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Study on separation of fine-particle ilmenite and mechanism using flocculation flotation with sodium oleate and polyacrylamide

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Abstract: In this paper, sodium oleate, polyacrylamide, soluble starch and sodium carboxymethyl cellulose were used as flocculants to study the flocculation and sedimentation behavior of microfine ilmenite. Sedimentation test shows that sodium oleate and polyacrylamide have good flocculation effect on ultrafine ilmenite. The flocculation rate of ilmenite can be further improved by the combination of sodium oleate and polyacrylamide. It was found that both flocculants could generate chemical adsorption with ilmenite surface, and they all react with Fe^{3+} on ilmenite surface. However, sodium oleate reacts with Fe^{3+} to form a water-insoluble iron oleate precipitate which coats the surface of the ilmenite and hinders the action of polyacrylamide and the remaining Fe^{3+}. This problem can be avoided by adding polyacrylamide followed by sodium oleate, and the flotation recovery can be increased significantly.

Keywords: sodium oleate, polyacrylamide, synergistic effect, ilmenite, flocculation flotation

1. Introduction

Titanium has been widely used because of its excellent physical and chemical properties, and the separation and recovery of ilmenite, one of the sources, has also attracted wide attention for a long time (Chen and Nakata, 2009; Chitichotpanya et al., 2019). Conventional grade ilmenite is mainly recovered by gravity separation, magnetic separation, flotation and electro-separation, and has a relatively mature technology (Chen et al., 2019; Zhao et al., 2019; Neradovsky et al., 2019). At present, the following methods are mainly used to recover the fine ilmenite produced by self-embedded fine-grained ilmenite and non-selective grinding. : 1) Adopt new mineral processing equipment, such as suspended cone coning concentrator, SSS type high gradient magnetic separator, centrifugal high gradient magnetic separator, magnetic shaker, magnetic chute, cyclone-static microbubble flotation column, etc (SUN, 2006; Xiao and Zhang, 2019; Farjana et al., 2018). These equipments can improve the recovery and grade of fine-grained ilmenite. However, the composite force field generated by the new equipment requires complex equipment support. The more complicated the equipment, the lower the stability, and the poor working environment of the ore dressing. The devices put forward higher requirements. 2) Flotation of

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ilmenite by combination agents, for example, a combination of arsenic, lauric acid and sodium dodecyl benzene sulfonate in a certain ratio can significantly increase the ilmenite flotation recovery. (Wang et al., 2017; Zhu et al., 2011; Li et al., 2016). However, there are many kinds of reagents added in the pulp during flotation, which brings great challenges to the treatment of mineral wastewater. 3) Use of combined separation process, such as magnetic separation-flotation combined process, suspension vibration gravity separation-flotation combined process, etc (Dobbins et al., 2007; Zeng et al., 2017; Lv et al., 2017). The combined separation process can reduce the content of mud in pulp, improve the environment of flotation pulp and reduce the use of chemicals. The disadvantages are numerous equipment, complex process, large investment in the early stage and inconvenient equipment management. 4) The introduction of microwave pretreatment technology to ilmenite dressing can improve the surface properties of ilmenite and improve the floatability of ilmenite (Xiao et al., 2019; Irannajad et al., 2014; Omran et al., 2015). However, the microwave pretreatment technology is difficult to achieve large-scale equipment, suitable for practical production needs to be further studied.

In view of the shortcomings of the above methods, a new technology of using high molecular flocculant to recover fine minerals has emerged. At present, the flocculation separation technology has achieved good results in the recovery and utilization of ultra-fine coal slime, ultra-fine sulfide ore and ultra-fine oxidized ore. Therefore, some scholars think that it is possible to recycle ultrafine ilmenite by using polymer flocculation (Forbes, 2011; Williams et al., 1997; Subrahmanyam and Forssberg, 1990). In addition, the use of polyacrylamide and its derivatives as flocculants for laboratory pure mineral flocculation behavior or selective flocculation separation of artificial mixed ore (Castro and Laskowski, 2015; Sung et al., 2018; Drzymala and Fuerstenau, 2014; Panda et al., 2018; Lapointe and Barbeau, 2018; Liu et al., 2014). However, the reasons for flocculation have not been explained in detail, and most of the trials are still in the laboratory research stage.

In this study, sodium carboxymethyl cellulose (CMC), soluble starch, polyacrylamide (HPAM) and sodium oleate (NaOL) were used as flocculants to flocculate with ultrafine ilmenite pure mineral to study the flocculation behavior of micrograined ilmenite and macromolecular agents. It was found that adding sodium oleate and polyacrylamide could complete the flocculation quickly. In order to improve the recovery of ultrafine ilmenite, two kinds of flocculants are used together to strengthen the flocculation effect. This paper mainly discusses the flocculation behavior of flocculants and fine-grained ilmenite and the mechanism of action of sodium oleate and polyacrylamide.

2. Materials and methods

2.1. Ore properties

The ilmenite samples used in this study were from a concentrator in panzhihua district, sichuan province, China. Chemical composition analysis of the samples (Table 1) show that the ore contains 48.6% TiO_2, the mineral can be identified as ilmenite pure mineral, and the X-ray diffraction pattern of the sample (Fig. 1) is basically consistent with the standard card of ilmenite (Table 2) (Berman and Aranovich, 1996).

Table 1. Chemical composition analysis results (%)

TFe	TiO_2	SiO_2	MnO	Al_2O_3	CaO	MgO
47.52	48.61	1.68	0.69	0.49	0.43	0.39
P_2O_5	SO_3	K_2O	ZrO_2	Cl	Na_2O	ZnO
0.06	0.03	0.02	0.02	0.02	0.02	0.02

Table 2. The main standard 2θ of ilmenite

Number	1	2	3	4	5	6	7	8
2Theta	23.79	32.484	35.25	40.283	48.697	53.007	61.538	63.269

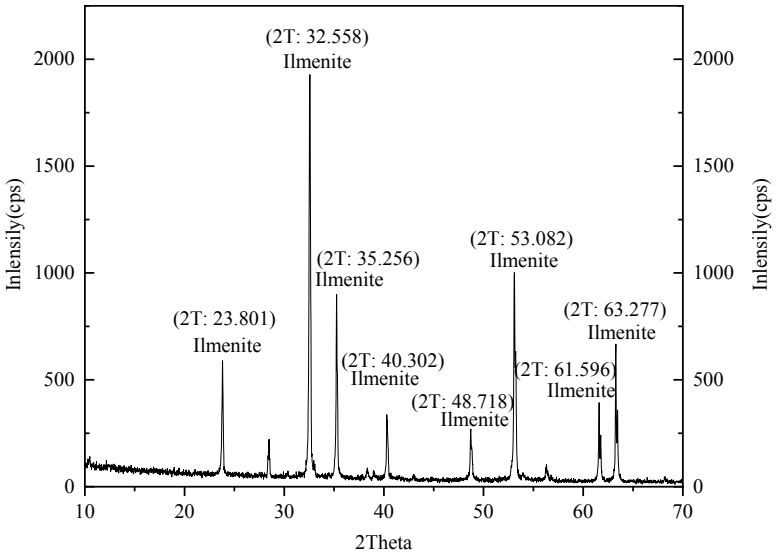

Fig. 1. X-ray diffraction (XRD) spectrum of the purified ilmenite sample

2.2. Particle size analysis

Prepare samples for grain size analysis by the following methods: 1.0 g of ilmenite ore was mixed with 20 ml of deionized water in a beaker and ultrasonically dispersed for 5 min. Particle size analysis was performed at 25℃ room temperature using a LS 13320 laser particle size analyzer (test range 0.375 to 2000 μm).

2.3. Test reagents

Polyacrylamide (CP, with a molecular weight of 3 million), Sodium oleate (CP), Soluble starch (AP), Sodium carboxymethyl cellulose (AP), Sodium hydroxide (AP), sulfuric acid (AP).

2.4. Sedimentation test of ultrafine ilmenite

Ilmenite and deionized water were fully mixed in a measuring tube with a solid-liquid ratio of 1:50, and the pH of mineral pulp was adjusted by sulfuric acid or sodium hydroxide to 6.5. The flocculation sedimentation test was conducted, and the settling time was 270s (calculated according to stokes sedimentation formula). One group did not add flocculant as the blank group, and the other groups used sodium oleate, soluble starch, polyacrylamide and sodium carboxymethyl cellulose as flocculant (Sodium oleate was 2×10^{-4} mol/L, soluble starch was 400 g/t, polyacrylamide was 80 g/t, and sodium carboxymethyl cellulose was 200 mg/L).

2.5. Characterization test of the mixing system of the two flocculants

The flotation method was used to evaluate the effect of adding flocculant on the separation and recovery of ilmenite. Methods as below: the XFG hanging trough flotation machine of 20ml was adopted, and the spindle speed was set at 1920 r/min. Each test, take 1g ore sample, mix it with deionization water and put it in the flotation machine, and start timing. At 2 min, the pH value was adjusted, at 5min, the agent was added and the original pH value was returned, at 8min, the manual foaming was started, and the foaming time was determined to be 5 min. The flotation products were dried and weighed, and the recovery was calculated.

2.6. Zeta potential measurements

The pure ilmenite minerals were milled to -2 μm size in an agate mortar to form 1g/L suspension. At room temperature of 25℃, 50mL of each measurement was taken, flocculant was added and pH value was adjusted. After constant temperature oscillation for 30min and rest for 10min, supernatant was

taken for Zeta potential measurements (Zetasizer Nano Zs90, Malvern Instruments, Britain). Each sample was tested 3 times and averaged.

2.7. Fourier transform infrared spectroscopy

Fourier transform infrared spectrum (FTIR) test adopts the American Version BM infrared spectrometer, which controls the measured wave number of 400 ~ 4000cm^{-1}, test temperature 25℃. Before the test, pure ilmenite minerals were ground to -2μm size, and 1.0g samples were taken to the flotation tank. Flocculant was added in the same treatment method as the flotation method, stirred for 10min, and then filtered. Deionized water with the same pH value was used for washing for 3 times before vacuum drying. KBr tablet method was adopted to test the infrared spectrum.

2.8. Microcalorimetry measurement

Under the condition of 25℃ ambient temperature and 40℃ test temperature, French SETARAM C80 mixed reaction calorimeter was adopted for the test.

The cavity for the calorimetric reaction consists of two thermopiles for placing the calorimetric reaction cell and the control reaction cell, respectively. The specific test procedure is as follows: 0.1 g of ilmenite ore is placed in the reaction cell, 1 ml of deionized water is added, and 1 ml of flocculant (2×10^{-4} mol/L sodium oleate or 80 g/t polyacrylamide) is added to the upper layer of the calorimetric reaction cell membrane, an equivalent amount of deionized water was added to the control cell. After the heat flow signal is stabilized, the upper layer liquid of the test group and the control group is simultaneously injected by the reaction cell matching device. Finally, data collection is performed.

In order to eliminate the relative wetting effect (Q_W) of deionized water combined with minerals, the final calorific value (Q_{ads}) of each test is subtracted from the calorific value (Q_W) by the measured calorific value (Q_r), namely formula (1).

$$Q_{ads} = Q_r - Q_w \tag{1}$$

It has been found that the calorific value (Q_W) produced by the relative wetting effect is negligible for measuring the calorific value (Q_r). That is, the final calorific value (Q_{ads}) of the test is equal to the measured calorific value (Q_r).

3. Results and discussions

3.1. sample size analysis results

The sample size analysis results are shown in Fig. 2. The test results show that d_{10}=2.610 μm, d_{50}=10.68 μm and d_{90}=22.80 μm in the samples, that is, the particle size of the samples used in the test is basically less than 23 μm, which is a fine grade mineral difficult to recover by traditional mineral processing methods.

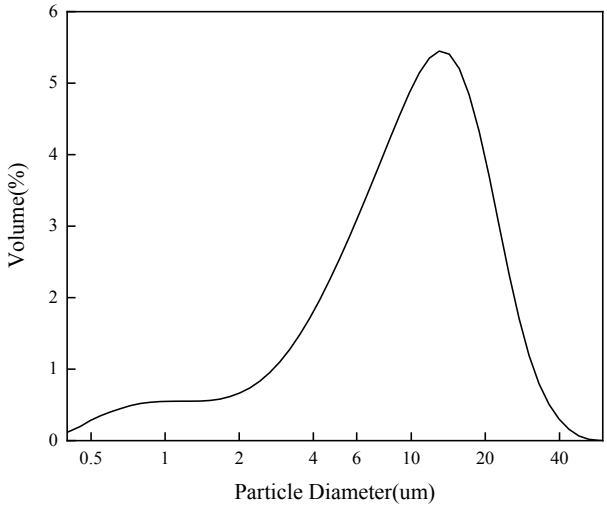

Fig. 2. Particle size analysis of raw ore

3.2. Effects of various flocculants on flocculation sedimentation of ultrafine ilmenite

Flocculation sedimentation test of ultrafine ilmenite was carried out with sodium oleate, soluble starch, polyacrylamide and sodium carboxymethyl cellulose as flocculants. The picture of settlement end point is shown in Fig. 3.

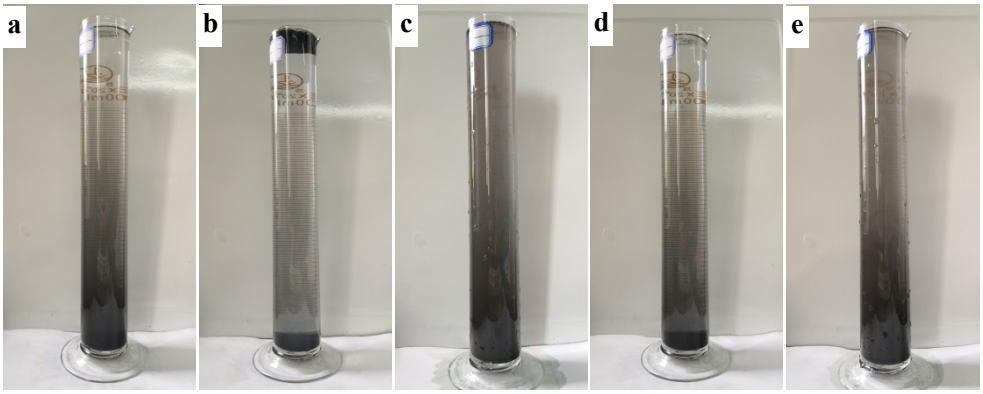

Fig. 3. Flocculation image of fine ilmenite. Left to right picture shows (a) blank group, (b) with sodium oleate, (c) with soluble starch, (d) with polyacrylamide, (e) with sodium carboxymethyl cellulose

According to Fig. 3, most ore particles in the blank group have settled after reaching the theoretical settlement time, but some fine particles are still suspended in the lower half of the measuring cylinder. The experimental results of the experimental group indicate that different types of flocculants have different degrees of promoting effect on the precipitation of ilmenite, but the effect of adding soluble starch and sodium carboxymethyl cellulose test group is not obvious; in the test group with polyacrylamide added, the ilmenite floc appeared in the lower layer of the measuring cylinder. During the test, it was found that polyacrylamide preferentially flocculated with the larger-sized ilmenite particles, and the settlement was completed quickly. The reason is that polyacrylamide itself, as a water-soluble polymer, forms a network structure with the combination of mechanical winding and hydrogen bond at the appropriate concentration (Tartaglia et al., 1997) , ilmenite particles larger than a certain size are coated, while ilmenite particles with smaller size can pass through the mesh and are difficult to be flocculated. It was found that the addition of sodium oleate can quickly complete flocculation and sedimentation, and form a loose porous sedimentation layer. Because sodium oleate has a certain hydrophobicity, sodium oleate and a part of fine ilmenite are floating on the liquid surface. The coarse-grained ilmenite and sodium oleate form a floc and settle to the bottom.

It can be concluded that soluble starch and sodium carboxymethyl cellulose are not suitable for flocculants with particle size smaller than 23 μm ultrafine ilmenite. Polyacrylamide can flocculate with ilmenite with coarse fraction, but the flocculation of ilmenite with fine particles is not satisfactory. Sodium oleate can act on coarse and fine ilmenite separately, so that the finer ilmenite particles float on the liquid surface, while the coarse fraction ones sink to the bottom. In order to investigate whether the sedimentation test is reproducible, the above-mentioned test process was repeated three times and it was found that the sedimentation phenomenon was basically the same.

In order to explore better flocculation conditions, the subsequent experiments mixed polyacrylamide and sodium oleate into the same system to study the combined flocculation of the two on micrograined ilmenite. The combined effects of the two agents are discussed below.

3.3. Mixing system of sodium oleate and polyacrylamide

Control flotation pulp pH=6.5, and Sodium oleate has a concentration of 2×10^{-4}mol/L and the dosage of polyacrylamide was 80g/t. The effects of different pharmaceutical systems on the recovery of ilmenite were investigated. The test results are shown in Table 3.

It can be seen from the Table 3 that the recovery of the experimental group only adding sodium oleate was higher than that of the experimental group only adding polyacrylamide, which was consistent with the sedimentation test. The recovery of sodium oleate and polyacrylamide in the two

Table 3. Effect of pharmaceutical system on recovery of ilmenite

Serial number	pH	Reagent scheme		Recovery (%)
		NaOL (mol/L)	HPAM (g/t)	
1	6.3	2×10^{-4}	0	69.51
2	6.5	0	80	30.54
3 *	6.4	2×10^{-4}	80	70.97
4 * *	6.4	2×10^{-4}	80	80.02

* No. 3 group, sodium oleate was added for 2 min and then polyacrylamide was added

** No. 4 group, polyacrylamide was added for 2 min, and then sodium oleate was added

experimental groups were higher than that of the experimental group using only one flocculant, which indicated that the combined action of the two flocculants was helpful to the formation of flocs and was recovered by flotation. It can also be concluded from the Table 3 that the adding order of two kinds of flocculation has a great influence on the test results. The sodium oleate was added for 2 min, and the recovery of the test group added with polyacrylamide was 70.97%, and the recovery of the test group was 80.02% after the first addition of polyacrylamide for 2 min. In order to determine the repeatability of the test, the flotation test was repeated several times and the experimental error was always less than ±0.5%. The flocs were analyzed microscopically, and the micrograph are shown in Fig. 4.

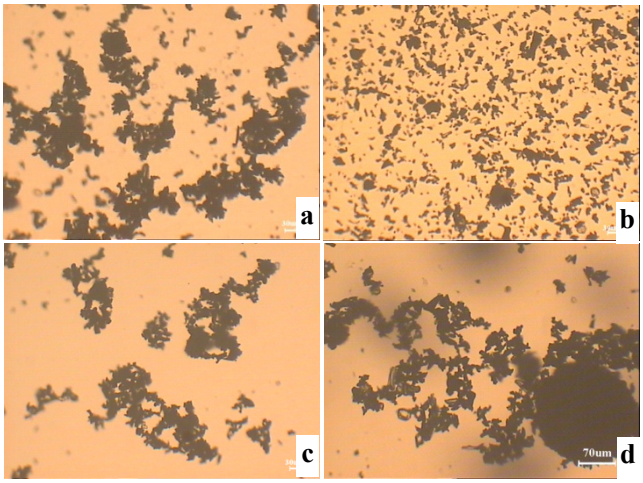

Fig. 4. Micrograph analysis results. Figures a, b, c and d represent respectively addition of 2×10^{-4}mol/L sodium oleate group, 80 g/t polyacrylamide group, 2×10^{-4} mol/L sodium oleate first and then 80g/t polyacrylamide group, first 80g/t polyacrylamide and then 2×10^{-4}mol/L sodium oleate group

According to figure 4a, a large number of loose chain floc appeared in the test group with sodium oleate as the flocculant alone, which was due to hydrophobic flocculation between sodium oleate and ilmenite, and floc formation between ilmenite through bridging. Several irregular aggregates of polyacrylamide treated ilmenite particles were found, but the aggregates were small in size and low in yield. Compared with the test group using only the sodium oleate, the test group with the first addition of sodium oleate and then the polyacrylamide was used. In addition to the more flocs formed in the system, the floc morphology did not differ much, which was consistent with the conclusion of flotation. Microscopic measurements showed that floc with particle size greater than 100μm appeared in the system, and there was a certain bridging phenomenon between the flocs. The result is shown in Fig. 4d. The reason for this phenomenon is that the polyacrylamide added first forms flocs with ilmenite of larger grain size, but these flocs are hydrophilic and difficult to recover by flotation, which is corresponding to the fact that the recovery of polyacrylamide low flotation recovery. The addition of sodium oleate partially flocculates with small particles of ilmenite, and the other part continues to flocculate with the remaining binding sites on the surface of the large particle ilmenite that has already

formed a floc. The hydrophobicity of the entire floc is increased, thereby increasing the flotation recovery.

3.4. Zeta potential analysis

As an efficient way to interpreter the trend of flotation efficiency and the modification performance caused by the presence of reagents, the zeta potential has long been used in experiments (Zouboulis and Avranas, 2000). The effect of different pharmaceutical systems on the surface potential of ilmenite in this experiment is shown in Fig. 5.

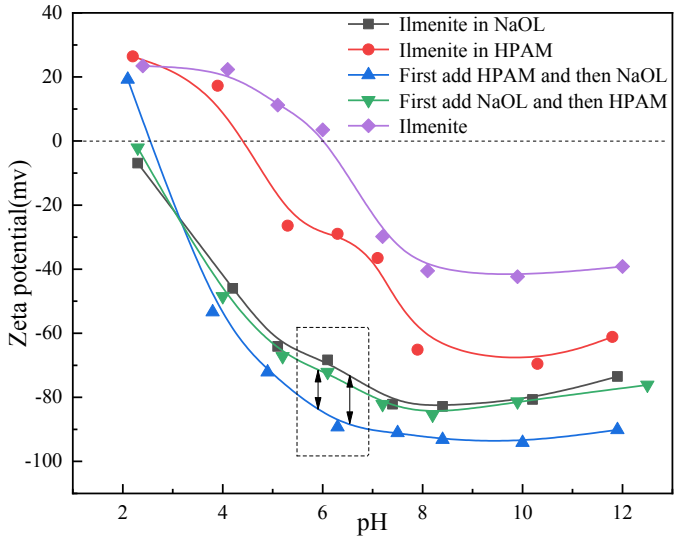

Fig. 5. Relationship between Zeta potential and pH of ilmenite after flocculant action

It can be seen from Fig. 5 that the isoelectric point (IEP) of ilmenite is pH=6.2 when no flocculant is added, which is consistent with the literature report (Liu et al., 2019). Within the pH range of the test, the Zeta potential of ilmenite was significantly negative shifted after NaOL or HPAM was added, and the negative shift of NaOL group was greater than that of HPAM group. This phenomenon indicates that NaOL has stronger adsorption on ilmenite than HPAM. In addition, the negative potential shift of the experimental group with the addition of two flocculants was greater than that of the experimental group with the use of one flocculant alone, indicating that the two flocculants had a synergistic effect on the adsorption of ilmenite to a certain extent, and the negative potential shift of the test group with HPAM and NaOL was larger than that with NaOL and HPAM. It can be inferred that the HPAM added first flocculated with the coarse ilmenite, and the fine ilmenite continued to flocculate with the subsequent NaOL, and further combined with the formed flocculate. That is to say, there are more reagents adsorbed on the surface of ilmenite, resulting in greater potentiodynamic changes. However, the first experimental group added with NaOL, because most of the ilmenite has formed floccules, causing the surface of the ilmenite to be hydrophobic, resulting in the lack of binding points of the HPAM added later, which did not exert flocculation, which is consistent with the experimental results.

3.5. FTIR analysis

In order to further determine the flocculation mechanism of sodium oleate and polyacrylamide on ilmenite, the infrared spectra of ilmenite under different reagent systems were characterized, as shown in Fig. 6.

According to Fig. 6(a), in the infrared spectrum of sodium oleate, the peaks at 2924 cm^{-1} and 2853 cm^{-1} are attributed to the C—H stretching vibration, the peaks at 1713, 1562, 1448 and 1423 cm^{-1} are attributed to the —COO— characteristic absorption peak (Feng et al., 2015). For polyacrylamide, the peaks at 2924 cm^{-1} for the $-CH_2$ characteristic absorption peak of anti-symmetric stretching vibration, the peaks at 2853 cm^{-1} for - CH_2 characteristic absorption peak of symmetric stretching vibration, the peaks at 1645 cm^{-1} are characteristic absorption peak of carbonyl group, the peaks at 1457 cm^{-1} are

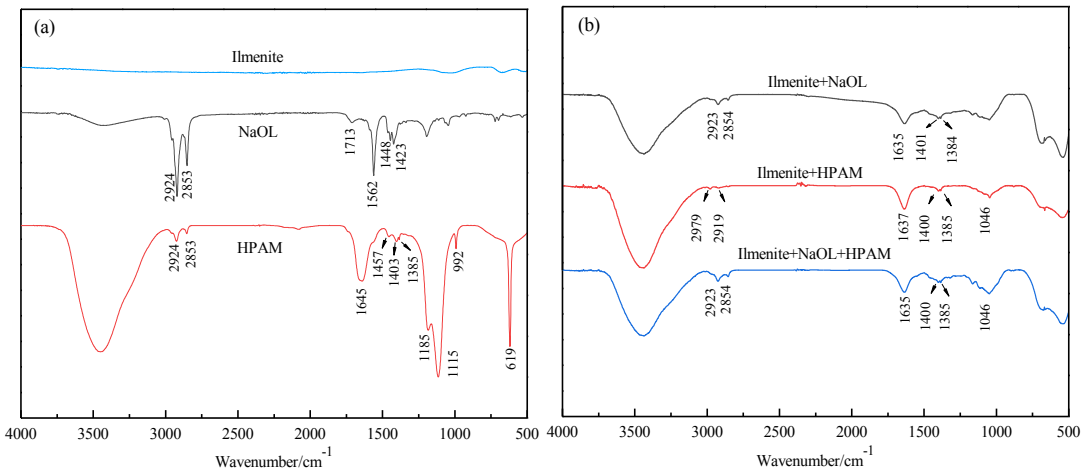

Fig. 6. Infrared spectra of ilmenite under different pharmaceutical systems

characteristic absorption peak of methylene deformation, the peaks at 1185 cm^{-1} and 1115 cm^{-1} the absorption peak of C—N was obvious in the spectrum of cationized products (Sadeghalvaad and Sabbaghi, 2015) . The sample is cationic polyacrylamide.

According to Fig. 6 (b), the infrared spectra of ilmenite have changed significantly after the interaction of ilmenite and sodium oleate at pulp pH=6.5. The absorption peaks at 2923 cm^{-1} and 2854 cm^{-1} belong to the shift of the symmetrical vibration absorption peaks of C—H bonds at 2924 cm^{-1} and 2853 cm^{-1} of sodium oleate, indicating that the reagent has developed with ilmenite. New absorption peaks appeared at 1635, 1401 and 1384 cm^{-1}, which belonged to the shift of carboxyl absorption peaks at 1713, 1562 and 1448 cm^{-1} in sodium oleate, and shifted 78, 161 and 64 cm^{-1}, respectively, indicating that chemical adsorption of sodium oleate and ilmenite took place. After interaction with polyacrylamide, the absorption peaks at 2979 cm^{-1} and 2919 cm^{-1} are the offset of symmetrical methylene vibration absorption peaks at 2924 cm^{-1} and 2853 cm^{-1} in polyacrylamide, which are 55 cm^{-1} and 66 cm^{-1} respectively; the absorption peaks at 1637 cm^{-1} belong to the offset of 1645 cm^{-1} carbonyl absorption peak, and the absorption peaks at 1400 cm^{-1} belong to 1457 cm^{-1} methylene, the migration of deformation absorption peaks is 8 cm^{-1} and 57 cm^{-1}, respectively, which indicates that chemical adsorption of polyacrylamide occurs on ilmenite surface. When sodium oleate and polyacrylamide interact together, the characteristic peaks of both of them shift in the infrared spectrum of ilmenite, indicating that sodium oleate and polyacrylamide have chemical adsorption on the ilmenite surface at the same time.

3.6. Microcalorimetric analysis

Record the change in heat generated by the different dosing methods of the two flocculants, thereby determining the severity of the adsorption reaction between the agent and the mineral.

Fig. 7 shows the typical thermal diagram of the reaction between mineral and flocculant. Fig. 7 (a) shows the thermal diagram of adding sodium oleate followed by polyacrylamide, and Fig. 7 (b) shows the thermal diagram of adding polyacrylamide followed by sodium oleate. We can conclude that as the reaction time goes on, the heat generated by the interaction between ilmenite and flocculant gradually increases, and the reaction reaches equilibrium after a period of time. According to the integral calculation of the analysis software, the reaction heats of Fig. 7 (a) and (b) are 51.25 J/g and 70.29 J/g, respectively, which indicate that the pharmaceutical system is first added with polyacrylamide and then sodium oleate. It can cause a more violent reaction between the agent and ilmenite.

$$M^{n+} + nOl^{-} = M(Ol)_n, \quad L_{S_i} = [M^{n+}][Ol^{-}]^n \tag{2}$$

$$Ol^{-} + H^{+} = HOl, \quad K^H = \frac{[HOl]}{[H^{+}][Ol^{-}]} \tag{3}$$

$$\alpha_{(Ol)} = 1 + K^H[H^{+}] \tag{4}$$

$$\alpha_{M^{n+}} = 1 + \beta_1[OH^{-}] + \beta_2[OH^{-}]^2 + \beta_3[OH^{-}]^3 + \beta_4[OH^{-}]^4 \tag{5}$$

$$\Delta G^{\theta}_{M^{n+}} = \mathrm{RT}\ln L'_S = RT\ln L_{S_i}\alpha_{M^{n+}}\alpha^n_{(Ol)} \tag{6}$$

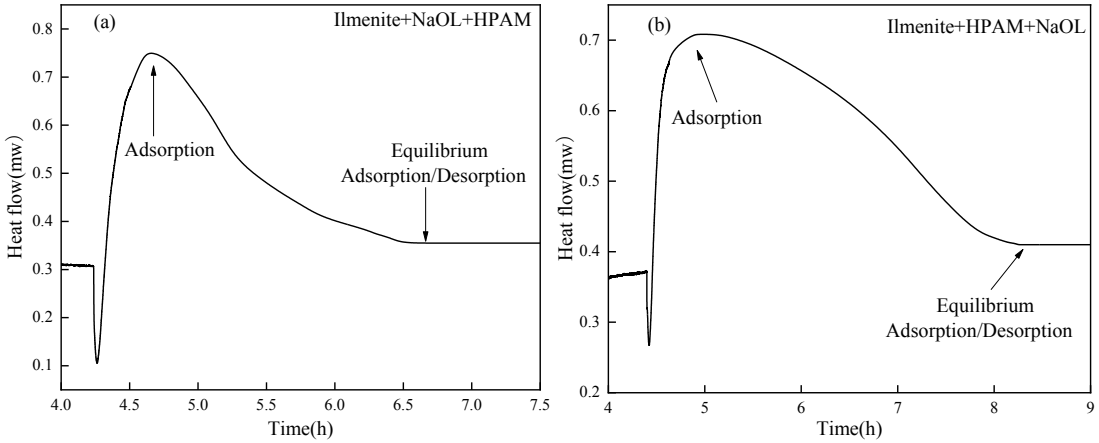

Fig. 7. Typical microcalorimetric curve for adsorption on ilmenite surface

According to a study on a titanium-water-oxygen-sodium oleate system (Luszczkiewicz et al., 1979), the chemical reaction between metal ions (Fe^{2+} /Fe^{3+}) and oleate ions, and the protonation reaction of oleate ions, side reaction coefficient, and standard Gibbs free energy change can be obtained as follows:

Where L_{S_i} represents the solubility product of the metal ion (Fe^{2+} $1\times10^{-15.4}$, Fe^{3+} $1\times10^{-34.2}$), L'_S represents the conditional solubility product, K^H represents the proton of the oleate ion Constant (1×106), $\alpha_{(Ol)}$, $\alpha_{M^{n+}}$ respectively represent the side reaction coefficient of oleate ion and metal ion, β_1, β_2, β_3, β_4 represent the hydroxyl complex of metal ion Cumulative stability constant (Table 4).

Table 4. Accumulation stability constants of metal ions hydroxyl complexes

Ion	β_1	β_2	β_3	β_4
Fe^{3+}	11.81	22.30	32.05	34.30
Fe^{2+}	4.50	7.40	10.00	9.60

According to equations (2) ~ (6), the relation between the standard gibbs free energy and pH of the reaction between metal ions and sodium oleate was calculated, as shown in Fig. 6.

According to Fig. 8, the Gibbs free energy of Fe^{3+} and oleate is larger than that of Fe^{2+} in the test pH range, which indicates that oleate is more likely to react with Fe^{3+} to produce oleate precipitation in the test pH range.

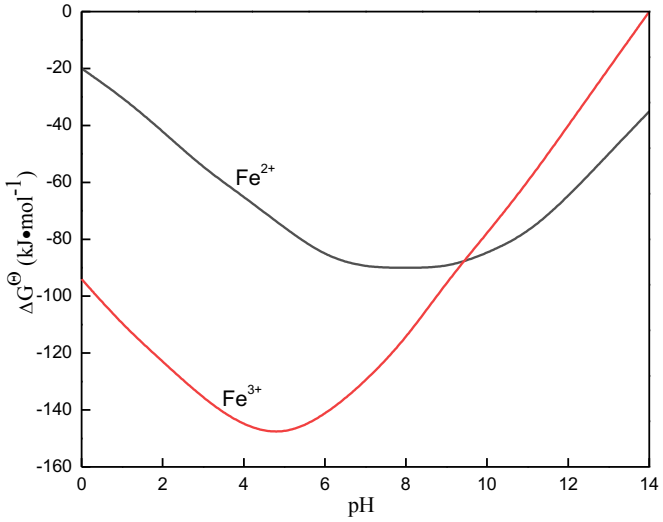

Fig. 8. Standard Gibbs free energy (ΔG^{θ}) for metal ions reacting with sodiumoleate as a function of the pH value

Research shows (Wang and Zhao, 1992; Sun et al., 2008) that Fe^{3+} is hydrolyzed and polymerized in aqueous solution to form multinuclear hydroxy bridge ions and form polar bonds and coordination bonds with the carboxyl groups of polyacrylamide and produce cross-linking. This indicates that polyacrylamide can react with Fe^{3+} on the surface of ilmenite. Combining with sedimentation test, it is determined that there is a competitive relationship between polyacrylamide and sodium oleate for flocculation of fine ilmenite. The first addition of polyacrylamide and Fe^{3+} forms a complex ion reaction to produce cross-linking effect, which makes part of ilmenite flocculate. The residual Fe^{3+} on the surface of ilmenite and the sodium oleate added after it continue to form iron oleate precipitation, which is wrapped on the surface of ilmenite, making the two flocculants closely bound to ilmenite, resulting in the appearance of giant pellet flocculants in microscopic photographs. The test group which first added sodium oleate blocked the residual Fe^{3+} and the post-added polyacrylamide due to the precipitation layer formed on the surface of ilmenite, resulting in a recovery difference of nearly 10% in the case of the same dosage.

4. Conclusions

1) Sodium oleate, soluble starch, polyacrylamide, sodium carboxymethylcellulose have flocculation effect on fine-grained ilmenite, but the actual flocculation effect is sodium oleate > polyacrylamide > sodium carboxymethyl cellulose > soluble starch.

2) The flocculation effect of fine-grained ilmenite is improved by using two kinds of flocculants of sodium oleate and polyacrylamide. Combined with Zeta potential analysis and infrared spectrum analysis, it is known that the flocculation of ilmenite by sodium oleate and polyacrylamide is chemical adsorption.

3) In the combined action system of polyacrylamide and sodium oleate, both flocculants react with Fe^{3+} on the surface of ilmenite. Adding polyacrylamide and then adding sodium oleate can prevent the formation of iron oleate precipitation from hindering the combination of minerals and flocculants. Compared with using only one flocculant or other dosing sequence, this dosing method can increase the flotation recovery by more than 10%.

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References

BERMAN, R.G., ARANOVICH, L.Y., 1996. *Optimized standard state and solution properties of minerals*. Contributions to Mineralogy and Petrology 126(1-2), 1-24.

CASTRO, S., LASKOWSKI, J.S., 2015. *Depressing effect of flocculants on molybdenite flotation*. Minerals Engineering 74, 13-19.

CHITICHOTPANYA, P., INPRASIT, T., CHITICHOTPANYA, C., 2019. *In vitro assessment of antibacterial potential and mechanical properties of Ag-TiO_2/WPU on medical cotton optimized with response surface methodology*. Journal of Natura Fibers 16(1), 88-99.

CHEN, P., HOU, P., ZHAI, J., SUN, W., 2019. *A novel method for the comprehensive utilization of iron and titanium resources from a refractory ore*. Separation and Purification Technology 226, 1-7.

CHEN, Y.C., NAKATA, K., 2009. *Microstructural characterization and mechanical properties in friction stir welding of aluminum and titanium dissimilar alloys*. Materials & Design 30(3), 469-474.

DOBBINS, M., DOMENICO, J., DUNN, P., 2007. *A discussion of magnetic separation techniques for concentrating ilmenite and chromite ore*. The 6th International Heavy Minerals Conference "Back to Basics", *The Southern African Institute of Mining and Metallurgy*.: 197-204.

DRZYMALA, J., FUERSTENAU, D.W., 2014. *Selective flocculation of hematite in quartz–hematite–ferric ion–polyacrylic acid system. Part 2. Effect of grinding and a hydrofluoric treatment on selectivity of flocculation*. International Journal of Mineral Processing 129, 1-5.

FARLANA, S.H., HUDA, N., MAHMUD, M.A.P., LANG, C., 2018. *Towards sustainable TiO_2 production: An investigation of environmental impacts of ilmenite and rutile processing routes in Australia*. Journal of Cleaner Production 196, 1016-1025.

FENG, B., LUO, X.P., WANG, J.Q., WANG, P.C., 2015. *The flotation separation of scheelite from calcite using acidified sodium silicate as depressant*. Minerals Engineering 80, 45-49.

FORBES E., 2011. *Shear, selective and temperature responsive flocculation: A comparison of fine particle flotation techniques*. International Journal of Mineral Processing 99(1-4), 1-10.

IRANNAJAD, M., MEHDILO, A., SALMANI, N.O., 2014. *Influence of microwave irradiation on ilmenite flotation behavior in the presence of different gangue minerals*. Separation and Purification Technology 132, 401-412.

LAPOINTE, M., BARBEAU, B., 2018. *Selection of media for the design of ballasted flocculation processes*. Water Research 147, 25-32.

LI, F., ZHONG, H, ZHAO, G, WANG, S., LIU, G., 2016. *Adsorption of a-hydroxyoctyl phosphonic acid to ilmenite/water interface and its application in flotation*. Colloids and Surfaces A: Physicochemical and Engineering Aspects 490, 67-73.

LIU, J., ZENG, Y., MAJID, E., NGUYEN, A.V., WANG, Y., WEN, S.M., 2019. *DFT simulation of S-species interaction with smithsonite (001) surface: effect of water molecule adsorption position*. Results in Physics, DIO: 10.1016/j.rinp.2019.102575

LIU W., HU Y., SUN W., 2014. *Separation of diaspore from bauxite by selective flocculation using hydrolyzed polyacrylamide*. Journal of Central South University 21(4), 1470-1476.

LUSZCZKIEWICZ, A., LEKKI, J., LASKOWSKI, J.S., 1979. *Flotability of ilmenite[C]//Treatment of Iron-Titanium Ores Round Table Seminar. Poland: PWN, Thirteenth International Mineral.*

LV, J.F., ZHANG, H.P., TONG, X., FAN, C L., YANG, W.T., ZHENG, Y.X., 2017. *Innovative methodology for recovering titanium and chromium from a raw ilmenite concentrate by magnetic separation after modifying magnetic properties*. Journal of Hazardous Materials 325, 251-260.

NERADOVSKY, Y., ALEKSEEVA, S.A., CHERNOUSENKO, E.V., 2019. *Mineralogy and process properties of Kolvitsky titanomagnetite ore*. IOP Conference Series: Earth and Environmental Science 262, 12050.

OMRAN, M., FABRITIUS, T., ELMAHDY, A.M., ABDEL-KHALEK, N.A., 2015. *Improvement of phosphorus removal from iron ore using combined microwave pretreatment and ultrasonic treatment*. Separation and Purification Technology 156, 724-737.

PANDA, L., BISWAL, S.K., VENUGOPAL, R., MANDRE, N.R., 2018. *Recovery of Ultra-Fine Iron Ore from Iron Ore Tailings*. Transactions of the Indian Institute of Metals 71(2), 463-468.

SADEGHALVAAD, M., SABBAGHI, S., 2015. *The effect of the TiO2/polyacrylamide nanocomposite on water-based drilling fluid properties*. Powder Technology 272, 113-119.*Processing Congress*, 164-182.

SUBRAHMANYAM, T.V., FORSSBERG, K.S.E., 1990. *Fine particles processing: shear-flocculation and carrier flotation – a review*. International Journal of Mineral Processing 30(3-4), 265-286.

SUN, B.Q., 2006. *Progress in China's Beneficiation Technology for Complex Refractory Iron Ore*. Metal Mine 3, 11-13.

SUNG, N.W., CONNAL, L.A., FORBES, E, MOHANARANGAM, K., FRANKS, G.V., 2018. *In situ study of aggregate sizes formed in chalcopyrite-quartz mixture using temperature-responsive polymers*. Advanced Powder Technology 29(8), 1940-1949.

SUN, W., LONG, J., XU, Z., MASLIYAH, J.H., 2008. *Study of Al (OH) 3− Polyacrylamide-Induced Pelleting Flocculation by Single Molecule Force Spectroscopy*. Langmuir 24(24), 14015-14021.

TARTAGLIA J.M., LOEFFLER J.P., 1997. *Turnlund T H. Polymer film for wrapping a stent structure: U.S. Patent 5,700,286*, 12-23.

WANG J., ZHAO F.L., 1992. *Crosslinking mechanism of multivalent metal ions with polyacrylamide*. J. China Univ. Pet 16, 32-39.

WANG W., ZHU, Y., ZHANG, S., DENG, J., HUANG, Y., YAN, W., 2017. *Flotation Behaviors of Perovskite, Titanaugite, and Magnesium Aluminate Spinel Using Octyl Hydroxamic Acid as the Collector*. Minerals 7(8), 134.

WILLIAMS, D.L., GANTT G E., BEHL S., WILLIS M.J., 1997. *Method for separating mixture of finely divided minerals: U.S. Patent 5,603,411*, 2-18.

XIAO, J.H., ZHANG, Y.S., 2019. *Recovering Cobalt and Sulfur in Low Grade Cobalt-Bearing V–Ti Magnetite Tailings Using Flotation Process*. *Processes 7*, 536.

XIAO, J.H., ZHOU, L.L., 2019. *Increasing Iron and Reducing Phosphorus Grades of Magnetic-Roasted High-Phosphorus Oolitic Iron Ore by Low-Intensity Magnetic Separation–Reverse Flotation*. *Processes 7*, 388.

ZENG, J., CHEN, L., YANG, R., TONG, X., REN, P., ZHENG, Y., 2017. *Centrifugal high gradient magnetic separation of fine ilmenite*. International Journal of Mineral Processing 168, 48-54.

ZHAO, X., MENG, Q., YUAN, Z., ZHANG, Y., LI, L., 2019. *Effect of sodium silicate on the magnetic separation of ilmenite from titanaugite by magnetite selective coating*. Powder Technology 344, 233-241.

ZHU, Y G., ZHANG, G.F., FENG, Q.M., YAN, D.C., WANG, W.Q., 2011. *Effect of surface dissolution on flotation separation of fine ilmenite from titanaugite*. Transactions of Nonferrous Metals Society of China 21(5), 1149-1154.

ZOUBOULIS, A.I., AVRANAS, A., 2000. *Treatment of oil-in-water emulsions by coagulation and dissolved-air flotation*. Colloids and Surfaces A: Physicochemical and Engineering Aspects 172(1), 153-161.