



# Anisotropic adsorption of oleate on diaspore and kaolinite crystals: Implications for their flotation separation



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## ABSTRACT

Comparative studies of flotation of oleate on diaspore and kaolinite in different particle size fractions (0.075–0.038 mm, 0.038–0.01 mm, 0–0.01 mm) are presented to investigate the influences of particle size. The flotation results show that the kaolinite recovery increases with a decrease in particle size, while the case of diaspore is the opposite. Chemisorptions of anionic oleate collector on the surface Al sites of the negatively charged diaspore and kaolinite are confirmed by zeta potential and FTIR measurements. Anisotropic surface bond densities are calculated based on surface crystal chemistry to characterize anisotropic wettability of mineral crystals. The increasing order of broken bond densities ( $D_b$ ) and hydrophobicity for different crystal planes of diaspore and kaolinite correlate well with increasing the number of broken Al–O bonds. The anisotropic adsorption of oleate on different crystal planes of diaspore and kaolinite are studied in terms of interaction energies computed by molecular dynamics (MD) simulations. The oleate is adsorbed more readily on (0 1 0) than (0 0 1) for diaspore. As for kaolinite, the oleate adsorption is considerably less on (0 0 1) as compared to (1 1 0). The conclusions drawn from purely theoretical computations are in good agreement with our experimental contact angle results.

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## 1. Introduction

Diasporic-bauxite is a major source for aluminium oxide production in China, which is characterized by its low mass ratio of  $\text{Al}_2\text{O}_3$  to  $\text{SiO}_2$  (A/S) [1]. Kaolinite is the dominant silica-bearing minerals in diasporic bauxites. This kind of bauxite ores cannot be treated economically by Bayer's process unless A/S in the ores is improved higher than 8. For the economical utilization of Chinese diasporic bauxites, flotation to increase A/S has been proved to be an efficient method [2].

On the one hand, reverse flotation to remove aluminosilicates from diasporic bauxite may be an effective processing method. Cationic collectors display a superior collecting power for the aluminosilicates (kaolinite, illite and pyrophyllite) to reverse flotation desilication for diasporic bauxites. Thereby various cationic collectors have been extensively studied in recent years. The main collectors cover alkylamines, tertiary amine, quaternary ammonium, acylamide, ether amine, polyamine, amidoamine and so on [3–7]. However, most of these cationic surfactants used as

collectors in desilication of bauxite ores by reverse floatation stay in the lab and cannot be widely applied in industry because of many shortcomings, such as high cost, low solubility, low biodegradability. On the other hand, due to fatty acids being green (low toxicity and renewable by hydrolysis of plant or animal) [8,9], direct flotation for diaspore with anionic collector (fatty acids) will be a better prospect of application.

In diasporic bauxite flotation, the minerals involved all contain broken Al–O bonds, although kaolinite also contains broken Si–O bonds. The challenge of this type of flotation systems is that the separation has to be based on subtle differences on the fractured surfaces among various minerals. These differences are often dictated by mineral crystal structures [10]. The diaspore [ $\alpha$ - $\text{AlO}(\text{OH})$ ] consists of hcp O sheets with Al filling two-thirds of the octahedral site [11]. Each occupied octahedron shares four edges with adjacent Al octahedral to form double chains in the *c* axis direction. These units are jointed to similar units by sharing the apical oxygens. Al occupies octahedrally coordinated sites between layers in such a way as to form strips of octahedron. The direction of these octahedrons defines the *c* parameter of the distance of the unit cell. The strips have a width of two octahedral and yield an orthorhombic cell in which *a* is twice the distance between oxygen layers. The coordination number of  $\text{Al}^{3+}$  is 6 and that of  $\text{O}^{2-}$

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is 3 [12]. Kaolinite [ $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ] is a two-layer-structured aluminosilicate, consisting of alternating layers of tetrahedral silicates and octahedral aluminum oxy-hydroxides. It has two kinds of different crystal planes, one of which is the basal plane (001), the other is the edge surfaces (010) and (110). Each layer has two different surfaces parallel to the (001) plane. First one (001) is formed from basal oxygen atoms of the tetrahedral ( $\text{SiO}_4$ ) sheet, while second one (001) is formed from surface hydroxyl groups of the octahedral ( $\text{AlO}_6$ ) sheet [13,14]. Generally, the surface chemical properties such as surface free energy, surface charge and surface hydrophobicity are governed by basal planes and edges [15,16]. It is also known that the surface properties at kaolinite basal planes and edges differ greatly. Recently, the surface charge and surface hydrophobicity of kaolinite (001) and (010) have been observed by Gupta and Yin et al. [17–19]. These investigations provided much useful information for us.

Several researches have been reported on the mechanisms of interaction of oleate with different aluminosilicate minerals, indicating that the oleate complexation with Al at the mineral surface is responsible for their flotation behaviour [20,21]. It is therefore that a proper understanding of surface Al sites cannot be neglected for the control of selectivity flotation for mineral with fatty acids. Rai et al. have recently demonstrated the interaction of oleate with spodumene, jadeite, feldspar and muscovite using molecular dynamics simulations [21]. We demonstrate in this paper how these important observations can be incorporated in diaspore and kaolinite for selective flotation among Chinese diasporic bauxites.

In the flotation separation technology, comminution is essential to liberate the valuable minerals from its gangue as well as to decrease the size [22,23]. Size reduction by mechanical crushing and grinding and flotation processes are closely connected. As mineral particles are gradually reduced in size, their shapes and surface properties become more important in particle processing operation [24]. Anisotropic surface properties of a mineral will vary depending on the mineral particles size factor. Hence, it is noted that as the particle size vary, the different crystal planes will play a different role in determining surface properties.

Our previous researches focused on the adsorption of cationic collectors on kaolinite based on its anisotropic surface crystal structure [7,25–28]. However, the anisotropic adsorption of anionic oleate collector on crystal planes of diaspore and kaolinite crystals has not been reported. In this study, the chemisorption mechanism of the carboxylate functional group of the anionic NaOL collector on diaspore and kaolinite is presented by zeta potential measurements and FTIR Analysis. The anisotropic hydrophobicity and adsorption of oleate on the different crystal planes diaspore and kaolinite are investigated by contact angle measurements and MD simulation. This study aims to profoundly investigate the effects of particle size on diaspore and kaolinite flotation. And anisotropic adsorption of oleate on diaspore and kaolinite will be explained based on surface crystal chemistry consideration.

## 2. Materials and methods

### 2.1. Materials

Diaspore and kaolinite were obtained from Xiaoguan of Henan province (China), Xiaoyi of Shanxi province (China), respectively. The samples were hand-picked, crushed and ground in a laboratory porcelain mill. Then, the powder samples were screened to three different size fractions (0.075–0.1 mm, 0.045–0.075 mm, and 0–0.045 mm). Chemical composition analysis and X-ray diffraction (XRD) were used to study the characteristics of chemical and mineral compositions. The results showed the purity of as-preparation diaspore and kaolinite is 92% and 90%, respectively.

Sodium oleate (NaOL) of chemical pure was used as collector. HCl and NaOH were used to adjust the pH of the system. The water for all experiments was deionized water (Resistivity =  $18.3\text{M}\Omega \times \text{cm}$ ).

### 2.2. Flotation

Flotation tests were carried out in a 40 mL hitch groove flotation cell. Mineral particles prepared (2 g) were placed in a plexiglass cell, and then filled with deionized water. HCl or NaOH was added to adjust the pH. After adding the desired amount of reagents, the suspension was agitated for 3 min. 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 products.

### 2.3. Zeta-potential measurements

A suspension containing 0.1 wt.% mineral particles grounded to  $-5\ \mu\text{m}$  in an agate mortar was prepared in the 1 mM KCl solution, and conditioned by magnetic stirring for 5 min. After settling for 10 min, the supernatant of dilute fine particle suspension was taken for zeta potential measurement. The zeta-potentials were measured using a Malvern Zetasizer Nano ZS90 (England) equipped with a rectangular electrophoresis cell. The conductivity and pH of the suspension were monitored continuously during the measurement and the environmental temperature was maintained at  $25^\circ\text{C}$ .

### 2.4. FTIR measurements

Fourier transform infrared (FTIR) spectra were recorded on a Nicolet 6700 spectrometer at  $25^\circ\text{C}$  in the range from  $4000$  to  $450\text{cm}^{-1}$ . Prior to the test, the pure minerals were grounded to less than  $5\ \mu\text{m}$  in an agate mortar before being conditioned with collectors. Spectra of the solids were taken with KBr pellets.

### 2.5. Calculation of surface broken bonds

A range of surface slabs was created from the bulk unit cell of diaspore and kaolinite at its Miller indices by Surface builder module in MS. The density of broken bonds for the creation of a certain surface was calculated according to

$$D_b = N_b/A \quad (1)$$

where  $D_b$  and  $N_b$  represent the surface broken bond density and the broken bond number per unit cell on a certain surface, respectively.  $A$  is the area of the surface unit cell [29].

### 2.6. Contact angle measurements

DSA 30 from KRUSS, Inc., Germany, was used to measure the contact angles on mineral surface in  $2 \times 10^{-4}\text{M}$  reagent solution by free sessile air bubble method. A hand-picked pure single crystal was prepared by exposing only the desired crystal plane while the other surfaces were masked by epoxy resin mold. The predominant cleavage plane of diaspore and kaolinite crystals was readily identifiable. The nominal crystal plane was prepared by cutting through a proper angle using rock cutter with a diamond saw blade. Then, the desired surface was polished by  $10\ \mu\text{m}$  alumina powder, washed thoroughly with water, conditioned in the reagent solution at  $25^\circ\text{C}$  for 30 min, and subjected to the contact angle measurement. The last process was repeated for the repolishing prior to each measurement.  $\text{NaNO}_3$  (1 mM solution) was used as the background electrolyte for contact angle measurements. The pH of the solution was adjusted individually using  $\text{HNO}_3$  and NaOH. An average

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