

PROCESSING OF FINE LITHIUM MINERAL TAILINGS

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ABSTRACT – Spodumene is a primary lithium source found in pegmatite deposits, typically associated with tantalite, cassiterite, quartz, and albite. Common processing methods for spodumene include dense medium separation (DMS), magnetic separation, and flotation. DMS exploits differences in specific density among minerals; however, the similar densities of spodumene and gangue minerals pose significant challenges to this method. This research aims to assess the potential of using DMS, as a processing method, to recover lithium from fine tailings generated by a tantalite processing plant in Brazil. Heavy liquid separation (HLS) tests were conducted on fine particle size fractions (850/150 μm), yielding high-grade lithium concentrates with up to 4.40% Li_2O . These results highlight the potential for DMS in the processing of fine lithium-bearing minerals.

Keywords: Spodumene, Lithium Recovery, Dense Media Separation, Processing.

INTRODUCTION

Lithium mineral processing plants typically encompass several stages, including comminution, dense medium separation, flotation, magnetic separation, and gravity concentration. Dense medium separation (DMS) is commonly employed as a pre-concentration stage in processing coarse size fractions ($+850 \mu\text{m}$) of spodumene, to separate gangue minerals before grinding [1]. According to Tadesse *et al.* [2], following the particle size adjustment through grinding and size classification, a gravity separation stage can be implemented to recover coproducts of tantalite and cassiterite. The flotation stage is essential for processing fine particles and generating high-grade concentrates, ensuring the successful flotation and separation of spodumene from the tailings. Ultimately, a magnetic separation stage may be required to remove substantial quantities of iron oxide-containing gangue minerals, for the final lithium concentrate. While there has been considerable advancement in studies related to spodumene concentration via flotation [3], relatively few studies discuss the concentration of spodumene using DMS [1].

Pegmatite processing using DMS can be complex due to the small difference in specific gravity between valuable and gangue minerals found in pegmatites. The specific gravity of spodumene ranges from 3.1 and 3.2 g.cm^{-3} , making it slightly heavier than most gangue minerals, including quartz (2.65 g.cm^{-3}), albite (2.60 g.cm^{-3}), and muscovite (2.8

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$\text{g}\cdot\text{cm}^{-3}$). Consequently, spodumene can sink in a dense medium with a suitably matched specific gravity, while gangue minerals will float [2].

This paper aims to evaluate the feasibility of using DMS as a spodumene concentration method, for minerals derived from fine tailings ($\sim 850\ \mu\text{m}$) from a tantalite processing plant. The analysis consists of tailings characterization through chemical and mineral analysis. Then, heavy liquid separation (HLS) laboratory tests using Bromoform were executed in different particle size fractions to determine the distribution of Li_2O in the sink and float products.

EXPERIMENTAL

Case study

The case study focuses on lithium fine tailings from a tantalite mineral processing plant of the Volta Grande mine, located in Nazareno in Minas Gerais state, Brazil. Nazareno lies within the Pegmatitic Province of São João del Rei, which hosts numerous pegmatitic bodies mineralized, with elements Sn, Nb, Ta, and Li. Commonly found minerals include spodumene, cassiterite, tantalite, columbite, and microlite. The Li-enriched pegmatitic bodies are particularly concentrated in the Nazareno region and named the Volta Grande pegmatite swarm [4]. The main products of this operation are tantalite and cassiterite, with lithium being a byproduct derived from reprocessing pegmatite tailings. Currently, lithium concentrates are produced by flotation and magnetic separation techniques.

Sample Preparation

About 20 kg of tailing samples were collected from the tantalite processing plant from the Volta Grande mine. A head sample of 2 kg was split into representative subsamples for chemical and mineral analysis, and heavy liquid separation (HLS) tests. Then each subsample was screened into five size fractions: $+850\ \mu\text{m}$, $-850/+500\ \mu\text{m}$, $-500/+297\ \mu\text{m}$, $-297/+149\ \mu\text{m}$, and $-149\ \mu\text{m}$.

Particle Size Analysis

Particle size distribution was carried out by wet sieving, performed on a series of Tyler sieves. The minimum mass of a representative sample, according to Pierre Gy's Theory, and the maximum mass to be retained on each screen were determined a total mass of 160 g. The wet sieving was done through the following process: first wet sieving ($-37\ \mu\text{m}/+2360\ \mu\text{m}$); the oversized material of each screen was filtered using a porous filter paper, dried, and weighed.

Mineral Analysis

The qualitative mineral identifications of the samples were performed by X-ray diffraction (XRD) using the total powder method. The samples for mineralogical characterization were prepared in powder form, by pulverization and homogenization of each sample. An X-ray diffractometer equipped with a copper tube ($\lambda = 1.5406\ \text{\AA}$) was used; the analysis was performed considering a 2θ array scan in the range of 5 to 90° ,

with an operating voltage of 45 kV, current intensity of 40 mA and collection time equal to 15 minutes. The diffractograms were obtained using specific software (X-ray Data Collector) and their interpretation was performed with the aid of another software (HighScorePlus), using the ASTM standard diffractogram database.

Chemical Analysis

The chemical content was determined by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). The samples were pulverized and dissolved in appropriate acids to convert target elements into a liquid solution. The solution was then filtered to remove solid residues and diluted with a suitable solvent to adjust element concentrations for ICP-OES detection. The sample prepared was introduced into the equipment via a nebulizer, generating a fine aerosol directed to the plasma torch. The data obtained were compared with reference standards for precise concentration determination.

Heavy Liquid Separation Tests

The heavy liquid separation (HLS) tests were performed with Bromoform (2.89 g/cm^3), under a laboratory fume hood. Due to chemical toxicity, personal protective equipment was used.

The tests were conducted in duplicate for the particle size fractions $+850 \mu\text{m}$, $-850/+500 \mu\text{m}$, $-500/+297 \mu\text{m}$, $-297/+149 \mu\text{m}$, and $-149 \mu\text{m}$. For each HLS test, approximately 20 g sample mass was added into 50 mL of Bromoform, using a separatory funnel to separate the heavier (sink) material from the light (float) material. Then, the material was stirred gently, every two minutes, to release the particles. After minerals separation, the sink material was removed by opening the funnel. The Bromoform was recovered by passing through the funnel opening, and therefore the float material was also recovered. The sink and float fractions were filtered using a glass funnel with filter paper, washed with ethyl alcohol to remove the Bromoform residues, and dried at room temperature. The sink and float products were weighed, and subsamples were taken for chemical and mineral analysis.

RESULTS AND DISCUSSION

Particle Size Analysis

Particle size analysis of the head sample allows an understanding of the distribution of grain sizes of tailings. Figure 1 shows that 80% of particles were smaller (P_{80}) than $869 \mu\text{m}$, which is interesting for this study (evaluate the feasibility of processing lithium minerals below $850 \mu\text{m}$); on the other hand, a coarser fraction is above $870 \mu\text{m}$; and 50% of the particles are passing (P_{50}) in $360 \mu\text{m}$.

Mineral Analysis

According to the XDR results shown in Figure 2, the main minerals to separate from the spodumene ($\text{LiAl}(\text{SiO}_3)$) are: quartz (SiO_2), albite ($\text{NaAlSi}_3\text{O}_8$), muscovite, ($\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$), and microcline ($\text{K}(\text{AlSi}_3\text{O}_8)$). The intensity of the diffraction peaks

indicates that quartz is the predominant mineral, suggesting that the tailings from the Volta Grande mine still contain a significant amount of free silica. The presence of albite and microcline indicates the presence of feldspars minerals, commonly found in pegmatites and granites. Although, spodumene has less intense peaks is related to a low concentration in the tailings. Additionally, the detection of muscovite implies the presence of phyllosilicate minerals, which could potentially impact a dense media separation process.

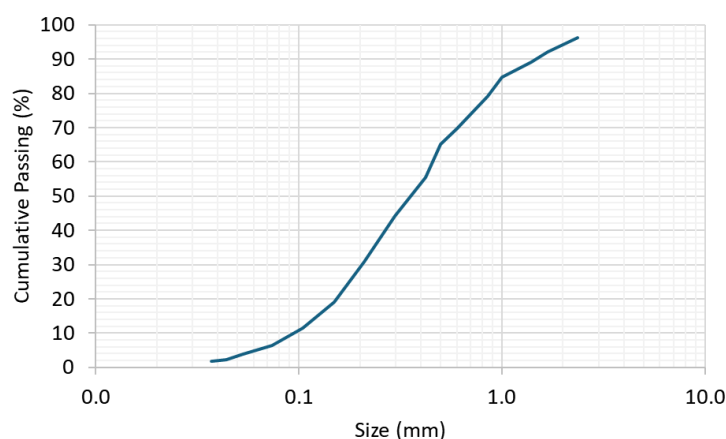


Figure 1 Particle size distribution of the tailing head sample from the Volta Grande mine

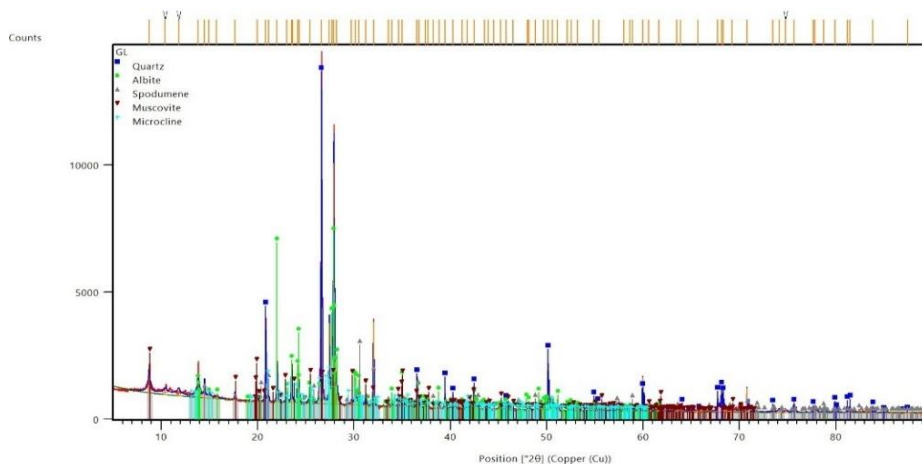


Figure 2 XRD mineral analysis of tailings head sample from the Volta Grande mine

Mineral Analysis

Chemical analysis confirmed the presence of the main minerals identified in the XRD analysis. The ICP-OES analysis detected the presence of SiO_2 , Al_2O_3 , Na_2O , and K_2O as the most abundant chemical components in the tailings head sample, as shown in Table 1.

Table 1 Chemical results (%) of the tailings head sample, as measured by ICP-OES

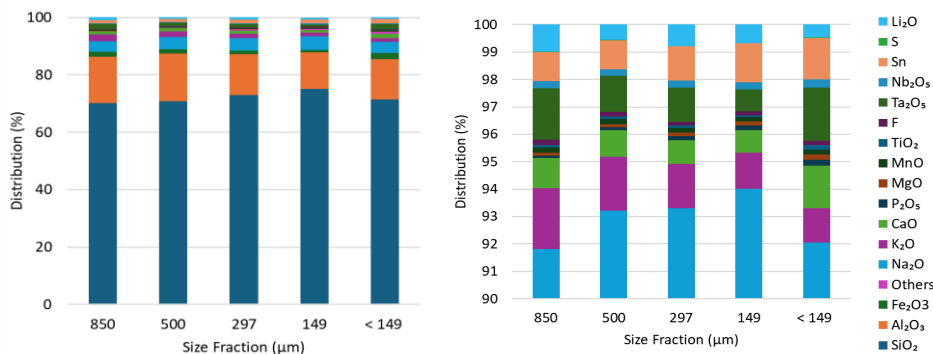
SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	Na ₂ O	K ₂ O	CaO	P ₂ O ₅	MgO
71.74	14.58	1.13	5.20	2.12	1.10	0.19	0.47
MnO	TiO ₂	F	Ta ₂ O ₅	Nb ₂ O ₅	Sn	S	Li ₂ O
0.18	0.08	0.19	1.60	0.28	1.23	0.02	1.05

The high silica content suggests that the tailings fraction consists of a substantial amount of non-lithium-bearing minerals. The grade of Fe₂O₃ indicates the presence of impurities in silicate minerals, which may influence the processing choice. A magnetic separation stage might be necessary if the material is intended for ceramics. According to Banks *et al.* [5], the spodumene concentrate should ideally contain less than 0.5% Fe₂O₃; however, regarding lithium extraction through chemical processing, Fe₂O₃ is not a significant concern.

The chemical components P₂O₅, F, and S may indicate the presence of phosphate minerals, fluorapatite, and sulfides, respectively. Fluorine may be associated with spodumene or the presence of residual fluorite.

The chemical analysis shows that valuable economic metals (Ti, Ta, Nb, Sn, and Li) are also present given that it is a tailing sample from tantalite and cassiterite concentration plants. The tailings have economic potential in lithium recovery, which may justify reprocessing. But, also, Ta₂O₅, Nb₂O₅, and Sn remain in the tailings, which may justify reprocessing to increase tantalum, niobium, and tin recovery.

Results from the granulochemical analysis of the head sample (Figure 3) identified higher grades of SiO₂ in all fractions (+850/-149 μm), and slightly higher of Al₂O₃. Related to the lower-grade components, Na₂O has the highest content in all size fractions. Finally, Li₂O has a higher grade in the fraction +850 μm.


Figure 3 Granulochemical analysis of tailings head sample of the Volta Grand mine

HLS Tests

Spodumene was separated from gangue minerals in the HLS tests using Bromoform. The distribution of Li₂O in dense medium products of different size fractions was determined based on the chemical content of this element provided by ICP-OES. The HLS

test results are shown in Table 2, which contains the Li₂O distribution (%) for float and sink products, in different size fractions.

Table 2 Results for the HLS tests of different particle size fractions in Bromoform

Size Fraction (μm)	Products (%)	Weight (%)	Li ₂ O (%)	Li ₂ O Distribution (%)
+850	< 2.89	67.13	0.12	5.10
	> 2.89	32.87	4.56	94.84
	Total	100.00	1.58	100.00
Size Fraction (μm)	Products (%)	Weight (%)	Li ₂ O (%)	Li ₂ O Distribution (%)
-850/+500	< 2.89	72.55	0.18	9.53
	> 2.89	27.45	4.52	90.52
	Total	100.00	1.37	100.00
Size Fraction (μm)	Products (%)	Weight (%)	Li ₂ O (%)	Li ₂ O Distribution (%)
-500/+297	< 2.89	76.89	0.07	5.13
	> 2.89	23.11	4.40	96.77
	Total	100.00	1.05	100.00
Size Fraction (μm)	Products (%)	Weight (%)	Li ₂ O (%)	Li ₂ O Distribution (%)
-297/+149	< 2.89	83.93	0.14	17.03
	> 2.89	16.07	3.56	83.00
	Total	100.00	0.69	100.00
Size Fraction (μm)	Products (%)	Weight (%)	Li ₂ O (%)	Li ₂ O Distribution (%)
-149	< 2.89	83.95	0.30	37.04
	> 2.89	16.05	2.67	63.06
	Total	100.00	0.68	100.00

A strong negative correlation exists between the Li₂O grade, the particle size fractions, the sink products, and the liberation of Li₂O minerals. Namely, lithium has a higher content in the coarser size fractions, as well as a greater distribution in the sink products as the granulometry increases, consequently its liberation.

Regarding the Li₂O distribution, over 90% of lithium is concentrated in the heavy fraction, demonstrating a high separation efficiency level, particularly for the size fractions: +850 μm; -850/+500 μm; and -500/+297 μm. In these size fractions, only about 5% of the lithium was found in the float fraction, indicating minimal loss in the tailings. Also, the sink fraction (> 2.89 g/cm³) concentrates most Li₂O, with grades above 4.40%. On the other hand, the float fraction (< 2.89 g/cm³) has low grades of Li₂O (between 0.07% and 0.18%).

In finer size fractions (-297/+149 and -149 μm), lithium content and distribution in the sink product decreases, possibly due to an increased feldspar content, as suggested by the granulochemical analysis. As noted by Banks *et al.* (1953), when spodumene

content decreases, feldspar content increases. This is significant because feldspar may be an important byproduct of the process and can be further recovered.

CONCLUSION

This paper aims to evaluate the feasibility of processing fine lithium mineral tailings using the dense medium separation method. Although many studies have investigated the application of DMS for the pre-concentration of spodumene in coarser particle size fractions (+ 840 μm), this work is unique in studying DMS applied to fine lithium tailings particles (- 840 μm).

The results of the HLS tests suggest that Dense Medium Separation (DMS) has the potential to effectively separate spodumene from gangue minerals such as quartz, albite, microcline, and muscovite. Most of the Li_2O content was found in the sink fraction (greater than 2.89 g/cm^3), whereas the float fraction exhibited low lithium contents. By adjusting the medium density according to particle size, it may be possible to further enhance the separation efficiency. Therefore, the reprocessing of tailings from the Volta Grande mine using DMS has the potential to be further used to improve the recovery of valuable metals.

ACKNOWLEDGEMENT

This work was funded by FAPEMIG and the FINEP in Brazil. The first author thanks the National Council for Scientific and Technological Development (CNPq) for financial support. We also appreciate AMG Mining for providing tailings samples and ICP-OES analysis from the Volta Grande Mine.

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