RESEARCH PAPER

STUDIES THE CRUCIAL ROLE OF SELECTION OF EXTRACTANT TO EXTRACT NIOBIUM FROM SULFURYL FLUORIDE SOLUTION AND OPTIMIZATION OF EXTRACTION CONDITIONS

Azamat Yessengaziyev*[1], Arailym Mukangaliyeva[1], Azamat Toishybek[1], Zaure Karshyga[1], Nurgaly Abdyldayev[1], Albina Yersaiynova[1], Nauryzbek Bakhytuly[1]

[1] Institute of Metallurgy and Ore Beneficiation, Satbayev University, Almaty, Kazakhstan

*Corresponding author: a.yessengaziyev@satbayev.university, Institute of Metallurgy and Ore Beneficiation, Satbayev University, Shevchenko str. 29/133, 050010 Almaty, Kazakhstan

ABSTRACT

The increasing demand for rare refractory metals such as niobium in high-tech industries requires the development of efficient and sustainable methods to extract them from secondary sources, including industrial by-products. This study studied niobium extraction from a fluoride-sulfuric acid solution obtained by leaching a niobium-containing intermediate product. A comprehensive assessment of various organic extractants, including methyl isobutyl ketone, tributyl phosphate, trioctylamine, and Cyanex 923, was performed, focusing on the recoverability of niobium from this solution. Experimental results show that Cyanex 923 is significantly superior to other extractants in efficacy. The extraction of niobium at different concentrations of this extractant in toluene and the ratios of organic and aqueous phases were studied. It is established that an increase in the contact time of the phases does not contribute to additional niobium recovery. Studies show that applying concentrated Cyanex 923 in toluene ensures complete recovery of niobium into the organic phase. The three-stage counter-current extraction shows a slightly higher niobium recovery efficiency than the single-stage process.

Keywords: niobium, solution; extraction; extractant; Cyanex 923.

INTRODUCTION

Rare refractory metals play an important role in modern industry due to their unique physical and chemical properties. These metals have a high melting point, excellent corrosion resistance, and mechanical strength, making them indispensable in such applications as aerospace, nuclear power, and the production of high-tech alloys. The high rates of development of these branches of technology determine the constantly growing demand for rare metals, which provides for further expansion of their production [1, 2]. The use of titanium-magnesium production wastes abundant in rare metals can contribute to the solution of this problem [3-5]. Niobium and zirconium are often companions of titanium. Therefore, it is found in titanium concentrates obtained from the ores of ilmenite deposits. Most of the niobium and zirconium fall and are concentrated in production waste at Ust-Kamenogorsk Titanium-Magnesium Plant JSC (UK TMP JSC) during the processing of titanium-containing raw materials. For example, the content of rare refractory metals is comparable to industrial concentrations in ores in the sublimations of dust chambers of titanium chlorinators. This waste is not recycled and accumulates in dumps, which creates environmental problems. Recycling dust chamber sublimations can bring significant economic benefits and improve the ecological situation around the plant.

The hydrometallurgical method is used to process niobium-containing raw materials, including the extraction and concentration of niobium. Niobium is resistant to the action of many acids and

salt solutions. It is practically unaffected by orthophosphoric, dilute sulfuric, or nitric acids. Only concentrated hydrochloric, sulfuric, and hydrofluoric acid solutions and their mixtures can be effectively used as reagents [6,7]. When the raw materials are treated with acids, niobium is extracted from the resulting solution by liquid extraction using organic extractants [8].

Solvent extraction is a widely used industrial method for separating and purifying niobium and tantalum from the leach liquors of these minerals. This process employs a variety of extractants, including ketones, alkyl-phosphorus esters, N-oxides, sulphoxides, and acidic alkyl-phosphorus extractants [9]. A few review papers are on recovering niobium and tantalum from their minerals by hydrometallurgy processes, including leaching followed by solvent extraction/precipitation [10,11].

The article [12] discusses the optimisation of niobium and tantalum extraction processes from minerals using trioctylamine as an extractant. The authors apply the Taguchi method to optimise such extraction parameters as the ratio of organic to aqueous phases, extractant concentration and temperature, which can achieve high niobium purity of up to 98.88% and significantly improve the efficiency of the process. Experiments show that TOA is an effective extractant for separating niobium and tantalum even at low concentrations of hydrofluoric acid, reducing environmental and operational risks. This paper demonstrates significant advances in the recovery and separation of these metals, making the process more suitable for industrial applications due to the increased efficiency and purity.

This study [13] presents a method for the solvent extraction of niobium using Aliquat 336S in xylene from ascorbic acid solutions within a pH range of 3.5-6.5. The extraction process involves stripping niobium from the organic phase with nitric acid. The results show that this method effectively separates niobium from metals like tantalum, vanadium, titanium, zirconium, thorium, and chromium, highlighting its capability to isolate niobium even in these interfering elements.

This review [14] comprehensively examines solvent extraction technologies for separating and purifying niobium and tantalum, focusing on extractants such as methyl isobutyl ketone, tri-butyl phosphate, cyclohexanone, and octanol-2. The study highlights MIBK dominance due to its advantageous physical properties, enabling high-purity extraction. Additionally, the review underscores the potential of using tertiary amines in fluoride-free solutions, emphasising the environmental benefits and urging further research into fluoride-free extraction systems.

The paper [15] discusses solvent extraction of high-purity tantalum and niobium compounds from fluoridesulphuric acid solutions resulting from the acidic decomposition of plumbomicrolite concentrate, proposing a flowsheet for sequential selective extraction of target components. The extraction of Ta was studied using triisoamylphosphate and octanol-1. The latter has proved to be effective for extracting both Ta and Nb. The optimal regimes for all extraction stages have been selected to provide high-quality target products (Ta_2O_5, K_2TaF_7, Nb_2O_5).

Analysis of scientific and technical literature shows that acid methods are most often used for the decomposition of rare-metal raw materials with the subsequent extraction of target components using extraction. Most research focuses on standard sources of rare metal raw materials, while little research is done to recover niobium and zirconium from titanium waste. A solution containing niobium, zirconium, and titanium was obtained from our research on two-stage leaching of dust chamber sublimations [16]. In this work, this fluoride-sulfuric acid solution is extracted to extract niobium and to study the behaviour of other components in the extraction process.

MATERIAL AND METHODS

A fluoride-sulfuric acid solution was obtained by leaching a previously obtained niobium-containing intermediate product for the extraction treatment. The composition of this extraction solution was as follows: g/l: 36.01 Ti_2O, 28.76 Al_2O_3, 21.27 Nb_2O_5, 17.24 Fe_2O_3, 13.19 ZrO_2, 503.81 H_2SO_4, 214.00 HF. Materials: Tributyl phosphate for extraction analysis, ≥99.0%); methyl isobutyl ketone MIBK (4-Methyl-2-pentanone, ACS reagent, ≥98.5%); Trialkyl phosphine oxides mixture (Cyanex 923) trioctylamine (trioctylamine ≥98.0%); kerosene (purified pure); toluene (toluene, ACS reagent, ≥99.7%). Equipment: Velp Scientifica DLS mixing device (Italy); LOIP LS-120 shaker (Russia); Laboratory glassware made of fluoroplastic and polypropylene.

A study of the IR spectra of extractants (**Fig. 1**) containing methyl isobutyl ketone, tributyl phosphate, and Cyanex 923 showed that the spectral characteristics were consistent with the expected compounds, as confirmed by the analysis of electronic databases.

Experimental procedure. Extraction was performed in polypropylene separation funnels where the organic phase and acid solution were placed. After the organic and aqueous phases were placed in the separation funnel, it was closed with a cork and shaken vigorously for 5 minutes. The tap was opened during this process several times to release the resulting vapours of volatile components. Then, the emulsion was left to stratify into two layers. It took at least 5 minutes. During separation, the lower organic layer was drained through the tap, and the upper water layer was drained through the upper opening of the separation

funnel. The studies were carried out at different ratios of the volumes of organic and aqueous phases of $V_o:V_{aq}$ at room temperature.
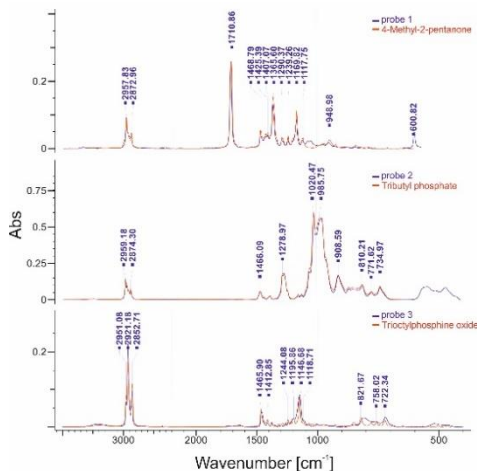

Fig. 1 Infrared spectrum of extractant samples

The distribution coefficient D was used as a characteristic of the extraction equilibrium:

$$D = \frac{C_{org}}{C_{aq}} \qquad (1.)$$

where C_{org} is the concentration of the substance in the organic phase, C_{aq} is the concentration in the aqueous phase. Two crucial technological characteristics of the process were directly related to the distribution coefficient. The first of these was recovery at a single extraction stage E:

$$E = \frac{D \cdot V_{org}}{V_{aq} + D \cdot V_{org}} \times 100\% \qquad (2.)$$

where V_{org} is the volume of the organic phase, V_{aq} is the volume of the aqueous phase.

The second characteristic was the β separation coefficient that was equal to the ratio of the distribution coefficients of the two elements:

$$\beta = \frac{D_A}{D_B} \qquad (3.)$$

where D_A and D_B are the distribution coefficients of substances A and B, respectively. The β value can be used to judge the efficiency of extraction used to separate this pair of elements.

Analysis methods. The content of niobium and other solution components was determined with the Optima 2000 DV inductively coupled plasma optical emission spectrometer (Perkin Elmer, USA). The spectra were obtained using the FT/IR-6X spectrometer in the 4000-400 cm^{-1} spectral range on the ATR PRO ONE X console. The spectra were analysed using unique literature and IR spectral databases for the KnowItAll software.

RESULTS AND DISCUSSION

Selection of organic extractant for niobium recovery from acid-leaching solutions

Neutral extractants play an important role in various stages of extraction processes, such as extraction, extraction purification,

and concentration, due to their chemical and physical properties. MIBK, which belongs to the category of neutral extractants, is in demand in the industry because of its characteristics. It is a highly volatile, colorless liquid with a pungent odour similar to acetone and belongs to the ketone class [17]. MIBK is well soluble in kerosene, forming a homogeneous mixture. It facilitates the extraction process, ensuring the extractant is evenly distributed throughout the solution.

The extraction of niobium from a fluoride-sulfuric acid solution can be different and depends on the presence of the fluorooniobate ion and its chemical activity in the system. It is known that at higher concentrations of HF (>35%) they are converted to non-hydrolyzed forms of NbF_6^-, $HNbF_6^-$ in accordance with the equations: $HNbOF_5^- + HF \rightarrow NbF_6^- + H_2O$ and $NbOF_5^{2-} + HF + 2H_3O^+ \rightarrow HNbF_6 + 3H_2O$. NbF_7^- and H_2NbF_7 are also formed [18].
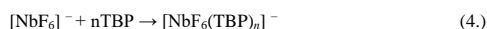
The distribution of components during extraction using 20% MIBK in kerosene is presented in **Table 1**.

Table 1 Distribution of components during extraction with a solution of MIBK in kerosene.

$V_o:V_{aq}$	Content in the phases, g/l						Degree of extraction into organic phase, %			Distribution coefficient, D			Separation coefficient, β	
	Nb_2O_5		ZrO_2		TiO_2		Nb_2O_5	ZrO_2	TiO_2	Nb_2O_5	ZrO_2	TiO_2	Nb_2O_5/ZrO_2	Nb_2O_5/TiO_2
	C_o	C_a	C_o	C_a	C_o	C_a								
2:1	0.61	20.07	0.74	11.69	2.26	31.48	5.73	11.30	12.56	0.03	0.06	0.07	0.48	0.43
1:1	0.06	21.23	0.67	12.52	4.50	31.50	0.28	5.07	12.51	0.003	0.05	0.14	0.06	0.02
1:2	0.06	21.26	1.70	12.34	9.01	31.50	0.13	6.43	12.51	0.003	0.14	0.29	0.03	0.01
1:4	0.11	21.26	0.11	13.16	18.02	31.50	0.13	0.20	12.51	0.01	0.01	0.57	0.71	0.01

During experiments conducted using MIBK, the extraction of niobium, zirconium, and titanium into an extract in one stage was very low over the entire range of ratios of the volume of organic and aqueous phases. MIBK showed low efficacy as an extracting agent.

The use of TBP for the extraction of rare metals from acidic solutions is a standard method in the chemical industry. TBP has a high selectivity for rare metals, making it possible to efficiently recover target metals even in the presence of other solution components. A simplified process for extraction of niobium from the test solution using TBP can be represented as follows:

$$[NbF_6]^- + nTBP \rightarrow [NbF_6(TBP)_n]^- \qquad (4.)$$

Similar reactions occur for $[HNbF_6]^-$, $[HNbF_7]^{2-}$ and $[H_2NbF_7]^-$, with TBP forming solvated complexes with these ions [19].

Table 2 presents experimental data on the distribution of components during the extraction of tributyl phosphate from fluoride-sulfuric acid solutions. The studies used 20% of TBP in kerosene

Table 2 Distribution of components during extraction with a solution of TBP in kerosene

$V_o:V_{aq}$	Content in the phases, g/l						Degree of extraction into organic phase, %			Distribution coefficient, D			Separation coefficient, β	
	Nb_2O_5		ZrO_2		TiO_2		Nb_2O_5	ZrO_2	TiO_2	Nb_2O_5	ZrO_2	TiO_2	Nb_2O_5/ZrO_2	Nb_2O_5/TiO_2
	C_o	C_a	C_o	C_a	C_o	C_a								
2:1	4.60	12.09	1.46	10.26	2.25	31.50	43.23	22.19	12.51	0.38	0.14	0.07	2.66	5.32
1:1	4.49	16.80	1.44	11.74	3.50	32.50	21.10	10.92	9.73	0.27	0.12	0.11	2.18	2.48
1:2	4.46	19.06	1.36	12.51	5.67	33.17	10.48	5.14	7.88	0.23	0.11	0.17	2.16	1.37
1:4	0.06	21.27	0.24	13.12	9.01	33.75	0.07	0.46	6.26	0.003	0.02	0.27	0.15	0.01

It can be seen from the data presented in **Table 2** that the degree of niobium recovery into the extract in one stage is 43.23% with the ratio $V_o:V_{aq} = 2:1$. For zirconium and titanium, extractions over the entire range of $V_o:V_{aq}$ ratios ranged from 0.46% to 22.19% and from 6.26% to 12.51%, respectively.

Cyanex 923 was used for further extraction assessment. It is a mixture of trialkyl phosphine oxides. Cyanex 923 can also be used as an extractant to extract metals from solutions, as they form complexes with metals and can efficiently extract and separate metals [20]. This extractant is distinguished by the fact that it contains the most electronegative substituent bound to the central atom, unlike TBP molecules. The most electronegative substituents are F –, Cl –, RO –. Their replacement with less electronophilic ones, for example, alkyl ones, increases the electron density on the active atom and, as a result, the extraction ability [21]. It is for this reason that the extraction capacity from trialkyl phosphates to trialkyl phosphoxides increases (**Fig. 2**):
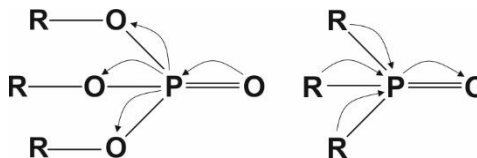

Fig. 2 Effect of substituents on the extraction capacity of trialkyl phosphates and trialkyl phosphoxides

Initial studies show that Cyanex 923's solubility in toluene is much better than in kerosene, which led to the choice of toluene as the diluent for these experiments. **Table 3** shows the distribution of the components during the extraction process using a solution containing 20% Cyanex 923 in toluene.

Table 3 Distribution of components during extraction with Cyanex 923 solution in toluene.

$V_o:V_{aq}$	Content in the phases, g/l						Degree of extraction into organic phase, %			Distribution coefficient, D			Separation coefficient, β	
	Nb_2O_5		ZrO_2		TiO_2		Nb_2O_5	ZrO_2	TiO_2	Nb_2O_5	ZrO_2	TiO_2	Nb_2O_5/ZrO_2	Nb_2O_5/TiO_2
	C_o	C_a	C_o	C_a	C_o	C_a								
2:1	10.51	0.27	3.23	6.73	12.76	10.49	98.75	49.01	70.85	39.52	0.48	1.22	82.24	32.51
1:1	17.39	3.90	1.86	11.33	13.01	22.99	81.67	14.07	36.14	4.46	0.16	0.57	27.21	7.87
1:2	23.09	9.75	1.35	12.52	4.50	33.75	54.21	5.10	6.26	2.37	0.11	0.13	22.03	17.74
1:4	25.26	14.98	2.66	12.52	4.67	34.84	29.65	5.04	3.24	1.69	0.21	0.13	7.94	12.57

The degree of niobium recovery in one stage was very high with a volume ratio of $V_o:V_{aq} = 2:1$, and is 98.75%. At the same time, the extraction of zirconium was 49.01%, and titanium - 70.85%. The data obtained demonstrate a fairly high cumulative extractability of all the components under consideration using Cyanex 923 in toluene. In this regard, it seems difficult to perform selective extraction of niobium under maximum saturation of the extractant. As the volume of the aqueous phase increases, the metal separation coefficients decrease which is particularly noticeable in the case of βNb/Zr.

The following extractant was used to extract - trioctylamine, an organic compound known as N,N,N-trioctylamine. TOA is capable to form stable complexes with many rare metals, such rare earth elements as thorium, uranium, chromium, etc. [22]. The solubility of anion exchange extractants in aliphatic diluents (kerosene) is often insufficient. There is a stratification of the organic phase into two ones: a light nonpolar phase that is a diluent with a small concentration of the extraction product and a heavy and viscous polar phase that is an extraction product with a small amount of diluent in several other systems during the extraction process. The stratification of the organic phase, or the appearance of the so-called third phase, leads to disruption of the operation of extraction equipment, and production conditions are generally unacceptable. Therefore, these experiments also used an aromatic hydrocarbon - toluene - as a diluent. **Table 4** shows the distribution of components during extraction with a solution of 20% TOA in toluene.

Table 4 Distribution of components during extraction with TOA solution in toluene.

$V_o:V_{aq}$	Content in the phases, g/l						Degree of extraction into organic phase, %			Distribution coefficient, D			Separation coefficient, β	
	Nb_2O_5		ZrO_2		TiO_2		Nb_2O_5	ZrO_2	TiO_2	Nb_2O_5	ZrO_2	TiO_2	Nb_2O_5/ZrO_2	Nb_2O_5/TiO_2
	C_o	C_a	C_o	C_a	C_o	C_a								
2:1	9.23	2.83	0.65	11.89	4.25	27.50	86.83	9.88	23.63	3.27	0.05	0.15	59.57	21.11
1:1	13.36	7.93	1.11	12.08	2.25	33.75	62.83	8.43	6.26	1.69	0.09	0.07	18.31	25.25
1:2	13.03	14.78	2.47	11.96	3.67	34.17	30.63	9.35	5.10	0.88	0.21	0.11	4.27	8.21
1:4	8.26	19.23	3.53	12.31	9.08	33.74	9.71	6.69	6.30	0.43	0.29	0.27	1.5	1.60

It can be seen from the analysis of the data presented in **Table 4** that the degree of niobium recovery in the extract in one step is significantly high with a ratio of organic and aqueous phases equal to 2:1. It amounts to 86.83%. At the same time, this value for zirconium is low and remains stable from 6.69 to 9.88% over the entire range of $V_o:V_{aq}$ values. The extraction of titanium into the extract with a ratio of organic and aqueous phases equal to 2:1 was 23.63%, than it decreased with an increase in the volume of the aqueous phase.

The inorganic substance that improves performance is called a precipitator during extraction. In most cases, these are non-extractable salts containing the counter-ion of the same name, which is part of the compound of the extracted metal. Adding a precipitant to an aqueous solution promotes the formation of better-extractable non-dissociated molecules or results in the formation of extractable complexes. In other words, the action of the precipitator is due to the hydration of the precipitator ion which reduces the concentration of unbound water which, in its turn, contributes to the dehydration of ions in the solution and an increase in their activity coefficients [23].

The effect of the salting-out agent on the extraction process was studied as part of our study. TBP was used as an extractant for extraction, and a 0.9 M solution of ammonium fluoride as a precipitant. The salting-out agent was added to the aqueous solution in doses of 6%, 10%, 14% and 20% of the volume of the aqueous solution. The ratio of the organic phase to the aqueous phase was 2:1, while the volume of added salting-out agent was not considered in the calculations. The results of the experiments are shown in **Table 5**.

Table 5 Distribution of components during extraction with a solution of TBP in kerosene, introducing a salting-out agent into the aqueous phase.

$V_o:V_{aq}$	NH_4F, %	Content in the phases, g/l						Degree of extraction into organic phase, %			Distribution coefficient, D			Separation coefficient, β	
		Nb_2O_5		ZrO_2		TiO_2		Nb_2O_5	ZrO_2	TiO_2	Nb_2O_5	ZrO_2	TiO_2	Nb_2O_5/ZrO_2	Nb_2O_5/TiO_2
		C_o	C_a	C_o	C_a	C_o	C_a								
2:1	6	13.78	7.51	7.76	5.42	3.00	33.00	64.78	58.86	8.34	1.84	1.43	0.09	1.28	20.18
	10	14.05	7.24	8.00	5.18	4.50	31.50	66.06	60.65	12.51	1.94	1.54	0.14	1.26	13.59
	14	14.20	7.09	8.25	4.93	4.67	31.33	66.74	62.54	12.97	2.00	1.67	0.15	1.20	13.43
	20	14.56	6.73	8.62	4.56	6.01	30.00	68.44	65.36	16.68	2.16	1.89	0.20	1.14	10.81

A change in the distribution of components was observed during the extraction process using a solution of 20% TBP in kerosene with the addition of a precipitant in the aqueous phase. There is a significant increase in the degree of recovery of niobium and zirconium compared to the experiments (see **Table 2**) where the precipitator was not used. The niobium recovery rate remained stable, ranging from 64.78% to 68.44%. Zirconium recovery increased significantly and ranged from 58.86 to 65.36% throughout the experiment, while titanium recovery remained low. It was determined that adding a salting-out agent in a volume corresponding to 6% of the volume of the aqueous solution is sufficient. The values of the distribution and separation coefficients are also shown in **Table 5**.

Determination of the optimal conditions for the extraction process of niobium from solutions by the selected extractant

The extractant Cyanex 923 was selected as the optimal reagent for the extraction of niobium from a fluoride-sulfuric acid solution based on the studies performed. The results of the studies indicate a significant efficiency of niobium extraction with a single extraction using this extractant. Besides, a significant co-extraction of other valuable co-components from the studied raw materials was found. A new batch of fluoride-sulfuric acid solution was prepared for subsequent studies to determine the optimal conditions for extraction processing. The chemical composition of this solution is as follows, g/l: 57.012 Ti_2O, 39.285 Al_2O_3, 26.526 Nb_2O_5, 43.315 Fe_2O_3, 13.459 ZrO_2, 521.1 H_2SO_4, 214.00 HF.

The main goal of this research stage was to determine the optimal ratio of the organic phase to the aqueous phase, at which the minimum amount of the organic phase is used up with high rates of niobium extraction into the extract. Studies were conducted

at different concentrations of Cyanex 923 in toluene: 30, 50 and 70%. The volumes of the organic phase to the water phase varied in the proportions of 1:1, 1:2, 1:4, 1:8, 1:10 and 1:20. The active mixing of the two phases in the separation funnels was 5 minutes for each sample. The data obtained during the experiments are shown in **Table 6**.

Table 6 Distribution of components at different concentrations of Cyanex 923 in toluene

V_o:V_{aq}	Content in the aqueous phase, g/dm³					Degree of extraction into organic phase, %					Distri-bution coeff., D (Nb_2O_5)	Separation coefficient, β	
	Nb_2O_5	ZrO_2	TiO_2	Fe_2O_3	Al_2O_3	Nb_2O_5	ZrO_2	TiO_2	Fe_2O_3	Al_2O_3		Nb_2O_5/Fe_2O_3	Nb_2O_5/Al_2O_3
30% Cyanex 923 in toluene													
1:1	2.43	6.56	29.00	28.85	29.63	90.85	51.27	49.14	33.39	24.59	9.93	19.82	30.47
1:2	7.42	9.74	46.52	30.35	32.57	72.03	27.67	18.41	29.92	17.10	5.15	6.03	12.48
1:4	14.48	9.87	50.00	32.67	35.68	45.42	26.65	12.29	24.57	9.17	3.33	2.55	8.25
1:8	20.37	10.85	55.01	31.86	39.29	23.20	19.38	3.51	26.45	0.00	2.42	0.84	-
1:10	22.32	11.72	55.01	32.96	39.29	15.86	12.94	3.51	23.90	0.00	1.88	0.60	-
1:20	24.32	12.80	57.01	36.65	39.29	8.32	4.92	0.00	15.39	0.00	1.81	0.50	-
50% Cyanex 923 in toluene													
1:1	0.00	4.62	13.00	30.03	28.76	100.00	65.71	77.20	30.67	26.78	-	-	-
1:2	3.45	9.57	38.01	30.18	28.76	86.99	28.93	33.33	30.33	26.78	13.37	15.36	18.28
1:4	13.55	9.57	50.00	33.51	38.47	48.91	28.93	12.29	22.64	2.07	3.83	2.11	45.32
1:8	18.53	10.82	55.01	35.90	39.29	30.16	19.63	3.51	17.11	0.00	3.45	2.09	-
1:10	19.87	11.76	55.01	31.92	39.29	25.11	12.62	3.51	26.31	0.00	3.35	0.94	-
1:20	22.80	12.57	54.98	35.89	39.29	14.03	6.59	3.57	17.14	0.00	3.26	0.79	-
70% Cyanex 923 in toluene													
1:1	0.00	3.25	8.49	27.35	28.79	100.00	75.86	85.10	36.85	26.71	-	-	-
1:2	0.00	9.55	29.00	31.43	32.10	100.00	29.03	49.14	27.43	18.29	-	-	-
1:4	2.92	10.32	42.01	33.77	35.49	88.98	23.30	26.31	22.04	9.67	32.29	28.55	75.42
1:8	13.96	10.86	50.00	37.17	39.29	47.38	19.32	12.29	14.19	0.00	7.20	5.44	-
1:10	18.31	11.06	50.00	35.84	39.29	30.99	17.83	12.29	17.26	0.00	4.49	2.15	-
1:20	22.11	12.29	55.01	35.72	38.33	16.63	8.66	3.51	17.53	2.43	3.99	0.94	8.00

A decrease in the recovery of niobium, zirconium and titanium from solutions is observed with an increase in the volume of the aqueous phase from 1 to 20 parts at all concentrations of Cyanex 923. There is an increase in the extraction of niobium into the extract, especially noticeable at high V_o:V_{aq} ratios with an increase in the extractant concentration. For example, the recovery of niobium to the organic phase increases from 8.32% to 16.63% with a ratio of V_o:$V_{aq} = 1$:20, with an increase in the concentration of Cyanex 923 from 30% to 70%.

In general, there is an increase in the separation coefficients of niobium with an increase in the concentration of the extractant. It is worth noting that niobium was completely extracted into the organic phase at 50% of Cyanex 923 in the ratio V_o:$V_{aq} = 1$:1, as well as at 70% of Cyanex 923 V_o:$V_{aq} = 1$:1, 1:2. As the extractant concentration increases, the Nb_2O_5/Fe_2O_3 and Nb_2O_5 separation coefficients also increase.

At a subsequent stage, studies were performed to analyze how the process's duration affects the extraction efficiency. Experiments were performed using a Cyanex 923 solution with a concentration of 70% at an organic to aqueous phase ratio of 1:4, with a contact time of 5, 10, 15, 20, 25, and 30 minutes (see **Table 7**).

Table 7 Influence of interaction time of organic and aqueous phases on the extraction process

τ, min	Content in the aqueous phase, g/dm³					Degree of extraction into organic phase, %					Distribu-tion co-eff., D (Nb_2O_5)	Separation coefficient, β	
	Nb_2O_5	ZrO_2	TiO_2	Fe_2O_3	Al_2O_3	Nb_2O_5	ZrO_2	TiO_2	Fe_2O_3	Al_2O_3		Nb_2O_5/Fe_2O_3	Nb_2O_5/Al_2O_3
5	2.92	10.32	42.01	33.77	35.49	88.98	23.30	26.31	22.04	9.67	32.29	28.55	75.42
10	3.80	8.76	40.01	27.22	36.93	85.69	34.93	29.82	33.06	5.99	23.95	12.12	93.91
15	3.12	8.35	42.01	25.02	35.66	88.23	37.96	26.31	38.49	9.23	29.99	11.98	73.70
20	4.22	8.78	40.01	25.70	35.92	84.09	34.77	29.82	36.81	8.57	21.14	9.07	56.38
25	3.10	8.94	40.01	22.35	35.92	88.32	33.57	29.82	45.04	8.57	30.24	9.22	80.65
30	3.46	9.15	40.01	24.61	35.59	86.96	32.04	29.82	39.50	9.41	26.67	10.21	64.21

An increase in the contact time of the τ phases did not result in additional niobium recovery; the percentage of niobium recovery ranged from ~84% to 89% throughout the study. At the same time, there was an increase and fluctuation in the extraction of zirconium and iron into the organic phase, which led to a decrease in the βNb_2O_5/Fe_2O_3 separation coefficient. In contrast, the recovery of aluminum into the organic phase decreased. The extraction of titanium into the extract remained at ~26-30% throughout the experiments.

The extraction of niobium under the selected optimal conditions of 70% Cyanex 923 in toluene with a ratio of V_o:$V_{aq} = 1$:4 can be improved if the process is carried out in a counterflow in several stages. A multi-stage countercurrent extraction process is the most efficient for efficiently recovering valuable metals from solutions at high rates and for separating components. A three-stage counter-current extraction was performed up to 5 cycles during our work. **Figure 3** shows a diagram of the extraction process. Each separation funnel, indicated by a number, corresponds to one theoretical step. Steps 1 to 3 form one cycle. The calculated volumes of the initial solution and extractant were mixed in a separation funnel. The process continued until the final phase of the extract in the separation funnel 1, and the final raffinate of the same cycle was obtained with a composition that did not change from cycle to cycle.

When the stock solution and extractant are introduced into the system periodically, the process is usually called batch extraction, where the formulations of the resulting products are variable. Based on it, the process implemented in separation funnels can be described as a step-by-step continuous countercurrent process after reaching a stationary state.

The ratio of phase volumes was maintained at the level of 1:4 during the experiment. The compositions of the final refinates and the degree of metal recovery in each cycle of the three-stage extraction process are presented in **Table 8**. Analysis of the results shows that the extraction of niobium into the extract in the three-stage countercurrent extraction is higher compared to the single-stage process, reaching the maximum value in the 3rd

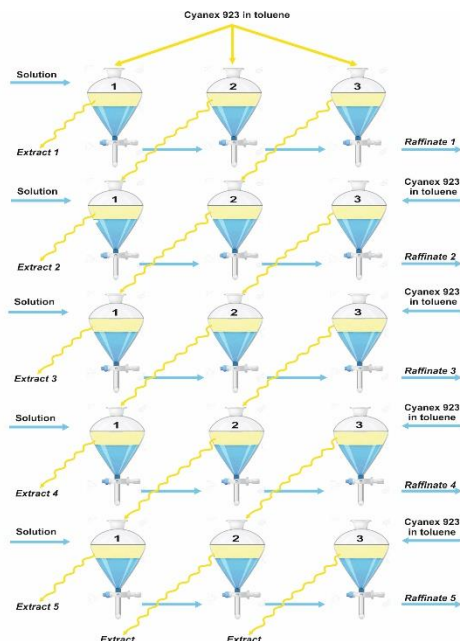cycle. This extraction method also observed an increase in the iron recovery rate.

Fig. 3 Three-stage countercurrent extraction scheme

The data show that during the three-stage countercurrent niobium extraction using Cyanex 923 in toluene at a concentration of 70% and an organic phase volume to water phase ratio of 1:4, niobium is extracted from 88.98% to 94.97%.

Thus, niobium can be efficiently extracted and concentrated with extraction with Cyanex 923 from fluoride-sulfuric acid solutions obtained from the processing of niobium-containing cake. The zirconium and titanium impurities present in the solutions are recovered in the range of ~20% to 40%. Depending on the experimental conditions, iron extractability varies from 22.04% to 53.77%. The three-step extraction results in an increase in the concentration and extraction of niobium into the extract. It is preferable to use Cyanex 923 with a concentration of 50% at a 1:1 ratio of organic phase volume to volume of the aqueous phase, as well as Cyanex 923 with a concentration of 70% at a ratio of 1:1 and 1:2 to obtain more concentrated niobium solutions. However, in this case, zirconium and titanium are co-extracted into the extract. Therefore, this approach may be of interest from the point of view of co-extracting zirconium and titanium with niobium, and then separating them in the reextraction process.

Table 8 Results of a three-stage countercurrent extraction study with the use of Cyanex 923 in toluene

Cycle No.	Content in the aqueous phase, g/dm3					Degree of extraction into organic phase, %					Distri-bution coeff., D (Nb₂O₅)	Separation coefficient, β	
	Nb_2O_5	ZrO_2	TiO_2	Fe_2O_3	Al_2O_3	Nb_2O_5	ZrO_2	TiO_2	Fe_2O_3	Al_2O_3		Nb₂O₅/ZrO₂	Nb₂O₅/TiO₂
1	1.73	10.59	40.01	24.61	35.59	93.47	21.35	29.82	39.50	9.41	57.30	21.94	137.94
2	1.72	10.57	38.01	27.07	36.67	93.52	21.46	33.33	33.45	6.67	57.70	28.70	201.98
3	1.33	8.27	37.34	18.80	35.63	94.97	38.57	34.50	53.77	9.30	75.58	16.25	184.24
4	2.66	9.44	40.01	19.11	35.63	89.99	29.87	29.82	53.00	9.30	35.96	7.97	87.66
5	2.63	9.25	38.01	19.27	34.29	90.10	31.28	33.33	52.63	12.72	36.40	8.19	62.45

CONCLUSION

Various classes of extractants were studied during the studies performed to extract niobium from a fluoride-sulfuric acid solution, including neutral oxygen-containing extractants, such as MIBK, TBP, Cyanex 923, and the anion exchange extractant TOA. Kerosene and toluene were used as diluents for extractants. The highest recovery rate of controlled elements was achieved by using Cyanex 923 in toluene. The degree of niobium recovery in one stage was 98.75%, zirconium recovery was 49.01%, and titanium recovery was 70.85%, with the ratio of organic phase to aqueous phase volumes equal to 2:1.

Extraction with a 20% TBP solution in kerosene and adding a precipitant to the aqueous phase significantly increased the recovery of niobium and zirconium compared to experiments without a precipitant. The recovery rate of niobium was stable in the range of 64.78%-68.44%, and zirconium was 58.86%-65.36% while the recovery of titanium remained low. Adding a precipitant of 6% of the aqueous solution volume effectively improved the extraction process with TBP.

Based on the research, the extractant Cyanex 923 was selected as the optimal reagent for removing niobium from a fluoride-sulfuric acid solution. It showed high efficiency in a single extraction.

Studies have been performed to determine the optimal ratio of organic and aqueous phases at different concentrations of Cyanex 923 in toluene (30, 50, 70%). The phase volumes varied in 1:1, 1:2, 1:4, 1:8, 1:10 and 1:20 proportions. It is established that an increase in the extractant concentration increases the separation coefficients of niobium. Complete recovery of niobium was achieved at 50% of Cyanex 923 (ratio $V_o:V_{aq}$ = 1:1) and 70% of Cyanex 923 (ratio $V_o:V_{aq}$ = 1:1, 1:2).

Analysis of the effect of the process duration showed that an increase in the contact time of the phases (5-30 minutes) did not lead to additional niobium recovery, the recovery rate remained within the range of 84.09%-88.98%.

A three-stage counter-current extraction with 70% Cyanex 923 (1:4 ratio) showed that niobium recovery exceeded the results of the single-step process, peaking in the third cycle at 94.97%.

REFERENCES

1. Ye.M. Zhilina, S.A. Krasikov, S.N. Agafonov, S.V. Zhidovinova, A.S. Russkikh, T.V. Osinkina: Trudy Kol'skogo

nauchnogo tsentra RAN, 2018, 269-271 (in Russian). https://doi.org/10.25702/KSC.2307-5252.2018.9.1.269-271

2. M.A. Alipovna, K.A. Karaulovich, P.A. Vladimirovich, A.Z. Zhanuzakovich, K.B. Bolatovna, W. Wieleba, N. Bakhytuly: Materials Science-Poland, 41(1), 2023, 1-14.

3. A.A. Ultarakova, A.M. Yessengaziyev, E.I. Kuldeyev, K.K. Kassymzhanov, O.Kh. Uldakhanov: Metalurgija, 60(3-4), 2021, 411-414.

4. A. Ultarakova, Z. Karshyga, N. Lokhova, A. Yessengaziyev, P. Burns: Complex Use of Mineral Resources, 325(2), 2023, 53-61. https://doi.org/10.31643/2023/6445.18

5. A. Yessengaziyev, A. Ultarakova, P. Burns: Complex Use of Mineral Resources, 320(1), 2022, 67-74. https://doi.org/10.31643/2022/6445.08

6. V.T. Kalinnikov, N.V. Zots, A.I. Nikolaev: Metallurgiya tsvetnykh i redkikh metallov: sb. st. Rossiysko-indiyskogo simpoz, M. 2002, 199-203 (in Russian).

7. B. Kenzhaliyev, T. Surkova, A. Berkinbayeva, Z. Baltabekova, K. Smailov: Metals, 14(6), 2024, 699. https://doi.org/10.3390/met14060699

8. M.J. Ungerer, D.J. Van der Westhuizen, G. Lachmann, H.M. Krieg: Hydrometallurgy, 144-145, 2014, 195-206. https://doi.org/10.1016/j.hydromet.2014.02.015

9. X. Yang, X. Wang, C. Wei, S. Zheng, Y. Zhang: Solvent Extraction Research and Development, Japan, 20, 2013, 159-168. https://doi.org/10.15261/serdj.20.159

10. S. Bhattacharyya, B. Ganguly: Journal of Radioanalytical and Nuclear Chemistry, 98, 1984, 247-253. https://doi.org/10.1007/bf02037087

11. O.S. Ayanda, F.A. Adekola: Journal of Minerals and Materials Characterization and Engineering, 10, 2011, 245-256. https://doi.org/10.4236/jmmce.2011.103016

12. S. Dutta, S. Mukhopadhyay, S. Gaddam, K. Shenoy, K.V. Mirji: Hydrometallurgy, 2020, 105522. https://doi.org/10.1016/j.hydromet.2020.105522

13. M. Karve, S. Khopkar: Talanta, 40(11), 1993, 1573-1578. https://doi.org/10.1016/0039-9140(93)80050-g

14. Z. Zhu, C.Y. Cheng: Hydrometallurgy 107, 2011, 112. https://doi.org/10.1016/j.hydromet.2010.12.015

15. S.M. Masloboeva, V.N. Lebedev, L.G. Arutyunyan: Vestnik MGTU, 13(4/2), 2010, 902-906 (in Russian).

16. A. Yessengaziyev, A. Toishybek, A. Mukangaliyeva, N. Abdyldayev, A. Yersaiynova: Complex Use of Mineral Resources, 331(4), 2024, 117-126. https://doi.org/10.31643/2024/6445.45

17. F. Habashi: *Handbook of Extractive Metallurgy*. Wiley-VCH, 1997.

18. A.G. Babkin, V.G. Mayorov, A.I. Nikolaev: Extraction of niobium, tantalum and other elements from fluoride solutions. L.: Nauka, 1988 (in Russian).

19. G. Singh: Hydrometallurgy, 40, 1996, 247-262. https://doi.org/10.1016/0304-386X(94)00054-7

20. E. Dziwiński, J. Szymanowski: Solvent Extraction and Ion Exchange, 16(6), 1998, 1515-1525. https://doi.org/10.1080/07366299808934592

21. G.M. Voldman: *Fundamentals of extraction and ion exchange processes of hydrometallurgy.* Moscow: Metallurgiya, 1982 (in Russian).

22. Y. Li, C. Cui, X. Ren, Y. Li: Desalination and Water Treatment, 54, 2015, 191199. https://doi.org/10.1080/19443994.2013.878670

23. G.M. Voldman, A.N. Zelikman: *Theory of hydrometallurgical processes. Textbook for universities.* 4th edition revised and expanded. Moscow: Intermet Inzhiniring, 2003 (in Russian).