

## Study of Xanthane (KAX) Adsorption on Galena : Separation by Flotation

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**Abstract:** The adsorption of anionic collectors (xanthate) on the surface of galena was studied using diffuse reflectance FTIR (DRIFT) and scanning electron micrograph (SEM) techniques. The effect of sulphite interaction with galena on the mechanism of potassium amyl xanthate (KAX) adsorption onto galena surfaces has been studied in situ using electrochemical potential, FTIR spectra and SEM have been used to identify the mechanism of interaction between sulphite and galena surfaces.

Activated galena with copper sulfate ( $10^{-4}$ M) has been investigated at pH 9.5 and potassium amyl xanthate ( $3 \cdot 10^{-2}$ M) concentration.

Potential ( $E_{opt}(PbS) = +55mV$ ); Adsorbed colloidal (Pb-AX,  $1109-1384Cm^{-1}$ ) is found even at high xanthate concentration, colloidal lead oxide/hydroxide particles have been imaged after  $10^{-4}$ M lead sulfate addition at pH 9.5.

The behaviour of this system is consistent with ion exchange between xanthate and hydroxide followed by oxidation to dixanthogen ( $X_2$ ,  $1276Cm^{-1}$ ) and diffusion of this species across the surface.

**Key words:** Galena, Xanthate (KAX), Adsorption, SEM, FTIR.

### Introduction

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

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 hydrophobic the surface of minerals G.W. Poling *et al.* (1963), M.C. Fuerstenau *et al.* (1982), J. Leppinen *et al.* (1995), N.P Finkelstain *et al.* (1997), and E. Mielezarski *et al.* (2003).

A 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 the spectroscopic methods, especially infrared (IR) spectroscopy correlated with scanning electron micrograph (SEM). Z. Nedjar *et al.* (2009).

The most commonly used thiol collectors are xanthates, which are alkali metal (e.g.  $Na^+, K^+$ ) salts of mono alkyl esters of dithiocarbonic acid (e.g. Potassium amyl xanthate :  $C_5H_{11}OCS_2K$ ). They are used as flotation agents in the recovery of metal sulphids (e.g. MeS: PbS galena). P.J. Harris *et al.* (1988).

The efficiency of xanthates as mineral collectors increases with the length of the carbon chain but results in a decrease in the selective flotation of minerals.

The activating effect of sodium sulphide is strongly time dependent. An increase in sulphidisation leads to an increase in the hydrophobicity of the mineral surface. Excess of copper sulfate acts as a depressant for oxidized lead and metal minerals because the adsorption of divalent sulphide ion on the surface of lead oxide minerals increases the negative charge which prevents the adsorption of collector. SEM and FTIR have been found to be useful techniques for elucidating the surface properties of solids, which may be relevant in applied aspects of mineral processing G.Ozbayoglu *et al.* (1994).

In the present investigation, the adsorption behavior effects of various amounts of anionic collectors on pure galena surfaces was verified using diffuse reflectance FT-IR, SEM and electrochemical potential studies.

## Experimental

### Materials and reagents

The galena sample was obtained from the Cheabet Elhamra mine, Algeria. The elemental composition of galena, see [Table 1].

**Table 1.** Chemical analysis of galena from Cheabet Elhamra mine

Mineral	Chemical elements present (wt. %)			
	<i>Pb</i>	<i>S</i>	<i>Fe</i>	<i>Cu</i>
Galena	83.32	9.97	2.39	0.74

The galena sample was crushed and the selected grains ground in an agate mortar. The galena fraction of -208+108 $\mu$ m was used in adsorption tests. The final grinding product (- 208 +108 $\mu$ m) was used for the SEM microscopy examination. The pH was adjusted using HCl and NaOH. Potassium amyl xanthate (KAX) solution prepared by dissolving the chemical grade KAX collector in purified water. The purification of xanthate includes dissolving commercial grade xanthate in acetone and its crystallization. Copper sulfate was used to introduce copper ions during the conditioning time. Galena was activated by copper at pH basic).

### Methods

Mineral suspensions of 3g galena 0.37 mm in size Z. Nedjar *et al* (1994). in 100 cm<sup>3</sup> of the solution were conditioned at the desired pH for 5 min after each reagent addition in the presence of various activators. 100 cm<sup>3</sup> of copper sulfate (10<sup>-4</sup> M) were used in potassium amyl xanthate (KAX 3.10<sup>-2</sup> M). It was conditioned in distilled water for 10 min at pH 9.5 and then electrophoretic mobility was measured. Electrochemical study was conducted using carbon matrix composite (CMC) electrode. Conditioned in copper solution at pH 9.5, pH was regulated with NaOH (10<sup>-1</sup> M) and HCl (10<sup>-1</sup>M).

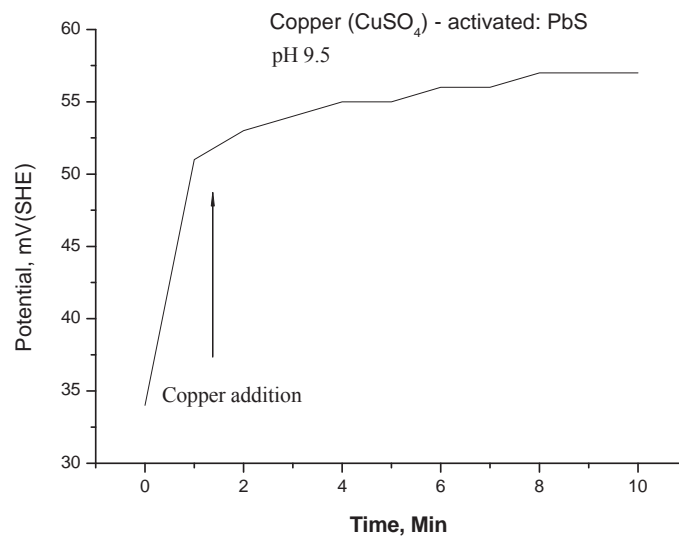
The scanning electron micrograph (SEM) type JSM-6390 is a high-performance device with a resolution of 3.0 nm. The customized GUI interface allows the instrument to be intuitively operated, and Smile Shot™ software ensures optimum operation settings. The JSM-6390 specimen chamber can accommodate a specimen 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<sup>-1</sup> 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<sup>-1</sup> were recorded for each sample.

## Results and discussion

### Studies of activation of galena by copper

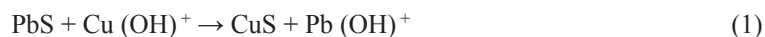
#### Rest Potential Measurement



**Fig. 1.** Rest potential measurement of galena in a  $10^{-4}$  M  $\text{CuSO}_4$  solution at pH 9.5

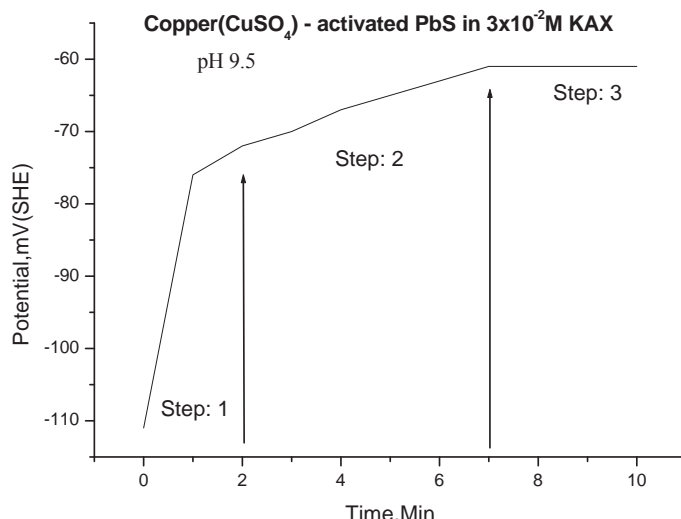
Figure 1 show the rest potential measurements of the galena in a  $10^{-4}$  M  $\text{CuSO}_4$  solution at pH 9.5 as a function of the activating time. It can be seen that the rest potential of the galena increases sharply upon the addition the copper solution, indicating that a new phase (copper (II) sulfide) is formed on the surface of galena. The potential reaches a plateau value of +55 mV; see [Figure 1], after approximately 10 minutes. The new phase (activation product) is probably  $\text{CuS}$ .

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



#### **Xanthate adsorption on copper-activated galena**

The interaction between collectors and surfaces plays an important role in understanding of interaction mechanisms of different reagents with the mineral surface. It is now widely accepted that there are two separate mechanisms by which collectors adsorb on the sulfide minerals. Firstly, there is the chemisorption mechanism where the adsorbed xanthate molecule forms chemical bond with metal atoms (Pb) at the sulfide ( $\text{PbS}$ ) surface. The other mechanism is electrochemical and involves electrochemical oxidation of the adsorbed collector molecules to give oxidation product species, which renders the galena surface hydrophobic J.D. Miller *et al* (1999). Results of galena surface oxidation to form hydrophobic and hydrophilic species depends strongly on potential. The rest potential measurement of galena activated with  $\text{CuSO}_4 10^{-4}\text{M}$  in  $3 \cdot 10^{-2}\text{M}$  KAX at pH 9.5 are shown in Fig.2.

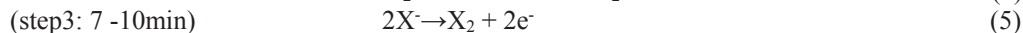
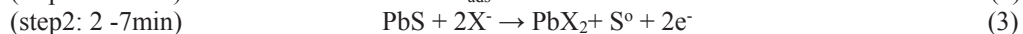
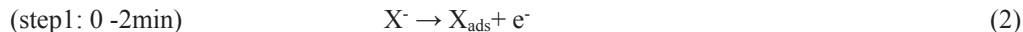


**Fig. 2.** Rest potential measurement of the galena activated with  $\text{CuSO}_4$   $10^{-4}\text{M}$  in  $3 \cdot 10^{-2}\text{M}$  KAX solution at pH 9.5

The rest potential measurement changes from: -111 mV to -61mV see [Figure 2].

As is known the solubility of  $\text{Pb-AX}$  ( $K_s = 1.20 \cdot 10^{-11}$ ) is considerably higher than that of  $\text{Pb(OH)}_2$  ( $K_s = 1.35 \cdot 10^{-19}$ ) and therefore xanthate (KAX) is not adsorbed on sphalerite S.L. Chryssoulis *et al* (1994). Therefore, copper activation is essential for flotation of galena. As is shown in Fig 2 galena can easily be activated with copper ions at pH 9.5. Addition of  $3 \cdot 10^{-2}\text{M}$  KAX resulted in formation of strongly hydrophobic  $\text{CuAX}$ , and very high adsorption R. Woods *et al* (1976).

The mechanism is:

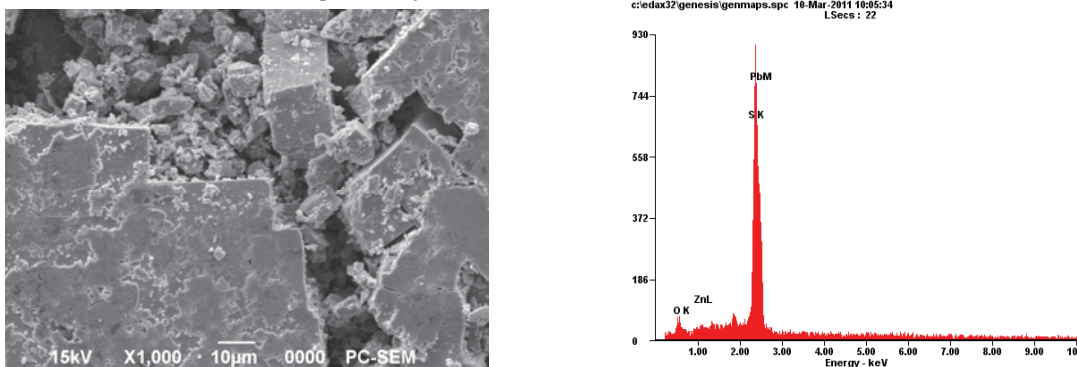


The expectation is that any of these species ( $\text{X}_{\text{ads}}$ ,  $\text{PbX}_2$ ,  $\text{S}^0$ ,  $\text{X}_2$ ) constitutes entities contributing to the hydrophobicity of the surface.

**Studies of xanthate (KAX) adsorption on copper activated galena using FTIR technique and SEM: Characterization of pure galena and xanthate (KAX) using FTIR technique and SEM**

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 *et al* (1992).

• Characterization of galena by SEM:

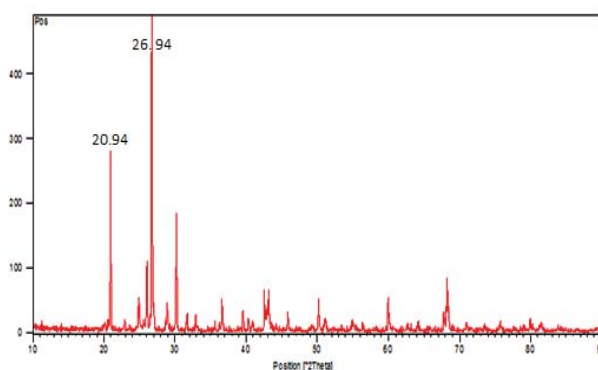


**Fig.3.** Field emission scanning electron micrograph of ground galena surface.

The characteristics and operating condition of the SEM technique have been fully described in other publications. 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 galena. The surface oxidation of galena 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 galena oxidizes considerably more slowly than the other sulfide minerals under these conditions. Further studies of PbS oxidation using SEM are still required. The physical nature of the oxidized layer formed initially on these surfaces can be seen in see [Figure 3], where a galena sample, ground initially in distilled water and allowed to condition for 10 minutes, was reground at that time and examined immediately using high resolution field emission SEM without coating at 15 KV.

**Characterization of galena by RX**

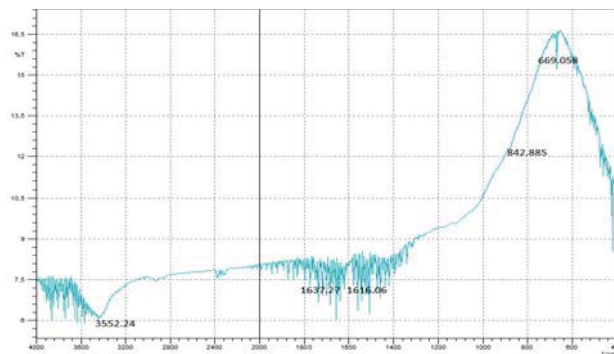
This method is used to identify the nature and structure of the crystallized products. See [Figure 4]. There is the diameter  $d_1=3.31$  and  $d_2=4.23$ ; the angle  $(^\circ 2\theta)_1=26.94$  and  $(^\circ 2\theta)_2=20.94$ .



**Fig.4.** RX spectra of galena

**Characterization of galena by FTIR**

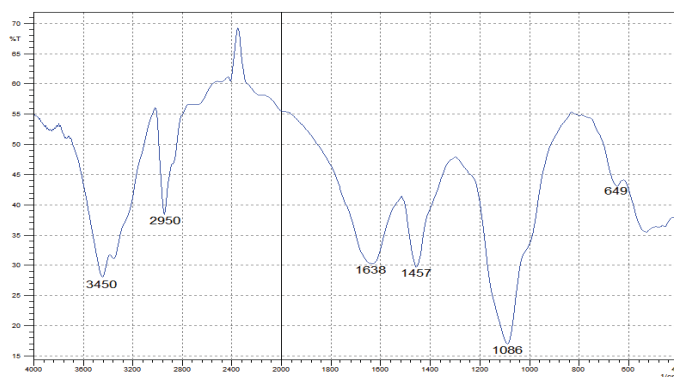
FTIR spectroscopic studies were carried out on galena samples both before and after adsorption. The assignments of the various bands and peaks made in this study are in reasonable agreement with those reported in the literature for similar functional groups. The FTIR spectra see [Figure 5]. A show the characteristic bands of galena in 669.058-842.885 $\text{Cm}^{-1}$  and 1616.06-1637.27  $\text{Cm}^{-1}$  corresponding to the carbonate  $\text{CO}_3^{2-}$  ion group are found to be active. The strong bands related to the presence of bound water (-OH) stretching is around 3552.24 $\text{Cm}^{-1}$ .



**Fig.5.** IR spectra of galena

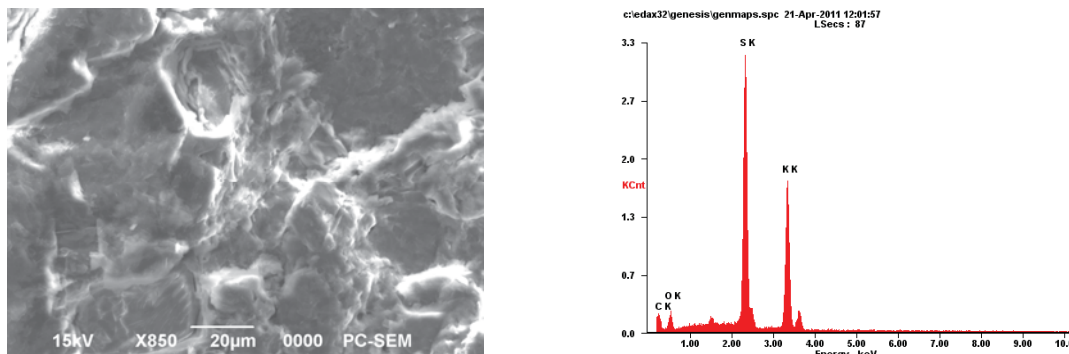
**Characterization of potassium amyl xanthate (KAX) by FTIR:**

The FTIR spectra of potassium amyl xanthate (KAX), see [Figure 6], the absorption band at 1080  $\text{Cm}^{-1}$  is related to (C=S) bands and two bands at 1457 and 1638  $\text{Cm}^{-1}$  is assigned to the bending vibration of (O-CS), the band at 2950  $\text{Cm}^{-1}$  which are characteristic of the hydrocarbon chain, the band at 3450  $\text{Cm}^{-1}$  is characteristic of (O-H) stretching S.L. Chryssoulis *et al* (1994).



**Fig.6.** IR spectra of KAX

**Characterization of potassium amyl xanthate (KAX) by SEM:**

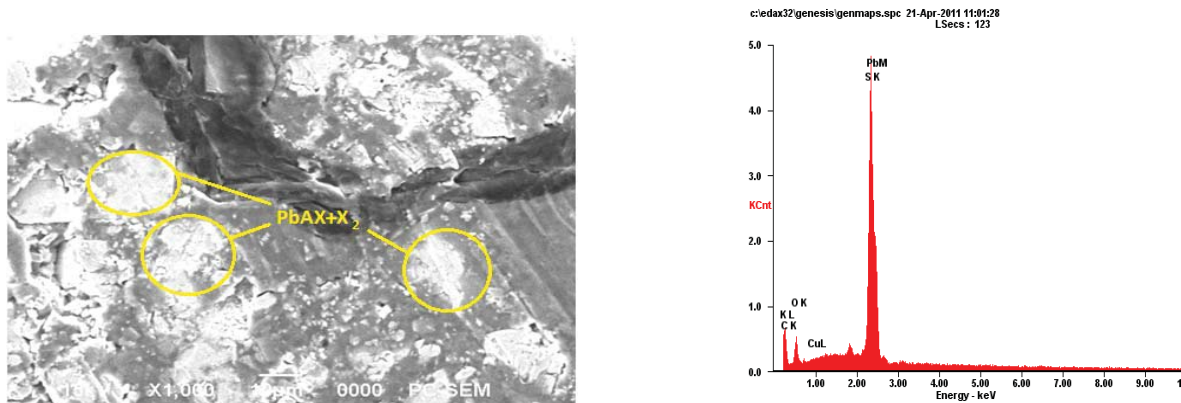


**Fig.7.** Field emission scanning electron micrograph of ground xanthate KAX surface

The characteristics and operating condition of the SEM technique have been fully described in other publications. It is well established that all xanthate KAX exhibit oxide and hydroxide species on their surface after exposure to air or aqueous solution. They have been observed in studies of xanthate (KAX) see [Figure7].

**Improving of xanthate adsorption on galena**

On copper-activated galena surfaces C.A Prestidje *et al* (1994), at low copper (II) additions and high affinity adsorption behavior, copper (I) amyl xanthate is the predominant surface species. The rate and extent of amyl xanthate adsorption are, however, decreased by extended conditioning periods apparently due to penetration of copper ions into the plomb sulfide lattice confirmed by SEM. Time dependence of  $3 \cdot 10^{-2}$  M KAX adsorption is then related to the subsequent back diffusion to the galena aqueous solution interface. At high copper sulfate ( $10^{-4}$  M) addition at pH 9.5, both dixanthogen and copper (I) amyl xanthate are detected on the galena surface.

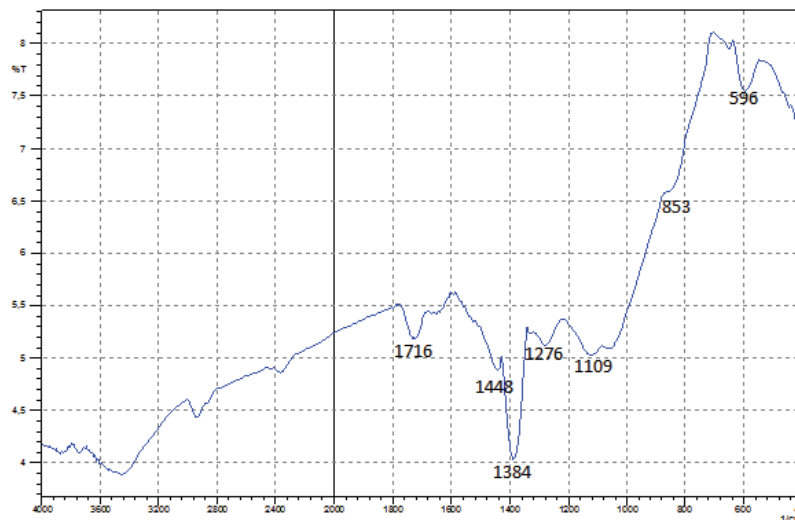


**Fig.8.** Field emission scanning electron micrograph of ground galena surface activated by copper sulfate  $10^{-4}$  M treated with KAX  $3 \cdot 10^{-2}$  M at pH 9.5 conditioned in water for 10 min

**Table 2.** Chemical analysis of galena activated by copper sulfate  $10^{-4}$  M treated with KAX  $3 \cdot 10^{-2}$  M at pH 9.5 conditioned in water for 10 min. (At: Atomic Percent, Wt: Weight Percent)

Elements	C	O	Cu	S	Pb
Wt. %	00.00	04.37	00.21	19.51	75.91
At %	00.00	21.82	00.27	48.63	29.28

Figure 8 display SEM of typical galena particle surface after pH 9.5 oxidation for 10 min in the presence of  $3 \cdot 10^{-2}$  M KAX. There appears to be evidence of the colloidal precipitates observed before copper sulfate and copper nitrate is present. The surface compositional information, see [Table 2]. (wt. Cu: 00.21 %).



**Fig.9.** IR spectra of galena activated by copper sulfate  $10^{-4}$  M treated with KAX  $3 \cdot 10^{-2}$  M at pH 9.5 conditioned in water for 10 min.

The infrared bands observed see [Figure 9], at  $1109\text{Cm}^{-1}$  are characteristic of (Pb-AX) and  $1276\text{Cm}^{-1}$  are characteristic of dixanthogene ( $\text{X}_2$  forms oxidized with the molecule of amyl xanthate) Z. Nedjar *et al* (2011).

**Conclusions**

1. The potassium amyl xanthate (KAX) has good collector ability on a sulphide mineral galena.
2. Activation of galena at lower potentials increases the copper uptake by the mineral.
3. Oxidation of galena at potential of +55 mV forms CuS product on galena in water for 10 min.
4. Using the SEM technique action of  $3 \cdot 10^{-2}$  M potassium amyl xanthate has been identified (adsorption to specific surface sites and colloidal precipitation from solution)
5. The FTIR spectra revealed the presence of copper on the surface of galena and this is confirmed the adsorption of KAX onto surface (Pb-AX,  $1109\text{-}1384\text{Cm}^{-1}$ ,  $\text{X}_2$ ,  $1276\text{Cm}^{-1}$ ).

It is suggested that copper cations exchange with those of plomb during copper activation of galena.

This study is ongoing and the results obtained will be discussed in a future work.



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