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The effect of calcium, magnesium, and sulphate ions on the surface properties of copper activated sphalerite

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ABSTRACT

Hydrophobicity and many other surface properties of copper (Cu) activated sphalerite can be changed by calcium, magnesium and sulphate ions in solutions, but have not been quantitatively investigated previously. Here, the effect of $Ca(NO_3)_2$, $Mg(NO_3)_2$, $MgSO_4$ and $CaSO_4$ on the surface properties of Cu-activated sphalerite was studied using contact angle (CA) measurements, X-ray photoelectron spectroscopy (XPS), and zeta potential measurements. The CA measurements show that the hydrophobicity of sphalerite developed after copper activation, but the presence of 30 mM $Ca(NO_3)_2$ or $Mg(NO_3)_2$ or $MgSO_4$ decreased its hydrophobicity: CA reduced from 67° to 48°. The presence of 30 mM of Ca^{2+} and SO_4^{2-} ions in solutions reduced CA further to 42°. This CA change could be due to the simultaneous presence of ionic calcium species and calcium sulphates that precipitated as gypsum. The XPS data show Cu presence on the sphalerite surface after copper activation in the salt solutions was in the Cu(I) state. The effect of $Ca(NO_3)_2$, $Mg(NO_3)_2$, $MgSO_4$ and $CaSO_4$ on the copper activated sphalerite surface appeared to be the same, namely a decrease in Cu(I) adsorption and polysulphide formation. Neither Ca^{2+} nor $CaSO_4$ were detected by surface analysis, but some Mg ions were found on the surface. Zeta potential measurements confirmed the presence of calcium and magnesium ions on the sphalerite surface. The role of calcium and magnesium ions in copper activation of sphalerite appears to be that of moderators which act to reduce the amount of Zn replaced by Cu on the sphalerite surface, whether SO_4 is present or not.

1. Introduction

Sphalerite (ZnS) is the principal source of the world's supply of zinc. The recovery of zinc from economic ore deposits usually involves sequential selective flotation with thiol collectors. It is generally accepted that inactivated sphalerite interacts weakly with short-chain thiol collectors. However, collector-induced flotation of sphalerite has been reported in the absence of added heavy-metal cations both at high pH (Leroux et al., 1987) and after conditioning in acidic media (Girczys et al., 1972; Marouf et al., 1986). It is well established that copper cations exchange with those of zinc (via an ion exchange mechanism) during copper activation of sphalerite (Finkelstein and Allison, 1976). However, the identity of the resulting copper-containing surface phase is still the subject of debate. Cases have been argued for the formation of covellite (CuS) (Cecile, 1985; Finkelstein and Allison, 1976) and chalcocite (Cu_2S) (Nefedov et al., 1980; Perry et al., 1984).

The activation mechanism in which sphalerite is conditioned with Cu(II) (normally as a nitrate or sulphate) prior to adsorption of xanthate, and its effects on subsequent flotation recovery, has been extensively studied. The following chemical exchange reaction has been generally accepted for sphalerite activation in a weakly acidic medium:

$$Cu_{aq}^{2+} + ZnS = CuS + Zn_{aq}^{2+} \quad (1)$$

By interaction between Cu_{surf}^{2+} and S^{2-} the second reaction would be an oxidation/reduction reaction. The reduction of the cupric ion that was exchanged with the Zn ion of sphalerite, and the concomitant oxidation of the sulphide to a polysulfide was sometimes presented by the following reaction: $2nCuS + 2e^- = 2Cu_2S + S_n{}^{2-}$. There would be a problem with this reaction, i.e., a chemical species has to get oxidized to supply the electrons needed by the reaction. Therefore, a better route without the requirement of electrons for the cupric ion exchange with Zn ions, as suggested by Fornasiero and Ralston (2006), is described by: $xZnS + Cu^{2+} = (ZnS)_{x-1}{\cdot}CuS + Zn^{2+}$ and $(ZnS)_{x-1}{\cdot}CuS = (ZnS)_{x-1}{\cdot}0.5Cu_2S_2$. Then, reduction of the exchanged cupric ion to the cuprous state, accompanied by the oxidation of the sulphide to disulphide to produce a cuprous disulphide, is described as follows:

$$2Cu_{surf}^{2+} + 2S^{2-} = Cu_2^{+}(S_2)_{surf}^{2-} \quad (2)$$

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Since $Cu_2^+(S_2)^{2-}_{surf}$ is a hydrophobic species, its presence on activated sphalerite provides an explanation for the observed flotation of copper-activated sphalerite in the absence of collector because the hydrophobic species are responsible for enabling flotation (Fornasiero and Ralston, 2006; Popov and Vucinic, 1990; Prestidge et al., 1997). The effect of salt ions on the formation of the hydrophobic species by reaction (2) can be important in flotation as discussed below.

Management of water resources has become an increasingly important issue in the world because it is closely related to the quality of human life and protection of the environment. Therefore, water reuse is a growing practice in many regions of the world, even in those countries that have not typically been considered to have problems with water scarcity (Bicak et al., 2012). Primary water supplies from bores containing high levels of salinity including calcium, magnesium and iron salts as potential precipitates are being used in several remote areas.

Calcium and sulphate ions are two of the most common species found in sulphide ore concentrator process water. The presence of calcium is due to the use of calcium hydroxide as a pH regulator and the dissolution of calcium-bearing minerals (e.g., calcite, dolomite, etc.) when they are present in the ore. In turn, a sulphate concentration above the saturation concentration for gypsum precipitation occurs due to the natural oxidation of sulphide minerals by atmospheric oxygen during grinding, conditioning, flotation and thickening. Typical process waters have calcium concentrations in the order of 700 mg/L, while sulphate concentrations may reach the saturation point (about 1700 mg/L) or greater (when water is at metastable equilibrium) (Deng et al., 2013; Grano et al., 1995; Levay et al., 2001; Sui et al., 2000, 1998).

Electrostatic interaction between calcium ions and sphalerite has been demonstrated previously (Davila-Pulido and Uribe-Salas, 2014; Deng et al., 2013; Duran et al., 1995; Ikumapayi, 2010; Moignard et al., 1977; Sui et al., 1998). Sui et al. (1998) showed an increase in the zeta potential of sphalerite in the presence of Ca or $CaSO_4$. They showed that the effect on zeta potential is due to Ca ions and not to the precipitates of $CaSO_4$, and attributed the increased zeta potential to the adsorption of Ca^{2+} or Ca-hydroxyl species. However, Lascelles et al. (2003) showed that calcium and magnesium have no effect on copper uptake on sphalerite at acidic or neutral conditions, but reduced copper uptake under highly alkaline conditions when pH exceeded that for the formation of the corresponding hydroxide precipitate. The zeta potential of sphalerite as a function of pH in deionized water, process water and deionized water containing different Ca^{2+} ion concentrations has also been investigated by Ikumapayi (2010). They found that calcium ions exist as divalent cations at pH 11.5, and that calcium hydroxide ($CaOH^+$) ions are the predominant species. Also, their adsorption is seen to decrease the magnitude of negative surface charge and is responsible for charge reversal.

Deng et al. (2013) investigated the zeta potential distributions of sphalerite in 800 ppm calcium solutions in the presence of copper and/or SIPX at pH 6.5. In 800 ppm calcium solutions, the zeta potential distribution of sphalerite shifts to a slightly less negative value of −12 mV in comparison with that in 10 mM KCl solution (−15 mV) (Deng et al., 2013). Davila-Pulido and Uribe-Salas (2014) found that the presence of either calcium or sulphate ions on their own does not have a significant effect on hydrophobicity caused by copper activation of sphalerite. Nevertheless, the simultaneous presence of both ions decreased the contact angle from 28.7° to 19.6°.

The aim of this work is to investigate further and quantify the fundamental interactions of sphalerite with copper, calcium, magnesium, and sulphate ions. This research is relevant to understanding their effects on the copper activation of sphalerite in flotation practice where such ions often occur in significant concentrations.

2. Experimental

2.1. Mineral and reagents

The sphalerite specimen was sourced from Wards Scientific (USA), mounted in metallographic resin and cut into thin sections. The final polished mounted section formed a disc of 30 mm diameter and approximately 2 mm thickness.

The buffer solution used in the experimental work consisted of a mixture of 0.05 M CH_3COONa and 0.05 M CH_3COOH (Reagent grade, ACS) to give pH 4.6. Water used for reagent preparation 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 $M\Omega\,cm^{-1}$. The reagents used in the study are shown in Table 1. Due to the high solubility of calcium nitrate and magnesium nitrate, we used these to chemicals to investigate only calcium or magnesium effects by prevention of calcium sulphate or magnesium sulphate precipitates formation.

2.2. Methodology

2.2.1. Contact angle measurement

For contact angle measurements the sphalerite specimen was mounted in metallographic resin, wet ground and polished with silicon carbide sandpaper (1200#) making use of ethanol and deionized water, then dried with nitrogen gas. Polishing was carried out before each test to renew the mineral surface. After specimen preparation, chemical conditioning was carried out using a two-stage process. Initially, 10 μL of either a calcium or magnesium solution was deposited on the surface and allowed to remain for 10 min, after which it was removed. Activation of the surface was then carried out with the deposition of 10 μL of a solution containing a combination of either calcium or magnesium ions and copper nitrate, simulating the expected conditions within industrial sphalerite flotation circuits. Upon completion of the conditioning process, the mounted specimen was cleaned and transferred to the contact angle measurement chamber (30 cm × 30 cm × 30 cm). Single sessile droplets of water were deposited on the sphalerite surfaces in a closed glass box to minimize possible external perturbations. The experiments were conducted at room temperature (22 ± 1 °C) and controlled relative humidity of 58 ± 1% (using a saturated $Mg(NO_3)_2$ salt solution within the chamber). Small sessile water droplets of 1 μL volume were gently deposited onto the flat solid surfaces using a pipet (Eppendorf Research, Germany) with precisely controllable volume. A progressive scan CCD camera (model XCD-SX910, Sony, Japan) fitted with a 10 × objective lens (Nikon, Japan) was used to capture transient pictures. A fibre light with a diffuser was used to illuminate the drop from behind. The video movies were then extracted into single images using Photron Fastcam Viewer 3 software (Photron) and further analysed using an in-house Matlab code for determining the droplet contact base radius and contact angle. Under all conditions, the experiments were repeated three times.

Table 1
Reagents used in the sphalerite surface preparation.

Chemicals	Grade (%)	Supplier
Copper nitrate, $Cu(NO_3)_2$	99	Sigma–Aldrich
Calcium sulphate, $CaSO_4$	99	Sigma–Aldrich
Magnesium sulphate, $MgSO_4$	99	Sigma–Aldrich
Calcium nitrate, $Ca(NO_3)_2$	99	Sigma–Aldrich
Magnesium nitrate, $Mg(NO_3)_2$	98	Sigma–Aldrich
Sodium sulphate, Na_2SO_4	99	Aldrich Chemical Company