



Efficient Recovery of Niobium and Tantalum from Ferrocolumbium Tantalum by a Continuous Leaching Process Using HF – H₂SO₄ – HNO₃ Synergistic System

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Abstract

A stable and continuous leaching process for niobium and tantalum extraction from ferrocolumbium tantalum (FT) was developed. The effects of initial concentration of HF and H₂SO₄, grinding fineness, leaching time, and temperature on the leaching rate of Ta, Nb, Fe, and Si were studied. Experimental results show that the leaching rates of Ta, Nb, Fe, and Si were enhanced by the increase of acid concentrate, fineness, leaching time, and leaching temperature. The optimum process conditions are HF initial concentration of 5 mol/L, H₂SO₄ initial concentration of 2.5 mol/L, –74 μm percentage of 65%, leaching time of 20 min, and leaching temperature of 25 °C. Continuous leaching of FT was carried out by feeding ore and acid every 20 min. By leaching with HF – H₂SO₄ for 4 h, then adding appropriate amount of HNO₃ into the solution and keeping for another 1 h, a high Nb extraction rate of 99.8% was achieved. The established method provides a promising technique for the high-efficiency separation of niobium and tantalum from FT.

Highlights

- The priority of metal extraction in HF–H₂SO₄ system is Si > Fe > Ta > Nb.
- Ferrocolumbium tantalum can be stable leached by introducing raw material and acid every 20 min.
- A high Nb extraction rate of 99.8% was achieved by the continuous leaching process.

Keywords Ferrocolumbium tantalum · Hydrofluoric acid – sulfuric acid · Continuous leaching · Niobium recovery

1 Introduction

Niobium and tantalum, characterized by high melting point, remarkable corrosion resistance, and good cold workability, are widely used in steel, petrochemical, electronics, and aerospace [1, 2]. The main ore sources for the production of tantalum and niobium include pyrochlore, microlite, tantalite, columbite, and columbo-tantalite [3]. Besides, some smelting slags (such as tin slag [4–7], iron slag, tungsten slag, etc.) and tantalum–niobium tailings are also important

raw materials for tantalum–niobium manufacture. Most tantalum–niobium minerals have a high chemical stability because tantalum–niobium exists in the form of pentoxide, which has strong chemical inertness and is difficult to dissolve.

Extraction of niobium–tantalum from abovementioned ores has been extensively studied in the past decades. The main procedures can be classified into alkali fusion [1, 8–10], hydrofluoric acid leaching [11], sulfuric acid leaching [12], and chlorination [7, 13]. For acid leaching method, hydrofluoric acid or sulfuric acid was employed as leaching agent to extract tantalum and niobium from mineral into the solution and then separate tantalum and niobium from impurities by solvent extraction or ion exchange. Currently, hydrofluoric acid leaching is the main industrial method for treating tantalum–niobium concentrates.

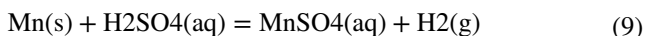
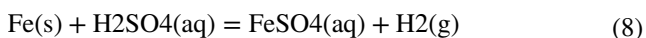
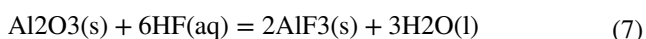
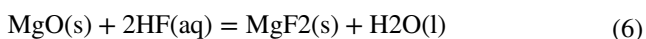
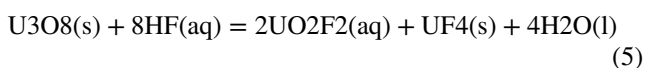
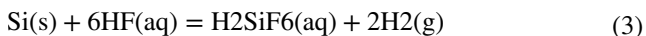
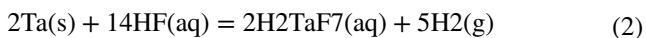
Tin slag is an important secondary resource for tantalum and niobium extraction [7]. In cassiterite smelting process, tantalum and niobium were enriched in the reducing slag

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along with other elements such as rare earth element, Ti, Si, Fe, Ca, Al, etc.; the (Ta + Nb)₂O₅ content approximately ranges from 1 to 25% [3]. Direct leaching of tin slag with such low metal grade is inefficient and economically undesirable. Therefore, enrichment methods for tin slag were developed. Combined acid-alkaline leaching is an efficient approach to enhance tantalum and niobium contents [6, 14]. Allain et al. [3] proposed a greener approach to selectively dissolve the slag amorphous matrix. A production with a 63% (Ta + Nb) oxide concentrate was obtained from a tin slag containing about 15% (Ta, Nb)₂O₅ through sequential acid and alkaline leaching steps. The author also studied the chlorination and carbochlorination of tantalum and niobium low-grade concentrate and high-grade concentrate produced from tin slag [15]. Results show that pretreatment of tin slag by a successive acid and basic leaching can eliminate the majority of Fe, Ca, Mn, Al, etc., and pure tantalum and niobium product was generated through carbochlorination at low temperatures. Besides, a common enrichment route is the reduction smelting of tin slag in electric furnaces followed by the dissolution or the chlorination of the upgraded materials and a purification step [16]. By carbon thermal reduction, Ta and Nb oxides along with ferric oxide and silicon dioxide were reduced to metal, generating a ferro-columbium tantalum (FT) and separating from the slag. Afterwards, the FT was subjected to acid leaching to extract Ta and Nb. The main reactions of FT in the HF – H₂SO₄ system are as follows:



During the leaching process, Nb, Ta, and Si mainly consume HF, while Fe mainly reacts with H₂SO₄, and impurities such as alkaline earth, rare earth, thorium, and uranium transform into insoluble fluorides and remain in the residue. A great amount of H₂ was produced during the leaching process of FT, and therefore the feeding rate must be strictly controlled to prevent the slurry escape and the potential safety hazard caused by high concentration of H₂. To date, researches on the acid decomposition of tantalum and niobium mainly focus on mineral raw materials, such as columbite [11] and tantalite [1, 17, 18], whereas few works have been done to evaluate the leaching behavior of FT in acid system.

In this work, a FT was leached by using HF – H₂SO₄ system, and the influences of acid concentration, grind fineness, leaching time, and leaching temperature on the extraction efficiency of tantalum and niobium were studied systematically. Finally, a continuous leaching process for FT was established based on the condition test.

2 Materials and Methods

2.1 Materials

The FT used in the experiment was acquired from a tantalum–niobium smelter in Guangdong province. The chemical composition shown in Table 1 indicates that the alloy mainly contains Si, Fe, Nb, and Ta, in addition to a small amount of MgO, Al₂O₃, MnO₂, and ThO₂. The characterization of FT is given in Fig. 1. Particle size analysis shows that the FT is fine particles with a mean diameter of ~7.87 μm (Fig. 1a) after ball-milling. X-ray diffraction (XRD) investigation (Fig. 1b) shows that the main crystalline phase in FT contains Fe₅Nb₃, Fe₂C, FeSi, Ca₂Al(AlSiO₇), and SiO₂, and part of FT exhibits as amorphous phase. The presence of Fe₂C suggests the occurrence of over-reduction during the carbon thermal reduction of tin slag. Scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDS) analysis of FT shown in Fig. 1c indicate that the main elements are Si, Fe, Nb, Ta, Al, etc., where Si, Fe, Nb, and Ta exhibit a similar distribution. The element mapping analysis further confirms the aggregation of Si, Fe, Nb, and Ta (Fig. 1d). The reagents used in the experiment are analytical grade HF with a concentration of ~40%, analytical grade H₂SO₄ with a concentration of ~98%, and analytical grade HNO₃ with a concentration of ~65%.

Table 1 Main chemical composition of FT (wt%)

Si	Fe	Nb	Ta	MgO	Al ₂ O ₃	MnO	ThO ₂	U
11.34	27.51	45.67	4.38	2.92	4.42	2.43	0.64	0.47

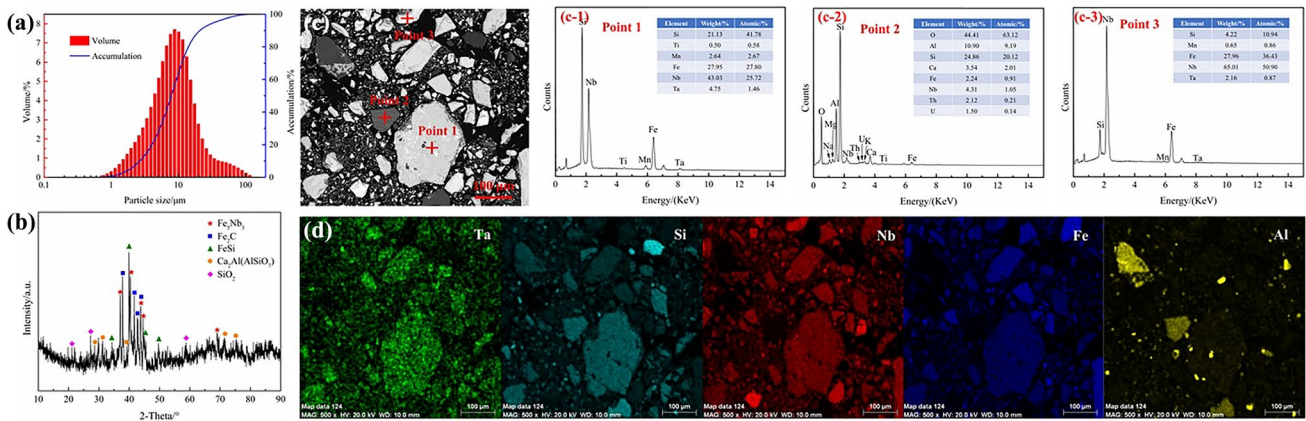


Fig. 1 Characterization of FT: **a** particle size distribution, **b** XRD analysis, **c** SEM and EDS analysis, and **d** element mapping analysis

Table 2 The tested factors and corresponding level range in this study

Factor	Level
HF and H ₂ SO ₄ concentrations	3 mol/L + 1.5 mol/L, 5 mol/L + 2.5 mol/L, and 7 mol/L + 3.5 mol/L
Ore fineness	–74 µm percentage of 55–85%
Leaching time	5–40 min
Leaching temperature	25–85 °C

2.2 Experimental Procedures

A total of 200 mL of acid solution with a certain concentration of HF and H₂SO₄ was loaded in a 1-L polytetrafluoroethylene beaker and then placed in a thermostatic water bath. Twenty grams of raw material was added to the solution after 15 min of heat preservation and stirred at 300 rpm. After leaching, the pulp was diluted by 300 mL of water to terminate the reaction and immediately filtered to collect the leaching liquor and leaching residue. The residue was washed, dried, and finely ground for analysis. The metal recovery rates were calculated by Eq. (10). All tested factors and its level range are listed in Table 2.

$$R_M = 1 - \frac{m_r \cdot \omega_M \cdot M_{\text{residue}}}{m_{\text{raw}} \cdot \omega_M \cdot M_{\text{raw}}} \times 100\% \tag{10}$$

where *M* denotes Nb, Ta, Fe, or Si; *m_r* is the weight of leaching residue; *ω_{M, residue}* is the metal content in the residue; *m_{raw}* is the weight of the raw material; and *ω_{M, raw}* is the metal content in the raw material.

2.3 Characterization

The chemical compositions of FT and leaching residue were determined by X-ray fluorescence spectrometry

(XRF, PANalytical-Axios^mAX, Almelo, Netherlands) and inductively coupled plasma–atomic emission spectroscopy (ICP–AES, PerkinElmer Optima–4300DV). Laser particle size analyzer (HORIBA LA-950) was used to measure the particle size distribution of FT and residue. XRD (X’PERT PRO MPD/PW3040, PANalytical B.V. Corporation, Almelo, Netherlands) analysis was carried out to investigate the phase composition of FT and residue. Microstructural characterizations of raw material and products were conducted by SEM (QUANTA 250FEG) equipped with an EDS (EDAX Genesis-SiLi) detector. The free acid concentration in the leachate after leaching was measured using titration method. Briefly, the total acid concentration in the leachate was first analyzed. Afterward, the leaching liquor was heated to volatilize the free HF, and the residual acid which mainly composed of H₂SO₄ was measured again.

3 Results and Discussion

3.1 Effect of Parameters

Figure 2a shows the effect of acid concentration on leaching rate of FT. Various HF and H₂SO₄ concentrations, namely, 3 mol/L + 1.5 mol/L (3 M + 1.5 M), 5 mol/L + 2.5 mol/L (5 M + 2.5 M), and 7 mol/L + 3.5 mol/L (7 M + 3.5 M), were studied. Notably, the recovery of Ta, Nb, Fe, and Si increases with the increase of acidity. The leaching rates exhibit a significant increase when the acidity increases from 3 M + 1.5 M to 5 M + 2.5 M and then tend to be stable with the further increase of acidity. It is noteworthy that high acidity is prone to elevate the foam height and hence causes an overswelling pulp.

Figure 2b shows the residue amount and slag composition obtained at various acidities. As the acidity increases, the residue amount gradually decreases, and the content of Ta, Nb, Fe, and Si shows a continuous decrease. The grade

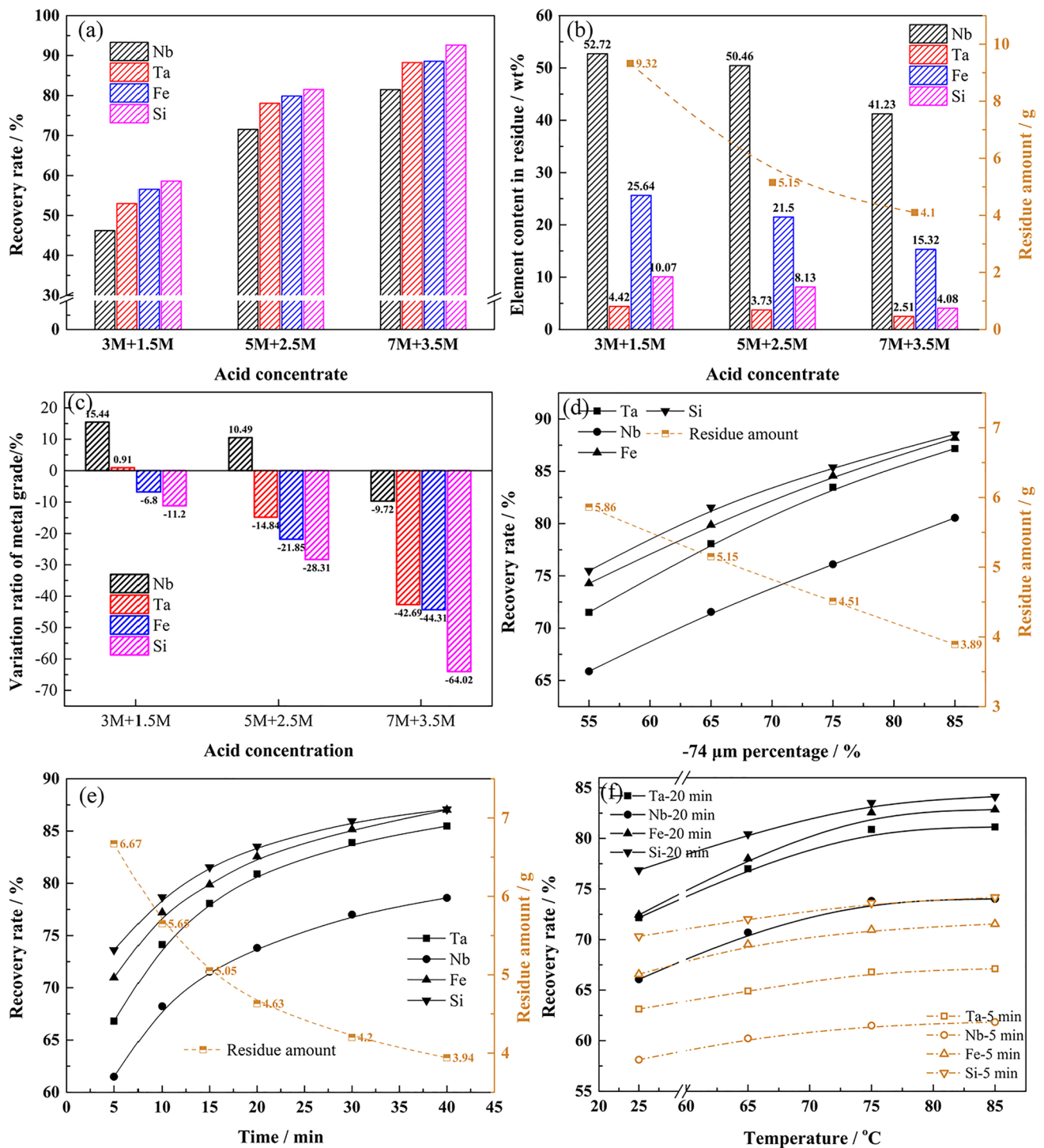


Fig. 2 Effect of acid concentrate ($-74 \mu\text{m}$ percentage: 65%, 15 min, 75 °C) on **a** the leaching efficiency of FT, **b** the element content and residue amount, and **c** relative variation ratio of element content; effects of **d** mineral fineness (5 M+2.5 M, 15 min, 75 °C), **e** leaching

time (5 M+2.5 M, $-74 \mu\text{m}$ percentage: 65%, 75 °C), and **f** temperature (5 M+2.5 M, $-74 \mu\text{m}$ percentage: 65%, 5 min and 20 min) on the leaching efficiency of FT

variation ratio (R_g) of different metal as a function of acidity, calculated by Eq. (11), is presented in Fig. 2c. Si shows the most significant decrease in all tested acidities, while

the recovery of Ta and Nb is less pronounced. It can be concluded that the priority of metal recovery in $\text{HF}-\text{H}_2\text{SO}_4$ system is $\text{Si} > \text{Fe} > \text{Ta} > \text{Nb}$, that is, the dissolution of Si and

Fe is dominant in the initial reaction stage compared to that of Ta and Nb. Considering the foam height and HF volatilization, 5 mol/L HF + 2.5 mol/L H₂SO₄ was selected as the optimal acidity.

$$R_g = \frac{\omega_{M, \text{residue}} - \omega_{M, \text{raw}}}{\omega_{M, \text{raw}}} \times 100\% \quad (11)$$

where R_g donates the variation ratio of Nb, Ta, Fe, and Si grade; $\omega_{M, \text{residue}}$ is the metal content in the residue; and $\omega_{M, \text{raw}}$ is the metal content in the raw material.

Figure 2d shows the effect of fineness on the leaching efficiency of FT. Clearly, the leaching rate was enhanced by increasing grinding fineness. The residue amount decreases from 5.86 to 3.89 g when the -74 μm percentage increases from 55 to 85%. The recovery rate of Nb is unsatisfactory, showing its maximum of 80.6% at -74 μm percentage of 85%. It was observed in the experiment that the generation of foams was sensitive to the fine granularity. A severe foam generation occurred in the case of 75% and 85% -74 μm percentage. Therefore, the optimal grinding fineness is chosen as -74 μm percentage of 65% considering the safety risk and the grinding cost.

Figure 2e shows the effect of leaching time on the leaching efficiency of FT. The recovery rate of Ta, Nb, Fe, and

Si shows a remarkable increase in the first 20 min and then slows down with prolonged time, which can be attributed to the decrease in liquid acidity. The variation of residue amount also confirms the significant dissolution at initial stage.

Figure 2f shows the effect of temperature on the leaching efficiency of FT. The recovery rate shows a slight increase by the elevated temperature, reaching at a steady level when the temperature exceeds 75 °C. Notably, the variation tendency of recovery rate obtained at 5 min is less pronounced. This is mainly because the alloy dissolution is an exothermic reaction. Considerable amounts of heat were generated at the initial leaching stage, reducing the temperature difference between leaching liquors. However, the increase in temperature may accelerate the volatilization of HF. Hence, it is advisable to control the leaching temperature at 25 °C since the increment of recovery rate resulted from temperature is non-significant.

3.2 Continuous Leaching

Based on the above test results, a continuous leaching test was carried out by acid supplementation and ore supplementation. The technological process is illustrated in Fig. 3. A total of 250 mL leaching liquor with HF and H₂SO₄

Fig. 3 Charging process of FT and acid for continuous leaching

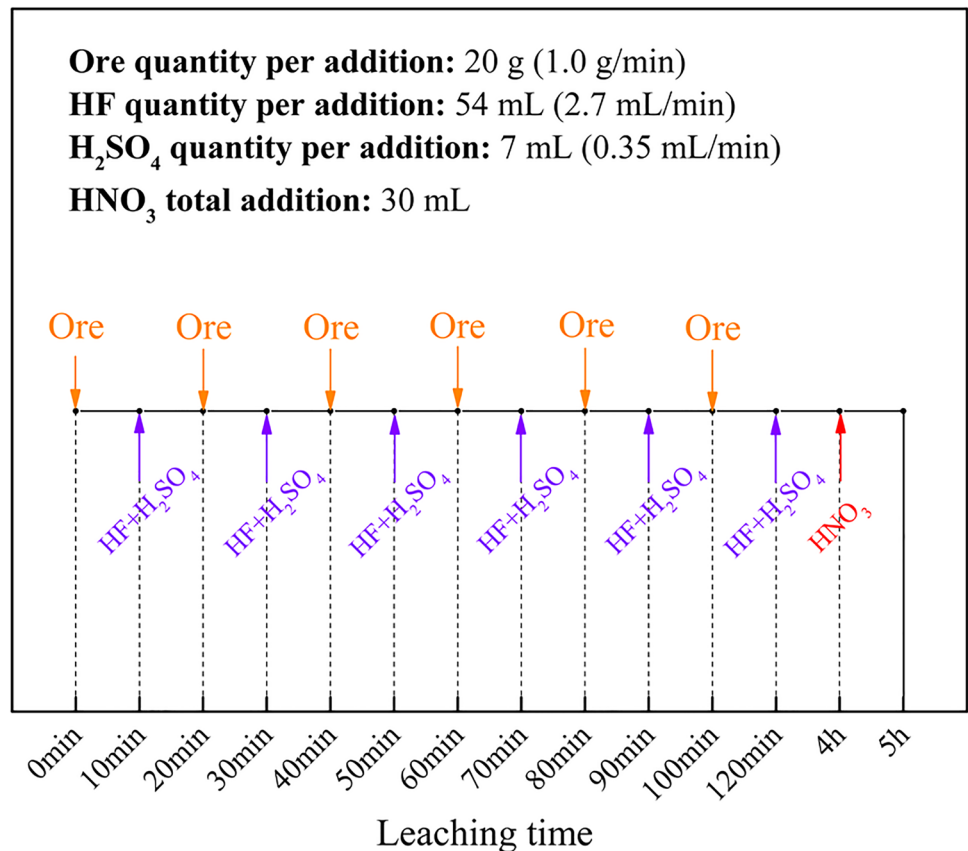


Table 3 The main chemical composition of the leaching residue (wt%)

Sample	F	Mg	Al	Si	Fe	Ca	Th	Pb	U	Nb	Ta	S
Residue at 4 h	14.62	6.18	9.95	0.31	1.11	2.86	4.30	7.45	8.01	36.05	0.44	2.31
Residue at 5 h	26.66	12.10	20.34	0.22	1.07	6.50	8.44	2.53	16.92	2.23	0.10	0.85

concentration of 5 mol/L and 2.5 mol/L, respectively, was prepared initially. Twenty grams of FT was loaded every 20 min, equivalent to an addition rate of 1.0 g/min. Fifty-four milliliter HF and 7 mL H₂SO₄ were added every 20 min (HF addition rate of 2.7 mL/min, H₂SO₄ addition rate of 0.35 mL/min) to keep the acidity in a sufficient level, that is, the HF and H₂SO₄ concentration in the leachate is close to the starting level. After leached for 4 h, 30 mL HNO₃ was introduced into the solution to resolve the residual niobium carbide.

Table 3 shows the chemical compositions of the residues obtained at 4 h and 5 h. After 4 h leaching, most Ta, Si, and Fe were extracted into the leachate, while the recovery efficiency of Nb is less favorable. By adding HNO₃, the Nb content in the residue was reduced to 2.23%, and a high Nb extraction yield of 99.8% was achieved. To acquire a deep insight of the phase transformation and composition change, a series of characterization analysis were performed. Figure 4a indicates that the residue becomes light after being treated by HNO₃. After decomposing for 4 h, the particle size of the residue decreases significantly compared with the raw material, while it shows a slight increase after being treated by HNO₃. The XRD pattern (Fig. 4c) shows that the main crystalline phases of the residue obtained at 4 h were identified as MgAlF₅·1.5H₂O, Nb₄C₃, Mg_{0.4}Al_{2.4}O₄, PbSO₄, and Al₂O₃. By the addition of HNO₃, peaks attributable to Nb₄C₃ disappeared and the diffraction peaks for PbSO₄ weakened, suggesting the dissolution of Nb and Pb from Nb₄C₃ and PbSO₄, respectively. Thus, the color change between the residues can be ascribed to the decomposition of Nb₄C₃. The undesirable Nb recovery after HF–H₂SO₄

leaching is due to the presence of niobium carbide, which may generate from the over-reduction of Nb₂O₅ during the smelting of tin slag. The SEM and EDS results shown in Fig. 4d further prove the presence of Nb₄C₃ (point 2) and Al₂O₃ (point 3). Most of the residue presents as fine particles with a diameter below 10 μm. After being treated by HNO₃, the size and quantity of Nb₄C₃ particles decreased, and the amount of Pb also reduced significantly. The XRD and SEM results correspond with each other, confirming the decomposition of Nb₄C₃ by HNO₃.

4 Conclusions

The recovery rate of Ta, Nb, Fe, and Si in the FT increases with the increase of acidity, fineness, leaching time, and temperature, but the foam generation was also enhanced. The priority of metal dissolution in HF–H₂SO₄ system is Si > Fe > Ta > Nb. The recovery rates of Si and Fe are superior to that of Ta and Nb. The optimal leaching parameters for FT are HF concentration of 5 mol/L, H₂SO₄ concentration of 2.5 mol/L, –74 μm percentage of 65%, leaching time of 20 min, and leaching temperature of 25 °C. Continuous and stable leaching of FT can be achieved by introducing raw material and acid every 20 min. After being decomposed by HF–H₂SO₄ for 4 h, and then further treated with HNO₃ for 1 h, a favorable Nb recovery rate of 99.8% was successfully obtained. The findings in this study provide a practicable strategy for stable and efficient recovery of ferrocolumbium tantalum.

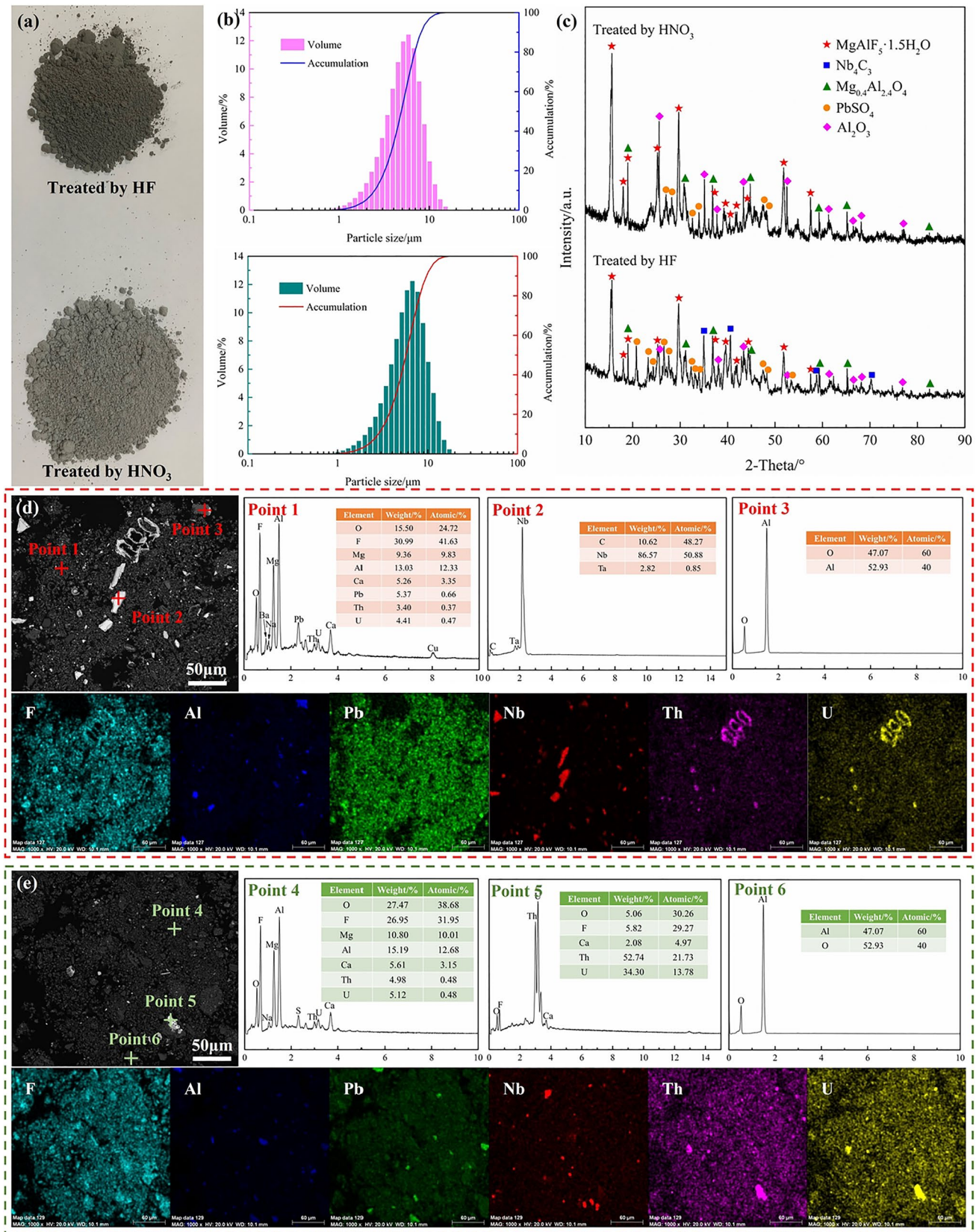


Fig. 4 Characterizations of the residues obtained after decomposing for 4 h and 5 h: **a** photograph of the residues, **b** particle size distribution, **c** XRD analysis, **d** SEM and EDS analysis of the residue after 4 h decomposing, **e** SEM and EDS analysis of the residue after 5 h decomposing

Author Contribution Jianfang Lyu: conceptualization, methodology, investigation, writing-original draft, writing-review and editing, and funding acquisition; Yong Liu: conceptualization, resources, and supervision; Zhiyuan Ma: investigation, writing-review and editing, and funding acquisition; Xianjin Lyu: methodology, investigation, and writing-review and editing; Jikui Zhou: resources and writing-review and editing.

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Declarations

Conflict of Interest The authors declare no competing interests.

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