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Influence of particle size on flotation separation of ilmenite, olivine, and pyroxene

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Abstract: The rock type in Panxi area is changing from gabbro type to olivine pyroxene type, which makes it difficult for enterprises to obtain better beneficiation indexes at present. In order to solve this problem, we use a variety of modern test techniques, such as zeta potential measurements, Fourier-transform infrared (FTIR) spectroscopy, adsorption amount measurements, and mineral-reagent interaction energy simulation to analyze the influence of particle size on mineral flotation behavior and the interaction of fine-grained minerals in this paper. The experiments results indicate that the presence of fine-grained (-19 μm) mineral particles is deleterious to the flotation of ilmenite, the ilmenite recovery decreases as the microfine grade content of pyroxene and olivine increases, distribution of narrow size minerals is beneficial to the minerals flotation performance, and the order of sodium oleate (NaOL) adsorption strength on different ilmenite crystal planes is (1011) > (0001). The research results of this paper deepen the understanding of the olivine type ilmenite resources in Panxi area, enrich the theoretical system of flotation separation of refractory ilmenite, and provide theoretical support for the key technical problems of flotation separation of ilmenite in Panxi area.

Keywords: olivine pyroxene, ilmenite, fine particles, narrow size, flotation separation

1. Introduction

Titanium (Ti) plays an irreplaceable role in high-tech fields, such as aerospace, weapon manufacturing, transportation, medical equipment (Bulatovic and Wyslouzil, 1999; Chen et al., 2013; Samal et al., 2009). After decades of exploitation of vanadium titanomagnetite (VTM) resources in Panxi area (southwest Sichuan province, China), most mines have entered the middle and deep mining. Panzhihua, Hongge, Baima, and Taihe are the four main mining areas in Panxi. With the increase of mining depth, the proportion of gabbro and pyroxene decreases gradually, while the proportion of olivine and peridotite increases, especially in Hongge mining area. (Yang et al., 2016b). Namely, the rock type has changed greatly from gabbro to olivine, with that type VTM resources are complex and difficult to separate. Additionally, the lack of corresponding separation technology makes it difficult for enterprises to obtain better beneficiation indexes and utilize such resources (Bai et al., 2012; Cheng et al., 2014). At present, in the process of deeply integrated exploration in Panxi, it is found that olivine pyroxene type ore resources account for more than 80% of the 3 billion tons of newly discovered VTM reserves, and the potential reserves are nearly 10 billion tons (Cheng et al., 2014). The objective evaluation on the economy and feasibility of recovery of the olivine pyroxene type VTM, has not been made yet. Besides, the process and technology to guide the rational utilization of refractory mineral resources in Panxi area are not available now.

The main beneficiation method of ilmenite is flotation. There are many factors affecting the flotation performance of ilmenite, such as the raw mineral properties, collectors' type, and the additional metal

ions. (Irannajad et al., 2014; Li et al., 2016; Parapari et al., 2017; Xu et al., 2017). It is found that pretreatment of ilmenite in certain ways can strengthen the flotation separation. Microwave irradiation can transform Fe^{2+} into Fe^{3+} on ilmenite surface, resulting in the increase of oleic acid adsorption amount and the formation of insoluble iron oleate, which was significantly increase the grade (from 21.3% to 22.1%) and recovery (from 71% to 82.5%) of TiO_2 (Irannajad et al., 2014). The same effect of microwave irradiation can be achieved by surface dissolution pretreatment of ilmenite with acid, and XPS analysis shows that the content of Fe^{3+} is also increased. The flotation recovery of ilmenite improves from 73.5% to 92.1% at a pH of 6.3, while that of olivine-pyroxene decreases from 59.6% to 44.6% (Parapari et al., 2017). In the pulp solution, the existence of some metal ions, such as Cu^{2+} and Pb^{2+} , can activate ilmenite flotation. Therefore, the flotation separation can be strengthened by adding appropriate amount of metal salt solution in the flotation process (Li et al., 2016; Xu et al., 2017). Many reagents have been employed for ilmenite flotation. It is found that combined use of collectors can achieve better results than single ones (Tian et al., 2017; Yang et al., 2016a).

A large number of fine mineral particles will be produced in crushing and grinding process, affecting ilmenite flotability. These fine particles have large solubility, and the dissolved components are readily to adsorb on the surface of minerals subsequently, which will weaken the selective adsorption of reagents, decrease the collision probability between particles and bubbles, and cause heterogeneous coagulation between particles. Hence, the flotation of fine minerals is always difficult in mineral processing (Johnson, 2006). In view of solving this problem, on the one hand, the bubble size is reduced to increase the collision and adhesion probability, such as the application of microbubbles in flotation column (Koh and Schwarz, 2003). On the other hand, selective agglomeration of fine particles is used to increase the apparent particle size of fine particles and realize flotation separation under conventional conditions, such as oil agglomeration flotation, carrier flotation, shear flocculation flotation and selective flocculation flotation (Johnson, 2006).

At present, the research on flotation separation of fine ilmenite has obtained certain achievements, but it didn't really solve the issue of low recovery. Therefore, it is an effective method to stop or reduce the production of fine ilmenite by selective grinding to address the difficulty of fine ilmenite flotation from the source. In this paper, ilmenite, titanite, and olivine are the main research objects in the flotation system of olivine type ilmenite in Panxi area. The basic theoretical system of flotation separation technology for olivine pyroxene type ilmenite was formed by studying the surface properties of minerals and the interaction between flotation reagents and mineral particles. It is of great significance on both theory and practice to solve the flotation separation issue of olivine pyroxene type ilmenite and improve the comprehensive utilization rate of VTM resources.

2. Materials and reagents

2.1. Materials

High grade samples of ilmenite, titanite, and olivine were obtained from Panzhihua (Sichuan province, China). These samples were repeatedly purified by magnetic separation and gravity separation. After being crushed and ground, the powdered samples were screen to four particle sizes (75-45, 45-25, 25-19, 19-0 μm), which were used in the flotation tests. For the FTIR analysis and zeta potential measurements, the samples were further ground to about 20 μm . Table 1.1 to Table 1.3 and Fig. 1.1 to Fig. 1.3 are the chemical composition and X-ray diffraction characterization results for the experiment samples respectively, confirming that the purity of the prepared samples was ~90%. The collector NaOL was chemically pure. In the experiment, H_2SO_4 and NaOH were used to adjust pH of the system. All reagents used in this study were analytical grade. Deionized water (resistivity: 18.3 $\text{M}\Omega \cdot \text{cm}$) was used for the microflotation tests.

Table 1.1. The chemical composition of ilmenite (mass %)

TiO_2	Fe_2O_3	MnO	CaO	Al_2O_3	MgO	SiO_2
50.05	41.76	0.62	0.10	0.45	5.50	1.52

Table 1.2. The chemical composition of titanaugite (mass %)

TiO ₂	Fe ₂ O ₃	MnO	CaO	Al ₂ O ₃	MgO	SiO ₂
0.37	16.862	0.048	2.10	11.53	22.39	46.70

Table 1.3. The chemical composition of olivine (mass %).

TiO ₂	Fe ₂ O ₃	MnO	CaO	Al ₂ O ₃	MgO	SiO ₂
0.60	9.27	0.13	0.10	0.50	49.15	40.25

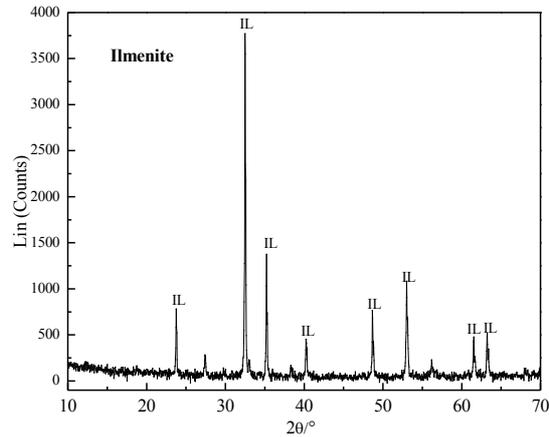


Fig. 1.1. XRD pattern of ilmenite

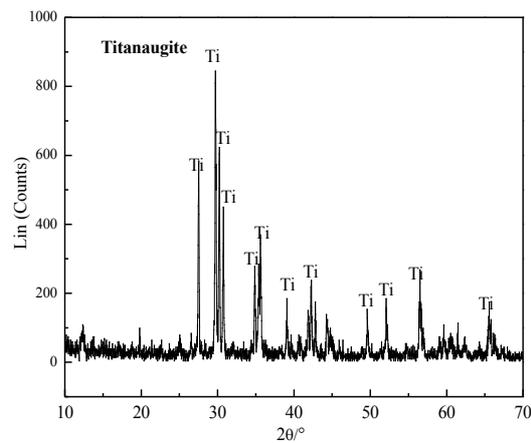


Fig. 1.2. XRD pattern of titanaugite

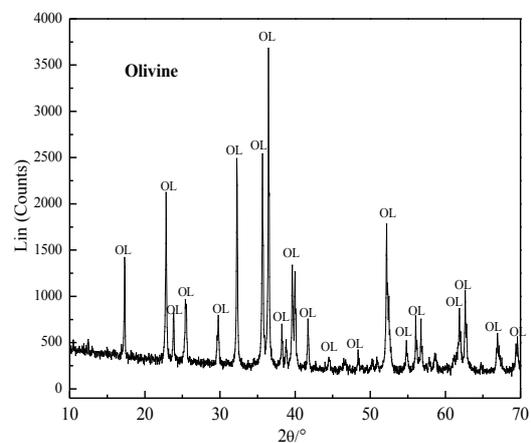


Fig. 1.3. XRD pattern of olivine

2.2. Micro-flotation tests

All of the micro-flotation tests were carried out in a flotation machine of XFG-1600 with impeller speed of 1600 rpm. For each test, 2.0 g mineral sample with desired particle sizes was added to a 40mL flotation cell. After the flotation pulp was conditioned to the desired pH, the desired dosage of reagents was added. The suspension was stirred for 5 min and each flotation was also conducted for 5 min. The concentrates and tailings were weighed separately after filtration and drying, and the recovery was calculated based on the dry weight. Moreover, every reported result was the average of triplicate parallel experiments. The environmental temperature was maintained at 25 °C.

2.3. Zeta-potential measurements

The zeta-potential measurements were carried out in a Malvern Zetasizer Nano ZS90 (England) equipped with a rectangular electrophoresis cell. The suspension containing 30 mg of the purified mineral particles (~20 µm) was prepared in 1mM NaCl background electrolyte solution, and conditioned by magnetic stirring for 5 min. The supernatant of the suspension was taken for zeta potential measurement after 10 min of settlement. The conductivity and pH of the suspension were monitored continuously during the measurement. The environmental temperature was maintained at 25 °C.

2.4. FTIR measurements

FTIR spectra were recorded from 4000 to 450 cm⁻¹ using a Spectrum One (version BM) spectrometer (Perkin Elmer, USA) at 25 °C. The purified mineral particles (2.0 g) used for FTIR measurements were ground to less than 2 µm. For each FTIR measurement, mineral sample was conditioned with certain reagents in a Plexiglas cell for 40 min. After being filtered, the sample was washed three times with ultrapure water, and then dried below 60°C under vacuum condition. The spectra of the samples were obtained using KBr disks.

2.5. Adsorption tests

Elementar liquid TOCII (German, Elementar Co.) was used to monitor the amount of adsorption. The pure mineral sample of 2.0 g was placed in a Plexiglas cell (40 mL), which was filled with 35 mL of deionized water before. The same procedure as micro-flotation tests was carried out for reaction of reagents with mineral particles. To obtain liquid supernatant used for the adsorption measurements, the suspension was settled for 10 min. The following equation was used to determine the amount of adsorbed reagents:

$$\Gamma = \frac{(C_0 - C) \cdot V}{m \cdot A} \quad (1)$$

where Γ is the adsorbed amount on specific surface area (mol/m²), C_0 and C are the initial and supernatant concentrations (mg/L), respectively, V is the solution volume (L), m is the mass of particles in the sample (g), and A is the mineral specific surface area (m²/g).

The specific surface area of ilmenite with different particle sizes was shown in Table 2.1.

Table 2.1. Specific surface of the different ilmenite size fractions

	ilmenite			
	45-75µm	38-45µm	19-38µm	0-19µm
Specific surface area (m ² /g)	0.537	0.943	1.302	1.669

2.6. Molecular dynamics simulations

The simulations were carried out via Forcite field in Material studio 6.0. The UFF force field was used to optimize the structural modeling, which was proved to be the most widely applicable calculation method. The initial configurations used to determine the minimum energy conformation of NaOL molecule were the same as that in our previous study (Hu et al., 2012; Xu et al., 2016). All the simulations were performed in a NVT (moles (N), volume (V) and temperature (T) are conserved) with a time step

of 1 fs and a total trajectory length of 300,000 steps. During the simulation, a Nose-Hoover thermostat was used to maintain the temperature at 298 K. With a cutoff of 1.25 nm, the Ewald method was used to calculate the non-bonded (van der Waals and Coulomb) interactions. In order to fully relax the system, a further 2 ns MD was performed and the trajectories of the last 1 ns were used for the analysis at the end of the above simulation.

The relative affinity between the ilmenite surface and the NaOL molecule can be quantified in terms of the interaction energy calculated as:

$$\Delta E = E_{\text{complex}} - (E_{\text{surface}} + E_{\text{adsorbate}}) \quad (2)$$

where E_{complex} denotes the total energy of the optimized reagent/mineral surface complex, while E_{surface} and $E_{\text{adsorbate}}$ are the energies of the free mineral surface and adsorbed molecules, separately (Xu et al., 2014). The more negative interaction energy (ΔE) value is, the more favorable interactions between the mineral surface and the collectors (Pradip et al., 2002). Therefore, via comparing ΔE value, it is easy to assess the relative strength of the interaction between adsorbed molecules and different mineral surfaces.

3. Results and discussion

3.1. Effect of particle size on mineral flotation

In the flotation practice, valueable minerals must not only achieve monomer dissociation, but also meet the flotation index of particle size. Some studies have shown that during the flotation process of minerals, the particle size together with the distribution of the mineral particles will also have a certain impact on the flotation index. The extreme coarse and fine particles mineral are more difficult to float, while intermediate particle sizes are relatively easy (Ng et al., 2015; Xu et al., 2016; Yin et al., 2011).

Most of the olivine type ilmenite minerals' particle size is fine, hence the particle size and distribution characteristics are particularly significant for effective flotation. Limited loading capacity of flotation bubbles determine that flotation cannot be achieved if the mineral particles are too coarse (Forbes, 2011; Lu et al., 1998; Van Oss et al., 1987). The recovery index is also not satisfying if the particles size is too fine, even if reaching monomer dissociation. Due to the large specific surface area and high activity of fine particles, the consumption of reagents will be increased, and the selectivity of reagents will be weakened. Slime inclusion in the bubble and covering on the surface of flotation concentrate will also affect the concentrate quality. The surface dissolution of fine particles intensifies, leading to the increase of excess ions and deterioration of flotation. Therefore, this paper intends to study the influence of different particle sizes on the floatability of minerals, and to explore the feasibility to enhance the flotation efficiency of olivine type ilmenite via improving the mineral particle size distribution.

3.1.1. Effect of particle size on mineral flotation behavior

The flotation results of ilmenite with different particle sizes as a function of pH are shown in Fig. 2.1. The recovery of ilmenite decreases with the decrease of its particle size. The recovery of 45-75 μm ilmenite is relatively high, reaching maximum 93%, but the recovery of ilmenite with particle size of -19 μm is less than 40% at pH 9.3. The reagent adsorption amount per unit surface decreases according to the decrease of mineral particle size. Under alkaline condition, the flotation behavior of ilmenite with particle size of 19-25 μm occurs abnormality, because the difference of ilmenite crystal surface is more notable in this size range.

Under different pH conditions, the titanite flotation results of different particle sizes are shown in Fig. 2.2. The flotation performance is affected by particle size distinctly. The smaller the particle size, the lower the flotation recovery. When the particle size is below -19 μm , the flotation recovery is less than 10%.

The flotation results of olivine with different particle sizes at different pH values are shown in Fig. 2.3. The effect of olivine with different particle size on flotation recovery is obviously different from that of titanite and ilmenite. The phenomenon that the recovery decreases with the decrease of particle size is not obvious in olivine flotation. Under different pH conditions, there is no significant difference in the size of olivine from 19-25, 25-45, and 45-75 μm . The recovery of -19 μm particle size is low, that is

less than 20% when the pH is 5.5 ~ 6.0. As showed the Figs 2.1, 2.2, and 2.3, the difference of titanaugite and olivine particle size has obvious influence on flotation recovery, rather than ilmenite at pH 6.0. Therefore, the flotation condition at pH 6.0 was determined for subsequent tests. The phenomenon that the difference of olivine particle size has obvious influence on flotation recovery also provides us with the idea of selective grind. By increasing the proportion of olivine in the grinding process, the flotation separation can be more effective.

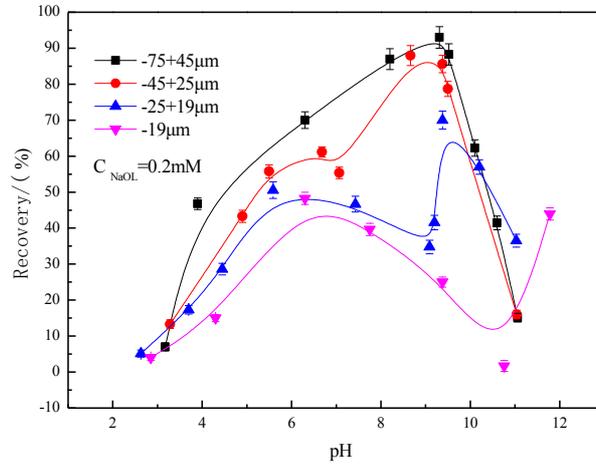


Fig. 2.1. The recovery of ilmenite with different sizes as a function of pH

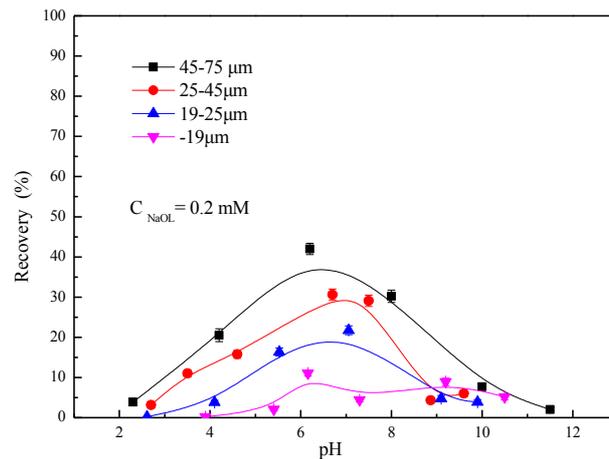


Fig. 2.2. The recovery of titanaugite with different sizes as a function of pH

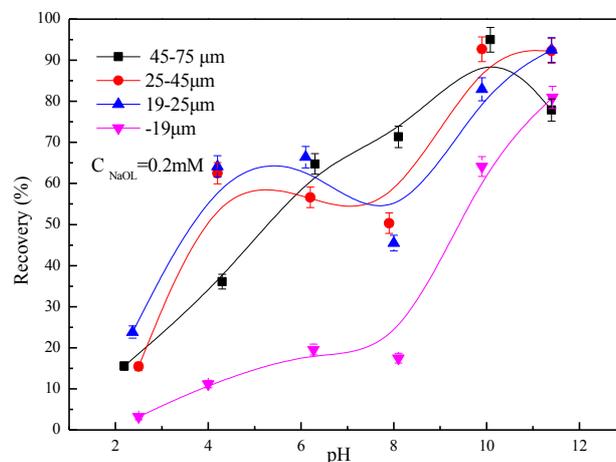


Fig. 2.3. The recovery of olivine with different sizes as a function of pH

3.1.2. Interaction of ultrafine olivine and titanite on ilmenite

As shown in Fig.2.4, when the NaOL dosage is 2×10^{-4} mol/L at pH condition of 6.0, it can be seen from the recovery curve that the ilmenite recovery witnesses a decline trend with the increase of the mass ratio of ultrafine olivine and titanite. Moreover, the influence of fine-grained olivine on ilmenite is greater than that of titanite. However, the recovery of ilmenite is slightly increased in both curves when the mass ratio is 10%, indicating that both olivine and titanite can activate ilmenite flotation to some extent when the content of ultrafine olivine and ilmenite is low.

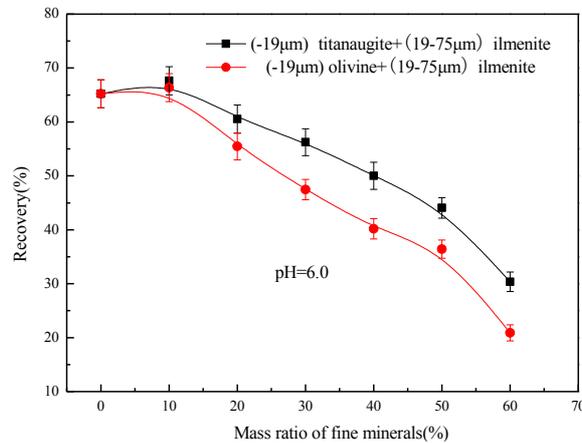


Fig. 2.4. Effect of fine particle size of titanium and olivine on separation of ilmenite.

3.2. Effect of narrow size mineral distribution on mineral flotation

The flotation effects of three minerals with different particle sizes were discussed in this section. It was found that the flotation efficiency of ilmenite was affected by the presence of $-19 \mu\text{m}$ gangue minerals from the interaction experiments of ultrafine olivine and titanopyroxene on ilmenite. Therefore, we hypothesized that strengthened flotation separation can be achieved by controlling the particle size distribution of minerals during grind. In order to verify it, NaOL was used as collector to carry out flotation experiments of -19 , $19-75$, and $-75 \mu\text{m}$, respectively, to research the influence of narrow particle size distribution on recovery.

Under the conditions of -19 , $19-75$, and $-75 \mu\text{m}$, the relationship between mineral flotation recovery and pH is shown in Fig. 2.5, Fig. 2.6 and Fig. 2.7. It can be seen that the recovery of ilmenite in $19-75 \mu\text{m}$ is significantly higher than that in $-75 \mu\text{m}$, which indicates that it is feasible to realize intensified flotation of ilmenite by controlling the particle size distribution of minerals. For gangue minerals olivine and titanite, the recovery of $19-75 \mu\text{m}$ particle size is also higher than that of full particle size $-75 \mu\text{m}$. the reason for this phenomenon is that fine-grained minerals will be coated on the surface of coarse-grained minerals, hence worsening flotation. Therefore, by reducing the production of fine-grained minerals in the grinding process, the strengthened flotation can be achieved.

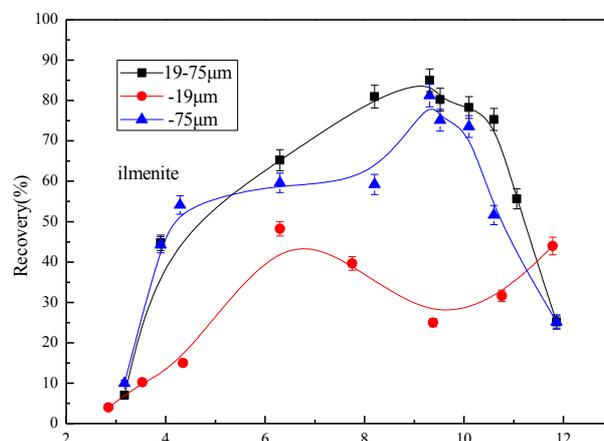


Fig. 2.5. The recovery of narrow particle size ilmenite as a function of pH ($C_{\text{Collector}}=2 \times 10^{-4}$ mol/L)

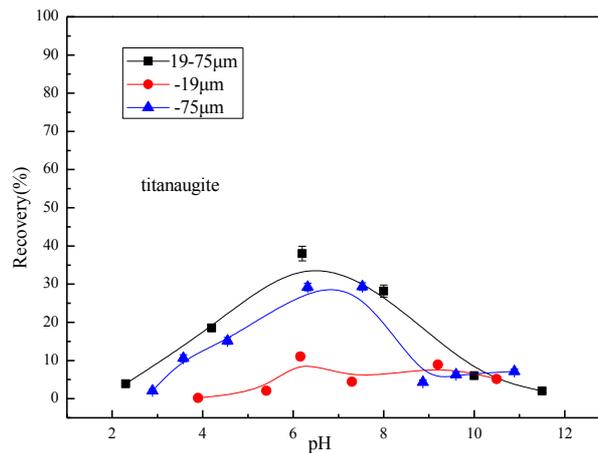


Fig. 2.6. The recovery of narrow partial size titanite as a function of pH ($C_{\text{Collector}}=2 \times 10^{-4}$ mol/L)

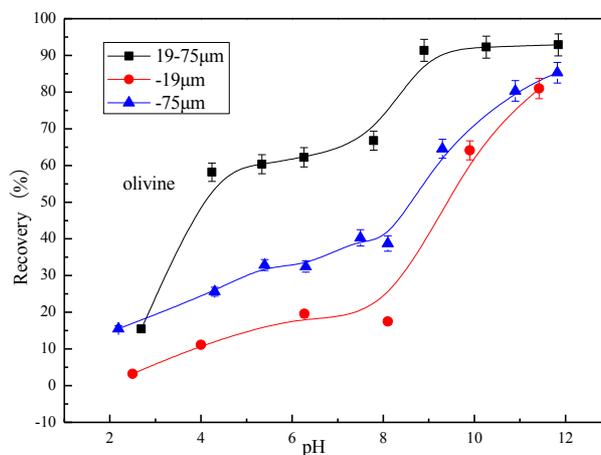


Fig. 2.7. The recovery of narrow particle size olivine as a function of pH ($C_{\text{Collector}}=2 \times 10^{-4}$ mol/L)

3.3. Analysis of flotation behavior difference of ilmenite with different particle size

In the process of crush and grind, the particle size of mineral gradually decreases, and the physical shape of mineral particles has increasing influence on its surface characteristics. Therefore, exposed surfaces that determine the surface properties of minerals are usually different with different particle sizes. Herein, ilmenite crystal is taken as an example to explain the difference of flotation behavior of different size mineral particles.

3.3.1. Adsorption behavior of ilmenite with different particle size

It can be seen from Fig.2.8 that there is no obvious characteristic peak in the infrared spectrum of ilmenite with wavenumber of $1000 \sim 4000 \text{ cm}^{-1}$. In the spectrum of NaOL, two adsorption peaks at 2920 and 2850 cm^{-1} are observed. They are the symmetrical vibrational adsorption peaks of C-H bond in $-\text{CH}_2-$ and $-\text{CH}_3$ in NaOL (Wang et al., 2020b), respectively. Peaks at 1560 , 1450 , and 1420 cm^{-1} represent the adsorption of carboxylate (Wang et al., 2020a). 1560 cm^{-1} is the asymmetric stretching vibration peak of $-\text{COO}-$ group in $\text{R}-\text{COOH}$, and the other two peaks are symmetrical vibration peaks. In the IR spectrum of NaOL interacting with ilmenite, symmetrical vibrational absorption peaks of $-\text{CH}_2-$ and $-\text{CH}_3$ move to 2930 and 2860 cm^{-1} , and new adsorption peaks appear at 1590 and 1465 , and 1560 and 1450 cm^{-1} . Compared to the vibration peak of carboxyl group, the wavenumber shift by 30 and 15 cm^{-1} respectively, illustrating the chemisorption of NaOL on the surface of ilmenite.

The surface charge and flotation behavior of minerals are affected by pH, which directly leads to the change of collector adsorption on mineral surface. Fig.2.9 shows the variation of the adsorption amount of NaOL on the surface of ilmenite with different particle sizes as a function of pH. As shown in Fig.2.9,

the adsorption capacity of ilmenite with the particle size of $-19\ \mu\text{m}$, $19\text{-}25\ \mu\text{m}$, $25\text{-}45\ \mu\text{m}$ and $45\text{-}75\ \mu\text{m}$ has the same tendency of change, increasing gradually with the increase of pH. In order to explain this phenomenon, the zeta-potential of ilmenite was measured. As shown in Fig.2.10, the greater the pH value is, the more negative charge on the ilmenite surface is. However, the adsorption amount increases, which indicates that the chief force is not electrostatic attraction. According to the general theory, the smaller the particle size is, the larger the specific surface area is, and hence the greater the surface energy is, so the adsorption capacity per unit area should be increased. However, from the adsorption curve, it is found that more coarse particle size of ilmenite has greater adsorption capacity of NaOL. The results show that smaller particle dissociate more crystal surfaces with poor adsorption ability (bottom surfaces). The larger the relative area of the bottom surface is, the smaller of adsorption amount per unit specific area is.

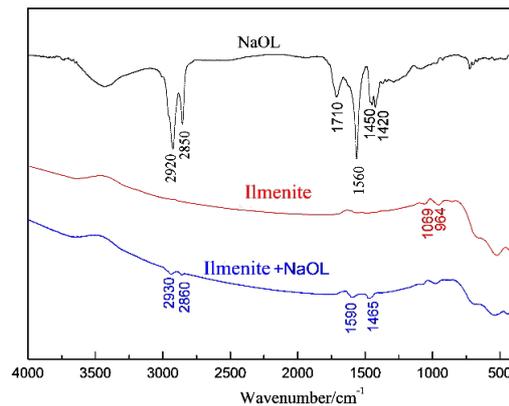


Fig. 2.8. FTIR of ilmenite before and after being treated by NaOL ($C_{\text{Collector}}=1\times 10^{-3}\text{mol/L}$, $\text{pH}=5.5\sim 6.0$)

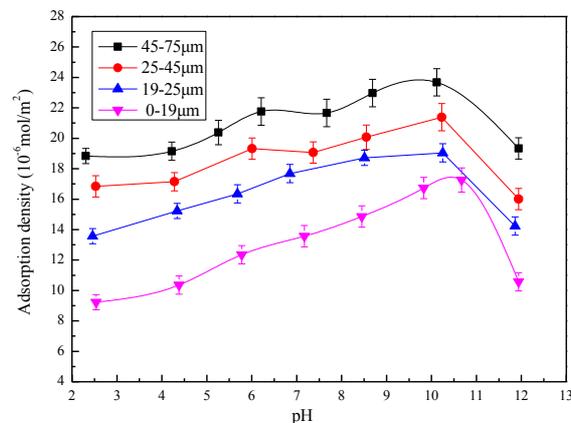


Fig. 2.9. The adsorption amount of NaOL on the surface of different ilmenite particle sizes

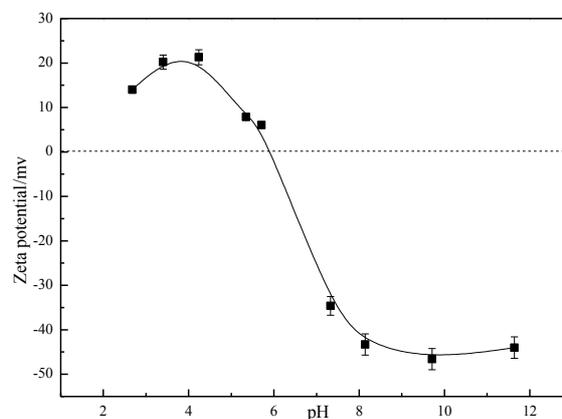


Fig. 2.10. The zeta potential of ilmenite as a function of pH

3.3.2. Anisotropy of interaction between sodium oleate and ilmenite

The geometry optimization and molecular dynamics simulation of different crystal planes and NaOL model were carried out to obtain the most stable configuration of flotation reagent interacted with mineral surface, and then the adsorption energy was calculated. The kinetic simulation parameters are as follows: in NVT system, the set temperature is 298K, the step size is 1.0 fs, the system is truncated to 18.5 nm, and the operation is 300 ps. The other parameters are selected by default. The interaction energy between ilmenite and NaOL was calculated, and the results are shown in Fig. 2.11.

According to Fig. 2.11, the order of interaction energy between NaOL and ilmenite crystal surfaces is $(1011) > (0001)$. When NaOL is adsorbed on the two different surfaces, the adsorption energy of (1011) surface is more negative, i.e., adsorption of NaOL with (1011) is the more stable than that with (0001) . In view of the difference of the flotation behavior with different particle sizes, the following reasons can be assumed according to the results of molecular dynamics simulation of ilmenite. For the short columnar ilmenite particles, the relative number and area of the edge surface (1011) and the bottom surface (0001) vary with the particle size changing. The more coarse ilmenite particle size has more proportion of edge surface (1011) with smaller surface energy, and hence stronger adsorption capacity for NaOL, so the flotation performance is better; when the particle size of ilmenite becomes finer, the proportion of fracture along the bottom surface (0001) with stronger chemical bond increases, but the interaction between (0001) and NaOL is weaker. Therefore, the flotation of fine ilmenite is poorer with the addition of same amount of NaOL. The schematic diagram of the relationship between crystal surface proportion and particle size variation is shown in Fig. 2.12. Furthermore, from the SEM images of different particle size ilmenite in Fig. 2.13, the proportion of short columnar ilmenite decreases with the particle size reducing, and that of bottom (0001) increases gradually, which is consistent with the inferred schematic diagram.

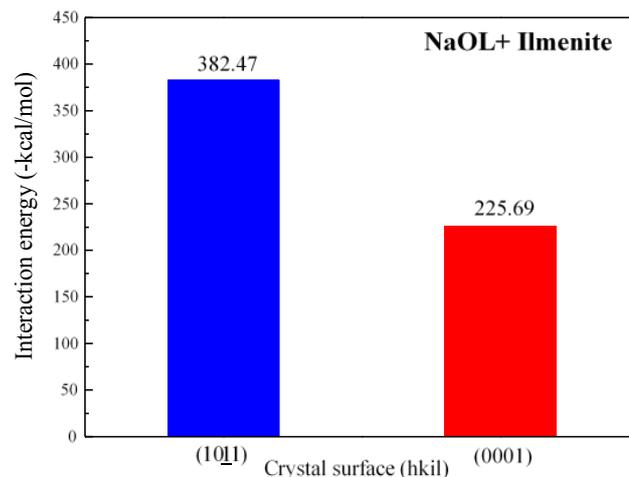


Fig. 2.11. Comparison of the interaction energy between NaOL and different ilmenite crystal surfaces

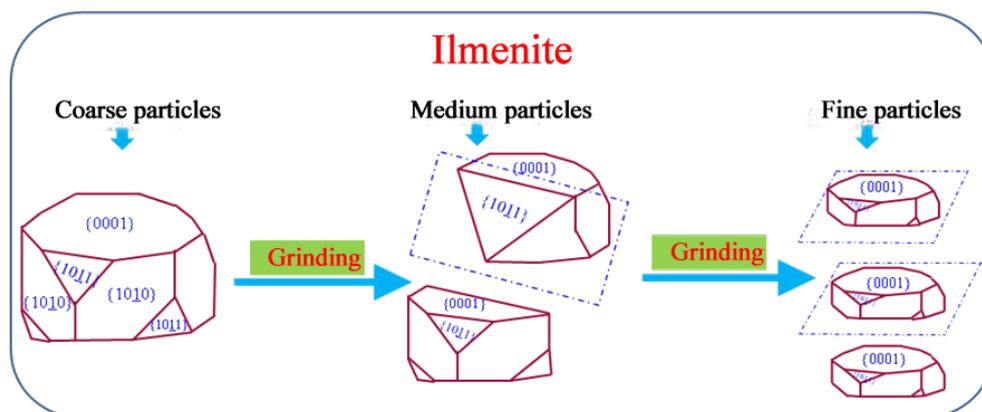


Fig. 2.12. Schematic of change in number of crystal planes of ilmenite with the decrease of particle size

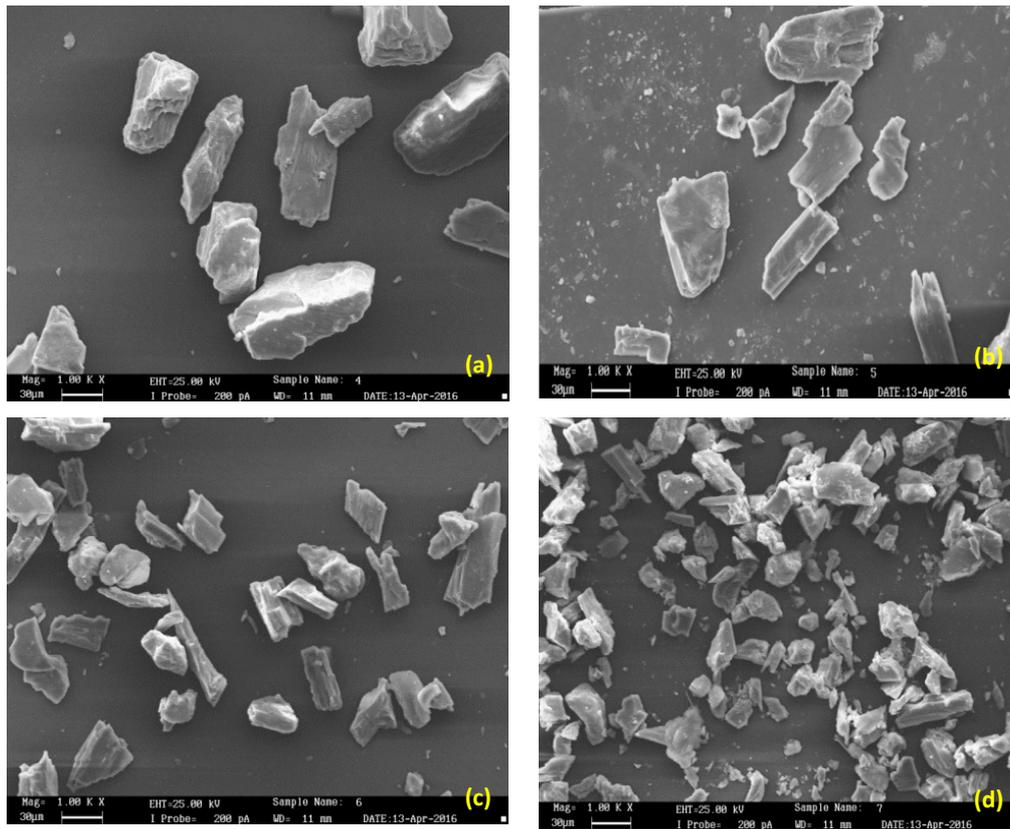


Fig. 2.13. Scanning electron microscopy of different sizes ilmenite (a)45-75 μm , (b)25-45 μm , (c)19-25 μm , and (d) -19 μm

4. Conclusions

(1) The recovery of ilmenite and titanaugite decreases with the decrease of particle size. When the particle size of olivine is -19 μm , the recovery is remarkably lower than other particle sizes. That is, the existence of fine mineral particles is not conducive to flotation.

(2) Interaction of ultrafine olivine and titanaugite on ilmenite results show that the recovery of ilmenite decreases with the increase of the content of ultrafine olivine and titanaugite, and the effect of fine-grained olivine on ilmenite is greater than that of titanaugite.

(3) The distribution of narrow particle size minerals is beneficial to improve the flotation performance through the influence of fine particle size (-19 μm) on the recovery of the three minerals. In order to strengthen the flotation separation of ilmenite from olivine and titanaugite, it is necessary to control and reduce the production of fine-grained minerals in the grind process.

(4) The reason for the difference of flotation behavior of ilmenite with different particle size is that the interaction ability of ilmenite crystal surface with NaOL is (1011) > (0001) via analyzing the crystal structure of ilmenite. The more coarse ilmenite particle size has more proportion of edge surface (1011) with stronger adsorption capacity for NaOL, leading to better flotation performance; when the particle size of ilmenite becomes finer, the proportion increased of fracture along the bottom surface (0001) with weaker interaction ability with NaOL, causing worse flotability.

This work provides valuable insights into the flotation separation of ilmenite, olivine, and pyroxene. Reducing the production of fine-grained minerals in the grinding process should be further investigated to improve the recovery and grade of TiO_2 .

Acknowledgements

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References

- BAI, Z.-J., ZHONG, H., LI, C., ZHU, W.-G., XU, G.-W., 2012. *Platinum-group elements in the oxide layers of the Hongge mafic-ultramafic intrusion, Emeishan Large Igneous Province, SW China*. *Ore Geology Reviews*, 46, 149-161.
- BULATOVIC, S., WYSLOUZIL, D., 1999. *Process development for treatment of complex perovskite, ilmenite and rutile ores*. *Minerals Engineering*, 12(12), 1407-1417.
- CHEN, D.-S., ZHAO, L.-S., TAO, Q., HU, G.-P., ZHAO, H.-X., JIE, L., WANG, L.-N., 2013. *Desilication from titanium-vanadium slag by alkaline leaching*. *Transactions of Nonferrous Metals Society of China*, 23(10), 3076-3082.
- CHENG, L., ZENG, L., REN, Z., WANG, Y., LUO, Z., 2014. *Timescale of emplacement of the Panzhihua gabbroic layered intrusion recorded in giant plagioclase at Sichuan Province, SW China*. *Lithos*, 204, 203-219.
- 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., NURI, O.S., 2014. *Influence of microwave irradiation on ilmenite flotation behavior in the presence of different gangue minerals*. *Separation and Purification Technology*, 132, 401-412.
- JOHNSON, N., 2006. *Liberated 0–10µm particles from sulphide ores, their production and separation – Recent developments and future needs*. *Minerals Engineering*, 19(6), 666-674.
- KOH, P., SCHWARZ, M., 2003. *CFD modelling of bubble-particle collision rates and efficiencies in a flotation cell*. *Minerals Engineering*, 16(11), 1055-1059.
- LI, F., ZHONG, H., WANG, S., LIU, G., 2016. *The activation mechanism of Cu (II) to ilmenite and subsequent flotation response to a-hydroxyoctyl phosphinic acid*. *Journal of Industrial and Engineering Chemistry*, 37, 123-130.
- LU, S., DING, Y., GUO, J., 1998. *Kinetics of fine particle aggregation in turbulence*. *Advances in Colloid and Interface Science*, 78(3), 197-235.
- NG, W.S., SONNIE, R., FORBES, E., FRANKS, G.V., 2015. *Flocculation/flotation of hematite fines with anionic temperature-responsive polymer acting as a selective flocculant and collector*. *Minerals Engineering*, 77, 64-71.
- PARAPARI, P.S., IRANNAJAD, M., MEHDILO, A., 2017. *Effect of acid surface dissolution pretreatment on the selective flotation of ilmenite from olivine and pyroxene*. *International Journal of Mineral Processing*.
- SAMAL, S., MOHAPATRA, B., MUKHERJEE, P., CHATTERJEE, S., 2009. *Integrated XRD, EPMA and XRF study of ilmenite and titania slag used in pigment production*. *Journal of Alloys and Compounds*, 474(1), 484-489.
- TIAN, J., XU, L., YANG, Y., LIU, J., ZENG, X., DENG, W., 2017. *Selective flotation separation of ilmenite from titanite using mixed anionic/cationic collectors*. *International Journal of Mineral Processing*.
- VAN OSS, C., CHAUDHURY, M., GOOD, R., 1987. *Monopolar surfaces*. *Advances in colloid and interface science*, 28, 35-64.
- WANG, Z., WU, H., XU, Y., SHU, K., FANG, S., XU, L., 2020a. *The effect of dissolved calcite species on the flotation of bastnaesite using sodium oleate*. *Minerals Engineering*, 145, 106095.
- WANG, Z., WU, H., XU, Y., SHU, K., YANG, J., LUO, L., XU, L., 2020b. *Effect of dissolved fluorite and barite species on the flotation and adsorption behavior of bastnaesite*. *Separation and Purification Technology*, 237, 116387.
- XU, L., HU, Y., WU, H., TIAN, J., LIU, J., GAO, Z., WANG, L., 2016. *Surface crystal chemistry of spodumene with different size fractions and implications for flotation*. *Separation and Purification Technology*, 169, 33-42.
- XU, L., TIAN, J., WU, H., LU, Z., YANG, Y., SUN, W., HU, Y., 2017. *Effect of Pb²⁺ ions on ilmenite flotation and adsorption of benzohydroxamic acid as a collector*. *Applied Surface Science*.
- YANG, Y., XU, L., LIU, Y., HAN, Y., 2016a. *Flotation separation of ilmenite from titanite using mixed collectors*. *Separation Science and Technology*, 51(11), 1840-1846.
- YANG, Y., XU, L., TIAN, J., LIU, Y., HAN, Y., 2016b. *Selective flotation of ilmenite from olivine using the acidified water glass as depressant*. *International Journal of Mineral Processing*, 157, 73-79.
- YIN, W.-Z., YANG, X.-S., ZHOU, D.-P., LI, Y.-J., LÜ, Z.-F., 2011. *Shear hydrophobic flocculation and flotation of ultrafine Anshan hematite using sodium oleate*. *Transactions of Nonferrous Metals Society of China*, 21(3), 652-664.