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Kinetic studies of amyl xanthate adsorption and bubble attachment to Cu-activated sphalerite and pyrite surfaces

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ABSTRACT

Kinetic studies of bubble attachment and amyl xanthate (AX) adsorption to $CuSO_4$ (Cu) activated sphalerite and pyrite surfaces were investigated by a novel in-situ approach with high-speed video microscopy (HSVM) and cryogenic X-ray photoelectron spectroscopic (Cryo-XPS). The drainage rate (DR) of thin films between the bubble and the surfaces was linked with the rate of AX adsorption onto the mineral surfaces. The single minerals studies revealed that the drainage (and adsorption) rate on polished pyrite was higher than on polished sphalerite after treatment with AX. However, the AX adsorption rate exhibited a higher value on the Cu-activated sphalerite than on the Cu-activated pyrite, indicating different surface components formed on the minerals surfaces and their different abilities to uptake Cu ions. Modeling AX adsorption rate on the unactivated and activated minerals by a pseudo-first order rate equation revealed the dependence of the drainage (and adsorption) rate on the initial AX concentration and the available active sites on the minerals surfaces. For the two minerals system, AX treatment results showed a significant drop in the adsorption rate of AX on the activated sphalerite with increasing the sphalerite to pyrite surface area ratio from 1:1 to 1:6. It confirmed the dependence of the AX adsorption rate on the available active sites on the minerals. Cryo-XPS confirmed that Cu-xanthate complex on the Cu-activated sphalerite and dixanthogen on the Cu-activated pyrite were the dominant surface components after treating with AX. It showed a selectivity of AX on the activated sphalerite with chemisorbed Cu-xanthate formation. However, consumption of AX with Cu-activated pyrite in the form of dixanthogen as well as Cu- or Fe-xanthate complexes were inevitable, especially when the available pyrite surface area was high in the mixed mineral system.

1. Introduction

Sphalerite is naturally an insulator with a band gap of 3.5 eV. Activation by Cu(II) results in the formation of a CuS-type conducting layer (with the band gap as low as 1.1 eV) on the sphalerite surfaces (Fornasiero and Ralston, 2006; Kartio et al., 1998). This reduced band gap aids in electron transfer reactions and allows the thiol collectors to form an insoluble collector complex on the sphalerite surface through mixed potential electrochemical reactions (Buckley et al., 1989; Kartio et al., 1998). Ab initio cluster model calculations have also shown that Cu atoms are incorporated into the sphalerite lattice enhance the electron acceptor ability of sphalerite (Porento and Hirva, 2005).

It has been accepted that Cu(I)-xanthate is the major surface species responsible for hydrophobicity of Cu-activated sphalerite (Leppinen, 1990; Mielczarski et al., 1989; Mikhlin et al., 2016b; Nefedov et al., 1980; Pattrick et al., 1999; Perry et al., 1984; Popov and Vucinic, 1990; Porento and Hirva, 2005; Prestidge et al., 1994; Termes and Richardson, 1986; Wang et al., 2013). However, dixanthogen adsorption is more prevalent on unactivated sphalerite (Pattrick et al., 1999) or when the Cu(II) concentration is low (Leppinen, 1990). Popov and Vucinic (1990) showed that, in acidic conditions, Cu(I)-xanthate was the dominant species on the Cu-activated sphalerite when the time of activation was only 2 min. The amount of Cu(I)-xanthate reduced when the activation time was prolonged from 2 to 45 min at a constant $CuSO_4$ concentration. For a short time of activation (2 min), i.e., under the rapid uptake regime, the increase in $CuSO_4$ concentration resulted in a higher amount of Cu(I)-xanthate formation on the sphalerite surface. However, Cu(I)-xanthate production was not higher with an increase in $CuSO_4$ concentration when the activation time was prolonged to 15 min. A long-time Cu-activation obviously involved migration of Cu ions under the sphalerite surface, a reduction of Cu(II) ions in solution, and consequently, a reduced formation of surface Cu(I)-xanthate.

It was also reported that, after Cu-activation of sphalerite in alkaline media, an exchange reaction between $Cu(OH)_{2(surface)}$ and X^- ions leads to $Cu(X)_{2(surface)}$ formation on the mineral surface, and subsequent

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decomposition of $Cu(X)_{2(surface)}$ forms Cu(I)-xanthate and dixanthogen (Fornasiero and Ralston, 1992; Mielczarski et al., 1979; Prestidge et al., 1994). The similar reaction could happen between $Fe(OH)_{2(surface)}$ and X^- ions in pyrite flotation using thiol collectors (Fornasiero and Ralston, 1992). However, the available literature (Fornasiero and Ralston, 1992; Leppinen, 1990; Mikhlin et al., 2016a; Wang and Forssberg, 1991) proposes that the dixanthogen would be the main surface product of the interaction of xanthate with pyrite.

Sphalerite Cu-activation kinetics (Dávila-Pulido et al., 2012; Ejtemaei and Nguyen, 2017a; Ralston and Healy, 1980a, 1980b) have been studied extensively. However, the presence of both sphalerite and pyrite minerals in solution can change the competition on Cu-activation and subsequent collector adsorption. In this present work, a novel technique for in-situ studies of drainage of liquid films and attachment, used in conjunction with XPS method, has been applied to investigate and compare the adsorption rate of AX on single and combined sphalerite and pyrite minerals activated by Cu. This study provides a better understanding of the effect of pyrite on xanthate adsorption rate of Cu-activated sphalerite.

2. Experimental

2.1. Mineral and reagents

Pure and natural sphalerite and pyrite used in our studies were obtained from Wards Scientific (USA). The chemical analysis the minerals surfaces by XPS showed negligible amount of impurities contained in the minerals (Ejtemaei and Nguyen, 2017b). They were cut into 5 mm × 5 mm sections and mounted in epoxy to the end of a small tube. The final polished mounted sections had an area of 25 mm^2 exposed to solutions. Water used for reagent preparation was purified using a reverse osmosis RIO's unit and an Ultrapure Academic Milli-Q system (Millipore, USA). The specific resistance of the Milli-Q water was 18.2 $M\Omega\ cm^{-1}$. Chemicals used in this study included $CuSO_4$ (99%, Sigma-Aldrich, Sydney, Australia) as an activator and potassium amyl xanthate (AX) as a collector.

2.2. Methodology

2.2.1. High-speed video microscopy (HSVM)

The experimental setup is shown in Fig. 1. A Fastcam SA3 High-Speed Camera Video Microscopy (HSVM) from Photron USA (San Diego, California, USA) was used to monitor the interaction between a freely rising bubble and the mineral surface. The interaction was recorded at a high frame rate of 10,000 fps. A needle with 0.184 mm inner diameter was connected to a syringe pump to generate a bubble with 1 mm diameter inside the cuvette of 1 cm × 1 cm × 5 cm (Fig. 1). The pump was operated at the pumping rate of 25 mL/h.

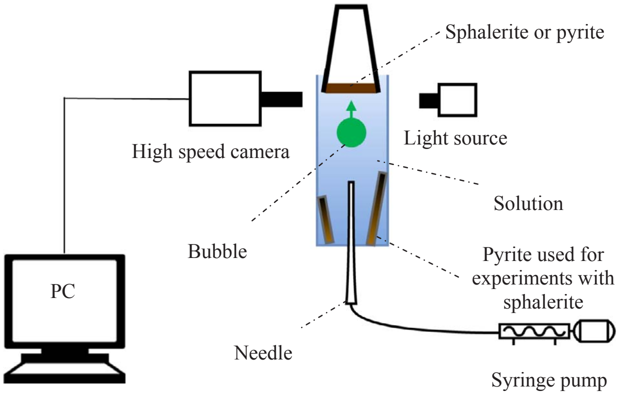

Fig. 1. Schematic of the experimental setup for monitoring the liquid film drainage and bubble-surface contact interaction (not to scale).

Before each experiment, the prepared mineral samples were wet polished using #1200 polishing paper for 1 min to produce a freshly smooth and clean mineral surface. Then the polished samples were immersed into the $CuSO_4$ solution with desired concentration for 10 min. The activated minerals were submerged into the measurement cuvette filled with AX. After a given treatment time to allow AX to adsorb to the mineral surface, a bubble generated by running the pump rose to and interacted with the surface. The interaction of the bubble with the mineral surface was monitored and recorded by HSVM. In the experiments with both sphalerite and pyrite minerals exposed to the solution, i.e., Cu-activation and AX treatment with different ratios of sphalerite to pyrite surface areas exposed to the solutions, small pieces of pyrite samples were polished with required surface area exposed to the solutions and were added into the solution contained in the cuvette at the same time with mounting sphalerite sample.

2.2.2. Cryogenic X-ray photoelectron spectroscopy (Cryo-XPS)

The X-ray photoelectron spectroscopy was carried out using a Kratos Axis ULTRA XPS (Kratos Analytical Ltd, UK) incorporating a 165 mm hemispherical electron energy analyzer. Monochromatic Al Kα X-rays (1486.6 eV) at 225 W (15 kV, 15 mA) was the incident radiation. Survey (wide) scans were taken at an analyzer pass energy of 160 eV and multiplex (narrow) high-resolution scans at 20 eV. Survey scans were carried out over 1200–0 eV binding energy range with 1.0 eV steps and a dwell time of 100 ms. Narrow high-resolution scans were run with 0.05 eV steps and 250 ms dwell time. Base pressure in the analysis chamber was 1.0×10^{-9} torr and during sample analysis 1.0×10^{-8} torr.

Atomic concentrations were calculated using the CasaXPS software (Version 2.3.14) and a Shirley baseline with Kratos library relative sensitivity factors. Peak fitting of the high-resolution data was also carried out using the Lorentz peak model within CasaXPS software.

The minerals were wet polished by polishing paper #1200 grit and cleaned with ethanol an Milli-Q water. The cleaned samples were activated with $CuSO_4$ for 10 min and then treated with AX for another 10 min. The samples were then rinsed with Milli-Q water and dried with nitrogen gas before transferring to the XPS chamber. The prepared samples pre-cooled to −165 °C and the analytical chamber of XPS was also −165 °C during the analysis. Spectra have been charge corrected using the main line of C 1s spectrum photoelectron peak (adventitious carbon) as an internal reference to account for sample charging, with an assigned BE of 284.8 eV. The cooling stage was applied using liquid nitrogen to reach −165 °C to avoid evaporation of elemental sulfur and dixanthogen under a high vacuum condition.

3. Results and discussion

3.1. Liquid film DR

3.1.1. AX adsorption onto the surfaces of sphalerite and pyrite

In the studies of collector adsorption onto a mineral surface, it has been accepted that the second order kinetics would be expected if the adsorption stage is rate-determining, and the rate of reaction should be proportional to the concentration of the collector in solution and the available adsorption sites on the mineral surface (Fredriksson et al., 2006). Therefore, in the case of sphalerite and pyrite Cu-activation and subsequent collector adsorption, we have the following kinetic model:

$$\frac{dx}{dt} = -k\,[A]_{surface}.\ [AX] \tag{1}$$

where k is the rate constant, x is the amount of AX adsorbed onto the mineral surface at time t, [AX] is the concentration of AX available at time t in the solution, and $[A]_{surface}$ is the "concentration" of available active sites at the sphalerite or pyrite surface that undergo electrochemical interaction with AX and have not been interacted by AX at time t. In a similar way developed for Cu uptake by sphalerite (Ejtemaei