

Characteristics of Nb and Ta in V–Cu Residue from the Purification Process of TiCl_4

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Received: 30 October 2016 / Accepted: 16 October 2017 / Published online: 23 October 2017
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Abstract Titanium tetrachloride is produced through the chlorination of a variety of titanium bearing ores. The chlorination step can produce a variety of metal chloride impurities, such as iron chlorides and vanadium chlorides. The technological process of removal vanadium with copper wires is widely used in China. In the process of removal vanadium, a solid and liquid mixture will be discharged as waste. V–Cu residue is a kind of solid waste filtered from the solid and liquid mixture generated in the purification process. V–Cu residue samples from Zunyi, Guizhou, China, were investigated using X-ray fluorescence spectroscopy, inductively coupled plasma optical emission spectrometry, X-ray diffraction, and scanning electron microscope. The results showed that this waste residue contained Ti (29%), Cu (9.87%), Cl (8.83%), V (5.77%), and an amount of niobium and tantalum. Mainly mineral phases were composed of vanadium niobium oxides, titanium niobium oxides, titanium oxides, and eriochalcite. Ti and V mainly existed in the form of oxides, as dense clumps, and were accompanied by a small amount of Nb. Cu in the V–Cu residue mainly existed in the form of chlorides, adsorbing on the surface of the Ti–V–Nb oxides.

Keywords Niobium and tantalum · V–Cu residue · Characteristics · Enrichment mechanism · Titanium

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Introduction

Titanium tetrachloride is generally produced by the reaction of chlorine with an intimate mixture of a titanium-bearing ore (or titanium compounds) and carbonaceous material [1]. Chlorination of titanium-bearing ores to yield crude titanium tetrachloride can produce many impurities, such as FeCl_3 , AlCl_3 , SiCl_4 , VOCl_3 etc. which are present in the crude TiCl_4 [2, 3]. The purification of TiCl_4 has been an on-going development effort more than 60 years [4]. Generally, crude titanium tetrachloride needs to be refined by physical and chemical methods, before the Kroll's magnesium reduction of refined titanium tetrachloride which has been widely utilized as an important intermediate in titanium sponge industry [5, 6]. Many of the low boiling point impurities, SiCl_4 , Cl_2 and HCl , and the high boiling point impurities, FeCl_3 and AlCl_3 , can be removed or separated by distillation. Vanadium removal is also essential. However, vanadium dissolves in crude TiCl_4 mainly as VOCl_3 and has a normal boiling point temperature of 400 K, only 9 °C below that of the titanium tetrachloride [7]. VOCl_3 can only be removed by chemical methods because its boiling point is very close to that of TiCl_4 [4, 8]. For removing vanadium, several reagents have been proposed [7, 9], such as hydrogen sulfide [4], organic matter, aluminum powder, copper powder and mineral oil. In China, reducing agent of copper wires is widely used to remove VOCl_3 from crude TiCl_4 because of lack of high grade copper powder [3, 10].

The technological process of removal vanadium with copper wires is simple, with good effect, and can separate other impurities [10], but the copper wires become invalid easily because reaction product can gradually accumulate on the wires surface and hinder the reaction [11]. Therefore, the copper wires must be periodically washed with water and hydrochloric acid. In the washing process, a solid and liquid

mixture will be discharged as waste. The solid waste separated from the mixture is derived from hydrolysis product of TiCl_4 and impurities, which is called V–Cu residue in this study, while liquid waste is rich in Cu, V, Ti and Cl, called V–Cu waste liquor.

A new clean method to recover both copper and vanadium from the copper–vanadium precipitate had been reported by Wang et al. [9], and then an integrated process for vanadium recovery from the precipitate was designed [11]. It is also investigated that the V–Cu residue contains a certain amount of niobium and tantalum, and it can be considered as a new type of resource because the contents of Nb and Ta in the waste are much higher than their industrial grades [12]. Niobium and tantalum are associated with the crude ore, and enrich in the crude titanium tetrachloride by the processing of chlorination. Ultimately, they enrich in the V–Cu residue after the process of purification of crude titanium tetrachloride. However, characteristics, occurrences and enrichment mechanism of Nb and Ta in the V–Cu residue have not been reported.

The aim of this work was to study the chemical composition, mineralogy, and micro texture of the V–Cu residue and to evaluate potentially value for recovering niobium and tantalum in the residue in future. The enrichment mechanism of Nb and Ta in the V–Cu residue will be also discussed.

Materials and Methods

Materials

The solid and liquid mixture sample used in this study was blue slurry, which was collected from Zunyi Titanium Industry Co. Ltd. The slurry was filtered to obtain white solid residue (V–Cu residue) and blue supernatant after being separated by centrifugal machine. The supernatant was acid with pH 0.5–2.0 [12], and it had been reported to recover V, Cu and Ti from the supernatant liquid [13–15]. After drying, the acidic V–Cu residue turned to be green. The homogeneous residue had to be ground and milled to a smaller size before characterization and examinations.

Analytical Methods

Several analytical methods were used to evaluate the V–Cu residue content to produce representative results. These methods included X-ray fluorescence spectroscopy (XRF), inductively coupled plasma optical emission spectrometry

(ICP-OES), and combustion and infrared identifications for total C and S amounts (C/S analyzer by LECO). The Volhard method was used for determination of chloride in the sample. Fluorine content in the sample was determined by ion selective electrode analysis method. The above-mentioned chemical composition were analyzed in ALS Laboratory Group—an Australian analytical lab in Guangzhou, China.

The X-ray diffraction analysis (XRD) was performed with a pulverized sample of the precipitate on a diffractometer (D/Max2200, Japan) with Cu $K\alpha$ radiation at State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences. The phase identification and content calculation were carried out with software JADE 6.

A scanning electron microscope JSM-6460LV equipped with an energy dispersion X-ray spectrometry system (EDS) was used to evaluate the composition and the texture of the residue particles at State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences.

Results and Discussion

Chemical Composition

Table 1 presents the major constituents of the V–Cu residue analyzed by XRF. The data showed that TiO_2 made up half of the chemical composition, indicative that Ti occurred as a high content composition in the V–Cu residue after the process of purification and washing process. Except Ti, V and Cu (determined by ICP-OES), the content of niobium (2.23 wt%) in the V–Cu residue was higher than other metals, such as Al, Fe, Si, Zr etc. Due to the limitations of XRF analysis and the particularity of the residue sample, unlike the geological samples, some metal oxides were not presented such as copper. ICP-OES analysis was employed for some minor or trace metals in the V–Cu residue sample (Table 2). The results of Ti, Nb, and Fe from ICP-OES are in agreement with those from XRF. From the ICP-OES analysis, the primary metal constituents of the V–Cu residue were Ti, Cu, V, Nb and Ta, of which the content accounted for nearly 50% of the weight. Approximately, Ta in the residue was one-tenth of Nb from Table 2. However, the abundance of niobium and tantalum in the earth's crust is near 20 and 2 $\mu\text{g/g}$ respectively [16]. The weathered crust Nb–Ta deposits in China were required to $(\text{Nb, Ta})_2\text{O}_5$ no less than 160–200 $\mu\text{g/g}$

Table 1 Main chemical composition of the V–Cu residue analyzed by XRF (wt%)

Element	TiO_2	V_2O_5	Nb_2O_5	Al_2O_3	Fe_2O_3	ZrO_2	SiO_2	CaO	MgO	MnO	P_2O_5	Cr_2O_3
Content	50.7	>5.0	3.47	1.09	0.50	0.26	0.12	0.09	0.03	0.01	0.03	<0.01

Table 2 Element composition of the V–Cu residue analyzed by ICP-OES (wt%)

Element	Ti	Cu	V	Nb	Ta	Fe	Ni	Pb	Sn
Content	29	9.87	5.77	2.23	0.23	0.3	0.01	0.01	0.01
Element	Mo	P	Mn	Zn	W	Cr	As	Sb	Co
Content	0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.005

Table 3 Non-metallic element composition of the V–Cu residue (wt%)

Element	Content	Method
Cl	8.83	ME-IR08, Volhard method
S	0.32	ME-IR08, C/S analyzer
C	0.12	CI-ELE81, C/S analyzer
F	0.009	F-ELE82, ion selective electrode analysis method

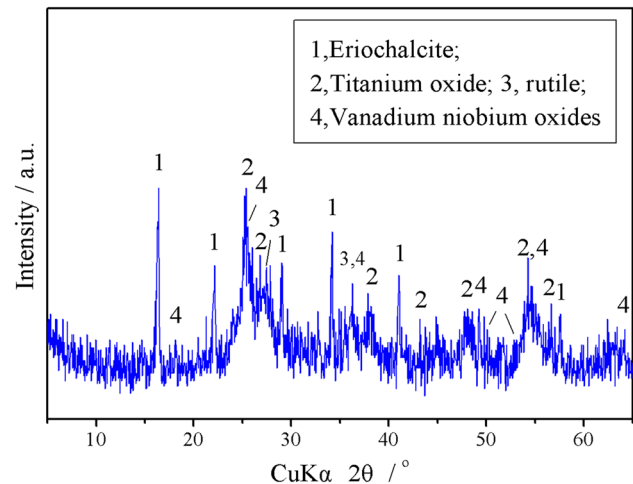
according to China Industry Standard. Both Nb and Ta are of great potential interest as for rare metal resource to recovery.

Table 3 presents the non-metallic element composition of the V–Cu residue and the analytical methods. Chlorine was the highest non-metallic element with a content of 8.83%, which was from the TiCl_4 and impurities and washing process of copper wires with hydrochloric acid. The total concentration of S, C, and F was lower than 0.5%.

Although the resources of niobium–tantalum ores are abundant in China, most of which are low-grade and difficult to decompose by hydrofluoric acid [17, 18]. It had been proved that Nb and Ta could be recovered from a tin-slag [19, 20]. Therefore, Nb and Ta in V–Cu residue should be considered to be extracted as potential resources when V, Cu are withdrawn for utilization.

X-ray Diffraction Analysis

The diffraction pattern of the V–Cu residue sample is shown in Fig. 1 and reveals a complicated mineral composition due to the hydrolysis reaction, which might take place during a rapid period. This diffraction pattern indicated that the residue was mainly consisted of vanadium niobium oxides ($\text{V}_2\text{Nb}_6\text{O}_{19}$, PDF: 33-1438), titanium oxides (Ti_3O_5 , PDF: 11-0217; TiO_2 , PDF: 11-1276), and eriochalcite ($\text{CuCl}_2 \cdot (\text{H}_2\text{O})_2$, PDF: 74-1052). The XRD of V–Cu residue sample presented complicated peaks, which may include other minor phases. The mineralogical phases identified using XRD correspond well with the chemical analysis of V–Cu residue.

**Fig. 1** X-ray diffraction pattern for the V–Cu residue

Morphological Characteristics

The backscattering scanning electron microscope images of the V–Cu residue particles with different magnification times are presented in Fig. 2. These images showed two different regions with different gray tonalities in the sample: gray regions and white spots or particles. The gray regions were dense, and with large blocky structures, while the spots were particulate matter, embedded in the large blocky structures or adhering on the surface of these gray regions.

The SEM-EDS results are consistent with the XRD analysis and the elemental distributions analysis. The white particulate matter was eriochalcite (see the EDS spectrum in Fig. 2c), and the gray regions were vanadium niobium oxides and titanium niobium oxides (see the EDS spectrum in Fig. 2c).

Figure 3 presents the backscattering scanning electron microscope images (a) and elemental distributions of Ti (b), V (c), Nb (d), Cu (e) and Cl (f) of the V–Cu residue particles. Distribution of tantalum was not operated because of its low concentration. The distributions of Ti, V and Nb were almost identical with the gray regions which were with compact structure, meanwhile, the distributions of Cu and Cl fitted well with the white spots and particles.

Overall, Ti and V mainly exist in the form of oxides, as dense clumps, which are accompanied by a small amount

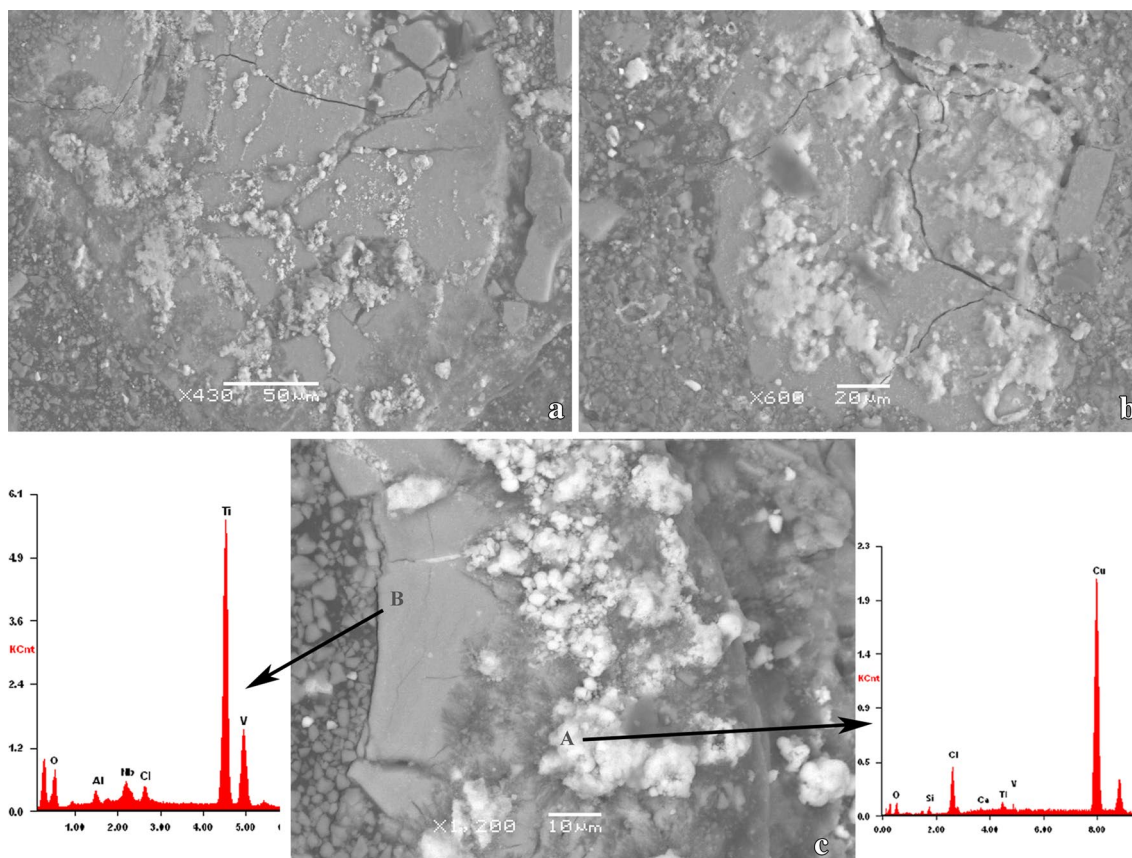


Fig. 2 Backscattering scanning electron microscope image of the V–Cu residue particles in different magnification times

of Nb. Cu in the V–Cu residue mainly exists in the form of chlorides, adsorbing on the surface of the Ti–V–Nb oxides.

Enrichment Mechanism of Nb and Ta

As mentioned earlier, Ti-bearing ore is associated with niobium and tantalum, most of which transferred into V–Cu residue with vanadium ultimately after the process of chlorination and purification of TiCl_4 . In the chloride process, TiO_2 and impurities were converted into their respective chlorides as follows [4, 21]:



Chloride slag, dust and fumes are produced in the chloride process; meanwhile the low boiling point impurities are as exhaust gas emission. Purification of TiCl_4 is made up of two steps, physical separation for removing Fe, Al etc. and chemical processing for removing V by reducing with copper (in Fig. 4). To remove most of these impurities in the physical separation step is based on condensation and distillation. Reducing the temperature from the

chlorination conditions solidifies many of the metal chlorides, as TiCl_4 is a liquid at room temperature and most metal chlorides are solids [4].

Vanadium has been mainly chloridized as VOCl_3 before the step of purification of TiCl_4 . When the VOCl_3 vapor contacts with copper wires, it is reduced to VOCl_2 as follows:

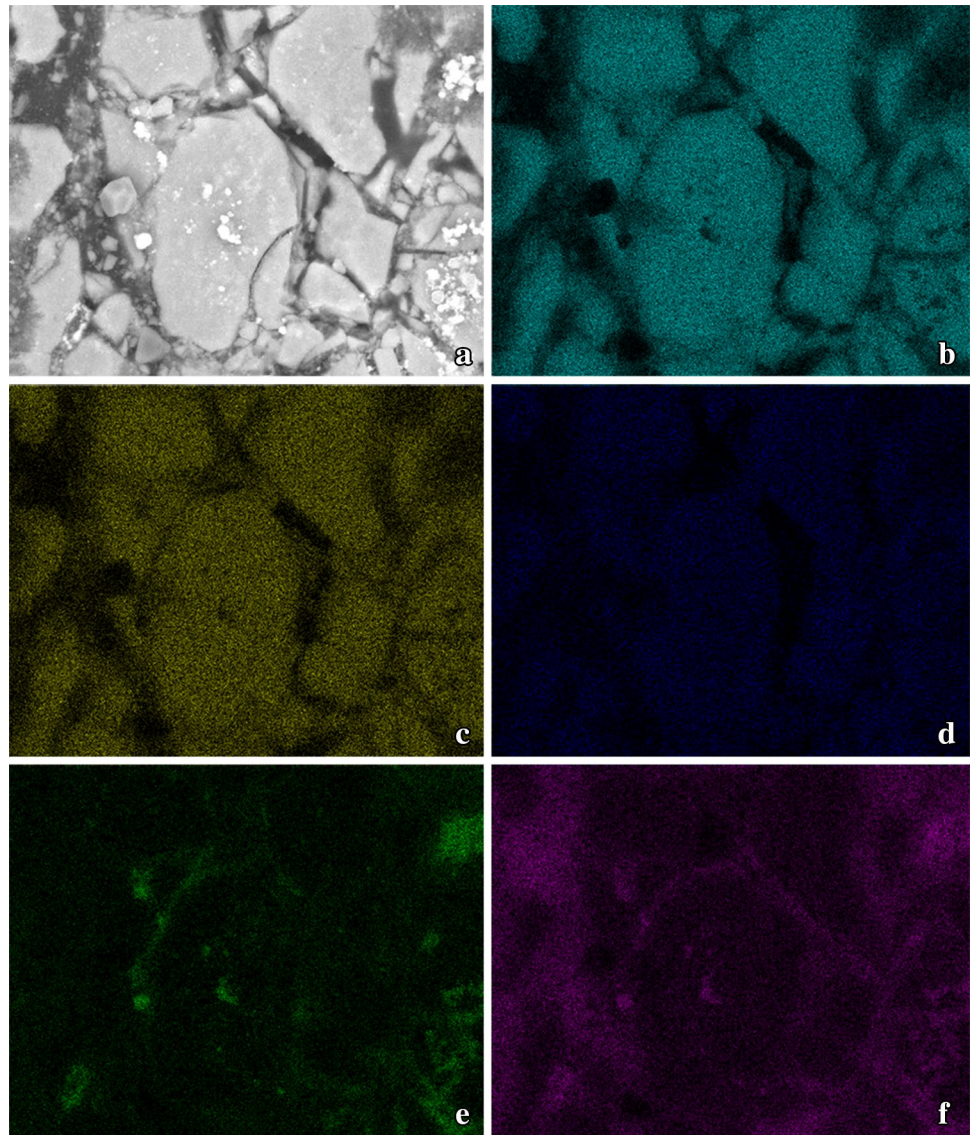


In the reduction process, the reaction product VOCl_2 and CuCl can gradually accumulate on the wires surface and hinder the reaction of VOCl_3 vapor with the copper wires. Therefore, the copper wires had to be periodically washed with water and hydrochloric acid for reutilization. In the washing process, the Cu^+ disproportionates into Cu and Cu^{2+} , the TiCl_4 hydrolyzes into TiO_2 and HCl, and the VOCl_2 dissolves into water [11].

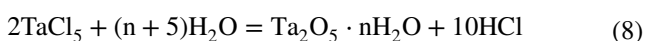
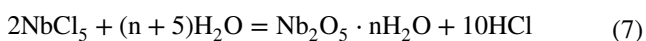
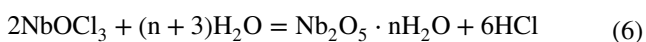


Vanadium, niobium and tantalum are members of the fifth group of the periodic table. The chemistry of the three

Fig. 3 Backscattering scanning electron microscope image (a) and elemental distributions of Ti (b), V (c), Nb (d), Cu (e), Cl (f) of the V–Cu residue particles



elements is very close, especially the second and third members. In the process of chlorination, niobium and tantalum should be mainly generated as the form of NbOCl_3 , NbCl_5 , TaCl_5 , and other chlorides or oxychlorides. VOCl_3 is reduced to VOCl_2 in the reduction process, whilst niobium, tantalum chlorides and oxychlorides do not react. In the washing process, NbOCl_3 , NbCl_5 and TaCl_5 can continuously hydrolyze with water as follow [10]:

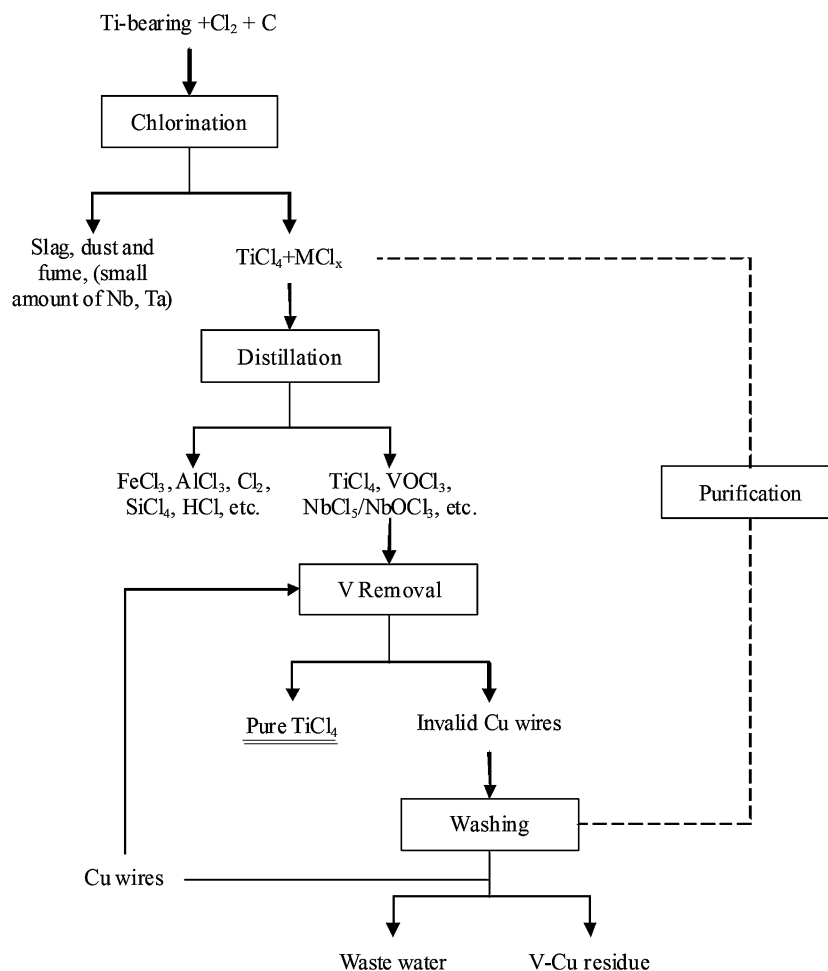


Conclusions

The chemical analyses reveal that the main constituents of the V–Cu residue are Ti (29 wt%), Cu (9.87 wt%), Cl (8.83 wt%), V (5.77 wt%), and an amount of 2.23 wt% of Nb and 0.23 wt% of Ta. The mineralogical analyses indicate that the residue is mainly composed of vanadium niobium oxides, titanium niobium oxides, titanium oxides, and eriochalcite. Ti, V and Nb mainly occur as the form of oxides, as dense clumps with compact structure. Cu in the V–Cu residue mainly exists in the form of chlorides, adsorbing on the surface of the Ti oxides.

Niobium and tantalum are chloridized firstly, and then dissolve in TiCl_4 together with vanadium, and eventually hydrolyze with water as oxides in the process of removal vanadium. The concentration of Nb and Ta in V–Cu

Fig. 4 Diagram of separation stages for TiCl_4 purification



residue is considerable, and it should be of potential interest when V and Cu are withdrawn as resources.

Acknowledgements The work is financially supported by the National Natural Science Foundation of China (Grant No. 41402039), Guizhou Provincial Science and Technology Foundation ([2016]1155) and Doctoral Program Foundation of Guizhou Normal University.

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