Alternative beneficiation of tantalite and removal of radioactive oxides from Ethiopian Kenticha pegmatite-spodumene ores

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Abstract: The beneficiation methods for Ethiopian Kenticha pegmatite–spodumene ores were assessed through mineralogical and quantitative analyses with X-ray diffraction (XRD) and energy-dispersive X-ray fluorescence (EDXRF). The tantalite in the upper zone of the Ken-

ticha pegmatite–spodumene deposit is 58.7wt% higher than that in the inner zone. XRD analysis revealed that the upper zone is dominated by manganocolumbite, whereas the inner zone is predominantly tantalite–Mn. Repeated cleaning and beneficiation of the upper-zone ore resulted in concentrate compositions of 57.34wt% of Ta_2O_5 and 5.41wt% of Nb_2O_5 . Washing the tantalite concentrates using 1vol% KOH and 1 M H₂SO₄ led to the removal of thorium and uranium radioactive oxides from the concentrate. The findings of this study suggest that the beneficiation and alkaline washing of Kenticha pegmatite–spodumene ores produce a high-grade export-quality tantalite concentrate with negligible radioactive oxides.

Keywords: beneficiation; manganocolumbite; pegmatite-spodumene; radioactive oxides; tantalite

1. Introduction

In the modern electronics and nuclear industries, both tantalum (Ta) and niobium (Nb) are key and critical metals [1–2]. Columbo–tantalite, which is the major source for these rare metals, occurs mainly in pegmatites associated with granites. The common name for the mineral is tantalite when tantalum predominates over columbium (Nb) and columbite/niobite when columbium is dominant [1,3]. The world resources available today may not meet future demands for Ta and Nb. These metals are recovered mainly from the minerals of "calton" (columbite-tantalite ore), which consists oxides of Ta and Nb (OTN) in the form of ((Fe,Mn)(Ta,Nb)₂O₆) and small amounts of other Ta oxides such as microlite, ixiolite, and wodginite [2–9]. The concentrates from this ore typically contain Ta₂O₅ between

10wt% and 60wt% in the case of concentrates from leading producers such as Greer Lake (Manitoba), Tanco pegmatites (Canada), Kenticha pegmatites (Ethiopia), Greenbushes and Wodgina pegmatites (Western Australia), Yichun complex (China), granitic pegmatites of the Pampean Ranges (Argentina), and rare-metal granitoids of the Eastern Desert (Egypt) [10]. The classification of pegmatite ores is based on the metamorphic environment, mineralogy, elemental composition, and texture; the ores are divided into classes, subclasses, types, and subtypes. On the basis of their mineralogical composition, the Li-Cs-Ta (LCT) family of the rare-element class is the economically most important family for Ta and Nb, and four pegmatite types (beryl, complex, albite-spodumene, spodumene) exist [6,11-17]. According to the mineralogical composition of Kenticha pegmatite, it is classified into beryl, feldspar-muscovite, albite-spodumene,



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and spodumene. Spodumene contains the highest compositions of Mn-tantalite, along with radioactive elements such as Th and U, which require careful removal for the concentrate product to meet export standards [13]. The beneficiation of OTN also requires the removal and separation of associated impurities from each other because Nb, Ta, Fe, and Ti are usually associated with one another in minerals. Because of their similar chemical properties, these elements are separated with difficulty [11–12]. This Kenticha pegmatite is the site of the open-pit tantalum mining operations and is the main subject of this paper.

According to Küster *et al.* [13] and Kim *et al.* [14], the Kenticha rare-element pegmatite (Ta–Li–Nb–Be–Cs) mineralized zone is located in the ophiolitic fold and thrust complex of southern (Oromia Regional State) Ethiopia, spanning approximately 2 km in length and 400–700 m in width, which represents a globally important tantalum source. Exploration by Ethiopian Mineral Petroleum and Biofuel Corporation (EMPBC) under the Federal Democratic Republic

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of Ethiopia. Ministry of Mines. Petroleum and Natural Gas is ongoing exporting high-grade or 50wt%-60wt% Ta₂O₅. The possible standby resource of primary Kenticha pegmatite ore is 17000 t at the Ta₂O₅ grade of 0.017wt%, whereas it was estimated to be 2400 t at 0.015wt% Ta₂O₅ in the weathered zone. The deposit of Kenticha is related to late Neoproterozoic I-type granites, a highly complex sub-horizontal pegmatite sheet with a thickness approaching 100 m and classified into three zones—the upper zone (UZ), the inner zone (IZ), and the lower zone (LZ), on the basis of the scheme of Černý and Ercit [13–15]. The exploitable and highly concentrated tantalite occurs in the UZ and is characterized by spodumene. Spodumene-bearing pegmatite is white (Fig. 1) and characteristically occurs in giant wedge-shaped crystals up to 4 m in length and with various Ta/Nb mass ratios from 3:1 to 1:1 and lower, which imitates the Ta mineralization potential. The Ta/Nb mass ratio is the highest in the spodumene unit, which is the focus of the present mining and future development for the extraction of Ta [13–17].



Fig. 1. View of the Kenticha pegmatite mined by EMPBC: (a) 20-m inner zone; (b) upper zone of the mined spodumene.

The beneficiation of tantalite ores often involves pre-concentration, feather concentration, and concentrate clean-up for less than 0.1wt% Ta2O5. The choice of any or all of these processes and their success would normally depend on the physiochemical properties of the ore, its Mn/Fe and Ta/Nb ratios, its response to magnetic fields, the presence of radioactive materials, the nature of the ore, and particularly the content of Ta₂O₅ in the ore relative to its associated minerals and impurities. The primary choice of the beneficiation process of an ore containing OTN usually starts with an enrichment step, which may involve mineral processing steps such as sizing and classification, washing, gravity separation, and magnetic separation steps [1-2]. However, the most well known beneficiation processes for concentrating tantalite ore are gravity and magnetic separations. Secondary ore concentration stages are generally required to increase the content of Ta2O5 before further processing to recover Ta and Nb and to remove associated Ta-bearing minerals, impurities, and radioactive elements to acceptable levels [1–2,18]. The chemical separation or purification of Ta and Nb from their minerals is a complex and difficult process, mainly because of the chemical and physical similarities between these two elements; for example, their ionic radii, resistance to chemical attack, and the ease with which their compounds are hydrolyzed in aqueous solutions are all similar [19]. Associated heavy minerals such as hematite, manganese oxides, and rutile are subsequently subjected to magnetic separation, where the hematite transformed to ferromagnetic magnetite is concentrated from nonmagnetic ore minerals [4].

Some studies have indicated the successful removal of up to 97wt% Fe and 86wt% Ti from tantalite using magnetic separation and 76.32wt% ThO₂ and 44.98wt% U₃O₈ radioactive elements using acid leaching from high-grade ores. In addition, 93.65wt% Nb and 93.6wt% Ta were recovered from a low-grade ore using a KOH roast–water leach system. However, approximately 80wt% Sn, 50wt% Ti, 20wt% Fe, and 20wt% Mn were also leached from

low-grade ores [5,20–22]. The separation of thorium from uranium was carried out using two different stripping steps to achieve recoveries of 99.6% ThO2 and 91.2% U3O8, along with 4.45% and 0.99% of Nb2O5 and Ta2O5, respectively [23-24]. Htwe and Lwin [5] studied the extraction of niobium oxide from columbite-tantalite concentrate containing 19.29wt% Nb₂O₅, 9.93wt% Ta₂O₅, and other impurities. A process involving acid digestion resulted in 74% Nb₂O₅. El-Hussaina and Mahdy [25] reported that a final product of 100% Nb₂O₅ and Ta₂O₅ was obtained when an Egyptian ore was leached using 4.3 N HF and 5.7 N H₂SO₄. Another study on the dissolution behaviors of Ta₂O₅, Nb₂O₅, and their mixture in KOH and H2O showed that the dissolution rate of tantalum increased and the dissolution rate of niobium decreased at 400°C [22]. Notably, however, these tests were carried out under relatively higher concentrations of acids and KOH at a higher temperature. High mineral acid concentrations can also affect the formation of niobium and tantalum complex species. The literature contains a few studies on the dissolution behavior of Ta2O5 and Nb2O5 with acids for high-grade tantalite ores and with alkaline solutions at room temperature for low-grade tantalite ores. However, to date, no work has been reported on washing as well as decomposition for high-grade tantalite ores using low concentrations of acids and alkaline solutions; therefore, in this work, we used 1 M H₂SO₄ and 1vol% KOH to remove radioactive oxides from the ore.

In this paper, we proposed an alternative approach to the beneficiation of two different OTN-bearing spodumene white sands from the same deposit. The efficiency of gravity and magnetic separation methods and the suitability of acid and alkaline washing for radioactive material removal from Ethiopian Kenticha tantalite sample ores were also investigated.

2. Experimental

2.1. Materials

The tantalite ore used for this investigation was sourced from the Kenticha tantalite mine in the regional state of Oromia, Ethiopia. The mineralogical purity of the ore was investigated using a Shimadzu Maxima-XRD-7000 X-ray diffractometer equipped with a Cu K_a radiation source (λ = 0.1540600 nm) operated at 40.0 kV and 30.0 mA. The resulting diffractograms were interpreted using the Diamond (version 4.2.2) software, the Match! (version 3.2.2) software, and the COD reference database. An energy-dispersive X-ray fluorescence (EDXRF 2800) was used for elemental analysis of the tantalite mineral and was calibrated using high-grade samples. Beneficiation of the ores was carried using a Frantz model LB1 magnetic barrier laboratory separator and a Laboratory LY model LY1000 \times 450 shaking table. The mass of the ores was measured using a Sartorius ENTRIS323-1S chemical weighing balance. Analytical-grade H₂SO₄ and KOH (Sigma-Aldrich) without further purification and doubly distilled water were used in this research.

2.2. Methods

As suggested by Küster et al. [13], to obtain an ore which have the highest tantalite content, we collected the sample ores from the UZ and the 20-m-depth IZ of the Kenticha pegmatite-spodumene ore deposit (Fig. 1, white-colored ore) currently mined by Ethiopian Mineral Petroleum and Biofuel Corporation (EMPBC). 10 kg samples (sample 1A and 1B) were milled manually with a mortar and pestle to less-than-200 to 400 and above-400 mesh sizes. This step was followed by washing and decantation to reject residues. The samples were then treated using shaking tables to recover the heavy brown-black portion of the ore. Further beneficiation was conducted by gravity separation (at 25°C and 250 r/min for 60 min) and magnetic separation according to schemes 1 and 2. The presence of magnetic minerals in nonmagnetic samples was checked using a permanent hand-held magnet.

The next step of beneficiation involved the removal of radioactive oxides such as uranium and thorium from the nonmagnetic portion of the sample. Approximately 2.0 g of a nonmagnetic fraction (sample 6) was accurately weighed and subsequently transferred to a pre-weighed 100-mL beaker. The washing was carried out using 1 M acid (H₂SO₄) and 1vol% alkaline (KOH) solutions at room temperature (20°C) and for a washing time of 1 min. The obtained slurry was centrifuged, and the supernatant liquid was decanted and stored for further study. The solid non-magnetic samples (samples 7 and 8) were dried in the open air for 2 d. Sample 8 was washed again with 1 M H₂SO₄ and 1vol% KOH solutions to obtain samples 10 and 11, respectively, to investigate whether further removal of radioactive materials could be achieved. The validity of the primary beneficiation was tested by mixing the light portion from Scheme 1 (i.e., sample 3) with the original ore in a mass ratio of 1:1 to obtain sample 1C (see Scheme 2). All samples except the low grades such as pegmatite-spodumene and residues were analyzed by powder X-ray diffraction (XRD) and energy-dispersive X-ray fluorescence (EDXRF). All measurements were carried out in triplicate.



Scheme 1. Systematic separation approach for the beneficiation of Kenticha pegmatite-spodumene ores. Sample 1A was taken from the upper zone of the deposit, and sample 1B was from the 20-m-deep inner zone of the currently mined deposit.



Scheme 2. Systematic connected approach for the beneficiation of Kenticha pegmatite–spodumene ores. Sample 1C was prepared by mixing a 1:1 mass ratio of pegmatite–spodumene ores with sample 3 of Scheme 1.

3. Results and discussion

3.1. Mineralogical studies of the Ethiopian Kenticha ore

The EDXRF quantitative analysis of ore samples from different mining zones revealed that the composition of the Kenticha ore deposit varies substantially depending on the mining locations. As evident from Tables 1 and 2, the Ta_2O_5 content in the highly concentrated zones was as high as 70wt%, whereas the Ta_2O_5 content in other zones was as low as 26wt%. However, the composition of Nb₂O₅ in the

low-Ta₂O₅-concentration zones was as high as 31wt%, although Nb₂O₅ contents as low as 7wt% have been reported. The amounts of U and Th oxides in the ore were noted because these are the major penalty elements. In the Kenticha pegmatite ore, certain parts of the coltan mineralization contain low levels of uranium and lithium. In most parts of the Kenticha coltan, the uranium content was above the critical level of 0.5wt% (Tables 1 and 2) and the lithium grade greater than 1.64wt% was obtained in the spodumene (results not shown) [26–29].

Table 1. EDXRF mineralogical analysis of the tantalite ore samples from the Kenticha deposit in Ethiopia (high-concentration lots).Source: EMPBC, Feb. 2016

Lot No.	$Ta_2O_5 / wt\%$	Nb_2O_5 / wt%	U_3O_8 / wt%	TiO_2 / wt%	SnO_2 / wt%	$ThO_2 / wt\%$	Sb / ppm
36	69.71	7.21	0.30	0.25	0.085	0.026	<20
52	67.42	10.84	0.56	0.28	0.210	0.088	<20
37	62.98	11.61	0.61	0.32	0.090	< 0.005	<20
53	61.57	12.95	0.86	0.39	0.320	0.086	<20
39	60.63	9.81	0.56	0.52	0.070	0.015	<20
54	60.23	12.55	1.19	0.41	0.340	0.091	< 0.001
32	60.13	15.19	0.55	0.24	0.090	0.025	<20
33	59.23	17.38	0.80	0.15	0.081	0.017	<20
35	58.93	9.06	0.42	0.42	0.079	0.024	<20
29	57.76	13.93	0.67	0.64	0.037	< 0.01	<20

Table 2. EDXRF mineralogical analysis of the tantalite ore samples from the Kenticha deposit in Ethiopia (low-concentration lots).Source: EMPBC, Feb. 2016

Lot No.	$Ta_2O_5 / wt\%$	Nb_2O_5 / wt%	U ₃ O ₈ / wt%	TiO_2 / wt%	SnO_2 / wt%	ThO ₂ / wt%	Sb / ppm
67	34.89	10.56	0.44	2.53	0.45	0.068	<20
80	34.86	21.87	<0.2	1.58	0.15	< 0.02	<20
68	34.83	13.32	0.90	0.90	0.69	0.019	<20
70	33.75	21.34	0.77	0.43	0.61	0.049	30
81	33.27	24.24	0.40	0.85	0.11	< 0.02	<20
71	33.01	26.33	0.52	0.39	0.63	0.015	<20
76	32.07	18.92	0.48	5.17	0.13	0.034	< 0.002
72	31.80	23.03	0.85	0.30	0.63	0.044	<20
83	30.87	26.72	0.43	1.31	0.10	0.200	<20
82	26.33	31.01	0.26	1.24	0.07	0.023	<20

3.2. Gravity and magnetic separation

The conventional method for the beneficiation of a tantalite ore is the gravity separation technique, which allows Taand Nb-bearing minerals to be concentrated together with other heavy minerals [4]. However, in the present study, the focus is the beneficiation of oxides of Ta and Nb with a view to generating economic value from the secondary ore concentrates in the Ta-bearing minerals. The other associated heavy-metal-containing minerals such as hematite, manganese oxide, and rutile were subsequently subjected to magnetic separation, where the hematite transformed to ferromagnetic magnetite was concentrated from nonmagnetic minerals [4]. Gravimetric analysis was carried out to determine the grade of Ta_2O_5 in the concentrates after gravity and magnetic separation. The particle size distribution of the sample used for this study is given in Table 3.

Table 3. Particle size distribution of pegmatite-spodumene ores

Sieve	Mass ret	ained / kg	Percentage retained / wt%			
size	Sample 1A	Sample 1B	Sample 1A	Sample 1B		
200	0.022	0.017	0.22	0.17		
250	0.015	0.012	0.15	0.12		
300	0.011	0.008	0.11	0.08		
350	0.008	0.005	0.08	0.05		
400	0.007	0.004	0.07	0.04		
>400	0.001	0.001	0.01	0.01		
Sum	0.64	0.047	0.64	0.47		

As shown in Table 4, the nonmagnetic (tantalite) fraction is higher in sample 1A than in sample 1B; in addition, the beneficiation with a mesh size of 200 produces the highest mass of retained tantalite. The gravimetric results indicate that sample 1A produces higher (58.7wt%) tantalite than sample 1B because of the meteorological conditions of the Kenticha deposit. The 20-m-deep mined samples have a lower tantalite mass fraction than the samples from the upper part of the deposit (sample 1A), as shown in Tables 1 and 2 [13-14]. Further studies using XRD (Fig. 2) indicate that the dominant phases in sample 1A are $Mn_{0.3}Nb_{0.24}O_2Ta_{0.42}$ (76.0mol%) and Nb_{0.61}Ta_{2.39}TeI₇ (20.6mol%). However, the primary phase in sample 1B was found to be a tantalite-(Mn) ((Fe_{0.09}Mn_{0.88}Nb_{0.28})₆Ta_{1.72}). Surprisingly, because of the absence of the fingerprint of OTN in the 30° of sample 1B, the chemical composition of sample 1A is expected to belong to manganocolumbite, including associated minerals (considered as residue in this study) [1,30-33].

Table 4. Concentrated mass of pegmatite-spodumene ores

Sample	Sample code	Mass / kg
	Theoretical*	0.015
1 4	Magnetic (5)	0.046
IA	Nonmagnetic (6)	0.022
	Nonmagnetic (Sample 1 + residue) (14)	0.045
1B	Theoretical*	0.015
	Magnetic (5)	0.027
	Nonmagnetic (6)	0.017

Note: *Theoretical data are based on Küster et al. [13].

General differences in the XRD patterns of samples 1A and 1B (Fig. 2) indicate the differences in mineralogy and the existence of additional elements in the tantalite ore. These results suggest that better enrichment of OTN requires removal and separation of associated impurities to improve the overall grade of Ta in the concentrate. Beneficiation of a mixture of pegmatite–spodumene ores with the residues (light and magnetic portions) (Scheme 2) is the best alternative approach for higher grades of tantalite ore over the primary beneficiation of pegmatite ore (Scheme 1). As shown in Table 5, sample 14 scored 57.34wt% of Ta₂O₅.



Fig. 2. Compositional XRD patterns of pegmatite–spodumene ore sample 1A from the upper zone and sample 1B from the 20-m-deep inner zone currently mined by EMPBC.

3.3. Acid and alkaline washing

The presence of radioactive elements such as Th and U in Kenticha tantalite complicates the transportation, handling, and processing of concentrates (see Th and U quantities from Tables 1 and 2) [13,14,26-29]. Acid and alkaline washing were used to assess the extent of removal of radioactive elements from the tantalite concentrates. Following washing with low-concentration acid and alkaline solutions, the chemical composition of the samples were analyzed by EDXRF; the results are presented in Table 5. Table 5 reveals that samples 6, 8, 11, 14 and u3 are mainly composed of Ta_2O_5 (> 45wt%), suggesting that the samples represent tantalite ores. According to the grades defined by the Tantalum-Niobium Study Center [33], such ores are considered to have excellent grades of tantalum. Samples 7, 10, and u represent columbite because they contain more Nb₂O₅ than Ta₂O₅ and also negligible amounts of Fe, Ti, Th, and U oxides. These results indicate that washing with dilute H₂SO₄ and KOH at room temperature resulted in the removal of the majority of radioactive oxides. However, washing the tantalite with 1 M H₂SO₄ solution resulted in a decrease in the percentage of Ta₂O₅ and an increase in the percentage of Nb₂O₅. By contrast, washing of tantalite with 1vol% KOH alkaline solution resulting in an increase in the percentage of Ta₂O₅ and a decrease in the percentage of Nb₂O₅. Therefore, washing the tantalite concentrate using dilute KOH is advisable to increase the percent of Ta_2O_5 before further extraction and to reduce the amount of radioactive elements. Notably, the limits for Th and U contents allowed in exportable concentrates are 0.1wt% ThO₂ and 0.1wt% U₃O₈ [1]. The beneficiation and washing procedures carried out in this study produce tantalite concentrates of acceptable quality that meet the essential requirements for safe handling, transport, and storage.

Comple 1A (comple on do)	Content / wt%							Mass ratio of
Sample TA (sample code)	Ta ₂ O ₅	K_2O	Nb_2O_5	TiO ₂	Fe ₂ O ₃	ThO ₂	U_3O_8	Ta/Nb
Magnetic (5)	6.25	0.41	10.15	5.33	80.23	0.06	0.10	0.62
Nonmagnetic (6)	45.71	0.67	5.51	Nd	Nd	0.04	Nd	8.30
Acid washed (7)	12.73	0.25	21.15	Nd	Nd	0.25	Nd	0.60
Alkaline washed (8)	45.04	0.41	5.49	Nd	Nd	0.00	Nd	8.20
Acid washed (10)	12.08	0.16	20.97	Nd	Nd	0.09	Nd	0.58
Alkaline washed (11)	45.09	0.65	5.41	Nd	Nd	0.00	Nd	8.33
Ore plus residue (14)	57.34	1.66	5.41	Nd	Nd	0.09	Nd	10.59
Acid washed (u)	11.31	1.36	14.13	Nd	0.00	0.08	Nd	0.80
Alkaline washed (u3)	62.12	1.32	5.15	Nd	0.00	0.00	Nd	12.06

 Table 5.
 Elemental analysis of concentrates by XRF

The predominant compound identified from samples 8, 11, and 14 upon washing was manganocolumbite, as evidenced by XRD analysis (Fig. 3) and the presence of Fe, Mn, Nb, Ta, and O [1,32]. The main mineral constituents of the residues were similar to those of the raw ore (sample 1A) with undissolved Ta_2O_5 in manganocolumbite peaks at 30° and 60°, which supports the elemental composition shown in Table 3 [1,30–33]. The absence of the core peak at 25° and the presence of a medium-intensity peak at 30° and a low-intensity peak at 60° in the XRD pattern of sample 5 are observed due to reduced Ta_2O_5 composition, whereas the existence of a sharp peak at 44° is attributed to a higher Fe₂O₃ concentration as compared to samples 1A and 14. These observations are in agreement with EDXRF results



Fig. 3. XRD spectra of the Kenticha pegmatite–spodumene ore (sample 1A), nonmagnetic fractions washed using 1vol% KOH (samples 8 and 11), the ore and residue mixture after concentration (sample 14), and the magnetic fraction (sample 5).

that confirm the main characteristics of magnetic materials [1,30–33]. Again, the results from samples 8 and 11 show that washing with dilute alkaline solution produces Kenticha tantalite concentrate of high quality that satisfies the Colton's criteria for exports.

4. Conclusions

In this study, the primary beneficiation methods of Kenticha pegmatite–spodumene ores were examined. The results led to the following conclusions:

(1) Ethiopian Kenticha pegmatite–spodumene beneficiates relatively easily with gravity and magnetic separation techniques, producing high-grade Ta and Nb oxide concentrates. The upper geographical zone of the deposit resulted in better quality tantalite concentrate as compared with the 20-m-deeper zone.

(2) Beneficiation of the mixture of pegmatite–spodumene ores with residues has shown best alternative approach for higher grade of tantalite ore over the primary beneficiation of pegmatite ore.

(3) When the tantalite concentrate was washed using 1 M H_2SO_4 , high yields of Nb_2O_5 with low levels of Th and U were obtained; by contrast, washing with 1vol% KOH resulted in the highest level of Ta_2O_5 , with almost no oxides of Th and U present.

(4) The EDXRF analysis of the magnetic fraction of tantalite concentrate indicated a low content of Th and U.

(5) The analysis using EDXRF and XRD has shown that Ethiopian tantalum ores are of high grade and can therefore be subjected to direct processing for tantalum and niobium products without the need for complex and costly concentration procedures.

(6) Knowledge of the presence of very low concentrations of radioactive oxides in the samples would assist in the design of appropriate beneficiation and extraction routes for similar deposits in Ethiopia.

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