Cassiterite Recovery from Tungsten Residues Through Centrifugal Gravity Concentration

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Abstract. Tungsten residues contain abundant valuable minerals that are difficult to be recovered by traditional gravity and flotation process. This study presents a route, centrifugal concentration for cassiterite recovery from tungsten residues through centrifugal concentrator. There were separated to three size fractions by experiment of elutriation using rotary flow analyser and cassiterite was observed by polarizing microscope and X-ray diffraction analysis. Results showed that after closed-circuit experiment of centrifugal concentration in the condition of roughing rotate speed of 850rpm, pulp mass concentration of 15%, washing water flow rate of 2L/S and concentrating rotate speed of 550rpm, the grade and recovery of Sn were 18.63% and 82.17% respectively. After closed-circuit experiment, Sn recovery of size fraction was calculated. Sn recovery of size fraction was 97.93% in size fraction of -37+20μm, 82.94% in size fraction of -20+10μm and 66.49% in size fraction of -10μm. This study demonstrates that the centrifugal concentration provides a promising process for the recovery of cassiterite from tungsten residues.

1. Introduction
China is one of the largest global producers of tungsten concentrate. The annual output of tungsten concentrate reach over 0.07 million tons from 2010 to 2013 (USGS, 2016). Tungsten residues are produced from tungsten hydrometallurgical process in world (Zhang et al., 2016). Most of the tungsten residues have to be stored because of strong alkalinity and contain contaminating heavy metals such as arsenic (As), cadmium (Cd) (Guan et al., 2016). The accumulation of tungsten residues has caused serious environmental problems, tungsten residues not only take up substantial farmland but also influence human health by polluting groundwater. Tungsten residues also contain a lot of useful metals such as tungsten(W), tin(sn), tantalum (Ta), niobium (Nb), so economic benefits from recycling metals are enormous (Zhang et al., 2003). However, few foreign researchers with regard to recovering valuable minerals from tungsten residues, great research effort has been made to develop green processes to treat tungsten residues in China. Dai yan-yang et al. have proposed a soda roasting, poaching and acid leaching process to recover Ta₂O₅, Nb₂O₅ from tungsten residues, in which tungsten residues are handled by roasting at 800℃ to 900℃, then leached with hydrochloric acid, enriched tungsten residues contain Ta₂O₅ plus Nb₂O₅ concentrate with grade of 15.89% and recovery of 79.46% (Dai Y et al., 2003).
however, hydrometallurgy process has some shortcomings such as high cost. Additionally, Luo xianping et al. have adopted a flotation process to recover Mo, Bi, W and a gravity separation process to recover Sn from tungsten residues (Luo et al., 2003). Because the particle of tungsten residues is relatively big, amount of Sn metal distributed in size fraction 37-76μm, when the particle of tungsten residues is very fine less than 37 μm, traditional gravity and flotation processes are no longer suitable.

In tungsten hydrometallurgical process (Guan et al., 2016), tungsten residues are formed by the following chemical reactions:

\[ \text{CaWO}_4(\text{s}) + 2\text{NaOH}(\text{aq}) = Na_2\text{WO}_4(\text{aq}) + \text{Ca(OH)}_2(\text{s}); \]
\[ (\text{Fe, Mn})\text{WO}_4(\text{s}) + 2\text{NaOH}(\text{aq}) = Na_2\text{WO}_4(\text{aq}) + (\text{Fe, Mn})(\text{OH})_2(\text{s}) \]

In chemical equations above, tungsten concentrate is transformed into sodium tungstate solution, however, cassiterite does not react with sodium hydroxide, so cassiterite is retained in tungsten residues.

Centrifugal concentrator is a high effective gravity equipment to recover micro-sized (less than 37μm) high-density minerals (Barry et al., 2006). This study exploits a new route, centrifugal gravity separation with Slon centrifugal concentrator, for the recovery of cassiterite from tungsten residues. Firstly, cassiterite is sufficiently dispersed under pulp of low mass concentration by high velocity mixing, and then collected by centrifugal gravity separation.

2. Experimental

2.1. Tungsten residues

Tungsten residues were obtained from Minmetals Smelting Plant (Jiangxi, China), one of largest smelts of W in China. Tungsten concentration including wolframite and scheelite is turned into tiny particles by wet milling, tungsten residues are obtained after leaching with sodium hydroxide at 80°C-180°C, pressure 0.8Mpa-2Mpa and pH 12-14. After filtration, the tungsten residues were over-dried for 2h at 90°C and then subjected to chemical composition analysis and X-ray diffraction (XRD) analysis.

2.2. Analytical methods

The tungsten residues sample was analyzed by chemical analysis methods using inductively coupled plasma-atomic emission spectrometry (ICP-AES, Optima 4300DV, American) and semiquantitative analysis with X-ray fluorescence (XRF, AXIOS, Netherlands), particle size of sample was analyzed by elutriation using rotary flow analyzer (XL-1, China), mineral composition by microscopic identification using polarizing microscope (PLM, XPV-600, China).

2.3. Tungsten residues characterization

Result of chemical composition analysis of the tungsten residues is shown in table1(XRF), table2(ICP-AES)

### Table 1. Result of chemical composition analysis of the tungsten residues (XRF).

| Elements | Al₂O₃ | As₂O₃ | Bi₂O₃ | CaO | CuO | F | Fe₂O₃ | I |
|----------|-------|-------|-------|-----|-----|---|-------|---|
| contents | 1.46  | 0.17  | 0.17  | 64.53 | 0.11 | 6.32 | 6.34  | 0.32 |
| Elements | K₂O | MgO | MnO | MoO₃ | Na₂O | Nb₂O₅ | PbO | SO₃ |
| contents | 0.07 | 0.27 | 1.32 | 0.11 | 3.88 | 0.37 | 3.36 | 1.78 |
| Elements | SiO₂ | SnO₂ | TiO₂ | WO₃ | ZnO |
| contents | 5.76 | 0.56 | 0.36 | 1.98 | 0.55 |

### Table 2. Result of chemical composition analysis of the tungsten residues (ICP-OES).

| Elements | WO₃ | Sn | Fe | Mn | CaO | S |
|----------|-----|----|----|----|-----|---|
| contents | 1.66 | 0.82 | 4.30 | 0.70 | 51.61 | 0.76 |
From the chemical composition analysis and the XRD result, it can be seen that calcium hydroxide and calcium fluoride were the mainly minerals. It can be inferred that tungsten concentrate is scheelite probably, fluorite is one of gangues. The valuable metals were mainly tungsten mineral (grade of WO$_3$ 1.66%), Sn mineral (garde 0.82%), which mainly existed in the form of scheelite, cassiterite from figure 2. Figure 2 shows also the gangues contains fluorite, pyroxene and quartz.

Table 3 shows the particle size distribution, the chemical grade and distributive of WO$_3$, Sn in the different size fractions. The size of all tungsten residue was less than 37um, indicating that the residues was already very fine. Furthermore, WO$_3$ and Sn were distributed in fine fraction, the size fraction of -10um occupied 62.01%, there were 52.08% of WO$_3$ and 60.39% of Sn. This results showed Sn was easier to recover than tungsten, the fine particle size was the most important influence factor in gravity seperation. In order to recover cassiterite effectively, the recovery of fine tin must be strengthened. Besides, there were 45.38% of WO$_3$ and 36.63% of Sn in the -37um+20um size fraction, this part of cassiterite was recoverable easily by centrifugal gravity separation process. As a result, the recovery of Sn metal from tungsten residues would be a big difficulty.

It was shown in figure 2 cassiterite and scheelite were irregular in shape, cassiterite particles were larger than scheelite particles. cassiterite and scheelite also were independent minerals and had been fully dissociated. This was beneficial to recovery of cassiterite using gravity separation process.

![Figure 1. The XRD of the tungsten residues sample.](image1)

![Figure 2. The PLM of the tungsten residues sample.](image2)
### Table 3. Elutriation characterization of the tungsten residues sample.

| Size fraction/μm | Occupancy/% | WO₃/% | Sn/% |
|------------------|-------------|-------|------|
|                  |             | Grade | Share | Grade | Share |
| -37+20           | 35.75       | 2.04  | 45.38 | 0.81  | 36.63 |
| -20+10           | 2.24        | 1.82  | 2.54  | 1.05  | 2.98  |
| -10              | 62.0        | 1.35  | 52.08 | 0.77  | 60.39 |
| Feed             | 100.00      | 1.61  | 100.00| 0.79  | 100.00|

![Diagram](image)

**Figure 3.** A centrifugal gravity separation flowsheet for the closed-circuit process of tungsten residue treatment.

### 2.4. Experimental approach

A 500 g of tungsten residue sample was transferred into a 5L stirring tank and pulped to 25wt.% using city water, the sample was well-diversified in the condition of 2000 rpm for 30min, after diversified, the centrifugal gravity separation procedure was carried out in a Slon 400M centrifugal separator machine. and then the pulp of tungsten residue was pumped into Slon 400M by a peristaltic pump. To find out the optimal conditions to recover cassiterite, a lot of experiments were made including: effect of rotating speed, dosage of washing water, pulp mass concentration on recovery of cassiterite. After centrifugal gravity separation, the tailings and the concentrates were filtered, dried, and weighted. Grade of Sn analysis was performed by ICP-AES, recovery of Sn was calculated by equation $\varepsilon = \gamma \beta \alpha$ Recovery $\gamma$ yield $\beta$ Grade of concentration $\alpha$ Grade of raw ore. A centrifugal gravity separation flowsheet for the closed-circuit process of tungsten residue treatment is shown in Figure 3.

Tests were carried out in an industrial yunxi type shaking table, with a rectangular shape of 4.50 m length and 1.50m width. There are two water supply points: feed water (near the feed box) and wash water. When tests begin, a 500 g of tungsten residue samp was pulped to 25wt.% using city water, which
was slowly transferred into feed box, the appropriate flow rate of feed water and wash water were adjusted. After shaking table gravity separation, the tailings, middlings and the concentrates were filtered, dried, and weighted. Grade of Sn analysis was performed by ICP-AES, recovery of Sn was calculated by equation $\varepsilon = \frac{\gamma \beta}{\alpha} \varepsilon$ Recovery $\gamma$ yield $\beta$ Grade of concentration $\alpha$ Grade of raw ore.

Tests were carried out in a laboratory suspended vibration concentrator, which was manufactured by China Yunnan deshang mining corp. it was an effective equipment for fine particle, when it worked, the table was suspended and meanwhile vibration. After suspended vibration concentrator gravity separation, the tailings and the concentrates were filtered, dried, and weighted. Grade of Sn analysis was performed by ICP-AES, recovery of Sn was calculated by equation $\varepsilon = \frac{\gamma \beta}{\alpha} \varepsilon$ Recovery $\gamma$ yield $\beta$ Grade of concentration $\alpha$ Grade of raw ore.

3. Results and Discussion

3.1. comparing with results of shaking table experiment and suspended vibration concentrator

Shaking table was a traditional gravity concentrator equipment, suspended vibration concentrator was a new film gravity equipment for fine-grains in the compounding force field.

Table 4. contrast test results of three gravity separation equipment

| Equipment                  | Condition                                      | Product    | Yield/ % | WO$_3$ Grade | WO$_3$ Recovery | Sn Grade | Sn Recovery |
|----------------------------|-----------------------------------------------|------------|----------|---------------|-----------------|----------|-------------|
| Centrifugal concentrator   | Rotate speed 750rpm washing water flow rate 2L/s pulp mass concentration 10% | concentrate | 6.69     | 2.82          | 19.28           | 5.58     | 80.53       |
|                            |                                               | tailing    | 93.31    | 1.56          | 80.72           | 0.18     | 19.47       |
|                            |                                               | feed       | 100.00   | 1.71          | 100.00           | 0.81     | 100.00      |
| suspended vibration        | Vibration frequency 20HZ, rotation period 4min, pulp mass concentration 15% | concentrate | 11.76    | 1.87          | 12.84           | 0.95     | 53.02       |
| concentrator               |                                               | tailing    | 13.35    | 1.76          | 13.71           | 0.46     | 13.64       |
|                            |                                               | feed       | 74.89    | 1.68          | 73.45           | 0.21     | 33.34       |
|                            |                                               | concentrate | 100.00   | 1.71          | 100.00           | 0.79     | 100.00      |
| Shaking table              | amplitude of table movement 16mm, frequency 320 cycles/min, inclination 2° | concentrate | 2.71     | 3.65          | 5.61            | 4.89     | 50.98       |
|                            |                                               | middling   | 6.52     | 2.54          | 9.40            | 0.67     | 10.87       |
|                            |                                               | tailing    | 90.77    | 1.65          | 84.99           | 0.26     | 38.14       |
|                            |                                               | feed       | 100.00   | 1.76          | 100.00           | 0.82     | 100.00      |

A series of gravity separation experiments were conducted to find out the optimal conditions to recovery Sn. The best test results were displayed for comparison by using three different gravity separation equipment. Table 4 showed obviously centrifugal concentrator was the most effective equipment, Sn grade of 5.58% and Sn recovery of 80.53% were obtained. Using suspended vibration concentrator and shaking table were gravity separator, obtaining Sn recovery of 53.02% and 50.98%. These results were lower than one obtained by centrifugal concentrator. At last, centrifugal concentrator was a kind of high-efficiency equipment to recovery Sn from tungsten residues.
3.2. Influence of roughing rotate speed on centrifugal separator

Rotate speed was a key condition in centrifugal gravity concentration, suitable speed was beneficial to the test results. As showed in Figure 4, When the rotate speed was 650rpm, the grade of Sn was only 4.36% and the recovery of Sn was 81.67%, while the grade and recovery of WO$_3$ were very low. When the rotate speed was increased up to 850rpm, the grade of Sn was increased to 5.17% and the recovery of Sn was increased to 86.73%. and then the grade and recovery of Sn was decreased with the increasing of rotational speed. Therefore, the roughing rotate speed of 650rpm was the optimal condition.

3.3. Influence of roughing pulp mass concentration on centrifugal separator

Low pulp mass concentration were good for separation of fine minerals and gangue in gravity separation, hence pulp mass concentration was set below 25%. The test results of pulp mass concentration were shown in Figure 5. The grade and recovery of Sn increased firstly and then decreased with the increase of pulp mass concentration. It was apparent that the grade of Sn was 5.22% and the recovery of Sn was 87.29%. When the pulp mass concentration was 15%, this is optimum condition for the test results.

3.4. Influence of roughing washing water flow rate on centrifugal separator

As showed in Figure 6, it is apparent that the grade and recovery of Sn first increased and then decreased with the washing water flow rate (up to 2L/S), reaching the maximal grade of 5.31% and recovery of 87.69%. with higher flow rate(up to 2.5L/S), the grade and recovery of Sn both decreased. So, washing water flow rate of 2L/S was the optimum condition.

3.5. Influence of concentrating rotate speed on centrifugal separator

In the concentrating process, rotate speed had a great influence on grade and recovery of Sn concentrate. It can be seen from the Figure 7 that optimum condition of concentrating rotate speed was 550rpm.

3.6. the closed-circuit process

Based on the optimal conditions: roughing rotate speed of 850rpm, pulp mass concentration of 15%, washing water flow rate of 2L/S and concentrating rotate speed of 550rpm. with one roughing-two concentration flowsheet to gain the Sn concentrate, as shown in Figure 3. Table 5 displayed the result of the closed-circuit process. Table 4 indicated the Sn was mainly recovered in the Sn concentrate with grade of 18.63% and recovery of 82.17%. the grade and recovery of WO$_3$ in Sn concentrate were very low. Figure 8 showed the phase of Sn in Sn concentrate was Cassiterite (SnO$_2$), it proved that Cassiterite was recovered using a centrifugal separator, but Scheelite was hardly recovered in tungsten residues.

| Product            | Yield/% | WO$_3$       | Sn           |
|--------------------|---------|--------------|--------------|
|                    |         | Grade/%      | Recovery/%   | Grade/%  | Recovery/% |
| Concentrate of Sn  | 3.75    | 2.16         | 4.85         | 18.63    | 82.17      |
| tailings           | 96.25   | 1.65         | 95.15        | 0.16     | 17.83      |
| total              | 100.00  | 1.67         | 100.00       | 0.85     | 100.00     |
Figure 4. The XRD of Sn concentrate the closed-circuit centrifugal gravity separation

Figure 5. Influence of roughing rotate speed on centrifugal separator

(roughing pulp mass concentration 15%, roughing washing water flow rate 2L/S)
Figure 6. Influence of roughing pulp mass concentration on centrifugal separator (roughing rotate speed 850rpm, roughing washing water flow rate 2L/S)

Figure 7. Influence of roughing washing water flow rate on centrifugal separator
(roughing rotate speed 850rpm, pulp mass concentration 15%)

Figure 8.
Figure 8. Influence of concentrating rotate speed on centrifugal separator

(roughing rotate speed 850rpm, pulp mass concentration 15%, roughing washing water flow rate 2L/S)

3.7. result of recovery of size fraction

Table 6. result of Sn recovery of size fraction

| Size fraction/μm | Tungsten residue/% | Tailing/% | Recovery of size fraction/% |
|------------------|--------------------|-----------|-----------------------------|
|                  | Yield | Grade | Yield | Grade |                     |
| -37+20           | 35.75 | 0.81  | 11.44 | 0.05  | 97.93                |
| -20+10           | 2.24  | 1.05  | 1.67  | 0.24  | 82.94                |
| -10              | 62.01 | 0.77  | 86.89 | 0.18  | 66.49                |

As was showed in Table 6, tailings of closed-circuit were separated to three size fractions by experiment of elutriation. Sn recovery of size fraction was calculated after closed-circuit experiment. Sn recovery of size fraction was 97.93% in size fraction of -37+20um, 82.94% in size fraction of -20+10um and 66.49% in size fraction of -10um. This was an excellent result.

4. Conclusion

In tungsten residues, Sn existed in mineral of Cassiterite and was distributed in fine fraction of -37um, fine particle seriously hampered the recovery of cassiterite, centrifugal concentration was an effective process to recover ultra-fine Cassiterite down to 10um. In centrifugal concentration work, obtaining Sn concentrate with Sn grade of 18.63% and Sn recovery of 82.17%. Compared with the original Sn grade of 0.79%, it was evidently a big progress. This process was easy to industrialize without any chemical agents in contrast to flotation. The study showed fine cassiterite was recovered successfully by Centrifugal Concentrator, it was proved cassiterite in size fraction of -37+20um can be recovered easily with Sn recovery of 97.93%, however Sn recovery in size fraction of -10um was down to 66.49%.
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