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Caustic potash assisted roasting of the Nigerian ferro-columbite concentrate and guanidine carbonate-induced precipitation: A novel technique for extraction of Nb–Ta mixed-oxides

Jean Baptiste Habinshuti [a,b,*], Jeanne Pauline Munganyinka [a,b], Adelana R. Adetunji [a,c], Brajendra Mishra [b], Himanshu Tanvar [b], Janvier Mukiza [d], Grace Ofori-Sarpong [e], Azikiwe Peter Onwualu [a]

[a] *Department of Materials Science and Engineering, African University of Science and Technology, Abuja, Nigeria*
[b] *Department of Mechanical Engineering, Worcester Polytechnic Institute, 100 Institute Road, Worcester, MA, 01609, USA*
[c] *Department of Materials Science and Engineering, Obafemi Awolowo University, Ile-Ife, Nigeria*
[d] *School of Education, College of Education, University of Rwanda, P.O. BOX 55, Rwamagana, Rwanda*
[e] *University of Mines and Technology, Tarkwa, Ghana*

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ABSTRACT

The current study focuses on alkali-assisted roasting, dissolution, and recovery of mixed oxides of niobium (Nb) and tantalum (Ta) from a ferro-columbite concentrate collected from Jos Plateau in Nigeria. Alkali-assisted roasting and water-based leaching to extract Nb and Ta using guanidine carbonate salt were adopted for sustainable extraction. The concentrate was roasted with caustic potash (KOH) as flux at optimized conditions (250 °C, 100% mass flux-to-concentrate ratio, 1 h) and leached with water. This resulted in dissolution of 97-96% Nb, 80-96% Ta, 92-91% W and 64-65% Mn for −250 and + 250 μm size fractions respectively while leaving behind in the residue most of Sn (94-83%) and Fe (79-81%). The amount of Nb and Ta dissolved were selectively recovered with novel application of guanidine carbonate salt as precipitating agent. High extraction yield (∼100%) was achieved. The final recovery of approximately 96% Nb and 85% Ta contained in the +250 μm concentrate feed sample was obtained under optimum conditions of 50 mg/mL guanidine. The (Nb,Ta)-guanidine precipitate obtained was then calcined at 900 °C for 1 h and converted into mixed $(Nb,Ta)_2O_5$ (97%) and removed the guanidine. Based on material balance, it was found that approximately 734.5 kg of (Nb,Ta)-guanidine precipitate with purity higher than 84% could be obtained from one tonne of ferro-columbite feed concentrate. The current technique of alkali-assisted roasting, dissolution, and recovery of mixed oxides of Nb and Ta is a novel process and presents an environmentally benign, and it is an efficient technique to replace the traditional method which uses an environmentally harmful hydrofluoric acid to extract Nb and Ta.

1. Introduction

Niobium (Nb) and tantalum (Ta) are refractory metals due to their unique properties such as extreme corrosion, shear, and high temperatures resistance. Nb has numerous applications; including production of ferro-niobium used as an additive to high-strength low-alloy steels. These structural alloys are widely used in manufacture of oil gas-pipelines, modern automobiles, and stainless steels for other various uses [1–4]. Further application of niobium is in the production of nickel, cobalt, and iron-based super-alloys used in aircraft engines components, heat-resistant and combustion equipment [2]. Nb is mainly imported and exported in form of ferro-niobium materials [1]. The global demand for ferro-niobium has risen and is expected to continue rising by over 8% per year, driven by the increasing global markets for steel in constructions, infrastructure and automotive applications as well as high-strength low-alloy steels [1,5]. The refined tantalum finds its broad applications in manufacturing of electronic components; and other high-technology products. These include capacitors and resistors used in mobile phones, computers, digital cameras; and super-alloys used in aerospace and automotive applications [3,6]; and bio-implants served

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* Corresponding author. Department of Materials Science and Engineering, African University of Science and Technology, Abuja, Nigeria.
E-mail address: hbaptiste@aust.edu.ng (J.B. Habinshuti).

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for biomedical applications [7].

Nb and Ta have a very strong geochemical coherence; they are always found together as oxides in the same mineral deposits [8,9]. The natural co-occurrence implies their co-extraction from primary resources [10]. The common raw materials used for the production of Nb include Nb–Ta containing ores and secondary resources such as scraps, and slags from cassiterite (SnO_2) smelting processes [11,12]. The economically important ores for sourcing Nb includes the Ta-free pyrochlore [$(Na,Ca)_2Nb_2O_6(OH,F)$], and the Nb,Ta mixed-oxides of the general formula [$(Fe,Mn)(Nb,Ta)_2O_6$] with various ratios of Nb-to-Ta [4]. The mineral is called 'columbite' when Nb is the predominant constituent (40–78% of Nb_2O_5) and 'tantalite' when Ta is the major component (38–86% of Ta_2O_5) [4]. In these materials, the isomorphism exists between Nb and Ta where they substitute each other freely, the same also exists for iron (Fe) and manganese (Mn) [13,14]. These minerals normally occur as accessory minerals disseminated in intrusive pegmatites, granitic pegmatites, and carbonatites of igneous rocks [15]. Rocks hosting Nb–Ta minerals are mined and processed to increase the grade of valuable minerals as columbite-tantalite concentrates. The principal method for beneficiation of (Nb,Ta)-ores is related to the higher densities of Nb, Ta and other (Nb,Ta)-carrier minerals that allow them to be concentrated by gravity separation [16]. However, losses of the fine Nb/Ta particles are reported especially for −150 and −200 mesh fractions and cyclone overflow slimes. This led to the very low recovery, ranging from 55% to ~65%. There is possibility to float (Nb,Ta) gravity tailings which would increase overall metallurgical recovery, but only few plants have tested this [16].

From an industrial viewpoint, current production and purification of these metals and their compounds is a complex process due to their very similar physical and chemical properties [17,18]. It involves decomposition and conversion of the Nb–Ta concentrate or ore into water-soluble compounds. Nb and Ta containing mineral ores can be decomposed or digested by concentrated hydrofluoric acid (HF) or its mixture with H_2SO_4 or alkali fusion at elevated temperature [19–21]. After digestion of the Nb and Ta mineral ore, the next step is to separate dissolved Nb and Ta from other associated impurities and subsequent separation of Nb and Ta from each other [22]. The first commercially successful process for production and separation of Nb and Ta is called the Marignac process. The process requires complexation of the two metal ions with fluoride ions (F^-) during their dissolutions [4,23,24]. The dissolution and complexation are accomplished by using a highly concentrated solution of HF or any other sources of fluoride ions. Advantages of fluoride media is that Nb and Ta are highly soluble and can form distinct complexes depending on the acidity level and metals concentration, thus difference in formed Nb and Ta complexes enables their separation. After dissolution, KF or KOH, or KCl is added to the reaction mixture for formation of K-salts (K_2NbOF_5 and K_2TaF_7). The resulting liquor solution is subjected to selective crystallization of the less soluble K_2TaF_7 followed by solvent decantation and filtration to recover Ta. Then the more soluble K_2NbOF_5 is recovered from solution as niobium oxide by precipitation via addition of ammonia solution. The drawback of the process is co-precipitation of multiple impurities such as Ti, Si, and Fe which contaminate the Nb_2O_5 [25].

The modern process uses liquid-liquid extraction to effect Nb and Ta loaded into the solution obtained after filtration of the slurry resulting from digestion of the Nb/Ta minerals with a mixture of HF and H_2SO_4 at elevated temperatures [26]. At higher acidic level (>8 M H_2SO_4), Nb and Ta are selectively extracted into organic phase leaving other dissolved impurities in aqueous phase. Lowering the acidity level 3–7.5 M H_2SO_4, Nb fluoride complex is back-extracted into flesh aqueous layer leaving the Ta into the organic layer. The Ta fluoride complex is then extracted from organic phase into aqueous layer at low acidic level ~ pH 7 by simply using water [18,26]. However, the process uses corrosive reagent and generates large amount of highly toxic fluoride solution, and it is only appropriate for high-grade Nb and Ta concentrates, thus recently alkaline media have caught growing attention for the extraction of Nb and Ta. In the process of solvent extraction performed in the presence of fluoride, organic solvents such as methyl isobutyl ketone, Octanol, Cyclohexanone, Tri-n-butyl phosphate (TBP), Alamine 336, bis (2-ethylhexyl) phosphoric acid (DEHPA) have been investigated for separation of Nb from Ta [27–29]. The hydrometallurgical production of Nb and Ta has been historically relying on the use of highly acidic media mentioned above which have many challenges including high energy demand, corrosivity, terrestrial acidification, and human toxicity [22, 30]. Thus, development of cost-effective and eco-friendly method for the recovery of Nb and Ta from primary and secondary resources has attracted the attention of many researchers [22,31].

The insolubility nature of compounds, minerals, and ores of Nb and Ta in minerals acids with exception of highly acidic solution of HF or its mixture with sulfuric acid, has led to an alkali-based process for dissolution of these resources. Alkaline roasting or alkaline leaching of Nb–Ta bearing ores produces highly water-soluble Nb–Ta compounds [32]. The alkali roasting process has been investigated using various fluxing and complexing agents for decomposition and dissolution of geological samples containing Nb and Ta [13,33]. The alkali processing is carried out either by direct leaching of the ore at high pressure and temperature or alkaline roasting (molten salt) to decompose the ore [27,31,34,35]. During roasting, caustic potash becomes fluid and reacts with the ore-particle where Nb_2O_5 and Ta_2O_5 convert into K_3NbO_4 and K_3TaO_4 which further hydrolyze easily and polymerize into polyoxometalate anionic species ($K_8Nb_6O_{19}$ and $K_8Ta_6O_{19}$) during the leaching [20,36, 37]. These species can be solubilized and leached out by water and recovered via precipitation or solvent extraction. After selective alkaline leaching, Nb and Ta must be precipitated out of the liquor solution to obtain commercial product or intermediate concentrate. Calcium-bearing reagents such as ($CaCl_2$, calcium acetate, or calcium hydroxide) have been reported to efficiently precipitate Nb and Ta as calcium hexaniobate and hexatantalate from alkaline solution [24]. High purity of mixed oxides $(Nb,Ta)_2O_5$ (99.3%) have been recovered from the alkali leach solution through evaporation, then crystallization, and phase transformation with diluted acid and calcination [34]. Nb and Ta have been precipitated as mixed oxides from strip solution of oxyfluoroniobic and fluorotantalic acids from alkaline liquor by addition of ammonia solution [4]. Acidification of the alkaline leach liquor solution containing polyoxometalate ions of Nb and Ta to pH 2–7 resulted in precipitation of these metals in form of hydrous pentoxides Eq. (1) but the process claimed not to be economic for recovering Nb and Ta [8, 38–40].

$$H_x(Ta,Nb)_6O_{19}{}^{x-8}{}_{(aq)} + (x-8)H^+{}_{(aq)} \rightarrow 3(Ta,Nb)_2O_{5(s)}.nH_2O_{(s)} + (4-3n)H_2O \tag{1}$$

$0 \le X \le 3$

Amines have been used as extractant in kerosene and produced a highly purified solution of niobium and tantalum [41]. Guanidine is an amine, strong base which forms a highly stable cation (guanidinium $C(NH_2)_3^+$) in aqueous solution due to its efficient resonance stabilization and solvation by water molecules [42]. Guanidine has proven the potential to rapidly and selectively precipitate Ta from a synthetic aqueous solution containing other metals such as Si and W [43]. Since Ta behaves similarly as Nb and always occur together in geological samples, therefore guanidine can be useful to extract these commodities.

The present study focuses on caustic potash assisted-roasting of columbite-Fe concentrate, water-based leaching and precipitation using guanidine carbonate salt to extract Nb and Ta from the liquor solution. Different roasting parameters such as temperature, mass flux-to-concentrate ratio and residence time were evaluated for high dissolution and elucidate the optimized conditions. Furthermore, recovery of mixed Nb and Ta from the optimized leach liquor solution is carried out with application of guanidine carbonate salt ($C_3H_{12}N_6O_3$). To the best of our knowledge, this would be the first-time guanidine amine salt was

Fig. 1. Mining site at Kwang, Jos Plateau, Nigeria.

utilized in the extractive metallurgy of Nb and Ta. The new processing flowsheet is environmentally friendly, does not require any toxic acidic reagents (such as HF) and results in higher extraction yield than existing methods.

2. Experimental

2.1. Materials

1.053 Kg of ferro-columbite concentrate (N-Jos Con) was obtained from S. Danboyi Rinn Nigeria Ltd located at Kwang, in Jos Plateau State of Nigeria, 9°49′52.0″N 8°54′50.0″E Fig. 1. The concentrated ore-sample as received from the mining company was dried, screened into two different size fractions, +250 and −250 μm with a sieve. The concentrate was analyzed with ICP-OES before and after sieving to see if further grinding was required to liberate Nb and Ta minerals. X-ray diffractometer was used for mineral phases identification (mineralogical compositions). Scanning Electron Microscopy attached with Energy Dispersive Spectroscopy (SEM/EDS) was also used for surface morphology analysis and to determine elemental and semi-quantitative chemical compositions of the concentrate sample. All chemical reagents used were of analytical grade. Guanidine carbonate salt (99%w/w) and potassium hydroxide (ACS reagent) pellets for analysis were purchased from Sigma Aldrich Inc.

2.2. Experimental procedure

Different mass flux-to-concentrate ratios (50–200%) were tested and assessed for alkaline assisted roasting decomposition and transformation of the Nb and Ta bearing phases into water-soluble compounds. The optimum conditions were determined for dissolution and extraction of these metals. Parameters investigated in the heat treatment and water based-leaching tests included temperature, flux-to-concentrate ratio, and roasting time. For sake of brevity, alkali roasting parameters were optimized without any size classification and furthermore optimized conditions were tested for different size class samples.

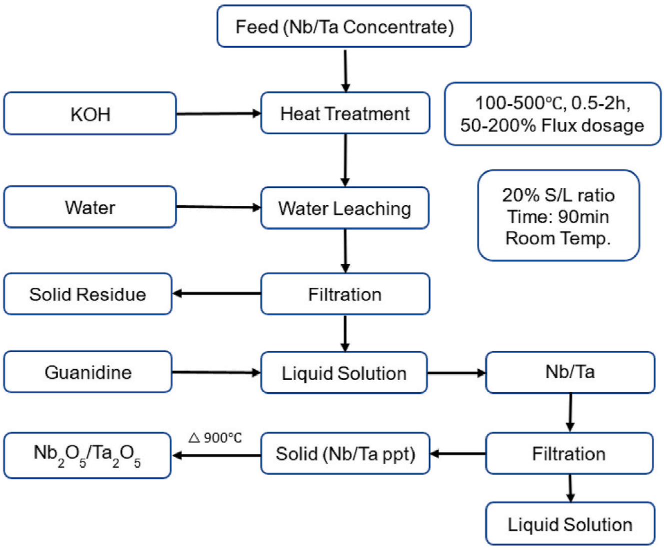


Fig. 2. Experimental flowsheet followed in this study.

In the first stage of heat treatment, 1.0 g of the concentrate sample was accurately weighed and thoroughly mixed with an appropriate weight (0.5–2.0 g) of ground pellets of KOH. The mixture was put in high quality alumina crucible. The roasting process was carried out in a muffle furnace (Mellen Microtherm). The furnace was pre-heated at specific desired temperature (100–500 °C) and when the temperature reached the preset value, a well-prepared sample was carefully introduced into the furnaceafter which the furnace was completely closed. The furnace was allowed to regain the desired temperature before the timer was started (0.5-2.0 hrs).After a particular time of roasting, the crucible was taken out of the furnace and the melt was allowed to cool at room temperature. After cooling, the melt was leached with 100 mL of deionized water and the resulting solid-liquid ratio of ~0.015–0.03 g/mL was stirred at room temperature for 90 min. Then, the slurry mixture was filtered on vacuum pump, and almost 100 mL of liquor solution was obtained. For leaching experiments carried out at room temperature (no roasting required), 2.0 g of concentrate were charged into 250 mL beaker containing 100 mL of 1 M KOH and stirred for 90 min. For each set of experiment performed, the solution and residue obtained after filtration were both analyzed with ICP-OES to determine the percentage content of Nb, Ta, Sn, Fe, and other impurities. Conditions for optimum dissolution of metals of interest were also determined. In addition to ICP-OES, the residue was analyzed with X-ray diffractometer to know the crystalline phases remained in the residue.

The optimized conditions were tested at large scale (15.0 g of sample and flux) and 1 L of deionized water was used for leaching these metals. The amount of Nb and Ta contained in the resulting pregnant leach solution (PLS) was recovered by precipitation using guanidine carbonate salt as precipitating agent. Appropriate volume of pregnant leach solution (200 mL) was measured from almost 1 L of PLS and 5–15.0 g of guanidine salt in solid form were added to the solution on continuous

Table 1
Chemical compositions of the ferro-columbite concentrate feed analyzed by ICP-OES.

Wt%	Nb_2O_5	Ta_2O_5	SnO_2	Fe_2O_3	MnO	SiO_2	Al_2O_3	WO_3
N-Jos Con	33.045	5.565	26.852	17.723	1.982	2.891	3.261	1.105
+250 μm	25.902	3.249	23.918	17.692	0.964	0.621	0.280	0.303
−250 μm	25.090	3.978	28.013	14.018	0.986	1.075	0.435	0.394

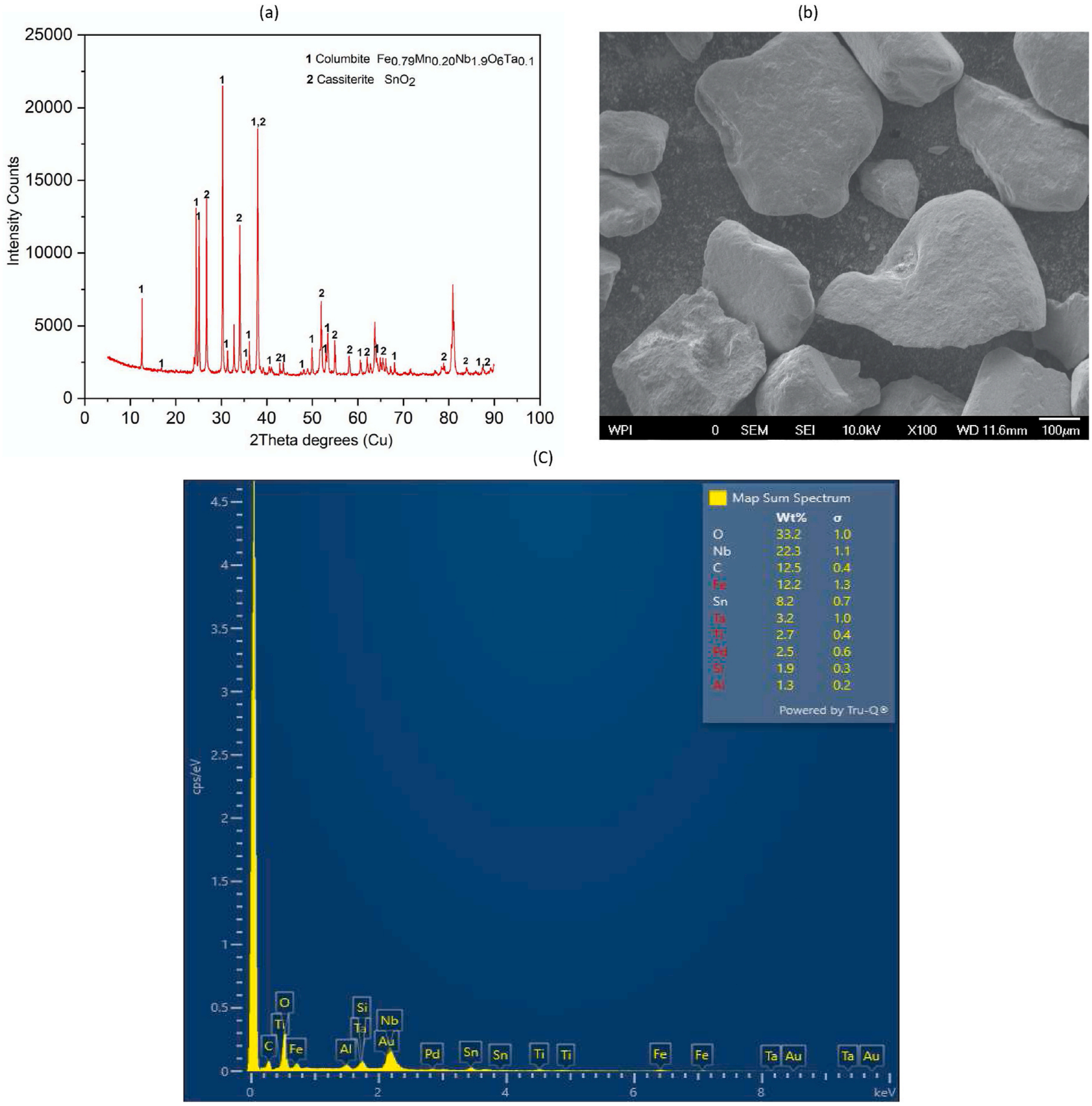
stirring to precipitate Nb and Ta. The Nb/Ta-guanidine precipitate appeared in the solution immediately in less than a minute. The mixture was stirred for 30 min to ensure complete precipitation. After 30 min, the mixture was filtered on vacuum pump and the precipitate was dried at 100 °C, both filtrate and precipitate were analyzed with ICP-OES for Nb, Ta, Sn, Fe, Mn, Si, and Al. The Nb/Ta-guanidine precipitate was then calcined at 900 °C for 1 h to convert precipitate into oxides of Nb and Ta and remove the guanidine. The percentage of element leached in the solution was determined by using the following expression:

$$\%\ \text{element leached} = \left(1 - \frac{Mr}{Mo}\right) \times 100 \quad (2)$$

where *Mr* is the weight of element in the residue after leaching *Mo* is the weight of element in the in the feed. The experimental flowsheet followed in this study is shown in Fig. 2.

2.3. Analytical techniques

The mineralogical characteristics were determined using PAN-Analytical Empyrean X-ray Diffractometer (XRD) with a Cu-Kα (λ = 0.1540 nm) radiation source operated at 45 kV and 40 mA at Worcester Polytechnic Institute (WPI), USA. The XRD samples were prepared by adding sufficient powder sample on a sample-holder and smoothen the surface to ensure a flat surface to the x-ray analyzer. The diffraction data were measured in 2-theta range of 5–90°, with a scanning rate of 2°/min and a step size of 0.02°. The diffractograms obtained were interpreted using X'Pert HighScore Plus software package (version 4.6a



	Wt%	σ
O	33.2	1.0
Nb	22.3	1.1
C	12.5	0.4
Fe	12.2	1.3
Sn	8.2	0.7
Ta	3.2	1.0
Ti	2.7	0.4
Pd	2.5	0.6
Si	1.9	0.3
Al	1.3	0.2

Fig. 3. Characterization of concentrate feed sample (a) XRD spectrum, (b) SEM micrograph, (c) EDS spectrum.

(4.6.1.23823)) matched with ICSD database. The Scanning Electron Microscopy attached with energy-dispersive x-ray spectroscopy (A JSM 700F SEM/EDS) was also used for surface morphology and elemental analysis of the investigated samples. The SEM/EDS powder sample was carefully prepared first by fixing a carbon double-sided sticker on sample holder and using a spoon to collect a small amount of sample and allow it to fall on the exposed side of the carbon sticker. Then, using air spray to remove the excess particles and mounting the sample into the specimen holder and now sample-specimen is ready to be inserted into SEM chamber.

The quantitative elemental compositions were determined using inductively coupled plasma-optical emission spectroscopy (PerkinElmer Optima 8000 ICP-OES) at WPI. The elemental analysis was performed at different spectral emission lines using RF Power of 1500W with a Plasma and Pump flow rate of 14.0 L/min, and 1.5 mL/min, respectively. The solid samples were prepared by fusing a mixture of 0.1 g powder sample and 1.0 g of fusion flux (lithium tetraborate) in a graphite crucible and put it in a preheated furnace at 1000 °C. After 1 h of heating, the melt was dissolved in 25% nitric acid. To ensure a complete dissolution of Nb/Ta, a small amount (1.5 mL) of concentrated hydrofluoric acid (40%) was added after 20 min of continuous stirring. After 90 min stirring was stopped and an appropriate volume of the solution was taken and diluted 10 or 100 times (depending on concentration of the analyte) with 2% nitric acid and then analyzed with ICP OES [44,45].

3. Results and discussions

3.1. Sample characterization

Chemistry and mineralogy of the Nb–Ta concentrate from Jos Plateau of Nigeria were analyzed before the size classification and heat treatment process. The chemical compositions of the concentrate under investigation were analyzed with ICP-OES Table 1. The mineralogical evaluation indicated that the main constituents of the sample are columbite-Fe (25.5% Nb_2O_5, 3.6% Ta_2O_5 and 15.8% Fe_2O_3) associated with cassiterite 25.9% SnO_2. XRD results confirmed the presence of Columbite and Cassiterite as the major mineral phases in the sample Fig. 3 (a). The SEM micrograph of the Nb–Ta concentrate at 100 magnifications in Fig. 3(b) depicts a smooth surface morphology characterized by particles of larges size of different shapes. The surface composition indicates presence of Nb (22.3%), Ta (3.2%), Fe (12.2%), and O (33.2%) as the major components of the columbite-Fe phase Fig. 3 (c). Some of Sn in form of cassiterite (SnO_2) was also detected with minor Al and Si oxides.

The Nb–Ta concentrate sample as received from the mining company was also screened with a sieve and classified into two different size fractions (+250 and −250 μm). Each fraction was analyzed to determine its compositions and crystalline phases present in the sample. The results of XRD analysis confirmed the presence of ferro-columbite phases associated with cassiterite and some iron and manganese oxides Fig. 3 (a). The chemical compositions information complemented with ICP-OES analysis, revealed no difference in chemical compositions between the two fractions. The main components present in each size fraction of the concentrate sample under investigation were columbite-Fe with average values of 25% Nb_2O_5, 3.5% Ta_2O_5 and 15.5% Fe_2O_3 accompanied with cassiterite, almost 25% SnO_2 Table 1.

3.2. Alkali roasting and water leaching

Minerals and ores of Nb and Ta in addition to their oxides are generally insoluble in mineral acids except in HF or in mixture of HF and H_2SO_4, which is not environmental benign. Thus, fusion of the geological samples containing Nb, and Ta is conducted to bring these metals of interest into the solution. A fusion process using KOH as flux was used to breakdown the components of the Nb–Ta concentrate into water-soluble compounds. In alkaline media ($8 \leq pH \leq 12$), Nb polymerizes into hydrated hexaniobate salts which are soluble, the solubility increases with decreasing concentration of alkaline solution and temperature, whereas Ta form similar salts at pH $\geq$ 12 [20]. The hexaniobate and hexatantalate salts are well-known (Nb,Ta)-species which are predominant in the solution with pH higher than ~10 [8].

$$(Fe,Mn)O(Ta,Nb)_2O_5 + 6KOH \rightarrow 2K_3(Ta,Nb)O_4 + (Fe,Mn)O + 3H_2O \quad (1)$$

$$6K_3(Ta,Nb)O_4 + 6H_2O \rightarrow K_8(Ta,Nb)_6O_{19}.H_2O + 10KOH \quad (2)$$

$$4FeO + O_2 \rightarrow 2Fe_2O_3 \quad (3)$$

$$2MnO + O_2 \rightarrow 2MnO_2 \quad (4)$$

$$Fe_2O_3 + 2KOH \rightarrow 2KFeO_2 + H_2O \quad (5)$$

$$MnO_2 + 2KOH \rightarrow K_2MnO_3 + H_2O \quad (6)$$

$$SnO_2 + 2KOH \rightarrow K_2SnO_3 + H_2O \quad (7)$$

$$SiO_2 + 2KOH \rightarrow K_2SiO_3 + H_2O \quad (8)$$

Scheme 1. [34].

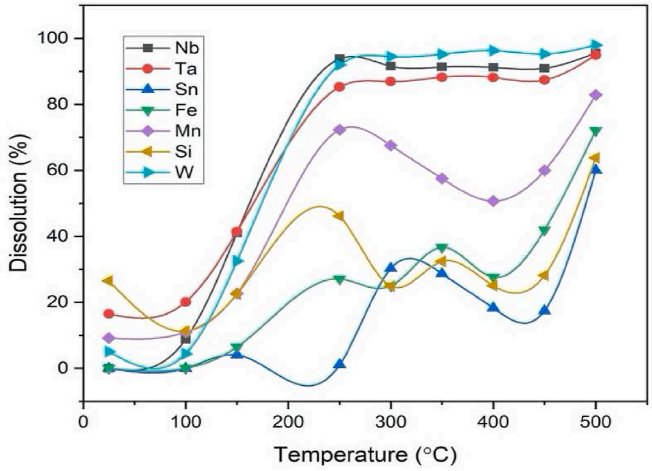


Fig. 4. Effect of temperature on dissolution of different elements at flux ratio 2:1 KOH: concentrate and 1 h heating duration.

During the alkali-assisted roasting (100–500 °C), the Nb–Ta and other elements contained in the concentrate feed sample react with molten KOH according to the mechanism of chemical reactions presented in Scheme 1. In the process, some of the Ta_2O_5 converts into soluble K_3TaO_4 and other part into insoluble $KTaO_3$ while Nb_2O_5 converts only into the soluble K_3NbO_4. However, depending on the alkali roasting conditions, the insoluble $KNbO_3$ can exist in the system via the isomorphism replacement between Nb^{5+} and Ta^{5+} where Nb can replace Ta and form a continuous solid solution of $KTaO_3$–$KNbO_3$. At low alkali concentration, the product is mainly the insoluble form of $KNbO_3$ ($KTaO_3$) and cannot be leached with water whereas at high alkali concentration, the product is mainly in the soluble form K_3NbO_4 (K_3TaO_4) Eq. (1) in Scheme 1. In addition to $K_3(Nb,Ta)O_4$ and $K(Nb,TaO_3)$, other salts resulting from Eqs. (5)–(8) in Scheme 1 of the roasting process goes immediately for leaching process. In the leaching, (Nb,Ta)-salts undergo hydrolyze and polymerize into water-soluble polyoxometalates species $K_8Nb_6O_{19}$ ($K_8Ta_6O_{19}$) which can be easily recovered [37]. On the other hand, FeO and MnO from Eq. (1) in Scheme 1 are oxidized by high temperature into Fe_2O_3 and MnO_2 with respect to Eqs. (3) and (4) in Scheme 1. The oxide products react with molten KOH to give salts $KFeO_2$ and K_2MnO_3 according to Eqs. (5) and (6) in Scheme 1 whereas SnO_2 and SiO_2 react to form salts K_2SnO_3 and K_2SiO_3 respectively as shown in Eqs. (7) and (8) in Scheme 1 [34].

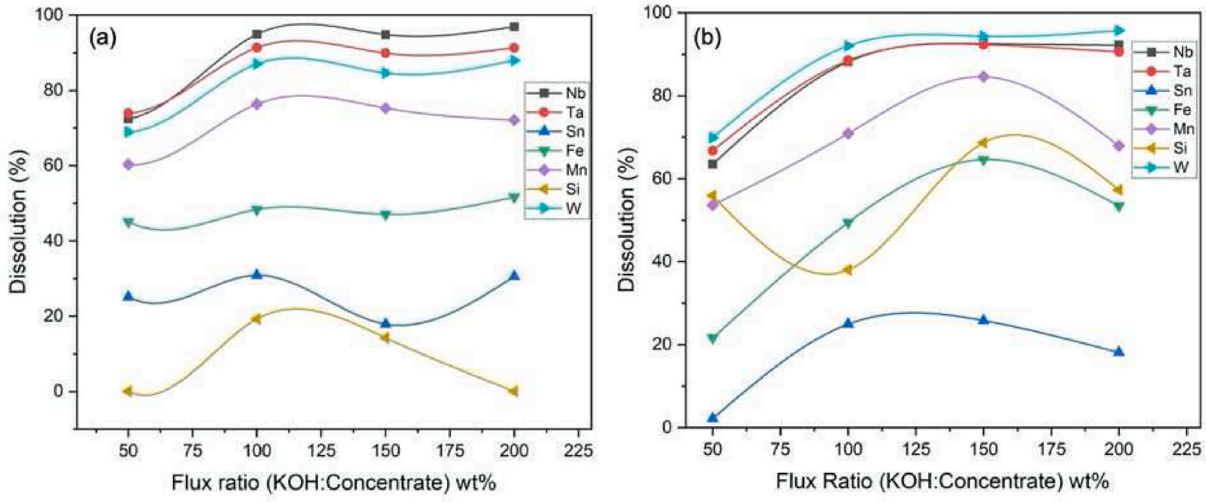


Fig. 5. Effect of flux-to-concentrate ratio on dissolution of elements in the concentrate at (a) 250 °C and (b) 500 °C.

3.2.1. *Effect of temperature on decomposition and dissolution of the niobium-tantalum concentrate*

The effect of temperature on dissolution of different elements at mass flux-to-concentrate ratio of 200% and 1 h heating time is shown in Fig. 4. From the figure, we can see that increasing of temperature has significant effect on dissolution of Nb and Ta. At the beginning, room temperature (25 °C), dissolution of Ta was minimum ($<$20%) while that of Nb was almost zero due to the insolubility nature of Nb/Ta minerals and compounds. Dissolution starts to increase at 100 °C through 150 °C, may be because of decrease in system's viscosity and mass transfer resistance at liquid-solid interface. At 250 °C, maximum dissolution for Nb (93.79%), Ta (85.23%) and W (91.93%) was achieved and no further change as temperature increases, reaction was completed at 250 °C. The dissolution of Mn, Fe, and Si start to decrease from their first maxima to minima at 400 °C, then increase again to the maximum at 500 °C. The dissolution of Fe (27.07%) and Sn (1.08%) was not significant at the beginning and start to increase at 150 °C through 350 °C, and decrease to 400 °C before attaining the maximum at 500 °C. This observed discrepancy in dissolution behavior between Nb, Ta and other elements is because the reaction of $(Nb,Ta)_2O_5$ with KOH occurs more readily than other reactions in the system. The behavior indicates efficient separation of Nb, Ta and W from Fe and Sn at 250 °C. The concentration of Mn, Si, Al, and W is relatively less in the starting feed and is of least concern to contaminate the final product.

3.2.2. *Effect of flux-to-concentrate on dissolution of niobium-tantalum concentrate*

Fig. 5 illustrates the effect of mass flux-to-concentrate ratio on the dissolution of different elements at 250 °C Figs. 5(a) and 500 °C Fig. 5 (b). Stoichiometrically from Eq. (1), almost 337 g of KOH would be required to convert 755 g of the Nb/Ta phases present in the concentrate feed sample. This is 44.5% flux-to concentrate ratio, thus the excess of KOH was beneficial to complete reaction and achieve optimum Nb/Ta dissolution since the concentrate is not 100% Nb and Ta compounds and other side reactions 5–8 will also occur. Therefore, at lower temperature 250 °C and 50% flux ratio, the dissolution of Nb, Ta, and W was minimum and start to increase to its maximum at a flux-to-concentrate ratio of 100% and remained almost constant as the flux-to-concentrate increases through 150% and 200%. At a mass flux-to-concentrate ratio of 100% approximately 94.88% Nb, 91.36% Ta, 48.37% Fe and 30.82% Sn dissolution was achieved. The dissolution of Mn, Fe and Sn decreased slowly from the maximum when flux-to-concentrate ratio increased from 100% through 150%–200%. At higher temperature Fig. 5(b) similar trend was observed with 100% flux-to-concentrate ratio being sufficient for highest dissolution value. Only dissolution of Si, Mn and Fe were improved slowly whereas that of Nb, Ta and Sn dropped relatively to that of lower temperature, may be due to the formation of insoluble compounds. As the ratio of flux-to-concentrate increases, dissolution of Nb, Ta and W also increases to the maximum at 100% flux ratio and approximately 88.54% Nb, 88.54% Ta, 49.47% Fe and 24.96% Sn were dissolved.

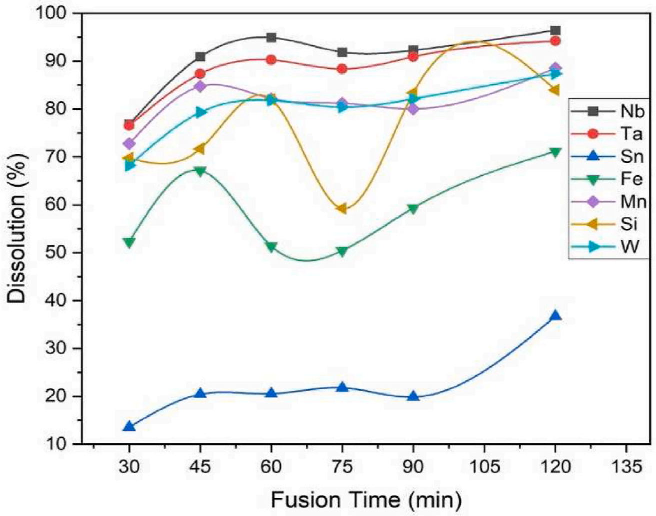


Fig. 6. Effect of fusion time on dissolution of different elements: flux-to-concentrate ratio 100%, and 250 °C temperature.

3.2.3. *Effect of roasting decomposition time*

The effect of roasting time on dissolution of different elements at 250 °C using 100% mass flux-to-concentrate ratio is shown in Fig. 6. The dissolution of Nb, Ta, W, and Mn increased with roasting time and reached equilibrium after 60 min of roasting. Sn showed least dissolution and remained in the residue in form of cassiterite as it is confirmed by XRD analysis of the residue. Fe was also dissolved at some extend and mainly found in the residue as hematite. Under optimal conditions 94.91% Nb, 90.24% Ta, 51.39% Fe and 20.57% Sn dissolution was obtained.

3.2.4. *Effect of particle size on alkali roasting*

Alkaline assisted roasting was performed using samples of two

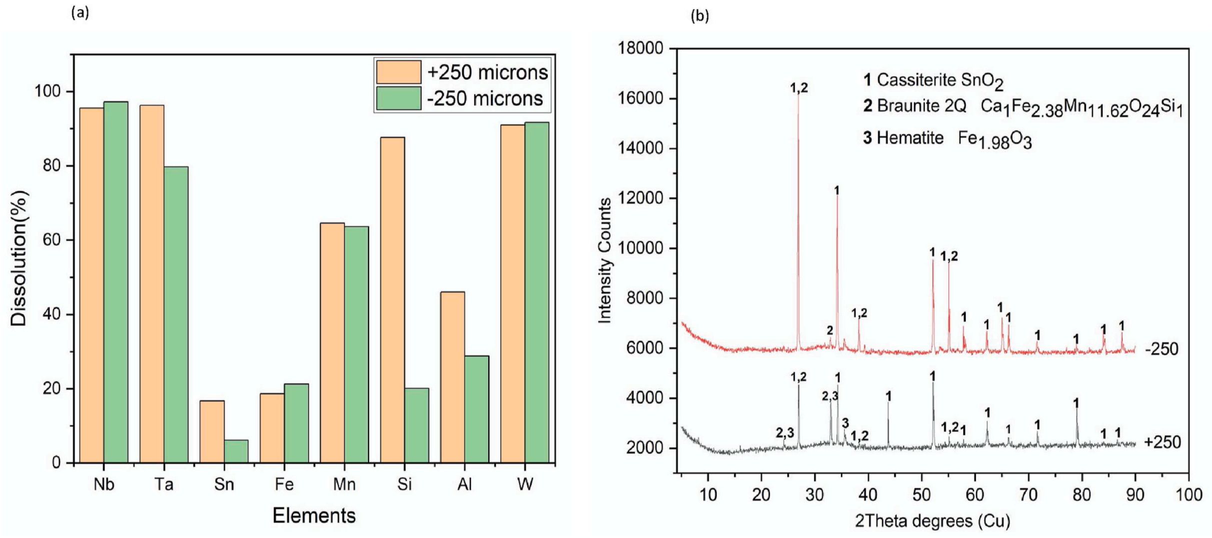


Fig. 7. (a) Alkaline dissolution of elements contained in the two size fractions +250 μm and −250 μm; (b) XRD spectrum of the residue obtained at different size fraction.

Table 2

Material balance for alkali roasting and water leaching of different size fractions at optimized conditions: 250 °C, flux ratio 100%, and 1 h roasting.

	+250 μm size fraction				−250 μm size fraction			
Elt	Feed (wt%)	Residue (wt%)	PLS (ppm)	Dissolution (%)	Feed (wt%)	Residue (wt%)	PLS (ppm)	Dissolution (%)
Nb	18.223	1.831	2754.120	95.536	19.030	3.164	2811.087	97.204
Ta	2.660	0.630	405.201	96.275	3.258	1.070	394.482	79.759
Sn	18.840	26.336	497.419	16.690	22.065	29.202	204.919	6.117
Fe	11.385	12.860	335.451	18.625	9.962	12.764	321.645	21.268
Mn	0.746	0.380	76.185	64.537	0.764	0.483	73.765	63.615
Si	0.290	0.461	40.240	87.620	0.503	0.583	15.328	20.091
Al	0.148	0.166	10.787	46.017	0.230	0.315	10.069	28.795
W	0.240	0.098	51.580	90.993	0.313	0.101	43.541	91.711
Weight(g)	15.345 g	8.702 g	970 mL	–	15.355 g	9.47 g	1012 mL	–

different size classes at optimized conditions (250 °C, flux-to-concentrate ratio 100%, and 1 h of roasting). The pregnant leach solution was subsequently collected for assessment and optimization of the Nb/Ta precipitation using guanidine. The roasting experiments were conducted using the oversize and undersize of the classified sample at a cutoff size of 250 μm. Different size fractions were tested to determine whether the material needs to be grounded to a finer particle size for minerals liberation.

The alkaline dissolution of the chemical elements contained in the Nb–Ta concentrate sample was found to be approximately the same within the two-size class as shown in Fig. 7(a). Similar dissolution trend indicates that the fusion process can effectively dissolve even the larger particles in the molten flux without any diffusion-based limitations and eliminates energy intensive for fine grinding requirements. The dissolution of Nb and Ta was found to be higher than 95% and 80% respectively, irrespective of the particle size. Dissolution of Mn and W was found to be approximately 65–64% and 91–92% respectively for +250 and −250-μm size fractions. Furthermore, dissolution of Fe, Sn, and Al was limited to a maximum of 17%, 19%, and 46% respectively. The particle size does not have a significant effect on the alkaline assisted dissolution of the main constituents of the concentrate sample under investigation.

The XRD spectrum of the residue obtained after roasting and leaching of the Nb–Ta concentrate depicts the presence of cassiterite as the major mineral phase. Other minor phases such as hematite and braunite were also detected in the residue Fig. 7(b). Because the reaction of $(Nb, Ta)_2O_5$ with KOH occurs more readily than others reactions involved and form highly soluble compounds while the insoluble remain in the residue. The hematite phase (α-Fe_2O_3) in residue may results from the oxidation of magnetite (Fe_3O_4) or the inversion of maghemite (γ-Fe_2O_3) when heated at temperature between 250 and 750 °C [46,47]. The braunite 2Q is a silicate mineral containing both iron and manganese. In presence of KOH, silicon in the ore first form soluble silicate K_2SiO_3 in equation 8 which transform into insoluble silicate that remained in the residue as braunite 2Q [34]. This agrees with the chemical composition information obtained from ICP-OES analysis, where the percentage content of Sn and Fe is high in the residue, whereas Nb and Ta get concentrated in the solution together with some dissolved Fe and Sn.

Furthermore, the elemental dissolution during leaching and corresponding materials balance are presented in Table 2. The PLS consist of approximately 2754–2811 ppm Nb, along with 405–394 ppm Ta, 204–497 ppm Sn, and 321–335 ppm Fe for +250 and −250μm size fractions respectively. Whereas the concentration of other elements (Mn, Si, Al, W) was less than 100 ppm. The concentration of Nb in PLS is significantly higher compared to other elements reflecting effective roasting and separation from other elements. The collected PLS was further processed to precipitate Nb–Ta values with novel application of guanidine amine salt as precipitating agent. The reported dissolution was calculated based on composition of PLS by using the following formula:

$$\% \; Dissol = \frac{(Conc \; of \; PLS \; in \; ppm*Volume \; (L)}{(wt\% \; of \; feed*total \; wt \; of \; feed)}*100 \tag{3}$$

3.3. *Precipitation of Nb–Ta from PLS using guanidine carbonate salt*

The PLS collected after alkaline heat treatment and water leaching process was processed to recover the dissolved Nb–Ta via precipitation

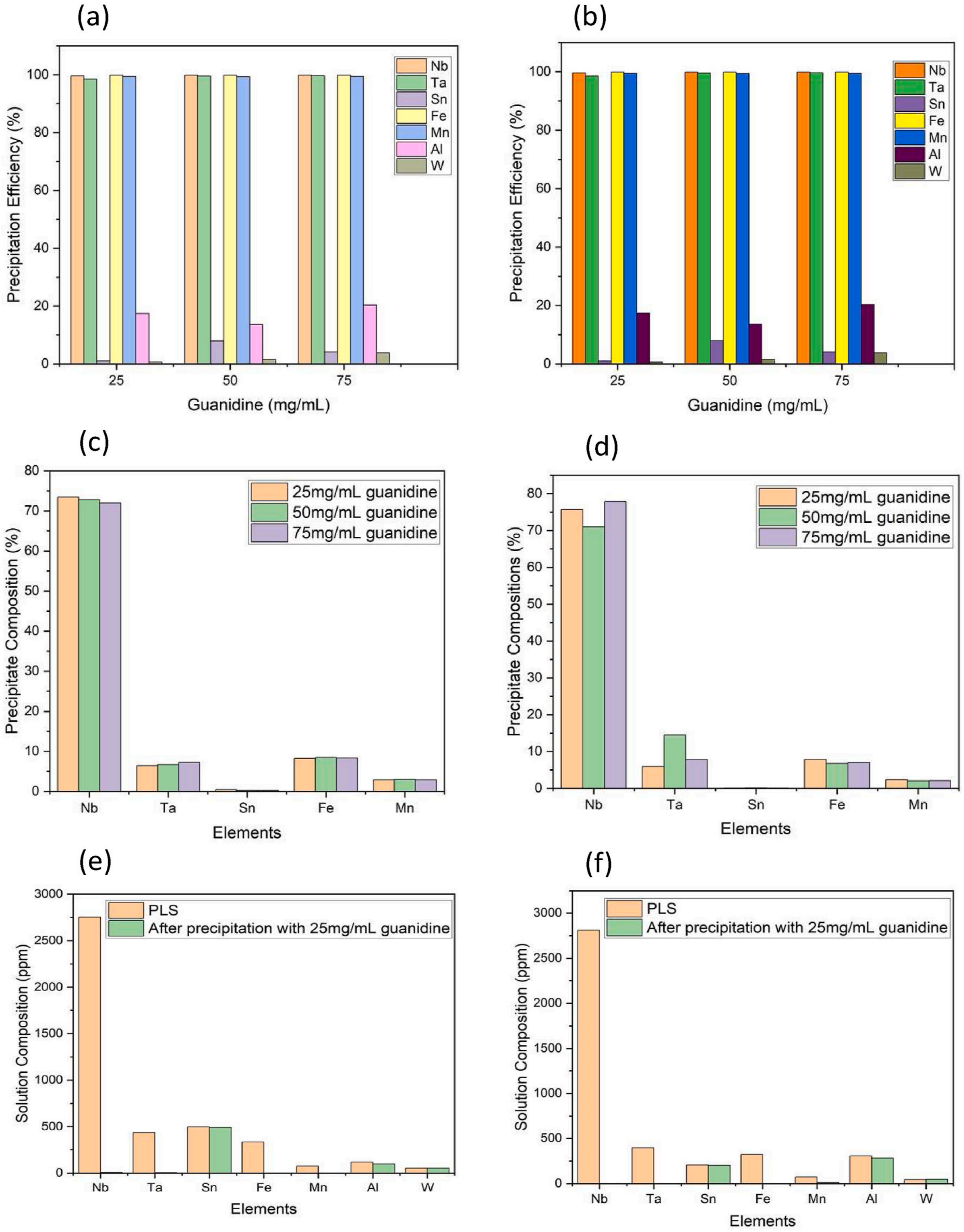


Fig. 8. Precipitation efficiency for (a) +250 μm size sample, (b) −250 μm size sample, Composition of precipitate at different guanidine dosage: (c) +250 μm size sample, (d) −250 μm size sample; Composition of PLS before and after precipitation (e) +250 μm size sample, (f) −250 μm size sample.

using Guanidine carbonate salt. Guanidine has proven the potential to rapidly and selectively precipitate Ta from a synthetic aqueous solution containing other metals such as Si and W [43]. When guanidine is added to an aqueous solution containing Nb and Ta; the guanidinium ion $C(NH_2)_3^+$ interacts electrostatically with ions of these metals (polyoxometalate) and a white precipitate is formed instantaneously Eq. (4) [43].

$$(\mathrm{Ta,Nb})_6\mathrm{O}_{19}{}^{8-}{}_{(aq)} + 8C(\mathrm{NH}_2)_3{}^{+}{}_{(aq)} \rightarrow \left(\mathrm{C(NH}_2)_3\right)_8(\mathrm{Ta,Nb})_6\mathrm{O}_{19\ (s)} \quad (4)$$

Precipitation of Nb and Ta using guanidine carbonate salt was carried out with PLS obtained from fusion and water leaching of +250 and −250μm size samples. Fig. 8(a) and (b) shows the Nb/Ta precipitation efficiency at different dosage of guanidine using PLS obtained from the two different size fractions. The precipitation efficiency was almost constant through increase of guanidine concentration and had no effect on the quality of precipitate. 25 mg/mL of guanidine was found sufficient to precipitate total amount of Nb and Ta reported in the PLS, however, the overall recovery of (Nb,Ta) decreases as guanidine increases. More than 99% precipitation efficiency was observed for Nb, Ta,

Table 3
Total recovery of Nb/Ta after guanidine precipitation (Roasting: 250 °C, flux ratio 100%, and 1 h roasting), Precipitation: 25, 50, 75 mg/mL guanidine, 30 min, 25 °C.

		+250 μm size fraction			−250 μm size fraction		
Elements	Guanidine (mg/mL)	Feed (%)	Precipitate (%)	Extraction (%)	Feed (%)	Precipitate (%)	Extraction (%)
Nb	25	18.223	25.075	95.249	19.030	27.468	97.726
Ta		2.660	3.065	79.748	3.258	3.022	62.799
Sn		18.839	0.155	0.568	22.065	0.032	0.099
Fe		11.385	2.564	15.590	9.962	2.618	17.791
Mn		0.746	0.587	54.427	0.764	0.500	44.325
Al		0.148	0.083	38.940	0.230	0.097	28.623
W		0.240	0.018	5.312	0.313	0.011	2.342
Weight(g)		15.000	10.380	–	15.000	10.160	–
Nb	50	18.223	24.035	96.897	19.030	25.686	93.631
Ta		2.660	3.083	85.134	3.258	3.757	79.981
Sn		18.839	0.082	0.320	22.065	0.041	0.127
Fe		11.385	2.545	16.422	9.962	2.231	15.534
Mn		0.746	0.586	57.681	0.764	0.443	40.231
Al		0.148	0.073	36.025	0.230	0.100	30.177
W		0.240	0.016	4.877	0.313	0.012	2.646
Weight(g)		15.000	11.02	–	15.000	10.4	–
Nb	75	18.223	22.526	87.564	19.030	25.458	90.572
Ta		2.660	3.153	83.948	3.258	3.597	74.751
Sn		18.839	0.079	0.296	22.065	0.028	0.085
Fe		11.385	2.375	14.781	9.962	2.081	14.139
Mn		0.746	0.538	51.071	0.764	0.411	36.388
Al		0.148	0.069	33.035	0.230	0.097	28.458
W		0.240	0.015	4.382	0.313	0.014	3.018
Weight(g)		15.000	10.62	–	15.000	10.16	–

Fe and Mn whereas a minimal amount of less than 20% of Sn, Al and W was co-precipitated with them. The composition of precipitate obtained is shown in Fig. 8(c) and (d). The precipitate composition was almost constant with variation of guanidine concentration. The precipitate obtained from liquor solution of −250 μm size fractions seems to have high percentage compositions relatively to that of +250 μm size fractions. The composition consists of approximately 79% Nb and 8.7% Ta along with 7.5% Fe and 1.4% Mn as minor impurities. Comparison of PLS and the solution obtained after precipitation is shown in Fig. 8(e) and (f). Concentration of Nb and Ta remained in the solution after guanidine precipitation were 3.32 and 1.56 ppm and 2.1 and 0.97 ppm for size fractions +250 and −250 μm respectively. The concentration of Sn, Al, and W in the solution remained unchanged after precipitation, this reflects their inert behaviors toward guanidine in the alkaline media. Contrary, the dissolved Fe and Mn were co-precipitated along with Nb–Ta as the main impurities of the precipitate. The expression used for calculating guanidine precipitation efficiency is given below:

$$\%\ \text{Precipitation Efficiency} = \left(1 - \frac{Mr}{Mo}\right) \times 100 \tag{5}$$

where ***Mr*** is the weight of element in solution obtained after guanidine precipitation and ***Mo*** is the weight of element in pregnant leach solution before precipitation.

From Table 3, at an optimum guanidine of 50 mg/mL, it is possible to obtain 734.5 kg of precipitate in form of (Nb,Ta)-guanidine salt from one tonne of the feed concentrate. By converting Nb and Ta into oxides, 4.201 g of (Nb,Ta)-mixed oxides were obtained from 15.0 g of feed concentrate, this gives 280.067 kg of mixed-oxides from one tonne of feed concentrate. Then, by comparing with $(\mathrm{Nb,Ta})_2\mathrm{O}_5$ presented in Table 1, for concentrate feed of +250 microns size fraction, it contains 29.151% of mixed $\mathrm{Nb_2O_5}$ and $\mathrm{Ta_2O_5}$, this would give 291.51 kg of $(\mathrm{Nb,Ta})_2\mathrm{O}_5$ from one tonne of the feed concentrate. Therefore, overall efficiency recovery of 96.06% for $(\mathrm{Nb,Ta})_2\mathrm{O}_5$ was obtained. The Nb/Ta-precipitate was calcined at 900 °C for 1 h to convert metals into oxides and remove the guanidine through evaporation in form of carbon and nitrogen oxides Eq. (6) [33,43].

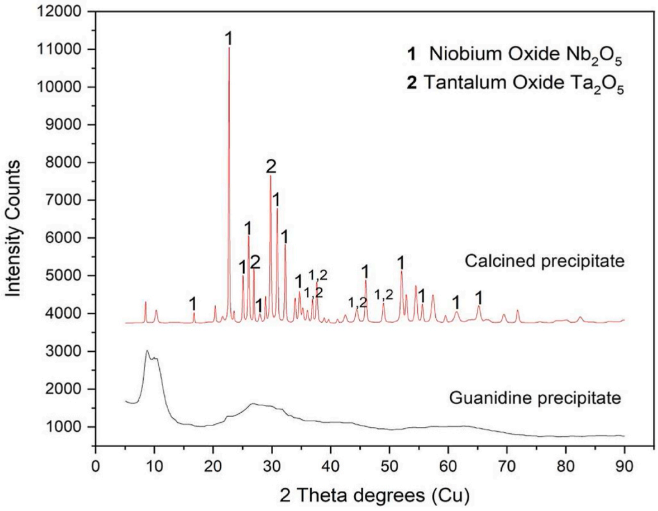
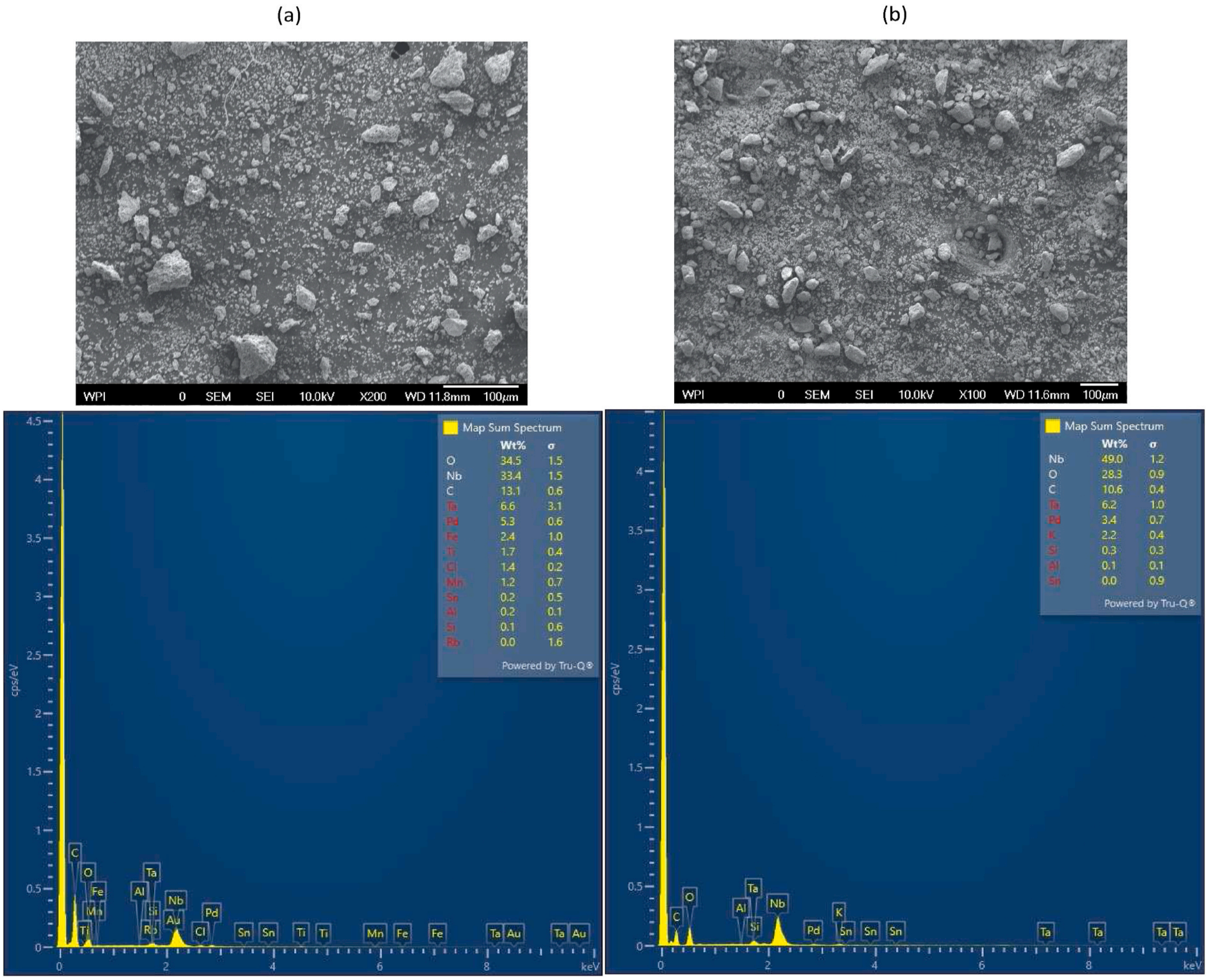


Fig. 9. XRD spectrum of Nb/Ta guanidine precipitate and calcined precipitate.

$$(\mathrm{C(NH_2)_3})_8(\mathrm{Ta,Nb})_6\mathrm{O}_{19\,(s)} \xrightarrow{900^\circ C} (\mathrm{Ta,Nb})_2\mathrm{O}_{5\,(s)} + CO_{2(g)} + NO_{x(g)} + H_2\mathrm{O}_{(g)} \tag{6}$$

The calcination resulted in mass loss of almost 50% and mixed oxides $(\mathrm{Nb,Ta})_2\mathrm{O}_5$ with purity of 97%. The XRD spectrum of Nb/Ta-guanidine precipitate and calcined precipitate presented in Fig. 9 depicts that the guanidine precipitate was amorphous, and no crystalline peak were obtained [43,48]. The amorphous precipitate converted into crystalline Nb/Ta oxide phases upon calcination at 900 °C for 1 h and is reflected in the XRD spectrum in Fig. 9. The calcination process destroyed and removed the guanidine in form of carbon and nitrogen oxides [43]. The SEM/EDS micrograph of guanidine precipitate and calcined product is shown in Fig. 10(a) and (b) where particles of the precipitate are characterized by smooth and uneven sized morphology mainly composed of Nb and Ta which was confirmed from results of EDS analysis. Micrograph of the calcined precipitate had a powdery texture and broken



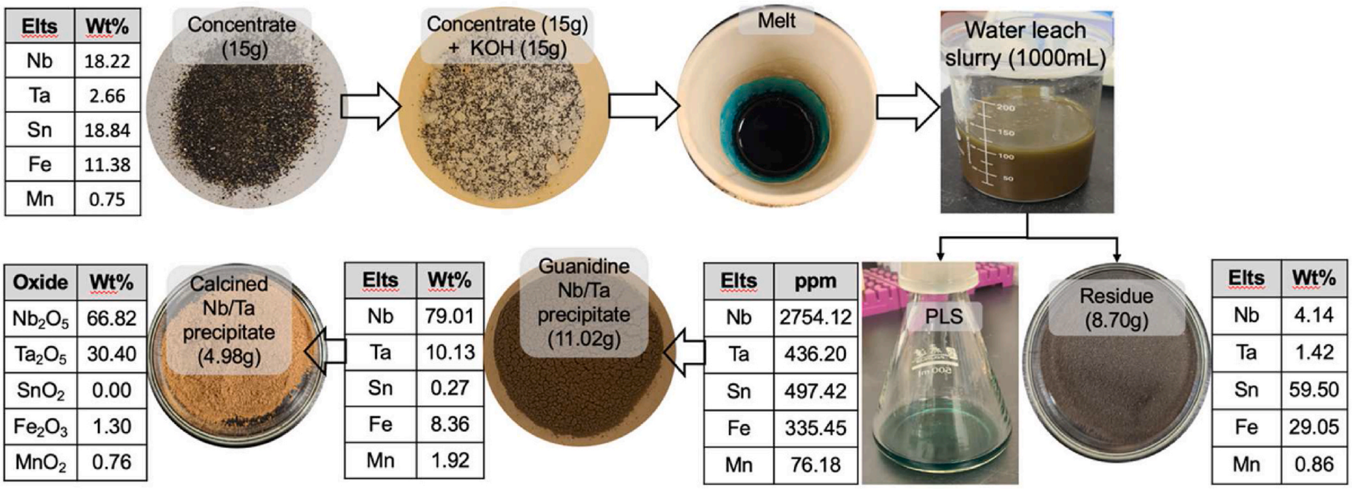
(a) Map Sum Spectrum

	Wt%	σ
O	34.5	1.5
Nb	33.4	1.5
C	13.1	0.6
Ta	6.6	3.1
Pd	5.3	0.6
Fe	2.4	1.0
Ti	1.7	0.4
Cl	1.4	0.2
Mn	1.2	0.7
Sn	0.2	0.5
Al	0.2	0.1
Si	0.1	0.6
Rb	0.0	1.6

(b) Map Sum Spectrum

	Wt%	σ
Nb	49.0	1.2
O	28.3	0.9
C	10.6	0.4
Ta	6.2	1.0
Pd	3.4	0.7
K	2.2	0.4
Si	0.3	0.3
Al	0.1	0.1
Sn	0.0	0.9

Fig. 10. (a) SEM/EDS of guanidine precipitate, (b) SEM/EDS of calcined Nb–Ta precipitate.



Elts	Wt%
Nb	18.22
Ta	2.66
Sn	18.84
Fe	11.38
Mn	0.75

Elts	Wt%
Nb	4.14
Ta	1.42
Sn	59.50
Fe	29.05
Mn	0.86

Elts	ppm
Nb	2754.12
Ta	436.20
Sn	497.42
Fe	335.45
Mn	76.18

Elts	Wt%
Nb	79.01
Ta	10.13
Sn	0.27
Fe	8.36
Mn	1.92

Oxide	Wt%
Nb_2O_5	66.82
Ta_2O_5	30.40
SnO_2	0.00
Fe_2O_3	1.30
MnO_2	0.76

Fig. 11. Sample specimen photographs at different stages of treatment.

surface morphology contrary to uncalcined precipitate.

Sample specimen photographs and composition at different stages of treatment are shown in Fig. 11 and the corresponding material balance and overall recovery values are presented in Table 3. Under the optimized conditions, Nb,Ta-guanidine precipitate with purity more than 84% was obtained. The calcination of the precipitate produced a mixed oxides of Nb and Ta having purity of 97%. The percentage recovery/extraction was calculated by using the following expression:

$$\%\,Recovery = \frac{(wt\%\ of\ element\ in\ precipitate * total\ weight\ of\ precipitate)}{(wt\%\ of\ element\ in\ the\ feed * total\ weight\ of\ feed)} * 100 \tag{7}$$

However, for +250 μm size fractions, recovery of Nb and Ta increases from 95 to 97% and from 80 to 85% respectively then decreases to their minimum of 86 and 84% with 25, 50 and 75 mg/mL of guanidine concentration. Contrary to the fine materials (−250 μm), the recovery of Nb decreased from 98 through 94 to 91% while that of Ta increased from 63 to 80% then decrease to 75% at 25, 50 and 75 mg/mL guanidine. The observed decrease in % recoveries may be related to the kinetics of the precipitation process which would require more investigations in the future studies. For some cases, due to calculation errors, there is a slight increase in % recoveries relatively to their % dissolutions but still in the same range.

4. Conclusion

The extraction of Nb–Ta from Ferro-columbite concentrate of Jos plateau (Nigeria) using alkali roasting, water-based leaching and precipitation with guanidine amine salt was investigated. Characterization of the concentrate sample under investigation indicated presence of columbite-Fe and cassiterite as main constituents with Nb_2O_5 (33.3% wt), Ta_2O_5 (5.5%wt), Fe_2O_3 (18%wt), MnO (2%wt) and SnO_2 (27%wt). The concentrated ore-sample was screened into two different size fractions, +250 and −250 μm with a sieve. The alkali assisted roasting and water leaching of the two size fractions at optimum conditions (250 °C, 100% flux-to-concentrate ratio and 1 h roasting) resulted in dissolution of 97–96 %wt Nb, 80-96 %wt Ta, 92-91 %wt W and 64-65%wt Mn respectively. The process leaves behind in the residue most of the Sn (94-83%wt), Fe (79-81%wt) and other associated impurities. The amount of Nb and Ta reported in the resulting liquor solution were recovered by precipitation using guanidine carbonate salt as precipitating agent. Guanidine salt effectively precipitated out total amount of Nb and Ta contained in the PLS. This resulted in a high recovery of almost 97% and 85% of the total amount of Nb and Ta contained in the +250 μm concentrate sample (feed) with optimum of 50 mg/mL guanidine. Irrespective of the size fractions, variation of guanidine does not show a significant effect on composition of the Nb–Ta precipitate. However, precipitate from −250μm size fraction seems to have high percentage compositions for Nb and Ta. Regardless of the guanidine concentration, higher Ta recoveries were achieved for +250 μm size whereas that of Nb were obtained for −250 μm except at 50 mg/mL guanidine. Based on material balance, it was found that approximately 734.5 kg of (Nb,Ta)-guanidine precipitate with purity higher than 84% could be obtained from one tonne of ferro-columbite feed concentrate. Since the content of Mn in the feed sample and PLS is not high and the extent at which iron dissolve is not such high (35%wt). In addition, their reaction with KOH is too slowly compared to that of Nb and Ta, thus their presence in the precipitate does not affect much the purity of the final product. The Nb–Ta guanidine precipitate obtained was then calcined at 900 °C for 1 h to convert the precipitate into mixed oxides of Nb and Ta and remove the guanidine. The calcination resulted in mass loss of almost 50% and $(Nb,Ta)_2O_5$ product with 97% purity containing Fe_2O_3 (1.3%) and MnO_2 (0.7%). The use of guanidine carbonate salt to recover Nb and Ta from aqueous solution is environmentally friendly process providing high yield (∼100%) and high potential to replace the traditional approach which use hydrofluoric acid.

Credit author statement

Jean Baptiste Habinshuti: Methodology, Writing – original draft, Investigation, and results interpretation. Jeanne Pauline Munganyinka: Visualization and Formal analysis. Adelana R. Adetunji: Writing – review & editing. Brajendra Mishra: Supervision and Resources. Janvier Mukiza: Conceptualization and Validation. Tanvar Himanshu: Formal analysis. Grace Ofori-Sarpong: Writing – review & editing. Azikiwe Peter Onwualu: Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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