Low-Acid Extraction of Tantalum from a Tantalum-Niobium Pulp by MIBK

Xiuli YANG,1,2 Xiaohui WANG,2* Chang WEI,1 Shili ZHENG2 and Yi ZHANG2
1 Faculty of Metallurgical and Energy Engineering, Kunming University of Science and Technology, 121 Avenue, Yunnan 650093, China
2 Institute of Process Engineering, Chinese Academy of Sciences, Zhongguancun Avenue, Beijing 100190, China
(Received March 15, 2012; Accepted April 12, 2012)

The technological parameters and the mechanism of low-acid pulp extraction of tantalum were investigated. The results show that hydrofluoric acid concentration, sulfuric acid concentration, organic to pulp phase ratio, the concentration of tantalum and niobium, contact time and temperature have a significant effect; optimum process operating parameters were established as follows: hydrofluoric acid concentration 1.6 mol/L, sulfuric acid concentration 0.6 mol/L, organic to pulp phase ratio 3:1, tantalum concentration 26.61 g/L, niobium concentration 11.64 g/L, contact time 5min and room temperature. Under these experimental conditions, tantalum extraction can reach more than 98% and the separation factors of Ta/Nb, Ta/Fe and Ta/Sn were maximal. According to slope analysis, the equimolar series method and the saturation capacity method, the extraction product was identified as \(3\text{MIBK} \cdot \text{H}_2\text{TaF}_7\).

1. Introduction

Tantalum and niobium are the important elements applied in many high-technology industries such as superconductors, electronic, energy and aerospace. About 61 % of tantalum is used for capacitors and about 90 % of niobium in the world is used in the iron and steel industry as additives [1].

The elements tantalum and niobium, because of their similar chemical properties, always occur together in nature [2]. Extraction as a method for separating and purifying niobium and tantalum, is widely used in industry [3,4]. A wide range of extractants has been used including: ketones, such as methyl isobutyl ketone (MIBK) and cyclo-hexanone; alkyl-phosphorus esters, e.g., tri-\(n\)-butyl phosphate (TBP) and trioctyl phosphate oxide (TOPO); \(N\)-oxides; sulphoxides; and acidic alkylphosphorus extractants, such
as di-2-ethylhexyl phosphoric acid (D2EHPA)—which were not very efficient—and long-chain alkylamines [5-10]. MIBK is the most commonly used extractant worldwide due to its lower density, lower water solubility, lower cost, higher chemical and operational stability, compared with other extractants [3, 11]. At present MIBK is commonly used in China, at Ningxia Orient Tantalum Industry Co., LTD and Guangdong Conghua Tantalum &Niobium Smeltery, which are two of the biggest tantalum and niobium producers in China. Therefore, methyl isobutyl ketone (MIBK) was used as the extractant.

All solvent extraction processes are exclusively operated in the presence of fluoride ions, most frequently in a mixture with a mineral acid such as sulfuric or hydrochloric acid. As this binary acid system is normally used for the digestion of tantalum and niobium concentrates, their solvent extraction is often carried out in the same system. Due to increasingly stringent regulations concerning the protection of human health and environment, the use of harmful fluorides must be reduced. Therefore, there is an urgent need to develop a new process for the separation and purification of niobium and tantalum.

Recently, a method for the separation and purification of niobium and tantalum was proposed with the objective to reduce fluorine pollution [12]. In this method, the pure solution containing only tantalum and niobium was extracted by MIBK. Based on this method, we proposed a new process to separate and purify tantalum and niobium in the tantalum-niobium pulp. This new process is based on the difference in tantalum and niobium extraction performance: niobium complexes in the solution are stronger Lewis acids than tantalum complexes. Therefore, the extraction of niobium with MIBK requires stronger solution acidity than that of tantalum. In the traditional process, tantalum and niobium were extracted simultaneously, followed by the back extraction and separation of tantalum and niobium respectively. In the new process, first tantalum was extracted, and then niobium was extracted. In comparison with the traditional process, the hydrofluoric acid concentration used in this process was reduced from 6 mol/L to 1.6 mol/L.

The purpose of the present work is to investigate the extraction behavior of tantalum, niobium, and other associated mineral impurities such as iron, manganese, aluminum, silicon and tin, and to obtain optimal operating parameters.

2. Experimental

2.1 Pulp and reagents

The tantalum and niobium pulps were obtained from the previous low-alkali decomposition process [13]. In the low-alkali decomposition process the tantalum-niobium ore is decomposed in a low alkali system under atmospheric pressure. The decomposition product contains some metatantalate and metaniobate salts, which are insoluble in hydrochloric acid or sulfuric acid, so a transformation agent was used to solubilise the metatantalate and metaniobate salts transformed in the solution for extraction. The mass concentrations of major elements in the pulp are shown in Table 1. In the pulp slag rate was 40%, including tin oxide and aluminosilicate.
<table>
<thead>
<tr>
<th>Elements</th>
<th>Ta</th>
<th>Nb</th>
<th>Fe</th>
<th>Al</th>
<th>Si</th>
<th>Mn</th>
<th>Sn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (g/L)</td>
<td>26.61</td>
<td>11.64</td>
<td>6.34</td>
<td>1.65</td>
<td>4.06</td>
<td>1.80</td>
<td>7.99</td>
</tr>
</tbody>
</table>

Methyl isobutyl ketone was of analytical grade, which was produced by Beijing Yili Chemical Co. Ltd, China. Hydrofluoric acid was of analytical grade, which was supplied by Beijing Beihua Fine Chemical Co. Ltd, China. Distilled water was used in the experiments.

### 2.2 Pulp extraction procedures

The pulp containing tantalum and niobium was equilibrated with different volumes of methyl isobutyl ketone by shaking in a separatory funnel for 10 min. The shaking speed was 240 rpm. This period of time which had been verified in preliminary tests was sufficient to achieve equilibrium.

The pulp after equilibrium was filtered. The concentrations of tantalum and niobium in the filtrate were measured by ICP-AES (ICP model; Perkins Elmer, OPTIMA 2100DV), after suitable dilution with distilled water and 12% (mass fraction) dihydroxysuccinic acid.

### 3. Results and Discussion

#### 3.1 Effect of hydrofluoric acid concentration on tantalum and niobium extraction

An important factor to be studied is the effect of hydrofluoric acid concentration. The effect of the hydrofluoric acid concentration on the extraction and separation of tantalum and niobium from the pulp is shown in Figure 1. It can be seen from Figure 1(a) that the percentage of extracted tantalum and niobium increased with increasing of hydrofluoric acid concentration. As the concentration of hydrofluoric acid increased from 1.2 mol/L to 1.6 mol/L, the degree of extraction of tantalum increased from 86% to about 98%. Similarly, the degree of extraction of niobium increased from 1% to 6%. Niobium extraction was far less than that of tantalum. In the extraction process, the lone pair of electrons on the oxygen atom of MIBK attracts hydrogen ions, which generates a cation. This cation combines with the tantalum complex anion electrostatically, which creates the complex $\text{H}_2\text{TaF}_n\cdot n\text{MIBK}$ which is hydrophobic and dissolves in methyl isobutyl ketone [14]. The separation factor is equal to the ratio of the distribution ratio of the two metals, which expresses the degree of separation of the two metals. Figure 1(b) shows that the separation factor of Ta/Nb reached a maximum and tantalum and niobium were well separated when the concentration of hydrofluoric acid was 1.6 mol/L. Meanwhile, the separation factors for Ta/Fe, Ta/Sn also reached a maximum. Most of the impurities stayed in the pulp, thus achieving the best separation of tantalum and impurities. Therefore, a hydrofluoric acid concentration of 1.6 mol/L is recommended.
3.2 Effect of sulfuric acid concentration on tantalum and niobium extraction

The effect of the sulfuric acid concentration on the extraction and separation of tantalum and niobium is shown in Figure 2. It can be seen from Figure 2(a) that tantalum extraction rate increased and then tended to level out as the sulfuric acid concentration increased. Niobium extraction increased when the sulfuric acid concentration increased. Sulfuric acid can combine with water molecules by hydration, so the number of free water molecules decreases. Therefore, the effective concentration of tantalum and niobium increases [15]. The effect of sulfuric acid on the extraction of niobium and tantalum with MIBK is a salting out effect [16]. Figure 2(b) shows that the separation factor of Ta/Nb reached a maximum when the concentration of sulfuric acid was 0.6 mol/L. Tantalum and niobium were well separated. Meanwhile, the separation factors of Ta/Fe, Ta/Sn also reached a maximum. Most of the impurities stayed in the pulp, thus achieving the best separation of tantalum and impurities. Therefore, a sulfuric acid concentration of 0.6 mol/L is recommended.
Figure 2. (a) Effect of sulfuric acid concentration on the extraction of tantalum and niobium and (b) Effect of sulfuric acid concentration on the separation factor of tantalum and other elements. Experimental conditions: hydrofluoric acid concentration 1.6 mol/L, Ta$_2$O$_5$ 26.61 g/L, Nb$_2$O$_5$ 11.64 g/L, phase ratio (organic/pulp, volume) 5:1, time 10 min, and room temperature

3.3 Effect of organic to pulp phase ratio on tantalum and niobium extraction

The effect of the phase ratio on the extraction and separation of tantalum and niobium from the pulp is shown in Figure 3. It can be seen from Figure 3(a) that, when the phase ratio increased, the degree of tantalum and niobium extraction increased, which can be attributed to the fact that more tantalum and niobium complexes combined with MIBK. The extraction of tantalum was almost completed at an O/A ratio of 3:1, but the extraction of niobium was small. Therefore the best separation of tantalum and niobium was achieved at an O/A ratio of 3:1. Figure 3(b) shows that the separation factor of Ta/Nb reached a maximum when the phase ratio was 3:1. Meanwhile, the separation factors of Ta/Fe, Ta/Sn also reached a maximum. Most of the impurities stayed in the pulp, thus achieving the best separation of tantalum and impurities. Therefore, a phase ratio of 3:1 is recommended.
3.4 Effect of the concentration of tantalum and niobium on tantalum and niobium extraction

The effect of tantalum and niobium concentration on the extraction and separation of tantalum and niobium from the pulp is shown in Figure 4. It can be seen from Figure 4(a) that the extraction of tantalum and niobium remained practically unchanged with increasing concentration of tantalum and niobium from 27 g/L to 50 g/L. Figure 4(b) shows that the separation factor for Ta/Nb decreased when the concentration of tantalum and niobium increased. However, when the concentration is low, the production capacity will decline and it is uneconomical. Therefore, a concentration of 38.25 g/L is recommended.

Figure 4. (a) Effect of Ta$_2$O$_5$ and Nb$_2$O$_5$ concentration on the extraction rate of tantalum and niobium and (b) Effect of Ta$_2$O$_5$ and Nb$_2$O$_5$ concentration on the separation factor of tantalum and other elements. Experimental conditions: hydrofluoric acid concentration 1.6 mol/L, sulfuric acid 0.6 mol/L, phase ratio (organic/pulp, volume) 3:1, time 10 min, and room temperature.
3.5 Effect of extraction time on tantalum and niobium extraction

The effect of extraction time on the extraction and separation of tantalum and niobium from the pulp is shown in Figure 5. It can be seen from Figure 5 that the extraction was very fast. The extraction was basically complete after only one minute. To ensure that the extraction equilibrium is fully achieved, a contact time of 5 min is recommended.

![Figure 5. Effect of time on the extraction of tantalum and niobium. Experimental conditions: hydrofluoric acid concentration 1.6 mol/L, sulfuric acid 0.6 mol/L, Ta_2O_5 26.61 g/L, Nb_2O_5 11.64 g/L, phase ratio (organic/pulp, volume) 3:1, and room temperature.](image)

3.6 Effect of temperature on tantalum and niobium extraction

The effect of the temperature on the extraction and separation of tantalum and niobium from the pulp is shown in Figure 6. Methyl isobutyl ketone is volatile and toxic, so it is not used at higher temperatures. Moreover, it can be seen from Figure 6 that the effect of temperature is not significant between 20°C and 50°C. However for MIBK such factors as high volatility and low flash point lead to high reagent losses and potentially dangerous operating conditions. Therefore, the recommended temperature is room temperature.

![Figure 6. Effect of temperature on the extraction of tantalum and niobium. Experimental conditions: hydrofluoric acid concentration 1.6 mol/L, sulfuric acid 0.6 mol/L, Ta_2O_5 26.64 g/L, Nb_2O_5 11.61 g/L, phase ratio (organic/pulp, volume) 3:1, and time 10 min.](image)

4. Mechanism of Tantalum Extraction

In order to be consistent with the above process, the mechanism of tantalum extraction was studied under the optimum process conditions: tantalum concentration 0.15 mol/L, hydrofluoric acid concentration 1.6 mol/L and sulfuric acid concentration 0.6mol/L. There are mainly H_2TaF_7 species in the pulp at a hydrofluoric acid concentration 1.6mol/L [14,16,18]. The predominant areas of TaF_6^2− and TaF_5^− complex species in the Ta_2O_5-HF-H_2O system are shown in Figure 7.
4.1 Slope method

The effect of pH, MIBK concentration, sulfate ion concentration and fluoride ion concentration were investigated. The plots of log D vs. log[SO₄²⁻], log[F⁻], pH and log[MIBK] are shown in Figure.8, Figure.9, Figure.10 and Figure.11 respectively. According to Figure 8, Figure 9, Figure 10 and Figure 11, the experimental points for log D vs. log[SO₄²⁻], log[F⁻], pH and log[MIBK] parameter all fall on a straight line, respectively, from which the slope can be obtained and are equal to 0.18, 7.06, -2.07 and 2.98 which can be rounded to be 0, 7, -2 and 3. Figure 8 shows that there is no sulfate ion involved into the reaction. Figure 9, Figure 10 and Figure 11 show that there are 2 hydrogen ions, 7 fluoride ions and 3 MIBK molecules involved into the reaction. Therefore, the extraction is considered to be as in Eq. (1).

$$3\text{MIBK} + 2\text{H}^+ + \text{TaF}_7^- = \text{H}_2\text{TaF}_6 \cdot 3\text{MIBK}$$ (1)
4.2 Equimolar series method [16, 19]

The sum of the molar concentration of the extractant in the organic phase and the molar concentration of tantalum in the aqueous phase is a constant value. When the hydrofluoric acid concentration is 1.6mol/L, the extraction is carried out for different ratios of the molar concentration of tantalum and the molar concentration of MIBK. The relationship of the extraction of tantalum and the ratio is shown in Figure 12. It can be seen from the Figure 12 that the ratio is 0.26 at the maximum extraction of tantalum. From this it can be concluded that the MIBK: $H_2TaF_7$ ratio is 3:1.

![Figure 11](image1.png)  ![Figure 12](image2.png)

**Figure 11.** The relationship between log[MIBK] and logD.

**Figure 12.** The relationship of the extraction of tantalum and the Ta MIBK molar ratio.

4.3 Saturated volumetric method

The extraction was carried out at a hydrofluoric acid concentration of 1.6 mol/L and a tantalum concentration 0.15mol/L. The concentration of tantalum in the aqueous was analyzed. The content of tantalum in the organic phase was calculated by the mass balance method. When the organic phase reached saturation extraction, the molar ratio of MIBK/Ta was 2.98:1. The result is consistent with that of the above methods.

5. Conclusion

1. According to a pilot study, low-acid pulp extraction is feasible.
2. Using this technology, the extraction rate of tantalum can reached to more than 98% at a hydrofluoric acid concentration of 1.6 mol/L, a sulfuric acid concentration of 0.6 mol/L, an organic to pulp phase ratio of 3:1, a tantalum concentration of 26.61 g/L, a niobium concentration of 11.64 g/L, a contract time of 5min and room temperature. Moreover, the separation of tantalum and niobium was very good under the above conditions.
3. The slope method, the equimolar series method and the saturated volumetric method were used to study the mechanism of tantalum extraction. The results of these methods are consistent. The MIBK:
H$_2$TaF$_7$ ratio is 3:1 in the extracted species.

Acknowledgement

This work was financially supported by Plan 863 Project of China (2009AA06Z103) and National Science Foundation of China (51004094).

References

6) J. Han, Y. Zhou, Rare Metals and Cemented Carbides, 32, 15-20 (2004).
12) J. Xu, “Basic research on the process of separating niobium and tantalum by extraction with MIBK in low concentration hydrofluoric acid system”, 2010, Beijing University of Chemical Technology, Beijing.