Selective flotation of smithsonite, quartz and calcite using alkyl diamine ether as collector

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Abstract: The flotation separation of smithsonite from calcite and quartz using a alkyl diamine ether (GE–609) as the collector was investigated through micro-flotation experiments and the real ore flotation experiments. The results show that GE–609 exhibits good collecting capability to three minerals without selectivity. The presence of sodium sulfide enhances the flotation of smithsonite and calcite while inhibits quartz. Moreover, both sodium silicate and sodium hexametaphosphate exhibit good selective inhibition to calcite. The real ore test results show that a zinc concentrate containing 23.51% Zn with the recovery of 71.02% is obtained in the closed-circuit test. To understand the adsorption of GE–609 on smithsonite surface, zeta potential measurement and FTIR analysis were carried out, and the results indicate that the collector GE–609 can adsorb on smithsonite surface through both electrostatic adsorption and chemical adsorption, and the presence of sodium sulfide enhances the adsorption of GE–609.

Key words: smithsonite; quartz; calcite; alkyl diamine ether; sodium sulfide; sulphidization flotation

1 Introduction

Although there is a wealth of zinc oxide ore resources in China, the lean ores occupy the most part, with the continuously increasing of exploration difficulty, the comprehensive utilization of low-grade zinc ores has become a pressing task. Smithsonite (ZnCO₃) is a typical oxidized zinc ore, and it usually appears in groups with calcite, quartz, dolomite and other gangue minerals. Therefore, it is required to achieve the separation in order to obtain a marketable product.

Flotation is a commonly used method for beneficiation of smithsonite [1–3], and two important methods have long been used. The one is direct flotation using fatty acids [4–6], chelating agents [7] or mercaptan [8] as collector, the other is sulphidization and then flotation with amines [9–11] or xanthates [12,13]. Although sodium silicate and sodium hexametaphosphate were used as depressants, the grade and recovery of zinc with oleic acid as the collector were lower than those obtained using the sulphidization-cationic flotation method [14]. In case of commercially available chelating agents, it is difficult to achieve large-scale application due to the lack of a long-chain hydrocarbon in the molecule [7]. For hexylmercaptan, the consumption is high [15]. Compared with sulphidization–flotation with xanthates, the technology of sulphidization–flotation with amines has been proved to be more effective in a large number of industrial practices, since it has advantages in sulphidization at normal temperature, without activation, and high selectivity.

The reagents used for sulphidizing the mineral mainly contain sodium sulphide, sodium hydrogen sulphide, elemental sulfur and sodium polysulfide. Sodium sulphide is cheaper than sodium hydrogen sulphide and also generates a high pH value [8,16]. The primary amines containing 8–18 carbon atoms exhibit strong collecting capability and selectivity to smithsonite after sulphidizing with sodium sulphide because they can react with copper and zinc to form complexes, but cannot react with calcium and magnesium [17,18]. However, the flotation is dependent on pH value [17], and amines show high sensitivity and poor selectivity for slimes which can deteriorate the flotation results [19].
Ether amine is obtained by introducing ether group into the hydrocarbon of an aliphatic amine, so it is easier to disperse in the pulp due to the lower melting point and higher solubility. GE-609 is a kind of alkyl diamine ether, and it has been successfully applied in the flotation practice of iron ore [20,21]. Compared with the common dodecylamine, GE-609 has better collecting capability and selectivity at the similar dosage. Furthermore, the use of GE-609 is more beneficial for actual production due to the less flotation foam with better brittleness. However, little effort has been devoted to the process and mechanism of smithsonite flotation with an ether amine as the collector. In this work, the main factors involved in the separation of smithsonite from calcite and quartz were investigated by micro-flotation experiments using GE-609 as the collector. And the adsorption of GE-609 on smithsonite surface was analyzed by zeta-potential measurement and Fourier transform infrared (FTIR) spectroscopy.

2 Experimental

2.1 Materials and reagents

The smithsonite sample was obtained from Yunnan province, China, and the calcite and quartz samples were obtained from Hunan province of China. They were crushed, ground and then sieved to collect the size fraction of 38–74 µm for the micro-flotation experiments. Based on the results of X-ray diffraction (XRD) and chemical analysis, the purities of the three samples are above 90%.

The real ore was obtained from Yunnan province, China. The chemical analysis results show that the raw sample contains 1.44% Pb, 7.04% Zn, 1.89% S, 4.72% Fe, 32.43% SiO₂, 18.62% CaO, and so on. Based on XRD detection, the main valuable minerals are cerusite and smithsonite, and the gangue minerals are mainly quartz and calcite, followed by mica, gypsum, dolomite and chlorite. The phase analysis results of Pb and Zn are shown in Table 1, and the results show that the oxidation rates of Pb and Zn are 82.88% and 84.79%, respectively. The separation technology for the raw ore is determined as Pb flotation and then Zn flotation. Since the main aim of this study is to investigate the selective flotation of smithsonite, calcite and quartz, so the experimental sample was the tailings produced by the Pb beneficiation process of sulphidization and then flotation with xanthates.

A alkyl diamine ether (GE-609) of industrial pure was used as the collector in this investigation, and its structural formula is \(\text{CH}_2(CH_2)_{n} \text{CH}_2 \text{O}(\text{CH}_2)_{n} \text{NH}(\text{CH}_2)_{n} \text{NH}_2\), \(n=6-16\). Solutions of HCl and NaOH were used to adjust pH value. Analytical grade sodium sulfide was used as an activator, and analytical grade sodium silicate and sodium hexametaphosphate were used as depressants. Distilled water was used for all experiments except the real ore flotation tests.

| Table 1 Phase analysis results of Pb and Zn in raw ore (mass fraction, %) |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Pb mineral      | Lead sulfate    | Lead oxide      | Lead sulfide    | Plumbojarosite  | Total           |
| Content        | 0.19            | 0.82            | 0.25            | 0.20            | 1.46            |
| Occupancy      | 13.01           | 56.16           | 17.12           | 13.70           | 100.00          |
| Zn mineral      | Zinc sulfate    | Zinc oxide      | Zinc sulfide    | Franklinite     | Total           |
| Content        | Trace           | 5.71            | 1.08            | 0.31            | 7.10            |
| Occupancy      | 80.42           | 15.21           | 4.37            | 100.00          |

2.2 Flotation experiment

The micro-flotation experiments were carried out in a 40 mL flotation cell at a constant stirring rate of 1600 r/min. For each test, 2 g of samples were separately conditioned with the corresponding reagents at a desired pH value for 3 min, and then floated for 4 min. At last, the concentrate and tailing were filtered, dried and weighed.

Flotation tests on the real ore sample were conducted in a series of 0.5–1.5 L flotation machine. The pH regulator, depressant and collector were successively added to perform the flotation. At last, the concentrate and tailing were separately dried, weighed and sampled to analyze the content of Zn to calculate the yield and recovery.

2.3 Zeta potential measurement

Zeta potentials of samples (~5 µm) were measured using a JS94H micro-electrophoresis meter (Shanghai, China). All measurements were conducted in a 1.0×10⁻⁴ mol/L KCl background electrolyte solution. The average value of three independent measurements was reported as the final result. The system error is less than 5%.

2.4 Infrared spectroscopy

The diffuse reflectance infrared spectra were obtained using a Nicolet FTIR-740 spectrometer (USA) to study the adsorption mechanism of GE-609 on smithsonite surface. Samples of ~2 µm fraction were used and prepared according to the conditions of micro-flotation tests.

3 Results and discussion

3.1 Micro-flotation studies

Flotation performance of smithsonite, quartz and calcite as a function of pH using 25 mg/L GE-609 as the collector is shown in Fig. 1. It can be seen that a rise in
pH from 6 to 10 improves the floatability of smithsonite with a maximum recovery of 85%. The recovery of quartz is approximately 100% in the pH range of 6–11, while it shows a sharp decrease when pH value is above 11. The floatability of calcite increases with the increase of pH value, and the flotation recovery is over 95% at pH 12.

Figure 3 shows the effect of sodium sulfide on the floatability of smithsonite, quartz and calcite at natural pH (7.0–7.5) and 10 mg/L GE–609. When the concentration of sodium sulfide is less than 300 mg/L, the recovery of smithsonite increases with increasing the concentration. After that, the flotation recovery of smithsonite has a little decrease, and the maximum recovery is about 96%. This confirms that over-sulphidization of the pulp decreases flotation recovery due to the high content of HS⁻ ion [6,10]. The calcite recovery increases with increasing sodium sulfide concentration, and it is about 90% when the concentration is above 500 mg/L. However, quartz shows a different flotation behavior, its recovery decreases as sodium sulfide concentration rises, and it is nearly 0 at 1000 mg/L sodium sulfide. Therefore, it is clearly show that the presence of sodium sulfide improves the flotation of smithsonite and calcite while it has depressing effect on quartz.

Using 10 mg/L GE–609 and 1000 mg/L sodium sulfide, the effects of sodium silicate and sodium hexametaphosphate concentration on the recovery of smithsonite and calcite were investigated, and the results are shown in Fig. 4. It can be seen that the recovery of calcite decreases from 90% to 10% at the sodium silicate concentration of 200 mg/L, where the recovery of smithsonite is still 95%. For sodium hexametaphosphate as the depressant, the recovery of calcite sharply decreases while the recovery of smithsonite has no obvious change, when the concentration is 3 mg/L, the recoveries of smithsonite and calcite are about 93% and 10%, respectively. According to these results, the flotation separation of smithsonite from calcite is possible to be achieved using sodium silicate or sodium hexametaphosphate as the depressant at an appropriate concentration.
The species $\text{Zn(OH)}_2(aq)$ of smithsonite samples without treatment was measured, and the results (Fig. 5) show that the isoelectric point (IEP) of smithsonite is found to be pH 7.3 in water, which agrees with those reported in the pH range of 7–8 [5,26]. The surface of smithsonite is positively charged at pH<7.3, and negatively charged at higher pH.

In the presence of GE–609, a series of processes occur, including the dissolution of GE–609, the adsorption of amine ions on smithsonite surface, chemical and/or electrochemical reactions, and the possible dissolution of some surface species. The zeta potential of smithsonite after GE–609 treatment shows that adding GE–609 makes the zeta potential more positive and the value of isoelectric point increases. The pH\_IEP of smithsonite rises from 7.3 to about 7.7 because of the adsorption of GE–609.

As shown in Fig. 6, the species $\text{RNH}_4^+$ dominates when pH<10.98, whereas the species $\text{RNH}_3(aq)$ and $\text{RNH}_2(aq)$ dominate when pH>10.98 [27]. Therefore, we can conclude that the more positive charge of smithsonite below pH 7.3 maybe be resulted from the reaction between $\text{RNH}_4^+$ and $\text{CO}_3^{2-}$ ions to form amine salts. In the pH range of 7.3–11, the smithsonite surface is negatively charged, the zeta potentials move to positive direction maybe due to the electrostatic adsorption of $\text{RNH}_4^+$ on smithsonite surface; whereas the zeta potentials almost keep unchanged above pH 11, possibly causing by the adsorption of $\text{RNH}_3(aq)$ and $\text{RNH}_2(aq)$ on the smithsonite surface in the form of Zn-amine complexes [28].

3.3.2 Infrared spectroscopy

Figure 7 shows the spectra of GE–609 adsorbed on smithsonite surface in the presence and absence of
sodium sulfide. As can be seen, the bands at 3381 and 3329 cm$^{-1}$ in the spectrum of GE–609 (a) are due to the stretching vibration of $\text{−NH}_2$, 1622 and 1570 cm$^{-1}$ are due to the bending vibration of $\text{−NH}_2$ and $\text{NH}_3$. The bands at 2924 and 2854 cm$^{-1}$ are assigned to $\text{−CH}_3$ and $\text{−CH}_2$ stretching. The adsorption band at 719 cm$^{-1}$ is due to the in-plane rocking vibration of $\text{−(CH}_3)_n$ ($n\geq 4$). Besides, the characteristic band at 1115 cm$^{-1}$ is due to the stretching vibration of C−O−C group [27].

The smithsonite spectrum (b) displays several bands, the bands at 870 and 743 cm$^{-1}$ correspond to the bending vibrations of CO$_3^{2−}$, 1444 cm$^{-1}$ is due to the asymmetric stretching vibration of CO$_3^{3−}$. The wide band at 3325 cm$^{-1}$ is due to the stretching vibration of $\text{−OH}$ [12]. After being treated with sodium sulfide (c), the C=O bands at 1444 cm$^{-1}$ partially disappear to form partially ZnS on the smithsonite surface. In the spectrum (d), there are several new bands after GE–609 treatment. Two new bands are observed at 2854 and 2923 cm$^{-1}$, assigned to $\text{−CH}_3$ and $\text{−CH}_2$ stretching. Two new bands at 3433 and 3334 cm$^{-1}$ are due to the stretching vibration of $\text{−NH}_2$. And a new band at 1180 cm$^{-1}$ is due to the stretching vibration of C−O−C group. Meanwhile, the characteristic smithsonite peak of 1444 cm$^{-1}$ assigned to CO$_3^{2−}$ vibration absorption has shifted to 1435 cm$^{-1}$. In the spectrum (e), the presence of sodium sulfide makes the intensity of alkyl chain bands and $\text{−NH}_2$ bands increase, which indicates the increased adsorption of GE–609 on smithsonite surface.

4 Conclusions

1) The alkyl diamine ether GE–609 exhibits good collecting capability to smithsonite, calcite and quartz, and it is unavoidable to use a depressant for their separation.

2) Sodium sulfide can improve the flotation of smithsonite and calcite while has depressing effect on quartz, both sodium silicate and sodium hexametaphosphate have selective inhibition to calcite at an appropriate concentration.

3) Zeta potential and FTIR analysis show that both electrostatic and chemical adsorption of GE–609 occur on smithsonite surface, and the presence of sodium sulfide enhances the adsorption of GE–609.

References

捕收剂烷基二醚胺对菱锌矿、石英和方解石选择性浮选的影响

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摘 要：通过单矿物浮选试验和实际矿山浮选试验考察了烷基二醚胺（GE-609）做捕收剂时，菱锌矿、石英和方解石的浮选性能。结果表明，GE-609 对 3 种矿物均有良好的捕收性能，浮选无选择性。硫化钠能增强菱锌矿和方解石的浮选但抑制石英。此外，水玻璃和六偏磷酸钠均对方解石表现出良好的选择性抑制作用。实际矿山浮选试验表明，最终闭路试验获得 Zn 品位为 23.51%，回收率为 71.02% 的锌精矿。通过动电位测试和红外光谱分析考察了 GE-609 在菱锌矿表面的吸附，结果表明，GE-609 在菱锌矿表面的吸附包括静电吸附和化学吸附，且硫化钠的存在增强了 BGE-609 在菱锌矿表面的吸附。

关键词：菱锌矿；石英；方解石；烷基二醚胺；硫化钠；硫化浮选

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