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Effects of diphosphonic acid on ilmenorutile collecting property and research of action mechanism

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Abstract: The effects of several collectors and their dosage on pure ilmenorutile at different pH values were studied and the collecting strength of several representative collectors was investigated. The experimental results indicate that diphosphonic acid is a good collector for ilmenorutile and the recovery of ilmenorutile ranges from 90.87% to 91.70% when the pulp pH value is 2.0-4.0 and the dosage is 75 mg/L. The sequence of collecting ability for several collectors is as follows: diphosphonic acid > TF279 > cyclic alkyl hydroximic acid > benzyl arsenic acid > salicylic hydroximic acid > alkyl hydroximic acid. Meanwhile, IAS (infrared absorption spectrum) and XPS (X-ray photoelectron spectroscopy) were used to detect and analyze the action mechanism of diphosphonic acid on ilmenorutile. IAS results showed that the characteristic absorption peak relating to P = O as well as P–O vibration occurred between wave numeber1 140 and 1 032 cm^{-1}, and diphosphonic acid had adsorbed on the surface of ilmenorutile. XPS results indicated that the binding energy of P2*P* peak of ilmenorutile had changed 0.45 eV after treated by diphosphonic acid. This proves that the adsorption is mainly chemical adsorption.

Key words: collector; diphosphonic acid; ilmenorutile; action mechanism

1 Introduction

So far, more than 130 niobium-containing minerals have been discovered, but only several kinds of niobium-containing minerals have industrial value, one of which is ilmenorutile. In 1950s and 1960s, niobium tapiolite was mainly recovered by physical separations, such as gravity separation, electromagnetic separation. But it was 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 ore-dressing separation and is widely used for processing niobium tapiolite in practical application [1].

High selective flotation reagents to different minerals depend on better flotation effects, especially high selective collectors. In recent years, a lot of research works have been done in aspects of the study and application of high selective collectors, and some high selective collectors for niobium-bearing minerals have been discovered and invented such as phosphonic acid, alkyl hydroximic acid. The reagents have gained better results in the research and production [2].

Anionic collectors can be used for the flotation of niobium-bearing minerals and so can cationic collectors, such as representative amine type collectors. In this paper, several better typical and high selective collectors were selected and their collecting properties were examined, finally, the optimum collector was sought out and its action mechanism was analyzed.

2 Experimental

2.1 Experimental sample

Ilmenorutile sample was from Xinqi, Jiangsu province, China. Its density and specific magnetic rate are 4.344 4 g/cm^3 and 28.9×10^{-6} cm^3/g, respectively. By chemical analysis, its main composition is Ti, 50.41%; Nb_2O_5, 0.082%, and T_{Fe}, 4.40% (mass fraction). The ilmenorutile sample of -43 μm was prepared by crushing, grinding and splitting. 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 (see **figure 1** and **table 1**) [3].

2.2 Experimental reagents

According to relative information and test experience, some typical acid types, such as arsenic acid types, phosphonic acid types and hydroximic acid types for niobium-containing minerals should be selected on purpose. In a word, benzyl arsenic acid, TF-279, diphosphonic acid, cyclic alkyl hydroximic acid, alkyl hydroximic acid and salicylic hydroximic acid are selected as collectors for the sample.

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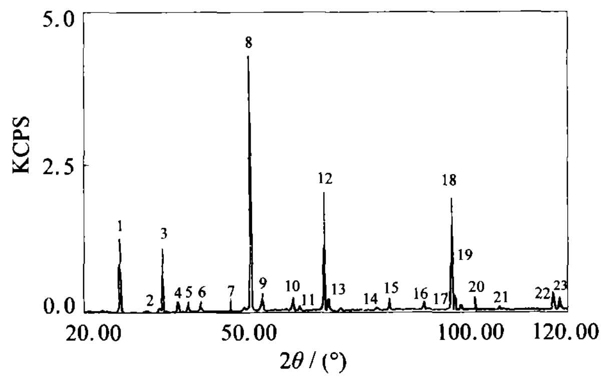

Figure 1 The graph of X-ray powder crystal diffraction on ilmenorutile.

Table 1 The analysis data of X-ray powder crystal diffraction on ilmenorutile [3]

Sequence number	Standard data		Reality measure data	
	d_s / nm	I/I_0	d_r / nm	I/I_0
1	0.2230	100	0.3274	30
2	0.2480	80	0.2484	26
3	0.2295	10	0.2296	5
4	0.2190	40	0.2181	5
5	0.2051	10	0.2052	4
6	0.1687	90	0.1684	100
7	0.1627	10	0.1622	8
8	0.1481	<10	0.1487	5
9	0.1454	<10	0.1454	2
10	0.1348	<10	0.1358	47
11	0.1096	<10	0.1093	3
12	0.1086	<10	0.1082	1
13	0.1041	<10	0.1042	45
14	0.0911	<10	0.0900	8
15	0.0903	<10	0.0900	6

2.3 Experimental scheme

(1) Experimental equipment. A XFGC-80 type aeration flotation cell was used in pure mineral flotation. The cell volume was 70mL. The pulp temperature was controlled between 25-30 ℃, and the impeller rotation speed was fixed at 2 000 r/min.

(2) Experimental step. Besides reagents type, pulp pH value and reagents dosage were principal factors affecting mineral flotation. According to the prime and second factor, firstly, pH test was done, and then reagents dosage test. The experiment step was as follows:

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

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

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

(d) Adding a drop of pine oil (frother) and agitating for 1 min pneumatically;

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

(f) 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 pH value constant 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 putting into the cell by pipet and foaming agent by syringe needle.

3 Floating test

Using benzyl arsenic acid, the maximum recovery of ilmenorutile was 63.64% (see **figure 2**) at pH 6.0. When TF-279 was used as collector, the recovery was seriously affected by pH value, it was up to 89.28% at pH 7.0. With diphosphonic acid, its recovery was kept between 90.87%-91.70% when the pH value was between 2.0 and 4.0. If pH value was over 4.0, the recovery would decrease obviously from 91.70% at pH 4.0 to 5.78% at pH 10.0. Using cyclic alkyl hydroximic acid, the maximum recovery was only 74.47% at pH 7.0. The collecting ability of alkyl hydroximic acid (C7) and salicylic hydroximic acid was weaker, the maximum recovery was 47.93% at pH 6.0 and 52.06% at pH 5.0, respectively.

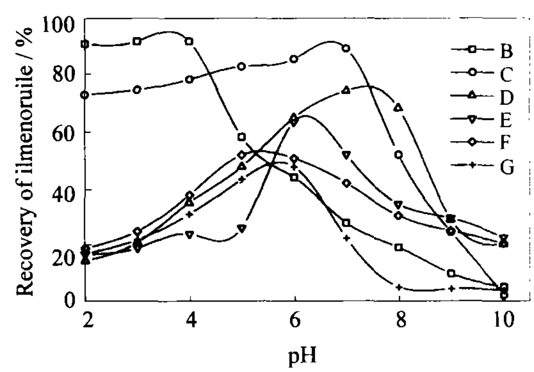

Figure 2 The effects of pH value on the recovery of ilmenorutile with different collectors, B: diphosphonic acid (50 mg/L); C: TF279 (80 mg/L); D: cyclic alkyl hydroximic (10 mg/L); E: benzyl arsionic acid (50 mg/L); F: salicylic hydroximic acid (5 mg/L); G: alkyl hydroximic acid (10 mg/L).

Figure 3 shows the effects of different concentration of collectors on the recovery of ilmenorutile at their optimum pH value. From curves in figure 2, the sequence of collecting ability of different collectors is diphosphonic acid > TF279 > cyclic alkyl hydroximic acid > benzyl arsenic acid > salicylic hydroximic acid > alkyl hydroximic acid.

Diphosphonic acid is that diphosphonic acid has better collecting property in strong acid pulp, but it can re-

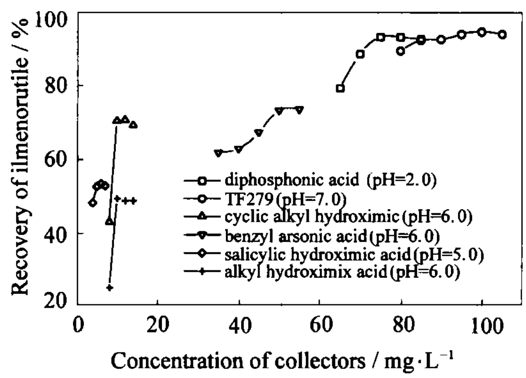

Figure 3 The effects of collector concentration on the recovery of ilmenorutile at their optimum pH value.

markably decrease the floatability of ilmenorutile in alkaline pulp.

4 Mechanism

The action mechanism of diphosphonic acid with ilmenorutile was studied by the determination of infrared absorption spectrum (IAS) and X-ray photoelectron spectroscopy (XPS).

4.1 IAS determination

The reagent adsorption type and bonding atom of functional group could be identified by IAS. The test sample were ilmenorutile and ilmenorutile treated by diphosphonic acid.

(1) The preparation of sample for IAS determination.

(a) The untreated sample preparation for determination. First, ilmenorutile was ground completely in an agate mortar and then 1.0 g sample was taken to determine.

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

1) Ilmenorutile was ground completely in advance in an agate mortar to make the sample as small as possible (about 2 μm) to enlarge the surface area of ilmenorutile. This would be benefit for adsorption of diphosphonic acid.

2) 150 mL diphosphonic acid of 1% (mass fraction) was prepared in a 200 mL beaker and pH value was adjusted to 2.0.

3) Adding 2.000 g ground ilmenorutile into the beaker, agitating for 2 h, controlling temperature between 25 and 30 ℃, adjusting pH value continuously to keep 2.0.

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 2.0. 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 a dryer for determination.

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

The IAS spectrum graph of ilmenorutile and ilmenorutile treated by diphosphonic acid was shown in **figure 4.**

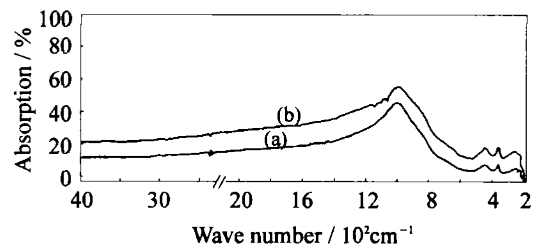

Figure 4 The IAS spectrum graph of ilmenorutile (a) and ilmenorutile treated by diphosphonic acid (b).

Meanwhile, the characteristic absorption peaks related to P=O and P–O vibration emerges at 1 140 and 1 032 cm^{-1}. The change of peak position signal is not remarkable, but it is enough to testify that diphosphonic acid has adsorbed onto the surface of ilmenorutile. In order to investigate the mechanism of reagent adsorption, it is necessary to do further analysis research with XPS [4].

4.2 XPS determination

Diphosphonic acid chemically consists of phosphorus, carbon, hydrogen and oxygen, *etc.* But as the carbon pollution can not be avoided from mineral surface, and oxygen is an innate component of all minerals, so neither oxygen nor carbon can become criterion of the existence of diphosphonic acid. In addition, hydrogen without inner layer electron can not be tested by XPS. Therefore, the existence of diphosphonic acid can only be decided by phosphorus.

(1) Sample preparation for XPS determination. The process of sample preparation for XPS determination is the same as that of sample preparation for IAS determination.

(2) The XPS complete spectrum of ilmenorutile and ilmenorutile treated by diphosphonic acid. **Figures 5** and **6** show the XPS complete spectrum of ilmenorutile and ilmenorutile treated by diphosphonic acid, respectively.

Figure 5 shows that the energy peaks of inherent Ti, O, Fe and polluted C appear. The content of Nb_2O_5 is so low in this sample and the niobium peak is not shown for the limited accuracy of the device. There occur P2*p* and C1*s* peaks in figure 6. C1*s* peak is intensified slightly and other element peaks are a little weak.

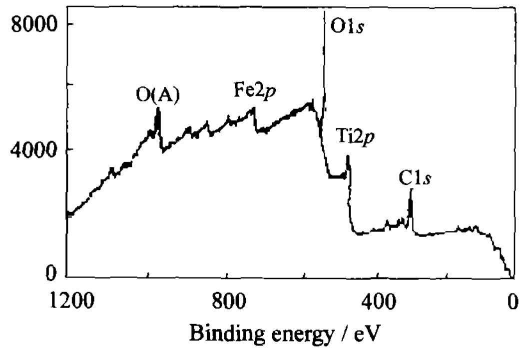

Figure 5 The XPS complete spectroscopy of ilmenorutile.

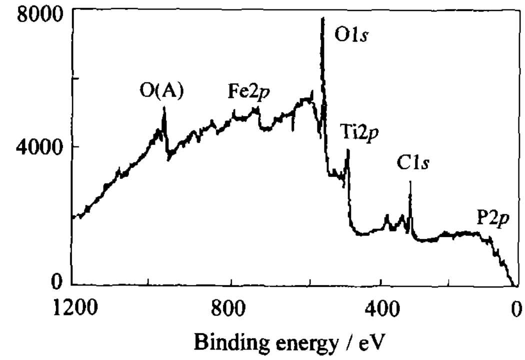

Figure 6 The XPS complete spectroscopy of ilmenorutile treated by diphosphonic acid.

The atom fraction on the surfaces of ilmenorutile and ilmenorutile treated by diphosphonic acid are listed in **table 2**.

Table 2 The atom fraction on the surface %

Sample	Ti2*p*	Fe2*p*	O1*s*	C1*s*	P2*p*
Ilmenorutile	14.74	3.52	45.09	36.65	0.00
Treated ilmenorutile	12.64	2.22	37.72	5.41	2.01

The atom fraction of P2*p* increased from zero to 2.01% after ilmenorutile was treated, and that of C1*s* upgraded from 36.65% to 45.41%. This indicates that the atom fraction of phosphorus and carbon on the surface of ilmenorutile is remarkably increased after ilmenorutile has been treated by diphosphonic acid. The reagent adsorption form at P2*p* peak position was further specified as shown in **figures 7** and **8**. The peak value is 132.50 eV in figure 7 and 132.95 eV in figure 8.

The difference is 0.45 eV. This indicates that the P2*p* peak position of ilmenorutile treated by diphosphonic acid has changed obviously and the chemical displacement of phosphorus has happened. Therefore, it is proved that diphosphonic acid adsorbs on the surface of ilmenorutile to make the atom fraction of phosphorus increase. Finally, it is testified that the main adsorption of diphosphonic acid on the surface of ilmenorutile is chemical adsorption.

5 Conclusions

(1) Diphosphonic acid is the most optimum collector among several collectors for ilmenorutile. The recovery of ilmenorutile in the flotation gained 90.87% to 91.70% dosages of 75 mg/L at pH 2.0-4.0. The collecting property of diphosphonic acid is superior to another collectors used in the flotation test. The sequence of collecting ability for several collectors is diphosphonic acid > TF279 > cyclic alkyl hydroximic acid > benzyl arsenic acid > salicylic hydroximic acid > alkyl hydroximic acid.

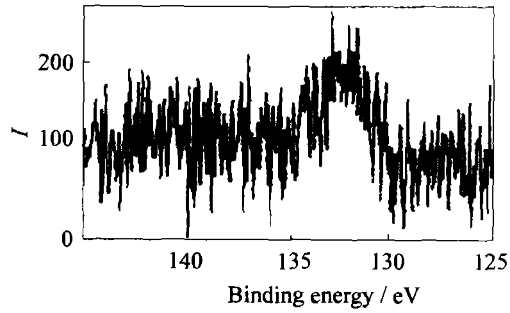

Figure 7 The P2*p* peak on the treated ilmenorutile.

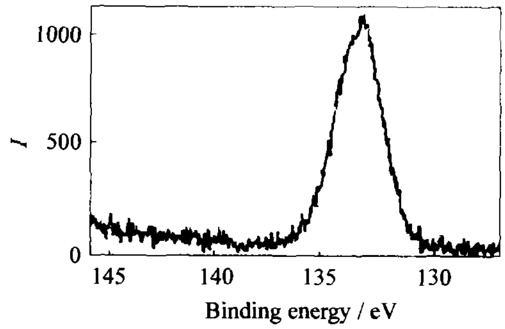

Figure 8 The P2*p* peak on the diphosphonic acid.

(2) IAS determination analysis showed that the characteristic absorption peak related to P=O and P–O occurred at wave number 1 140 and 1 032 cm^{-1}. This means the adsorption of diphosphonic acid on the surface of ilmenorutile has happened.

(3) XPS determination analysis indicated that the binding energy at P2*p* peak position for ilmenorutile and ilmenorutile treated by diphosphonic acid had changed 0.45 eV. It is obviously proved that the adsorption form of reagent is chiefly chemical adsorption.

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