



Metal recovery from TiCl_4 slurry by evaporation and acid leaching

X. Xiang¹, X. Wang², W. Xia¹, and J. Yin¹

Affiliation:

¹School of Metallurgical and Materials Engineering, Central South University, Changsha, China.

²School of Metallurgy and Environment, Chongqing University of Science and Technology, Chongqing, China.

Correspondence to:

X. Xiang

Email:

xxycsu@163.com

Dates:

Received: 5 Apr. 2018

Revised: 12 Jul. 2018

Accepted: 29 Oct. 2018

Published: April 2019

How to cite:

Xiang, X., Wang, X., Xia, W., and Yin, J.

Metal recovery from TiCl_4 slurry by evaporation and acid leaching. The Southern African Institute of Mining and Metallurgy

DOI ID:

<http://dx.doi.org/10.17159/2411-9717/85-192-1/2019>

ORCID ID:

X. Xiang

<https://orcid.org/0000-0002-7080-7980>

Synopsis

TiCl_4 slurry containing valuable metals is an unavoidable by-product of the titanium ore chlorination process. The recovery of these valuable metals, which include titanium, niobium, tantalum, and aluminum, is an urgent issue to tackle in the titanium industry. The results of this investigation show that the valuable metallic elements can be recovered from the slurry by evaporation in a sealed container and leaching with dilute hydrochloric acid. After evaporation at 200°C for 60 minutes, nearly 99% of the titanium was recovered in the form of TiCl_4 , which was formed by the reaction of the TiO_2 in the slurry with AlCl_3 . After evaporation, metals like niobium, aluminum, and tantalum remained in the residue. By leaching with 2.1 mol/L HCl at a L/S ratio of 6:1 mL/g at 80°C for 60 minutes, the soluble metals, such as aluminum, iron, and copper were all removed from the residue, and the niobium and tantalum were further enriched in the leach residue. A concentrate containing 53.40 wt% Nb and 5.57 wt% Ta was obtained by washing the leach residue with dilute aqueous ammonia under stirring. A potential waste water purifying agent containing 263.75 g/L AlCl_3 was produced by purifying the leaching solution with $\text{Al}(\text{OH})_3$ and modified polyacrylamide.

Keywords

TiCl_4 slurry, niobium, recovery, evaporation, leaching.

Introduction

Titanium tetrachloride (TiCl_4) is an important intermediate in titanium metallurgy that is widely used in the production of titania and titanium sponge (Akhtar, Xiong, and Pratsinis, 1991). In conventional titanium metallurgical processes, high-titanium materials such as synthetic rutile and high-titanium slag are reacted with chlorine to produce TiCl_4 in a fluidized-bed furnace. Accompanying elements, such as Al, Nb, and Fe also react with chlorine to form chlorides, which are mixed with gaseous TiCl_4 (Anderson, 1917). In the condensation process, gaseous TiCl_4 is refrigerated and high-boiling-point chlorides are precipitated in the liquid TiCl_4 to form a slurry containing 50–60 wt% TiCl_4 (Wang, Xiang, and Wang, 2012).

Various methods have been proposed to recover TiCl_4 from the slurry, including microwave heating and spray drying (Wang, Xiang, and Wang, 2012; Wang *et al.*, 2010a). To date, the only way to recover the TiCl_4 is to return the slurry to the fluidized-bed furnace. However, this causes fluctuations in the temperature in the furnace, resulting in incomplete reaction between titanium-rich materials and chlorine. Therefore, the slurry is often rinsed with water and neutralized by adding lime, which caused serious environmental pollution and wastes a valuable resource (Roy, Bhatt, and Rajagopal, 2003).

The TiCl_4 slurry contains considerable quantities of niobium (Wang *et al.*, 2012), which is one of the accompanying elements in titanium ore. Niobium is a rare metal that is widely used in steel, electronics, and other high-tech industries (Miller, 1959a; He, Liu, and Zhang, 1998). In nature, niobium is often associated with titanium, tantalum, the rare earth elements, and tin (Gupta and Suri, 1994; Miller, 1959b), and is usually recovered by hydrometallurgical methods such as decomposing tantalum-niobium concentrate with hydrofluoric acid (El-Hussaini, 2001; Gupta and Suri, 1994; Wang *et al.*, 2010) and leaching niobium from low-grade niobium materials with concentrated KOH solution (Zhou, Zheng, and Zhang, 2005; Wang *et al.*, 2009a; Zhou *et al.*, 2005b). These methods cannot be used to recover niobium from the slurry because of the high content of TiCl_4 . However, the niobium can be easily recovered from the slurry by leaching after the TiCl_4 has been removed by evaporation (Fran, 1978).

The objective of this study is to transform the slurry from a waste material into a valuable resource and reduce pollution. The methods employed include evaporation of the slurry in a sealed container and leaching of the residue with dilute hydrochloric acid.

Metal recovery from $TiCl_4$ slurry by evaporation and acid leaching

Experimental

Materials and analysis

All the chemical reagents used in this study were analytical grade, and deionized water was used. The $TiCl_4$ slurry was obtained from Zunyi Titanium Industry Co. Ltd. Its chemical composition is listed in Table I. It was found that about 80% of the titanium existed as $TiCl_4$ in the slurry, which was confirmed by washing the slurry with CCl_4 .

The contents of titanium, aluminum, niobium *etc.* were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a PS-6 Plasma Spectrovac, Baird (USA). Samples analysed for niobium were dissolved in hydrofluoric acid and hydrochloric acid (Lima and Conte, 2003; Lu and Makishima, 2007; Yang and Pin, 2002). The X-ray diffraction (XRD) patterns were recorded on a Rigaku Miniflex diffractometer with Cu K X-ray radiation at 35 kV and 20 mA.

Experimental procedure

Table I shows that the contents of titanium, aluminum, and niobium are much higher than those of other metallic elements in the slurry. Hence, the experimental work focused on the recovery of titanium, niobium, and aluminum. The experimental procedure was performed as shown in Figure 1. First, $TiCl_4$ was recovered from the slurry by evaporation and condensation. The residue was then leached with dilute hydrochloric acid to remove the aluminium and enrich the niobium content. The leach residue was washed with ammonia solution and filtered to recover a niobium concentrate. The leaching solution was purified to produce an $AlCl_3$ solution, which could be used as a purifying agent in waste water treatment.

Figure 2 is a schematic of the experimental set-up for $TiCl_4$ recovery from the slurry. During the operating process, the slurry (25 g each test) was added into a 50 ml stopper flask which was heated by an oil bath. $TiCl_4$ in the slurry was volatilized from the flask and condensed in the forced-water condenser with a vortex tube. The liquid $TiCl_4$ was collected in a calibrated measuring cylinder. After evaporation for the required time, the residue was removed and weighed.

The leaching experiments were conducted in a 300 ml glass flask, which was heated by a water bath. After the required contact time, the suspension was vacuum-filtered. The leach residue was washed with ammonia solution while stirring to remove residual chlorine, then dried and analysed for niobium and other elements.

Experimental fundamentals

From Table I, it can be seen that the slurry was mainly composed of chlorine, titanium, aluminum, and niobium. Most of the titanium in the slurry was in the forms of $TiCl_4$ and TiO_2

(Wang, Xiang, and Wang 2012). During evaporation, $TiCl_4$ was preferentially vaporized from the slurry as its boiling point is lower than that of other chlorides such as $AlCl_3$, $NbCl_5$, and $FeCl_3$ (Dean, 1985; Lide, 1991). During evaporation, complex chemical reactions can take place in the slurry (Den, 2010), expressed as follows:

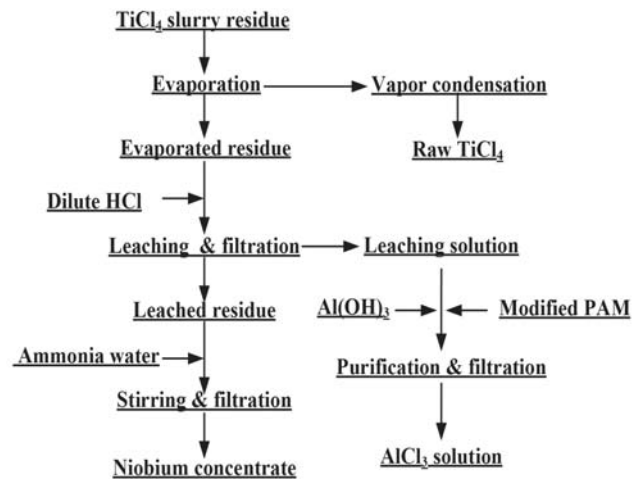


Figure 1—Schematic flow sheet of metal recovery from $TiCl_4$ slurry residue

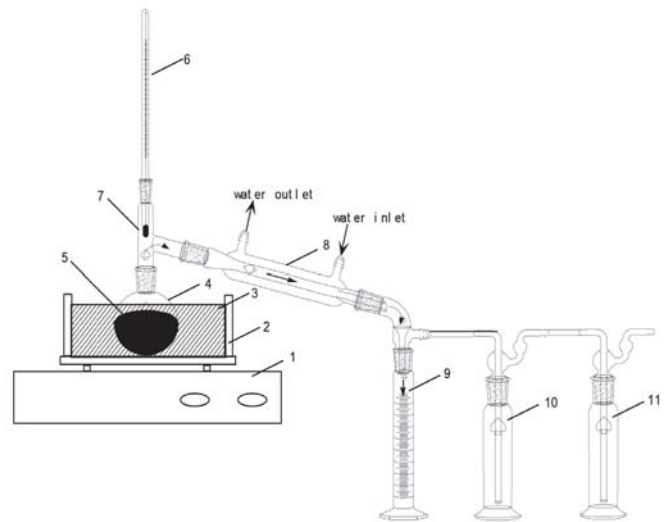


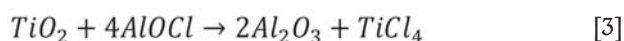
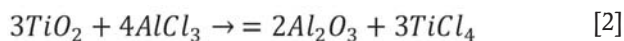
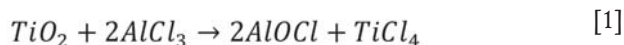
Figure 2—Schematic of the experimental set-up for $TiCl_4$ recovery from $TiCl_4$ slurry residue: (1) shaker, (2) heating tape, (3) oil bath, (4) distillation flask, (5) slurry, (6) heat indicator, (7) still head, (8) condenser, (9) measuring cylinder, (10) filtering flask with dried NaOH, (11) filtering flask with silica gel desiccant

Table I

Composition of the $TiCl_4$ slurry and products (wt%)

Material	O	Al	Cl	Ti	Nb	Fe	Cu	Ta	Zr
$TiCl_4$ slurry	10.36	7.68	61.63	17.41	2.23	0.10	0.33	0.23	0.22
Evaporation residue	41.26	25.93	21.32	0.79	7.71	0.32	1.01	0.79	0.75
Leache residue	49.87	1.59	8.01	1.75	30.49	0.08	0.14	3.18	2.95
Nb concentrate	28.14	2.95	0.82	3.60	53.40	0.14	0.23	5.57	5.18

Metal recovery from TiCl₄ slurry by evaporation and acid leaching



The free energy changes of reactions [1]–[5] at 200°C are listed in Table II. As seen, the reactions can occur when the slurry is heated to 200°C. Although the free energy changes are different, the reactions are not selective as they take place not in solution but in the slurry. Therefore the TiO₂ in the slurry can transform into TiCl₄, which then vaporizes. Hence, by controlling the evaporation temperature, titanium can be effectively separated and recovered from the slurry. Subsequently, aluminum, iron, and copper remaining in the residue can be easily leached with dilute hydrochloric acid, while the niobium, zirconium, and tantalum are insoluble in dilute acid (Dean, 1985; Zhu and Cheng, 2011; Gibalo, 1970). After washing with ammonia solution, chloride remaining in the leached residue is almost completely removed. Therefore, the niobium contained in the slurry can be effectively enriched by using the process shown in Figure 1.

Results and discussion

TiCl₄ slurry evaporation

Effect of evaporation temperature

Figure 3 shows the effect of temperature on the evaporation of titanium, niobium, and aluminium from the slurry over 60 minutes of heating. It was found experimentally that only when the temperature was increased to 145°C could liquid TiCl₄ be observed in the condenser, because the temperature difference between the oil bath and the still head outlet was about 25°C. In order to avoid the evaporation of high-boiling-point chlorides, the test temperature was changed from 150°C to 220°C. As can be seen, the evaporation of titanium increased considerably as the temperature increased from 150 to 164°C, and then increased very slowly in the range of 164–220°C. After evaporation at 164°C for 60 minutes, 3.5% of the titanium remained in the residue, decreasing to 1.5% when the temperature was raised to 200°C. This can be attributed to the reaction between TiO₂ and gaseous AlCl₃, because the sublimation temperature of AlCl₃ is 178°C (Dean, 1985).

Figure 3 shows that the evaporation of titanium reached up to 98.5% at 200°C, while the evaporations of niobium and aluminium were 0.1% and 13.27% respectively. With further increases in temperature, the evaporation of titanium remained

Reaction	[1]	[2]	[3]	[4]	[5]
ΔG	-134.41	-317.58	-48.76	-264.85	-12.69

constant, while the evaporation of niobium and aluminium increased quickly, which might be due to the evaporation of AlCl₃ and NbCl₅. Table III gives the vapour pressures of chlorides at different temperatures (Dean, 1985). As can be seen, the vapour pressure of AlCl₃ and NbCl₅ increases with increasing temperature, and the vapour pressures of AlCl₃ and NbCl₅ are higher than those of TaCl₅ and ZrCl₄ at temperatures below 200°C. However, it is interesting to see that the evaporation of AlCl₃ is lower than expected, which may be due to the inhibitory effect of TiO₂ and Nb₂O₅. Therefore, to separate and recover TiCl₄ from the slurry, the evaporation temperature should not exceed 200°C.

Effect of evaporation time

Figure 4 shows the effect of varying evaporation time from 5 to 40 minutes on the evaporation of titanium at different temperatures. It can be seen that the evaporation of titanium was fast initially, and then gradually slowed as evaporation neared completion. The times needed for evaporation at temperatures 220°C, 200°C, 180°C, and 160°C were 25, 30, 35, and 40 minutes respectively, which indicates that the lower the evaporation temperature and the less the amount of TiCl₄ remaining in the slurry, the more difficult the evaporation of titanium from the residue. From Figures 3 and 4, it can be determined that the recovery of titanium from the slurry should be carried out in the temperature range of 180–200°C for more than 35 minutes.

The residue obtained by evaporating the slurry at 200°C for 60 minutes (see Table I) was used for niobium recovery experiments. As can be seen from Table I, after evaporation, the content of titanium decreased from 17.41 wt% to 0.79 wt% while the contents of aluminium, niobium, zirconium, tantalum,

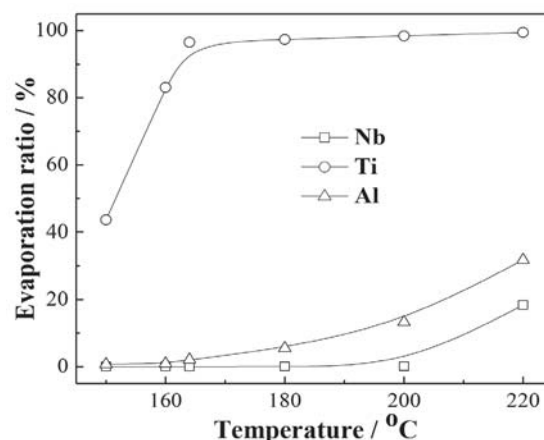


Figure 3—Effect of temperature on titanium evaporation

Temperature (°C)	150	160	180	200	220
AlCl ₃	14.62	31.25	127.33	—	—
NbCl ₅	6.51	9.29	18.02	33.10	57.79
TaCl ₅	6.06	8.81	17.68	33.48	60.19
ZrCl ₄	1.28	1.97	4.41	9.22	18.14

Metal recovery from $TiCl_4$ slurry by evaporation and acid leaching

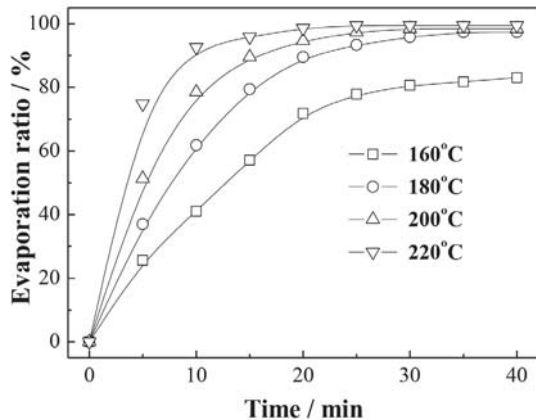


Figure 4—Effect of time on titanium evaporation at different temperatures

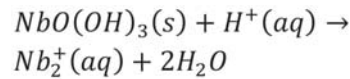
copper, and iron all increased proportionally. Compared with a titanium content of 29.6 wt% in the residue obtained by spray drying with argon at about 250°C (Wang *et al.*, 2012), it can be seen that evaporation in a closed container is an effective method of recovering titanium from the slurry. During the evaporation process, 66.7 wt% of the slurry evaporated to form a yellowish distillate with a $TiCl_4$ content of 97.5%, together with some impurities such as $AlCl_3$, $NbCl_5$, and $FeCl_3$. Therefore, the distillate represents a crude titanium tetrachloride and could be used to produce pigment or titanium sponge after purification (Den, 2010). Figure 5 shows the XRD pattern of the residue from evaporation. As seen from Figure 5 and Table I, the high-boiling-point chlorides and oxides all remained in the residue, indicating that the most appropriate method of separating and recovering titanium from $TiCl_4$ slurry is to evaporate the slurry in a closed container at 200°C for 60 minutes.

Leaching of the evaporation residue

It can be seen from Table I that the metallic elements contained in the evaporation residue can be divided into two types – those that are soluble in dilute hydrochloric acid, which include aluminum, copper, and iron, and those that are insoluble, including niobium, zirconium, and tantalum (Dean, 1985). The content of aluminum in the residue is much higher than that of copper and iron. Therefore, this paper focuses on the separation of aluminum and niobium.

Effect of acid concentration

The effect of acid concentration on the separation of aluminum and niobium was tested at 30°C at a liquid-to-solid ratio of 6:1 mL/g and leaching time of 120 minutes. Figure 6 shows that the acid concentration was an important factor in the separation. The leaching ratio of aluminum increased with increasing acid concentration, with more than 97% of the aluminum being leached when the acid concentration increased to 2.1 mol/L. A further increase in acid concentration had little effect. The remaining aluminum might be occluded by the leach residue. The leaching ratio of niobium was nearly zero at an acid concentration below 1.7 mol/L, and increased quickly at acid concentrations over 2.1 mol/L. This could be attributed to the dissolution of niobium oxides at high acid concentrations (El-Hussaini and Mahdy, 2002), and the possible reaction is given in Equation [6]. Therefore, to separate aluminum from niobium, the preferred hydrochloric acid concentration was determined to be 2.1 mol/L.



[6]

Effect of temperature

The effect of temperature on the leaching of the residue from evaporation is illustrated in Figure 7. The experiments were performed with liquid-to-solid ratio of 6:1 mL/g, and a leaching time of 120 minutes in 2.1 mol/L HCl. As can be seen from Figure 7, the effect of temperature on aluminum leaching was slight, while the effect on niobium leaching was more pronounced. As the temperature was increased from 30°C to 70°C, leaching of niobium decreased slowly, which might be attributed to hydrolysis of niobium in the leaching solution. Only 1.28% of the niobium was leached at 70°C, and further increase of temperature had little effect. Therefore, keeping the leaching temperature over 70°C is propitious for the enrichment of niobium.

Effect of time

Figure 8 shows the results obtained by varying the leaching time from 5 to 120 minutes at 80°C with a liquid-to-solid ratio of 6:1 mL/g in 2.1 mol/L HCl. As can be seen, 95% of the aluminum

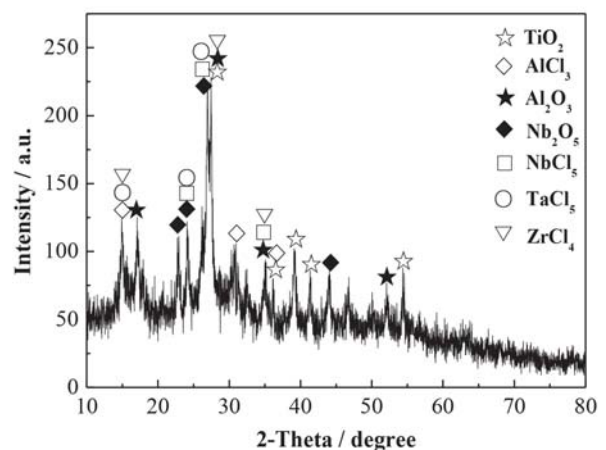


Figure 5—XRD pattern of the residue from evaporation

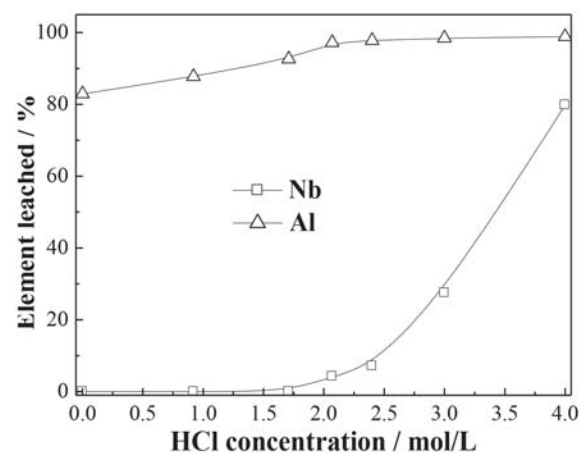


Figure 6—Effect of acid concentration on the leaching of Al and Nb from the evaporation residue

Metal recovery from $TiCl_4$ slurry by evaporation and acid leaching

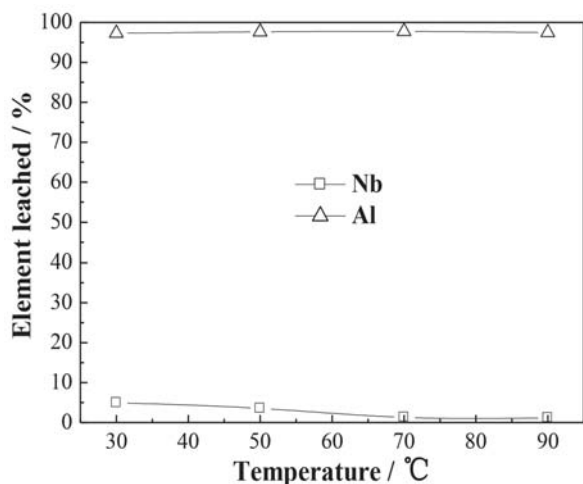


Figure 7—Effect of temperature on the leaching of Al and Nb from the evaporation residue

was leached within 5 minutes, while only 5% of the niobium was leached. During the experiment, it was found that once the residue was added into the hydrochloric acid solution under stirring, the solid became suspended in the solution and the amount decreased appreciably. This indicated that aluminum contained in the evaporation residue dissolved easily in dilute hydrochloric acid. As the leaching time increased, the leaching ratio of aluminum increased slowly, while the leaching ratio of niobium decreased markedly. With a leaching time of 60 minutes, the leaching ratio of aluminum increased to 97.67%, while that of niobium decreased to 1.39%. The leaching ratio of niobium remained almost constant with further increases in leaching time. As aluminum was leached, the acidity of the leaching solution decreased rapidly, which caused the hydrolysis precipitate of niobium to dissolve in the solution. Therefore, a contact time of 60 minutes was selected for the following experiments.

Effect of liquid-to-solid ratio

The effect of liquid-to-solid (L/S) ratio was examined in 2.1 mol/L HCl at 80°C for 60 minutes. The results are presented in Figure 9. As can be seen, the leaching ratio of aluminum increased from 80.16% to 97.73% when the L/S ratio increased from 2:1 to 6:1 mL/g, and then remained constant. However, the leaching ratio of niobium remained almost constant as the L/S ratio increase from 2:1 to 6:1 mL/g. At a L/S ratio over 6:1 mL/g, the leaching ratio of niobium increased markedly. Therefore, a L/S ratio of 6:1 mL/g was considered appropriate in this work.

The compositions of the leached residue and leaching solution are listed in Table I and Table IV respectively, obtained by treating the evaporation residue with a L/S ratio of 6:1 mL/g in 2.1 mol/L HCl at 80°C for 60 minutes. As can be seen, aluminum, iron, and copper were almost completely leached from the evaporation residue, while the leaching of chlorine

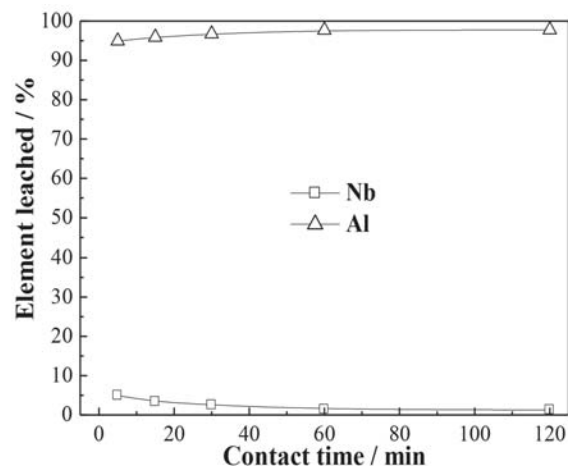


Figure 8—Effect of time on the leaching of Al and Nb from the evaporation residue

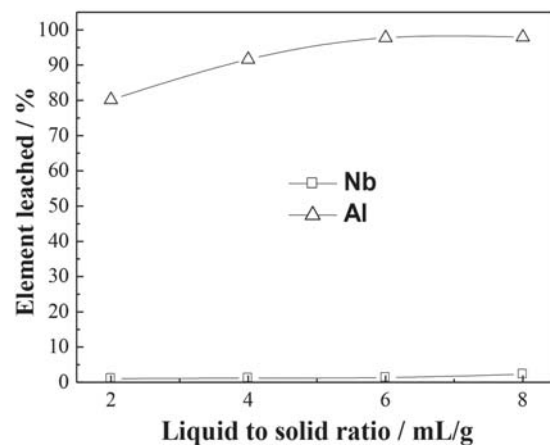


Figure 9—Effect of liquid-to-solid ratio on the leaching of Al and Nb from evaporation residue

was only about 85%. This indicated that the leached residue might contain oxychlorides (Rodrigues and Silva, 2010; Guo and Wang, 2009). In order to remove the residual chlorine, the leached residue was washed with 2 mol/L aqueous ammonia at a L/S ratio of 4:1 mL/g under stirring at room temperature for 30 minutes and then filtered. After drying at 115°C for 24 hours, a niobium concentrate with the composition listed in Table I was obtained. Table I shows that after evaporation of the $TiCl_4$ slurry in a closed container, leaching of the residue with dilute HCl, and washing with dilute ammonia, the niobium, tantalum, and zirconium contents in the slurry were enriched dramatically. Although the content of Nb was 53.40 wt% in the concentrate, which is equivalent to 76.39 wt% of Nb_2O_5 , it was found that the niobium in the concentrate was amorphous. Figure 10 shows the XRD pattern of the niobium concentrate roasted at 600°C for 4 hours. As seen, the Nb_2O_5 changed from amorphous to crystalline

Table IV

Compositions of leaching solution before and after purification

Constituent	Al (g/L)	Ti (mg/L)	Nb (mg/L)	Fe (mg/L)	Cu (mg/L)	Ta (mg/L)	Zr (mg/L)	H ⁺ (mol/L)
Before purification	41.87	588	146	481	1568	116	248	1.39
After purification	53.37	2.7	1.2	3.6	5.3	1.5	1.1	pH=3.6

Metal recovery from TiCl_4 slurry by evaporation and acid leaching

after roasting. It can also be seen from Table I that the Nb_2O_5 plus Ta_2O_5 content can reach up to 83.19wt% in the Nb concentrate. Therefore, this is a high-quality raw material for extracting niobium and tantalum by hydrofluoric acid decomposition and solvent extraction (El-Hussaini, 2001; Gupta and Suri, 1994; Guo and Wang, 2009).

Purification of leaching solution

Table IV shows that the leaching solution contains aluminum, iron, copper, titanium, niobium, zirconium, and tantalum. To recover aluminum, the impurities should be removed from the solution. The pH of the solution was adjusted to 3.5 by adding 36 g of $\text{Al}(\text{OH})_3$ to 1000 mL of leaching solution, which caused Fe, Ti, Zr, Nb, and Ta to precipitate. Subsequently, modified polyacrylamide (PAM) was added to remove Cu and other trace heavy metals before filtration (Li *et al.*, 2010). The composition of the purified solution after filtration is listed in Table IV. The purified solution contained 263.75 g/L AlCl_3 , which can be used as a purifying agent for waste water (Zhao *et al.*, 2009).

Conclusions

Experiments confirmed that the valuable metals in TiCl_4 slurry can be recovered by evaporation and acid leaching. In this process, TiCl_4 , niobium concentrate, and AlCl_3 solution were obtained separately. More than 98% of the titanium was recovered from the slurry by evaporation at 200°C for 60 minutes. The residue was leached with 2.1 mol/L HCl at a L/S ratio of 6:1 at 80°C for 60 minutes, then washed with 2 mol/L aqueous ammonia at a L/S ratio of 4:1 mL/g under stirring at room temperature for 30 minutes. After filtration, a niobium concentrate containing 53.40 wt% Nb and 5.57 wt% Ta was obtained. The leaching solution was purified by adding $\text{Al}(\text{OH})_3$ and modified polyacrylamide, and a solution containing 263.75 g/L AlCl_3 was produced. Future work will focus on testing the performance of the purified leaching solution during wastewater treatment.

Acknowledgements

The authors would like to thank the National Natural Science Foundation of China (No. 51604055 and No. 51674057) and the Chongqing Research Program of Basic Research and Frontier Technology (cstc2016jcyjA0645) for their financial support of this work.

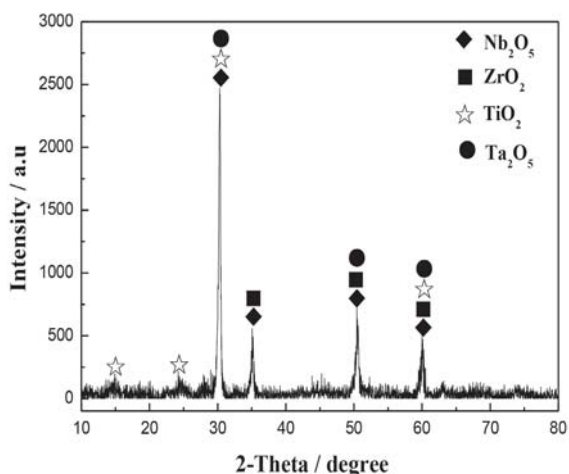


Figure 10—XRD pattern of the roasted niobium concentrate

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