MINING SCIENCE AND TECHNOLOGY (RUSSIA)
ГОРНЫЕ НАУКИ И ТЕХНОЛОГИИ
2021;6(3):158–169

eISSN 2500-0632
https://mst.misis.ru/

BENEFICIATION AND PROCESSING OF NATURAL AND TECHNOGENIC RAW MATERIALS

Research article

https://doi.org/10.17073/2500-0632-2021-3-158-169

Prospects for selective-and-advanced recovery of rhenium from pregnant solutions of in-situ leaching of uranium ores at Dobrovolnoye deposit

A. A. Rudenko[1], **I. D. Troshkina**[2] ✉, **V. V. Danileyko**[1], **O. S. Barabanov**[3], **F. Ya. Vatsura**[2]

[1] *JSC "RUSBURMASH", Moscow, Russian Federation;*

[2] *Mendeleev University of Chemical Technology of Russia, Moscow, Russian Federation*

[3] *JSC ARMZ (Atomredmetzoloto Uranium Holding Co., the Rosatom's mining division), Moscow, Russian Federation*

✉ *tid@muctr.ru*

Abstract

Analysis of exploration materials and market conditions showed that by-product recovery of rhenium, one of the rarest strategic elements of the periodic system, was not always effective in processing the whole volume of pregnant uranium-bearing solutions. The main goal of the research was to develop an effective method for recovery rhenium from pregnant solutions in in-situ uranium leaching. The objectives of the research were as follows: evaluation of the possibility of selective-and-advanced recovery of rhenium from ores by in-situ leaching method and comparison of the technological advantages of the new proposed method with the known ones. The study involved the analysis of historical geological, mineralogical and geochemical information on the Dobrovolnoye deposit and analysis of technological aspects of by-product recovery of rhenium in the world practice. A selective-and-advanced scheme of rhenium recovery from pregnant uranium-bearing sulfate (sulfuric acid) solutions of the Dobrovolnoye deposit ISL (Russia) using mobile installations was proposed. The process has the following features: zoning of production blocks when constructing injection and extraction (pumping) wells; piping of selective extraction wells into a separate collecting pipe; implementation of advanced rhenium sorption. The process implementation makes it possible to obtain rhenium from economically viable areas of the uranium deposit. The mobile installation includes the following main units: a filter for purification (aftertreatment) to remove suspension, a chain of sorption apparatuses (sorption filters or columns), connecting fittings, control and measuring instruments. The sorption apparatuses are filled with rhenium-selective ionite (ion exchanger). As a selective sorbent for the primary concentration of rhenium from sulfate solutions (pH 2), weakly basic nitrogen-bearing ionites containing amine functional groups of various types can be used. If further concentration of rhenium is required, in order to unify the equipment used, materials with a mobile extractant phase (so-called TVEXs (solid extractants or Levextrel resins in English literature) and so-called "impregnated" or "impregnates"), such as TVEX-DIDA containing diisododecyl amine, or TAA-impregnate containing trialkylamine, can be used. Rhenium desorption from these materials is carried out by an ammonia solution, which allows producing rough ammonium perrhenate from the eluate. Economic aspects of the rhenium selective-and-advanced technology were evaluated. Implementation of the recovery selective-and-advanced technology allows obtaining rhenium from economically-viable areas of the uranium deposit.

Keywords

uranium, in-situ leaching, Kurgan region, rhenium, sulfuric acid, recovery scheme, production block, differentiation, optimization, productivity, selectivity

For citation

Rudenko A. A., Troshkina I. D., Danileyko V. V., Barabanov O. S., Vatsura F. Ya. Prospects for selective-and-advanced recovery of rhenium from pregnant solutions of in-situ leaching of uranium ores at Dobrovolnoye deposit. *Mining Science and Technology (Russia)*. 2021;6(3):158–169. https://doi.org/10.17073/2500-0632-2021-3-158-169

MINING SCIENCE AND TECHNOLOGY (RUSSIA)
ГОРНЫЕ НАУКИ И ТЕХНОЛОГИИ
2021;6(3):158–169

eISSN 2500-0632
https://mst.misis.ru/

ОБОГАЩЕНИЕ, ПЕРЕРАБОТКА МИНЕРАЛЬНОГО И ТЕХНОГЕННОГО СЫРЬЯ

Научная статья

Перспективы селективно-опережающего извлечения рения из продуктивных растворов подземного выщелачивания урановых руд месторождения Добровольное

А. А. Руденко[1], **И. Д. Трошкина**[2] ✉, **В. В. Данилейко**[1], **О. С. Барабанов**[3], **Ф. Я. Вацура**[2]

[1] *АО «РУСБУРМАШ», г. Москва, Российская Федерация*

[2] *Российский химико-технологический университет имени Д. И. Менделеева (РХТУ им. Д. И. Менделеева), г. Москва, Российская Федерация*

[3] *АО «АРМЗ», г. Москва, Российская Федерация*

✉ *tid@muctr.ru*

Аннотация

Анализ геологоразведочных материалов и рыночной конъюнктуры показал, что попутное извлечение одного из самых редких стратегических элементов периодической системы – рения – не всегда эффективно при переработке всего объема продуктивных урансодержащих растворов. Основная цель исследований – разработка эффективного способа извлечения рения из продуктивных растворов при скважинном подземном выщелачивании урана. Задачами исследований являлись: оценка возможности селективно-опережающего извлечения рения из руд способом скважинного подземного выщелачивания и сопоставление технологических преимуществ нового предлагаемого способа с известными. В работе использован анализ геологической, минералого-геохимической информации предыдущих лет изучения месторождения Добровольное и анализ технологических аспектов попутной добычи рения в мировой практике. Предложена селективно-опережающая схема извлечения рения из продуктивных сернокислых урановых растворов подземного выщелачивания урановых руд месторождения Добровольное (Курганская область, Россия) с использованием мобильных установок. Технология имеет следующие отличия: зонирование эксплуатационных блоков при сооружении закачных и откачных скважин; обвязку откачных селективных скважин в отдельный коллектор; осуществление опережающей сорбции рения. Ее осуществление дает возможность получать рений из экономически выгодных участков месторождения урана. Мобильная установка включает следующие основные узлы: фильтр для очистки (доочистки) от взвесей, каскад сорбционных аппаратов (сорбционных фильтров или колонн), соединительную арматуру, контрольно-измерительные приборы. Сорбционные аппараты заполняются селективным на рений ионитом. В качестве селективного сорбента для первичного концентрирования рения из сернокислых растворов (pH 2) могут быть использованы слабоосновные азотсодержащие иониты, содержащие функциональные группы аминов различного типа. При необходимости дальнейшего концентрирования рения с целью унификации используемого оборудования можно применить материалы с подвижной фазой экстрагента (твэксы или импрегнаты), например, ТВЭКС-ДИДА, содержащий диизододециламин, или импрегнат-ТАА, содержащий триалкиламин. Десорбция рения с этих материалов осуществляется раствором аммиака, что позволяет получить из элюата черновой перренат аммония. Оценены экономические аспекты селективно-опережающей технологии рения. Реализация технологии селективно-опережающего извлечения дает возможность получать рений из экономически выгодных участков месторождения урана.

Ключевые слова

уран, скважинное выщелачивание, Курганская область, рений, серная кислота, схема извлечения, добычной блок, дифференциация, оптимизация, продуктивность, селективность

Для цитирования

Rudenko A. A., Troshkina I. D., Danileyko V. V., Barabanov O. S., Vatsura F. Ya. Prospects for selective-and-advanced recovery of rhenium from pregnant solutions of in-situ leaching of uranium ores at Dobrovolnoye deposit. *Mining Science and Technology (Russia)*. 2021;6(3):158–169. https://doi.org/10.17073/2500-0632-2021-3-158-169

Introduction

The main direction in the development strategy of the mineral resource base (MRB) of the Russian Federation uranium mining industry for the next decade is primarily expansion of MRB in the area of operating mining enterprises, JSC "Dalur", JSC "Khiagda" and PJSC "PPGKhO", suitable for the development with the use of two geotechnologies: well in-situ leaching (ISL) and in-situ block leaching [1].

Creation of new modern technologies for natural resources development involves application of environmentally sound methods, which include in-situ leaching, their integrated development and the maximum possible degree of processing for the products demanded by the national economy. Integrated processing of natural resources as a basis for creation of low-waste technologies is understood as the use of all mineral components of raw materials by turning them into useful products by combining several productions within one enterprise. Often, when extracting two or more components from raw materials, the lower concentration limit of processing viability decreases.

Along with the main task of uranium raw materials integrated processing – by-product recovery of its valuable components, which are of an economic nature, utilization of solid waste and recovery of reagents from water and gas waste are also important. Uranium itself is recovered as by-product from copper and gold ores, as well as from phosphorite. The share of such by-product uranium is ~9 % of the whole uranium recovery.

Complex uranium ores are divided into two main groups [2]:

1. Ores in which uranium and associated elements are contained in a single mineral (vanadium and uranium in carnotite, phosphorus and uranium in apatite, niobium and uranium in hatchettolite, zirconium and uranium in malacone). The useful components cannot be separated by mechanical beneficiation methods and can only be separated by chemical processing of the ores.

2. Ores in which uranium and associated elements are represented by different mineral forms or carriers (ores containing non-ferrous metal sulfides and arsenides, native silver, gold, bismuth). In this case, separate production of concentrates is possible by methods of mechanical beneficiation.

The following elements accompany uranium in ores: gold, vanadium, molybdenum, rare earth elements, yttrium, rhenium, copper, nickel, cobalt, arsenic, and phosphorus. Thorium, scandium, and selenium are present to a lesser extent. It should be noted that grade (concentration) of these elements in the ores is often too low to ensure economically viable separation and recovery, but on the other hand, it is high enough to affect the quality of the primary uranium concentrate, "yellow cake". In this connection, the task of integrated processing of uranium raw materials is also connected with the task of improving the quality of the main commercial product of uranium processing.

Profitability of integrated processing is determined by the lower concentration limit, evaluation of which for two-component ores at different uranium grade is given in [3]. It should be noted that the most cost-effective in the world uranium recovery from ores with an average uranium grade of 0.06% was achieved in the course of processing of complex ores of Olympic Dam copper-gold-silver-bearing uranium deposit in Australia.

The most promising method of uranium ore leaching, in-situ leaching (ISL) (with the use of wells), produces so-called pregnant solutions, which along with the target component, uranium, contain a number of by-products, among which rhenium and scandium are of high value and strategic importance. The lower concentration threshold of rhenium in them is less than 0.02 mg/l [3].

Rhenium is one of the least abundant elements of the periodic system. The existence of rhenium was predicted in 1871 by D.I. Mendeleev, who called it eco-manganese. It was discovered in Germany in 1925 as the last stable element in the periodic system. The melting point of this metal is 3180 °C, second only to tungsten. At the same time, rhenium is distinguished by plasticity among the most refractory brittle metals (tungsten, molybdenum, and others). Alloys based on refractory metals have high mechanical strength as well as resistance to thermal deformation, creep, and oxidation. Superalloys – alloys based on metals of group VIII (nickel, iron, and cobalt) are distinguished among them [4]. The most high-temperature cast complex-alloyed nickel-based alloys capable of operating at temperatures of 1050–1100 °C for hundreds and thousands of hours under high static and dynamic loads typically account for 40–50 % of the total weight of an aircraft engine and are widely used in working and nozzle blades, turbine rotor disks, combustion chamber parts [5, 6]. These superalloys also contain other elements such as rhenium, chromium, cobalt, tungsten, tantalum, molybdenum, hafnium, titanium, aluminum. Up to 40% of the total weight of the superalloys belong to them. Alloys of the fifth generation contain ruthenium along with rhenium [7]. Rhenium is one of the most effective alloying components in monocrystalline alloys: its effect on the heat resistance enhancement is due to its increased solubility in nickel γ-solid solution, the increase in the lattice spacing and solidus temperature, the decrease in the alloying elements diffusion coefficients [7].

The development of aerospace engineering in the world is determined by the use of rhenium heat-resistant monocrystalline nickel-based superalloys. The sector of heat-resistant alloys consumes more than 80% of total rhenium production (~70 t, 2021)[1]. This field of rhenium application has dominated since the end of the last century [4]. The remaining part of rhenium is indispensable in the composition of platinum-rhenium catalysts for high quality gasoline and in electronics [4].

The rhenium mineral raw -material base of Russia is presented by low-grade molybdenite concentrates, which can be produced from ores of deposits Sorskoye, Zhirekeskoye, Lobash, etc., and also by fumarole gases of Kudryavy volcano (Iturup island, Kurils, Sakhalin region), included in the State Balance Sheet of Reserves, but not processed.

By-product recovery of rhenium from pregnant solutions of Dobrovolnoye uranium deposit ore ISL (in the area of the operating mining enterprise JSC “Dalur”) seems to be a timely scientific and practical task.

The main goal of the research was to develop an effective method for recovery rhenium from pregnant solutions in in-situ uranium leaching.

The objectives of the research were as follows: evaluation of the possibility of selective and advanced recovery of rhenium from ores by in-situ leaching method and comparison of the technological advantages of the new proposed method with the known ones.

The study involved the analysis of historical geological, mineralogical and geochemical information on the Dobrovolnoye deposit and analysis of technological aspects of by-product recovery of rhenium in the world practice.

Brief analysis of by-product rhenium recovery technologies

Because of ultralow Re crystal abundance ($7 \cdot 10^{-4}$ %), rhenium in world practice is recovered only as a by-product in integrated processing of molybdenum and copper ores. Molybdenum concentrates from copper-porphyry deposits, which provide about 80 % of world production of rhenium (Chile, Peru, USA and Canada), serve as the main raw material for rhenium production. Among other sources the important place belongs to stratiform deposits of copper, from which the main amount of rhenium is extracted in CIS countries. Cuprous ores of the Dzhezkazgan deposit in Kazakhstan remain the largest source of this metal in Asia. Own minerals of rhenium are rare (dzhezkazganite – rhenium sulfide, rheniite – rhenium sulfide) and have no practical value [4].

Uranium ores as an additional raw material source of rhenium are known since 50th of the last century: in the USA, ~1 t of rhenium was produced from molybdenum-uranium ores [4]. In the CIS, stratified-infiltration exogenous deposits developed by in-situ leaching are located in the largest in the world Near-Tien-Shan Uranium-Ore Province. The grade of rhenium in the ores of these deposits ranges from 0.02 to 2 g/t [8].The highest grade of rhenium was found in Central Kyzyl Kum in ores of “uchkuduk type” (0.6-2.0 g/t on average), whereas in adjacent Syr-Darya and Chu-Sarysu provinces the grade was much less (0.2-0.5 g/t Re) [9]. Rhenium was first detected in 1978 at the North Kanimekh deposit in solutions of in-situ uranium leaching. It was found to be most effectively extracted by ISL with the use of oxygenated natural water. The universal form of Re migration in oxygenated groundwater is the perrhenate ion ReO_4^-, the concentration of which reaches as much as milligrams per liter, whereas its common concentration values are about 0.0n μg/L [8].

In Russia, Re content in uranium ore occurrences of the Russian platform was evaluated [10]. The content of rhenium in these objects is insignificant.

Process flow diagrams based, as a rule, on the use of sorption method were developed for recovery of minor valuable elements from pregnant solutions of in-situ leaching [11]. For example, vanadium can be extracted by using VPK chelating ionite (ion-exchanger) and VP-1p anionite (anion exchanger) for its concentration; for scandium recovery, AFI-22 ion-exchanger is applied.

It should be noted that the highest profitability, 540 %, was demonstrated by rhenium recovery [12]. From sulfate pregnant solutions, rhenium together with uranium is absorbed by strong-basic anion exchanger AM-p. Selective desorption of rhenium is carried out with acidic solutions containing nitrate ions (NO_3^- – 80–90 g/L, HNO_3 – 4–4,5 %). Rhenium is extracted from eluates (with Re concentration of 10–15 mg/L) by a solution of trialkylamine fraction C7–C9 in kerosene with the addition of decanol as modifier. The content of rhenium in the extract reaches 8 g/L, which allows its re-extraction with ammonia solution in the solid-phase version. Flow diagram of by-product recovery of rhenium from ISL sulfate solutions is presented in Fig. 1 [11].

To extract rhenium from circulating solutions of in-situ leaching after uranium sorption (The Republic of Uzbekistan), the composite extracting polymer KEP-200 by Purolite company was used [12, 13]. Recent studies of rhenium sorption from model sulfate (pH 1.54) and bicarbonate (pH 7.1) solutions demonstrated the efficiency of strong-basic anion exchanger V0-020 [15]. From 2008 to 2011, at two operating sorption installations of Navoi Mining and Metallurgical Combine, ~3 tons of ammonium perrhenate of AP-0 grade were produced [15, 16].

---

[1] USGS Mineral Commodity Yearbook 2021. https://doi.org/10.3133/mcs2021

In the territory of the Russian Federation, rhenium was not extracted from solutions of uranium in-situ leaching on commercial scale.

Characteristics of the developing Dobrovolnoye deposit

Development of deposits by the ISL method in the Trans-Urals is conducted by JSC Dalur uranium mining company, located in the village of Uksyanskoye, Dalmatovskiy district of Kurgan region. The district is well developed and is crossed by the Sverdlovsk-Kurgan-Petropavlovsk and Chelyabinsk-Kurgan railroads, as well as dense network of regional and national roads. The routes of the main oil pipelines pass through the district.

Uranium mineralization in the Trans-Urals territory (Fig. 2) is mainly presented by uranium deposits and occurrences in the Upper Jurassic - Lower Cretaceous paleo-valleys, cut into the crystalline rocks of the pre-Jurassic basement. The currently developed Miass and Uysko-Tobolsky ore districts, which include three deposits: Dalmatovskoye, Khokhlovskoye, Dobrovolnoye and a large group of ore occurrences, are of commercial importance.

Paleo-valleys extend for tens of kilometers at the width of 2–5 km. The deposits are elongated (up to 20 km long) ribbon-like zones of uranium-bearing rocks in paleo-valleys. The source of uranium and associated metals is probably the rocks of the Jurassic basement, which underwent intense chemical weathering.

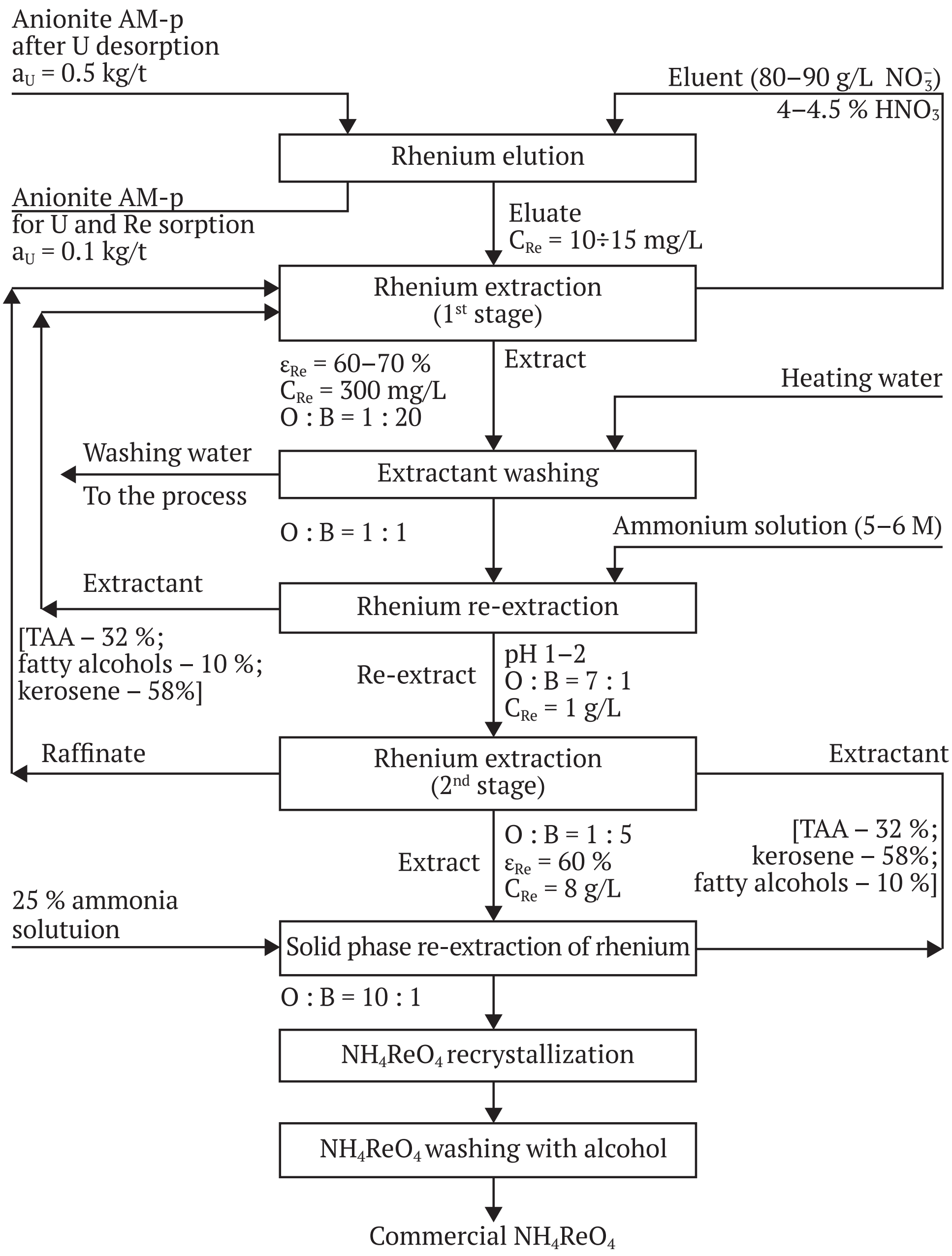


Fig. 1. Flow diagram of rhenium by-product recovery from uranium in-situ leaching solutions [11]

Gravel-sandy sediments rhythmically alternating in the section well permeable with clayey aquicludes allow distinguishing three water-permeable sub-horizons (aquifers) in the section. In the absence of an aquiclude between sediments of the first and second rhythms, the lower and middle aquifers are combined into one. The upper aquifer lies at a depth of 435–517 m. The average thickness is 13 m. The upper aquiclude for the aquifer is presented by clays of Koskolskaya red-colored strata, and the bottom aquiclude is composed of clayey sediments 3–15 m thick. The filtration coefficient varies from 0.8 to 23.5 m/day. The aquifers occur at depths of 513–567 m. Their average thickness is 30 m, varying from 4.5 to 44 m. The upper aquiclude is presented by clayey sediments of the second rhythm of 3–20 m thick, and the lower one is the basement rocks. The filtration coefficient varies from 5.0 to 20.7 m/day.

Chemistry of the Middle-Upper Jurassic ore-bearing aquifer system within the deposit is characterized by prevailing hydrocarbonates, sulfates, and sodium chlorides. The waters are saline with salinity of 11.1–13.0 g/dm^3, pH 7.2–7.5. Uranium concentration in the water is up to $7.8 \cdot 10^{-6}$ g/dm^3, hydrogen sulfide concentration is up to 1.5 mg/dm^3, Eh ranges from +60 to +120 mV. The aquifer waters are high-pressure. Estimated water head above the day surface is 41–47 m.

Mineral composition of uranium ores of Trans-Urals deposits is uniform and typical for exogenous deposits of hydrogenous type. Ore-bearing sandy sediments up to 20 m thick have aluminosilicate composition, %: SiO_2, 78.5; Al_2O_3, 12.5; CO_2, 0.2 (with maximum content not exceeding 2.0); iron, 1–3; sulfide sulfur, 0.1–1.6. More than 95 % of uranium occur in its own mineral form of uranium oxides (nasturan), represented by several generations, and silicates (coffinite). The ratio of nasturan and coffinite in the ores is approximately 1:1. The radioactive equilibrium coefficient is ~1. In uranium grade, the ores belong to the class of poor and low-grade; the average uranium grade in ores of the deposits is 0.03–0.05 %. The age of mineralization determined by the uranium-lead method for all the deposits is about 140 million years.

Technological properties of the ores of the deposits are identical; the ores are suitable for uranium leaching with sulfate (sulfuric acid) solutions.

Rhenium-rare earth-uranium deposit Dobrovolnoye was discovered in 1986 by Turgai Crew No. 89. The State Balance Sheet of Reserves accounted for in the deposit: 339.0 tons of uranium in C1 category; 7060.0 tons of uranium in C2 category; 5656 tons of uranium in P1 category. Depth of occurrence of the uranium ores is 480–700 meters. Average uranium grade in ore bodies of the deposit is 0.028–0.057 %. Resources and reserves of rhenium are 5.59 tons in P1 category and 10.6 tons in C2 category[2].

Fig. 2. Dobrovolnoye deposit location map

---

[2] Luchinin I. L. Report on the results of preliminary exploration of rhenium-rare earth-uranium deposit Dobrovolnoye. Turgai Party No. 89. Yekaterinburg; 1994.

Rhenium, except for its own mineral form (rhenium sulfides), was identified in the form of sorption impurity in nasturan, pyrite, marcasite and clay matter.

The contents of rhenium in the ores by grade classes are as follows: up to 1 g/t – 71 %, from 1 to 10 g/t – 29 %. High grades of the rhenium are confined to subzones of poor "gray" uranium ores and their "rich" subzones; 15–20 % of the rhenium ores are located in subzone of "whitish" rocks. A schematic section and distribution of rhenium along the exploration section (profile) are shown in Fig. 3.

Selective-and-advanced recovery of rhenium from pregnant sulfate solutions of in-situ leaching

Currently, multivariate methods of recovery of minerals by in-situ leaching, particularly for uranium, are known. At the same time, only rare elements – rhenium and scandium – are so far extracted from pregnant solutions after uranium recovery. Rhenium is extracted on commercial scale in Uzbekistan at the Navoi Mining and Metallurgical Combine [13]. Other methods described in the patents of Russia[3], Kazakhstan[4] and others, as well as in papers [13, 16–19] and monographs [11], prescribe the recovery of rhenium from the whole volume of uranium-bearing solutions.

The main drawback of the known methods is that recovery of rhenium and other associated components from pregnant uranium solutions is supposed to be carried out after sorption of uranium from the pregnant solution – from the so-called "sorption mother liquors". In this case it is necessary to process equivalent volumes of solutions with low concentrations of the associated components in the total volume of the solutions. For example, the concentration of rhenium in pregnant uranium solutions is 0.3–0.8 mg/L (0.5 mg/L in average), which predetermines the necessity to construct additional modules for processing of the solutions, commensurable with the core uranium production. The capital and operating costs of such production can withstand the profitability of the by-product recovery only when peak market prices for the metals are reached. This makes by-product recovery of rhenium and other rare elements under such process flow sheets vulnerable.

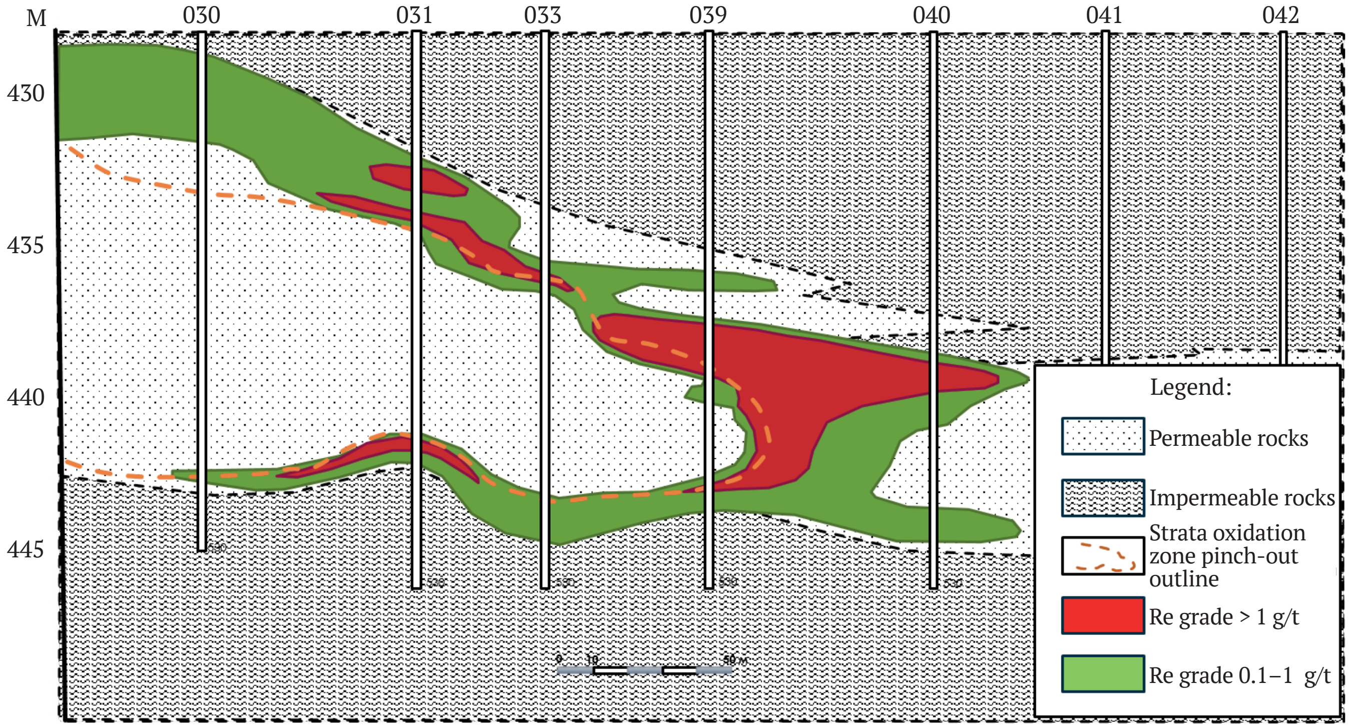


Fig. 3. Distribution of rhenium along the profile 65+400 at Dobrovolnoye deposit

---

[3] Tolstov E. A., Mikhin O. A., Pershin M. E. et al. Method for rhenium recovery from solutions. RF Patent No. 2294392 dated 24.05.2005.

[4] Kozhakhmetov S. K., Kopbaeva M. P., Panova E. N. et al. Method of processing pregnant solutions of in-situ leaching of rhenium-containing uranium ores. RK Patent No. 22659 dated 02.04.2012; Kozhakhmetov S. K., Kopbaeva M. P., Panova E. N. et al. Method of processing pregnant solutions of in-situ leaching of rhenium-containing uranium ores. RK Patent No. 23507 dated 02.04.2012; Kozhakhmetov S. K., Kopbaeva M. P., Panova E. N. et al. Method of processing pregnant solutions of in-situ leaching of rhenium-containing uranium ores. RK Patent No. 26780 dated 02.04.2012.

It is possible to calculate preliminary average concentration of rhenium (C_m, g/dm^3) in pregnant solution during the whole leaching period on the basis of its extracted quantity and total volume V, m^3, of the pregnant solution using the following formula [20]:

$$C_m = 10^2 P_m \frac{\varepsilon}{V},$$

where P_m – total ore reserves in the section, t; ε – degree of metal recovery, fractions of unit; V – volume of leaching solution, m^3.

At initial grade of rhenium in ores more than 2 g/t, concentration of rhenium in pregnant solution is more than 1 mg/L (Fig. 4).

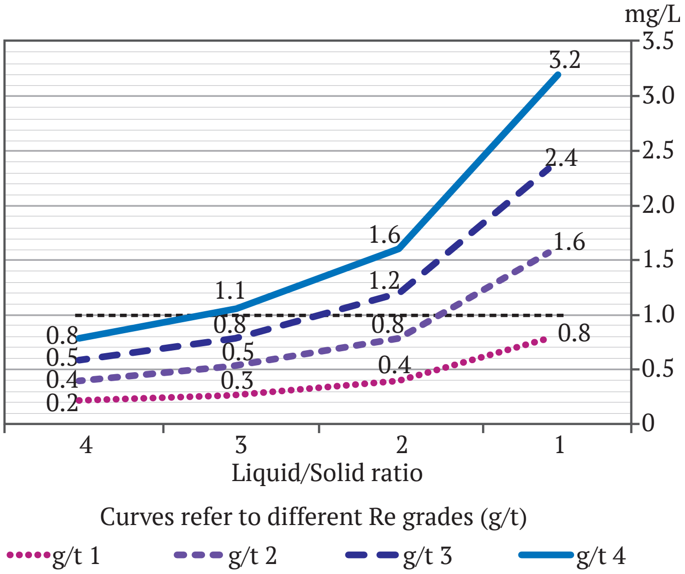


Fig. 4. Rhenium concentration in solution as a function of rhenium ore grade

In this paper we considered the possibility of changing the sequence of operations for by-product recovery of rhenium from solutions by using selective-advanced recovery[5]. An example of the implementation of such a method of recovery is shown in Fig. 5.

Ore production block (*1*) shall be drilled by technological injection (*2*) and pumping (*3*) wells which shall be tested with leaching solution by the "Push-Pull" method after their construction. Based on the results of the analysis of solutions for rhenium, the zones (*4*) of pumping wells location with rhenium concentration in the solution less than 1 mg/l and the zones (*5*) of pumping well location (*6*) with rhenium concentration more than 1 mg/l were differentiated. For the pumping wells with rhenium concentration more than 1 mg/l, piping was created to direct the solutions into a separate pumping collecting pipe (*7*), and solutions were sent for advanced sorption (*9*) with the following production of ammonium perrhenate. After the rhenium sorption, the uranium-containing solutions entered cumulative collecting pipe (*8*) and undergone standard uranium sorption/desorption cycles at the facility for processing uranium-containing solutions (*10*) to produce the finished product ("yellow cake"). The "sorption mother liquor" are supplemented with sulfuric acid and sent through collecting pipe (*11*) for ore leaching through injection wells (2).

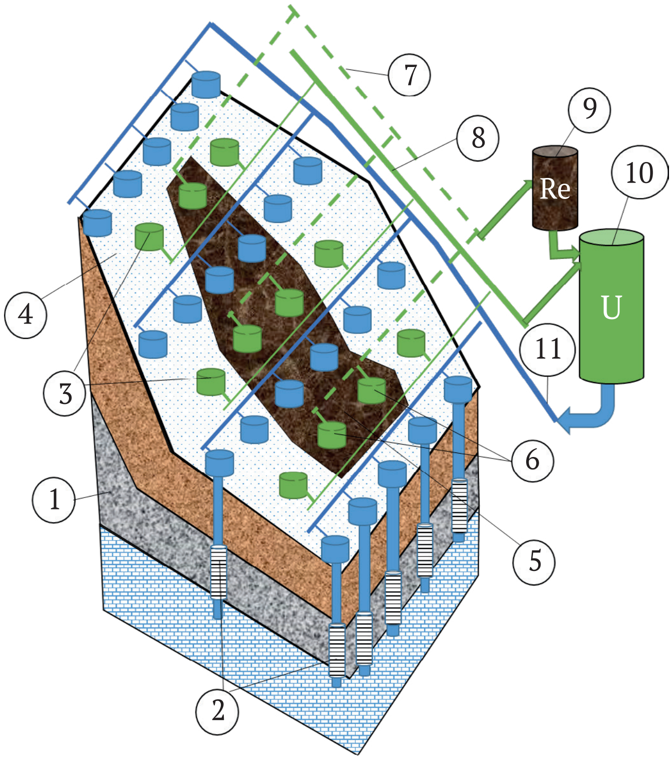


Fig. 5. Schematic diagram of the selective-advanced recovery of rhenium

A variant of a mobile version of the sorption installation for the conditions of in-situ leaching is currently under development.

The installation can provide timely recovery of by-product components through the method of selective-advanced processing of rhenium-containing solutions in the mobile version. The mobile installation includes the following main units: a filter for purification (aftertreatment) to remove suspension, a chain of sorption apparatuses (sorption filters or columns), connecting fittings, control and measuring instruments. The sorption apparatuses are filled with a rhenium-selective ionite (ion exchanger). The installation operates as follows: pregnant solution, containing valuable by-product components, after removal of impurities at the filter or in pond with aftertreatment at the filter, goes to sorption apparatus filled with a ion-exchanger.

---

[5] Rudenko A. A., Troshkina I. D., Danileiko V. V. Method of extraction of minerals by in-situ leaching. Positive decision on the application for invention No. 2020129776 (priority from 08.09.2020) dated 28.09.2021

After complete saturation with valuable component the sorption apparatus is switched off and transported to the core shop of uranium solutions processing or to the nearby facility on processing of rhenium-containing materials for washing, desorption and the subsequent concentration of rhenium to produce, for example, rough ammonium perrhenate of AR-1 grade. The sorption apparatus with the regenerated ion exchanger is returned for connection to the installation apparatus cascade.

Depending on the infrastructure of the in-situ leaching wellfield it is possible to carry out washing, desorption and subsequent concentration operations (process stages) to produce the commercial salt in the area occupied by the mobile installation, with increasing the number of necessary apparatuses.

As a selective sorbent for the primary concentration of rhenium from sulfate solutions (pH 2), weakly basic nitrogen-bearing ionites containing amine functional groups of various types, modified activated carbon, fibrous materials of different composition[6] can be used [4, 21, 22–24]. Sorbents based on natural raw materials – lignin [25] and composites with bamboo [26] – were prepared for rhenium recovery from acid solutions.

Interaction of rhenium in solution in the form of perrhenate ion with frequently used in practice weakly basic anion exchangers containing secondary amine groups occurs through the mechanism of ion exchange of perrhenate ion ReO_4^- to sulfate ion (the form in which the anion exchanger is present). The reaction can proceed according to the equation:

$$(RNH_2)SO_4^{2-} + 2ReO_4^- \leftrightarrow 2RNH_2(ReO_4) + SO_4^{2-},$$

where R is hydrocarbon radical.

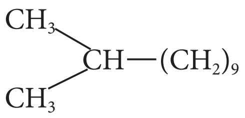
If further concentration of rhenium is required, in order to unify the equipment used, materials with a mobile extractant phase, such as Levextrel resins or impregnates [35], sorption on which allows avoiding fire-hazardous extraction process stage, can be used. The impregnates are produced by impregnating the carrier with the extractant. An alternative way to create materials of this type is the introduction of the extractant into the matrix during its synthesis, to be carried out, for example, in the mode of suspension copolymerization of styrene with divinylbenzene in the presence of a radical polymerization initiator. The materials produced by this method are called solid extractants (“tvex” in Russia; in the English-language literature, these are called Levextrel resins). Despite fundamentally different methods of production, impregnates and Levextrel resins are similar in structure and properties. Unlike ion exchangers, these sorption materials do not swell in aqueous solutions and retain their mechanical strength in both wet and air-dry state that allows their use in modern high-performance equipment.

In terms of density, bulk weight, mechanical strength impregnates and Levextrel resins are similar to sorbents, whereas the mechanism of recovery of components by impregnates and Levextrel resins is similar to the extraction mechanism. The capacitive and kinetic characteristics of these materials are determined mainly by the porous structure, type and state of the extractant in the matrix. A characteristic feature of Levextrel resins and impregnates is the absence of chemical bond between the extractant and the polymer matrix. Due to the liquid phase mobility, these materials have improved kinetic characteristics.

Extractants of different classes are used in their production. TVEX-DIDA containing diisododecyl amine was developed and produced in Research Institute VNIIHT JSC. Interaction of perrhenate ion with this extractant proceeds according to the reaction:

$$(R_2NH_2)_2SO_4 + 2ReO_4^- \leftrightarrow 2R_2NH_2(ReO_4) + SO_4^{2-},$$

where R –



$$\begin{matrix}CH_3 & \\ & CH{-}(CH_2)_9 \\ CH_3 & \end{matrix}$$

is hydrocarbon radical.

The sorption characteristics of this material and impregnates containing amines, such as trialkylamine (TAA-impregnate), studied at the Mendeleev Russian University of Chemical Technology, allow to use them for concentration of rhenium [28]. Desorption of rhenium from these materials is carried out by ammonia solution, which allows producing rough ammonium perrhenate (from the eluate). Its following purification by electrodialysis method allows improvement of quality of the finished rhenium commercial product to grade AP-0 (GOST 31411-2009 “Ammonium perrhenate. Technical Specifications”. Date of the GOST enactment: 01.01.2011) [4, 14, 18].

The implementation of processes using Levextrel resins or impregnates allows to eliminate the use of toxic, volatile and fire-hazardous organic diluents, avoid difficulties associated with the separation of hard-to-dissolve emulsions (“third phase”), reduces the pollution of waste water with organic reagents – compared with liquid extraction process. The processes with the use of impregnates and Levextrel resins are significantly less energy-intensive than traditional sorption processes due to high degree of metal concentration.

---

[6] Troshkina I. D., Balanovsky N. V., Vanin I. A. et al. Method for the recovery of rhenium from uranium solutions. RF Patent No. 2627838 dated 23.03.2016.

Economic aspects of the method of selective-advanced recovery of rhenium from pregnant solutions of uranium in-situ leaching

Economic efficiency of the method of selective-advanced recovery of rhenium is due to the following:

– costs of ore extraction and preparation for processing, etc. are deducted in estimating the cost of rhenium production;

– the impacts on the sorbent designated for extracting the main component, uranium, decreases;

– the quality of the uranium commercial product is improved;

– the volume of rhenium solutions to be processed decreases;

– the capital cost of construction of the processing plant for rhenium is reduced;

– the operating costs and associated expenses decrease;

– the economic attractiveness of the deposit increases.

Conclusions

1. For expanding the mineral raw material base, the method of selective-and-advanced recovery of rhenium, one of the valuable associated components of complex polymetallic uranium ores of the Dobrovolnoye deposit (JSC Dalur, Russia), very important metal of superalloys for the aerospace industry of the national economy was proposed.

2. For the first time the proposed technology has the following features:

– zoning of production blocks when constructing injection and extraction (pumping) wells;

– piping of selective extraction wells into a separate collecting pipe;

– implementation of advanced rhenium sorption.

3. Implementation of the recovery selective-and-advanced technology allows obtaining rhenium from economically-viable areas of the uranium deposit. In this case a mobile facility can be used as the equipment for the technology implementation, the main unit of which is a sorption unit filled with a rhenium-selective ion-exchanger from a group of weakly basic nitrogen-containing ion-exchangers with functional groups of amines of various types. If further concentration of rhenium is required, in order to unify the equipment used, materials with a mobile extractant phase, such as TVEX-DIDA (Levextrel resin) containing diisododecyl amine, or TAA impregnate containing trialkylamine, can be used. Rhenium desorption from these materials is carried out with an ammonia solution, which allows obtaining rough ammonium perrhenate from the eluate.

References

1. Akimova I. D., Babkin A. S., Ivanov A. G. et al.; Solodov I. N. (ed.). *Uranium geotechnology (Russian experience)*. Moscow: ARMZ; 2017. 541 p. (In Russ.)

2. Kislyakov Ya. M., Mashkovtsev G. A., Miguta A. K. et al. *Uranium*. Handbook. Moscow: CJSC Geoinformmark Publ.; 1997. 70 p. (In Russ.)

3. Lebedev V. M. Nuclear fuel cycle: Technologies, Safety, Economy. Moscow: Energoatomizdat Publ.; 2005. 316 p. (In Russ.)

4. Palant A. A., Troshkina I. D., Chekmarev A. M., Kostylev A. I. Technology of Rhenium. Moscow: Galleya-Print LLC Publ.; 2015. 329 p. (In Russ.)

5. Kablov E. N., Bondarenko Yu. A., Kolodyazhny M. Yu., Surova V. A., Narsky A. R. Prospects for the creation of high-temperature heatresistant alloys based on refractory matrices and natural composites. *Voprosy Materialovedeniya*. 2020;(4):64–78. (In Russ.) https://doi.org/10.22349/1994-6716-2020-104-4-64-78

6. Petrushin N. V., Ospennikova O. G., Elyutin E. S. Rhenium in single crystal nickel-based superalloys for gas turbine engine blades. *Aviatsionnye Materialy and Tekhnologii*. (In Russ.). 2014;(S5):5–16.

7. Kablov E. N., Karpov Yu. A., Titov V. I., Karfidova E. N., Kudryavtseva G. S., Gundobin N. V. Determination of Rhenium and Ruthenium in Nanostructured Heat-Resistant Nickel Alloys for Aerospace Equipment. *Zavodskaya laboratoriya. Diagnostika*. 2014;80(1):6–12. (In Russ.). URL: http://old-zldm.ru/upload/iblock/820/1028686120148001006.pdf

8. Luzanovsky A. G., Turamuradov I. B., Turesebekov A. Kh. Prospective features of rhenium and osmium extraction from gold-uranium ores and oil shale of Kyzyl Kum. *Gorniy Vestnik Uzbekistana*. 2007;(1):31–33. (In Russ.). URL: http://gorniyvestnik.uz/assets/uploads/pdf/2007-yanvar-mart.pdf

9. Karimov Kh. K., Bobonorov N. S. et al. *Uchkuduk type uranium deposits of the Republic of Uzbekistan*. Tashkent: FAN Publ., 1996. 336 p. (In Russ.).

10. Levchenko E. N., Bykhovskiy L. Z., Spiridonov I. G., Klyucharev D. S. Features of accounting rare metal reserves. *Razvedka i Okhrana Nedr*. 2019;(1):45–51. (In Russ.)

11. Laverov N. P., Abdulmanov I. G., Brovin K. G. et al. Underground leaching of polyelement ores. Moscow: Publishing house of Academy of Mining Sciences; 1998. 446 p. (In Russ.)

12. Ortikov I. S., Nebera V. P. Recovery of rhenium from uranium leach solutions in Kyzylkum province. *Tsvetnye Metally*. 2010;(3):78–83. (In Russ.).

13. Volkov V. P., Meshcheryakov N. M., Nikitin N. V., Mikhaylenko M. A. Industrial experience of sorptive extraction of rhenium from the circulating leach solutions of uranium. *Tsvetnye Metally*. 2012;(7):64–67. (In Russ.).

14. Sharafutdinov U. Z., Kurbanov M. A., Alikulov Sh. Sh., Ganieva D. S. Adsorption properties of anion-exchange resins in joint uranium and rhenium sorption during in-situ uranium leaching. *Mining Informational and Analytical Bulletin*. 2021;(3-1):136–146. (In Russ.). https://doi.org/10.25018/0236_1493_2021_31_0_136

15. Volkov V. P., Mikhin O. A., Pershin M. E. Commercial experience of rhenium recovery from ISL uranium-containing solutions with producing pure salts of ammonium perrhenate. In: *Actual problems of uranium industry. Proceedings of the V International Scientific-Practical Conference*. Almaty: Viva-Promotion LLP Publ.; 2008. P. 353

16. Volkov V. P., Mescheryakov N. M. Sorptive recovery of rhenium from circulating solutions of uranium in situ leaching operation at Navoi GMK, Uzbekistan. In: *7th Int. Symp. on Technetium and Rhenium – Science and Utilization (ISTR-2011)*. 04–08 July 2011. Moscow: Publishing House Granitsa; 2011. P. 107.

17. Sanakulov K. S., Petukhov O. F., Kurbanov M. A. Investigation and development of hybrid recovery of rhenium during in-situ ore leaching. Gornyi Zhurnal. 2018;(9):69–73. (In Russ.). https://doi.org/10.17580/gzh.2018.09.10

18. Zagorodnaya A. N., Abisheva Z. S., Ponomareva E. I., Bobrova V. V. Combined sorption-extraction-electrodialysis process for producing ammonium perrhenate from uranium-containing solutions. *Tsvetnye Metally*. 2010;(8):59–62. (In Russ.)

19. Zagorodnyaya A. N., Abisheva Z. S., Sharipova A. S., Sadykanova S. E., Bochevskaya Ye. G., Atanova O. V. Sorption of rhenium and uranium by strong base anion exchange resin from solutions with different anion composition. *Hydrometallurgy*. 2013;(131–132):127–132. https://doi.org/10.1016/j.hydromet.2012.11.003

20. Beletsky V. I., Bogatkov L. K., Volkov N. I. et al.; Skorovarov D. I. (ed.). *Handbook of Uranium Geotechnology*. Moscow: Energoatomizdat Publ.; 1997. 672 p.

21. Nesterov Yu. V. Ionites and Ion Exchange. Sorption Technology in Uranium and Other Metals Mining by In-situ Leaching Methods. Moscow: Unicorn Izdat LLC Publ.; 2007. P. 204

22. Blokhin A. A., Mikhaylenko M. A. Ion-exchange sorption in the hydrometallurgy of rhenium: a review. *Tsvetnye Metally*. 2019;(10):18–27. (In Russ.). https://doi.org/10.17580/tsm.2019.10.03

23. Fathi M. B., Rezai B., Alamdari E. K. Competitive adsorption characteristics of rhenium in single and binary (Re-Mo) systems using Purolite A170. *International Journal of Mineral Processing*. 2018;169:1–6. https://doi.org/10.1016/j.minpro.2017.10.003

24. Wang Y., Wang C. Recent advances of rhenium separation and enrichment in China: Industrial processes and laboratory trials. *Chinese Chemical Letters*. 2018;29(3):345–352. https://doi.org/10.1016/j.cclet.2018.01.001

25. Chopabayeva N. Sorption and desorption of rhenium ions by lignin sorbents. *Journal of Chemical Technology and Metallurgy*. 2019;54(3):585–594. URL: https://dl.uctm.edu/journal/node/j2019-3/17_18-56_p_585-594.pdf

26. Hui Hu, Longli Sun, Bangqiang Jiang, Huixiong Wu, Qingming Huang, Xiaohui Chen. Low concentration Re(VII) recovery from acidic solution by Cu-biochar composite prepared from bamboo (Acidosasa longiligula) shoot shell. *Minerals Engineering*. 2018;124:123–136. https://doi.org/10.1016/j.mineng.2018.05.021

27. Troshkina I. D., Obruchnikova Y. A., Pestov S. M. Metal sorption by materials with a mobile phase of extractants. *Russian Journal of General Chemistry*. 2019;89:2721–2732. https://doi.org/10.1134/S107036321912048X (Orig. ver.: Troshkina I. D., Obruchnikova Y. A., Pestov S. M. Metal sorption by materials with a mobile phase of extractants. *Rossiiskii Khimicheskii Zhurnal*. 2017;61(4):54–65. (In Russ.))

28. Troshkina I. D., Balanovskyi N. V., Obruchnikova Ya. A., Vatsura F. Ya., Vanin I. A., Zhukova O. A., Ratchina K. A. Recovery of rhenium by amine-contained sorbents. In: *10th International Symposium on Technetium and Rhenium – Science and Utilization (ISTR-2018)*. 03–06 October 2018. Moscow: Publishing House Granitsa; 2018. https://doi.org/10.13140/RG.2.2.31744.07686

Information about the authors

Alexey A. Rudenko – Cand. Sci. (Geol. and Min.), Deputy Head of the Analysis and Expertise Department, JSC “RUSBURMASH”, Moscow, Russian Federation; e-mail Rudall2007@yandex.ru

Irina D. Troshkina – Dr. Sci (Eng.), Professor, Department of Technology of Rare Elements and Nanomaterials Based on Them, Mendeleev University of Chemical Technology of Russia, Moscow, Russian Federation; ORCID 0000-0002-5523-0247, Scopus ID 6603490618; e-mail tid@muctr.ru

Vladimir V. Danileyko – Dr. Sci (Eng.), Director for Special Projects, JSC “RUSBURMASH”, Moscow, Russian Federation; e-mail danileykovv@gmail.com

Oleg S. Barabanov – Cand. Sci. (Econ.), First Deputy General Director, JSC ARMZ (Atomredmetzoloto Uranium Holding Co., the Rosatom’s mining division), Moscow, Russian Federation; e-mail OleStBarabanov@armz.ru

Fedor Ya. Vatsura – PhD student, Department of Technology of Rare Elements and Nanomaterials Based on Them, Mendeleev University of Chemical Technology of Russia, Moscow, Russian Federation; Scopus ID 57200650509; e-mail fedotik_r2s@mail.ru

Received	28.07.2021
Revised	22.08.2021
Accepted	15.09.2021