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A comparison study of the flotation and adsorption behaviors of diaspore and kaolinite with quaternary ammonium collectors

Hao Jiang [a,*], Zhongcheng Sun [a], Longhua Xu [a,b], Yuehua Hu [a], Kai Huang [a], Shusheng Zhu [a]

[a] School of Minerals Processing and Bioengineering, Central South University, Changsha 410083, China
[b] Key Laboratory of Solid Waste Treatment and Resource Recycle Ministry of Education, Southwest University of Science and Technology, Mianyang 621010, China

ABSTRACT

The flotation and adsorption behaviors of two quaternary ammonium collectors DTAC (dodecyl trimethyl ammonium chloride) and CTAC (cetyltrimethyl ammonium chloride) on diaspore and kaolinite were investigated in this work. The flotation recovery of diaspore increases with the increase of pH and the decrease of particle size, however, the situations for kaolinite are opposite. Furthermore, the influence of pH on flotation of kaolinite decreases with the decrease of particle size, and for the fine particles (undersize 0.045 mm), the flotation recovery with CTAC which has a longer hydrocarbon chain and is believed to have a stronger collecting ability is lower than that with DTAC. The dramatic differences of the flotation behaviors between diaspore and kaolinite are correlated to the differences of their crystal structures. The morphologies of diaspore and kaolinite particles in different size were studied by SEM. The kaolinite particles have much larger specific surface areas (about 7 times) than the diaspore particles due to their layered structure. This leads to the differences of collector adsorption behaviors on kaolinite and diaspore and results in the different flotation behavior.

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1. Introduction

Diaspore-type bauxite is the major aluminum resource in China. However, for most of them, the mass ratio of Al_2O_3 to SiO_2 (A/S) is between 4 and 6, which should be improved to meet the basic condition ($A/S > 10$) of Bayer process (Liu et al., 2011; Zhong et al., 2008). The reverse flotation for silica removal was developed as an economical way to improve the A/S ratio (Hu et al., 2003; Jiang et al., 2001). Reverse flotation is widely used in mineral processing such as reverse flotation of coal (Stonestreet and Franzidis, 1992) and reverse flotation of iron ore (Dos Santos and Oliveira, 2007). In the reverse flotation of diaspore-type bauxite, gangue minerals (mainly kaolinite, etc.) are floated from valuable minerals (mainly diaspore).

During the latest ten years, many studies have been conducted to investigate the flotation behaviors of kaolinite and diaspore in order to understand and control the diasporic bauxite reverse flotation (Cao et al., 2004; Hu et al., 2003, 2005; Jiang et al., 2001; Liu et al., 2011; Ma et al., 2009; Zhong et al., 2008). Cationic collectors such as alkyl quaternary ammonium salts (Hu et al., 2003), amino amides (Zhao et al., 2003a,b), polyamine and ether amine (Cao et al., 2004) were tested and proved to be effective collectors for bauxite reverse flotation. However, some situations such as the flotation recovery of kaolinite decreases with the pH increase (Hu et al., 2005; Jiang et al., 2001) are abnormal and their mechanisms are not very clear.

Generally, many flotation phenomena can be interpreted by considering the adsorption of collectors and modifying reagents. Several experimental techniques such as electron spin resonance (Chandar et al., 1987b; Waterman et al., 1986), UV spectroscopy and fluorescence probe studies (Chandar et al., 1987a; Somasundaran et al., 1986), and Raman spectroscopy (Somasundaran et al., 1989) have been employed to study the adsorption mechanisms as well as the structure of adsorbed collectors. The adsorption of cationic collectors on dioxide minerals is governed mainly by the electrostatic interaction and hydrophobic interaction (Cases and Villieras, 1992) which includes interaction between the collector and the surface as well as the interaction between collector molecules. Initially, collector cations adsorb physically as individual ions on the negatively charged surface sites. In this stage, the cations exchange with protons or other counterions present at the solid–water interface (Tahani et al., 1999). Once the surface charge has been neutralized, the adsorption will only increase if the interaction of the hydrophobic part of the collector for water can promote self-association and consequently, adsorption (Tahani et al., 1999).

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* Corresponding author. Tel.: +86 731 88830204; fax: +86 731 88830815.
  E-mail address: jianghao-1@126.com (H. Jiang).

To make a contribution toward the understanding of the bauxite reverse flotation, the flotation and adsorption behaviors of diaspore and kaolinite in different size fractions with two quaternary ammonium collectors (DTAC and CTAC) were studied. The morphologies of the particles in different sizes were characterized by SEM and AFM. The differences of flotation behaviors between diaspore and kaolinite were interpreted by focusing on the differences of crystal structure and adsorption behaviors of collectors.

2. Experimental

2.1. Minerals and chemicals

Kaolinite and diaspore were obtained from Xiaoguan in Henan province, China and Xiaoyi in Shanxi province, China, respectively. The samples were handpicked and ground by porcelain mill and sieved into three size fractions (0.075–0.1 mm, 0.045–0.075 mm and −0.045 mm). The purity of minerals samples determined by chemical composition analysis (Table 1) and X-ray diffractometry (XRD) indicates that they are sufficiently pure to meet the requirements of subsequent experiments.

DTAC and CTAC of analytical grade from Nanjing Robiot Co., Ltd. were used as collectors as well as frothers. Bromothymol blue (BTB) of analytical grade from Damao Chemical Reagent Factory China was used as an indicator. HCl and NaOH of analytical grade from Damao Chemical Reagent Factory China were used to adjust the pH of the system. Deionized water was used in this experiment.

2.2. Methods

Flotation tests of pure minerals were performed in a 40 mL plexiglass cell filled with distilled water by using 2 g of desired size fraction samples for each test. The rotational speed in the cell during flotation was 1600 rpm. The pH was adjusted to a desired value with addition of HCl and NaOH. The samples were conditioned with reagents for 5 min in the cell at 1600 rpm. The flotation was conducted for 4 min. The froth products and tails were weighed respectively after filtration and drying, and the recovery was calculated based on the mass of the products.

Zeta potentials were determined using a Brookhaven ZetaPlus Zeta Potential Analyzer (USA). The mineral samples were ground to −2 μm and the suspensions concentration 0.04wt% was prepared in the 1×10^{-3} mol/L NaCl solution.

The morphologies of the particles in different sizes obtained by sedimentation were characterized by SEM (JEOL, JSM-5600LV, Japan) and TMAFM (DI Nanoscope multimodeV, USA). The specific surface area of diaspore and kaolinite in different size ranges were determined by the BET nitrogen adsorption.

The amount of collectors adsorbed on minerals surfaces was determined by UV spectrophotometry (Unico UV-2012, China) in this work. At a pH 7.5–8.5 buffer solution of phosphate, the color of bromothymol blue solution will decrease due to the association reaction between quaternary ammonium saltsand bromothymol blue. This phenomenon enables the determination of quaternary ammonium concentration by spectrophotometric method (Wu et al., 2002). We used the same method as that of Wu et al.

(2002) to determine the concentration of quaternary ammonium. 10.0 ml quaternary ammonium salts sample solution with unknown concentration, 2.0 ml 0.5 wt% emulsifier OP solution, 5 ml 2.5×10^{-4} mol/L bromothymol blue solution, and 2.5 ml pH 7.7 buffer solution prepared from disodium hydrogen phosphate and potassium dihydrogenphosphate were added in an 80 ml beaker. After sufficient mixing through shaking the beaker, the absorbance of the solution at 618 nm wavelength was determined by UV spectrophotometry (Unico UV-2012, China). The quaternary ammonium salts concentration of the sample solution was then determined by comparing the absorbance to the standard curve obtained at the same conditions but the known ammonium salts concentration of the sample solution. If the determined concentration exceeds 5×10^{-5} mol/L, the sample solution was diluted and retested again due to the breaking of Bear's law according to the test of standard sample.

Pure mineral sample (2 g) of desired size fraction was placed in the 40 mL plexiglass cell filled with distilled water. The pH was adjusted to a desired value with the addition of HCl and NaOH. The samples were conditioned with collectors for 5 min in the flotation cell at 1600 rpm. The solid particles were then separated by centrifugation at 12,000 r/min for 10 min. The concentration of the collector in the supernatant solution (residual collector concentration) was determined by UV spectrophotometry. The amount of collector adsorbed on the mineral particles was calculated as (Beaussart et al., 2009):

$$\Gamma = \frac{V(C_0 - C)}{mA} \qquad (1)$$

where C_0 and C are the initial and supernatant concentrations, respectively; V is the solution volume; m is the amount of the particles per sample; A is the particle specific surface area.

3. Results

3.1. Flotation results of diaspore and kaolinite

Fig. 1 shows the flotation results of diaspore and kaolinite with DTAC and CTAC as a function of the solution pH. The initial concentration of DTAC and CTAC are 4×10^{-4} mol/L. It is evident that the flotation recovery of diaspore with DTAC and CTAC increases with the increase of solution pH and the decrease of the particle size fraction. However, the situations are completely opposite for the flotation of kaolinite. The flotation recovery of kaolinite decreases with increasing the pH value, which is consistent with previous literatures (Hu et al., 2003; Jiang et al., 2001), but for the fine particles (undersize 0.045 mm), the decreases are mostly vanished. The flotation recovery with CTAC which has a longer hydrocarbon chain is better than that with DTAC for both diaspore and kaolinite except for the fine kaolinite (undersize 0.045 mm).

3.2. Zeta potential of diaspore and kaolinite

As shown in Fig. 2, the zeta potential of diaspore and kaolinite in water decreases with the increase of pH, and the zeta potential of diaspore is higher than that of kaolinite. These are consistent with many previous literatures (Hu et al., 2003, 2005; Liu et al., 2011).

Table 1
Chemical analyses of the pure minerals (%).

Mineral	Al$_2$O$_3$	SiO$_2$	Fe$_2$O$_3$	TiO$_2$	CaO	MgO	K$_2$O	Na$_2$O	LOI[a]
Diaspore	80.98	0.78	0.29	2.84	0.01	0.046	0.007	0.025	14.5
Kaolinite	39.2	43.67	0.32	1.98	0.01	0.068	0.094	0.028	13.98

[a] Loss on ignition.