

## Assessment Of Beneficiation Routes Of Tantalite Ores From Key Locations In Nigeria

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### Abstract:

*The beneficiation methods for some tantalite ores from selected deposits in Nigeria have been assessed through mineralogical and compositional analyses of the ores. Tantalite ores obtained from eight different well-known locations of the mineral in the country were analyzed with <sup>109</sup>Cd excitation source Energy Dispersive X-ray spectrometry using the emission-transmission method of quantification. The major minerals detected and quantified include TiO<sub>2</sub>, MnO, Fe<sub>2</sub>O<sub>3</sub>, Ta<sub>2</sub>O<sub>5</sub>, Nb<sub>2</sub>O<sub>5</sub>, WO<sub>3</sub>, Th and U. Impurity elements such as Hf, Zn, Zr, Co, Pb, Rb, and Y were also observed and evaluated. Our analyses further show that Ta<sub>2</sub>O<sub>5</sub> in the ores ranged from a minimum concentration of about 8% in Otu to about 60% in the Egbe deposits, while the Nb<sub>2</sub>O<sub>5</sub> concentrations in the ores ranged from about 20% to 37.5% with the highest coming from the Ofiki deposit. Based on these results and the work of other authors, we deduced that clean-up operations might be adequate for Ta extraction from most of the tantalite deposits in Nigeria. The consideration of simplicity and cost of process favours the direct dissolution of the ores in HF for the clean-up operations.*

**Keywords:** Tantalite ores, Elemental Composition, EDXRF

### INTRODUCTION

Nigeria is blessed with abundant mineral resources. These include vast deposits of coal, cassiterite, columbite, marble, limestone, clay, bitumen and tantalite. While some of these minerals are currently mined, several others have been identified to have huge potentials of being exploited in commercial scale. The Federal Government of Nigeria is paying renewed attention to the solid mineral sector; therefore, development activities in the sub-sector are expected to increase many-fold. Recent studies conducted by the Raw Materials Research and Development Council (RMRDC) have shown that the need to develop capacity for processing of these minerals into intermediate products is the most important requirement of the solid mineral sector in the country [1].

The recovery of tantalite in Nigeria dates back to the 1940's as a by-product of cassiterite mining [2, 3]. Later, large tonnages of granite containing about 0.26% Nb<sub>2</sub>O<sub>5</sub> in urania pyrochlore (3.1% U<sub>3</sub>O<sub>8</sub>, 3.3% ThO<sub>2</sub>, 37.5% Nb<sub>2</sub>O<sub>5</sub> and 3.5% Ta<sub>2</sub>O<sub>5</sub>) were

identified. The reserves were however not confirmed. Primary deposits of huge economic value of the ore have now been reported in various parts of the country [4, 5, 6]. Indeed, Nigeria is currently rated to be the 7<sup>th</sup> largest producer of tantalum resources in the world [7]. The production in 2004 was estimated at 25 metric tons.

Tantalite is the most important mineral form of tantalum, a specialty metal used mainly in the electronics industry for the manufacture of capacitors and in several specialty alloy applications. The beneficiation of tantalite ores usually involves pre-concentration, primary concentration and concentrate clean up. The choice of any or all of these processes would depend on the nature of the ore, particularly the content of Ta<sub>2</sub>O<sub>5</sub> in the ore relative to its associated minerals and impurities. Typically, mechanically mined ores contain less than 0.1% Ta<sub>2</sub>O<sub>5</sub>, and would therefore essentially require enrichment through the three processes stated above. The concentration processes may be carried out by wet gravity, magnetic or electrostatic methods or by flotation to produce concentrates containing up to 70% combined Ta<sub>2</sub>O<sub>5</sub> and Nb<sub>2</sub>O<sub>5</sub> to meet extraction requirements. However, the universally employed method for the concentration of tantalite ores is gravity separation – the separation of two or more minerals as a result of differences in specific gravity and their movement in response to the force of gravity and one or more other forces [8, 9]. Other methods, when used, are employed in the final cleanup of gravity concentrates.

Furthermore, Burt [10] had noted that concentrates suitable for further processing to recover Ta are generally required to exceed 25% Ta<sub>2</sub>O<sub>5</sub>, with 50% combined Ta<sub>2</sub>O<sub>5</sub> and Nb<sub>2</sub>O<sub>5</sub>. Primary ores with these Ta<sub>2</sub>O<sub>5</sub> and Nb<sub>2</sub>O<sub>5</sub> contents would only need clean-up operations for Ta extraction processes. The clean-up operation results in the removal of associated minerals and impurity elements to a tolerable extent. Typical associated minerals include zircon, rutile, monazite, cassiterite, ilmenite, garnet, uranium and thorium minerals, beryl, spodumene, tourmaline and, in some cases, aquamarines and gold: light minerals such as quartz and feldspar may also be present due to inefficient primary concentration.

A number of reports [11, 12] have given the mineralogical composition of Ta-Nb ores obtained from a few locations in the middle belt region of Nigeria. However, the limitation of these previous works is the failure to relate the results to an upgrading process for a value-added Nigerian tantalite.

The main objective of this work is to assess the appropriate beneficiation schemes by identifying the associated elements and impurity elements in samples obtained from notable tantalite deposits across Nigeria. The associated elements are known to contribute to the physical characteristics of the Ta mineral and these characteristics dictate the beneficiation methods. The outcome of the work reported here would therefore provide critical information about the appropriate routes for the beneficiation processes needed for value addition to the Nigerian tantalum industry.

## MATERIALS AND METHODS

Eight samples were collected from different notable deposits in Nigeria. The sources are Egbe, Komu, Nassarawa, Agunrege, Baba Ode, Ofiki, Igbo Ijaye and Otu. Six of the locations are in Oyo State in the South Western Nigeria; one location is in Kogi State while one is in Nassarawa State, both deposits located within the middle belt region of the country. The samples were obtained from miners in the study areas. The miners employ manual methods of mining, in which the samples would have been upgraded to some extent by hand sorting. Measurements of the major constituents and trace elements were carried out using a radioisotope source Energy Dispersive X-Ray Fluorescence (EDXRF) Spectrometer at the Centre for Energy Research and Training, Ahmadu Bello University, Zaria, Nigeria.

The samples were ground manually to powder with an agate mortar and pestle to grain size of less than 125  $\mu\text{m}$ . Pellets of 19 mm diameter were prepared from 0.3 – 0.5g powder mixed with three drops of organic liquid binder and then pressed at 10 tons with a hydraulic press. Measurements were performed using an annular 25 mm  $^{109}\text{Cd}$  as the excitation source, which emits Ag-K X-rays (22.1 keV) in which case all elements with lower characteristic excitation energies were accessible for detection in the samples. The system further consists of a Si(Li) detector, with a resolution of 170 eV for the 5.90 keV line, coupled to a computer controlled ADC-card. Further details about the system have been given elsewhere [11, 13,14].

Quantitative analysis of the samples was carried out using the Emission-Transmission (E-T) method, for which a number of quantification methods has been developed and applied [13 – 18]. These quantification methods provide different approaches to correct the matrix absorption as well as enhancement effects. In this work quantification was carried out using a modified version of E-T method [11, 19, 20], which involves the use of pure target material (Mo) to measure the absorption factors in the sample. The Mo target serves as a source of monochromatic X-rays, which are excited through the sample by primary radiation and then penetrate the sample on the way to the detector. In this way, the absorption factor is experimentally determined. The program then uses this factor in the quantification of concentration of the elements. In addition, the contribution to the Mo-K peak intensity by the Zr-K is subtracted for each sample. The spectra for the samples were collected for 3000s with the  $^{109}\text{Cd}$  and the spectra were then evaluated using the AXIL- QXAS program [21]. It was noted that very light mineral associations of the Ta ores could not be determined due to the absence of an  $^{55}\text{Fe}$  excitation source.

## RESULTS AND DISCUSSION

The results of the mineralogical analysis including a number of impurities/trace elements are shown in Table 1. The results show that the Egbe sample contains the highest  $\text{Ta}_2\text{O}_5$  content at 59.58%. The  $\text{Ta}_2\text{O}_5$  contents of Komu, Nassarawa, Agunrege,

Baba Ode, Ofiki, Igbo Ijaye and Otu ore samples are respectively 49.57%, 46.15%, 45.42%, 42.00%, 36.63%, 23.64% and 8.00%. The results further showed that the samples also contain appreciable amounts of Nb<sub>2</sub>O<sub>5</sub> and TiO<sub>2</sub>. Other mineral ores/phases identified and quantified include MnO, Fe<sub>2</sub>O<sub>3</sub>, WO<sub>3</sub>, Th and U. Impurities/trace elements such as Hf, Zn, Zr, Co, Pb, Rb, and Y were also determined.

*Table 1: Mineralogical Analysis of Tantalum Ore Samples From 8 Different Locations in Nigeria.*

Oxide	Egbe	Komu	Nassarawa	Agunrege	Baba Ode	Ofiki	Igbo Ijaye	Otu
TiO <sub>2</sub> %	-	-	3.81 ±0.42	1.64 ±0.37	2.34 ±0.42	1.05 ±0.33	20.36 ±0.58	33.38 ±0.67
MnO%	4.15 ±0.10	9.03 ±0.17	5.80 ±0.13	6.69 ±0.14	8.62 ±0.17	10.10 ±0.18	3.46 ±0.12	0.74 ±0.09
Fe <sub>2</sub> O <sub>3</sub> %	7.76 ±0.18	3.51 ±0.14	10.69 ±0.23	7.37 ±0.18	4.69 ±0.16	2.86 ±0.13	9.66 ±0.21	9.70 ±0.20
Ta <sub>2</sub> O <sub>5</sub> %	59.58 ±0.62	49.57 ±0.54	46.15 ±0.52	45.42 ±0.49	42.00 ±0.46	36.63 ±0.42	23.64 ±0.40	8.00 ±0.17
Nb <sub>2</sub> O <sub>5</sub> %	19.74 ±0.17	29.18 ±0.23	24.86 ±0.20	31.18 ±0.26	32.90 ±0.26	37.48 ±0.29	28.90 ±0.29	22.43 ±0.17
WO <sub>3</sub> %	-	0.38 ±0.13	1.80 ±0.14	-	-	-	0.32 ±0.09	0.17 ±0.05
SnO <sub>2</sub> %	-	-	8.43 ±1.97	-	-	-	-	-
Hf%	0.22 ±0.05	0.26 ±0.05	0.31 ±0.05	0.18 ±0.05	0.17 ±0.05	0.11 ±0.04	0.13 ±0.04	-
Zn%	-	0.22 ±0.03	0.09 ±0.03	-	0.09 ±0.03	0.07 ±0.02	-	-
Zr%	0.31 ±0.01	0.12 ±0.01	0.26 ±0.01	0.15 ±0.01	0.22 ±0.01	0.17 ±0.01	0.06 ±0.01	0.06 ±0.01
Pb (ppm)	489 ±146	570 ±146	1720 ±195	-	1010 ±168	720 ±146	-	-
Rb ppm)	-	120 ±47	-	-	-	-	-	-
Y ppm)	(	-	333 ±51	-	-	-	-	-
ThO <sub>2</sub> %	0.34	0.03	0.15	0.02	0.02	0.05	0.03	0.01
U <sub>3</sub> O <sub>8</sub> %	0.17	0.37	0.65	0.42	0.94	1.57	0.28	0.27

The elemental Ta content in the respective ore samples are 48.79%, 40.59%, 37.79%, 37.19%, 34.39%, 30%, 19.36% and 6.55% respectively for Egbe, Komu, Nassarawa, Agunrege Baba Ode, Ofiki, Igbo Ijaye and Otu. An earlier work by Funtua [11] put the Ta content in the central pegmatite region around Jos, Nassarawa and Jama'a areas of central Nigeria at between 21 and about 30%. We note that this figure is somehow less than the Nassarawa ore found to be about 38% in the current investigation. The difference could probably be explained in terms of the diversity in the ore contents from site to site and from ore vein to ore vein.

In terms of beneficiation, the density of Ta-Nb minerals allows concentration with other heavy minerals by gravity methods; sluices, jigs, spirals and shaking tables are used in conjunction with screen sizing; other processes, when used, are employed in the final cleanup of gravity concentrates. Ta-Nb is separated from other heavy minerals by a combination of high-tension electrostatic and high-intensity electromagnetic means.

Concentrates from Nigerian placer deposits, which are worked primarily for cassiterite, are dried and treated by magnetic separators to remove the magnetic constituents: magnetite, ilmenite, columbite, monazite and magnetic cassiterite. The magnetic fraction is then re-treated to separate the different minerals. Columbite, monazite and magnetic cassiterite are weakly magnetic. Columbite and magnetic cassiterite are separated on air flotation tables, whereas columbite and monazite are separated electrostatically [2]. Classification, screening, and desliming are employed as adjuncts, depending on the composition of the ore. Treatment schemes vary from the most primitive hand methods to extremely complex modern plants [22]. The liberation of values from waste must be carried out with care, since all tantalum minerals are friable, and, according to Burt [10], concentration efficiency decreases with decreasing particle size.

Gravity plant concentrate, grading approximately 25%  $Ta_2O_5$  is generally upgraded to 50% in a clean-up plant. The Nb content in the ore is very important. Concentrates suitable for further processing to recover Ta are generally required to exceed 25%  $Ta_2O_5$ , with 50% combined  $Ta_2O_5$  and  $Nb_2O_5$  [10]. The ores below this level of  $Ta_2O_5 - Nb_2O_5$  content need to be enriched by methods discussed above. The tantalum ores from Egbe, Komu, Nassarawa, Agunrige, Baba Ode and Ofiki all have  $Ta_2O_5 - Nb_2O_5$  combined content of about 70%, with the  $Ta_2O_5$  contents of over 25%. Thus these ores can be subjected directly to clean-up operations, without pre-concentration or primary concentration, for the removal of associated minerals. Many of the ores may even be subjected to direct hydrometallurgical extraction processes without going through clean-up operations. This is because their  $Ta_2O_5$  contents fall into categories for which technologies have specifically been developed as raw materials of different origins and grades [23], as shown in Table 2. The ore sample from Igbo Ijaye, which contains 23.64%  $Ta_2O_5$ , is rich enough for primary concentration, while the Otu ore sample, with 8%  $Ta_2O_5$ , would be enriched right from the pre-concentration stage (Table 3). These two ore samples were however found to have a high  $TiO_2$  content of 20.36% and 33.38% respectively. Although the Otu figure is lower than that of a recently studied rutile sample [24], it would be appropriate to treat the ore primarily for rutile recovery and then secondary recovery for tantalite and niobite.

Table 2: Correlation between technology and raw material input [23]

Technology	Raw Material Input	%Ta/ $Ta_2O_5$
Pyrometallurgy	Low – Medium Grade Tin Slags	2 – 10% $Ta_2O_5$
Chlorination	Alloys, Scraps	40 – 100% Ta
Hydrometallurgy	Natural Ores	20 – 40% $Ta_2O_5$
	Synthetic Concentrates	20 – 40% $Ta_2O_5$
	High Grade Tin Slags	>15% $Ta_2O_5$

The main associations of  $Ta_2O_5$  in the ores under investigation apart from  $Nb_2O_5$  and rutile are hematite, wolframite, uranium, cassiterite minerals as well as hafnium, zinc and zirconium elements with other trace elements. We note that because  $TiO_2$  and MnO are paramagnetic and  $Fe_2O_3$  is ferromagnetic, they can be separated from the ore by magnetic separation, whereas electrostatic separation can be employed to remove cassiterite, hematite, ilmenite, tantalite, niobite and wolframite, which are electrically

conducting, from the ore, leaving the non-conducting zirconium compounds in the gangue. An earlier work by our group [25] had not been able to present the data shown in this work on the impurity/trace element contents of the ores. Most of these elements would go into the gangue during the elimination of the major constituents by the physical and subsequent chemical methods.

*Table 3: Recommended beneficiation routes for different grades of Ta<sub>2</sub>O<sub>5</sub> ores (Adapted from table provided by Burt, [10])*

Ta <sub>2</sub> O <sub>5</sub> Content (%)	Sample Sources Content (%Ta <sub>2</sub> O <sub>5</sub> )	Beneficiation Route
<10	Out (8.00)	Preconcentration (sizing, gravity separation)
10 – 25	Igbo Ijaye (23.64)	Primary concentration (jigs and sluices) Hydraulic classification Stage treatment (spirals, shaking tables)
>25	Egbe (59.58), Komu (49.57, Nassarawa (46.15), Agunrege (45.42), Baba Ode (42.00), Ofiki (36.63)	Concentrate clean-up (floatation, leaching, magnetic or electrostatic separation)

We note further that based on the characteristics of the ores analysed in this study, a preliminary treatment for the samples would be fusion with K<sub>2</sub>CO<sub>3</sub>, which would separate Sn, Fe, Mn and TiO<sub>2</sub> from the earth acids [26]. The approach in this case, is to fuse at red heat with threefold excess of K<sub>2</sub>CO<sub>3</sub>, dissolve the fused mass in water, filter, then precipitate the tantalum and niobium as the sodium salts. However, the number of steps and amount of reagents required could make this process expensive. Gustion and Pilloton [26] observed that direct dissolution of ores in HF as a clean-up operation would not always produce adequate solution for separation by crystallization or liquid extraction. Thus an alternative route to effect a rough purification is to fuse them with caustic. The fused mass would then be leached with water to remove excess caustic, Sn and W. The Ta and Nb, in the form of complex tantalates and niobates, are insoluble. An acid leach would then dissolve Fe, Mn, Alkalies, and alkaline earths, leaving as a residue a mixture of the acids, Ti, and traces of other contaminants. However, Gustion and Pilloton [26] showed that six additional operations must be added to those required by direct HF dissolution in order to accomplish this. These are caustic fusion, crushing of the fusion mass, water leach, filtration of water-leach liquor, acid leach and filtration of acid-leach liquor. The caustic fusion step is a high-labour operation. Furthermore, the labour requirements for each filtration step are about the same as for direct dissolution, so that filtration costs rise 100-200% over the direct dissolution operation. Leaching in water requires about 50% as much labour as direct dissolution, but since leaching in acid is comparable to direct dissolution the wet processing of the upgraded ores altogether requires about 100-150% more labour than a direct dissolution operation. The consideration of simplicity and cost of process therefore favours the direct dissolution of the ores in HF to dissolve Ta, Nb, Fe, Ti, Mn and W. In practice, the advantages and disadvantages of caustic fusion prior to the HF leach must be carefully evaluated. The decision to use caustic fusion depends mainly on the type of ore that is treated and on the method of separation used. If chemical and equilibria data were available for the

dissolution process, it might be possible to maximize Ta and Nb dissolution with minimum dissolution of the gangue material.

Finally, it is appropriate to mention here that depending on the country or region of exportation, some Ta/Nb minerals cannot be shipped out of their country of origin because of their levels of radioactivity. The limits of allowed uranium and thorium oxide contents are 0.1 %U<sub>3</sub>O<sub>8</sub> and 0.1%ThO<sub>2</sub> [27]. All the ore samples under investigation would not pass through such transportation regulation for their U<sub>3</sub>O<sub>8</sub> content while Egbe and Nassarawa samples would not pass through as a result of their ThO<sub>2</sub> content. This measure in principle could create a market problem for the tantalite ores originating from these Nigerian deposits. Where there are ready buyers because of the strategic importance of the end product, i.e. the tantalum metal/compounds, the crude ore is substantially reduced in value because of their radioactive contents. However, Krismer and Hoppe [28] have developed a process for the recovery of the non-radioactive metal compounds from the ores containing complexes of U and Th. The gangue can now be treated to recover uranium as an additional economic by-product [29].

## CONCLUSION

The analysis of the tantalum ores from eight different notable deposits in Nigeria using EDXRF spectrometry has shown that the Nigerian tantalum ores are of relatively high quality and can therefore be subjected to direct processing for tantalum products without the need for complex and costly preconcentration procedures. The consideration of simplicity and cost of process favours the direct dissolution of the ores in HF. The simultaneous evaluation of rutile and niobium in the ores allows for the assessment of the suitability of the ores for primary/secondary recovery processes of rutile and niobium products. In addition, the XRF technique offers the possibility of determining other major constituents such as Fe, Mn, W, Th, U, Hf, Zn and Zr. The tantalite mineral can be separated from the ore leaving the radioactive elements in the gangue, the secondary recovery of which is an added economic advantage. The knowledge of the presence of Co, Pb, Rb, and Y, as well as radioactive elements in the samples would assist in evaluating co-dissolved species as well as the development of appropriate beneficiation routes for value-addition to the mineral in Nigeria.

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