

Flotation separation of low grade and complex rutile ore in Zaoyang and interaction of rutile with octyl hydroxamic acid

WANG Jun, LIU Bei, CHENG hongwei, LI Kaiyun, QIN Wenqing, QIU Guanzhou
(School of Minerals Processing and Bioengineering, Central South University)

Abstract: The flotation separation of rutile ore in Zaoyang was investigated by raw ore experiments and pure mineral tests. The mechanism of rutile with octyl hydroxamic acid (OHA) as collector was further studied by Zeta potential measurement and Infrared spectrum measurement. Raw ore experiment results indicate that rutile can be recycled effectually by using C5~9 hydroxamic acid as collector. The rutile grading of flotation concentrate can reach to 43.25% with the recovery of 69.10%.The pure mineral tests indicate that octyl hydroxamic acid(OHA) is an effective collector of rutile and andradite, and rutile can be activated remarkably by lead nitrate while andradite not. Sodium fluosilicate was found to be an effective selective depressor for andradite. Zeta potential measurements and Infrared spectrum measurements indicate chemisorption and physically absorption are occurred on the surface of rutile with OHA and stable pentabasic chelate are formed.

Key words: rutile; andradite; sodium fluosilicate; flotation separating; infrared spectroscopy

0 Introduction

Rutile is a common mineral in the nature which is widely used. Rutile is a crucial material in extracting metallic titanium and titanium alloy, it's the best source for making titanium dioxide, meanwhile it is the major raw material of slap-up welding electrode, minute quantity rutile can be taken as jewel[1,2].

There is a large reserve volume of rutile in china which mainly contains low grade primary ores of about 86% rutile resource and small part rutile placer ores of about rutile resource 14% [3]. Primary rutile ores are tousle and distribute sporadic, the grade of ores are poor and the recovery of rutile is low, though the reserve of rutile placer ores is small, they are easy to be mined and processed and are the major to be exploit in rutile resource.

The problem of processing rutile ores at present are as follows[4]: (a) The scale of dressing plant of rutile ores is small and the cost is high. (b) The beneficiation technology is not mature and the dressing equipment is behindhand. (c) The comprehensive utilization of rutile ores is low. (d)The dressing technology of rutile ores is very difficult to separate.

Primary rutile ores are in large amount and are the major target object in the future, while relatively they are refractory ores[5,6], so it's very necessary to reasonably develop and utilize ores resource. Meanwhile, rutile ores haven't gotten effective use at present, the great problem is the inefficiency of mineral processing technology, nevertheless, flotation method is a key to solve the difficult of rutile's processing[7].

The rutile ore in Zaoyang city ,China that has been exploited and utilized is a extra big primary rutile ore deposit, Its grade of TiO₂ is 3.06%,the main valuable mineral is rutile and the main associated minerals are hornblende and andradite that closely coexist with rutile and the recovery is not high all the time. The separation between rutile and amphibole is easy to realize while the separation of rutile from andradite is difficult to deal with, and the latter is

Foundations: the National Natural Science Foundation of China (No. 51474254);Program for New Century Excellent Talents in University (No.NCET-13-0595);Ph.D. Programs Foundation of Ministry of Education of China (No. 20120162110008)

Brief author introduction:WANG Jun(1977-),male,vice proffessor,mineral processing. E-mail: wjqw2000@126.com

the vital constraint to improve the grade of rutile in the mineral processing. So it is crucial to study the separation between these two minerals. Gravity separation can't separate them since their specific gravity are 4.4 and 4.1 respectively, magnetic separation is also difficult to dispose since the irons which exit with isomorphism in the rutile lattice make the rutile magnetic and the andradite is moderate magnetic[7,8].So the applicable way to separate rutile and andradite is the flotation method.

This work discusses the flotation on the separation between rutile and andradite and the process flow of Zaoyang rutile's concentration by flotation through the pure mineral tests and the actual ore experiment. The interactions between collector and the pure minerals are also investigated..

1 Materials and experiments

1.1 materials

The pure mineral samples of rutile and andradite were gained by gravity and magnetic separation of rutile ores from Zaoyang, Hubei, China. Then they were ground to fine particles by using a ceramic ball mill, and production of (0.038-0.074) mm was achieved by screening. The X-ray diffractions of rutile and andradite are as follows(Fig.1 and Fig.2) and the purity of rutile and andradite were 93% and 98%, respectively.

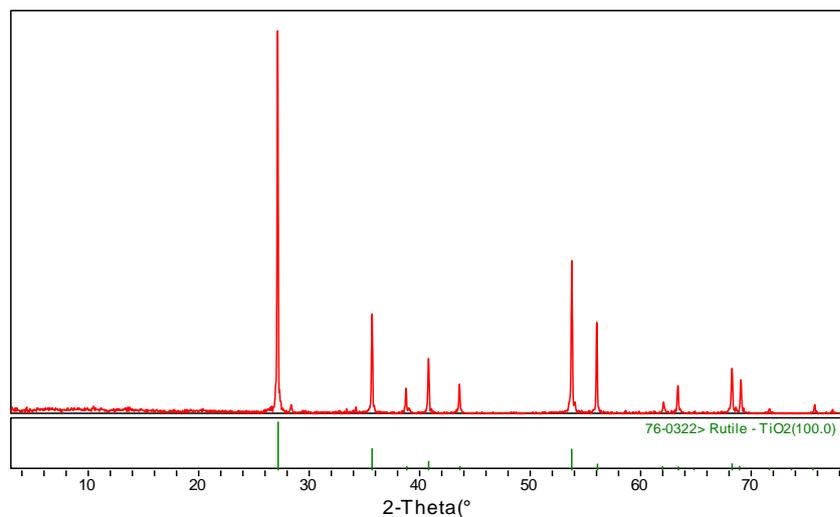


Fig. 1 Result of X-ray diffraction of rutile

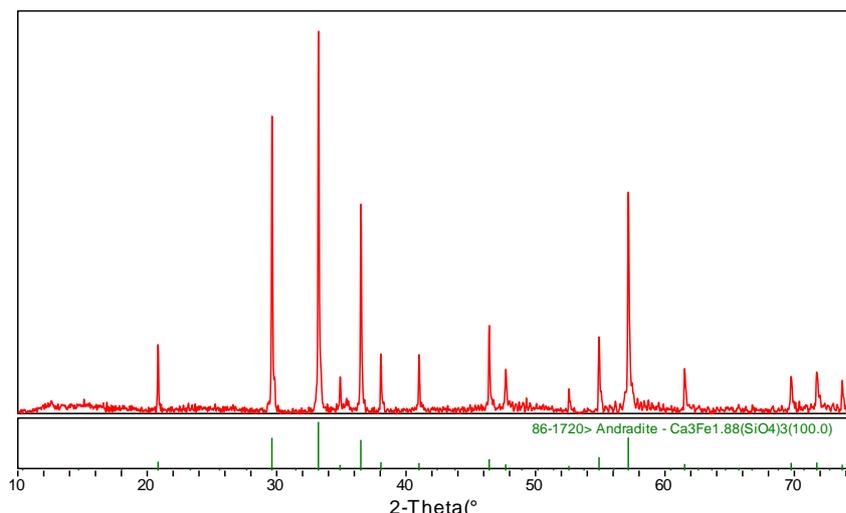


Fig.2 Result of X-ray diffraction of andradite

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The raw ore samples were taken from primary rutile ores in Zaoyang. The multi-element analysis and Titanium phase analysis were showed in Table 1 and Table 2. Most of titanium-bearing minerals were rutile, less are andradite and titanite, etc.

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Table 1 Multi- element analysis results of run-of-mine ore(%)

Constituent	TFe	SiO ₂	Al ₂ O ₃	CaO	MgO
Content	10.81	41.52	15.65	8.05	6.06

Table 2 Result of Ti phase composition's analysis(%)

Phase	TTiO ₂	ilmenite	titanomagnetite	Titanite and others	rutile
Content	3.06	0.33	0.01	0.38	2.34
Distribution	100	10.78	0.33	12.41	76.47

1.2 Experimental methods

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1.2.1 Flotation tests

Pure mineral experiments were carried out in XFG type hanging trough flotation machine of 50mL. The sample of 2.0g was used each time. The temperature of tests were 25°C and the flotation time was 3min. Reagents of chemical-pure and distilled water were used in flotation.

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Raw ore experiments were performed in a XFG 1.5L and 0.5L single-cell flotation machine. In the test, the grinding fineness is 82.09% which refers to the distribution of particles' size under 0.074mm, ores of 500g were conditioned in 650mL tap water at 20~25°C, then pH regulator and activator were added and stirred for 3min respectively, afterwards sodium fluosilicate and combined reagent of C5~9 hydroxamic acid and BAA were added successively and pulp was conditioned for 5min, then followed by 5min flotation.

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1.2.2 Zeta potential measurement

The zeta potentials of mineral were done by using JS94H micro-electrophoresis apparatus. 0.03g of rutile samples under -5µm were stirred in 50mL of distilled water for 3min with pH regulators in the presence or absence of OHA (conditioned for 5min). Following that the suspensions were stewing for 4min, then they were transferred to the the cell of micro-electrophoresis machine for the measurement.

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1.2.3 IR spectrum measurement

50mL of distilled water was added into the beaker with 3g of rutile samples under $-5\mu\text{m}$, and then they were stirred for 30min with the addition of 2.5g of OHA. Afterwards, the solution was filtered and the solid was washed with 4 times by distilled water of pH 9.7, then it was dried naturally and sent to the analysis room for measurement. Infrared spectrometric (IR) of OHA, the pure mineral treated and untreated by collector were conducted by using infrared spectrometer of Nicolet Model Nexus 670.

2 Results and discussion

2.1 Raw ore experiment

The major exploitable useful mineral in raw ore taken from Zaoyang of China is rutile, the main gangue minerals include andradite, hornblende, epidote, chlorite, paragonite and so on. After a series of tests, a terminal technological process of flotation was settled down. The flotation tests were carried out according to the circuit of Fig.3. Test results are given in Table 3. For a feed grading 2.96% rutile, a flotation concentrate was obtained grading 43.25% rutile at recovery of 69.10%. Apparently rutile can be gathered and recycled effectively under the reagents system that lead nitrate is as activator, sodium fluosilicate acts as depressor, the combination of Benzyl arsonic acid (BAA) and C_{5-9} hydroxamic acid are collectors. The results would meet the industrial demand of rutile after the test conditions are optimized.

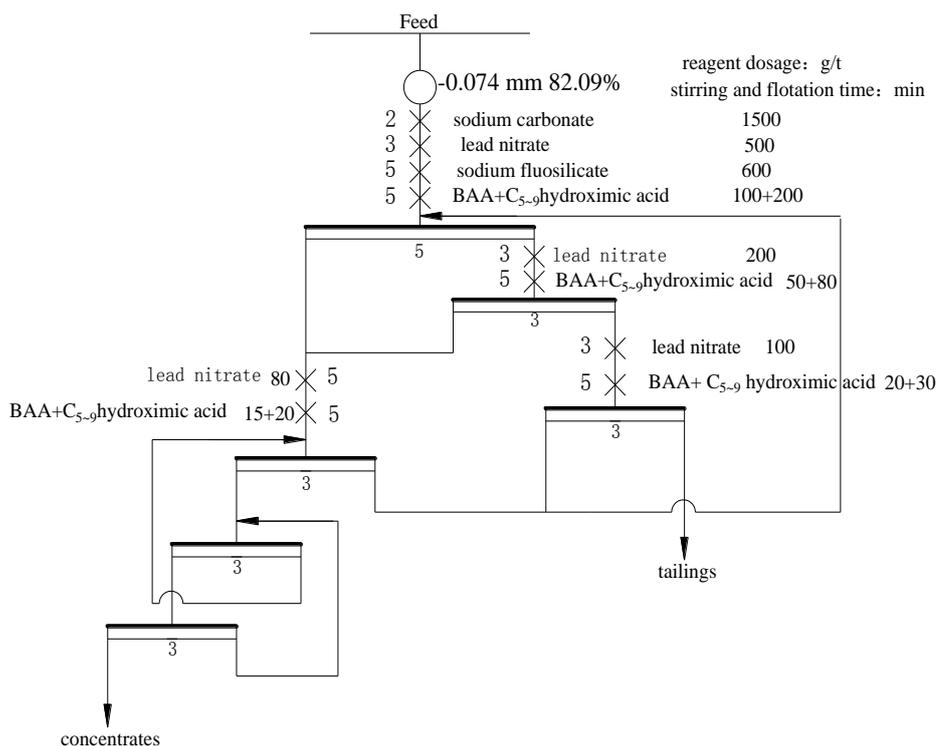


Fig.3 The circuit and reagent regime of flotation experiments

Table.3 Flotation circuit results of raw ore(%)

Product	Yield	Grade of TiO ₂	Recovery of TiO ₂
Concentrate	4.73	43.25	69.10
Tailing	95.27	0.96	31.90
Feed	100.00	2.96	100.00

2.2 Pure mineral tests

2.2.1 Flotation test

The effect of pH on the floatability of rutile and andradite in the presence of OHA is shown in Fig. 4. It is evident that as the increasing of pH, the recovery of rutile and andradite raise gradually, when the pH is about 9.5~10, the recovery reach their maximum, while pH exceed 10.0, the recovery descend sharply. The recovery of rutile is slightly higher than andradite in the pH value range of 3.5~7, while it's opposite in the pH value range of 7~11.

The effect of OHA concentration on two minerals at pH9.7 is shown in Fig.5. It reveals that the recovery of minerals increases as the usage of OHA increasing and recovery of rutile increases faster than andradite. It can be concluded that rutile and andradite can't be separated from each other in the presence of OHA and without regulators addition.

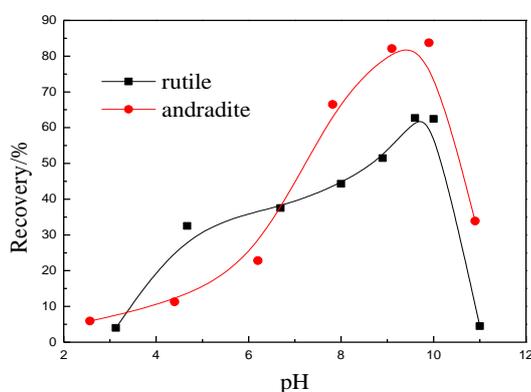


Fig.4 Effect of medium pH on minerals flotation (C_{OHA}=40mg/L)

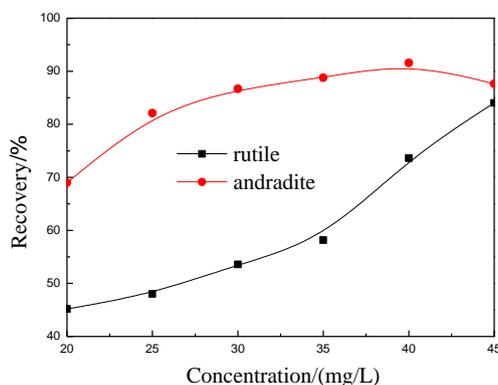


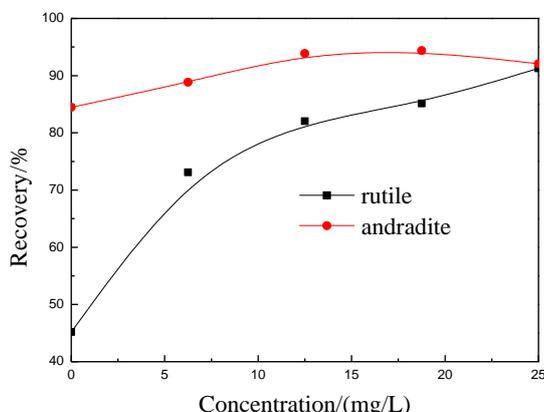
Fig.5 Effect of concentration of OHA on minerals flotation (pH=9.7)

2.2.2 Influence of activator lead nitrate on f minerals

Lead nitrate is an effective reagent of rutile^[9]. The electronegativity of oxygen atom^[10] exposed on the surface of rutile is 3.5, while that of lead ion is 1.6, therefore there can be a strong affinity between them. Lead ion can easily adsorb on the surface of rutile and become the active point, so it can increase the floatability of rutile.

Fig.6 shows the effect of lead nitrate concentration on the flotation of rutile and andradite. It's

135 shown that lead nitrate could activate these two minerals, particularly the activation to rutile is remarkable. As the increasing of lead nitrate concentration, the recovery of rutile raises greatly, while it is slow as for andradite whose increment is only about 10%. It can be concluded that lead nitrate has a good selectivity of activation to rutile and a weak activation to andradite.

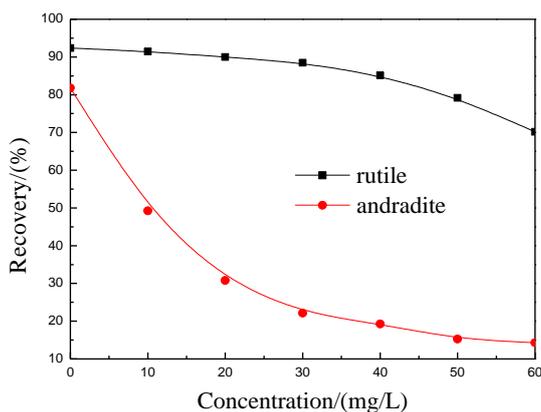


140 Fig.6 Effect of lead nitrate concentration on minerals flotation (pH=9.8, C_{OHA}=45mg/L)

2.2.3 The influence of sodium fluosilicate for the flotation of pure minerals

Sodium fluosilicate is a kind of depressor that is used widely, it can suppress a variety of silicate minerals^[11,12]. Fig.7 shows the effect of sodium fluosilicate concentration on minerals.

145 Fig.7 shows when sodium fluosilicate is applied in process, the recovery of andradite decreases quickly, it reduces to 15% and keeps steady at the concentration of 50mg/L of sodium fluosilicate. While the recovery of rutile decreases slowly and only drops to 75% with the increasing of concentration of depressor. It suggests that there is a selectivity of sodium fluosilicate to rutile and andradite. So we can conclude rutile can be successfully separated from andradite by using lead nitrate as an activator, sodium fluosilicate as a depressor and OHA as a collector.



150 Fig.7 Effect of the sodium fluosilicate concentration on minerals flotation (pH=9.7, Pb(NO₃)₂=25mg/L, C_{OHA}=45mg/L)

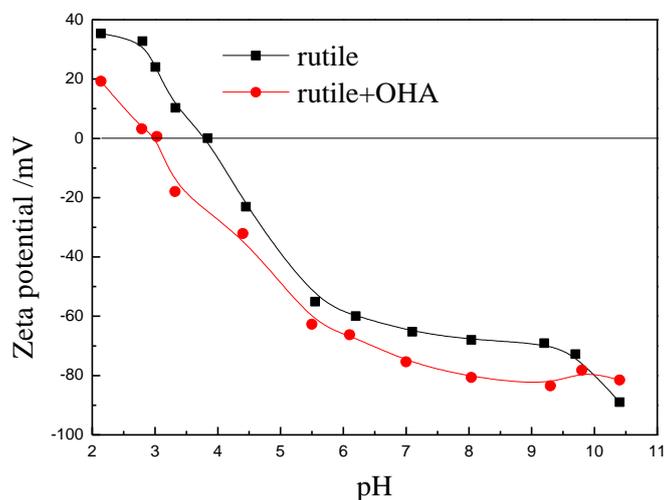
155 2.3 Mechanism of rutile with OHA

In this part, the action mechanism of rutile with OHA was investigated using Zeta potential measurements and IR Spectrum analysis methods.

2.3.1 Zeta potential measurements

160 Zeta potential is a vital parameter to describe the electrically charged situation of mineral in the flotation system. As for oxidized ores, they will absorb or dissociate H^+ and then get charged positively or positively in the systems of different pH owing to the exposed metal particles easily getting hydroxylation^[13-15].

The zeta potential of rutile treated or untreated with OHA is shown in Fig.8. It's indicated that the addition of OHA can bring down the zeta potential of rutile. The point of zero charge (PZC) of rutile in distilled water is about 3.9, which conforms to the literature^[21], while the PZC of rutile reduces to 3.1 after treated with OCT. When pH is <3.9, rutile charges positively, bits of hydroxyl oxime acid radical ions dissociated from hydroxamic acid and absorbed on the surface of rutile, leading to the zeta potential decrease. This verifies the lower recovery of rutile in pure mineral s flotation due to few collectors' adsorption. When $3.9 < \text{pH} < 9.8$, rutile charges negatively, meanwhile as the pH raises, most hydroxamic acid dissolves to electronegative hydroxyl oxime acid radical, while zeta potential of rutile treated with OHA still reduces, this may be explained that electronegative hydroxyl oxime acid radical adsorbs on positively charged titanium ions by chemical forces. While pH is about 9.8, the pK_a of OHA, the recovery of rutile reaches its maximum, it can be explained that the concentration of hydroxyl oxime acid radical ions gets its maximal level, thus adsorbing and surfacing the rutile. When pH is >9.8, the zeta potential of rutile treated with collector even overtops its zeta potential in distilled water, and the recovery of rutile decreases sharply, this may because there is titanium hydroxide generated on the surface of rutile in strongly alkaline medium then rutile is depressed and the its recovery reduces^[14,16].



180 Fig.8 Zeta potentials of rutile treated and untreated with OHA ($C_{\text{OHA}} = 40\text{mg/L}$)

2.3.2 Infrared spectrum measurements

In order to explain the hypothesis of chemisorption, the infrared spectrum measurements were studied. Fig.9 shows the IR spectrum of OHA and rutile treated with and without OHA.

185 It can be observed in Fig.9 that 3254.0cm^{-1} is the character stretching vibration overlap peak of N-H and O-H, 1662.5cm^{-1} is the stretching vibration peak of C=N, 1623.0cm^{-1} is the bending

vibration peak of N-H, 1118.4 cm^{-1} and 971.9 cm^{-1} is the stretching vibration peak of C-N and N-O respectively in IR spectrum of OHA^[17,18].

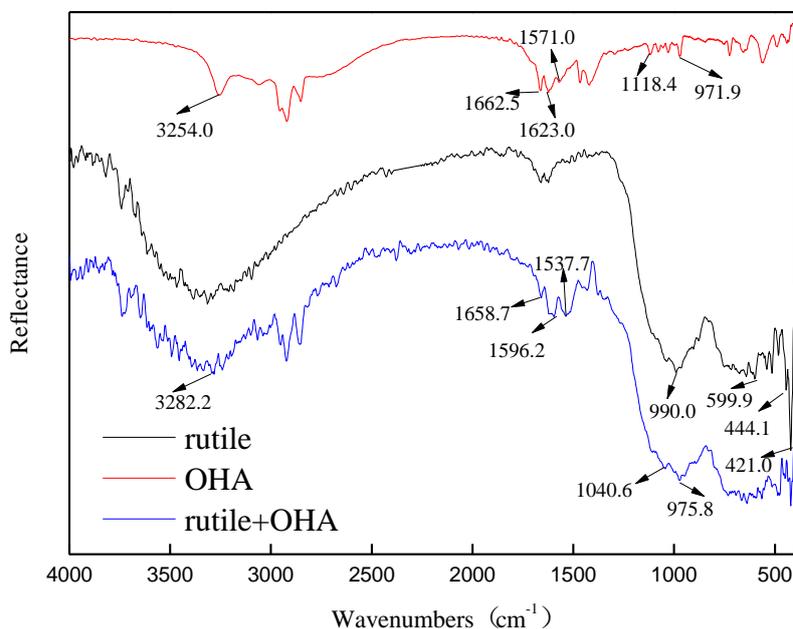


Fig.9 Infrared spectra of OHA and rutile treated with and without OHA

190 While in IR spectrum of rutile treated with OHA, the stretching vibration overlap peak of N-H and O-H appear at 3282.2 cm^{-1} with a excursion approach 30, the stretching vibration peak of C=N drifts to 1658.7 cm^{-1} , a adsorption peak at 1596.2 cm^{-1} characteristic C=O of OHA, the stretching bending vibration peak of N-H and the stretching vibration peak of N-O skew to 1537.7 cm^{-1} and 975.8 cm^{-1} respectively. The remarkable excursions of these major functional groups indicate that oxygen atoms are bonded with titanium ions So it can be concluded that OHA has a chemisorption on the surface of rutile^[19,20]. This can be explained that the electronegativity of Ti is 1.54 which is less than that of H^[21], and the polarity of Ti-O is great than that of H-O, then the hydroxyl ions of hydroxylated Ti ions are replaced by octyl hydroxyl oxime acid radicals that means the oxygen atoms and nitrogen atoms of the collector bond with Ti ions and form chelates.

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200 When Ti bonds with O and O, they forms pentabasic chelate, while Ti combines with O and N, they form quaternary chelate^[22,23]. The model of the reaction between hydroxamic acid and titanium ion can be described as Fig.10^[23,24]:

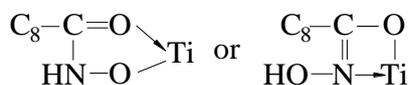


Fig.10 The model of the reaction between OHA and Ti

205 There are some reports^[21,22] indicate that the tension of quaternary chelate is large and the stability is poor, so tendency of forming quaternary chelate is small, while the trend of electron donating ability of O is bigger than that of N, besides the common ligancy of metal atoms is 6 at its largest, so metal ions and hydroxyl oxime acid often form the more stable pentabasic chelate which is the major product.

210 3 Conclusions

(1) The raw ores tests of Zaoyang indicate that rutile can be concentrated effectively, TiO_2

grade of rutile can be raised from 3.06% to 43.25%, and the recovery can reach 69.10% by the closed circuit of one-roughing, two-scavenging and three-cleaning using lead nitrate as a activator, sodium fluosilicate as a depressor and a combination reagents of C₅₋₉ hydroxamic acid and benzyl arsenic acid as collectors.

(2) The pure mineral tests indicate that OHA is an effective collector of rutile and andradite, and lead nitrate can activate rutile remarkably and andradite weakly, while sodium fluosilicate is an effective selective depressor for andradite. Rutile can be separated from andradite by using lead nitrate as activator, sodium fluosilicate as a depressor and OHA as a collector.

(3) The PZC of rutile is about 3.9, it drifts to 3.1 as the addition of OHA. The zeta potential of rutile shifts to more negative direction with a adsorption of the collector, the IR spectrum shows that OHA adsorbs on the surface of rutile by chemical forces and pentabasic chelate between OHA and Ti is forming

Acknowledgments

This work was supported by the National Natural Science Foundation of China (project No. 51474254), Program for New Century Excellent Talents in University (project No.NCET-13-0595) and Ph.D. Programs Foundation of Ministry of Education of China (project No. 20120162110008). We want to express our sincere appreciations for these financial supports. Besides, we want to thank CNMC and DYNC for their support for the experiment.

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285 枣阳低品位复杂金红石矿的浮选分离及与 辛基羟肟酸相互作用机理

王军, 刘贝, 程宏伟, 李开运, 覃文庆, 邱冠周
(中南大学资源加工与生物工程, 长沙 410083)

摘要: 通过实际矿石试验、纯矿物试验研究了枣阳金红石的浮选分离, 并通过 Zeta 动电位测试、红外光谱测试进一步探索了辛基羟肟酸与金红石的作用机理。实际矿石试验表明,
290 C5~9 异羟肟酸和苄基肟酸 (BAA) 的混合捕收剂可以有效捕收金红石, 浮选精矿达到 43.25%, 回收率为 69.10%。单矿物试验表明, 辛基羟肟酸 (OHA) 是金红石和钙铁榴石有效捕收剂, 铅盐可以显著活化金红石而对钙铁榴石活化作用较弱。同时, 研究发现氟硅酸钠是钙铁榴石有效的选择性抑制剂。Zeta 电位测量和红外光谱的测量表明, 辛基羟肟酸在金红石表面发生了化学吸附和物理吸附, 并形成了稳定的五元螯合物。

295 关键词: 金红石, 钙铁榴石, 氟硅酸钠, 浮选分离, 红外光谱
中图分类号: TD91