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Collecting property of diphosphonic acid for niobite

Hao Ren, Feifei Ji, Guilan Song, and Shuxiang Zhang

School of Chemistry and Chemical Engineering, Jinan University, Jinan 250022, China

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Abstract: The effect of several collectors on the niobite synthetized under the condition of varying pH values and dosages were studied. The collecting property of several representative collectors was also investigated. The experimental result shows that diphosphonic acid is a good collector for niobite. Its recovery is about 84.24%-91.17% when the pH value of the pulp is less than 5.0 and the dosage of diphosphonic acid is 140 mg/L. The sequences of the selectivity and collecting capacity of the collectors were compared. Infrared absorption spectrum (IAS) and X-ray photoelectron spectroscopy (XPS) were used to detect and analyze the adsorption mechanism of diphosphonic acid on the surface of niobite. The IAS result indicates that diphosphonic acid is indeed adsorbed on the surface of niobite, and the XPS result shows that the binding energy of P_{2p} peak of niobite treated by diphosphonic acid has changed 2.85 eV. It confirms that the adsorption belongs to a chemisorption type.

Key words: collector; diphosphonic acid; niobite; collecting property

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. Over 130 types of niobium-containing minerals were discovered, but only a few of them had industrial value, niobite was one [1-3].

The processing of niobium-containing minerals was very difficult due to the fine mineral particle size and complicated composition. In the middle period of last century, niobium-containing tapiolite was mainly reclaimed by physical separations, such as gravity separation, electromagnetic separation *etc.* But it was difficult for gravity separation to process the primary slime and secondary slime of niobium-containing tapiolite as well as low-grade fine particle disseminated minerals. Nowadays, flotation is an effective and economical mineral processing method and is widely used for processing the niobium-containing minerals in practical applications.

For different minerals, highly selective flotation reagents decide the flotation effect, especially high selective collectors. In recent years, a lot of work has been done on the application of high selective collectors, and some high selective collectors for niobium-bearing minerals have been discovered and invented. The reagents have obtained better results in research and production.

Some typical and highly selective collectors were chosen and their collecting properties were investigated in this paper. At the same time, the optimum collector was picked out and its reaction mechanism was discussed.

2 Experimental

2.1 Sample

Niobite is a useful mineral, and dolomite is the intergrowth gangue with niobite.

(1) Preparation of niobite.

It was too difficult to obtain pure niobite from original mineral. Therefore pure niobite was synthesized by de-oxidation-baking method [4-5]. The synthesized niobite is a gray crystal or black crystal, and the crystal size is about 2.0 mm. The result of chemical analysis indicates that the purity of the sample is up to 95.84% and can meet the need for the experiment. In the meanwhile, the results of X-ray powder crystal diffraction and the correlation data of diffraction intensity (I) and crystal surface distance *(d)* have testified that the sample has better representation [6-7] (see **figure 1** and **table 1).**

(2) Preparation of dolomite.

Dolomite is mostly the intergrowth gangue with niobite. It was from the Leiyang region, Hunan province, China. Its density is 2.843 g/cm^3 and its purity is 98.2%.

Corresponding author: Hao Ren. E-mail: rhjf@sina.com

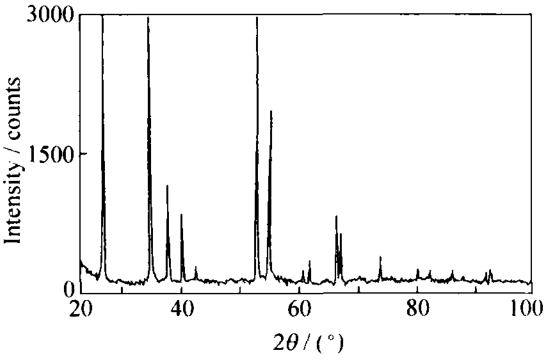

Figure 1 Graph of X-ray powder crystal diffraction for synthetic niobite.

Table 1 Analysis data of X-ray powder crystal diffraction for synthetic niobite

Sequence number	Standard data		Measured data	
	d_s / nm	I / I_0	d_r / nm	I / I_0
1	0.3230	100	0.3242	100
2	0.2557	70	0.2558	50
3	0.2350	12	0.2352	16
4	0.2246	10	0.2233	12
5	0.2101	2	0.2105	4
6	–	–	0.2047	2
7	–	–	0.1805	2
8	0.1730	40	0.1742	55
9	0.1661	10	0.1653	25
10	0.1524	3	0.1515	4
11	0.1485	5	0.1479	6
12	0.1393	10	0.1390	12
13	0.1385	10	0.1375	10
14	0.1335	1	0.1335	2
15	0.1278	4	0.1285	6

All the samples were prepared by comminution, ore sorting, porcelain ball grinding, screening and splitting so that they could pass through 325-mesh screen. The datum also showed that all the samples could meet the demand of the experiment.

2.2 Reagents

According to the correlative information [8-10] and test experience [11-13], some typical acids for niobium-containing minerals were selected on purpose, such as benzyl arsonic acid, alkyl hydroximic acid ($C_{7\text{-}9}$), α-styrolphosphonic, diphosphonic acid and alkyl sulfonated amber acid were selected as collectors for the sample. Hydrochloric acid and sodium hydroxide were used to adjust the pH value.

23 Scheme

The XFGC-80 aeration flotation cell was used for **the** niobite flotation. The volume of the cell was 70 m**L. The pulp** temperature was controlled between 25-30°C **and** the rotation speed of the propeller was fixed **at 2000** r/min. The pulp pH value and reagent dosages are the principal factors affecting the mineral flotation besides the reagent types.

The pulp was adjusted continuously to keep the pH value constant in the flotation operation. The pH regulating agents were sodium hydroxide (1wt%) and hydrochloric acid (1wt%). The fitting collector dosage was added into the cell by pipe, then a little drop of foaming agent was added by syringe needle.

3 Flotation test

Figure 2 shows the effect of different collectors on the recovery of two minerals. The two minerals could not be separated effectively when benzyl arsonic acid, alkyl hydroximic acid ($C_{7\text{-}9}$), α-styrolphosphonic acid, and alkyl sulfonated amber acid were used as the collectors (see figures 2(a)-(c) and (e)). However, diphosphonic acid shows a better selectivity. Figure 2(d) shows that niobite can be separated effectively from dolomite. The recovery of dolomite is about 24%-40% and that of niobite is about 84.24%-91.17% when the pH value is less than 5.0. The recovery difference goes to enlarge in strong acid pulp. And the results of repeat tests attest its reliability.

From the curves in figure 2, the sequence of selectivity of different collectors is diphosphonic acid > benzyl arsonic acid > alkyl sulfonated amber acid > α-styrolphosphonic acid > alkyl hydroximic acid ($C_{7\text{-}9}$). Diphosphonic acid has a better collecting property to niobite in a strong acid pulp, and it can remarkably decrease the floatability of niobite in an alkaline pulp.

Figure 3 shows the effect of the collector concentration on the niobite recovery at an optimum pH value. It also shows that the sequence of collecting ability of the five collectors is alkyl hydroximic acid ($C_{7\text{-}9}$) > diphosphonic acid > alkyl sulfonated amber acid > benzyl arsonic acid > α-styrolphosphonic acid.

4 Mechanism analysis

The action mechanism of diphosphonic acid on niobite was studied by infrared absorption spectroscopy (IAS) measurement and X-ray photoelectron spectroscopy (XPS) determination.

4.1 IAS measurement [14-15]

The bonding atom of function group and the reagent absorbing form could be identified by IAS. The tested samples were niobite and the niobite treated by diphosphonic acid.

(1) The sample preparation for IAS measurement.

(a) Preparation of the sample untreated for determination. First, niobite was ground completely in an **ag-**

ate mortar to make the sample size less than 2 μm, then 1.0 g sample was taken for determination.

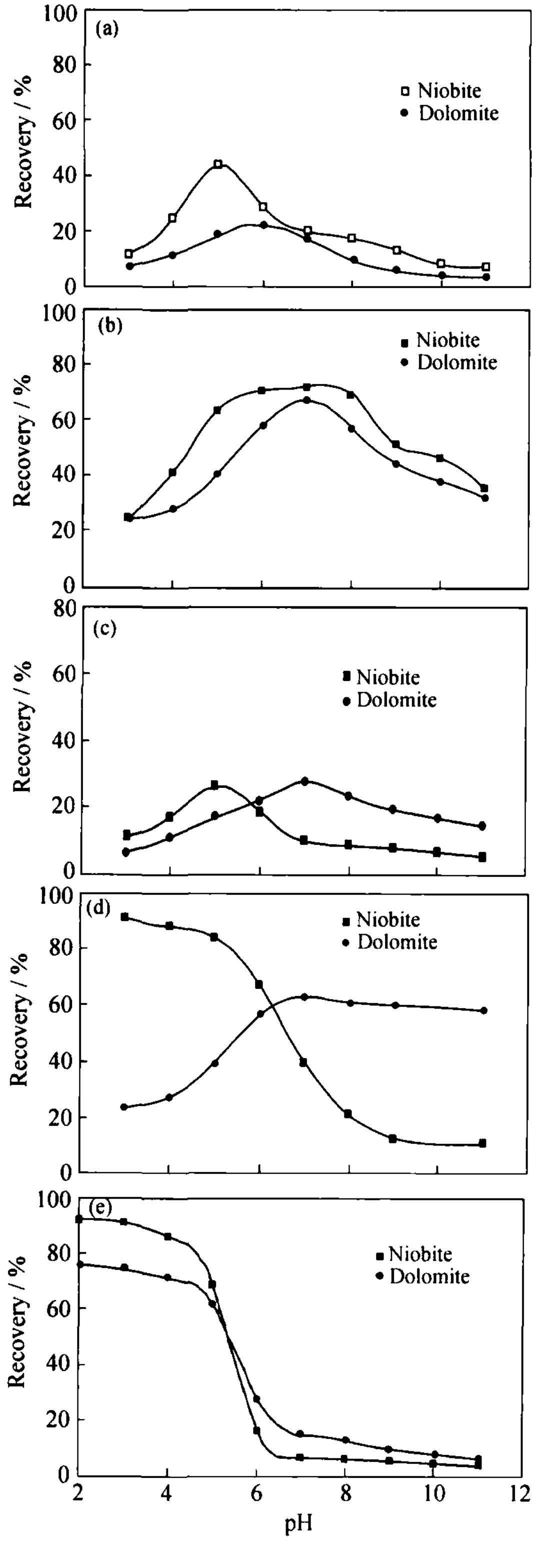

Figure 2 Effect of pH values on the recovery of niobite and dolomite with different collectors: (a) benzyl arsonic acid, 300 mg/L; (b) alkyl hydroximic acid, 100 mh/L; (c) α-styrolphosphonic acid, 400 mg/L; (d) diphosphonic acid, 140 mg/L; (e) alkyl sulfonated amber acid, 600 mg/L.

(b) The sample treated by chemical agent for determination.

I) The niobite was ground completely in advance in an agate mortar to make the sample size less than 2 μm in order to enlarge the surface area of niobite. The adsorption of diphosphonic acid would benefit from this.

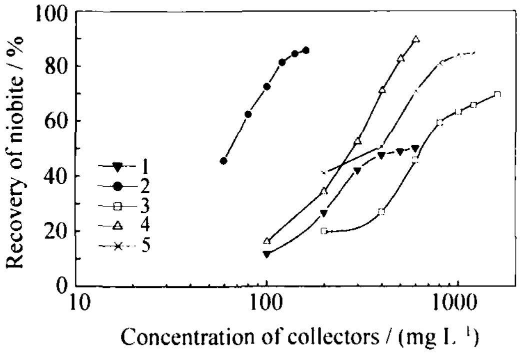

Figure 3 Effects of collector concentration on the recovery of niobite at an optimum pH value. 1—benzyl arsonic acid (pH=5.0); 2—C_{7-9} alkyl hydroximic acid (pH=7.0); 3—α-styrolphosphonic acid (pH=5.0); 4—diphosphonic acid (pH=5.0); 5—alkyl sulfonated amber acid (pH=7.0).

II) 150 mL 1.0wt% diphosphonic acid solution was prepared in a 200 mL beaker and the pH value was adjusted to 5.0.

III) Adding 2.000 g ground niobite into the beaker, agitating for 2 h, controlling the temperature between 25 and 30°C, and adjusting the pH value continuously at 5.0.

IV) The solid-liquid separation was done by a centrifugal filter. The filter liquor was drained.

V) The filter cake was washed by the de-ionized water whose pH value was 5.0. Such washing was done 5 times to make the solvent reagents in the liquid to the minimum degree.

VI) The sample was dried below 60°C and kept in an airer for determination.

(2) The IAS spectrum graph of niobite and the niobite treated by diphosphonic acid

Figures 4-6 show the IAS spectrum graphs of diphosphonic acid, niobite, and the niobite treated by diphosphonic acid.

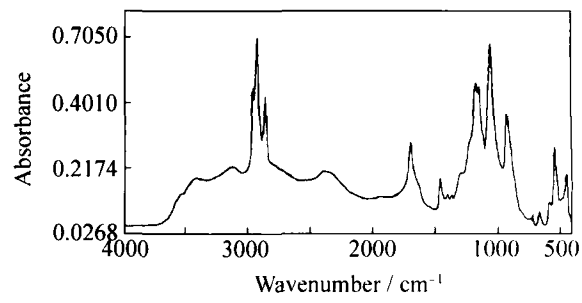

Figure 4 IAS spectrum of diphosphonic acid.

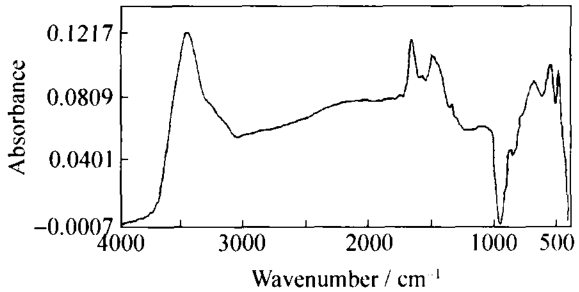

Figure 5 IAS spectrum of niobite.

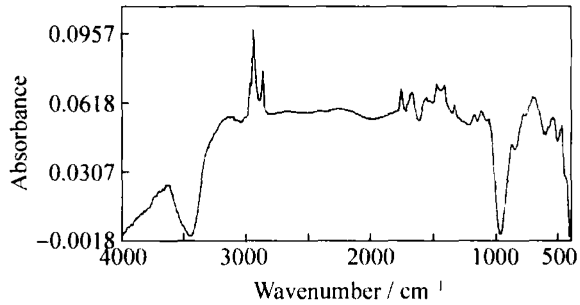

Figure 6 IAS spectrum of the niobite treated by diphosphonic acid.

Comparing figures 5 with 6, the shape of the IAS spectrums graph of niobite and the niobite treated by diphosphonic acid are different observably. The characteristic absorption peaks related to methyl and submethyl vibration appear at 2957, 2924, and 2854 cm^{-1} respectively in figure 6. It shows that some organics were absorbed. Otherwise, the characteristic absorption peaks related to P-O vibration emerge at 1049, 1115, and 1169 cm^{-1} respectively in figure 6. It is well known that the characteristic absorption peak related to P-O vibration emerges at 1062 cm^{-1} in figure 5, and emerges at 1049 cm^{-1} in figure 6. It can be found that the peak position of P-O characteristic absorption changes 13 cm^{-1}. The change is remarkable. It is testified obviously that the diphosphonic acid had has been adsorbed on the surface of niobite. It is necessary to do further analysis with XPS in order to study the mechanism of reagent adsorption.

4.2 XPS determination

Diphosphonic acid mostly comprises of phosphorus, carbon, hydrogen and oxygen, *etc.* Neither oxygen nor carbon can be used as the criterion of the existence of diphosphonic acid because the carbon pollution can not be avoided from the surface of mineral, and oxygen is an innate component of all minerals. In addition, hydrogen without inner layer electrons can not be tested by XPS. Therefore, the existence of diphosphonic **acid** on the surface of niobite can only be decided by **phosphorus** element [15].

(1) **Preparation** of the sample for XPS determination.

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

(2) XPS complete spectra of niobite and the niobite treated by diphosphonic acid.

Figures 7 and **8** show the XPS complete spectra of niobite and the niobite treated by diphosphonic acid, respectively.

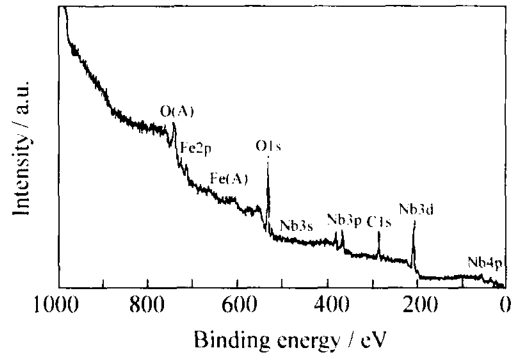

Figure 7 XPS complete spectroscopy of niobite.

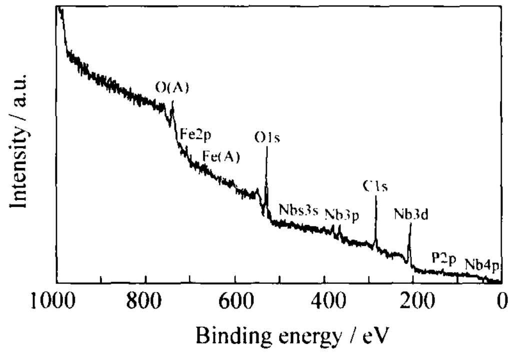

Figure 8 XPS complete spectroscopy of the niobite treated by diphosphonic acid.

The energy peaks of inherent Nb, Fe, O and polluted C appear in figure 7. P_{2p} and C_{1s} peaks appear in figure 8, and C_{1s} peak is intensified observably and other elements peaks are weaken observably. The atom ratios on the surfaces of niobite to the niobite treated by diphosphonic acid are listed in **table 2.**

Table 2 Atom ratios on the niobite surface

Sample	Te/Nb	P/Nb	C/Nb	O/Nb
Niobite	0.98	0.00	4.09	3.90
Niobite treated	0.85	0.37	10.09	4.99

The atom ratios of P/Nb increased from 0 to 0.37% after the niobite was treated, and that of C/Nb upgraded from 4.09% to 10.09%. This indicates that the atom ratios of P/Nb and C/Nb on the surface of the niobite increase remarkably after niobite has been treated by diphosphonic acid. The reagent adsorption form **at the** P_{2p} peak position is further specified in **figures 9 and 10.**

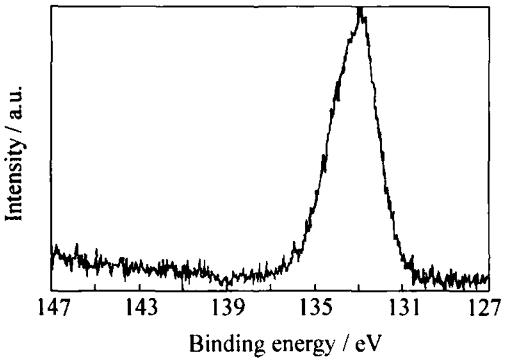

Figure 9 P_{2p} **peak on the diphosphonic acid.**

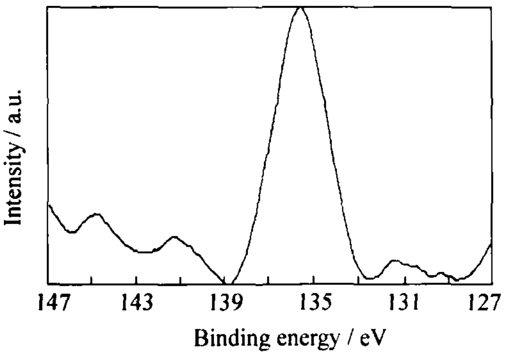

Figure 10 P_{2p} **peak on the niobite treated by diphosphonic acid.**

5 Conclusions

(1) Diphosphonic acid is the optimum collector for niobite. The recovery of niobite is between 84.24% and 91.17% at a dosage of 140 mg/L and the pH value less than 5.0.

(2) Diphosphonic acid is a good selective collector for niobite. The sequence of selectivity of different collectors is diphosphonic acid > benzyl arsonic acid > alkyl sulfonated amber acid > α-styrolphosphonic acid > alkyl hydroximic acid (C_{7-9}).

(3) The collecting property of diphosphonic acid is better than that of the other collectors tested. The sequence of collecting ability for several collectors is alkyl hydroximic acid (C_{7-9}) > diphosphonic acid > alkyl sulfonated amber acid > benzyl arsonic acid > α-styrolphosphonic acid.

(4) IAS measurements show that the characteristic absorption peak related to P-O emerges at 1049, 1115, and 1169 cm^{-1}. This indicates that the adsorption of diphosphonic acid on the surface of niobite has taken place.

(5) XPS determination analysis shows that the binding energy at the P_{2p} peak position for niobite and the niobite treated by diphosphonic acid has changed 2.85 eV. It is confirmed that the adsorption of the reagent belongs to a chemisorption type.

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