

Article

# Selective Recovery of Mushistonite from Gravity Tailings of Copper–Tin Minerals in Tajikistan

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**Abstract:** Tajikistan has abundant copper–tin resources. In this study, mineralogical analysis of copper–tin ores from the Mushiston deposit of Tajikistan indicates that tin mainly occurred in mushistonite, cassiterite, and stannite, while copper mainly occurred in mushistonite, malachite, azurite, and stannite. The total grades of tin (Sn) and copper (Cu) were 0.65% and 0.66%, respectively, and the dissemination size of copper–tin minerals ranged from 4  $\mu\text{m}$  to over 200  $\mu\text{m}$ . Coarse particles of copper–tin minerals were partially recovered by shaking table concentrators with a low recovery rate. Based on the mineralogical analysis, flotation recovery was used for the first time on the fine particles of copper–tin minerals, including mushistonite, from shaking table tailings. Single factor flotation experiments, open circuit flotation tests, and closed circuit flotation tests were performed to determine the optimized flotation conditions. Results indicated that benzohydroxamic acid ( $\text{C}_6\text{H}_5\text{CONHOH}$ ) and lead nitrate could effectively recover the mushistonite, cooperating with other depressants. The final concentrate contained 13.28% Sn, with a recovery rate of 61.56%, and 18.51% Cu, with a recovery rate of 86.52%. This method proved effective for the exploitation and use of this type of copper–tin resource in Tajikistan.

**Keywords:** mushistonite; copper–tin tailings; flotation; benzohydroxamic acid

## 1. Introduction

Tajikistan has abundant mineral resources. More than 400 different mineral deposits have been confirmed through systematic geological investigations. The main deposits of tin ores are found within the Zarafshan–Hisar geological and structural zone, in Central and South Pamir of Tajikistan. The tin resources total about 73 thousand tons [1]. The primary raw material deposit of tin in the Zarafshan–Hisar zone is found in Mushiston. This unique species of tin ore was originally discovered in the Penjikent region of Tajikistan by geologists in the 1960s, but was not named at that time [2,3]. Later, in 1984, the deposit was officially called mushistonite, after the name of the place where it was first discovered in Penjikent, Tajikistan [4–6].

Mushistonite is a malachite-green mineral with a dull luster, and recognized as a copper–tin-hydroxide mineral. Its general molecular formula is  $(\text{Cu,Fe,Zn})\text{Sn}(\text{OH})_6$ , with a framework of corner-linked  $\text{BB}'(\text{OH})_6$  octahedra [7]. Mushistonite has also been found in Sichuan, China and South Dakota, U.S., with slightly different chemical element content [5,8,9].

Mushistonite is a rare mineral, distributed in several areas around the world, and is not exploited on a large commercial scale currently. Few research reports have studied the exploitation and use of mushistonite [10,11]. In recent years, some companies and researchers have tentatively exploited the mine and established a small-scale minerals concentration factory. Coarse particle size fractions of cassiterite, chalcopyrite, and malachite were recovered by gravity separation using shaking tables.

The factory attempted to recover the fine particle size fraction of copper and tin minerals, including mushistonite, using the sulfidation flotation method, but failed.

Research studies have indicated that oxide minerals, such as cassiterite and scheelite, could establish hydroxylated surfaces in the flotation pulp. Benzohydroxamic acid (BHA) and lead ions react with the hydroxyl groups and co-absorb on the hydroxylated surface. As a result, cassiterite and scheelite could be selectively recovered by flotation, using BHA as a collector and lead nitrate as an activator [12–16]. According to the chemical composition and crystal structure of mushistonite mentioned above, hydroxyl groups are present within the mineral's own natural structure. The strength of the hydrogen bonds between hydroxyl groups is weak, and easily broken to form hydroxylated surfaces with grinding. We considered that hydroxyl groups on the surface of mushistonite could react with BHA and lead ions, and be selectively recovered by flotation. Based on this hypothesis, process mineralogy and the flotation of copper–tin tailings were studied to recover mushistonite. Experimental results confirmed that flotation of copper–tin tailings, using BHA as the collector, was feasible. It provided an economical and realistic method for the use of mushistonite.

## 2. Materials and Methods

### 2.1. Minerals and Reagents

The raw ore samples were collected from the crushing workshop of the Yukuang Panjakent copper–tin mine concentration plant in Northwest Tajikistan. The samples used for flotation experiments were obtained from the shaking table tailings of this plant (Figure 1). To ensure the representativeness of the samples, sampling work was performed during the normal producing period in the plant. The sampling work was sustained for 30 min each time, one time every half day, for three continuous days. All samples were fully mixed after being dried in the natural air environment.

The collector BHA was 98% pure, and other reagents used in this study, including lead nitrate as activator, sodium carbonate and hydrochloric acid as pH modifiers, carboxymethyl cellulose (CMC) and sodium fluorosilicate (SSF) as depressants, as well as terpeneol as a frother, were all analytical grade. All reagents were separately dissolved into deionized water to prepare the compound solutions used in each test.

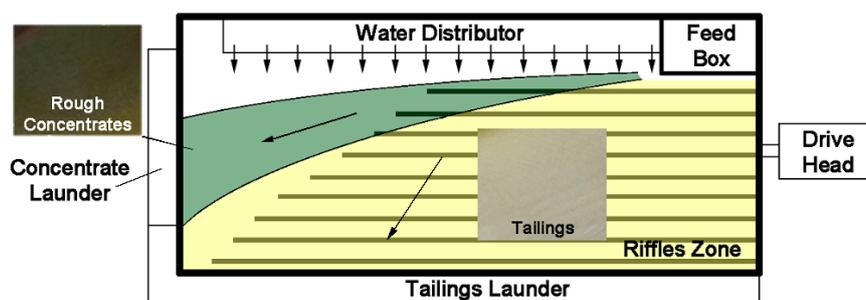


Figure 1. Samples used for flotation tests were obtained from the shaking table tailings.

### 2.2. Analysis Methods

Mineral identifications of the raw ore were performed using X-ray diffraction, transmission polarized optical microscopy, and scanning electron microscopy (SEM) with energy dispersive analytical attachment. Quantitative mineralogical compositions could also be calculated, but using special methods [17,18]. Chemical compositions of raw ore and flotation ore samples were detected with X-ray fluorescence spectrometry and chemical analysis, which was sufficient to evaluate the result of flotation.

### 2.3. Flotation Experiments

Flotation experiments on the gravity process tailings were performed in a series of XFG type flotation machines (Jilin Prospecting Machinery Factory, Changchun, China). Single factor experiments were performed in a 3.0 L flotation cell, while open circuit and closed circuit experiments were conducted in the 3.0 L, 1.0 L, 500 mL, 250 mL, and 100 mL flotation cells. A 1000 g dosage of ore sample was treated for each experiment. Flotation parameters were controlled at a pulp temperature of 293 K and a stirring speed of 1910 r/min. After each flotation experiment, the products were collected, filtered, dried, weighed, and detected by Axios X-ray fluorescence spectrometry (PANalytical B.V., Almelo, The Netherlands), after which the recovery rates of Sn and Cu were calculated.

## 3. Results and Discussion

### 3.1. Mineralogical Analysis

Mineral composition, chemical formula, specific gravity (a range of values found in the literature), and dissemination size of the raw ore are listed in Table 1. Valuable minerals in the raw ore included mushistonite, cassiterite, stannite, malachite, and azurite. Gangue minerals included dolomite, quartz, calcite, talcum, limonite, sericite, and other impurities.

**Table 1.** Mineral composition, chemical formula, specific gravity, and dissemination size of the raw ore.

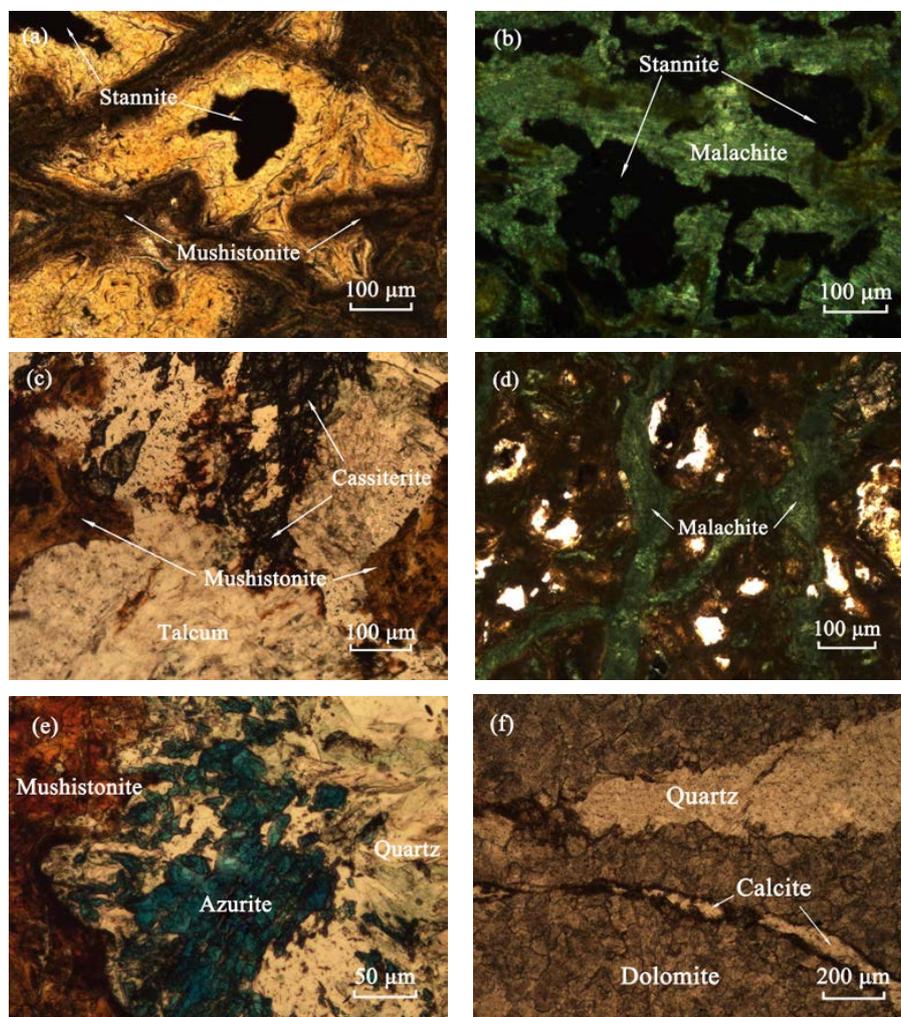
Mineral Composition	Chemical Formula	Specific Gravity	Dissemination Size (mm)
Mushistonite	(Cu,Fe,Zn)Sn(OH) <sub>6</sub>	4.0–4.4	0.01–0.5
Cassiterite	SnO <sub>2</sub>	6.8–7.0	0.014–0.2
Stannite	Cu <sub>2</sub> FeSnS <sub>4</sub>	4.3–4.5	0.004–0.6
Malachite	Cu <sub>2</sub> [CO <sub>3</sub> ](OH) <sub>2</sub>	3.9–4.0	0.004–0.8
Azurite	Cu <sub>3</sub> [CO <sub>3</sub> ] <sub>2</sub> (OH) <sub>2</sub>	3.7–3.9	0.01–0.3
Dolomite	CaMg(CO <sub>3</sub> ) <sub>2</sub>	2.8–2.9	0.06–0.25
Quartz	SiO <sub>2</sub>	2.2–2.6	>0.004
Calcite	CaCO <sub>3</sub>	2.7	>0.004
Talcum	Mg <sub>3</sub> [Si <sub>4</sub> O <sub>10</sub> ](OH) <sub>2</sub>	2.6–2.8	0.004–0.2
Limonite	Fe <sub>2</sub> O <sub>3</sub> ·nH <sub>2</sub> O	3.3–4.0	0.004–0.2
Sericite	K{Al <sub>2</sub> [AlSi <sub>3</sub> O <sub>10</sub> ](OH) <sub>2</sub> }	2.6–2.7	0.004–0.1
Others	-	-	-

Tin was distributed among three different minerals: mushistonite, cassiterite, and stannite. The total grade of Sn was 0.65%. As observed in transmission polarized optical microscopy DM4 (Leica Microsystems Inc., Wetzlar, Germany), mushistonite was the result of stannite alteration, and presented with a yellowish-brown color and a greasy luster. It had a homogeneous colloidal distribution and a dense disseminated structure along the crevice of the stannite, mixing with malachite, azurite, and cassiterite, as shown in Figure 2a,c,e. Stannite presented with a black color and a metallic luster, and was distributed in mushistonite and malachite, as illustrated in Figure 2a,b. Cassiterite presented with a brownish-black to light brown color, and had a greasy luster with an aggregate or scattered disseminated distribution, as exhibited in Figure 2c.

Copper was mainly distributed among four different minerals: malachite, azurite, mushistonite, and stannite. The total grade of Cu was 0.66%. Malachite presented with an emerald green color and a glassy luster. It had an inhomogeneous, disseminated distribution when confounding with stannite, or an aggregate, thin vein-type distribution along the crevice of quartz, as shown in Figure 2b,d. Azurite presented with an azure color and a glassy luster, and had an aggregate distribution when confounding with mushistonite and quartz, as exhibited in Figure 2e.

The main gangue minerals were dolomite, quartz, and calcite. The gangue mineral with the highest content in the raw ore was dolomite, with a mass content of 61.20%. Dolomite presented with a light gray color and a glassy luster, and its crystal was turbid. It had a hypidiomorphic granular texture, and the granules were closely inlaid with each other, as shown in Figure 2f. Quartz presented

with a white color and a glassy luster. It existed as veins, including granules of varying sizes and inhomogeneous distributions, as shown in Figure 2e,f. Calcite also presented with a white color and a glassy luster. It had an allotriomorphic granular texture and an aggregate vein-type distribution along the crevice of the raw ore, as exhibited in Figure 2f.



**Figure 2.** Optical microscope images of the raw ore, dissemination characteristic of main minerals.

Mineralogical analysis of the raw ore indicated that the dissemination size of the copper–tin minerals ranged widely, from 4  $\mu\text{m}$  to more than 200  $\mu\text{m}$ . Coarse particles of copper–tin minerals could be recovered using the gravity concentration process. Cassiterite, malachite, and azurite were partially recovered by shaking table concentrators in the producing plant. The recovery rate of Sn through this process was around 10.91%, and that of Cu was 13.89%, which are both low overall recovery rates. Therefore, a new method to improve the recovery rates of Sn and Cu in the shaking table tailings was required.

Yield, grade, and distribution of Cu and Sn in each particle size fraction of the shaking table tailings are listed in Table 2. As the particle size decreased, the grades of both Cu and Sn increased. Although the yield of the +75  $\mu\text{m}$  fraction was over 40%, both the grade and the distribution of Cu and Sn were low in this fraction, which indicated that the copper–tin minerals in this coarse fraction mostly amassed to the shaking table concentrates. Similarly, although the grades of Cu and Sn in the –18  $\mu\text{m}$  fraction were higher than in other fractions, the yield of this fraction was only 4.41%, and the distribution of Cu and Sn in this fraction were both less than 8%. Hence, over 88% of tin minerals

and over 86% of copper minerals in the shaking table tailings were distributed in the size fractions of 18  $\mu\text{m}$  to 75  $\mu\text{m}$ , for which the shaking table concentrator was ineffective.

**Table 2.** Grade and distribution of Cu and Sn in each particle size fraction of shaking table tailings.

Size Fraction ( $\mu\text{m}$ )	Yield (%)	Sn		Cu	
		Grade (%)	Distribution (%)	Grade (%)	Distribution (%)
+75	40.26	0.054	3.75	0.081	5.76
−75 + 38	24.37	0.89	37.41	0.86	37.04
−38 + 18	30.96	0.96	51.27	0.91	49.79
−18 + 10	3.66	0.99	6.25	0.95	6.14
−10	0.75	1.02	1.32	0.96	1.27
Total	100	0.58	100	0.57	100

The content percentage of the elements in the shaking table tailings are listed in Table 3. The content of Sn and Cu were 0.58% and 0.57%, respectively. Zn was only distributed in mushistonite instead of in an independent zinc mineral, and could not be separately recovered.

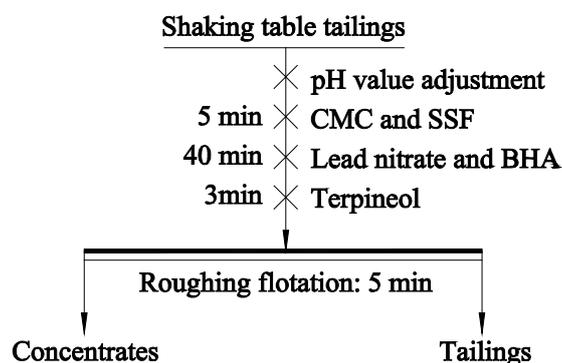
**Table 3.** Percentage contents of main elements in the shaking table tailings.

Component	Sn	Cu	Zn	CaO	SiO <sub>2</sub>	MgO	Al <sub>2</sub> O <sub>3</sub>	FeO	K <sub>2</sub> O	S
Content (%)	0.58	0.57	0.48	27.76	22.59	12.08	3.84	1.58	0.83	0.12

### 3.2. Flotation Experiments of Copper–Tin Minerals

Based on mineralogical analysis, the valuable minerals being recovered were distributed in the 18–75  $\mu\text{m}$  size fractions. The liberation degree of tin- and copper-bearing minerals in this fraction was high, and no further grinding was necessary.

The effects of each reagent dosage on copper–tin minerals flotation were investigated following the process shown in Figure 3. The pulp temperature was controlled at 293 K. CMC and SSF were added into the pulp simultaneously and mixed for 5 min. Lead nitrate and BHA were added into the pulp simultaneously and mixed for 40 min. The terpeneol dosage was moderated, according to the foam volume, and mixed for 3 min. Air filling and flotation time was 5 min. The grade and recovery of Sn and Cu in the concentrates and tailings were detected and calculated.

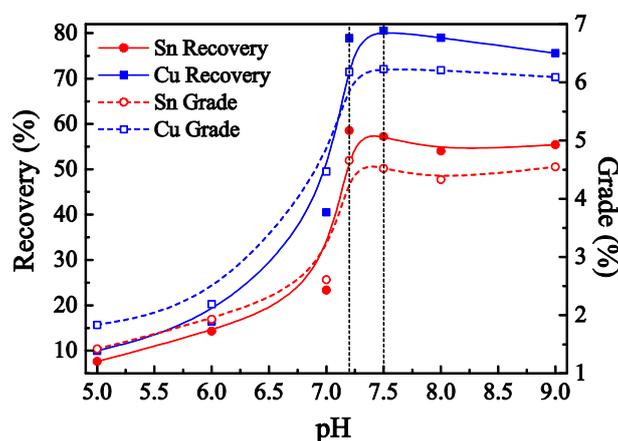


**Figure 3.** Rough flotation flowchart of the shaking table tailings (BHA—Benzohydroxamic acid; CMC—carboxymethyl cellulose; SSF—sodium fluorosilicate).

#### 3.2.1. Effect of Pulp pH Value

Sodium carbonate and hydrochloric acid were used to adjust the pulp pH value [19]. The flotation recovery and grade of Sn and Cu, as a function of pulp pH value from 5.0 to 9.0, are exhibited in

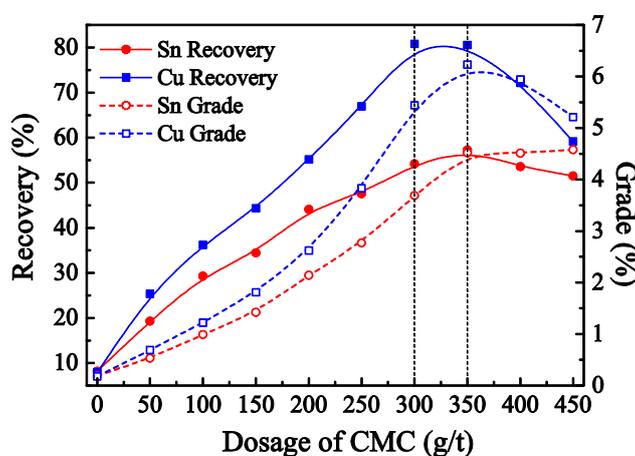
Figure 4. As the pulp pH value was adjusted to approximately 7.2, the recovery and grade of Sn both reached their peak values, with a recovery of 58.53% and a grade of 4.66%. At the same pH value, the recovery and grade of Cu were 78.92% and 6.18%, respectively. As the pulp pH value increased from 7.2 to 7.5, the recovery and grade of Cu both reached their peak values, with a recovery of 80.58% and a grade of 6.23%. The recovery and grade of Sn slightly decreased, but the recovery remained at 57.22% and the grade at 4.52%. Experiments on the pulp pH value indicated that the optimum pH value range for both elements was 7.2–7.5.



**Figure 4.** Flotation recovery and grade of Sn and Cu as a function of pulp pH value (carboxymethyl cellulose (CMC) 350 g/t; sodium fluorosilicate (SSF) 250 g/t; lead nitrate 200 g/t; Benzohydroxamic acid (BHA) 2000 g/t; Terpeneol 25 g/t).

### 3.2.2. Effects of Depressant CMC

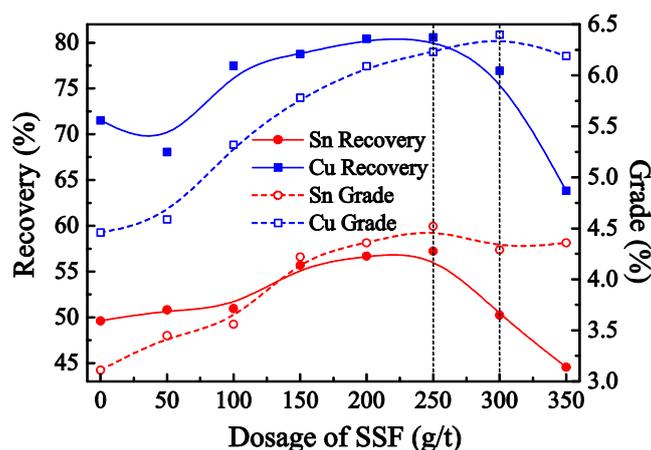
CMC was reported to be an effective depressant for carbonate minerals, including dolomite and calcite [20–22]. The flotation recovery and grade of Sn and Cu, as a function of dosage of CMC from 0 to 450 g/t, are exhibited in Figure 5. When the CMC dosage was 300 g/t, the recovery of Cu reached its peak value of 80.81%. As the dosage of CMC increased to 350 g/t, the grade and recovery of Sn and the grade of Cu reached high values, at 4.52%, 57.22% and 6.23%, respectively. The recovery of Cu was still 80.58%, with no significant variation as the dosage of CMC increased from 300 g/t to 350 g/t. Experiments on the effects of the depressant CMC indicated that the optimum dosage of CMC was 350 g/t.



**Figure 5.** Flotation recovery and grade of Sn and Cu as a function of dosage of CMC (pH = 7.2–7.5; SSF 250 g/t; lead nitrate 200 g/t; BHA 2000 g/t; terpeneol 25 g/t).

### 3.2.3. Effects of Depressant SSF

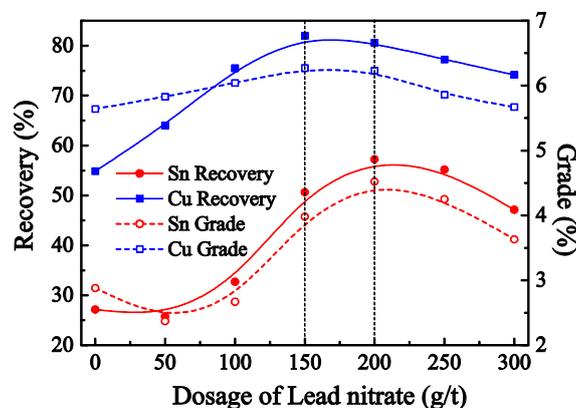
SSF was applied as an effective depressant for silicon-containing minerals (including quartz) in flotation [23–25]. The flotation recovery and grade of Sn and Cu as a function of SSF dosage from 0 to 350 g/t are shown in Figure 6. When the dosage of SSF was 250 g/t, the recovery and grade of Sn, as well as the recovery of Cu, all reached their peak values of 57.22%, 4.52%, and 80.58%, respectively. As the dosage of SSF increased from 250 g/t to 300 g/t, the grade of Cu reached its peak value of 6.40%, an inconspicuous increase, but the recovery and grade of Sn and the recovery of Cu all sharply decreased. Experiments on the effects of the depressant SSF indicated that the optimum dosage of SSF was 250 g/t.



**Figure 6.** Flotation recovery and grade of Sn and Cu as a function of dosage of SSF (pH = 7.2–7.5; CMC 350 g/t; lead nitrate 200 g/t; BHA 2000 g/t; terpeneol 25 g/t).

### 3.2.4. Effects of Activator Lead Nitrate

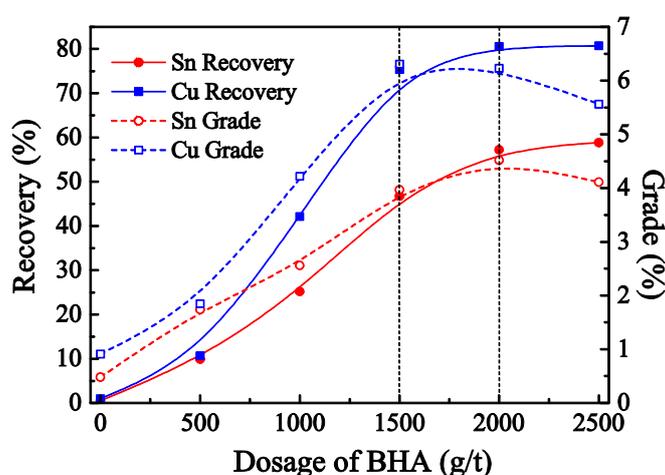
Lead nitrate was applied as the most common and effective activator for tin or tungsten oxide minerals (including cassiterite and scheelite) in flotation [26–28]. The flotation recovery and grade of Sn and Cu, as a function of the dosage of lead nitrate from 0 to 300 g/t, are shown in Figure 7. When the dosage of lead nitrate was 150 g/t, the recovery and grade of Cu both reached their peak values of 82.00% and 6.27%, respectively. As the dosage of lead nitrate increased from 150 g/t to 200 g/t, the recovery and grade of Sn both reached their peak values of 57.22% and 4.52%, respectively. The recovery and grade of Cu slightly decreased, but the variation was not significant. Experiments on the effects of the activator lead nitrate indicated that the optimum dosage of lead nitrate was 200 g/t.



**Figure 7.** Flotation recovery and grade of Sn and Cu as a function of the dosage of lead nitrate (pH = 7.2–7.5; CMC 350 g/t; SSF 250 g/t; BHA 2000 g/t; terpeneol 25 g/t).

### 3.2.5. Effects of Collector BHA

BHA has been used as an effective collector for tin or tungsten oxide minerals, including cassiterite and scheelite, and has begun to be used in the cassiterite and scheelite flotation industries [29–31]. The flotation recovery and grade of Sn and Cu, as a function of the dosage of BHA from 0 to 2500 g/t, is shown in Figure 8. When the dosage of BHA was 1500 g/t, the grade of Cu reached its peak value of 6.31%. As the dosage of BHA increased from 1500 g/t to 2000 g/t, the grade of Sn reached its peak value of 4.52%, and the grade of Cu decreased slightly, although not significantly. The recovery of both Sn and Cu had an increasing trend as the dosage of BHA increased, and reached high values, 57.22% and 80.58%, respectively, at the dosage of 2000 g/t. The dosage of BHA increased continuously from 2000 g/t to 2500 g/t; the recovery of Sn and Cu exhibited no significant variation, but the grade of Cu and Sn dropped obviously. Experiments on the effects of BHA indicated that the optimum dosage of BHA was 2000 g/t.



**Figure 8.** Flotation recovery and grade of Sn and Cu as a function of the dosage of BHA (pH = 7.2–7.5; CMC 350 g/t; SSF 250 g/t; lead nitrate 200 g/t; terpineol 25 g/t).

### 3.2.6. Closed Circuit Flotation Tests

The bench-scale closed circuit flotation tests of the shaking table tailings from Tajikistan were performed based on single factor experiments and open circuit tests, with optimized flotation conditions. After further adjustments and optimizing the flotation conditions, the closed circuit flotation flowchart of the shaking table tailings was established following the process shown in Figure 9. By adopting single-stage roughing, two-stage scavenging, and four-stage cleaning flotation, the results were obtained and calculated as shown in Table 4. The concentrate was a copper–tin mixture product that contained 13.28% Sn, with a recovery rate of 61.56%, and a Cu content of 18.51%, with a recovery rate of 86.52%. Experimental results confirmed that selective flotation of copper–tin minerals, including mushistonite, from the shaking table tailings in Tajikistan, using BHA as the collector and lead nitrate as the activator, in cooperation with other depressants, is feasible. These results provided a basis for the exploitation and use of this type of mineral in Tajikistan.

**Table 4.** Results of the bench-scale closed circuit flotation experiments of shaking table tailings.

Product	Yield (%)	Sn		Cu	
		Grade (%)	Distribution (%)	Grade (%)	Distribution (%)
Concentrates	2.71	13.28	61.57	18.51	86.52
Final Tailings	97.29	0.23	38.43	0.08	13.48
Feed	100	0.58	100	0.57	100

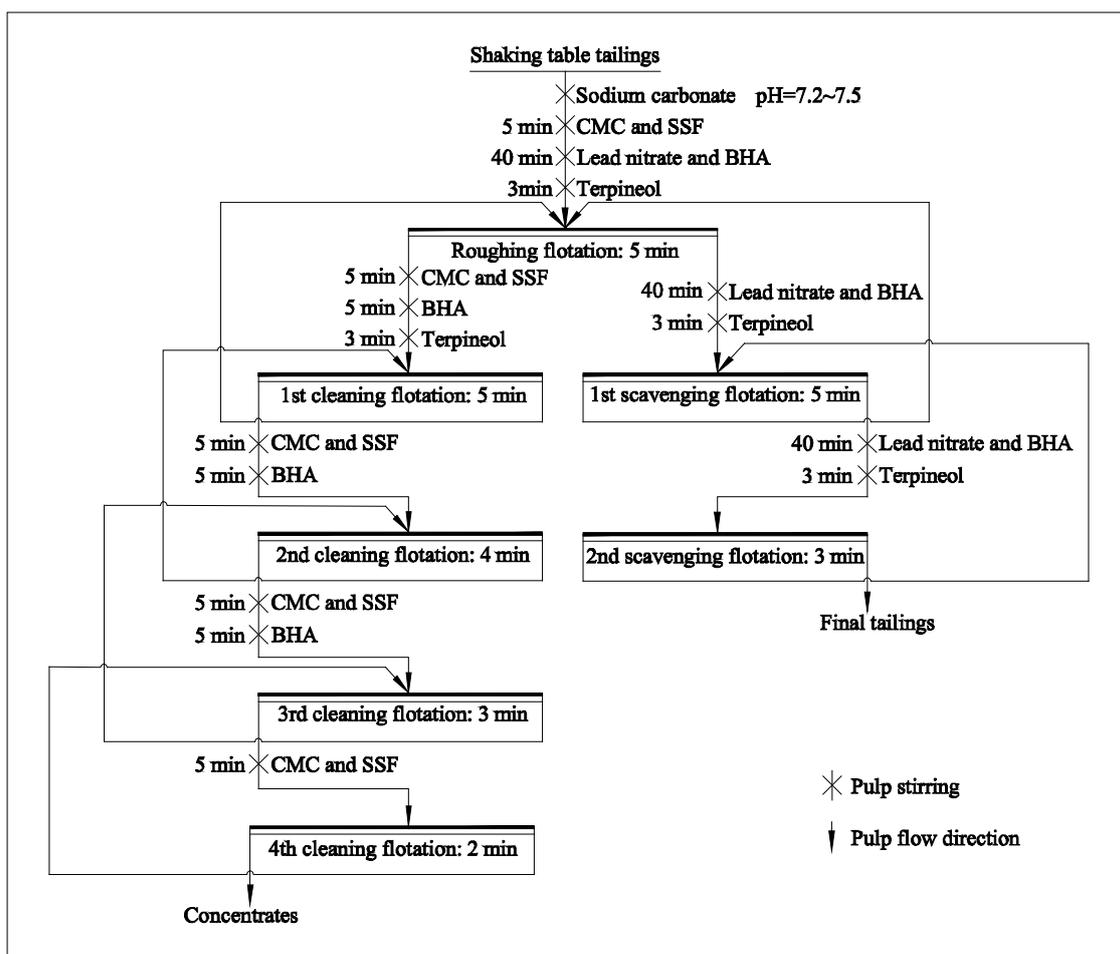


Figure 9. The bench-scale closed circuit flotation flowchart of the shaking table tailings.

#### 4. Conclusions

Mineralogical analysis of the copper–tin minerals from the Mushiston deposit in Tajikistan indicated that tin mainly occurred in mushistonite, cassiterite, and stannite, while copper mainly occurred in mushistonite, malachite, azurite and stannite. The total grade of Sn was 0.65%, and that of Cu was 0.66%. The main gangue minerals were dolomite, quartz, and calcite. Dissemination size of the copper–tin minerals ranged widely, from 4  $\mu\text{m}$  to more than 200  $\mu\text{m}$ .

Copper–tin minerals in coarse particles were partially recovered by shaking table concentrators in a gravity concentration process, but with an overall low recovery rate. The valuable minerals to be recovered were mainly distributed in the 18  $\mu\text{m}$  to 75  $\mu\text{m}$  size fractions of the shaking table tailings. Flotation was applied in this study, for the first time, to selectively recover the copper–tin minerals of shaking table tailings in Tajikistan. Results of the bench-scale closed circuit flotation tests indicated that selective flotation of copper–tin minerals, including mushistonite, using BHA as the collector and lead nitrate as the activator, in cooperation with other depressants, is feasible. The resulting concentrate contained 13.28% Sn with a recovery of 61.56%, and the concentrate contained 18.51% of Cu with a recovery of 86.52%.

Flotation of copper–tin minerals from the shaking table tailings in Tajikistan is an effective method for the exploitation and use of this type of resource. Separation of Cu and Sn in the mushistonite will be the next step of research, based on the work completed by Yang et al. [32].

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**Author Contributions:** Yuehua Hu and Wei Sun provided the research ideas and guidance; Lei Sun designed and performed the experiments, and wrote the paper as well; Zhiyong Gao revised the manuscripts; Mengjie Tian contributed the experiment performances.

**Conflicts of Interest:** The authors declare no conflict of interest.

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