A comparative study of the attachment of air bubbles onto sphalerite and pyrite surfaces activated by copper sulphate

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A B S T R A C T

Pyrite is a gangue mineral in the flotation of sphalerite activated by copper sulphate (CS). In this study, the attachment of air bubbles onto sphalerite and pyrite surfaces activated by CS was comparatively studied using a novel approach with High-Speed Video Microscopy (HSVM) and X-ray photoelectron spectroscopic (XPS). HSVM allowed for the in-situ determination of the liquid film Drainage Rate (DR) and Contact Angle (CA) of the bubble attachment. The results showed that after the activation sphalerite became hydrophobic by the formation of polysulphide as confirmed by XPS while pyrite remained hydrophilic. With increasing activation time and CS concentration, both DR and CA on the sphalerite surface rapidly increased at the beginning and reached constant values, while those on pyrite remained unchanged. The changes in the CA values of the sphalerite was successfully modelled by considering a second-order rate process for the CS activation which was proportional to initial copper concentration and available Zn active sites on the sphalerite surface. If both sphalerite and pyrite were simultaneously exposed to CS solutions (but not in the physical contact), the rate of CS activation of sphalerite remained unchanged when the ratio of sphalerite to pyrite surface areas exposed to CS solutions was equal to 1:1. However, the activation rate of sphalerite significantly dropped with increasing the sphalerite:pyrite surface area ratio from 1:3 to 1:6. The effect of the surface area ratio on the CS activation rate was prominent at activation times higher than 3 min. The XPS results for the mixed minerals showed the reduction in sphalerite Cu/Zn exchange and polysulphide/Cu ratios with increasing available pyrite surface area in CS solutions, indicating the significant drop in the CS activation of sphalerite in the presence of pyrite. The outcomes of this study provided further insights into the selective flotation of sphalerite from pyrite.

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1. Introduction

The activation mechanism of sphalerite (ZnS) by copper sulphate (CS) prior to adsorption of xanthate in flotation has been extensively studied in literature (Gerson et al., 1999; Jain and Fuerstenau, 1985; Kartio et al., 1998; Prestidge et al., 1997; Ralston and Healy, 1980a,b; Wang et al., 1989b). However, sphalerite is not the only sulphide mineral that its flotation behaviour can be affected by the presence of Cu ions. The possibility of inadvertent CS activation of pyrite (FeS_2), a gangue mineral in sphalerite flotation, and its undesirable flotation are the factors accounting for the effective separation of sphalerite from pyrite (Dichmann and Finch, 2001; Peng and Grano, 2010; Shen et al., 2001; Weisener and Gerson, 2000). Therefore, the presence of pyrite during the CS activation of sphalerite plays a significant role in the activation process affecting the activation kinetics.

CS activation kinetics of sphalerite in the absence of many other minerals has been widely investigated (Allison et al., 1982; Chen, 1999; Dávila-Pulido et al., 2012; Finkelstein and Allison, 1976; Jain and Fuerstenau, 1985; Wang et al., 1989a). Finkelstein and Allison (Finkelstein and Allison, 1976) found that sphalerite CS activation took place in two stages: The first stage was limited to a few monolayers, but it was rapid (less than a second). The first stage was dependent on the properties of the CS solution. Detailed studies of CS activation kinetics of sphalerite (Ralston and Healy, 1980a,b) with a Cu-selective electrode disclosed that Cu ion uptake displayed a clear linear dependence on the logarithmic scale of activation time for the initial, rapid activation step (up to 1.5 min) at pH 4–6.5. After the initial activation step, it was observed that Cu ion uptake data followed fairly closely the logarithmic dependence on time in the interval 1.5–15 min i.e. $\Gamma = k \log_{10} t + \text{constant}$. After 15 min, the rate equation was not well described by the model (Ralston and Healy, 1980a,b).

Pugh and Tjus (1987) studied the kinetics of CS activation of sphalerite by measuring zeta potentials as a function of ageing time after 20 min activation in a copper hydroxide solution. They

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observed charge reversal on the sphalerite surface due to the accumulation of copper hydroxide species on the sphalerite surface between pH = 6 and pH = 8. However, the copper hydroxide coating on sphalerite surface was depleted over a period. It was reflected by the reduction in positive zeta potential, and the sphalerite surface would be eventually converted into copper sulphide. The decrease in the zeta potential was found to be a linear function of the square root of time (parabolic kinetics) and a function of the ratio of Cu ion concentration to the total surface area of sphalerites. Wang et al. (1989a) also investigated the sphalerite activation by CS in acidic and neutral pH media. It was concluded from their study that the parabolic stage (second stage) started after about 5 min, whereas the rate of the second stage was unaffected by the pH of the solution, and the rate of the first stage increased when the pH was increased from 5 to 6. ∗∗Chen et al. (1999) used the electrochemical method to study Cu ion uptake kinetics at acidic and neutral pHs based on the intensity of the anodic peak arisen from the CS activation of sphalerite. They also confirmed the two stages of activation mechanism where the rapid first stage took up to 10 min; then a slow second stage was followed. At about pH 5, Cu monolayers formed after about 30 min. Under the neutral pH condition, the Cu ion uptake was very fast for the first 10 min and then reached saturation, which was equivalent to about 2.5 monolayers of Cu. A second order model reported by Finkelstein (1997) for CS activation of sphalerite was applied by Dávila-Pulido et al. (2012) to study the kinetics of CS activation of sphalerite. They confirmed that the activation kinetics obeyed the second order model.

Despite comprehensive studies on the CS activation of sphalerite, there is a relative paucity of comparative studies into the CS adsorption kinetics of mixed sphalerite and pyrite, and the possible competition between sphalerite and pyrite for Cu ions. This paper focuses on the probable competition between sphalerite and pyrite during the CS activation using in-situ High-Speed Video Microscopy (HSVM) and X-ray photoelectron spectroscopy (XPS) techniques to monitor hydrophobicity, surface components of sphalerite after CS activation in the presence of pyrite with the different surface area, and the Cu activation kinetics. This study aims to gain a better understanding of the effect of pyrite on the CS activation kinetics of sphalerite and the selective flotation of sphalerite.

2. Experimental

2.1. Materials

The sphalerite and pyrite samples were obtained from Wards Scientific (USA). They were cut into 5 mm × 5 mm sections and were mounted in a resin to the end of a small plastic tube. The exposure area of the final polished mounted section was 25 mm². Water used for reagent preparation and experiments was purified using a reverse osmosis RIO's unit and an Ultrapure Academic Milli-Q system (Millipore). The specific resistance of the Milli-Q water was 18.2 MΩ cm^{-1}. $CuSO_4$ (99%, Sigma-Aldrich) was used to activate the sphalerite and pyrite.

2.2. Methods

2.2.1. In-situ studies of film drainage rate and contact angle measurements

The experimental setup for monitoring the liquid film drainage and bubble-surface contact interaction is shown in Fig. 1. High-speed camera video microscopy (HSVM) (Fastcam SA3, Photron, USA) was used to monitor the interaction between a freely rising bubble and the mineral surface. The bubble-flat surface interaction
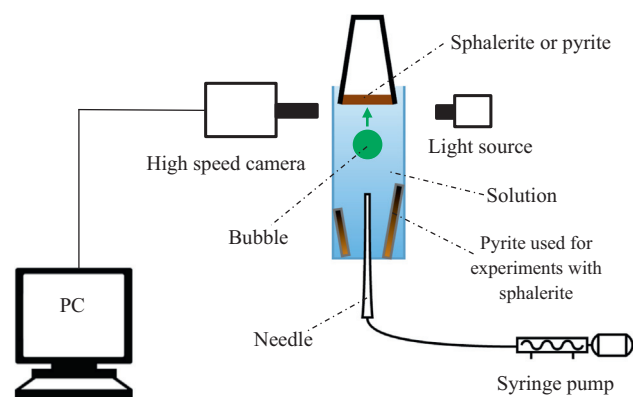

Fig. 1. Schematic of the experimental setup for monitoring the liquid film drainage and bubble-mineral surface contact interaction (not to scale).

was recorded at a high frame rate of 10,000 fps. A needle with 0.184 mm inner diameter was connected to a syringe infusion 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.

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 measurement cuvette filled with desired solution (e.g., $CuSO_4$), and after a given activation time a bubble was generated by running the pump, and interaction of bubble with the mineral surface was monitored and recorded. In the experiments with different ratios of sphalerite to pyrite surface areas exposed to CS solutions, small pieces of pyrite samples with the required surface areas were polished and then plunged into the cuvette at the same time with mounting sphalerite sample to the solution.

2.2.2. X-ray photoelectron spectroscopy (XPS)

The X-ray photoelectron spectroscopy analysis was carried out using a Kratos Axis ULTRA X-ray Photoelectron Spectrometer incorporating a 165 mm hemispherical electron energy analyser. 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 analyser 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 1.0×10^{-8} torr during sample analysis.

Atomic concentrations were calculated using the CasaXPS version 2.3.14 software and a Shirley baseline with Kratos library relative sensitivity factors. Peak fitting of the high-resolution data was also carried out using the CasaXPS software.

The XPS spectra were corrected using the main line of the carbon 1 s 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 sulphur in a high vacuum condition.

3. Results and discussion

3.1. Cu activation kinetics studies with single minerals

3.1.1. Drainage rate

The attachment of hydrophobic particles to air bubbles is a well-known process in froth flotation. A few steps involved in