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Study of the leaching process for dust chamber sublimates followed by the extraction of niobium and zirconium into solution

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ABSTRACT
The material composition of the sublimates from dust chambers in titanium chlorinators has been studied by chemical, X-ray and microprobe analysis methods. Studies of the phase composition of dust chamber sublimates have shown that the object consists of aqueous and anhydrous chloride phases to a greater extent. Two forms of niobium present, such as oxychloride and oxide niobium were found. The presence of zirconium in sublimates has a chloride and oxychloride nature. Experiments for the aqueous leaching of dust chamber sublimates were conducted to determine the optimal process conditions: S:L ratio = 1:8, leaching time = 1 hour, temperature = 25°C. Studies were conducted to choose an acidic reagent for cake leaching followed by the conversion of niobium and zirconium into a solution. A solution consisting of $HF+H_2SO_4$ was selected as an acidic reagent for cake leaching. Optimal conditions for the extraction of niobium and zirconium into solution were established, such as 25% [18M HF] +75% [7M H_2SO_4], S:L ratio = 1:3, temperature = 90 °C, duration of the leaching process = 120 minutes. Under these leaching conditions, the extraction of niobium, zirconium, and titanium into solution was 94.06%, 84.95% and 32.35%, respectively. The elemental and phase composition of the residue from acid leaching of cake were determined.

Keywords: niobium, dust chamber sublimates, leaching, acid, solution.

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Introduction

In general, rare metals determine the development of such important fields as semiconductor electronics, nuclear power, aviation and rocket engineering, electro-vacuum technology, as well as the production of special steels and hard, heat-resistant and anticorrosive alloys. Rare refractory transition metals which form alloys of intermetallic compounds and solid solutions characterized by high intermolecular adhesion of atoms in crystals may be considered particularly in demand. The high rates of development of these technology branches determine the continuous increase in demand for rare metals which provides for further expansion of their production [[1], [2], [3]]. The use of titanium-magnesium production waste abundant in rare metals can contribute to solving this problem [4]. Niobium and zirconium are a common satellite of titanium: therefore, they are found in titanium concentrates obtained from ores of ilmenite deposits. At Ust-Kamenogorsk Titanium and Magnesium Plant (UKTMP) JSC, during the processing of titanium-containing raw materials, the largest part of niobium and zirconium enters and concentrates in production waste.

When titanium tetrachloride is produced, a large amount of spent melt and pulps of chlorinators, sublimates and sludge of dust chambers is formed. An analysis of the distribution of niobium in solid waste from the chlorination process for titanium slags of the Ust-Kamenogorsk Titanium and Magnesium Plant shows that the highest content of niobium is found in dust chamber sublimates. Depending on the volume of titanium tetrachloride production, up to 3.2 t/day of DC sublimates are formed and contain such valuable components as KCl, NaCl, $FeCl_2$, $FeCl_3$, $MnCl_2$, $CrCl_3$, $TiCl_4$, $NbCl_5$, $ZrCl_4$, $ThCl_4$, $A1C1_3$, $ScCl_3$, $TaCl_5$. At the plant, DC distillates are washed with water, the resulting chloride pulp is discharged into an acidic sewer and then neutralized with lime milk. Here, all valuable components in the sublimates accumulate in sludge accumulators [[5], [6]].

Niobium is resistant to many acids and salt solutions. Orthophosphoric, diluted sulfuric and nitric acids have practically no effect on niobium. Only concentrated solutions of hydrochloric, sulfuric and hydrofluoric acid or their mixtures can be effectively used as reagents [[7], [8]].

There are well-known methods of hydrochloric acid opening for natural and secondary titanium, niobium and tantalum raw materials [[9], [10], [11]]. The work [12] studies the kinetics of niobium leaching with hydrochloric acid from titanium-magnesium production waste. The experiments determine the effect of the parameters of the leaching temperature (25-90 °C), HCl concentration (0.5 - 4 M), stirring rate (100-500 rpm) and the solid-liquid ratio. The maximum niobium extraction degree of more than 90% was achieved in 60 minutes by leaching residues in 4 M HCl at 70°C.

The work [13] studies the conditions for the niobium and tantalum leaching from the columbite concentrate of the Zashikhinskiy deposit with a solution of hydrofluoric and sulfuric acids. We can see that the concentration of acids and the temperature of the solution have a decisive effect on the extraction degree of both elements. In contrast, the dispersion of the concentrate and the duration of phase contact have a lesser effect. Under conditions ensuring the production of solutions with a total content of niobium and tantalum of at least 110-130 g/L. Large-scale laboratory tests of the process for the extraction of niobium 97.6% and tantalum 93.7% were performed. The separation of niobium and tantalum using 1-octanol as an extractant for the production of experimental samples of niobium oxide and tantalum oxide was studied under the conditions of a continuous extraction cascade.

Zirconium is also chemically resistant in many aggressive environments. Zirconium interacts with acids only when there are conditions for the oxidation of acids and the formation of anionic complexes. It reacts neither with hydrochloric and sulfuric acids (up to 50%) nor with alkali solutions. It interacts with nitric acid and Aqua regia at above 100 °C. It is soluble in hydrofluoric and hot concentrated (above 50%) sulfuric acids [14].

The work studies the effect of nitric, sulfuric and hydrochloric acids on the morphology, elemental composition, structural and chemical transformations of the mineral surface and the leaching efficiency of zirconium (eudialyte) concentrate with the use of a complex of modern analytical methods [15]. Specific features in the eudialyte destruction nature and the degree of the effect of various acids have been found.

The analysis of the scientific and technical literature shows that acidic methods of decomposition followed by selective extraction of the target components are used to a greater extent to open rare metal raw materials. Moreover, most studies in the literature are devoted to qualified sources of rare metal raw materials, and there are very few studies on the extraction of niobium and zirconium from titanium production waste. The main purpose of this research is to conduct experimental studies to leach dust chamber sublimates, followed by the extraction of niobium and zirconium into an acidic solution.

Materials and methods

Materials. Mineral acids are high-purity hydrofluoric acid, chemically pure sulfuric acid, and chemically pure hydrochloric acid. A sample of the sublimates from dust chambers in titanium chlorinators was provided by UKTMP JSC. Content of the main components of dust chamber sublimates, wt. %: 7.44 Ti; 6.5 Fe; 5.025 K; 4.899 Al; 2.539 Zr; 1.105 Na; 0.797 Nb; 0.359 Si; 0.214 Mg; 44.35 Cl; 24.053 O.

Equipment. Shimadzu TW423L analytical balance (Japan); Velp Scientifica LS top-drive agitator (Italy); IV-6 vibration damper (Russia); LT-111a circulation thermostat (Russia); SNOL drying cabinet (Lithuania).

Experiment method. Agitation leaching of DC sublimates with water was performed with the use of a weight of 50 g, at different ratios of S:L, temperature, time and at a stirring rate of 300 rpm. After filtration, the resulting cakes were dried to a constant weight and tested. Subsequent acid leaching of the niobium-containing cake was performed similarly, using a wide range of process parameters. The liquid phase was filtered at the end of the process. The precipitate was washed with warm water to remove residual acid. The resulting solutions and cakes were analyzed for the content of niobium, zirconium, titanium, aluminum, and iron.

Analysis methods. X-ray phase analysis was performed with the BRUKER D8 ADVANCE device (Germany). X-ray fluorescence analysis was performed with Venus 200 PANalytical B.V. wave dispersion spectrometer (Holland). Chemical analysis of samples was performed with Optima 2000 DV, an optical emission spectrometer with inductively coupled plasma (United States). Electron probe analysis was performed with JEOL JXA 8230 microanalyzer (Japan).

Results and discussion

Physical and chemical study of dust chamber sublimates and their treatment with the removal of water-soluble components. The results of the X-ray phase analysis are shown in Figure 1. For the most part, the object of study consists of aqueous and anhydrous chloride phases: Erythrosiderite $K_2(FeCl_5(H_2O))$, aqueous chloraluminite $AlCl_3(H_2O)_6$, rokühnite $FeCl_2(H_2O)_2$, sodium chloride NaCl, zirconium chloride $ZrCl_2$, niobium oxychloride $NbOCl_3$.The oxide components of the sublimate include the phases of rutile $Ti_{0.924}O_2$, titanium oxide Ti_6O_{11}, and niobium-aluminium-titanium oxide $Ti_{0.8}Al_{0.1}Nb_{0.1}O_2$.

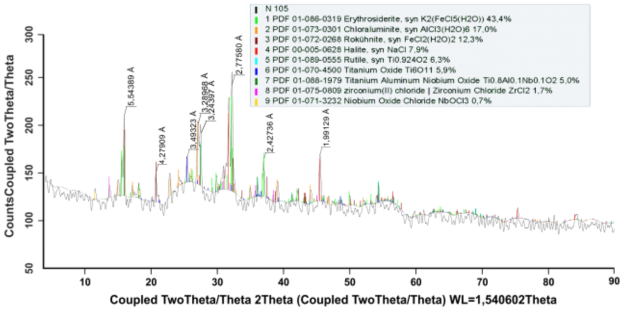
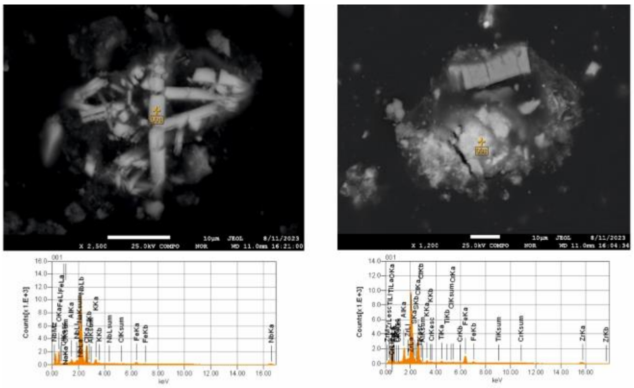


Figure 1 – Diffractogram of DC sublimates



Chemical formula		ms%	mol%	Sigma	Net	K ratio	Line
O	38.54	72.38	0.42	416748	0.0928929		K
Na	1.11	1.45	0.13	72358	0.0057195		K
Al	1.03	1.15	0.07	157205	0.0062511		K
Cl	8.47	7.18	0.09	1078888	0.0585941		K
K	2.18	1.67	0.12	276350	0.0189778		K
Fe	2.00	1.07	0.19	173162	0.0199245		K
Nb	46.67	15.09	0.18	5514982	0.4090875		L
Total	100.00	100.00					

Chemical formula		ms%	mol%	Sigma	Net	K ratio	Line
O	36.28	68.81	0.20	474713	0.1036698		K
Al	3.13	3.52	0.04	529360	0.0206232		K
S	1.38	1.31	0.05	171199	0.0093187		K
Cl	9.34	8.00	0.05	1251948	0.0666156		K
K	0.67	0.52	0.06	95637	0.0064347		K
Ti	0.61	0.39	0.06	79620	0.0057210		K
Cr	0.48	0.28	0.08	56477	0.0049377		K
Fe	5.57	3.03	0.09	527004	0.0594101		K
Zr	42.51	14.14	0.10	4955320	0.3675531		L
Total	100.00	100.00					

Figure 2 – COMPO image of DC sublimate. A particle of niobium and zirconium oxychlorides

A detailed study of the mineral structure of the DC sublimate sample was performed with the use of an electron probe microscope in the mode of backscattered electrons (COMPO). Several mineral points were analyzed using the electron probe microscope. Figure 2 shows particles of niobium (×2500) and zirconium (×1200) oxychlorides with a spectrum of various impurities.

Most hydrochloric acid salts are known to be freely soluble in water. Erythrosiderite contained in DC sublimates is a crystallohydrate of a complex salt of iron, potassium and hydrochloric acid $FeCl_3 \cdot 2KCl \cdot H_2O$. It is yellowish-red in color, hygroscopic, and soluble in water [16]. Hydrates of aluminum and iron chlorides are also hygroscopic crystalline substances that are easily soluble in water [[17], [18]]. Sodium chloride is the sodium salt of hydrochloric acid. It is moderately soluble in water and has a solubility that is slightly dependent on temperature. It is significantly reduced in the presence of chlorides of other metals. Pure sodium chloride is non-hygroscopic [19]. Zirconium oxide-dichloride has good solubility in cold water and is hydrolyzed in aqueous solution at above 70°C [20]. Niobium chloride and niobium oxychloride decompose with water, resulting in the formation of hydrated niobium pentoxide [21].

Experiments were conducted on its aqueous leaching taking into account the water-solubility of the chloride phases in DC sublimates. Table 1 shows the effect of the S:L ratio on the extraction degree of the main components of sublimating into the cake. Leaching experiments were performed at room temperature for 4 hours.

When the S:L ratio increases during the leaching of DC sublimates, a gradual decrease in cake yield is observed. The obtained pulps were filtered at a leisurely pace. At S: L = 1:10, the weight of the cake decreased 4 times while a slight decrease in the degree of niobium extraction into the cake was reported. When sublimates were leached at S: L= 1:8, the extraction of niobium into the cake was 83.85%. Ferric chloride showed high solubility in an aqueous medium and a relatively insignificant transition into cake. When the S:L ratio changes from 1:4 to 1:10, the extraction of aluminum and zirconium into the cake gradually decreases. At the same time, titanium showed low solubility and accumulation in the cake.

Table 2 shows the results of experiments on the effect of the leaching duration on the extraction degree of the main components of sublimating into the cake. The experiments were performed at process durations of 1,2,4,6 hours, temperature of 25°C, and S: L ratio of 1: 8.

Table 1 – Effect of the S:L ratio on the extraction degree of the main components of sublimating into the cake

S:L ratio	Cake yield, %	Content in cake, %					Extraction into cake, %				
		Ti	Fe	Al	Zr	Nb	Ti	Fe	Al	Zr	Nb
1:4	28.00	24.23	7.45	19.67	4.14	2.25	91.19	32.08	62.72	45.63	79.15
1:6	27.60	24.34	5.45	16.71	4.13	2.29	90.31	23.13	52.51	44.87	79.41
1:8	27.00	25.74	3.59	13.42	3.93	2.48	93.42	14.92	41.26	41.76	83.85
1:10 AM	22.72	30.17	3.44	11.37	3.93	2.53	92.13	12.01	29.43	35.17	72.24

Table 2 - Effect of leaching duration on the extraction degree of the main components of sublimate into the cake

Time, h	Cake yield, %	Content in cake, %					Extraction into cake, %				
		Ti	Fe	Al	Zr	Nb	Ti	Fe	Al	Zr	Nb
1	32.80	20.96	2.72	11.80	3.91	2.06	92.40	13.70	44.09	50.45	84.57
2	35.00	19.60	2.53	10.98	3.73	1.91	92.22	13.64	43.77	51.38	83.70
4	27.00	25.74	3.59	13.42	3.93	2.48	93.42	14.92	41.26	41.76	83.85
6	29.00	24.23	3.23	10.65	3.53	2.09	94.44	14.39	35.17	40.30	75.87

Table 3 - Effect of temperature on the extraction degree of the main components of sublimate into the cake

T, ºC	Cake yield, %	Content in cake, %					Extraction into cake, %				
		Ti	Fe	Al	Zr	Nb	Ti	Fe	Al	Zr	Nb
25	32.80	20.96	2.72	11.80	3.91	2.06	92.40	13.70	44.09	50.45	84.57
45	36.46	18.77	7.04	10.50	3.22	1.79	91.99	39.49	43.62	46.25	81.84
65	37.24	17.99	9.02	9.93	4.22	1.75	90.07	51.69	42.13	61.85	81.77
90	37.40	17.61	11.87	10.69	5.10	1.80	88.53	68.32	45.54	75.12	84.47

At a leaching duration of 1 hour, the extraction of niobium and zirconium into the cake was 84.57% and 50.45%, respectively. The table of the dependence of the extraction of sublimate components into cake on the duration of the experiment shows that when the duration increases, there is a decrease in the extraction of niobium and zirconium into cake, niobium and zirconium are leached into the solution. Therefore, the optimal leaching duration should be considered 1 hour for maximum extraction of the target components into the cake.

Table 3 shows the results of experiments on the effect of temperature on the extraction degree of the main components of sublimating into the cake. The study was performed at leaching temperatures of 25, 45, 65 and 90°C, and the following process parameters were kept constant: S: L ratio = 1: 8, duration = 4 hours, stirring rate = 300 rpm.

The results of the study presented in Table 3 show that increased leaching temperature leads to a slight increase in cake yield. At 90°C, the cake yield was 37.40%. There was a slight increase in the extraction of iron, aluminum, and zirconium into the cake, including chlorine cake, by 19.71%. It is worth noting that an increase in temperature forms a gel-like, viscous pulp which is difficult to filter. It has been established that an increase in the temperature of the leaching process has a negative effect in terms of the conversion of chlorides into solution.

Therefore, the optimal conditions for the aqueous leaching of DC sublimates are S: L ratio = 1: 8, leaching time = 1 hour, and temperature = 25°C. At the same time, the extraction of niobium, titanium, aluminum, iron and zirconium into the cake was 84.57%, 92.40%, 44.09%, 13.70%, and 50.45%, respectively.

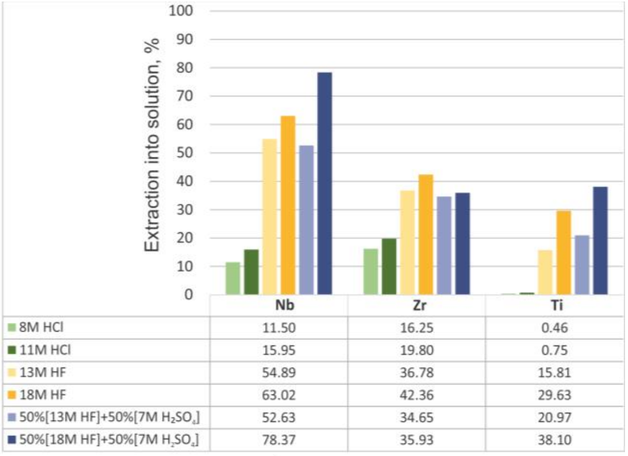
Choice of an acidic reagent for the conversion of niobium and zirconium into solution. The choice of solvents depends on many factors, including the corrosive effect on equipment, regenerability, and cost but not limited to the chemical and physical nature of the starting material. Besides, the state of rare refractory metals in acidic solutions is characterized by an extraordinary complexity and variety of forms. They can exist in the form of cationic and anionic mono- and polynuclear complex particles. Consequently, the subsequent extraction depends largely on the form of their existence in

Table 4 – Content of Nb, Zr, Ti, Al, Fe in solution

Acidic reagent	Cake yield, %	Content in solution, g/L				
		Nb	Zr	Ti	Al	Fe
8M HCl	75.18	1.09	3.41	0.51	6.81	8.38
11M HCl	81.62	1.59	4.35	0.88	7.77	9.43
13M HF	55.60	6.75	9.47	22.37	20.47	16.38
18M HF	33.42	6.74	9.49	36.69	18.41	17.54
50%[13M HF]+50%[7M H_2SO_4]	70.68	5.10	7.01	25.12	17.31	16.70
50%[18M HF]+50%[7M H_2SO_4]	59.92	7.62	7.18	45.60	23.06	15.41

aqueous solutions which, in turn, are determined by their concentration of metal, and mineral acid, as well as the nature and concentration of other components.

To conduct experiments on acid leaching, 2 kg of cake was accumulated under the established optimal conditions of aqueous leaching of DC sublimates. Chemical composition of cake, wt.%: 28.33 Ti; 9.53 Al; 4.89 Zr; 3.66 Fe; 2.34 Nb; 1.5 Si; 33.28 O; 6.83 Cl; 0.46 Mn, etc. To compare the effectiveness of different acids concerning the conversion of the maximum amount of niobium and zirconium into filtrate, the niobium-containing cake was leached with solutions of HCl, HF and a mixture of acids with the composition of 50%HF+ 50%H_2SO_4. Considering that the completeness of the solubility of niobium and zirconium is achieved only in concentrated acids, agitation leaching of the cake was performed with the following solutions: 8M HCl, 11M HCl, 13M HF, 18M HF, 7M H_2SO_4. The cake suspension was processed for 2 hours at 25 °C and S:L ratio = 1:3. At the end of the process, the liquid phase was filtered. The precipitate was washed with warm water to remove residual acid. The resulting solutions were analyzed for the content of niobium, zirconium, titanium, aluminum, and iron. The results are shown in Table 4.



	Nb	Zr	Ti
8M HCl	11.50	16.25	0.46
11M HCl	15.95	19.80	0.75
13M HF	54.89	36.78	15.81
18M HF	63.02	42.36	29.63
50%[13M HF]+50%[7M H_2SO_4]	52.63	34.65	20.97
50%[18M HF]+50%[7M H_2SO_4]	78.37	35.93	38.10

Figure 3 – Dependence of the extraction degree of niobium, zirconium and titanium on the concentration and composition of the leaching solution

The graph of the dependence of the extraction degree of niobium, zirconium and titanium on the concentration and composition of the leaching solution was constructed. It is shown in Figure 3.

Studies on the identification of the effect of HCl, HF, HF+H_2SO_4 on the degree of niobium extraction into the solution at a temperature of 25°C, the S:L ratio=1:3 and the agitation time of 2 hours showed the advantage of hydrofluoric acid and a HF+H_2SO_4 mixture. When using hydrochloric acid under similar leaching conditions, the extraction of niobium and zirconium is 15.95% and 19.8%, respectively. Accordingly, about the conversion of niobium and zirconium into solution, concentrated hydrochloric acid turned out to be ineffective. The use of a mixture of hydrofluoric and sulfuric acids for cake leaching made it possible to achieve a relatively high extraction of the target components into the solution. The use of this mixture also helps to save on relatively expensive hydrofluoric acid. Therefore, a mixture of 50% [18M HF] + 50% [7M H_2SO_4] was chosen as the acidic reagent for cake leaching.

Study of the effect of various parameters on acid leaching of cake. Experiments on the effect of the ratio of a mixture of hydrofluoric and sulfuric acids were performed under the following conditions: S:L ratio=1:3, temperature = 25°C, duration = 240 minutes, stirring intensity = 300 rpm and acid ratios of 10% [18M HF] + 90% [5M H_2SO_4], 25% [18MHF] + 75% [5M H_2SO_4], 35% [18M HF] + 65% [7M H_2SO_4], 50% [18M HF] + 50% [7M H_2SO_4].

Figure 4 shows a histogram of the extraction of Nb, Zr, and Ti into solution at different ratios of hydrofluoric and sulfuric acids.

The figure shows that, in general, when the proportion of hydrofluoric acid in the mixture increases from 10% to 50%, the extraction of controlled elements into solution increases from 48.57 to 78.37% for niobium, from 27.67 to 35.93% for zirconium, and from 11.86 to 38.10% for titanium. The cake yield varies from 59.92% to

72.74%. At ratios of 35% [18M HF] +65% [7M H_2SO_4], 50% [18M HF] + 50% [7M H_2SO_4], the contamination of the solution with titanium and other impurities was higher; consequently, 25% [18M HF] +75% [7M H_2SO_4] was accepted as the optimal ratio of a mixture of hydrofluoric and sulfuric acids for the studied raw materials, at which the extraction of niobium and zirconium into solution is 75.75% and 30.3%, respectively. Further experiments on the effect of various parameters on the process of leaching niobium-containing cake were performed at the above ratio of hydrofluoric and sulfuric acids.

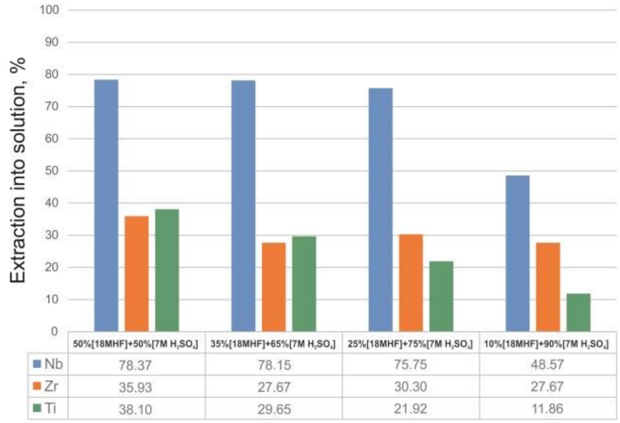


Figure 4 – Histogram of the extraction of Nb, Zr, and Ti into solution at different ratios of hydrofluoric and sulfuric acids

Studies to leach niobium-containing cake at different ratios of solid and liquid phases were performed using solutions of a mixture of 25% [18M HF] +75% [7M H_2SO_4], temperature = 25°C, duration = 240 minutes, mixing intensity = 300 rpm. The results of the research are shown in Figure 5.

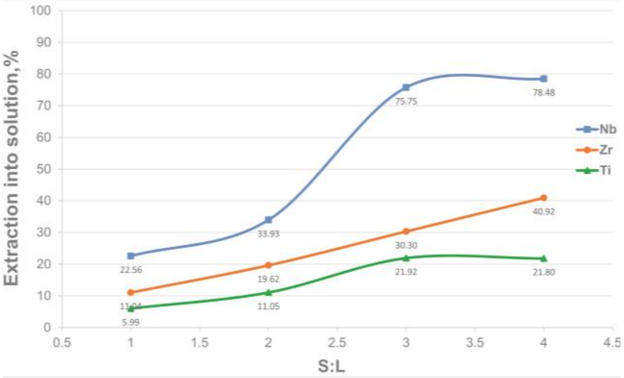


Figure 5 – Dependence of the extraction of Nb, Zr, Ti into solution on the S:L ratio at 25%HF+75% H_2SO_4

The figure shows that the extraction of niobium into solution increases dynamically in the range of S:L ratios from 1:2 to 1:4. At the same time, the extraction of niobium into solution is comparatively lower at S:L ratios of 1:1 and 1:2. The extraction of zirconium and titanium into solution with a change in the S:L ratio increases in the range from ~ 11 to ~ 41% and from ~ 6 to ~ 22%, respectively. For that matter, these mineral forms of zirconium and titanium were moderately dissolved in solution under experimental conditions and remained mostly in the cake. Therefore, taking into account the consumption of the reagent during leaching, the S:L ratio = 1:3 can be considered the best option.

Further, the studies were performed at leaching temperatures of 25, 45, 65, 90°C and while maintaining constant the following process parameters: 25%HF + 75%H_2SO_4, S:L ratio =1:3, holding time = 240 minutes, and pulp stirring rate = 300 rpm. The results of the research are shown in Figure 6.

When the temperature of the leaching process increases, an increase in the extraction of Nb and Zr into the solution is reported. At the same time, there is a slight increase in the extraction of titanium into solution. In general, the increase in temperature had a positive effect on the intensification of the leaching process. At a leaching temperature of 90°C, the extraction into solution reached 94.73% for niobium, 33.67% for titanium, and 83.53% for zirconium. The cake yield varied between ~ 22 and 29%.

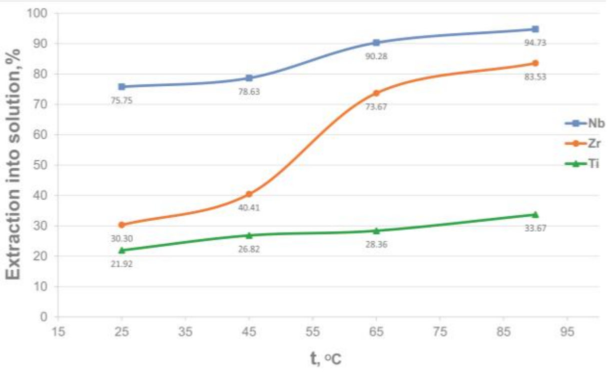


Figure 6 – Dependence of the extraction of Nb, Zr, Ti into solution on the temperature at 25%HF+75% H_2SO_4

Experiments on the duration of leaching were performed while maintaining the duration of the process of 30, 60, 120 and 240 minutes, a temperature of 90°C, a ratio of S:L = 1:3 and a pulp stirring rate of 300 rpm. The experimental results are shown in Figure 7.

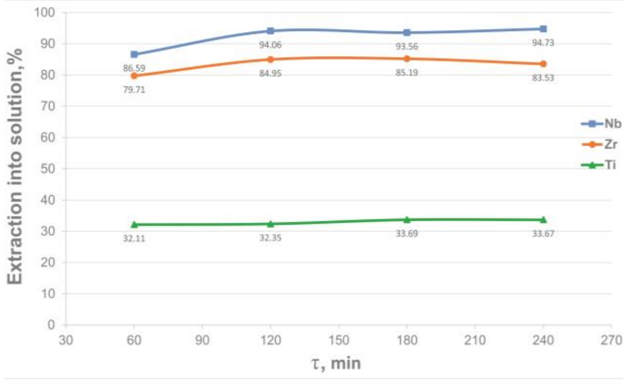


Figure 7 – Dependence of the extraction of Nb, Zr, Ti into solution on duration at 25%HF+75% H_2SO_4

The extraction of niobium into the solution was 94.06% at a leaching duration of 120 minutes. Then, in the interval of the leaching duration of 120-240 minutes, it was kept at the level of ~ 93-95%. Over the entire period, the extraction of zirconium into solution was also consistently high, on average fluctuating in the range of ~80-85%. Titanium extraction is kept almost at the same level in the range of ~32-34%. The equilibrium in the system is established after 120 minutes of holding of pulp; therefore; there is no need to carry out the leaching process for more than 120 minutes. X-ray fluorescence analysis of the leaching residue was performed, wt. %: 55.22 Ti; 4.47 Fe; 1.04 Al; 0.75 Zr; 0.26 Nb; 0.21 Mg; 23.27 O; 7.5 Cl, etc.

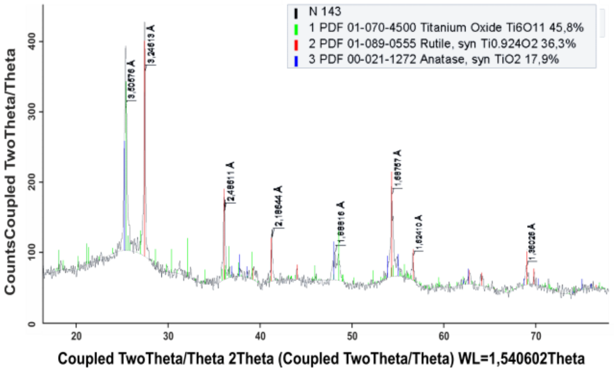


Figure 8 – X-ray phase analysis of residual cake

According to the results of the XRF analysis (see Figure 8), the cake consists of titanium oxides of various natures, wt. %: 45,8 Ti_6O_{11}; 36,3 $Ti_{0.924}O_2$; 17,9 TiO_2.

Thus, as a result of the experimental work on acid leaching of cake, the optimal conditions for the extraction of niobium and zirconium into solution were determined and are 25%HF +75%H_2SO_4, S:L ratio = 1:3, temperature = 90°C, duration of the leaching process = 120 minutes. At the same time, the extraction of niobium into solution reached 94.06%, and the extraction of zirconium and titanium into solution amounted to 84.95% and 32.35%, respectively.

Conclusions

We studied the material composition of the sublimates from dust chambers in titanium chlorinators. Chemical and X-ray fluorescence analyses determined the content of the main components, wt. %: 7.44 Ti; 6.5 Fe; 5.025 K; 4.899 Al; 2.539 Zr; 1.105 Na; 0.797 Nb; 0.359 Si; 0.214 Mg; 44.35 Cl; 24.053 O.

X-ray phase analysis found the presence of the following phases: erythrosiderite K_2 ($FeCl_5(H_2O)$), aqueous chloraluminite $AlCl_3(H_2O)_6$, rokühnite $FeCl_2(H_2O)_2$, sodium chloride NaCl, rutile $Ti_{0.924}O_2$, iron titanate $Fe_3Ti_3O_{10}$, zirconium chloride $ZrCl_2$ and niobium oxychloride $NbOCl_3$.

The study of the mineral structure of the DC sublimate sample using an electron probe microscope determined the presence of particles of niobium and zirconium oxychlorides.

Taking into account the water-solubility of the chloride phases in DC sublimates, experiments were conducted on its aqueous leaching at various parameters. The optimal conditions for aqueous leaching are S:L ratio = 1:8, leaching time = 1 hour, and temperature = 25°C. At the same time, the extraction of niobium, titanium, aluminum, iron and zirconium into the cake was 84.57%, 92.40%, 44.09 %, 13.70 %, and 50.45%, respectively.

We determined the quantitative elemental composition of a sample of niobium-containing cake obtained under optimal conditions of aqueous leaching, wt. %: 20.96 Ti; 11.8 Al; 3.91 Zr; 2.72 Fe; 2.06 Nb; 1.5 Si; 0.94 Na; 0.33 K; 0.15 Mg; 45.68 O; 6.8 Cl, etc.

Studies on the identification of the effect of HCl, HF, HF+H_2SO_4 on the degree of niobium extraction into the solution at a temperature of 25°C, the S:L ratio=1:3 and the agitation time of 2 hours showed the advantage of hydrofluoric acid and a HF+H_2SO_4 mixture. A mixture of 50% [18M HF] +50% [7M H_2SO_4] was chosen as the acidic reagent for cake leaching.

According to the results of the studies on the Study of the effect of various parameters on acid leaching of cake, optimal conditions for the extraction of niobium and zirconium into solution

were established: 25% [18M HF] +75% [7M H_2SO_4], S:L ratio = 1:3, temperature = 90 °C, duration of the leaching process = 120 minutes. Under these leaching conditions, the extraction of niobium, zirconium, and titanium into solution was 94.06%, 84.95% and 32.35%, respectively. X-ray fluorescence analysis of the residue, mass was performed, wt.%: 55.22 Ti; 4.47 Fe; 1.04 Al; 0.75 Zr; 0.26 Nb; 0.21 Mg; 23.27 O; 7.5 Cl, etc. Based on the results of the XRD analysis, the phase composition of the residue, mass, was determined; wt. %: 45,8 Ti_6O_{11}; 36,3 $Ti_{0.924}O_2$; 17,9 TiO_2.

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Ниобий мен цирконий ерітіндіге шығарылатын шаң камераларының возгондарын шаймалау процесін зерттеу

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ТҮЙІНДЕМЕ

Химиялық, рентгендік және микрозондтық талдау әдістерімен титан хлораторларының шаң камераларының возгондарының заттық құрамы зерттелді. Шаң камераларының возгондарының фазалық құрамын зерттеу нәтижесінде олардың сулы және сусыз хлоридті фазалардан тұратыны анықталды. Возгондарда ниобий екі түрде - оксихлорид және оксид түрінде болады. Цирконий хлоридті және оксихлоридті сипатқа ие. Шаң камералары возгондарын сумен шаймалау бойынша тәжірибелер жүргізіліп, процестің оңтайлы жағдайлары анықталды: Қ:С=1:8, шаймалау уақыты 1 сағат, температура 25 ^{0}С. Ниобий мен цирконийді ерітіндіге айналдыра отырып, сүзіндіні шаймалау үшін реагентті таңдау бойынша зерттеулер жүргізілді. Реагент ретінде HF + H_2SO_4 қышқылдарының қоспасынан тұратын ерітінді таңдалды. Ерітіндіге ниобий мен цирконийді алудың оңтайлы шарттары белгіленді: 25%[18m HF] +75%[7M H_2SO_4], Қ:С = 1: 3, температура 90 °C, шаймалау процесінің ұзақтығы 120 мин. Осы шаймалау жағдайында ниобийдің ерітіндіге өтуі 94,06%, цирконийдің 84,95%, титанның 32,35% болды. Сүзіндіні қышқылмен шаймалаудан қалған қалдықтың элементтік және фазалық құрамы анықталды.

Түйін сөздер: ниобий, шаң камераларының возгондары, шаймалау, қышқыл, ерітінді.

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Исследование процесса выщелачивания возгонов пылевых камер с извлечением ниобия и циркония в раствор

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АННОТАЦИЯ

Изучен вещественный состав возгонов пылевых камер титановых хлораторов методами химического, рентгеновского и микрозондового анализа. Исследования фазового состава возгонов пылевых камер показало, что объект в большей степени состоит из водных и безводных хлоридных фаз. Выявлены две формы присутствия ниобия - оксихлоридной и окисидной. Нахождения циркония в возгонах имеет хлоридную и оксихлоридную природу. Проведены опыты по водному выщелачиванию возгонов пылевых камер с определением оптимальных условий процесса: Т:Ж=1:8, время выщелачивания 1 часа, температура 25 ^{0}С. Проведены исследования по выбору кислотного реагента для выщелачивания кека с переводом ниобия и циркония в раствор. В качестве кислотного реагента для выщелачивания кека выбран раствор, состоящий из смеси $HF+H_2SO_4$. Установлены оптимальные условия извлечения ниобия и циркония в раствор: 25%[18M HF] +75%[7M H_2SO_4], Т:Ж = 1:3, температура 90 °С, продолжительность процесса выщелачивания 120 мин. При данных условиях выщелачивания, извлечение в раствор ниобия 94,06%, циркония 84,95%, титана 32,35%. Определен элементный и фазовый состав остатка от кислотного выщелачивания кека.

Ключевые слова: ниобий, возгоны пылевых камер, выщелачивание, кислота, раствор.

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