

Reverse flotation separation on diaspora and kaolinite in the presence of cationic polyacrylamide polymers^①

LIU Guang-yi(刘广义), ZHONG Hong(钟宏), LU Yiping(卢毅屏), FENG Qiming(冯其明)
(College of Chemistry and Chemical Engineering, Central South University, Changsha 410083, China)

Abstract: Based on the analyses of crystal structures and surface properties of diaspora and kaolinite, an effective diaspora depressant, CPAM (cationic polyacrylamide) polymers was discovered by single minerals tests, separation experiments of artificial mixed minerals, zetapotential and adsorption measurement. The reverse flotation separation on diaspora and kaolinite can be carried out using collector dodecylamine acetate and depressant CPAM under pH 5.5~8.5. On the surfaces of diaspora, there are a large amount of active aluminum atoms. They can bond with $-C(O)NH_2$ groups in CPAM and make the $-CH_2N^+(CH_3)_3$ groups in CPAM orient toward the outer surfaces of diaspora, which prevents a majority of the dodecylamine cations from adsorbing on diaspora, enhances hydrophilicity of diaspora, and depresses the floatability of diaspora. But for kaolinite, CPAM polymers have little effect on its floatability.

Key words: cationic polyacrylamide; reverse flotation; diaspora; kaolinite

CLC number: TD 923

Document code: A

1 INTRODUCTION

China is rich in diaspora bauxite resources^[1, 2] which possess special properties such as high grade of both Al_2O_3 and SiO_2 and low Fe content, but the Al/Si (mass ratio of Al_2O_3 to SiO_2) value is low. In order to treat the diaspora bauxite, united methods and sintering methods^[3] are still applied although suffering from disadvantages including complex technology flow chart, high energy consumption, high production cost, and restraining further development of alumina industry. However, by improving bauxite Al/Si > 10, we can choose more advanced alumina production technology—Bayer Methods.

Froth flotation is one of the most widely used processes for beneficiation of ores containing valuable minerals. It is especially used for separating finely ground valuable minerals from the associated gangue or for separating valuable minerals from one another. For diaspora bauxites, the flotation technology is applied to get high quality material for Bayer technology by improving Al/Si values of bauxites.

The speciality of diaspora bauxites is that the grade of valuable mineral diaspora is high and the grade of associated gangue silicates such as kaolinite is low. If a routine flotation flow chart is used, the yield of diaspora concentrate is over 80%, but it still suffers from many disadvantages for commercial production. Aiming at overcoming those disadvantages,

the reverse floatation^[4-7], floating silicates such as kaolinite from diaspora bauxites, is applied in this study.

2 EXPERIMENTAL

2.1 Minerals

Diaspora was obtained from Mianchi Bauxites, Henan Province, China. Kaolinite was obtained from geological museum of China. They are 95% in purity by chemical and spectroscopical analyses. Diaspora and kaolinite were ground to particles with diameter $\leq 4 \mu m$ and BET $1.14 m^2 g^{-1}$ for diaspora and $11.34 m^2 g^{-1}$ for kaolinite.

2.2 Reagents and experimental apparatus

1) Reagents

Dodecylamine, acetic acid, hydrochloric acid and caustic soda are AR grade. CPAM-1 having about 10%, CPAM-2 having 20% and CPAM-3 having 35% cation by mass respectively are commercial purity.

2) Apparatus

pHS-3C pH meter, UV-3000 spectrometer, Zetaplus electrophoresis instrument, XFD hanging-cell flotation machine.

2.3 Experimental methods

A 40 mL flotation cell was fed with 2 g sample

① **Foundation item:** Project(96-122-01-01) supported by the Key Program of 9th Five-year Plan of China

Received date: 2002-09-16; **Accepted date:** 2002-12-23

Correspondence: LIU Guang-yi, Candidate for Doctor; Tel: + 86-731-8830603; E-mail: Huangyi.Liu@163.com

of minerals and suitable amount of distilled water was added. The tests were carried out in hanging-cell flotation machine with procedures shown in Fig. 1.

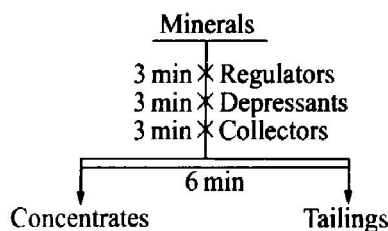


Fig. 1 Minerals flotation testing flow chart

3 RESULTS AND DISCUSSION

3.1 Single minerals flotation tests

3.1.1 pH value tests

Fig. 2 demonstrates that the floatabilities of diaspor and kaolinite are similar in whole pH range, with only a little difference under pH 2~6. Theoretically, the reverse flotation separation on them can partly be implemented under these pH values. But for industrial practice, an obvious disadvantage under acidity circumstances is that the processing equipments are easily corroded. In order to increase the floatability difference between diaspor and kaolinite and to improve the pulp pH values, regulators or depressants are very essential in this flotation system.

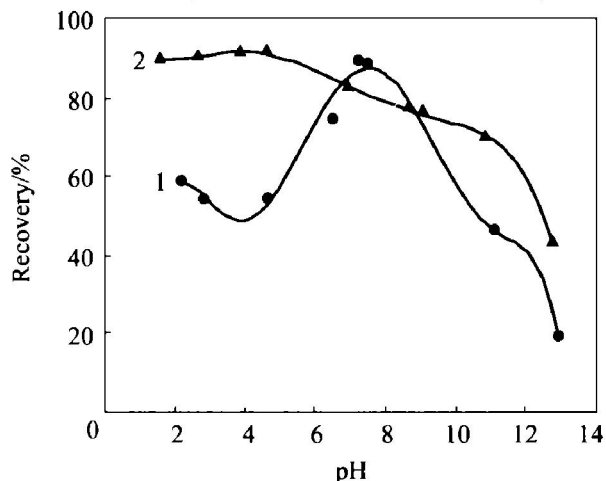


Fig. 2 Flotation recovery of diaspor and kaolinite under different pH values and using $4 \times 10^{-4} \text{ mol/L}$ dodecylamine acetate
1—Diaspor; 2—Kaolinite

3.1.2 Dosage of CPAM

Fig. 3 shows that CPAM-1, CPAM-2 and CPAM-3 have little effect on the floatability of kaolinite, and efficiently reject diaspor being floated out. The rejection abilities of these CPAMs are followed as this sequence: CPAM-3 > CPAM-2 > CPAM-1, identical to their cationic contents: CPAM-3 > CPAM-2 > CPAM-1.

3.1.3 pH values tests in the presence of CPAM-3

Fig. 4 shows that kaolinite has excellent floa-

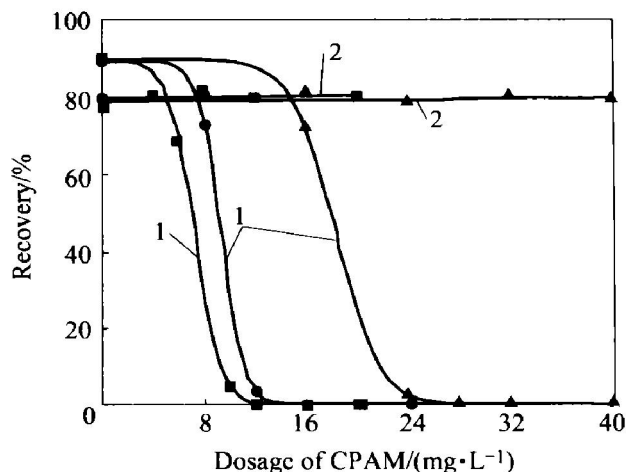


Fig. 3 Flotation recovery of diaspor and kaolinite as function of dosage of CPAM

1—Diaspor; 2—Kaolinite. ■—CPAM-3;
●—CPAM-2; ▲—CPAM-1;

pH = 7.5; dodecylamine acetate: $4 \times 10^{-4} \text{ mol/L}$

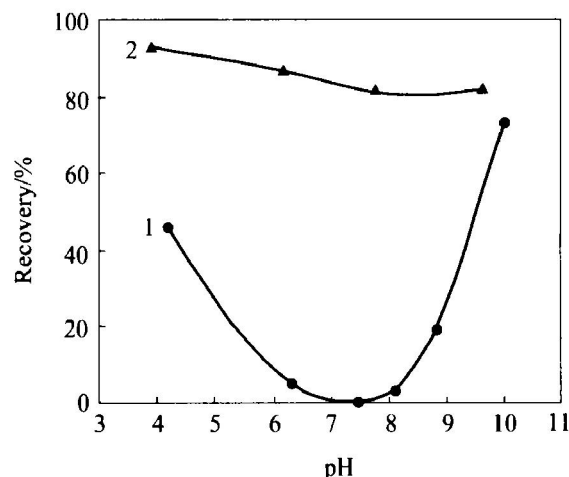


Fig. 4 Recovery of diaspor and kaolinite as function of pH value in the presence of CPAM-3

1—Diaspor; 2—Kaolinite. CPAM-3: 12 mg/L ;

dodecylamine acetate: $4 \times 10^{-4} \text{ mol/L}$

tability under pH 4~10, but diaspor is effectively rejected by CPAM-3 in pH 5.5~8.5. So the reverse flotation separation on diaspor and kaolinite can be brought about under this pH value.

3.2 Separation tests of artificial mixed minerals

Based on the results of single minerals tests, separation tests of artificial mixed minerals were conducted employing mass ratio 1:1 of diaspor to kaolinite. The results obtained was plotted in Fig. 5. It shows that the reverse flotation separation on diaspor and kaolinite succeed under such conditions as pH = 7.5, dosage of dodecylamine acetate $4 \times 10^{-4} \text{ mol/L}$, and CPAM-3 over 4 mg/L at an excellent diaspor rejection.

3.3 Zeta potential

3.3.1 pH value

Fig. 6 demonstrates that the point of zero charge is at pH 5.3 and pH 3.1 for diaspor and kaolinite,

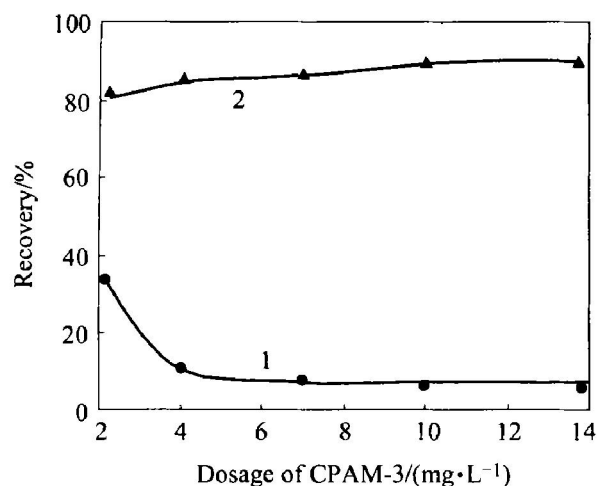


Fig. 5 Results for separation experiments of artificial mixed minerals

1—Diaspore; 2—Kaolinite. dodecylamine acetate: $4 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$; pH = 7.5

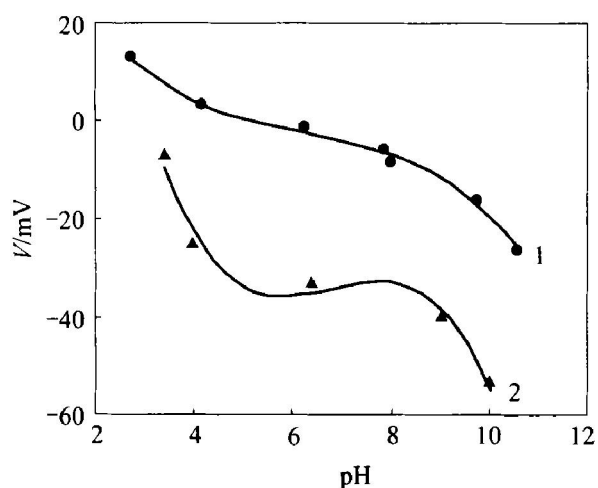


Fig. 6 Zeta potential as function of pH value
1—Diaspore; 2—Kaolinite

respectively. When pH value is over 5.5, the surfaces of diaspor and kaolinite show negative charge and both of them can be floated out using cationic collector dodecylamine. The Zeta potential of diaspor is more positive than that of kaolinite at the same pH value. i. e., the amount of aluminum atoms on diaspor surfaces is much more than that on kaolinite surfaces.

3.3.2 Dodecylamine acetate

Fig. 7 shows that the Zeta potential of diaspor and kaolinite increases with increasing dosage of dodecylamine acetate, which indicates that cationic dodecylamine can adsorb on the surfaces of both minerals and the amount of adsorption increases with increasing concentration of dodecylamine acetate. Fig. 7 also demonstrates that collector dodecylamine acetate shows multilayer physical adsorption on the surfaces of both minerals when its concentration is higher.

3.3.3 CPAM-3

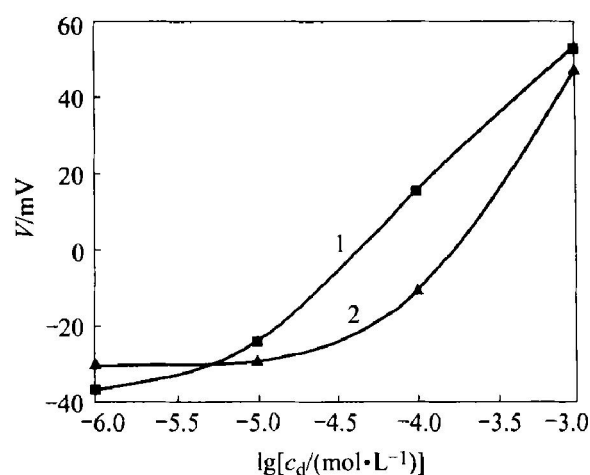


Fig. 7 Zeta potential as function of dosage of dodecylamine acetate (c_d)

1—Diaspore; 2—Kaolinite. pH = 7.5–7.8

Fig. 8 shows that the Zeta potential of diaspor increases and the Zeta potential of kaolinite decreases with increasing dosage of CPAM-3 in the presence of dodecylamine acetate of $10^{-4} \text{ mol} \cdot \text{L}^{-1}$. On the surfaces of diaspor, there are a large number of active aluminum atoms. They can bond with $-\text{C}(\text{O})\text{NH}_2$ groups in CPAM and make $-\text{CH}_2\text{N}^+(\text{CH}_3)_3$ groups in CPAM orient to the outer surfaces of diaspor, which enhances its Zeta potential. But for kaolinite, CPAM-3 polymers adsorb on its surfaces mainly by $-\text{CH}_2\text{N}^+(\text{CH}_3)_3$ groups in CPAM. On one hand, the competition adsorption between $-\text{CH}_2\text{N}^+(\text{CH}_3)_3$ groups and dodecylamine cation maybe decrease the adsorption capacity of dodecylamine on the surfaces of kaolinite. On the other hand, $-\text{C}(\text{O})\text{NH}_2$ groups orient to the outer surfaces of kaolinite. These decrease the Zeta potential of kaolinite.

3.4 Adsorption measurement

The results of adsorption measurement obtain

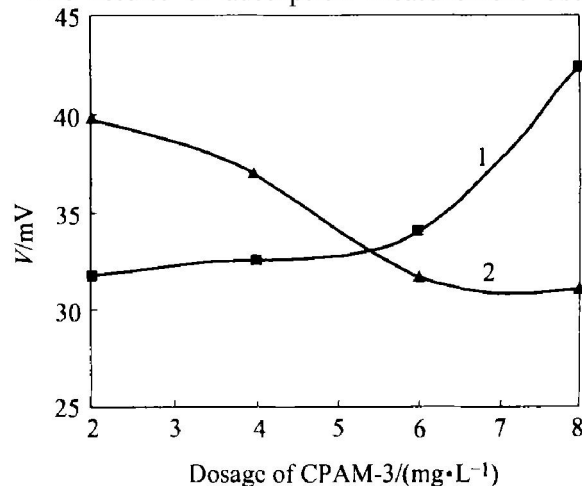


Fig. 8 Zeta potential as function of dosage of CPAM-3 in the presence of dodecylamine acetate

1—Diaspore; 2—Kaolinite. dodecylamine acetate: $10^{-4} \text{ mol} \cdot \text{L}^{-1}$; pH = 7.5–7.8

ed is listed in Table 1. It shows that the amount of dodecylamine acetate adsorbed on the surfaces of diaspo-re decreases by 68.5% in the presence of CPAM-3. Under the same circumstances, the amount of do-decylamine acetate adsorbed on the surfaces of kaolin-ite only decreases by 0.4%. The results of adsorption capacity measurement indicates that CPAM-3 poly-mers have little effect on the amount of dodecylamine acetate adsorbed on the surfaces of kaolinite, whereas greatly decrease the amount of dodecylamine acetate adsorbed on the surfaces of diaspo-re. During reverse flotation processing, the use of depressant CPAM-3 can remarkably increase the difference of floatability between diaspo-re and kaolinite, which is of great ad-vantage to minerals separation.

Table 1 Relation of adsorptive capacity on surfaces of minerals and CPAM-3

CPAM-3	Adsorptive capacity/ ($10^{-6} \text{ mol} \cdot \text{m}^{-2}$)		Conditions
	Diaspo-re	Kaolinite	
0	7.30	1.240	Dodecylamine acetate: $4 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$
$20 \text{ mg} \cdot \text{L}^{-1}$	2.30	1.235	pH= 7.5 ~ 7.8

3.5 Discussion

Solution chemistry of dodecylamine^[8] shows that dodecylamine is mainly present in the form of $\text{C}_{12}\text{H}_{25}\text{NH}_3^+$ in aqueous solution under pH 5.5 ~ 8.5. So dodecylamine easily adsorbs on the surfaces of both diaspo-re and kaolinite whose Zeta potential is nega-tive.

Chemical formula of diaspo-re is $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ or $\alpha\text{-AlOOH}$. Diaspo-re belongs to rhombic crystal series and has the crystal structure of diaspo-re. When diaspo-re is ground to finer particles, the bond of $\text{Al}-\text{O}$ is broken, which exposes a large number of active alu-minum atoms on the surfaces of diaspo-re and enhances positive charge of diaspo-re in aqueous solution. The PZC of diaspo-re is high^[1,9,10].

Chemical formula of kaolinite is $\text{Al}_4(\text{Si}_4\text{O}_{10})\text{-(OH)}_6$. Kaolinite belongs to triclinic minerals and is a typical aluminum silicate ratio of 1:1 layer structure. While kaolinite is ground to finer particles, the inter-layer hydrogen bond is easily broken, but the bond of $\text{Al}-\text{O}$ and $\text{Si}-\text{O}$ is difficultly broken. The number of active aluminum atoms on the surfaces of kaolinite is small and its PZC is low.

$-\text{C}(\text{O})\text{NH}_2$ groups in CPAM polymers can bond with the active aluminum on the surfaces of di-aspo-re and kaolinite. On the surfaces of diaspo-re,

there are a large amount of active aluminum atoms. They can bond with $-\text{C}(\text{O})\text{NH}_2$ groups and make $-\text{CH}_2\text{N}^+(\text{CH}_3)_3$ groups in CPAM orient to the outer surfaces of diaspo-re, which prevents a majority of do-decylamine cations from adsorbing on diaspo-re, en-hances hydrophilicity of diaspo-re, and rejects diaspo-re floated out. Both $-\text{C}(\text{O})\text{NH}_2$ groups and $-\text{CH}_2\text{N}^+(\text{CH}_3)_3$ groups in CPAM polymers can adsorb on the surfaces of kaolinite. The $-\text{CH}_2\text{N}^+(\text{CH}_3)_3$ groups do not orient to the outer surfaces of kaolinite. Dodecylamine cation adsorbs more easily on kaolinite than $-\text{CH}_2\text{N}^+(\text{CH}_3)_3$ groups do, which limit the accessi-bility of the nitrogen to participate in attachment to the negatively charged surfaces of kaolinite. CPAM-3 polymers have little effect on the floatability of kaol-inite using collector dodecylamine cation.

REFERENCES

- [1] LIU Guang-yi. A Study on Flotation and Desilication of Diaspo-re Bauxites [D]. Changsha: Central South Uni-versity of Technology, 1999. (in Chinese)
- [2] LU Yǎ-ping, ZHANG Guǒ-fang, FENG Qǐ-ming, et al. A novel collector RL for flotation of bauxite [J]. J Cent South Univ Technol, 2002, 9(1): 21 ~ 24.
- [3] CHENG Dai, LIAN Dǎ-nou. Production actuality and de-velopment of bauxite industry in China [J]. Light Met-als, 1997(1): 12 ~ 19. (in Chinese)
- [4] LUO Zhao-jun, HU Yue-hua, WANG Dian-zuo, et al. Mechanism of dispersion and aggregation in reverse flota-tion for bauxite [J]. The Chinese Journal of Nonferrous Metals, 2001, 11(4): 680 ~ 684. (in Chinese)
- [5] JIANG Tao, HU Yue-hua, QIN Wen-qing, et al. Mechanism of flotation for diaspo-re and aluminium-silicate minerals with alkylamine collectors [J]. The Chinese Journal of Nonferrous Metals, 2001, 11(4): 688 ~ 692. (in Chinese)
- [6] Mehrotra, Vikram P. Collecting agents for use in the froth flotation of silica-containing ores [P]. US 4725351, 1988.
- [7] CAO Xue-feng, HU Yue-hua, JIANG Yu-ren, et al. Flotation mechanism of aluminium silicate minerals with N-dodecyl-1,3-diaminopropane [J]. The Chinese Journal of Nonferrous Metals, 2001, 11(4): 693 ~ 696. (in Chi-nese)
- [8] HU Yue-hua, WANG Dian-zuo. The Solution Chemistry of Flotation [M]. Changsha: Hunan Peoples Press, 1989. (in Chinese)
- [9] YIN Wan-zhong, HAN Yue-xin, WEI Xin-chao, et al. The crystal chemical analysis of the flotability of diaspo-re and kaolinite [J]. Metal Mine, 2001(6): 29 ~ 33. (in Chinese)
- [10] CUI Jǐ-rang, FANG Qǐ-xue, HUANG Guǒ-zhi. Crystal structures and surface properties of diaspo-re and kaolinite [J]. Non-ferrous Metals, 1999(4): 25 ~ 30. (in Chinese)

(Edited by HUANG Jin-song)