

## ORIGINAL RESEARCH ARTICLE

# Thermodynamic stability diagram of the copper/water/amyloxanthate flotation system

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### ABSTRACT

The purpose of this work was to obtain the thermodynamic stability diagram that characterizes the copper/water/amyloxanthate flotation system, as part of the theoretical foundation necessary for the analysis of the copper ion flotation process with the flotation collector reagent potassium amyloxanthate. From the system of fundamental chemical reactions and with the help of the Medusa software, the Eh-pH diagram was obtained, in which the stability zones of the different chemical species are defined and it is established that in the pH range from 4 to 13, the xanthogenic species of copper(I) and (II) coexist, whose ratio decreases with the increase of pH.

**Keywords:** Eh-pH Diagram; Xanthate; Copper Amyloxanthate; Copper; Ionic Flotation

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## 1. Introduction

O-alkyldithiocarbonate reagents, known as xanthates, are compounds of heteropolar molecular structure, with a non-polar carbon chain and a polar sulfhydryl (-SH) group<sup>[1,2]</sup>. They are used as collectors in the flotation of sulfide minerals<sup>[3,4]</sup>, mainly ethylxanthate<sup>[5-7]</sup>, but their high chemical reactivity with heavy metals<sup>[2,8]</sup> stimulates their use in the treatment of waste solutions.

The results achieved with the application of this technique depend primarily on the pH of the medium. For example, in ionic dissolved air flotation of copper(II), zinc and arsenic(V) ions from synthetic solutions of individual ions and mixtures, sodium ethylxanthate and diethylxanthate are used as collectors<sup>[9,10]</sup>. Copper removal in the pH range between 2.5 and 5.5 is not affected but requires a 10 % excess of collector reagent. These works show satisfactory results. However, for pH below 4.7, partial decomposition of ethylxanthate is verified<sup>[8,11-13]</sup>, and the effect on process efficiency is not mentioned. The use of sodium diethylxanthate as a collector, in spite of exhibiting similar properties and showing good results in the collection of copper and zinc, is limited by the cost of obtaining it<sup>[14]</sup>.

Lazaridis *et al.*<sup>[15]</sup> report the application of the same ethylxanthate flotation technique on copper, iron and nickel systems independently and in their mixtures. The results showed that nickel remains in solution for acidic conditions, while copper and iron species float together and gradually increase their recovery until reaching maximum values from pH 6. If the pH of the system is equal to 2, the recovery values are associated with the initial copper and iron species float together and gradually increase their recovery until reaching maximum values from

pH 6. If the pH of the system is equal to 2, the recovery values are associated with the initial copper concentration; if its magnitude is low, copper recovery is reduced to 50% and iron to 25%, otherwise, about 80% is removed. It is possible that the result is associated with the decomposition of ethylxanthate; its half-life at pH 2.5 is 120 s<sup>[16]</sup>, which coincides with the results achieved during ionic flotation of copper from mine wastewater<sup>[17]</sup>, according to the conditions established by Stalidis *et al.*<sup>[9]</sup> involving high acidity. Favorable results are obtained only when twice the stoichiometric amount of ethylxanthate is used.

The works<sup>[9,15]</sup> on the separation of copper ions with ethylxanthate by flotation show a contradiction regarding the pH value at which optimum recovery values are reached. Stalidis *et al.*<sup>[9]</sup> stated that this result is achieved under acidic conditions, where the process is efficient and independent of pH, while Lazaridis *et al.*<sup>[15]</sup> state that it is only possible to achieve similar results for pH above 6. This indicates that it is necessary to accurately determine the stable zone according to the pH value of copper ions captured by xanthomonas in the flotation process.

The thermodynamic stability diagrams, as a function of pH, are an essential tool in the theoretical analysis of the interactions of a given system. In the case of the copper/sulfur/water/ethylxanthate system in the construction of the Eh-Ph diagram<sup>[18,19]</sup>, copper(I) ethylxanthate was considered to be the initial product of the oxidation of ethylxanthate with calcocite. However, it has been reported<sup>[20]</sup> that such a diagram does not adequately predict the observed flotation behavior, because the limiting value of flotation potential is lower than the expected value in the diagram.

According to Woods *et al.*<sup>[20]</sup>, this discrepancy can be explained by the fact that under these conditions, the formation of chemisorption species requires a lower potential than that required for the formation of copper(I) ethylxanthate. Such species were included by these authors in the construction of new diagrams in the copper/water/ethylxanthate and chalcocite/water/ethylxanthate systems. The predictions made in these diagrams are in corre-

spondence with the critical potential and the upper limit of pH value for the flotation of pyrrhotite, which is related to the upper limit of stability of copper(I) ethylxanthate, determined in both systems by the oxidation of the copper(I) complex to copper(II) oxide and dixanthate.

Although these diagrams are applicable to copper ore flotation, the copper(II) ethylxanthate phase is not considered. It is suggested that there is no evidence that it is a stable phase. However, the half-life of the xanthogenated copper(II) species is known to be 6 h<sup>[21]</sup>, if obtained from amyloxanthate.

Although some works report that the decomposition of the ethylxanthate species in aqueous media occurs in several stages<sup>[8,11,22-24]</sup>, this mechanism is not well known. Proof of this is that the pH ranges of the stability zones for the reported species do not coincide<sup>[25]</sup>. Evidence also shows that the length of the carbon chain of the collectors causes changes in this zone and in the kinetics of their decomposition<sup>[26]</sup>.

With the elements provided it is not possible to predict the reproducibility of the reported diagrams for xanthates that differ in carbon chain length. The reported Eh-pH diagrams do not accurately describe the copper/water/amyloxanthate system under study in the present investigation. Therefore, it is necessary to establish the diagram for this system, which should give a more accurate answer to the behavior of copper species during flotation treatment with potassium amyloxanthate of solutions carrying this species, with respect to the system reported by Hapel and Pomianowski<sup>[27]</sup> for ethylxanthate.

The definition of the stability zone, both of the amyloxanthate ion and of the complexes formed as a function of pH, as well as the reaction system defined to obtain the diagram is of vital importance.

## 2. Materials and methods

### 2.1 Experimental procedure

#### 2.1.1 Definition of the system of chemical reactions for the construction of the Eh-pH diagram

The system of equilibrium chemical reactions and reduction potential equations used in the con-

struction of the thermodynamic stability diagram of the copper/water/amyloxanthate system is shown in

**Table 1.**

**Table 1.** Chemical reactions and equations of the reduction potential

NO.	System reactions $\text{Cu}/\text{H}_2\text{O}/\text{C}_5\text{H}_{11}\text{OCS}_2^-$	Equations of reduction potential and pH
1	$\text{HAmX}(\text{ac}) \rightleftharpoons \text{AmX}^-(\text{ac}) + \text{H}^+(\text{ac})$	$\text{pH} = 1.72 + \log\left(\frac{\text{AmX}^-}{\text{HAmX}}\right)$
2	$(\text{Am})\text{X}_2(\text{ac}) + 2e^- \rightleftharpoons 2\text{AmX}^-(\text{ac})$	$E = -0.077 - 0.059 \log(\text{AmX}^-)$
3	$1/2(\text{AmX})_2(\text{ac}) + e^- + \text{H}^+(\text{ac}) \rightleftharpoons \text{HAmX}(\text{ac})$	$E = 0.179 - 0.059\text{pH}$
4	$\text{Cu}^{+2}(\text{ac}) + \text{H}_2\text{O} \rightleftharpoons \text{CuO}(\text{s}) + 2\text{H}^+(\text{ac})$	$\text{pH} = 3.83 - \log(\text{Cu}^{+2})$
5	$\text{Cu}^{+2}(\text{ac}) + e^- \rightleftharpoons \text{Cu}^+(\text{ac})$	$E = 0.168 - 0.059 \log\left(\frac{\text{Cu}^+}{\text{Cu}^{+2}}\right)$
6	$\text{CuO}(\text{s}) + 2\text{H}^+(\text{ac}) + 2e^- \rightleftharpoons \text{Cu}(\text{s}) + \text{H}_2\text{O}$	$E = 0.564 - 0.059\text{pH}$
7	$\text{CuAmX}(\text{s}) + e^- \rightleftharpoons \text{Cu}(\text{s}) + \text{AmX}(\text{ac})$	$E = -0.538 - 0.059 \log(\text{AmX}^-)$
8	$\text{CuAmX}(\text{s}) + e^- + \text{H}^+(\text{ac}) \rightleftharpoons \text{Cu}(\text{s}) + \text{HAmX}(\text{ac})$	$E = -0.189 - 0.059\text{pH}$
9	$1/2\text{Cu}_2\text{O}(\text{s}) + \text{H}^+(\text{ac}) + e^- \rightleftharpoons \text{Cu}(\text{s}) + 1/2\text{H}_2\text{O}$	$E = 0.46 - 0.059\text{pH}$
10	$1/2\text{Cu}_2\text{O}(\text{s}) + \text{AmX}^-(\text{ac}) + \text{H}^+(\text{ac}) \rightleftharpoons \text{CuAmX}(\text{s}) + 1/2\text{H}_2\text{O}$	$\text{pH} = 16.88 + \log(\text{AmX}^-)$
11	$1/2\text{Cu}_2\text{O}(\text{s}) + 1/2\text{H}_2\text{O} \rightleftharpoons \text{CuO}(\text{s}) + \text{H}^+(\text{ac}) + e^-$	$E = 0.66 - 0.059\text{pH}$
12	$\text{Cu}_2(\text{AmX})_2(\text{ac}) + e^- \rightleftharpoons \text{CuAmX}(\text{s}) + \text{AmX}^-(\text{ac})$	$E = -0.027 - 0.059 \log(\text{AmX}^-)$
13	$(\text{AmX})_2(\text{ac}) + \text{Cu}^{+2}(\text{ac}) + 2e^- \rightleftharpoons \text{Cu}(\text{AmX})_2(\text{ac})$	$E = 0.543 - \frac{0.059}{2} \log\left(\frac{\text{Cu}(\text{AmX})_2}{(\text{Cu}^{+2})(\text{AmX})_2}\right)$
14	$\text{Cu}(\text{AmX})_2(\text{ac}) + e^- + \text{H}^+(\text{ac}) \rightleftharpoons \text{CuAmX}(\text{ac}) + \text{HAmX}(\text{ac})$	$E = 0.075 - 0.059 \log\left(\frac{\text{HAmX}}{\text{Cu}(\text{AmX})_2}\right) - 0.059\text{pH}$
15	$\text{CuO}(\text{s}) + \text{AmX}^-(\text{ac}) + e^- + 2\text{H}^+(\text{ac}) \rightleftharpoons \text{CuAmX}(\text{s}) + \text{H}_2\text{O}$	$E = 1.66 - 0.059 \log(\text{AmX}^-) - 0.059\text{pH}$
16	$\text{CuO}(\text{s}) + 1/2(\text{AmX})_2(\text{ac}) + 2e^- + 2\text{H}^+(\text{ac}) \rightleftharpoons \text{CuAmX}(\text{s}) + \text{H}_2\text{O}$	$E = 0.795 + \frac{0.059}{2} \log(\text{AmX})_2 - 0.059\text{pH}$
17	$\text{CuO}(\text{s}) + (\text{AmX})_2(\text{ac}) + 2\text{H}^+(\text{ac}) + 2e^- \rightleftharpoons \text{Cu}(\text{AmX})_2(\text{ac}) + \text{H}_2\text{O}$	$E = 0.77 - \frac{0.059}{2} \log\left(\frac{\text{Cu}(\text{AmX})_2}{\text{AmX}}\right)_2 - 0.059\text{pH}$
18	$\text{Cu}(\text{ac}) + \text{H}_2\text{O} \rightleftharpoons \text{CuO}(\text{s}) + 2\text{H}^+(\text{ac}) + e^-$	$E = 0.88 - 0.118\text{pH}$

**Amx-amyloxanthate**( $\text{C}_5\text{H}_{11}\text{OCS}_2^-$ )

**(Amx)<sub>2</sub>-amyldiixanthate**( $\text{C}_5\text{H}_{11}\text{OCS}_2)_2$ )

The construction of the diagram was carried out with the help of the Medusa software<sup>[28]</sup> of the Department of Inorganic Chemistry of the Royal Institute of Technology, Great Britain, which contains a database from log K to 298 K; the software allows the modification and creation of diagrams from supplied data.

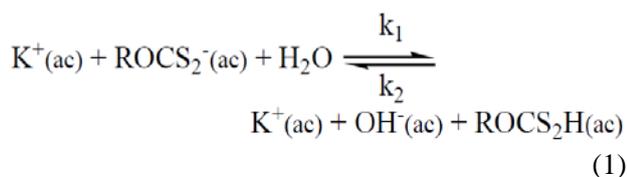
The potential value  $1.59 \cdot 10^{-2}$  eV<sup>[3]</sup> for the  $(\text{Amx})_2/\text{Amx}^-(\text{Am-amil}; \text{X-xantato})$  pair was used in the construction of the diagram. The equilibrium constant value for the copper(II) amyloxanthate

complex formation reaction is  $3.7 \cdot 10^{9[21]}$ ; for the copper(I) amyloxanthate complex formation reaction the experimental value 0.3467 was used<sup>[29]</sup>.

### 3. Results and discussion

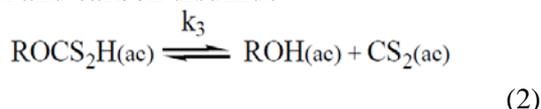
In the analysis of xanthogenic systems, the decomposition of ethylxanthate in aqueous media must be considered; for this purpose, six stages have been proposed<sup>[8,25,30]</sup>.

**Stage 1: Hydrolysis of xanthate ion and formation of xanthic acid**



Where R represents the carbon chain.

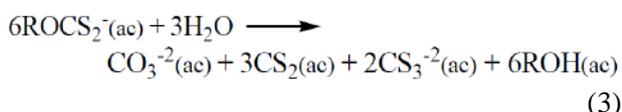
**Stage 2: Decomposition of xanthic acid to alcohol and carbon disulfide**



Where  $k_1$ ,  $k_2$  and  $k_3$  are the velocity constants.

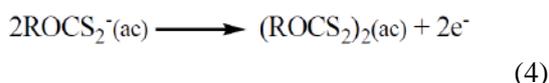
Both reaction equations are verified in acid medium. Iwasaki and Cooke<sup>[11]</sup> reported that the ethylxanthate ion and ethylxanthic acid are in equilibrium in a pH range from 0.10 to 4.71, corresponding to the value of the dissociation constant of ethylxanthic acid, which is considered a moderately weak acid ( $\text{pK}_a = 1.6$ )<sup>[31]</sup>.

**Stage 3: Hydrolytic decomposition of xanthate ion**



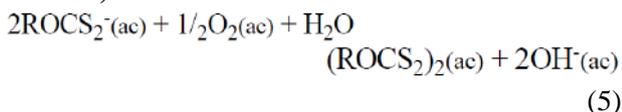
This stage can occur in neutral and alkaline media, however, some authors consider that the reaction occurs only when  $\text{pH} > 13$ <sup>[1,5,12,25]</sup>. According to Pomianowsky and Leja<sup>[23]</sup>, the decomposition of trithiocarbonate into carbon disulfide and sulfur,  $\text{CS}_2$  and  $\text{S}^{2-}$ , can occur in parallel.

**Stage 4: Oxidation to dixanthate**



Zohir *et al.*<sup>[32]</sup> propose that the above reaction equation is independent of the reduction potential, unlike the mechanism that takes place in the presence of dissolved oxygen in the aqueous medium:

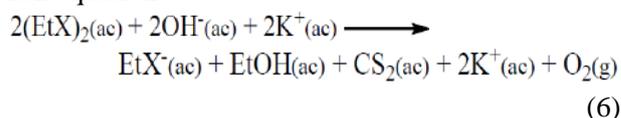
**4.a)**



The magnitude of the reaction corresponding to stage 4.a is very small and reaches equilibrium in neutral medium after oxidation of 5%–10%; its extent depends on the pH of the medium. Its development is more significant with increasing hydrocarbon chain length<sup>[8]</sup>. Correspondingly, the value

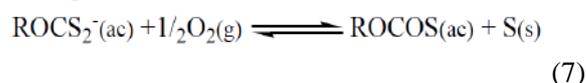
of the oxidation potential also increases; it is 0.04 eV and -0.159 eV for methylxanthate and n-amyldixanthate respectively<sup>[33]</sup>. The above information indicates that the behavior of xanthates in aqueous media, according to the number of carbon atoms in the chain, may differ as a function of the pH conditions of the medium. Similarly, the values of the molar absorptivity coefficient are modified<sup>[34]</sup>.

The oxidation reactions to dixanthate have been considered irreversible and dixanthate unreactive, but studies by Pomianowsky and Leja<sup>[23]</sup> showed that this species reacts under alkaline conditions and gives rise to the ethylxanthate ion and carbon disulfide<sup>[12]</sup> according to the following reaction equation.



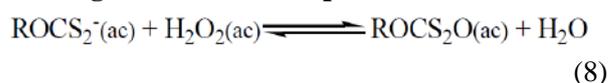
The development of the last two stages needs specific conditions to be verified<sup>[24]</sup>.

**Stage 5: Oxidation to monothiocarbonate**



According to Harris and Filkenstein<sup>[24]</sup>, the formation of monothiocarbonate requires the participation of sulfide where the reactants are previously adsorbed; the sulfide acts as a catalyst.

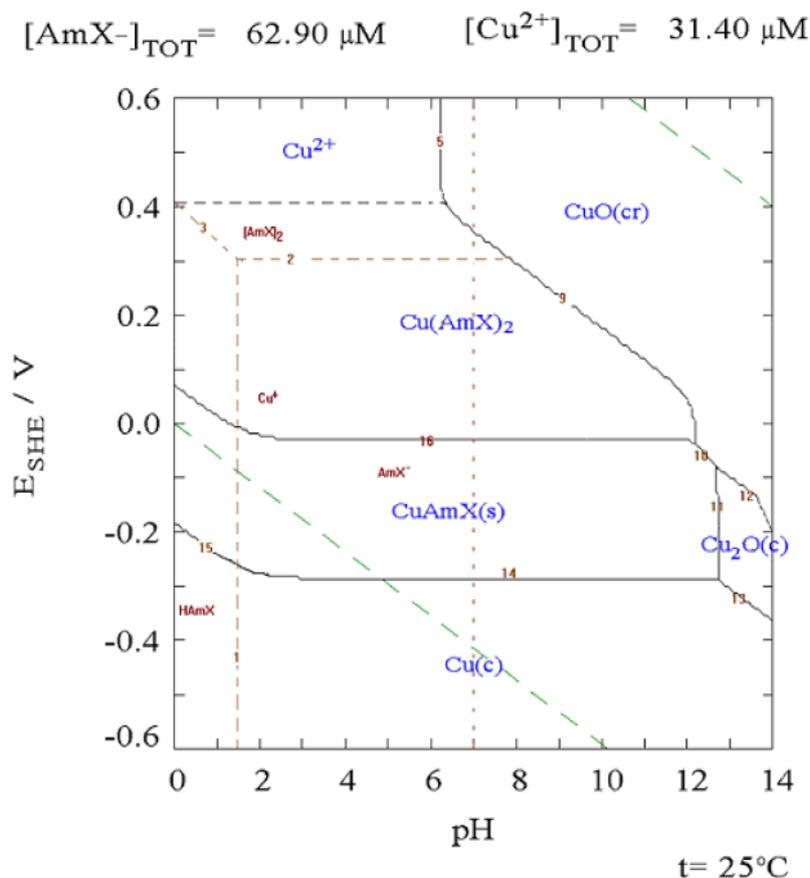
**Stage 6: Oxidation to perxanthate**



In the case of perxanthate, its presence has been recorded under specific conditions of alkalinity and high degree of oxidation<sup>[12,14]</sup>.

Although the steps have been generalized, there is a contradiction between the pH range of ethylxanthate decomposition in acidic media<sup>[11]</sup> and its application results in flotation at similar pH values<sup>[9,17]</sup>. Moreover, the effect caused by increasing the number of carbon atoms on the pH range in which such transformations manifest themselves has not been tested. Although it is well known that the stability of xanthate has been improved, and the decomposition kinetics has slowed down with the increase of carbon chain, these aspects have a significant impact during the interaction between xan-

that species and metal ions present in a solution.



**Figure 1.** Thermodynamic stability diagram of the copper/water/amyloxanthate system.

### 3.1 Potential-pH diagram of the copper/water/amyloxanthate system

**Figure 1** shows the thermodynamic stability diagram for the copper/water/amyloxanthate system.

It is observed that the stability zones of the xanthogenic copper species coexist practically up to pH equal to 13 units. As can be seen, the conditions of the potential of the medium play a decisive role in the predominance of one of the species during the flotation process. In a comparative analysis of this diagram and the one reported by Hepel and Pomianowski<sup>[27]</sup> for potassium ethylxanthate under the same conditions, the variation in the stability zones of the compounds with amyloxanthate, with respect to the one formed with ethylxanthate, was verified, mainly due to the reduction of the potential value at which they are stable.

As for the pH value, no significant changes are shown in the stability zones of the different species. Compared with short chain xanthates, The difference in stability of amyloxanthate is based on the

speed of decomposition, and its kinetics is slow<sup>[26]</sup>. This characteristic favors the use of amyloxanthate with respect to ethylxanthate in processes where greater stability of its complexes is required for their separation by flotation.

## 4. Conclusions

The thermodynamic stability diagram for the copper/water/amyloxanthate system is established. The analysis showed that the xanthogenic species of copper(I) and (II) coexist in the pH range of 4 to 13, and their ratio decreases with the increase of pH.

## Conflict of interest

The authors declared no conflict of interest.

## References

1. Somasundaran P, Moudgil BM. Reagents in minerals technology. Florida: CRC Press; 1988.
2. Roy KM. Xanthates. In: Ullmann's encyclopedia of industrial chemistry.
3. Crozier RD. Flotation: Theory, reagents and ore

- testing. 1<sup>st</sup> ed. Oxford: Pergamon Press; 1992.
4. Fuerstenau DW. Advances in flotation technology. SME: Littleton; 1999. p. 3–21.
  5. Dudenkov S, Shubov L, Glazunov L. Fundamentos de la teoría y la práctica de empleo de reactivos de flotación (Spanish) [Theoretical and practical basis for the use of flotation reagents]. Moscow: Mir Publishers; 1980.
  6. Harris PJ. Reagents in mineral technology. New York: Marcel Dekker; 1988.
  7. Abramov AA, Forssberg KSE. Chemistry and optimal conditions for copper minerals flotation: Theory and practice. *Mineral Processing and Extractive Metallurgy Review* 2005; 26: 77–143.
  8. Rao SR. Xanthates and related compounds. 1<sup>st</sup> ed. New York: Marcel Dekker; 1971. p. 1–504.
  9. Stalidis GA, Matis KA, Lazaridis NK. Selective separation of Cu, Zn, and As from solution by flotation techniques. *Separation Science and Technology* 1989; 24(1): 97–109.
  10. Matis KA, Mavros P. Recovery of metals by ion flotation from dilute aqueous solutions. *Separation and Purification Methods* 1991; 20: 1–48.
  11. Iwasaki I, Cooke SRB. The decomposition of xanthate in acid solution. *Journal of the American Chemical Society* 1958; 80: 285–288.
  12. Tipman RN, Leja J. Reactivity of xanthate and dixanthogen in aqueous solution of different pH. *Colloid and Polymer Science* 1975; 253: 4–10.
  13. Sun Z, Forsling W. The degradation kinetics of ethyl-xanthate as a function of pH in aqueous solution. *Minerals Engineering* 1997; 10(4): 389–400.
  14. Leja J. Surface chemistry of froth flotation. New York: Plenum Press; 1982. p. 1228.
  15. Lazaridis NK, Matis KA, Stalidis GA, *et al.* Dissolved-air flotation of metal ions. *Separation Science and Technology* 1992; 27(13): 1743–1758.
  16. Kakovsky I. Physicochemical properties of some flotation reagent and their salts with ions of heavy iron-ferrous metals. *Proceedings of the Second International Congress of Surface Activity*; London. 1957. p. 225–237.
  17. Lazaridis NK, Peleka EN, Karapantsios ThD, *et al.* Copper removal from effluents by various separation techniques. *Hydrometallurgy* 2004; 74(1–2): 149–156.
  18. Basilio C, Pritzker MD, Yoon RH. Thermodynamics, electrochemistry and flotation of the chalcocite-potassium ethyl xanthate system. 114th AIME Annual Meeting; 1985 Feb 24–27; New York. 1985. p. 85–86.
  19. Young CA. Nonstoichiometry of chalcocite in water-xanthate systems [MSc thesis]. Virginia Polytechnic Institute and State University; 1987. p. 296.
  20. Woods R, Young CA, Yoon RH. Ethyl xanthate chemisorption isotherms and Eh-pH diagrams for the copper/water/xanthate and chalcocite/water/xanthate systems. *International Journal of Mineral Processing* 1990; 30: 17–33.
  21. Joly HA, Majerus R, Westaway KC. The effect of diethylenetriamine on the formation of Cu<sup>2+</sup>, Ni<sup>2+</sup>, and Fe<sup>3+</sup> amyl xanthate ion complexes. *Minerals Engineering* 2004; 17: 1023–1036.
  22. Klauditz W. The ripening of viscose. *Tech-Wise*; 1939. p. 251–259.
  23. Pomianowski A, Leja J. Spectrophotometric study of xanthate and dixanthogen solutions. *Canadian Journal Chemistry* 1963; 41: 2219–2230.
  24. Harris PJ, Filkenstein NP. Interactions between sulphide minerals and xanthates, I. The formation of monothiocarbonate at galena and pyrite surfaces. *International Journal of Mineral Processing* 1975; 2(1): 77–100.
  25. Obregón H. Xantatos en sistemas de flotación (Spanish) [Xanthates in flotation systems]. *Reacciones Fenómenos y Mecanismos* 1990; 5.
  26. Donato P, Cases JM, Kongolo M, *et al.* Stability of the amylxanthate ion as a function of pH: Modelling and comparison with the ethylxanthate ion. *International Journal of Mineral Processing* 1989; 25: 1–16.
  27. Hepel T, Pomianowski A. Diagrams of electrochemical equilibria of the system copper-potassium ethylxanthate-water at 25 °C. *International Journal of Mineral Processing* 1977; 4: 245–361.
  28. Puigdomenech I. Software equilibrio químico (Spanish) [Chemical equilibrium software]. Royal Institute of Technology 2004.
  29. Ramírez Serrano B. Remoción por flotación iónica de iones cobre con (Spanish) [Removal by ionic flotation of copper ions with potassium amylxanthate] [PhD thesis]. Moa: Instituto Superior Minero Metalúrgico; 2011. p. 120.
  30. Bulatovic SM. Handbook of flotation reagents. Chemistry, theory and practice: Flotation of sulfide ores. Amsterdam: Elsevier; 2007. p. 443.
  31. AGPS. Sodium ethyl xanthate. 1995. p. 1–64.
  32. Zohir N, Mustapha B, Abd-Elbaki D. Synthesis and structural characterization of xanthate (KEX) in sight of their utilization in the processes of sulphides flotation. *Journal of Minerals and Materials Characterization and Engineering* 2009; 8(6): 469–477.
  33. Jones MH, Woodcock JT. Dixanthogen determination in flotation liquors by solvent extraction and ultraviolet spectrometry. *Analytical Chemistry* 1986; 58: 588–591.
  34. Jones MH, Woodcock JT. Ultraviolet spectrometry of flotation reagents with special reference to the determination of xanthate in flotation liquors. London: Chameleon Press; 1973. p. 110.