

# The role of copper and lead in the activation of pyrite in xanthate and non-xanthate systems

E.T. Pecina <sup>a,\*</sup>, A. Uribe <sup>b</sup>, F. Nava <sup>b</sup>, J.A. Finch <sup>c</sup>

<sup>a</sup> CIMAV, Miguel de Cervantes 120, Compl. Ind. Chihuahua, C.P. 31109, Chihuahua, Chih., Mexico

<sup>b</sup> CINVESTAV-IPN, Unidad Saltillo, Ramos Arizpe, A.P. 663, C.P. 25900, Coah., Mexico

<sup>c</sup> McGill University, Montreal, Quebec, Canada H3A 2B2

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## Abstract

Lead and copper activation of pyrite in the presence of thiol collectors was examined by means of cyclic voltammetry and microflotation techniques. Di-isobutyl dithiophosphinate (Aerophine 3418A) and alkyl thionocarbamate (AERO 3894) were employed as collector of lead and copper, respectively. Otherwise, isopropyl xanthate (IPX) was also used as a collector of both: lead and copper. The results revealed that in the presence of non-conventional collectors, the increase in pyrite recovery due to the activation by copper and lead species, was noticeably smaller than that exhibited when xanthate (IPX) was used. The electrochemical response of pyrite indicates that lead activation favors the formation of dixanthogen. In non-xanthate systems, the voltammograms of pyrite remained unaffected regardless of the activation by lead or copper species.

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## 1. Introduction

The hydrolyzed metal species are very active constituents of the flotation pulp. The interaction of these species with the minerals shows a remarkable effect upon the floatability of sulfides. Activation is one of the most important phenomena identified in the flotation of sulfides. This is related to the adsorption or precipitation of metal species onto the mineral surface, creating sites with affinity towards the collector.

Pyrite (FeS<sub>2</sub>) is the most abundant of the sulfide minerals. It is considered as a worthless mineral (i.e., gangue type) during the flotation of the metal-base sulfides (Pb/Cu/Zn), and is only appreciated when it is associated with precious metals such as gold. The conventional practice of sulfide flotation establishes that successful depression of pyrite may be performed by following a conventional

scheme of flotation, where xanthates and traditional flotation reagents are involved. Nevertheless, the presence of non-liberated pyrite particles within the valuable mineral concentrates (Pb, Zn and Cu concentrates) implies the emergence of phenomena such as inadvertent activation of pyrite with concomitant metal species.

The precise identities of the reaction products of activators with sulfides have not been clearly established. The complexity of sulfides systems due to concurrence of the electrochemical and chemical processes, seems to be responsible for the controversy that exists around sulfide activation. Studies on pyrite activation with metal ions (e.g., Cu<sup>2+</sup> and Pb<sup>2+</sup>), have shown that activation under alkaline conditions, involves complex interactions between sulfides and their products, hydroxides and hydrolyzed species. The activation products have been established as: a sulfide resulting from the adsorbed metal species; a complex oxidized sulfide (COS, representing the variety of species having nominal valences between 0 and –2, produced as the result of both, the oxidation of the sulfide and the

\* Corresponding author. Tel.: +52 614 4391100; fax: +52 614 4391130.  
E-mail address: [teresa.pecina@cimav.edu.mx](mailto:teresa.pecina@cimav.edu.mx) (E.T. Pecina).

adsorption of divalent metal ions); the adsorbed or precipitated hydrolyzed species (hydroxides and hydroxo complexes); and as elemental sulfur produced during the electrochemical adsorption of divalent cations ( $\text{Cu}^{2+}$ ) (Wang and Forssberg, 1989; Wang et al., 1989; Senior and Trahar, 1991; Smart, 1991; Finkelstein, 1997).

A number of studies have been published revealing the nature of the product derived from the interaction between the thiol collectors and the activated mineral. Dixanthogen and metal xanthates have been frequently detected by spectroscopy techniques (e.g., FTIR) (Leppinen, 1990; Senior and Trahar, 1991; Zhang et al., 1997).

The available literature (Fuerstenau et al., 1968; Gardner and Woods, 1977; Leppinen, 1990) establishes that the dixanthogen ( $\text{X}_2$ ) is the main hydrophobic product of the interaction of xanthate with pyrite. The process involved is of electrochemical nature:



The oxidation potential of dixanthogen for a specific xanthate concentration, may be computed from the Nernst equation, as follows:

$$\text{Eh}_{\text{X}_2} = E_{\text{X}^-/\text{X}_2}^0 - 0.059 \log[\text{X}^-] \quad (2)$$

where  $E_{\text{X}^-/\text{X}_2}^0$  is the standard potential of the half cell given in Eq. (1), and  $[\text{X}^-]$  is the molar xanthate concentration.

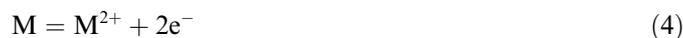
Thus, it is expected that xanthate will be oxidized to dixanthogen if the redox potential of the aqueous solution is increased above the value given by Eq. (2).

Ferrous and ferric ions from pyrite dissolution/oxidation do not have a significant chemical affinity for thiol collectors; however, if copper or lead species adsorb/precipitate onto the mineral, the sites with the products of the activation may react according to the following mechanisms.

A chemical reaction between the xanthate ion  $\text{X}^-$ , and the metallic sites of the mineral surface (activation products) may occur to form a metal-collector compound. The mechanism involved may be regarded as a two step-process consisting of an electrochemical reaction (e), such as those represented in Eqs. (3) and (4), followed by a chemical reaction (c), as that represented in Eq. (5): For sulfides:



For metallic electrodes:



Chemical reaction for the formation of the metal-collector compound:



The redox potential for the formation of the metal-collector compound is computed with Eq. (6) for sulfides, and Eq. (7) for metallic electrodes (Woods, 1971):

$$\text{Eh}_{\text{MX}_2} = E_{\text{MS}/\text{M}^{2+}}^0 - 0.059 \log[\text{X}^-] \quad (6)$$

$$\text{Eh}_{\text{MX}_2} = E_{\text{M}/\text{M}^{2+}}^0 - 0.059 \log[\text{X}^-] \quad (7)$$

where  $E_{\text{MS}/\text{M}^{2+}}^0$  and  $E_{\text{M}/\text{M}^{2+}}^0$  are the standard potential of the half cells of Eqs. (3) and (4), respectively, and  $\text{X}^-$  is the molar xanthate concentration.

The relation may be expressed in terms of the solubility product of the metal xanthate,  $K_{\text{sp}}$  (Woods, 1988). In this case, xanthate concentration ( $\text{X}^-$ ) is substituted by the inverse of the  $K_{\text{sp}}$ . For example, for Eq. (7):

$$\text{Eh}_{\text{MX}_2} = E_{\text{M}/\text{M}^{2+}}^0 + 0.059 \log[K_{\text{sp}}] \quad (8)$$

Xanthate may chemisorbed (i.e., without transfer of charge) by replacing a ion of similar charge. Hydroxyl ions could be adsorbed under most conditions in moderately alkaline medium and may be replaced readily by xanthate ion.



According to Woods (1988), electrochemical adsorption or charge transfer chemisorption (Eq. (10)) is an intermediate process in the formation of dithiolates, and may be regarded as precursor in the development of metal-thiol compounds onto the mineral. This occurs at lower potential compared to that of the compound formation.



Other collectors have obtained less attention than xanthates. With regard to thionocarbamates (TC), a standard potential for the isopropyl thionocarbamate (Z200) dimer formation has been reported ( $E^0 = 0.195 \text{ V}$ ); however, as stated by Woods (1988), “the oxidation products have not been well characterized and the significance of the measured potential is open to question”.

With respect to the effect of metal activation of pyrite in non-xanthate systems, the experimental evidence suggests similar behavior to that identified for xanthates. Nagaraj and Brinen (1995) studied the activation of gangue minerals using secondary ion mass spectroscopy (SIMS), and found that the adsorption of thionocarbamate is enhanced when pyrite is activated by copper ions. Unfortunately the precise nature of the hydrophobic species could not be identified. Basilio and Yoon (1992), in their voltammetric study, found an increase of current at  $-200 \text{ mV}$ , using a chalcopyrite electrode in presence of thionocarbamate (IBECTC, *O*-isobutyl-*N*-ethoxycarbonyl thionocarbamate). The peak was only observed at a sweep rate of  $1 \text{ V/s}$ ; at slow rates, such as those used in this study ( $20 \text{ mV/s}$ ), the voltammogram of chalcopyrite did not show the anodic wave related to the oxidation of IBECTC. The authors also stated that the interaction mechanism of IBECTC with copper ions involves the release of a proton ( $\text{H}^+$ ) from the collector molecule followed by the formation of a copper-collector compound. Dithiophosphinate (DTPI) emits a signal too weak to be detected in FTIR spectra; on the contrary, TOF-SIMS appears to be a helpful tool in the detection of the collector, as revealed by the work of Piantadosi and Smart (2002). These authors identified

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