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Effect of hydroxamic acid starch on reverse flotation desilicate from diasporic bauxite①

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[Abstract] It is important to depress diaspore effectively in order to remove silicates from diasporic bauxite. A new water soluble polymer hydroxamic acid starch (HA-starch) was prepared. The effects of the product on the diaspore and kaolinite flotation were investigated and its reactive mechanism was studied by zeta potential measurement and FTIR. The results show that HA-starch can depress diaspore while make positive effect on kaolinite flotation at low pH value(pH below 6). The flotation recovery of diaspore was sharply decreased with the increase of concentration of HA-starch. The chemical adsorption of HA-starch on the surface of diaspore was revealed.

[Key words] hydroxamic acid starch; reverse flotation; diasporic bauxite; desilicate

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1 INTRODUCTION

There are plenty of bauxite resources in China. However the most of bauxite (more than 90%) is diasporic-bauxite with low ratio of aluminum oxide to silica (A/S= 5~ 6). The diaspore is difficult to be dissolved under normal pressure and processed by conventional Bayer's process. The complicated processing methods such as sintering technology has been used to treat such diasporic-bauxite to produce aluminum oxide. The high production cost and environmental problem with these technologies made the development of Chinese aluminum industry confront predicament. Economically, it is required to remove silicates from diasporic-bauxite to obtain a concentrate with the ratio of A/S above 11 and the recovery of Al_2O_3 above 87%, which can be easily treated in Bayer's process[1, 2]. Flotation is an effective separation technology and the reverse flotation which can remove most silicate minerals from bauxite has been recently paid much attention from industry. In the reverse flotation, to depress diaspore is one of the key factors. Our recent studies show that the organic polymer with lots of groups may be good depressant for diaspore[3, 4].

Starch is an important natural polysaccharide. The macromolecule is highly hydrophilic, due to the presence of several OH-groups in its basic structural unit D-glucose. It has been found with broad application as flocculant/depressant in the mineral processing, such as in the separation of iron ores (reverse flotation of quartz with the depression of hematite by starches) and the direct flotation of carbonic phosphate ores (depression of calcite)[5~ 6]. But in the reverse flotation desilicate from bauxite, it shows a poor selectivity and depressing effect. It requires to modify the structure of starch to improve its depressing activity.

Hydroxamic acids are regarded as a kind of replaced derivative with the nitrogen-bound hydrogen in the hydroxylamine molecule, and are expressed by a general formula R—CO—NHOH(R= alkyl or aryl). It has the tautomerism of keto and enol types. The keto form predominates in an acid medium and the enol form in an alkaline medium[7]. They are known to form complexes with a large number of metal ions (including Al^{3+}). In this regards, it is necessary to introduce the hydroxamic acid group into starch molecule to improve the depressing effect on diaspore.

In the present work, the starch was modified and the product was identified by spectra. its activity in flotation of diaspore and kaolinite was investigated.

2 EXPERIMENTAL

2.1 Synthesis of hydroxamic acid starch(HA-starch)

Synthesis of hydroxamic acid starch involved two steps: the synthesis of carboxymethyl starch esters (CMSE), and the CMSE reacts with hydroxylamine to obtain HA-starch. The steps are shown as follows.

$$\text{Starch-OH} + \text{NaOH} \rightarrow \text{Starch-O-Na} + H_2O$$

$$\text{Starch-O-Na} + ClCH_2COOCH_2CH_3 + NaOH \rightarrow \text{Strach-}OCH_2COOCH_2CH_3 + NaCl + H_2O$$

$$\text{Strach-}OCH_2COOCH_2CH_3 + NHOH\cdot HCl + NaOH \rightarrow \text{Starch-}OCH_2CONHON + NaOH + H_2O$$

The solvent plays an important role in the reaction. It has reported that different solvents and compositions have different effects on the carboxymethylation of cellulose and the iso-propanol—water system exhibits a positive effect to increase the degree of substitution[8, 9]. In

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the present work, iso-propanol—water solution was used as reaction solvent. The detailed preparation procedure will be reported elsewhere.

2.2 Mineral samples

Diaspore and kaolinite samples were hand picked from Henan Province and Zhejiang Province respectively. Both samples were dry ground in a porcelain ball mill and dry screened to obtained the fractions in the size range of − 98 μm. The purity of kaolinite and diaspore sample was over 85%. All the reagents used are AR grade. Double distilled water was used in all tests.

2.3 FTIR

The FTIR of starch, HAS and their reaction products with minerals were recorded with Nicolet FTIR-740.

2.4 Flotation test

The flotation tests were carried out in a microflotation cell with a volume of 30 mL. Stirring rate is 2 000 r/min. 3 g of mineral was used in each test. The pH was modified with 0.1 mol/L HCl or 0.1 mol/L NaOH and measured on a pHs-2 acidity meter. After adding HA-starch or starch and collector dodecylamine, the pulp was stirred and the mineral was floated for 4 min. The floated product and the tailing fractions were separately filtered, dried and weighed. The recoveries are expressed on a weight basis.

2.5 Zeta potential measurement

The mineral samples were further ground to − 5 μm in agate mortar. 50 mg sample was dispersed in 50 mL double distilled water each time. Conditioning the pH of mineral suspension with HCl or NaOH at room temperature (23 ℃) and then adding the reagents, the zeta potentials were determined with a Zeta Potential Analyzer (Zeta plus V3.52) after stirring 5 min.

3 RESULTS AND DISCUSSION

3.1 Effect of starch on flotation of diaspore and kaolinite

The effect of pH on the floatability of diaspore and kaolinite is illustrated in Figs. 1 and 2. It can be seen that the flotation recovery of diaspore increases with increase of pH up to about 7.5 and thereafter decreases, while that of kaolinite sharply decreases with increase of pH. Diaspore exhibits a good floatability than kaolinite in wide pH region in absence of starch. It is difficult in flotation to float kaolinite from bauxite and thus effective depressant for diaspore is required. It also follows from Figs. 1 and 2 that the natural starch has little effect on the flotation of diaspore and kaolinite. HA-starch depresses the flotation of diaspore evidently at pH< 8 and shows some activation on the flotation of kaolinite around pH4.

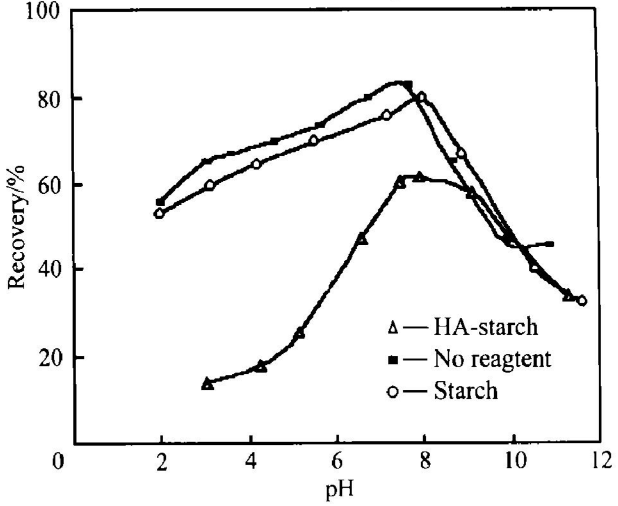

Fig. 1 Flotation recovery of diaspore as function of pH

DDA: 40 mg/L; starch and HA-starch: 40 mg/L

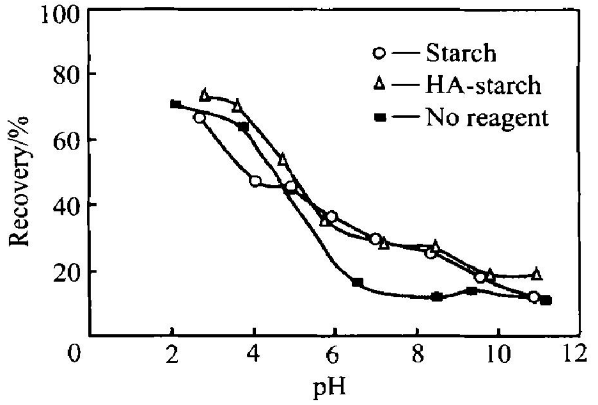

Fig. 2 Flotation recovery of kaolinite as function of pH

DDA: 40 mg/L; starch and HA-starch: 40 mg/L

The effect of starch and HA-starch concentration on diaspore and kaolinite is shown in Fig. 3. It is clearly demonstrated that in the pH range of 3.8~ 4.2, HA-starch significantly depresses diaspore, while there is even a marginal active effect on kaolinite flotation, which will facilitate the selective flotation separation of kaolinite from diaspore in flotation bauxite. In the case of natural starch, it has little effect on the floatablity of the minerals.

3.2 Effect of starches on zeta potential of diaspore and kaolinite

Zeta potentials of diaspore and kaolinite as a function of pH in the absence and presence of starch and HA-starch are shown in Fig. 4 and Fig. 5 respectively.

The isoelectric point (IEP) of diaspore in distilled water is found to be located around pH 6.0. The positive zeta potential decreases slowly with the increase of pH up to pH6. The negative zeta potential increase sharply with increase of pH at pH> 6. The addition of starch and HA-starch reduces the positive electro-

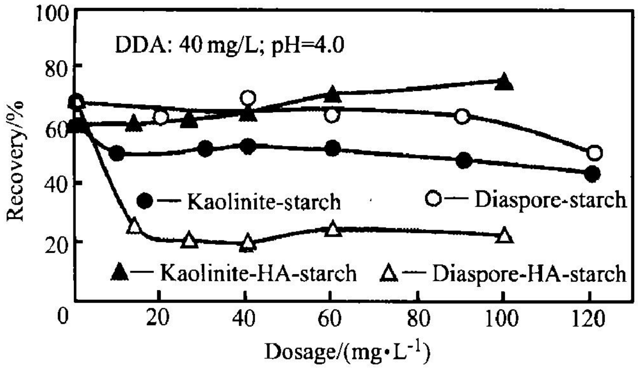

Fig. 3 Effect of reagents concentration on diaspore and kaolinite flotation

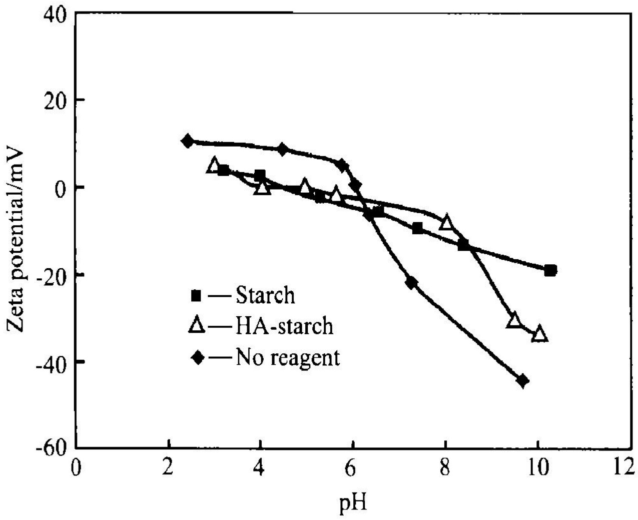

Fig. 4 Zeta potential of diaspore as function of pH

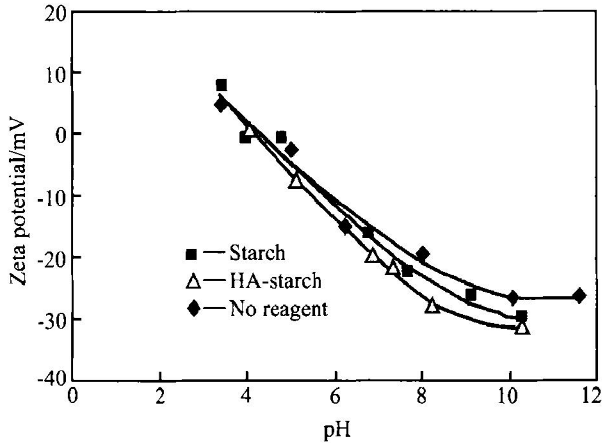

Fig. 5 Zeta potential of kaolinite as function of pH

phoretic mobility values of diaspore. IEP of diaspore decreases to pH about 4 and 5 respectively. At high pH range, the addition of starch also reduces the negative zeta potentials. Since the polymer appears merely to reduce the electrophoretic mobility in absolute magnitude under all the pH conditions studied, the primary effect of the large macromolecule seems to be to shift the slipping plane further away from the interface. This result suggests that some conformational rearrangements of the macromolecules take place with starch and HA-starch addition. These observations are in consonance with the results of the effect of the adsorption of non-ionic polymer molecules on the zeta potential reported by many researchers[10].

In the case of kaolinite, HA-starch and starch have no effect on the zeta potentials of kaolinite with increase in pH up to about 7.5, but beyond 7.5, they increase slightly the negative electrophoretic mobility of kaolinite. It may conclude that HA-starch and starch are easier adsorbed by diaspore than kaolinite.

3.3 FTIR spectra of interaction between starch and minerals

Comparison of the IR spectra of starch and its derivative is shown in Fig. 6. It is clear that the IR of HA-starch is different from that of starch. New bands appeared at 1 597 cm^{-1} —stretching of —C ═ O and —C ═ N, 1 403 cm^{-1} — symmetric stretching of —COO —, 1 333 cm^{-1} —bending of the O —H, 835 cm^{-1} and 934 cm^{-1} due to stretching vibration of C —N and N —O respectively. The evidence proved that the starch be modified and the hydroxamic acid group was introduced into the starch molecule.

Fig. 7 shows the FTIR spectra of diaspore in absence and presence of starch and HA-starch. Fig. 8 shows the FTIR spectra of kaolinite in absence and present of starch and HA-starch.

1) Infrared peak value of diaspore

2 119 cm^{-1}, 1 989 cm^{-1} stretching of O —H on the surface; 1 088 cm^{-1}, 970 cm^{-1} bending of O —H on the surface; 745 cm^{-1} due to the stretching of Al —O.

2) Infrared spectra of kaolinite

1 112 cm^{-1}, 1 005 cm^{-1} stretching of Si —O; 791 cm^{-1} and the peak followed contribute to vibration of Si — O —Si or Al —O —Si.

3) Infrared spectra of diaspore treated with HA-starch

The shift of diaspore bands at 2 119 cm^{-1}, 1 088 cm^{-1}, 970 cm^{-1} to 2 121 cm^{-1}, 1 078 cm^{-1} and 968 cm^{-1} respectively, may be attributable to the hydrogen bond between the diaspore and HA-starch.

The shift of HA-starch band at 1 597 cm^{-1}, 1 403 cm^{-1} to 1 650 cm^{-1} and 1 456 cm^{-1} respectively, may be due to the chemical interaction between HA-starch and diaspore.

In the infrared spectra of kaolinite treated with HA-starch, the characteristic peak of HA-starch at 1 597 cm^{-1}, 934 cm^{-1}, 835 cm^{-1} shifted, so chemical adsorption may also takes place between kaolinite and HA-starch.

Infrared spectra of diaspore and kaolinite treated with starch is different from that of diaspore and kaolinite untreated with reagent. There appear new peaks, which means the reagents were adsorbed on the mineral surface. But the bands shifted always related to the vibration of O —H, it indicates that there is hydrogen bond between minerals and the starch.

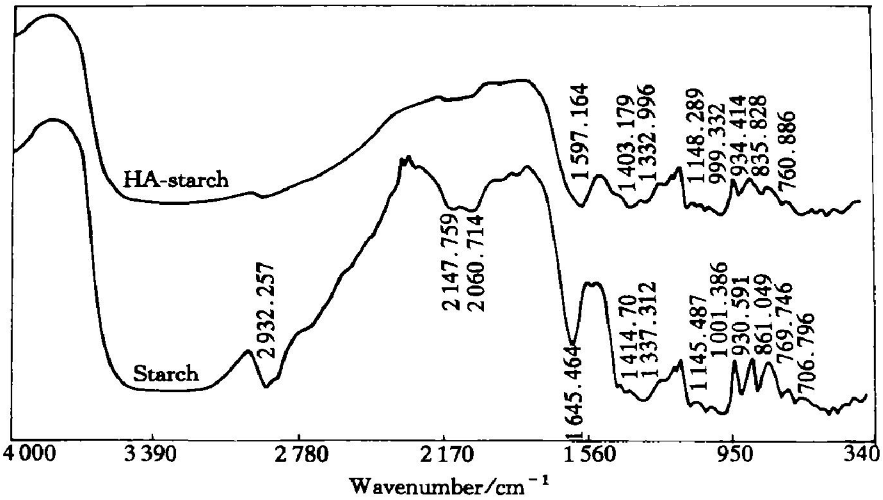

Fig. 6 FTIR spectra of starch and HA-starch

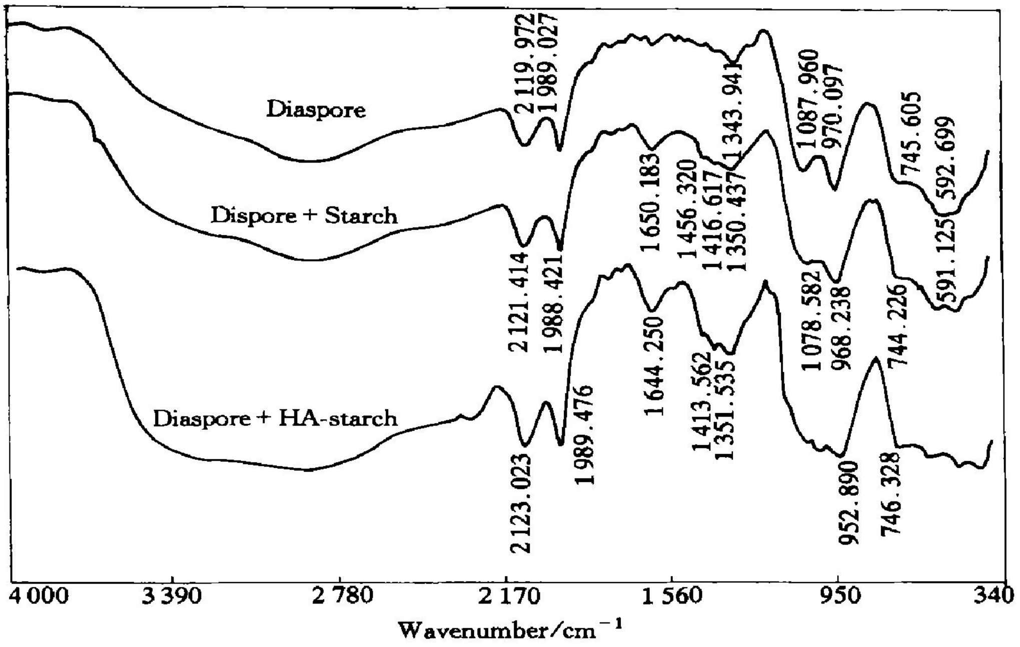

Fig. 7 FTIR spectra of diaspore in presence and absence of starch and HA-starch

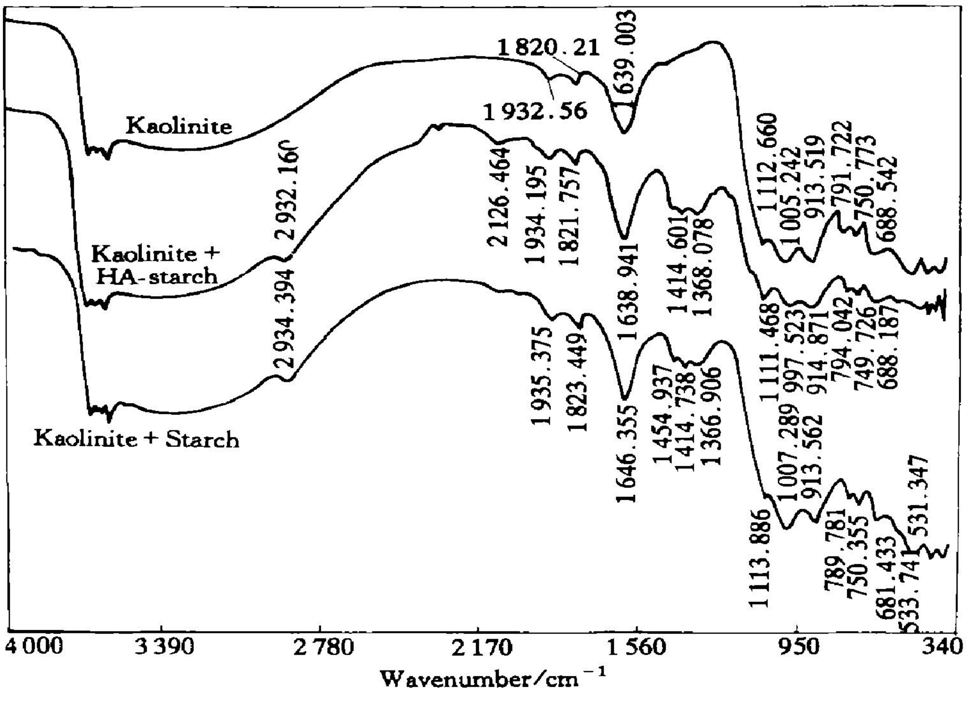

Fig. 8 FTIR spectra of kaolinite in present with starch and HA-starch

The study on the breakage bonds of diaspore and kaolinite shows that there are plenty of broken Al—O bonds on the surface of diaspore while there are a few on the surface of kaolinite. Al is belong to hard acid element, it is easy to react with reagents which have high electronegativity groups. The HA-starch has a lot of hydroxamic groups and carboxyl groups. The electronegativity of these groups is over 4.0, which can react with Al^{3+}. So HA-starch can depress diaspore flotation effectively.

4 CONCLUTIONS

1) The starch ramification ——HA-starch can be prepared by two-steps of the synthesis of CMSE, and the CMSE reacts with hydroxylamine and exhibits a better flotation property;

2) HAS demonstrates a good depressing effect on diaspore flotation while plays some active effect on kaolinite flotation at pH below 6.

3) Water soluble HAS adsorbs on the surface of diaspore mainly by chemical adsorption or hydrogen bonding. It affects the zeta potential of diaspore and makes diaspore particle surface hydrophilic, resulting in decreasing of recovery of diaspore.

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