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Review on development of low-grade scheelite recovery from molybdenum tailings in Luanchuan, China: A case study of Luoyang Yulu Mining Company

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Abstract: Luanchuan area is one of the regions with the largest scale of scheelite beneficiation and the largest output of scheelite concentrate in the world. After years of innovation and progress, the beneficiation technology of low-grade scheelite associated with molybdenum tailings in Luanchuan area is becoming more and more perfect. In this study, the development process of low-grade scheelite recycling technology in Luanchuan area was reviewed, including raw ore properties, beneficiation process, flotation equipment and flotation reagents. Meanwhile, taking Luoyang Yulu Mining Co., Ltd. as an example, the effects of various technical transformations such as the optimization of the beneficiation process, the column−machine combined process, and the high-efficiency flotation reagents were elucidated in detail. However, the recycling technology of low-grade scheelite of Luanchuan area is still possible to be improved. As a result, coupled with the latest research progress, the development direction of low-grade scheelite beneficiation in Luanchuan area was also prospected. It is of great significance to further improve the recovery efficiency of low-grade scheelite resources in Luanchuan area and this can provide technical reference for other scheelite plants.
Key words: scheelite; low-grade ore; beneficiation; flotation; recovery

1 Introduction

As a typical rare metal, tungsten has a large density, stable chemical properties, and good electrical and thermal conductivity [1,2]. It is an important modern high-tech material. The tungsten-containing cemented carbides are known as "industrial teeth" and widely used in the manufacture of drills, milling cutters and various molds [3,4]. The tungsten−copper alloy is a very effective contact material for the production of parts such as knife switches, circuit breakers, and spot welding-electrodes [5,6]. High-density tungsten alloys can be used in the manufacture of rotors for gyroscopes, counterweights and controlling rudders for aircrafts, radiation shields and baskets for radioisotopes. Tungsten compounds such as WS_2 are applied to solid lubricants and catalysts in the preparation of synthetic gasoline [7,8]. Alloys of tungsten and other refractory metals are always employed in thermal strength materials in aero-engines and other instrument [9]. Due to its important application, tungsten is listed as a

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strategic metal by major countries and economies in the world such as China, USA, and the European Union [10].

China's tungsten resource reserves and tungsten output are both ranked first in the world [11]. By the end of 2018, China's remaining WO_3 reserves reached 10715.7 kt [12]. In 2017, 83.16% of the world's tungsten concentrates were produced in China [13]. The scheelite is one of the crucial types of tungsten resources in China. However, most of the scheelite deposits in China are barren, and the WO_3 grade of more than 90% of scheelite is lower than 0.5% [14]. The scheelite deposits in China are characterized by diverse mineral compositions, complex associated relationships and great difficulty in beneficiation processing. The scheelite is generally considered to be recycled together with other useful minerals in the deposit to ensure economic viability [2].

The Luanchuan area of Luoyang is rich in molybdenum and tungsten resources and has the largest scheelite processing scale in the world [15−17]. Among them, the Sandaozhuang molybdenum−tungsten mine of China Molybdenum Group Co., Ltd. (CMOC) is the largest molybdenum deposit with proven molybdenum reserves and the second largest tungsten deposit with proven tungsten reserves in China. The Sandaozhuang molybdenum−tungsten mine has an ore reserve of 583 Mt, a molybdenum metal content of 672500 t, and an average Mo grade of 0.115%. The tungsten metal content of associated scheelite is 502500 t, and the average WO_3 grade is 0.117% [18]. However, in the early stages, due to the low grade of WO_3 in the raw ore, it was difficult to produce scheelite concentrate that met metallurgical requirements (WO_3 grade >50%) while ensuring an ideal scheelite recovery [19]. Therefore, CMOC only carried out molybdenum recycling, and the scheelite in the molybdenum tailings was discharged into the tailings pond [20]. The discarding of scheelite not only causes the waste of resources, but also increases the load of tailings pond, which is a huge hidden danger of environment and safety. In recent years, with the promotion of the novel tungsten metallurgy process of tungsten hydrometallurgy based on direct solvent extraction from alkaline medium and synergistic decomposition of scheelite by sulfuric−phosphorous mixed acid, the grade requirement of tungsten concentrate (WO_3 grade >20%) is reduced, which created conditions for the remining of low-grade scheelite in molybdenum tailings [21−24].

At present, the recycling of low-grade scheelite in molybdenum tailings in the Luanchuan area has been successfully performed on three beneficiation plants, with a total processing capacity of 57000 t/d. Among them, Luoyang Yulu mining company (LYYL) is the earliest scheelite plant. In 2017, the output of tungsten in the Luanchuan area exceeded 11.7 kt, accounting for about 6% of the world's tungsten output, making it the world's largest tungsten producer [25]. The large-scale recycling of low-grade associated scheelite in Luanchuan area not only consolidates the advantages of China's tungsten resources, but also reduces the pressure on the environment, making the entire mining process more efficient and cleaner.

In this work, the development of low-grade scheelite recovery from molybdenum tailings in Luanchuan area is reviewed, including ore properties, beneficiation process, flotation equipment, flotation reagents and prospect. Meanwhile, taking LYYL, the pioneer of beneficiation technology innovation of low-grade scheelite in molybdenum tailings, as an example, the scheelite beneficiation indexes before and after each technological innovation are elucidated. This review summarizes the innovations in the beneficiation technology of low-grade scheelite from molybdenum tailings in Luanchuan area, which can provide directions for the subsequent researches, as well as a reference for the recycling of other similar associated scheelite.

2 Ore properties

Based on the research results of LYYL's technological mineralogy and other related research results, the properties of raw ore and molybdenum tailings of Sandaozhuang deposit are summarized.

2.1 Composition and content of ore

The relevant studies have indicated that the ore composition of the Sandaozhuang molybdenum−tungsten deposit is dominated by skarn, accounting for 70%−80%, and the remaining 20%−30% are mainly diopside hornfels and wollastonite hornfels [26,27]. According to the results of mineral liberation analyzer (MLA) from LYYL (Table 1), the main valuable metallic minerals in the raw ore are scheelite and molybdenite; other metallic minerals available are pyrite, pyrrhotite and hematite/limonite; the gangue minerals of high content are wollastonite, garnet and pyroxene, followed by quartz, calcite/dolomite, feldspar, fluorite, montmorillonite, mica, hornblende, apatite, chlorite, talc, serpentine and sphene; other trace minerals are wolframite, rutile, ilmenite, siderite, zircon, monazite, allanite and magnesite.

According to the detailed exploration results of the entire mining area, the WO_3 grade of the raw ore is mostly between 0.04% and 0.15% [20]. The multi-element chemical analysis and tungsten chemical phase analysis results of molybdenum tailings in LYYL are shown in Table 2 and Table 3, respectively.

The multi-element chemical analysis result indicated that the grade of WO_3 in the molybdenum tailings is 0.067% and the main chemical components of gangue are SiO_2 and CaO, accounting for 44.04% and 36.23%, respectively, followed by Al_2O_3, MgO and K_2O. The tungsten phase was analyzed by selective leaching. The result of tungsten phase chemical analysis showed that the distribution rates of WO_3 in scheelite, wolframite and tungstite are 94.29%, 4.28% and 1.43%, respectively.

2.2 Occurrence of scheelite

The particle size statistical results of the scheelite in the raw ore under scanning electron microscope of MLA are presented in Table 4. The results showed that the scheelite has the characteristic of uneven fine-grained distribution and 90% of the scheelite particles are between 0.59 mm and 0.074 mm. If an ideal liberation degree liberation of scheelite is obtained, the reasonable grinding fineness is 0.074 mm. However, due to the difference in the reasonable grinding fineness of molybdenite flotation and scheelite flotation, the particles with the size of 0.074 mm in molybdenum tailings only account for about 60% in actual production. The sieve analysis results of molybdenum tailings indicate that 77.80% of WO_3 is distributed in the fine particles below 0.074 mm (Table 5).

The liberation degree of scheelite and the proportions of different associated minerals of scheelite in molybdenum tailings are given in Tables 6 and 7, respectively. The results indicated that the liberated scheelite particles only account for 67.83% of scheelite particles, and the rich associated mineral particles (the volume content of scheelite in the locked particles >3/4) account for 19.22%. The total distribution rate of liberated particles and rich associated mineral particles is 87.05%. Among the associated minerals, garnet, diopside/amphibole and wollastonite are most closely related to scheelite, followed by quartz/feldspar, fluorite and calcite. The high liberation degree is beneficial to the separation of scheelite and other minerals. However, due to the limitation of site and cost, a large number of tests are still needed to verify the feasibility of regrinding the

Table 1 Content of major minerals in raw ore (wt.%)

Scheelite	Molybdenite	Pyrite	Pyrrhotite	Hematite /lignite	Garnet	Wollastonite
0.12	0.24	0.29	0.41	0.19	21.03	35.32
Pyroxene	Hornblende	Quartz	Feldspar	Mica	Dolomite/calcite	Fluorite
13.78	1.21	8.50	4.21	2.40	5.21	2.74
Chlorite	Montmorillonite	Talc	Serpentine	Sphene	Apatite	Others
0.35	2.70	0.34	0.12	0.10	0.43	0.28

Table 2 Multi-element chemical analysis results of molybdenum tailings (wt.%)

WO_3	Mo	Fe	SiO_2	Al_2O_3	CaO	MgO
0.067	0.015	6.1	44.04	4.52	36.23	1.86
Na_2O	K_2O	S	F	C	Ignition loss	Others
0.42	0.96	0.38	1.49	0.73	2.83	0.36

Table 3 Tungsten phase chemical analysis results of molybdenum tailings

Phase	WO_3 grade/%	Distribution/%
Scheelite	0.066	94.29
Wolframite	0.003	4.28
Tungstite	0.001	1.43
Total	0.07	100

Table 4 Statistical results of scheelite particle size distribution in raw ore

Particle size/mm	Distribution/%	Cumulative distribution/%
0.59−0.42	9.71	9.71
0.42−0.30	13.65	23.36
0.30−0.21	24.31	47.67
0.21−0.15	18.43	66.10
0.15−0.105	14.29	80.39
0.105−0.074	10.16	90.55
0.074−0.052	4.38	94.93
0.052−0.037	2.80	97.73
0.037−0.026	1.65	99.38
0.026−0.019	0.46	99.84
0.019−0.010	0.14	99.98
<0.010	0.02	100.00

Table 5 Sieve analysis results of molybdenum tailings

Particle size/mm	Distribution/%	Grade of WO_3/%	Distribution of WO_3/%
>0.150	18.25	0.025	7.14
0.150−0.074	21.66	0.045	15.06
0.074−0.045	14.59	0.058	13.20
0.045−0.038	6.53	0.081	8.25
0.038	38.97	0.093	56.35
Total	100.00	0.064	100.00

Table 6 Liberation degree of scheelite in molybdenum tailings (%)

Liberated particle	Locked particle			
	>3/4	3/4−1/2	1/2−1/4	<1/4
67.83	19.22	6.36	3.49	3.10

molybdenum tailings to obtain more liberated scheelite particles.

Most of scheelite particles in the molybdenum tailings are in the form of irregular granular. The coarse particles are larger than 0.4 mm, the fine particles are only about 0.01 mm, and the majority of scheelite particles are between 0.02 mm and 0.3 mm. The results of energy dispersive spectrometer (EDS) analysis showed that the scheelite particles contain 24.19% of CaO, 68.43% of WO_3, 7.10% of MoO_3, 0.24% of FeO and 0.03% of MnO on average (Table 8). The chemical composition of scheelite particles is varied. Due to the isomorphous substitution, most scheelite particles contain a certain amount of Mo, and some particles are changed from pure scheelite to molybdenum-bearing scheelite, and even develop into powellite. In addition, a very small amount of calcium atoms in scheelite are replaced by iron and manganese atoms. The substitution of molybdenum for tungsten in scheelite particles may lead to the decrease of WO_3 grade in scheelite concentrate. However, the content of WO_3 in scheelite particles reaches 68.43%, which is far more than the current requirements of scheelite metallurgy technology. In addition, the molybdenum in scheelite concentrate can be recovered by extraction during the metallurgical process [21−23].

Table 7 Proportions of different associated minerals of scheelite in molybdenum tailings

Associated mineral	Distribution/%
Molybdenite	0.39
Sulphide	0.32
Garnet	25.17
Wollastonite	19.15
Diopside/Amphibole	23.46
Quartz/Feldspar	11.47
Fluorite	7.46
Mica	0.89
Calcite	7.46
Others	3.79
Total	100.00

The back scattered electron images (BSE) and MLA further present the particle morphology of scheelite (Figs. 1 and 2). Some fine scheelite is embedded among the particles of calcite and diopside (Fig. 1(a)). Irregular scheelite containing extremely fine molybdenite is embedded among gangue particles composed of garnet and feldspar (Fig. 1(b)). Mineral association composed of scheelite, powellite and molybdenite are embedded

Table 8 EDS analysis results of scheelite particles (wt.%)

No.	CaO	FeO	MnO	WO_3	MoO_3
1	28.03	0.80	0.00	54.80	16.36
2	21.48	0.25	0.00	78.27	0.00
3	26.69	0.36	0.03	52.85	20.07
4	22.61	0.10	0.00	76.13	1.17
5	22.76	0.30	0.02	72.38	4.54
6	22.54	0.30	0.00	74.07	3.10
7	23.92	0.00	0.00	72.94	3.14
8	21.41	0.13	0.00	78.46	0.00
9	26.68	0.39	0.14	62.00	10.78
10	22.16	0.22	0.00	75.96	1.66
11	22.23	0.00	0.00	77.55	0.22
12	23.12	0.18	0.04	69.04	7.62
13	26.02	0.23	0.00	55.07	18.68
14	21.23	0.51	0.00	78.26	0.00
15	25.56	0.39	0.00	69.57	4.47
16	23.44	0.17	0.00	71.18	5.20
17	26.88	0.29	0.04	57.72	15.07
18	22.41	0.31	0.00	73.99	3.29
19	25.66	0.21	0.11	62.57	11.45
20	24.88	0.50	0.24	74.37	0.00
21	23.28	0.17	0.00	76.55	0.00
22	22.48	0.15	0.00	71.86	5.51
23	26.46	0.57	0.01	71.09	1.87
24	26.92	0.09	0.00	57.93	15.06
25	21.28	0.12	0.00	78.60	0.00
26	27.84	0.27	0.00	48.59	23.30
27	26.14	0.03	0.12	57.90	15.81
28	26.07	0.10	0.13	59.27	14.43
29	23.25	0.05	0.00	71.49	5.20
30	22.41	0.12	0.00	72.54	4.93
Average	24.19	0.24	0.03	68.43	7.10

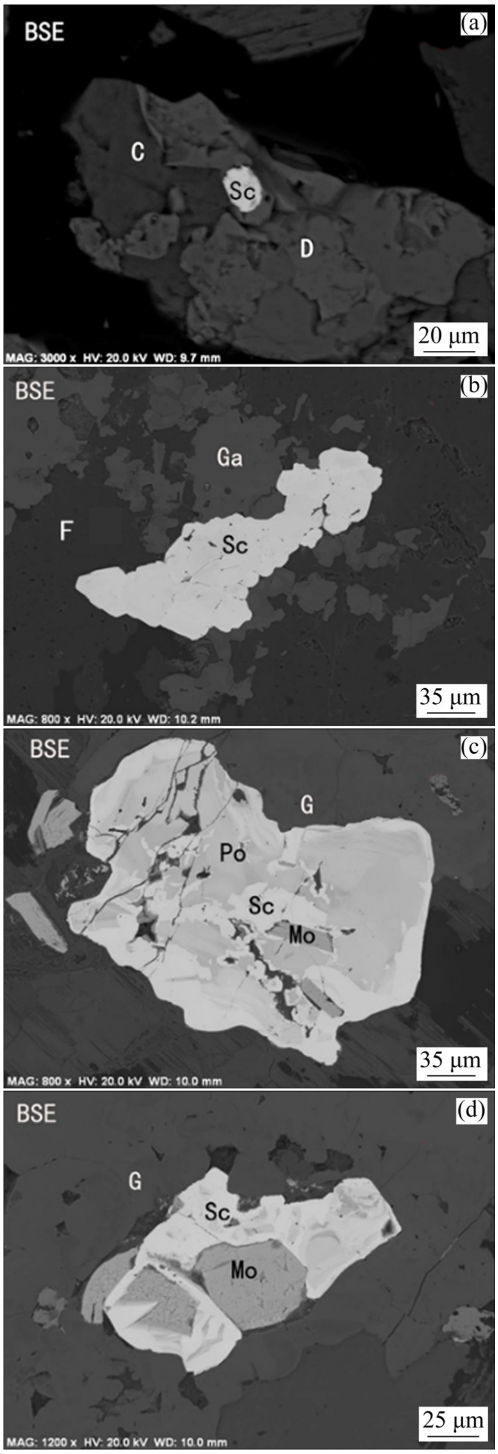

Fig. 1 BSE images of some scheelite particles in raw ore: (a) Sc−Scheelite, C−Calcite, and D−Diopside; (b) Sc−Scheelite, Ga−Garnet, and B−Feldspar; (c) Sc−Scheelite, Po−Powellite, Mo−Molybdenum, and G−Gangue; (d) Sc−Scheelite, Mo−Molybdenum, and G−Gangue

in the gangue (Fig. 1(c)). Molybdenite is either embedded along the edge of scheelite or wrapped in scheelite (Fig. 1(d)).

3 Beneficiation process

The study on the recycling technology of low-grade scheelite in molybdenum tailings in Luanchuan area has been going on for about forty years. Before the large-scale production, the laboratory-scale research process of low-grade scheelite recycling technology is summarized in Table 9. In preliminary study, gravity beneficiation

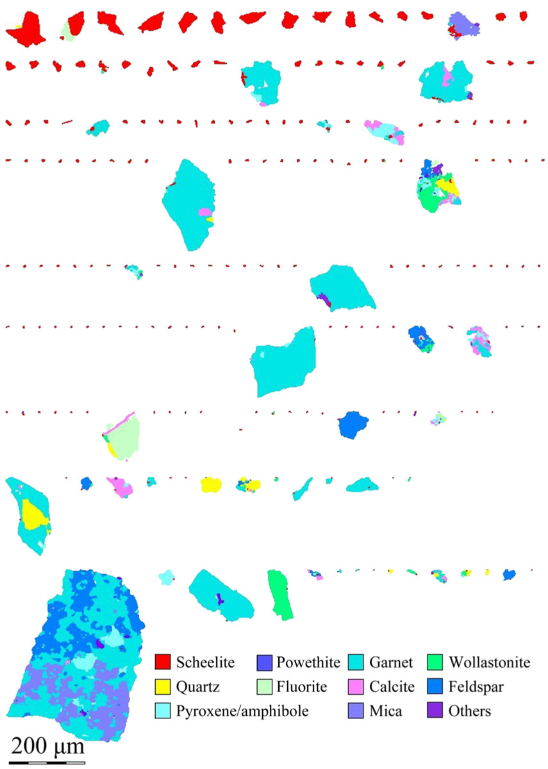

Fig. 2 Particle morphology of scheelite in molybdenum tailings

was used as the first choice for the recycling of low-grade scheelite. However, as described in Table 5, most of the scheelite is distributed in fine particles. Therefore, it is inefficient to recover low-grade scheelite by gravity beneficiation. It was not until 2000 that the main process of "room temperature flotation + heating flotation" was finalized. In order to stabilize the WO_3 grade of scheelite concentrate above 50%, a pickling process was employed in the follow-up study.

LYYL's 4500 t/d experimental beneficiation plant was completed and put into operation in 2004 on the basis of the "room temperature flotation + heating flotation + pickling" process. With the revolution of tungsten metallurgy technology, the pickling process was cancelled shortly after the operation of the plant. Meanwhile, the WO_3 grade requirement of the feeding was also reduced. After a large number of tests to verify smooth operation, the processing scale was expanded to 14500 t/d in 2007. Then, the beneficiation process of LYYL was used as a reference to build the other scheelite plants.

As a result, the beneficiation process of low-grade scheelite in Luanchuan area is divided into two stages: roughing stage (room temperature flotation) and cleaning stage (heating flotation). The purpose of roughing stage is to recover scheelite and remove gangue minerals as much as possible. The purpose of cleaning stage is to improve the quality of final concentrate and met market requirements, and the WO_3 grade of final concentrate needs to reach above 20% [28].

3.1 Roughing stage

As presented in Fig. 3, the scheelite roughing stage in Luanchuan area includes one roughing and two scavenging. The Sandaozhuang molybdenum−tungsten deposit is open-cast mining, while the

Table 9 Research course of low-grade scheelite recycling technology

Period	Beneficiation process	Beneficiation index		
		Grade of feeding/%	Grade of concentrate/%	Recovery/ %
1979−11—1980−12	Room temperature flotation + Heating flotation + Shaking table gravity separation	0.11	22.53−68.02	41.02−80.06
1980−12—1981−07	Heating flotation	0.12−0.15	65	70−80
1983−07	Spiral chute−shaking table combined process	−	71	44.09
1981−12—1984−01	Shaking table gravity separation	−	65	30
1987	Roughing: Spiral chute gravity separation	0.159	0.42	36.9
1987—1988	Roughing: Gravity−flotation combined process	0.147	0.458	40.96
1985—1989	Magnetic−gravity combined process	0.102	72.22	32.41
1999	Gravity−flotation combined process	0.23	66.85	67.53
2000	Room temperature flotation + Heating flotation	0.149	40.38	80.82
2000−12—2001−05	Room temperature flotation + Heating flotation + Pickling	0.143	53.66	71.82

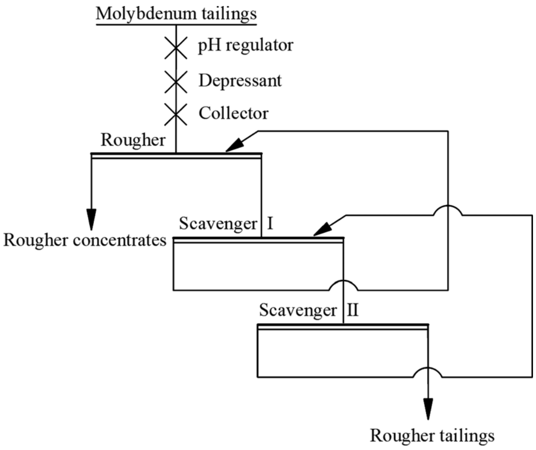

Fig. 3 Flowsheet of roughing stage [28]

content of scheelite in the surface and depth of the deposit is low. Therefore, the WO_3 grade of molybdenum tailings tends to increase first and then decrease. The barren feeding is one of the crucial reasons for the low recovery efficiency of the roughing stage in the early phase. The indexes and technology upgrades of LYYL in the roughing stage from 2007 to 2017 are shown in Fig. 4. In 2007, 2008 and 2009, the WO_3 grades of molybdenum tailings are only 0.051%, 0.045%, and 0.057%, respectively, the recoveries of the roughing stage are 58.37%, 64.42%, and 65.75%, respectively, and the WO_3 grades of rough concentrates are 1.11%, 1.10%, and 1.27%, respectively. With the improvement of feeding grade and the upgrading of technological, the efficiency of scheelite roughing stage is continuously improved. From 2013 to 2017, the recovery of scheelite roughing stage is stable at more than 75.00%, and the WO_3 grade of rough concentrate is stable at above 1.50%.

3.2 Cleaning stage

The other calcium-bearing minerals in Sandaozhuang deposit such as fluorite, calcite and apatite are similar to scheelite in floatability and difficult to separate in the scheelite flotation process. Large amounts of calcite and fluorite are found in scheelite rough concentrates in Luanchuan area. In order to inhibit calcium-bearing gangue minerals more effectively, the heating flotation process, also known as Petrov process, is introduced in the cleaning stage [29,30].

The principle of Petrov process is to selectively remove the collector adsorbed on the surface of the gangue by using the difference between the film desorption velocity of the collector adsorbed on the surface of scheelite and that on the surface of gangue minerals under high temperature. The main steps of Petrov process in Luanchuan are as follows: First, the scheelite rough concentrate containing calcite and fluorite is concentrated to a solid concentration of 60%−70% and sodium silicate is added. Then, the slurry is heated to 90−95 °C and stirred for 30−60 min. Finally, the rough concentrate is diluted with water to a content of 20%−25% and the scheelite flotation is carried out at room temperature [29].

Before February 2009, there was only one Petrov process operation in the scheelite cleaning

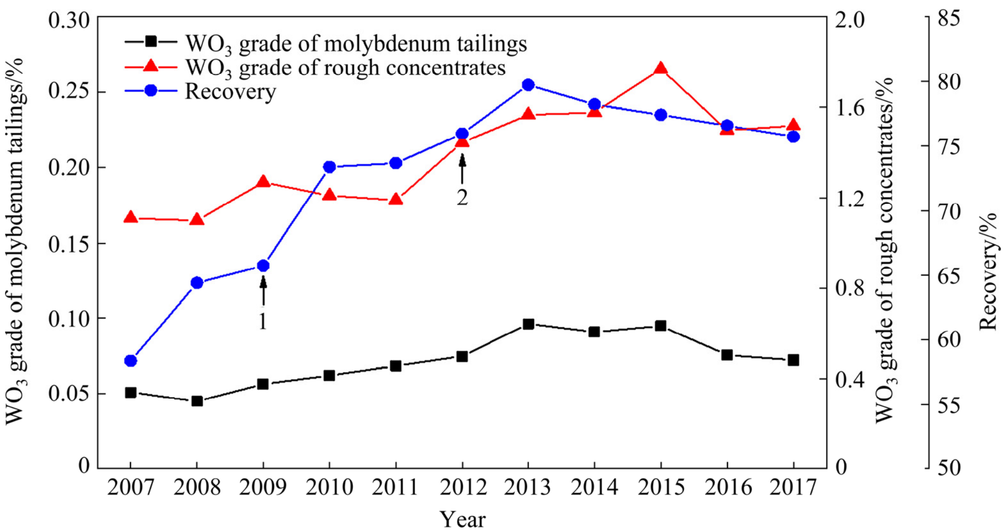

Fig. 4 Indexes of roughing stage (1−Application of new collector; 2−Application of column−machine combined process)

stage in LYYL. However, in order to make the WO_3 grade of final scheelite concentrate over 28% to achieve better economic benefits, the final scheelite concentrate is subjected to a second Petrov process operation to strengthen the inhibition effect on the calcium-containing gangues. As shown in Fig. 5, after defoaming and rinsing the scheelite concentrate obtained by the first Petrov process operation, most of coarse liberated scheelite or rich associated mineral particles in the concentrates are separated by shaking table so as to alleviate the burden of the second Petrov process operation. The shaking table tailings are subjected to the second Petrov process operation. The flotation concentrates of second Petrov process operation and shaking table concentrates are combined as the final scheelite concentrates.

The indexes of LYYL's cleaning stage before and after the transformation are given in Table 10. The results indicated that compared with the indexes before the transformation, the average recovery after the transformation dropped from 90.04% to 89.00%, and the WO_3 grade increased from 19.52% to 31.81%. In the case of a small loss of recovery, the purpose of improving the final concentrate grade is achieved.

In August 2014, LYYL changed the flotation equipment of cleaning stage from the inflatable

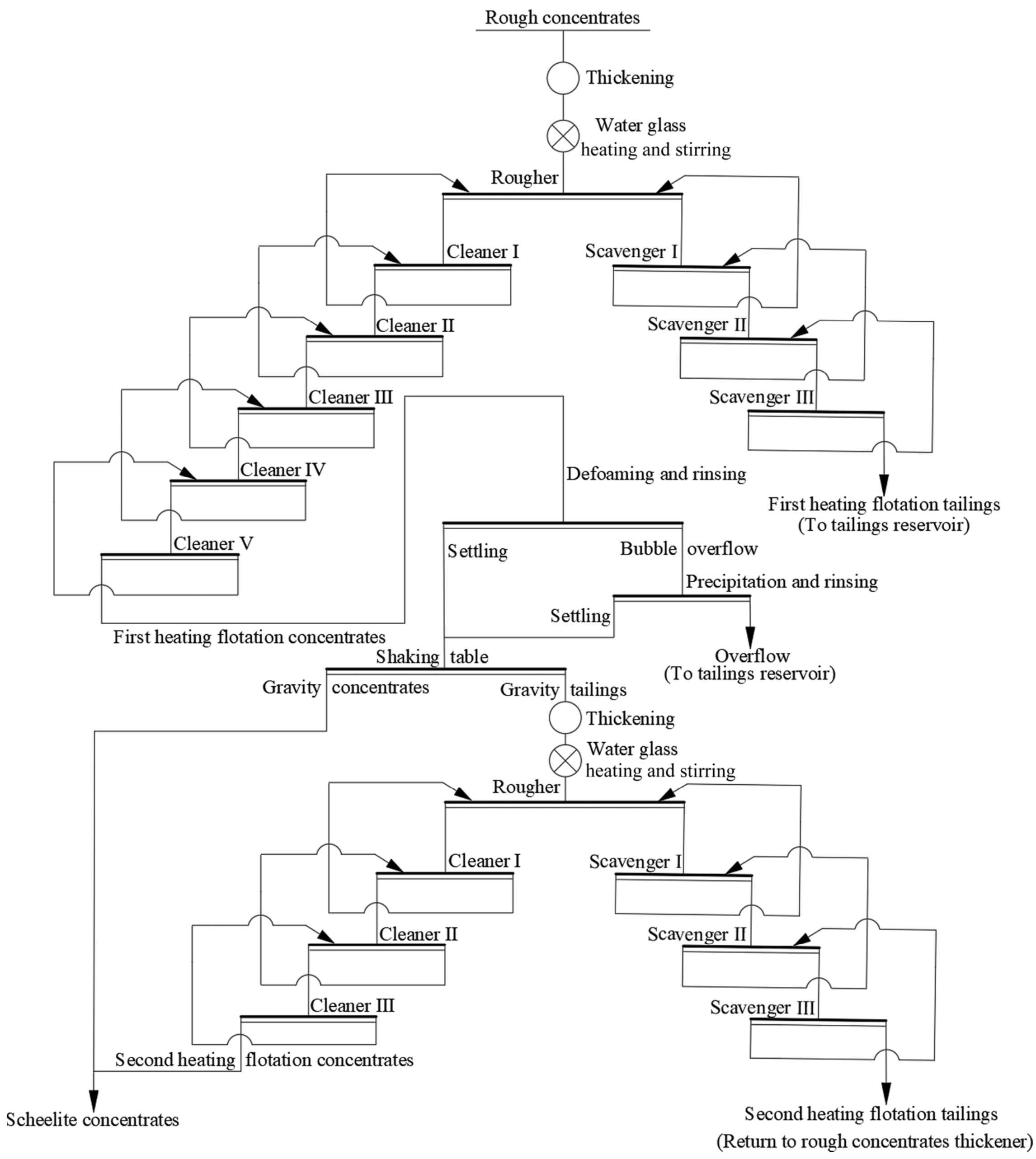

Fig. 5 Flowsheet of cleaning stage (From February 2009 to July 2014)

mechanical agitation flotation machine to a combination of flotation machine and flotation column. The column−machine combination significantly improved the flotation efficiency and shortened the flotation process in the cleaning stage (Fig. 6) [26]. The indexes of cleaning stage in recent years are given in Fig. 7. The results indicated that the WO_3 grade of the final concentrates can still be maintained at more than 30% and the scheelite recovery of the cleaning stage has increased to over 95% since 2015.

4 Flotation equipment

The scheelite plants in Luanchuan area initially used flotation machines as flotation equipment. For example, the SL jet flotation machine and the conventional BS-K inflatable mechanical agitation flotation machine were employed in the roughing stage and the cleaning stage of LYYL, respectively. The working principle of the SL jet flotation machine is as follows: after the mixture of slurry and flotation reagents is pressurized by the mortar pump, it is sprayed from the nozzle to the plenum chamber at high speed to form a vacuum to inhale air and generate mineralized bubbles to realize the mineral separation [31]. The inflatable mechanical agitation flotation machine mineralizes the entrained air with the target mineral by agitation [32]. The schematic diagrams of SL jet flotation machine and BS-K inflatable mechanical agitation flotation machine are shown in Fig. 8 and Fig. 9, respectively.

Whether it is a jet flotation machine or an inflatable mechanical agitation flotation machine, it has a strong mechanical mixing effect, and the travel of the mineralized bubbles to the foam layer is short, and the suspended mineral particles are not

Table 10 Indexes of cleaning stage before and after transformation

Before				After			
Date	WO_3 grade/%		Recovery/%	Date	WO_3 grade/%		Recovery/%
	Rough concentrates	Final concentrates			Rough concentrates	Final concentrates	
2008−11	1.21	21.47	90.39	2009−02	1.13	32.65	88.68
2008−12	1.13	20.28	90.31	2009−03	1.21	33.49	89.96
2009−01	1.14	16.8	92.43	2009−04	1.18	29.29	88.34
Average	1.16	19.52	91.04	Average	1.17	31.81	89

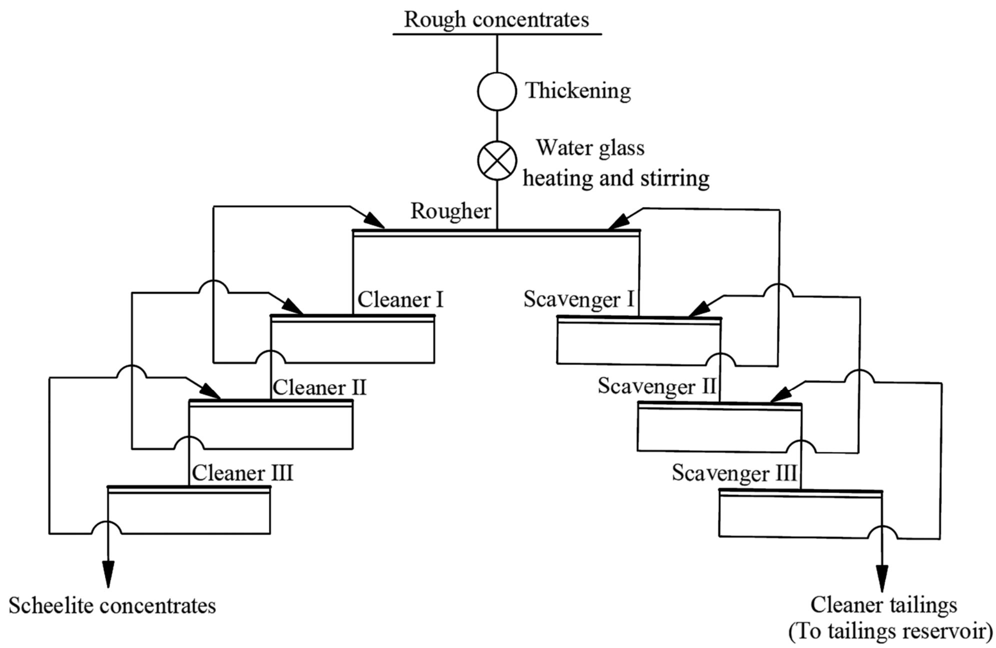

Fig. 6 Flowsheet of cleaning stage (From August 2014 to now)

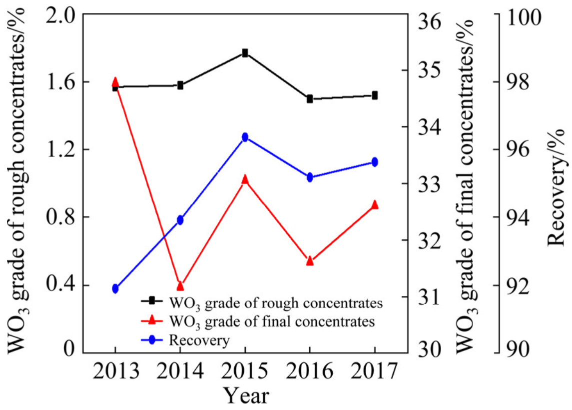

Fig. 7 Indexes of cleaning stage in recent years

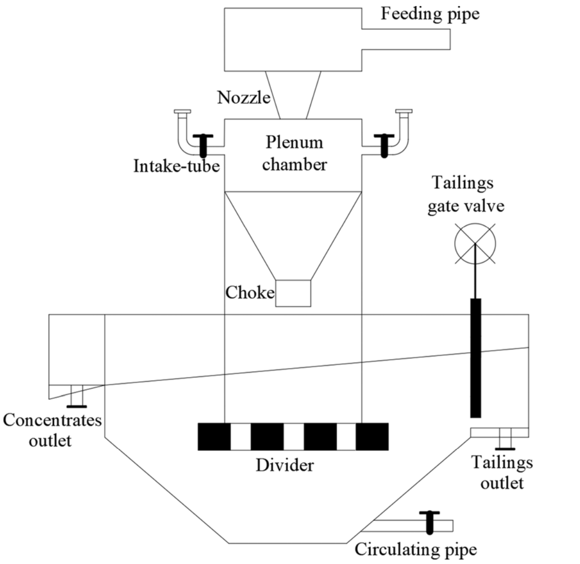

Fig. 8 Schematic diagram of SL jet flotation machine [31]

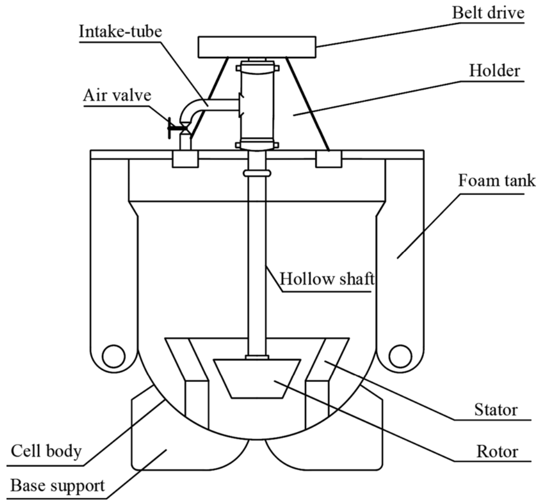

Fig. 9 Schematic diagram of BS-K inflatable mechanical agitation flotation machine [33]

easy to sink. Therefore, the flotation machine is effective when it is used to recover minerals with coarse particles or high density, but it has serious gangue entrainment and the obtained concentrate is of low grade. However, the flotation column has obvious advantages in improving the grade of concentrate, and is characterized by simple structure, large processing capacity and low energy consumption, but it has a poor recovery effect on heavy particulate minerals [34]. The schematic diagram of CCF flotation column is presented in Fig. 10. The slurry and the bubbles move toward

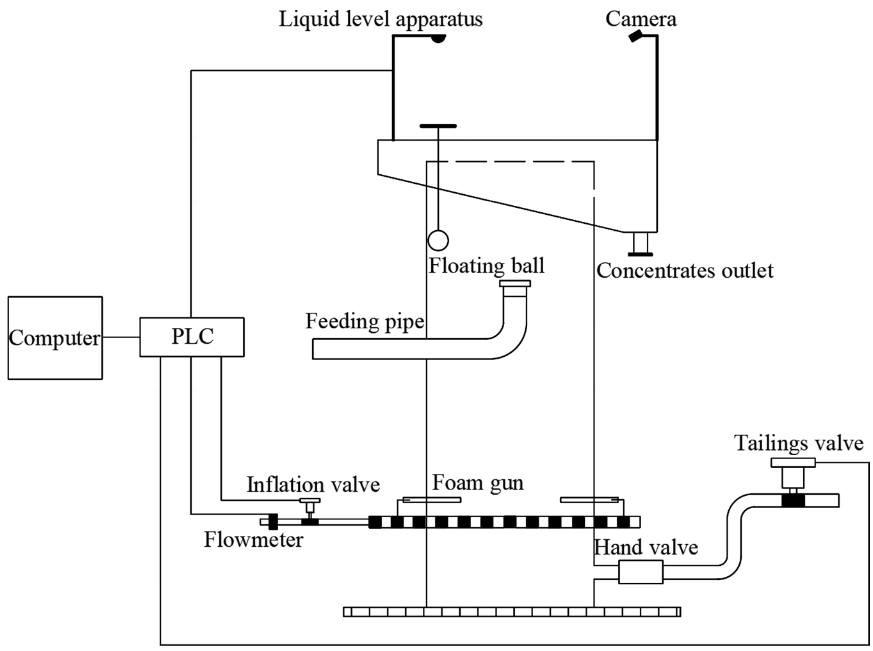

Fig. 10 Schematic diagram of CCF flotation column [35]

each other and fully act to form mineralized bubbles. The mineralized bubbles rise to the foam phase zone and are washed by the rinse water to cause the entrained gangue minerals to fall back into slurry, resulting in secondary enrichment [36,37].

As a result, in order to further improve the recovery efficiency of low-grade scheelite and shorten the process, the column−machine combined process was successively carried out in Luanchuan area after repeated trials and demonstrations [38]. At the end of 2011, the combined process transformation in roughing stage of LYYL was completed. The equipment of roughing and first scavenging in roughing stage were changed from SL jet flotation machine to CCF flotation column, and the original SL jet flotation machine was still applied in the secondary scavenging [34]. As given in Table 11, after the transformation, the enrichment ratio was increased from 17.35 to 19.39, the recovery was increased from 73.68% to 75.97%, the processing capacity was increased from 14500 to 18000 t/d, but the installation power was decreased from 1440 to 930 kW.

In August 2014, the equipment of roughing and cleaning in cleaning stage was changed from BS-K flotation machine to CCF flotation column, and the original BS-K flotation machine was retained in scavenging [35,39]. As presented in Fig. 11, the WO_3 grade of final concentrate decreased from 31.77% to 30.54%, but the recovery of cleaning stage increased from 92.74% to 96.07%. The WO_3 grade of the final scheelite concentrate still remained above 30%, but the recovery of cleaning stage increased significantly.

The application of flotation column in scheelite roughing and cleaning improves the grade of concentrate, and the application of flotation machine in scavenging reduces the loss of heavy particle minerals and ensures the scheelite recovery rate. The results indicated that the combined process not only enhances the beneficiation index, but also lowers the beneficiation cost.

5 Flotation reagent

A typical reagent scheme is employed in the roughing stage of low-grade scheelite in Luanchuan area, which is called “sodium carbonate flotation

Table 11 Indexes before and after transformation of roughing stage

Flotation equipment	Year	WO_3 grade/%		Recovery/%	Enrichment ratio	Processing capacity/($t\cdot d^{-1}$)	Installed power/kW
		Molybdenum tailings	Rough concentrate				
Jet flotation machine	2011	0.0686	1.19	73.68	17.35	14500	1440
Column−machine combination	2012	0.0748	1.45	75.97	19.39	18000	930

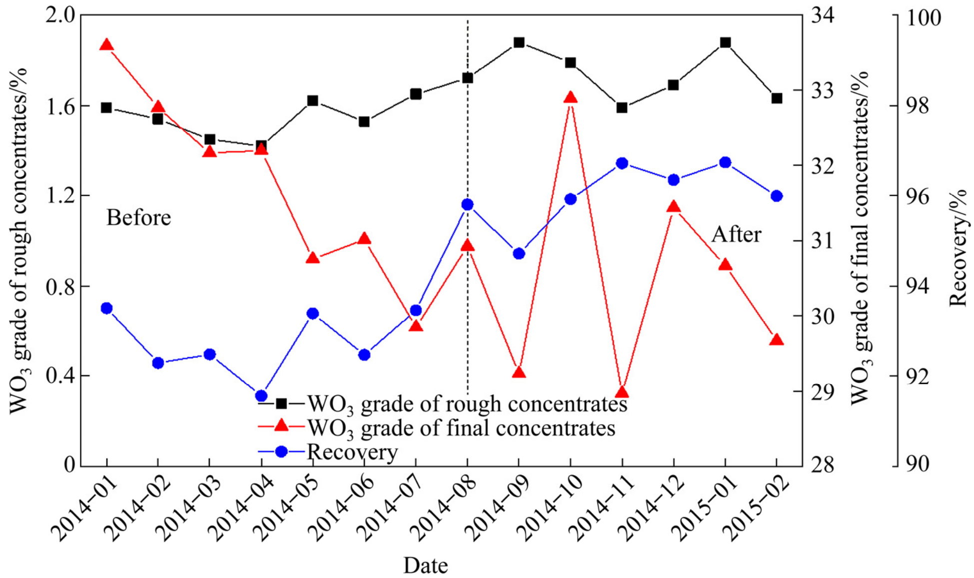

Fig. 11 Indexes before and after transformation of cleaning stage

process". The reagent scheme uses sodium carbonate as a pH regulator, sodium silicate as an inhibitor, and fatty acid or fatty acid salt as a collector [40−42].

The optimum slurry pH value of scheelite flotation is relatively alkaline [41]. Sodium carbonate can not only adjust the slurry pH, but also promote the dispersion of slurry and eliminate calcium and magnesium ions, and create suitable conditions for the adsorption of collectors on the surface of scheelite [43]. According to the properties of the molybdenum tailings in Luanchuan, the slurry pH value of the scheelite roughing stage is controlled between 9.0 and 10.5 by adding sodium carbonate [27].

The dominate silicic species $SiO(OH)_3^-$ and $Si(OH)_4$ generated by the hydrolysis of sodium silicate can be adsorbed on the surface of gangue minerals to form complexes, which can enhance the hydrophilicity of gangue minerals and inhibit the gangue minerals [41]. The combination of sodium carbonate and sodium silicate can produce a synergistic effect to strengthen the inhibition of gangue minerals. The surface carbonation induced by the prior addition of sodium carbonate, leads to an acid-based reaction on the surface that results in the formation of the deprotonated forms of silica, which are more susceptible to adsorption on the gangue mineral surface [44−46]. However, the selective inhibition effect of sodium silicate on calcium-containing gangue minerals is limited during the roughing of Luanchuan low-grade scheelite, and the excessive sodium silicate will also inhibit scheelite [41]. In order to improve the scheelite rough concentrate grade in Luanchuan area, KANG et al [47] used etidronic acid instead of sodium silicate and increased the rough concentrate grade from 1.22% to 1.68%. The improvement of roughing concentrate grade not only saved 17% of the subsequent cleaning cost, but also increased the cleaning recovery by 7%. The combined inhibitor of ATM and acidified sodium silicate was also introduced in the laboratory to improve the rough concentrate grade. In the case that the roughing recovery has not decreased, the rough concentrate grade was increased from 0.62% to 1.42% [48,49]. The industrial promotion of these novel inhibitors is still in their infancy.

Originally, oleic acid was used as the collector of scheelite in Luanchuan area. The poor dispersibility of oleic acid at low temperatures leads to a sharp decline in the recovery of the scheelite roughing stage in winter. In the first and fourth quarters of each year, the temperature in Luanchuan area is relatively low, and the slurry temperature of the scheelite roughing stage is generally between 8 and 15 °C. As shown in Fig. 12, in 2008, the average recovery of the scheelite roughing stage in the first and fourth quarters of LYYL was 3.64% lower than that in the second and third quarters. Among them, the difference in the roughing recovery between February and May is the largest, reaching 9.57%. In August 2009, oleic acid was replaced by FX-6, a scheelite collector with better low-temperature collecting ability. According to the relevant reports, FX-6 is a mixture of sodium fatty acids with different chain lengths and surfactants with different functional groups [27,50]. As presented in Fig. 13, after the application of the new collector FX-6, the average roughing recovery from

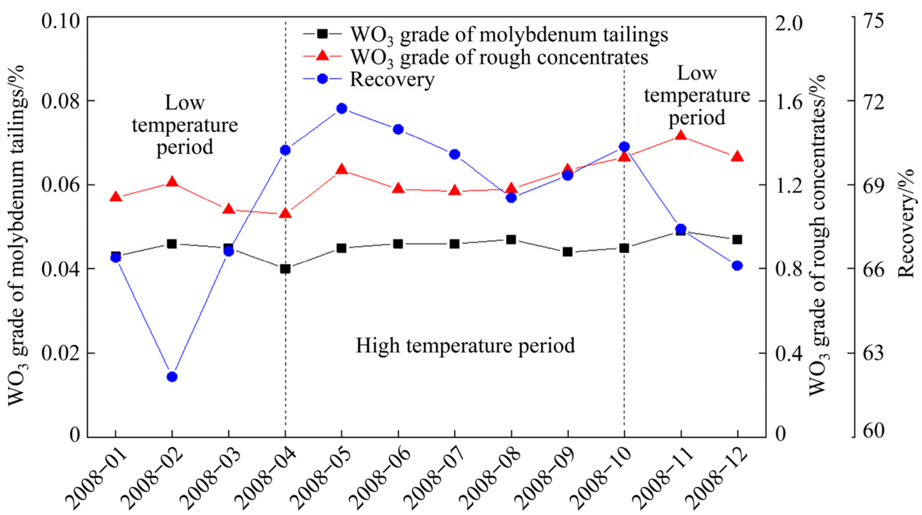

Fig. 12 Monthly roughing production indexes of LYYL in 2008

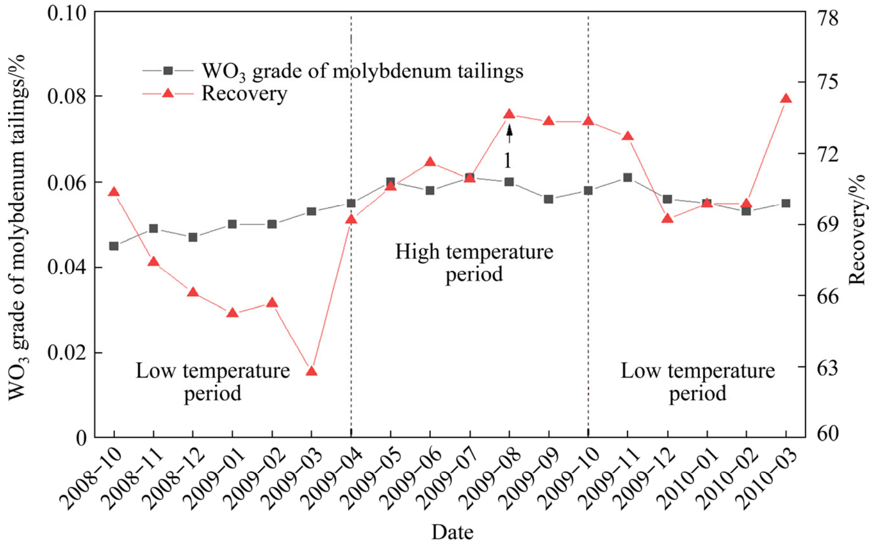

Fig. 13 Monthly roughing production indexes of LYYL from October 2008 to March 2010 (1−Introduction of FX-6)

October 2009 to March 2010 is 71.55%, an increase of 5.29% year-on-year, which is the same as the average recovery from April 2009 to September 2009. Its good performance may be attributed to the synergistic effect between fatty acids with different chain lengths and different saturations [51].

Sodium silicate is the main flotation reagent in the cleaning stage, but there are few studies on the detailed mechanism of sodium silicate in the Petrov process. It was found in the actual production process that the dosage of sodium silicate in the Petrov process is affected by the modulus (the mole ratio of SiO_2 to Na_2O). As given in Table 12, the dosage of sodium silicate with a modulus of 2.0 in the Petrov process is lower than that with a modulus of 3.0 and the indexes of Petrov process have little change. As a result, the original sodium silicate was completely replaced by sodium silicate with a modulus of 2.0 [52].

Table 12 Comparison of dosage of sodium silicate with different moduli in Petrov process of LYYL [52]

Modulus	Date	Dosage of sodium silicate to raw ore/(kg·t^{-1})	WO_3 grade of final concentrates/%	Recovery of cleaning/%
3.0	2010−03	3.69	26.63	94.30
	2010−04	7.07	30.52	87.79
	2010−05	4.25	29.63	97.80
2.0	2010−06	1.88	30.63	90.66
	2010−07	2.09	34.65	91.32
	2010−08	2.70	31.46	96.84

6 Prospect

After the development for decades, the beneficiation technology of low-grade scheelite in Luanchuan area has become relatively mature. However, there are still some issues worthy of further study. The existing problems are summarized and solutions are proposed in combination with the advanced technologies, as follows:

(1) Stabilizing and improving the roughing recovery of scheelite in ultra-low temperature environment. In 2017, The annual recovery of the scheelite roughing stage reached 75.74%. However, affected by the extremely cold weather that has never been encountered, the recovery of the scheelite roughing stage in the fourth quarter of 2017 was only 70.54%. The slurry temperature in the fourth quarter of 2017 was lower than 8 °C for a long time, and the dispersibility of the collector was deteriorated, resulting in the resource and economic losses.

According to relevant researches, the combination of fatty acid collectors and other surfactants is an effective way to improve the recovery of scheelite in ultra-low temperature environments. The addition of polyoxyethylene ether nonionic surfactant can improve the dispersibility and hard water resistance of fatty acid collector [53]. Therefore, it can be applied to the low-temperature flotation of scheelite, apatite, fluorite, bauxite and other minerals. The research results indicate that polyoxyethylene ether surfactants can make sodium oleate obtain higher surface property under low temperature environment and increase the adsorption amount of sodium oleate on the surface of scheelite [54,55]. The beneficial effect of nonylphenol polyethylene glycol ether surfactants was tested in the flotation of phosphate ores. The results showed that the nonylphenol polyethylene glycol ether surfactant reduced the surface tension of the sodium oleate solution and improved the flotation foam properties, thereby increasing the recovery of the phosphate ores [53]. FILIPPOV et al [56] found that fatty alcohol and oleic acid were co-adsorbed on the surface of calcium-containing minerals, which increased the hydrophobicity of the mineral surface and improved the flotation recovery.

Different surfactants have different synergistic effects. The effect of multi-surfactant compounding system on the recovery efficiency of low-grade scheelite in Luanchuan area in low temperature environment is worthy of in-depth study.

(2) Improving the WO_3 grade of scheelite rough concentrate. The high-grade rough concentrate is beneficial to reducing the load of the cleaning stage and improving the quality of the final scheelite concentrate. As given in Table 13, the main components in the rough concentrate of LYYL are CaF_2, $CaCO_3$ and SiO_2. The separation of scheelite and calcium-containing gangue minerals is always a challenge in mineral processing [57,58]. However, it is feasible to achieve efficient flotation separation of scheelite, fluorite and calcite by developing more selective collectors and inhibitors, thereby improving the grade of scheelite rough concentrate [59,60].

Table 13 Multi-element chemical analysis result of rough concentrate and final concentrate (wt.%)

Component	Rough concentrate	Final concentrate
WO_3	1.67	31.95
P_2O_5	3.29	11.97
CaF_2	22.42	14.62
$CaCO_3$	34.59	31.67
SiO_2	18.41	3.09

A large number of research results have indicated that the metal−organic complexes formed by the mixture of lead nitrate and hydroxamic acid can improve the flotation efficiency of tungsten minerals and calcium gangue minerals [61−63]. However, the application of this reagent scheme in scheelite flotation is still mainly confined to batch flotation test, and the main limiting factors of its industrial application are as follows: (1) Economic benefits. In the case of LYYL, the total cost of collector, sodium silicate and slurry heating in the existing process is RMB ¥ 5 per ton of raw ore (Table 14). If hydroxamic acid and lead nitrate are introduced, the collector cost rises to about RMB ¥ 20 per ton of raw ore due to its more expensive price and larger dosage. Even if the Petrov process could be replaced, it would not be acceptable for such low-grade scheelite in Luanchuan. (2) Environmental problems. Based on China’s current environmental policy, the application of lead nitrate and the production of hydroxamic acid are strictly restricted.

Table 14 Price and consumption of main consumables of LYYL

Item	Price/ (RMB ¥·t^{-1})	Consumption/ (g·t^{-1})	Cost/ (RMB ¥·t^{-1})
Sodium carbonate	1500	1800	2.7
Sodium silicate	600	3000	1.8
Collector	8000	200	1.6
Natural gas*	2.5	0.64	1.6

*Measured in m^3

Other novel collectors, such as amide-hydroxamic acid, quaternary ammonium salt, and cation/anion collector mixed by dodecyl amine and sodium oleate, are considered to have better selectivity and collection capacity than fatty acid collectors [64−67].

The novel inhibitors are also the focuses of research. The mixture of oxalic acid and sodium silicate in a ratio of 3:1 exhibits a good selective inhibition effect on calcite and can achieve efficient separation of scheelite and calcite [68]. Other novel inhibitors such as phytic acid, calcium lignosulphonate, sodium alginate, dextran sulfate sodium, guar gum and xanthan gum also have excellent selective inhibition effect on calcium-containing gangue minerals [47,69−72]. The structures of these inhibitors generally contain hydrophilic groups such as hydroxyl, carboxylic acid, phosphoric acid, and sulfonic acid. The results of mechanism studies indicate that these inhibitors can be selectively chemically adsorbed on the surface of gangue minerals through the bonding of their hydrophilic groups and calcium ions on the surface of gangue minerals [73−75]. The pre-adsorption of inhibitors prevents the further adsorption of collectors on the surface of gangues, thus achieving the separation of scheelite and calcium-containing gangue [76,77].

On the basis of the above researches, the application of these novel flotation regents in improving the grade of scheelite rough concentrate in Luanchuan area can be popularized. However, the economic benefits of these novel reagents should be strictly calculated to ensure the sustainability of the recovery of low-grade scheelite in Luanchuan area.

(3) Realizing the whole process of normal temperature flotation. The whole process of normal temperature flotation will save energy consumption of pulp heating and drastically reduce the beneficiation cost of low-grade scheelite. The above-mentioned novel flotation reagents are undoubtedly one of the crucial paths to realize normal temperature flotation [18].

In addition, the centrifugal gravity separation equipment such as Falcon and Knelson concentrators have been successfully applied to the separation process of scheelite form skarns in recent years. The research results show that these equipments can reject most calcium-bearing gangue minerals such as fluorite and apatite [78,79]. It may be a beneficial attempt to introduce the new equipment into the beneficiation process of low-grade scheelite in Luanchuan area to remove most of the gangues in the rough concentrate in advance to replace the Petrov process. However, the technical indicators and economic benefits of the entire process also need to be given adequate attention.

(4) Recycling other associated resources. The molybdenum tailings also contain a certain amount of fluorite. Fluorite is a nonrenewable nonmetallic strategic resource. The value of fluorite in the molybdenum tailings in Luanchuan is comparable to that of scheelite. The recycling of fluorite is of great significance to the comprehensive utilization of resources [80]. Laboratory-scale studies were carried out on the recovery of fluorite from scheelite rough concentrate and scheelite tailings. The results presented that no matter which process was introduced, the fluorite grade can reach about 93%, and the fluorite recovery can reach about 45%. The quality of fluorite concentrate meets the standards of metallurgical grades. Industrialization of fluorite recycling is the focus of future research [80,81].

7 Conclusions

(1) The associated scheelite resources in the molybdenum tailings in Luanchuan area have undergone a process from discarding as tailings to large-scale recovery, which is of great significance to ensure the advantages of China's tungsten resources and avoid the loss of resources.

(2) After several years of exploration and innovation, the beneficiation process, beneficiation equipment and flotation reagents of low-grade scheelite have been fully developed. The optimization of the beneficiation process, the column−machine combined process, and the high-efficiency flotation reagents have greatly improved the indexes of low-grade scheelite recovery.

(3) The beneficiation level of low-grade scheelite in Luanchuan area still has a lot of room for improvement. It is worth further study and promotion for high selective flotation reagents, recycling of associated resources and so on.

Acknowledgments

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从栾川钼尾矿中回收低品位白钨矿的研究进展：以洛阳豫鹭矿业有限责任公司为例

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摘 要：栾川地区是世界上白钨矿选矿规模最大、白钨矿精矿产量最多的地区之一。经过多年的创新和进步，从栾川地区的钼尾矿中回收低品位伴生白钨矿的选矿技术日臻完善。作者针对栾川地区低品位白钨矿回收技术的发展历程进行总结，包括原矿性质、选矿工艺、浮选设备和浮选药剂等。同时，以洛阳豫鹭矿业有限责任公司为例，详细阐述选矿工艺优化、柱−机联合工艺、高效浮选药剂等各项技术改造取得的效果。栾川地区低品位白钨矿的回收技术仍有进步空间。结合最新研究进展，展望栾川地区低品位白钨矿选矿技术的发展方向。这对于进一步提高栾川地区低品位白钨矿资源的回收效率具有重要意义，可为其他白钨矿厂提供技术参考。

关键词：白钨矿；低品位矿；选矿；浮选；回收

(Edited by Bing YANG)