Effects and Mechanisms of Grinding Media on the Flotation Behavior of Scheelite

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ABSTRACT: Grinding, an essential procedure for size reduction and fresh surface exposure of mineral particles, plays an important role in mineral flotation. The grinding media are the key factors for effective grinding and thus for successful flotation. In this study, ceramic ball (CB) and cast iron ball (CIB), two representative grinding media, were chosen to investigate the effects and mechanisms of grinding media on the flotation behavior of scheelite. The results of pure scheelite flotation show that scheelite ground by CB has a better floatability than that ground by CIB. Scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) and X-ray photoelectron spectroscopy (XPS) analyses indicate that there are Fe species, namely, elemental iron (Fe), ferrous oxide (FeO), and iron oxyhydroxide (FeOOH), coated on the surfaces of scheelite ground by CIB but not in the case of scheelite ground by CB. The dissolved oxygen (DO) and inductively coupled plasma-atomic emission spectroscopy (ICP-AES) tests show that Fe ions exist in the CIB grinding slurry but not in the case of CB grinding slurry. Compared with the CB grinding slurry, the CIB grinding slurry has a lower DO content and higher Ca ion concentration. Zeta potential results reveal that the Fe species in the CIB grinding reduce the NaOl adsorption on the scheelite surfaces. Finally, the deleterious effect of CIB grinding on the flotation behavior of scheelite is verified by the actual scheelite ore flotation experiments.

1. INTRODUCTION

Tungsten, a rare metal element, is located at the VIB group of the sixth period of the periodic table. Its atomic number is 74, and its relative atomic mass is 183.85. While having the highest melting point (3410 °C) of all metals, tungsten has a density of 19.35 g/cm³ and is categorized as a heavy metal. Tungsten has the highest melting point (3410 °C) of all metals, tungsten has a density of 19.35 g/cm³ and is categorized as a heavy metal. Tungsten has already been widely used in many fields such as chemistry, mining, electronics, metallurgy, etc. Scheelite (CaWO₄) and wolframite ((Fe, Mn)WO₄) are the two main tungsten-bearing minerals that are being mined commercially. However, with the increasing depletion of the easily beneficiated wolframite resources, scheelite resources are being exploited more and more broadly and play an important role in tungsten production.¹

Flotation is the most widely used beneficiation method in the mining industry. In most scheelite flotation plants, the flotation recoveries are merely 60−85%, such as Cantung mine (75−79%) in Canada,² Shizhuyuan mine (65%) in Hunan Province, China,³ and a skarn scheelite type (71%) in Jiangxi Province, China.⁴ A great amount of research has been conducted to improve the flotation recovery of scheelite with the focus on the flotation reagents.⁵−⁹ For example, Han et al.¹⁰ combined the Pb²⁺ ions with benzohydroxamic acid (BHA) to self-assemble the Pb-BHA complex, which showed superior selective collecting ability for scheelite compared with Pb²⁺ ions added before BHA. In the Shizhuyuan mine, using Pb-BHA as the collector increased the flotation recovery by 12.57%.¹⁰

While improved scheelite flotation recovery can be obtained via flotation reagent adjustment, an important factor (grinding media) that could potentially affect the scheelite flotation performance is ignored by researchers. It is well known that cast iron ball (CIB) is the first choice for scheelite grinding because of its cheap price and high grinding efficiency. However, using CIB in grinding inevitably results in Fe contaminations. It has been reported that Fe contamination has deleterious effects on flotation of a great number of minerals, such as sulfide minerals,¹¹−¹³ platinum group metal (PGM),¹⁴ carbonate minerals,¹⁵ and so on, whereas using inert grinding media such as ceramic ball (CB) can enhance the sulfide flotation performance.¹⁶−¹⁹ Nevertheless, Zhu and Yu²⁰ and Hu and Sun²¹ found that using CIB in grinding could...
increase the flotation recovery of beryl and spodumene. The adhered iron fillings on the fresh beryl and spodumene surfaces would be oxidized to Fe ions, which activated the flotation of beryl and spodumene. Therefore, it can be concluded that the CIB in grinding can have different effects on flotation depending on the minerals processed. However, the effects of CIB grinding on the flotation behavior of scheelite are still unclear. Herein, this research investigated the effects of grinding media on the flotation behavior of scheelite. CIB and CB were chosen as the grinding media and tested in parallel. The mechanisms were revealed by zeta potential measurements, dissolved oxygen (DO) tests, inductively coupled plasma-atomic emission spectroscopy (ICP-AES) tests, scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) tests, and X-ray photoelectron spectroscopy (XPS) tests.

2. RESULTS AND DISCUSSION

2.1. Pure Scheelite Flotation Performance. To investigate the effects of NaOl concentration on the flotation behavior of scheelite ground by CB and CIB in parallel, pure scheelite flotation experiments were conducted as a function of NaOl concentration, and the results are shown in Figure 1a. It can be seen that when the NaOl concentration is lower than $1.0 \times 10^{-4}$ mol/L, the flotation recoveries of scheelite increase gradually with the increase of NaOl concentration. The two flotation curves shown in Figure 1a reach their highest levels at $1.0 \times 10^{-4}$ mol/L NaOl concentration. After that, the flotation recoveries of scheelite remain at about 84.0% for CB and 69.0% for CIB until $1.5 \times 10^{-4}$ mol/L NaOl concentration. However, when the NaOl concentration is above $1.5 \times 10^{-4}$ mol/L, the flotation recoveries of scheelite show a slight decrease with increasing NaOl concentration, which may result from the multilayer adsorption of NaOl on the scheelite surface or the formation of NaOl micelles.22 Clearly, within the experimental NaOl concentration, the flotation recoveries of scheelite ground by CB are always higher than those of scheelite ground by CIB.

Figure 1b shows the effects of slurry pH, across the pH range of 6–12, on the scheelite flotation ground by CB and CIB in parallel as a function of NaOl concentration and (b) slurry pH.

![Figure 1](https://dx.doi.org/10.1021/acs.omega.0c05104)
parallel at 1.0 × 10⁻⁴ mol/L NaOl concentration. With the increase of slurry pH, the flotation recoveries of scheelite increase very slightly and reached their highest level at pH 9.0–10.0. Above the slurry pH 10.0, the flotation recoveries of scheelite first decrease very slightly (pH < 11.0) and then sharply (pH > 11.0) with increasing slurry pH. This sharp decrease may be induced by the competitive adsorption between NaOl and abundant OH⁻ for the active Ca sites on the scheelite surface.²³,²⁴ However, across the experimental slurry pH range, the flotation recoveries of scheelite ground by CB are higher than those of scheelite ground by CIB. According to the flotation results shown in Figure 1, it can be concluded that scheelite ground by CB has a better performance in subsequent flotation than that ground by CIB.

2.2. SEM-EDS Analysis. As flotation is a method based on the physicochemical characteristics of mineral surfaces, the surface morphology and elemental composition are the predominant factors in determining mineral flotation behavior. Figure 2 shows the SEM-EDS results of scheelite surfaces subjected to different grinding media. From Figure 2a, it can be known that the surfaces of scheelite ground by CB are smooth and clean without small particles visible on the surface. Figure 2b shows the EDS image of scheelite ground by CB. It shows that the elements Ca, W, and O are all detected on the scheelite surfaces, which are the constituent elements of scheelite. No impurity element is found on their surfaces. However, when the scheelite is ground by CIB, the surfaces are rough and uneven as shown in Figure 2c. It is evident that there are small particles coated on their surfaces. Figure 2d shows the EDS image of scheelite ground by CIB. Besides the elements Ca, W, and O, Fe is also detected, which originates from the grinding media of CIB. This indicates that there are Fe contaminations from the CIB grinding coated on the scheelite surfaces but not in the case of CB grinding.

2.3. DO and ICP-AES Analysis. Figure 3 shows the contents of DO, Ca, and Fe ions in the pulp of scheelite ground by CB and CIB in parallel. The DO contents of the scheelite pulp ground by CB and CIB are 8.36 and 5.14 ppm, respectively. The lower content of DO in the CIB grinding is due to the consumption of oxygen in galvanic reactions.²⁵ Additionally, the Ca ion concentration in the pulp of scheelite particles ground by CIB is significantly higher than that in the pulp of scheelite particles ground by CB. This indicates a considerably increased dissolution of the scheelite surface in the CIB grinding, which in turn will reduce the flotation recovery of scheelite.²⁶ Regarding the Fe ion concentration, 0.078 mg/L Fe ion concentration is detected in the CIB grinding but not in the case of CB grinding. This indicates that the Fe contaminations exist in the scheelite pulp using CIB as the grinding media, in line with the SEM-EDS results.

2.4. Zeta Potential Analysis. The zeta potentials of scheelite particles ground by CB and CIB, respectively, in the absence and presence of NaOl were measured, and the results are shown in Figure 4. In the absence of NaOl, the zeta potential of scheelite is negatively charged and decreases with increasing slurry pH, which is consistent with the published literature.²⁶,²⁷ However, it should be noted that the zeta potential of scheelite ground by CB is higher than that of scheelite ground by CIB. This may be caused by the coating of positively hydrophilic Fe species generated in the CIB grinding on the scheelite surfaces.²⁸ In the presence of NaOl, the zeta potential of scheelite shifts to a more negative value, indicating the chemisorption of the anionic carboxylate functional group in NaOl onto the negatively charged scheelite surfaces.²⁹,³⁰ Figure 4 also shows that the decreases in zeta potential of scheelite particles before and after NaOl adsorption are larger for CB grinding than for CIB grinding, indicating that more NaOl is adsorbed on the surfaces of scheelite ground by CB. This may be caused by the coating of the hydrophilic Fe species, which not only cover the Ca²⁺ active sites, which are essential for NaOl adsorption, but also increase the hydrophilicity of scheelite surfaces.³¹,³² This thickens the hydration film, which in turn makes the NaOl adsorption more difficult.³³,³⁴

2.5. XPS Analysis. To have further knowledge of the elemental compositions and states of scheelite surfaces ground by CB and CIB in parallel, XPS tests were conducted, and the results are shown in Figure 5. From Figure 5a, it can be seen that the peaks of Ca2p, O1s, W4f, and C1s are all detected on the surfaces of scheelite ground by CIB and CB. Ca, O, and W are the constitution elements of scheelite, while C is the background element for XPS tests. Additionally, it can be seen that a weak Fe2p peak at 711.3 eV is shown in the survey spectra of scheelite ground by CIB, which further proves that there are Fe-containing species coated on the scheelite surfaces in CIB grinding. Figure 5b shows the atomic concentrations of Ca, O, W, C, and Fe on the surfaces of scheelite ground by CB and CIB in parallel. It can be known that 1.36% Fe is found on...
the scheelite surfaces ground by CIB but not in the case of those ground by CB. Besides, in the case of CIB grinding, the calcium content on the scheelite surfaces is lower while the oxygen content is slightly higher than those in the case of CB grinding. These may be attributed to the galvanic reactions in CIB grinding, which consume the oxygen to form Fe–O species and cover the active calcium sites on the scheelite surfaces.31,32,35

To identify the chemical states of Fe and O on the scheelite surfaces, the Fe2p2/3 and O1s narrow spectra of scheelite ground by CB and CIB in parallel were analyzed through peak fitting, and the results are shown in Figure 6. As shown in Figure 6a, when the scheelite is ground by CIB, there are five different peaks in the spectra of Fe2p3/2. The peak at 706.70 eV is ascribed to elemental iron (Fe),36,37 and the peaks at 709.45 and 711.30 eV are attributed to ferrous oxide (FeO) and iron oxyhydroxide (FeOOH), respectively.38,39 Additionally, the peaks at 715.25 and 716.60 eV are the satellites of FeO and FeOOH, respectively.40 Figure 6b shows the O1s narrow spectra of scheelite ground by CB and CIB in parallel. When
the scheelite is ground by CB, there are only two peaks in the spectra of O1s, which are assigned to the W−O group at 530.49 eV and Ca−O group at 532.03 eV.31,42 However, when the scheelite is ground by CIB, four different peaks appear in the narrow spectra of O1s. The peaks of the W−O group and Ca−O group shift to 530.55 and 532.45 eV, respectively. Additionally, the peaks at 529.80 and 531.51 eV are assigned to Fe(II)−O and Fe(III)−O, respectively, indicating that there are Fe−O species, namely, Fe(II)−O and Fe(III)−O, on the scheelite surfaces ground by CIB.

It can be concluded from Figure 6 that there are elemental iron, iron oxide, and iron oxyhydroxide species generated on the scheelite surfaces ground by CIB but not in the case of scheelite surfaces ground by CB. Elemental iron may originate from the worn parts of CIB, while iron oxide and iron oxyhydroxide can be identified from the galvanic reactions in CIB grinding. The reaction mechanisms can be shown as follows:

As illustrated in Figure 7, in the presence of oxygen and water, the galvanic reactions can take place between the CIB media. The reactions are as follows:43,44

\[ \text{anodic oxidation: } \text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \quad (1) \]

\[ \text{cathodic reduction: } \text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- \quad (2) \]

\[ \text{hydroxylation: } \text{Fe}^{2+} + 2\text{H}_2\text{O} \rightarrow \text{FeO} + \text{H}_2\text{O} \quad (3) \]

\[ \text{Fe}^{3+} + 3\text{OH}^- \rightarrow \text{Fe(OH)}_3 \rightarrow \text{FeOOH} + \text{H}_2\text{O} \quad (5) \]

The galvanic reactions will result in the worn parts of CIB and the formation of iron oxide and iron oxyhydroxide. In the grinding, these hydrophilic Fe species can coat the scheelite surfaces under the collision and extraction of CIB.

### 2.6. Actual Scheelite Ore Flotation Performance

To verify the effects of grinding media on the flotation performance of actual scheelite ore, the flotation experiments of actual scheelite ore samples ground by CB and CIB in parallel were conducted, and the results are shown in Figure 8. The flotation recovery was calculated according to the WO3 grade of the scheelite flotation feed. Flotation efficiency was chosen to evaluate the flotation performance. The formula of flotation efficiency is as follows:

\[
E = \frac{\left( e - \gamma \right)}{\left( 1 - \frac{\alpha}{\beta} \right)} \times 100 \%
\]

In the above formula, \( E \) is the flotation efficiency; \( \epsilon \) and \( \gamma \) are the flotation recovery and flotation yield of rougher concentrates, respectively; \( \alpha \) is the WO3 grade of scheelite flotation feed; and \( \beta \) is the WO3 grade in pure scheelite, which accounts for 80.52%.

From Figure 8, it is clear that the WO3 grade and recovery of rougher concentrates in CB grinding are higher than those of rougher concentrates in CIB grinding. Additionally, the flotation efficiency in the CB grinding is 79.18%, while in the CIB grinding, the flotation efficiency is merely 76.63%, illustrating that the flotation performance is better when the actual scheelite ore is ground by CB. Meanwhile, Figure 8 also shows that the slurry color of the actual scheelite ore ground by CB is gray. In contrast, when the actual scheelite ore is ground by CIB, the slurry color is dark green, indicating that the slurry is contaminated when using CIB in grinding.

It is worth noting that in addition to Fe contamination, the difference in mill geometries could contribute to the distinct flotation response when different types of mills are used. Continued work is needed to decouple the effect of Fe contamination and mill geometries on the flotation behavior of mineral particles.

### 3. CONCLUSIONS

In this study, the effects and mechanisms of grinding media (CB and CIB) on the flotation behavior of scheelite were investigated through pure mineral flotation, actual scheelite ore flotation, SEM-EDS tests, XPS tests, zeta potential measurements, DO, and ICP-AES tests. The results indicate that pure scheelite ground by CIB has a lower flotation recovery than that ground by CB, which is attributed to the coating of Fe species (Fe, FeO, FeOOH) on CIB ground scheelite surfaces, which in turn impede the subsequent adsorption of NaOl. The actual scheelite ore flotation results are in good agreement with the pure scheelite flotation results, which verifies the Fe contaminations in the CIB grinding from a real ore perspective. This research will guide the grinding medium selection in beneficiation of scheelite ore in industry and effectively improve the scheelite flotation performance, which is significant in the efficient use of tungsten resources.

### 4. EXPERIMENTAL SECTION

#### 4.1. Materials and Reagents

The pure scheelite samples were collected from Jiangxi Province, China. The massive crystals were hand-ground by a hammer to ~1.7 mm and hand-selected for the high-purity parts. The chemical multielement analysis results of the pure scheelite samples (Table 1) show that the WO3 grade is 76.98%, which indicates that the purity of pure scheelite samples is as high as 95.56%. The X-ray diffraction (XRD) patterns of the pure scheelite samples (Figure 9) further show the high purity of the samples.

The actual scheelite ore samples used in batch flotation experiments were collected from a scheelite beneficiation plant.

#### Table 1. Chemical Multielement Analysis Results of the Pure Scheelite Samples

| element | CaO | WO3 | SiO2 | MgO | Al2O3 | Fe | purity |
|---------|-----|-----|------|-----|-------|----|--------|
| content/% | 18.54 | 76.98 | 1.16 | 0.98 | 1.22 | 95.56 |
samples. The WO₃ grade of the samples is 0.45%. The main gangue minerals are quartz, calcite, and fluoride with contents of 51.53, 13.14, and 8.51%, respectively. Table 3 shows the phase analysis of tungsten in the actual scheelite ore samples. It shows that the tungsten-bearing mineral is scheelite, which accounts for 95.11%, with only 3.11% wolframite and 1.78% tungstate.

Sodium oleate (NaOl, C₁₈H₃₃O₂Na, analytical grade) used as the collector was purchased from Shanghai Maikun Chemical Co., Ltd., China. Hydrochloric acid (HCl, analytical grade) and sodium hydroxide (NaOH, analytical grade) were bought from Sinopharm Chemical Reagent Co., Ltd., China. Hydrochloric acid (HCl, analytical grade) and sodium hydroxide (NaOH, analytical grade) were used as the pH modifiers. Sodium carbonate (Na₂CO₃, analytical grade) was used as the pH modifier NaOl were added sequentially and stirred for 2 and 3 min, respectively. After that, the concentrates were collected for about 4 min, and both the concentrates and tailings were filtered, dried, and weighed to calculate the flotation recovery. The flotation flowsheet of pure scheelite samples is shown in Figure 10.

The actual scheelite ore samples were ground using a laboratory conical ball mill (HLXMQ-Φ240 × 90, Wuhan Hengle Mineral Engineering Equipment Co., Ltd.) and a tumbling mill (5-II, Haoqiang Machinery Factory, Yixing town, Jiangsu Province, China) equipped with a 5.0 L ceramic pot. The laboratory conical ball mill was filled with CIB, and the mill shell composition was cast iron; meanwhile, the tumbling mill was filled with CB, and the mill shell composition was ceramic. For each grinding, the medium filling rate and grinding concentration were 50.0 and 50.0%, respectively. The −75 μm fractions of the ground products accounted for about 62.0%, which was consistent with the scheelite beneficiation plant. The flotation experiments of actual scheelite ore samples were conducted in a 1.5 L HLXFD flotation machine manufactured by Wuhan Hengle Mineral Engineering Equipment Co., Ltd., China. For each experiment, 800 g of the ground products and 1200 g of tap water were mixed. Then the reagents were added sequentially and stirred according to the distribution rate of the flotation machine. After flotation, the rougher concentrates and tailings were filtered, dried, and weighed to calculate the flotation recovery.

4.3. Zeta Potential Measurements. Zeta potential measurements were carried out using a Zetasizer Nano ZS90 analyzer manufactured by Malvern Panalytical Ltd., England. A
Figure 11. Flotation flowsheet of actual scheelite ore samples.

Dilute suspension was prepared by adding 50 mg of pure scheelite samples to 35 mL of KCl solution (10^{-2} mol/L) and stirred with a magnetic stirrer for 2 min. Then, the pH modifier and NaOl were added sequentially and stirred for 2 and 3 min, respectively. After that, the suspension was allowed to settle naturally for 10 min. The upper layer of the suspension was sucked out and injected into the testing sample cell for measurement. Each measurement was repeated three times at 25 °C, and the average was calculated.

4.4. DO and ICP-AES Tests. After grinding, the slurry of pure scheelite samples ground by CIB and CB in parallel was transferred into sealed beakers for settlement. After settlement, the upper clarified liquid was decanted for DO tests (AZ8403, Hengxin Technology Co., Ltd., China) and ICP-AES tests (ICPE-9800, Shimadzu Corporation, Japan).

4.5. SEM-EDS Tests. Scanning electron microscopy (SEM, JSM-6610, JEOL Ltd., Japan) coupled with energy dispersive spectroscopy (EDS, QUANTAX200-30, Bruker Corporation, Germany) was applied to observe the surface topography and elemental composition of scheelite ground by CIB and CB in parallel.

4.6. XPS Tests. To analyze the elemental composition and elemental states of scheelite surfaces ground by CIB and CB in parallel, XPS tests were conducted using an X-ray photoelectron spectrometer (ESCALAB 250 XI, Thermo Fisher Scientific, USA). The testing parameters were as follows: Al Kα (hν = 1486.6 eV) energy resource, 8 × 10^{-10} Pa of the analytical chamber vacuum, 12.5 kV of the testing voltage, and 16 mA of the testing current. All the binding energies were referred to the C1s (284.80 eV).

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References

(1) Kupka, N.; Rudolph, M. Froth flotation of scheelite - A review. Int. J. Min. Sci. Technol. 2018, 28, 373–384.
(2) Leal-Ayala, D. R.; Allwood, J. M.; Petavratzi, E.; Brown, T. J.; Gunn, G. Mapping the global flow of tungsten to identify key material efficiency and supply security opportunities. Resour. Conserv. Recycl. 2015, 103, 19–28.
(3) Han, H.; Hu, Y.; Sun, W.; Li, X.; Cao, C.; Liu, R.; Yue, T.; Meng, X.; Guo, Y.; Wang, J.; Gao, Z.; Chen, P.; Huang, W.; Liu, J.; Xie, J.; Chen, Y. Fatty acid flotation versus BHA flotation of tungsten minerals and their performance in flotation practice. Int. J. Miner. Process. 2017, 159, 22–29.
(4) Peng, H.; Jiao, W.; Wu, D. Improvement on the flotation performance of scheelite ore. Met. Mine 2017, 495, 106–110.
(5) Gao, Z.; Bai, D.; Sun, W.; Cao, X.; Hu, Y. Selective flotation of scheelite from calcite and fluorite using a collector mixture. Miner. Eng. 2015, 72, 23–26.
(6) Yao, W.; Li, M.; Zhang, M.; Cui, R.; Shi, J.; Ning, J. Effect of Zn^{2+} and its addition sequence on flotation separation of scheelite from calcite using water glass. Colloids Surf., A 2020, 124394.
(7) Bo, F.; Xianping, L.; Jinqing, W.; Pengcheng, W. The flotation separation of scheelite from calcite using acidified sodium silicate as depressant. Miner. Eng. 2015, 80, 45–49.
(8) Dong, L.; Jiao, F.; Qin, W.; Zhu, H.; Jia, W. Effect of acidified water glass on the flotation separation of scheelite from calcite using mixed cationic/anionic collectors. *Appl. Surf. Sci.* 2018, 444, 747−756.

(9) Feng, B.; Guo, W.; Peng, J.; Zhang, W. Separation of scheelite and calcite using calcium lignosulphonate as depressant. *Sep. Purif. Technol.* 2018, 199, 346−350.

(10) Han, H.; Liu, L.; Hu, Y.-H.; Sun, W.; Li, X.-D. A novel flotation scheme: selective flotation of tungsten minerals from calcium minerals using Pb-BHA complexes in Shizhujuan. *Rare Met.* 2017, 36, 533−540.

(11) Huang, G.; Grano, S.; Skinner, W. Galvanic interaction between grinding media and arsenopyrite and its effect on flotation: Part II. Effect of grinding on flotation. *Int. J. Miner. Process.* 2006, 78, 198–213.

(12) Corin, K. C.; Song, Z. G.; Wise, J. G.; O’Connor, C. T. Effect of using different grinding media on the flotation of a base metal sulphide ore. *Miner. Eng.* 2018, 126, 24−27.

(13) Grano, S.; Ralston, J.; Smart, R. S. C. Influence of electrochemical environment on the flotation behaviour of Mt. Isa copper and lead-zinc ore. *Int. J. Miner. Process.* 1990, 30, 69−97.

(14) Song, Z. G.; Corin, K. C.; Wise, J. G.; O’Connor, C. T. Effect of different grinding media composition on the flotation of a PGM ore. *Miner. Eng.* 2018, 124, 74−76.

(15) Song, Z. G.; Sun, C. Y. Effect of grinding media on the flotation of carbonate using sodium oleate as collector. *China Min. Mag.* 2009, 18, 94−97.

(16) Peng, Y.; Grano, S.; Fornasiero, D.; Ralston, J. Control of grinding conditions in the flotation of chalcoprite and its separation from pyrite. *Int. J. Miner. Process.* 2003, 69, 87−100.

(17) Zhang, X.; Han, Y.; Gao, P.; Li, Y. Effects of grinding media on grinding products and flotation performance of chalcopyrite. *Miner. Eng.* 2020, 160, 106070.

(18) Rabieh, A.; Albijanic, B.; Eksteen, J. Influence of grinding media and water quality on flotation performance of gold bearing pyrite. *Miner. Eng.* 2017, 112, 68−76.

(19) Deng, J.; Lai, H.; Chen, M.; Glen, M.; Wen, S.; Zhao, B.; Liu, Z.; Yang, H.; Liu, M.; Huang, L.; Guan, S.; Wang, P. Effect of iron concentration on the crystallization and electronic structure of sphalerite/marmatite: A DFT study. *Miner. Eng.* 2019, 136, 168−174.

(20) Zhu, J.; Yu, M. Mechanisms of the activation and flotation separation of spodumene from beryl by cast iron grinding media. *Hunan Nonferrous Met.* 2019, 9, 332−336.

(21) Hu, Z.; Sun, C. Effects and mechanisms of different grinding media on the flotation behaviors of beryl and spodumene. *Minerals* 2019, 9, 666−679.

(22) Jiang, Y. *Resource Processing;* 1st. ed; Wang, D.; Qiu, G.; Hu, Y., Ed.; Science Press: Beijing, 2014; pp. 246−248.

(23) Li, C.; Gao, Z. Tune surface physicochemical property of fluoride particles by regulating the exposure degree of crystal surfaces. *Miner. Eng.* 2018, 128, 123−132.

(24) Lu, Y.; Drelich, J.; Miller, J. D. Wetting of francolite and quartz and its significance in the flotation of phosphate rock. *Miner. Eng.* 1997, 10, 1219−1231.

(25) Dong, L.; Zhu, H.; Jiao, F.; Qin, W.; Jia, W. Effect of calcium ions on scheelite flotation using mixed collectors. *Sep. Sci. Technol.* 2019, 54, 153−162.

(26) Han, H.; Hu, Y.; Sun, W.; Li, X.; Chen, K.; Zhu, Y.; Nguyen, A. V.; Tian, M.; Wang, L.; Yue, T.; Liu, R.; Gao, Z.; Chen, P.; Zhang, C.; Wang, J.; Wei, Z.; Wang, R. Novel catalysis mechanisms of benzenoaromatic acid adsorption by lead ions and changes in the surface of scheelite particles. *Miner. Eng.* 2018, 119, 11−22.

(27) Gao, Z.; Hu, Y.; Sun, W.; Drelich, J. W. Surface charge anisotropy of scheelite crystals. *Langmuir* 2016, 32, 6282−6288.

(28) Yu, Y.; Ma, L.; Cao, M.; Liu, Q. Slime coatings in froth flotation: A review. *Miner. Eng.* 2017, 114, 26−36.

(29) Xu, L.; Hu, Y.; Dong, F.; Gao, Z.; Wu, H.; Wang, Z. Anisotropic adsorption of oleate on diaspore and kaolinite crystals: Implications for their flotation separation. *Appl. Surf. Sci.* 2014, 321, 331−338.

(30) Deng, J.; Liu, C.; Yang, S.; Li, H.; Liu, Y. Flotation separation of barite from calcite using acidified water glass as the depressant. *Colloids Surf., A* 2019, 123605.

(31) Stone, A. T.; Morgan, J. J. Reduction and dissolution of manganese (III) and manganese (IV) oxides by organics. 1. Reaction with hydroquinone. *Environ. Sci. Technol.* 1984, 18, 450−456.

(32) Jin, S. S.; Zhang, L. M.; He, J. Z. Review of reactions of manganese oxides with organic compounds and applications of MnO₂ in environmental remediation. *Acta Sci. Circumstantiae* 2008, 18, 2394−2403.

(33) Dong, L.; Jiao, F.; Qin, W.; Zhu, H.; Jia, W. New insights into the carboxymethyl cellulose adsorption on scheelite and calcite: adsorption mechanism, AFM imaging and adsorption model. *Appl. Surf. Sci.* 2019, 463, 105−114.

(34) Tian, M.; Gao, Z.; Sun, W.; Han, H.; Sun, L.; Hu, Y. Activation role of lead ions in benzenoaromatic acid flotation of oxide minerals: New perspective and new practice. *J. Colloid Interface Sci.* 2018, 529, 150−160.

(35) Yao, W.; Li, M.; Zhang, M.; Qian, G.; Cui, R.; Ning, J. Effect of grinding media on the flotation behavior of fluorite using sodium oleate as a collector. *Physicochem. Probl. Miner. Process.* 2020, 56, 556−565.

(36) National Institute of Standards and Technology X-ray Photoelectron Spectroscopy Database; https://srdata.nist.gov/xps/Default.aspx.

(37) Yao, W.; Li, M.; Zhang, M.; Cui, R.; Jiang, H.; Li, Y.; Zhou, S. Effects of grinding media on flotation performance of calcite. *Miner. Eng.* 2019, 132, 92−94.

(38) Yang, S.; Peng, T.; Li, H.; Feng, Q.; Qiu, X. Flotation mechanism of wolframite with varied components Fe/Mn. *Miner. Process. Extr. Metall. Rev.* 2016, 37, 34−41.

(39) Cai, J.; Deng, J.; Wen, S.; Zhang, Y.; Wu, D.; Luo, H.; Cheng, G. Surface modification and flotation improvement of ilmenite by using sodium hypochlorite as oxidant and activator. *J. Mater. Res. Technol.* 2020, 9, 3368−3377.

(40) Thermo Scientific XPS Knowledge Base - XPS Simplified; https://xpsimplified.com/periodictable.php.

(41) Yao, W.; Li, M.; Zhang, M.; Cui, R.; Shi, J.; Ning, J. Decoupling the effects of solid and liquid phases in a Pb-water glass mixture on the selective flotation separation of scheelite from calcite. *Miner. Eng.* 2020, 106423.

(42) Wei, Z.; Hu, Y.; Han, H.; Sun, W.; Wang, R.; Wang, J. Selective flotation of scheelite from calcite using Al₂Na₃SiO₉ polymer as depressant and Pb-BHA complexes as collector. *Miner. Eng.* 2018, 120, 29−34.

(43) Hu, Y.; Wu, M.; Liu, R.; Sun, W. A review on the electrochemistry of galena flotation. *Miner. Eng.* 2020, 106272.

(44) Zhang, X.; Han, Y.; Kwatira, S. K. Effects of grinding media on grinding products and flotation performance of sulfide ores. *Miner. Process. Extr. Metall. Rev.* 2020, 1.