

The Study of the Kinetic Characteristics of Sorption of Scandium of Ion Exchanger Purolite MTS9580 from Return Circulating Solutions of Underground Leaching of Uranium Ores

U. Yessimkanova^{1*}, M. Mataev¹, M. Alekhina², M. Kopbaeva³,
A. Berezovskiy³, Dr D. Dreisinger⁴

¹Al-Farabi Kazakh National University, 71 Al-Farabi ave., Almaty, Kazakhstan

²D. Mendeleev University of Chemical Technology of Russia, 9 Miusskaya pl., Moscow, Russia

³"Institute of High Technologies" LLP, 168 Bogenbai Batyr str., Almaty, Kazakhstan

⁴University of British Columbia, Department of Materials Engineering, 309-6350 Stores Road, Vancouver, Canada

Article info

Received:
14 September 2019

Received in revised form:
28 November 2019

Accepted:
17 February 2020

Keywords:

Scandium
Rare-earth metals
Sorption
Static mode
Dynamic mode

Abstract

This paper presents the results of a study of experiments on the sorption characteristics of phosphorus-containing ion exchangers Purolite MTS9580 (functional group – derivatives of phosphonic acid) and Lewatit TP260 (functional group – aminomethylphosphonic acid) on scandium. Using the method of low-temperature nitrogen adsorption, structural characteristics of selected ion exchangers Purolite MTS9580 and Lewatit TP260 respectively were measured. The specific surface of Purolite MTS9580 and Lewatit TP260 ion exchangers was measured as 5.1 and 4.5 m²/g, respectively. The obtained values indicate the presence of a macroporous structure in the ion exchangers. Experiments were carried out on the sorption of scandium and critical impurities in a static mode and dynamic mode while varying the acidity of the initial mother liquor of the sorption of uranium. Comparison of scandium sorption from pre-acidified uranium sorption mother liquor with Lewatit TP260 and Purolite MTS9580 ion exchangers showed an advantage for MTS9580 resin. The MTS9580 resin had an exchange capacity of 200 mg Sc/dm³ versus 59.7 mg Sc/dm³ for TP260. The dynamic exchange capacity of Purolite MTS9580 is much lower in relation to harmful impurities as Al, Fe, Ca, etc.

1. Introduction

Scandium is a precious and rare metal due to the high cost of scandium and the complex metallurgical processes of its isolation and purification. Scandium is used in high-strength aluminum alloys, solid oxide fuel cells, electronics and in laser technology and magnets [1, 2, 3]. A mixture containing scandium oxide in combination with an Al-CoCrFeNi alloy was investigated, which led to the discovery of a promising nanodiamond composite [4]. Due to its low content in mineral ores, scandium is usually isolated from various sources, such as uranium production solutions [5], as a by-product from tailings processing, titanium pigment produc-

tion waste [6], ilmenite chlorination waste, tungsten processing residues [7] and red mud [8, 9].

Among sources rich in rare-earth elements, the intermediate products of processing of uranium ores – solutions of underground leaching of uranium are very promising for scandium supply. The peculiarities of processing solutions of underground leaching of uranium include, as a rule, a low rare earth elements content and a complex chemical composition. In this regard, many technologies developed by industry for concentrating and extracting REEs are unsuitable and inefficient. Sorption extraction of REEs seems most appropriate at the stage of primary concentration.

The complexity of the scandium recovery process technology depends on various types and amounts of impurities, such as Al, Fe, and Ca.

*Corresponding author. E-mail: umitka.89@mail.ru

Numerous researchers [10, 11, 12] have studied the extraction of scandium from uranium production. It is known that phosphorus-containing ion exchangers are the most effective sorbents for the concentration of scandium from solutions of complex multicomponent composition [13].

The purpose of this work was to extract scandium from return circulating solutions of underground leaching of uranium ores and to study the kinetic characteristics of phosphorus-containing ion exchangers for scandium.

2. Experimental part

A search was made for phosphorus-containing ion exchangers to extract scandium from uranium leach solutions. Two types of ion exchange resins were investigated in scandium sorption experiments:

1. Lewatit TP260, functional group – amino-methylphosphonic acid, with a particle size of 0.47–0.81 mm;

2. Purolite MTS9580, functional group – derivatives of phosphonic acid, with a particle size of 0.52–0.60 mm;

To determine the structural characteristics of the Purolite MTS9580 and Lewatit TP260 ion exchangers, nitrogen adsorption isotherms were measured at 77 K using a Sorbi MS instrument (META, Novosibirsk, Russia). Before measuring isotherms using a Sorbi Prep instrument, samples were degassed at 105 °C in a nitrogen stream. The specific surface area of the samples was calculated using the BET equation. The distribution of pore volumes by their diameters was calculated by the BJH method.

To establish the sorption characteristics of the MTS9580, experiments were carried out on the sorption of scandium and impurities in static and dynamic modes with a change in the acidity of the initial mother liquor of sorption of uranium. Sorption was carried out at room temperature (20 °C).

The chemical composition of the mother liquor of sorption of uranium for experiments is shown in Table 1.

Preparation of ion exchangers for testing was carried out in accordance with State standard (State standard 10896-78. Ion-exchange resins. Preparation of specimens for test, 1980-01-01).

For test experiments on sorption under static conditions, a volume ratio of phases $V_{\text{solution}}/V_{\text{resin}}$ of 1000: 1 was used. The duration of the contact was 24 h. Sampling for analysis in an amount of 10 ml is carried out at intervals: after 1, 2, 4, 6, 8, 12, 16, 20, 24 h.

At the end of sorption, solid and liquid samples were analyzed for scandium, rare-earth metals and impurities using an inductively coupled plasma mass spectrometer model ICAP-Qc from Thermo Fisher Scientific, Maltham, MA, USA. The relative standard error of the method for determining scandium, REE and uranium is 0.66%, 0.67%, and 0.1%.

The equilibrium static exchange capacity of the dry ion exchanger according to Sc (per element) was determined by the difference in the Sc concentrations in the initial mother liquor and the solution after sorption and was calculated by the Eq. 1:

$$\text{SEC} = \frac{(C_1 - C_2) \times V_s}{m_{\text{resin}}}, \text{ mg/g} \quad (1)$$

where, C_1 – concentration of Sc in the initial solution, g/dm³; C_2 – concentration of Sc in solution after sorption, g/dm³; V_s – volume of the solution taken for testing, dm³; m_{resin} – mass of a sample of dry ion exchanger in H⁺ form, g.

To study the sorption process under dynamic conditions, a pre-swollen ion exchanger was placed in Plexiglas ($V = 30 \text{ cm}^3$) columns and the test solution was passed through the fixed volume of the ion exchanger until it was completely saturated with a valuable component. The solution was supplied “from the bottom up” using a peristaltic pump with a constant flow rate of 0.3 dm³/h for sorption. In this case, 10 $V_{\text{solution}}/V_{\text{resin}}$ per hour.

In the calculation, the ratio of the concentration of the target element in the mother liquor (C_e) to the concentration in the incoming solution (C_0) was used as a function of the duration or volume

Table 1
The chemical composition of the initial mother liquor of sorption of uranium

Elements	Sc	U	pH	H ₂ SO ₄	Ce	Nb	Y	Fe ²⁺	Fe ³⁺	Al	Th
Content, mg/dm ³	0.34	1.9	2	n.a.	3.82	6.25	1.66	40	140	160	0.084

of the missed solution. The integral area under the output curve allows you to find the number of adsorbed target element. The total amount of sorbed element, Q (DEC) was calculated by the Eq. 2:

$$Q = \frac{\sum (C_0 * V - C_e * V) * 1000}{V_{resin}}, \text{ mg / dm}^3 \quad (2)$$

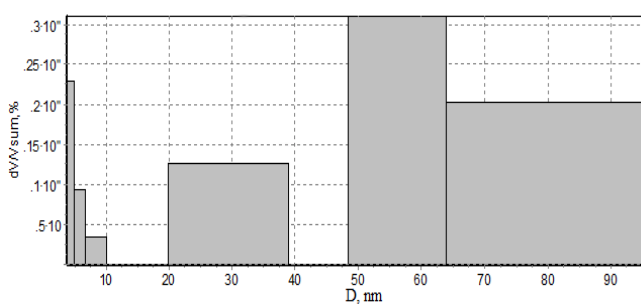
where, C_0 – initial concentration, mg/dm^3 ; C_e – concentration of the element in solution passing through the column, mg/dm^3 V_{resin} – volume of the resin in the column, 30 ml; V – volume of solution passing through the column, cm^3 .

3. Results and discussion

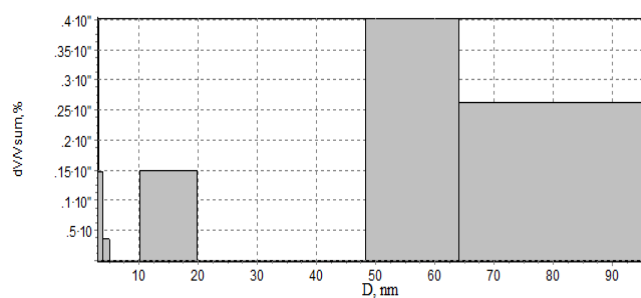
The specific surface of Purolite MTS9580 and Lewatit TP260 ion exchangers was measured as 5.1 and 4.5 m^2/g , respectively. The distribution of pore volumes by their diameters is given in Fig. 1.

The values obtained indicate the presence of a macroporous structure in ion exchangers. The proportion of large pores (diameter 50–90 nm) is the same for both resins, but the fraction of small pores in Purolite MTS9580 (20–40 nm) is slightly higher compared to Lewatit TP260 (10–20 nm), which suggests the best kinetic characteristics of Purolite MTS9580 with respect to metal cations.

It should be noted that ion-exchange resins swell



(a)



(b)

Fig. 1. Pore diameter distribution for Purolite MTS9580 (a) and Lewatit TP260 (b) ion exchangers.

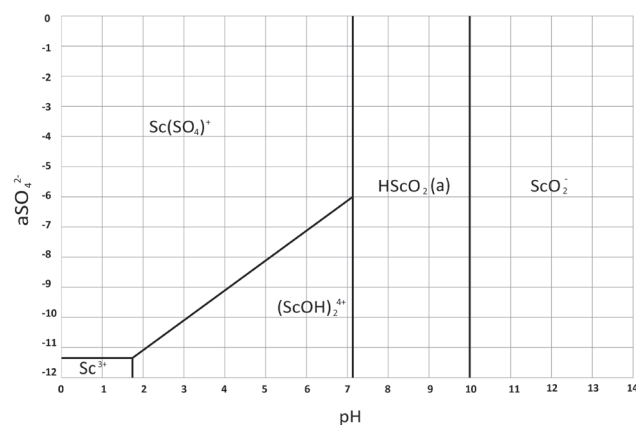


Fig. 2. Scandium state diagram in sulfate solutions depending on the concentration of sulfate ions and the pH of the solution at 25 °C [15].

upon contact with aqueous solutions, as a result of which the pore sizes of ion exchangers in a swollen state can radically differ from the pores of ion exchangers in dry form, due to this circumstance, the data presented are only comparative.

One of the known methods for enlarging the exchange capacity of weakly acid cation exchangers for the target component is to increase the acidity of the initial sorption solution. Based on thermodynamic calculations performed in [14], the prevailing form of Sc(III) in acid sulfate solutions is $\text{Sc}(\text{SO}_4)^+$ (Fig. 2) and cation exchange is considered as the main mechanism of interaction of this ion with the functional groups of the studied sorbent.

To establish the sorption characteristics of MTS9580 ion exchanger, experiments were carried out on the sorption of scandium and impurities in a static mode with varying the acidity of the initial mother liquor of sorption of uranium. The kinetic sorption curve of scandium is presented in Fig. 3.

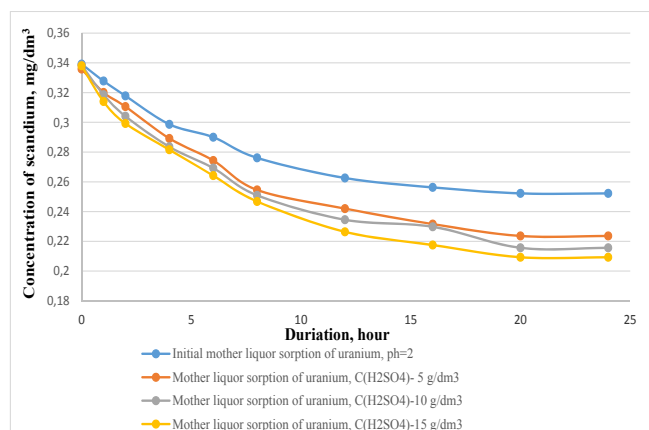


Fig. 3. Kinetic curves of scandium sorption on MTS9580 ion exchanger from mother solutions of uranium sorption with different acidity at 20 °C.

Table 2
Comparative data on the static exchange capacity (SEC) of TP260 and MTS9580 for scandium and impurities (calculated by the equation

Element	SEC, mg/g							
	Mother liquor solution (init.), pH – 2	Mother liquor solution, H ₂ SO ₄ – 5 g/dm ³	Mother liquor solution, H ₂ SO ₄ – 10 g/dm ³	Mother liquor solution, H ₂ SO ₄ – 15 g/dm ³	Mother liquor solution (init.), pH – 2	Mother liquor solution, H ₂ SO ₄ – 5 g/dm ³	Mother liquor solution, H ₂ SO ₄ – 10 g/dm ³	Mother liquor solution, H ₂ SO ₄ – 15 g/dm ³
	TP 260				MTS9580			
Sc	0.118	0.154	0.211	0.223	0.144	0.185	0.285	0.384
Ce	1.481	1.419	1.066	1.052	0.032	0.020	0.011	0.009
Dy	0.090	0.090	0.075	0.070	0.013	0.011	0.006	0.004
Er	0.035	0.041	0.029	0.026	0.006	0.004	0.003	-
Eu	0.035	0.035	0.030	0.029	0.002	0.001	0.00079	0.00059
Gd	0.148	0.149	0.120	0.114	0.023	0.023	0.014	0.013
La	0.464	0.398	0.277	0.273	-	-	-	-
Nd	0.643	0.615	0.495	0.482	0.005	-	-	-
Fe	7.746	6.616	5.773	5.314	6.915	7.891	5.601	5.705
Th	0.167	0.277	0.237	0.248	0.098	0.137	0.097	0.130
U	0.497	0.423	0.249	0.402	0.366	0.443	0.532	0.581
Al	1.067	0.978	0.710	0.613	0.093	0.073	0.047	0.039
Ca	0.893	0.432	0.425	0.358	0.410	0.343	0.531	0.429

Figure 3 shows the advantage of sorption of scandium by the MTS9580 ion exchanger, provided that the sorption mother liquor of uranium is pre-acidified with sulfuric acid to 15 g/dm³.

Table 2 shows comparative data on the static exchange capacity of TP260 and MTS9580 ion exchangers obtained by sorption of scandium from the mother liquor of sorption of uranium of various acidity (5 g/dm³, 10 g/dm³, 15 g/dm³). Scandium recovery increases with decreasing pH, i.e., as the dissociation of ion-exchange groups is suppressed (the dissociation constants of phosphonic acid at the first and second steps are 1.8 and 6.7, respectively, the dissociation pH at 2 steps is 2.6 [15]) and with an increase in the fraction of sorbed ions due to complexation with the functional group of the ion exchanger. Data on TP260 resin was studied in [16].

From the data in Table 2, it can be seen that, compared to the TP260 ion exchanger, the MTS9580 ion exchanger has a clear advantage: when sorbing from a solution with an acid different from the acidity of the initial mother liquor, a higher scandium capacity is achieved, which gradually increases with increasing sulfuric acid concentration in

the uranium sorption mother liquor. The exchange capacity of the MTS9580 ion exchangers for rare-earth metals and harmful impurities is gradually decreasing.

The data obtained determine the choice of resin MTS9580 for further experiments on the sorption of scandium in the dynamic mode from the mother liquor of sorption of uranium with acidification up to 15 g/dm³.

Figures 4–8 show the output sorption curves of scandium and impurities on MTS9580 resin.

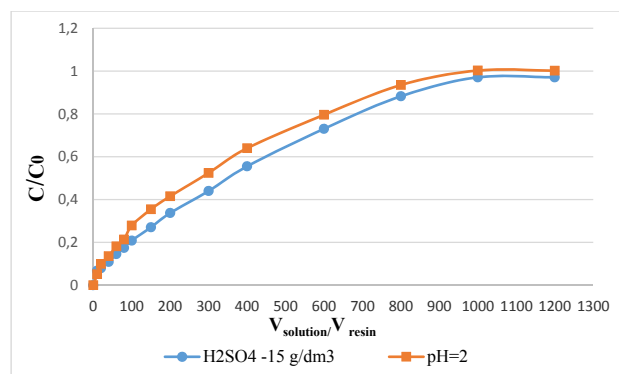


Fig. 4. The output sorption curves of scandium on the ion exchanger MTS9580 at 20 °C.

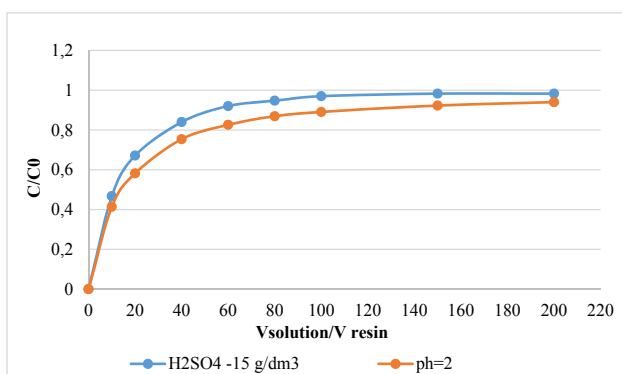


Fig. 5. The output sorption curves of iron on the ion exchanger MTS9580 at 20 °C.

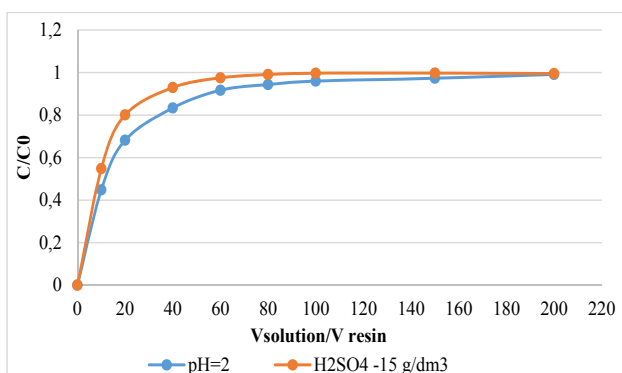


Fig. 6. The output sorption curves of aluminum on the ion exchanger MTS9580 at 20 °C.

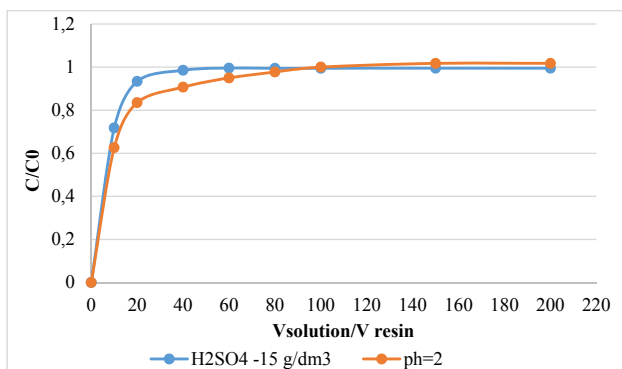


Fig. 7. The output sorption curves of neodymium on the ion exchanger MTS9580 at 20 °C.

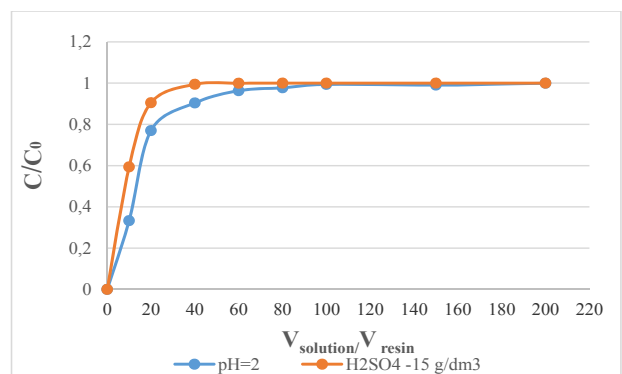


Fig. 8. The output sorption curves of thorium on the ion exchanger MTS9580 at 20 °C.

Analysis of the graphs presented in Figs. 5–8 suggests that the sorption of impurities and rare-earth metals under dynamic conditions ceases after passing the first 100–150 bed volumes (Figs. 5, 6 – 150 bed volumes, Figs. 7, 8 – 100 bed volumes) of the solution, while scandium sorption continues even after passing 800 specific volumes of acidified mother liquor of sorption of uranium. This indicates the high selectivity of the MTS9580 ion exchanger for scandium. To completely saturate the MTS9580 with scandium, it is necessary to pass 1200 bed volumes of the solution. The sorption data of scandium from acidified (to 15 g/dm³ H₂SO₄) mother liquor sorption of uranium using ion exchangers TP260 and MTS9580 are summarized in Table 3.

The dynamic exchange capacity of MTS9580 for scandium is more than 3 times higher than that of TP260, and the DEC values for rare-earth metals and harmful impurities in MTS9580 are much lower. These results indicate a higher selectivity of MTS9580 for scandium compared to TP260.

Table 3

Dynamic exchange capacities (DEC) of ion exchangers TP260 and MTS9580 for scandium and impurities (calculated by the Eq. 2)

Element	DEC, mg/dm ³	
	TP-260	MTS9580
Sc	59.7	200
Dy	19.2	4.46
Ce	357	53.7
Nd	136	21.1
La	124	20.3
Y	66.8	19.2
Al	308	80.2
Fe	2868	1254
Th	112	36.6
Ca	342	168

4. Conclusion

Comparison of the sorption indices of scandium from pre-acidified H₂SO₄ to 15 g/dm³ of sorption uranium mother liquor on Lewatit TP260 and Purolite MTS9580 ion exchangers showed the advantage of using the latter: a higher dynamic exchange capacity of 200 mg/dm³ was achieved compared to 59.7 mg/dm³ for TP260, and DOE in relation to harmful impurities for this sorbent is much lower. Based on the studies, the Purolite MTS9580 ion

exchanger can be recommended as a selective adsorbent for the isolation of scandium from sorption of uranium mother liquor.

Acknowledgments

The work was carried out in laboratory for research and analysis of materials «Institute for High Technologies» LLP (subsidiary of NAC Kazatomprom, Almaty, Kazakhstan).

References

- [1]. A. Belosludtsev, Y. Yakimov, R. Mroczyński, S. Stanionytė, M. Skapas, D. Buinovskis, N. Kyžas, *Physica Status Solidi (a)* 216 (2019). DOI: [10.1002/pssa.201900122](https://doi.org/10.1002/pssa.201900122)
- [2]. D. Cheikh, K. Lee, W. Peng, A. Zevalkink, J.-P. Fleurial, S.K. Bux, *Materials* 12 (2019) 734. DOI: [10.3390/ma12050734](https://doi.org/10.3390/ma12050734)
- [3]. K. Skotnicová, G.S. Burkhanov, T. Cegan, N.B. Kolchugina, A.A. Lukin, O. Životsky, P.A. Prokofev, M. Kurska, J. Jurica, Yu. Koshkid'ko. *Journal of Physics: Conference Series* 1134 (2018) 012055. DOI: [10.1088/1742-6596/1134/1/012055](https://doi.org/10.1088/1742-6596/1134/1/012055)
- [4]. S. Riva, Scandium metal processing for aerospace application, 2018. DOI: [10.23889/SUthesis.39867](https://doi.org/10.23889/SUthesis.39867)
- [5]. T.V. Molchanova, I.D. Akimova, A.V. Tatarnikov, *Russian Metallurgy (Metally)* 2019 (2019) 674–679. DOI: [10.1134/S0036029519070103](https://doi.org/10.1134/S0036029519070103)
- [6]. H. Qiu, M. Wang, Y. Xie, J. Song, T. Huang, X.-M. Li, T. He, *Process Saf. Environ.* 121 (2019) 118–124. DOI: [10.1016/j.psep.2018.10.027](https://doi.org/10.1016/j.psep.2018.10.027)
- [7]. H. Nie, Y. Wang, Y. Wang, Z. Zhao, Y. Dong, X. Sun, *Hydrometallurgy* 175 (2018) 117–123. DOI: [10.1016/j.hydromet.2017.10.026](https://doi.org/10.1016/j.hydromet.2017.10.026)
- [8]. O.V. Petrakova, A.B. Kozyrev, A.G. Suss, S.N. Gorbachev, A.V. Panov, *Light Metals* (2019) 1407–1413. DOI: [10.1007/978-3-030-05864-7_176](https://doi.org/10.1007/978-3-030-05864-7_176)
- [9]. E.M. Peters, Ş. Kaya, C. Dittrich, K. Forsberg, *Journal of Sustainable Metallurgy* 5 (2019) 48–56. DOI: [10.1007/s40831-019-00210-4](https://doi.org/10.1007/s40831-019-00210-4)
- [10]. D.A. Kondrutsky, E.V. Kirillov, V.N. Rychkov, E.V. Kirillov, G.M. Bunkov, E.S. Vostrov, V.A. Tretyakov, G.R. Gadzhiev, N.A. Poponin, D.V. Smyshlyaev, Solid extractant with high dynamic exchange capacity for scandium extraction and method for its production. Federal Service for Intellectual Property, 13/04/2018. Patent No. 2650410 (in Russ.)
- [11]. Yu.V. Sokolova, K.Yu. Pirozhenko, The sorption of scandium from sulfuric acid solution on industrial phosphorus-containing ion exchange resins. *Sorbtsionnye i khromatograficheskie Protsessy* [Sorption and chromatographic processes] 15 (2015) 563–570 (in Russ.).
- [12]. U.M. Yessimkanova, M.M. Mataev, M.P. Kopbaeva, A.V. Berezovsky, M.B. Alekhina, *Khimicheskaja promyshlennost' segodnja* [Chemical Industry Today] 5 (2019) 24–27 (in Russ.).
- [13]. A.V. Tatarnikov, M.A. Mikhailenko, Selection of sorbents for the extraction of scandium and rare earth elements from solutions of complex composition, Collection of materials of the international scientific-practical conference “Actual issues of obtaining and applying REM and RM - 2017, Moscow, June 21–22, 2017, “Institute” GINCVETMET” (in Russ.).
- [14]. Shenxu Bao, W. Hawker, J. Vaughan, *Solvent Extr. Ion Exc.* 36 (2017) 100–113. DOI: [10.1080/07366299.2017.1412917](https://doi.org/10.1080/07366299.2017.1412917)
- [15]. Yu.Yu. Lurie Handbook of analytical chemistry, M.: Chemistry, 1989, P. 448 (in Russ.).
- [16]. M.P. Kopbaeva, A.V. Berezovsky, A.T. Kumarbekova, U.M. Yessimkanova, A.K. Torebekov. The increase in acidity of weakly acid cation exchanger according to scandium due to an increase in the acidity of the initial solution. Collection of reports of the International Innovation School “Prospects and Technologies for Diversifying the Activities of NAC Kazatomprom JSC, 2018, P. 187–190 (in Russ.).