

Nature of (001) and (00 $\bar{1}$) faces and flocculation flotation of kaolinite^①

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Abstract: Flotation mechanism of kaolinite was investigated through flotation test, SEM analysis and quantum chemical simulation calculation. It is shown that the (001) face of kaolinite easily adsorb cationic collector to exhibit hydrophobicity; the (00 $\bar{1}$) face is easily interacted with the reagent carrying the group of high electronegativity (—O—, —N—, F—) to show hydrophilicity. The cationic and anionic polyacrylamide are adsorbed onto the (001) face of kaolinite and the flocculation of kaolinite particles may take place; the (001) faces are exposed to interact with cationic collector to be rendered hydrophobicity. Thus, the macromolecules can evidently enhance the flotation of kaolinite in alkaline media.

Key words: cleavage face; flotation; modified macromolecule; flocculation; kaolinite

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1 INTRODUCTION

The diasporic bauxite resource in China is characterized by high content of Al_2O_3 and SiO_2 and low mass ratio of Al_2O_3 to SiO_2 , the ratio is usually 5 ~ 8. The diasporic bauxite with low mass ratio of Al_2O_3 to SiO_2 cannot be directly processed by Bayer's technology. The sintering or combination of sintering and Bayer process are often used to treat such diasporic bauxite, showing energy-intensive and environmental unfriendly^[1]. It is required to increase the mass ratio of Al_2O_3 to SiO_2 to above 10 by physical separation so that the Bayer's process can be applied directly^[2, 3].

In the diasporic bauxite, the valuable mineral is diasporite which accounts for about 70% of total mass. The main gangue minerals are kaolinite, pyrophyllite, illite and small amount of titanium and iron impurities. In order to effectively remove aluminosilicate minerals from bauxite, it is necessary to understand the surface properties and flotation behavior of the aluminosilicates in bauxite. Because the silicate minerals occur in the majority of cases as gangue minerals in many ore deposits and need to be depressed, there were a lot of researches on the flotation behavior of silicates^[4-6]. Fuerstenau and Fuerstenau^[7] summarized in detail the crystal chemistry, electrical double layer properties and their correlation with flotation behavior of silicates such as orthosilicates, sheet silicates, framework silicates etc.

However, in the course of reverse flotation of diasporic bauxite, it is required to float the kaolinite,

pyrophyllite and illite, and to depress the diasporite. The three aluminosilicates belong to the sheet silicates, but they exhibit different natures of cleaved surfaces. The difficulty is that these minerals all have the broken Al—O bonds on the cleaved surface in addition to having the broken Si—O bonds. These broken bonds control their surface behavior, although there are a lot of researches on the layer charge, cation-retention capacity, adsorption, hydrophilicity and hydrophobicity related to the adsorption about the aluminosilicate minerals^[8-11], there are few reports on the flotation of kaolinite, especially the flotation of the kaolinite from the bauxite deposits. Our previous works show that when a common long chain alkyl amine is used as a collector, kaolinite exhibits good floatability in acidic media and poor flotation in alkaline media. The soft kaolinite shows better floatability than hard kaolinite^[12]. The wettability and floatability of kaolinite are closely related to its crystal structure and the type and number of the broken bonds on various cleavage faces^[13]. In the present work, the flocculating activation flotation of kaolinite was further investigated in the light of flotation tests, molecular dynamics simulation and SEM analysis.

2 EXPERIMENTAL

2.1 Materials

Hand-picked kaolinite, taken from Pingdingshan, Henan province in China, was crushed and

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ground in a porcelain mill. The ≤ 0.098 mm fraction was used in flotation tests; the purity of kaolinite is above 90%. The dodecylammium acetate (DDA) of analytically pure was used as collector; HCl and NaOH were used to adjust pH value, double distilled water was used in all the tests. The modified polyacrylamides included cationic and anionic (PAM).

2.2 Flotation test

Single mineral flotation tests were carried out in a micro-flotation cell. The mineral suspension was prepared by adding 3 g minerals to 40 mL of solutions under agitation. The pH of the mineral suspension was first adjusted to a desired value by adding concentrated NaOH or HCl solutions, then the modified PAM solution was added while conditioning for 3 min. The collector solution was then added and the suspension was conditioned for 2 min without aeration, then floated for 4 min. The floated and unfloated particles were respectively collected, filtered and dried in a well-ventilated oven at 120 °C. The recovery was calculated based on solid mass distributions between the two products.

2.3 SEM analysis

Samples were examined on a scanning electron microscope (Noran Jeol model JSM-5600LV). 3 g of mineral samples were added into 40 mL of pure water, sequential addition of modifiers, the suspension was agitated for 2 min. A suspension drop with 5 mm in diameter was created on the sheet glass using a micro dropper. The sample was then air-dried at ambient temperature.

2.4 Quantum chemistry calculation

MNDO (modified neglecting differential overlap) method was employed to calculate the interaction between collector and mineral surface. All the calculation and model construction and optimization were taken on C2 software. The Mopac module was used, and calculation task was assigned to 'POTENTIAL'. The crystal structure was construct from experiment data (Bish). Gaussian 98 using function 6-31G* was employed to optimize the reagent structure before calculation.

3 RESULTS AND DISCUSSION

3.1 Nature of cleaved (001) and (00 $\bar{1}$) planes of kaolinite

During the comminution, kaolinite is cleaved at long basal faces (001) and edges (010) and (110). Because of two layer structure, there exist two (001) faces with equivalent amount and different natures, respectively defined as (001) and (00 $\bar{1}$) faces. Fig. 1 (a) shows the surface group on (001) basal face of kaolinite. It is dominated by bond of Si–O of tetra-

hedral [SiO₄]. Per cell face contains 6 high electronegativity oxygen atoms per cell face, which makes (001) face easily form H-bond with hydrogen or adsorbed positive ion. Fig. 1(b) demonstrates the surface group on (00 $\bar{1}$) basal face of kaolinite, which mainly consists of [AlO₂(OH)₄] octahedral. Each cell contains 6 low electronegativity hydrogen atoms, which form H-bond with high electronegativity groups such as O, F, and N.

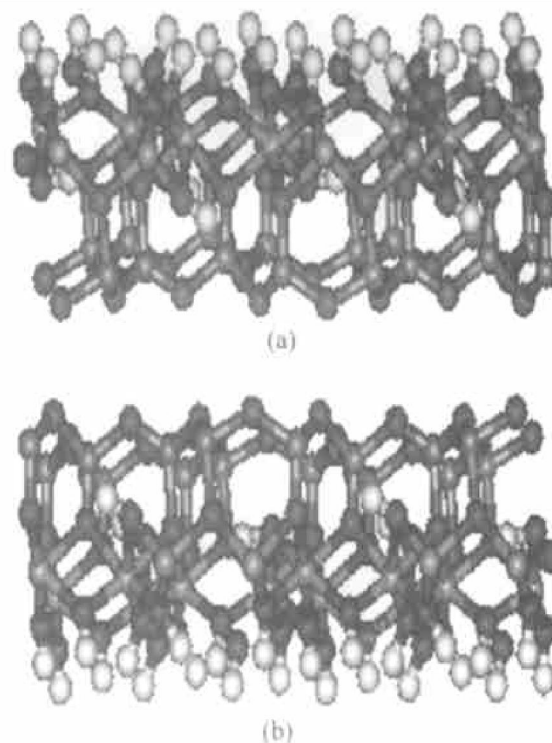


Fig. 1 Atom arrangement on kaolinite surface (a) —(001) face; (b) —(00 $\bar{1}$) face

3.2 Molecular dynamic simulation of DDA adsorption on (001) and (00 $\bar{1}$) faces

The different mechanisms of amine adsorption on (001) and (00 $\bar{1}$) faces may be due to the difference of these two faces. The molecular dynamic simulation of the adsorption of dodecylamine on (001) and (00 $\bar{1}$) faces of kaolin are conducted in terms of the models in Fig. 1. The change of total energy of DDA adsorption on kaolin, the bond distance and bond angle of Si–O bond of kaolinite surface after adsorbing DDA, were calculated. The results are shown in Fig. 2. Fig. 2 shows the energy-distance curves of DDA adsorbing on (001) and (00 $\bar{1}$) faces of kaolinite. The lower the energy is, the easier the adsorption and the more stable the adsorption state. It can be seen from Fig. 2 that when DDA molecule is close to the (00 $\bar{1}$) face, only a small energy barrier exists at 0.27 nm. The DDA molecule is easily adsorbed onto the (00 $\bar{1}$) face by overcoming the small energy barrier and the interaction energy decreases with the decrease of the distance and reaches at 0.15 nm, which is usually the minimum distance of contact equilibrium^[14, 15].

However, the total energy of interaction be-

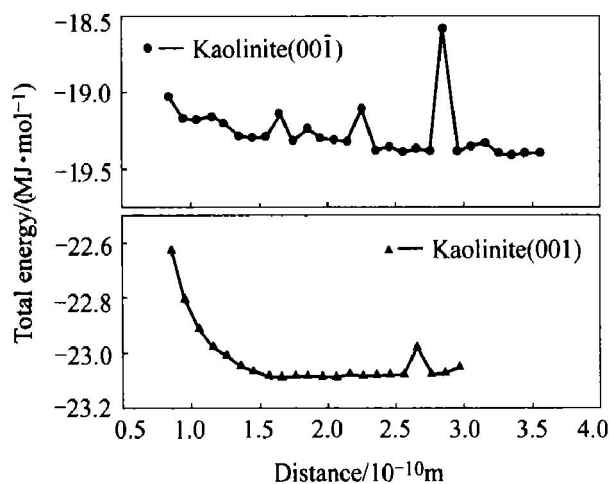


Fig. 2 Energy-distance curve of DDA molecule adsorption on kaolinite (001) face and (001) face

tween DDA and (001) face of kaolinite is irregularly changed and there exists a high energy barrier. And the total energy tends to grow up when DDA molecule closes the (001) face. It indicates the difficulty of DDA adsorption on kaolinite (001) face. Fig. 3 shows the change of bond distance of Si-O, the bond angle of Si-O-Si on kaolinite (001) face when the DDA molecule closes to the (001) face. The bond distance increases from 0.1861 nm to 0.1891 nm, bond angle increases from 105.86° to 104.9°. Based on chemical bond theory, the chemical bond is formed when the electron cloud is gathered between two atoms. For the bond of given compound, its bond distance and angle is fixed and changed only when the system is attacked by other active substance. Thus, it may be derived from Fig. 3 that the change of bond distance and bond angle of Si-O of kaolinite (001) face may result from the interaction (H-bond) between DDA molecule and surface oxygen atom. There-

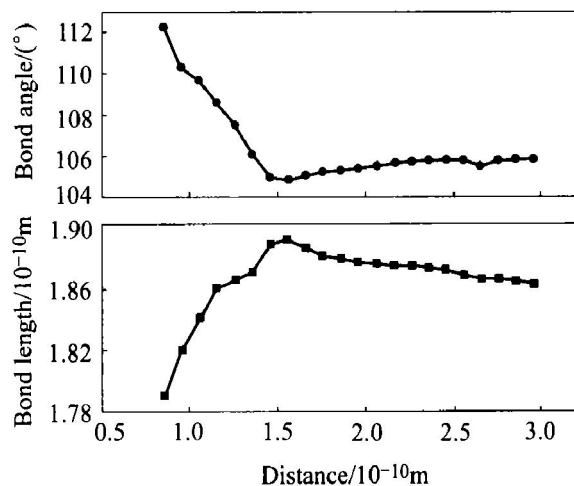


Fig. 3 Change of bond distance and bond angle of surface Si-O during adsorption of DDA on (001) face of kaolinite

fore, the flotation of kaolinite may be enhanced by increasing the amount of exposed (001) face and decreasing the amount of (001) face.

3.3 Aggregation of kaolinite through (001) face using polymers and activation flotation

In order to decrease the amount of (001) face of kaolinite particles, two modified polyacrylamide were synthesized and used to flocculate the kaolinite particles. The modified PAM with -O-, -COO- groups may form H-bond with surface hydroxyl on (001) face. Kaolinite particles may be flocculated through (001) face as shown in Fig. 3. The SEM images of the kaolinite are shown in Fig. 4, it can be seen that the kaolin particles are dispersed well in the absence of modified PAM, there are gaps and holes among particles. In the presence of modified PAM, the bigger flocculates are observed, there are few gaps and holes among particles. In this case, (001) faces become the

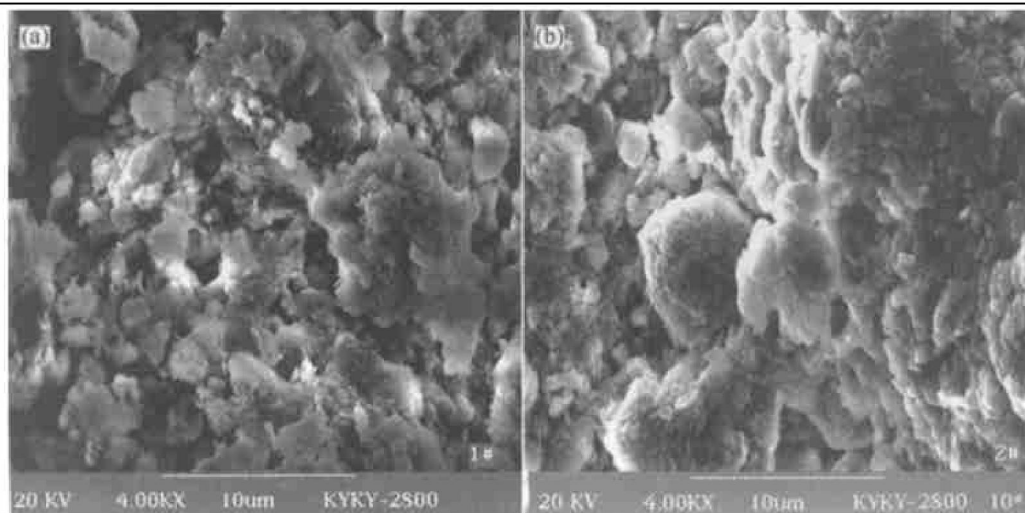


Fig. 4 SEM images of kaolinite treated in different conditions
(a) —Without modified polyacrylamide; (b) —With modified polyacrylamide

dominant to determine the surface wettability and floatability. The (001) faces are easily interacted with cation collector to become hydrophobicity, result in activation flotation of kaolin. Fig. 5 shows the cation flotation results of kaolin in the presence and absence of modified PAM. In the absence of modified PAM, kaolin exhibits better floatability only in acidic media, and very poor floatability in neutral and alkaline media. By addition of modified PAM, the flotation of kaolin is greatly enhanced in wider pH range, especially at alkaline range. The recovery of kaolinite between pH 6 ~ 11 is increased from < 20% to > 80%. The model of flocculating activating flotation of kaolin can be schematically shown in Fig. 6.

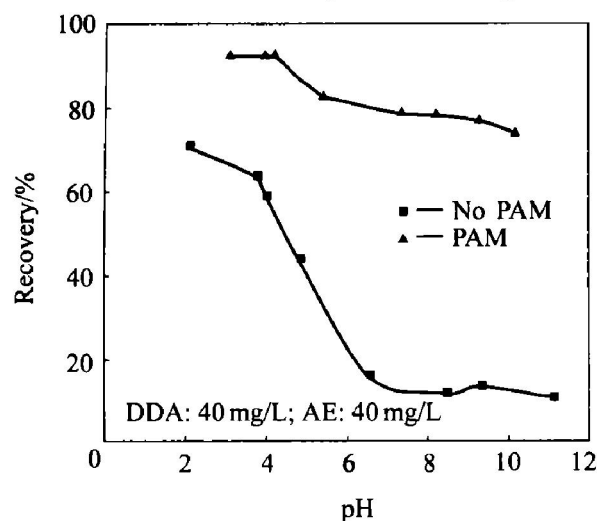


Fig. 5 Flotation recovery of kaolinite as function of pH with dodecylamine as collector

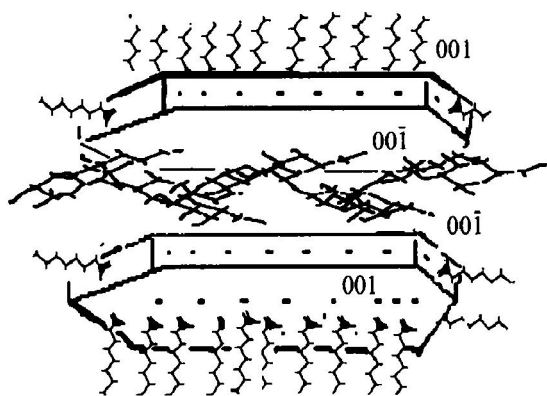


Fig. 6 Schematic model of activation flotation of kaolinite by macromolecular flocculation

4 CONCLUSIONS

Kaolin usually be cleaved to produce (001), (00 $\bar{1}$) basal faces and edge faces, (001) face is the active surface adsorbing cation collector, (00 $\bar{1}$) face is not easily interacted with cationic collector. The modified PAM is selectively adsorbed onto

(00 $\bar{1}$) face to make kaolin particles be flocculated through increasing the amount of exposed (001) faces, and decreasing the amount of (00 $\bar{1}$) faces become hydrophobicity by adsorbing cation collector. The flotation of kaolin is activated in wide pH range by addition of modified PAM.

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