

Article

Mineralogical Characteristics of Pegmatite Tailings and Beneficiation Assessment of Pollucite in Recovering Cesium

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Abstract: The technological mineralogical characteristics of cesium-containing minerals in tailings were examined by means of chemical analysis, the energy spectrum analysis method, and MLA (mineral liberation analyzer) to determine the element content, phase analysis, associated mineral components, degree of liberation, particle size, etc. The results showed that the samples mainly contained spodumene, quartz, feldspar, mica, and other minerals. Pollucite was the main cesium-containing mineral in the sample, which had a cesium oxide content that was as high as 34.58%. The mineral content of pollucite in the sample was relatively low—only 1.23%. The pollucite monomer content and the amount of rich intergrowth was 85.25%, and the metal distribution of cesium in the +0.074 mm sample was as high as 87.06%. Spodumene was the main mineral associated with pollucite. The beneficiation evaluation of this tailing sample was conducted using a combined process that integrated desliming, magnetic separation, and froth flotation, and a pollucite concentrate containing 4.45% Cs₂O was obtained with a 63.71 recovery rate. This indicates that little pollucite was removed by means of desliming and magnetic separation before froth flotation recovery, but during the froth flotation stage in spodumene and feldspar, a large pollucite loss was observed. Therefore, to improve pollucite recovery, a pollucite-specific adsorption reagent should be synthesized.

Keywords: feasibility; pollucite; mineralogical characteristics; tailing; froth flotation



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1. Introduction

Cesium is an important rare metal element that has great application prospects in ion rocket engines, in the information industry, in medicine, as a catalyst, and in other contexts [1–3]. At present, the main source of cesium extraction is pollucite, but with the depletion of high-grade cesium resources [4], the clean and efficient utilization of low-grade cesium resources and secondary resources has attracted attention.

World-class TANCO pegmatite, which is located in Bernic Lake, is the most significant rare metal deposit in Manitoba. This highly fractionated lithium–cesium–tantalum(LCT)-type pegmatite contains several distinct mineralogical zones that have historically been mined for Li, Ta, Cs, Rb, and Be ores. Currently, the TANCO mine produces pollucite for the manufacture of cesium formate, which is used for high-density and low-viscosity drilling as well as in the completion fluid that is primarily used in oil and gas wells. The development of the West TMA of the TANCO Mine was approved in 1991 through alterations made to Environment Act License No. 973. The placement of tailings in the West TMA started in 1991 and has continued to the present, with approximately three million tons of tailings having been deposited there to date.

The occurrence state and property state of minerals are the key factors for determining the ore washability, and it is very important to accurately determine the occurrence state of useful minerals and the parameters of the useful minerals in any ore [5,6]. Therefore,

the key to the development and utilization of low-grade secondary tailings lies in the mineralogical study of these kinds of tailings using a systematic process to determine the mineral composition of the ore, the dissemination characteristics of the minerals, and the occurrence state of useful minerals in the tailings. Its purpose is to reveal the key factors of valuable mineral recovery to formulate the best recovery process suitable for ore properties.

There are two types of tailings in the TANCO mine; the east part of the mine contains tailings from the smelting and chemical industry, and the west part of the mine contains tailings left by ore dressing. In this paper, a systematic process mineralogy study of the TANCO west tailings was carried out to determine the types of minerals as well as the occurrence and dissemination characteristics of the cesium in the tailings, and an automatic mineral analysis system (Mineral Liberation Analyzer, MLA) was used to determine and analyze the minerals that were found to contain cesium. According to the process mineralogical characteristics of cesium-bearing minerals in the sample and the test pollucite beneficiation results, an evaluation determining pollucite recovery from the sample was carried out. The purpose of this study was to provide suggestions for the rational secondary development and utilization of tailings to recover cesium-containing minerals.

2. Materials and Methods

2.1. Samples

The ore sample was taken from the comprehensive ore sample (1000 kg) of TANCO west tailings. The ore sample was dried naturally, mixed, and divided to obtain the sample (200 kg) required for the test, and the sample was reserved for preparation. The silt particles in the sample were fine, and the overall size of the particles was less than 0.6 mm. Some of the mica flakes had widths that were more than 1.0 mm. Mica, quartz, feldspar, and other minerals were able to be initially identified by the naked eye.

2.2. Methods

The chemical composition of the sample was determined. The major elements were analyzed by means of X-ray fluorescence (XRF) using a sequential EDX-7000 spectrophotometer (Shimazu, Kyoto, Japan). Minor elements were measured by inductively coupled plasma-mass spectroscopy (ICP-MS) (PlasmaQuant MS Q, Analytik Jena AG, Jena, Germany).

Mineralogical characterization was carried out by various methods, including mineral liberation analysis (MLA), X-ray diffraction analysis (XRD), and optical microscopy analysis.

MLA system is an automatic mineral analyzer that is mainly used to accurately test the mineralogical characteristics and parameters of the process, such as mineral composition and content, particle size distribution, degree of liberation, mineral occurrence, the dissemination relationship, etc. The MLA system is composed of a scanning electron microscope (Jeol JSM6510, Japan Electronics Co., Ltd., Tokyo, Japan), an energy dispersive spectrometer (Genesis XM2 EDS, EDAX Inc., Berwyn, IL, USA), and MLA software (Suit2.9, JKTeck, Brisbane, Australia). MLA measurements were performed at 20 kV with a 1.5-micron pixel resolution using the XBSE method. The working principle of MLA is to use backscattered images to distinguish between different phases and to combine these images with the energy dispersive spectrometer to collect and analyze relevant information and then use image analysis technology to calculate and process the obtained data.

XRD patterns were recorded using a Rigaku D/MaxrA rotating anode X-ray diffractometer equipped with a Cu K α tube and an Ni filter ($\lambda = 0.1542$ nm) at a scanning rate of $0.0167^\circ/\text{s}$.

Optical microscopy analysis was performed on a ZEISS Axioskop 40 microscope.

Samples were taken to determine the feed sample particle size distribution of the ore using a laser particle size instrument (Bettersize 2000, Dandong Baxter Instrument Co., Ltd., Dandong, China).

To prepare the ore for froth flotation, the sample (1000 g) was screened by a sieve with a mesh size of 0.15 mm. The oversize particles were ground to $-150\ \mu\text{m}$ and were deslimed afterward. After desliming, magnetic separation was conducted to purify the froth flotation

feed by removing the Fe minerals. After magnetic separation, froth flotation was adopted. Froth flotation experiments were conducted using a 1.5 L stirred froth flotation cell. The slurry was stirred at 660 rpm. The solid content in the cell was then adjusted to 33% via the addition of approximately 1.2 L of tap water. In the stage of mica flotation, the pH value of the pulp was 7. After mica flotation, the pH value of the pulp was controlled at 9 with NaOH (AR, Macklin). The collector (details was shown in Table 1) and frother (MIBC, Macklin) were added at the selected dosages. The pH was readjusted before the addition of the reagent to ensure that froth flotation occurred at the target pH during the conditioning period, which was set at 3 min.

Table 1. Collector in different froth flotation states.

Froth Flotation Stage	Collector	Reagent Grade	Reagent Company
Mica	3030C	-	Solvi
Spodumene and Feldspar	Oxidized paraffin soap 731 odium oleate	Industrial grade	Bei Zhen City Lvfen Chemical plant, Jinzhou, China
Pollucite	Ether amine T-49	Industrial grade	Yunnan Yuntong Tiefeng ore dressing Pharmaceutical Co., Ltd., Chuxiong, China

Wet screening was carried out using an XSB-88 standard vibration sieve machine.

A wet magnetic separator (XCSQ 50 × 70) manufactured by Wuhan Exploration Machinery Co., Ltd. was used to run the tests. The magnetic field intensity was 1 Tesla, and the magnetic concentration was 20%.

A hydrocyclone (JAX-75) was used for desliming, the pulp concentration was 12% (solid–liquid weight ratio), and the working pressure was 0.4 Mpa.

3. Results and Discussion

3.1. Chemical Composition and Analysis

The sample was analyzed by XRF analysis and multi-element analysis, and the analysis and test results are shown in Tables 2 and 3, respectively. The main chemical components in the sample were SiO₂, Al₂O₃, Na₂O, and K₂O. The Li₂O, Rb₂O, and Cs₂O contents in the sample were 1.16%, 0.34%, and 0.51%, respectively, which are close to the mining grade of pegmatitic granite, and the mining index was able to be reached at the current metal price. Lithium, cesium, and rubidium were the main target elements for recovery in the sample.

Table 2. Semi-quantitative analysis results of XRF.

Element	Rb	Cs	Ta	Ga	Ge	Cu	Zn	Sr
Content, %	0.158	0.286	0.01	0.008	0.001	0.005	0.007	0.003
Element	Zr	Ti	Cr	Fe	Mn	Si	Al	Ca
Content, %	0.001	0.017	0.006	0.373	0.072	33.53	7.133	0.222
Element	Mg	K	Na	P	S	F		
Content, %	0.032	1.6	2.91	0.64	0.01	0.32		

Table 3. Results of chemical multi-element analysis.

Constituent	Li ₂ O	Rb ₂ O	Cs ₂ O	Ta ₂ O ₅	Nb ₂ O ₅	FeO	MnO	F
Content, %	1.16	0.34	0.51	0.037	0.006	0.43	0.069	0.21
Constituent	Al ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	SiO ₂	P	Ig
Content, %	13.52	0.34	0.063	1.93	3.64	74.51	0.48	2.755

Table 4 shows that cesium mainly exists as an independent mineral of pollucite, comprising 83.33% of the total elemental cesium. About 13% of the cesium in the sample was distributed in mica. Therefore, cesium can be fully recovered by recovering pollucite and mica.

Table 4. Results of chemical cesium phase analysis.

Cesium Phase	Cs ₂ O in Mica	Cs ₂ O in Pollucite	Cs ₂ O in Others	Total
Content, %	0.067	0.424	0.018	0.509
Proportion of total cesium, %	13.16	83.30	3.54	100.00

3.2. Mineral Composition and Content of Sample

The XRD results for the samples are shown in Figure 1, and the relative weight contents of the main minerals in the sample are shown in Figure 2. Through microscopic identification, XRD, and MLA, the main minerals in the sample were determined to be quartz, feldspar (mainly albite, followed by orthoclase), spodumene, and mica, followed by hornblende, pollucite, phosphoponite, and apatite, among others. The results show that the main lithium-bearing minerals were spodumene and mica, followed by phosphoponite; the main rubidium-bearing mineral was determined to be mica, followed by feldspar; and the main cesium-bearing mineral was pollucite, followed by mica.

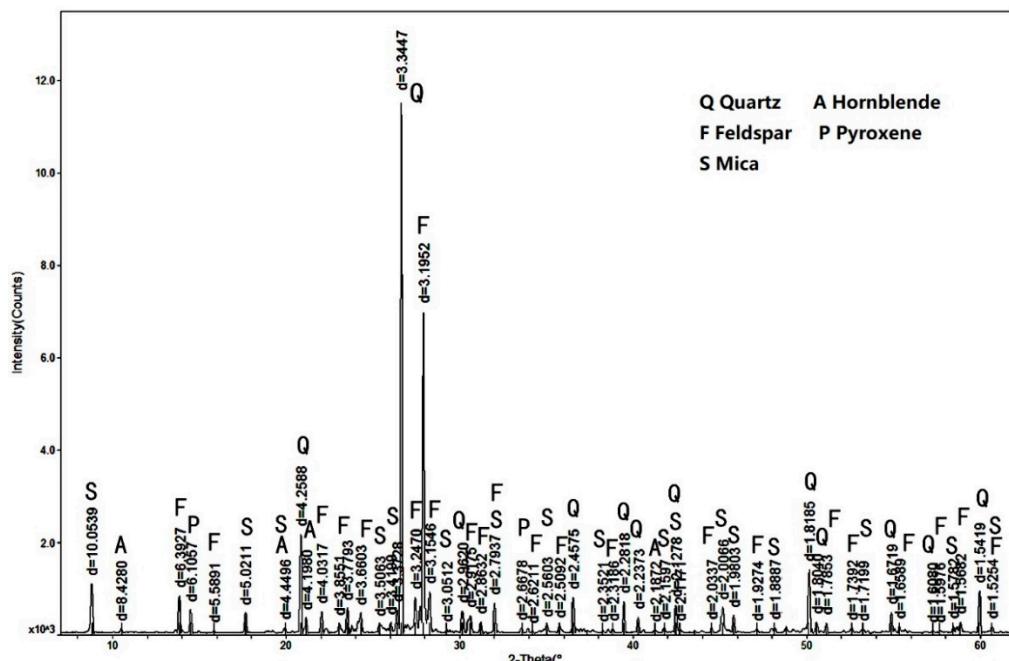


Figure 1. XRD analysis results of the sample.

3.3. Size Characteristics of Main Cesium-Bearing Minerals

The results of the size characteristics of pollucite and mica are shown in Figure 3. In general, pollucite and mica had coarse particles that were less than 0.6 mm in size. In a +0.075 mm sample, mica accounted for 57.74%, and pollucite accounted for more than 70%. In +0.038 mm samples, mica accounted for 83.82%, and pollucite accounted for more than 90%. The metal distribution of cesium in the +0.074 mm sample was as high as 87.06%. Both cesium-containing minerals had coarse particles and demonstrated reasonable froth flotation recovery.

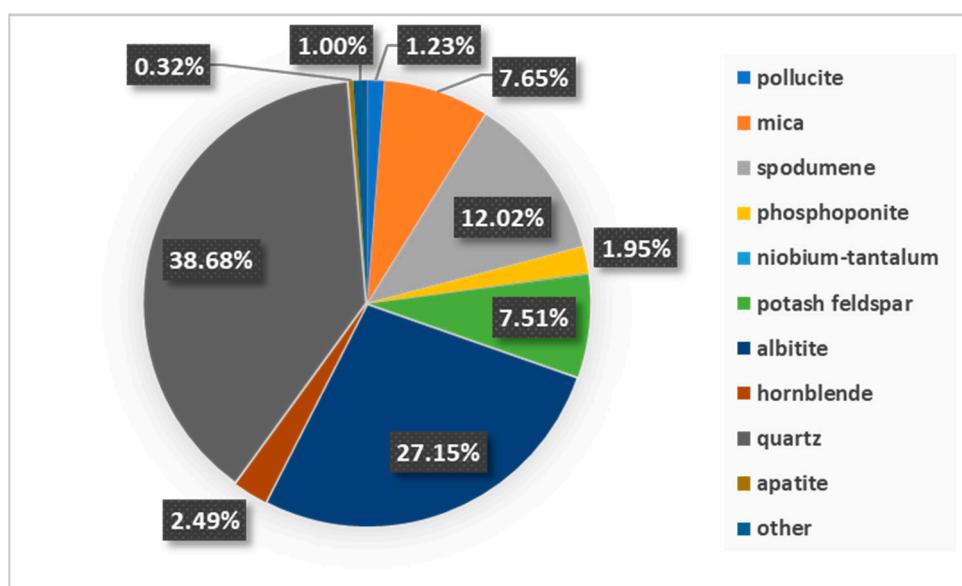


Figure 2. Results determining the mineral composition and content.

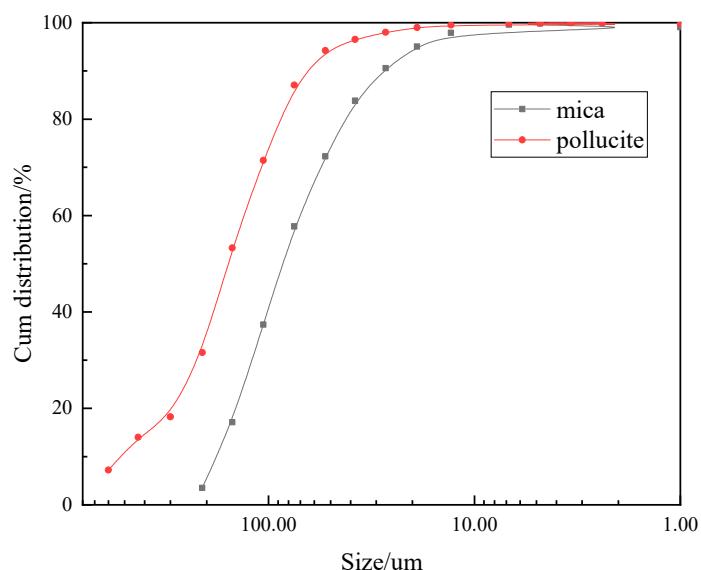


Figure 3. Cumulative distribution curve of particle size of the main cesium-containing minerals.

3.4. Degree of Liberation of Cesium-Bearing Minerals

The results determining the degree of liberation in pollucite and mica are shown in Table 5. The degrees of liberation for mica and pollucite were high. Mica had a higher dissociation degree than pollucite. The sum of the pollucite monomer and rich intergrowth ($>3/4$) was 85.25%, and that of mica was more than 90%. Judging from the dissemination feature of the minerals, the sample can be separated without grinding.

Table 5. Liberation degrees of pollucite and mica.

Mineral	Monomer, %	Intergrowth, %			
		>3/4	3/4~1/2	1/2~1/4	<1/4
pollucite	76.33	8.92	10.77	2.57	1.41
mica	84.38	6.45	4.86	2.45	1.86

3.5. Cesium Content in Cesium-Bearing Minerals

The results of the energy spectrum micro-domain composition analysis determining the main cesium-bearing minerals are shown in Tables 6 and 7 and Figure 4. The average Cs_2O content in mica was only 0.31%, while the average Cs_2O content in pollucite was 34.58%. Because of the low cesium oxide content in mica, mica is not the main mineral for cesium recovery. There was a relatively high cesium oxide content in pollucite, meaning that a high-grade cesium concentrate can be obtained via pollucite recovery.

Table 6. Energy spectrum micro-domain composition analysis for pollucite.

Number	Content, %				
	Cs_2O	Rb_2O	Na_2O	Al_2O_3	SiO_2
1	34.39	0.00	2.23	17.16	44.73
2	33.56	0.00	2.63	17.27	45.04
4	34.46	0.00	2.62	16.81	44.61
5	33.24	0.00	2.66	17.44	45.15
6	34.15	0.88	2.20	16.63	44.65
7	33.88	0.55	2.35	16.82	44.89
8	33.74	0.00	2.67	16.99	45.10
9	36.86	0.00	1.55	15.29	44.81
Average	34.28	0.18	2.36	16.80	44.87

Table 7. Energy spectrum micro-domain composition analysis of mica.

Number	Content, %				
	Cs_2O	Rb_2O	K_2O	FeO	MnO
1	0.12	2.55	11.09	0.37	0.05
2	0.16	2.69	10.09	0.81	0.08
3	0.59	4.08	9.19	0.25	0.88
4	0.08	3.39	9.92	0.58	0.06
5	0.05	2.24	10.70	0.96	0.22
6	0.72	3.10	10.38	0.99	0.37
7	0.16	2.40	10.48	1.26	0.05
8	0.15	2.28	10.99	1.29	0.05
9	0.30	3.54	9.11	2.43	0.11
Average	0.25	2.84	10.36	0.81	0.22

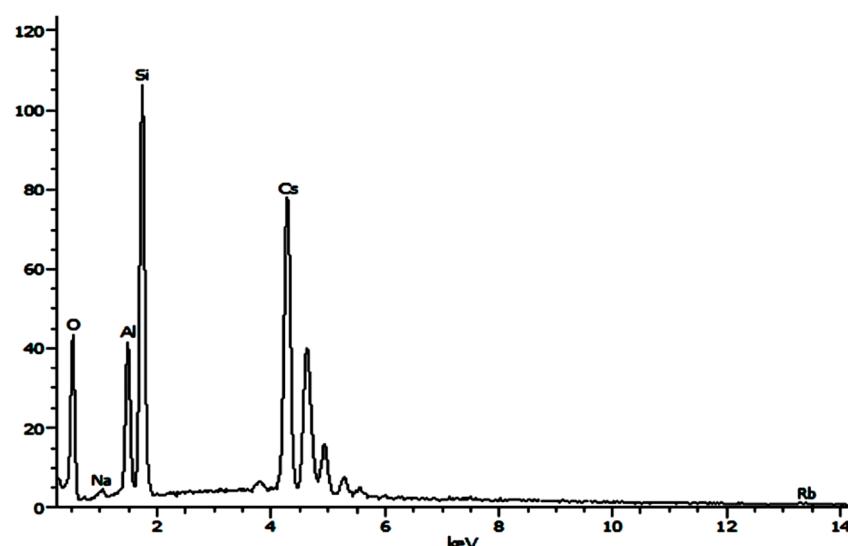


Figure 4. X-ray energy spectrum composition diagram for pollucite.

3.6. Occurrence of Cesium-Bearing Minerals

The embedded characteristics results showing the relationship between cesium-bearing minerals and other minerals are shown in Figures 5–7. Pollucite was an independent mineral of cesium in the samples and existed in both granular and irregular fine-grained aggregate forms. Pollucite was found in a wide range of sizes, generally between 30 µm and 300 µm. Most pollucite was single or shows rich intergrowth, and a small amount of pollucite was embedded in other minerals. Undissociated pollucite was closely intercalated with spodumene, and spodumene is commonly found in intercalated minerals.

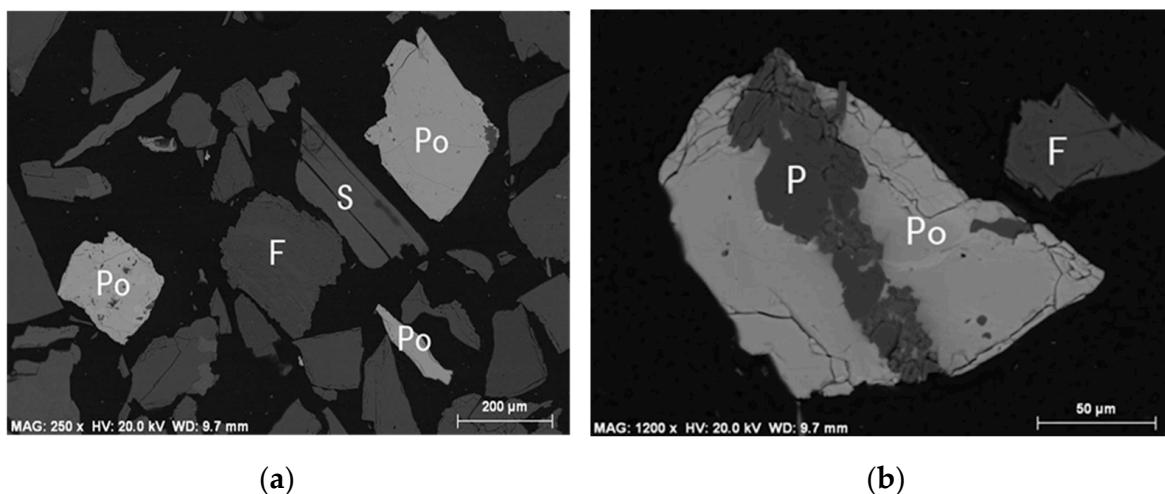


Figure 5. Characteristics of pollucite (Po), albite (F), spodumene (P), and mica (S): (a) pollucite occurs as a monomer; (b) intergrowth of coarse-grained pollucite and spodumene.

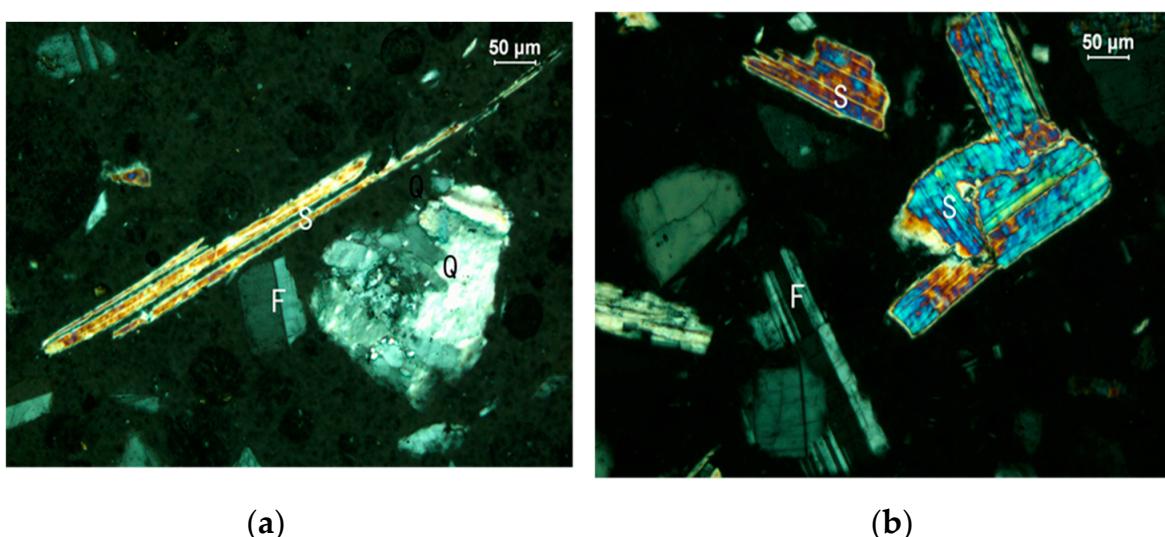


Figure 6. Orthogonal polarization diagram of mica (S), albite (F), and quartz (Q): (a) mica exists in the form of thin strips; (b) mica exists in the form of flakes.

Mica is mainly composed of muscovite (lepidolite) and occasionally biotite. Mica usually has a flaky or scaly shape, and flakes are usually less than 0.03 mm thick. Mica can have different particle sizes, with muscovite with a sheet width of more than 1.0 mm being able to be seen with the naked eye, but fine and scaly mica can be microscopic and less than 0.02 mm in size. Coarse-grained mica is mostly found in the monomer state, in which fine feldspar and other minerals are sometimes disseminated; fine lepidolite is often closely interlocked with feldspar, quartz, and other minerals.

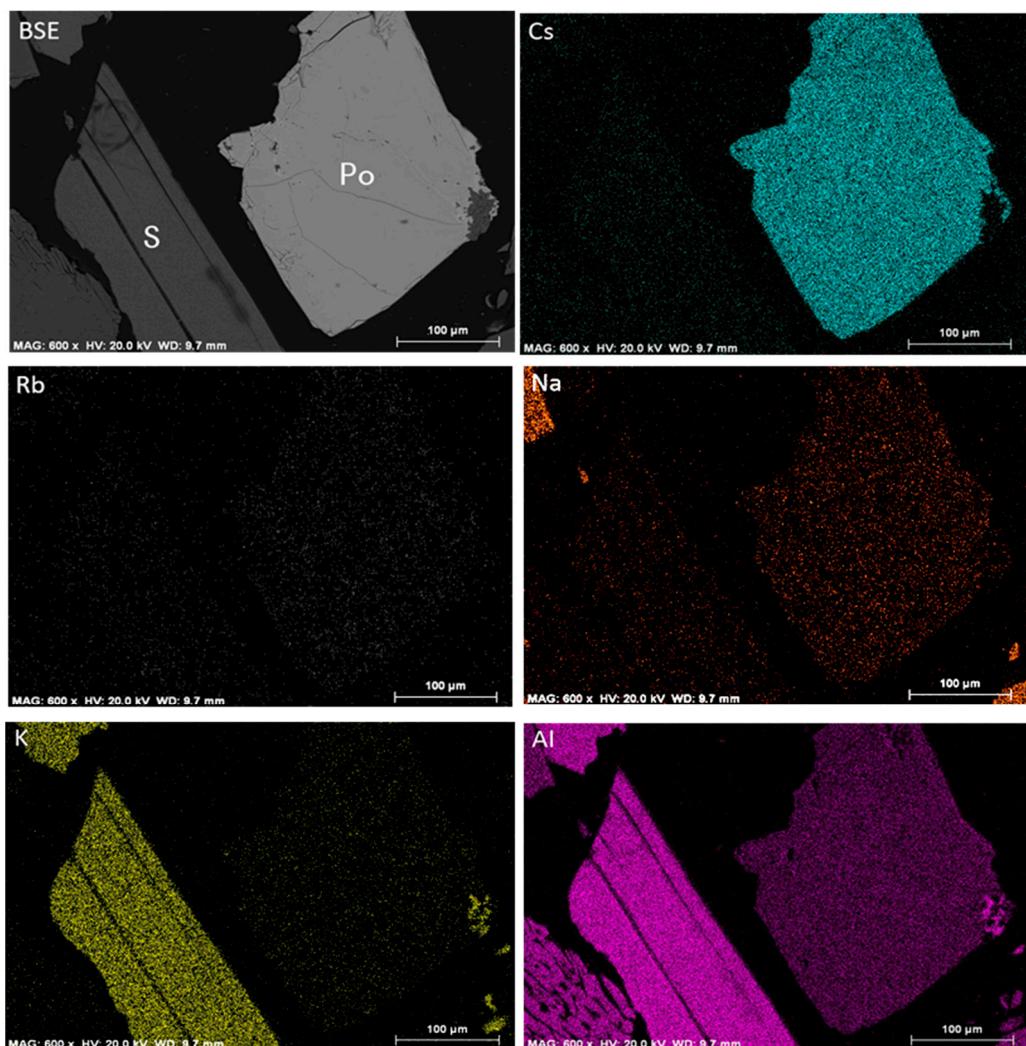


Figure 7. SEM–EDS spectrum of pollucite (Po) and mica (S).

3.7. Pollucite Beneficiation

In the sample, Cs_2O was present at a concentration of 0.51%, and cesium oxide mainly existed in the form of pollucite, with only a small portion existing in the form of mica. Pollucite has a high degree of liberation. The occurrence state of cesium indicates that most cesium can be effectively enriched by froth flotation, and cesium's maximum possible recovery is 80.26%.

In the sample, the cesium oxide content in pollucite was higher, and the particle size of the pollucite in the sample was in a range that is suitable for froth flotation and has a high liberation degree, indicating that this portion of the pollucite can be floated without grinding. However, the coarse pollucite fraction with a low froth flotation efficiency still needs to be ground. During the grinding and froth flotation process, minerals are often contaminated by multivalent cations, which, in turn, affect mineral floatability. The research shows that Ca^{2+} , Mg^{2+} , Al^{3+} , and other cations can activate silicate minerals in specific conditions.

There were some Fe minerals (hematite, limonite, etc.) in the samples, and the Fe minerals needed to be removed by magnetic separation before the pollucite was recovered by means of froth flotation. This is because these Fe minerals will compete with pollucite minerals during the froth flotation process.

In general, it is easy for minerals to react with adequate reagents and under adequate froth flotation conditions without slime, and these minerals have good floatability [7,8]. However, in nature, pegmatite ore is often weathered and easily covered by slime particles,

which has a greater impact on froth flotation. During the froth flotation process, a large amount of slime adheres to the surface of useful minerals and gangue minerals, reducing the floatability of useful minerals and improving the floatability of gangue minerals, thus reducing the differences in floatability between them.

When the pulp contains slime and metal ions, it can seriously affect the floatability difference between pollucite and the gangue minerals [9–11]. Therefore, pretreatment should be carried out before the pollucite floatation to remove any impurities and slime on the mineral surface to create favorable conditions for the subsequent froth flotation process.

According to the above analysis and the mineralogical characteristics of the samples, pollucite beneficiation tests were carried out in accordance with Figure 8. During the process, particles larger than 0.15 mm in size were screened out first because spodumene and pollucite intergrowth are common in the +0.15 mm size fraction. Desliming was also essential. Although there was little slime in the sample, the slime had great interference with the ability of silicate minerals to float, so it is suggested to remove the slime before commencing froth flotation. At the same time, the Fe minerals in the sample had a great interference on the froth flotation of silicate minerals, and these could be removed by means of magnetic separation. During the froth flotation stage, the reagent is important, specifically the selectivity of the collector. Because the pollucite, albite, spodumene, and quartz in the samples are silicate minerals, the surfaces of these minerals are very similar. The test results are shown in Table 8. Pollucite concentrate with a Cs_2O grade of 4.45% and a Cs_2O recovery rate of 63.71% was obtained. There was a large gap (about 20 percentage points for pollucite recovery) between the test index and maximum pollucite recovery. Pollucite loss was the largest during the spodumene and feldspar froth floatation stage, which may be because spodumene, feldspar, and pollucite are silicate minerals and because these minerals have similar surface properties. Additionally, the collectors that were used during the floatation process, sodium oleate and 731, have limited selectivity, resulting in the spodumene and feldspar also catching some of the pollucite during the froth floatation stage. In order to obtain a higher pollucite recovery rate, other special pollucite activators or collectors should be explored in the future.

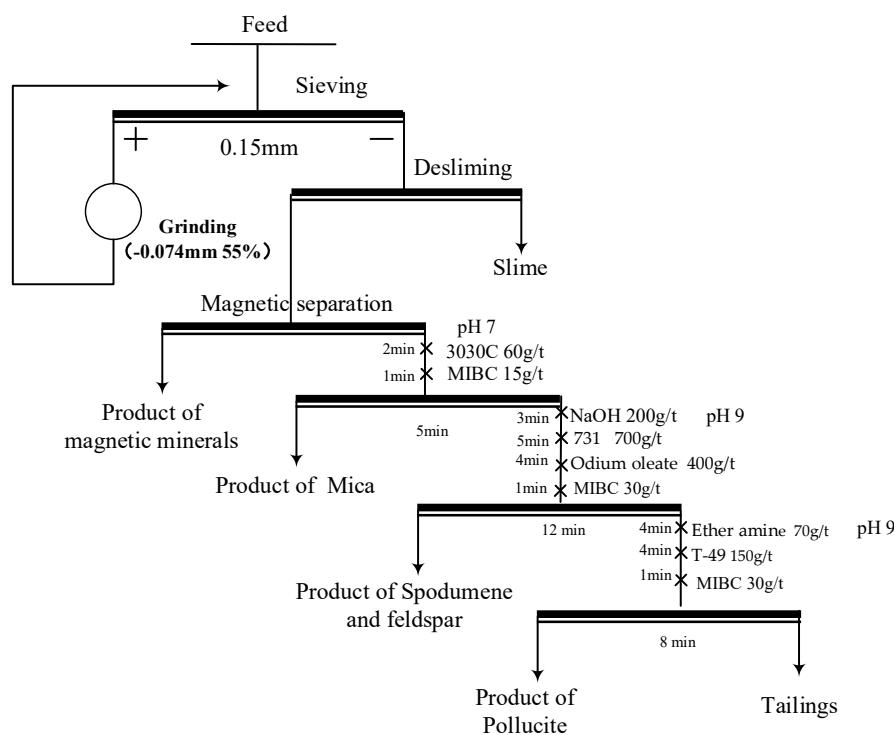


Figure 8. Beneficiation flowsheet for pollucite.

Table 8. Pollucite beneficiation results.

Product	Yield, %	Grade (Cs_2O), %	Recovery (Cs_2O), %
Slime	8.92	0.22	3.88
Fe minerals	3.04	0.21	1.26
Mica	7.21	0.32	4.56
Spodumene and feldspar	43.06	0.22	18.73
Pollucite	7.24	4.45	63.71
Tailings	30.53	0.13	7.85
Feed	100.00	0.51	100.00

4. Conclusions

The cesium oxide content in the sample was 0.5%, which is higher than that of common granite raw ore and allows for comprehensive utilization. The cesium in the sample mainly existed in the form of pollucite and pollucite with a higher liberation degree (the monomer and rich intergrowth was 85.25%), and this is within the appropriate particle size range that is suitable for froth flotation. The maximum cesium recovery rate was determined to be 80.26% according to the process mineralogy analysis.

The analysis of the results of the beneficiation test shows that it is feasible to recover pollucite from tailings. During the pollucite recovery process, it is important to consider the influence of Fe minerals, mud, and metal ions on pollucite recovery when using froth flotation. Before recovering pollucite using froth flotation, it is necessary to eliminate the interference of these factors to the maximum extent possible to create a good froth flotation environment for pollucite floatation. However, pollucite, feldspar, spodumene, and mica are silicate minerals with similar surface properties, and presently, there is no special collector or activator for pollucite froth flotation, indicating that pollucite recovery during the froth flotation process needs to be further improved.

Author Contributions: Y.C. and Y.S. conceived of and designed the experiments; Y.C., J.W., Y.S., W.L. and S.L. performed the experiments; Y.C. and Y.L. analyzed the data; Y.C. and W.L. wrote the paper. All authors have read and agreed to the published version of the manuscript.

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