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Preliminary Investigation on the Thermodynamic Evaluation and Phase Evolution of Soda Ash-Assisted Roast Treatment of Alluvial Columbite for Recovery of Niobium and Tantalum

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Alkaline roasting of a low-grade alluvial silica-based columbite bearing mineral from the Rayfield–Jos deposits (located in South Jos, Plateau state, Federal Republic of Nigeria) was conducted with specific emphasis on the evaluation of thermodynamic reactions as well as the mineral phase evolution during the extraction of Nb and Ta. An isothermal roasting procedure was investigated in order to understand the effects of different soda ash to sample mass ratios as well as the roasting temperatures on the measure or rate of the recoveries of Nb and Ta complexes. Thus, the feasibility rate of a successful alluvial columbite mineral roasting was determined to be influenced by certain optimal process conditions or optimum values of the study parameters, such as alkali to sample mass ratio and, more essentially, the roasting temperature. Therefore, the thermodynamic feasibility of the alkali-carbothermic roasting procedure was also investigated and the resulting chemical reactions were evaluated using the HSC chemistry 9.0 software. Premised on this, the results obtained as well as the thermodynamic data realized from the study demonstrated the feasibility of successful dissolutions of Nb and Ta into a pregnant leached-liquor stream (PLS), without the use of the conventional harmful, hazardous, toxic, and environmentally unfriendly hydrofluoric (HF) acid.

INTRODUCTION

Niobium and tantalum are ubiquitous in a broad range of industries including aerospace, telecommunications, nuclear energy, and iron and steel making.^{1–3} These elements primarily exist as mixed oxides in minerals such as columbite–tantalite (coltan) and pyrochlore–microlite, and can also be found in lower grades or concentrations in other

minerals, such as the secondary mineral sources of columbite, tantalite, and coltan, and also in euxenite, struverite, loparite, fergusonite, samarskite, mossaite, tapiolite, and cassiterite minerals.^{1,4} The global demand for these elements along with the rarity of their high-grade primary mineral ores is notable, hence they are currently classified as “critical elements.”^{1,4–8} Thus, various factors contribute to the inevitable need to explore and exploit the low-grade or secondary mineral sources of columbite, tantalite, or coltan, such as their mineral tailings as well as other heavy mineral tailings containing Nb and Ta. These factors include the

pervasive nature of the metallic elements in numerous technological and engineering applications, along with the sparse nature of their ores, low crustal abundance in primary mineral deposits (Nb, 20–25 ppm) and Ta (2 ppm), and the low-grade composition of the available columbite/tantalite or coltan mineral ores.^{1,2,5–10}

Low-grade niobium and tantalum mineral ores are known for their diverse mineralogy, and are mostly found together with oxides of iron, manganese, zirconium, silicon, titanium, tin, and aluminum.^{1,2,11} As such, the extraction process includes several mineral pre-treatment procedures, upgrades, and beneficiation processes, all targeted at eliminating these gangue impurities or selective dissolution of niobium and tantalum. Here, various processes based on pyrometallurgy and hydrometallurgy or in combination have been adopted.^{1–4} Common ones include alkali fusion accompanied by acid leaching, chlorination, ammonium fluoride (NH_4F) or ammonium bifluoride (NH_4HF_2) fusion, direct hydrofluoric (HF) acid dissolution or leaching, direct sulfuric (H_2SO_4) acid dissolution or in a combination with hydrofluoric (HF) acid, as well as alkaline solution dissolution.^{1,4–6,12–27} The conventional process method of extracting and recovering Nb and Ta is usually conducted hydrometallurgically, often employing the use of aqueous dissolution and subsequent solvent extraction, ionic exchange, or other separation and purification processes.^{1–5,28} However, some of these process routes are carried out under harsh aqueous media conditions of very toxic, concentrated, hazardous, and with corrosive chemicals through several complex beneficiation and separation steps. This could be chiefly attributed to the high level of insolubility of Nb and Ta as well as other refractory metallic oxides in somewhat milder conditions. In addition to this, the chemical and physical similarities of Nb and Ta, along with other refractory elements, tend to increase their separation difficulty and, overall, increase the extraction process complexity.^{1–4}

Different hydrometallurgical process methods of Nb/Ta recovery have been developed and established, practiced industrially and employed commercially over the past decades. For instance, a hydrometallurgical method called the “marignac process” for the extraction of Nb and Ta was developed by Jean Charles Galissard de Marignac in 1866. It involved the use of fractional crystallization to separate Ta and Nb as potassium heptafluorotantalate ($\text{K}_2[\text{TaF}_7]$) and potassium oxypentafluoronioate monohydrate ($\text{K}_2[\text{NbOF}_5]\text{H}_2\text{O}$), respectively. This in turn is reduced to obtain metals of certain purity, most times through electro-winning in fused salts, as reported by Nzeh et al.¹ However, a new process, liquid–liquid extraction was established in the twentieth century, which replaced marignac. This method was developed in 1957 by the Ames Laboratory in collaboration with

U.S. Bureau of Mines, and utilizes the acid solubility differences of Nb and Ta fluoride ions in organic solvent media at different acidic levels.^{1–3} Albeit the aforementioned approaches are quite effective, they often require harsh, hazardous, toxic, and corrosive operational conditions, including moderately elevated temperatures and lixiviant concentrations.^{1–4,12,17,28–32} They are also designed for medium to high-grade mineral ores; thus, direct application to low-grade mineral ores will significantly reduce the economic benefits while aggravating the environmental impact of the whole process.

Following the inherent limitations of the conventional pyrometallurgical and hydrometallurgical approaches to the recovery of these elements from their mineral ores, the alkali roast-water leaching system is a more suitable and sustainable approach which was proposed and recommended by Nzeh et al.^{1–3} It entails a pyro-hydrometallurgical process that converts niobium and tantalum in the mineral ores into compounds of varied polarity and magnetic properties. Here, niobium/tantalum-bearing mineral ores are roasted with alkalis in inert, oxidizing or reducing conditions, with the tantalum and niobium converted to tantalates and niobates of varied polarity and magnetic properties. This approach, as shown by several studies, can be achieved using a broad range of alkali complexes and/or salts including NaOH, Na_2CO_3 , KOH, and K_2CO_3 , among others.^{1–4,22,23,26} However, the results obtained from the investigations conducted by these researchers indicated that the nature of the compounds formed was highly dependent on the molar ratio of alkali complex/salt to mineral ore and roasting conditions including temperature.

Thus, it has been shown that a high alkali (KOH) to ore molar ratio favors the formation of water-soluble niobates and tantalates while a high roasting temperature, confirmed via thermodynamic evaluation of the possible reactions and quantitative analysis, facilitates the formation of water-soluble tantalates and niobates.^{4,23} In another study using sodium carbonate (NaCO_3) as alkali source, Ghambi et al.³³ confirmed that temperatures and amounts of alkali salts also influence the magnetic properties of the formed compounds. Shikika et al.⁴ advocated roasting at temperatures above 550°C to avoid the formation of the undesirable KTaO_3 and KNbO_3 , and Ghambi et al.³³ showed that roasting above 900°C has an insignificant effect on the nature of the compounds formed. However, there is no information on potential reactions and products between 550°C and 900°C. Furthermore, these studies showed that alkali tantalates and niobates exhibit similar solubility and magnetic properties. They overlooked the influence of the chemistry of the mineral-bearing ores, and this is often neglected despite the fact that variations in the origin and chemical composition of the ores can lead to the formation of undesirable compounds.^{1–3}

Additionally, alkali roast-water leaching has been shown by numerous researchers to be a facile, eco-friendly, and economical approach to recovering niobium and tantalum from low- and high-grade ores.^{22,23,33} There are, however, few studies on its application in the recovery of these critical metals from concentrates. Phase transformations occurring during the roasting of low-grade ores and concentrates with high gangue content have a significant effect on the overall product formation.^{33,34} Hence, there is a need for more studies using ores or mineral deposits, especially low-grade ones from different sources. Comprehensive understanding of the role of the origin of the ores, and the temperature and alkali mass ratio on the thermodynamics and formation of water-soluble compounds and recovery efficiencies is imperative for the future commercialization of this facile process. Following the above context, this work explored the thermodynamics feasibility of soda ash (sodium carbonate)-assisted reductive roasting of an alluvial silica-based columbite mineral (SBCM) from Rayfield–Jos minefields, South Jos, in Plateau state, Federal Republic of Nigeria. Unlike the works of Shikika et al.⁴ and Ghambi et al.,³³ possible reactions and products which can be influenced by impurities

were investigated. In addition, and, different from the study carried out by Ghambi et al.,³³ this present study has investigated the use of lower temperatures for the reductive roasting of low-grade Nb/Ta minerals. This study is of relevance as it provides the possibility of reducing the amount of energy consumed or required for the process, as well as reducing the cost of the process. Hence, this study presents the feasibility of employing lower roasting temperatures on a low-grade Nb/Ta mineral, and, as such, the resulting effects are discussed.

MATERIALS AND METHODS

Materials

About 25 kg of alluvial silica-based columbite mineral (ASBCM) was sourced from Rayfield–Jos minefields, located in Rayfield, South Jos, Plateau state, Federal Republic of Nigeria. As-received samples were concentrated using in situ gravity separation and screened (average particle size = 150 + 90 μm). Further homogenization was carried out, and a representative sample (1 kg) was obtained using a 10-way riffle splitter. The ASBCM deposit was characterized and the results are

Table I. Ultimate composition analysis of the bituminous coal sample utilized during reductive roasting

Compound	Fixed carbon	Ash	Water	Volatile	Sulfur
Composition (wt.%)	71.17	10.06	7.17	11.60	0.23



Fig. 1. Rayfield–Jos ASBCM: (a) bag of as-received sample (25 kg), (b) washed and dried sample.

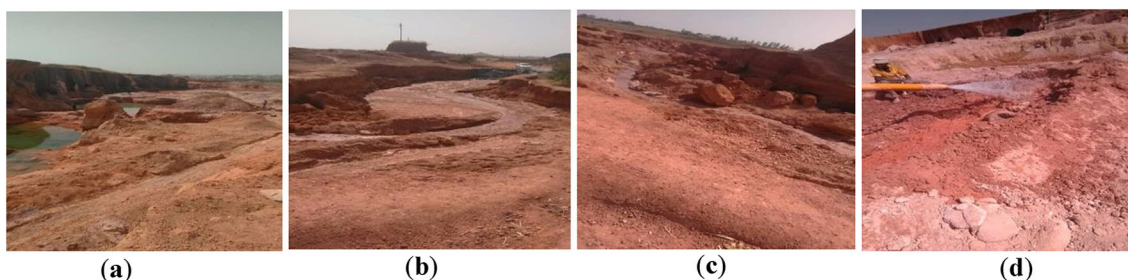


Fig. 2. (a–d) Different areas of the Rayfield–Jos minefields at Rayfield, South of Jos, Plateau state, Nigeria.

Table II. Roasting conditions

Parameters	Levels		
	550	650	750
Temperature (°C)	550	650	750
Alkali: sample mass ratio (wt.%)	2:1	4:1	6:1

presented in the “[Characterization and Analysis](#)” section. Different quantities of anhydrous soda ash (Na_2CO_3 , 99.5 wt.%) were used for the roasting, while a specific (constant) amount of South African bituminous coal served as the carbon source and the reductant needed to create a reducing atmosphere during roasting (see [Table I](#) for the ultimate analysis of the coal). [Figures 1 and 2](#), respectively, show samples of the Rayfield–Jos ASBCM and certain areas of the minefields at Rayfield, in South Jos, where the samples were collected.

Method

Roasting Procedure

An amount of 50 g of ASBCM, with various or varying specific ratios of soda ash, were pre-mixed using an IKA RW 20 digital overhead stirrer or mixer. About 100 g of bituminous coal was utilized in order to produce a reducing atmosphere. Each sample consisted of pre-determined amount of ASBCM and soda ash of varied alkali reagent to sample mass ratios. The pre-mixed samples were placed in 200-ml cylindrical ceramic crucibles, which were placed in a muffle furnace and then roasted at furnace temperatures between 550°C and 750°C for 1 h. On completion, the roasted mineral samples were removed from the furnace and allowed to cool to room temperature before being subjected to a water-leaching procedure. The parameters and parameter range or process conditions are depicted in [Table II](#).

Thermodynamic Analysis of Reductive Soda Ash Roasting

The thermodynamics of the reductive soda ash roasting procedure of ASBCM (in a reducing atmosphere) was performed using the HSC chemistry 9.0 commercial software.

Characterization and Analysis

Mineralogical Analysis

I. X-ray diffraction (XRD)

Mineralogical compositional analysis of the ASBCM was performed using X-ray diffraction (XRD; X’pert Pro; PANalytical) with phases present in the as-received ASBCM samples and the roasted samples characterized using a diffractometer with fixed receiving slits with iron (Fe)-filtered $\text{Co-K}\alpha$ radiation ($\gamma = 1.789 \text{ \AA}$) and a monochromatized $\text{Cu-K}\alpha$ radiation source ($\gamma = 1.5406 \text{ \AA}$) at a scanning

angle range of $2\theta = 10\text{--}90^\circ$ and a scan rate of $0.02^\circ \text{ s}^{-1}$. Phases present in the ASBCM mineral particles were matched and identified using X’pert Highscore Plus software.

Microstructural and Morphological Analysis

I. Optical microscopy (OPM)

Optical microscopy was conducted using OPM (BX 51 TRF; Olympus) on the columbite test sample. This was used to produce and examine the sample photomicrographs. The process adopted a combination of light and lenses to magnify the material image at different magnifications including 5 \times , 10 \times , 15 \times , and 20 \times . The objective lens was made up of two operational features which includes magnifications (ranging from 5 \times to 100 \times) and the numerical aperture (ranging from 0.14 to 0.7) corresponding to the focal lengths of 40–2 mm, respectively.

ii. Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS)

Scanning electron microscopy (SEM) along with energy dispersive spectroscopy (EDS) were used for morphological evaluation and elemental compositional analysis. A high-performance field-emission-scanning electron microscopy (FE-SEM; JSM-7600F; Joel, Japan) was used to examine the surface morphology and dispersion of homogenized columbite mineral test samples using secondary electron imaging. An energy dispersive X-ray spectrometer detector (Oxford X-Max) with an INCA X-Stream pulse analyzing software and back-scattered electron imaging detector equipped to the FE-SEM gave the elemental composition and surface topography of the columbite samples. The test samples were coated with conductive carbon with the aid of a carbon tape/vacuum coater and positioned for analysis. The INCA analyzer was set at an acquisition time of 70 s and 2 s process time. The FE-SEM analysis was conducted applying a spectrum range of about 1–20 keV and an accelerated voltage of about 20–30 kV incident electron energy beam for all the surfaces. The obtained SEM micrographs were subjected to ImageJ software for porosity determination.

Chemical Composition Analysis

I. X-ray fluorescence (XRF)

X-ray fluorescence (XRF; ARL Perform’X Sequential; Thermo Scientific) chemical composition analysis was conducted on the test sample (as seen in [Table III](#)). The mineral samples were prepared as boric acid powder briquettes and then XRF as well as Uniquant software was used to analyze both the test and reference mineral samples, respectively. This software was, however, set to detect all the elements ranging from Na to U in the periodic table and to report the elements above the limits of detection. Values were normalized, as there was no

Table III. ED-XRF analysis of the sample of ASBCM from Rayfield–Jos

Element	SiO ₂	ZrO ₂	Nb ₂ O ₅	Fe ₂ O ₃	TiO ₂	Al ₂ O ₃	SnO ₂	Ta ₂ O ₅	Others
Composition (wt.%)	69.60	9.88	6.60	4.58	2.39	1.90	0.99	0.70	3.36

Others oxides of Mn, Hf, P, Ce, Ca, Mg, Cr, W, Y, K, and U in minute amounts.

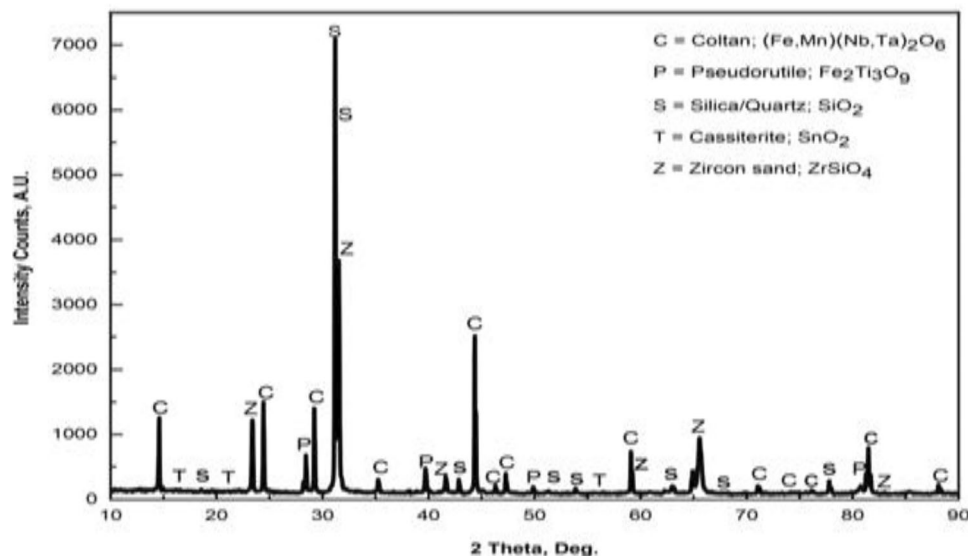


Fig. 3. XRD pattern of the ASBCM mineral.

loss on ignition (LOI) in determining the crystal water and changes in oxidation state.

RESULT AND DISCUSSION

Characterization of the As-Received ASBCM Samples

The data in Table III show the chemical composition of the as-received ASBCM measured using XRF. The ASBCM consisted of silica (SiO₂), zirconium dioxide (ZrO₂), niobium penta-oxide (Nb₂O₅), iron III oxide (Fe₂O₃), titanium dioxide (TiO₂), and oxides of aluminum (Al₂O₃) and tin (SnO₂), and minute amounts (< 1 wt.%) of HfO₃, Ta₂O₅, P₂O₅, CeO₅, MnO, CaO, MgO, SO₃, Cr₂O₃, WO₃, Y₂O₃, and K₂O. As shown, the ASBCM contains less than 25 wt.% of niobium and tantalum oxides and hence can be classified as a low-grade source.^{1–3,35–38} The XRD spectra of the as-received ASBCM in Fig. 3 confirm the presence of coltan, zirconia sand, quartz, cassiterite, and pseudorutile. Thus, in line with the literature,^{11,16,28,37,38} and also corroborated by the chemical analysis, it is evident that the main mineral constituents of the low-grade mineral deposit are thought to be columbite, quartz, and zirconia.

However, as already identified by the XRF analysis, quartz is the most dominant mineral and the major gangue in the ASBCM. Hence, the presence of a high composition of silica in the alluvial columbite mineral explains its low-grade nature. Furthermore, the OPM photomicrographs in Fig. 4a indicate the presence of quartz/silica, zirconia, and columbite particles embedded in each other. On the other hand, SEM analysis shows the presence of a significant amount of aggregate mineral particulates in particle sizes ranging mainly between 150 and 500 μm, and of shapes varying from sub-hedral (columbite mineral), sub-angular (quartz/silica), and spherical to sub-angular (zirconia) (Fig. 4b). This further corroborates the results of the OPM test. This is, however, in agreement with the reports from the literature corroborating the microscopic analysis that was conducted and reported by Ayeni et al.²⁹ Furthermore, Fig. 4c indicates significant micropores found within the particles. A maximum pore area of about 46.8% and a total average porosity of 45.0% were determined. EDS, with the results shown in Table IV, was conducted at three different spectra (Fig. 4d) and showed the presence of significant quantities of Nb, Ta, Si, Fe, Mn, Zr, and Al. Some of these elements might have been covered by silica, hence their absence in the XRD spectra in Fig. 3.

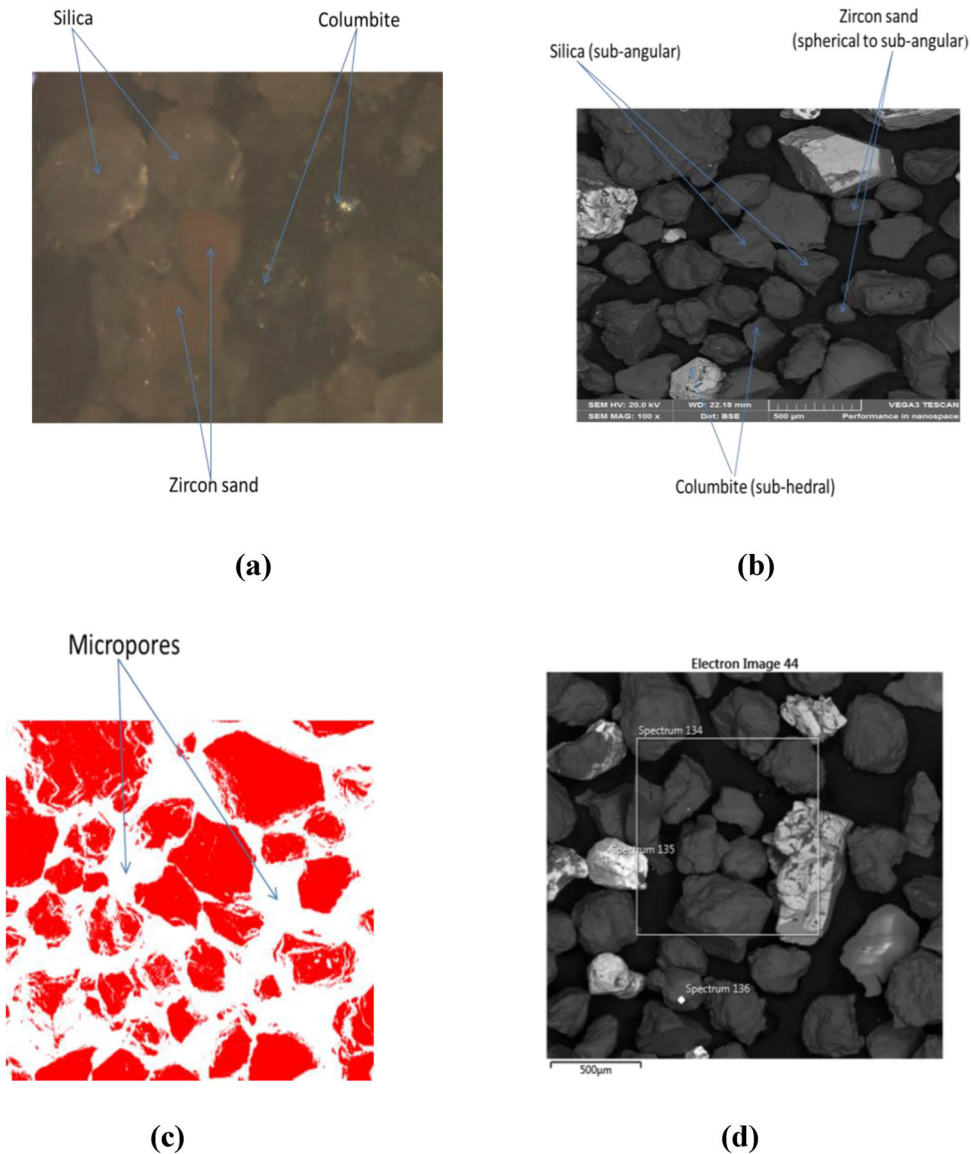


Fig. 4. (a) OPM and (b–d) SEM microstructural views of the Rayfield–Jos ASBCM samples.

Table IV. EDS spectra of the identified areas in Fig. 4d

Elements	Elemental composition		
	Spectrum 134 (wt.%)	Spectrum 135 (wt.%)	Spectrum 136 (wt.%)
O	44.5	55.7	48.7
Nb	–	16.9	1.2
Ta	–	0.3	–
Fe	0.7	5.9	2.8
Mn	–	0.2	–
Si	21.5	11.1	45.1
Al	1.3	9.8	2.2
Zr	31.9	–	–

Reductive Alkali-Assisted Roasting of the ASBCM Samples

Reductive roasting was conducted on the ASBCM samples and the reduced-roasted samples were physically examined and observed. Thus, Fig. 5 shows images of the reduced-roasted samples at the different roasting temperatures of 550°C, 650°C, and 750°C at constant alkali-to-sample mass ratios (A-S ratios), as well as the A-S ratios of 2:1, 4:1, and 6:1 at constant temperatures, respectively, indicating the color and texture variations of the different samples. It can be seen from Fig. 5 that there were

color variations as a result of the different A-S ratios. Therefore, as the A-S ratio increased from 2:1 to 4:1 and then to 6:1, the sample color became lighter. Furthermore, as the roasting temperature increased from 550°C to 650°C and then to 750°C, the particles of the samples were fused and agglomerated. This could be attributed to the fusion that occurred between the mineral particulates at the higher temperature of 750°C, as the further increase to 750°C led to the formation of sodium salts of aluminium and silica, such as sodium aluminosilicate (NaAlSiO_4), and, more essentially, to the formation of sodium niobates (Na(Nb,Ta)O_3).



Fig. 5. Roasted samples at different roasting temperatures and alkali-to-sample mass ratios: (a) 2:1 A-S ratio at 550°C, (b) 2:1 A-S ratio at 650°C, (c) 2:1 A-S ratio at 750°C, (d) 4:1 A-S ratio at 550°C, (e) 4:1 A-S ratio at 650°C, (f) 4:1 A-S ratio at 750°C, (g) 6:1 A-S ratio at 550°C, (h) 6:1 A-S ratio at 650°C, (i) 6:1 A-S ratio at 750°C.

Effect of Temperature and Alkali-to Sample Mass Ratio

In this study, the roasting temperatures were varied in order to conduct preliminary investigations on the influence of temperature on the evolution of the alkali salt (Na_2CO_3) of Nb, Ta, and other mineral contents, such as Fe, Mn, Ti, Zr, and Sim as well as the investigation of the feasibility of the formation of soluble alkali salts, most essentially soluble sodium niobates and/or sodium tantalates. The XRD phase patterns for the roasting temperatures between 550°C and 750°C at constant A-S ratios, and with different alkali-to-sample mass ratios between 2:1 and 6:1 at constant temperatures, can be seen in Fig. 6. Furthermore, the SEM and EDS analyses in Fig. 7 and Table V, respectively, corroborate the XRD results and the phase patterns realized (Fig. 6). The SEM results therefore indicated the agglomeration of different mineral particulates as a result of the fusion that occurred between the various mineral constituent particles.

Thus, the influence of different roasting temperatures at constant A-S ratios on the phase evolution during the roasting of ASBCM is shown in Fig. 6. The decomposition of the soda ash and coltan, and the formation of sodium tantalates and niobates is endothermic, and hence were significantly enhanced as the roasting temperature increased from 550°C to 750°C. For instance, XRD of the samples roasted at 550°C and at an A-S ratio kept constant at 2:1 (Fig. 6a) shows the presence of residual soda ash and intense peaks corresponding to coltan, which signifies incomplete decomposition of the coltan and utilization of the soda ash at that temperature. A further increase up to 750°C leads to the formation of sodium salts, such as NaAlSiO_4 and $\text{Na}(\text{Nb},\text{Ta})\text{O}_3$, and partially decomposed coltan ores, such as $\text{Fe}(\text{Ta},\text{Nb})_2\text{O}_6$ and $\text{Mn}(\text{Ta},\text{Nb})_2\text{O}_6$. The temperature also favored the fusion of gangue materials to form intermetallics, such as MnSiO_4 , and lovozerite-type structures such as $\text{Na}_2\text{Ti}_2\text{Si}_2\text{O}_9$ (lorenzenite) and $\text{Na}_6\text{MnTiSi}_6\text{O}_{18}$ (kazakovite). Although these reactions shown in Fig. 6 intensified above 550°C and affirms the need for a high roasting temperature, complete decomposition of coltan did not occur at 750°C. Thus, an increment in roasting time rather than temperature will be more beneficial.

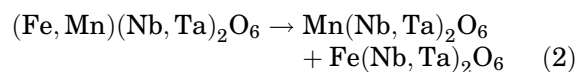
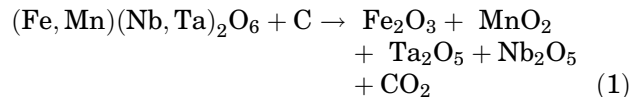
In a study by Ghambi et al.,³³ it was shown that, during the decomposition of coltan and formation of sodium compounds with gangue (SiO_2 , Al_2O_3 etc.), niobium and tantalum oxides are thermodynamically feasible at temperatures above 550°C. Several studies on the influence of temperature on the phase evolution of alkali-fused minerals and concentrates have also shown that increasing temperature favors the fusion of gangue materials to form intermetallic compounds. In addition, the formation of iron (Fe) complexes observed from both XRD phases and

SEM spectra in Figs. 6 and 7, respectively, and also in Table V, can feasibly be physically separated from the valuable alkaline salts, which are the sodium niobates (NaNbO_3) and sodium tantalates (NaTaO_3). Theoretically, this implies that adopting appropriate and proper particle size reductions by applying a comminution process (crushing and grinding), the Fe complexes can be separated from the alkaline salts of interest by the use of a dry or, more essentially, wet magnetic concentration process technique.

On the other hand, the influence of the alkali content (alkali-to-sample ratio) was investigated in order to assess and evaluate the physicochemical changes that occur during the alkali reductive roasting of the ASBCM sample. Thus, Fig. 6b and c respectively shows the influence of the mass ratio of alkali (at specific temperatures) on the decomposition of columbite–tantalite (coltan) in the ASBCM. As shown in Fig. 6, increasing the mass ratio of alkali enhances the decomposition of coltan and the formation of sodium niobates and tantalates. The results shown in Fig. 6 also indicate that the alkaline salts are a close match in phase patterns with monoclinic Na_3NbO_4 and monoclinic Na_3TaO_4 . This is in line with the reports of Sanchez-Segado et al.³² and Ghambi et al.³³ In addition, the results also explain the triggered change in crystallography that occurred on the reduced-roasted ASBCM products when relatively high alkali consumption (alkali-to-sample ratio) was employed. However, at lower alkali to sample mass ratio (2:1), no significant change occurred on the crystallography of the reduced-roasted ASBCM products, especially at lower roasting temperatures.

Thermodynamics of the Reductive Roasting

Ferro-columbite bearing ASBCM contain impurities such as Sn, Fe, Mn, Al, Ti and Zr present as oxides, as shown in the XRF result and confirmed by the EDS result. Thus, several possible side reactions are thermodynamically favored to occur during the alkali-assisted reductive roasting. Possible reactions as summarized in Eqs. 1 to 16 include partial reduction of coltan ore, alkali fusion of partially reduced tantalates and niobates, and fusion reactions involving intermediate compounds, gangue, and soda ash:



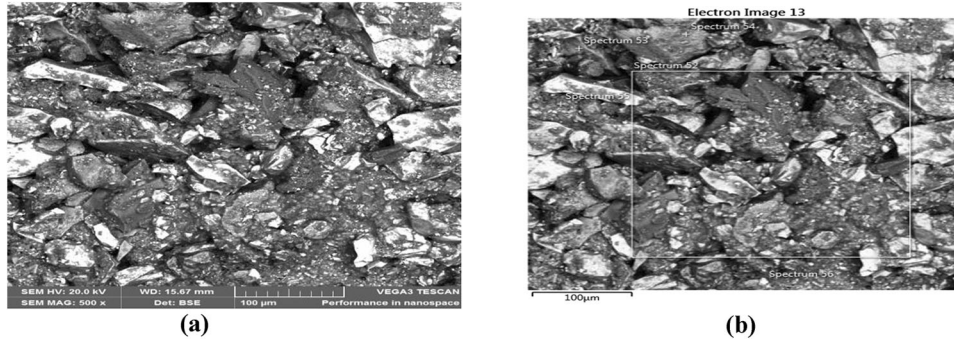
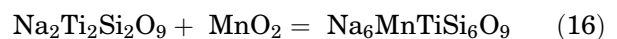
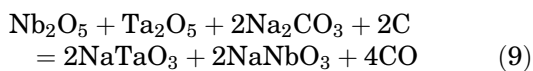
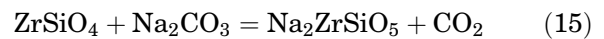
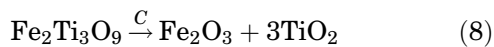
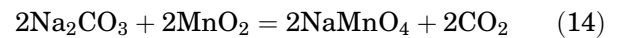
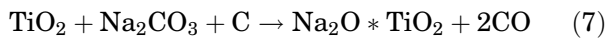
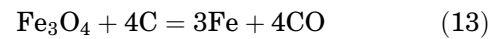
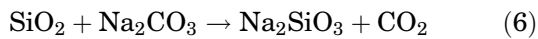
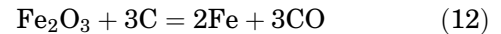
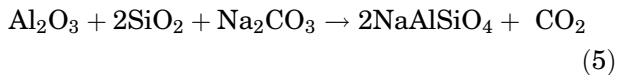
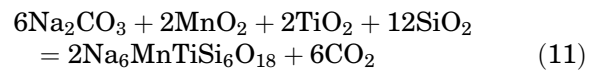
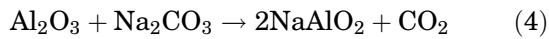
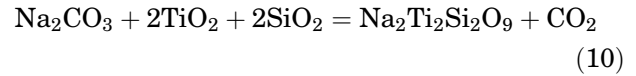
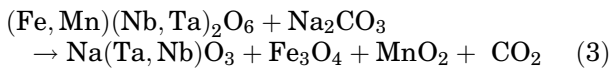


Fig. 7. (a) SEM micro-structural image of reduced-roasted ASBCM sample at 650°C; (b) SEM micro-structural image showing different spectra.

Table V. EDS spectra of the identified areas in Fig. 7b

Elements	Elemental compositions				
	Spectrum 52 (wt.%)	Spectrum 53 (wt.%)	Spectrum 54 (wt.%)	Spectrum 55 (wt.%)	Spectrum 56 (wt.%)
O	37.7	36.8	21.6	35.6	30.1
Nb	6.0	1.2	1.1	2.5	2.2
Ta	0.4	–	–	–	0.3
Fe	9.3	12.6	27.9	4.7	16.8
Mn	0.6	0.7	1.7	0.4	–
Si	1.6	0.3	0.3	0.3	0.4
Al	0.3	0.1	–	–	0.2
Sn	–	–	–	–	20.1
Na	29.5	30.3	18.0	43.8	19.5
Ca	0.5	–	–	–	–
Ti	4.6	4.7	29.5	2.2	4.7
V	–	0.2	–	–	–



Further analysis using HSC Chemistry 9.0 commercial software was carried out to elucidate the mechanism and evaluate the spontaneity of possible reactions taking place during the roasting of the ore in the temperature range of 550–750°C. Figure 6 shows that the formation of sodium niobates and

tantalates, and undesirable compounds such as NaAlSiO_4 , is feasible within the temperature range of the reactions. It is therefore evident that the reaction involving ZrSiO_4 with sodium carbonate (Eq. 15) is feasible in the studied temperature range. However, the absence of compounds such as $\text{Na}_2\text{ZrSiO}_5$ indicates the formation of amorphous phases, as shown by the absence of sodium zirconates in the XRD spectra (Fig. 6). In addition, roasting leads to the formation of compounds that may be intermediate for subsequent reactions. Pseudorutile can be decomposed to Fe_2O_3 and TiO_2 , whereas oxides of Nb, Ta, and Mn can be formed from the decomposition of coltan. Therefore, lovozerite-type structures such as lorenzenite and kazakovite (in Fig. 6a, b and c), as well as the aluminosilicates present in Fig. 6b and c, might have been formed from the fusion reactions involving these intermediate compounds. Thus, we propose that $\text{Na}_2\text{Ti}_2\text{Si}_2\text{O}_9$ might have been formed from the fusion of sodium carbonate, quartz/silica, and titanium oxide. A similar reaction has also been observed by researchers³³ on certain heavy minerals and mineral sand molds.

CONCLUSION

This study has demonstrated the feasibility of processing alluvial silica-based columbite minerals (ASBCM) into niobium and tantalum oxides, employing a procedure that is based on alkali-assisted carbothermic reduction of columbite–tantalite minerals. The study employed the use of a solid carbon (bituminous coal) in the presence of an alkali reagent within the roasting temperature range of 550–750°C and without the use of hydrofluoric (HF) acid as the dissolution medium. From the study, it can be concluded that alkali roasting of a low-grade columbite mineral using soda ash may lead to the formation of water-soluble compounds. The temperature parameter has been investigated to strongly influence the evolution of water-soluble phases, and also lead to the formation of inter-metallic compounds. Furthermore, above the temperature of 550°C, the alkali-to-sample mass ratio did not seem to have a very significant influence. This finding might be as a result of the fusion of the intermediate compounds with Na_2CO_3 , which will subsequently lead to the consumption of the soda ash. Finally, the presence of gangue minerals, such as SiO_2 , tend to increase the consumption of the soda ash and, thus, affect the formation of the useful/valuable compounds. Therefore, a prior and efficient primary mineral concentration and beneficiation process of the low-grade alluvial silica-based columbite mineral (ASBCM) is required in order to eliminate the silica content and other mineral gangues, as well as to upgrade the Nb and Ta content in the mineral. In addition, therefore, the optimization process of the various steps of the reductive roasting procedure is imperative and

should be conducted, placing particular emphasis on the formation of the valuable soluble sodium niobate and sodium tantalate complexes (which are of interest) and also the separation of Fe complexes from the aforementioned valuable complexes using a wet magnetic concentration process as well as further separation or purification processes of the mixed Nb and Ta penta-oxides (Nb_2O_5 and Ta_2O_5). Overall, this research paper has presented a thermodynamic feasibility study, and has evaluated feasible chemical and thermodynamic reactions involved in a soda ash-assisted carbothermic–alluvial columbite reductive roasting, employing lower roasting temperatures on a low-grade Nb/Ta mineral, and the resulting effects are discussed.

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COMPETING INTEREST

The authors hereby declare that there are no known (financial) competing interests or conflicts of interests related to this article which could influence or affect the study.

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