemical interaction of platinum-xanthate, that the formation of dixanthogen may involve the following reactions in addition to reaction (5):



The overall reaction combining reactions (7) and (8) is equivalent to reaction (6).

6 Copper in xanthate-free borate solutions

It is generally agreed that in alkaline solutions Cu_2O , CuO and $\text{Cu}(\text{OH})_2$ are formed on the surfaces of copper electrode upon anodically polarized, namely :



For a pH value of 9.2, the equilibrium potentials of reactions (9), (10), and (11) are -318 mV, -120 mV, and -42 mV respectively. These values reveal that the formation of Cu_2O , CuO and $\text{Cu}(\text{OH})_2$ is possible from -318 mV to before oxygen evolution potential.

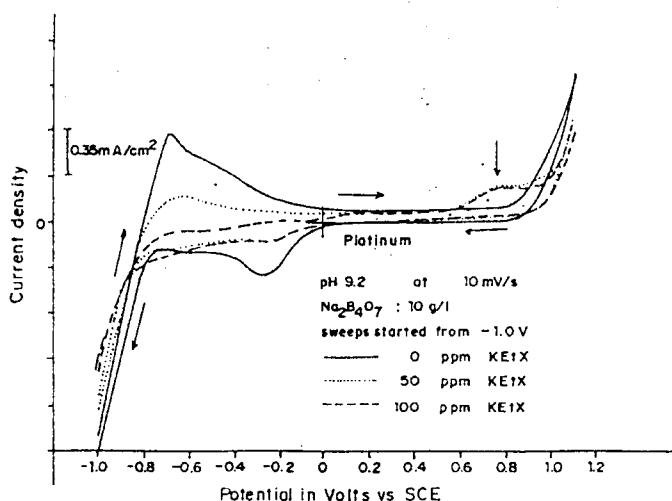


Figure 4 Voltammograms obtained on a platinum electrode dipped in xanthate containing borate solutions for a potential sweep rate of 10 mV/s .

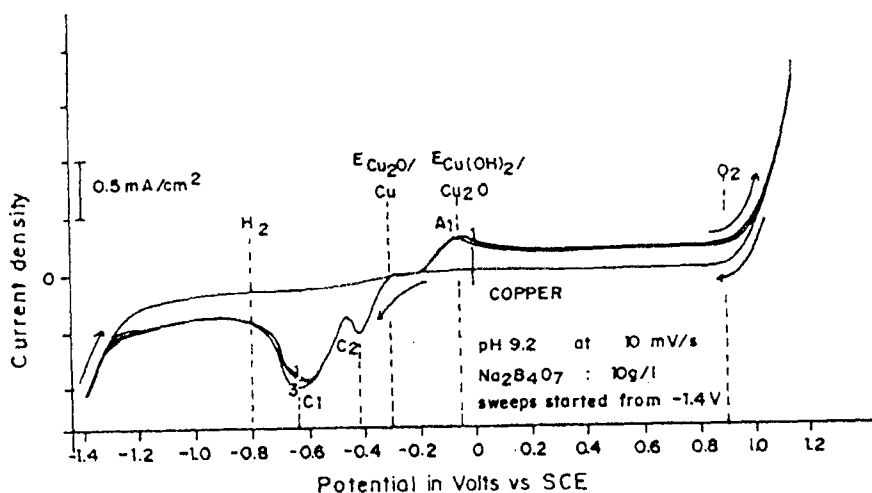


Figure 5 Voltammograms of a copper electrode dipped in xanthate-free borate solutions

Fig. 5 shows voltammograms of copper electrode dipped in a borate solution at pH 9.2 for a potential sweep rate of 10 mV/s. The potentials were positively polarized from the hydrogen evolution potential region to +1200 mV and were reversed back to the negative potentials.

As the potential is raised during a sweep cycle, a peak related to the oxidation of copper is observed on the positive current region followed by potential plateaus which may be associated with the passivation effect. On the negative current region two peaks are observed. It can be seen that one of the peaks on the negative current region is much broader than the other, this suggests that there is a two-stage reduction of the products formed during anodic potential sweep, namely reduction of CuO to Cu_2O and Cu_2O to Cu and the peak which is narrower can be assimilated to the reduction of $\text{Cu}(\text{OH})_2$ to Cu_2O .

To gain further insight into the processes of oxidation and reduction of copper, a potentiodynamic measurement was conducted with successively increased of the reversing potential. The potential of a copper electrode was positively polarized at a potential sweep rate of 10

mV/s from -1400 mV and then negatively reversed at -300, -200, -100, 50, 400, 600 and 1200 mV. The results are shown in Fig. 6.

Voltammograms shown in Fig. 6 reveal the sensitivity of the cathodic current peaks to the reversing potential. The increase in the value of the reversing potential increased the current in the negative potential region between -700 mV and -200 mV. There are two cathodic current peaks in this potential region, which are identified as C1 and C2 peaks. The C1 peak is observed firstly when the reversing potential is equal to -100 mV (curve 3); since the equilibrium potentials of reactions (10) and (11) are smaller than -100 mV and C1 peak is much broader than C2 peak, is likely that C1 peak may be associated with the reduction of both CuO to Cu_2O and Cu_2O to Cu . Moreover, when the reversing potential is increased to 50 mV which is higher than the equilibrium potential of $\text{Cu}(\text{OH})_2$ formation as indicated by reaction (11), the first cathodic current peak, C2 appears at ca. -200 mV, this behavior suggests that reduction of $\text{Cu}(\text{OH})_2$ to Cu_2O takes place at C2 peak.

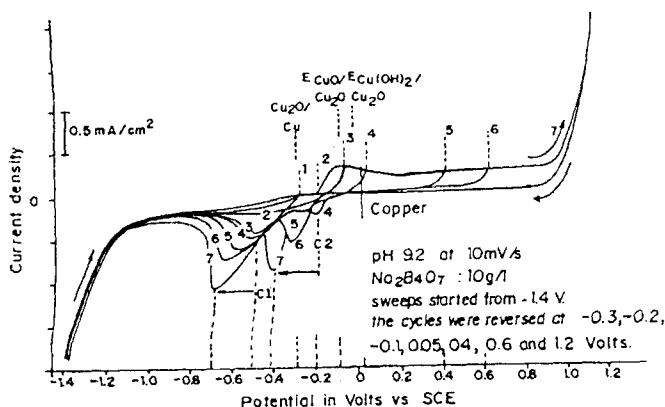


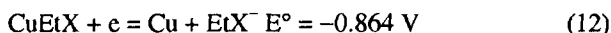
Figure 6 Voltammograms of a copper electrode dipped in a xanthate-free borate solution for a potential sweep rate of 10 mV/s showing the influence of reversing potential

7 Copper in xanthate containing borate solutions

Figure 7 shows the potentiodynamics traces of a copper electrode dipped in borate solutions containing from 50 ppm up to 200 ppm KETX.

The potential sweep rate was 10 mV/s. The shape of the voltammograms changes considerably compared to those shown in Fig. 6. As potential is raised from -1400 mV, four anodic current peaks are observed, namely, A1, A2, A3 and A4. On reversing the potential sweep at +1200 mV only three cathodic current peaks are observed i.e. C1, C2 and C3 in the negative potential region.

The thermodynamic data of Hepel and Pomianowski (1977) suggest that xanthate ions may react spontaneously with copper surfaces lead to the formation CuEtX and Cu(EtX)₂:



The voltammograms in Fig.7 display a quite well defined peak at ca. -650 mV. This peak which is labeled as A1 can be related to the formation of CuEtX as indicated by reaction (12). For a xanthate concentration of 50 ppm this reaction has an equilibrium potential at -657 mV. The second peak in the polarization curves, indicated by A2 peak at ca. -500 mV, is expected to represent the formation of Cu(EtX)₂ as indicated by reaction (13). The height of A2 peak is greater than that of A1 peak showing a difference of charge transfer, one electron for reaction (12) and two for reaction (13).

As previously mentioned, dixanthogen may be formed by the oxidation of xanthate ions according to equation (5). For a xanthate concentration of 200 ppm the equilibrium reaction of dixanthogen formation may occur at -150 mV. There is no peak in Fig.7 that can be related

to the formation of dixanthogen. It seems thus that according to the results of potentiodynamic method, there is no clear indication that reaction (5) may occur on copper electrodes, although quite a small potential sweep rate has been used.

The height A4 peak is almost constant but it is shifted to more positive values with increasing xanthate concentration. Since there is no cathodic current peak, decomposition of CuEtX species as oxidation reactions are suggested to occur at this peak.

It can be seen that the onset of A4 peak is shifted to more positive value with increasing xanthate concentration.

It can be seen from Figure 7 that the height of A3 peak which related to the oxidation of copper electrode decreases at increasing xanthate concentration. This suggests that the oxidation of copper electrode is inhibited with the presence of xanthate ions in the solution.

A similar phenomenon is shown by C3 peak, its current density decreases with increasing xanthate concentration. It is reasonably therefore to relate A3 peak with C3 peak representing the oxidation-reduction of copper electrode in aqueous xanthate borate solutions.

Observation at C1 and C2 reduction peaks suggests to relate with reactions (12) and (13) since their cathodic current densities increase with increasing xanthate concentration indicating the increase of the amount of copper-xanthate species formed previously. The A1 peak is related to C1 peak while A2 peak to the one of C2 peak.

The SACV-test results in xanthate containing solutions (Fig.8) reveal a sharp decrease of the Rapp-value between -800 and -450 mV with a minimum value at -650 mV. This potential region may correspond to the formation of CuEtX as expressed by reactions:

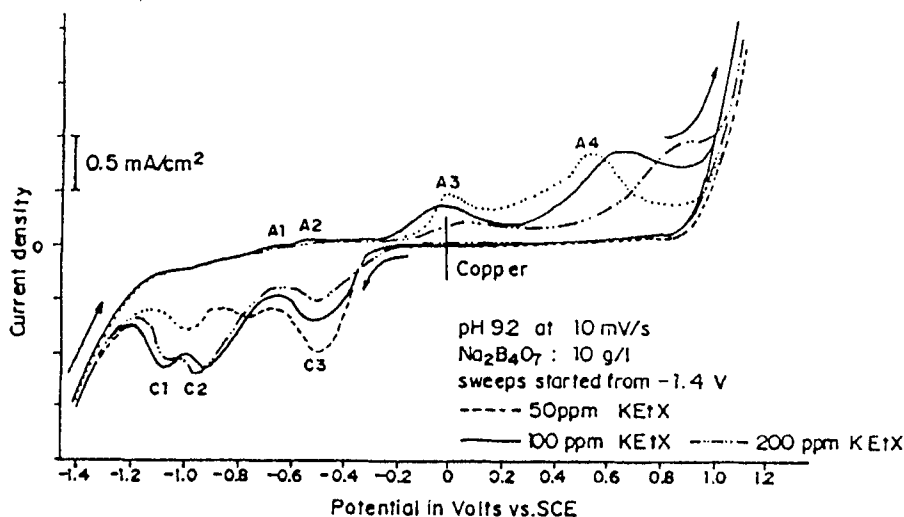


Figure 7 Voltammograms of a copper dipped in borate solutions containing different xanthate concentrations for a potential sweep rate of 10 mV/s

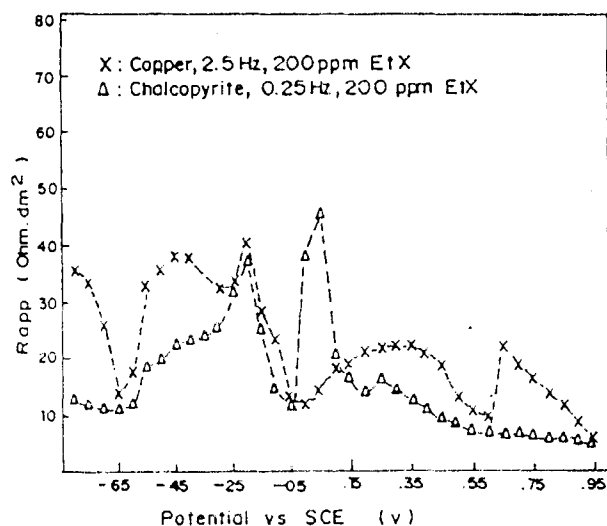
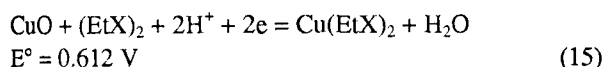
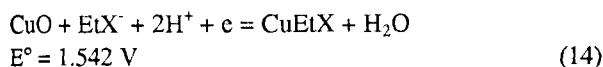
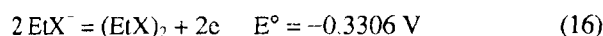


Figure 8 SACV-test results of copper and chalcopyrite



Between -200 and 0 mV, Rapp decreases with increasing potential. This phenomenon can be linked to the possible formation of dioxanthogen mentioned by Roos et. al (1988) and indicated by reaction :



with regard to the minimum values of Rapp in the range of $+500$ up to $+800$ mV and above $+800$ mV. A link with oxygen evolution can be made. A similar phenomenon was observed in SACV-tests on platinum at a frequency of 2.5 Hz for potentials at $+700$ and $+950$ mV reported by Roos et. al in 1988. However, in case of copper, the Rapp-value decreases above $+550$ mV with increasing xanthate concentration (Ross et. al 1990). This indicates that besides the oxygen evolution additional reactions do occur. The decomposition of Cu-EtX species according to the reactions (12) and (13) (Hepel and Pomianowski, 1977) is such a possibility.

The microflotation-electrochemical cell results on copper particles are shown in Fig. 9. The flotability of copper is strongly potential dependent. The onset of flotability is observed at -800 mV and may thus be related to the formation of CuEtX according to reaction (12). The flotability raises up to 40% between -600 and -300 mV. This effect can be related to the formation of $\text{Cu}(\text{EtX})_2$ according to reaction (13). A small decrease in flotability is observed at -100 mV which is followed by a remarkable increase at $+100$ mV. It is anticipated that a competition between the oxidation of copper resulting in the formation of Cu_2O according to reaction (9) and oxidation resulting in Cu-EtX species, e.g. reactions (14) and (15), may reduce the flotability at -100 mV. This is further substantiated by HAVC voltammograms shown

in Fig.6, from which a decrease of the A3 peak height related to reaction (12) with xanthate addition can be seen. The voltammograms shown in Fig. 7 display quite well defined peaks (A1 and A2) at ca. -650 mV that can be related to reaction (14).

The remarkable flotability at $+100$ mV indicates that dioxanthogen which can be formed above -150 mV greatly influences the flotability of copper. When the potential is further raised above $+200$ mV, flotation is suppressed. It is believed therefore that Cu-EtX species may undergo decomposition above $+200$ mV. Furthermore, this is confirmed by the appearance of current peaks, labeled as A4 in the voltammograms of copper dipped in xanthate solutions, shown in Fig. 7.

8 Chalcopyrite-xanthate interaction

Electrochemical micro-flotation tests for chalcopyrite are shown in Fig. 9. The onset of this flotability is observed at -400 mV. It is clear that the onset of flotability coincides well with the equilibrium potential of the reaction proposed by Richardson and Walker in 1985 :

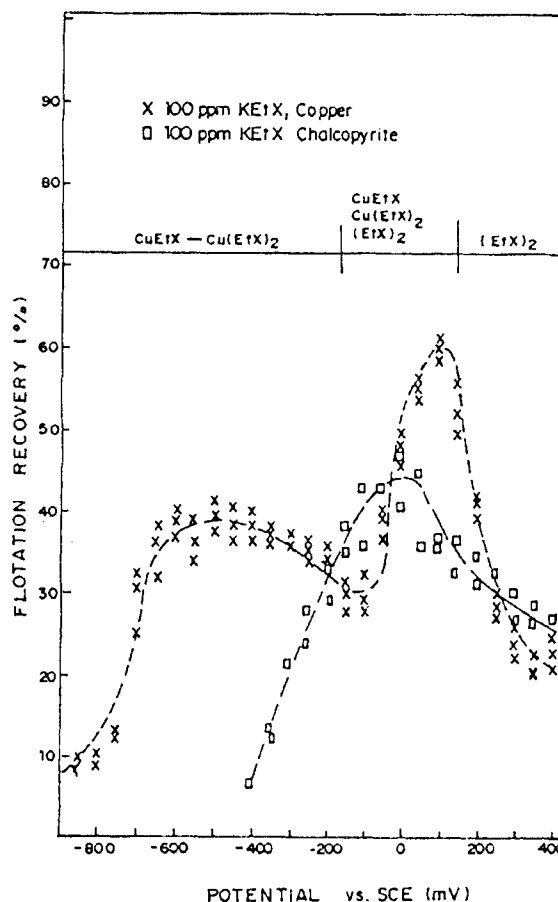
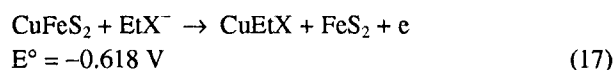


Figure 9 Flotation-test results in microflotation-electrochemical cell (Roos et.al 1990a)

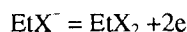
where chalcopyrite reacts directly with xanthate ions. Since equation (17) derives CuEtX and, as shown previously, that CuEtX is a species responsible for the hydrophobization of copper particles, CuEtX seems also to be responsible for the onset of flotation of chalcopyrite at -400 mV. Reaction (17) can occur before the dixanthogen formation, and there is no doubt that CuEtX participates in the hydrophobization of chalcopyrite. This conclusion is in agreement with the Rapp value of chalcopyrite shown in Fig. 8 (Roos et. al, 1988).

The recovery of chalcopyrite increases further at increasing potential and reaches a maximum at ca. 0 mV. In analogy with the copper flotation, this can be related to the dixanthogen formation at potentials above -150 mV. Indeed the Rapp-values measured in a 200 ppm KEtX solution at a frequency of 0.25 Hz show a sharp decrease at -200 to 50 mV (Fig. 8).

From a further observation of the Rapp values between +150 up to +250 mV, there is evidence that Cu-EtX species decompose in this potential region. The Rapp value decreases with increasing potential.

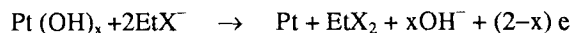
9 Conclusions

The formation of dixanthogen at platinum electrode besides due to the oxidation of ethyl xanthate ions according to:

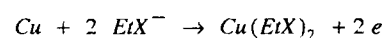
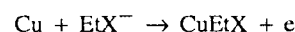


$$E = -0.3261 - 0.0591 \log [\text{EtX}^-] \text{ Volt}$$

may also be formed by an exchange reaction between OH chemisorbed on the platinum surfaces and xanthate ions at highly positive potentials:



From the electrochemical study carried out on copper electrodes in aqueous xanthate borate solutions, it becomes apparent that Cu-EtX species such as CuEtX and Cu(EtX)₂ may be responsible for the hydrophobization of copper surfaces. The formation of these species by direct reactions between copper surfaces and xanthate ions is expected to occur above -700 mV according to reactions



However, although the use of a fairly slow linear potential sweep to modulate an electrochemical process has received a wide application to interpret the phenomena observed in the electrochemical system, LPSV studies on the anodic oxidation of copper in xanthate alkaline solutions have not showed a fundamental understanding concerning the reaction mechanisms of dixanthogen formation.

It is shown that besides Cu-EtX species, dixanthogen also influences the flotability of copper particles. However, dixanthogen alone is not sufficient to render copper particles floatable. Further it is shown that flotability is suppressed above +200 mV, and this can be related to the decomposition of Cu-EtX species.

From SACV-tests on chalcopyrite, it becomes evident that besides dixanthogen, CuEtX may also be formed by a direct reaction between chalcopyrite and xanthate ions at potential above -300 mV. The flotation-tests confirmed that dixanthogen alone is not sufficient to render chalcopyrite mineral floatable since the flotability decreases at potentials where the decomposition of Cu-EtX species occurs namely above +100 mV.

10 References

1. Feldberg, S.W., Enke, C.G. and Bricker, C.E., Formation and Dissolution of Platinum Oxide Film : Mechanism and Kinetics, *J. Electrochem. Soc.*, **111** (7), 826-834 (1963).
2. Roos, J.R., Celis, J.P., Sudarsono, A.S., Investigation of Xanthate Interaction on Platinum and Chalcopyrite by Small Amplitude Cyclic Voltammetry, *Int. J. of Mineral Processing*, **24**, 91-110 (1988).
3. Roos, J.R., Celis, J.P., Sudarsono, A.S., Electrochemical Control of Metallic Copper and Chalcopyrite-Xanthate Flotation, *Int. J. of Mineral Processing*, **28**, 231-245 (1990).
4. Gardner, Jr., Woods, R., The Use of A Particulate Bed Electrode for The Electrochemical Investigation of Metal and Various Sulphide Flotation, *Aust. J. Chem.*, **26**, 1635-1644 (1973).
5. Hepel, T. Pomianowski, A., Diagrams of Electrochemical Equilibria of The System Copper-Potassium Ethyl Xanthate-Water at 25° C, *Int. J. of Mineral Process*, **4**, 345-361 (1977).
6. Richardson, P.E., Walker, G.W., The Flotation of Chalcopyrite, Bornite, Chalcocite and Pyrite in An Electrochemical-Flotation Cell, XVth Int. Mineral Process. Congr., Cannes, France, Tome II, 198-210 (1985).
7. Sudarsono, A.S., 1988a., Small Amplitude Cyclic Voltammetric Study of Xanthate Flotation of Copper-Sulphide Minerals, Ph. D. Thesis, Katholieke Universiteit Leuven, Belgium, January 1988.
8. Sudarsono, A.S., 1988b., Analisis Kronopotensio-metrik Arus Balik pada Interaksi Elektrokimia Platina-Xanthate, *Proc. ITB*, 1988.
9. Walker, G.W., Stout III, Richardson, P.E., Electrochemical Flotation of Sulfides: Reactions of Chalcocite in Aqueous Solutions, *Int. J. of Mineral. Process*, **12**, 55-72 (1984).