



Effect of sodium pyrophosphate on the flotation separation of chalcopyrite from galena

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ABSTRACT

The effect of sodium pyrophosphate (SPH) on the separation of chalcopyrite from galena was examined through flotation, adsorption, electrokinetic studies and infrared spectral analysis. Differential flotation tests indicate that satisfactory separation can be achieved within the pH range from 2.5 to 6 using SPH to depress the galena, but not the chalcopyrite when *O*-isopropyl-*N*-ethyl thionocarbamate (IPETC) is used as the collector. The electrophoretic mobilities of both the minerals dramatically become negatively charged following SPH adsorption in the pH range from 2.5 to 12. The infrared spectral analysis suggests that chemical adsorption occurs on galena surface treated by SPH, indicating that a chelate complex has formed. At weakly acidic pH values, the adsorption density of IPETC onto galena is significantly reduced in the presence of SPH. However, the amount of IPETC adsorbed onto chalcopyrite almost remains at the same level. Since the observed adsorption density of IPETC onto chalcopyrite is quite high compared to galena, the observed flotation results are explained. A possible mechanism for the interaction between the two sulphide minerals and SPH is discussed.

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1. Introduction

Many polymetallic sulfide ores contain copper and lead minerals. Generally, the most common treatment methods include: (1) Bulk copper/lead flotation followed by copper/lead separation; (2) Sequential copper/lead flotation [1,2]. The main difficulty with the differential separation of chalcopyrite from galena lies in the extremely similar floatability of these two minerals.

The list of depressants used to facilitate separation has long included sulphur-oxy depressants added in the form of sulphite, bisulphate, metabisulphite or sulphur dioxide, as well as sodium dichromate or cyanide [3]. Of these agents, dichromate and cyanide have been the most common used. They are, however, known to be toxic and their use is often associated with environmental hazards and a large loss of precious metals from the mineral concentrates. Therefore, selective, non-toxic and bio-degradable agents are required.

The application of some cyanide-free and bichromate-free flotation depressants has been recently reported for both laboratory and commercial process. Much progress has been made. In particular, organic depressants are a diverse, cost-efficient, and readily available series of agents that have gained importance and attention [4]. For instance, dextrin selectively depressed galena while chalcopyrite was floated with a xanthate collector using NaOH to adjust

pH [5]. Carboxymethyl cellulose (CMC), especially in combination with Na_2SiO_3 and Na_2CO_3 , has been widely applied to depress galena in the flotation separation of chalcopyrite from it [6–8]. Sodium polyacrylate has also been used as an effective galena depressant during Cu/Pb separation [9]. Liu et al. have shown that ferrochrome lignosulfonate added to the pulp slightly decreases the recovery of chalcopyrite while galena was dramatically depressed [10].

Polyphosphates, due to their low price, non-toxicity and excellent chemical properties, have been extensively used in the field of mineral processing recently mainly as dispersants and depressants.

Previous investigation of polyphosphates as dispersants revealed an increased stability of suspensions due to increasing repulsion between particles. This occurred either because of increased electrostatic repulsion or because close approach of the particles is prevented by repulsive steric interactions, or by a combination of the two [11].

The ability of polyphosphates to form soluble complexes with divalent metal ions has been long known for a long time and is of great interest due to the ability of polyphosphates to act as selective depressant. Lu et al. have reported that the obvious depressed performance of sodium hexametaphosphate (SHX) on the floatability of barite [12]. Bulatovic et al. have shown that a new depressant based on dichromate complexed with carboxymethyl cellulose (CMC) and sodium phosphate (Na_2HPO_4) was being used for copper/lead separation in the Raura plant [1]. Rashchi et al. concluded that mechanism by which polyphosphates controlled contaminant metal ions was: (1) A blocking mechanism where a metal ion-polyphosphate complex formed on the surface, thereby

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inhibiting further adsorption of the collector; or (2) A cleaning mechanism where the metal ion-polyphosphate complex selectively solubilized the metal ion thereby removing it from the surface [13]. Ding et al. proposed the mechanism that sodium hexametaphosphate (SHX) depressed almandine and the mechanism can be divided into two parts: (1) SHX is chemically adsorbed onto the surface of almandine and thus induced strong hydrophilic forces; and (2) SHX selectively dissolves calcium from almandine surface, thereby reducing the number of active calcium sites, which decreased the adsorption of collector, i.e. a cleaning action [14]. This mechanism is compatible with the findings by Parsonage et al. who concluded the mechanism of triphosphate depression of calcite, apatite and dolomite involved triphosphate adsorbed at cation sites conferred a highly negative zeta potential to the mineral and thereby reduced the adsorption of collector [15].

Electrokinetic potential studies and X-ray photoelectron spectroscopy performed by Zhang and Fang indicated that the selective adsorption of sodium pyrophosphate onto the mineral surfaces contributed to the different chemical activation seen from that additive [16]. It was also shown that sodium pyrophosphate preferentially adsorb to metallic ions at a position located on microcline surface, as well as reacts with metallic ions to produce complexes that precipitate onto microcline surface, this increases the differential adsorption of sodium pyrophosphate onto the mineral surface. Other references have reported that flotation of galena is improved by removing Ca and Mg ions with hexametaphosphate [13,17]. Galena was strongly depressed in the presence of these cations, but after the addition of hexametaphosphate, galena recovery was regained, especially within the pH range from 8 to 10, this is a form of blocking action. The results of a new technology for separating bulk copper/lead concentrate investigated by Liu show that sodium pyrophosphate, especially in combination with CMC acts as a selective depressant of galena that could produce satisfactory separation performance [18].

Reports describing the use of polyphosphates as a depressant during sulfide mineral separations are not scarce, but the reaction mechanism behind the observed results is not well documented. The subject of this study is the flotation separation of chalcopyrite from galena using sodium pyrophosphate to depress the galena in an acidic pH range. In the presence of sodium pyrophosphate, the flotation behavior of chalcopyrite and galena and a possible mechanism was investigated using zeta potential measurement, adsorption test and infrared spectral analysis.

2. Experimental

2.1. Materials

Samples of chalcopyrite and galena were obtained from Yunnan and Guangxi, respectively. The crystals were first hand picked from the mine and then crushed, pulverized and dry screened to size fractions of $-74\ \mu\text{m}$ and $-38\ \mu\text{m}$, those two samples were used for the micro-flotation and adsorption test, respectively. A similar method was used to prepared $-2\ \mu\text{m}$ size fraction for electrokinetic potential studies. These samples were stored in sealed glass bottles to prevent further surface oxidation and to ensure reproducibility of the tests. The chemical analysis of the chalcopyrite revealed a composition (mass percent) of 38.30% Cu, 23.24% Fe, 31.99% S and 0.81% Pb, while the galena sample contained 84.61% Pb, 1.96% Fe, and 10.12% S.

The collectors used were *O*-isopropyl-*N*-ethyl thionocarbamate (IPETC) and ammonium dibutyl dithiophosphate (ADTP), these were industrial grade reagents supplied by the Zhuzhou Flotation Reagents Factory in Hunan province. Sodium pyrophosphate (SPH) was of analytical grade. Dilute solutions of sodium hydroxide

and hydrochloric acid were used to adjust the pH value. Solutions all the reagents were prepared using distilled water.

2.2. Flotation tests

Flotation was carried out in a micro-flotation cell with an effective volume of approximately 40 mL. A 2.0 g sample of the material ($-74\ \mu\text{m} + 38\ \mu\text{m}$ particle size fraction) was used for each experiment and the sample was cleaned by ultrasonic treatment prior to the tests. After one minute of agitation, the pH value of the suspension was adjusted. Then the depressant, the collector and the frother were added sequentially. The conditioning time was 2, 5 and 1 min, respectively. The flotation time was set to 2 min. The froth fractions of flotation were filtered to remove excess of water, dried and analyzed for copper and lead.

2.3. Infrared spectrum measurement

Sodium pyrophosphate (SPH), chalcopyrite, galena and their interaction products (chalcopyrite-SPH, galena-SPH) were used as samples for these tests. A known mass of mineral sample (1.0 g) was combined with 20 mL of SPH solution at pH 5.5 and then ground in a carnelian agate mortar and pestle for 30 min, filtrated, and rinsed 2 or 3 times using the corresponding pH buffer solution. The treated sample was dried in a vacuum desiccator, and then used for FTIR reflection spectra measurement. The infrared spectra were recorded using NEXUS-470 spectrometer.

2.4. Adsorption tests

The adsorption density of IPETC onto chalcopyrite and galena, both in the absence and presence of SPH over the pH range from 4.5 to 6 was determined by measuring the adsorption at a wavelength of 204 nm, an ultra-violet (UV-1810) spectroscopy was used for this test. A 2.0 g sample of $-38\ \mu\text{m}$ sized mineral was pulped with 40 mL distilled water. After the addition of a known amount of the desired reagents, the solution was agitated for 15 min using a stir followed by centrifugation at 4500 rpm for 10 min using a high speed refrigerated centrifuge. The suspensions were then filtered through filter paper. Finally the solution after adsorptions was measured with the UV spectrometer. The amount of IPETC adsorbed on the chalcopyrite and galena was calculated from the difference between the initial and residual IPETC concentration in the solution. The average BET specific surface area for the ground chalcopyrite and galena samples was 0.26 and 0.13 m^2/g .

2.5. Electrokinetic potential studies

The zeta potentials of chalcopyrite and galena conditioned with and without SPH were measured as a function of pH. A 0.1 g sample of pure mineral was first ground to $-2\ \mu\text{m}$, and then transferred into a 100 mL beaker containing a 50 mL solution of potassium chloride at an ionic strength of $10^{-2}\ \text{M}$. The conditioning procedure aforementioned in flotation tests was identical for these electrokinetic studies. After conditioning, a small part of the suspension was transferred into a standard cuvette for zeta potential measurement using a Coulter Delta 440SX instrument. The solution temperature was maintained at $25.0 \pm 0.5\ ^\circ\text{C}$. Then measurements were taken and the average was presented as the measured zeta potential.

3. Results and discussion

3.1. Flotation studies

3.1.1. Collector performance of IPETC and ADTP

Fig. 1 compares of collector performance of IPETC and ADTP for the flotation of chalcopyrite and galena as a function of pH is made

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