



Effects of salinity on xanthate adsorption on sphalerite and bubble–sphalerite interactions



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ABSTRACT

The adsorption of amyl xanthate on sphalerite in NaCl solutions of different concentrations and in saline water (viz. simulated sea water) and the surface properties of treated minerals were investigated. The interactions between xanthate treated sphalerite particles and air bubbles were examined using induction time measurement, which revealed that the salt ions could inhibit the adsorption of xanthate on sphalerite due to the competitive adsorption, but also could compress the electrical double layer at mineral/water interface. The induction time of sphalerite treated in potassium amyl xanthate (PAX) with saline water was shorter than that of sphalerite treated in PAX with NaCl of the same ion concentration, which implies that the water composition (e.g. Ca^{2+} , Mg^{2+}) could play an important role in the bubble–particle interaction. The hydrophobicity, chemical composition, and charge property of PAX treated sphalerite surfaces were characterized using contact angle measurement, Cryo-X-ray photoelectron spectroscopy (Cryo-XPS) and zeta potential determination, respectively, which support the inhibition effect of salt ions on the xanthate adsorption on sphalerite. In the case of saline water, the xanthate decomposition products were confirmed by XPS, which could further lower the hydrophobicity of the treated sphalerite. Our results provide insights into the basic understanding of the salinity effects on the xanthate adsorption on sphalerite and the bubble–mineral interactions in flotation.

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1. Introduction

Sphalerite (zinc sulfide mineral) is the most important source of zinc metal, and zinc sulfide itself also has many applications such as lubricant additives (Moreno et al., 2011) and photocatalysts (Chandra and Gerson, 2009). Alkyl xanthates are commonly used collectors for sphalerite flotation to separate sphalerite from other valuable minerals (Harmer et al., 2008) or gauge minerals (e.g. clays) (Wang and Peng, 2014). Xanthate ions adsorb on mineral surfaces to render the mineral surfaces hydrophobic, which facilitates the attachment of air bubbles onto mineral particles and consequently benefits the flotation. Because zinc (II) alkylxanthates are more soluble in water than most other heavy-metal alkylxanthates (Fuerstenau et al., 1985), the floatability of sphalerite with xanthates as collectors is relatively poor, especially when the alkyl chains of xanthates are shorter than amyl due to the weak hydrophobicity of zinc (II) alkylxanthates with short chains (Leja, 1982). Nevertheless, sphalerite is still floatable with xanthates as collectors. Fuerstenau et al. (1974) studied the flotation of sphalerite with alkylxanthates of various carbon chain lengths as

a function of pH and xanthate concentration. The flotation recovery increases with increasing the xanthate concentration and carbon chain length. At pH 2–6, with 2.5×10^{-4} M amyl xanthate, the flotation recovery is higher than 80%. Combined with the infrared absorption spectroscopy data, the authors concluded that the formation and adsorption of bulk precipitated zinc (II) alkylxanthates on the alkyl chains of chemisorbed xanthates is necessary to render sphalerite surface hydrophobic for bubble attachment (Fuerstenau et al., 1974). Patrick et al. applied so-called fluorescence reflection extended X-ray absorption fine structure (REFLEXAFS) to study xanthate adsorption mechanism. To avoid the problem of differentiating between sulfur in the xanthate and the ZnS substrate, ZnSe was used as an iso-structural analogue of ZnS. On addition of sodium isopropyl xanthate, the evidence of direct interaction of xanthate S and Zn in unactivated ZnSe at pH 5 was observed (Patrick et al., 1999). Song et al. investigated the adsorption of ethyl and amyl xanthate ions on sphalerite fines using electrophoretic light-scattering (ELS) measurements (Song et al., 2001a). They found that the adsorption of xanthate ions on sphalerite is nonuniform, which could be responsible for the poor flotation recovery. The adsorption of xanthate ions on sphalerite also causes the hydrophobic flocculation of sphalerite fine particles,

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which enlarges the sphalerite particle size and subsequently improves the floatability of mineral fines (Song et al., 2001b).

Due to the shortage of available fresh water sources and restrictions for disposal of used water to the environment for mineral processing industry, recycled water and seawater have been applied for mineral flotation (Castro and Laskowski, 2011; Drelich and Miller, 2012; Farrokhpay and Zanin, 2012; Moreno et al., 2011; Wang and Peng, 2014). The high salinity condition and complex aqueous media could cause various challenging issues in mineral processing, and the effects of process water quality on recovery and grades of valuable minerals were discussed in the recent International Symposium on Water in Mineral Processing (Drelich, 2012). In flotation process, the presence of salt ions and the elevated salinity can affect the structure of water (e.g. “structure making” or “structure breaking”) in vicinity of mineral particles, particle properties (e.g. hydration layer and electrical double layer), and bubble properties (e.g. bubble coalescence and froth stability) (Bérubé and de Bruyn, 1968; Du and Miller, 2007; Johnson et al., 2000; Ozdemir et al., 2007; Ralston and Healy, 1973; Shi et al., 2014a,b; Teng et al., 2011; Wang and Peng, 2014), which in turn influences the mineral–bubble interaction and flotation efficiency. Understanding the impact of complex aqueous solution conditions, particularly the high salinity environment, on the adsorption of collectors (e.g. xanthate) on sulfide minerals and their surface properties is of both fundamental and practical importance. In this work, sphalerite was chosen as a model sulfide mineral, and the adsorption of xanthate ions on sphalerite in solutions of different salinity was investigated. The interactions between xanthate treated sphalerite and air bubbles were examined via induction time measurements to elucidate the effects of ions and solution salinity on the attachment of bubbles to treated sphalerite. The physicochemical surface properties of the mineral particles were investigated by contact angle measurement, X-ray photoelectron spectroscopy (XPS) analysis and zeta potential determination.

2. Experimental

2.1. Materials

Sphalerite (Crystalline) was purchased from Ward's Natural Science, and was milled and dry-screened to collect 75–150 μm size fractions for induction time measurement. Potassium amyl xanthate ($\text{C}_6\text{H}_{11}\text{OS}_2\text{K}$, Prospec Chemicals Ltd., Canada), sodium chloride (NaCl , ACS certified, Fisher Scientific), sodium hydroxide (NaOH , ACS certified, Fisher Scientific), hydrochloric acid (HCl , 1 M, ACS certified, Fisher Scientific), calcium sulfate hemihydrate ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$, ACS certified, Fisher Scientific), magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, ACS certified, Fisher Scientific) sodium sulfate anhydrous (Na_2SO_4 , ACS certified, Fisher Scientific) were used as received.

All aqueous solutions were prepared using Milli-Q water (Millipore deionized, 18.2 $\text{M}\Omega\text{ cm}$ resistivity). Potassium amyl xanthate (PAX) was purified by adding 100 g xanthate into 1000 mL warm acetone at 40 $^\circ\text{C}$ on a water bath, stirring for a few minutes and precipitated by ether following an established method (Rao, 1971; Teng et al., 2012). The so-called “saline water” in this work was prepared based on recent reports about saline water in mineral flotation (Bruce and Seaman, 2014; Ji et al., 2013), which was a simulated mixture of seawater and reclaimed process water. Only major ions were considered to make up the saline water, and the composition of saline water is shown in Table 1.

2.2. Induction time measurement

The induction time measurements were conducted using a home-built induction timer and following a procedure reported

Table 1
Ion concentrations (M) in saline water.

Ion	Cl^-	SO_4^{2-}	Na^+	K^+	Ca^{2+}	Mg^{2+}
Concentration	0.423	0.0225	0.383	0.0108	0.00775	0.0411

previously (Gu et al., 2003). Briefly, silicon wafer was placed on top of a Teflon stage in a transparent rectangular glass cell to provide a flat substrate, and a desired testing solution was poured into the cell and sphalerite particles (75–150 μm size fractions) were spread on the silicon wafer to form a particle bed. A fresh captive bubble with diameter of 1.5 mm, held on a capillary tube, was pushed against the particle bed in the testing solution for a controlled contact time. The approaching speed of bubble was 4 cm s^{-1} . The initial distance between the air bubble and the particle bed was fixed at 0.25 mm and the bubble displacement was 0.4 mm. A video camera was used to provide a side view of the bubble and particle bed to determine whether attachment of particles to the bubble surface occurred during the desired controlled time. Fig. 1 shows a typical side-view microscopic image of sphalerite particles attached to an air bubble in aqueous solution. The bubble approach process was repeated 20 times against different positions on the particle bed. A distribution of the attachment probability was plotted as a function of contact time. The contact time with 50% of attachment probability was referred to as the induction time (Ye et al., 1989). Before each measurement, sphalerite particles were soaked in 0.01 M HCl for 5 min and then washed 5 times with Milli-Q water. The cleaned particles were treated in conditioning solutions (5×10^{-4} M PAX with various ion concentrations at pH 5) for 10 min and washed 5 times with Milli-Q water, and then transferred into testing solutions (with various ion concentrations at pH 5, free of collector). The terms of conditioning solution and testing solution are used throughout this work. The pH of the conditioning solutions and testing solutions was fixed at pH 5, under which sphalerite was reported to show good flotation recovery with xanthate as collector (even without Cu activation) (Fuerstenau et al., 1974; Harmer et al., 2008; Song et al., 2001b), to investigate the effect of solution salinity on xanthate adsorption on sphalerite and bubble–sphalerite interaction.

2.3. Contact angle measurement

The sessile drop technique was used to measure contact angles of water on sphalerite surfaces. Sphalerite minerals were freshly crushed, polished by using SiC paper from 60 to 1200 grit, rinsed with Milli-Q water, and then dried by N_2 (Wang et al., 2013). Then the minerals were treated in a desired conditioning solution

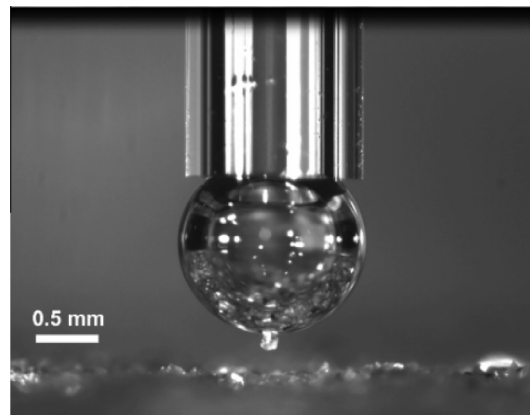


Fig. 1. A typical microscopic image taken during induction time tests for mineral particles attached to an air bubble in aqueous solution.

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