



Full Length Article

Comparative study on the copper activation and xanthate adsorption on sphalerite and marmatite surfaces

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ARTICLE INFO

Article history:

Received 8 June 2017

Revised 30 December 2017

Accepted 4 January 2018

Available online 6 January 2018

Keywords:

Sphalerite

Fe impurity

Copper activation

Xanthate adsorption

LEIS

ToF-SIMS

ABSTRACT

The copper activation and potassium butyl xanthate (PBX) adsorption on sphalerite and marmatite surfaces were comparatively investigated using in situ local electrochemical impedance spectroscopy (LEIS), time-of-flight secondary ion mass spectrometry (ToF-SIMS) and surface adsorption tests. Comparing the LEIS and surface adsorption results, it was found that the activation time is a key factor influencing the copper activation and PBX adsorption on marmatite surface, but it has a negligible influence on sphalerite. For a short activation time within 10 min, the Fe impurity in marmatite shows an adverse influence on the speed of Cu adsorption and ion exchange as well as on the subsequent PBX adsorption. For a long activation time of 30 min, the LEIS, ToF-SIMS and surface adsorption results suggested that the Fe impurity in marmatite enhances the copper adsorption, whereas such enhanced copper adsorption of marmatite cannot result in corresponding enhancing of PBX adsorption. DFT result showed that the Fe impurity in marmatite has harmful influence on the PBX interaction with the Cu-activated surface by increasing the interaction energy. ToF-SIMS result further indicated that the Cu distribution in the outermost surface of marmatite is less than that of the sphalerite, which also results in the less PBX adsorption for the marmatite.

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1. Introduction

Sphalerite (ZnS) is the most abundant Zn-bearing mineral, whereas it has an inferior natural floatability and responds not well to short chain xanthate collectors. As a result, additional activators, such as copper sulfate (CuSO₄), are generally required to treat the mineral surface to enhance the adsorption of collector molecules [1–3]. The chemical composition of natural sphalerite varies considerably with the ore deposits, due to the substitution of other impurities in the mineral lattice [4]. One of the most common impurities occurred in the lattice is iron (Fe), which substitutes for zinc in the sphalerite lattice. In this case, it forms marmatite (Zn_xFe_{1-x}S) and ultra-high marmatite, when the content of iron in sphalerite exceeds 6% and 20%, respectively [5].

The Fe impurity in the mineral lattice significantly affects the surface reactivity, copper activation, collector adsorption and subsequent sphalerite flotation. For example, it was reported that the presence of Fe decreases the band gap of sphalerite and affects its

reactivity [6]. Using synthetic sphalerite with different iron contents, Solecki et al. [7] have pointed out that the adsorption of Cu²⁺ decreased with increasing iron concentration in sphalerite, and increasing the iron content results in the decreased attachment of xanthate on copper-activated sphalerite surface. These results were further confirmed by Buckley's investigations on two natural sphalerite samples with different iron contents using XPS analysis [8]. Recently, the study of Boulton et al. [9] on the flotation of two natural sphalerite samples with high iron (12.5 wt%) and low iron (0.3 wt%) has also concluded that the presence of iron in the sphalerite lattice has a detrimental effect on the flotation of sphalerite as it reduces the copper activation, which in turn results in the reduction of xanthate adsorption as copper (I) xanthate. However, these previous studies investigating the effect of iron content in sphalerite on copper activation, collector adsorption and subsequent sphalerite flotation have led to conflicting results [6–10]. Using natural sphalerite with varying iron content, Gigowski et al. [10] found that xanthate was preferentially adsorbed on the copper activated iron-rich sphalerite. Also, using a combination of electron microprobe analysis (EPA), atomic force microscopy (AFM) and XPS on five different sphalerite samples with various iron content, Harmer et al. [6] demonstrated that the amount of Cu²⁺ adsorbed on sphalerite surface increased with

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increase in the iron content of sphalerite; in addition, the samples with higher iron content undergo a more rapid oxidation than those with lower iron content, and thus the iron further contributes to Cu^{2+} adsorption.

In spite of these valuable investigative works, the precise mechanism responsible for the effect of iron content in sphalerite on copper activation and collector adsorption is still a contentious issue. One of the most influencing factors which results in the discrepancies from these works is the non-situ studying of mineral surface layer coated by copper and collector molecules [11,12]. Scanning electrochemical probe technologies such as scanning electrochemical microscopy (SECM) and local electrochemical impedance spectroscopy (LEIS) provide a powerful in situ examining of surface properties of substrate, like the surface defects, surface heterogeneities and surface reactivity [13–15]. In recent years, SECM has been successfully applied to the fundamental study of froth flotation. It was firstly reported by Wang et al. [12] to study the copper activation and xanthate adsorption on sphalerite surface; it was found that the unactivated and activated sphalerite surfaces have negative current feedback and partially positive current feedback, respectively, implying the formation of Cu_2S on the surface. Using SECM, Liu et al. [16] and Xiao et al. [17] studied the adsorption of new collectors (iPOPECTU and BOPECTU) on chalcopyrite surface, and pointed out that there might be some new substance formed on chalcopyrite surface, which resulted in the decrease of the current response. However, there is little information on the application of LEIS in froth flotation.

Time of flight secondary ion mass spectrometry (ToF-SIMS) is a very sensitive technique for analyzing and mapping the chemical composition of solid surfaces and thin films [18–21]. In the field of flotation, it was mainly used for investigation the adsorption of flotation reagents on the mineral surface [22–26], study the hydrophobicity of mineral particles [27,28], identifying the relationship between mineral surface chemistry and contact angle [29–32], optimization of the flotation condition [33], and evaluation of grinding effects [34,35]. However, ToF-SIMS can inevitably cause certain degrees of surface damages of the sample during the analysis.

In this work, LEIS was employed, for the first time, to in situ comparatively investigate the copper activation and potassium butyl xanthate (PBX) adsorption on sphalerite and marmatite surfaces. After that, the surface layer compositions of sphalerite and marmatite were further analyzed by ToF-SIMS. Moreover, the adsorption of copper and PBX on sphalerite and marmatite surfaces was also investigated by inductively coupled plasma-atomic emission spectrometry (ICP-AES) and ultraviolet spectrophotometer, respectively. Combining the LEIS, ToF-SIMS and surface adsorption tests, the investigation illuminates the discrepancy of copper activation and xanthate adsorption on sphalerite and marmatite surfaces.

2. Materials and experimental method

2.1. Description of materials

The materials used for the present study are natural pure sphalerite and marmatite, with very low and high Fe content, respectively. The sphalerite is from southwest Yunnan province of China with a yellow–brown color and the marmatite is from Guangxi province of China with a dark color. The two materials were soaked in a 1% concentration of hydrochloric acid solution for 1 hour, cleaned with ultrasonic and then air-dried; after that, they were hand-ground in a mortar and pestle, and sieved to obtain a particle size around 90% below 74 μm for subsequent surface adsorption tests. The chemical compositions of the materials are shown in Table 1.

Table 1
Chemical composition of materials.

Sample	Element content (wt%)				
	Zn	S	Fe	Pb	SiO_2
Sphalerite	64.84	32.81	0.19	0.014	1.21
Marmatite	50.68	33.39	13.18	0.38	<0.50

From Table 1, the sphalerite sample contains 64.84 wt% Zn and 32.81 wt% S, only with 0.19 wt% Fe and some minor impurities of Pb and SiO_2 . However, the marmatite contains 50.68 wt% Zn and 33.39 wt% S, with a high Fe content of 13.18 wt%. In addition, the X-ray diffraction (XRD) (D/Max 2200, Rigaku, Japan) was used to further analyze the composition and crystal structure of the materials, with the result shown in Fig. 1.

The XRD result of Fig. 1 confirms that the two materials belong to a cubic structure sphalerite ($\beta\text{-ZnS}$) with no apparent impurities. However, the diffraction peak intensity of marmatite is obviously lower than that of sphalerite. This is due to the effect of Fe impurity in marmatite.

2.2. LEIS experiments

To conduct the LEIS scanning of sphalerite and marmatite surfaces under the same electrochemical system, the small blocky sphalerite and marmatite were adhered together with epoxy resins to form one substrate. After that, the substrate was polished by hand with wet silicon carbide paper in the sequence of 240, 320, 400, 600, 800 and 1200 grit, and then was further polished with 5 μm alumina powder suspensions. The freshly polished substrate of sphalerite and marmatite was ultrasonically washed in ethanol and Milli-Q water for 5 min, respectively. The cleaned substrate was dried by highly pure N_2 . Then, the freshly prepared substrate was immediately transferred into a 1L electrochemical cell for LEIS experiments. The LEIS experiments were performed on a scanning electrochemical work station (Versa SCAN, AMETEK Inc, USA), with the schematic diagram of LEIS measurement of sphalerite and marmatite surfaces illustrated in Fig. 2.

A Pt dual-element probe with 5 μm radius was used as the LEIS tip. The tip was polished on a micro-polishing cloth with 0.05 μm alumina powder suspension and rinsed thoroughly with ethanol and Milli-Q water before use. A freshly prepared substrate was mounted at the bottom of a LEIS cell with its surface exposed to the electrolyte solution. A Pt wire was used as a counter electrode, and an Ag/AgCl electrode was used as a reference electrode. It should be noted that in LEIS measurements, the substrate does not need to be electrically connected to an external circuit, as required in traditional electro analytical techniques.

LEIS measurements were made from the ratio of the applied AC voltage to the local AC current density. The applied voltage (V_{applied}) was the potential difference between the working and reference electrodes. The local AC current density (I_{local}) was calculated using Ohm's law:

$$I_{\text{local}} = \frac{\kappa V_{\text{probe}}}{d} \quad (1)$$

where κ is the conductivity of the electrolyte and V_{probe} is the potential difference of Pt dual-element Probe; d is the distance between two probes positioned on and in a conical plastic holder: one protrudes from the tip of the cone and the other is a ring placed around the cone 3 mm from the tip. The local impedance Z_{local} is calculated by Eq. (2):

$$Z_{\text{local}} = \frac{V_{\text{applied}}}{I_{\text{local}}} \quad (2)$$

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