JOM, Vol. 70, No. 12, 2018
https://doi.org/10.1007/s11837-018-3187-3

Separation of Radioactive Elements from Ethiopian Kenticha Pegmatite Ore by Hydrometallurgical Methods

MULUGETA SISAY CHERU,[1,6] ALBERTO VELÁZQUEZ DEL ROSARIO,[2]
ABUBEKER YIMAM ALI,[3] GOITOM GEBREYOHANES BERHE,[4]
and BOGALE TADESSE[5]

1.—School of Materials Science and Engineering, Jimma University, P.O. BOX 378, Jimma, Ethiopia. 2.—Federal Technical and Vocational, Education and Training Institute, Addis Ababa, Ethiopia. 3.—School of Chemical and Bio Engineering, Addis Ababa Institute of Technology, Addis Ababa, Ethiopia. 4.—Department of Chemistry, Mekelle University, PO Box 823, Mekelle, Ethiopia. 5.—Western Australian School of Mines, Curtin University, Kalgoorlie, WA 6430, Australia. 6.—e-mail: mulugetajimma07@gmail.com

The leaching and extraction behavior of uranium and thorium from a high-grade Ethiopian pegmatite ore in a mixture of hydrofluoric acid and sulfuric acid has been investigated. The effects of variables such as the temperature, particle size, acid concentration, and leaching time were studied. The leaching efficiency of uranium increased with increasing temperature to 150°C, at which 96% removal of uranium was achieved. Particles in the size range of − 100 + 75 μm resulted in the highest leaching of uranium, while formation of a colloidal suspension was observed when using a fine particle size fraction (− 75 μm). The dissolution of uranium increased with increasing leaching time. No significant systematic dependence of the leachability of thorium on the above variables was observed. Optimum extraction of uranium and thorium using D_2EHPA was obtained when using aqueous/organic phase volume ratio of 1:1, solvent concentration of 0.3 M, and contact time of 20 min.

INTRODUCTION

Tantalum (Ta) and niobium (Nb) are key elements in modern society due to their wide applications in the electronics and nuclear industries. Pegmatites are major sources of Ta and Nb, with active mining operations in Brazil, Australia, Canada, Mozambique, and Ethiopia.[1] The primary source of Ta/Nb is the columbite–tantalite mineral. Ta and Nb also exist in a number of other minerals as complex oxides and hydroxides, including microlite, wodginite, euxenite, and ixiolite.[2] In columbite–tantalite ores, Ta and Nb often occur in association with thorium (Th), uranium (U), titanium, and rare-earth elements.[3]

Extraction of Ta and Nb from pegmatite ores containing radioactive elements such as thorium and uranium presents significant environmental challenges. Exposure of people and the environment to radiation can occur during mining and processing of ores, during handling and transportation of concentrates containing radioactive materials, or from wastes generated by processing plants. Generally, the allowable limits of U and Th in tantalum/niobium minerals and concentrates for export purposes are set at 0.1% U_3O_8 and 0.1% ThO_2.[4] Thus, safe removal of Th and U from minerals and concentrates as early as possible is critical to avoid exposure to radioactive materials during processing, handling, transportation, and tailings disposal.

Acid leaching is commonly employed to recover uranium and thorium from pegmatite ores. Sulfuric acid decomposition of ore from the Eastern Desert of Egypt, consisting of euxenite, betafite, thorite, and zircon, resulted in ThO_2 and U_3O_8 dissolution rates of 86.5% and 91.1%, respectively.[5] In another study, a mixture of H_2SO_4 and HNO_3 at 1:3 ratio resulted in leaching efficiency of 86% and 60% for thorium and uranium, respectively.[6] The low recovery of uranium was attributed to the refractory nature of the host mineral. Presence of reactive gangue minerals during leaching leads to low U recovery.[7] Sulfuric acid leaching of betafite showed preferential leachability of U over Ti, Ta, and Nb, which are commonly found in pegmatite ores.[8] Use of HF for recovery of tantalum and niobium and removal of radioactive and other impurities from pegmatite ores has been reported in a number of studies.[9–12] For example, HF was used for direct dissolution of tantalite ore to remove both uranium and thorium from the concentrate.[13]

Solvent extraction is used to remove radioactive elements from leach liquors. Solvents such as tributyl phosphate (TBP) and other organophosphorus compounds are used as uranium extractants.[14] TBP was reported to be the simplest and most efficient solvent, as it gives more reliable results in terms of separation of uranium from trace metals.[7,15] A mixture of solvents was found to lead to high efficiency and selectivity for uranium extraction.[16]

Mineralogical factors associated with ores, including the degree of liberation, mineral association, and gangue mineral composition, play key roles in successful removal of Th and U from ores and concentrates.[6,7,16,17] For instance, differences in the U leaching efficiency of 53% were observed for two natural betafite samples over various processing conditions.[18,19] Thus, it is expected that removal of radioactive elements could be more effective for some types of ores than others based on certain mineralogical factors. The aim of the present study is to investigate the leaching behavior of a pegmatite ore from Kenticha Mine, Southern Ethiopia, which contains relatively high amounts of radioactive U and Th oxides.[20] Leaching experiments were conducted using a mixture of HF and H_2SO_4. The effects of variables including temperature, leaching time, particle size, and HF:H_2SO_4 ratio on the removal efficiency of radioactive oxides was investigated.

EXPERIMENTAL PROCEDURES

Materials

A pegmatite ore sample was collected from five different zones of Kenticha Mine, Southern Ethiopia. Analytical-grade reagents (Sigma Aldrich) HF (48% wt/wt) and H_2SO_4 (98% wt/wt) were used for leaching. Di(2-ethylhexyl) phosphoric acid (D_2EHPA) was used for extraction, while ammonium fluoride and sodium carbonate were used for stripping. Deionized water was used for dilution and solution preparation. The particle size was analyzed using standard mesh sieves (No 72 PAT), according to ASTM standard.[21] Elemental analysis of feed samples and leached residues was conducted using energy-dispersive x-ray fluorescence (EDXRF, Epsilon 3^{XLE}, PANalytical, The Netherlands). Solutions were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES). Changes in topography and composition before and after leaching of the sample were studied using scanning electron microscopy (SEM) equipped with energy-dispersive spectroscopy (EDS) (JEOL JSM-848). Thermogravimetric analysis–differential thermal analysis (DTA–TGA, STA 409 PC) was used for stability measurements by recording the rate of weight loss of the sample with increase in temperature, and to investigate the moisture content of the ore and the presence of impurities that decomposed at higher temperature.

Methods

The parent pegmatite ore was enriched to tantalite concentrate by gravity and magnetic separation. Details of this beneficiation process can be found elsewhere.[10] The composition of the tantalite concentrate for the pegmatite samples collected from various zones showed significant variation in the U and Th distribution from one zone to another, with the highest U_3O_8 and ThO_2 concentrations recorded as 1.32 wt.% and 0.6 wt.%, respectively. The concentrate was milled to obtain particle size fractions of -75 μm, $-100 + 75$ μm, and $-250 + 100$ μm. Each leaching experiment was conducted on a sample of 10 g in an autoclave with 250-mL Teflon [polytetrafluoroethylene (PTFE)] beakers placed on a hot plate with variable temperature and stirring rate of 250 rpm. Extraction of U and Th was conducted using D_2EHPA at 50°C, pH 2, and various solvent concentrations (0.1–0.3 M). The aqueous (containing Nb and Ta) and organic (containing U and Th) phases were separated using a separation funnel when equilibrium was reached (20 min), and the extraction efficiency of U and Th into the organic phase was calculated. Then, U and Th stripping was conducted using sodium carbonate and ammonium fluoride, respectively. All experiments were repeated at least five times, and the mean value for each test is reported.

RESULTS AND DISCUSSION

Preliminary tests were conducted to determine the most effective HF:H_2SO_4 ratio leading to reasonable decomposition of the solid sample. The HF:H_2SO_4 ratio of 3:1 (N:N) was found to be most appropriate, based on the amount of undissolved residue left over after leaching. During mixed-acid leaching, while HF may be useful for decomposition of silicate minerals, H_2SO_4 may ionize to form sulfate, bisulfate, and hydrogen ions. These species react with hexavalent uranium (UO_2^{2+}) to produce uranyl sulfate and complex uranyl sulfate anions according to the following reactions:[22]

$$UO_3 + 2H^+ \rightarrow UO_2^{2+} + H_2O \tag{1}$$

$$UO_2^{2+} + SO_4^{2-} \rightarrow UO_2SO_4 \tag{2}$$

$$UO_2SO_4 + SO_4^{2-} \rightarrow \left[UO_2(SO_4)_2\right]^{2-} \tag{3}$$

$$\left[UO_2(SO_4)_2\right]^{2-} + SO_4^{2-} \rightarrow \left[UO_2(SO_4)_3\right]^{4-} \tag{4}$$

Dissolved uranium may occur in any of the above forms, depending upon the acid and uranium concentrations, temperature, and other system variables. In the following sections, the effects of the leaching temperature, time, particle size, and acid-to-ore ratio on the dissolution of U and Th are described.

Effect of Temperature

The effect of temperature on the uranium and thorium leaching from tantalite using HF:H_2SO_4 ratio of 3:1 was studied in the range from 90°C to 170°C. Figure 1 shows the percentage of U and Th dissolved during leaching at various temperatures. The leaching efficiency of U increased with increasing temperature up to 150°C, after which a slight decrease was observed. Compared with the amount of U in the initial sample (1.32 wt.%), 96% dissolution was observed at 150°C. The dependence of the leaching of Th on temperature was somewhat mixed, with a decreasing trend in the temperature range from 90°C to 130°C but increasing trend in the temperature range from 130°C to 170°C, with the highest dissolution of 85% obtained at 170°C. The high dissolution of thorium at lower temperatures may be due to formation of soluble sulfate octahydrate [$Th(SO_4)_2{\cdot}8H_2O$].[23] At higher temperatures, HF may be the main reason for Th dissolution.

Effect of Particle Size

It is known that particle size generally plays a major role in leaching processes. In this study, particle size fractions of − 75 μm, − 100 + 75 μm, and − 250 + 100 μm were considered. The highest leaching of U of 95% was found when using the − 100 + 75 μm particle size fraction. When using the finer particle size range (− 75 μm), the leaching of U was 91%. A complex solution forms during leaching at this size fraction, hindering separation. Complex aluminosilicates in pegmatite ores may undergo dissolution in H_2SO_4; For example, Eq. 5 shows one possible reaction for montmorillonite which leads to formation of silicic acid:

$$
\begin{aligned}
&(\mathrm{Mg,Ca})\mathrm{O}\cdot\mathrm{Al_2O_35SiO_2}\cdot n\mathrm{H_2O}+4\mathrm{H_2SO_4}\\
&\quad\rightarrow\mathrm{Al_2(SO_4)_3}+5\mathrm{H_2SiO_3}+(\mathrm{Mg,Ca})\mathrm{SO_4}\\
&\qquad+(n-1)\mathrm{H_2O}
\end{aligned}
\tag{5}
$$

The silicic acid forms colloids, which then precipitate as a gel, causing difficulty in subsequent processing steps. The formation of a colloidal suspension when using the − 75 μm particle size may be due to Reaction 5 occurring during leaching. In this study, overgrinding resulted in increased pulp viscosity, which adversely affected the leaching rate. The lowest leaching of U (75%) was observed for the − 250 + 100 μm size fraction, probably due to poorly liberated U- and Th-bearing minerals becoming less accessible for leaching. A similar trend in leachability with particle size was observed for Th.

Effect of Leaching Time

The effect of time on the leaching efficiency of U and Th with 3HF + H_2SO_4 was studied for leaching times of 1–4 h. Figure 2 shows that the dissolution of uranium increased with increasing leaching time, whereas no systematic variation in the leaching rate with time was observed for thorium.

Based on the optimum leaching conditions identified above, a comparison of the U and Th removal for samples collected from five different zones of the Kenticha deposit is presented in Table I. It can be seen that U_3O_8 and ThO_2 contents as low as 0.01 wt.% (zone 1) were observed in the residues after leaching, indicating almost complete removal of these radioactive oxides. On the other hand, relatively low Ta and Nb dissolutions were observed

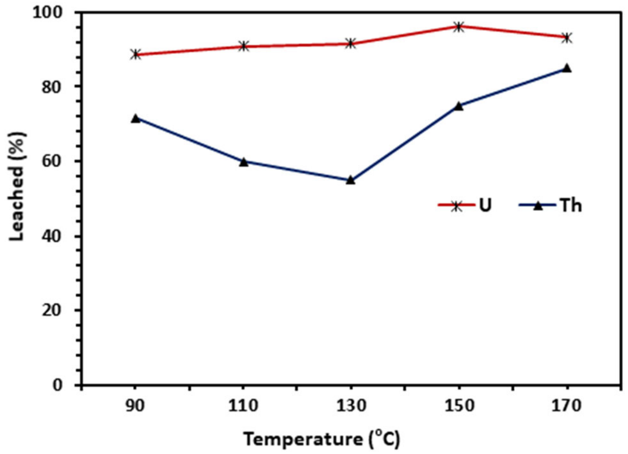


Fig. 1. Leaching of U and Th using HF:H_2SO_4 molar ratio of 3:1 at various temperatures with leaching time of 3 h.

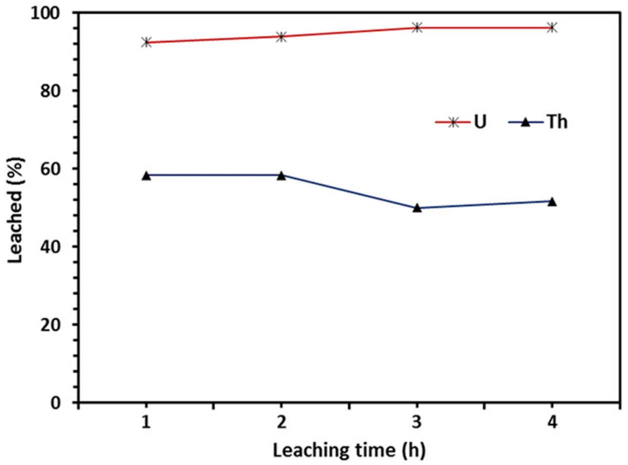


Fig. 2. Effect of time on leaching of U and Th using HF:H_2SO_4 molar ratio of 3:1 at temperature of 150°C.

in this study, in agreement with other studies conducted on similar ores.[6,24]

Characterization of Tantalite before and after Leaching

Thermogravimetric Analysis

The stability of the tantalite ore was analyzed using TGA-DTA. Figure 3a shows that the weight loss in the pegmatite ore on heating to 1000°C was insignificant (1.6%). Differential thermal analysis (green line) revealed a heat of transition of less than zero at the maximum temperature (endothermic process). Figure 3b indicates that the weight loss for a HF/H_2SO_4-treated sample reached up to 40% relative to the feed. The initial loss in weight between 90°C and 150°C is attributed to evolution of gaseous H_2O and any adsorbed HF. Sublimation of $TaOF_3$(g) was seen at about 280°C, and decomposition of niobium dioxyfluoride (NbO_2F) and tantalum dioxyfluoride (TaO_2F) was observed at about 650°C and 720°C, respectively.[25] The significant weight loss at 1000°C shows the vulnerability of grain boundaries to breakage after acid dissolution.

SEM–EDS Analysis

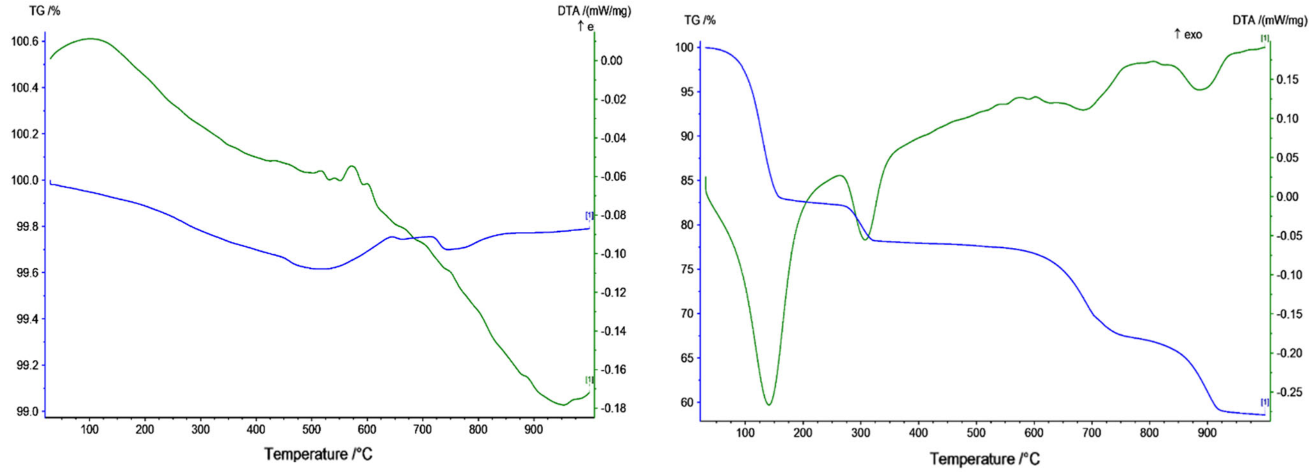
The morphology and composition of the acid-treated sample were analyzed by SEM–EDS. A comparison of the changes in topography and composition between the feed pegmatite ore and the acid-treated tantalite is shown in Fig. 4a and b, respectively. Coarse-grained homogeneous topography with few grain boundaries was observed for the tantalite feed (Fig. 4a). The corresponding EDS results indicated presence of uranium, thorium, and tantalum, as expected. The acid-treated sample shown in Fig. 4b appears to be porous in comparison with the parent ore. This morphology most likely resulted due to leaching of U, Th, Ta, and other species via the action of HF and H_2SO_4. The corresponding EDS spectra revealed absence of U and Th with presence of Ta, Nb, Mn, and Fe, which can be attributed to the high amount of undissolved ferrocolumbite in the ore.

Solvent Extraction

Extraction of uranium and thorium from the acid leach liquor was conducted using the highly selec-

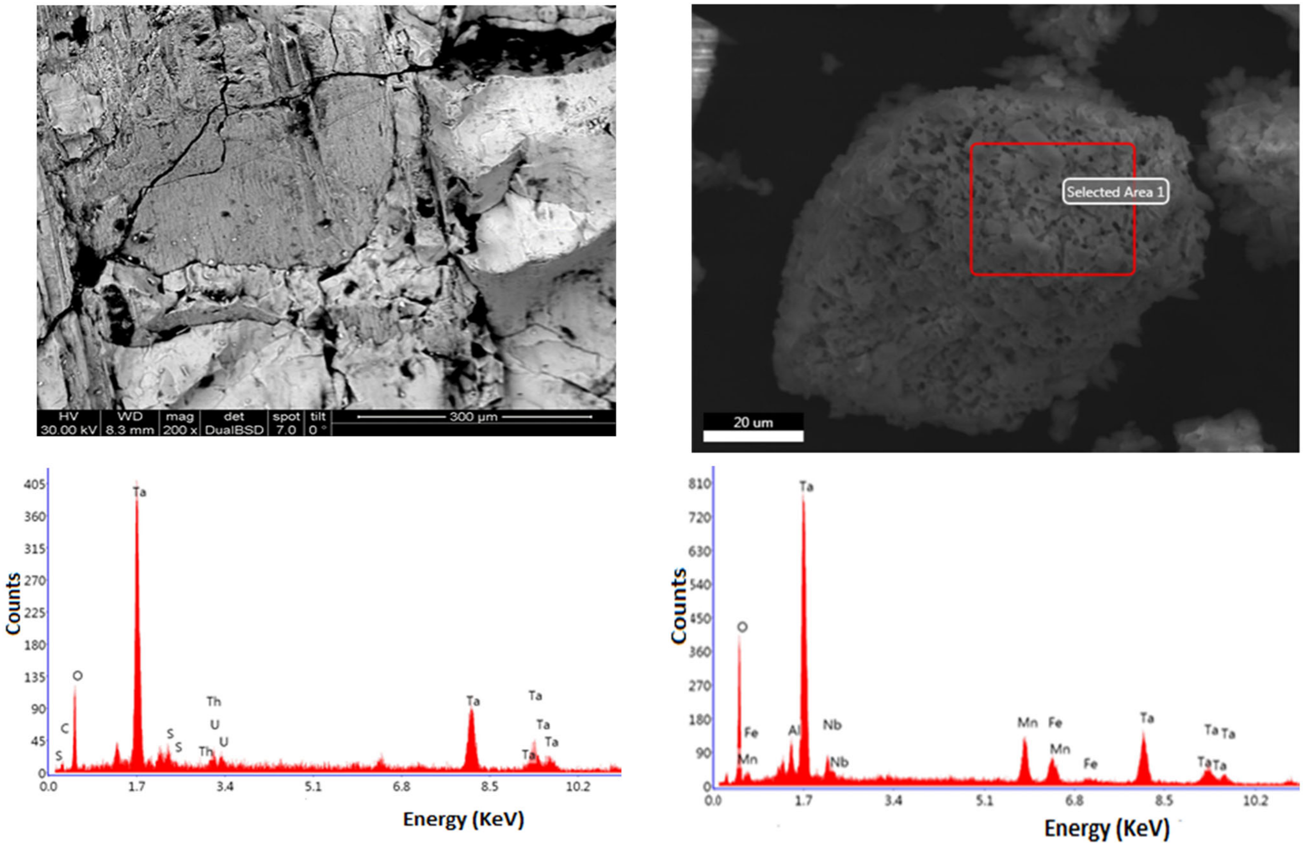
Table I. Elemental analysis of enriched tantalite ore before and after leaching with 3HF + 1H_2SO_4 from various deposit zones (denoted 1 to 5) of the Kenticha area. Contact time of 3 h, temperature 150°C, particle size −100 + 75 μm

	Ta_2O_5 (wt.%)		Nb_2O_5 (wt.%)		U_3O_8 (wt.%)		ThO_2 (wt.%)		TiO_2 (wt.%)	
Zone	Before	After	Before	After	Before	After	Before	After	Before	After
1	46.24	41.9	18.98	7.30	1.10	0.12	0.37	0.19	0.65	0.52
2	52.98	43.4	20.23	6.63	1.32	0.05	0.60	0.10	0.73	0.34
3	49.52	39.2	18.08	5.50	1.05	0.07	0.53	0.14	0.66	0.41
4	60.12	38.8	11.52	3.40	1.00	0.05	0.07	0.17	0.43	0.38
5	50.19	32.4	19.80	7.20	0.99	0.01	0.26	0.01	0.65	0.42



(a) (b)

Fig. 3. TGA-DTA results of the (a) raw sample and (b) sample treated with HF:H_2SO_4 molar ratio of 3:1 at 150°C for 3 h.



(a) **(b)**

Fig. 4. SEM micrograph and EDS results of (a) pegmatite ore and (b) tantalite residue after leaching in HF:H_2SO_4 mixture at molar ratio of 3:1.

tive D_2EHPA[16] with various contact times, solvent concentrations, and aqueous/organic ratios at pH 2. Extraction equilibrium was reached at contact time of 20 min, at which the uranium extraction efficiency was 98% while that of thorium was 91% at aqueous/organic phase volume ratio of 1:1. Upon varying the aqueous/organic phase volume ratio from 1:1 to 1:3, a slight decrease (2%) in extraction efficiency was observed. The extraction efficiency of uranium increased by about 23% when increasing the D_2EHPA concentration from 0.1 M to 0.3 M. In this study, the highest extraction efficiencies for uranium and thorium were obtained at aqueous/organic phase volume ratio of 1:1, D_2EHPA concentration of 0.3 M, and contact time of 20 min.

CONCLUSION

The efficiency of removal of uranium and thorium from pegmatite ore by acid leaching followed by solvent extraction was investigated. Mineralogical analysis revealed that the tantalite concentrate beneficiated from pegmatite ore contained high concentrations of radioactive elements such as uranium and thorium. Use of leaching temperature of 150°C, particle size of $-100+75$ μm, and HF:H_2SO_4 ratio of 3:1 resulted in higher dissolution of uranium. The dependence of the leachability of thorium on the above variables was not systematic. D_2EHPA was found to be an effective extractant. At the experimental conditions considered in this study, satisfactory removal of radioactive elements from the concentrate was achieved, which could potentially meet handling and transport guidelines.

ACKNOWLEDGEMENTS

The authors would like to thank the Ethiopian Mineral Petroleum and Biofuel Corporation, Ethiopian Conformity Assessment Enterprise, Jimma University, Addis Ababa University, and Grace Trading for financial and in-kind assistance.

REFERENCES

1. M. Nete and W. Purcell, *Emerging Trends in Chemical Sciences*, ed. P. Ramasami, B.M. Gupta, L.S. Jhaumeer, and K.W.H. Li (Basel: Springer, 2018), p. 267.
2. J.B. Lambert, *Kirk-Othmer Encyclopedia of Chemical Technology*, eds. D. Othmer and R.E. Kirk (Hoboken: Wiley, 2011).
3. S.B. Dampare, B.J.B. Nyarko, S. Osae, E.H.K. Akaho, D.K. Asiedu, Y. Serfor-Armah, and P. Nude, *J. Radioanal. Nucl. Chem.* 265, 53 (2005).
4. G.J. Simandl, Tantalum market and resources: an overview. *B. C. Geol. Surv.* 1, 313 (2001).
5. O.M. EL-Husaini and M.N. EL-Hazek, *Eur. J. Miner. Process. Environ. Protec.* 5, 7 (2005).
6. O.M. El-Hussaini and M.A. Mahdy, *Hydrometallurgy* 64, 219 (2002).

7. V. Madakkaruppan, A. Pius, T. Sreenivas, and C. Sarbajna, *J. Radioanal. Nucl. Chem.* 309, 493 (2016).
8. K.C.A. Nettleton, A.N. Nikoloski, and M.D. Costa, *Hydrometallurgy* 157, 270 (2015).
9. M. Nete, W. Purcell, and J.T. Nel, *JOM* 68, 556 (2016).
10. G.G. Berhe, V.R. Alberto, B. Tadesse, A. Yimam, and G. Woldetinsae, *Physicochem. Probl. Miner. Process.* 54, 406 (2018).
11. C.K. Gupta and A.K. Suri, *Extractive Metallurgy of Niobium* (Boca Raton: CRC Press, 1994).
12. V.G. Maiorov, A.I. Nikolaev, and V.K. Kopkov, *Russ. J. Appl. Chem.* 74, 363 (2001).
13. A.R. Adetunji, W.O. Siyanbola, I.I. Funtua, S.O. Olusunle, A.A. Afonja, and O.O. Adewoye, *J. Miner. Mater. Charact. Eng.* 4, 85 (2005).
14. J.R. Kumar, J.S. Kim, J.Y. Lee, and H.S.A. Yoon, *Sep. Purif. Rev.* 40, 77 (2014).
15. A.H. Orabi, *J. Rad. Res. Appl. Sci.* 6, 1 (2013).
16. K. Kiegiel, A. Abramowska, P. Biełuszka, G. Zakrzewska-Kołtuniewicz, and S. Wołkowicz, *J. Radioanal. Nucl. Chem.* 311, 589 (2017).
17. D. Gajda, K. Kiegiel, G. Zakrzewska-Kołtuniewicz, E. Chajduk, and S. Wołkowicz, *J. Radioanal. Nucl. Chem.* 303, 521 (2015).
18. S.A. McMaster, R. Ram, F. Charalambous, M.I. Pownceby, J. Tardio, and S.K. Bhargava, *J. Hazard. Mater.* 280, 478 (2014).
19. S.A. McMaster, R. Ram, J. Tardio, and S.K. Bhargava, *International Symposium on Uranium Raw Material for the Nuclear Fuel Cycle*, ed. J. Zellinger (Vienna: World Nuclear Association, 2014).
20. D. Küster, R.L. Romer, D. Tolessa, D. Zerihun, K. Bheemalingeswara, F. Melcher, and T. Oberthür, *Miner. Deposita* 44, 1 (2009).
21. ASTM D6913/D6913 M-17, Standard Test Methods for Particle-Size Distribution (Gradation) of Soils Using Sieve Analysis (ASTM International, West Conshohocken, PA, 2017), https://compass.astm.org/EDIT/html_annot.cgi?D6913+17. Accessed 22 Mar 2018.
22. R.C. Merritt, *The Extractive Metallurgy of Uranium* (Golden: Colorado School of Mines Research Institute, 1971), pp. 59–61.
23. H.D. Mathur and O.P. Tandon, *Chemistry of Rare Elements* (New Delhi: S. Chand, 1986), p. 93.
24. M. Nete, F. Koko, T. Theron, W. Purcell, and J.T. Nel, *Int. J. Miner. Metall. Mater.* 21, 1153 (2014).
25. A.D. Pienaar, J.B. Wagener, and P.L. Crouse, *Int. J. Miner. Process.* 114, 7 (2012).