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THE TECHNOLOGY OF EXTRACTION AND ENRICHMENT OF SCANDIUM FROM URANIUM-PHOSPHORUS-RARE EARTH CONCENTRATE

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The paper presents the results of pilot tests of scandium extraction technology from uranium-rare-earth phosphorite to obtain high-purity scandium oxide Sc_2O_3. It is shown that scandium in phosphorites is accompanied by thorium and rare earth elements (REE), which requires the development of a technology for the complex processing of raw materials. Scandium with a purity of 99.0% was obtained from a concentrate of various degrees of enrichment and shavings of scandium alloys by dissolving them in sulfuric acid, extraction, and selective precipitation with oxalic acid. In the process of testing, scandium oxides were obtained with a purity of 99.0; 99.9, and 99.99%, suitable, for example, for the production of alloys based on magnesium for medical purposes.

INTRODUCTION

Scandium is a diffuse rare metal that is used as an alloying element for alloys based on aluminum, iron, and magnesium. The extraction of scandium in the world remains limited since it does not have its minerals and is found as an associated element in the minerals of titanium, zirconium, uranium, in oxide or phosphate compounds [1]. Metal scandium and aluminum-scandium alloys are used in aviation and space technology.

Sources of scandium in Ukraine are the following:

– zircon and ilmenite concentrate;

– brown coal;

– uranium raw materials;

– technogenic waste of alumina production (red mud).

Scandium reserves in Ukraine are the largest in Europe. The content of scandium in minerals and ores ranges from 0.001 to 0.02%.

The value of scandium for modern technology is determined by national interests, for example, in the United States there is a federal strategy for ensuring the supply of critical minerals, incl. scandium. The price of scandium reaches $100/kg [2].

Small volumes of production (only 18.9 t of scandium were obtained in 2018) determine its high cost. The amount of scandium used depends on its purity and cost. For the production of master alloys and alloys with aluminum grades 01570 and 01521, the purity of the metal must reach 99% [3].

In the 21st century, new areas of application for magnesium alloys with scandium with a purity of at least 99.98% began to develop. The content of impurities is not more than 0.001% for thorium, strontium, beryllium, cadmium, mercury, and chromium; 0.002% – for iron, copper, and nickel. The content of scandium can range from 5 to 15% since it is precisely these limits that provide high ductility and strength, a grain size of less than 3.0 μm, good shaping properties, and high corrosion resistance. The biological compatibility of the alloy with the composition of blood and blood vessels makes it possible to manufacture a wide range of products (screws, bolts, stents, plates, brackets, tubular meshes, markers, and catheter windings). The low corrosion rate of the alloy at the level of 2 mg/(cm^2·day) ensures the necessary durability of products made from it. Over time, the alloy dissolves in the blood without negative consequences for human health [4].

High-purity scandium can be obtained in the process of extraction isolation and its purification from accompanying impurities, incl. REE, uranium, thorium, and radioactive products of their decay, which are part of phosphorite [7–9].

The purpose of this work is to develop, test and optimize a pilot technology for processing complex uranium-rare-earth phosphorite with a scandium content of 0.02%, obtaining high-purity scandium compounds from it with the release of thorium, radium, polonium, and actinium into a total concentrate for disposal; recycling of reagents, as well as 40…60% scandium concentrate and metal chips and Al-Sc alloys.

MATERIALS AND METHODS

For pilot testing of the processing of phosphorus raw materials with the production of high-purity scandium oxide, the uranium-rare earth concentrate "Melovoye" of the following composition was used (Table 1).

Table 1

Chemical and mineralogical composition of ore concentrate

Component	U	P_2O_5	ΣTR_2O_3	CaO	FeS_2	Sc	F	Th	Mineralogical composition		
									francolite	pyrite	clay
Content, %	0.188	20.8	0.79	36.6	14.4	0.02	1.6	0.1	65	15	20

Leaching of the concentrate was carried out with melange – a mixture of nitric and sulfuric acids in a ratio of 1:1. The primary concentration of scandium from the nitrate-phosphate solution (NPS) after leaching the

concentrate with melange was carried out by precipitation with ammonia to pH = 0.9 and iron to pH ≤ 1.35. Uranium, thorium, scandium, REE, and radioactive isotopes passed into the collective chemical concentrate (CCC).

The quality of CCC was determined by the content of uranium, total REE (ΣTR_2O_3), thorium, phosphorus, scandium, and impurities (Fe, Al, Ca). After filtration and washing of CCC, it was leached with a solution of 45% HNO_3 under various technological conditions. In the course of the research, the yield and chemical composition of the solid and liquid phases were determined. Experimental tests were carried out according to the technological scheme shown in Fig. 1.

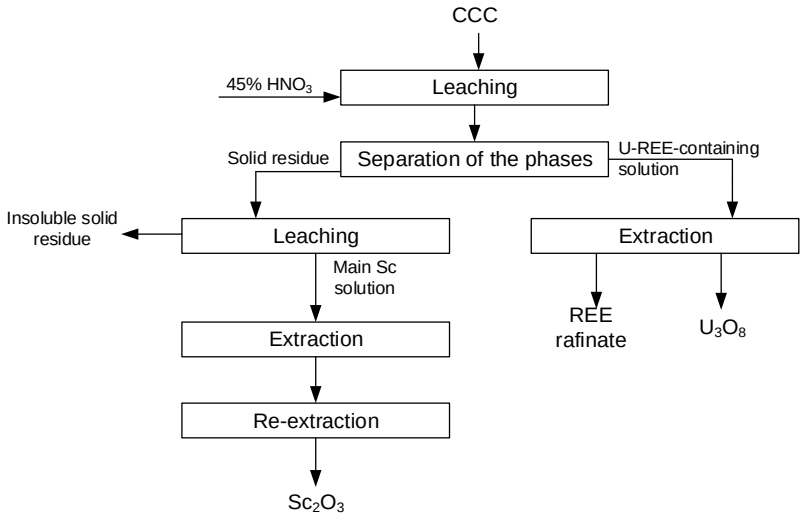

Fig. 1. Flow sheet of CCC enrichment

Testing of the processing technology for 40…60% scandium concentrates was carried out according to the technological scheme shown in Fig. 2.

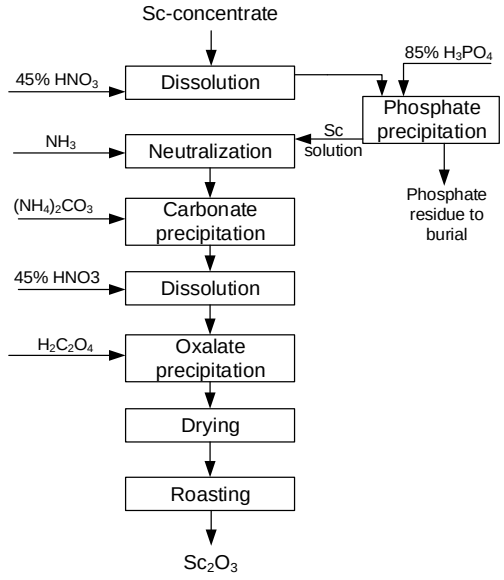

Fig. 2. Flow sheet for the processing of scandium concentrates

Processing of metal waste (shavings) of aluminum alloys with a scandium content of 0.2% was carried out using sulfuric acid, followed by purification of scandium solutions by extraction and utilization of aluminum sulfate in the production of alumina alum. In the course of the study, the optimal parameters of each process were studied.

Impurity metal oxides were analyzed by the volumetric method, REE oxides were analyzed by the spectral method. The radioactivity of the products was measured by the X-ray spectral method. The scandium content in the intermediates was determined by the atomic absorption method.

RESULTS AND DISCUSSION

In the course of the research, the conditions for the primary concentration of uranium, REE, thorium, and scandium were determined, with their transfer to the CCC:

– pH = 1.3…1.4;
– temperature ≤ 45 °C;
– deposition time – 0.5 h;
– electronic moving force (EMF) – 150…160 mV;
– consumption of iron chips – 31.8 kg/t;
– residual content of uranium – 10 mg/l;
– NPS output – 2.44 m^3/t;
– CCC yield – 43.8 kg/t.

The process of transferring elements from the ore solution to the CCC is described by the equations:

$$UO_2(NO_3)_2 + Fe + 2H_3PO_4 \rightarrow U(HPO_4)_2 + Fe(NO_3)_2 + 2H_2O; \quad (1)$$

$$TR(NO_3)_3 + Fe + H_3PO_4 \rightarrow TRPO_4 + FePO_4 + 3HNO_3; \quad (2)$$

$$Sc(NO_3)_3 + Fe + H_3PO_4 \rightarrow ScPO_4 + FePO_4 + 3HNO_3. \quad (3)$$

Extraction of REE from solution to concentrate equals 83.6%; uranium – 99.4%; phosphorus – 15%; scandium – 99.5%. The composition of the CCC is given in Table 2.

Table 2

Chemical composition of CCC

Component	ΣTR_2O_3	U	P_2O_5	Fe	CaO	F	Th	Sc	C	H_2O
Content, %	11.73	3.97	38.7	10.1	5.20	2.7	0.4	8.4	8.54	43.5

During the tests, the optimal conditions for CCC leaching were determined:

– hydraulic module on pulping – 1:3;
– temperature – 45…50 °C;
– opening time – 1.0 h;
– mixing time – 2.0 h;
– excess acidity in HNO_3 – 100…120 g/l;
– EMF – 700 mV.

The leaching process can be described by the following equations:

$$U(HPO_4)_2 + 4HNO_3 \rightarrow UO_2(NO_3)_2 + 2H_3PO_4 + 2NO_2; \quad (4)$$

$$Th(HPO_4)_2 + 4HNO_3 \rightarrow Th(NO_3)_4 + 2H_3PO_4. \quad (5)$$

The consumption of nitric acid was 36.5 kg/t, and the extraction of uranium, ΣTR_2O_3, and scandium from the concentrate into solution was 98.2; 98.4%, and 12.0%, respectively. The output of the solution was 0.16 m^3/t. Complete dissolution of the insoluble residue is unacceptable, because. the concentration of phosphorus can reach 130 g/L, iron – 50 g/L, which will make it impossible to extract uranium. The composition of the solution for extraction is given in Table 3.

Table 3

Composition of the extraction solution

Component	ΣTR_2O_3	U	Th	Sc	P_2O_5	CaO	Fe
Content, g/L	18-27	6…9	0.7	0.04	60	30	12

The yield of insoluble residue was 16…17 kg/t, as a result, the concentration of scandium in the solid phase increased to 0.4%, and most of the radioactive elements quantitatively passed into the solution. The resulting NPS was sent to the extraction purification of uranium to obtain a concentrate of uranium oxide, and the extraction raffinate was sent to the sorption separation of the REE concentrate. Phosphorus, after the release of rare earth elements, returned to the production of fertilizer. The scandium-enriched insoluble precipitate after the first leaching was leached with 45% nitric acid. The composition of the solid phase after leaching is given in Table 4.

Table 4

Chemical composition of the solid phase after leaching

Component	ΣTR_2O_3	U	P_2O_5	CaO	Fe_2O_3	Th	Sc	SiO_2	HNO_3	Al
Content, %	6…10	0.2…0.6	2.7…3.5	0.4	30…50	10…15	1…2	0.7–…1.5	300	0.08

Radioactivity i.r. was $22.94 \cdot 10^3$ Bq/g. Liquid phase composition after the second leaching i.r. nitric acid is given in Table 5.

Table 5

Chemical composition of the liquid phase after the second leaching

Excess acidity, g/L	Content, g/L		Extraction of scandium, %			
	Sc	U	from residue	% of CCC	from CCC	total
310	0.115	1.5…2.0	93.0	83.0	12.0	95.0
300	0.116	1.5…2.0	93.0	83.0	12.0	95.0
250	0.116	1.5…2.0	92.8	82.8	12.0	94.8
230	0.116	1.5…2.0	92.8	82.8	12.0	94.8
220	0.090	1.5…2.0	72.0	64.3	12.0	76.3
200	0.084	1.5	67.2	60.0	12.0	72.0
300	0.120	2.0	–	83.0	12.0	95.0

The optimal process conditions are:

– excess acidity 250 g/l;
– temperature 80 °C;
– leaching time 8 h;
– solid to liquid ratio (S:L) before leaching – 1:5.

The yield of insoluble residue after the second leaching was ≤ 3 kg/t. The main component of the insoluble residue (i. r.) is iron phosphate, which, after washing, is sent for burial, and the radioactivity exceeded the allowable rate of 3.7 Bq/g. Thorium and part of the radioactive impurities remain in the i. r., while scandium is absent.

The process of the final dissolution of the insoluble residue with nitric acid can be described by the following equations:

$$U(HPO_4)_2 + 4HNO_3 \rightarrow UO_2(NO_3)_2 + 2H_3PO_4 + 2NO_2\uparrow; \quad (6)$$

$$Th(HPO_4)_2 + 4HNO_3 \rightarrow Th(NO_3)_4 + 2H_3PO_4; \quad (7)$$

$$FePO_4 + 3HNO_3 \rightarrow Fe(NO_3)_3 + H_3PO_4; \quad (8)$$

$$ScPO_4 + 3HNO_3 \rightarrow Sc(NO_3)_3 + H_3PO_4. \quad (9)$$

Radioactive elements almost completely passed into the nitric acid solution. To extract scandium from the solution, extractants of the following compositions were selected.

Composition 1: diisooctylmethylphosphonate (DiOMF) – 3%; trialkylmethylammonium (TAMA) – 5%; kerosene – 92%.

Composition 2: tributyl phosphate (TBP) – 10%; heteroradical phosphine oxide (FOR) – 30%; carbo-ammonia salts – 60%.

Composition 1 was used in stages I and III of extraction, and composition 2 – in stages II and IV. The chemical composition of the solution after leaching is given in Table 6.

Table 6

The composition of the solution after leaching

Component	ΣTR_2O_3	U	Th	Sc	P_2O_5	Fe	HNO_3
Content, g/L	≤12.0	≤0.8	≤5.0	≤0.1	≤10.0	60	≤300

During the experiments, the optimal parameters of each extraction queue were determined (Fig. 3).

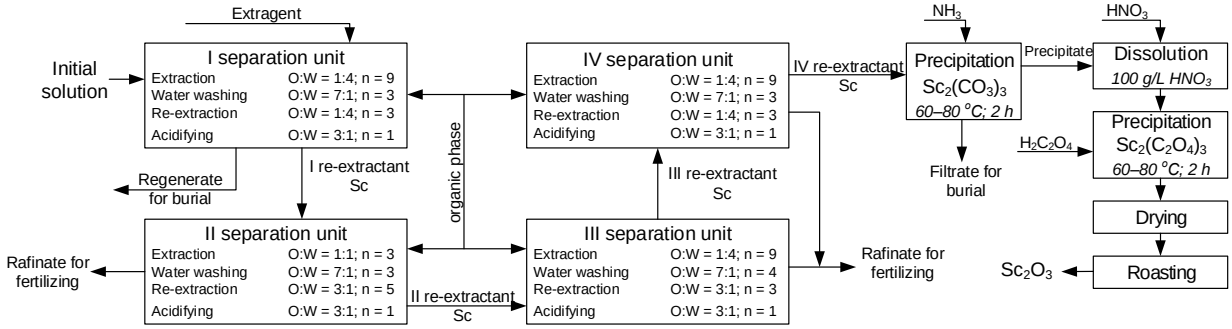

Fig. 3. Flow sheet for the isolation and purification of scandium by the extraction method

The purpose of the first purification extraction is to extract uranium and radioactive isotopes from the solution and convert the scandium into a raffinate. The purpose of the second stage of extraction is to isolate scandium and obtain pure fertilizer reagents. The purpose of the third stage is to deeply purify scandium from radioactive impurities. The raffinate of the third stage of extraction was sent to the extraction of the fourth stage, where it was saturated with scandium and, after washing with distilled water, was sent to the re-extraction of 20% $(NH_4)_2CO_3$. The Sc concentration in the carbonate re-extract reached 10 g/L. The Sc carbonate re-extract was treated with ammonia to pH = 12 to convert scandium from the complex compound to an insoluble carbonate. For complete settling and filtration, the suspension was heated to 80 °C and cooled to 40 °C. The dissolution of scandium carbonate 47% HNO_3 occurs most effectively at an excess acidity of 90±10 g/L.

$$Sc(NO_3)_3 + 3H_2C_2O_4 \rightarrow Sc_2(C_2O_4)_3\downarrow + 6HNO_3. \quad (10)$$

Process temperature – 80 °C, duration – 4 h. Oxalic acid was used in dry form with a consumption of 4 kg per 1 kg of scandium. The precipitate was dried in quartz cuvettes at 120 °C, and calcined at 750 °C for 16 h.

Extraction on all separation units is carried out in countercurrent at organic to water phases ratio (O:W) = 1:1. Water washing of the saturated organic phase is carried out at a ratio of 5:1. Saturation of the water phase by nitric acid is carried out until it is saturated with 100 g/L. Re-extraction of the organic phase was carried out with a 20% ammonium carbonate solution. After the fourth separation unit, scandium carbonate is a pure product, from which scandium oxide is obtained after oxalate treatment of scandium nitrate solution.

To isolate scandium from a 40…60% concentrate, a technological scheme was developed, shown in Fig. 2. The resulting product was 99% Sc_2O_3 in quality. The content of the main impurities in the finished product is shown in Table 7.

Table 7

Impurity content in Sc_2O_3

Component	Fe_2O_3	Al_2O_3	P_2O_5	CaO	CuO	SiO_2	MgO	Y_2O_3	ZrO_2	TiO_2
Content, %	< 0.05	< 0.01	< 0.02	< 0.05	< 0.01	< 0.05	< 0.01	< 0.05	< 0.10	< 0.05

Further purification of scandium oxide up to 99.99% is possible using known methods, for example, using formic acid, which forms a precipitate of scandium formicate at an excess acidity of 80 g/L [5].

Processing of 40% scandium concentrate using 45% nitric acid showed that the optimal process parameters are: S:L = 1:10, temperature 90 °C, time 1 h, HNO_3 concentration 500…700 g/L. Analysis of the aqueous phase showed the presence of Al, Ti, Zr, Fe, Mn, Ca, Si, and P_2O_5 impurities. The scandium concentration averaged 30 g/L.

The dissolution reaction of scandium oxide is described by the equation:

$$Sc_2O_3 + HNO_3 \rightarrow 2Sc(NO_3)_3 + 3H_2O. \quad (11)$$

To precipitate impurities, 85% phosphoric acid was used according to the reaction:

$$3Me(NO_3)_4 + H_3PO_4 \rightarrow Me_3(PO_4)_4 + 12HNO_3, \quad (12)$$

where Me – Ti, Zr.

The consumption of phosphoric acid was 2 L/m^3 of solution. The scandium remained in the solution. The solid phase of phosphates contained 2…3% scandium and was stockpiled for future processing. The solution was neutralized with a 20% ammonia solution for 30 min to pH = 1, then dry ammonium carbonate was added to its content in the solution of 2…3 g/L. This made it possible to isolate scandium in the form of $Sc_2(CO_3)_3$ crystals within 40 min. Thorium and part of the alkaline earth elements remain in the solution. The reaction can be described by the equation:

$$Sc(NO_3)_3 + 3(NH_4)_2CO_3 \rightarrow Sc_2(CO_3)_3 + 6NH_4NO_3. \quad (13)$$

When the concentration of carbonate ions exceeds 5 g/L, scandium carbonate passes into a soluble carbonate complex, which is undesirable.

After scandium carbonate is dissolved in nitric acid at an excess acidity of 100 g/L and scandium is precipitated with oxalic acid at 80 °C for 4 h, scandium oxalate is precipitated according to the reaction:

$Sc(NO_3)_3 + H_2C_2O_4 \rightarrow Sc(C_2O_4)_3\downarrow + 6HNO_3$. (14)

The precipitate was washed three times with a 3% oxalic acid solution and dried at 100…120 °C. After calcination, which was carried out in two stages (for 6 h at 500 °C and 10 h at 700 °C), scandium oxide was obtained by the reaction:

$Sc(C_2O_4)_3 + O_2 \rightarrow Sc_2O_3 + 5CO_2\uparrow + CO\uparrow$. (15)

The resulting product had a purity of 99% and was sent to the production of 2% aluminoscandium literature according to the technology described in [6].

The chemical composition of the studied shavings of aluminoscandium alloy grade 01570 is as follows, %: Al is the base; Mg – 6.5; Mn – 0.5; Zr – 0.1; Sc – 0.28; Cu – 0.1; Si – 0.2; Fe – 0.3.

The dissolution of the chips was carried out with nitric and sulfuric acids, and alkali. As is known, nitric acid does not completely dissolve chips, which leads to scandium loss [1]. In this case, it is necessary to process a nitrate solution of aluminum and magnesium. Therefore, alkaline and sulfuric acid methods of dissolution were investigated.

The alkaline method is designed for the dissolution of aluminum in an excess of NaOH solution [1]. This method is more efficient than the use of nitric acid, because aluminum is completely transferred into the solution, and scandium remains in the precipitate. The presence of aluminum makes it possible to obtain liquid products, for example, ammonia-aluminum alum, which has a wide range of applications.

The dissolution of chips in sulfuric acid is described by the equation:

$2Al + 3H_2SO_4 + 18H_2O \rightarrow Al_2(SO_4)_3 \cdot 18H_2O + 3H_2\uparrow$.(16)

The interaction of aluminum alloy shavings with sulfuric acid makes it possible to convert aluminum and scandium into solution in 3 h. An extractant of the composition 10% FOR, 5% TBP, and 85% kerosene was used for the extraction of scandium.

Based on the results of the experiments, a technological scheme for processing alloy shavings with the extraction of scandium was proposed (Fig. 4).

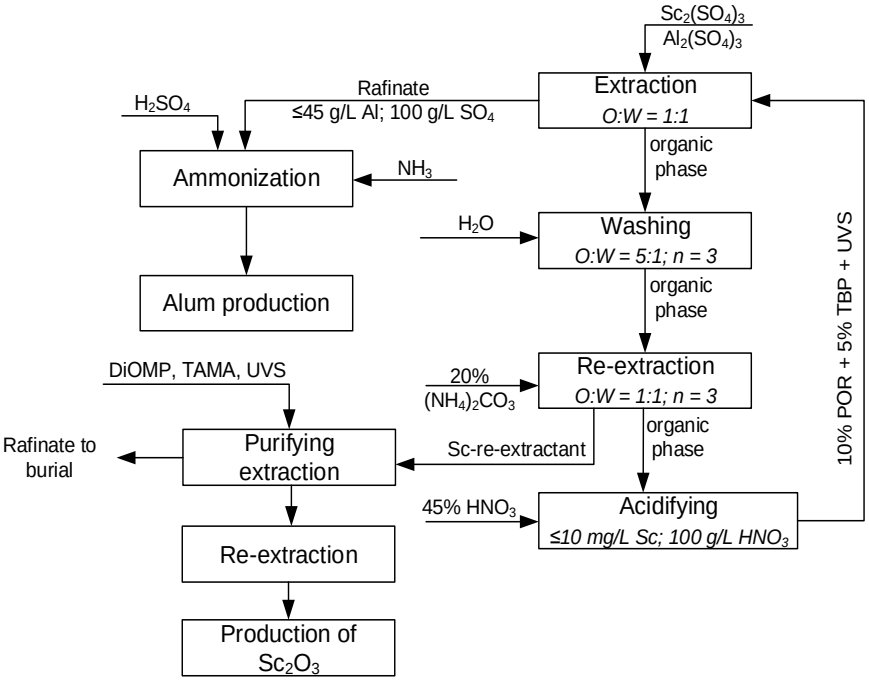

Fig. 4. Flow sheet for processing chips of aluminum-scandium alloys

The chemical composition of the scandium sulfuric acid solution was as follows, g/l: Sc – 0.05; Al – 45.0; Mg – 3.6; Th – 0.007; H_2SO_4 – 100. The content of radioactive impurities in the solution reached, Bq/L: ^{210}Po – 0.7…2.1; ^{226}Ra – 2.2; ^{227}Ac – 0.7. The contact time at each stage of extraction is 5 min, and the re-extraction is 15 min. The phase separation time is 60 s. The obtained alum corresponded to the standard OST 95-28-79, their yield was 1.6 t per 1 t of chips.

A.I. Shabanov, V.A. Spitsin, and A.I. Silkina took part in the work.

CONCLUSIONS

1. Pilot tests of the complex technology for the enrichment of scandium raw materials were carried out. The optimal technological parameters for the processes of separation of valuable components and their purification from radioactive impurities Ra, Po, Ac, and Th have been determined.

2. The results obtained made it possible to develop a technological process for the complex processing of uranium-phosphorus-rare earth concentrate, consisting of the following stages:

– precipitation of scandium in the form of phosphate at pH = 1.4;

– the selective dissolution of U, Th, and REE in 45% HNO_3;

– extraction purification of Sc from U, Th products of their decay.

3. Studies have been carried out on the processing of metal shavings of an alloy of aluminum with scandium. A technological scheme with the use of sulfuric acid, extraction, and concentration of scandium with the production of alumina alum is proposed. It has

been shown that scandium can be successfully purified using an extractant of 10% FOR and 5% TBP in kerosene, while its content in the raffinate does not exceed 10 mg/L.

4. Studies have been carried out on the processing of 40…60% scandium concentrate to obtain scandium oxide with a purity of 99.0%. It is shown that the method of scandium oxalate purification makes it possible to obtain Sc_2O_3 with a purity of 99.0%.

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ТЕХНОЛОГІЯ ВИЛУЧЕННЯ ТА ЗБАГАЧЕННЯ СКАНДІЮ З УРАН-ФОСФОР-РІДКІСНО-ЗЕМЕЛЬНОГО КОНЦЕНТРАТУ

А.П. Мухачев, Д.О. Єлатонцев, О.А. Харитонова

Викладено результати дослідно-промислових випробувань технології вилучення скандію з уран-рідкісно-земельного фосфориту з отриманням високочистого оксиду скандію. Показано, що у фосфоритах скандію супроводжують торій та рідкісно-земельні елементи (РЗЕ), що потребує розробки технології комплексної переробки сировини. Скандій чистотою 99,0% отримували з концентрату різного ступеня збагачення та стружки сплавів скандію методами розчинення їх в азотній кислоті, екстракції та селективного осадження щавлевою кислотою. В процесі випробувань були отримані оксиди скандію Sc_2O_3 чистотою 99,0, 99,9 і 99,99%, придатні для отримання сплавів на основі магнію медичного призначення.