

## Recovery of Niobium Pentaoxide and Ammonium Sulfate from Titanium-Magnesium Production Waste

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### ABSTRACT

This study was aimed to investigate the development of a technology for the extraction of niobium pentaoxide and ammonium sulfate from titanium-magnesium production waste, specifically, the sublimates of dust chamber into concentrate in the form of niobium pentoxide. Optimal conditions for washing the niobium hydroxide precipitate by repulping with hot (60–70°C) distilled water, drying at 200°C for 6 hours were determined. The influence of temperature and duration of the process was studied. Optimal conditions for the dynamic desorption of niobium from saturated ionite (Purolite A100) was determined. The results further indicated that the optimum quantity of the solution of desorption with sulfuric acid was equal to 5.5% and ammonium oxalate was equal to 4%, while temperature and the flow rate of the desorbing solution was 22–27°C and 6 rpm, respectively. The study of the precipitation of niobium from sulfuric acid desorbates showed that the interaction of niobium ions with ammonia takes place at a low rate. The degree of precipitation of niobium hydroxide equal to 99.6% was achieved in 7 hours of agitation of the suspension at a temperature of 22–25°C.

**Keywords:** titanium residue, sludge, leaching, niobium chloride, niobium pentaoxide, purification, dust chamber, sublimation, desorption, ammonium sulfate.

### INTRODUCTION

Niobium (Nb) is a rare metal used in the production of high-strength low-alloy steel which is decrypted as HSLA (Sanz et al., 2022). Along with that, it is used in the industry of ferroniobium and it constituted more than 90% of niobium production. Niobium is considered as one of the most critical in the countries such as USA, EU and Japan. According to the study by The European Commission (European Commission, Directorate-General for Internal Market, Industry, Entrepreneurship and SMEs., 2017) niobium is included to the list of the most critical metals for EU together with 20 metals.

Niobium is distinguished by the fact that it combines a high level of corrosion resistance with low weight. Niobium is also used as a material for medical implants because of its high level

of biological compatibility. Niobium pentoxide is used as a catalyst in the chemical engineering. Therefore, the additional extraction of niobium from industrial waste is relevant (Nzeh et al., 2022).

Niobium is generally a companion element of titanium along with vanadium, zirconium and hafnium. Also, niobium is mainly hosted in titanium concentrates such as ilmenite and rutile (Bollaert et al., 2023). The reserves of residue in sludge accumulated at “Ust-Kamenogorsk Titanium and Magnesium Plant” JSC (“UKTMP” JSC, Kazakhstan) amount to 1,270 thousand tons (Shayakhmetov et al., 1998). These residues contain from 0.4% to 2% niobium, and it is almost similar to the niobium content in primary ores of pyrochlore carbonatites (Mitchell, 2015).

According to the analysis by “UKTMP” JSC the niobium content in the sublimates of dust chambers ranges between 0.26 and 0.6%. In

accordance with the technology, the sublimates from dust chambers are washed away with water. As a result, chloride pulp is discharged into acidic sewage. Subsequently, it is neutralized with lime milk (Khudaibergenov, 1996). These accumulated wastes from sludge collectors and sublimates from dust chambers might be a potential resource of niobium oxide and ammonium sulfate, which is used in alloying, capacitors and fertilizers, respectively.

An analysis of the available literature review shows that most studies have been conducted for high-grade niobium-containing raw materials (Shikika et al., 2020). Moreover, very few studies have been conducted on the recovery of niobium from titanium production waste (Baigenzhenov et al., 2021; Kudryavsky, 2004).

In the study of these authors (Utlarkova et al., 2016) a method for recovery niobium from dust chamber sublimates developed. This included their leaching with a solution of sulfuric acid and chloride distillation of cakes, subsequent hydrolytic treatment of sublimates in order to obtain a niobium-bearing product.

Generally, model solutions are used in niobium sorption in accordance with many studies (Ghosh et al., 2015). Therefore, most of these studies are of limited use in industry, since the leaching process solutions obtained in industry are complex in composition and consist of several metal ions and other compounds.

(Khabyev et al., 2022) investigated kinetic studies of the recovery of niobium from titanium chloride solution. The authors used two types of cation exchange resins KU-2-8H and Purolite-C104 respectively. As a result of sorption experiments, for both cationites, optimal conditions were at a concentration of HCl-3,0 M,  $m - 1,0$  g resin dose, duration – 3,5, temperature – at room condition. This study also demonstrated that, the kinetic data fitted well with the pseudo-second-order model ( $R^2 \geq 0.989$ ). In other studies, the authors studied (Utlarkova et al., 2023) niobium sorption from chloride solutions by using anion-exchange sorbents (Amberlite IRA-67, Purolite A-100, AB-17-8, and AN-2FN). Among them, Purolite A-100 was more suitable for Nb recovery and niobium recovery degree was 41.5%. According to its adsorption kinetic research, the most acceptable isotherm model was Langmuir and it fitted well with correlation coefficient  $R^2 = 0.999$ .

The literature review shows that research is currently being conducted on the sorption

extraction of niobium, some of which have been brought to the stage of pilot tests. However, the widespread introduction of ion exchange technology into hydrometallurgy is hindered by the complex composition of solutions containing rare metals. The selection of a sorbent for practical problem solving is an important step, since its modification affects the efficiency of niobium sorption. Therefore, modern scientific research is aimed at finding new sorbents to create a competitive technology for sorption extraction of niobium from technological and production solutions.

The purpose of the research lies in the search for a highly efficient ionite, the justification of its use and the study of the effect of impurity components on the kinetics of niobium sorption in complex technological solutions.

## MATERIALS AND METHODS

Studies on the recovery of niobium oxide and ammonium sulfate consisted of the following stages: preparation of raw materials, leaching followed by sorption, desorption, precipitation and filtration.

Materials and equipment. Precipitation of niobium hydroxide was carried out in glass thermostatically controlled reactors. In the experiments, a 25% ammonia solution (JSC Ural Chemical Reagents Plant) and a solution after desorption with a niobium concentration of  $6.59 \text{ g/dm}^3$  were used.

The method of the investigation. An ammonia solution was added to the initial solution while stirring until the required pH was reached. Then, mixing was turned off. After that, the niobium hydroxide precipitate was washed by repulping with water at a ratio of S:L = 1:8. Before filtration, the pulp was settled in order to obtain clarified and condensed parts.

The precipitation of particles from 3 to 100 microns in size obeys Stokes' law, and their precipitation rates can be determined by the formula

$$\omega = d^2 \cdot \frac{\rho_1 - \rho_2}{18\mu} \quad (1)$$

where:  $\omega$  is the precipitation rate, m/s;

$d$  is the particle diameter,

$\rho_1$  and  $\rho_2$  – density of solid and liquid phases,  $\text{kg/m}^3$ ;

$\mu$  is the viscosity of the medium,  $\text{Pa} \cdot \text{s}$ .

Particles with a diameter of 0.1 microns are practically not precipitated. Since  $p_1$  and  $p_2$  is a constant value under experimental conditions, the precipitation rate can be influenced by changes in the diameter of the particles  $d$  and the viscosity of the medium  $\mu$ .

In order to reduce the viscosity of the pulp, thickening and washing were carried out at a temperature of 40–45°C. In addition, the increased temperature helps to strengthen the pulp particles.

The effect of the final pH on the precipitation depth of niobium in the form of hydroxide was studied in the range of pH values of the pulp 5.5–9.5. (Braun et al., 2002). The filtration rate was determined at one time.

Methods of analysis. The X-ray phase analysis of the sludge was carried out on a diffractometer D8 Advance (BRUKER), Cu-K $\alpha$  radiation. The data processing of diffractogram data and calculation of interplane distances were carried out using EVA software. The decoding of samples and the search for phases were carried out according to the Search/match program using the Database of ASTM cards.

X-ray fluorescence analysis was carried out on a spectrometer with wave dispersion Venus 200 (Panalytical B.V., the Netherlands).

Chemical analysis of the samples was carried out on an optical emission spectrometer with inductively coupled plasma Optima 2000 DV (USA, Perkin Elmer).

## RESULTS AND DISCUSSION

From the experimental data (Table 1), it follows that the optimal pH value is precipitation equal to 9.0. Under these conditions, a high degree of extraction of niobium into the precipitate in the form of hydroxide and the highest filtration rate of the suspension are ensured.

The niobium hydroxide precipitate was washed by repulping with hot (60–70°C) distilled water. The washed precipitate was dried at 200°C for 6 hours. The moisture loss was 50%. Niobium hydroxide retained its amorphous form with partial crystallization (Figure 1).

Thus, the use of a 25% ammonia solution for the precipitation of niobium at a pH value of 9.0 medium makes it possible to obtain amorphous niobium hydroxide. Whereas, the degree of extraction of niobium showed that 99.4% of niobium passed into sediment.

### Determination of optimal conditions for the desorption of niobium with a solution of sulfuric acid

Currently, the requirements for the eco-friendly technologies have increased, reducing the amount of waste due to their processing to obtain commercial products.

In technologies based on ion exchange processes, sorption from solution to ionite and desorption of target components into solution are of particular importance. In this case, determination of the optimal desorption mode is a necessary condition for the effectiveness of the technology being developed for the extraction of niobium from dust chamber sublimates. For that reason, sulfuric acid (JSC ‘Base №1 of chemical reagents’, Russian Federation), and Purolite A100 ionite were used in the experiments. The niobium content in saturated ionite was 35.6 mg/g.

Niobium desorption was carried out under dynamic conditions. In this purpose chromatographic column with an internal diameter of 8.6 mm was used, the height of the ionite layer was 40 cm. Niobium was desorbed with a solution of sulfuric acid with a concentration of 5.5% in the presence of 4.4% ammonium oxalate. The transmission rate of the desorbing solution is 6 rpm. To calculate

**Table 1.** Influence of the pH value of the medium on the precipitation of niobium

Equilibrium values		The degree of extraction of niobium into the sediment, %	Filtration rate, m <sup>3</sup> /m <sup>2</sup> ·h
pH	Concentration of niobium in solution, g/dm <sup>3</sup>		
5.42	5.80	12.0	0.479
6.88	0.88	86.7	0.500
7.19	0.52	92.1	0.597
8.29	0.17	97.4	0.670
9.00	0.04	99.4	0.678
9.60	0.05	99.2	0.672

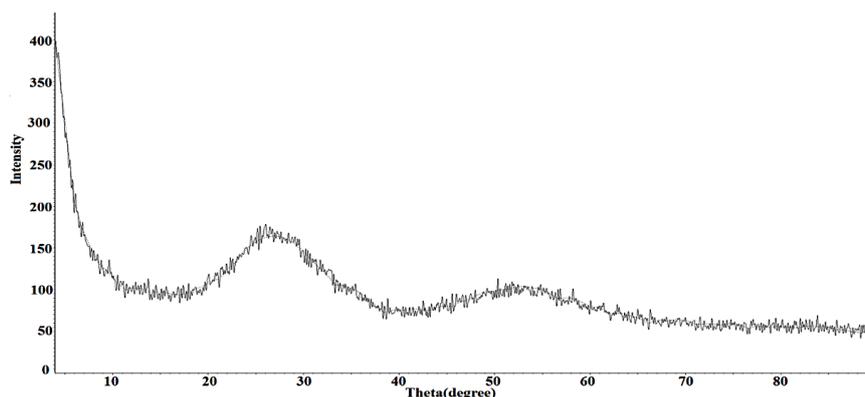


Figure 1. Diffractogram of niobium hydroxide

the process of niobium desorption from saturated ionite Purolite A100, a stage has been established that determines the speed of the entire process.

The study of the effect of the volume of the desorbing solution passed through the ionite and the duration of the process on the residual niobium content in the ionite showed that the amount of niobium entering the solution is proportional to the volume of the passed desorbent, the output curve is stretched, which corresponds to the strength of the bond of niobium with ionite. A slight increase in the desorption rate with an increase in the flow rate of the desorbing solution (Figure 2 and Figure 3) indicates a certain effect on the process of external diffusion.

For a small diffusion time, the approximation is valid (Kokotov et al., 1986):

$$F = \frac{A}{W} \sqrt{\frac{Dt}{\pi}} \quad (2)$$

where:  $W$  is the volume of the ionite,  
 $A$  is the transfer surface.

When processing the experimental data shown in Figure 2 and Figure 3, a more convenient equation for technological calculations was obtained, showing the relationship between the desorption time  $t_{des}$  (min) and the residual content of niobium in ionite ( $C$ ) with expressed as:

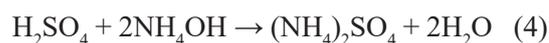
$$t_{des} = k \frac{C^0 - C(855.3 + 63V)}{VC} \quad (3)$$

where:  $C^0$  and  $C$  – the content of niobium ions in ionite at  $t = 0$  and  $t = t_{des}$ , mg-eq/dm<sup>3</sup>,  
 $k$  – proportionality coefficient,  
 $V$  – linear flow rate, m<sup>3</sup>/h.

Thus, optimal conditions for the dynamic desorption of niobium from saturated Purolite A100 ionite were determined: a desorbing solution containing 5.5% sulfuric acid and 4% ammonium oxalate; temperature 22–27°C, the flow rate of the desorbing solution is 6 rpm. Precipitation of niobium hydroxide from a sulfuric acid solution.

The desorbate at room temperature 23–25°C was treated with concentrated ammonia solutions and the resulting suspension was stirred at a speed of 600 rpm until pH 9.0 was reached. At the same time, the concentration of niobium in the mother liquor was 0.04–0.05 g/dm<sup>3</sup>. Then the suspension was filtered, the precipitate was washed.

It is established that the precipitation of niobium begins only after the neutralization of sulfuric acid by reaction (4).

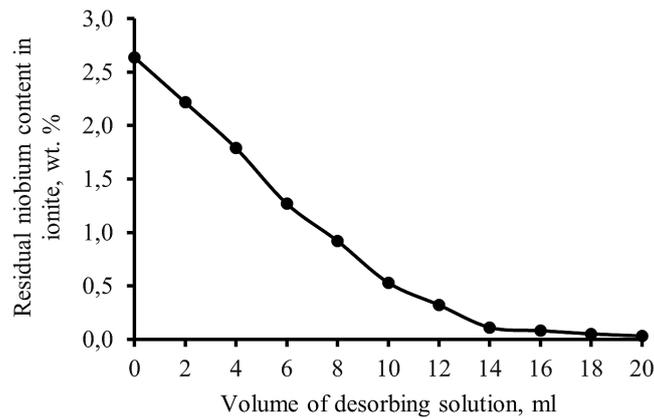


Excess ammonia suppresses the hydrolysis of ammonium sulfate, and the reaction becomes irreversible.

Precipitation of niobium hydroxide occurs at a low rate (Figure 4). The process ends completely after 7 hours of agitation suspension. The resulting precipitate was dried at 105°C and calcined at 900°C.

Thus, the study of the process of precipitation of niobium from sulfuric acid desorbates showed that the interaction of niobium ions with ammonia takes place at a low rate. The degree of precipitation of niobium hydroxide equal to 99.6% is achieved in 7 hours of agitation of the suspension at a temperature of 22–25°C.

The purpose of conducting large-scale laboratory tests of the developed technology for recovery niobium from titanium-magnesium



**Figure 2.** Dependence of the residual niobium content in ionite on the volume of the desorbing solution

production waste is to clarify and process the parameters of technological conversions.

The test materials were the sublimate of dust chambers presented by “UKTMP” JSC. The contents of the main components are given in Table 2.

The sublimate of dust chambers differs from the sludge accumulator precipitation by a high content of aluminum, iron, niobium and a low content of silicon. In this regard, it became necessary to clarify the modes of leaching niobium into the solution for sorption.

Leaching was carried out in glass cups with a volume of 2 dm<sup>3</sup>. Dust chamber sublimates were introduced into the hydrochloric acid solution in the ratio L:S = 1:5 and the pulp was stirred for 2 hours at a temperature of 25°C. The pulp was filtered and the resulting solution was analyzed for the content of niobium, aluminum and iron.

The results of the study of the effect of hydrochloric acid concentration and leaching indicators are shown in Table 3.

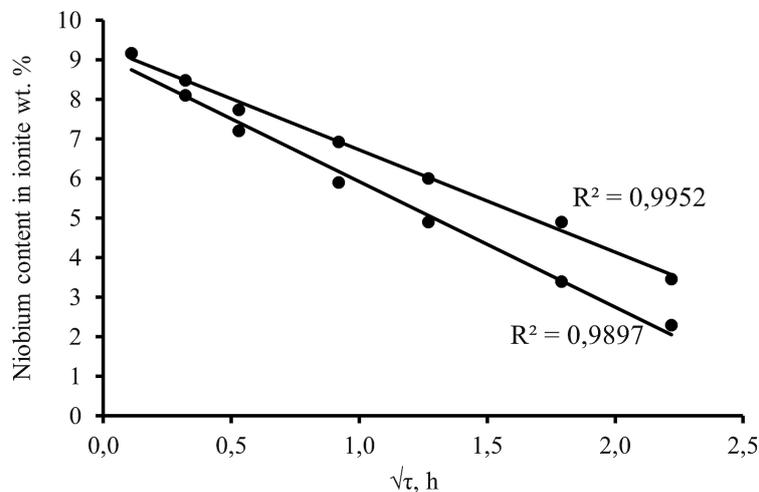
The obtained results confirmed that the concentration of hydrochloric acid equal to 20% allows achieving a high degree of niobium extraction in solution.

Niobium sorption was carried out under dynamic conditions at the installation shown in Figure 5.

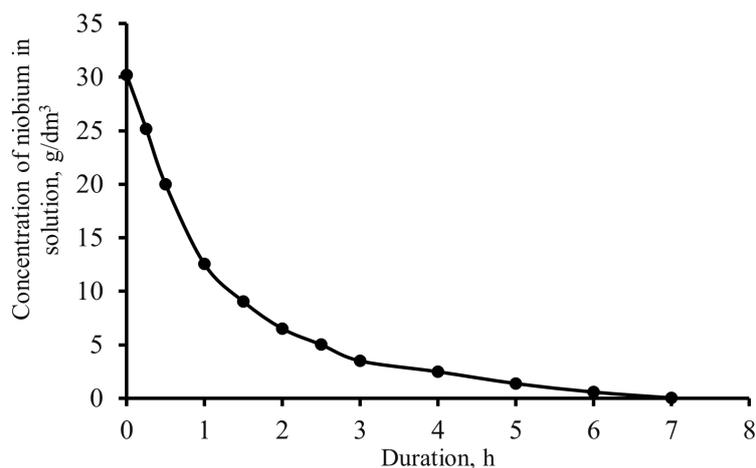
During the tests, a column with an internal diameter of 60 mm and a filter layer height of 290 mm was used. The transmission rate of the solution was 29 cm·h<sup>-1</sup>.

The niobium content in saturated Purolite A100 ionites is 35.6%. Desorption was carried out with a solution containing 5.5% sulfuric acid and 4% ammonium oxalate. The linear velocity of the solution is 0.3 cm/min.

The niobium content in the resulting solution is 30.12 g/dm<sup>3</sup>. Precipitation of niobium hydroxide was carried out with a concentrated ammonia solution at room temperature. The duration of agitation of the suspension was 7 hours. The filtered and washed precipitate was dried at 105°C to a



**Figure 3.** Dependence of the residual niobium content in ionite on the duration of the desorption process



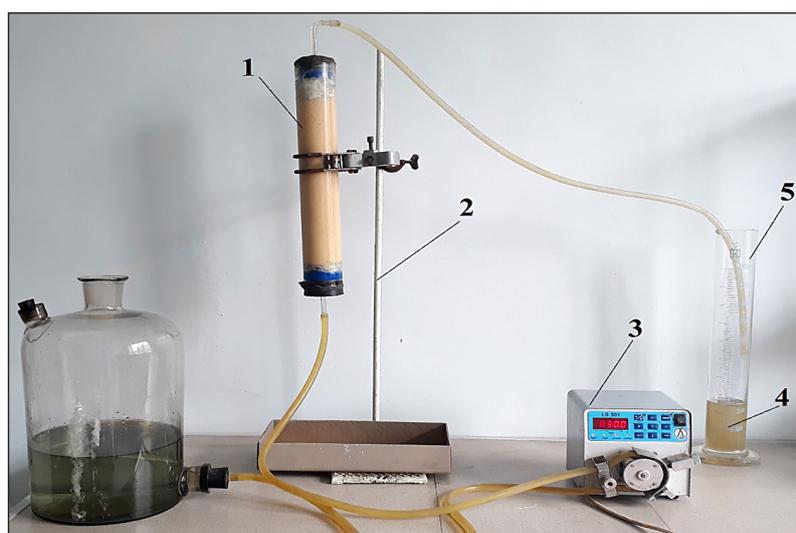
**Figure 4.** Dependence of the residual concentration of niobium in solution on the duration of interaction with ammonia

**Table 2.** The content of the main components of the dust chamber sublimates, wt. %

Ti	Nb	Ca	Mg	Al	Si	Fe	Mn	V	Cl
2.18	0.78	0.11	0.06	7.51	0.11	4.04	0.08	0.01	46.23

**Table 3.** Effect of hydrochloric acid concentration on niobium, aluminum and iron from dust chamber sublimates

Concentration HCl, %	Volume of filtrates, sm <sup>3</sup>	Content in solution, g/dm <sup>3</sup>			Extraction into solution, %		
		Nb	Al	Fe	Nb	Al	Fe
15	1419	0.98	14.16	6.91	59.6	89.2	81.3
20	1380	1.56	15.59	8.13	92.1	95.5	92.6



**Figure 5.** Installation for conducting pilot tests of the developed technology:  
 1 – sorption column; 2 – retort stand; 3 – peristaltic pump;  
 4 – solution; 5 – dimensional cylinder

constant weight and calcined at a temperature of 900°C for 2 hours.

The resulting niobium pentoxide (Figure 6) was analyzed by spectral analysis (Table 4). The content of the main substance is 99.6%.

**Investigation of the possibility of obtaining ammonium sulfate from the mother liquor after precipitation of niobium oxide**

According to (Hadlocon et al., 2015) ammonium sulfate is produced by wet method. At the same time, the presence of excess sulfuric acid in an amount of 5–7% in the solution of ammonium sulfate is necessary to prevent ammonia losses during evaporation.

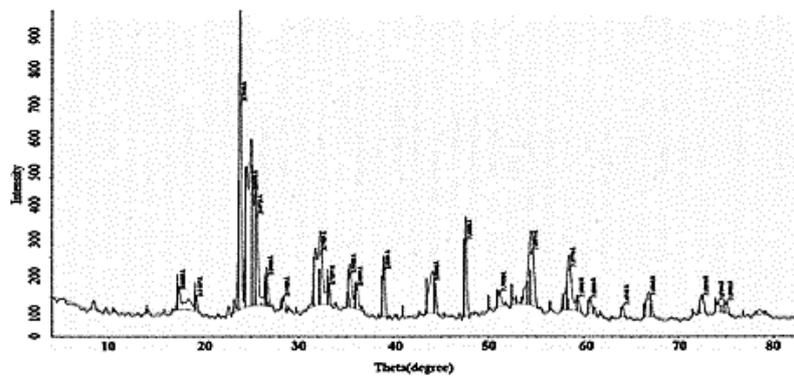
Sulfuric acid was injected into the mother solution with pH 9 in the required amount and evaporated at 110°C. During the formation of ammonium sulfate crystals, separation from the mother liquor was carried out on a centrifuge. The resulting ammonium sulfate was dried at a temperature of 110°C to a constant weight.

X-ray phase analysis of the obtained sample showed that ammonium sulfate is formed under the studied conditions

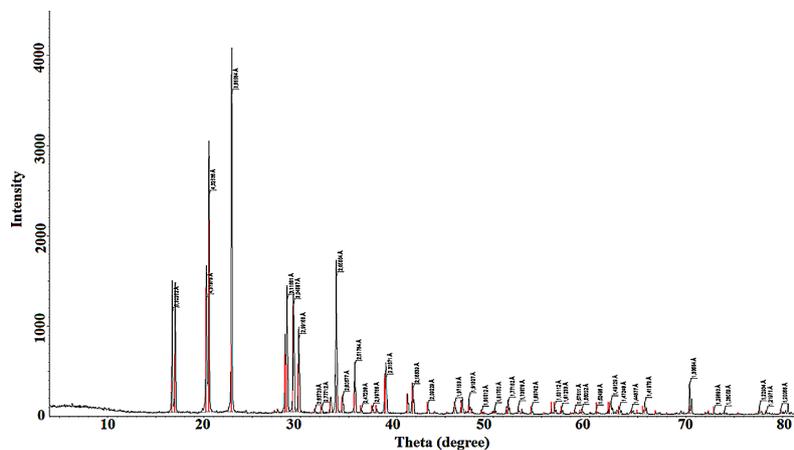
Ammonium sulfate is used in agriculture as a nitrogen fertilizer. The nitrogen content is 20.5–21.0%. By its physical properties, ammonium sulfate is better than ammonium nitrate – it is not explosive and much less hygroscopic. Thus, laboratory tests of the developed

**Table 4.** Content of controlled impurities, ppm

Ti	Al	Zr	V	Co	Sn	Mn	Mg
< 3	< 4	< 1	< 2	< 0,2	< 1	< 1	< 1
Si	Fe	Cr	Ni	Mo	Ca	Cu	Pb
< 3	< 1	< 1	< 0,5	< 3	< 3	< 0,5	< 1



**Figure 6.** Diffractogram of niobium pentoxide



**Figure 7.** Diffractogram of ammonium sulfate

technology for recovery niobium from titanium–magnesium production waste have confirmed the results of laboratory studies. The technological parameters of the main processing have been worked out and refined.

## CONCLUSIONS

Optimal conditions for washing the niobium hydroxide precipitate by repulping with hot (60–70°C) distilled water, drying at 200°C for 6 hours. Moisture loss was 50%. Niobium hydroxide retained its amorphous form with partial crystallization. The use of a 25% ammonia solution for the precipitation of niobium at a pH value of 9.0 allows to obtain amorphous niobium hydroxide. At the same time, the degree of extraction of niobium into the sediment is 99.4%.

The results of large-scale laboratory tests were as follows:

- optimal conditions for the dynamic desorption of niobium from saturated Purolite A100 ionite have been determined: a desorbing solution containing 5.5% sulfuric acid and 4% ammonium oxalate; temperature 22–27°C, the flow rate of the desorbing solution is 6 rpm. Precipitation of niobium hydroxide from a sulfuric acid solution.
- a study of the precipitation of niobium from sulfuric acid desorbates showed that the interaction of niobium ions with ammonia occurs at a low rate. The degree of precipitation of niobium hydroxide equal to 99.6% is achieved in 7 hours of agitation of the suspension at a temperature of 22–25°C.

Large-scale laboratory tests of the developed technology for recovery niobium from titanium – magnesium production waste confirmed the results of laboratory studies. The technological parameters of the main processing have been worked out and refined.

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