

Electrochemistry of Copper Activation of Sphalerite and Potassium Isobutyl Xanthate (KIBX) Synthesized Collectors Adsorption

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Abstract

In this study, we suggest proceeding to an experimental study concerning the synthesis of new organo metallic product xanthate (KIBX) by intermittent method and their use in the processes of sulphides flotation.

The adsorption of potassium isobutyl xanthate (KIBX $3 \cdot 10^{-3} M$) on sphalerite has been studied using electrochemical potential, FTIR technique and SEM. Non activated minerals and minerals activated with copper sulfate ($10^{-4} M$) and copper nitrate ($10^{-4} M$) have been investigated at pH 7.5. Surface species have been identified by FTIR and correlated with SEM. After copper sulfate activation, copper xanthate exists on all of the minerals studied.

Neutral pH is the most suitable for potassium isobutyl xanthate adsorption on sphalerite.

Keywords: *Flotation, Adsorption, Xanthate (KIBX), Sphalerite*

1. Introduction

Although copper sulfate was used as an activator many years before xanthate was adopted to flotation, it is believed that copper activation of galena was accidentally introduced to galena flotation in 1914 (Ralston, et al, 1930).

Since then, numerous experiments have been conducted to study the activation process and the subsequent xanthate adsorption in order to achieve better selectivity and recovery in galena flotation.

The past eight decades has seen significant improvement on galena flotation thanks to better understanding of the activation and xanthate adsorption process.

It is generally accepted today that galena floats poorly with short chain xanthate collectors. This was clearly established by Gaudin in 1930, who resolved earlier uncertainty by his demonstration that with pure unactivated galena no recovery was obtained with ethyl xanthate, a moderate recovery with amyl xanthate, and complete

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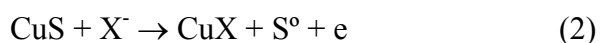
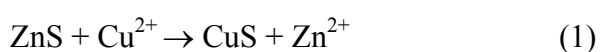
recovery with hexyl xanthate. Similarly, Wark and Cox (1934) were able to measure the critical pH values for galena flotation with amyl xanthate but not with ethyl xanthate. There are several explanations for the relatively weak interaction between galena and short chain xanthate.

Some suggested that zinc xanthate is so soluble that it would dissolve from the mineral surface, while others suggested that the high band gap of galena makes it kinetically inert towards the adsorption of anions such as xanthate. Maust and Richardson (1976) proposed that the electron-to-hole ratio at the surface is too high to permit the lower xanthates to chemisorb.

Due to the reasons described above, an activation process is required prior to the flotation via Reaction (1).

The activation product (CuS-like species) can then react with xanthate to form insoluble copper xanthate species through an electrochemical reaction such as Reaction (2).

The insoluble CuX species will render the mineral surface hydrophobic.



The interaction between collectors and surfaces plays an important role and the understanding of the interaction mechanisms of different reagents with mineral surface is significant in achieving selective flotation.

It is now widely accepted that there are two separate mechanisms by which collectors

adsorb on sulphide minerals. Firstly, there is the chemisorptions mechanism where the adsorbed xanthate molecule forms a chemical bond with metal atoms at the sulphide surface. The other mechanism is electrochemical, and involves the electrochemical oxidation of the adsorbed collector molecules to give Oxidation product species, which renders the sulphide surface hydrophobic.

Much of the research was focused on the action of hydrophobic xanthate type surfactants on sulphide minerals. Different possibilities have been suggested in literature to explain how xanthates can render the surface of minerals hydrophobic.

Sphalerite (ZnS) is a major source of zinc metal. It usually coexists with other sulfide minerals such as chalcopyrite, galena and pyrite. Its beneficiation is accomplished by adsorption using short-chain thiol collectors such as xanthate.

Separation of minerals from ores is a very important industrial process. The most commonly applied separation method is flotation, which ensures the required relation between the hydrophobic and hydrophilic properties on the surface of the mineral particles [1].

Distinct progress in identifying the structure of the surface products formed on the mineral surface after the sorption of the collector has been achieved with the aid of electrochemical methods, especially potential control, correlated with scanning electron micrograph (SEM) [10].

The effect of potential on copper activation and the mechanism of the xanthate adsorption on sphalerite at neutral pH were studied using electrochemical and controlled

potential measurement techniques.

In the present investigation, the adsorption pattern with various amounts of anionic collectors (KIBX) on pure sphalerite surfaces was verified using electrochemical processes and SEM studies. According to Hintikka and Leppinen (1990) selective flotation of sulfide minerals can be achieved by potential control.

2. Experimental

2-1. Materials and reagents

The sphalerite sample was obtained from the Chaabet Elhamra mine, Algeria. The elemental composition of sphalerite is shown in Table 1.

Table 1. Chemical analysis of sphalerite from Cheabet Elhamra mine.

Mineral	Chemical Elements Present (wt. %)			
	Zn	S	Fe	Cu
Sphalerite	41.64	39.38	13.71	0.14

The sphalerite sample was crushed and the selected grains ground in an agate mortar. The sphalerite fraction of -208+108 μ m was used in adsorption tests. The final grinding product (- 208 +108 μ m) was used for the SEM microscopy examination. The pH was adjusted using HCl (10^{-1} M) and NaOH (10^{-1} M). Potassium isobutyl xanthate (KIBX) solution was prepared by dissolving the chemical grade KIBX collector in purified water. The purification of xanthate includes dissolving commercial grade xanthate in acetone and its crystallization (KIBX were stirred for about 2 hours in acetone 50ml, the recrystallized solid was filtered off and washed with a few ml of dry ether). Copper nitrate and copper sulfate were used to

introduce copper ions during the conditioning time. Sphalerite was activated by copper at a neutral pH).

2-2. Methods

Mineral suspensions of 4g sphalerite 0.444 mm in size [9] in 100 cm³ of the solution were conditioned at pH 7.5 for 5 min after each reagent addition in the presence of various activators. One hundred cm³ of copper sulfate (10^{-4} M) and copper nitrate (10^{-4} M) were used in potassium isobutyl xanthate (KIBX 3.10^{-3} M). This was conditioned in distilled water for 15 min at pH 7.5 and then electrophoretic mobility was measured. Electrochemical study was conducted using carbon matrix composite (CMC) electrode. Conditioned in copper solution at pH 7.5, pH was regulated with NaOH (10^{-1} M) and HCl (10^{-1} M).

The scanning electron micrograph (SEM) type JSM-6390 is a high-performance device with a resolution of 3.0 nm. The customized GUI interface allows the instrument to be intuitively operated, and Smile Shot™ software ensures optimum operation settings. The JSM-6390 specimen chamber can accommodate a specimen of up to 152 mm in diameter. Standard automated features include auto focus/auto stigmator, autogun (saturation, bias and alignment), and automatic contrast and brightness.

FT-IR measurements were recorded on a SHIMADZU 8400S FTIR spectrometer in the region of 400-4000 Cm⁻¹ supplied with OMNIC software. The tablets were prepared by grinding 2mg of the solid sample with 50 mg of KBr. Before every analysis, the background was collected and subtracted

from the spectrum of the sample. Two hundred scans at a resolution of 4 Cm^{-1} were recorded for each sample.

Several surface sensitive techniques, capable of analyzing the first few atomic layers of the mineral surface have been used for more than ten years in a variety of studies related to the mechanisms of oxidation and adsorption in sulfide mineral flotation. The significance of these techniques is that they provide not only a compositional analysis of the surface but also information on chemical states (oxidation, bonding) and spatial distribution of adsorbed species on individual particles and complex mixtures of minerals as a function of depth through the surface layers (Amira 1992, 1994; Smart 1991).

3. Results and discussion

3-1. Studies of activation of sphalerite by copper

Rest potential measurement

Figs. 1 and 2 show the rest potential measurements of the sphalerite in a 10^{-4} M CuSO_4 and in 10^{-4} M $\text{Cu}(\text{NO}_3)_2$ solution at pH 7.5 as a function of the activating time. It can be seen that the rest potential of the sphalerite increases sharply upon addition of the copper solution, indicating that a new phase (copper (II) sulfide) is formed on the surface of sphalerite. The potential reaches a plateau value of 23 mV (Fig. 1) and 45mV (Fig. 2) after approximately 30 minutes; the new phase (activation product) is probably CuS.

The initial positive potential can be attributed to the adsorption of $\text{Cu}(\text{OH})^+$ on ZnS surface. Some $\text{Cu}(\text{OH})^+$ is transferred into CuS via reaction:

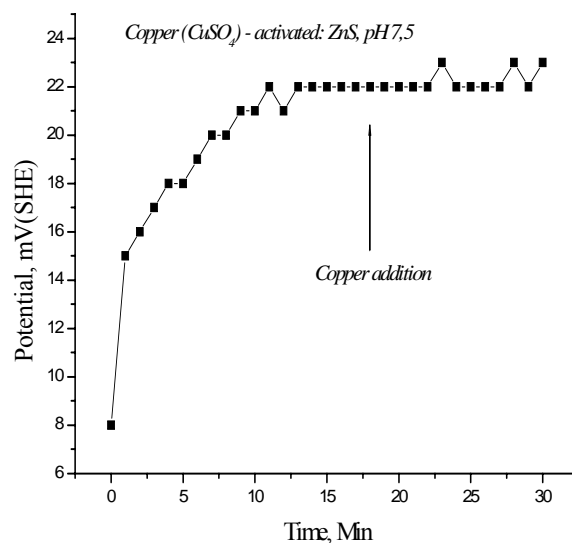


Figure 1. Rest potential measurement of sphalerite in a 10^{-4} M CuSO_4 solution at pH 7.5.

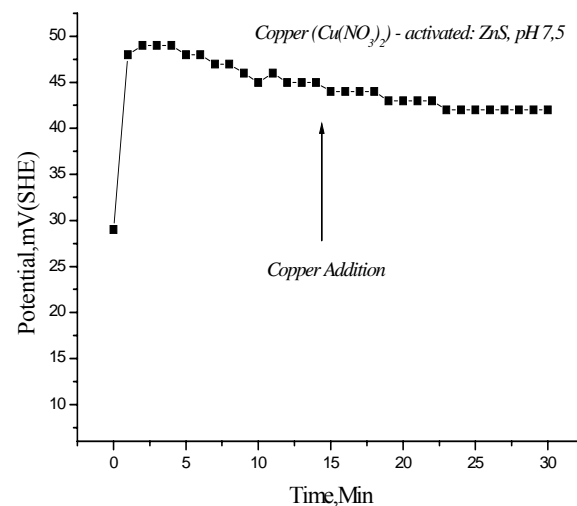


Figure 2. Rest potential measurement of sphalerite in a 10^{-4} M $\text{Cu}(\text{NO}_3)_2$ solution at pH 7.5.

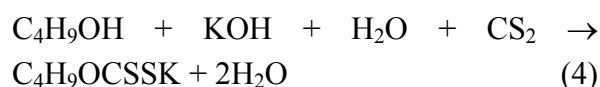


3-2. Xanthate KIBX adsorption on copper-activated sphalerite

3-2-1. Synthesis of potassium iso butyl xanthate (KIBX) by the discontinuous method

During the intermittent method, in the basic solution of alcohol, consisting of 0.5 mole of

isobutylique alcohol, 0.5 mole of water, 0.5 mole of potassium hydroxide and 0.5 mole of disulfure of carbon (CS_2) were slowly added. After that, we separated the deposit of xanthate, which, after addition of all the portions of disulfure of carbon represents constitutently formed crystals. This method achieves high quality xanthates, obtained using Eq. (4). (Superior activity of xanthate is 90 %).



Results of sphalerite surface oxidation to form hydrophobic and hydrophilic species depends strongly on potential. The rest potential measurement of sphalerite activated with $\text{CuSO}_4 10^{-4}\text{M}$ and $\text{Cu}(\text{NO}_3)_2 10^{-4}\text{M}$ in $3 \cdot 10^{-3}\text{M}$ KIBX at pH 7.5 is shown in Figs. 3 and 4.

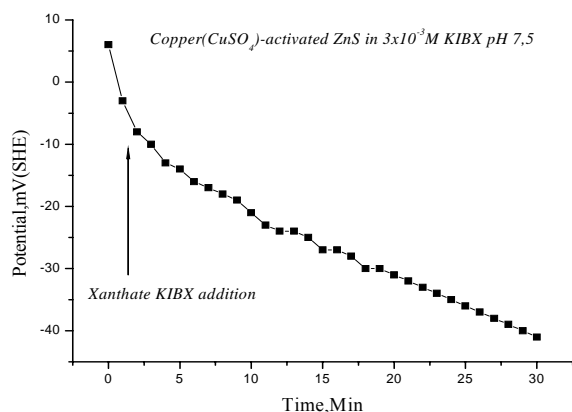


Figure 3. Rest potential measurement of the sphalerite activated with $\text{CuSO}_4 10^{-4}\text{M}$ in $3 \cdot 10^{-3}\text{M}$ KIBX solution at pH 7.5.

Addition of $3 \cdot 10^{-3}\text{M}$ KIBX at pH 7.5 does not increase the recovery of sphalerite in the absence of copper ions. The rest potential measurement changes to -15mV (Fig. 5).

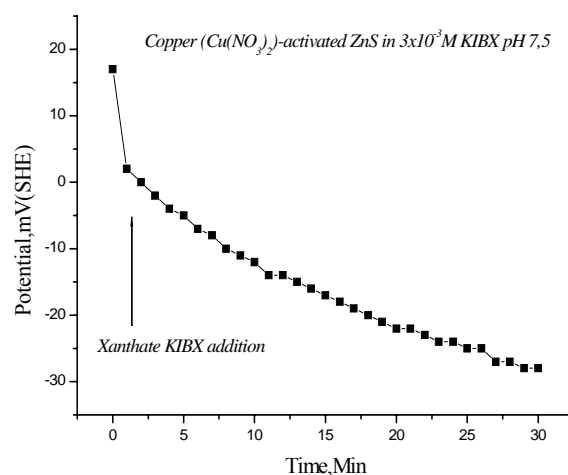


Figure 4. Rest potential measurement of the sphalerite activated with $\text{Cu}(\text{NO}_3)_2 10^{-4}\text{M}$ in $3 \cdot 10^{-3}\text{M}$ KIBX solution at pH 7.5.

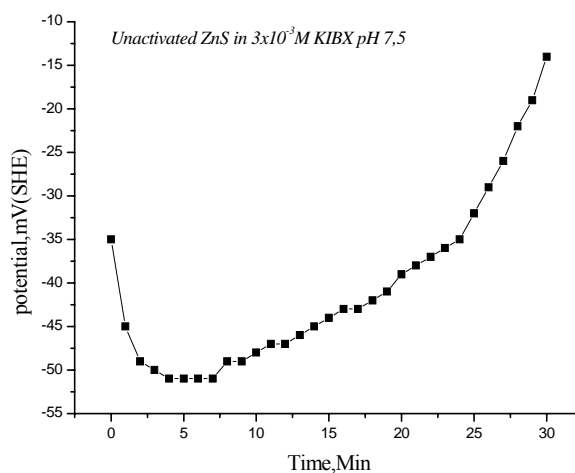


Figure 5. Rest potential measurement of the unactivated sphalerite in $3 \cdot 10^{-3}\text{M}$ KIBX solution at pH 7.5.

As is known, the solubility of Zn-IBX is considerably higher than that of $\text{Zn}(\text{OH})_2$ and therefore xanthate (KIBX) is not adsorbed on sphalerite [6].

Therefore, copper activation is essential for flotation of sphalerite. As is shown in Figs 3 and 4. Sphalerite can easily be activated with copper ions at pH 7.5. Addition of $3 \cdot 10^{-3}\text{M}$ KIBX resulted in formation of strongly

hydrophobic Cu-IBX, and very high adsorption [5].

3-3. Improving xanthate adsorption on copper activated sphalerite using FTIR technique and SEM

3-3-1. Characterization of sphalerite by XRD

According to Fig. 6, the diameters are $d_1=3.116$ and $d_2=1.909$; the angles are $(^\circ 2\theta)_1=28.614$ and $(^\circ 2\theta)_2=47.573$.

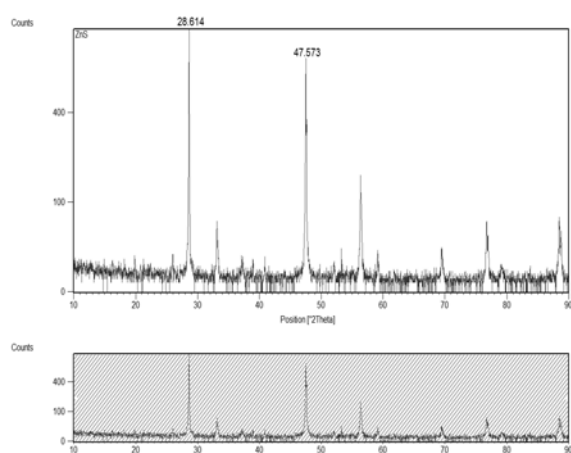


Figure 6. XRD spectra of sphalerite.

3-3-2. Characterization of sphalerite by FTIR

FTIR spectroscopic studies were carried out on sphalerite and potassium isobutyl xanthate (KIBX) samples both before and after adsorption.

Assignments of the various bands and peaks made in this study are in reasonable agreement with those reported in the literature for similar functional groups.

The FTIR spectra (Fig. 7) show the characteristic bands of sphalerite in 610, 1103, 1535 and 1635 cm^{-1} corresponding to the carbonate CO_3^{2-} ion group are active.

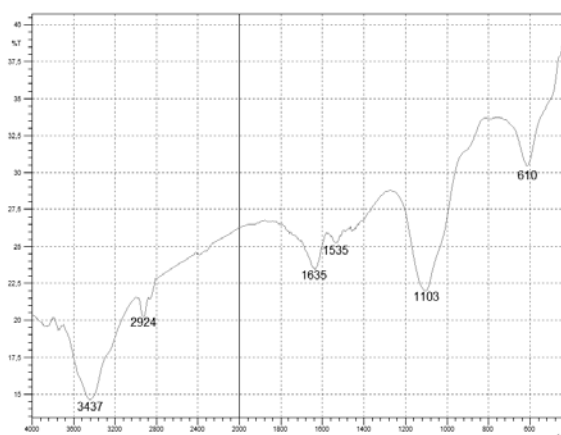


Figure 7. IR spectra of sphalerite.

The strong bands related to the presence of bound water (-OH) stretching are around 3437cm^{-1} .

3-3-3. Characterization of potassium isobutyl xanthate (KIBX) by FTIR

FTIR spectra of potassium isobutyl xanthate (KIBX) (Fig. 8) absorption band at 1009-1144 cm^{-1} is related to (C=S) bands, and two bands at 1384 and 1638 cm^{-1} are assigned to the bending vibration of (O-CS), the band at 2950 cm^{-1} which is characteristic of the hydrocarbon chain and the band at 3450 cm^{-1} which is characteristic of (O-H) stretching [8].

3-3-4 Characterization of sphalerite by SEM

It is well established that all metal sulfide minerals exhibit oxide and hydroxide species on their surface after exposure to air or aqueous solution. They have been observed in studies of sphalerite.

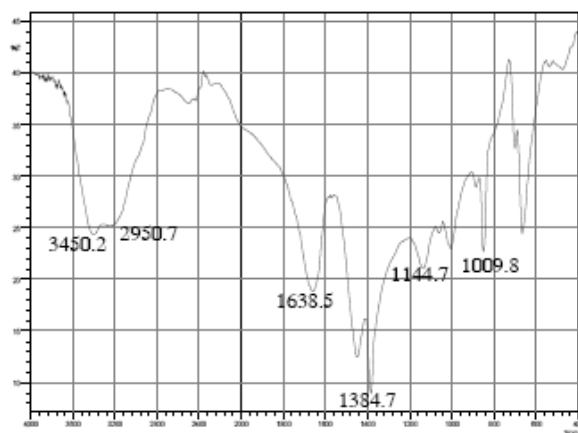


Figure 8. IR spectra of KIBX.

The surface oxidation of galena has been less systematically studied than that of other sulfide minerals but the pattern of reaction appears to be similar. It has been suggested that galena oxidizes considerably more slowly than the other sulfide minerals under these conditions. Further studies of ZnS oxidation using SEM are still required. The physical nature of the oxidized layer formed initially on these surfaces can be seen in Fig. 9 where a sphalerite sample, ground initially in distilled water and allowed to condition for 30 minutes, was reground at that time and examined immediately using high resolution field emission SEM without coating at 15 KV, 5 μ m.

3-3-5. Characterization of potassium isobutyl xanthate (KIBX) by XRD

According to Fig. 9, the diameters are $d_1=3.0008$ and $d_2 = 2.9697$; and the angles $(^\circ 2\theta)_1= 29.749$ and $(^\circ 2\theta)_2 = 54.949$.

3-4. Studies of potassium isobutyl xanthate (KIBX) adsorption on copper activated sphalerite using FTIR technique and SEM

The characteristics and operating condition

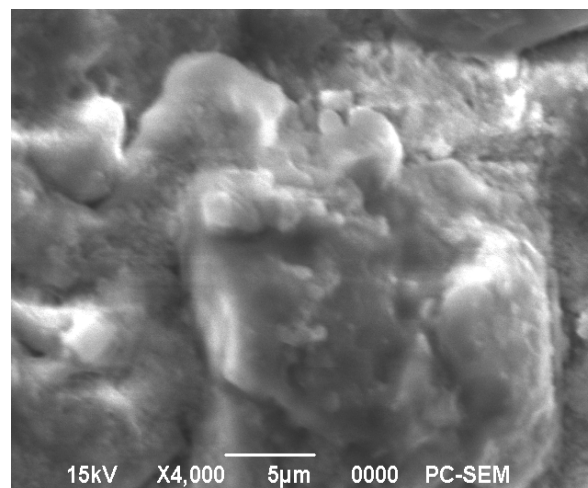


Figure 9. SEM of KIBX.

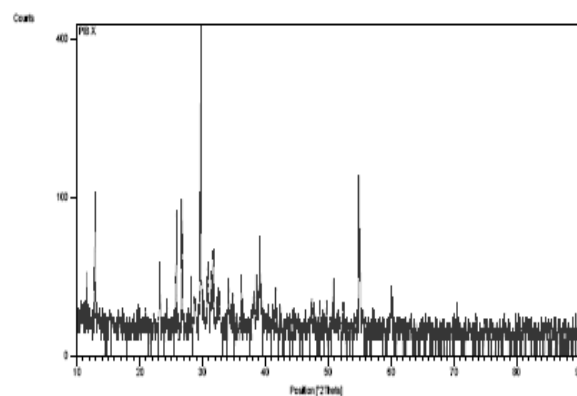


Figure 10. XRD spectra of KIBX synthesized.

of the SEM technique have been fully described in other publications (Smart 1991; O'Connor 1992; Chryssoulis 1994). It is well established that all metal sulfide minerals exhibit oxide and hydroxide species on their surface after exposure to air or aqueous solution. They have been observed in studies of sphalerite (2,12). The surface oxidation of sphalerite has been less systematically studied than those of other sulfide minerals but the pattern of reaction appears to be similar. It has been suggested that sphalerite oxidizes considerably more slowly than the other sulfide minerals under these conditions

[2]. Further studies of ZnS oxidation using SEM are still required. The physical nature of the oxidized layer formed initially on these surfaces can be seen in Figs. 11 and 12 where a sphalerite sample, ground initially in distilled water and allowed to condition for 30 minutes, was reground at that time and examined immediately using high resolution field emission SEM without coating at 15 KV.

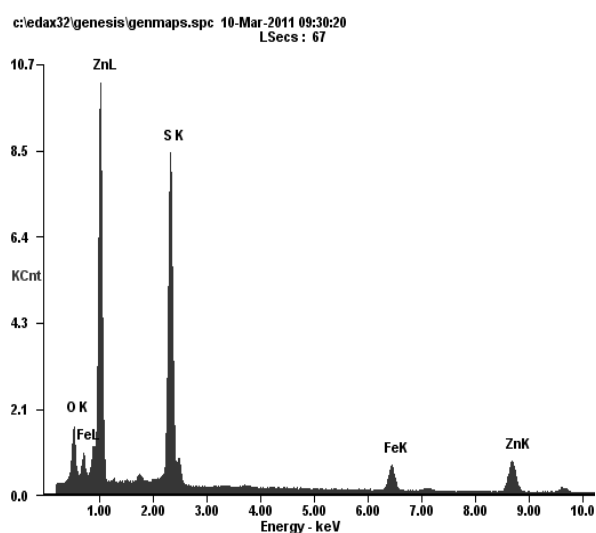
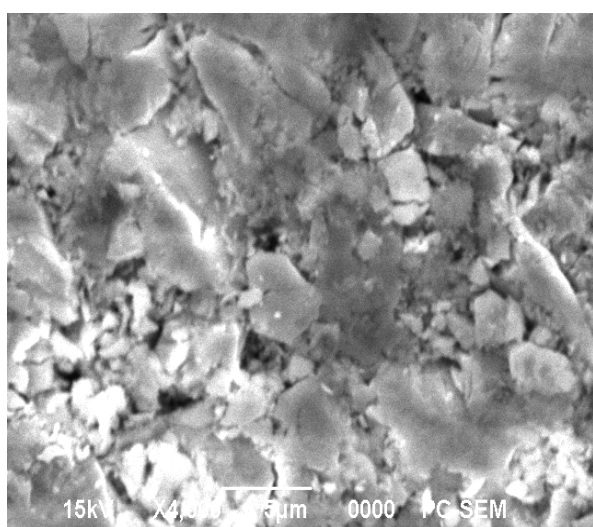


Figure 11. Field emission scanning electron micrograph of ground sphalerite surface activated by copper sulfate 10^{-4} M treated with KIBX $3 \cdot 10^{-3}$ M at pH 7.5 conditioned in water for 30 min.

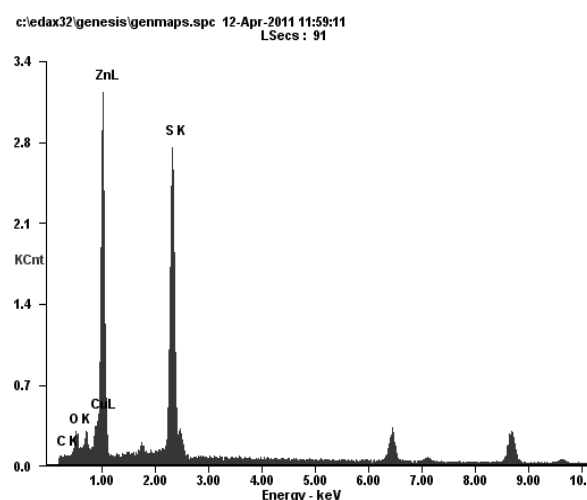
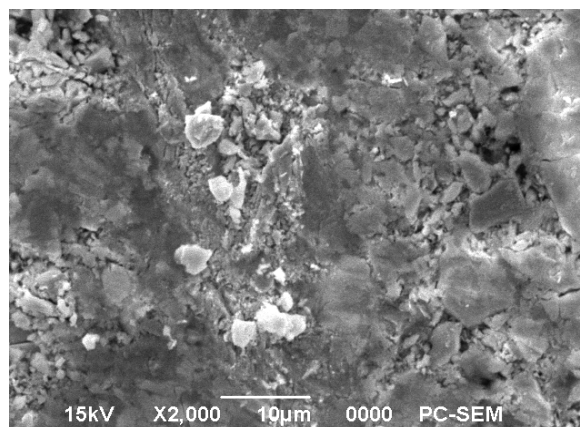
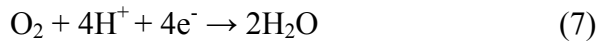


Figure 12. Field emission scanning electron micrograph of ground sphalerite surface activated by copper nitrate 10^{-4} M treated with KIBX $3 \cdot 10^{-3}$ M at pH 7.5 conditioned in water for 30 min.

Figs. 11 and 12 display SEM of typical sphalerite particle surface after pH 7.5 oxidation for 30 min in the presence of KIBX. There appears to be evidence of the colloidal precipitates observed before copper sulfate and copper nitrate are present.

Selective flotation of sulfide minerals is normally carried out using thiol-based collectors including xanthate (Potassium isobutyl xanthate, KIBX). The mechanism [13] is:





The expectation is that any of these species (IBX_{ads} , ZnIBX_2 , S^0 , IBX_2) constitutes entities contributing to the hydrophobicity of the surface. On copper-activated sphalerite surfaces [12] at low copper (II) additions and high affinity adsorption behavior, copper (I) isobutyl xanthate is the predominant surface species. The rate and extent of isobutyl xanthate adsorption are, however, decreased by extended conditioning periods apparently due to penetration of copper ions into the zinc sulfide lattice confirmed by SEM.

Time dependence of KIBX adsorption is then related to the subsequent back diffusion to the sphalerite aqueous solution interface. At high copper sulfate or copper nitrate (10^{-4} M) addition at pH 7.5, both dixanthogen and copper (I) isobutyl xanthate are detected on the sphalerite surface.

The infrared bands observed in Figs. (13a, 13b) at 1093.6 cm^{-1} and 1019.6 cm^{-1} are characteristic of (Zn-IBX) and 1264.9 cm^{-1} and 1273.3 cm^{-1} are characteristic of dixanthogene (IBX_2) forms oxidized with the molecule of isobutyl xanthate).

4. Conclusions

1. The potassium isobutyl xanthate (KIBX) has good collector ability on a sulphide mineral sphalerite.
2. Oxidation of sphalerite at potential of +23 mV forms CuS and Cu_2S product on sphalerite in water for 30 min.

3. Addition of KIBX at pH 7.5 conditioned in water for 30 min inactivated sphalerite and did not increase the recovery of sphalerite in the absence of copper ions but no evidence of the colloidal precipitates was observed before potassium isobutyl xanthate is present.

4. The FTIR spectra revealed the presence of copper on the surface of sphalerite and this is confirmed by the adsorption of KIBX onto surface:

(Zn-BIX, 1093.6 cm^{-1} 1019.66 cm^{-1} , (IBX_2), $1294.6.56 \text{ cm}^{-1}$ 1273.36 cm^{-1}).

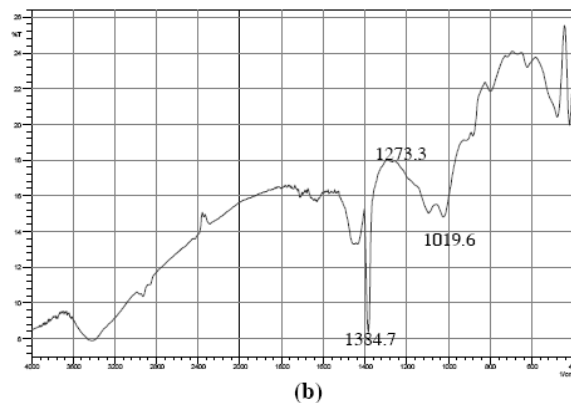
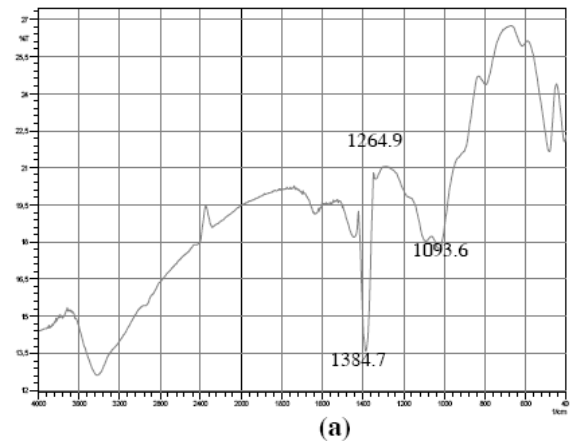


Figure 13. IR spectra of sphalerite activated by copper sulfate 10^{-4} M(a) and copper nitrate 10^{-4} M(b) treated with KIBX $3 \cdot 10^{-3}$ M at pH 7.5 conditioned in water for 30 min.

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