ABSTRACT

of dissertation work for the Doctor of Philosophy (Ph.D.)
6D072000 – «Chemical technology of inorganic substances»

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Development of technology for extracting the associated rare earth metals in underground uranium leaching

The relevance of the research topic

Uranium deposits in Kazakhstan can serve as sources for the extraction of many rare and rare earth metals (REM), including such as rhenium, scandium, vanadium, selenium, yttrium and lanthanides. They are used in the production of high-tech materials for the aerospace and electronics industries. The uranium deposit belongs to the category of polyelement, in the ore of which, on average can be contained (g/t): 0,25 Re, 3,3 Sc, 106 REM. Due to the large volume of circulating solution of Underground Borehole Leaching (UBL), the extraction of scandium, rhenium and rare-earth metals may be of industrial interest.

In order to expand the resource base and production organization of R &RM for 2021-2025 since 25th of October the roadmap has been adopted. The roadmap presents the whole direction for prospecting for the extraction of REM technology. Domestic enterprises LLP "Institute of High Technologies", which is a subsidiary of NAC Kazatomprom JSC, acted as the responsible executor in this area.

In this regard, it seems relevant to develop selective methods for extracting and concentrating REM to isolate them from the selected object of study: diluted radioactive sulfuric acid solutions formed after the sorption of uranium from productive UBL of ores in Kazakhstan.

Purpose of the thesis is selection of the most promising associated useful component (AUC) from an economic point of view. The development of a highly efficient and economically acceptable technology for the associated extraction of the selected AUC from the mother solutions of uranium sorption during underground uranium leaching at the deposits of NAC Kazatomprom JSC.

Research objectives:

1. Determine the current content of associated components in technological solutions of 8 mines of NAC Kazatomprom JSC with the choice of the most attractive deposit in terms of efficient extraction of RM and REM. Determine the most economically promising AUC for its extraction from mother solutions of uranium sorption;
2. To carry out the selection of the most effective sorbents for the extraction of AUC from the uranium sorption mother liquor;
3. To study the statics, kinetics and dynamics of AUC sorption using various cation exchangers;

4. To develop a method for efficient desorption of UAC from the selected sorbent;

5. To develop the second stage of AUC concentration from the desorbate;

6. Develop a technology for extracting UAC from MSU to obtain the final product on an industrial scale. Calculate the material balance of the AUC movement in the developed technology;

7. Conduct a feasibility study of the developed technology
extraction of UAC.

The object of the thesis: rare earth metals, cation exchange resins, scandium.

The subject of the thesis: leaching, sorption, desorption of scandium, REM from the mother liquor of uranium sorption.

The scientific novelty of the thesis results obtained is ascertained by the fact that for the first time:

1. For the first time, the processes of sorption of scandium and other rare earth metals by the phosphorus-containing cation exchanger Purolite MTS 9580 have been studied in relation to real technological solutions of UBL of uranium ores in Kazakhstan.

2. For the first time, the kinetic and dynamic characteristics of the sorption process were investigated and established, the separation and distribution coefficients, the kinetic coefficient and the diffusion coefficient were determined.

3. For the first time, a technological scheme for obtaining scandium oxide with their specific consumption rates, annual consumption of reagents, characteristics of all columns, flows, overloads are described.

Practical significance.

1. The possibility of extracting scandium from uranium UBL solutions without significant changes in the main technology used at the «6» deposit for uranium extraction has been shown. The developed technology for extracting scandium can be implemented on a pilot scale at other uranium mining enterprises.

2. A patent was obtained for a method for extracting scandium from uranium sorption mother liquors with Purolite MTS 9580 ion-exchange resin.

3. A preliminary calculation of the technical and economic indicators for the technological scheme was carried out, which showed a moderate profitability of extracting scandium from industrial solutions of uranium UBL. Annual average net profit is predicted to be $ 557,000/year.

The main provisions to be defended:

• acidification of the initial uranium sorption mother liquor to a concentration of H2SO4 15 g/dm^3 increases the exchange capacity of the Purolite MTS9580 cation exchanger for scandium up to 200 mg/dm^3;

• the use of fractional desorption makes it possible to separate scandium and major impurities to obtain desorbate rich in scandium content;

• repeated sorption of scandium on Ambersep 920U anion exchanger with saturation up to 0.4 kg/m^3 and subsequent desorption of scandium with nitrate solutions makes it possible to obtain richer (220 mg/dm^3) and purer commercial desorbate for subsequent direct precipitation of scandium;

• the technological scheme of sorption-desorption extraction of scandium from return solutions of underground borehole leaching of uranium at mine «6» provides a productivity of 0.101 kg/hour of scandium oxide.

The main results of the study:

1. Based on the study of geological materials, the study of the composition of uranium ore and productive solutions of underground borehole leaching, as well as the analysis of the world metal market, it has been shown that scandium can be considered as a promising component for associated extraction from industrial solutions.

- The cost of marketable products on the world market, $ /kg: scandium oxide - 2000-4200; ammonium perrhenate - 900-1200; ∑ REM - 20-25.

The most attractive in terms of scandium content in uranium sorption mother liquor is deposit «6»;

2. Purolite MTS9580 ion exchange resin has been found to have the highest scandium selectivity than other sorbents. The static exchange capacity of the Purolite MTS9580 sorbent is maximum - 0.049 mg / cm^3, respectively, the separation coefficient (β_{Sc} /E) and the distribution coefficient (D_E) of scandium for MTS 9580 are higher relative to other resins. The condition of preliminary acidification of the initial MSU to the content of H_2SO_4 15 g/dm^3 made it possible to increase the exchange capacity of Purolite MTS9580 for scandium by a factor of 3 (200 mg/dm^3) compared to TP260, while the exchange capacity of Purolite MTS9580 for REM and harmful impurities is significantly lower, than TP260;

3. Based on the study of scandium sorption kinetics with Purolite MTS9580 ion exchanger from uranium sorption mother, it was established that the mechanism of the sorption process is complex. Scandium sorption process with Purolite MTS9580 ion exchanger is limited by gel diffusion. The chemical stage of the scandium sorption process on the Purolite MTS9580 cation exchanger is described by a pseudo-second order model (R^2 = 0.999);

4. The mechanism of scandium sorption from sulfuric acid solutions on Purolite MTS9580 is proposed. IR spectroscopy confirmed the formation of a coordination bond between scandium ions and the MTS9580 functional group;

5. The selected composition of the desorbing solution (H_2SO_4 - 110 g/dm^3, Na_2CO_3 - 150 g/dm^3) confirmed its effectiveness in the desorption of scandium from the MTS9580 ion exchanger. Scandium content ~ 40 mg/dm^3 in carbonate desorbate with MTS9580 of average composition, against 10 mg/dm^3 obtained in desorbate with TP 260; low content of harmful impurities and REM in carbonate desorbate;

6. Ambersep 920U anion exchange resin was used for the second concentration. Full dynamic exchange capacity was achieved after passing 110 beats. volumes of the solution, the content of scandium in the resin was 420 mg/dm^3. The degree of scandium concentration was -5.5. Composition of commercial desorbate after the second sorption concentration: Sc - 220 mg/dm^3, Al - 0.03 mg/dm^3, Fe - 0.07 mg/dm^3, Ca - 0.03 mg/dm^3, Th - 2.7 mg/dm^3, NO_3 - 80 g/dm^3;

7) For the first time, a detailed scheme for the production of Sc_2O_3 with a complete material balance, specific consumption rates, annual consumption of reagents, characteristics of all columns, flows, reloads has been developed. The feasibility study of the developed technological scheme for the extraction of scandium from mother liquors of uranium sorption at Mine «6», taking into account the changes made, showed moderate profitability: an average net profit of $557,000 per year is expected.

Relation of the thesis with research and government programs

The dissertation work was carried out within the framework of the Roadmap for research work on expanding the resource base and organizing the production of REM.

Description doctoral contribution to the preparation of each publication.

The doctoral student was directly involved in the sorption, desorption, obtaining experimental data, processing and interpreting experimental results, and also took part in the implementation of physicochemical studies for the design of the article «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» in journal «Eurasian Chemico-Technological Journal» (2020.−Vol. 22.−P.135-140. IF 0,871 Quartile Q3 https://doi.org/10.18321/ectj961).

The doctoral student was directly involved in the search for a literature review, sorption, obtaining experimental data, processing and interpreting experimental results, and also took part in the implementation of physicochemical studies for the design of the patent for invention «Sposob izvlecheniya skandiya iz matochnyh rastvorov sorbcii urana» (in Russian) (№34597).

The doctoral student was directly involved in the leaching, obtaining experimental data, processing and interpreting experimental results, and also took part in the implementation of physicochemical studies for the design of the article «Izuchenie processa vyshchelachivaniya skandiya iz uranovoj rudy filtracionnom metodom » (in Russian) in journal «Uspekhi v himii i himicheskoj tekhnologii » (collection of scientific papers Vol. XXXIII, № 1 (211). – M.: D. Mendeleev University of Chemical Technology of Russia, У78. 2019. − P.74).

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The doctoral student was directly involved in the desorption, obtaining experimental data, processing and interpreting experimental results, and also took part in the implementation of physicochemical studies for the design of the article «Razdelnaya desorbciya skandiya i primesej» (in Russian) in journal «Himicheskij zhurnal Kazahstana» (№1, **UDC 546.63**. 2020.−P.169-182.).

The doctoral student was directly involved in the leaching, sorption, desorption, obtaining experimental data, processing and interpreting experimental results, and also took part in the implementation of physicochemical studies for the design of the article

«Vybor sorbenta dlya koncentrirovaniya skandiya iz rastvorov mnogokomponentnogo sostava » (in Russian) in journal «Himicheskij zhurnal Kazahstana» (№1, **UDC 546.63**. 2020.− P.189-197.).

The doctoral student was directly involved in the sorption, desorption, obtaining experimental data, processing and interpreting experimental results and also took part in the implementation of physicochemical studies for the design of the article «Povyshenie emkosti slabokislotnogo kationita po skandiyu za schet uvelicheniya kislotnosti iskhodnogo rastvora» (in Russian) in the collection of reports of the International School of Innovation «Perspektivy i tekhnologii dlya diversifikacii deyatel'nosti AO «NAK «Kazatomprom» (2018 y.).

The doctoral student was directly involved in data collection, sorption, desorption, processing and interpretation of experimental results, and also took part in the implementation of physicochemical studies for the design of the article «Izuchenie soderzhaniya redkozemel'nyh metallov v rastvorah podzemnogo vyshchelachivaniya atomnoj promyshlennosti Kazahstana» (in Russian) in conference materials V International Scientific Conference Modern Problems of Condensed Matter Physics Nanotechnology and Nanomaterials (2018 y.).

Volume and structure of the thesis.

The thesis consists of an introduction, seven sections, a conclusion, and a list of references. The work is presented on 149 pages, contains 57 figures, 38 tables, and 101 bibliographical references.