

## Article

# Simultaneous Recovery of Niobium and Sulfur from Carbonate Niobite Ore with Flotation

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**Abstract:** Exploring new ways to acquire niobium resources is essential to resolve niobium supply risks, due to the fact that, at present, 99% of niobium is controlled by only two countries. In the present work, a flotation technique was applied to separate niobium from low-grade niobite ore. To maximize the utilization of the original ore resources, pre-flotation was conducted to recover sulfur and eliminate the adverse effects of sulfide on niobite flotation. The obtained sulfur grade and recovery were 33.74% and 92.04%, respectively, and its concentration ratio was 40x. As for the niobite flotation, a closed-circuit experiment with one rougher flotation, three cleaner flotations, and two scavenger flotations was carried out to achieve the maximum niobite recovery. To further improve the niobite recovery, a leaching process with diluted HCl was employed; the final obtained Nb<sub>2</sub>O<sub>5</sub> grade and recovery were 30.19% and 65.04%, respectively, and the concentration ratio reached 242x. Moreover, the economic evaluation implies that the flotation process can attract great positive interest.

**Keywords:** niobite; flotation; collector; grade; recovery



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## 1. Introduction

Niobium, a rare metal with high melting and boiling points, is widely used in stainless steels and alloys, along with the nuclear and superconductor industries. Niobite is a very important niobium-containing industrial mineral. At present, about 90% and 9% of worldwide ferroniobium production is from Brazil and Canada, respectively [1]. Although the current production rate is enough to meet the globally increasing demand, there are predictable niobium supply risks resulting from the highly concentrated ferroniobium production regions [2]. The many niobite resources in the world can diversify global ferroniobium production. However, numerous deposits are quite refractory, leading to uneconomical development through presently used routes of mineral processing [3–5].

Froth flotation, as one effective technique used for the selective separation of valuable minerals from their associated gangue minerals, would be an efficient method to obtain niobium. Pyrochlore and niobite are the main commercial niobium-containing minerals, which are usually derived from various carbonatite deposits. These minerals can be recovered via multistage separation processes including magnetic separation, or flotation of sulfides and carbonates, followed by pyrochlore and niobite flotation with various collectors and other modifiers [6–8]. It is worth noting that the collector plays an essential role in the flotation process; numerous collectors are developed to obtain a higher mineral recovery and grade. Gibson studied the flotation of pyrochlore from carbonatite tailings with benzohydroxamic acid as a collector; a 1.54% Nb<sub>2</sub>O<sub>5</sub> grade and a 93% Nb<sub>2</sub>O<sub>5</sub> recovery were achieved [9]. Furthermore, Gibson studied the flotation and mechanism of pyrochlore

in silicate gangues with amine as a cationic collector [10]. Liu reported that the octyl hydroxamic acid and sodium oleate could separately be used as collectors to recover pyrochlore as a function of particle size [11]. Chen et al., found that a niobite recovery ranging from 82% to 91% could be obtained when octyl diphosphonic acid was used as a collector [12]. Ren et al., studied the collection performance of salicylhydroxamic acid and methylenediphosphonic acid for niobite flotation, and two niobite flotation rates of 17% and 19% were observed [13]. In addition, He et al., found that a combined collector of salicylhydroxamic acid and ammonium dibutyl dithiophosphate could help to improve the tantalum niobium flotation [14]. Recently, benzyl arsenic acid has been proven as an efficient reagent in flotation for collecting and recovering various metallic minerals, such as cassiterite, tungsten, rutile, tantalum, niobium, etc. [15,16]. However, there are few reports focusing on its flotation superiority on niobite as an effective collector [17]. It is important and meaningful to carry out studies on niobite flotation with benzyl arsenic acid to prevent risk to the niobium supply.

In this study, the upgrade potential of a carbonatite niobite ore by flotation with benzyl arsenic acid as a collector was investigated. A pre-flotation was conducted to recover sulfur from the ore in order to eliminate its effect on the recovery and grade of niobite. To attain the highest possible recovery and grade of niobite, the flotation experiments were carried out as detailed, as a function of the activator, depressor, and collector. Furthermore, a closed-circuit experiment and an acid treatment process were employed to further improve the recovery and grade of niobite. The results provide a new insight for developing flotation reagents for niobium.

## 2. Materials and Methods

The carbonatite niobite ore was obtained from a niobium rare-earth deposit in Hubei Province. The mineral was firstly crushed into particles, then ground to a smaller size and, finally, sieved to the required size fraction. The sample with 90% of the size fraction under 0.074 mm was used for flotation. The results of X-ray diffraction patterns displayed in Figure 1 indicate that the carbonatite niobite ore mainly consisted of calcite, muscovite, biotite, albite, dolomite, quartz, fluorapatite, and pyrite. There was no obvious peak of the niobite observed, because of its rather low grade, which is consistent with the X-ray fluorescence analysis of niobite in Table 1. As shown in Table 1, the niobite contained only 0.533% rare earth oxide and 0.125% Nb<sub>2</sub>O<sub>5</sub>. In addition, the niobite contained a lot of CaO and small amounts of SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, MgO, P<sub>2</sub>O<sub>5</sub>, and Al<sub>2</sub>O<sub>3</sub>. There was a large loss of 31.765%, which may have resulted from the decomposition of carbonates. The carboxymethyl cellulose (CMC), MB xanthic acid sodium (MB), 2# oil, Pb(NO)<sub>3</sub>, benzohydroxamic acid (BHA), and styryl phosphonic acid (SPA) were purchased from Sinopharm Group Co., Ltd. (Shanghai, China). The collector was prepared in the lab based on benzyl arsenic acid, and termed as DB-11. All of the experiments were conducted using tap water in the lab.

**Table 1.** XRF analysis of the carbonate niobite ore.

Oxides	REO	Nb <sub>2</sub> O <sub>5</sub>	SiO <sub>2</sub>	CaO	Al <sub>2</sub> O <sub>3</sub>	MgO	Na <sub>2</sub> O	K <sub>2</sub> O
Content (%)	0.533	0.125	4.95	48.85	1.7	2.54	0.11	1.06
Oxides	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	S	MnO	Fe <sub>2</sub> O <sub>3</sub>	Lost	Organic carbon	
Content (%)	0.23	2.13	0.85	0.95	4.12	31.765	0.62	

The flotation experiments were carried out on an XFG-II flotation machine (8 L flotation cell, 2000 rpm impeller speed). The flotation sheet is presented in Figure 2. Firstly, 3000 g of niobite ore was added to the flotation cell and then stirred for 2 min. Then, the CMC depressor, MB collector and 2# oil frother were successively added to the slurry with intervals of 2 min. Finally, the froth products were collected as the sulfur concentrate, and

the tailings were collected for niobite flotation with the  $Pb(NO_3)_3$  activator, CMC depressor, DB-11 collector, and 2# oil frother.

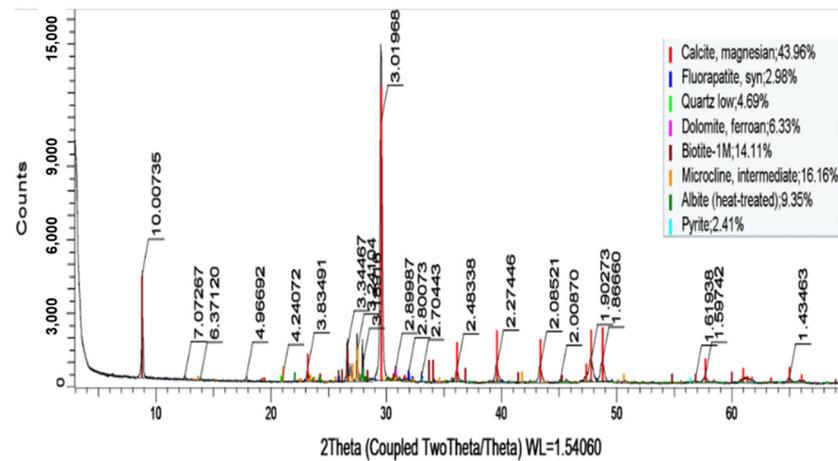


Figure 1. XRD patterns of the carbonate niobite ore.

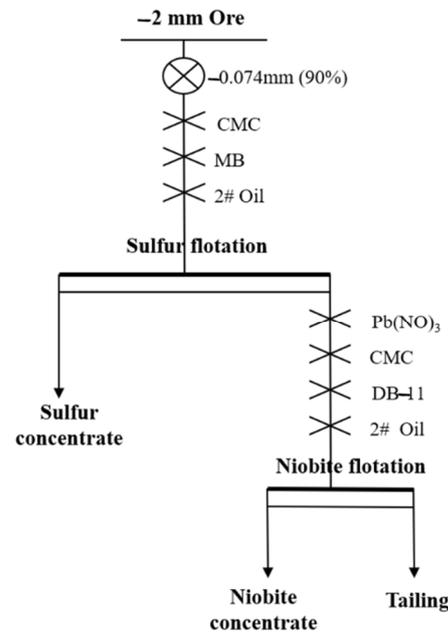


Figure 2. The flotation sheet of the general condition of the niobite ore.

### 3. Results

#### 3.1. Recovery of Sulfur

##### 3.1.1. Effect of CMC Dosage on Sulfur Flotation

Due to the ore containing a certain amount of pyrite, it is better to separate the pyrite before niobite flotation so as to avoid the adverse effect of pyrite on niobium recovery. At the same time, the separated pyrite can bring good recovery of sulfur. To obtain a good separation efficiency, the effect of the CMC depressor dosage on sulfur grade and recovery in the sulfur concentrate and  $Nb_2O_5$  grade and recovery in the tailings were recorded, as shown in Figure 3. As can be seen in Figure 3a, the sulfur grade increased gradually with increasing CMC dosage, and almost reached a balance after 150 g/t MB, reaching 25%. As for the sulfur recovery, it first increased and then slightly decreased when the CMC dosage was above 150 g/t. The higher sulfur grade and recovery means that more pyrite is separated from the niobite ore, which can result in the improvement of the  $Nb_2O_5$  grade and recovery in the tailings. As shown in Figure 3b, it can be seen that the  $Nb_2O_5$  grade in the tailings is proportional to CMC dosage, whereas the recovery remains stable

without any significant change, further demonstrating that the removal of sulfur in advance would increase the Nb<sub>2</sub>O<sub>5</sub> contents in the tailings, which would be better for the effective recovery of valuable metals. Based on Figure 3a,b, the 150 g/t CMC is more acceptable in the sulfur flotation.

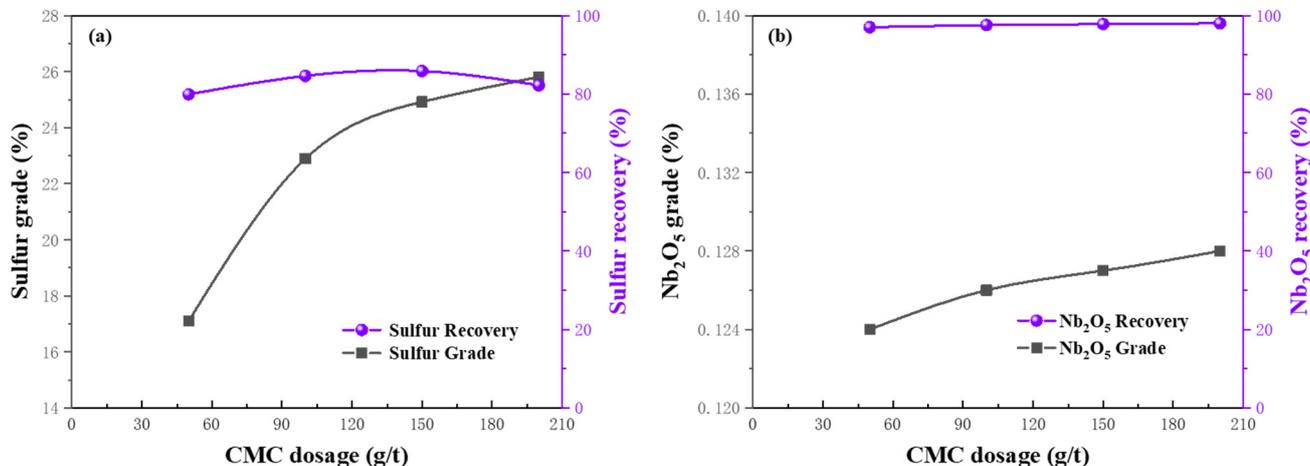


Figure 3. The effect of CMC dosage on (a) sulfur and (b) Nb<sub>2</sub>O<sub>5</sub> grade and recovery.

### 3.1.2. Effect of MB Dosage on Sulfur Flotation

Figure 4 shows the impact of MB collector dosage on the grade and recovery of sulfur in concentrate and Nb<sub>2</sub>O<sub>5</sub> in tailings. It can be seen in Figure 4a that the sulfur grade grows very quickly when the MB dosage ranges from 200 g/t to 300 g/t, and then reduces slowly. The sulfur grade at 300 g/t is 27.08%, which enables sulfur to reach a high concentration ratio of 32x. On the other hand, the sulfur recovery experiences a marginal increase and reaches its biggest value when the MB dosage is 300 g/t, which is consistent with the results for sulfur grade. As for the Nb<sub>2</sub>O<sub>5</sub> grade and recovery in the tailings, it can be seen (Figure 4b) that the tendency is similar to that in Figure 3b, where the recovery maintains a high value around 98% without any change. The Nb<sub>2</sub>O<sub>5</sub> grade decreased to 0.127% under the optimal MB dosage, which is a little lower than that in Figure 3b (0.128%), demonstrating that regulating the MB dosage could effectively improve the recovery of sulfur and maintain the valuable Nb<sub>2</sub>O<sub>5</sub> contents in the tailings for further treatment. Here, an MB dosage of 300 g/t was chosen for the following experiments.

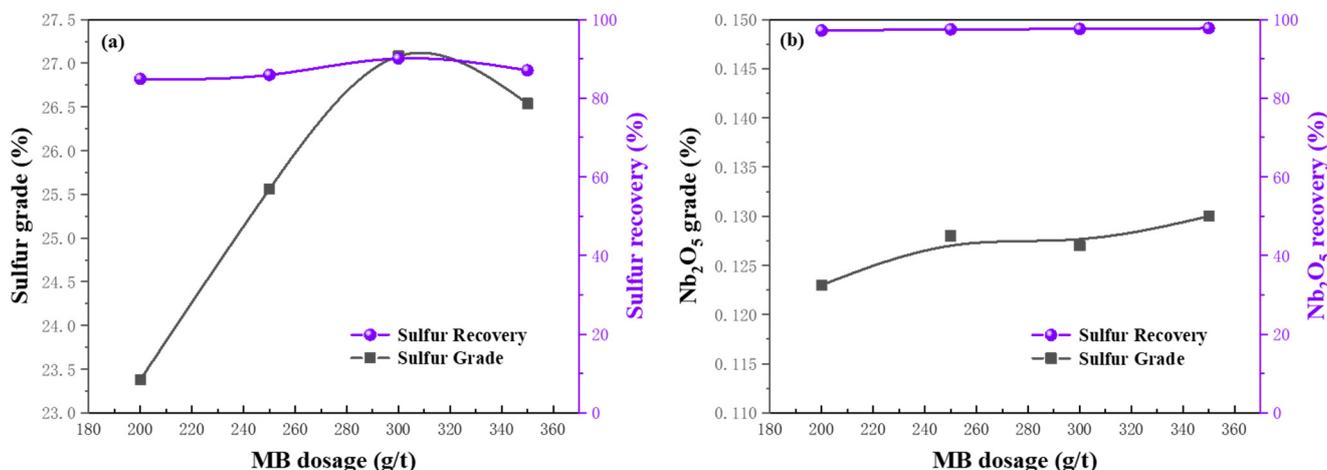
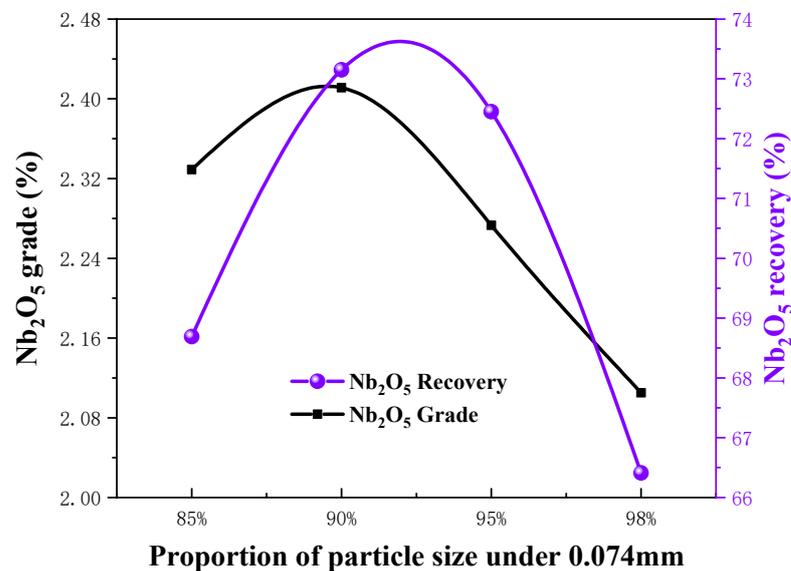


Figure 4. The effect of MB dosage on (a) sulfur and (b) Nb<sub>2</sub>O<sub>5</sub> grade and recovery.

### 3.2. Recovery of Niobite

#### 3.2.1. Effect of Grinding Fineness on Niobite Flotation

To obtain a good grade and recovery of niobite, a suitable niobite particle size—but not excessively small fine mud—is essential for the flotation process. Figure 5 displays the effect of the proportion of particle size under 0.074 mm on niobite flotation. It can be seen that both the  $\text{Nb}_2\text{O}_5$  grade and  $\text{Nb}_2\text{O}_5$  recovery achieve their best performance at 90% proportion of particle size under 0.074 mm. The results indicate that the niobite ore is completely liberated under this condition. Moreover, the  $\text{Nb}_2\text{O}_5$  grade and recovery decrease sharply when the proportion is lower or higher than 90%; this is mainly due to the fact that a finer grinding would generate more slimes and then deteriorate the flotation performance through entrainment. The ore with many incompletely liberated particles would also affect the interaction between the collector and the particles, thereby leading to a low grade and recovery. As a result, 90% proportion of particle size under 0.074 mm is the best choice of grinding size for niobite flotation.



**Figure 5.** The effect of particle size under 0.074 mm on  $\text{Nb}_2\text{O}_5$  grade and recovery.

#### 3.2.2. Effect of DB-11 Dosage on Niobite Flotation

The collector plays a crucial role in flotation, directly deciding whether the niobite can be well recovered at high quality. To further optimize the  $\text{Nb}_2\text{O}_5$  grade and recovery, the influence of DB-11 dosage on flotation is illustrated in Figure 6. With increasing DB-11 dosage, the  $\text{Nb}_2\text{O}_5$  grade shows a rapid reduction after 700 g/t, and the  $\text{Nb}_2\text{O}_5$  recovery sustains a small increase, with a pause between 700 and 800 g/t. Considering the  $\text{Nb}_2\text{O}_5$  grade of 3.95% and  $\text{Nb}_2\text{O}_5$  recovery of 68%, the results suggest that a DB-11 dosage of 700 g/t is the best choice in the flotation.

#### 3.2.3. Effect of $\text{Pb}(\text{NO}_3)_2$ Dosage on Niobite Flotation

In order to improve the flotation efficiency of niobite, a  $\text{Pb}(\text{NO}_3)_2$  activator was added to the ore pulp; Figure 7 presents the effect of the dosage of  $\text{Pb}(\text{NO}_3)_2$  on the  $\text{Nb}_2\text{O}_5$  grade and recovery. When increasing the quantity of  $\text{Pb}(\text{NO}_3)_2$  from 300 to 600 g/t, there was only small fluctuation in the  $\text{Nb}_2\text{O}_5$  grade, while the  $\text{Nb}_2\text{O}_5$  recovery changed a lot. As  $\text{Pb}(\text{NO}_3)_2$  increased from 300 to 400 g/t, the  $\text{Nb}_2\text{O}_5$  recovery increased sharply from 56% to 67.5%, while it decreased a little to 63.8% as  $\text{Pb}(\text{NO}_3)_2$  increased from 400 to 600 g/t. These interesting results can be attributed to the fact that there was not enough of the activator at lower  $\text{Pb}^{2+}$  concentrations, while  $\text{Pb}^{2+}$  may have generated precipitate at a higher activator concentration. Thus, 400 g/t of  $\text{Pb}(\text{NO}_3)_2$  activator is more suitable for the niobite flotation.

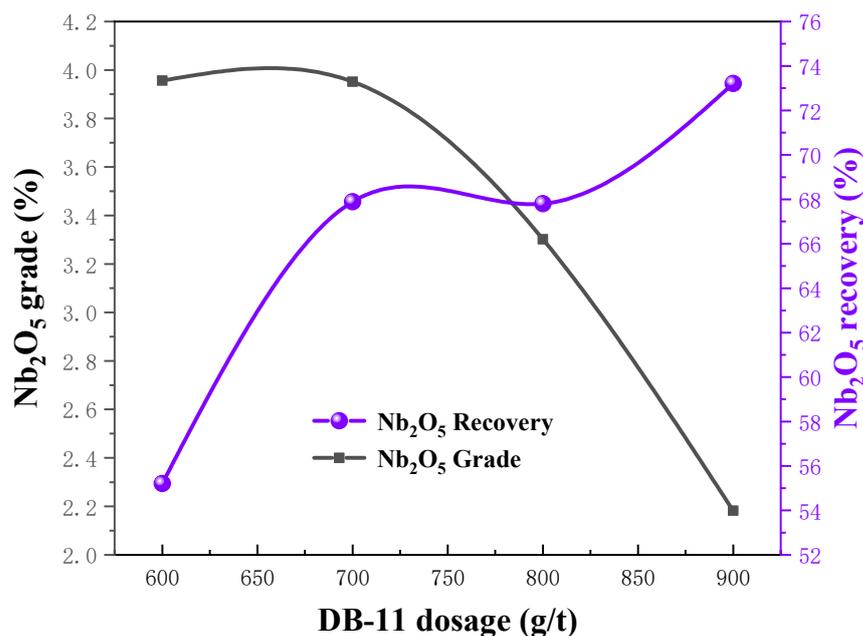


Figure 6. The effect of DB-11 dosage on Nb<sub>2</sub>O<sub>5</sub> grade and recovery.

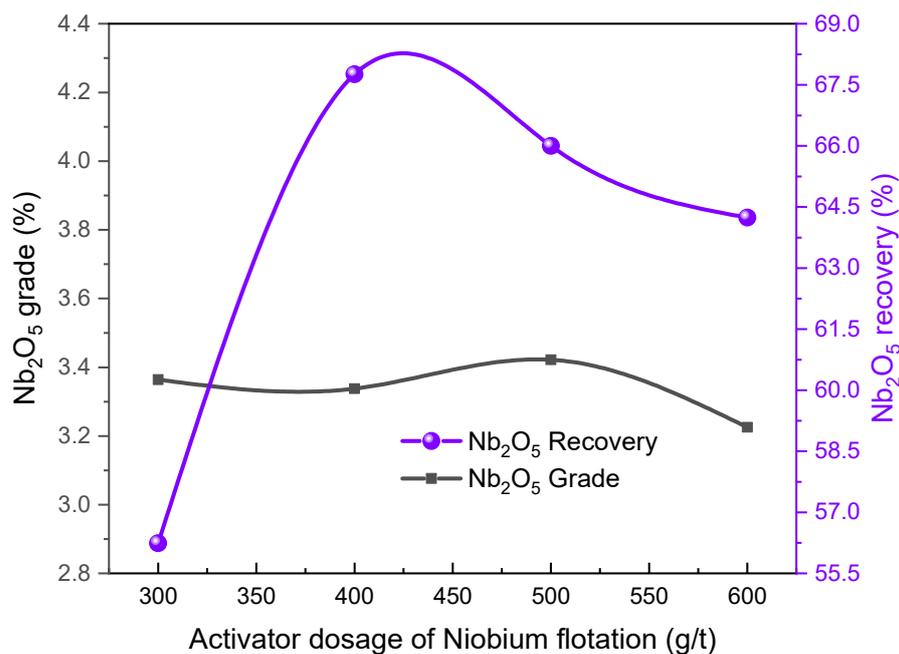


Figure 7. The effect Pb(NO<sub>3</sub>)<sub>2</sub> dosage on Nb<sub>2</sub>O<sub>5</sub> grade and recovery.

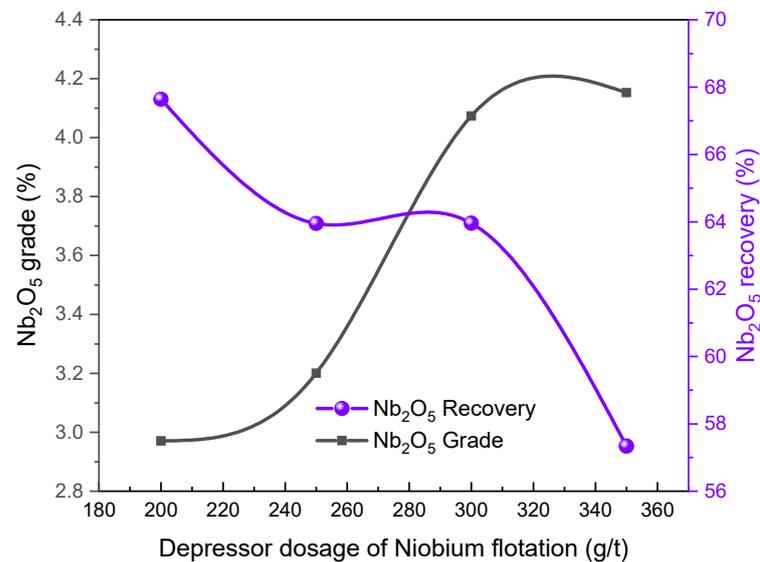
### 3.2.4. Effect of CMC Dosage on Niobite Flotation

Because of the widespread existence of calcite microcline and biotite, a depressor is necessary to control the gangue and achieve a better niobite flotation. As seen in Figure 8, with increasing depressor dosage, the Nb<sub>2</sub>O<sub>5</sub> grade continuously grows, and almost reaches equilibrium at 4.2% after 300 g/t. However, the depressor displays a certain adverse effect on the Nb<sub>2</sub>O<sub>5</sub> recovery, which continuously declines, with a rebound at 300 g/t CMC. To balance the Nb<sub>2</sub>O<sub>5</sub> grade and recovery, 300 g/t of CMC was chosen for the following flotation experiments.

### 3.2.5. Optimization of Niobite Concentrate Flotation

In the previous experiment, it was found the concentration ratio of Nb<sub>2</sub>O<sub>5</sub> was only about 34x, which is not enough for a good flotation. Thus, a second flotation for niobite

concentrate (concentrate flotation I) was carried out to improve the concentrate grade. To achieve a better  $\text{Nb}_2\text{O}_5$  grade and recovery, three different flotation reagent systems were employed to optimize concentrate flotation I, as shown in Figure 9. As can be seen, the addition of the collector and depressor causes a great impact on  $\text{Nb}_2\text{O}_5$  recovery, but little on  $\text{Nb}_2\text{O}_5$  grade; a certain increase in the collector can greatly improve the  $\text{Nb}_2\text{O}_5$  recovery, while too much of the depressor will lead to a reduction in  $\text{Nb}_2\text{O}_5$  recovery. Thus, 10 g/t collector and 15 g/t depressor were used; the  $\text{Nb}_2\text{O}_5$  grade was 12.03%, and the obtained concentration ratio was about 96x as compared to the original ore. In order to further improve the  $\text{Nb}_2\text{O}_5$  grade and concentration ratio, a concentrate flotation II with only 8 g/t collector and a concentrate III without any reagent were conducted. After three concentrate flotations, the  $\text{Nb}_2\text{O}_5$  grade was found to reach 23.48%, which exceeds most niobium froth flotations; meanwhile, the concentration ratio reached about 190x that of the original ore. However, although the  $\text{Nb}_2\text{O}_5$  grade was very high, its  $\text{Nb}_2\text{O}_5$  recovery was only 25.6%, which is unacceptable for the niobite flotation. Thus, a closed-circuit experiment is required to improve the  $\text{Nb}_2\text{O}_5$  recovery in the following experiment.



**Figure 8.** The effect of CMC dosage on  $\text{Nb}_2\text{O}_5$  grade and recovery.

### 3.3. Closed-Circuit Experiment

Based on the above experimental conditions, a closed-circuit experiment was conducted, and the flotation sheet is shown in Figure 10. For the sulfur concentrate, there was a sulfur grade of 33.74% and a sulfur recovery of 92.04%, and the sulfur concentration ratio reached 40x. As for the niobite concentrate, it had an REO of 1.04%,  $\text{Nb}_2\text{O}_5$  grade of 19.11%, and  $\text{Nb}_2\text{O}_5$  recovery of 69.61%, and the  $\text{Nb}_2\text{O}_5$  concentration ratio reached 153x. The XRF analysis (Table 2) of niobite concentrate shows that the main chemical components are  $\text{Nb}_2\text{O}_5$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{CaO}$ , and  $\text{MgO}$ , demonstrating that although the niobite is concentrated, a certain degree of impurity needs to be further removed.

**Table 2.** XRF analysis of niobite concentrate after flotation.

Oxides	REO	$\text{Nb}_2\text{O}_5$	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{CaO}$	$\text{MgO}$
Content (%)	1.04	19.11	3.47	0.9	25.25	14.08	2.83
Oxides	$\text{TiO}_2$	$\text{MnO}$	S	$\text{P}_2\text{O}_5$	$\text{K}_2\text{O}$	$\text{Na}_2\text{O}$	Lost
Content (%)	18.05	0.78	2.12	1.94	0.36	0.3	10.81

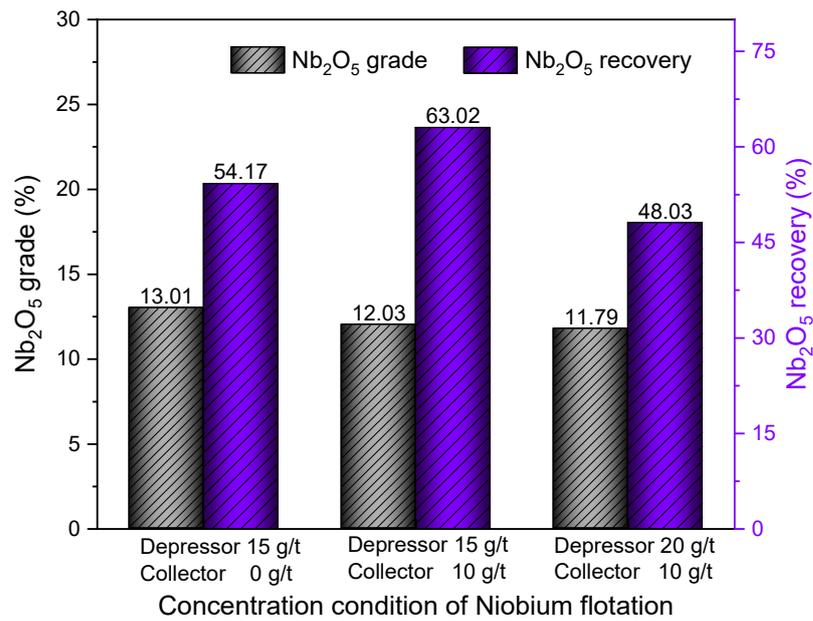


Figure 9. The effect of reagent system on Nb<sub>2</sub>O<sub>5</sub> grade and recovery of niobite concentrate.

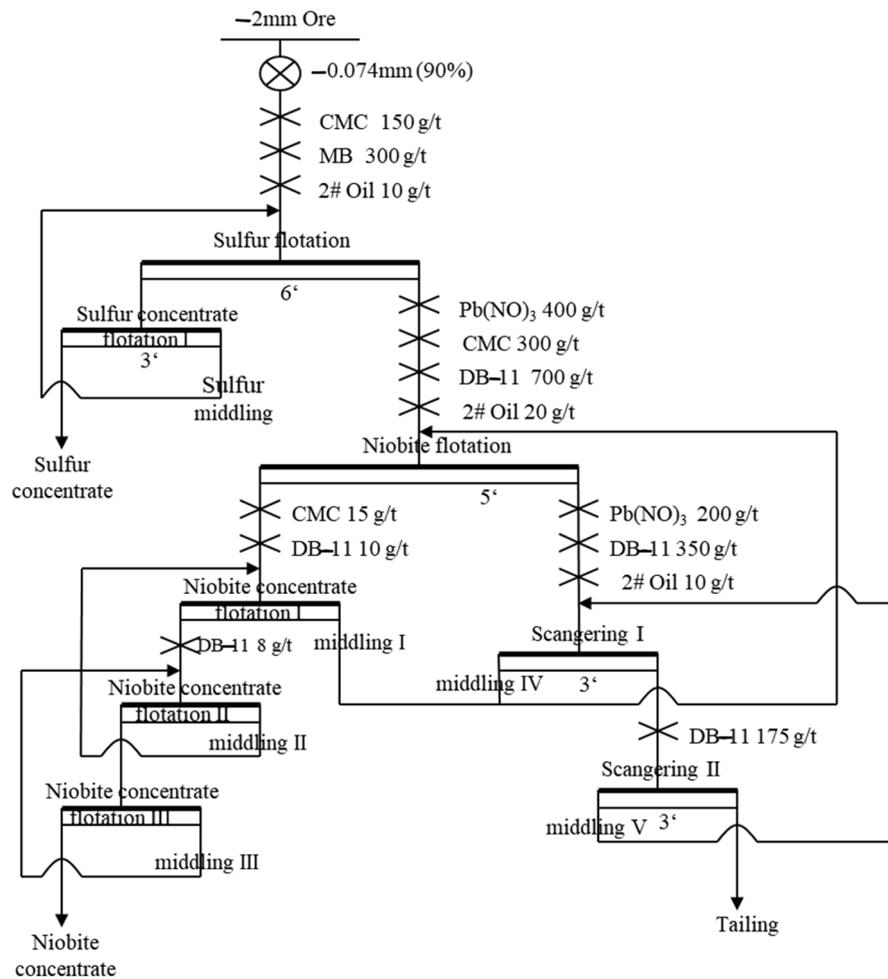


Figure 10. The closed-circuit experiment of niobite flotation.

### 3.4. Leaching of Niobite Concentrate

Considering the existence of CaO and MgO in the niobite concentrate, diluted HCl solution (9 wt%) was used to remove impurities. Five grams of sample was added to a 1.5 mL diluted HCl solution, and then stirred for 30 min at room temperature, after which we finally filtrated and dried the sample. After the leaching with diluted HCl, from Table 3 it can be seen that the Nb<sub>2</sub>O<sub>5</sub> grade and recovery in niobite reached 30.19% and 65.04%, respectively, with a concentration ratio of 242x. The results suggest that the flotation–leaching process can efficiently concentrate and recover niobium from complex low-niobium-grade carbonate niobite with the use of technology.

**Table 3.** XRF analysis of niobite concentrate washed with diluted HCl.

Oxides	REO	Nb <sub>2</sub> O <sub>5</sub>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO
Content (%)	1.81	30.19	5.29	1.26	26.6	0.54	0.01
Oxides	TiO <sub>2</sub>	MnO	S	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O	Na <sub>2</sub> O	Lost
Content (%)	25.71	0.5	3.67	0.13	0.37	0.24	3.68

### 3.5. Economic Evaluation

Practical application of niobium recovery is a complex engineering project; in order to verify the application possibility and profitability of our process, a simple economic evaluation was conducted, the results of which are listed in Table 4. As can be seen, the total expenditure for the niobite ore, water and electricity, auxiliary materials, and others was about CNY 54,060.00/t (excluding tax). At present, the price of this Nb<sub>2</sub>O<sub>5</sub> grade (30%) niobite concentrate is about CNY 100,000.00/ton or more. Thus, there is a difference of more than CNY 46,000.00/t. In addition, the production of 1 ton of niobite concentrate can produce 5.37 tons of high-quality sulfur concentrate (S grade 33.74%), which will further improve the interest after sale.

**Table 4.** Estimation of the economic benefit for production of 1 ton of niobite concentrate.

Items	Units	Unit Consumption	Unit Price	Sum (CNY)
Original ore	Mining	Ton	388	15,520.00
	Transport	Ton	388	5820.00
Water and electricity	Water	Ton	1300	1300.00
	Electricity	KW/h	2500	2500.00
Auxiliary materials	Activator	Kg	139.54	2511.00
	Depressor	Kg	70.00	45.00
	CMC	Kg	35.00	280.00
	MB	Kg	70.00	840.00
	DB-11	Kg	280.00	22,400.00
	Hydrochloric acid	Kg	80.00	400.00
	2# oil	Kg	9.30	63.00
	Lube			80.00
Others	Machinery depreciation and maintenance			150.00
	Salary and other			1800.00
	Management cost			200.00
	Contingencies			150.00
Total				54,060.00

#### 4. Conclusions

Herein, DB-11 was chosen as a collector to achieve the effective recovery of niobite. The applicability and feasibility of DB-11 in real low-grade carbonate niobite ore were evaluated by means of flotation tests in terms of single-factor experiments, as well as open- and closed-circuit experiments. Moreover, the potential practical application of the niobite flotation recovery was verified through a simple economic evaluation. The flotation results indicate that DB-11 shows an excellent collecting effect on niobite—a 19.11% Nb<sub>2</sub>O<sub>5</sub> grade and a 69.61% Nb<sub>2</sub>O<sub>5</sub> recovery were achieved, and the concentration ratio was 153x. After leaching of the niobite flotation concentrate, an improved Nb<sub>2</sub>O<sub>5</sub> grade of 30.19% and a much higher concentration ratio of 242x were obtained. In addition, a high-quality sulfur product with a sulfur grade of 33.74% and sulfur recovery of 92.04% was achieved simultaneously, which is very beneficial to the comprehensive utilization of carbonate niobite ore.

**Author Contributions:** Investigation, S.L.; methodology, S.L.; resources, S.L.; supervision, S.S.; writing—original draft, S.L.; writing—review & editing, S.S., H.Y., L.Y. All authors have read and agreed to the published version of the manuscript.

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

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