PURIFICATION OF RARE EARTH ELEMENTS FROM THORIUM, URANIUM, AND RADIOACTIVE ISOTOPES

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This article presents the results of industrial tests of the technology of sorption, precipitation and extraction purification of the concentrate of rare earth elements (REE) from radioactive decay products of the uranium and thorium series. It has been shown that the combination of sorption, selective precipitation, and extraction processes makes it possible to effectively purify REE from U, Th, Po, Ra, RaD, and Ac and to obtain radiation-safe nitrogen-containing solutions for the production of fertilizers and individual REE.

INTRODUCTION

Uranium and rare earth elements (REE), gadolinium, dysprosium, and europium are an integral part of the fuel for nuclear reactors. The main source of the medium-heavy fraction of REE until 1991 was the Melovoe deposit (Kazakhstan). The concentrate mined there was distinguished by a unique composition: along with uranium (0.2%) and phosphorus (20%), the yttrium content reached 18%, the sum of gadolinium and dysprosium – 35%; europium – 0.8% [1, 2].

In force until 1991 capacities for the processing of phosphorites, the production of uranium and phosphorus fertilizers in Ukraine are mothballed due to the lack of raw materials. Currently, the only explored deposit of complex phosphorite ores in Ukraine, containing uranium, thorium and REE, is the Novopoltavskoe deposit in the Zaporizhzhia region [3]. When implementing the State Program for the creation of nuclear fuel, it can become the main source of gadolinium, dysprosium and europium, with the associated extraction of uranium and phosphorus.

A prerequisite for the production of REE is their deep purification from impurities, incl. from uranium and thorium, as well as from radioactive products of their decay (Ra, Po, Pb, Ac). The processing technology of uranium-rare earth phosphate ores is complex, multistage, fine technologies of sorption and extraction are used at the final stages of processing.

Phosphorites are atypical uranium-containing raw materials, which contain P_2O_5, uranium, REE, as well as scandium and thorium [4, 5]. The associated extraction of phosphorus, in the form of phosphorus fertilizers, significantly reduces the cost of uranium and REE. In the production of uranium and REE, as well as for the nuclear power industry in general, the main issue is the radiation safety of personnel and the protection of the environment from radioactive contamination. This becomes especially important when reprocessing radioactive spent nuclear fuel (SNF), which contains fissile isotopes of uranium and other elements. Effective reprocessing of SNF to separate uranium and plutonium is possible only with the use of chemical technologies that are well mastered by the nuclear industry.

The work aims to present the results of industrial tests of the technology for the purification of REE concentrate obtained during the processing of phosphate compounds and the extraction of uranium from radioactive elements to the level of sanitary standards of Ukraine.

RESEARCH METHODS

To select the methods for separating U, P_2O_5, REE and purifying them from radioactive impurities, a chemical analysis of the REE concentrate after the extraction of uranium was carried out. To separate the REE and the phosphate ion, the process of sorption of the REE raffinate on the KU-2-8 cation exchanger with an NHO_3 content of 50…100 g/dm^3 was chosen. The raffinate after sorption, containing phosphorus and other non-radioactive elements, corresponded to the 97 Radiation Safety Standards for Ukraine (the NRBU-97) according standards and was sent to obtain nitrogen-phosphorus fertilizer of the "Nitrofos" type. To achieve the maximum capacity of KU-2-8 for REE and radioactive elements, the extraction raffinate was diluted with a solution obtained as a result of washing the saturated resin before sorption. In the course of sorption, the optimal P_2O_5: REE ratio was determined, at which their separation was the most complete. Saturated cation exchanger, after washing to remove F^- and PO_4^{3-} ions, was subjected to desorption with a mixture of HNO_3 and NH_4NO_3. In the process of sorption, the capacity of the cation exchanger, the kinetics of the process, and the residual content of REE in the raffinate were determined.

After desorption, the residual capacity of the cation exchanger, the elemental composition of the eluate, incl. content of Th, U, Po, Ra, Ac, Pb. For desorption, a regenerating solution with an optimal ratio of $HNO_3:NH_4NO_3$ was selected. Iron-thorium cake was precipitated from the eluate with ammonia at pH = 4.0. To extract REE, the cake was repulped with water at S:L = 1:4 and a temperature of 65 °C.

The filtrate was sent to wash the saturated cation exchanger. The eluate, after separation of Fe-Th cake, was sent to the precipitation of REE hydroxides at pH = 8.0…9.0. The precipitate of REE hydroxides was dissolved in 45% HNO_3 at an excess acidity of
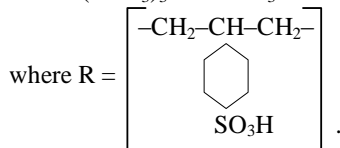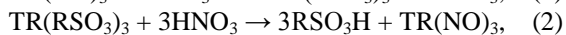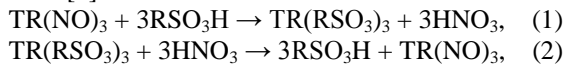
$20\ldots40$ g/dm^3. H_2O_2 was introduced into the solution to convert Ce^{4+} to Ce^{3+}, to separate it during extraction, after which it was sent for sulfide purification from radioactive elements. For this, the salts $Ba(NO_3)_2$, $Pb(NO_3)_2$, Na_2S, and $K_4[Fe(CN)_6]$ were used. The released H_2S was absorbed by a soda solution and sent to the preparation of a 10% Na_2S solution.

The precipitated radioactive impurities (Ra, Po, RaD) and uranium were sent together with Fe-Th cake for repulpation, and after washing with REE – for disposal. The REE solution was analyzed for the content of Po, Ra, Ac, and NH_4NO_3 was sent for purification from ^{227}Ac by extraction using tributyl phosphate (TBP). During the tests, the following was determined: the ratio of the volumes of the organic and aqueous phases (O:A) at all stages; the content of REE and ^{227}Ac in the extractant and extraction raffinates; the content of radioactive impurities. Residual radioactivity in products, according to OSP-72/87 supplied to the national economy, should not exceed 0.01% of equilibrium thorium and uranium or 10^{-10} Ci/g for the sum of the following elements: ^{228}Ra, ^{228}Th, ^{234}U, ^{230}U, ^{226}Ra, ^{210}Pb, ^{210}Po, ^{227}Ac.

For the rapid determination of the ^{227}Ac content in the REE, an improved method was used [6, 7], within which the intensity of the γ-radiation from the accumulated daughter elements of the actinium series in the calcined REE residue was measured.

RESULT AND DISCUSSION

The processes of sorption and desorption of REE on the KU-2-8 cation exchanger are described by the equations [8]:
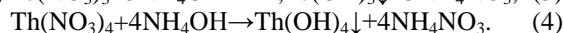
$$TR(NO)_3 + 3RSO_3H \rightarrow TR(RSO_3)_3 + 3HNO_3, \quad (1)$$
$$TR(RSO_3)_3 + 3HNO_3 \rightarrow 3RSO_3H + TR(NO)_3, \quad (2)$$

where R =

$$\begin{bmatrix} -CH_2-CH-CH_2- \\ \bigcirc \\ SO_3H \end{bmatrix}.$$

The PO_4^{3-} and NO_3^- anions are not sorbed by the resin. During sorption, the concentration of H^+ ions in the solution increases. The kinetics of the process provides a sorption duration of no more than 20 min. The completeness of the REE sorption, within the excess HNO_3 content of $70\ldots100$ g/dm^3, does not depend on acidity. At the same time, at acidity less than 40 g/dm^3 of HNO_3, the precipitation of REE phosphate occurs, which leads to their losses [9].

It was determined that the solution for sorption should have the following composition, g/dm^3: REE – $20\ldots25$; the ratio P_2O_5:REE ≤ 2. The capacity of KU-2-8 in such conditions was, kg/t: REE – $40\ldots60$; Fe_2O_3 – 40; CaO – 25. The ratio of flows of resin and solution was maintained at a level of 1:4. The raffinate after extraction separation of uranium and REE contained, g/dm^3: REE – $19\ldots25$; U ≤ 0.01; P_2O_5 – $35\ldots50$; HNO_3 – $100\ldots150$; Fe_2O_3 – $9\ldots14$; CaO < 35; F < 0.01; Th – $0.1\ldots0.3$. In terms of the content of radioactive elements, the raffinate did not meet the NRB standards.

Desorption was carried out at a ratio of resin and regenerating solution flows of 1:2. The composition of the eluate after desorption, g/dm^3: REE – 12; P_2O_5 – 2.0; Fe_2O_3 – 2.5; Al – 3.0; Th – 0.1; U – 0.02. The completeness of the desorption process reached 100%.

The REE eluate containing radioactive isotopes was sent to the precipitation of thorium and iron hydroxides at pH = $3.5\ldots4.5$ and a temperature of 70 °C according to the reactions:

$$Al, Fe(NO_3)_3 + 3NH_4OH \rightarrow Al, Fe(OH)_3\downarrow + 3NH_4NO_3, \quad (3)$$
$$Th(NO_3)_4 + 4NH_4OH \rightarrow Th(OH)_4\downarrow + 4NH_4NO_3. \quad (4)$$

To intensify the process of filtration of hydroxides, a flocculant polyacrylamide (PAA) is added in the form of a 0.1% solution. Repulpation of Fe-Th cake allows reducing the loss of REE by 4 times. The technological scheme for the purification of REE from phosphorus and thorium is shown in Fig. 1.
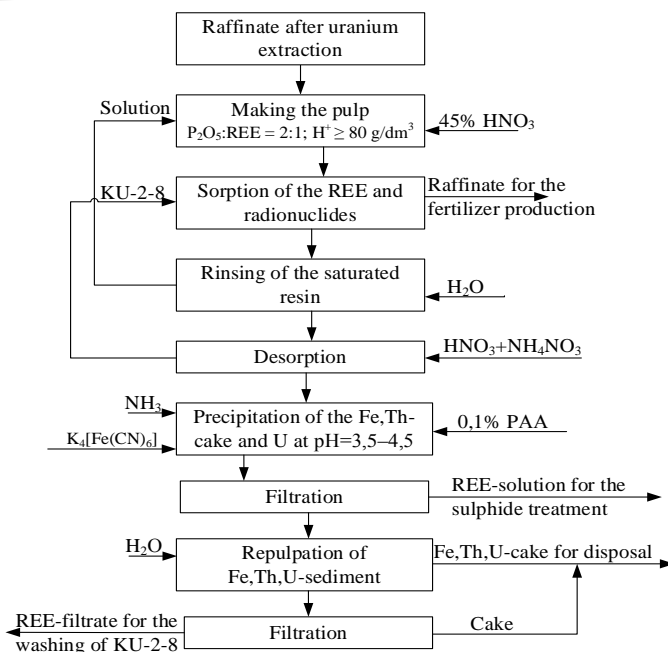

*Fig. 1. Technological scheme for the separation of impurities from REE*

The precipitation of the REE concentrate is described by the reaction:

$$TR(NO_3)_3 + 3NH_4OH \rightarrow TR(OH)_3\downarrow + 3NH_4NO_3. \quad (5)$$

Chemical composition of REE hydroxides, %: $REE \geq 90$; $CaO \leq 4.0$; $Fe_2O_3 \leq 0.5$; $P_2O_5 \leq 1.0$; $Th+U \leq 0.2$. The dissolution of the REE concentrate with nitric acid occurs according to the reaction:

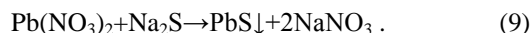$$TR(OH)_3 + 3HNO_3 \rightarrow TR(NO_3)_3 + 3H_2O. \quad (6)$$

Nitrate solutions of REE are an oxidizing agent, and the used precipitant (Na_2S) is a strong reducing agent. Under reducing conditions, with an excess of H_2S, the isotopes of lead and polonium will be retained in the sediment [10]. In the absence of an excess of H_2S, the decomposition of the sulfide precipitate and the transition of lead and polonium isotopes into the solution will take place. The solubility of PbS depends on the pH of the solution, therefore, during sulfide purification, it is required to conduct the process in a certain range of pH values. Sodium sulfide (Na_2S) at $pH = 2.5...2.8$ almost completely transforms into H_2S by the reaction:

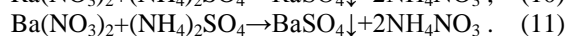$$2HNO_3 + Na_2S \rightarrow H_2S\uparrow + 2NaNO_3. \quad (7)$$
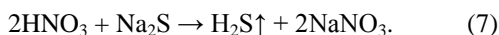
This phenomenon is undesirable; therefore, constant pH control is required for complete precipitation of lead and polonium sulfides. The transition of lead and polonium into solution is observed only when the values of the redox potential change from negative values to positive ones, relative to the silver chloride electrode [11]. The completeness of uranium deposition is achieved by adding $K_4[Fe(CN)_6]$ according to the reaction:

$$UO_2(NO_3)_2 + K_4[Fe(CN)_6] \rightarrow K_2(UO_2)[Fe(CN)_6]\downarrow + 2KNO_3. \quad (8)$$
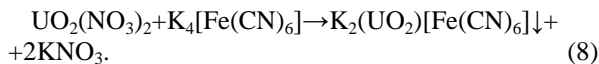
During the deposition of lead by the reaction:

$$Pb(NO_3)_2 + Na_2S \rightarrow PbS\downarrow + 2NaNO_3. \quad (9)$$

The pH rises to 0.7 and the ORP should not exceed -60 mV. ^{226}Ra precipitated from solution in the form of sulfate together with $BaSO_4$ according to the reactions:

$$Ra(NO_3)_2 + (NH_4)_2SO_4 \rightarrow RaSO_4\downarrow + 2NH_4NO_3, \quad (10)$$
$$Ba(NO_3)_2 + (NH_4)_2SO_4 \rightarrow BaSO_4\downarrow + 2NH_4NO_3. \quad (11)$$

Together with $Ba(NO_3)_2$, $Pb(NO_3)_2$ is introduced, which is a polonium co-precipitator. In the course of the experiment, the optimal consumption of reagents was determined, which was (per 100 kg of REE), kg: $Ba(NO_3)_2 - 0.5$; $K_4[Fe(CN)_6] - 0.13$; $Na_2S - 0.5$; $H_2SO_4 - 0.4$; $Pb(NO_3)_2 - 0.24$.

The precipitation of Fe-Th cake and sulfide purification of the REE concentrate do not provide purification from ^{227}Ac, a daughter product of the radioactive decay of uranium, since this element is similar in chemical properties to lanthanum. As a result, anemones increase the total radioactivity of REEs when they are divided into groups.

A solution after purification from radioactive elements, containing REE nitrates in an amount of 100 and 200 g/dm^3 NH_4NO_3, as well as impurities, in terms of the calcined product, %: $Fe < 0.5$; $CaO < 4.0$; $F < 1.5$; $Cl < 0.2$; $SO_4 < 0.25$; $P_2O_5 < 1.0$ has an increased content of actinium – $50 \cdot 10^{-10}$ Ci/g, at a rate of $1 \cdot 10^{-10}$ Ci/g.

In the course of the experiments, a technological scheme for the purification of REE from uranium and radioactive impurities, except for actinium, was developed (Fig. 2).
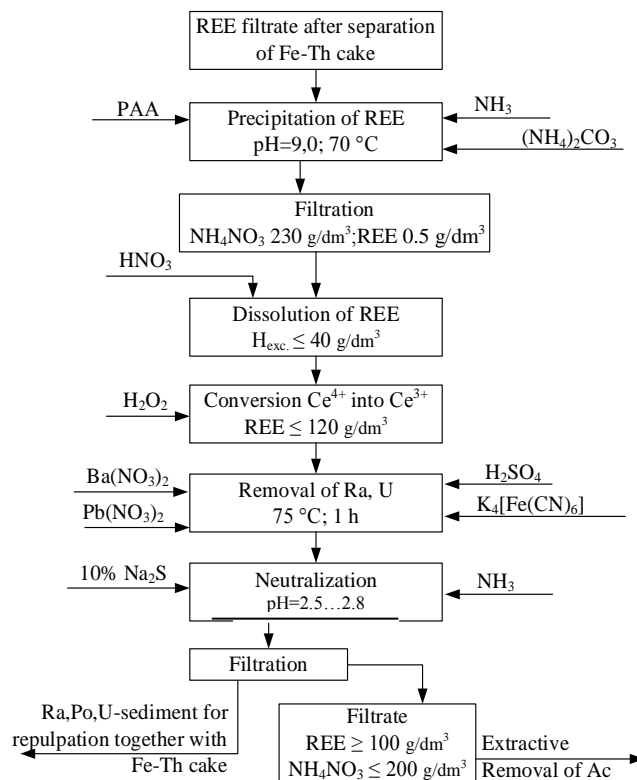

Fig. 2. Technological scheme for cleaning REE from uranium and radioactive elements

After separation of Th, Po, Ra, Pb, the REE filtrate was sent for extraction purification from ^{227}Ac. The REE extraction process using TBP is described by the equation:

$$TR(NO_3)_3 + TBP \cdot HNO_3 \rightarrow TBP \cdot TR(NO_3)_3 + HNO_3 . \quad (12)$$

The efficiency of the process depends on the concentration of REE in the solution, as well as the presence of a salting-out agent – the NH_4NO_3 salt. The efficiency criterion is the composition of the regenerate, which must contain the minimum amount of REE and the maximum possible amount of non-radioactive impurities and ^{227}Ac, so as not to return it to the cycle. During the experiments, it was determined that an increase in the concentration of REE to 300 g/dm^3 and

NH_4NO_3 to 400 g/dm^3 promotes an increase in the extraction of REE and purification of the concentrate from ^{227}Ac to sanitary standards.

The purified REE concentrate before separation into groups contained ^{210}Po $10^{-11}...10^{-12}$ Ci/g and ^{226}Ra $10^{-10}...10^{-11}$ Ci/g, which meets the requirements of NRB. The ^{227}Ac content determines the radioactivity at the level of 10^{-11} Ci/g, while the analysis duration according to the new method [6, 7] was 5 days instead of 15 according to the standard one. This significantly reduces the cost of products.

As a result of industrial tests, a technological scheme for the purification of REE from actinium was developed (Fig. 3).
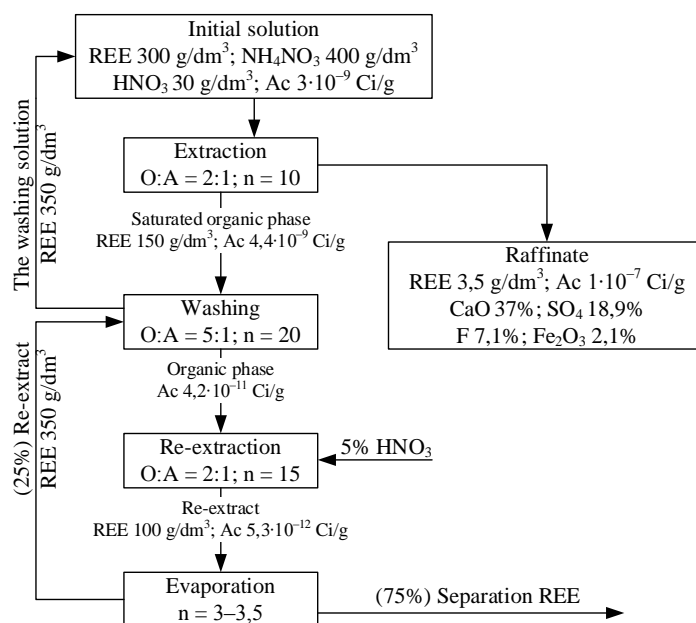

Fig. 3. Technological scheme for the extraction of REE from actinium

The proposed composition of the flow ratios at the stages of extraction, washing, and stripping made it possible to increase the extraction of REE up to 93%.

CONCLUSION

1. The release of thorium and iron hydroxides at pH = 4.0 ensures the release of thorium from the solution to the level of sanitary standards.

2. The use of Na_2S and $Pb(NO_3)_2$ gives positive results in the purification from the radioactive isotope ^{210}Po, and the use of $K_4[Fe(CN)_6]$ makes it possible to achieve almost complete separation of uranium.

3. The rational sequence of the introduction of reagents (2% $Pb(NO_3)_2$, 5...10% Na_2S) made it possible to ensure the purification of the radioactive isotope ^{226}Ra to the sanitary standards.

4. A prerequisite for the purification of REE from ^{226}Ra is the introduction of the SO_4^{2-} ion in the form of H_2SO_4 or $(NH_4)_2SO_4$.

5. The process of extraction purification of REE from the radioactive isotope ^{227}Ac allows to reduce its content to sanitary standards ($4 \cdot 10^{-11}$ Ci/g) and obtain a lanthanum concentrate with a purity of 99.88%. In this case, the extraction of REE into the purified solution is 93%.

6. The combination of the proposed methods for the isolation of radioactive isotopes ensures the safe work of personnel during the separation of the REE concentrate. The results of the study make it possible to use the considered technological methods for SNF reprocessing.

REFERENCES

1. *ИТС 24-2017 Производство редких и редкоземельных металлов.* М.: «Бюро НДТ», 2017, с. 202.

2. J.I. Skorovarov et al. Recovery of rare earth elements from phosphorites in the USSR // *J. Alloys Comp.* 1992, v. 180, p. 71.

3. Е.Г. Мусич, В.Г. Верховцев. *Фосфорсодержащие руды Украины: Сборник научных трудов Института геохимии окружающей среды.* 2017, т. 27, с. 171.

4. Г.И. Авдонин и др. Оценка возможности добычи урана из фосфоритовых руд // *Разведка и охрана недр.* 2017, №12, с. 43-48.

5. *Практика переработки уранового сырья* / Под ред. Г.А. Машковцева. М.: ВИМС, 2008, с. 269.

6. И.Е. Старик, Е.Е. Щепотьева. *Методы определения радиоактивных природных образований*. М.: «Госгеолиздат», 1946, с. 97.

7. Х.В. Межигорская и др. *Способ определения* ^{227}Ac. Заявка на а.с. СССР 014069 30.01.1969.

8. B.S. Kolychev. Application of sorption and solvent extraction processes in the hydrometallurgy of uranium // *Sov. J. Atomic Energy.* 1960, N 6, p. 368.

9. B.N. Laskorin et al. A filtration-free method of processing uranium ores // *Atomic Energy.* 1977, N 43, p. 1127.

10. L.I. Vodolazov, V.V. Shatalov, T.V. Molchanova. Methods for desorption of uranium and other valuable components from saturated ion exchangers // *Atomic Energy.* 1999, N 87, p. 731.

11. D.I. Skorovarov, E.A. Semenova, I.F. Yakhonin. Modern trends in the development of hydrometallurgical processes for extracting uranium from ore // *Atomic Energy.* 1986, N 61, p. 814.

ОЧИСТКА КОНЦЕНТРАТА РЗЭ ОТ ТОРИЯ, УРАНА И РАДИОАКТИВНЫХ ПРИМЕСЕЙ

А.П. Мухачев, Д.А. Елатонцев, Е.А. Харитонова

Изложены результаты промышленных испытаний технологии сорбционной, осадительной и экстракционной очисток концентрата редкоземельных элементов (РЗЭ) от радиоактивных продуктов распада уранового и ториевого рядов. Показано, что сочетание процессов сорбции, избирательного осаждения и экстракции позволяет эффективно очищать РЗЭ от U, Th, Po, Ra, RaD и Ac и получать радиационно безопасные азотосодержащие растворы для производства удобрений и индивидуальных РЗЭ.

ОЧИЩЕННЯ КОНЦЕНТРАТУ РЗЕ ВІД ТОРІЮ, УРАНУ І РАДІОАКТИВНИХ ДОМІШОК

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

Викладено результати промислових випробувань технології сорбційної, осаджувальної і екстракційної очисток концентрату рідкісноземельних елементів (РЗЕ) від радіоактивних продуктів розпаду уранового та торієвого рядів. Показано, що поєднання процесів сорбції, виборчого осадження та екстракції дозволяє ефективно очищати РЗЕ від U, Th, Po, Ra, RaD і Ac і отримувати радіаційно безпечні розчини, які містять азот, для виробництва добрив та індивідуальних РЗЕ.