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Characterization of zinc sulfide species on smithsonite surfaces during sulfidation processing: Effect of ammonia liquor

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ABSTRACT

The interaction between sulfide-ion species and smithsonite surfaces in the absence with and without ammonia liquor was investigated. The results of zeta potential and sulfide ion adsorption indicated that $\text{NH}_3 \cdot \text{H}_2\text{O}$ addition promoted the transfer of sulfur in the pulp solutions onto the smithsonite surfaces. Time-of-flight secondary ion mass spectrometry and X-ray photo-electron spectroscopy analysis indicated that the zinc sulfide species was composed of zinc monosulfide and zinc polysulfide and was reinforced by $\text{NH}_3 \cdot \text{H}_2\text{O}$ addition. The distribution ratio of polysulfide in the whole S species increased. The results shed light on reinforcement of the smithsonite sulfidation mechanism with ammonia liquor addition.

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Introduction

Usually, zinc is mainly concentrated from zinc sulfide minerals with conventional flotation techniques. However, with the increasing depletion of zinc sulfide ores and restrictions on sulfur emission, the beneficiation of oxidized zinc ores has assumed great importance in recent years [1–3]. Smithsonite (ZnCO_3) is an important zinc oxide mineral and is commonly used as a study object to investigate the flotation behavior of zinc oxide with various flotation reagents [4–6]. Compared with its corresponding sulfide mineral, smithsonite exhibits inferior floatability. Sulfidation–flotation is commonly performed to recover zinc metal from smithsonite ores [7–9]. This process involves sulfidation of the smithsonite using sulfurizing reagents to allow sulfide collectors to recover the targeted base zinc oxides. Amine collector is commonly used to recover smithsonite ores after sulfidation. However, the main disadvantage for sulfidation–amine flotation processing lies in the severe influence of slime. The amount of sulfidizing reagents and pulp pH must be carefully controlled in amine flotation [10,11]. Thus, desliming prior to flotation is usually required during this process, which causes loss of fine smithsonite minerals [12,13].

Sulfidation–xanthate flotation is effective for beneficiating smithsonite ores. In this approach, sulfidation is a vital step, but a key link in sulfidation is difficult to attain. The common problem when using Na_2S as the sulfidizing reagent is the contradiction between Na_2S concentration and smithsonite floatability, that is, low Na_2S concentration cannot adequately vulcanize the mineral surface, whereas sulfide collectors are inhibited at high Na_2S concentrations, consequently diminishing smithsonite floatability. Thus, extreme operating conditions must be applied to strictly control Na_2S addition to the pulp suspension prior to collection. This process prevents the adverse effects of inappropriate sulfide dosage on flotation. Additional, many sulfidation techniques, such as surface, mechano-chemical [14,15], hydrothermal [16–19], and roasting sulfidation [9,20,21] have been studied for zinc oxide sulfidation. Many studies present screenings of sulfurizing techniques for zinc oxide sulfidation; however, surface sulfidation is one of the best candidates because it is easier to operate and is more economically feasible than other techniques. Thus, investigating the effective surface sulfidation technique to beneficiate zinc oxide minerals is a worthwhile endeavor.

Using smithsonite surface sulfidation with Na_2S as a sulfurizing reagent has been widely studied. The sulfidation mechanism of smithsonite involves the following [22–24]: (I) ion-exchange reaction between sulfide and carbonate ions on the smithsonite surface and (II) metal sulfide precipitation adsorption, in which sulfide ions react with metal ion components, forming metal sulfide and adsorbing on the smithsonite surfaces. Mehdilo et al.

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[25] showed that smithsonite surfaces were completely converted into ZnS at high Na₂S concentrations, and the mineral surface was coated with a dense sulfide film. Navidi Kashani and Rashchi [7] demonstrated the formation of zinc sulfide on smithsonite surfaces with Na₂S addition, and that the number of zinc sulfide layers was limited. Wu et al. [26] suggested that zinc sulfide film deposited on smithsonite surfaces after Na₂S treatment. Feng and Wen [27] indicated that zinc sulfide species formed on the surface of smithsonite after sulfidation, and its contents increased as Na₂S concentration increased. In conclusion, numerous studies on smithsonite surface sulfidation have been conducted, but minimal information is available regarding the reinforced sulfidation mechanism of smithsonite and zinc sulfide species on smithsonite surfaces. Zinc sulfide species on smithsonite surfaces, such as monosulfide and zinc polysulfide, are important for smithsonite hydrophobicity and floatability [28,29]. Hence, studying the reinforced smithsonite surface sulfidation behaviors and mechanisms, as well as investigating the zinc sulfide species on smithsonite surfaces, is important to improve flotation performance. This study explored the industrial application of sulfidation-xanthate flotation.

Ammonia liquor is a mixture that dissociates in water. It dissolves oxidized ores to form $[M(NH_3)_i]^{2+}$ ions ($i=1, 2, 3, 4$) [30–32]. When these sulfurized compounds form MS, where M is a metal element and S is sulfur, more active sites become available for collector binding than for sulfurized metal oxides, thus improving the flotation performance. Motivated by these observations, we investigated the characterization of zinc sulfide species on smithsonite surfaces during sulfidation with the addition of NH₃·H₂O. We focused on the reinforced sulfidation mechanism of smithsonite using two sulfidation mechanisms.

In this work, the effect of ammonia liquor on zinc sulfide species formation on smithsonite surfaces during sulfidation was investigated via inductively coupled plasma (ICP) analysis, zeta-potential determination, and X-ray photo-electron spectroscopy (XPS). Moreover, time-of-flight secondary ion mass spectrometry (TOF-SIMS) was used innovatively to characterize the smithsonite surface. The results shed light on the reinforcement of the smithsonite surface sulfidation mechanism with the addition of ammonia liquor, and therefore provided theoretical basis for the sulfidation-xanthate flotation technique of zinc oxide ores.

Experimental

Materials and reagents

The original smithsonite samples used in all experiments were obtained from the Yunnan Province, China. The samples were prepared by stage crushing and dry grinding in a mill (MM400, Retsch, Germany). The ground products were sieved using a standard screen to achieve a particle fraction of $-74 + 38 \mu\text{m}$ smithsonite. Main chemical analysis showed that the test samples contained 49.69% Zn and low levels of mineral impurities. X-ray diffraction (XRD) pattern of sample is shown in Fig. 1, and only the smithsonite crystal was observed. The diffraction peak was well consistent with the data presented in the JCPDS card (No. 83-1765) [27]. Analytical-grade Na₂S·9H₂O was employed as sulfidizing agent. Sodium hydroxide (NaOH), hydrochloric acid (HCl), and ammonia liquor (NH₃·H₂O) with more than 98% purity were used. Pure deionized water with a resistivity of 18 MU obtained from a Milli-Q50 system (Billerica, MA, USA) was used in all experiments.

Sulfide-ion adsorption experiments

Each 2 g of the smithsonite samples with particle size fractions of $-74 + 38 \mu\text{m}$ were added to two different solutions, one of which

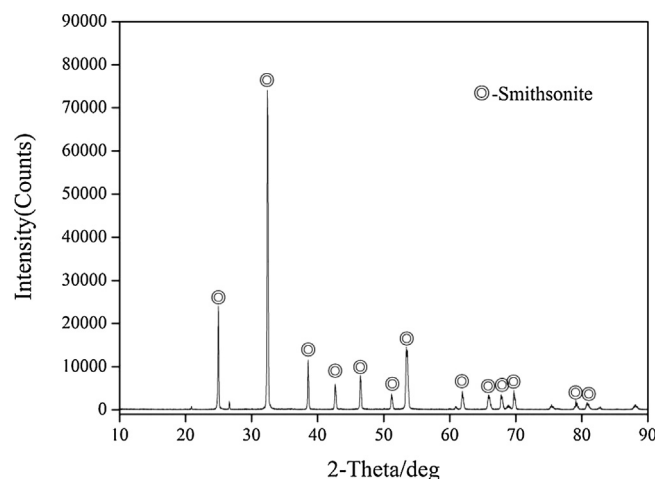


Fig. 1. XRD pattern of original smithsonite.

is a Na₂S solution and the other is a mixture of NH₃·H₂O and Na₂S, to obtain a 5% pulp concentration. The NH₃·H₂O and Na₂S concentrations were 1.5×10^{-3} mol/L. The solutions were mechanically stirred in a beaker for 30 min with samples periodically taken for kinetic monitoring. The residual sulfur content in the supernatant was measured by ICP-MS using a centrifuge (TL-4.7W, SCI, China) for solid–liquid separation.

Zeta potential determinations

Zetesizer-3000HS (Malvern Instrument Ltd.) was used for zeta potential determinations. All the samples were thoroughly equilibrated, and the measurements were recorded from a diluted suspension of 1% solids by weight. Zeta potentials of the samples were recorded through artificial determination at different pH conditions with hydrochloric acid and sodium hydroxide solution as regulating agents. Zeta potential values were measured thrice with a maximum standard deviation of ± 2.0 mV, and an average value was recorded.

TOF-SIMS analysis

Composition mapping of the smithsonite surface during sulfidation was accomplished by TOF-SIMS analysis using a ToF-SIMS⁵ spectrometer (ION-TOF, Munster, Germany) equipped with a bismuth liquid ion source. The primary ion beam of 25 keV Bi³⁺ was operated in a static mode with a primary pulsed beam current of 1.12 pA. The area of each sample for spectra acquisition was $150 \mu\text{m} \times 150 \mu\text{m}$. The sputter ion of 1 KeV O₂ was used with a sputter current of 227.79 nA, and the sputter area was $500 \mu\text{m} \times 500 \mu\text{m}$. The analysis time was 2 min/frame, and the primary ion dose was $\leq 10^{10}$ ions/cm², which ensured static conditions and minimal surface damage. Negative ion spectra were collected from each individual region of interest (ROI). Three ROIs were investigated at samples pretreated with different conditions to obtain statistically significant results. Prior to statistical analysis of mean, the intensities of the prominent secondary ions in the TOF-SIMS spectra were normalized to the total ion yield. The analysis was conducted in a vacuum on the order of at least 10^{-7} Pa. Sample charging was neutralized with an electron flood gun.

To prepare the samples for TOF-SIMS analysis, we freshly fractured the pure smithsonite chunk samples. After washing in Milli-Q water by ultrasonication, the freshly fractured samples were conditioned with laboratory test operating conditions. The contrast tests conditions were as follows. Two freshly fractured samples were mixed with 30 mL of deionized water in a 50 mL

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