Colloids and Surfaces A: Physicochem. Eng. Aspects 486 (2015) 145–152

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

A study of adsorption mechanism of dodecylamine on sphalerite

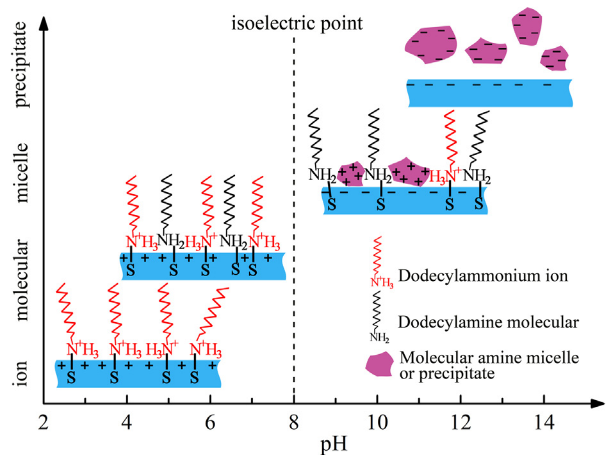
Shihong Xu[a], Jue Kou[a,*], Tichang Sun[a], Kwangsok Jong[a,b]

[a] *School of Civil and Environmental Engineering, University of Science and Technology Beijing, Beijing 100083, China*
[b] *Mineral Processing Engineering Department, School of Mining Engineering, KimChaek University of Technology, Pyongyang 999093, Democratic People's Republic of Korea*

HIGHLIGHTS

- A new flotation mechanism of sphalerite using dodecylamine as collector is proposed.
- Dodecylammonium ions could chemisorb with sulfur atoms (in ZnS form) by N atoms.
- The neutral molecular dodecylamine could screen the electrostatic repulsion between positive-charged head groups.
- Negatively charged dodecylamine precipitates inhibit sphalerite flotation.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 18 June 2015
Received in revised form 8 September 2015
Accepted 16 September 2015
Available online 21 September 2015

Keywords:
Long-chain primary amines
Dodecylamine
Sphalerite
Adsorption mechanism
XPS
Adsorption layer structure

ABSTRACT

Long-chain primary amines are not only good collectors for silicate minerals, but, they can also float some metallic sulfides. However, the flotation mechanism of sulfide minerals using long-chain primary amines as collector is uncertain. In this paper, the flotation performance and adsorption mechanism of dodecylamine in the flotation of sphalerite was studied using micro flotation tests, zeta potential measurements, XPS analysis and FTIR measurements. The dodecylamine showed better sphalerite flotation performance over a wide pH range even at a low collector dosage. The spectroscopic data in combination with zeta potential showed that: (1) chemisorption occurred between the N atoms in dodecylammonium ions (RNH_3^+) and the sulfur atoms in ZnS over the pH range from 1 to 13. The molecular dodecylamines (RNH_2) could also adsorb via H-bonds with other sulfur atoms; (2) the molecular dodecylamine absorbed onto the sphalerite surface may screen the electrostatic repulsion between the positive-charged head groups ($-NH_3^+$) absorbed onto the sphalerite surface, which increased the density of absorbed amine and further enhanced the surface hydrophobicity; (3) in the alkaline pH range, the dodecylamine colloidal precipitates appeared, and the zeta potential of the colloidal precipitates changed from positive to negative as the pH increased. As a result, positively charged precipitates electrostatically adsorbed onto the negatively charged sphalerite surface thus enhancing the flotation recoveries, while negatively charged precipitates inhibited sphalerite flotation.

* Corresponding author.
E-mail address: koujue@ustb.edu.cn (J. Kou).

http://dx.doi.org/10.1016/j.colsurfa.2015.09.040
0927-7757/

1. Introduction

Xanthates are the most commonly used collectors in the flotation of sphalerite. Unfortunately, sphalerite does not respond well to short chain thiol collectors, unless it is activated by some transition metal ions [1]. In contrast, sphalerite can float well with low concentration dodecylamine over a wide pH range without activation [2–7].

Dodecylamine is a commonly used cationic weak-electrolyte-collector. Since long-chain primary amines are good collectors for the common silicate minerals it has been suggested that investigators have omitted them from consideration as collectors for the selective flotation of metallic sulfides [4]. There have been several investigations on the use of long-chain primary amines for the flotation of sphalerite. As early as the 1940s, Ralston patented the process of separating zinc sulphide from lead sulfide by using primary long-chain aliphatic amine [2,3]. Kellogg [4] investigated the mechanism of dodecylamine as a collector for the flotation of galena-sphalerite ores by conducting contact-angle measurements and analysis of the aqueous solution. He postulated that the water repellency was induced by the formation of a zinc–amine complex ($[Zn(RNH_2)_x]^{2+}$) on the surface of the sphalerite. Laskowski systematically studied the colloid chemistry of primary amines [5,6] and a subsequent study [7] suggested that after a sufficiently long conditioning time, a very strong, chemical interaction between the dodecylamine (even when in a colloidal form) and the sphalerite occurred. However, the author did not point out what the chemical interactions and reaction products were.

In practice, long-chain primary amines are used to float zinc oxide minerals after sulfidization using sodium sulfide [8–11]. It is generally accepted that the hydrosulfide ions (HS^-) are the predominant species in the pH range of sulfidization and flotation ($10 < pH < 13$) and therefore it causes the mineral surface to become negatively charged, which favors the electrostatic adsorption of amines [12–15]. On the one hand, the sulfidization process converts the oxide mineral surface to a sulfide surface. This process includes: (1) the dissolution of Na_2S, in which HS^- and S^{2-} ions form in the aqueous suspension; (2) the adsorption of HS^- and S^{2-} ions on the mineral surfaces; (3) the chemical and/or electrochemical reactions, in which sulfide forms on the surfaces; and (4) the possible dissolution of some surface species [16]. On the other hand, amine exists in the pulp mainly in the form of $RNH_{2(aq)}$ in the flotation pH range ($10 < pH < 13$), and the RNH_2 can link with the Zn^{2+} ions (in ZnS form) through coordination bonds formed by N atoms, resulting in zinc-amine complexes or hydroxyl ions produced on the surface [17,18]. Therefore, the flotation of sulfidized zinc oxide minerals using primary amine can be treated as the flotation of zinc sulfide using the primary amine collector.

Although the flotation mechanism of sphalerite using primary amines as a collector has been studied by several investigators, the flotation mechanism, reaction processes and associated surface reaction products still remain controversial. In this paper, we studied the flotation mechanism of sphalerite using primary amine. The flotation performances of dodecylamine in floating pure sphalerite mineral were studied by micro-flotation, and the flotation mechanism was evaluated by zeta potential measurements, XPS analysis and FTIR measurements.

2. Materials and methods

2.1. Materials

The sphalerite sample used in the present studies had a purity of 97.73% based on chemical and X-ray diffraction (XRD) analysis (Fig. 1). It assayed 65.57% Zn, 0.93% Si, 0.07% Fe, 0.04% Cu and 0.09% Pb using ICP. The sphalerite rock samples were crushed, hand-sorted, ground in an agate mortar and dry-screened to collect the −75 + 45 mm size fraction, which was used for micro-flotation tests and the −45 mm fine fraction was reserved for other measurements.

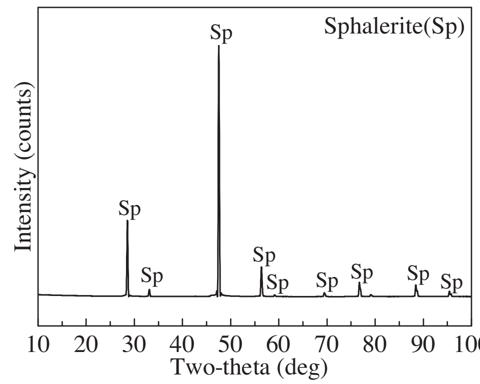


Fig. 1. X-ray diffraction of sphalerite sample in the present study.

The dodecylamine hydrochloride (DACl) was purchased from Sigma-Aldrich with purity of 99% and was used without further purification. Other chemicals used in the study were analytical grade reagents. Hydrochloric acid and sodium hydroxide were utilized to adjust the pH. Deionized water was used throughout the experiments.

2.2. Micro-flotation test

Micro-flotation tests were conduct to recover sphalerite to assess the effect of dodecylamine hydrochloride concentration and pH using a XFGII5 flotation machine (mechanical agitation) with a 30 mL effective cell volume under an 1700 rpm impeller speed. Exactly 2 g of sphalerite sample and 30 mL distilled water were transferred to the cell and conditioned for 2 min. Aqueous solutions of sodium hydroxide or hydrochloric acid was then added and conditioned for 2 min to adjust the pulp pH values. After the addition of aqueous dodecylamine hydrochloride at a desired concentration, the pulp was conditioned for 2 min. Then flotation was conducted for 5 min. Both froth and tailings products were collected, dried, and weighed. The mineral recoveries were calculated based on the dry weights of the obtained products.

2.3. Zeta potential measurement

The zeta potential measurements were carried out using a Zeta Potential and Particle Size Analyzer (Brookhaven Instruments, USA). A 0.05 g sample of pure sphalerite was ground to 5 μm in an agate mortar and pestle grinder and then transferred into a 100 mL beaker containing 50 mL solution of 1×10^{-3} mol/L KCl background electrolyte. For collector treatment, the conditioning procedures were conducted using the same conditions as in the flotation tests as presented in Section 2.2. The zeta potential of colloidal dodecylamine [19,20] at alkaline pH was measured in the 1×10^{-3} mol/L KCl background electrolyte solution. The pH of the suspension at the time of measurement was recorded and the environmental temperature was maintained at 25.0 ± 0.5 °C.

2.4. X-ray photoelectron spectroscopy

The XPS measurements were performed using a Thermo Scientific ESCALAB 250Xi instrument under ultrahigh vacuum conditions and using an Al Kα source ($h\nu$ 1486.60 eV) over a specific area of 500 μm. The high resolution XPS spectra were collected using a