## N E W S OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN SERIES OF GEOLOGY AND TECHNICAL SCIENCES

ISSN 2224-5278 Volume 4, Number 442 (2020), 156 – 165

https://doi.org/10.32014/2020.2518-170X.96

UDC 622.775; 544.47;

## N. S. Ivanov, A. Z. Abilmagzhanov, N. M. Shokobayev, I. Y. Adelbayev, A. E. Nurtazina

JSC "D. V. Sokolskiy Institute of Fuel, Catalysis and Electrochemistry", Almaty, Kazakhstan. E-mail: xumuk777@mail.ru, a.abilmagzhanov@ifce.kz, nurlan.shokobayev@flsmidth.com, clerikc88@mail.ru, nurtazina.aizhan@bk.ru

# SCANDIUM EXTRACTION BY PHOSPHORUS-CONTAINING SORBENTS

Abstract. The research and development of a highly effective, economically acceptable technology for scandium extracting from in-situ leaching solutions of uranium is an urgent scientific and technical task. An effective way of separation and purification of scandium is considered to be extraction from various solutions, among which organic acid phosphorus extractants are the most promising. This article is aimed at studying the equilibrium scandium sorption characteristics from model solutions of organophosphorus ion exchangers. Scandium sorption was carried out under static and dynamic conditions. In the furtherance of desired goal, scandium sorption by phosphorus-containing ion exchangers Lewatit TP272, Lewatit TP260, D2EHPA and DRPO from model solutions was studied. Sorption isotherms and integrated kinetic curves of scandium sorption were obtained. For the studied ion exchangers, the values of static exchange capacity and total dynamic exchange capacity for scandium were determined. Saturation on the TP260 ion exchanger at 700 sp.vol. equal to 0.027 kg/m<sup>3</sup> and on D2EHPA ion exchanger at 2382 sp.vol. equal to 0.236 kg/m<sup>3</sup> were obtained during passed volumes. It was found that desorption degree with scandium-saturated Lewatit TP260 ion exchanger using a solution of 200 g/dm<sup>3</sup> Na<sub>2</sub>CO<sub>3</sub> at room temperature was 87.26%, whereas with TVEX D2EHPA ion exchanger using solutions of sodium carbonate Na<sub>2</sub>CO<sub>3</sub> (200 g/dm<sup>3</sup>) and hydrofluoric acid HF (3.5M) was about 100%. When using a solution of ammonium fluoride  $NH_4HF_2$ , scandium extraction degree was 76%. A carbonate-alkaline solution of 0.5M NaOH + 1M Na<sub>2</sub>CO<sub>3</sub> and sodium salt solution of hydrofluoric acid 3.5M NaF showed low desorption characteristics. Obtained results made it possible to select Lewatit TP260 and D2EHPA ion exchangers for further study of scandium sorption extraction.

Key words: scandium, sorption, desorption, extraction, degree of extraction, exchange capacity, filtrate.

**Introduction.** Scandium (Sc) is one of the most expensive rare metals with a small volume of industrial production. Despite the significant content in the earth's crust, scandium rarely forms its own deposits. The reason is that Sc does not combine with ore-forming anions. In this regard, scandium is usually stands out as a byproduct in the processing of tailings and residues of various sources, such as uranium production solutions, titanium pigment production waste, ilmenite chlorination waste, wolframium and red mud sludge processing residues [1-3]. The main line of scandium application is the production of aluminum-based allovs used in the aerospace industry, in the manufacture of sports equipment and firearms. This is facilitated by the unique properties of scandium alloys, such as a combination of high strength and low weight, heat resistance and mechanical strength. In illumination engineering scandium iodide is used as an additive in halide lamps, which are one of the most effective light sources [4-7]. Scandium is a typical dissipated lithophylic element, found exceptionally in the form of oxide compounds. Scandium's own minerals - thortveitite  $Sc_2[Si_2O_7]$  and sterrettite  $ScPO_4*2H_2O$  - rare and do not have industrial significance. The problem of industrial production of scandium is solved by using dissipated scandium, extracted simultaneously from ores of non-ferrous and rare metals. The scandium content in these products does not exceed tenths of a percent. Scandium oxide of various qualifications is the final product of the described schemes [8-11]. One of the main scandium sources is uranium ores containing  $10^{-3}$  -  $10^{-4}$ %. Global uranium manufacturing in 2016 amounted to 62,366 tons, of which 39.4% was produced in Kazakhstan, followed by Canada (22%), Australia (10%), Niger (5.8%) and Russia (4.8%) [12]. Accordingly, scandium extraction as a by-product in uranium processing is great consequence. Currently, the processing of uranium-containing leaching solutions for scandium recovery typically uses hydrometallurgical processes, which are mainly associated with leaching, precipitation, liquid extraction and related technologies such as ion exchange and liquid membrane extraction [13-15].

Liquid extraction is one of the well-established hydrometallurgical methods for concentrating scandium and purifying leaching solutions of scandium-containing raw materials. The technology for the scandium isolation is complicated by the fact that the multicomponent composition of scandium-containing solutions necessitates a combination of different methods of concentration and purification. Process flowsheets for the scandium extraction are quite difficult, so the question of developing effective methods of extraction concentrating and separation from impurities remains particularly relevant. Review of the above process engineering solutions for scandium concentrating [16-23] indicates the efficiency of sorption and the variety of ion-exchange resins used. To concentrate scandium from productive solutions of uranium in-situ leaching acid extractants are often used. Most commonly the extraction of a metal ion (Mn<sup>n+</sup>) with an acid extractant at a high concentration of an element in the organic phase proceeds according to the cation exchange mechanism [18]. For scandium sorption from acidic solutions of complex salt composition, it is preferable to use highly selective phosphorus-containing ion exchangers with high scandium sorbability even when extracted from strongly acidic solutions. In turn, these acidic extractants are divided into phosphoric, phosphonic and phosphinic [22-27].

**Experimental procedure.** Scandium sorption was investigated using a sulfuric acid solution simulating ISL uranium solutions. Standardized test solution for scandium sorption with a volume of  $60 \text{ dm}^3$  was prepared by dissolving scandium oxide  $\text{Sc}_2\text{O}_3$  with a purity of 99.9% in a hot solution of 60% sulfuric acid (CP 94.6%) at a temperature of  $80^{\circ}\text{C}$  for 0.5 hour. Investigation process of scandium extraction from sulfate solutions was carried out using phosphorus-containing ion exchangers, main specifications of which are presented in table 1. The following solutions were used in the experiments: sodium carbonate Na<sub>2</sub>CO<sub>3</sub>, ammonium biflouride NH<sub>4</sub>HF<sub>2</sub>, fluohydric acid HF, sodium fluoride NaF, sodium hydroxide NaOH, citric acid C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>.

**Research methods.** Before work samples of ion exchangers were preconditioned with hydrochloric acid and caustic soda solutions according to the procedure described in [28]. Cation exchangers were converted to  $H^+$  form, polyampholytes to the  $H^+$  and  $SO_4^{2-}$  form when working with sulfuric solutions. Further, the resins were transferred to the working form by holding for 24 hours in the appropriate medium, after which they were washed with distilled water to a pH of 3-3.5.

Investigation of sorption under static conditions, a weighed portion of the resin in the range from 0.04 to 4 g was placed in a container with a volume of 5 dm<sup>3</sup>, a certain amount of solution with a known concentration of scandium was injected into it and the container was hermetically closed and placed on a LS110 radial shaker. Taking into account the extremely low concentrations of scandium, the study under static conditions was carried out with a large ratio of the solution volume to the weight of the ion exchanger V:W=1000:1 (5 dm<sup>3</sup>:5 g). Stirring of the container was carried out to prevent resin's particles deposition for 48 hours.

Resin	Functional groups	Matrix type	Granules size in the air-dry state, mm						
Chelating resins									
Lewatit TP272	bis(2,4,4-trimethylpentyl)phosphinic acid	macroporous, cross-linked polystyrene	0.30÷1.60						
Lewatit TP260	aminomethylphosphonic acid	macroporous, cross-linked polystyrene	0.40÷1.25						
	Solid extract	tants							
D2EHPA	di-(2-ethylhexyl)phosphoric acid	macroporous, hypercrosslinked polystyrene	0.65+2.50						
DRPO	different radical phosphine oxide	macroporous, hypercrosslinked polystyrene	0.25÷0.80						

Table 1 - The main specifications of the resins used in the work

Stirring of the container was carried out to prevent resin's particles deposition for 48 hours. Samples for analysis were taken at certain time intervals without interrupting the experiment. System's volumetric change as a result of sampling did not exceed 5%. Sorption isotherm from the solution was taken off varying the ratio of the solution volume to the ion exchanger mass V:m. The solution was contacted with the resin also until equilibrium was established. The equilibrium static exchange capacity (SEC), calculated by the residual scandium content in the solution, was determined by the formula 1:

$$SEC = \frac{C_0 - C_e}{C_0} \cdot \frac{V}{m},\tag{1}$$

where:  $C_0$  - scandium concentration in the initial solution, mg/dm<sup>3</sup> or mmol/dm<sup>3</sup>;  $C_e$  - the equilibrium concentration of scandium in solution after sorption, mg/dm<sup>3</sup> or mmol/dm<sup>3</sup>; V - the volume of solution taken for testing, dm<sup>3</sup>; m - ion exchanger's sample weight, g.

Investigation of sorption under dynamic conditions, prehydrated in distilled water and converted into the desired form, the ion exchanger was placed in a  $30 \text{cm}^3$  organic glass column (the ratio of the height of the sorbent layer to the diameter h/d = 4.8:1). The solution was passed from bottom to top through an ion exchanger until the resin was completely saturated with scandium. The specific load was 10 sp.vol./sp.vol./hour. At a controlled flow rate, the solution at the column outlet was fractionally selected for analysis. Throughput raterate was set using a peristaltic pump. Total dynamic exchange capacity (TDEC) was calculated by the formula 2. Solutions were analyzed by inductively coupled plasma atomic emission method on an Optima 8300DV spectrometer from Perkin Elmer, LLC.

$$TDEC = \frac{(C_0 - C_a) \cdot V}{m_{i.e.}} \tag{2}$$

where:  $C_0$  - scandium concentration in the initial solution, mg/dm<sup>3</sup> or mmol/dm<sup>3</sup>;  $C_a$  - an average scandium concentration in solution, mg/dm<sup>3</sup> or mmol/dm<sup>3</sup>; V - passed solution volume, dm<sup>3</sup>;  $m_{i.e.}$  - ion exchanger's sample weight, g.

The distribution coefficient of scandium was calculated by the formula 3:

$$K_d = \frac{(C_0 - C) \cdot V}{C \cdot m} \tag{3}$$

where:  $K_d$  - distribution coefficient of scandium,  $cm^3/g$ ;  $C_0$  - scandium concentration in the initial solution, mg/dm<sup>3</sup> or mmol/dm<sup>3</sup>; C - scandium concentration in mother solution, mg/dm<sup>3</sup> or mmol/dm<sup>3</sup>; V - passed solution volume, dm<sup>3</sup>; *m* - ion exchanger's sample weight, g.

**Result and discussion.** Sorption isotherm characterizes the state of ion-exchange equilibrium at a constant temperature. Researches of scandium sorption isotherm were carried out at a concentration range as close as possible to the technological conditions of uranium leaching. Scandium sorption isotherms on an ion exchangers were removed by varying the initial concentration in the solution from 0.03 to  $0.6 \text{ mg/dm}^3$  ( $0.67*10^{-3} \div 13.3*10^{-3} \text{ mmol/dm}^3$ ). The value of ion exchanger's capacity was calculated by the formula 1, the distribution coefficient by the formula 3. Research results of scandium sorption isotherms are shown in table 2.

Table 2 - Results of scandium sorption isotherms research

Ion exchanger	Scandium equilibrium concentration in the solution, mmol/dm <sup>3</sup> *10 <sup>3</sup>	Ion exchanger capacity, mmol/g*10 <sup>3</sup>	Distribution coefficient K <sub>d</sub> , cm <sup>3</sup> /g	
	1.68	2.14	1756.0	
	3.95	4.16	1112.8	
TP272	6.12	5.10	914.6	
	8.28	6.42	1194.8	
	12.24	10.14	862.8	
	1.28	1.15	1108.6	
	4.12	2.86	689.6	
TP260	7.76	3.66	788.0	
	10.21	4.85	646.6	
	12.80	6.82	658.8	

			Coninuation of table 2
	1.16	4.08	3546.2
	3.42	8.95	4122.3
D2EHPA	6.00	14.56	4852.6
	9.20	20.12	3896.2
	12.48	27.82	3452.5
	1.32	1.24	666.5
	3.44	2.75	768.8
DRPO	7.22	6.54	844.0
	9.12	7.26	716.8
	12.42	9.96	708.6

As can be seen from the graphs in figure 1, scandium sorption isotherms within the studied concentration range are close to rectilinearly type. Isotherms were processed by the instrumentality of the Langmuir and Henry equations [29]. The processing results in coordinates 1/E-1/C (Langmuir equation) and E-C (Henry equation) are presented in table 3.





Based on the presented results analysis, it can be concluded that there is no significant difference between the correlation coefficients in the two equations for the studied resins in the selected concentration range and conditions.

Ion exchanger	Equation	Concentration range, mmol/dm <sup>3</sup> *10 <sup>3</sup>	Constant K, dm <sup>3</sup> /g (Henry) or g/mmol (Langmuir)	Correlating coefficient, R <sup>2</sup>
TD272	Henry	1 69+12 24	1.12	0.8692
Langmuir	1.06+12.24	198.622	0.7458	
TD260	Henry	1 29 12 90	0.72	0.9742
TP260	Langmuir	1.28+12.80	108.55	0.9413
DIFIDA	Henry	1 16 10 49	3.56	0.9826
DZEHFA	Langmuir	1.10+12.46	16.68	0.9748
DBBO	Henry	1 22 - 12 42	0.82	0.9832
DRFO	Langmuir	1.32712.42	3.10	0.9812

Table 3 – Scandium sorption isotherm processing results

Scandium sorption kinetic characteristics were studied by the limited-volume method in an installation with a thermostatically controlled cell at temperatures of 293 K in such a way that the exchange process occurred in a stirred solution with a volume of 5000 cm<sup>3</sup> with an initial composition of

0.22 mg/dm<sup>3</sup>. In this case, sorbed ion concentration in the solution changes during the experiment, which affects the speed of the process. With sufficiently intensive mixing, an equilibrium distribution of the ion concentration in the entire solution volume is achieved, excluded layers directly adjacent to the grain layer (boundary layer). The integrated kinetic sorption curves of scandium, considered at a temperature of 293K, are shown in figure 2.



Figure 2 – Integrated kinetic curves of sorption of scandium from model solutions with TP272, TP260, D2EHPA, and DRPO ion exchangers at a temperature of 293K

Figure 2 shows that TP260 ion exchanger showed the lowest kinetic and capacitive indices, TP272 and DRPO ion exchangers are saturated with scandium in about 6 hours, while D2EHPA resin exhibits a lower saturation rate at a significantly higher equilibrium capacity. However, the strong affinity of the ion exchanger to the recoverable element expectedly complicates scandium subsequent extraction from the resin phase during desorption. Obtained results made it possible to select Lewatit TP260 and D2EHPA ion exchangers for further study of scandium sorption extraction. Before scandium sorption on selected ion exchangers under dynamic conditions, an experiment was conducted in a static mode. In this case, the ratio of L:S was 1000:1 (5 dm<sup>3</sup> of scandium-containing solution: 5g of resin). The container was stirred to prevent resin's particles from occurring for 48 hours, after which a sample of the solution was taken and analyzed for scandium under dynamic conditions was carried out according to the procedure described above, from a sulfate solution at a specific load of 10 sp.vol./ sp.vol./hour. The results of scandium sorption on the ion exchangers TP260 and D2EHPA are shown in tables 5 and 6. With the passed volume of solutions, the calculated saturation of 0.027kg/m<sup>3</sup> was obtained.

Table 4 –	Results	of	scandium	sorption	in	static	conditions
				1			

Ion avahangar	Sc concentr	ration, mg/dm <sup>3</sup>	Extraction degree 94	Resin capacity, kg/m <sup>3</sup>	
Ton exchanger	initial	final	Extraction degree, 76		
TP260	0.196	0.155	16.72	0.031	
D2EHPA	0.180	0.139	25.27	0.047	

Table 5 - Results of scandium sorption on the ion exchange TP260

Specific volume, unit	0	100	200	300	400	500	600	700	α, kg/m <sup>3</sup>
Sc concentration, mg/dm <sup>3</sup>	0.186	0.081	0.157	0.161	0.180	0.184	0.183	0.176	0.027

Specific volume, unit	0	150	320	486	650	780	942	1120	α, kg/m <sup>3</sup>
Sc concentration, mg/dm <sup>3</sup>	0.186	0.028	0.063	0.098	0.104	0.104	0.084	0.069	
Specific volume, unit	1190	1430	1566	1678	1860	2059	2218	2382	0.148
Sc concentration, mg/dm <sup>3</sup>	0.062	0.058	0.055	0.057	0.058	0.064	0.069	0.072	

Table 6 - Results of scandium sorption on the ion exchange D2EHPA

Saturation was 0.148 kg/m<sup>3</sup>, with the passed solution volume; the following calculated saturation was obtained: 0.236 kg/m<sup>3</sup>. Thus, it was possible to obtain saturation on the TP260 ion exchanger at 700 sp.vol. equal to 0.027 kg/m<sup>3</sup> and on D2EHPA ion exchanger at 2382 sp.vol. equal to 0.236 kg/m<sup>3</sup>. Scandium was desorbed from saturated ion exchangers in organic glass columns with a volume of 30 cm<sup>3</sup> (the ratio of the height of the sorbent layer to diameter h/d = 4.8:1) filled with a saturated resin from a previous sorption experiment. From the bottom up, a desorption solution was passed through a clamped ion exchanger using a peristaltic pump, and the specific load was 1 sp.vol./sp.vol./h. At a controlled flow rate, sorption filtrates were fractionally selected for analysis. Scandium desorption from saturated Lewatit TP260 ion exchanger was carried out under dynamic conditions with a sodium carbonate solution Na<sub>2</sub>CO<sub>3</sub> with a concentration of 200 g/dm<sup>3</sup>. Main results of the experiment on the scandium desorption from resin TP260 are shown in table 7 and figure 3.

Specific volume, unit	0	1	2	3	4	5	6	7	8	9	10
Sc concentration, mg/dm <sup>3</sup>	0	1.98	6.25	4.56	2.40	1.22	0.84	0.62	0.45	0.23	0.23
Sc extraction, %	0	5.64	18.12	37.24	57.22	70.15	81.15	82.20	84.36	85.52	87.26

Table 7 - Results of scandium desorption from resin TP 260 in dynamic conditions





Figure 3 - Scandium desorption curve and degree of scandium extraction from TP260 resin

Desorption degree with scandium-saturated Lewatit TP260 ion exchanger using 200 g/dm<sup>3</sup> Na<sub>2</sub>CO<sub>3</sub> and passing 10 sp.vol. at room temperature it was 87.26%, which allows making a conclusion about effectiveness of selected scandium desorbent. Scandium desorption from saturated TVEX D2EHPA ion exchanger was carried out under static conditions using various desorption solutions. The volume of saturated D2EHPA resin for each experiment was 5 cm<sup>3</sup>. Desorption solutions volume was 200 cm<sup>3</sup>. Desorption solutions of the following concentration were used: 200 g/dm<sup>3</sup> Na<sub>2</sub>CO<sub>3</sub>; 3.5M NH<sub>4</sub>HF<sub>2</sub>; 3.5M HF; 3.5M NaF; 0.5M NaOH + 1M Na<sub>2</sub>CO<sub>3</sub>; 5% citric acid. Results of scandium desorption from resin TVEX D2EHPA in static conditions are shown in table 8 and figure 4. It was established in [30] that scandium can be extracted from D2EHPA with carbonate - alkaline solutions or solutions of hydrofluoric acid or its salts. But then again, carbonate-alkaline solutions application for scandium desorption from TVEX is unacceptable, because D2EHPA will be emulsified and washed out from the TVEX's phase. Certain salts of hydrofluoric acid are also unallowable, as this will lead to the formation of sparingly soluble complex salts in TVEX's phase.

Description colution	Scan	Extraction					
Desoroning solution	1	2	4	6	12	24	degree, %
Na <sub>2</sub> CO <sub>3</sub>	0.60	1.13	2.33	3.10	4.33	7.05	~100
$NH_4HF_2$	1.8	2.62	3.35	3.65	3.75	4.32	76
HF	4.74	5.53	5.86	6.27	6.56	7.22	~100
NaF	0.0025	0.068	0.068	0.065	0.070	0.096	2
$NaOH + Na_2CO_3$	0.48	0.85	1.15	1.20	1.15	1.09	13
Citric acid	0	0	0	0	0	0	0

Table 8 - Results of scandium desorption from resin TVEX D2EHPA in static conditions



Figure 4 – Kinetic curve of scandium desorption from TVEX D2EHPA resin using various desorption solutions and extraction degree from the resin

From the data presented in table 8 and figure 4, it can be seen that when using solutions of sodium carbonate  $Na_2CO_3$  (200 g/dm<sup>3</sup>) and hydrofluoric acid HF (3.5M) as desorption solutions, almost complete scandium desorption from the TVEX D2EHPA resin was observed in static conditions. Nevertheless, a carbonate-alkaline solution of 0.5M NaOH + 1M Na<sub>2</sub>CO<sub>3</sub> and a 3.5M solution of sodium salt of hydrofluoric acid NaF showed very low desorption characteristics. An ammonium fluoride NH<sub>4</sub>HF<sub>2</sub> solution, devoid of the disadvantages of carbonate-alkaline desorbates, is applied to desorb scandium from phosphorus-containing ion exchangers. In our experiments desorption degree with scandium-saturated TVEX D2EHPA ion exchanger using a 3.5M solution of NH<sub>4</sub>HF<sub>2</sub> at room temperature was 76%. As can be seen, the desorption results obtained are in good agreement with the literature.

**Conclusion.** Scandium equilibrium sorption characteristics from model solutions by organophosphorus ion exchangers were studied. Scandium sorption by selected ion exchangers was carried out under static and dynamic conditions. Saturation on the TP260 ion exchanger at 700 sp.vol. equal to  $0.027 \text{ kg/m}^3$ and on D2EHPA ion exchanger at 2382 sp.vol. equal to  $0.236 \text{ kg/m}^3$  were obtained during passed volumes. It was found that desorption degree with scandium-saturated Lewatit TP260 ion exchanger using a solution of 200 g/dm<sup>3</sup> Na<sub>2</sub>CO<sub>3</sub> was 87.26%; whereas with TVEX D2EHPA ion exchanger using solutions of sodium carbonate Na<sub>2</sub>CO<sub>3</sub> (200 g/dm<sup>3</sup>) and hydrofluoric acid HF (3.5M) was about 100%. A carbonate-alkaline solution of 0.5M NaOH + 1M Na<sub>2</sub>CO<sub>3</sub> and sodium salt solution of hydrofluoric acid 3.5M NaF showed low desorption characteristics. Consequently, phosphorus-containing ion exchangers Lewatit TP260 and TVEX D2EHPA can be proposed as promising sorbents for scandium extraction from uranium in-situ leaching solutions.

**Funding.** The research was carried out within the framework of the project AP05133140 "Development and testing of resource-saving technologies for extraction of valuable byproducts during the processing of uranium ores with a comprehensive assessment of its profitability and investment attractiveness" due to scientific projects financing under the of the Scientific Committee of the Ministry of Education and Science of the Republic of Kazakhstan.

#### Н. С. Иванов, А. З. Абильмагжанов, Н. М. Шокобаев, И. Е. Адельбаев, А. Е. Нуртазина

«Д.В. Сокольский атындағы жанармай, катализ және электрохимия институты» АҚ, Алматы, Қазақстан

## ФОСФОРЛЫ СОРБЕНТТЕРМЕН СКАНДИЙДІ БӨЛІП АЛУ

Аннотация. Ғылымды қажет ететін инновациялық технолоғиялардың дамуы сирек кездесетін жер элементтерін өндіру әрі пайдалануға байланысты, олардың арасында скандий перспективті. Скандийдің ықтимал қайнаркөзінің бірі – уранды жерасты шаймалау ерітінділері. Қазақстанда скандий өндірісінің мығым әлеуеті бар. Уранды жерасты сілтісіздендіру арқылы скандий алудың жоғары тиімді, экономикалық тұрғыдан тиімді технолоғиясын зерттеу және әзірлеу өзекті ғылыми-техникалық міндет болып саналады. Скандийді бөлудің және тазартудың ең тиімді әдісі – әртүрлі ерітінділер экстракциясы. Орғанофосфор

қышқылының экстрагенттері скандийді экстракция және скандийді басқа элементтерден бөлу үшін перспективті болып келеді.

Зерттеу аясында фосфорлы Lewatit TP272, Lewatit TP260, ҚЭ Д2ЭГФҚ (қатты экстрагент ди-(2этилгексил) фосфор қышқылы) және ФОР (түрлі радикалды фосфин оксиді) иониттерімен модельді ерітінділерден скандий сорбциясы зерттелді. Сорбциялық изотермалар және скандий сорбциясыныц интегралды кинетикалық қисықтары алынды. Зерттелетін иониттер үшін скандийдіц статикалық алмасу сыйымдылығы және толық динамикалық алмасу мүмкіндігі анықталды. Алынган нәтижелер скандийдіц сорбциялық экстракциясын одан әрі зерттеу үшіп Lewatit TP260 және ҚЭ Д2ЭГФҚ иониттерін таңдауға мүмкіндік берді.

Сорбцияны статикалық жағдайда зерттеуде 0,04 ден 4 г дейінгі шайырдың өлшенген бөлігі 5 дм<sup>3</sup> көлеміндегі контейнерге орналастырылды, оган нақты скандий концентрациясы бар ерітіндінің белгілі бір мөлшері енгізілді, контейнерді мықтап жауып, LS110 радиалды шайқаушыга салынды. Зерттеу ерітінді көлемінің ионит массасына шексіз қатынасы арқылы жүргізілді С:Қ 1000:1 (5дм<sup>3</sup>:5 г). Динамикалық жағдайда сорбцияны зерттеуде ионит 30 см3 органикалық әйнек баганына орналастырылды (сорбент қабаты биіктігінің диаметрге қатынасы h/d = 4,8:1). Ерітінді түбінен жогарыга шайыр скандиймен қаныққанга дейін ионит қабаты арқылы өткізілді. Меншікті жүктеме 10 меншікті көлем/менш.көл./сағат болды. Ерітінділердің өткізіп алынган көлемі бойынша ТР260 ионитте 700 менш.көл. қанықтырылды (ол 0,027 кг/м<sup>3</sup> тең) және Д2ЭГФҚ ионитте 2382 менш.көл. (ол 0,266 кг/м<sup>3</sup> тең).

Динамикалық жагдайда қаныққан иониттен Lewatit TP260 натрий карбонаты Na<sub>2</sub>CO<sub>3</sub> ерітіндісімен (концентрациясы 200 г/дм<sup>3</sup>) скандийді десорбциялау үдерісі жүзеге асырылды. Бөлме температурасындағы десорбция дәрежесі 87,26% көрсетті. Қаныққан ҚЭ Д2ЭГФҚ иониттен скандийді десорбциясы түрлі десобциялық ерітінділерді қолдана отырып, статикалық жағдайда жүргізілді. Төмендегі концентрациядағы десорбциялық ерітінділерді қолдана отырып, статикалық жағдайда жүргізілді. Төмендегі концентрациядағы десорбциялық ерітінділер пайдаланылды: 200 г/дм<sup>3</sup> Na<sub>2</sub>CO<sub>3</sub>; 3,5M NH<sub>4</sub>HF<sub>2</sub>; 3,5M HF; 3,5M NaF; 0,5M NaOH + 1M Na<sub>2</sub>CO<sub>3</sub>; 5% – лимон қышқылының ерітіндісі (сітіс асіd). Натрий карбонаты Na<sub>2</sub>CO<sub>3</sub> ерітіндісін және гидрофторлы қышқылды HF десорбциялық ерітінді ретінде пайдалану кезінде статикалық жағдайда ҚЭ Д2ЭГФҚ шайырынан скандийдің толық десорбциясы байқалды. Аммоний фторидінің NH<sub>4</sub>HF<sub>2</sub> ерітіндісін колданганда скандийдің бөліп алу дәрежесі 76% көрсетті. Карбонатты-сілтілі ерітіндісі және натрий тұзының гидрофторлы қышқылының ерітіндісі NaF аса төмен десорбция сипаттамаларын көрсетті.

**Түйін сөздер:** скандий, сорбция, десорбция, экстракция, бөліп алу дәрежесі, алмасу сыйымдылығы, сүзінді.

#### Н. С. Иванов, А. З. Абильмагжанов, Н. М. Шокобаев, И. Е. Адельбаев, А. Е. Нуртазина

АО "Институт топлива, катализа и электрохимии им. Д. В. Сокольского", Алматы, Казахстан

## ИЗВЛЕЧЕНИЕ СКАНДИЯ ФОСФОРСОДЕРЖАЩИМИ СОРБЕНТАМИ

Аннотация. Развитие наукоемких инновационных технологий связано с получением и применением редкоземельных элементов, среди которых перспективным является скандий. Один из потенциальных источников скандия – растворы подземного выщелачивания урана. Казахстан обладает необходимым потенциалом для производства скандия. Исследование и разработка высокоэффективной, экономически приемлемой технологии извлечения скандия из растворов подземного выщелачивания урана является актуальной научнотехнической задачей. Наиболее эффективным способом разделения и очистки скандия является экстракция из различных растворов. Кислотные фосфорорганические экстрагенты являются перспективными для экстракции и отделения скандия от других элементов.

В рамках работы проведены исследования сорбции скандия фосфорсодержащими ионитами Lewatit TP272, Lewatit TP260, ТВЭКС Д2ЭГФК и ФОР из модельных растворов. Получены изотермы сорбции и интегральные кинетические кривые сорбции скандия. Для исследуемых ионитов определены значения СОЕ и ПДОЕ по скандию. Полученные результаты позволили выбрать иониты Lewatit TP260 и Д2ЭГФК для дальнейшего изучения сорбционного извлечения скандия.

При исследовании сорбции в статических условиях навеску смолы в диапазоне от 0,04 до 4 г помещали в емкость объемом 5 дм<sup>3</sup>, вводили в нее определенное количество раствора с известной концентрацией скандия, герметично закрывали емкость и ставили ее на радиальный шейкер LS110. Исследование в статических условиях проводили при большом соотношении объема раствора к массе ионита Ж:Т 1000 : 1 (5дм<sup>3</sup> : 5 г). При изучении сорбции в динамических условиях ионит помещали в колонку из оргстекла объемом 30 см<sup>3</sup> (отношение высоты слоя сорбента к диаметру h/d = 4,8:1). Через слой ионита пропускали раствор снизувверх до полного насыщения смолы скандием. Удельная нагрузка составляла 10 уд.об./уд.об./час. При пропущенных объемах растворов удалось получить насыщение на ионите ТР260 при 700 уд.об. равным 0,027 кг/м<sup>3</sup> и на ионите Д2ЭГФК при 2382 уд.об. равным 0,236 кг/м<sup>3</sup>. Десорбцию скандия с насыщенного ионита Lewatit TP260 проводили в динамических условиях раствором карбоната натрия с концентрацией 200 г/дм<sup>3</sup> Na<sub>2</sub>CO<sub>3</sub>. Степень десорбции при комнатной температуре составила 87,26 %. Десорбцию скандия с насыщенного ионита TBЭКС Д2ЭГФК проводили в статических условиях с использованием различных десорбирующих растворов. Были использованы десорбирующие растворы следующей концентрации: 200 г/дм<sup>3</sup> Na<sub>2</sub>CO<sub>3</sub>; 3,5M NH<sub>4</sub>HF<sub>2</sub>; 3,5M HF; 3,5M NaF; 0,5M NaOH + 1M Na<sub>2</sub>CO<sub>3</sub>; 5% – раствор лимонной кислоты (citric acid). При использовании растворов карбоната натрия Na<sub>2</sub>CO<sub>3</sub> и фтористоводородной кислоты HF в качестве десорбирующих растворов наблюдалась практически полная десорбция скандия со смолы TBЭКС Д2ЭГФК в статических условиях. При использовании раствора фторида аммония NH<sub>4</sub>HF<sub>2</sub> степень извлечения скандия составила 76%. Карбонатно-щелочной раствор и раствор натриевой соли фтористоводородной кислоты NaF показали весьма низкие десорбирующие характеристики.

Ключевые слова: скандий, сорбция, десорбция, экстракция, степень извлечения, обменная емкость, фильтрат.

#### **Information about authors:**

Ivanov Nikolai Sergeevich, Candidate of Chemical Sciences, Leading Researcher in Laboratory of Applied Research, JSC "D.V. Sokolskiy Institute of Fuel, Catalysis and Electrochemistry", Almaty, Kazakhstan; n.ivanov@ifce.kz; https://orcid.org/0000-0002-2153-2802

Abilmagzhanov Arlan Zainutallaevich, Candidate of Chemical Sciences, head of Applied Research laboratory of JSC "D.V. Sokolskiy Institute of Fuel, Catalysis and Electrochemistry", Almaty, Kazakhstan; a.abilmagzhanov@ifce.kz; https://orcid.org/0000-0001-8355-8031

Shokobayev Nurlan Maratovich, PhD, Junior Researcher in Laboratory of Applied Research of JSC "D.V. Sokolskiy Institute of Fuel, Catalysis and Electrochemistry", Almaty, Kazakhstan; nurlanshokobayev@gmail.com; https://orcid.org/0000-0003-1697-4638

Adelbayev Iskander Yersayanovich, master's degree, senior engineer in Laboratory of Applied Research of JSC "D.V. Sokolskiy Institute of Fuel, Catalysis and Electrochemistry", Almaty, Kazakhstan; clerikc88@mail.ru; https://orcid.org/0000-0003-1435-8583

Nurtazina Aizhan Erkinbekkyzy. PhD student, master's degree, senior engineer of Applied Research laboratory of JSC "D.V. Sokolskiy Institute of Fuel, Catalysis and Electrochemistry", Almaty, Kazakhstan; nurtazina.aizhan@bk.ru; https://orcid.org/0000-0001-7202-5344

#### REFERENCES

[1] Duyvesteyn P.C., Putnam G.F. (2014) Scandium. A review of the element, its characteristics, and current and emerging commercial applications, EMC Metals Corporation. http://www.scandiummining.com/site/assets/files/5740/scandium-white-paperemc-website-june-2014-.pdf (in Eng.).

[2] Gupta C.K., Krishnamurthy N. (2016) Extractive metallurgy of rare earths, Taylor & Francis Group, LLC CRC. ISBN: 1466576340 (in Eng.).

[3] U.S. Geological Survey (2017) Mineral Commodity Summaries, January. 147 p. https://minerals.usgs.gov/minerals/pubs/commodity/scandium/mcs-2017-scand.pdf (in Eng.).

[4] Venkateswarlu K., Rajinikanth V., Ajoy K.R., Cheng X., Langdon T.G. (2010) Effect of a scandium addition on an A1-2% Si alloy processed by ecap, Rev.Adv.Mater.Sci, 25: 4: 99-106 (in Eng.).

[5] Zaki A. (2003) The Properties and Application of Scandium-Reinforced Aluminum, JOM: the journal of the Minerals, Metals & Materials Society, 55: 35-39 (in Eng.).

[6] Ryset J. (2005) Norwegian Scandium in aluminium alloys, International Materials Reviews, 50: 19-44 (in Eng.).

[7] Mertin S., Heinz B., Rattunde O., Christmann G., Dubois M., Nocolay S., Muralt P. (2018) Piezoelectric and structural properties of c-axis textured aluminium scandium nitride thin films up to high scandium content, Surface and Coatings Technology, 343: 2-6 (in Eng.).

[8] Komissarova L.N. (2001) Inorganic and analytical chemistry of scandium, M.: Editorial URSS. 512 p. (in Russ.).

[9] Horovitz C.T., Gschneidner K.A., Melson G.A., Youngblood D.H., Schock H.H. (1975) Scandium its occurrence, physics, metallurgy, biology and technology, New York: Academic Press. 598 p. (in Eng.).

[10] Wang W., Pranolo Y., Cheng C. (2011) Metallurgical processes for scandium recovery from various resources: A review, Hydrometallurgy, 108: 100-108 (in Eng.).

[11] Lenczowski B., Wiesheu R. (1997) Scandium – A Carrent Review of its deposits, reserves, production, and technical use, Erzmetall, 50: 10: 631-639 (in Eng.).

[12] Uranium Production Figures 2010-2019, Production from mines (2020) Electronic resource. https://www.world-nuclear.org/information-library/facts-and-figures/uranium-production-figures.aspx (in Eng.).

[13] Smirnov A.L., Titova S.M., Rychkov V.N., Bunkov G.M., Semenishchev V.S., Kirillov E.V., Poponin N.N., Svirsky I.A. (2017) Study of scandium and thorium sorption from uranium leach liquors, J. Radioanal. Nucl. Chem, 312: 277–283 (in Eng.).

[14] Ross J.R., Rosenbaum J.B. (1962) Reconnaissance of scandium sources and recovery of scandium from uranium mill solutions, US Department of the Interior. 16 p. (in Eng.).

[15] Lash L.D., Ross J.R. (1961) Vitro chemical recovers costly scandium from uranium solutions, Min. Eng, 13: 966–969 (in Eng.).

[16] Wang W., Pranolo Y., Cheng C.Y. (2011) Metallurgical processes for scandium recovery from various resources: a review, Hydrometallurgy, 108: 100-108 (in Eng.).

[17] Michael C. (2008) Liquid–Liquid Extraction and Liquid Membranes in the perspective of the twenty-first century. In book: Solvent Extraction and Liquid Membranes, CRC Press: Taylor & Francis. 344 p. (in Eng.).

[18] Wang W., Cheng C.Y. (2011) Separation and purification of scandium by solvent extraction and related technologies: a review, Journal of Chemical Technology & Biotechnology, 86: 10: 1237-1246 (in Eng.).

[19] Korovin V.Y., Randarevich S.B. (1991) Synthesis, properties and application of solid extractants [Sintez, svojstva i primenenie tverdyh ekstragentov] 5: 3-13 (in Russ.).

[20] Korovin V., Shestak Y., Pogorelov Y., Cortina J.L. (2008) Solid Polymeric Extractants (TVEX): Synthesis, Extraction Characterization and Application for Metal Extraction Processes, Solvent Extraction and Liquid Membranes. Fundamentals and Applications in New Materials. Boca Raton: CRC Press. P. 261-301 (in Eng.).

[21] Xu S., Li S. (1996) Review of the extractive metallurgy of scandium in China (1978–1991), Hydrometallurgy, 42: 337-343 (in Eng.).

[22] Singh R.K., Dhadke P.M. (2003) Extraction and separation of candium(III) from perchloratemedia by D2EHPA and PC-88A, Bull Chem Technol Macedonia, 22: 1-11 (in Eng.).

[23] Xue L.Z., Li D.Q. (1992) Extraction of scandium(III), yttrium(III), lanthanides(III) and iron(III) from hydrochloric acid solutions with di-(2-ethylhexyl) phosphinic acid, Chinese J Appl Chem, 9: 21-25 (in Eng.).

[24] Li Y., Li Q., Zhang G., Zeng L., Cao Z., Guan W., Wang L. (2018) Separation and recovery of scandium and titanium from spent sulfuric acid solution from the titanium dioxide production process, Hydrometallurgy, 178: 1-6. doi:10.1016/j.hydromet.2018.01.019 (in Eng.).

[25] Li G., Ye Q., B Deng Q., Luo J., Rao M., Peng Zh., Jiang T. (2018) Extraction of scandium from scandium-rich material derived from bauxite ore residues, Hydrometallurg, 176: 62-68. doi:10.1016/j.hydromet.2018.01.007 (in Eng.).

[26] Qureshi IH, McClendon LT, Lafleur PD (1969) Extraction studies of the Group IIIB-VIIB elements and the lanthanides utilizing Bis(2-Ethyl- Hexyl) Oryhophosphoric acid, Radiochim Acta, 12: 107-111 (in Eng.).

[27] Zlobina E.V., Pak L.O. (2013) The use of binary extractants for the extraction of scandium [Primenenie binarnyh ekstragentov dlya izvlecheniya skandiya] 4: 72: 168-176 (in Russ.).

[28] Polyanskij N.G., Gorbunov G.V., Polyanskaya N.L. (1976) Methods of research of ion exchangers, M.: Chemistry. 208 p. (in Russ.).

[29] Lebedev K.B., Kazancev E.I., Rozmanov V.M., Paholkov V.S., Chemezov V.A. (1975) Ionites in non-ferrous metallurgy, M.: Metallurgy. 352 p. (in Russ.).

[30] Wang W., Pranolo Y., Cheng C.Y. (2013) Recovery of scandium from synthetic red mud leach solutions by solvent extraction with D2EHPA, Sep. Purif. Technol, 108: 96-102 (in Eng.).