

A THEORETICAL STUDY OF THE EFFECT OF CARBOXYL HYDROXAMIC ACID ON THE FLOTATION BEHAVIOR OF DIASPORE AND ALUMINOSILICATE MINERALS

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Abstract—The collector for separating diasporic bauxite serves as a type of flotation reagent by adsorbing selectively on diaspore to make it hydrophobic enough to separate it from the aluminosilicates. Although the flotation process is considered economical in the desilication of Chinese diasporic bauxite, the existing collectors fail to separate these ores because of their poor adsorption selectivity over other minerals. The present study was an attempt to seek a collector for selective flotation of diaspore over aluminosilicates. A novel carboxyl hydroxamic acid compound, 2,2-bis(hydroxycarbamoyl) decanoic acid (BHDA), was designed and synthesized, and the flotation behavior of diaspore, kaolinite, and illite was investigated by flotation tests with BHDA. The interactions between the BHDA and the minerals were also explored by Fourier-transform infrared spectroscopy (FTIR), zeta-potential measurement, and density functional theory (DFT) calculation. Using BHDA as the collector, the pulp pH value affected the floatability of diaspore significantly while the floatability of kaolinite or illite was unaffected or only slightly affected. The dosage of BHDA had little effect on the floatability of the three minerals. The greatest difference in floatability between diaspore and aluminosilicates occurred at mid-range pulp pH (7). Large shifts in characteristic absorption peaks and new absorption peaks were observed for BHDA-treated diaspore but were absent from BHDA-treated aluminosilicates. The change in the negative zeta potential of diaspore was also greater than those of aluminosilicates in the presence of BHDA. The O atoms in the carboxyl and hydroxycarbamoyl of BHDA have highly negative charges, and favorable stereo conditions existed to form five- or six-membered rings, resulting in their coordination with the Al atoms of diaspore, leading to chemisorption in chelate rings; the adsorption of BHDA on kaolinite or illite, on the other hand, was mainly physical in nature. The BHDA was, therefore, highly selective in the flotation between diaspore and aluminosilicates and possibly suitable for the separation of diasporic bauxite.

Key Words—Aluminosilicate Minerals, Bauxite, Collector, DFT Calculation, Diaspore, Synthesis.

INTRODUCTION

Bauxite resources are abundant in China but >98% of them are diasporic bauxite. The gangue minerals in diasporic bauxite resources are mainly kaolinite, illite, and pyrophyllite, balanced by a small amount of Ti and Fe impurities (Xu *et al.*, 2004). The diasporic bauxite has a high grade of aluminum and silicon, but a low mass ratio of Al₂O₃ to SiO₂ (A/S) (Liu and Du, 2000; Lu *et al.*, 2002; Chen and Zhao, 2000). The diasporic bauxite, therefore, cannot be used directly by the Bayer process (Feng *et al.*, 2004). Complex workflows such as a sintering process and a combined (Bayer and sintering) process have been developed and applied to produce alumina from diasporic bauxite ore with A/S < 8 in China (Cheng and Yan, 1997; Chen and Peng, 1997). As the aforementioned methods do not compare well with the Bayer process, a new flotation-Bayer process was developed to produce alumina (Huang *et al.*, 1999), where the A/S can be increased to ~8–10 from ~3–5 in

order to obtain Bayer raw materials (Fang and Huang, 2000; Liu and Liu, 2005).

Flotation desilication has been investigated extensively since the beginning of the 1990s. Great progress has been made in the theory and practice for the flotation separation between diaspore and aluminosilicates, especially in the fields of mineral crystal structure, surface properties, the flotation mechanism of the reagent, flotation-solution chemistry, and flotation techniques (Zhang *et al.*, 2006; Yin *et al.*, 2001; Chen *et al.*, 2006; Huang *et al.*, 2006; Ling *et al.*, 2006). The flotation reagents, including collector, inhibitor, modifier, *etc.*, are among the most critical elements of the flotation-separation process. For the flotation of diaspore, traditional collectors and their mixtures have been reported widely (Wang *et al.*, 2003; Hu *et al.*, 2004, 2005). A number of new collectors have been studied in the flotation of aluminosilicate minerals (Yu *et al.*, 2009; Zhao and Chen, 2009; Xia *et al.*, 2009; Li and Cheng, 2008), none of which is selective enough to separate diaspore from aluminosilicate minerals.

Two important issues need to be addressed for the rational design of flotation reagents, namely the selection of appropriate functional groups which can interact

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specifically with the surface of the target mineral and the design of an appropriate molecular conformation which is favorable to its function (Padip *et al.*, 2002). Pradip (1994) suggested that reagents with two or more functional groups appropriately spaced enhance their stereochemical compatibility, and make them likely to be more selective than conventional monofunctional reagents. In other words, the more functional groups a reagent molecule has, the greater its selectivity. In previous work (Jiang *et al.*, 2001) a collector, COBA (a monocarboxyl monohydroxamic acid), was found to float diaspore well and the collecting performance on diaspore depended heavily on the coexistence of the carboxyl and hydroxycarbamoyl groups in the COBA molecular structure. To develop this type of collector, with improved selectivity, another multifunctional compound was designed for detailed investigation. A novel collector, 2,2-bis(hydroxycarbamoyl)decanoic acid (BHDA), was designed and synthesized, and then its flotation performance with respect to diaspore, kaolinite, and illite was investigated. As fundamental studies of the reagent–mineral interaction form the basis for the design of a collector, the interaction mechanism between BHDA and the minerals was studied using FTIR spectroscopy and zeta-potential measurements. In order

to illustrate the interaction mechanism, DFT calculation was applied to study the molecular properties of BHDA. The results of both the flotation tests and investigations of the mechanism indicated that the BHDA was a highly selective collector for the flotation between diaspore and aluminosilicate minerals.

METHODS AND MATERIALS

Synthesis

The detailed procedure that was designed for synthesizing BHDA (Figure 1) is as follows:

Tricarbo methoxymethane. Dry xylene (100 mL) and sodium (3.25 g) were placed in a 250 mL three-necked flask with an upright condenser, a pressure-equalizing dropping funnel, and a mercury-sealed stirrer. The flask was heated to $\sim 90^{\circ}\text{C}$ in an oil bath until the sodium melted and then the mixture was stirred until the sodium was broken up into fine (~ 1 mm in diameter) globules. Methyl malonate (17.2 g) was added over a period of 5 to 10 min. The mixture was stirred while cooling and, when the temperature reached $\sim 65^{\circ}\text{C}$, methyl chloroformate (12 mL) was added over a period of 5–10 min. The mixture obtained was warmed to boiling point ($\sim 130^{\circ}\text{C}$)

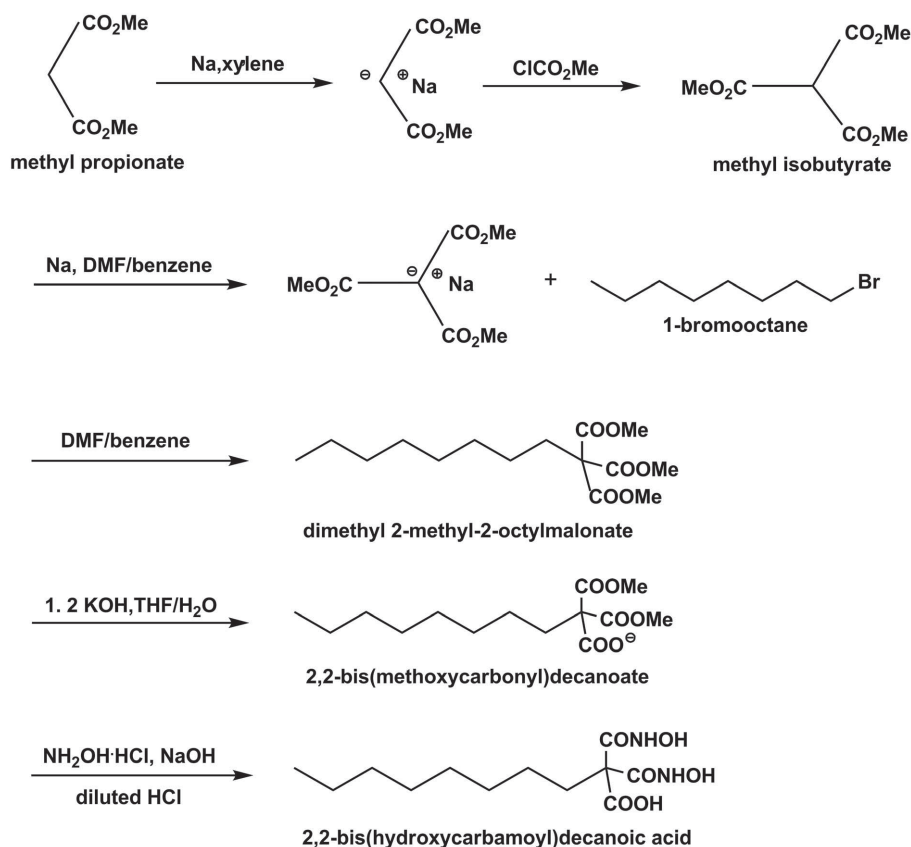


Figure 1. Means of synthesizing BHDA.

over a period of 20 min and then stirred at that temperature for 5 h. The reaction product was cooled to room temperature and 100 mL of water was added. The xylene layer was separated (after adding water, the mixture obtained was left to stand for several minutes after which the xylene layer and the water layer separated; the xylene layer was removed immediately), washed with water, dried over calcium chloride, filtered at atmospheric pressure through a filter paper (pore size of 10–15 μm), and distilled under reduced pressure (the original pressure was ~ 20 kPa and the new pressure ~ 13.3 kPa; the pressures were achieved by mechanical vacuum pump). After the solvent was removed, tricarbomethoxymethane was distilled at 128–142°/2.4 kPa. The yield of crude product was 21 g.

Tricarbomethoxynonane. A solvent consisting of dry (H_2O -free) dimethylformamide/benzene mixture (1:1) (20 mL) and sodium (0.58 g) were placed in a 250 mL three-necked flask with an upright condenser, a pressure-equalized dropping funnel, and a mercury-sealed stirrer. The flask was heated in an oil bath until the sodium melted, and then the mixture was stirred until the sodium was broken up into fine globules (~ 1 mm in diameter). Tricarbomethoxymethane (10 g) was added and stirred for 15 min, and then 1-bromooctane (11 mL) was added dropwise at 90°C and stirred for 4 h. The reaction product was cooled and toluene (100 mL) was added. The solution obtained was washed with saturated NaHCO_3 (4×100 mL), dried over anhydrous MgSO_4 , concentrated *in vacuo*, and dried in a high-vacuum oven at 40°C overnight to produce the desired product with a yield of 95%.

2,2-Bis(methoxycarbonyl)decanoic acid. Tetrahydrofuran (20 mL) and tricarbomethoxynonane (10 g) were placed in a 100 mL flask with magnetic stirrer using a pressure-equalized dropping funnel. A solution prepared from KOH (2.23 g) in water (10 mL) was added slowly at room temperature and stirred for 1.5 h. The reaction product was washed with water and acidified slowly to pH 3.5–4 (by adding 1 mol/L HCl). After the extra water was removed, the mixture was dried by evaporation at reduced pressure (~ 13.3 kPa) to produce the desired product with a yield of 90%.

2,2-Bis(hydroxycarbamoyl)decanoic acid (BHDA). Hydroxylamine hydrochloride (2.09 g) dissolved in methanol (10 mL) and sodium hydroxide (1.2 g) dissolved in methanol (15 mL) were mixed in a 100 mL flask submerged in an ice-salt bath under a layer of nitrogen. The precipitation of sodium chloride was allowed to occur for 5 min, and then the salt was removed by filtration. 2,2-Bis(methoxycarbonyl)decanoic acid (2.88 g) was added to the free hydroxylamine and the solution was stirred for 4 h. A white crystal which initially precipitated was obtained by filtration. After washing with methanol and drying in under vacuum at 45°C, the crystal was dissolved in 10 mL of ice-cold water. The solution obtained was acidified slowly with 1 mol/L hydrochloric acid and dried by evaporation at reduced pressure (~ 13.3 kPa) to produce the final product as paste.

The product synthesized was characterized using a FTIR-740 infrared spectrometer (Nicolet Instrument Corporation, Madison, Wisconsin, USA) and elemental analyzer (Elementar Analysensysteme GmbH, Hanau, Germany), and the results (Table 1) confirmed that the structure of the compound synthesized corresponded with that of the compound designed.

Materials and reagents

Diaspore, kaolinite, and illite were obtained from Henan province, China. All the mineral samples were hand-picked, ground in a porcelain mill, and passed through a 200 mesh sieve to obtain particles of <74 μm . The purity of the minerals was identified as being at least 90% by chemical content analysis for Al_2O_3 , SiO_2 , *etc.* and by X-ray diffraction (XRD). The chemical analyses of the three samples were as follows: diaspore – 80.32% Al_2O_3 , 0.71% SiO_2 , 0.04% K_2O ; kaolinite – 36.83% Al_2O_3 , 40.60% SiO_2 , 0.06% K_2O ; and illite – 34.81% Al_2O_3 , 42.53% SiO_2 , 7.61% K_2O . The pH modifiers employed were of analytical grade hydrochloric acid or sodium hydroxide, and distilled water was used for all parts of the tests.

Flotation test

Flotation tests were conducted in an XFG-35 flotation machine made by Liyuan Mining & Metallurgical Equipment Co., Ltd., Nanchang, Jiangxi Province,

Table 1. Elemental and FTIR analysis of BHDA.

Compound	Formula	Elemental analysis (%)						Characteristic FTIR bands cm^{-1}
		Calculated			Found			
		C	H	N	C	H	N	
BHDA	$\text{C}_{12}\text{H}_{24}\text{O}_6\text{N}_2$	49.32	8.22	9.59	49.33	8.25	9.49	3224(OH), 2922($-\text{CH}_2$), 1736(C=O in COOH), 1666(C=O in CONHOH), 1593(C–N)

China. A 35 mL flotation cell was used and the impeller speed was fixed at 1650 revolutions min^{-1} . Mineral samples (2 g) and distilled water (30 mL) were placed in the cell and stirred for 5 min. The pH of the mineral suspension was adjusted to the desired value by adding aqueous hydrochloric acid solution or sodium hydroxide solution. After adding the desired amount of collector, the suspension was agitated for 2 min and then the flotation was carried out for 4 min. The floated and unfloated fraction in the suspension were collected separately, filtered, and dried in a well ventilated oven at 105°C. The flotation recovery ratio was calculated based on the mass ratio of the floated fraction to the sum of the floated and unfloated fraction.

FTIR spectroscopy

The infrared spectra of samples were recorded with the aforementioned FTIR-740 infrared spectrophotometer using the KBr technique. The mineral samples used for this purpose were ground in an agate mortar to $<5 \mu\text{m}$. To obtain the samples tested, 50 mg of the mineral samples ($<5 \mu\text{m}$) was added to 30 mL of aqueous solution with or without 2×10^{-4} mol/L BHDA at pH 7 and 25°C, and the mixtures were stirred for 30 min, filtered, and dried for 24 h in a vacuum oven at $<35^\circ\text{C}$. A pellet was prepared from a mixture of ~ 5 mg of the sample and ~ 200 mg of KBr; the IR spectra were recorded immediately over the range 400 to 4000 cm^{-1} (at a resolution of 4 cm^{-1} , at high sensitivity, and with 16 scans taken of each sample).

Zeta-potential measurements

The zeta potential of minerals was measured with a Zetaplus zeta potential analyzer (Brookhaven Instruments Corporation, Holtsville, New York, USA), and the minerals tested were ground to $<5 \mu\text{m}$ (determined by the zeta potential analyzer) in an agate mortar. The mineral suspension was prepared to contain 0.01% (mass fraction) solid content in distilled water. The suspension pH was measured at the end of agitation with a PHS-3C pH meter (Shanghai Rex Instrument Co., Ltd., Shanghai, China). KNO_3 solution of 1×10^{-3} mol/L was used as the supporting electrolyte. The agitated suspension was transferred to the square sample vessel and the zeta potential was then recorded. Three independent suspensions prepared under the same conditions were used to obtain the average value of the zeta potential, and the measurement error was within ± 0.5 mV.

DFT calculation

The DFT calculations were performed using the UB3LYP/6-31+G(d) (Becke, 1993) level in the *Gaussian 03W* program package (Frisch *et al.*, 2003). The harmonic vibrational frequencies were calculated at the same level of theory in order to identify the local minima and to estimate the corresponding zero-point vibrational energy. Atomic-charge values and frontier orbitals,

namely the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), were employed to describe the reactivity of the molecules.

RESULTS AND DISCUSSION

Flotation behavior of diaspore and aluminosilicates with BHDA

The effects of pH value on the floatability of diaspore, kaolinite, or illite using BHDA as collector (Figure 2) revealed that the flotation recovery of diaspore increased and then decreased with increase in the pulp pH value, while the recoveries of kaolinite and illite changed little and were very small in the pH range of ~ 3 –11. The maximum recovery of diaspore was $>95\%$ at pH 7, where the recovery of kaolinite or illite was $<25\%$.

The influences of BHDA concentration on the flotation recovery of diaspore, kaolinite, and illite (Figure 3) indicated that the recovery of diaspore increases with increased dosage of BHDA at pH 7, while the recovery ratio of kaolinite and illite remained small throughout the tested range and became immune to the dosage change when the concentration of BHDA was $>6 \times 10^{-4}$ mol/L. When the flotation recovery of diaspore was $>99\%$, the maximum recoveries of the two aluminosilicates was $<25\%$.

The flotation tests using BHDA as the collector indicated that the pH value of the pulp significantly affected the floatability of diaspore while it had little or no effect on that of kaolinite or illite (Figure 2); the dosage of BHDA had only a small effect on the floatability of all three minerals (Figure 3). Under the same experimental conditions, the flotation recovery ratio of diaspore was considerably greater than that of kaolinite or illite. The separation of diaspore from aluminosilicate minerals seems more feasible using BHDA as the collector.

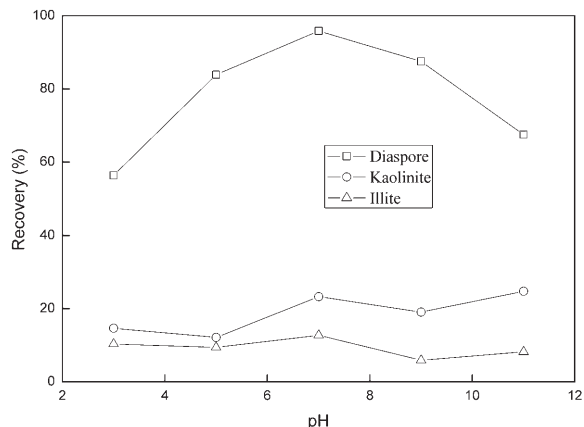


Figure 2. The flotation recoveries of three minerals as a function of pH using 2×10^{-4} mol/L BHDA as the collector.

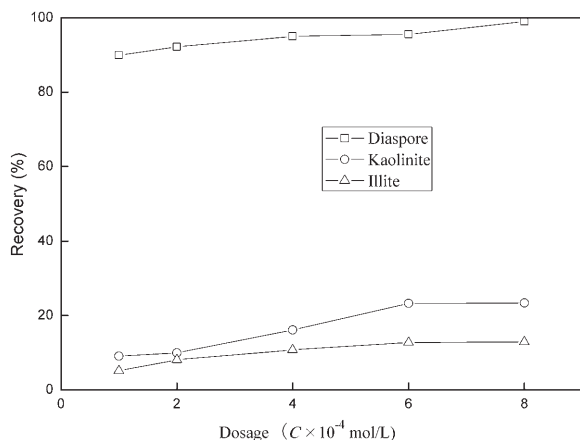


Figure 3. Flotation recoveries of the minerals as a function of BHDA dosage at pH 7.

Analysis of FTIR spectra of BHDA adsorbed on minerals

The FTIR spectra of diaspore, kaolinite, and illite (before treatment with BHDA) at pH 7 (Figure 4a–c) were similar to those reported previously (Peng and Liu, 1982; Wen, 1989). The aluminosilicate minerals have characteristic O–H vibrations at 3620 cm^{-1} , 3659 cm^{-1} , 3670 cm^{-1} , and 3696 cm^{-1} for kaolinite (Figure 4b), and at 3631 cm^{-1} for illite (Figure 4c). The locations of these

absorption peaks are usually sensitive to the interaction of organic molecules, as demonstrated by Elbokl and Detellier (2006), who, using IR spectroscopy, reported the intercalation of polystyrene into the interlamellar spaces of kaolinite.

The FTIR spectra of diaspore treated and untreated with 2.0×10^{-4} mol/L BHDA at pH 7 (Figure 4a) revealed that the stretching-vibration peak of OH at 2924 cm^{-1} shifted to 2917 cm^{-1} ; the inside and outside bending vibrational mode of OH at 2118 cm^{-1} and 1985 cm^{-1} shifted to 2116 and 1983 cm^{-1} , respectively; the inside and outside bending vibration of OH at 962 cm^{-1} and 1066 cm^{-1} shifted to 960 cm^{-1} and 1070 cm^{-1} , respectively; the stretching-vibration peak of Al–O at 746 cm^{-1} shifted to 748 cm^{-1} . Such small shifts of these absorption peaks (other than the stretching-vibration peak of OH) are insufficient to confirm that BHDA was chemisorbed on diaspore. The absorption peak of CH was not observed in the spectra of diaspore treated with BHDA due to its overlapping with the stretching vibration peak of OH at 2917 cm^{-1} of diaspore, while absorption peaks of NH of –CONHOH at 3422 cm^{-1} and of C=O of –COOH at 1726 cm^{-1} in BHDA were observed. Comparison of the spectra of the BHDA-treated and untreated diaspore revealed that the absorption peak of C=O presents a large shift from 1736 cm^{-1} to 1726 cm^{-1} while the absorption peak of NH presented quite a small shift, indicating that NH did not react with diaspore while

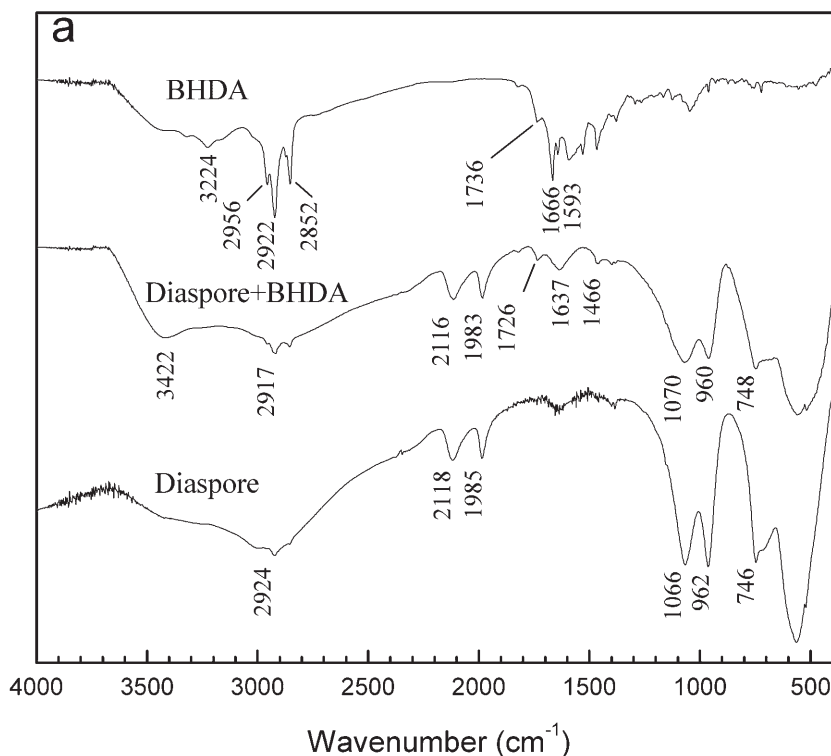
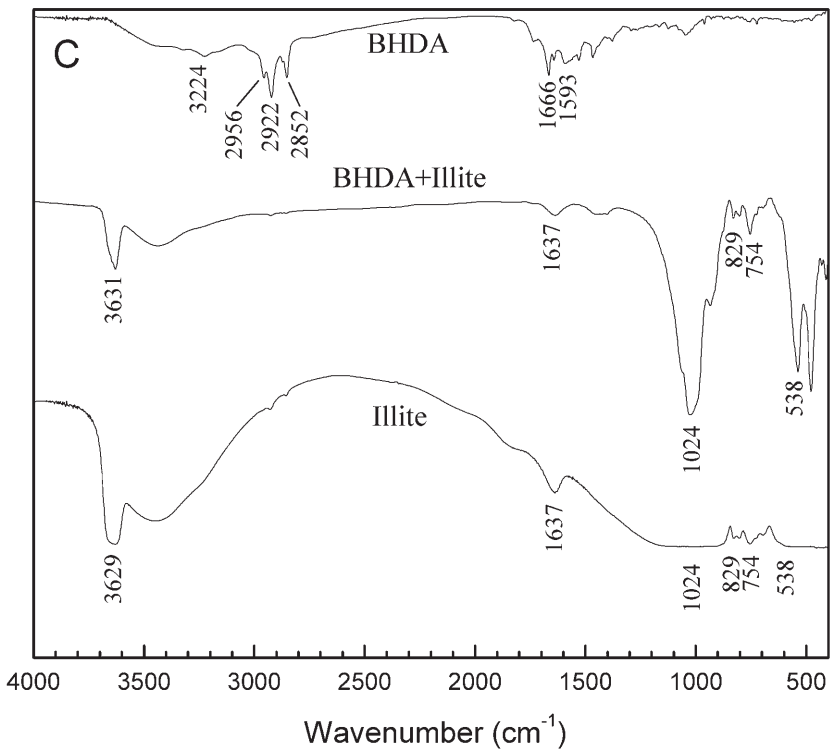
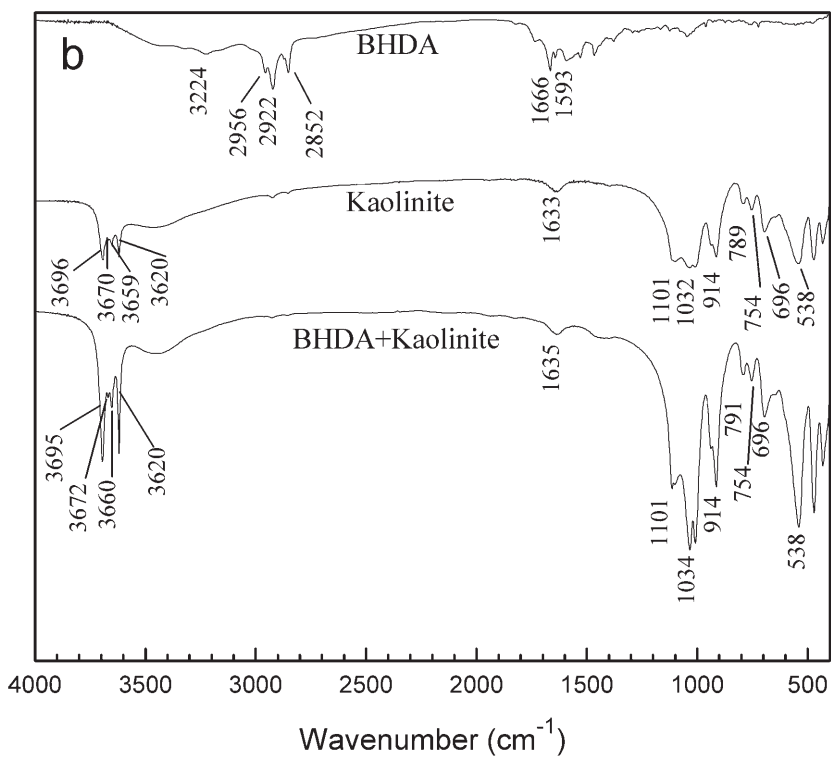


Figure 4 (*this and facing page*). FTIR spectra of the three minerals untreated and treated with 2.0×10^{-4} mol/L BHDA at pH 7.

C=O in -COOH did. Two new absorption peaks occurred at 1637 cm^{-1} and 1466 cm^{-1} in the spectra of diaspore treated with BHDA. The shifts of these absorption peaks

and the occurrence of new absorption peaks indicate that the interaction between BHDA and diaspore is chemical adsorption.



The FTIR spectra of kaolinite not treated with BHDA (Figure 4b) revealed a weak absorption peak at 1633 cm^{-1} attributed to the bending mode of H–O–H; the O–H stretching region of kaolinite is characterized by peaks at 3620 cm^{-1} , 3659 cm^{-1} , 3670 cm^{-1} , and 3696 cm^{-1} ; the Si–O stretching region is characterized by peaks at 1101 cm^{-1} and 1032 cm^{-1} ; the band at 914 cm^{-1} is due to the AlAl–OH deformation; and the bands at 789 cm^{-1} and 754 cm^{-1} are attributed to vibration of Si–O–Si and Al–O–Si, respectively. Comparison of the spectra of the BHDA-treated and untreated kaolinite revealed that the shifts of characteristic absorption peaks are very small and no new absorption peak was found and so adsorption of BHDA on the kaolinite surface may well be physical adsorption.

The FTIR spectra of illite not treated with BHDA (Figure 4c) revealed a band centered at 3629 cm^{-1} which is mainly due to the structural inner OH stretching modes of the octahedral sheet of the layer and 1637 cm^{-1} which is attributed to the HOH deformation of adsorbed free water in illite; the peak at 1024 cm^{-1} represents the stretching vibration of Si–O; the band at 829 cm^{-1} is due to Al–Mg–OH deformation and the one at 754 cm^{-1} derives from the vibration Al–O–Si, respectively. Comparison of the spectra of the untreated and BHDA-treated illite revealed that only the peak at 3629 cm^{-1} shifted slightly. Similar to kaolinite, the shift of characteristic absorption peaks was very small and no new absorption peak was found in the spectra of illite treated with BHDA. Again, the suggestion is that the adsorption of BHDA on the illite surface was physical adsorption.

Electrokinetic behavior of minerals in the presence and absence of BHDA

Electrokinetic phenomena of mineral suspensions were studied to understand better the interactions

between BHDA and the minerals. The zeta potentials of minerals where no BHDA was present (Figure 5) revealed that the three minerals show similar zeta potential response to the change of the suspension pH value. The isoelectric point (IEP) of diaspore, kaolinite, and illite where no BHDA was present is 6.0, 3.6, and 3.0, respectively. When $2.0 \times 10^{-4}\text{ mol/L}$ BHDA was introduced into the pulp, the zeta potentials of diaspore (Figure 5) shifted rapidly to negative values in the pH range 5–9 while those of kaolinite and illite changed little under the same conditions. On the contrary, at lower pH ($\text{pH} < 3$) or higher pH ($\text{pH} > 10$), the introduction of BHDA had only a small effect on the zeta potential of diaspore. This phenomenon may involve two crucial factors of zeta potential, *i.e.* the difference in the composition of the mineral/water interface and BHDA under different pH values and the amounts of broken Al–O bonds on the cleavage planes of minerals.

The zeta potential of diaspore is derived from the broken Al–O bonds followed by adsorption of water and deprotonation. The possible composition in the diaspore/water interface, without BHDA, at different pH (Figure 6a), suggested by Liu *et al.* (2007), indicated that the compositions were mainly A and B species at $\text{pH} < 5.5$; B, C, and D species at $5.5 < \text{pH} < 8.5$; and D and F species at $\text{pH} > 8.5$. The dissociation constant of BHDA suggests that BHDA under different pH values (Figure 6b) is mainly H_3L species at $\text{pH} < 4$, H_2L^- species at $4 < \text{pH} < 8.5$, HL^{2-} species at $8.5 < \text{pH} < 10.5$, and L^{3-} species at $\text{pH} > 10.5$. When BHDA was introduced into the pulp in the pH range of 5–9, anionic H_2L^- and HL^{2-} , as the main species of BHDA, replaced the H_2O and OH^- groups of the B, C, and D species in the diaspore/water interface, resulting in a significant shift to the negative zeta-potential region. However, at lower pH ($\text{pH} < 3$), H_3L as the main species of BHDA

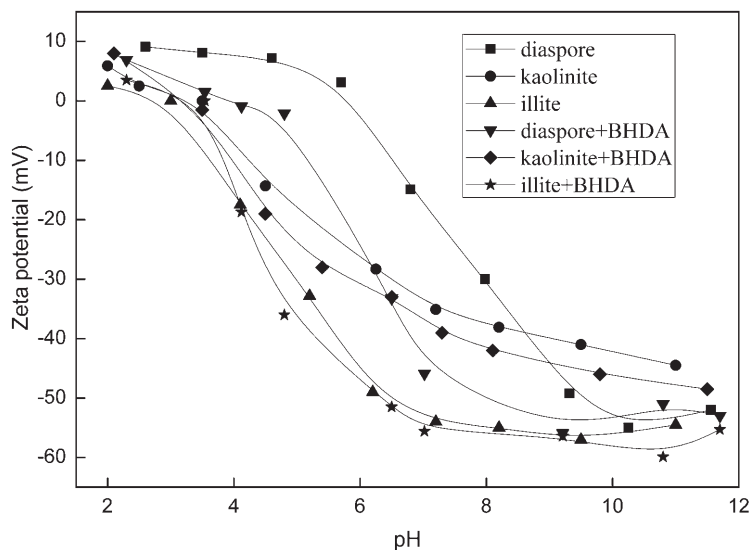


Figure 5. Relationship between zeta potential of minerals and pH with and without BHDA as a collector.

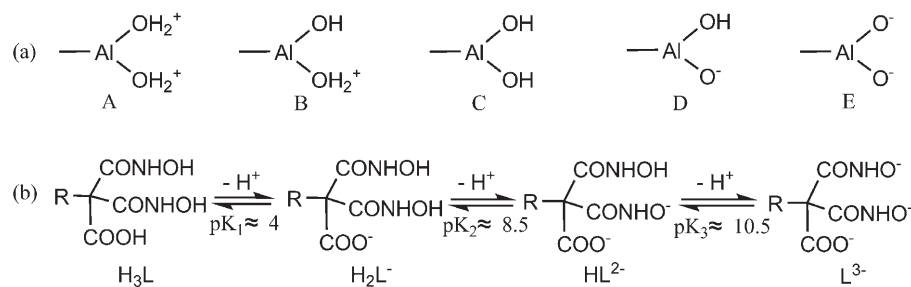


Figure 6. Possible composition under different pH values: (a) diaspore/water interface – A and B at $\text{pH} < 5.5$; B, C, and D at $5.5 < \text{pH} < 8.5$; D and E at $\text{pH} > 8.5$; and (b) BHDA aqueous solution – H_3L at $\text{pH} < 4$; H_2L^- at $4 < \text{pH} < 8.5$; HL^{2-} at $8.5 < \text{pH} < 10.5$; L^{3-} at $\text{pH} > 10.5$.

substituted for the H_2O group of the A species in diaspore/water interface, bringing little change to the zeta-potential; at higher pH ($\text{pH} > 10$), HL^{2-} (including a small quantity of L^{3-}) as the main species of BHDA took the place of the O^{2-} group of E species in the diaspore/water interface, only slightly affecting the zeta potential. These may be the reasons why BHDA affects the zeta potential of diaspore in the pH range 5–9 more than that at very low or very high pH values. According to the interactions between BHDA and diaspore mentioned above, BHDA should float diaspore strongly throughout the whole pH range. In fact, when $\text{pH} < 3$ or $\text{pH} > 10$, the increase in the number of easily hydrated A or E species in the diaspore surface will improve its hydrophilicity and some of the BHDA will be decomposed by hydrolysis reaction, resulting in a decrease in its flotation recovery.

By comparison, more broken Al–O bonds are found on the cleavage planes of diaspore than on those of aluminosilicates. The greater the number of Al sites exposed on the mineral surface, the more BHDA molecules that interact with the mineral. As a result, BHDA makes the zeta potential of diaspore shift rapidly to the negative value while those of kaolinite and illite change little. Kaolinite and illite are layer-structured aluminosilicates. Many $\text{Si}-\text{O}^-$ or $\text{Si}-\text{OH}$ species and few $\text{Al}-\text{OH}_2^+$, $\text{Al}-\text{OH}$, or $\text{Al}-\text{O}^-$ species are exposed on the surfaces of aluminosilicate minerals at pH 2–12 (Liu, *et al.*, 2007), where BHDA should be adsorbed mainly by $\text{Si}-\text{O}^- \cdots \text{H}-\text{O}$, $\text{Si}-\text{O}^- \cdots \text{H}-\text{N}$, $\text{Si}-\text{OH} \cdots \text{O}$, $\text{Al}-\text{OH}_2^+ \cdots \text{O}$, and $\text{Al}-\text{O}^- \cdots \text{H}-\text{N}$ hydrogen bonds. Accordingly, BHDA cannot be adsorbed efficiently on the surfaces of aluminosilicate minerals due to the weak hydrogen bonds, giving rise to the slight negative shift and the small flotation recovery.

DFT calculation results

On the basis of the optimized geometry of BHDA (Figure 7), the DFT calculation of BHDA was conducted. The HOMO and LUMO are commonly responsible for the reactivity of the molecule and are sometimes referred to collectively as frontier orbitals for they are molecular orbitals at extreme energy and are

involved in most chemical reactions. The HOMO is generally associated with the molecule's capacity for donating electrons while the LUMO reflects the molecule's ability to accept electrons. The HOMO or LUMO energy is an important factor but not the most critical in terms of the nucleophilic or electrophilic behavior of the molecule. In addition, the electron density is another fundamental concept which has been cited frequently to help understand the chemical reactivity of a molecule as well as explain the phenomena of nucleophilic and electrophilic attack on a molecular system.

The HOMO drawing (Figure 8), obtained using *GaussView* 3.0 (GaussView, 2003), revealed that the HOMO consists mainly of the atomic orbitals of O26, O30, O32, O35, O38, N27, and N36. The two hydroxycarbonyl groups donate more to the HOMO than the carboxyl group, suggesting that the hydroxycarbonyl groups should be more active than the carboxyl group in the BHDA molecule.

The LUMO consists mainly of the atomic orbitals of O, N, and C atoms (Figure 9). A large delocalized orbit can be found in the common area, which is apt to accept 2p-orbital electrons of Al at the mineral surface to form a feedback π -bond. This feedback bond, as one of the interactions between BHDA and diaspore, plays an important role in the formation of a strong adsorption.

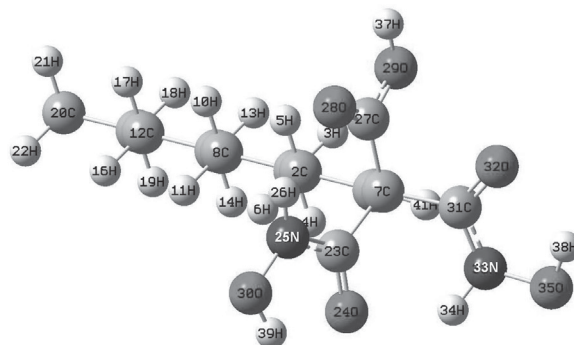


Figure 7. The optimized geometry of BHDA at B3LYP/6-31+G(d) level.

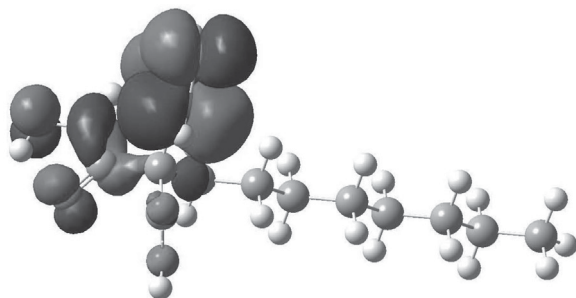


Figure 8. The HOMO for the BHDA, isovalue = 0.02.

This may be another reason to interpret the difference in collecting performance of BHDA on the three minerals (Figure 2).

The geometrical parameters of BHDA (Table 2) showed that the bond distances in the N27-containing hydroxycarbamoyl group are much shorter than those in the N36-containing hydroxycarbamoyl group. The dihedral angles are 4.8° for $\tau(\text{O32-N27-C25-O26})$ and -177.0° for $\tau(\text{O32-N27-C25-C8})$ in the N27-containing hydroxycarbamoyl group, while those of the N36-containing hydroxycarbamoyl group are 10.3° for $\tau(\text{O38-N36-C34-C35})$ and -172.1° for $\tau(\text{O38-N36-C34-C8})$. These imply that O, C=O, and N in the N27-containing hydroxycarbamoyl group lie almost in the same plane, where the orbitals can be delocalized sufficiently to produce a better overlap and a stronger electron fluidity than the N36-containing hydroxycarbamoyl group. Perhaps it is this favorable delocalization that wins more participation for the N27-containing hydroxycarbamoyl group in the formation of the HOMO.

All six O atoms in the BHDA molecule contain lone pair electrons, three of which are in the C=O groups and the others are in -OH conjugated with the bond N-C=O. All these O atoms can donate electrons to the empty orbital, which has been confirmed by the second-order perturbative estimates of donor-acceptor interactions of the lone-pair atoms on the Natural Bond Orbital (NBO) basis (Table 3). The O atoms and N atoms which have lone electron pairs donate electrons readily to other empty orbitals. As the electronegativity of N is less than that of O, the electrons of N atoms would flow toward O

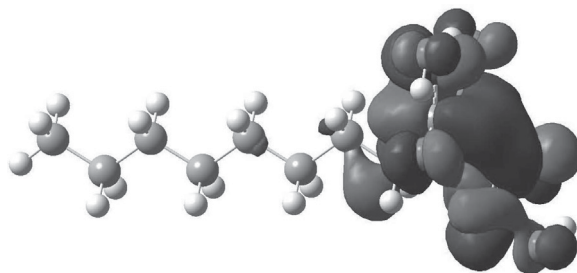


Figure 9. The LUMO for the BHDA, isovalue = 0.002.

atoms in the delocalization process, with the result that O atoms exhibit greater natural charge (Table 2) and reactivity. A reasonable prediction, therefore, is that the HOMO can donate the reactive frontier electrons of the O atoms in BHDA to the Al cations on the mineral surfaces to form a strong chemical bond.

In the geometric structure of BHDA, the two O atoms in the -C(O)NHOH groups are ~4–5 atoms apart, appropriate to form the five- or six-membered ring when bonded to the Al atom on the mineral surface. The DFT calculation results of the BHDA molecule showed that -C(O)NHOH is more active than -COOH and much more likely to donate electrons to the empty p-orbital of the Al atom. Accordingly, the interaction model of BHDA and diaspore can be deduced as follows: the O atoms in the BHDA molecule bond to the Al atom on the diaspore surface to form a chelate ring during which the hydroxycarbamoyl groups play a predominant role while the carboxylic group plays a subsidiary one which can enhance the collecting capacity of the BHDA molecule.

The crystal structure of diaspore [$\alpha\text{-AlO}(\text{OH})$] consists of hexagonal close-packed oxygen sheets with Al atoms filling two-thirds of the octahedral sites (Newman, 1987). Each occupied octahedron shares four edges with adjacent Al octahedra, forming double chains in the *c*-axis direction. These units are joined together by sharing the apical O atoms. Aluminum atoms occupy octahedrally coordinated sites between layers in such a way as to form strips of octahedra. When subjected to grinding, diaspore breaks along the 010 crystal planes where the binding force is weakest. Comminution

Table 2. Calculated natural charge, HOMO and LUMO energies, and geometrical parameters of BHDA.

Eigenvalues (a.u.)		Natural charge	— Geometrical parameters —	
HOMO	LUMO		Bond distances (Å)	Dihedral angle ($^\circ$)
-0.25959	-0.04497	^8C : -0.1461 ^5C : -0.2262	$r(\text{C25-N27}) = 1.33$	$\tau(\text{O38-N36-C34-C35}) = 10.3$
		^{26}O : -0.3513 ^{27}N : -0.1566	$r(\text{C34-N36}) = 1.35$	$\tau(\text{O32-N27-C25-O26}) = 4.8$
		^{29}C : 0.4304 ^{30}O : -0.3099	$r(\text{N27-O32}) = 1.39$	$\tau(\text{O32-N27-C25-C8}) = -176.9$
		^{31}O : -0.3475 ^{32}O : -0.2818	$r(\text{N36-O38}) = 1.40$	$\tau(\text{O38-N36-C34-C8}) = -172.1$
		^{35}O : -0.3212 ^{34}C : 0.3264		
		^{36}N : -0.1709 ^{38}O : -0.2880		

Table 3. Donor-acceptor interactions of atoms with lone-pair electrons.

Donor NBO	Acceptor orbitals	Stabilization energy (atomic units of energy)
LP (1) O 26	RY*(1)C25	7.39
	BD*(1)N36 – H37	1.37
LP (2) O 26	BD*(1)C8 – C25	9.39
	BD*(1)C25 – N27	10.79
LP (1) N 27	BD*(1)C25 – O26	2.15
	BD*(2)C25 – O26	25.86
LP (1) O 30	RY*(1)C29	7.70
	BD*(1)C8 – C29	9.15
LP (2) O 30	BD*(1)C29 – O31	15.82
	BD*(2)C29 – O30	25.22
LP (2) O 31	BD*(1)C29 – O30	4.13
LP (1) O 31	BD*(1)C29 – O30	4.13
LP (1) O 32	BD*(1)C25 – N27	2.08
LP (1) O 35	RY*(1)C34	7.68
LP (2) O 35	BD*(1)C8 – C34	11.58
LP (2) O 35	BD*(1)C34 – N36	11.11
LP (1) N 36	BD*(2)C34 – O35	15.83
LP (1) O 38	BD*(1)C34 – N36	1.79

LP: 1-center valence lone pair; RY*: 1-center Rydberg orbital; BD*: 2-center anti-bonding orbital
Single (1) or double (2) bond in the atom pair

destroys ionic/covalent Al–O bonds, resulting in a surface of unsaturated bonds or an ionic surface (Hu, 2003). This unsaturated surface of the diaspore tends to accept the electrons from the collector to form bonds, consequently making the separation of diaspore from the aluminosilicate minerals possible.

Because of the different structures of the diaspore and the aluminosilicate minerals, the degree of active Al–O site density on the surfaces of the minerals decreased in the order: diaspore > kaolinite > illite. The flotation separation of diaspore from the two aluminosilicate minerals may be accomplished by taking advantage of the differences in the number and nature of the broken Al–O bonds among these minerals. The ratio of the broken Al–O to Si–O bonds per unit area on the various edge surfaces decreases in the order: diaspore > kaolinite > illite. The ratio of the broken Al–O to Si–O bonds plays a dominant role in the surface properties of minerals (Guan *et al.*, 2009). The amount of active Al³⁺ on the surfaces of minerals will significantly influence the floatability of minerals. As diaspore has the largest broken-bond ratio, it achieves a better floatability than aluminosilicate minerals in the presence of BHDA.

The theoretical results, therefore, indicate that BHDA has excellent selectivity for the flotation of diaspore, which is in agreement with the experimental results and offers a theoretical foundation for the separation of diaspore from aluminosilicate minerals.

SUMMARY AND CONCLUSIONS

A novel 2,2-bis(hydroxycarbamoyl)decanoic acid (BHDA) was designed and synthesized by implanting

mono-carboxyl and double-hydroxycarbamoyl within the same molecule. The degree of floatability of three minerals using BHDA as the collector decreases in the order: diaspore > kaolinite > illite, and BHDA exhibits excellent collecting power for the diaspore flotation compared with that for kaolinite and illite. The FTIR spectra and the zeta potentials indicated that the adsorption of BHDA on the diaspore surface was chemical in nature, while that on kaolinite and illite was mainly physical in nature. The DFT calculation results of the BHDA molecule showed that the O atoms in the molecule tended to bond with the Al atoms of diaspore to form chelate rings and supported the high selectivity and collecting capacity of BHDA for the diaspore flotation. In brief, BHDA may be useful as a highly efficient collector for the separation of diaspore from aluminosilicate minerals.

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REFERENCES

- Becke, A.D. (1993) Density-functional thermochemistry. III. The role of exact exchange. *Journal of Chemical Physics*, **98**, 5648–5652.
- Chen, J.H. and Zhao, Q.J. (2000) Technical progress in last ten years and future development direction of Chinese alumina industry. *Light Metals*, **10**, 3–7.
- Chen, W.K. and Peng, G.C. (1997) *The Digestion Technology of Diasporic Bauxite*. Beijing, Metallurgical Industry Press,

- China.
- Chen, X.Q., Chen, X.H., Ma, J.W., and Chen, Z.Y. (2006) Study on the research of lower grade bauxite dressing and desilication. *Light Metals*, **10**, 13–16.
- Cheng, D. and Yan, D.O. (1997) Production actuality and development of bauxite industry in China. *Light Metals*, **1**, 12–19.
- Elbokl, T.A. and Detellier, C. (2006) Aluminosilicate nano-hybrid materials intercalation of polystyrene in kaolinite. *Journal of Physics and Chemistry of Solids*, **67**, 950–955.
- Fang, Q.X. and Huang, G.Z., (2000) The character of bauxite and the technology of flotation desilicate in China. *Metallic Ore Dressing Abroad*, **5**, 11–16.
- Feng, Q.M., Chen, Y.D., Lu, Y.P., Chen, Y., OU, L.M., and Zhang, G.F. (2004) Density functional theory study of diasporic (α -AlOOH) bulk and (010) surface. *The Chinese Journal of Nonferrous Metals*, **4**, 670–675.
- Frisch, M.J., Trucks, G.W., Schlegel, H.B. and Scuseria, G.E. (2003) *Gaussian 03, Revision C.01*. Gaussian, Inc., Wallingford CT.
- GassView (2003) *Revision 3.1*. Gaussian, Inc., Pittsburgh, Pennsylvania, USA.
- Guan, F., Zhong, H.G., Liu, Y., Zhao, S.G., and Xia, L.Y. (2009) Flotation of aluminosilicate minerals using alkyl-guanidine collectors. *The Transactions of Nonferrous Metals Society of China*, **19**, 228–234.
- Hu, Y. (2003) Progress in flotation de-silica. *The Transactions of Nonferrous Metals Society of China*, **13**, 656–662.
- Hu, Y.H., Sun, W., and Jiang, H. (2005) The anomalous behavior of kaolinite flotation with dodecyl amine collector as explained from crystal structure considerations. *International Journal of Mineral Processing*, **76**, 163–172.
- Hu, Y.Y., Sun, W., Li, H.P., and Xu, Z.H. (2004) Role of macromolecules in kaolinite flotation. *Minerals Engineering*, **17**, 1017–1022.
- Huang, C.B., Wang, Y.H., and Lan, Y. (2006) Mechanism of selective flocculation separation of diasporic-bauxite with organic flocculent HSPA. *The Chinese Journal of Nonferrous Metals*, **7**, 1250–1256.
- Huang, G.Z., Fang, Q.X., Gui, J.R., and Rang, J. (1999) The casting silicate means and studying evolution of bauxite. *Light Metals*, **5**, 16–20.
- Jiang, Y.R., Hu, Y.H., and Cao, X.F. (2001) Synthesis and structure-activity relationships of carboxyl Hydroxidoxime in Bauxite Flotation. *The Chinese Journal of Nonferrous Metals*, **4**, 702–706.
- Li, S.Q. and Cheng, X.C. (2008) Application of C01 and B01 etc in sluminosilicate reverse flotation. *Nonferrous Metals*, **2**, 96–98.
- Ling, S.S., Zhang, X.L., Shang, X., and Zhang, W.B. (2006) Overview on physical desilicate flotation of bauxite mineral. *Metallic Ore Dressing Abroad*, **43**, 9–12.
- Liu, J.R. and Liu, X.M. (2005) Application of treating middle and low grade bauxite by Ore-dressing Bayer process in alumina production. *Light Metals*, **4**, 11–14.
- Liu, Z.F. and Du, Y.J. (2000) Overall analysis of Chinese bauxite resource. *Light Metals*, **12**, 8–13.
- Liu, G., Zhong, H., Hu, Y., Zhao, S., and Xia, L. (2007) The role of cationic polyacrylamide in the reverse flotation of diasporic bauxite. *Minerals Engineering*, **20**, 1191–1199.
- Lu, Y.P., Zhang, G.F., Feng, Q.M., and O, L.M. (2002) A novel collector RL for flotation of bauxite. *Journal of Central South University of Technology*, **9**, 21–24.
- Newman, A.C.D. (1987) *Chemistry of Clays and Clay Minerals*. Longman Group, UK, Limited, Essex, UK, pp. 168–169.
- Padip, Rai, B., Rao, T.K., Krishnamurthy, S., Vetrivel, R., Mielczarski, J., and Cases, JM. (2002) Molecular modeling of interactions of diphosphonic acid based surfactants with calcium minerals. *Langmuir*, **18**, 932–940.
- Peng, W.S. and Liu, G.K. (1982) *Graph of Minerals Infrared Spectra*. Science and Technology Press, Beijing, China.
- Pradip (1994) Proceedings of symposium on reagent for better metallurgy (P.S. Mulukutla, editor). *SME-AIME*, **24**, 245.
- Wang, Y.H., Hu, Y.H., and Chen, X.Q. (2003) Aluminum-silicates flotation with quaternary ammonium salt. *Transactions of Nonferrous Metals Society of China*, **13**, 715–719.
- Wen, L. (1989) *Mineral Infrared Spectroscopy*. Chongqing University Press, Chongqing, China.
- Xia, L.Y., Liu, G.Y., Zhong, H., Wang, S.A., and Zhao, S.G. (2009) Flotation separation of diasporic from aluminosilicates by using dodecylguanidine. *The Chinese Journal of Nonferrous Metals*, **3**, 562–569.
- Xu, Z.H., Plitt, V., and Liu, Q. (2004) Recent advances in reverse flotation of diasporic ores – A Chinese experience. *Minerals Engineering*, **17**, 1007–1015.
- Yin, W.Z., Han, Y.X., Wei, X.C., Zhai, Y.C., and Tian, Y.W. (2001) The crystal chemical analysis of the floatability of diasporite and kaolinite. *Metal Mine*, **6**, 29–33.
- Yu, X.Y., Zhong, H., and Liu, G.Y. (2009) Research on novel flotation collector of aluminosilicate minerals. *Journal of JiangXi University of Science and Technology*, **5**, 21–24.
- Zhang, L.H., He, J.H., and Zhang, Y. (2006) Status and countermeasure of alumina industry in China. *Light Metals*, **2**, 3–7.
- Zhao, S.G. and Chen, Y.C. (2009) The study on aluminosilicate minerals flotation using alkyl-guanidine. *Conservation and Utilization of Mineral Resources*, **4**, 36–40.

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