Results in Physics 10 (2018) 250–255

Contents lists available at ScienceDirect

Results in Physics

journal homepage: www.elsevier.com/locate/rinp

Detrimental effects of slimes on the flotation of rutile from eclogite ore

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ARTICLE INFO

Keywords:
Rutile
Eclogite
Slimes
De-sliming flotation

ABSTRACT

The detrimental effects of slimes on the flotation of rutile from eclogite ore have been studied in this work in order to improve the separation efficiency of the flotation. The study was performed through particle size distribution measurement and mineralogical analysis. The results have demonstrated that the slimes were enriched in the concentrates, which became seriously with the increase of slime contents in feed ore. The presence of slimes resulted in the involvement of a large amount of omphacite and garnet into the concentrates, deteriorating the flotation selectivity in both of fine and coarse size fraction. Accordingly, de-sliming pretreatment was applied to the flotation, which significantly improved the flotation efficiency of rutile from eclogite ore for increasing TiO_2 grade and recovery of concentrates.

Introduction

Rutile is one of the favored minerals for manufacturing titanium white pigment [1], high quality welding electrodes [2,3], photocatalyst in solar cells [4]. It is also a good material for bone grafting [5].

In world, the major rutile deposits may be divided into four types, including metamorphic, igneous-related, sedimentary and weathered. In China, the sedimentary deposits are economically most important, followed by metamorphic deposits such as the eclogite type. Rutile in sedimentary deposits accounts only 14% of the Chinese reserves of economic sources [6]. Due to the depletion of easily processed rutile from sedimentary deposits and the increasing demand for titanium, particular focus has been given to rutile-bearing eclogites. The eclogites originated by high-pressure and temperature alteration of Proterozoic, Fe-Ti rich, gabbroic rocks. They were strongly deformed under eclogite-facies metamorphism and thereafter variably affected by retrograde processes [7]. Eclogite ore is a type of rutile resource with high economic value due to its large-scale reserves, good continuity of ore deposits and easy for exploitation [5].

The mineral fines are produced inevitably in the grinding process for adequate liberation of the particles [8]; mineral fines (slimes) are known to have a detrimental effect on minerals flotation. Slimes could increase the reagent consumption and pulp viscosity. In addition, slimes are liable to get into froth phase via composite particles, slime coatings as well as froth entrainment [9]. It was reported that the medium density fraction which mainly contained clay-coal composite particles greatly decreased the flotation recovery of the pure coal, but the heavy fraction which mainly comprised clays only depressed the flotation to a much less extent. The authors proposed that the great depression caused by the medium density fraction was due to the partial hydrophobicity of the clay-coal composite particles. They argued that the hydrophobic side of the composite particles could adhere to the coal surface by hydrophobic force, exposing the hydrophilic side to the water [10]. Due to electrostatic attraction between opposite charged coarse and fine particles [11,12], slimes coating on value mineral surface formed a hydrophilic “armor”, which reduced the efficiency of bubble–coal attachment [10]. Thus, the presence of clay slimes decreased the recovery and flotation rate of coarse coal [13]. In microcrystalline graphite flotation, majority of sericite fines was recovered into concentrates as a result of froth entrainment, partly recovered by entrapment, affecting the flotation selectivity [14]. The presence of gangue slimes would cause a low flotation separation efficiency in

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https://doi.org/10.1016/j.rinp.2018.06.013
Received 5 May 2018; Received in revised form 1 June 2018; Accepted 9 June 2018
Available online 10 June 2018

Table 1
Chemical composition of the ore sample (wt%).

Component	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO
Content	2.03	5.83	12.55	45.84	0.58	0.13	0.22	11.63
Component	ZnO	BaO	Fe_2O_3	MnO	SrO	TiO_2	LOSS	
Content	0.014	0.041	16.51	0.24	0.013	3.96	0.42	

ilmenite flotation [15]. A good result can be obtained in rutile flotation when the gravity separation was carried out in advance [16]. Thereby, the presence of slimes led to low recovery and grade of flotation concentrate [17,18].

The objective of this study is to investigate the specific effect of slimes on flotation of rutile from eclogite ore and to approach into the mechanisms of the detrimental effect. Also, a de-sliming pretreatment for improving the flotation efficiency is presented.

Experimental

Materials and reagents

The rutile ore used in this study was obtained from Donghai, Jiangsu province, China. The raw ore was blended and riffled thoroughly to prepare sub-samples for mineralogy analysis. The results of an X-ray fluorescence chemical analysis of the ore sample are presented in Table 1. According to Table 1, the raw ore is extraordinarily rich in the elements of iron and silicon, and low in titanium. The TiO_2 content of this sample is 3.96%, which reveals that it belongs to a low-grade ore.

In addition, X-ray diffraction (Bruker, Braun, Germany) was used to further analyze the composition of the raw ore, with the result shown in Fig. 1. The main gangue minerals associated with rutile are omphacite, garnet, quartz, albite and biotite. As shown in Table 1, there are very small impurities in the ore sample, but they cannot be detected using XRD because of their very low contents.

In flotation test, composite collector (Styryl phosphonic acid and n-octyl alcohol) was added to induce the hydrophobicity of valuable minerals. Lead nitrate, and sodium fluorosilicate were used as activator and depressant, respectively. The sodium silicate was used as slurry dispersant to prevent the non-selective coagulation of slimes during the flotation. And the frother was terpene. Lead nitrate, sodium fluorosilicate, n-octyl alcohol were analytical grade and were purchased from Sinopharm Chemical Reagent Co., Ltd., China. Industrial grade styryl phosphonic acid (SPA) and sodium silicate were supplied by Chengdu reagent factory, China. In terms of the sample used in this study, no additional pH regulator was added, and the experiments were

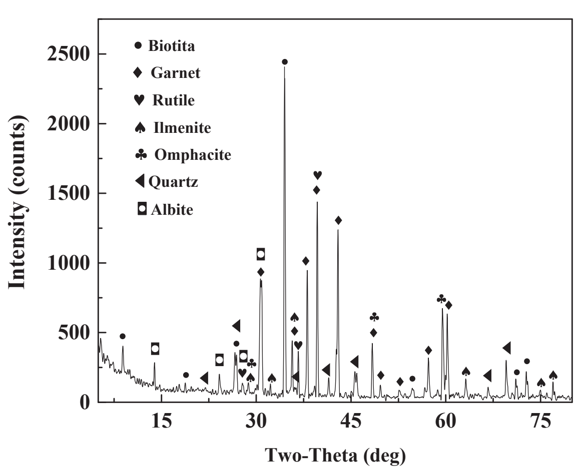

Fig. 1. X-ray diffraction pattern of the sample ore.

performed under natural pH around 4. The reagents used for experiments were prepared daily prior to the flotation tests using tap water.

Samples preparation

In order to increase the recovery of valuable minerals, raw ore, has to be ground to a much smaller size. However, by doing so, gangue minerals are also ground finely. And both fines (gangue and valuable mineral particles) can experience entrainment [18], while the entrainment of fine gangue mineral particles ($-45\,\mu m$) into the froth can be one of the reasons for the difficulty in obtaining qualified concentrates [19]. Thus, in this work, the fines ($-32\,\mu m$) are collectively called "slimes".

Flotation samples preparation

The raw ore with different slime contents was ground in porcelain ball mill and a sample of 500 g was used each time, and then samples with different slime contents (2.56%, 8.91% and 19.88%, respectively) were obtained. The grades of the as-prepared mineral samples were 4.05%, 4.14% and 3.82%, successively.

De-sliming flotation samples preparation

The rutile sample grading 3.96% used in de-sliming flotation was ground to 45% passing 74 μm using a porcelain ball mill at a pulp density of 50% (by weight). After grinding, the materials were then stirred in a container with 20 cm diameter and 2000 ml volume. The de-slime yields including 0%, 4.69%, 8.4%, 12.28%, 14.35% and 16.49% were chosen for these tests. De-slime yield was the amount of slime discarded via de-sliming pretreatment.

The procedures for preparing these samples are as follows: (1) The samples were placed into the container and the slurry was adjusted to achieve calibration of 2000 ml by adding tap water. (2) An agitator was then applied to achieve homogeneous dispersion of suspension with a stirring speed of 500 rpm for 10 s. The height from the blender impeller to the bottom of the container was 400 ml. (3) After stirring, settlement is needed. The upper solution was then scraped out by siphonage and 1400 ml of upper solution was aspirated each time. (4) After siphonage, the tap water was then added to pulp and conditioned the calibration to 2000 ml.

The sample with de-slime yield 0% was the ground product of raw ore. The settling time of the remaining five samples were 3 min, 2 min, 1.25 min, 1 min and 0.5 min, respectively. Step 3 to step 4 were required to repeat three times. A flow chart of preparation process is shown in Fig. 2.

Flotation tests

To investigate the effects of slimes on the flotation of rutile from eclogite ore, batch flotation tests of samples with different slime contents (2.56%, 8.91%, and 19.88%, respectively) were performed. The flotation concentrates were subjected to determine the particle size distribution, mineral composition and distribution of Ti in different size fractions.

Flotation tests were performed in a XFDII (1.5 L) mechanically agitated flotation machine with an agitation speed of 1750 rpm. First, the samples with different slime contents were conditioned for 3 min; next, lead nitrate (300 g/t), sodium fluorosilicate (800 g/t), sodium silicate (200 g/t), styryl phosphonic acid (600 g/t), n-octyl alcohol (30 g/t) and terpene were added staged to pulp and agitated for 3 min after each addition; then, the flotation time lasted for 4 min, and the froth product was scraped out as concentrates and the pulp left in cell was tailing; finally, the concentrates and tailing were dewatered, dried and weighed. The flowsheet of the rougher flotation is shown in Fig. 3.

The de-sliming treatment was conducted via siphonage to mitigate the detrimental effects of slimes on flotation. After pretreatment, the flotation tests were performed as described above. The flowsheet of the

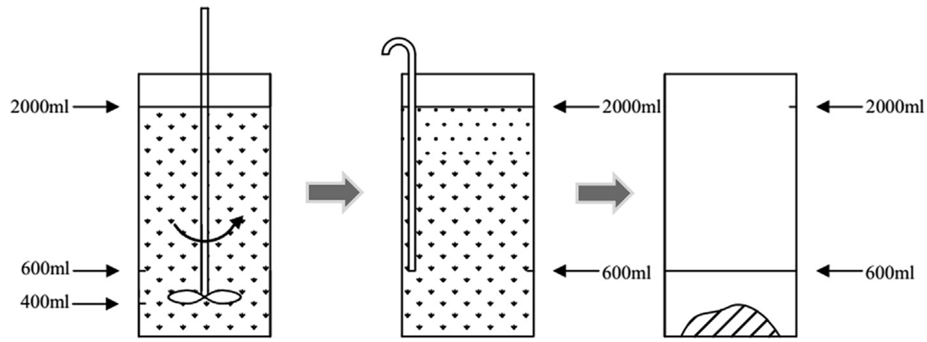

Fig. 2. Steps for preparing samples with different de-slime yield.

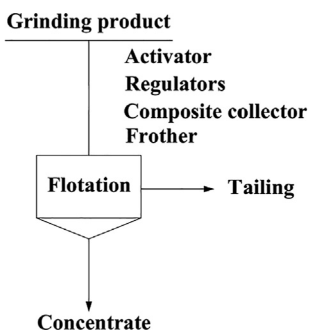

Fig. 3. Flowsheet of flotation tests.

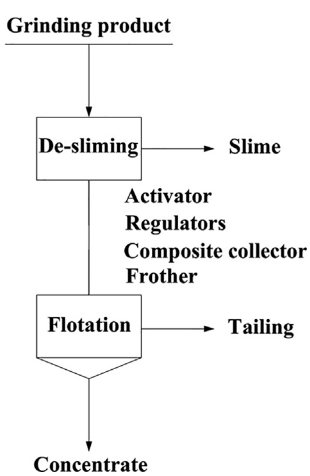

Fig. 4. Flowsheet of de-sliming flotation tests.

de-sliming flotation test is shown in Fig. 4.

Measurements

To explore the effect of slimes on the flotation selectivity, the flotation concentrates of samples with different slime contents were chosen for mineralogy analysis. The mineralogical analyses were done on a mineral liberation analyzer (Quanta 650) using polished thin sections with diameter of 30 mm. The particle detected was then analyzed using energy dispersive X-ray analyses.

Particle size analyses of flotation feeds and concentrates were conducted on laser particle size analyzer (Malvern, UK). Samples were placed in an ultrasonic bath for 1.5 min before measurement. An average result can be obtained due to the measurement of the subsamples in triplicate.

Results and discussion

Slimes in flotation concentrates

The flotation feeds and concentrates are analyzed by a laser particle size analyzer in terms of the distribution of particle size. The differences of particle size distribution between flotation feeds and concentrates are shown in Fig. 5a, b and c. It is observed that there is an enrichment of slimes into froth concentrates during the flotation of rutile from eclogite ore, and new peak forms for each concentrate around 32 μm size fraction.

Table 2 gives the slime contents recovered in flotation concentrates (namely, −32 μm). An increase in the slime contents in feeds result in a significant increase in the slime contents recovery in concentrates due to the upward momentum resulting in a greater water recovery and hence higher solids entrainment [20,21]. When the slime contents in feeds are 19.88%, the total amount of slime contents recovered in concentrates increased by about 10%. It is expected that entrainment is a mechanical transfer process by which gangue mineral particles suspended in water enter the flotation froth, move upwards, and finally leave the flotation cell with the mineral particles recovered by true flotation. It plays a vital role in the processing of ores with a large proportion of fine particles [9].

Deterioration of flotation selectivity

Mechanical entrainment of fine mineral particles is one of the main reasons which leads to the poor flotation selectivity.

To investigate the flotation selectivity of sample in different size fraction, sieve analyses of flotation concentrates are conducted. And five size fractions including −32 μm, −45 + 32 μm, −75 + 45 μm. −109 + 75 μm and +109 μm are chosen for the tests. TiO_2 grade and recovery of concentrates for each size fraction are analyzed and the results are presented in Fig. 6a and b. As shown in Fig. 6a, (1) For the fine size fraction (−32 μm), with the slime contents in feeds increasing from 2.56% to 19.88%, the TiO_2 grade of concentrates decreases from 68.39% to 17.12%. The sample with slime contents 2.56% in feeds performs the highest TiO_2 grade, which may be ascribed to the presence of major amount of valuable mineral particles instead of gangue mineral particles. The poor flotation selectivity of −32 μm size fraction may be attributed to the froth entrainment of fine gangue minerals [22]. Similarly, the entrainment of fine Fe-bearing particles (−45 μm) into the froth can be one of the problems for obtaining tailings with low Fe content during the reverse flotation of quartz [19]. (2) For the coarse size fraction (+32 μm), interestedly, the TiO_2 grade of concentrates also sharply decreases when slime contents in feeds increase up to 19.88%. It may be attributed to the non-selective absorption of depressant by slimes with large amount, resulting in a failure of depression of coarse gangue minerals [23]. The presence of high amount of slimes substantially increases reagents consumption in both flotation routes and the detrimental effect of slimes cannot be fully corrected by

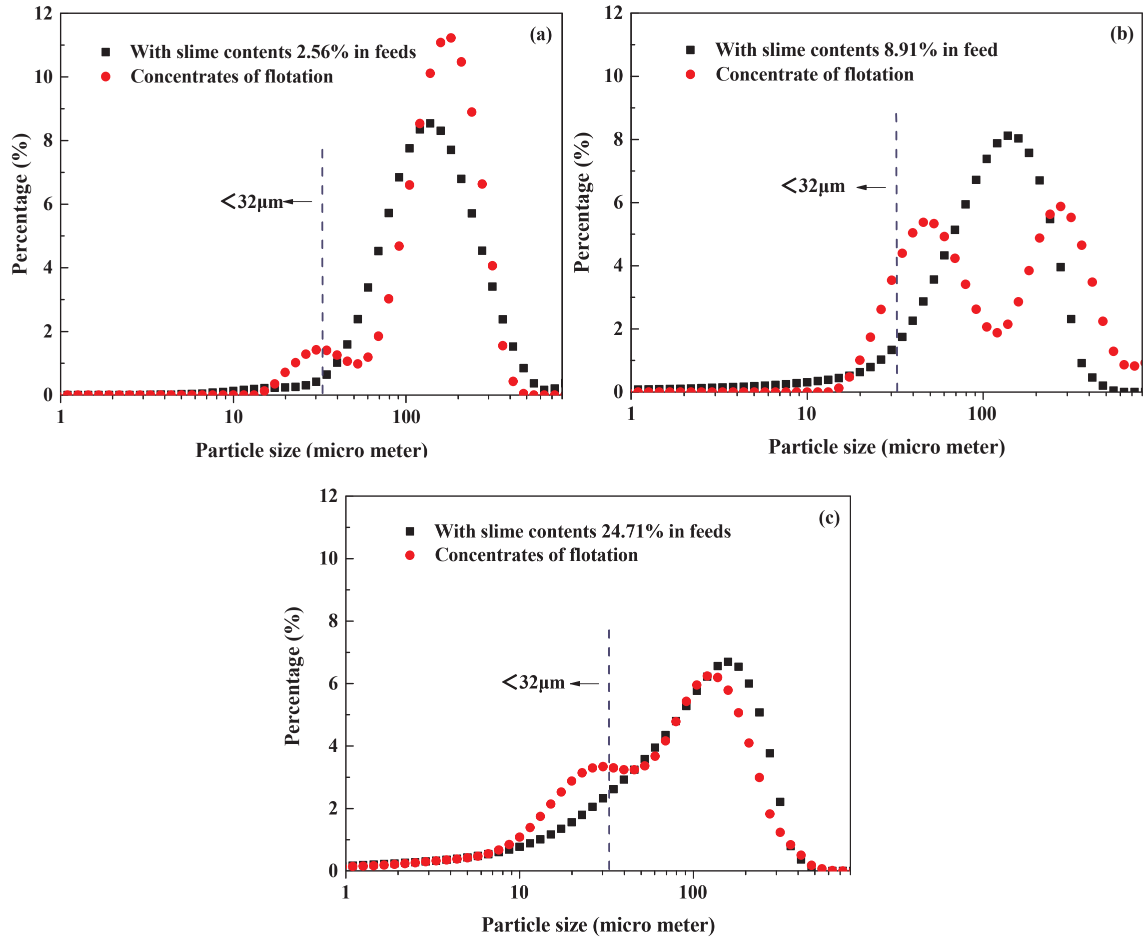

Fig. 5. Particle size distribution of flotation feeds and concentrates.

Table 2
Comparison of slime (−32 μm) contents in flotation feeds and concentrates.

Slime contents in feeds (wt.%)	2.56	8.91	19.88
Slime contents in concentrates (wt.%)	5.76	11.22	29.96

adding more reagents [24]. For +109 μm size fraction, the apparent grade decreases may be attributed to the presence of incomplete liberation of coarse particles.

As shown in Fig. 6b, (1) For fine size fraction (−32 μm), the recovery of the sample with slime contents 2.56% in feeds is around 5% and performs relatively lower than that of other two samples. (2) For coarse size fraction (+32 μm), the TiO_2 recovery of these three samples

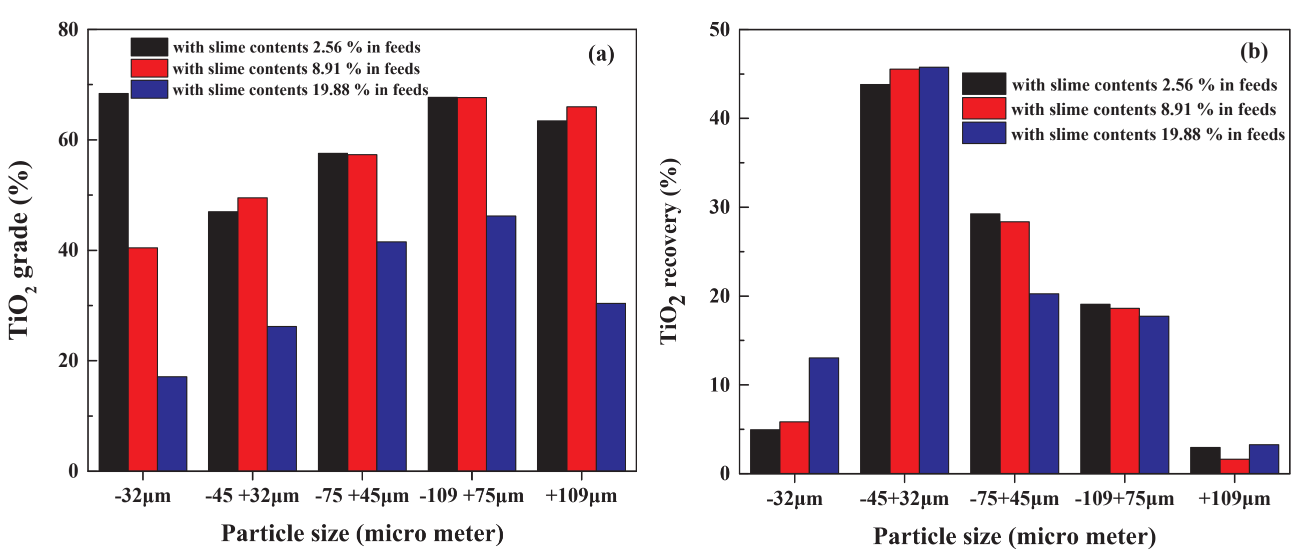

Fig. 6. TiO_2 grade (a) and recovery (b) as a function of particle size.

Table 3
Mineral composition of the flotation concentrates (wt%).

Minerals	Omphacite	Garnet	Rutile	Ilmenite	Quartz	Albite	Clay	Others
Slime contents (2.56%)	7.87	6.61	48.86	31.28	0.38	0.29	0.38	4.33
Slime contents (8.91%)	25.57	16.88	30.5	20.96	0.51	0.55	1.7	3.33
Slime contents (19.88%)	23.86	44.83	11.74	11.71	0.89	1.17	0.99	4.81

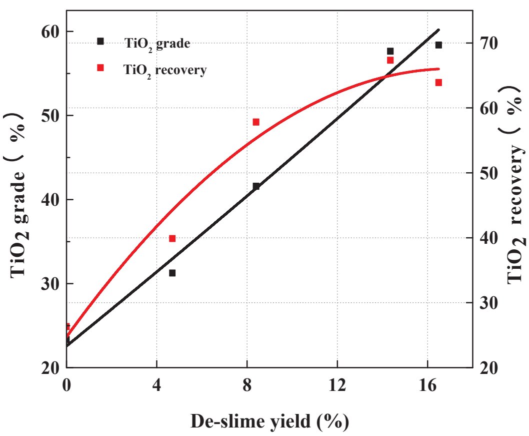

Fig. 7. The performance of rougher flotation process as a function of de-slime yield.

show no significant discrepancy. For +109 μm size fraction, the flotation of coarse mineral particles is always low due to their detachment from bubbles in the high turbulent regions of flotation cells [25]. In addition, it was reported that the liberation degree of coarser size fraction is lower than that of the finer size fraction, resulting in a low flotation recovery and flotation rate, especially for particles with a lower liberation class and coarser size [26,27].

Effect of slimes on the selectivity of minerals

For a direct investigation on the influence of slimes on the selectivity of minerals (valuable minerals and gangue minerals), the mineral compositions of flotation concentrates are determined by MLA. The results are presented in Table 3.

Table 3 shows that a large amount of omphacite and garnet report into concentrates, which result in the dilution of flotation concentrates. Other gangue minerals such as quartz, albite, clay slightly reduce the TiO_2 content of flotation concentrates. Generally, the presence of fine particles of gangue more strongly affects the quality of the separation, as a result of the high degree of entrainment [28].

It is observed that with an increase of slime contents in feeds, the amount of omphacite and garnet that report into concentrates increase significantly. When the slime contents are 2.56%, the amount of omphacite and garnet in flotation concentrates are only 7.87% and 6.61%. While, the amount of omphacite and garnet in flotation concentrates sharply increase to 23.86% and 44.83%, when the slime contents in feeds increase to 19.88%. Accordingly, the content of rutile and ilmenite in concentrates obviously decrease with an increase of slime contents in feeds. These results are in good agreement with the conclusions drawn in section 3.2. It was reported that a high content of fines increases the required cationic collector dose and reduces the selectivity. However, when the fines < 20 μm in size were removed from the flotation feeds, the selectivity increased dramatically [29]. Not surprisingly, an increase in the slime contents in feeds result in a significant increase in the involvement of a large amount of omphacite and garnet, this phenomenon may be ascribed to the entrainment of fine gangue minerals (garnet and omphacite fines) and a failure depression of coarse garnet and omphacite particles.

Improvement of flotation performance through de-sliming pretreatment

Omphacite and garnet fines are easily entrained into the froth and result in a low-grade product. De-sliming was found to be indispensable before flotation to mitigate the detrimental effect of fine gangue mineral particles and improve the flotation performance [30,31]. Therefore, de-sliming pretreatment is conducted to improve the flotation selectivity.

The TiO_2 grade and recovery of flotation concentrates as a function of the de-slime yield are shown in Fig. 7. It can be seen that both TiO_2 grade and recovery of flotation concentrates are persistently improved with the de-slime yield increasing. The TiO_2 grade increases from 23.34% to 57.65% with the de-slime yield increasing from 0% to 14.35%. The results suggest that froth entrainment of gangue fines is reduced and the depression of coarse gangue minerals is improved by de-sliming. It is noteworthy that TiO_2 recovery of flotation concentrates sharply increases from 26.32% to 67.33% when the de-slime yield increases from 0% to 14.35%. It was reported that without de-sliming, the flotation of smithsonite consumes more sodium sulfide (12000 g/t) and yields a lower recovery of Zn (29.4%) than that with de-sliming operation [32]. The results suggest that de-sliming is an effective measure to erase the reagents consumption by slimes and improve the flotation recovery.

Conclusions

(1) In the rutile flotation from eclogite ore, slimes were enriched in the concentrates, leading to a worse separation efficiency.
(2) The mechanism was that a large amount of omphacite and garnet were collected into the concentrates, deteriorating the flotation selectivity in both of fine size fraction and coarse size fraction.
(3) A de-sliming pretreatment before the flotation could greatly improve the efficiency for increasing TiO_2 grade and recovery of concentrates.

Acknowledgments

The financial supports for this work from the Ministry of Land and Resources of China (201511063-2), the Natural Science Foundation of Hubei Province of China (2016CFA013) is gratefully acknowledged.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.rinp.2018.06.013.

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