

Available online at www.sciencedirect.com



Transactions of Nonferrous Metals Society of China

www.tnmsc.cn



Trans. Nonferrous Met. Soc. China 34(2024) 1275-1287

# Effect of ammonia on sulfidization flotation of heterogenite and its mechanism

Guo-fan ZHANG<sup>1,2</sup>, Yong-qiang GAO<sup>1</sup>, Meng-tao WANG<sup>1</sup>

 School of Minerals Processing and Bioengineering, Central South University, Changsha 410083, China;
 Key Laboratory of Hunan Province for Clean and Efficient Utilization of Strategic Calcium-containing Mineral Resources, Central South University, Changsha 410083, China

Received 14 May 2023; accepted 8 November 2023

**Abstract:** Ammonium ion was introduced to enhance the sulfidization of heterogenite, the main cobalt oxide mineral. The flotation recovery was significantly improved from less than 20% to over 70%. Micro flotation and FT-IR analyses indicated that ammonium ions enhanced the adsorption intensity of xanthate and improved the flotation recovery of heterogenite. Zeta potential, ICP-OES, and XPS tests further illustrated that cobalt on the surface of heterogenite was transferred to the liquid phase by forming ammonia complexes, thereby increasing the sulfur adsorption sites on the mineral surface and promoting sulfidization. This study will contribute to a better understanding of the flotation behavior of heterogenite; ammonium activity; sulfidization flotation; cobalt oxide ore

# **1** Introduction

Cobalt, as a key metal for new energy storage materials, is widely used in lithium batteries due to its excellent electrochemical properties [1]. The consumption of cobalt will continue to expand in the foreseeable future, and most of the new demands should be realized by increasing the production capacity [2]. Cobalt resources are heavily concentrated in the Central African Copper Belt, especially in the Democratic Republic of Congo, which accounts for about half of the world's cobalt reserves and more than 70% of its output [3,4] and is the most important source of cobalt. Cobalt in cobalt oxide ores can be extracted by hydrometallurgy; however, when the content of alkaline gangue in cobalt oxide ores is very high and the cobalt grade is low, the process consumes high amounts of acids and easily poses a threat to

the environment. In this regard, cobalt oxide ore ores should be enriched by mineral processing using flotation [5]. However, the flotation recovery of cobalt is typically less than 50% for mixed sulfur-oxygen cobalt ores. Multiple collectors are used to enhance flotation recovery [6,7], which is determined by the oxidation rate of the ore [8]. Heterogenite is the most important cobalt oxide mineral in the sedimentary copper-cobalt ores of the Central African Copper Belt [9]. Heterogenite has various complex crystal structures, which mainly consist of crystalline varieties with a composition close to the formula CoOOH, as well as crypto-crystalline or amorphous varieties that have varying amounts of copper, nickel, iron, and bivalent cobalt [10]. Heterogenite has complex interfacial properties, which leads to limited flotation recovery [11].

Sulfidization flotation is an efficient and economical method used to recover the oxidized

Corresponding author: Meng-tao WANG, Tel: +86-17671669382, E-mail: wang.mt@foxmail.com DOI: 10.1016/S1003-6326(24)66470-8

<sup>1003-6326/© 2024</sup> The Nonferrous Metals Society of China. Published by Elsevier Ltd & Science Press

This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/)

minerals [10,12], such as malachite, smithsonite, and cerussite. In our previous study, we found that heterogenite is difficult to obtain satisfactory flotation recovery by direct sulfidization. As such, new methods should be explored to enhance sulfidization. Sulfidization flotation can be enhanced mainly bv sulfidization roasting. dissolved oxygen regulation, metal ion activation, and ammonium ion enhancement. The pretreatment of sulfidization roasting can decompose zinc carbonate into zincate at high temperatures, and it will react with sulfidization reagents to form stable sulfide film zinc sulfide on the surface to facilitate flotation recovery [13]. Our previous work showed that low dissolved oxygen levels can enhance sulfidization and increase the flotation recovery of smithsonite [14]. These methods have not yet been applied in industry due to their harsh operating conditions and high energy consumption. Lead ions can be pre-adsorbed on the malachite surface in the form of  $Pb(OH)^+$ , to improve the surface sulfidization effect and promote the adsorption of collectors [15]. JANUSZ et al [16] reported that the adsorption of Cu<sup>2+</sup> can activate the sulfidization flotation of synthetic zinc carbonate. ZHAO et al [17] showed the Cu is present on the smithsonite surface as -O-Cu complex, which increases the number of active sites for S adsorption and promotes the sulfidization effect of smithsonite. The use of ammonia pre-treatment has been widely studied to enhance the sulfidization flotation of oxidized minerals. FENG et al [18,19] conducted solution chemistry calculations and concluded that NH<sub>3</sub> acts on hydroxymetal species; this phenomenon is unfavorable for sulfidization to form complexes of metals and NH<sub>3</sub>, which results in the formation of more S<sup>2-</sup>adsorption active sites on the mineral surface. LIU et al [20] determined the activation effect of NH<sub>3</sub> on malachite and found that the adsorption of NH3 on the surface of malachite is very limited. Sulfide particles generated on the surface in the presence of NH<sub>3</sub> are larger and more stable. Hence, NH3 acts as an intermediary to promote the nucleation and growth of sulfide products, and more stable and dense sulfides are beneficial to malachite flotation.

Metal ions can generate new phases on the surface of oxidized minerals. This process is beneficial to the sulfidization of oxidized minerals and increases collector adsorption and flotation recovery. Ammonium ions can form a complex with many metals [21], specifically copper, nickel, and cobalt, generating extremely stable chelates  $(Co(NH_3)_6^{3+})$ , and  $\lg \beta = 35.20$  [22]. To avoid the influence of alkaline gangues, researchers have attempted to extract valance metals through ammonia leaching, which is insensitive to alkaline gangues [23]. Therefore, the addition of metal ions or the pretreatment of ammonium ions has great potential to improve the sulfidization flotation recovery of heterogenite.

In this study, we introduced various metal ions and ammonium ions to enhance the sulfidization of heterogenite and improve the flotation recovery. The effect of adding ammonium ions on the adsorption of the collector was studied using Fourier transform infrared (FT-IR) spectrometer. The mechanism of action of ammonium ions on the sulfidization of heterogenite was identified by zeta potential measurement, inductively coupled plasma optical emission spectrometry (ICP-OES), and X-ray photoelectron spectroscopy (XPS). This work contributes to a deep understanding of heterogenite sulfidization and provides guidance for its flotation recovery.

# 2 Experimental

#### 2.1 Materials and reagents

Copper-cobalt mixed oxide ores and pure heterogenite samples were obtained from Democratic Republic of Congo. The copper-cobalt mixed oxide ore was ground to be <1.5 mm with ceramic jars and zirconia balls, concentrated with a shaking table and high-intensity magnetic separation machine, and then screened out to be  $38-74 \,\mu\text{m}$  for flotation and sulfur ions adsorption tests. The pure heterogenite samples were manually selected and ground with ceramic jars and zirconia balls. The <10 µm particles were screened for FTIR analysis, zeta potential measurement, and XPS analysis. The selected highgrade copper-cobalt mixed oxide ore and pure heterogenite were analyzed by X-ray diffraction (XRD) (Fig. 1) and X-ray fluorescence (XRF) (Table 1). The main minerals of the copper-cobalt mixed oxide ore are malachite and heterogenite. The pure heterogenite sample has good agreement with the standard card of heterogenite (PDF No. 07-0169) and the content of cobalt is 51.43%, indicating the high purity of the sample.



Fig. 1 X-ray diffraction pattern of samples: (a) Copper-cobalt mixed oxide ore; (b) Pure heterogenite

Table 1 X-ray fluorescence results for samples

Sample	Co	Cu	Fe	Mn	Ni	Р	Ca	Si	Mg
Cu–Co mixed oxide ore	20.36	16.32	20.36	_	0.18	0.60	0.67	9.25	1.13
Pure heterogenite	51.43	6.16	0.98	2.83	_	0.30	0.25	0.73	0.22

Analytical grade NH<sub>4</sub>Cl, CuSO<sub>4</sub>·5H<sub>2</sub>O, Pb(NO<sub>3</sub>)<sub>2</sub>, and FeCl<sub>2</sub>, which are cation sources, were purchased from Sinopharm Chemical Reagent Co. Ltd., China. Na<sub>2</sub>S·9H<sub>2</sub>O (analytical grade), potassium amyl xanthate (PAX, >98 wt.%), and methyl isobutyl carbinol (MIBC, >99 wt.%) were used as sulfidization reagents, collectors, and foaming reagents, respectively. The pulp pH was adjusted by adding dilute hydrochloric acid (HCl) and sodium hydroxide (NaOH). The water used for all experiments and measurements was deionized (DI) water.

#### 2.2 Micro-flotation experiments

Flotation experiments were carried out with an XFG flotation machine by using a 40 mL flotation cell, impeller tip speed of 1992 r/min and airflow rate of 0.3 m<sup>3</sup>/h. The flowsheet for the flotation experiments is shown in Fig. 2. For each test, 2 g of sample and 35 mL of DI water were fed into the flotation cell. The pulp was stirred for 2 min; if needed, cations were added and agitated for 3 min. Flotation reagents were sequentially added at scheduled concentrations and stirred. The desired pH was adjusted and the solution was stirred for another 2 min. The foam product was scraped off manually, and all products were filtered, dried, weighed, and analyzed for elemental content. The flotation recovery of heterogenite was calculated



Fig. 2 Flowsheet of flotation experiments

according to Co grades of the concentrate and feed. The dosages of PAX and MIBC in all flotation experiments were  $4 \times 10^{-3}$  mol/L and  $20 \mu g/L$ , respectively.

### 2.3 FT-IR spectral analysis

Fourier-transform infrared spectroscopy (FT-IR) analysis was performed using a Bruker Alpha FTIR spectrometer (Nicolet 6700, Thermo Scientific, USA), with a resolution of 4 cm<sup>-1</sup>, to reveal the reaction of reagents with mineral particles. 0.5 g of minerals were ground to less than 2  $\mu$ m, added to a 40 mL conical beaker containing 35 mL of DI water, and stirred. The pH was adjusted, and reagents were added sequentially with the same amount as in the flotation experiment. The

solution was stirred thoroughly for 15 min, centrifuged, washed repeatedly with DI water three times, dried in a vacuum drying oven, and analyzed by infrared spectroscopy using the KBr press disk method.

#### 2.4 Zeta potential measurements

Zeta potential measurements were performed using ZETASIZER Nano-Zs90 series (Malvern Instruments, UK) to reveal the mechanism underlying the reaction between the reagents and mineral particles.  $1 \times 10^{-3}$  mol/L KCl was used as the background electrolyte solution. In brief, 20 mg of <10 µm fractions were collected into a 50 mL conical beaker containing 35 mL of DI water. The pH of the solution was adjusted, and it was then added with the predetermined reagents, stirred for 5 min, and allowed to standing for 3 min. The upper layer solution was extracted for zeta potential measurements. Measurement under each condition was conducted three times and the average value was taken as the final value.

#### 2.5 Ions concentration measurements

The amount of reagents adsorbed on the mineral surface can be calculated from the discrepancy between the original and residual concentrations of the solution before and after the adsorption of the reagent on the mineral surface. About 2 g of minerals and 40 mL of DI water were placed into a 50 mL conical beaker and stirred with a magnetic stirrer at 2000 r/min for 2 min. The solution was added with a certain amount of reagents sequentially and stirred for a certain time. The supernatant (2 mL) was obtained, centrifuged and diluted to measure S concentration. The content of Co was determined using the procedure for S content, and the amount of sample used was 0.5 g each time.

The concentrations of S and Co were measured using SPECTRO BLUEII inductively coupled plasma optical emission spectrometer (ICP-OES) (SPECTRO Analytical Instruments, Germany), using a predefined concentration calibration standard curve before testing. The amount of the reagent absorbed was calculated by Eq. (1):

$$\tau = c_1 - c_2 \tag{1}$$

where  $\tau$  is the adsorption of reagent on mineral surfaces (mg/L);  $c_1$  and  $c_2$  are the concentrations of reagents before and after adsorption, respectively (mg/L).

#### 2.6 X-ray photoelectron spectroscopy analysis

The sample preparation is the same as that in Section 2.3. XPS analysis was performed using Thermo Scientific K-Alpha (Thermo Fisher, USA). Individual spectra were analyzed, and the atomic fractions of elements using Advantage software were calculated.

# **3** Results and discussion

#### 3.1 Micro-flotation test results

Micro-flotation tests were performed to investigate the sulfidization flotation behavior of heterogenite in the absence and presence of cations by using  $4 \times 10^{-3}$  mol/L PAX as the collector. Figure 3 presents the effect of cation concentration on the recovery of sulfidization flotation. Without the addition of ions, the flotation recovery of heterogenite was only 18% using  $2 \times 10^{-3}$  mol/L Na<sub>2</sub>S pretreatment at pH 10. As such, recovery of heterogenite by the pretreatment of sulfidization alone was difficult. As shown in Fig. 3, the effect of cations on the sulfidization flotation behavior of heterogenite was different. The sulfidization flotation recovery of heterogenite decreased as the concentration of Fe<sup>2+</sup> ions increased, showing that the existence of Fe<sup>2+</sup> inhibited the sulfidization flotation of heterogenite. The addition of small amounts of Cu<sup>2+</sup> and Pb<sup>2+</sup> ions could increase the sulfidization flotation recovery of heterogenite, but the increase was relatively small, ranging from 18% to about 40%. The recovery decreased significantly with further increase in ion concentration. The results indicated that Cu<sup>2+</sup> and Pb<sup>2+</sup> could enhance



**Fig. 3** Flotation recovery of heterogenite as function of concentration of different cations (Na<sub>2</sub>S:  $2 \times 10^{-3}$  mol/L; PAX:  $4 \times 10^{-3}$  mol/L; pH=10)

the sulfidization flotation of heterogenite to a certain extent, but the dose added was critical. The effect of  $NH_4^+$  on the sulfidization flotation of heterogenite differed from that of the above ions. A small amount of  $NH_4^+$  had little effect on the sulfidization flotation of heterogenite. When the dosage of  $NH_4^+$  was more than  $5 \times 10^{-4}$  mol/L, the flotation recovery of heterogenite increased significantly with increasing dosage of  $NH_4^+$  and it exceeded 70% as the dosage of  $NH_4^+$  reached  $20 \times 10^{-4}$  mol/L. Hence, the  $NH_4^+$  ion considerably activated the sulfidization flotation of heterogenite.

The effect of pulp pH on the sulfidization flotation of heterogenite in the absence and presence of ammonium ions was further studied and the results are shown in Fig. 4. As shown in Fig. 4, the flotation recovery of heterogenite was below 20% across entire pH range with pretreatment of Na<sub>2</sub>S alone, indicating the challenge of recovering heterogenite by traditional sulfidization flotation. Interestingly, the addition of ammonia ions changed this situation. After the addition of ammonium ions, the flotation recovery of heterogenite increased significantly over the entire pH range. The finding indicated that ammonium ions had a strong activation effect on the sulfidization flotation of heterogenite. Regardless of the presence or absence of ammonium ions, the sulfidization flotation recovery of heterogenite decreased at a pH above 10, probably due to the formation of hydroxyl compounds on the heterogenite surface. As such, the suitable pH range for the sulfidization flotation of heterogenite was below 10.



**Fig. 4** Recovery of heterogenite as function of pH in absence and presence of  $NH_4^+$  (Na<sub>2</sub>S: 2×10<sup>-3</sup> mol/L;  $NH_4^+$ : 2×10<sup>-3</sup> mol/L; PAX: 4×10<sup>-3</sup> mol/L; pH=10)

#### **3.2 FT-IR measurement results**

FT-IR measurements were conducted under different reagent schemes at pH 10 to investigate the adsorption mechanism of reagents on heterogenite. The FT-IR spectra of PAX and heterogenite with/without the treatment of reagents are depicted in Figs. 5 and 6, respectively. As seen in Fig. 5, bond peaks at 2957.19 and 2873.33 cm<sup>-1</sup> correspond to C—H bond stretching vibration absorption, and those at 1242.56 and 1159.01 cm<sup>-1</sup> could be attributed to C—O—C bond asymmetry and symmetry stretching vibration, respectively. The C=S stretching vibration peaks of PAX were found at 1117.99 and 1083.33 cm<sup>-1</sup> [24,25].



Fig. 5 FT-IR spectrum of PAX



**Fig. 6** FT-IR spectra of heterogenite in absence and presence of flotation reagents (Na<sub>2</sub>S:  $2 \times 10^{-3}$  mol/L; NH<sub>4</sub><sup>+</sup>:  $2 \times 10^{-3}$  mol/L; PAX:  $4 \times 10^{-3}$  mol/L; pH=10)

Figure 6 presents the spectra of heterogenite with the treatment of different reagents. After the treatment of PAX, the characteristic absorption peaks at 2956.41 and 2876.33 cm<sup>-1</sup> could be attributed to the C—H stretching vibration of PAX,

indicating the adsorption of PAX on the surface of heterogenite. Moreover, the C—O—C stretching vibration peaks shifted from 1242.56 and 1159.01 cm<sup>-1</sup> to 1249.26 and 1193.41 cm<sup>-1</sup>, and the C—S vibration peaks shifted from 1117.99 and 1080.33 cm<sup>-1</sup> to 1142.82 and 1035.63 cm<sup>-1</sup>, respectively. These peak shifts indicated the chemical adsorption of PAX on the heterogenite surface [26].

Figure 6 shows a large difference among the pretreatment reagents on the adsorption amount of PAX. Without any pretreatment, only a weak characteristic peak appeared. The characteristic peak intensity was enhanced by the pretreatment of Na<sub>2</sub>S, but the magnitude was limited. It is worth noting that the addition of NH<sub>4</sub><sup>+</sup> changed this situation significantly. For samples treated with  $NH_4^+$  before sulfidization, the intensity of the characteristic absorption peak of PAX was significantly enhanced. This indicated that the amount of PAX adsorbed on the heterogenite surface increased significantly due to the introduction of NH<sub>4</sub><sup>+</sup>. Therefore, the benefits of NH<sub>4</sub><sup>+</sup> to the flotation recovery of heterogenite could be attributed to the significant increase in the adsorption capacity of PAX.

It is well known that  $NH_4^+$  ions have a strong chelating effect on metal ions. The properties of the heterogenite surface might be changed by adding  $NH_4^+$  before sulfidization. Therefore, a series of studies were further performed to characterize the effect of  $NH_4^+$  on the surface properties and sulfidization of heterogenite.

#### 3.3 Zeta potential

The adsorption of reagents on the mineral surface may affect their electrical properties, and zeta potential measurements of heterogenite as a function of pulp pH under different reagent schemes were performed. As depicted in Fig. 7, the zeta potential of bare heterogenite decreased with increasing pH. The isoelectric point (IEP) was approximately at pH=9.0, different from the results of previous studies (5.5–8) [27]. This inconsistency could be attributed to the difference in the type and amount of lattice-substituted elements in the mineral crystals [10]. With the addition of ammonium ions, the zeta potential of samples increased slightly at pH>8, which might be related

to the distribution species of ammonium ions at different pH levels. When the pH is lower than 8, the species of  $NH_4^+$  was the dominant species, and its adsorption would lead to an increase in zeta potential. However, the hydrolysis products of ammonium mainly existed in the form of  $NH_3(aq)$ , adsorbed, and complexed with Co sites on the surface of heterogenite, indicating a negligible effect on surface electrical properties. The result of analysis was in good agreement with the zeta potential measurement results.



Fig. 7 Zeta potentials of heterogenite as function of pH in absence and presence of flotation reagents (Na<sub>2</sub>S:  $2\times10^{-3}$  mol/L; NH<sub>4</sub><sup>+</sup>:  $2\times10^{-3}$  mol/L)

The zeta potential of heterogenite treated with Na<sub>2</sub>S shifted negatively at pH below 10, and the IEP moved to around pH 5, indicating the adsorption of S<sup>2-</sup> and the formation of new species of Co-S on the surface of heterogenite. The introduction of ammonium ions under acidic and neutral conditions had little effect on the zeta of heterogenite with potential sulfidization. compared with only However, sulfidization treatment, the surface zeta potential was decreased by the addition of ammonium ions under alkaline conditions, proving that the adsorption of NH<sub>4</sub><sup>+</sup> facilitated the adsorption and interaction of Na<sub>2</sub>S with heterogenite.

#### 3.4 Sulfur ions absorption amount

To research the effect of  $NH_4^+$  on the sulfidization of heterogenite, the adsorption amount of sulfur ions on the heterogenite surface with and without  $NH_4^+$  was measured by ICP-OES (Fig. 8). The amount of sulfur ions adsorbed on the surface of heterogenite gradually increased with increasing

adsorption time in the presence and absence of  $NH_4^+$ . The value reached the maximum after 4 min. After the adsorption of sulfur ions reached the equilibrium, it did not change much with increasing action time. Compared with direct sulfidization, the adsorption amount of sulfur ions on the surface of heterogenite increased greatly with  $NH_4^+$  activation and the maximum adsorption amount reached 2.28 times than that of direct sulfidization, further confirming the enhanced effect of  $NH_4^+$  on heterogenite sulfidization. This finding may be partly because the adsorption of S on the surface of oxidized ore is usually in the form of  $HS^-$ , and the dissociation of  $NH_4^+$  to  $NH_3$  and that of  $S^{2-}$  to  $HS^-$  have a mutual promotion effect [28].



Fig. 8 Absorption amount of sulfur ions as function of time in absence and presence of  $NH_4^+$  (Na<sub>2</sub>S:  $2 \times 10^{-3}$  mol/L;  $NH_4^+$ :  $2 \times 10^{-3}$  mol/L; pH=10)

#### 3.5 XPS analysis results

Zeta potential measurements and sulfur ion adsorption showed that the addition of ammonium ions promoted the transformation of sulfide ions from the pulp to the surface of heterogenite, which might be accompanied by the formation of new species. XPS analysis was further conducted to directly investigate the effect of sulfidization on the chemical composition and change of valence of heterogenite surfaces with and without the addition of ammonium ions.

The contents of Co, N, O, and S on the surface of heterogenite samples under different conditions detected by the XPS spectra are shown in Table 2. The content of cobalt on the heterogenite surface reached 19.62 at.%, which provided active sites for surface sulfidization and adsorption of collectors. After sulfidization, elemental sulfur appeared, and

the content was only 2.99 at.% on the mineral surface, which might not effectively promote the subsequent collector adsorption. The addition of ammonium ions before sulfidization could effectively promote the adsorption of sulfur ions. The content of sulfur element on the heterogenite surface increased from 2.99 to 9.35 at.%. The results are consistent with the results of ICP-OES measurements, confirming that  $NH_4^+$ can substantially promote the surface sulfidization of heterogenite. It is noteworthy that heterogenite treated with  $NH_4^+$  alone or  $NH_4^+$  and  $Na_2S$  both showed low elemental content of N on the surface (1.24 and 1.70 at.%, respectively), which may suggest that the activation of heterogenite sulfidization by NH<sub>4</sub><sup>+</sup> did not work by adsorption onto the surface.

 Table 2 Contents of element on heterogenite surfaces

 under different conditions (at.%)

*					
Sample	Co 2p	N1s	O1s	S 2p	
Untreated heterogenite	19.62	_	80.38	_	
Heterogenite $+ \mathrm{NH}_4^+$	20.43	1.24	78.33	-	
Heterogenite $+$ Na <sub>2</sub> S	20.98	_	76.03	2.99	
Heterogenite + $NH_4^+$ + $Na_2S$	17.84	1.70	71.11	9.35	
					i

The S 2p high-resolution XPS spectra and the distribution of each species are shown in Fig. 9 and Table 3, respectively. Curve fitting of the S 2p high-resolution peaks of the sulfidized heterogenite samples suggested that they were all resolved into three components. After treatment with Na<sub>2</sub>S alone, the divided peaks at binding energy of 167.79, 163.56 and 162.08 eV for S  $2p_{3/2}$  were attributed to sulfates, polysulfides and sulfides [29-32]; the distribution of three species relative to the total S was 29.79%, 35.61% and 34.60%, respectively. As for the sample treated with  $NH_4^+$  and  $Na_2S$ , the divided peaks at binding energies of 168.20, 163.48 and 162.34 eV for S  $2p_{3/2}$  were attributed to sulfates, polysulfides and sulfides, and the distribution of the three species relative to the total S was 31.89%, 42.50% and 25.61%, respectively. In general, sulphate is not favorable to flotation, whereas sulfide is [33]. The proportions of sulphate and sulfide relative to total S were approximately the same. Hence, the promotion of heterogenite sulfidization by NH<sub>4</sub><sup>+</sup> was mainly achieved by increasing the sulfur adsorption amount.



**Fig. 9** High-resolution XPS spectra of S2p of sulfidized heterogenite in absence (a) and presence (b) of  $NH_4^+$  ( $NH_4^+$ :  $2 \times 10^{-3} \text{ mol/L}$ ;  $Na_2S$ :  $2 \times 10^{-3} \text{ mol/L}$ ; pH=10)

**Table 3** Binding energy and distribution of S species of sulfidized heterogenite in absence and presence of  $NH_4^+$  ( $NH_4^+$ :  $2 \times 10^{-3}$  mol/L;  $Na_2S$ :  $2 \times 10^{-3}$  mol/L; pH=10)

Chemical	In absence	of $\mathrm{NH}_4^+$	In presence of $NH_4^+$			
state	Binding energy/eV	Distribution/at.%	Binding energy/eV	Distribution/at.%		
$\mathrm{SO}_4^{2-}$	167.79, 169.04	29.79	168.20, 169.26	31.89		
$\mathbf{S}_n^{2-}$	163.56, 164.74	35.61	163.48, 164.74	42.50		
$S^{2-}$	162.08, 163.14	34.60	162.34, 163.58	25.61		

The XPS pattern of Co, a transition metal, is characterized by multiple cleavages, with the peaks of some compounds overlapping. Cobalt on the heterogenite surface with or without reagents, has various forms, including cobalt oxides, sulfides, and sulfates, so the peak fitting of Co on the surface of heterogenite was very complicated. According to previous studies [34], the divalent oxide of cobalt has peaks around 780 and 782 eV, while the trivalent oxide has peaks around 780 and 781 eV. The presence of all three peaks implies the simultaneous presence of Co(II)-O and Co(III)-O. Furthermore, divalent cobalt had a satellite peak of around 785 eV, while trivalent cobalt is around 790 eV [35], and the Co  $2p_{1/2}$ - $2p_{3/2}$  spin-orbit level energy spacing ( $\Delta E$ ) close to 16 eV is considered to be high-spin Co(II) and that close to 15 eV is considered to be low-spin Co(III) [36,37].

Combining the divided Co 2p spectrum (Fig. 10), S 2p spectrum (Fig. 9) and Co  $2p_{3/2}$  spectral fitting parameters (Table 4), we can tentatively determine the species corresponding to the cobalt peaks. The spectrum of untreated heterogenite (Fig. 10(a)) can be divided into three main peaks at 780.15, 781.38 and 783.26 eV, and a

satellite peak at 789.98 eV, which agrees well with the characteristic spectral peaks of heterogenite (CoOOH) [34,35]. By comparing Figs. 10(b) with 10(a), a new satellite peak with a binding energy of 784.37 eV appeared on the heterogenite surface after treatment with NH<sub>4</sub><sup>+</sup>, indicating that Co on the heterogenite surface underwent a valence shift from trivalent to divalent. Based on the comparison between Figs. 10(c) and 10(a), two new peaks located at binding energy values of 779.68 and 781.98 eV appeared after treatment with Na<sub>2</sub>S alone. The peak at 781.98 eV can be attributed to Co(II)—O bond, CoSO4, and CoS [38-41], while the peak at 779.68 eV could be attributed to Co(III) polysulfides [42,43]. The peaks located at 780.01, and 780.88 eV and the satellite peak at 790.01 eV were indicative of Co(III)-O bond [34,44]. For heterogenite treated with  $NH_4^+$  and  $Na_2S$  (Fig. 10(d)), the binding energy value of 781.98 eV could be attributed to Co(II)-O, CoSO4, and CoS, leading to 779.78 eV for Co(III) polysulfides, 780.24 eV, and 780.94 and 790.33 eV to form a Co(III)-O bond.

Through the above analysis, we noticed a trend of transition from Co(III) into Co(II) on the



**Fig. 10** High-resolution XPS spectra of Co 2p of heterogenite samples: (a) Untreated; (b) Treated with  $NH_4^+$ ; (c) Treated with  $Na_2S$ ; (d) Treated with  $NH_4^+$  and  $Na_2S$  ( $NH_4^+$ :  $2 \times 10^{-3}$  mol/L;  $Na_2S$ :  $2 \times 10^{-3}$  mol/L; pH=10)

**Table 4** Binding energy and distribution of S species of sulfidized heterogenite under different conditions ( $NH_4^+$ :  $2 \times 10^{-3} \text{ mol/L}$ ;  $Na_2S$ :  $2 \times 10^{-3} \text{ mol/L}$ ; pH=10)

Heterogenite			Heterogenite $+ Na_2S$			Heterogenite $+ NH_4^+ + Na_2S$			
Position/ eV	Split energy, $\Delta E/eV$	Peak area proportion/%	Position/ eV	Split energy, $\Delta E/eV$	Peak area proportion/%	Position/ eV	Split energy, $\Delta E/eV$	Peak area proportion/%	
780.15	15.10	54.58	779.68	14.94	18.43	779.78	15.00	16.67	
781.38	15.35	23.66	780.01	15.11	24.27	780.24	15.07	16.26	
783.26	15.10	11.83	780.88	15.36	27.55	780.94	15.40	25.21	
789.98	15.30	9.92	781.98	15.76	17.52	781.89	15.79	30.69	
			785.88	15.77	8.03	785.83	15.79	6.50	
			790.01	15.12	4.20	790.33	14.7	4.67	

heterogenite surface after interaction with  $NH_4^+$ ,  $Na_2S$ , or both. The peaks near 720 and 786 eV are the fingerprint peaks of Co(II). The distinction of spin-orbit splitting energy ( $\Delta E$ ) can also support this judgment. Changes in the percentage of Co(II) can be qualitatively inferred from the percentage of the fitted peak area. As shown in Table 4, the percentage of Co(II) increased from 25.55% to 37.19% after treatment with  $NH_4^+$  and  $Na_2S$  compared with that after treatment with  $Na_2S$  alone. Hence,

 $NH_4^+$  can promote the conversion of Co(III) into Co(II). The redox reaction only occurs when  $Na_2S$  interacts with active Co(III), so it can be assumed that more conversion of Co(III) into Co(II) is exactly caused by the presence of more active Co sites on the heterogenite surface for sulfur ion adsorption.

Based on the above experimental and measurement results, the conceivable mechanism of  $NH_4^+$  in promoting the sulfidization flotation of heterogenite is shown in Fig. 11. The addition of

Guo-fan ZHANG, et al/Trans. Nonferrous Met. Soc. China 34(2024) 1275-1287



Fig. 11 Schematic diagram of mechanism of ammonia ions promoting sulfidization of heterogenite

 $NH_4^+$  ions modifies the heterogenite surface morphology by transferring Co from the surface to the liquid phase to provide additional active sites for sulfur adsorption, rather than be adsorbed onto the heterogeneous surface. More S adsorption favors the adsorption of the collector PAX, leading to the hydrophobic flotation of the heterogenite particles.

The lg C-pH relationship for the NH<sub>4</sub><sup>+</sup>-Co<sup>3+</sup>-H<sub>2</sub>O system was calculated using Visual MINTEQ software (Fig. 12). Ammonia and cobalt are present



Fig. 12 Distribution of cobalt and ammonia complexes in  $NH_4^+$ - $Co^{3+}$ - $H_2O$  system as function of pH ( $Co^{3+}$ : 2.7×10<sup>-4</sup> mol/L;  $NH_4^+$ : 2×10<sup>-3</sup> mol/L)

predominantly as the complex  $Co(NH_3)_6OH^{2+}$ , at pH 10. Co on the surface of heterogenite may be transferred to the liquid phase via specific reactions.

To verify the results, we measured the concentration of Co in the pulp before and after the interaction of heterogenite with  $NH_4^+$  and conducted ICP-OES (Fig. 13). The solubility of Co increased greatly after the interaction with  $NH_4^+$ , indicating the reasonableness of the results from the side.



Fig. 13 Concentration of Co in liquid phase as function of time in absence and presence of  $NH_4^+$  ( $NH_4^+$ :  $2\times10^{-3}$  mol/L; pH=10)

# **4** Conclusions

(1)  $NH_4^+$  could increase the adsorption of PAX on the heterogenite surface, thereby greatly enhancing sulfide flotation and increasing the flotation recovery from less than 20% to more than 70%.

(2) The zeta potential and sulfur adsorption measurements demonstrated that the transfer of cobalt ammonia into the liquid phase by complexation could form stable complexes under weakly alkaline conditions. This phenomenon created more lattice vacancies on the surface of heterogenite particles and increased the amount of sulfur adsorption active sites.

(3) XPS analysis indicated that the sulfur adsorption products on the heterogeneity surface were sulfide and sulfate. The addition of  $NH_4^+$  could produce more active Co sites, which could interact with S, thereby promoting the adsorption of S.

#### **CRediT** authorship contribution statement

**Guo-fan ZHANG:** Supervision, Funding acquisition, Resources, Conceptualization; **Yong-qiang GAO:** Conceptualization, Data curation, Writing – Original draft; **Meng-tao WANG:** Methodology, Validation, Formal analysis, Writing – Review & editing.

#### **Declaration of competing interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Acknowledgments

The authors would like to acknowledge the support from the National Key Research and Development Program of China (No. 2022YFC2904601).

#### References

- QU Li-li, HE Ya-qun, FU Yuan-peng, XIE Wei-ning, YE Cui-ling, LU Qi-chang, LI Jin-long, LI Jia-hao, PANG Zhi-bo. Enhancement of leaching of cobalt and lithium from spent lithium-ion batteries by mechanochemical process [J]. Transactions of Nonferrous Metals Society of China, 2022, 32(4): 1325–1335.
- [2] SMITH C G. Always the bridesmaid, never the bride: Cobalt geology and resources [J]. Transactions of the Institutions of Mining and Metallurgy Section B–Applied Earth Science, 2001, 110: B75–B80.

- [3] ZENG An-qi, CHEN Wu, RASMUSSEN K D, ZHU Xue-hong, LUNDHAUG M, MÜLLER D B, TAN Juan, KEIDING J K, LIU Li-tao, DAI Tao, WANG An-jian, LIU Gang. Battery technology and recycling alone will not save the electric mobility transition from future cobalt shortages [J]. Nature Communications, 2022, 13(1): 1341.
- [4] CAILTEUX J L H, KAMPUNZU A B, LEROUGE C, KAPUTO A K, MILESI J P. Genesis of sediment-hosted stratiform copper-cobalt deposits, central African Copperbelt [J]. Journal of African Earth Sciences, 2005, 42(1/2/3/4/5): 134–158.
- [5] BARTON I F, YANG He-xiong, BARTON M D. The mineralogy, geochemistry, and metallurgy of cobalt in the rhombohedral carbonates [J]. Canadian Mineralogist, 2014, 52(4): 653–669.
- [6] MUSUKU B. Enhancing the recoveries and grades of cobalt from Nchanga and Konkola Ores of KCM [D]. Lusaka, Zambia: The University of Zambia, 2013.
- [7] TIJSSELING L T, DEHAINE Q, ROLLINSON G K, GLASS H J. Flotation of mixed oxide sulphide coppercobalt minerals using xanthate, dithiophosphate, thiocarbamate and blended collectors [J]. Minerals Engineering, 2019, 138: 246–256.
- [8] DEHAINE Q, TIJSSELING L T, GLASS H J, TORMANEN T, BUTCHER A R. Geometallurgy of cobalt ores: A review [J]. Minerals Engineering, 2021, 160: 106656.
- [9] SANTORO L, TSHIPENG S, PIRARD E, BOUZAHZAH H, KANIKI A, HERRINGTON R. Mineralogical reconciliation of cobalt recovery from the acid leaching of oxide ores from five deposits in Katanga (DRC) [J]. Minerals Engineering, 2019, 137: 277–289.
- [10] BULATOVIC S M. Flotation of oxide copper and copper cobalt ores [M]// BULATOVIC S M. Handbook of Flotation Reagents: Chemistry, Theory and Practice. Amsterdam: Elsevier, 2010: 47–65.
- [11] KONGOLO K, KIPOKA M, MINANGA K, MPOYO M. Improving the efficiency of oxide copper-cobalt ores flotation by combination of sulphidisers [J]. Minerals Engineering, 2003, 16: 1023–1026.
- [12] SHUNGU T, VERMAUT N, FERRON C J. Recent trends in the Gecamines copper-cobalt flotation plants [J]. Mining, Metallurgy & Exploration, 1988, 5(3): 163–170.
- [13] LÜ Jin-fang, TONG Xiong, ZHENG Yong-xing, XIE Xian, WANG Cong-bing. Study on the surface sulfidization behavior of smithsonite at high temperature [J]. Applied Surface Science, 2018, 437: 13–18.
- [14] WANG Meng-tao, ZHANG Guo-fan, CHEN Yan-fei, ZHAO Lei. Effect of dissolved oxygen on the sulfidization flotation of smithsonite [J]. Minerals Engineering, 2022, 186: 107741.
- [15] WANG Mei-li, ZHAO Wen-juan, HAN Guang, FENG Qi-cheng. Utilization of lead ions to improve surface hydrophobicity and flotation recovery of sulfidized smithsonite [J]. Colloids and Surfaces a–Physicochemical and Engineering Aspects, 2023, 663: 131126.
- [16] JANUSZ W, SZYMULA M, SZCZYPA J. Flotation of synthetic zinc carbonate using potassium ethylxanthate [J]. International Journal of Mineral Processing, 1983, 11(2): 79–88.
- [17] ZHAO Wen-juan, YANG Bin, LIU Dian-wen, FENG

Qi-cheng. Effect of copper ions on sulfidization flotation of smithsonite: Surface properties and adsorption mechanism [J]. Colloids and Surfaces a–Physicochemical and Engineering Aspects, 2022, 650: 129515.

- [18] FENG Qi-cheng, WEN Shu-ming, BAI Xu, CHANG Wei-hua, CUI Chuan-fa, ZHAO Wen-juan. Surface modification of smithsonite with ammonia to enhance the formation of sulfidization products and its response to flotation [J]. Minerals Engineering, 2019, 137: 1–9.
- [19] FENG Qi-cheng, ZHAO Wen-juan, WEN Shu-ming. Ammonia modification for enhancing adsorption of sulfide species onto malachite surfaces and implications for flotation [J]. Journal of Alloys and Compounds, 2018, 744: 301–309.
- [20] LIU Rui-zeng, LIU Zhi-cheng, LI Jian-min, AO Shun-fu, PEI Bin, LIU Dian-wen, LI Jia-lei. Reexamining the role of ammonium ions in the sulfidization, xanthate-flotation of malachite [J]. Minerals, 2020, 10(6): 537.
- [21] MENG Xing-hui, HAN K N. The principles and applications of ammonia leaching of metals—A review [J]. Mineral Processing and Extractive Metallurgy Review, 1996, 16(1): 23–61.
- [22] YU Jian-cheng, MA Bao-zhong, SHAO Shuang, WANG Cheng-yan, CHEN Yong-qiang, ZHANG Wen-juan. Cobalt recovery and microspherical cobalt tetroxide preparation from ammonia leaching solution of spent lithium-ion batteries [J]. Transactions of Nonferrous Metals Society of China, 2022, 32(9): 3136–3148.
- [23] BOWELL R J, GROGAN J, HUTTON-ASHKENNY M, BROUGH C, PENMAN K, SAPSFORD D J. Geometallurgy of uranium deposits [J]. Minerals Engineering, 2011, 24: 1305–1313.
- [24] KHOSO S A, HU Yue-hua, LYU Fei, LIU Run-qing, SUN Wei. Selective separation of chalcopyrite from pyrite with a novel non-hazardous biodegradable depressant [J]. Journal of Cleaner Production, 2019, 232: 888–897.
- [25] KHOSO S A, GAO Zhi-yong TIAN Meng-jie, HU Yue-hua, SUN Wei. Adsorption and depression mechanism of an environmentally friendly reagent in differential flotation of Cu–Fe sulphides [J]. J Mater Res Technol, 2019, 8(6): 5422–5431.
- [26] MOHAMMADKHANI M, ABDOLLAHY M, KHALESI M R. Investigation of mechanism of adsorption of xanthate and hydroxamate on malachite [J]. Journal of Mining and Environment, 2020, 11(3): 921–933.
- [27] EVRARD L. Study of the buoyancy of hydrated oxides of cobalt from the heterogenite group: Improvement of their flotation using alkyl hydroxamates [D]. Belgium: University of Louvain, 1971. (in French)
- [28] BAI Shao-jun, LI Chun-long, FU Xian-yu, DING Zhen, WEN Shu-ming. Promoting sulfidation of smithsonite by zinc sulfide species increase with addition of ammonium chloride and its effect on flotation performance [J]. Minerals Engineering, 2018, 125: 190–199.
- [29] WU Song-ping, LU Ming-jia, TIAN Xiao-dong, JIANG Chan. A facile route to graphene-covered and carbonencapsulated CoSO<sub>4</sub> nanoparticles as anode materials for lithium-ion batteries [J]. Chemical Engineering Journal, 2017, 313: 610–618.
- [30] ZHANG Yan, LI Qian, SUN Shao-kang, LIU Xiao-liang,

JIANG Tao, LYU Xian-jun, HE Ying-he. Electrochemical behaviour of the oxidative dissolution of arsenopyrite catalysed by Ag<sup>+</sup> in 9K culture medium [J]. Colloids and Surfaces a–Physicochemical and Engineering Aspects, 2021, 614: 126169.

- [31] WANG Hai-yan, YANG Ying, LI Qing-hao, LU Wen, NING Ji-qiang, ZHONG Yi-jun, ZHANG Zi-yang, HU Yong. Molecule-assisted modulation of the high-valence Co<sup>3+</sup> in 3D honeycomb-like Co<sub>x</sub>S<sub>y</sub> networks for high-performance solid-state asymmetric supercapacitors [J]. Science China Materials, 2020, 64(4): 840–851.
- [32] HAN Guang, WEN Shu-ming, WANG Han, FENG Qi-cheng. Enhanced sulfidization flotation of cuprite by surface modification with hydrogen peroxide [J]. Transactions of Nonferrous Metals Society of China, 2021, 31(11): 3564–3578.
- [33] ZHANG Qian, WEN Shu-ming, FENG Qi-cheng. Effect of CuSO4 on sulfidized cerussite surface properties and its response to the flotation behavior [J]. Applied Surface Science, 2022, 589: 152956.
- [34] YANG Jing, LIU Hong-wei, MARTENS W N, FROST R L. Synthesis and characterization of cobalt hydroxide, cobalt oxyhydroxide, and cobalt oxide nanodiscs [J]. Journal of Physical Chemistry C, 2010, 114(1): 111–119.
- [35] BIESINGER M C, PAYNE B P, GROSVENOR A P, LAU L W M, GERSON A R, SMART R S. Resolving surface chemical states in XPS analysis of first row transition metals, oxides and hydroxides: Cr, Mn, Fe, Co and Ni [J]. Applied Surface Science, 2011, 257(7): 2717–2730.
- [36] OKU M. X-ray photoelectron spectrum of low-spin Co(III) in LiCoO<sub>2</sub> [J]. Journal of Solid State Chemistry, 1978, 23(1/2): 177–185.
- [37] IVILL M, PEARTON S J, RAWAL S, LEU L, SADIK P, DAS R, HEBARD A F, CHISHOLM M, BUDAI J D, NORTON D P. Structure and magnetism of cobalt-doped ZnO thin films [J]. New Journal of Physics, 2008, 10(6): 065002.
- [38] OKAMOTO Y, ADACHI T, NAGATA K, ODAWARA M, IMANAKA T. Effects of starting cobalt salt upon the cobalt-alumina interactions and hydrodesulfurization activity of CoO/Al<sub>2</sub>O<sub>3</sub> [J]. Applied Catalysis, 1991, 73(2): 249–265.
- [39] BREYSSE M, BENNETT B A, CHADWICK D, VRINAT M. Structure and HDS activity of Co-Mo catalysts: A comparison of alumina and carbon supports [J]. Bulletin des Sociétés Chimiques Belges, 2010, 90: 1271–1278.
- [40] MA Yong-peng, XU Teng-fei, WANG Jian-dong, SHI Yan-ru, WANG Hong-yan, XIONG Fei-gen, XU Hao-miao, MA Yun-xia, ZHANG Hong-zhong. Superior Hg<sup>0</sup> capture performance and SO<sub>2</sub> resistance of Co–Mn binary metal oxide-modified layered MCM-22 zeolite for SO<sub>2</sub>-containing flue gas [J]. Environmental Science and Pollution Research, 2021, 28(13): 16447–16457.
- [41] MIAO Wen-fang, ZHANG Yu, LI Hao-tian, ZHANG Zi-hao, LI Ling, YU Ze, ZHANG Wen-ming. ZIF-8/ZIF-67-derived 3D amorphous carbon-encapsulated CoS/NCNTs supported on CoS-coated carbon nanofibers as an advanced potassium-ion battery anode [J]. Journal of Materials Chemistry A, 2019, 7(10): 5504–5512.
- [42] LOUSSOT C, AFANASIEV P, VRINAT M, JOBIC H,

1286

LEVERD P C. Amorphous cobalt oxysulfide as a hydrogen trap [J]. Chemistry of Materials, 2006, 18(24): 5659–5668.

[43] DENG Ding-rong, XUE Fei, JIA Yue-ju, YE Jian-chuan, BAI Cheng-dong, ZHENG Ming-sen, DONG Quan-feng. Co(4)N nanosheet assembled mesoporous sphere as a matrix for ultrahigh sulfur content lithium-sulfur batteries [J]. ACS Nano, 2017, 11(6): 6031–6039.

[44] YANG You-ping, LIU Ren-sheng, HUANG Ke-long, WANG Li-ping, LIU Su-qin, ZENG Wen-wen. Preparation and electrochemical performance of nanosized Co<sub>3</sub>O<sub>4</sub> via hydrothermal method [J]. Transactions of Nonferrous Metals Society of China, 2007, 17(6): 1334–1338.

# 氨离子对水钴矿硫化浮选的影响及其机理

张国范1,2, 高永强1, 王梦涛1

1. 中南大学 资源加工与生物工程学院,长沙 410083;
 2. 中南大学 战略含钙矿物清洁高效利用湖南省重点实验室,长沙 410083

摘 要:引入氨离子强化主要的氧化钴矿物(水钴矿)的硫化,使其浮选回收率从不到 20% 显著提高到 70% 以上。 微浮选和傅立叶变换红外分析表明,氨离子增强黄药的吸附强度,从而提高水钴矿的浮选回收率。Zeta 电位、ICP-OES 和 XPS 测试进一步表明,水钴矿表面的钴可通过形成氨配合物而转移到液相中,从而增加矿物表面的硫吸 附位点,促进硫化。这项研究将有助于更好地理解水钴矿的浮选行为,并为高效回收氧化钴矿提供有价值的参考。 关键词:水钴矿;氨离子活化;硫化浮选;氧化钴矿

(Edited by Bing YANG)