[Article ID] 1003- 6326(2001)03- 0430- 04

Interaction and flotation of diaspore with alkylamine hydrochlorides①

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[Abstract] Electrokinetics and flotation of diaspore in solutions of different alkylamine hydrochlorides (with 12, 14 and 16 carbon atoms) were studied. The point of zero charge (PZC) of diaspore was determined by measuring zeta potential (streaming potential method) as a function of pH. Dodecyl-, tetradecyl- and hexadecylamine hydrochloride ions seem to be strongly adsorbed on the interface because they make the zeta potential more positive as the concentration increases. The PZC of diaspore is determined at pH 5.7. Flotation of diaspore was studied and shown to be influenced by the chain length of collectors and both collector and hydrogen ion concentration. The optimal experimental flotation conditions as pH and concentrations agreed well with that predicted from solution chemistry calculations, and the floatability of diaspore is poor while the pH value of flotation system is too high or low. The results of calculation also predict a wide pH range of effective flotation with increasing collector concentration.

[Key words] flotation; alkyl amine; diaspore
[CLC number] TD 923; TD 952 **[Document code]** A

1 INTRODUCTION

Flotation is one of the most versatile technologies used in mineral processing. The separation of minerals by flotation has been proven effective when particles to be floated can be made selectively hydrophobic. The hydrophobicity is often induced by the adsorption of collector and the flotation selectivity is achieved by using specific reagents, including activators, depressants and pH regulators.

The diasporic bauxite is the main resource of bauxite. It is important and essential to determine the floatability and electrokinetics from both scientific and practical point of view. The technological schemes of positive-flotation or reverse-flotation separation of aluminum-silicate minerals from diasporic bauxite were suggested[1, 2]. The positive-flotation separation of bauxite is to depress aluminum silicate gangue minerals such as illite, kaolinite and pyrophillite, and use anionic collectors to float diaspore. The conventional reagents are, fatty acid as collector, phosphate as depressant and dispersant, and sodium carbonate as pH modifier[3]. But the separation of diaspore by positive-flotation has two disadvantages: 1) the ore need to be ground finely, which make the product fine and containing much water and affect negatively on the filtration; 2) the concentrate yield is high (> 80%)[4], the flotation reagent consumption is high and it may be remained in concentrate, and affected the next Bayer process. Reverse-flotation separation of bauxite is to depress diaspore, and the aluminum-silicate minerals are floated with cationic or anionic collectors. The reverse-flotation separation of bauxite is characterized as: 1) it is to be prone to coarse grinding; 2) the yield of the diasporic product is low, so the consumption of flotation reagent will reduce, and the cost is less and the diasporic concentrate may not contain surfactants. This will reduce the negative effect of flotation reagents on Bayer process; 3) the concentrate is easy to filtrate.

In general, cationic collectors of the alkylamine type are now currently employed in recovering oxide minerals, specially in reverse-flotation separation of silicate ore and iron ore[5], and in the industrial beneficiation of phosphate ores[6]. In a previous paper, the mechanisms involved in the adsorption of the alkyl amine hydrochlorides on the fluorite/solution interface have been discussed[7]. However, very few results are found in the literature on the floatability and electrokinetics of diaspore with alkyl amine hydrochlorides, but it is very important for the flotation separation of diaspore from aluminum-silicate minerals.

The purpose of the present work is to gain information on the flotation behavior of diaspore as it is influenced by: 1) the chain length of the collector; 2) the effect of collector and hydrogen ion concentrations. On the other hand, the role played by the surface charge in determining the adsorption of flotation reagents is of a great importance in understanding of flotation behavior of this type of minerals. No systematic study of the floatability and of diaspore at alkyl amine hydrochlorides solution has been reported, although the reagent used in flotation has been

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① **[Foundation item]** Project (G1999064901) supported by the State Key Fundamental Research Progra
[Received date] 2000- 12- 06; **[Accepted date]** 2001- 01- 08

recognized of late. To improve the efficiency of alkyl amine hydrochlorides used in flotation, it is essential to understand the mechanisms of dodecyl-, tetradecyl- and hexadecylamine hydrochloride on diaspore surface, and determine the characteristics of electrokinetic and floatability.

2 EXPERIMENTAL

Diaspore was from the Great Wall Aluminum Corporation of China. The crystals was selected by hand, crushed and ground in a porcelain mortar, and the 0.039~ 0.15 mm fraction, which assayed about 79% Al_2O_3, was used in flotation. The purity of diaspore is about 90%. The alkylamines transformed in alkylamines hydrochloride following the Ralston method[8]. Double distilled water was used in all the experiments described here and the suspension pH was adjusted using HCl and NaOH stock solutions.

A 40 ml laboratory flotation cell was used. Mineral particles (2 g) were placed in the ploxglass cell that was then filled with distilled water. After introducing desired amount of reagents, the pulp was agitated for three minutes. The flotation was conducted with the aeration under the natural suction effect of mechanical stirring for three minutes, and the recovery was calculated as the percentage of minerals floated. Electrophoretic mobility measurement was conducted using an MRK electrophoresis apparatus with a flat cell manufactured in Japan. The suspension made in a 10^{-3} mol/L KNO_3 supporting electrolyte solution with a solid for liquid ratio of 0.05∶100 was conditioned at 25 ℃. The electrophoretic mobility was then measured with the aid of optical microscope. About 40 different particles were counted to obtain the average mobility from which zeta potential was calculated using the Smoluchowski equation.

3 RESULTS AND DISCUSSION

3.1 Flotation

The flotation recovery of diaspore as a function of pH, using 1.0×10^{-4} mol/L collector, is presented in Fig. 1. As shown in this figure, flotation recovery of diaspore increase with pH, and diaspore has well floatability from pH 2.0 to 7.0, from pH 2.0 to 8.5, and from pH 2.5 to 10.0 using dodecyl-, tetradecyl- and hexadecylamine hydrochloride as collector respectively.

The data shown in Fig. 2 are for alkylamine hydrochlorides (with 12, 14 and 16 carbon atoms). As can be seen, the recovery can be increased continuously with collector concentrations at pH= 6.0 while the concentration is less than 10×10^{-4} mol/L. There is a strong tendency for the flotation recovery of diaspore to increase both with collector concentration and with chain length of this collector. According to the experimental results of Fig. 1 and Fig. 2, we can assert that as the chain length increase, there is a decrease in the concentration value at which a given flotation recovery is obtained. It should be remembered that the longer the alkyl chain, the greater the collector adsorption density, and both adsorption and flotation recovery are known to be related to each other[5, 9].

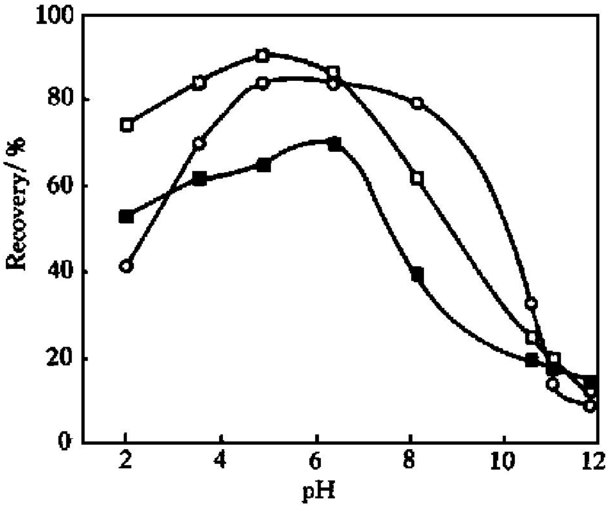

Fig. 1 Effect of pH on flotation of diaspore with alkylamine hydrochloride as collector at 25 ℃
(■—Dodecylamine; □—Tetradecylamine; ○—Hexadecylamine)

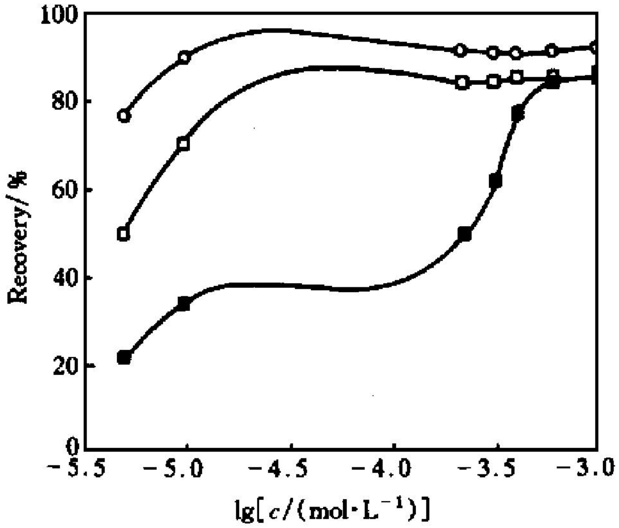

Fig. 2 Effect of alkylamine hydrochloride concentration on flotation of diaspore at pH 6.0, 25 ℃
(■—Dodecylamine; □—Tetradecylamine; ○—Hexadecylamine)

3.2 Zeta potential measurement

According to Ref. [10], the point of zero charge (PZC) of a mineral depends on the p*K* of the function groups, i. e. of the surface chemical composition. As can be seen in Fig. 3, the obtained PZC is pH 5.7. The diaspore showed an isoelectric point of pH above which it is negatively charged.

Fig. 4 shows the zeta potential of diaspore in solution of dodecyl-, tetradecyl- and hexadecylamine hydrochloride, the conditioning time of the mineral with the collector was always chosen of 20 min, corresponding to the actual residence time of the pulp in flotation process. The experiments have been carried out at constant pH of 6. 0. Similar trends were observed for the three considered alkyl chains. At the low concentration, the zeta potential remains nearly constant while a sudden increase takes place as soon as a certain concentration is reached, which being lower for longer alkyl chains.

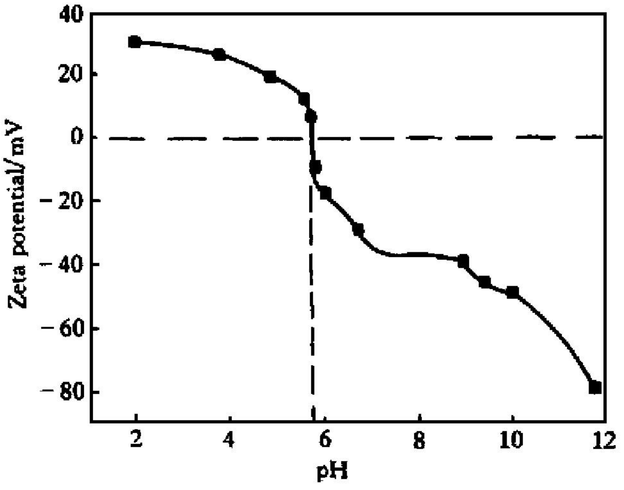

Fig. 3 Zeta potential of diaspore as function of pH at 25 ℃

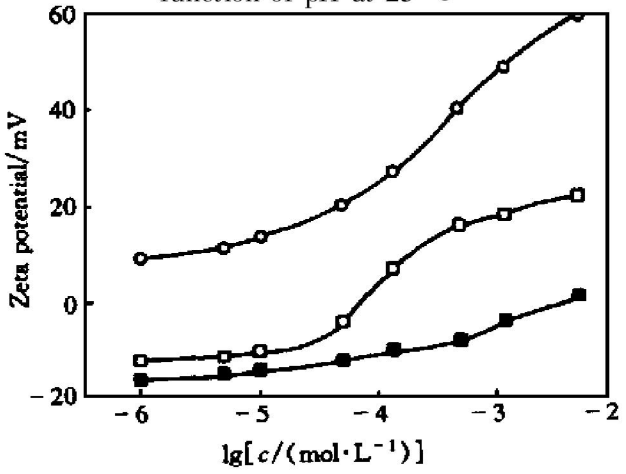

Fig. 4 Zeta potential of diaspore as function of alkylamine hydrochloride concentration at pH 6. 0, 25 ℃
(■ —Dodecylamine; □ —Tetradecylamine; ○—Hexadecylamine)

The point of zero charge of a mineral has been shown to be an important characteristic because the adsorption of various organic and inorganic ions will be governed by the location of the solution properties such as pH value with respect to PZC[11]. It is generally accepted that cationic surfactants are adsorbed essentially on the negative sites by electrostatic adsorption. From Fig. 3, the pH increases, the negative charge of the diaspore surface increases. Also, when the pH decreases, the positive character will then be increased. Fig. 4 shows that the zeta potential of diaspore increase abruptly at concentrations exceed 5×10^{-4} mol/L, 5×10^{-5} mol/L, and 10^{-5} mol/L respectively for dodecyl-, tetradecyl- and hexadecylamine hydrochloride. Zeta potential also changes from negative to positive when increasing the solution concentration, suggesting that the alkylamine ions adsorbed strongly on diaspore surface and that some type of specific adsorption can be assumed to take place in higher concentration region. Since pH determines both magnitude and sign of the surface charge, changes of the pH will affect the required collector concentration to obtain a determined recovery by flotation. The lower recovery obtained in the acid region could be attributed to the less negative values of the zeta potential.

The equilibrium of cationic collectors in solution are

$$RNH_3\cdot Cl \text{ — } RNH_3^+ + Cl^-$$

$$RNH_3^+ \text{ — } RNH_2 + H^+$$

$$K_a = [H^+][RNH_2]/[RNH_3^+]$$

$$pH - pK_a = \lg[RNH_2] - \lg[RNH_3^+]$$

There is a possible competition between H^+ ions and $R—NH_3^+$ ions for occupying the negative sites at the mineral surface. $R—NH_3^+$ are principally responsible for the collecting effect in the acid region. It is generally known that the floatability increase with the increase of the ratio $[RNH_3^+]/[H^+]$. The tendency towards better flotation when the alkaline pH region is attained, except for the highest values of pH, which could be due to the electrostatic contribution, since the surface charges become more negative under this condition. But the neutral molecules (RNH_2) must increase with the increase of pH. According to Hu et al[12, 13] this is due to the depressing effect of the neutral amine. From Fig. 1, we can find the flotation recovery of diaspore drops abruptly beyond pH 7. 8 , pH 9. 0 , and pH 10. 4 respectively for dodecyl-, tetradecyl- and hexadecylamine hydrochloride.

4 CONCLUSIONS

1) The point of zero charge of diaspore is determined at pH 5. 7.

2) Dodecyl-, tetradecyl- and hexadecylamine hydrochloride ions seem to be strongly adsorbed on the interface, because they change the sign of the zeta potential from negative to positive as the concentration increase.

3) Flotation recovery of diaspore, for a given concentration of alkylamine, increases with the num-

ber of carbon atoms of the chain.

4) Better flotation recovery is obtained as the pH increase, except for the highest values of pH.

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(Edited by LONG Huai-zhong)