

Article

Extraction of Ta and Nb from a Coltan Bearing Ore by Means of Ammonium Bifluoride Fluorination and Sulfuric Acid Leaching

Alidor Shikika ^{1,2,*} , Francois Zabene ² , Fabrice Muvundja ^{2,3} , Mac C. Mugumaoderha ^{2,3,4},
Julien L. Colaux ⁴ , Mohamed Aatach ¹  and Stoyan Gaydardzhiev ¹

¹ GeMMe-Mineral Processing and Recycling, University of Liège, 4000 Liege, Belgium; Mohamed.Aatach@uliege.be (M.A.); s.gaydardzhiev@uliege.be (S.G.)

² Unité de Recherche en Sciences et Technologies Innovantes des Matériaux et de l'Environnement (URSTIME), Institut Supérieur Pédagogique de Bukavu (ISP Bukavu), Bukavu B.P. 854, Democratic Republic of the Congo; fzabene@gmail.com (F.Z.); amisimuv@yahoo.fr (F.M.); mugcubaka@gmail.com (M.C.M.)

³ Centre de Recherche en Environnement et Géo-Ressources (CREGÉR), Université Catholique de Bukavu (UC Bukavu), Bukavu B.P. 285, Democratic Republic of the Congo

⁴ Namur Institute of Structured Matter (NISM), Synthesis, Irradiation and Analysis of Materials Platform (SIAM), University of Namur, 5000 Namur, Belgium; julien.colaux@unamur.be

* Correspondence: ashikika@uliege.be; Tel.: +32-465629352

Abstract: A novel approach for Ta and Nb extraction consisting of the pre-treatment of a coltan-bearing ore with an ammonium bifluoride sub-molten salt and subsequent acid leaching has been studied. The effects from ore granulometry, ammonium bifluoride (ABF) to ore mass ratio, temperature and duration of fluorination on the degree of Ta and Nb extraction were examined. The ABF to ore ratio and process temperature were found to have the most pronounced impact on extraction efficiency. The following optimal process conditions were determined: ore granulometric fraction ($-75 + 45 \mu\text{m}$), ABF-ore (5/1), fluorination temperature (200 °C) and fluorination time (2.5 h). Maintaining these parameters enabled about 94% of Ta and 95% of Nb to be brought into solution during the sulfuric-acid-leaching stage. A comparison of the proposed method with previously reported studies suggests that due to the effects of mechanical agitation and the recirculation of the HF-containing gaseous phase back into the process, the dosage rate of ABF at the fluorination stage could be reduced significantly without sacrificing the overall recovery of Ta and Nb. In such a way, the approach could offer added environmental benefits since release of fluoride-containing effluents into the environment could be limited.

Keywords: ammonium bifluoride (ABF); fluorination; tantalum; niobium; coltan ore; sub-molten salt-assisted leaching



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1. Introduction

Tantalum (Ta) and niobium (Nb) are two refractory metals with similar physical and chemical properties that are almost always found in nature as paired metals. Tantalum has a high thermal and electrical conductivity and is well known for its high resistance to acid attack and corrosion [1,2]. Niobium is characterized by an elevated melting point, relatively low density and quite marked magnetic and superconductive properties [2]. These unique properties determine their irreplaceable position and use in specific sectors of the electronics industry, in defense-equipment manufacturing, steel making, cutting-tools fabrication, etc. The extractive metallurgy of Ta and Nb is complex since it requires various metallurgical techniques such as leaching, solvent extraction, precipitation of hydroxides and their subsequent calcination [3,4]. The leaching of Ta and Nb still remains quite a challenge, since the process requires highly aggressive conditions. The currently existing processes for leaching of Ta–Nb ores mainly use HF–H₂SO₄-based media and temperatures between 80–100 °C. Under these conditions, the majority of the studies

being done [5–7] are reporting to be able to recover more than 90% of Ta and Nb from tantalite $(\text{Fe,Mn})\text{O}(\text{Ta,Nb})_2\text{O}_5$ or columbite $(\text{Fe,Mn})\text{O}(\text{Nb,Ta})_2\text{O}_5$, which justifies the wider industrial-scale use of hydrofluoric acid for Ta and Nb leaching.

Alternative non-fluoride based lixiviants, including H_2SO_4 and HCl have also been investigated for processing Ta and Nb containing ores [8–11]. However, while some of them demonstrate reasonable leaching yields, others are witnessing low recoveries and metal yields when compared to the HF process. This is due to the fact that Ta and Nb complexes containing non-fluoride lixiviants are as a rule characterized by an extreme tendency towards hydrolysis, hydrolytic polymerization and precipitation from solutions [7]. Moreover, these complexes do not possess the desired differences in chemical and physical behavior, which is a prerequisite for the facilitation of their downstream separation [12]. Moreover, Ta and Nb are among the metals that passivate directly in aqueous solution without passing through corrosion zones, as evidenced by the Pourbaix diagrams in Figures 1 and 2. This passivation is often attributed to the formation of a thin layer of Nb or Ta oxide on the mineral surfaces [1,13], which explains the low recoveries of Nb and Ta during the leaching stage. To counterbalance this passivation, Welham [14] proposed a sort of mechanical activation by pursuing the fine milling of the ore ahead of leaching. The same study reported that an ore milled for 50 h dissolves 4500 times more rapidly in a hydrochloric acid environment than one only milled for 2 h. However, since milling the ore for 50 h is undoubtedly an energy intensive operation that precludes its industrial deployment, Welham [14] recommends leaching in hydrofluoric acid instead.

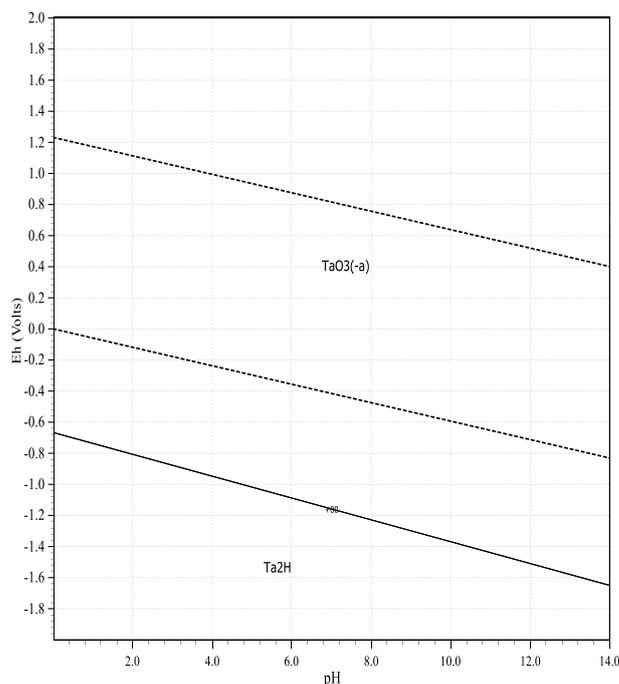


Figure 1. Potential/pH diagram for the system Ta- H_2O at 25 °C (HSC Chemistry 10).

Other studies have been carried out with the aim of drastically reducing the amount of hydrofluoric acid or fluorine used in leaching, while keeping the recoveries of Ta and Nb above 90%. Among these studies, Rodriguez et al. [15] were able to bring 91% of Ta and 95% of Nb into solution by leaching a ferrocolumbite ore with a mixture of HF (15%) and tartaric acid $\text{C}_4\text{H}_6\text{O}_6$ (15%) at 220 °C. Yang et al. [16] were able to demonstrate an extraction rate of over 93% Ta and 96% Nb from manganotantalite $\text{Mn}(\text{Ta,Nb})_2\text{O}_6$ under pressure leaching at 200 °C using a mixture of 50% H_2SO_4 and NH_4F . Other approaches based on the production of Ta–Nb concentrates have been proposed in several studies [17–19]; however, they do not feature Ta and Nb separation.

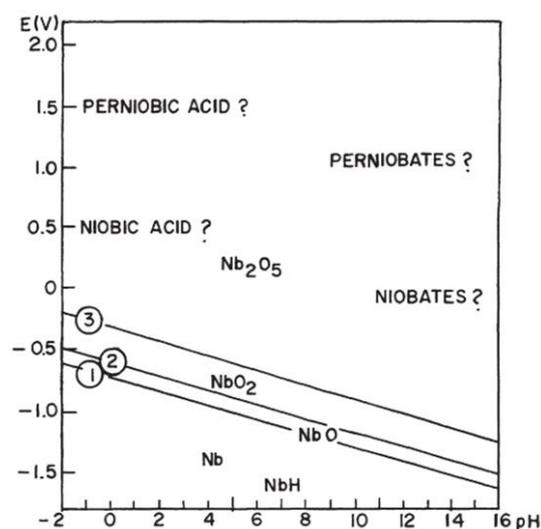
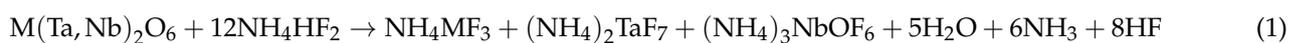


Figure 2. Potential/pH diagram for the system Nb-H₂O at 25 °C [13].

Currently, alkaline processes are being studied as an alternative to the HF process for Ta and Nb extraction; however, they remain on a laboratory scale only [20,21]. It should be noted that despite the excellent metallurgical performance offered by the alkaline approach, an efficient separation and purification of Ta and Nb from the resulting alkaline solutions is still difficult to achieve. The reason behind this is that most of the extractants of Ta and Nb are customized for use only in acidic solutions, and more precisely, in hydrofluoric acid media [22]. In addition, the hydrofluoric complexes of Ta and Nb are sufficiently stable when bound to the extracting reagents and do possess traits enabling their efficient separation [23]. Therefore, it is not surprising that the current and future developments in the extractive metallurgy of Ta and Nb have been oriented towards the fluoride-based lixiviants.

Recently, the ammonium bifluoride (ABF, NH₄F·HF) has attracted appreciable attention as a potential fluorination agent for the extraction of transition and refractory metals. ABF belongs to the group of strong fluorination agents, having a reactivity closer to that of fluorine and/or hydrofluoric acid [24–26]. This salt is known to present the least hazardous form of HF in terms of transport and handling. At room temperature, ABF presents as a non-volatile, crystalline substance and is environmentally safe [26–29]. It is relatively inexpensive, easily recycled from gaseous compounds and does not require special equipment to use [23]. In addition, the leachates from an ABF-based process possess low acidity, which offers the possibility of selectively extracting Ta ahead of Nb.

Studies on the possibility of digesting Ta and Nb ores with ABF have already been conducted [30–32]; however, the effect of the process parameters on both of the metals' recoveries was not investigated in detail. The process basically consisted of the fusion of the ABF mixture with the ore inside a muffle furnace at temperatures close to 200 °C with the generation of water-soluble ammonium fluorides. The global reaction of a coltan fluorination could be thus represented as follows [30]:



where M is Fe or Mn.

It has been shown for this process that the degree of Ta and Nb recovery largely depends on the ABF-ore mass ratio, with high ratios being suggested as a consequence. For instance, Purcell et al. [32] were able to use up to a 1/10 ore-ABF mass ratio to recover about 91% of Ta and 96% of Nb. Kabangu and Crouse [30] used an ore-ABF mass ratio of 1/30 to demonstrate 97.2% Nb and 98.7% Ta recovery. However, these elevated mass ratios to maximize the extraction levels of Ta and Nb could undoubtedly contribute to high process costs. Moreover, the process generates NH₃ and HF as a gas phase, both

being harmful to the environment. Therefore, the potential industrial application of such processes should be preceded by fundamental, in-depth studies that aim to reduce both the consumption of ABF and the emission levels of fluoride-based gaseous effluents. The possibility of recovering and condensing the gases that are generated during the ABF fusion with the NH_4F form has been also documented [23,29]. This option could offer a technical, economic and environmental advantage since the fluoride will be maintained in a concentrated state inside the reaction medium and the release of harmful gases will be prevented.

The current study focuses on this problem by proposing a process that is based on a slow-speed agitative fluorination (300 rpm) involving the continuous reflux of the $\text{NH}_3 + \text{HF}$ gases as NH_4F back into the process. It is believed that the examination of key process parameters such as the ore-particle size, ABF-ore mass ratio, temperature and duration of the fluorination process and their effect on the Ta and Nb recoveries will fill the existing knowledge gap in the field and contribute to the rise of industrial interest.

2. Materials and Methods

2.1. Materials

A representative sample of coltan ore was collected within the perimeter of the Lulingu district (South Kivu, province of the Democratic Republic of the Congo). The ore was dried, crushed and sieved using a 2 mm sieve. The resulting material was homogenized, and a representative sub-sample was collected and prepared for characterization and testing.

ABF with an analytical purity of 99% was obtained from VWR (Avantor) and was used as a fluorination agent, and sulfuric acid (98%, $\rho = 1.84$), supplied by Central Drug House, was used for the leaching of the fluorinated product. Distilled water was employed for the preparation of solutions and washing of residues.

2.2. Ore Characterization

The input ore and the process-derived streams were characterized by three independent techniques: PIXE, XRD and SEM. Multi-element and quantitative PIXE (Particle Induced X-ray emission) was used to determine the chemical composition of the ore (Table 1). This technique offers the advantage of performing an analysis without the need for time-consuming digestion and thus reduces the uncertainties associated with sample preparation. The analysis was carried out on a PIXE-SIAM platform using simultaneously two detectors (SSD and RX LGe) and two particles detectors (PIPS). The SSD was equipped with a magnetic filter to disable backscattered particles without cutting off the low-energy X-rays, while the LGe was used with a large solid angle and a thick Mylar absorber (250 μm) to allow us measuring high-energy X-rays with a good sensitivity. Particles detectors were mainly used to determine the collected charge on the sample. The set of 4 spectra was self-consistently analyzed to derive mean composition of each sample. These assays indicated that the concentration of Ta and Nb in the ore were 8.43% and 41%, respectively.

Table 1. Chemical composition of the studied coltan ore.

Element	Nb	Ta	Fe	Mn	Al	Si
Content (wt. %)	41	8.43	7.43	4.4	1.79	1.5
Element	Ti	W	Sn	Zr	Ce	Na
Content (wt. %)	1.6	0.62	0.57	0.18	0.11	0.05
Element	Mg	Ca	Zn	K		
Content (wt. ppm)	923	510	391	636		

The mineral-phase analysis of the ore was carried out by an X-ray Bruker D8-ECO diffractometer with $\text{CuK}\alpha$ radiations ($\lambda = 19373 \text{ \AA}$). The sample was pulverized before being scanned between 5 and $75^\circ 2\theta$ at a rate of $0.02^\circ 2\theta$ per second. The identification of all the minerals from the XRD patterns was done with a Panalytical Xpert

suite and the WebPDF4 + ICDD relational database. The identified major mineral phases are shown in Figure 3, indicating that Ta and Nb were essentially found as columbite ($(\text{Fe},\text{Mn})\text{O}(\text{Nb},\text{Ta})_2\text{O}_5$ (89%). The other minerals of eventual economic interest are cassiterite (SnO_2) and tapiolite $(\text{Fe},\text{Mn})(\text{Ta},\text{Nb})_2\text{O}_6$, while the major gangue-forming mineral is quartz (SiO_2).

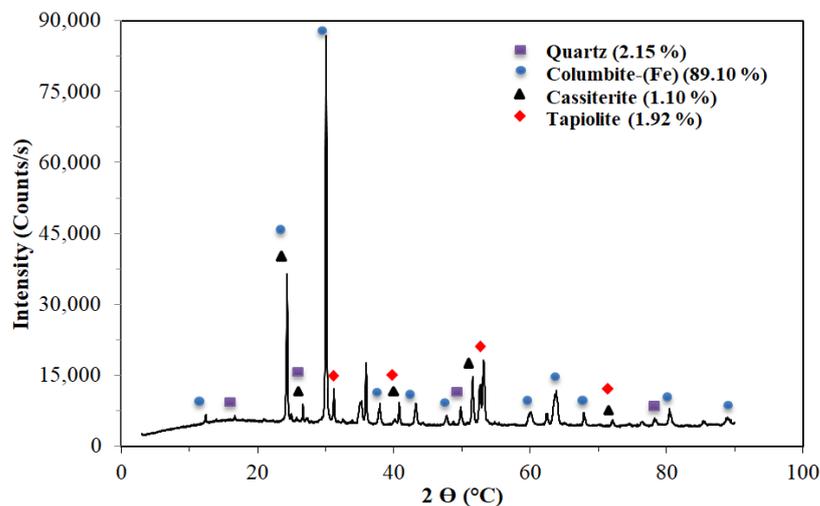


Figure 3. XRD pattern of the raw coltan ore.

The above analysis was complemented by an automated mineralogy characterization using a SEM-based ZEISS (Sigma 300) system. The system was equipped with two Bruker XFlash 6I30 X-ray energy dispersion spectrometers (EDS). The SEM-EDS analyses were carried out with a probe current of 2.3 nA and an accelerating voltage of 20 kV at a working distance of 8.5 mm. The obtained BSE images, shown in Figure 4, again indicate coltan as the main Ta- and Nb-carrying mineral. The remaining minerals that are present include cassiterite, ilmenite, rutile, with quartz being identified as gangue phase.

2.3. Experimental Procedure

The two-step experimental procedure consisted of the fluorination of the coltan sample followed by sulfuric-acid leaching. The experiments were performed inside a fluoroplastic (Teflon) vessel. The setup shown in Figure 5 enabled the performance of an agitative fluorination (at 300 rpm) while the vessel was coupled to a unit that condensed the $(\text{HF} + \text{NH}_3)$ gases as NH_4F . The fluorination was always performed on a 5 g coltan sample. A predetermined amount of ABF was added with respect to the required ABF-ore mass ratio and the mixture was introduced into a vessel that had been heated in advance to the desired temperature. At the same time, the reactor was closed with a Teflon cover coupled to a PP condenser in which cooling water was circulated. Magnetic stirring was then started and the reaction was carried out for a given time duration. After a certain time, the fluorinated product was cooled down to room temperature and then leached with 200 mL of 2N sulfuric acid solution. The leaching step was performed at room temperature while stirring at 600 rpm for a fixed duration of 30 min. These conditions were kept constant since the current study was focused merely on the effect of fluorination as the pre-treatment step. Upon leaching completion, the unreacted residue and the pregnant leach solution (PLS) were separated by filtration. The resulting phases (liquid and solid) formed the filtrate (PLS) and the leached cake, respectively. The latter was washed thoroughly with distilled water to remove traces of fluorine, dried in an oven at 60 °C for 24 h and finally weighed. The dried residue was then analyzed by PIXE with limits of detection from 10 ppm to

1000 ppm, and uncertainties from 5 to 20% depending of the element under interest. The coltan dissolution yield and Ta- and Nb-leaching recovery were calculated as follows:

$$\text{Dissolution yield} = \left(1 - \frac{M_r}{M_i}\right) \times 100 \quad (2)$$

$$\text{Ta or Nb recovery} = \left(1 - \frac{M_r \times C_r}{M_i \times C_i}\right) \times 100 \quad (3)$$

where M_i is the weight of the input ore before fluorination, M_r is the weight of insoluble residue, C_i is the initial concentration (wt. %) of the metal (Nb or Ta) in the ore before fluorination, and C_r is the concentration (wt. %) of the metal in the insoluble residue.

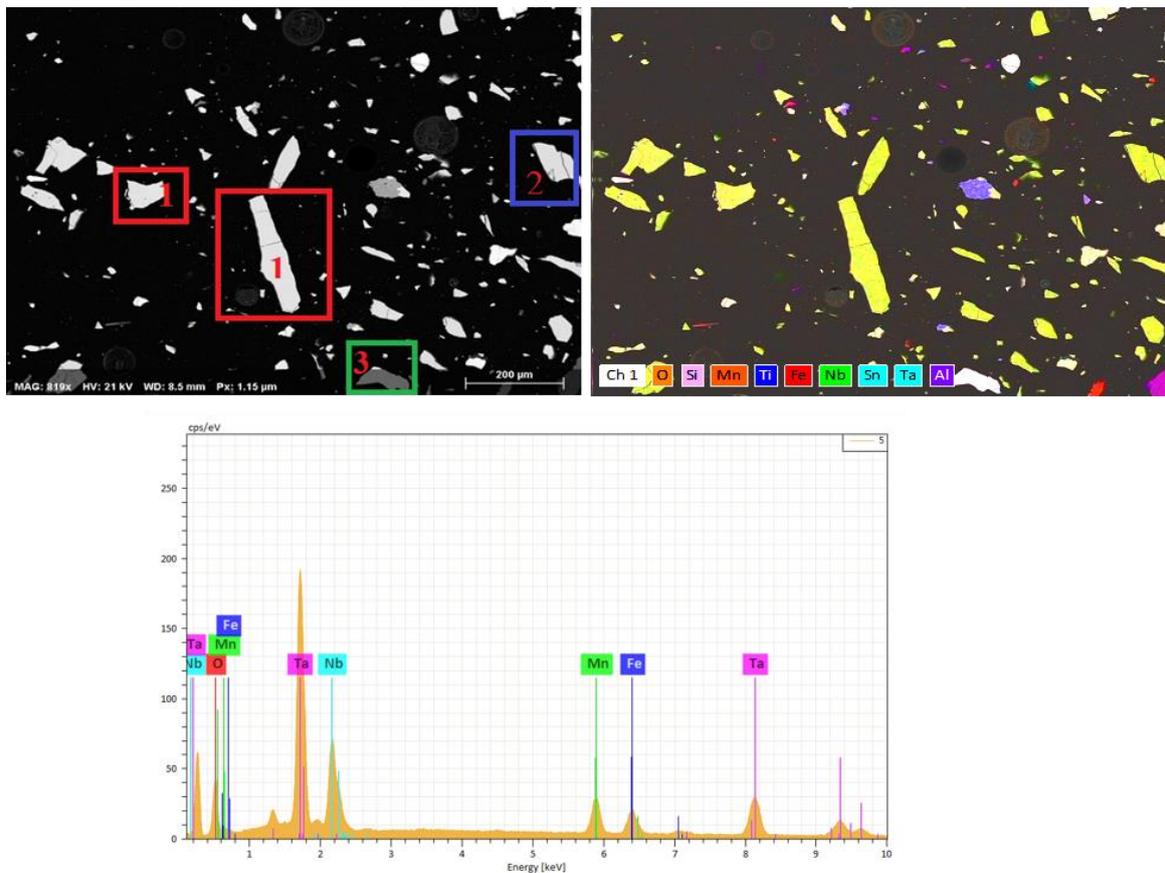


Figure 4. BSE view of the raw coltan ore with major mineral phases (1-coltan, 2-cassiterite, 3-quartz) and EDS mapping for Nb, Ta, Fe, and Mn, with EDS spectrum of coltan.

It should be noted that although the fluorination tests were carried out under agitation, the effect of agitation speed was not investigated since the reaction occurs in a sub-molten salt medium and the fluorination product tends to form an amorphous phase. Nevertheless, the agitation promotes the contact between the ore and the ABE, which is essential to promote the reaction kinetics.

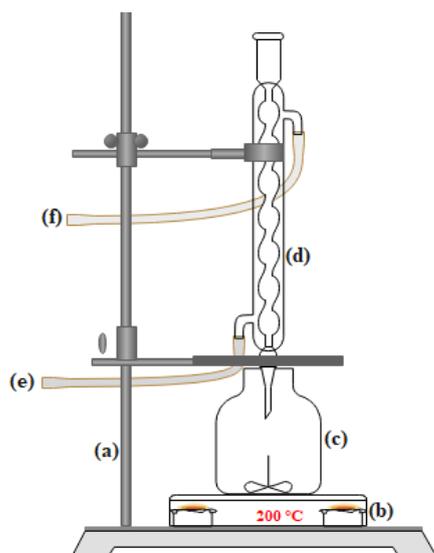


Figure 5. Agitative fluorination set-up for Ta and Nb extraction (a) ring stand, (b) magnetic stirrer with heating plate, (c) Teflon vessel, (d) reflux condenser, (e) cooling water input, and (f) cooling water output).

3. Results and Discussion

3.1. Effect of Ore Particles Size

In order to study the effects of the particle size of the ore, the material was sieved into four granulometric fractions, and the Ta and Nb content of each is presented in Table 2. It can be seen that both metals are distributed in a relatively uniform way inside the four granulometric fractions.

Table 2. Nb and Ta concentrations in the tested granulometric fractions.

Granulometric Fraction	Nb (wt. %)	Ta (wt. %)
−75 + 45 μm	40.99	8.43
−105 + 75 μm	42.71	8.37
−150 + 105 μm	42.50	8.90
−212 + 150 μm	40.46	8.32

The effects of the particle size on Ta and Nb recoveries was investigated at a temperature of 200 °C, using an ABF-ore mass ratio of 3/1. The results shown in Figure 6 indicate that the leaching recovery of Ta and Nb increases concomitant to the decrease in ore-particle size. This observation can be explained by the increased surface area of the material, which itself is one common way to increase the hydrometallurgical results up to a certain extent.

It can be seen from Figure 6 that the ore-particle size has a pronounced effect on Ta and Nb extraction. The fluorination kinetics are faster for the very fine particle fractions (−75 + 45 μm). Indeed, the fluorination of Ta and Nb is known as the chemisorption process, which is highly dependent on the available surfaces of the phases [16]. Finer particles offering larger specific surface areas are therefore more susceptible to the chemical adsorption of the fluorine ions, which logically is reflected by higher recoveries. The obtained results also show that Nb, being less refractory, dissolves more easily than Ta. Moreover, since the atomic radius of Nb (0.69 Å) is larger than that of Ta (0.64 Å), bringing Nb into solution is easier than Ta [16].

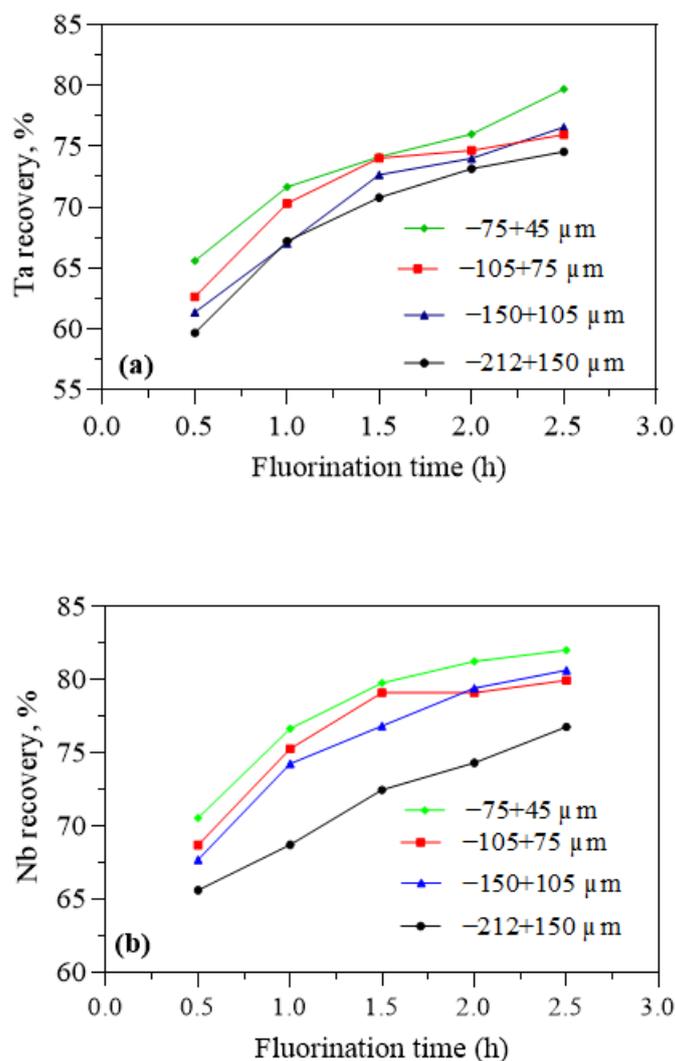


Figure 6. Effect of material particle sizes on Ta (a) and Nb (b) recoveries.

The mass loss of the coltan ore is also an important performance criterion when one considers processing routes based on a fluoride-based lixiviant. It has been reported that the mass loss is generally above 90% when the ore is treated with hydrofluoric acid at concentrations higher than 10% [6,7,33]. In the case of a prospective ABF-based process, the maximum mass loss observed for the $-75-45 \mu\text{m}$ size range is close to 78% (Figure 7), corresponding to Ta and Nb recoveries of about 80% and 82%, respectively.

The PIXE analysis of the leach residue (Figure 8) that corresponded to a mass loss of 78% revealed relatively high levels of remaining Ta and Nb. For instance, considering the fact that Fe, Mn, Ta and Nb are the most common metals that accompany coltan ores, it can be seen that the chemical composition of the residue does not deviate significantly compared to that of the feed. This finding suggests that the non-leached particles remaining in the residue were fluorinated to a lesser extent. Therefore, it could be assumed that fluorine ions were deficient inside the reactive medium, leading to the partial fluorination of Ta and Nb. Therefore, in order to obtain higher extraction yields, it has been decided to increase the ABF-ore mass ratio, which is known to be one of the key process parameters.

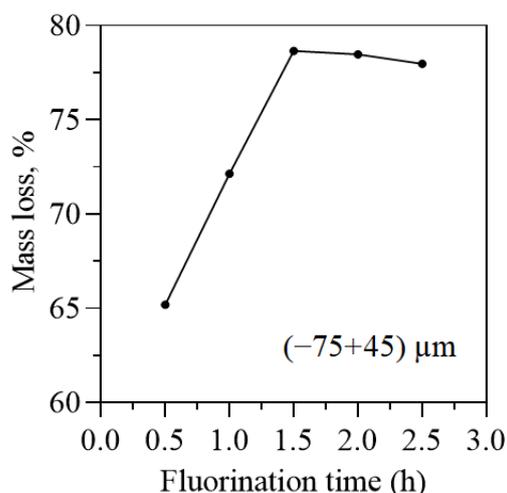


Figure 7. Mass loss vs. fluorination time (ABF-ore mass ratio: 3/1, fusion temperature: 200 °C).

3.2. Effect of ABF-Ore Mass Ratio on Ta and Nb Recovery

The influence of the ABF-ore mass ratio on the process efficiency was studied at a temperature of 200 °C using the granulometric fraction of $-75-45\ \mu\text{m}$ and the results are depicted in Figure 9.

The results pictured in Figure 9 leave little doubt that the ABF-ore mass ratio has quite a significant influence on the degree of Ta and Nb recovery. Studies done elsewhere have reported that in order to guarantee Ta and Nb recoveries close to 90%, ABF-ore mass ratios of 10/1 [31,32] or even up to 30/1 [30] have to be used. The mass ratios that were reported in these studies can be justified, since the tested methodology has always involved the subsequent evaporation of the fluorinating reagent and hence, its withdrawal from the reaction area, while this is not the case in the current study. In our configuration, the majority of the generated gases are not evacuated, but rather recycled back into the reactive medium. It can be seen that increasing the ABF-ore mass ratios to above 3 provoked a concomitant increase in Ta and Nb recoveries. In support of this assumption, the PIXE spectrum seen in Figure 10 illustrates marked differences in comparison to the spectrum presented in Figure 8. Figure 10 undoubtedly suggests that the Ta and Nb contents in the leached material are well below that of the feed ore and of the residue obtained with an ABF-ore mass ratio of 3/1. However, at ABF-ore mass ratios of 4/1 and 5/1 and a fluorination duration of 2.5 h, the increase in Ta and Nb recoveries is less evident and does not exceed 3% on a comparative basis. The mass ratio of 5/1 could nevertheless be retained as an optimal one since it secured nearly 94% and 95% recovery of Ta and Nb, respectively. It can be also deduced that the process can be characterized as environmentally safe in terms of discharging fluorine anions into the environment.

3.3. Effect of Fluorination Temperature on Ta and Nb Recovery

The effect of the variation in fluorination temperature was studied in the range of 130–200 °C. The temperature of 130 °C has been chosen as a starting point of the study since this temperature is slightly above the melting point of the ABF. The ABF-ore mass ratio was kept at 5/1 and the granulometric fraction of $-75-45\ \mu\text{m}$ was used again. The results from these series are given in Figure 11.

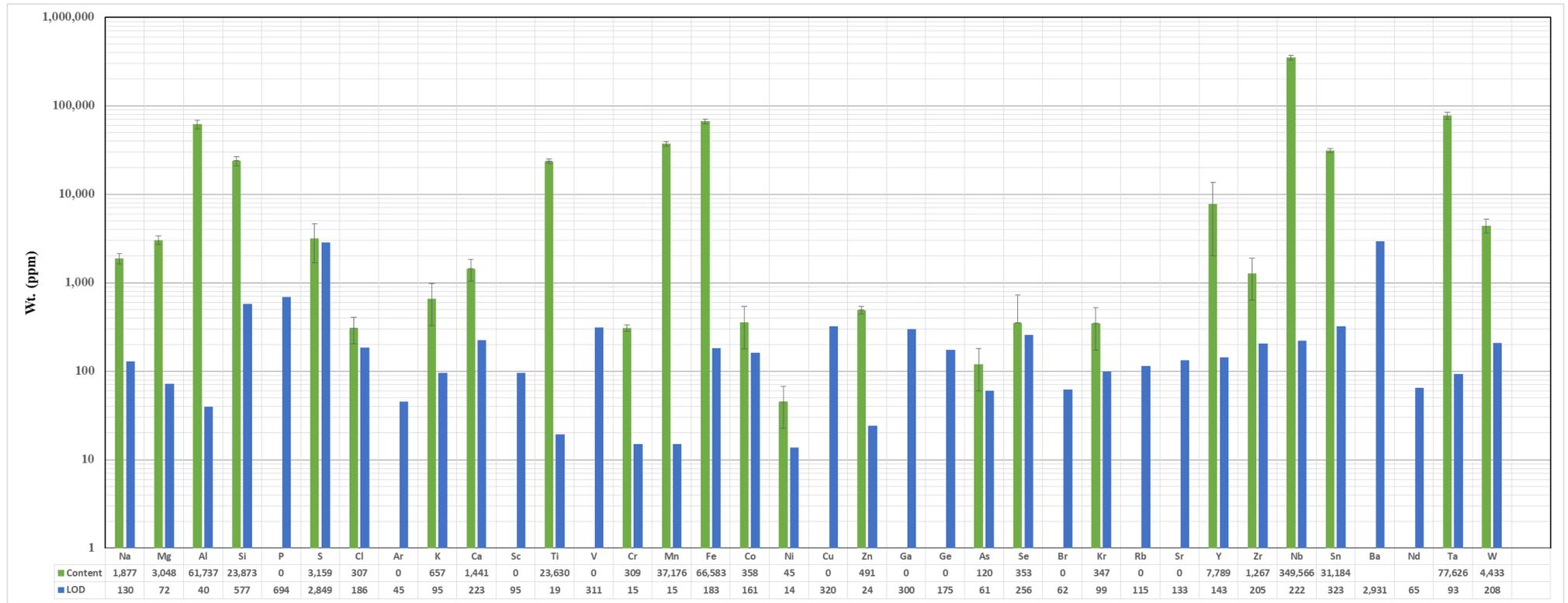


Figure 8. PIXE spectrum of the leaching residue (ore-particle size range: -75–45 μm, ABF-Ore: 3/1, fusion temperature: 200 °C, fluorination duration: 2.5 h).

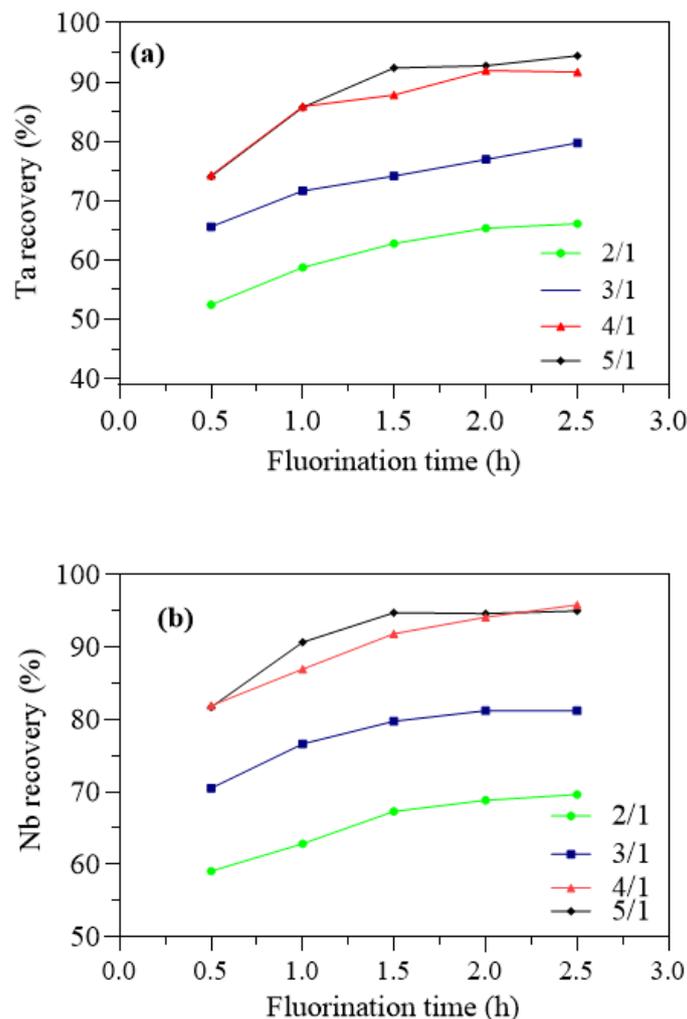


Figure 9. Ta (a) and Nb (b) recovery for different fluorination times and ABF-ore mass ratios.

It can be seen from Figure 11 that a notable rise in Ta and Nb recovery was observed when the fluorination temperature was increased above 130 °C. When the fluorination was run for a 2.5 h duration at 150 °C, about 85% Ta and 88% Nb were recovered, while at 130 °C, only 64% Ta and 69% Nb recovery was recovered. This marked difference can be explained by the difference in the kinetic constants, which is a rate determining factor for each level of the studied temperatures. Logically, a fluorination temperature of 200 °C secured the highest recoveries of Ta and Nb.

The above results also show that the fluorination efficiency of Ta and Nb depends strongly on temperature, given the fact that the fluorination of Ta and Nb oxides is an endothermic process [23]. It is obvious that the fluorination of Ta and Nb can take place at lower temperatures, provided that hydrofluoric acid is used as a fluorination agent. However, in the case of alternative fluorinating agents such as ammonium fluoride or ammonium bifluoride, higher temperatures are required for the respective process to be accomplished [23]. Based on the above, the following optimal operating conditions can ultimately be suggested: a particle size range of $-75-45\ \mu\text{m}$, an ABF-ore mass ratio of 5/1, a fluorination temperature of 200 °C, and a process duration of 2.5 h. These conditions can guarantee Ta and Nb recoveries in the range of 94–95%. The resulting PLS (pregnant leaching solution) has a chemical composition that is presented in Table 3, with respect to the major elements.

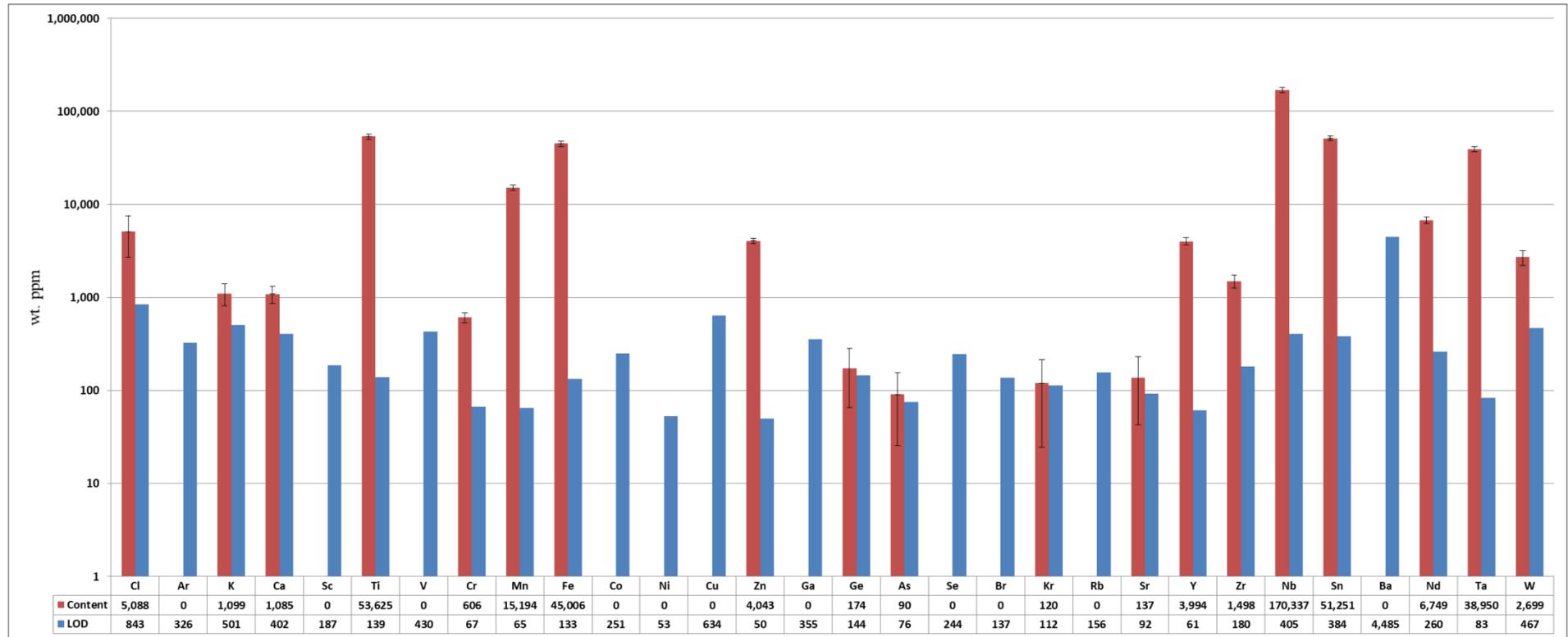


Figure 10. PIXE spectrum of the leaching residue (ore-particle size range: $-75-45 \mu\text{m}$, ABF-Ore: 5/1, fusion temperature: $200 \text{ }^\circ\text{C}$, fluorination duration: 2.5 h).

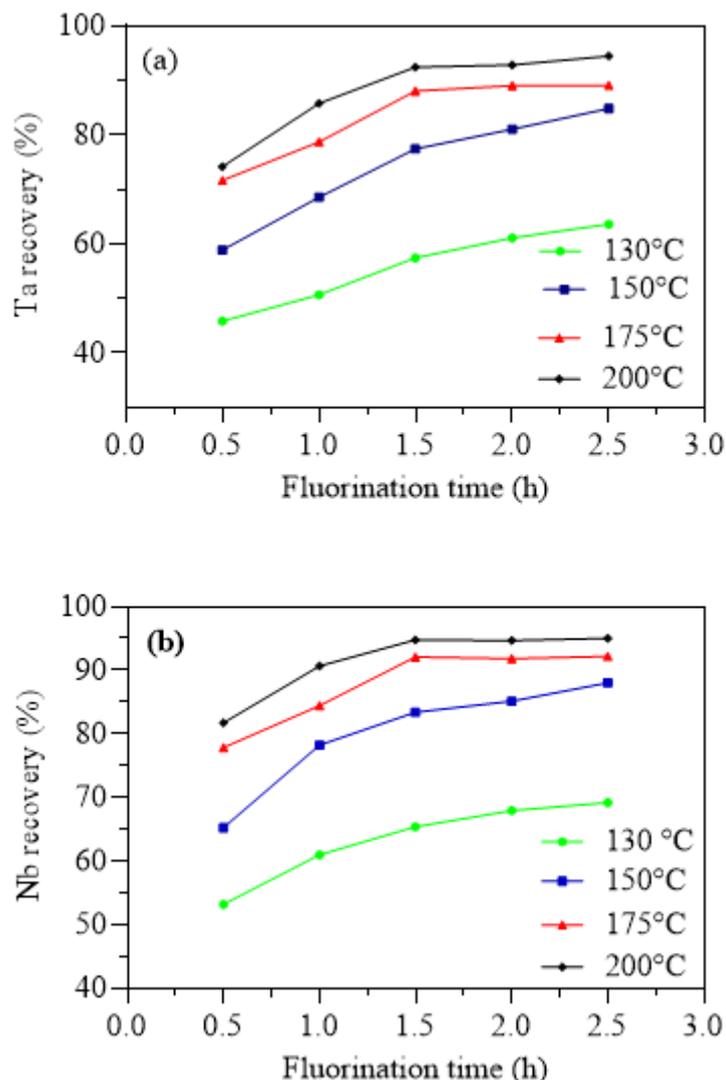


Figure 11. Effect of fluorination temperature on Ta (a) and Nb (b) recovery with time.

Table 3. Chemical composition of resulting solution from fluorination and sulfuric acid leaching.

Element	Ta	Nb	Fe	Mn	Si	Ti
Content (g/L)	2.01	9.74	1.68	1.05	0.37	0.22

Apart from the studied parameters at their variation levels, the agitation and the existing reflux of the HF-based gases that are generated during fluorination play an important role in the extraction of Ta and Nb. The agitation speed has to be maintained so as to ensure an optimal contact between the ABF and the ore particles. On one hand, such a contact leads to improved kinetics and minimizes the consumption of ABF, while maximizing the yield of the reaction, thereby leading to high recoveries of Ta and Nb at relatively low ABF-ore mass ratios; on the other hand, the reflux of the generated fluorination gases creates conditions for reaction medium fluidization, as the medium tends towards an amorphous phase. Under such conditions, the ABF reacts in a similar to HF, which can explain the satisfactory recovery levels obtained for Ta and Nb.

The general flowsheet of Figure 12 summarizes the procedure and steps described in this article. The resulting solution is further processed via solvent extraction to purify and separate Ta and Nb.

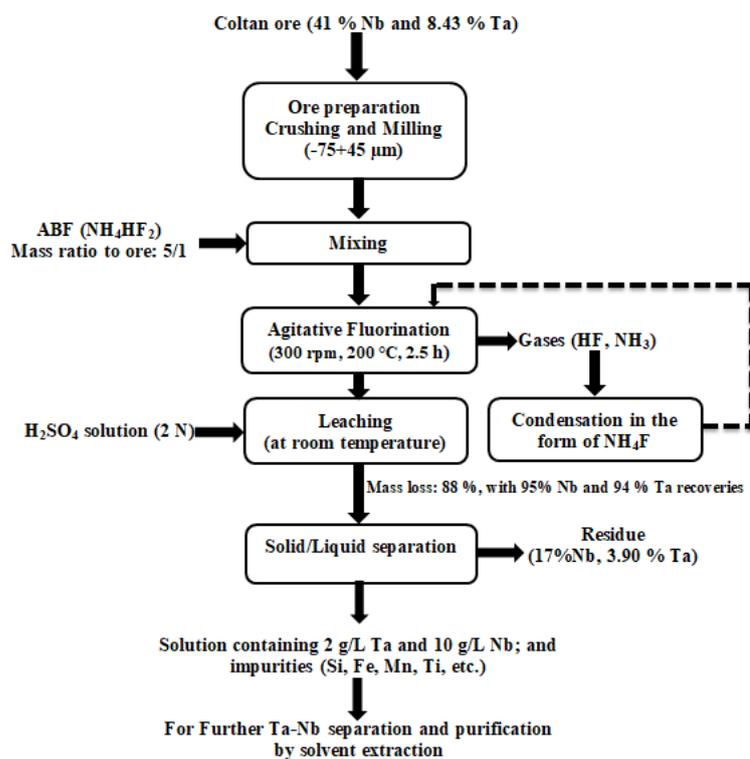


Figure 12. Flow chart for ABF fluorination and sulfuric acid leaching of the coltan ore.

3.4. Characterization of the Leaching Residues

In order to understand the mechanism of the phase conversions during the ABF sub-molten fluorination and the acid leaching, the leaching residues from the tests where the ABF-ore mass ratio and temperature were found to have the largest influence on the degree of fluorination were analyzed by XRD. To this end, Figure 13 compares the XRD patterns of the residues after fluorination at ABF-ore mass ratios of 3/1 and 5/1 with the patterns of the raw coltan ore.

From the XRD patterns collected in Figure 13, it can be seen that there is no formation of new crystalline structures. It can also be seen that after fluorination and subsequent acid leaching, the characteristic peaks corresponding to the coltan ore significantly decreased. This suggests that the mineral particles were attacked to a significant extent during the ABF sub-molten treatment. In other words, the minerals were converted with a part of the mineral phase remaining intact. The observed peak decreases were more pronounced for the case when the fluorination was performed at a mass ratio of 5/1 than at 3/1, which may explain the high recovery of Ta and Nb at the 5/1 ratio.

In addition, Figure 13 shows that as the ABF-ore mass ratio increases from 3/1 to 5/1, the peaks corresponding to quartz (gangue) disappear almost completely, which is due to the increased solubility of the compounds formed by the reaction between the ABF and the quartz. This is also valid for the other impurities accompanying the ore, as it is known that the fluoro-ammonium salts of tin, titanium, aluminum, iron, etc., are highly soluble in sulfuric acid solutions. From a practical view point and in order to yield high-purity compounds of Ta and Nb, these impurities have to be removed from the leachates by performing the solvent-extraction steps.

The XRD patterns of the leaching residues from the tests at different fluorination temperatures are compared in Figure 14.

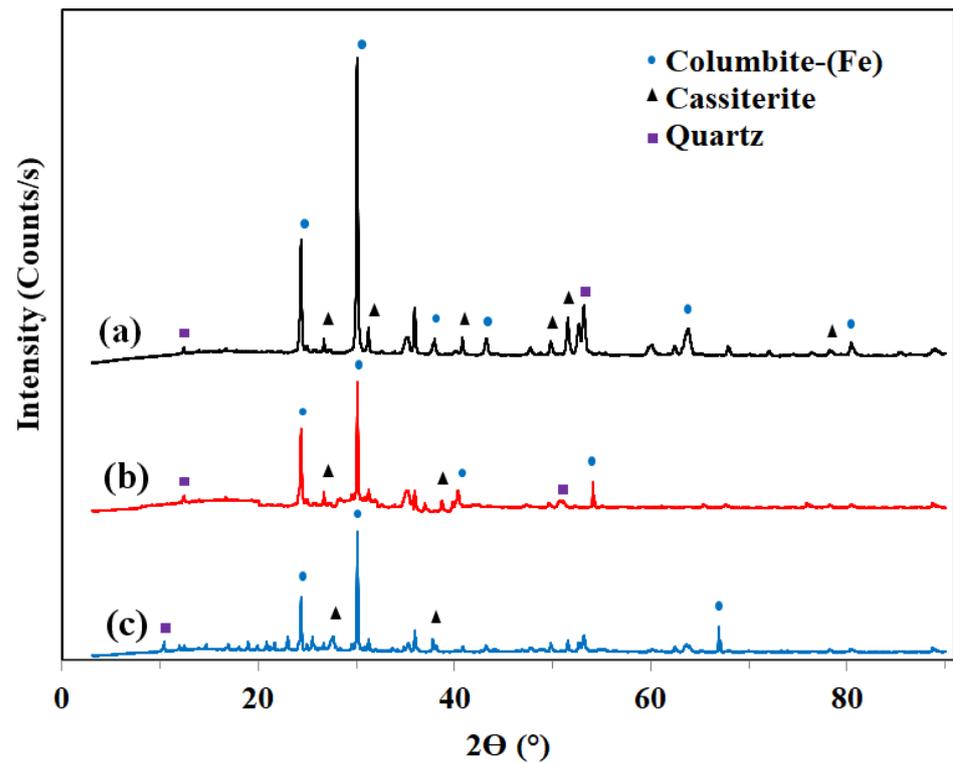


Figure 13. XRD patterns of the raw coltan ore (a) and residues from fluorination and acid leaching at 200 °C, 2.5 h, ABF-ore: 3/1 (b), 5/1 (c).

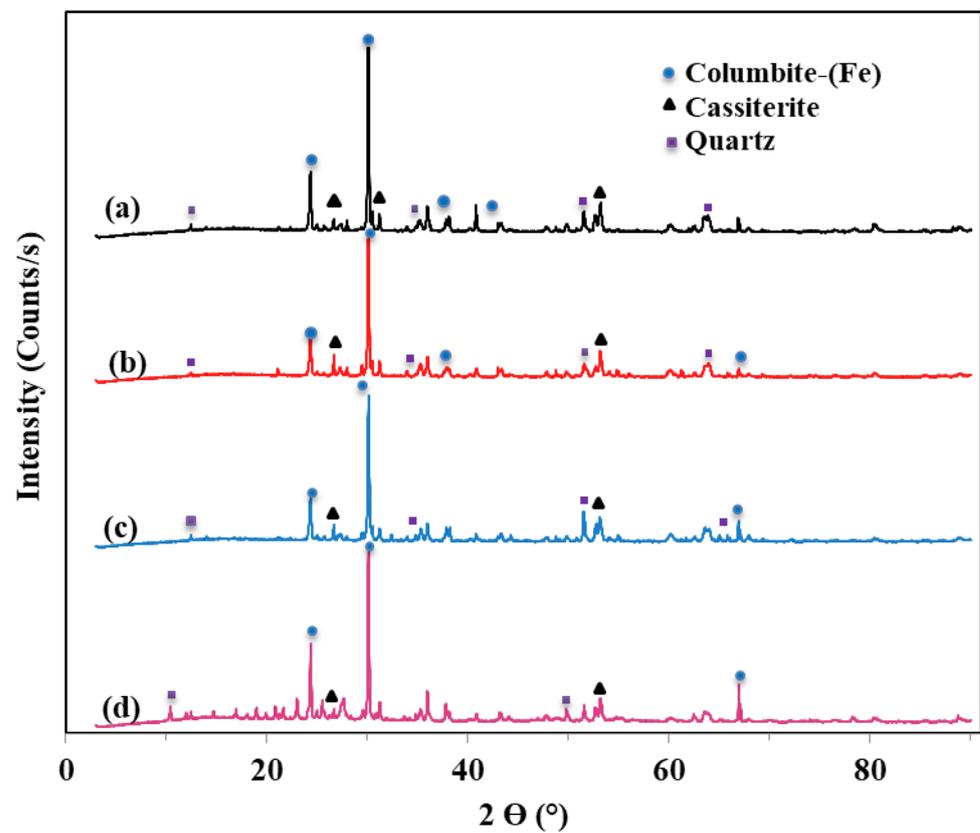


Figure 14. XRD patterns of the leaching residues after fluorination at various temperature ranges: 130 °C (a), 150 °C (b), 175 °C (c) and 200 °C (d); ABF-ore mass ratio: 5/1, fluorination duration: 2.5 h.

The patterns in Figure 14 suggest that with the increase in fluorination temperature, the heights of the diffraction peaks for the coltan ore gradually decrease, suggesting an enhanced degree of fluorination. This provokes the increased reactivity of the coltan ore, resulting in the more efficient acid leaching of Ta and Nb. The XRD pattern corresponding to the residue resulting from the fluorination temperature of 130 °C shows diffraction peaks similar to those of the feed ore, thus indicating an incomplete fluorination of the coltan. This observation explains, on the one hand, the relatively low recovery of Ta and Nb that is observed at this temperature, and on the other hand, confirms that ABF-based fluorination is an endothermic process, which is promoted when the process temperature increases.

4. Conclusions

The effects of key operational parameters of a two-stage process that involves fluorination followed by sulfuric-acid leaching on the degree of Ta and Nb extraction has been studied. The results demonstrate the feasibility of a new approach to processing coltan ore from a deposit of economic potential.

It was determined that running the fluorination process at a temperature of 200 °C, an ABF-ore mass ratio of 5/1, an ore granulometry range of $-75-45\ \mu\text{m}$ and a duration of 2.5 h can guarantee an acceptable recovery of Ta and Nb during the subsequent sulfuric-acid leaching. Under these conditions, about 94% of Ta and 95% of Nb were recovered in the resulting leachate and had concentrations of around 10 g/L Nb and 2 g/L Ta.

Although preliminary, the presented findings mark an opportunity to establish a viable alternative to the currently practiced HF route in view of the industrial processing of Ta-Nb ores. Moreover, after an indispensable upscaling phase, the prospective process based on the tested approach could bring added benefits in terms of a reduced ABF consumption and a low environmental footprint. This is feasible thanks to the possibility of maintaining optimal agitation speed while simultaneously refluxing the generated gases back into the fluorination stage. This operational mode helps to reduce ABF consumption while keeping Ta and Nb recoveries at economically acceptable levels.

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