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Flotation of fine kaolinite using dodecylamine chloride/fatty acids mixture as collector

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ABSTRACT

In order to improve the flotation recovery of fine kaolinite, mixed dodecylamine chloride/fatty acid was used as collector in kaolinite flotation process.

The performance of dodecylamine chloride/fatty acid mixture collector on kaolinite flotation was investigated using flotation test and computational method. Surface tension measurement, contact angle measurement and image analysis were also used to study the flotation behavior of dodecylamine chloride and mixture collectors. The flotation results showed that much higher kaolinite flotation recovery was obtained in the presence of dodecylamine chloride/octanoic acid mixture compared with that in the presence of dodecylamine chloride alone. Surface tension measurements indicated that the mixed dodecylamine chloride/octanoic acid collector was more efficient at decreasing the air–water interfacial tension. Molecular dynamics simulation showed that the octanoic acid molecules were interleaved among dodecylamine chloride ions and co-adsorbed at the kaolinite (001) surface. The relative concentration of water molecules near kaolinite (001) surface further decreased in the presence of dodecylamine chloride/octanoic acid compared with that in the presence of dodecylamine chloride alone, which indicated a much stronger hydrophobicity of the kaolinite (001) surface.

1. Introduction

Flotation is one of the prime mineral processing methods that has found wide application from separation of complex ores such as sulphides of lead–zinc and copper–zinc to platinum, nickel and gold hosting sulphides, to oxides like hematite, cassiterite, oxidised minerals such as malachite, cerussite and finally to non-metallic ores like fluorites, phosphates as well as coal [1–5]. Clay minerals are among the most important and useful industrial minerals because they have many applications. However, clays or phyllosilicates, for example kaolinite, pyrophyllite, illite, montmorillinite, are also very common gangue minerals in the processing of mineral resources, and are difficult to remove from valuable minerals and energy resources, e.g. oil sands, potash, phosphate, bauxite, rare earth resources, metal sulphide ores (copper, nickel) [6–7]. In some cases it is desired to depress kaolinite during flotation while in other cases the kaolinite is removed by reverse flotation [8–9]. In bauxite flotation, recent studies have suggested that reverse flotation is economically favored over the direct flotation process as well as coals [2,10–12].

During the latest ten years, many studies have been conducted to investigate the flotation behaviors of kaolinite [10–12]. Recently, many researchers have been dedicated to developing new cationic collectors which can improve the flotation behavior of kaolinite from bauxite, and a large variety of the collector types have been investigated, such as the primary amine, tertiary amines and quaternary amines [11, 13–14].

However, during their researches, they found that fine kaolinite particles (0–0.045 mm) showed poorer floatability compared with coarse kaolinite particles. The flotation recovery of fine kaolinite was even <10% over a wide pH range. Several probable reasons were discussed in their research [15–16]. In this paper, mixtures made of dodecylamine chloride and fatty acid were prepared and used as cationic collector for fine kaolinite flotation. Flotation results with these mixture collectors were compared with each other. Moreover, computational calculations were used to obtain information on the adsorption mechanism of the mixture collectors on the kaolinite (001) surface to elucidate the adsorptive characteristics of the mixture collector toward the kaolinite (001) surface.

2. Experimental

2.1. Minerals and reagents

Kaolinite samples were obtained from Xiaoyi, Shanxi province in China. The samples were hand-picked, crushed and ground in a

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laboratory porcelain mill. Then the sample was screened and size fraction (0–0.045 mm) was used in the experiments. Chemical composition analysis and X-ray diffractometry were used to study the characteristics of chemical and mineral compositions (Fig. 1). The size distribution of the kaolinite sample was showed in Fig. 2. The purity of the kaolinite sample was about 90% by chemical analysis and X-ray diffraction. The BET surface area of the sample was 3.114 m^2/g.

The collector, dodecylamine hydrochloride (DAH), with a purity of 99.5%, was purchased from Aladdin Reagent. The concentration of the DAH solution was 0.134 mol/L. Hydrochloric acid (HCl) and sodium hydroxide (NaOH) were used as pH regulators. HCl and NaOH used in this study were of analytical grade obtained from Aladdin Reagent. Reagent grade fatty acids were supplied by Aladdin Reagent. The following fatty acids were used: *n*-octanoic acid, C8 (purity ≥ 98%), *n*-capric acid, C10 (purity ≥ 98%), dodecanoic acid, C12 (purity ≥ 98%). All fatty acids were used as received. Each fatty acid was mixed with 50 mL DAH solution and stirred with a magnetic stirrer at 50 °C until a homogeneous mixture was obtained. The molar ratio of DAH and fatty acid was 1:1 and 2:1, respectively. The full names and the shortcuts of all reagents were listed in Table 1.

2.2. Flotation tests

Flotation tests were carried out in a 50 mL XFD laboratory flotation cell. In all flotation tests, a 4 g sample was used. The impeller speed in both conditioning and flotation processes is 1800 rpm. The pH was adjusted to a desired value with addition of HCl and NaOH. It is noted that we did not measure the pulp pH after minerals were added into the water; the pH was referred to water pH in all the tests. During the flotation process, the additional water used to keep the pulp level was the same pH value with that of the system. The samples were conditioned with reagents for 30 s. Each flotation test was performed for 5 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.

2.3. Surface tension measurement

Surface tension measurements were determined by the du Nouy ring method using a LAUDA (TEIC) Tensiometer. The instrument was calibrated against double distilled water. Measurements were made at intervals of a few minutes until successive values agreed within a standard deviation of 0.1 mN/m or less. The CMC values were determined graphically as the intersection point of the two linear portions of the plot [17].

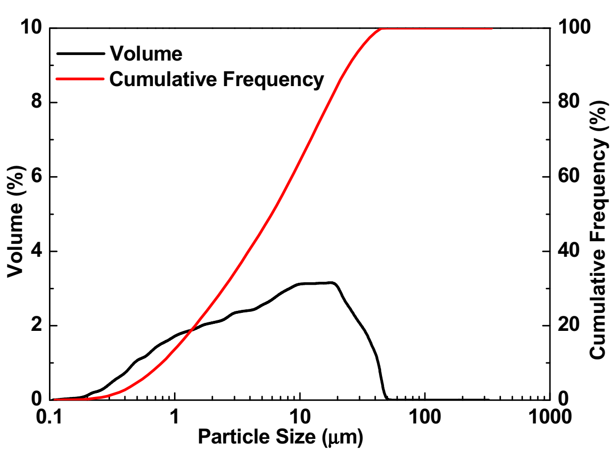

Fig. 1. Size distribution of the kaolinite sample.

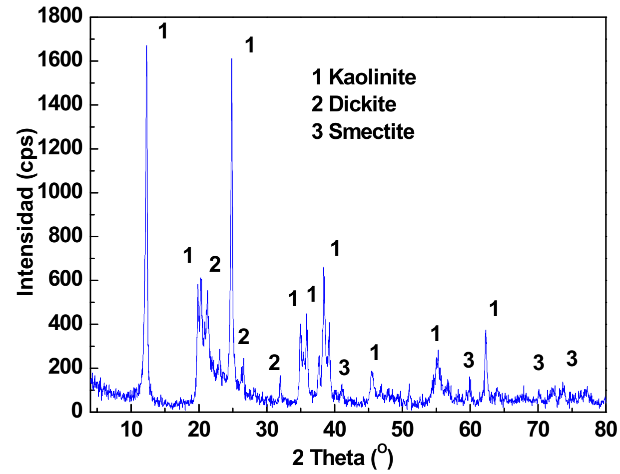

Fig. 2. XRD patterns of the kaolinite sample.

2.4. Contact angle measurements

DSA 30 from KRUSS, Inc. (Germany) was used to measure the contact angles on mineral surface in different reagent solution by sessile drop method. In each test, 4 g kaolinite (−0.045 mm) was first stirred with a magnetic stirrer in different collector solution with adjusted pH values for 30 min. And the suspension was filtered and dried at 30 °C. Then the kaolinite sample was performed at 10 M pressure for 1 min using a FW-4A powder compressing machine (China). The measurements were repeated at least four times and each contact angle data point presented in this paper was the average value of at least three measurements.

2.5. Image analysis

An optical microscope equipped with a digital camera was used to observe the mixture collectors. The collector was prepared by dropping it on a glass plate, followed by putting a thin glass slide on the sample to fix it. During the observation, the collectors were photographed [18].

2.6. Computational details

All simulations were performed in Accelrys Material Studio 6.0 (MS) modeling package. CASTEP module included in MS software was used to optimize the crystal structure of kaolinite; DAH and fatty acid molecules were optimized using DMOL3 module. The exchange-correlation function used was the generalized gradient approximation (GGA) developed by Perdew-Burke-Ernzerhof (PBE). The energy cut-off for the plane-wave basis was 300 eV. The convergence criterion for self-consistent field tolerance was 1.0×10^{-6} eV/atom. Universe force field (UFF) was applied for all Molecular Dynamics simulations. Since many experts have successfully demonstrated that UFF could be used to simulate aluminosilicate with reasonable accuracy while other force fields could not [19–20]. The aqueous layer contained one thousand water molecules with identical length and width to those in the mineral

Table 1
The shortcuts of all reagents.

Full name	Shortcut
Dodecylamine hydrochloride	DAH
Hydrochloric acid	HCL
Sodium hydroxide	NaOH
n-Octanoic acid/DAH mixture	C8D
n-Capric acid/DAH mixture	C10D
Dodecanoic acid/DAH mixture	C12D