A Study on Recycling Fine Wolframite Slime by “Flotation Desulfurization-Centrifugal Preconcentration-Flotation Wolframite” Process

Guanghua Ai¹,², Yanfei Liu¹

¹Faculty of Resource & Environmental Engineering
Jiangxi University of Science & Technology
Ganzhou, Jiangxi, China
²Jiangxi Key Laboratory of Mining Engineering
Ganzhou, Jiangxi, China

Abstract—In order to solve the problems of recycling difficulties, complicated recycling processes and low recycling rate of fine wolframite slime, this paper adopted a new technological process of “Flotation desulfurization-Centrifugal preconcentration-Flotation wolframite” to recycle real fine wolframite slime samples in a wolframite slime workshop, examined the influences of centrifuge working conditions, flotation reagents system, auxiliary collector and other conditions on the indicators of fine wolframite slime, optimized the corresponding technological conditions and operation parameters, and finally conducted close-circuit experiments on basis of above. The experimental results showed that, through new process, we could obtain tungsten concentrate with WO₃ content of 36.87% and recovery rate of 62.90%, which separation indexes were significantly superior to previous indexes in all gravity separation process of “Grading-Coarse grain table-Fine centrifugal”; under circumstances of same grade of fine wolframite slime ore, the grade of wolframite concentrate was increased by 15.22% through new process than previous process. This technology provides a new technological pathway to high-efficiency recycling of fine wolframite slime.

Keywords—Fine wolframite slime; Centrifugal preconcentration; Combined collector; Auxiliary collector; New process

I. INTRODUCTION

China owns the most abundant reserves of tungsten in the world, about 40% of the total reserves. Though tungsten is a kind of preponderant mineral resources, it is crisp, easily over-crushing and slimed, and its surfaces are apt to be contaminated by fine gangue mineral stuff so that lose original flotation performance and thus hard to recycle. According to statistics, all around the world, about one-fifth of tungsten are lost in tailings by form of slime yearly, which may result in waste of resources and environmental pollution. Due to high specific gravity of wolframite, it is favorable to use gravity separation method to remove away gangue mineral of much different specific gravity. This method is featured by low cost, simple process and low environmental pollution. However, the wolframite is tough but crisp, thus extremely easy to suffer from over crushing during ore grinding; besides, the gravity separation method is inefficient in recycling fine fraction wolframite, resulting in that a lot of tungsten existing in fine slime are lost in tailings. Therefore, to efficiently recycle wolframite mineral from fine wolframite slime is an important way to improve comprehensive recycling rate of tungsten. Today, as wolframite resources exhaust day by day, it will be particularly vital to utilize high-efficiency preparation equipment, simple and feasible process and efficient beneficiation reagents to recycle fine wolframite slime[1-4]. This paper took the fine wolframite slime sample as the object of research, a mixture of original and secondary fine slimes under proportion of 1:3 that acquired from a fine wolframite slime workshop in Dayu County, Jiangxi Province, and aimed at developing an efficient recycling process of fine wolframite slime. With “Flotation desulfurization - Centrifugal preconcentration - Flotation wolframite”, a flotation-separation-flotation technological process[5-11], it is favorably to recycle fine wolframite slime with WO₃ content of 36.87%, recycling ratio of tungsten concentration 62.90% and recycling rate of 86.01% via flotation operation, while new process enables it to realize an increased grade of wolframite concentrate by 15.22% than previous process.

II. ORE PROPERTIES

This mine belongs to Wolframite cassiterite stringer filling - hydrothermal quartz vein type polymetallic deposit. In which, the main ore minerals include wolframite and cassiterite, and the associated minerals primarily include chalcopyrite, galena, sphalerite, molybdenite and pyrite as well as small amounts of scheelite, bismuthinite, bornite, arsenopyrite, limonite, etc. a majority of gangue minerals are quartz, followed by sericite, lepidolite, fluorite, epidote, tourmaline, beryl, topaz, pyrophyllite, chlorite, etc. The analysis results of the chemical composition of fine Wolframite slime and the chemical phase of tungsten in fine Wolframite slime are shown in Table.1 and 2. The size distribution of fine Wolframite slime and the tungsten distribution rate are shown in Table.3.
### TABLE 1 ANALYSIS RESULT OF THE CHEMICAL CONTENTS OF FINE WOLFRAMITE (%)

<table>
<thead>
<tr>
<th>Composition</th>
<th>WO₃</th>
<th>Sn</th>
<th>Cu</th>
<th>S</th>
<th>Pb</th>
<th>Zn</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content</td>
<td>0.26</td>
<td>0.09</td>
<td>0.15</td>
<td>0.76</td>
<td>0.14</td>
<td>0.17</td>
<td>0.018</td>
</tr>
<tr>
<td>Composition</td>
<td>Bi</td>
<td>Fe</td>
<td>CaO</td>
<td>SiO₂</td>
<td>CaF₂</td>
<td>Al₂O₃</td>
<td>P</td>
</tr>
<tr>
<td>Content</td>
<td>0.053</td>
<td>4.87</td>
<td>0.86</td>
<td>63.86</td>
<td>0.09</td>
<td>8.49</td>
<td>0.09</td>
</tr>
</tbody>
</table>

### TABLE 2 ANALYSIS RESULT OF THE CHEMICAL PHASE OF TUNGSTEN IN FINE WOLFRAMITE (%)

<table>
<thead>
<tr>
<th>Chemical Phase</th>
<th>Tungsten in wolframite</th>
<th>Tungsten in scheelite</th>
<th>Tungsten in other phase</th>
<th>Total tungsten content</th>
</tr>
</thead>
<tbody>
<tr>
<td>WO₃</td>
<td>0.227</td>
<td>0.033</td>
<td>0.003</td>
<td>0.26</td>
</tr>
<tr>
<td>Distribution rate</td>
<td>86.31</td>
<td>12.55</td>
<td>1.14</td>
<td>100.00</td>
</tr>
</tbody>
</table>

As can be seen in table 1 and 2, the grade of WO₃ is as low as 0.26% in wolframite fine slime ore. While in fine wolframite slime, tungsten mainly exists in the form of wolframite; in scheelite, tungsten only occupies 12.55%; and there is few tungstite.

### TABLE 3 SIZE COMPOSITION AND TUNGSTEN DISTRIBUTION IN FINE WOLFRAMITE (%)

<table>
<thead>
<tr>
<th>Size fraction (mm)</th>
<th>Yield</th>
<th>Cumulative yield</th>
<th>WO₃ grade</th>
<th>WO₃ distribution rate</th>
<th>WO₃ cumulative distribution rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>+0.15</td>
<td>3.35</td>
<td>3.35</td>
<td>0.07</td>
<td>0.89</td>
<td>0.89</td>
</tr>
<tr>
<td>0.15+0.074</td>
<td>15.4</td>
<td>18.76</td>
<td>0.13</td>
<td>7.60</td>
<td>8.49</td>
</tr>
<tr>
<td>0.074+0.053</td>
<td>25.4</td>
<td>44.24</td>
<td>0.36</td>
<td>34.80</td>
<td>43.29</td>
</tr>
<tr>
<td>0.053+0.038</td>
<td>9.86</td>
<td>54.10</td>
<td>0.24</td>
<td>8.98</td>
<td>52.27</td>
</tr>
<tr>
<td>0.038+0.01</td>
<td>30.7</td>
<td>84.87</td>
<td>0.34</td>
<td>39.69</td>
<td>91.96</td>
</tr>
<tr>
<td>-0.01</td>
<td>15.1</td>
<td>100.00</td>
<td>0.04</td>
<td>8.04</td>
<td>100.00</td>
</tr>
<tr>
<td>Σ</td>
<td>100.00</td>
<td>/</td>
<td>0.26</td>
<td>100.00</td>
<td>/</td>
</tr>
</tbody>
</table>

As can be seen in table 3, the yield of fine slime ore with size fraction of -0.074mm reaches up to 81.24%, either does WO₃ distribution rate reach up to 91.51%, which indicates a very fine distribution granularity of tungsten minerals.

### III. EXPERIMENT

#### A. Experimental Reagents

In the experiment, the beneficiation reagents basically include butyl xanthate, terpenic oil, sodium silicate, lead nitrate, 731, salicylaldoxime and TBP, all which are industrial reagents used for beneficiation plants. The water is civil tap water.

#### B. Experimental Equipment

The main experimental equipment are XMQ-240×90 conical mill, XFD & XFG series flotation machine, SLon-1600 centrifugal concentrator, precision pH meter.

### IV. RESULTS AND ANALYSIS

#### A. Fine Wolframite Slime Flotation Desulfurization Experiment and Results

Since the oxide ore flotation collector can easily collect sulfide ore, and fine slime ore only contains 0.76% of sulfur, thereby, sulfide ore will not only increase reagents consumption but also mix with rough tungsten concentrate to seriously deteriorate the tungsten concentration process. So, it is necessary to implement flotation desulfurization before fine wolframite slime flotation process[12]. Each time, we shall take 1kg fine wolframite slim ore and test in 3L single slot flotation machine. The trial test of collector showed that, butyl xanthate had a better effect on flotation desulfurization of wolframite fine slime, so we used butyl xanthate as desulfurization collector and then adopted secondary roughing process to conduct some experiments for investigating the effect of butyl xanthate dosage on desulfurization, experimental result as shown in Fig. (2).
Fig.(2) indicates that, judging by the sulfur recycling index and how many WO3 loss from sulfur concentrate, as butyl xanthate dosage increases, the sulfur grade decrease in tailings and the sulfur recycling ratio is gradually improved in sulfur concentrate, however, tungsten increasingly losses in sulfur concentrate. Under overall consideration, when butyl xanthate dosage is composed by 40g/t during I-stage roughing and 20g/t during II-stage roughing, it is probably to acquire a high sulfur recycling ratio and a low tungsten loss rate.

B. Centrifugal Preconcentration Experiment and Results

Due to low grade and high mud content of fine wolframite slime, it is difficult to obtain satisfactory separation indexes. As a result, we carried out preconcentration experiment of fine wolframite slime desulfurized tailings by SLon-1600 centrifugal concentrator. The experiment adopted roughing-scavenging process in experiment of centrifugal preconcentration condition including centrifuge speed, feeding concentration, rinse water volume and feeding speed, etc[13]. Table 4 shows the experimental results under optimum conditions of centrifuge speed 500r/min, feeding concentration 20%, rinse water volume 3L/min and feeding speed 20L/min.

<table>
<thead>
<tr>
<th>Product</th>
<th>Yield</th>
<th>WO3 Grade</th>
<th>WO3 Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfide concentrate</td>
<td>4.71</td>
<td>0.31</td>
<td>5.55</td>
</tr>
<tr>
<td>Rough tungsten concentrate</td>
<td>26.94</td>
<td>0.72</td>
<td>73.68</td>
</tr>
<tr>
<td>Tailings</td>
<td>68.35</td>
<td>0.08</td>
<td>20.77</td>
</tr>
<tr>
<td>Raw ore</td>
<td>100.00</td>
<td>0.26</td>
<td>100.00</td>
</tr>
</tbody>
</table>

From the results in table 4, through centrifugal preconcentration of wolframite fine slime by SLon-1600 centrifugal machine, we obtained satisfactory rough tungsten concentrate with WO3 content of 0.72% and recycling ratio up to 73.68%. The gravity separation preconcentration experiment improved the grade of the selected fine wolframite slime under floatation, at the same time, greatly reduced the feeding volume and mud content in fine wolframite slime floatation, saved a lot of floatation reagents, and brought down the subsequent beneficitation costs.

C. Wolframite Fine Slime Flotation Experiment and Result

1) Experiment of the Influence of Sodium Silicate Dosage on Grading Indexes of Fine Wolframite Slime

Taking rough centrifugal concentrate as feeding in fine wolframite slime floatation experiment, the mono-mineral experiment and production practice show, optimum wolframite flotation pulp is neutral or weak alkaline environment with pH value of 7.0–9.0. Nevertheless, the experimental gangue inhibitor was sodium silicate, which is a kind of weak acid and alkaline salt that may hydrolyze in aqueous solution to display alkalinity. For this reason, in general, no pH regulators is necessary in wolframite flotation experiment, and sodium silicate can inhibit quartz, silicate minerals and calcite. We examined the influence of sodium silicate dosage on targets of wolframite floatation under lead nitrate dosage of 200g/t and 731 dosage of 200g/t, and the experimental results are shown in Fig. (3).

2) Experiment of the Influence of Lead Nitrate Dosage on Grading Indexes of Fine Wolframite Slime

Recently, lead nitrate is the most frequently used and effective activator in wolframite flotation. The mono-mineral experiment indicates that lead nitrate has significant activation to wolframite, and its dosage significantly impacts the wolframite floatation indexes. We examined the influence of lead nitrate dosage on wolframite floatation indexes under sodium silicate dosage of 400g/t, it indicates the best WO3 recycling indexes: grade 4.22% and recycling ratio up to 68.94%.

From the results in Fig. (3), the grade of rough tungsten concentrate increases with sodium silicate dosage, but excessive sodium silicate dosage may inhibit wolframite so that WO3 recycling ratio initially slightly rises and later entirely tends to decrease. Under sodium silicate dosage of 400g/t, it indicates the best WO3 recycling indexes: grade 4.22% and recycling ratio up to 68.94%.
As can be seen in Fig. (4), as lead nitrate dosage increases, the WO3 grade displays no significant change, but wolframite recycling ratio largely raise up. When lead nitrate dosage is 300g/t, the wolframite recycling ratio reaches up to 75.82%; while increasing the dosage to 400g/t, the wolframite recycling ratio rapidly falls, which is possibly caused by that excessive lead nitrate dosage results in the elevated negative value of wolframite surface potential. In consequence, we decided that a proper lead nitrate dosage shall be 300g/t in roughing of fine wolframite slime.

3) Experiment of the Influence of Collector Kind on Grading Indexes of Fine Wolframite Slime

Selecting appropriate collector is crucial for flotation indexes[14]. Under same conditions beside of collector, we implemented collector species experiment to compare and screen the conventional fatty acid collector, chelating collector and the combined collector of previous two species. We examined the influence of various collectors on wolframite flotation indexes under sodium silicate dosage of 400g/t, lead nitrate dosage of 300g/t and collector dosage of 200g/t, and the experimental results are shown in Fig. (5).

It can be concluded from Fig. (5) that, regarding single collector, only 731 has good effect on fine wolframite slime beneficiation, while the results of benzoxyhydroxamic acid, salicylaldoxime and oleic acid are not satisfactory; the results of two combined collectors are better than 731; under proportion of 731:salicylaldoxime=9:1 (i.e. a combined collector mixed with 731 dosage 180g/t and salicylaldoxime dosage 20g/t), we can acquire optimum results in grading of fine wolframite slime with WO3 content of 4.98% in rough tungsten concentrate and recovery ratio up to 82.61%. 

4) Experiment of the Influence of Combined Collector on Grading Indexes of Fine Wolframite Slime

We examined the influence of combined collector (mixture by proportion of 731:salicylaldoxime=9:1) dosage on wolframite flotation indexes under sodium silicate dosage of 400g/t and lead nitrate dosage of 300g/t, and the experimental results are shown in Fig. (6).

It can be concluded from Fig. (6) that, when combined collector dosage increases, the yield of rough tungsten concentrate constantly increases, WO3 grade obviously tends to decrease and WO3 recovery rate unceasingly yet slowly rises. Considering both grade and recovery ratio, it is better to make total combined collector dosage be 200g/t, under which condition, we can get WO3 grade of 5.12% and recovery ratio of 81.26%.

5) Experiment of the Influence of Auxiliary Collector on Grading Indexes of Fine Wolframite Slime

In order to explore whether TBP (tributyl phosphate) could exert auxiliary effect on fine wolframite slime floatation via combined collector, we made combined collector dosage experiment. We examined the influence of auxiliary collector TBP on wolframite flotation indexes under sodium silicate dosage of 400g/t, lead nitrate dosage of 300g/t and 731/salicylaldoxime combined collector dosage of 200g/t, and the experimental results are shown in Fig. (7).
The results in Fig. (7) manifests that, as TBP dosage increases, the recovery of WO3 firstly slightly increases; under TBP usage of 40g/t, the WO3 recovery reaches up to 83.90%; then after continue adding TBP, the recovery sharply decreases. So we can conclude from the experiment that TBP can effectively help to enhance flotation effect of combined collector, but excessive dosage may diminish the concentrate foam and let indexes abruptly fall down, which warn us to strictly control TBP dosage.

D. Fine Wolframite Slime Beneficiation Opened-circuit Experiment and Results

On the basis of conditionl experiment, we utilized roughing twice in desulfurization operation, a roughing once-scavenging once process in centrifugal gravity preconcentration and a roughing once-concentrating three times-scavenging three times in flotation operation. See opened-circuit experimental results in table 5.

E. Fine Wolframite Slime Beneficiation Closed-circuit Experiment and Results

On the basis of opened-circuit experiment, we conducted a laboratory full-process small-scaled closed-circuit experiment. See experimental process in Fig. (8) and experimental results in table 6.
From the results of closed-circuit experiment, the “Flotation desulfurization-Centrifugal preconcentration - Flotation wolframite” method, a new flotation-gravity-flotation process, can preferably recycle fine wolframite slime. Furthermore, the preconcentration function of centrifuge separator enables us to enhance the grade of wolframite flotation feeding ore, to cut down the dosage of wolframite floatation feeding ore and to sharply bring down total reagent dosage during the whole process, which avails cost saving and environmental protection. By full-process laboratory small-scaled closed-circuit experiment, we obtained tungsten concentrate with WO3 content of 36.87%, a recovery rate of 62.90% and the flotation operation recovery up to 86.01%.

F. Comparison between New Process and Field Technological Indexes for Fine Wolframite Slime Beneficiation

The mine adopted a full gravity separation process of “Grading-Coarse grain table-Fine centrifuge” process to treat original and secondary fine wolframite slime. According to the statistics data provided by the mine, their tungsten recovery is 61.62% and final grade of WO3 in tungsten concentrate is 21.65%; the 60%~80% of concomitant sulfide ore in fine slime are lost in tailings. We made a comparison between the indexes obtained from using new process of “Flotation desulfurization-Centrifugal preconcentration - Floatation wolframite” and the indexes obtained under previously field all gravity separation process, see results in table. 7.
TABLE 7 RESULTS OF THE NEW PROCESS COMPARED WITH THE ORIGINAL TECHNICAL INDEX

<table>
<thead>
<tr>
<th>Process</th>
<th>Product</th>
<th>Yield (%)</th>
<th>WO3 Grade (%)</th>
<th>WO3 Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>New process</td>
<td>Concentrate</td>
<td>0.45</td>
<td>36.87</td>
<td>62.90</td>
</tr>
<tr>
<td></td>
<td>Tailings</td>
<td>99.55</td>
<td>0.10</td>
<td>37.10</td>
</tr>
<tr>
<td></td>
<td>Raw ore</td>
<td>100.00</td>
<td>0.26</td>
<td>100.00</td>
</tr>
<tr>
<td>Original process</td>
<td>Concentrate</td>
<td>0.74</td>
<td>21.65</td>
<td>61.62</td>
</tr>
<tr>
<td></td>
<td>Tailings</td>
<td>99.26</td>
<td>0.10</td>
<td>38.38</td>
</tr>
<tr>
<td></td>
<td>Raw ore</td>
<td>100.00</td>
<td>0.26</td>
<td>100.00</td>
</tr>
<tr>
<td>Target contrast</td>
<td>Under same raw ore grade, the new process can improve the wolframite concentrate grade by 15.22% and acquire equivalent recovery rate</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

As is known from experimental results, we can obtain superior indexes through adopting the new technological process of “Flotation desulfurization-Centrifugal preconcentration - Flotation wolframite” in beneficiation than adopting the all gravity separation process of “Grading-Coarse grain table-Fine centrifuge. Under the same grade of raw ore, the new process can improve the grade of wolframite concentrate by 15.22% and acquire equivalent recovery rate.

V. CONCLUSION

(1) The test raw ore is a mixture of original and secondary fine wolframite slime which originates from a mine in Ganzhou and contains 0.26% of WO3. The tungsten phase results show, in fine slime, tungsten mainly exists in the form of wolframite; in scheelite, tungsten only accounts 12.55%; and there is few tungstite. Besides, due to very fine granularity of fine slime raw ore, the yield of -0.074mm granularity is over 80%, the yield of -0.038 granularity reaches up to 45.9%. The recovery indexes are unsatisfactory using conventional gravity separation recovery method.

(2) Regarding this fine wolframite slime, we adopted “Flotation desulfurization-Centrifugal preconcentration - Flotation wolframite” process for separation, and in flotation operation, we adopted sodium silicate as gangue inhibitor, lead nitrate as activator, mixture of 731 and salicylaldoxime (731/salicylaldoxime=9:1) as wolframite collector and TBP as auxiliary collector, and finally carried out the “roughing once-concentration three times- scavenging twice” closed-circuit process, so that obtained a tungsten concentrate with WO3 content of 36.87%. Since 731 is also capable to powerfully collect small amount of scheelite in fine wolframite slime, therefore, flotation WO3 recovery is as high as 86.01% and the whole process WO3 recovery is 62.90%.

(3) The 731 and salicylaldoxime combined collector and auxiliary collector TBP are successfully used in the actual fine wolframite slime flotation experiment, which proves that such combined collector could easily collect wolframite, and TBP could excellently assist the combined collector.

(4) We can obtain superior separation indexes through adopting the new technological process of “Flotation desulfurization-Centrifugal preconcentration - Flotation wolframite” in beneficiation than adopting the all gravity separation process of “Grading-Coarse grain table-Fine centrifuge. Under the same grade and equivalent recovery of raw ore, the new process can improve the grade of wolframite concentrate by 15.22%.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflicts of interest.

ACKNOWLEDGMENT

This work is supported by the Natural Science Foundation of China (No.51564014).

REFERENCES


