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Selective flotation separation of ilmenite from titanaugite using mixed anionic/cationic collectors

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ABSTRACT

The flotation behavior of ilmenite and titanaugite using anionic collector sodium oleate (NaOL), cationic collector dodecylamine acetate (DAA) and the mixed anionic/cationic collector (NaOL-DAA) was investigated through micro-flotation experiments, zeta potential measurements, Fourier transform infrared (FTIR) analyses, and the artificially mixed minerals flotation experiments. The results of the microflotation experiments indicate that DAA exhibits good flotation performance to both ilmenite and titanaugite at a pH > 6.0. The flotation separation of ilmenite from titanaugite can be performed using the mixed NaOL-DAA in a wide pH range of 5.0–7.0. In this pH range, the recovery of ilmenite remains constant at approximately 90%, while the recovery of titanaugite remains <25%. The best separation result can be achieved with NaOL-DAA molar ratios of 10:1. The results of the zeta potential experiments and the FTIR analyses indicate that the adsorption of the mixed collector, NaOL-DAA, on the ilmenite surface is larger than on the titanaugite surface and that the NaOL-DAA complex might be mainly adsorbed on the ilmenite surface by chemical adsorption, apart from electrostatic adsorption. The synthetic mineral mixture micro-flotation results demonstrate that, compared to NaOL, NaOL-DAA not only increases the recovery and grade of the TiO_2 by 7.02% and 6.71%, respectively, but also decreases the reagent consumption by half.

1. Introduction

Honored as "the third metal", Ti has played an irreplaceable role in a variety of fields, including aerospace, the military industry, transportation, and environmental protection, and in medical devices (Bulatovic and Wyslouzil, 2009; Chen et al., 2013; Samal et al., 2009). Ilmenite ore (since the remaining amount of the other main TiO_2 containing mineral, rutile, is limited) is ranked as one of the major sources of Ti dioxide and titanium metal. Ilmenite ($FeTiO_3$), with a structure similar to hematite, belongs to the titanate of ferrous iron. As Mehdilo et al. (2013, 2015) said "Along the direction of the triad axis, pairs of Ti ions alternate with pairs of Fe^{+2} ions; thus each cation layer is a mixture of Fe^{+2} and Ti^{+4}".

The Panzhihua area, located in the Sichuan province of China, possesses the largest deposits of vanadium-titanium magnetite with a reserve of >10 billion tons (Han et al., 2011; Wang et al., 2015). Because ilmenite is freely disseminated in the gangue in these ores, physical methods can barely achieve an effective separation (Zhang et al., 2011). Thus, flotation, with its excellent separation performance, is preferentially chosen as the main method for processing the ilmenite ore (Bulatovic and Wyslouzil, 2009; Mehrabani et al., 2010).

Fatty acid collectors such as sodium oleate, naphthenic soap, and oxidized paraffin soap are widely used industrially in the flotation separation of ilmenite from the gangue minerals (Hosseini and Forssberg, 2013; Liu et al., 2015; Xu et al., 2015). On one hand, ilmenite is freely distributed in the gangue minerals, while on the other hand, the grade of the titanium minerals is decreasing. Although the anionic collectors mentioned above have good selectivity over the ilmenite flotation, they are increasingly powerless to guarantee an appreciable flotation recovery (Fan et al., 2009). The cationic collectors, namely amine, are extensively applied in the flotation of metal oxide ore and silicate ore such as zinc oxide mineral, bauxite, mica and quartz (Pugh et al., 1996; Sekulić et al., 2004; Yu et al., 2016).The main flotation characteristic of the cationic collectors is that they can achieve a relatively high recovery but, at the same time, they can hardly guarantee the required selectivity (Al-Thyabat, 2012). Considering the characteristics of the anionic and the cationic collectors, the theory of mixing the anionic collector and the cationic collector comes into consideration.

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In recent years, the use of mixed collectors has become an inevitable trend in terms of their superior selectivity (Rao and Forssberg, 1997; Vidyadhar et al., 2012). For example, our previous research indicated that the mixed collectors consisting of NaOL and benzohydroxamic acid could achieve fairly good results in the flotation separation of ilmenite and titanaugite ($Ca(Mg,Fe,Ti)(Si,Al)_2O_6$) (Yang et al., 2016). Among a variety of combinations of collector types, the mixed anionic/cationic surfactants exhibit many unique properties in addition to their advantages over price and solubility (Ejtemaei et al., 2014; Heyes et al., 2013). Due to the strong electrostatic interactions between oppositely charged head groups, the mixed anionic/cationic surfactants system demonstrates a better flotation performance (Sohrabi et al., 2008; Yoshimura and Esumi, 2004). Xu et al. (2016) found that the mixed anionic/cationic collectors not only decreased collector consumption but also increased the recovery and grade of Li_2O concentrates in the flotation separation of spodumene from feldspar. Wang et al. (2015) discovered that the mixed anionic/cationic collectors exhibited selective collection for muscovite when quartz coexists, allowing preferential flotation separation in a strong alkaline condition. However, to the best of our knowledge, although numerous studies have been performed to detect the flotation performance of the mixed anionic/cationic collector, investigation of the flotation performance and the adsorption mechanism of the mixed cationic/anionic collectors on ilmenite and its gangue mineral has not previously been documented.

Through the investigation, our objective is to understand the flotation performance and the underlying adsorption mechanism of the mixed anionic/cationic surfactants on ilmenite flotation separation from titanaugite.

2. Experiment

2.1. Materials and reagents

The same sample of ilmenite and titanaugite as our previous research was obtained from Panzhihua in the Sichuan province (China) (Yang et al., 2016). After being hand-selected, crushed, ground and screened, the powder sample of −75 + 38 μm fractions was used in the flotation tests. The samples used for the Fourier transform infrared (FTIR) analysis and the zeta potential measurement were further ground to about −20 μm. The chemical composition and the X-ray diffractometry of the ilmenite and titanaugite used for the study of the chemical characteristics and mineral compositions are shown in Table 1 and Fig. 1. The results showed the purity of the prepared ilmenite and titanaugite are ~90%. The mass ratio of the artificially mixed minerals, consisting of ilmenite and titanaugite, was 2:3 and the corresponding TiO_2 grade of the artificially mixed minerals was 21.5%. The samples of DAA and NaOL used as collectors were chemically pure. The DAA was prepared by mixing equimolar amounts of the dodecylamine and acetic acid. The mixed NaOL-DAA at different ratios of NaOL to DAA was prepared by adding desired amount of one reagent to the other reagent solution and stirring for 5 min. What should be mentioned was that the addition orders of the two reagents didn't obviously affect the flotation performance of the mixed collectors. To avoid precipitation, the mixed NaOL and DAA were freshly prepared before usage. H_2SO_4 and NaOH were used to adjust the pH of the system. Deionized water (resistivity = 18.3 MΩ∗cm) was used for the micro-flotation tests.

Table 1
Chemical compositions of the purified samples (mass fraction, %).

Sample	TiO_2	FeO	MgO	Al_2O_3	SiO_2	CaO	MnO
Ilmenite	50.90	38.81	5.06	0.89	1.51	0.31	0.64
Titanaugite	1.88	13.61	12.53	5.95	41.78	16.53	0.26

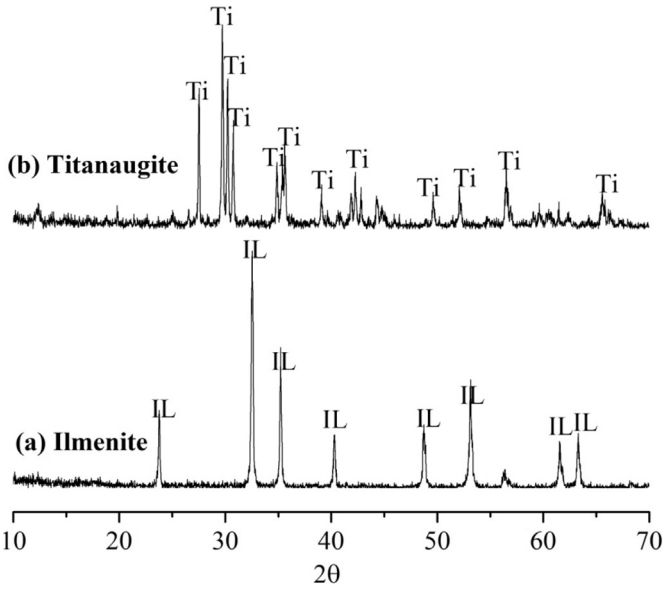

Fig. 1. XRD patterns of the purified samples (a) ilmenite, (b) titanaugite (IL = ilmenite, Ti = titanaugite).

2.2. Flotation tests

Both the single mineral (2 g) flotation and the artificial mixed minerals (3 g) flotation were conducted in a 40 mL hitch groove flotation cell with a spindle speed of 1600 rpm. The artificial mixed minerals consisted of 1.2 g of ilmenite and 1.8 g of titanaugite. After adding the desired amount of reagents, the suspension was stirred for 3 min during which the pH of the solution was adjusted to the desired value. The flotation was conducted for 4 min. The froth products and tails were weighed separately after filtration and drying, and the recovery was calculated based on the dry weight of the product. The flotation grades of ilmenite and titanaugite were assessed by the method of ammonium ferric sulfate titration in a synthetic mineral mixture flotation. The detailed procedures for chemical analysis were as follows: First, melted by potassium pyrophosphate, the sample was leached by acid; Second, under the condition of air isolation, titanium was reduced from tetravalence to tervalence by aluminum foil in hydrochloric acid and sulfuric acid solution; Third, using ammonium thiocyanate solution as indicator, the titration end-point was gotten when the solution turned to stable orange red by adding ammonium ferric sulfate standard solution. Each experiment was repeated three times and the average was reported as the final value. The standard deviation, which is presented as an error bar, was calculated by using Origin 9.2, based on the normal distribution of three measurement results.

2.3. Zeta potential measurement

The zeta potentials were measured using a Zetasizer Nano Zs90 (England). The measurement temperature was maintained at 25 °C. The suspension was prepared by adding 30 mg of the purified mineral particles to 40 mL of ultrapure water and sodium sulfate Na_2SO_4 (1×10^{-4} mol/L) as background electrolyte was added as background electrolyte. After being conditioned by magnetic stirring for 5 min and settling for 10 min, the supernatant of the dilute fine particle suspension was taken for the zeta potential measurement. The conductivity and pH of the suspension were monitored continuously during the measurement. Each sample was measured at least three times and their averages were taken as the final result.