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Effect and mechanism of diphosphonic acid on flotation characteristic of fersmite and intergrowth gangue①

REN Hao(任 浩), JI Fei-fei(纪绯绯), ZHANG Shu-xiang(张书香),
(School of Chemistry and Chemical Engineering, Ji'nan University, Ji'nan 250022, China)

Abstract: The effect of several collectors and their dosage on the flotation characteristics of the synthetical fersmite at different pH values, the collecting strength and selectivity of several representative collectors were investigated. The experimental results indicate that diphosphonic acid is a good collector for fersmite and recovery of fersmite ranges from 83.27% to 85.10% when the pulp pH value is at 2.5－5.0 and the dosage is 20 mg/L. The rank sequence of selectivity for several collectors is as follows: diphosphonic acid > benzyl arsonic acid > α-styrolphosphonic acid> alkyl hydroximic acid (C_{7-9}) > cyclic alkyl hydroximic acid. At the same time, Infrared Absorption Spectrum (IAS) and X-ray Photoelectron Spectroscopy (XPS) were used to detect and analyze the action mechanism of diphosphonic acid on fersmite. IAS results show that the characteristic absorption peak relating to P═O as well as P—O vibration occurs between wave number 1 178 cm^{-1}, 1 142 cm^{-1}, 1 087 cm^{-1} and 934 cm^{-1}, and diphosphonic acid is adsorbed on the surface of fersmite. XPS results indicate that the binding energy of P 2p peak of fersmite treated by diphosphonic acid is increased by 3.85 eV. It is proved that the adsorption is mainly chemical adsorption.

Key words: flotation; collector; diphosphonic acid; fersmite
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1 INTRODUCTION

The reserves of niobium-containing minerals in China take the second place in the world, and distribute mainly in Baiyunebo of Inner Mongolia, Taimei of Guangdong Province and Yichun of Jiangxi Province, etc. Niobium-containing minerals were discovered over 130 kinds, but only a few of them had industrial value. Fersmite is one of the several valued industrial niobium-containing minerals[1, 2].

The processing of niobium-containing minerals is too difficult due to their fine size and numerous species and complex composing. In middle period of last century, niobium tapiolite was mainly reclaimed by physical separations, such as gravity separation, electromagnetic separation. But it is difficult for gravity separation to process primary slime and secondary slime of niobium tapiolite as well as low-grade fine particles disseminated minerals. Nowadays, flotation is an effective and economical mineral processing and is widely used for processing niobium-containing in the practical application.

For different minerals, high selectivity flotation reagents depend on good flotation effect, especially high selectivity collectors. In recent years, a lot of research works have been done in the study and application of high selectivity collectors, and some high selectivity collectors for niobium-bearing minerals have been discovered and invented. The reagents have obtained better results in the research and production.

In this paper, typical and high selectivity collectors are selected and their collecting properties are investigated. At the same time, the optimum collector is got and its action mechanism is analyzed.

2 EXPERIMENTAL

2.1 Experimental sample

It is much difficult to obtain pure fersmite from original mineral. So pure fersmite was synthesized by oxidation-baking[3]. The fersmite synthesized is a colourless transparent crystal or white powder. The main component of the fersmite was $CaNb_2O_6$, as shown in Fig. 1. The result of chemical analysis indicated that the purity of the sample could be up to 99.48% when Nb_2O_5 was 82.15% in the fersmite and the sample could meet the need of the experiment. In the meanwhile, the results of X-ray diffraction and the correlation data of diffraction intensity (I) and crystal surface distance (d) testified that the sample has better representation(Fig. 1 and Table 1)[4]. In Table 2, it was shown that the summary of intergrowth gangue with fersmite and the datum also showed that the intergrowth gangue could meet the need of the experiment.

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Correspondence: REN Hao, PhD; Tel: +86-531-2765959; E-mail: rhjf@sina.com

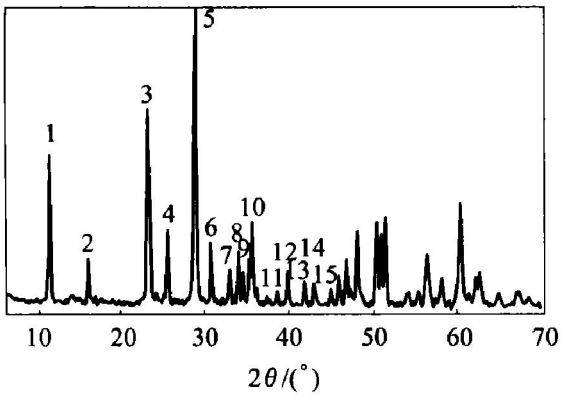

Fig. 1 X-ray diffraction pattern of synthetical fersmite powder

Table 1 Analysis data of X-ray diffraction on synthetical fersmite powder

Sequence number	Measured data		Standard data*	
	d/Å	I/I_0	d/Å	I/I_0
1	7.506	21	7.470	40
2	5.381	8	5.340	20
3	3.770	27	3.950	60
4	3.440	11	3.428	20
5	3.060	100	3.049	100
6	2.879	10	2.863	30
7	2.688	6	2.681	10
8	2.612	9	2.606	20
9	2.574	6	2.564	10
10	2.520	8	2.510	30
11	2.498	12	2.498	30
12	2.316	3	2.306	10
13	2.250	6	2.242	20
14	2.091	5	2.090	20
15	1.768	7	1.768	50

* JCPDS(18-302)

Table 2 Intergrowth gangue with fersmite

Name	Producing area	Purification method	Density/ ($g \cdot cm^{-3}$)	Purity/ %
Limonite	Tongguanshan region, Anhui Province	Comminution-ore sorting-porcelain ball grinding-screening	4.034	95.8
Nephelite	Baiyunebo region, Inner Mongolia	Shaking tabe-wetting high intensity magnetic-screening	3.552	95.0
Dolomite	Laiyang region, Hunan Province	Comminution-ore sorting-porcelain ball grinding-screening	2.843	98.2

2.2 Experimental reagents

According to correlative information[5-7] and tested experience[8, 9], some typical acids for niobium-containing minerals separation should be selected on purpose, such as arsonic acids, phosphonic acids and hydroximic acids. In a word, benzyl arsonic acid, α-styrolphosphonic, diphosphonic acid, cyclic alkyl hydroximic acid, alkyl hydroximic acid were selected as collectors for the sample.

2.3 Experimental scheme

2.3.1 Experimental equipment

The XFGC-80 aeration flotation cell was used in the fersmite flotation. The volume of the cell was 70 mL. The pulp temperature was controlled at 25 - 30 ℃ and the rotation speed of the impeller was fixed at 2 000 r/min.

2.3.2 Experimental step

1) Weighing sample 1.000 g, the degree of accuracy was 1 mg;

2) Adding 65 mL deionized water in the flotation cell, agitating for 2 min and adjusting pH value in th pulp to preset value;

3) Adding predetermined amount of collector, agitating for 4 min;

4) Adding a drop of frother and agitating for 1 min pneumatically;

5) Skimming froth for 3 min, the speed of froth skimmer was 35 r/ min;

6) Filtering and drying froth and bottom-flow, weighing and recording. If necessary, these products should be examined chemically.

The pulp was adjusted continuously to keep the constant pH value in the flotation operation. The pH regulating agent was sodium hydroxide (1%, mass fraction) and sulfuric acid (1%, mass fraction). Collector solution of fitting mass fraction was put into the cell by pipet and foaming agent by syringe with pipe-needle.

3 FLOATING TEST AND RESULTS

Effect of different collectors on the recovery of four minerals is shown in Fig. 2. Four minerals could not be separated effectively each other when benzyl arsonic acid, cyclic alkyl hydroximic acid, alkyl hydroximic acid (C_{7-9}) and α-styrolphosphonic acid were used as collector (Figs. 2 (a) - (d)). However, diphosphonic acid showed the good selectivity when it was used as collector of the niobium-containing minerals. Nephelite was hardly floatable when pH value was at 2.0 - 11.0. The recovery of dolomite was up to maximum at pH 6.0 and it decreased obviously when pH value was less than 6.0. The recovery of fersmite was from 82.3% to 85.2% when pH value was at 2.5 - 5.0. In the meanwhile, Fig. 2 (e)

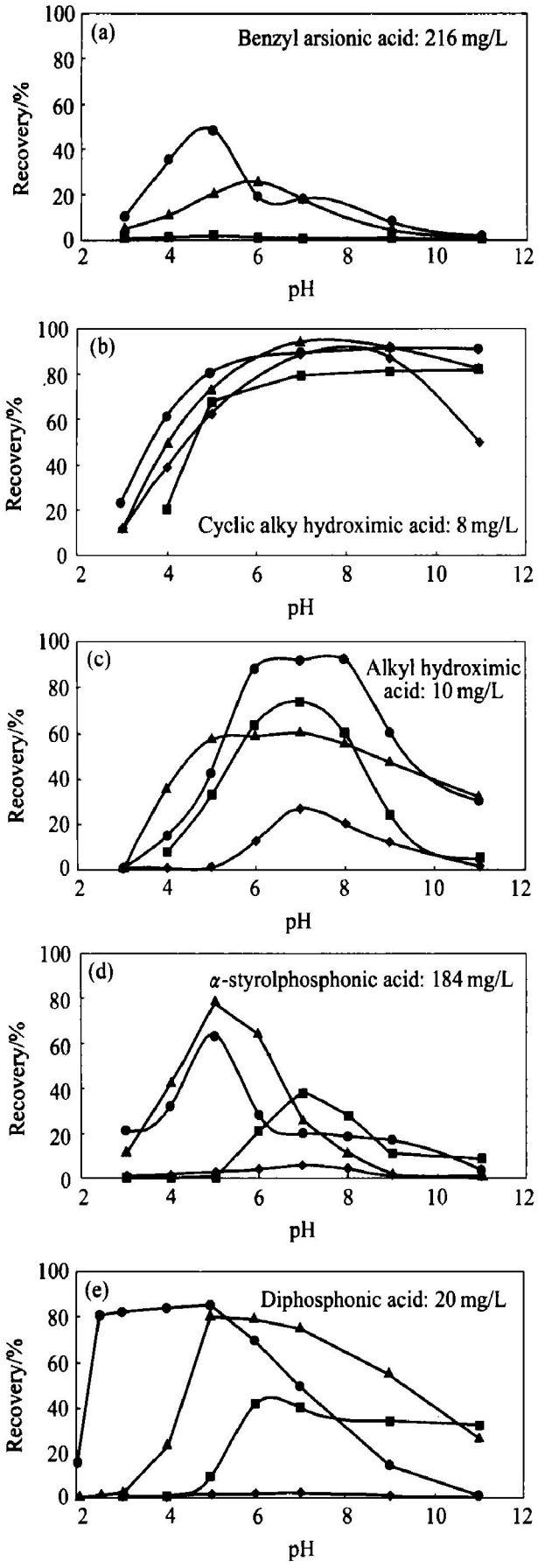

Fig. 2 Relationship between pH value and recovery of different minerals with different collectors
●—Fersmite; ▲—Limonite;
◆—Nephelite; ■—Dolomite

shows that fersmite could be separated effectively from its intergrowth gangue when pH value was at 2.0 – 4.0, and the results of repeated tests attested its reliability. The rank sequence of selectivity of different collectors is diphosphonic acid > benzyl arsonic acid> α-styrolphosphonic acid> alkyl hydroximic acid (C_{7-9}) > cyclic alkyl hydroximic acid .

Fig. 3 shows that the effects of different concentration of collectors on the recovery of fersmite at their optimum pH value. The rank sequence of collecting ability of the collectors is cyclic alkyl hydroximic acid > alkyl hydroximic acid (C_{7-9}) > diphosphonic acid > α-styrolphosphonic and > benzyl arsonic acid.

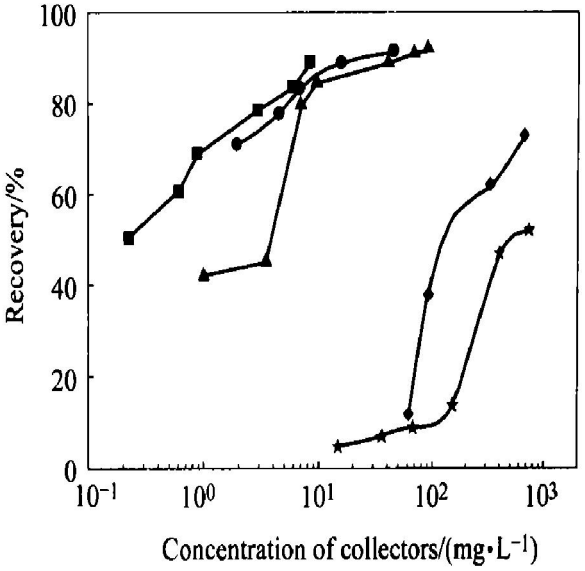

Fig. 3 Effects of collector concentration on recovery of fersmite at optimum pH value
■—Cyclic alkyl hydroximic acid (pH= 7.0);
●— Alkyl hydroximic acid (pH= 6.0);
▲—Diphosphonic acid (pH= 5.0);
◆—α-styrolphosphonic acid (pH= 5.0);
★—Benzyl arsonic acid (pH= 5.0)

Diphosphonic acid had good collecting property for fersmite between pH 2.5 and 5.0, while it could decrease remarkably the recovery of fersmite when pH value was more than 5.0 or less than 2.5.

4 MECHANISM ANALYSIS

The action mechanism of diphosphonic acid for fersmite was studied by the determination of Infrared Absorption Spectrum (IAS) and X-ray Photoelectron Spectroscopy (XPS).

4.1 IAS Determination[10, 11]

The bonding atom of functional group and reagent adsorption form could be identified by IAS. The test sample was fersmite and fersmite treated by diphosphonic acid.

4.1.1 Preparation of sample for IAS determination

a) The preparation of sample untreated for determination. First, fersmite was ground primarily in an agate mortar and then 1.000 g sample was taken for determination.

b) The sample treated by chemical agent for determination

1) Fersmite was ground completely in advance in an agate mortar to make the size of sample less than 2 μm in order to enlarge the surface area of fersmite. This would benefit adsorption of diphosphonic acid.

2) 150 mL diphosphonic acid of 1.0% was prepared in 200 mL beaker and pH value was adjusted to 5.0.

3) Adding 2.000 g ground fersmite into the beaker, agitating for 2.0 h, controlling temperature at 25 – 30 ℃, adjusting pH value continuously to keep pH 5.0.

4) Solid-liquid separation was done by a centrifugal filter. Filter liquor was drained.

5) The filter cake was washed by deionized water whose pH value was 5.0. Such washing had been done for 5 times to make the solvent reagents in the liquid to the minimum degree.

6) The sample was dried below 30 ℃ and kept in the air for determination.

4.1.2 IAS spectrum graph of fersmite and fersmite treated by diphosphonic acid

Fig. 4 and Fig. 5 show that the IAS spectra of fersmite and fersmite treated by diphosphonic acid. The difference spectrum of fersmite and fersmite treated by diphosphonic acid is shown in Fig. 6.

The characteristic absorption peaks related to methyl and methylene vibration appeared respectively at 1 465 cm^{-1}, 2 854 cm^{-1}, 2 925 cm^{-1} and 2 957 cm^{-1} (as shown in Fig. 5). The characteristic absorption peaks related to P═O and P—O vibration emerged at 1 178 cm^{-1}, 1 142 cm^{-1}, 1 087 cm^{-1} and 934 cm^{-1} (as shown in Fig. 6). Comparing Fig. 4 with Fig. 5, you could find the peak position of P—O characteristic absorption changed by 25 cm^{-1}. The change was remarkable, and it was enough to testify that diphosphonic acid had happened to adsorption on the surface of fersmite. It is necessary to do further analysis and study with XPS in order to research the mechanism of reagent adsorption.

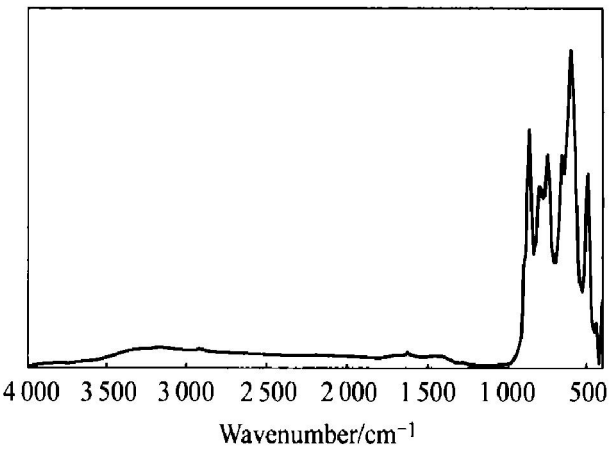

Fig. 4 IAS spectrum of fersmite

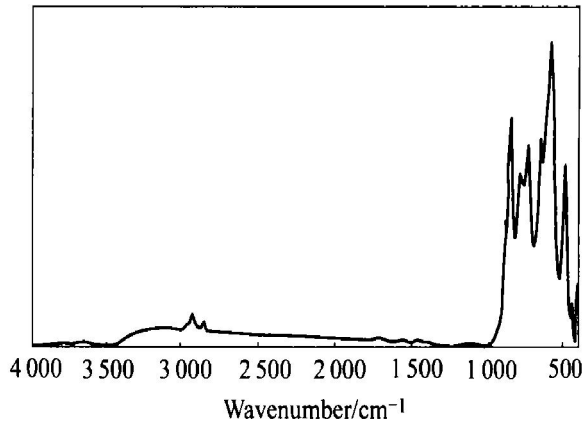

Fig. 5 IAS spectrum of fersmite treated by diphosphonic acid

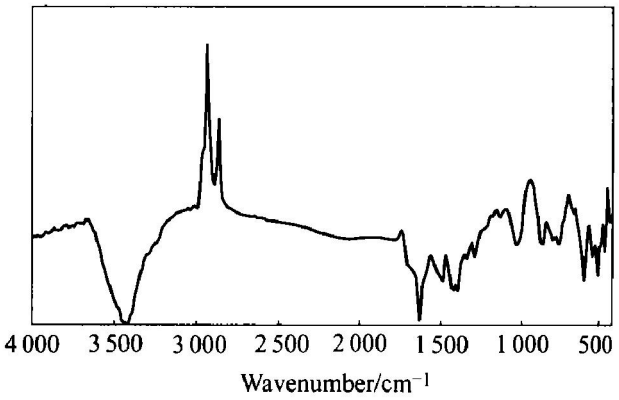

Fig. 6 Difference spectrum of fersmite and fersmite treated by diphosphonic acid

4.2 XPS determination[11]

Diphosphonic acid is mostly comprised of phosphorus, carbon, hydrogen and oxygen, etc. Neither oxygen nor carbon could become the criterion of the existence of diphosphonic acid because the carbon pollution could not be avoided from the surface of mineral, and oxygen was an innate component of all minerals. In addition, hydrogen without inner layer electron could not be tested by XPS. Therefore, the existence of diphosphonic acid on the surface of fersmite could only be decided by phosphorus element.

The process of the sample preparation for XPS determination was the same as that of sample preparation for IAS determination.

Fig. 7 and Fig. 8 show that the XPS complete spectra of fersmite and fersmite treated by diphosphonic acid, respectively.

The energy peaks of inherent Nb, O, Ca and polluted C appear in Fig. 7. P 2p and C 1s peaks are

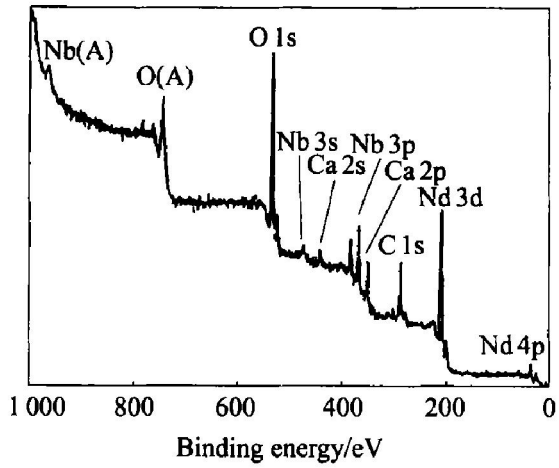

Fig. 7 XPS complete spectroscopy of fersmite

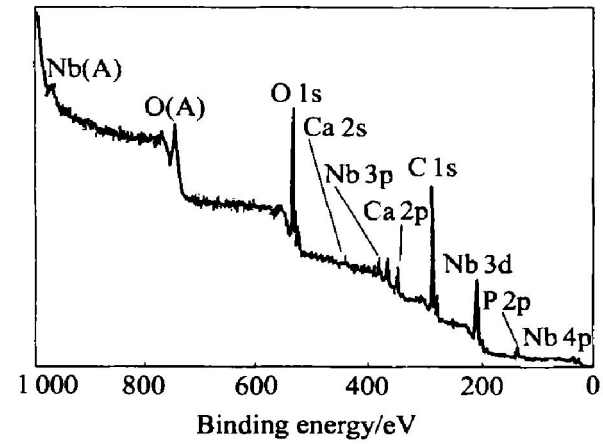

Fig. 8 XPS complete spectroscopy of fersmite treated by diphosphonic acid

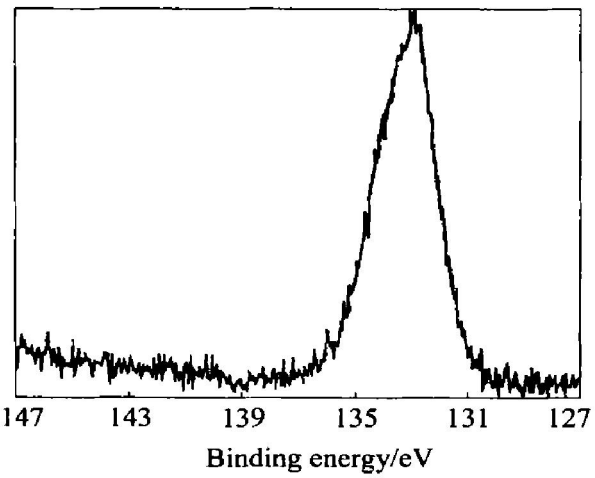

Fig. 9 P 2p peak on diphosphonic acid

shown in Fig. 9. C 1s peak was intensified observably and other elements peaks were weakened.

The atom fraction on the surfaces of fersmite and fersmite treated by diphosphonic acid are listed in Table 3.

The atom fraction of P / Nb increased from 0.01% to 0.96% after fersmite was treated, and that of C/Nb upgraded from 3.06% to 12.30%. This indicates that the atom fraction of phosphorus and carbon on the surface of fersmite was remarkably increased after fersmite had been treated by diphosphonic acid. The reagent adsorption mode at P 2p peak position is further specified in Fig. 9 and Fig. 10.

Table 3 Atom fraction on fersmite surface

Sample	Ca/Nb	P/Nb	C/Nb	O/Nb
Fersmite	0.47	0.01	3.06	3.57
Fersmite treated	0.68	0.96	12.30	6.02

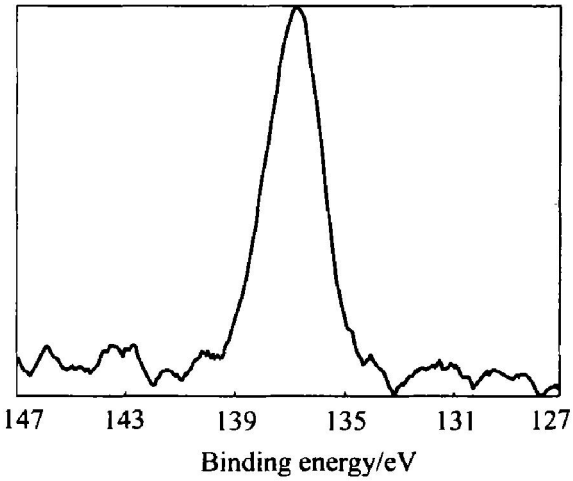

Fig. 10 P 2p peak on treated fersmite

The peak value was 132.95 eV in Fig. 9 and 136.80 eV in Fig. 10. The difference was 3.85 eV. This indicates that the P 2p peak position of fersmite treated by diphosphonic acid had changed obviously and the chemical displacement of phosphorus had happened. Therefore, it is proved that diphosphonic acid adsorbs on the surface of fersmite to make the atom fraction of phosphorus increase. Finally, it is testified that the main adsorption of diphosphonic acid on the surface of fersmite was chemical adsorption.

5 CONCLUSIONS

1) Diphosphonic acid is the optimum collector of several collectors for fersmite. The recovery of fersmite is from 83.27% to 85.10% when dosage is 20 mg/L at pH 2.5 ~ 5.0 .

2) Diphosphonic acid is the good selectivity collector for fersmite. The rank sequence of selectivity of different collectors is diphosphonic acid > benzyl arsonic acid> α-styrolphosphonic acid > alkyl hydroximic acid(C_{7-9}) > cyclic alkyl hydroximic acid .

3) The collecting property of diphosphonic acid is superior to other collectors. The rank sequence of collecting ability for several collectors is cyclic alkyl hydroximic acid> alkyl hydroximic acid (C_{7-9}) > diphosphonic acid> α-styrolphosphonic and > benzyl

arsonic acid.

4) IAS determination analysis shows that the characteristic absorption peak relates to P ═ O and P —O occurred at 1 178, 1 142, 1 087 and 934 cm^{-1}. This means the adsorption of diphosphonic acid on the surface of fersmite has happened.

5) XPS determination analysis indicates the binding energy at P 2p peak position for fersmite and fersmite treated by diphosphonic acid is changed by 3.85 eV. It is obviously proved that the adsorption mode of reagent is chiefly chemical adsorption.

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