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SECONDARY RAW MATERIALS OF RADIOACTIVE METALS

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Main kinds of secondary raw materials containing radioactive metals are given. Technologies of reprocessing spent nuclear fuel and certain types of waste of nuclear industry including production of radionuclide molybdenum-99 are considered.

INTRODUCTION

In our previous papers [1–3] technologies of recovery of radioactive metals from secondary raw materials such as uranium shavings, waste of uranium-molybdenum alloy, scrap of fuel elements coated with magnesium-beryllium alloy, uranium-fluorine-containing waste, americium-containing solutions were considered. In the present work new publications (for the period 2016–2018) devoted generally to reprocessing spent nuclear fuel and production of radionuclide molybdenum-99 are reviewed.

SPENT NUCLEAR FUEL (SNF)

Methods of reprocessing SNF from nuclear plants can be classified on aqueous and non-aqueous [4, 5]. Only hydrometallurgical technology of reprocessing SNF from thermal reactors is realized now on a commercial scale. This is so-called PUREX process based on liquid extraction with the use of tributhyl phosphate (TBP). Plutonium recovered at reprocessing can be used as MOX fuel, i. e. UO_2-PuO_2 mixture. That fuel is most effectively to use in fast neutron reactors allowing creating closed nuclear fuel cycle based on fast neutrons.

PUREX process that uses solution of 30 % TBP in paraffin as extracting agent provides, in according to the work [6], recovery of uranium, plutonium, neptunium, and technetium in first extraction cycle and separation of neptunium and technetium from plutonium with uranium stream and with final purification of uranium and plutonium from admixtures in refining cycles. In power reactors of PWR and BWR types the burnup of SNF increases from 0.5 to 70 GW·days per tonne, therefore content of transuranium elements and fission products in it increases. Some of them are extracted by TBP and some (molybdenum, zirconium, barium) tend to sludge at dissolution of SNF and evaporation.

The same authors report about development of process chart of first extraction cycle of SNF reprocessing using 50% solution of TBP in isoparaffin which includes like previous case the separation of transplutonium elements (TPE) and rare-earth elements (REE) into individual fraction [7]. As salting-out agent at extraction of TPE and REE trivalent iron nitrate with concentration up to 2 mol/L or ammonium nitrate with concentration up to 6 mol/L were used. At verifying technology on real highly active raffinate from reprocessing SNF of WWER-100 reactor, TPE were extracted 99.9 % for two interacts and successfully reextracted.

Authors of two previous works patented extraction mixture and method for extraction of TPE and REE from highly active raffinate from reprocessing SNF [8]. Extraction mixture contains organophosphorus extraction agent in polar solvent and method consists in joint extraction of TPE and REE by this mixture, washing extraction agent from admixtures, and reextraction. The method can be combined with additional separation of TPE and yttrium REE using as extraction agent of strong organophosphorus acid or its zirconium salt in individual cycle.

Procedure for the use of extraction processes at the Siberian Chemical Complex is described in the work [9]. It includes choice of extraction agent, calculation of extraction process, and choice of equipment. The report indicates that during affinage of natural uranium at reprocessing SNF, enriched nuclear fuel, and waste uranium containing solvents neutral extraction agents are most appropriate.

Prospects for reprocessing SNF based on U-Th alloy are considered in the work [10]. Extraction of Th^{4+}, U^{6+} and accompanying metals ions from nitrate solutions was carried out by dihexyloctanamide (DHOA) and TBP. At that the modelled waste and commercial solvents Solvesso 100 and Shellsol D70 were used.

For recovery of thorium and REE from radioactive residues the extraction agent Cyanex 572 dissolved in kerosene was tested [11]. Its capacity for thorium and REE was 0.3 and 1.0 mol/L, respectively. The fullest separation of thorium and REE was achieved in 10 stages of extraction-reextraction.

The method for reprocessing of irradiated nuclear fuel proposed in work [12] consist in autoclave dissolution of SNF in nitric or muriatic acid at a temperature of 400…500 ºC and a pressure of 30-40 MPa. At that, the lanthanides (Ce, Pr, Tb, Nd, Sm) don't form oxides and remain in solution and solid U_3O_8 and UO_3 uranium oxide particles can be used for production of mixed oxide nuclear fuel.

Electrochemical and physical properties of actinides and lanthanides for developing technologies of its recovery from SNF were studied in the work [13]. The investigations curried out in LiCl-KCl melt of eutectic composition.

The technology for reprocessing SNF proposed in the work [14] consists in electrorefining raw materials in melted salts with aluminum cathodes and chlorination for separation of actinides from Ac-Al melt deposited on cathode. Last operation consists in three stages. The first stage is distillation of salts clumped by cathode deposit; the second one is chlorination of Ac-Al melt by

$HCl-Cl_2$ gas mixture at 300…400 ºC with obtaining aluminum and actinium chlorides; the third one is sublimation of $AlCl_3$. As actinide phase, UCl_4, $NdCl_4$ or $PuCl_3$ were obtained.

The problem of reprocessing SNF by electrochemical method with the use of the FFC Cambridge process was the subject of the work [15]. As applied to SNF, the technology consists in production from spent radioactive metal oxides of cathode briquettes and its subsequent electrochemical reduction to metals which are easier to separate as compared with current pyrometallurgical methods for separation of uranium from plutonium and cerium. Investigations were carried out in melts of $CaCl_2$ at 810 ºC and LiCl – $CaCl_2$ at 600 ºC.

At reprocessing SNF cesium is recovered from it by coprecipitation with salts of iron, nickel, zinc or ammonium, as well as sorption and extraction. Most selective extraction agents for cesium are solutions of macrocyclic polyethers (crown ethers) in organic solvents. To improve extraction processes, in the work [16] so new activator as $(CF_3SO_2)_2NSi$ is proposed. It allows extracting cesium with a rather high partition coefficient from neutral solvents.

To recover americium from SNF and refine it from plutonium and uranium in the patent [17] it is proposed to use electrolysis in molten chloride with liquid cadmium or bismuth electrodes. Yield of americium was 99.5 %. After separation of americium, liquid cathode was returned to electrolysis.

Active irradiation of SNF was curried out in the work [18] for purpose to develop improved procedure of differential registration of damping electrons (DDA) for SNF. The procedure can by applied to solve next problems: 1 – restoration after loss of knowledge accumulated in organization; 2 – checking recorded incoming mass of plutonium on reprocessing unit; 3 – quantitative definition of mass of plutonium sending from one object to other in terms of estimation of variations between sender and recipient data; and 4 – stopping of assurance for nuclear materials in storage facility of spent fuel. Systems based on neutron generators have been used for decades to measure radioactivity of waste in reprocessing plants and when general analyzing containers with waste and never to analyze completely spent fuel assembly being much more actively reproducing system than waste and having respectively much more difficult behavior.

SNF tailing dumps contain up to 80 ppm uranium. In the work [19] a new technique to recover uranium involving pretreatment of raw material by diluted alkali and sulfuric acid is presented. When NaOH and Na_2CO_3 are used (leaching mode: alkali concentration 10 g/l, liquid to solid ratio 20, mixing speed 400 rpm, duration 2 h), there are 13 ppm and 7.5 ppm respectively in tailings. Proposed technology has next advantages compared with conventional direct acid leaching as low energy consumption, high efficiently, lower amount of impurities in recovered product.

OTHER KINDS OF WASTE

Spent uranium-zirconium fuel elements in addition to uranium and zirconium contain aluminum and silicon. Main operations of the technology proposed in the work [20] devoted to recovery of uranium from this secondary material are fragmentation of waste to size of 20…40 mm, oxidation of fragments in air at a temperature 1000…1250 ºC during 8…10 h, and treatment of oxidized fragments by 3…6 N nitric acid at a solid to liquid ratio 1:(3…6), temperature of 70…90 ºC during 4…6 h. High-temperature oxidation leads to the formation of ZrO_2, SiO_2, α-Al_2O_3 oxides of acid-resistant modification and uranium continues to be able to dissolve in the nitric acid. Due to low content of Zr, Al, and Si in nitrate uranium-containing solution it can be reprocessed by single peroxide deposition without going through extraction. The technology provides the extraction of uranium more than 98%. At that, non-dissolved residue contains less than 0.5 wt.% of uranium and can be transferred to the category of low-level radioactive waste. The technology is patented as method of reprocessing of uranium-zirconium waste in form of fuel elements [21].

The technology of reprocessing zirconium-containing intermediate product of the uranium production is given in the work [22]. The technology consist in following operations: washing of zirconium concentrate by solutions of sodium bicarbonate and sulphuric acid in mode of pH control, step-by-step leaching of enriched zirconium concentrate by sulphuric acid, precipitation of zirconium hydroxide, drying, and calcination of residue with production of zirconium dioxide (more than 90% ZrO_2) which contains, %: 67.1 Zr and 0.001 U. Obtained technical ZrO_2 on amount of main substance can be used to prepare DZ (ДЦ) grade powders according to the technical specification TU 342-2000 that is applied for plasma spraying of heat protective coatings in aviation and aerospace engineering.

In the work [23] a process of acid and carbonate dissolution of uranium waste was study and new techniques for selective deposition of oxalates of fission products from uranium-containing solutions were developed that allow reducing the fission products content in uranium by 2000…8000 times. New techniques to recovery uranium from oxalate mother liquors provide uranium deposition degree at least 90%.

The method to recovery rhenium from uranium-containing solutions according to the patent [24] consist in sorption of rhenium by weak basic nanostructured anionite on styrene-acrylate matrix that contains functional groups of cyclohexylamine in amount of 1.9…3.0 mg-eq/g. The technical result is increase of recovery selectivity for rhenium in respect to uranium and decrease in the number of sorption-desorption stages at purification of eluted solutions of rhenium from uranium.

The method to recovery americium from liquid radioactive waste consist in next operations: joint extraction of americium and REE from nitrate radioactive solution by solution of neutral organic extracting agent in polar organofluoric solvent, washing of organic phase saturated with metals, and selective reextraction of americium which allows to separate it from all rare earth metals in single extraction cycle [25]. As extracting agent the tetraalkylamide of diglycolic acid was used and as reextracting agent such solution, g/l: 5…20 of complexone, 5…60 of nitrogen-containing organic acid, 60…240 of salting-out agent.

Technologies to recover uranium, thorium and REE from various industrial wastes are described in review [26].

Experience of obtaining REE concentrate from highly active waste of factory RT-1 is described in the work [26]. Waste contained uranium, aluminum and REE. Developed technology consisted in combining methods of alkali and oxalate deposition. Purification factors of REE from uranium in the stage of oxalate deposition were at least 12. The technology allowed selecting REE fraction from solutions of highly active waste of complex salt composition and at that providing effective removal from REE concentrate up to 99% of aluminum and more than 90% of uranium.

PRODUCTION OF RADIONUCLIDE MOLYBDENUM-99

Radionuclide molybdenum-99 relates to radiopharmaceutical preparations. It is the parent radionuclide for charging generators of technetium-99m. It is obtained at irradiation of targets with highly enriched uranium. The report [28] discussed the transfer of current production of Mo-99 to low enriched uranium (LEU). After alkali and acid schemes of reprocessing irradiated targets was considered, it was found that rational alternative at transfer to LEU targets is dissolution of the irradiated targets in nitric acid with subsequent direct recovery of Mo-99 from the solution by sorption on aluminum oxide.

The modes of sorption recovery of Mo-99 from solution on aluminum oxide were studied in work [29]. Obtained results show a low sensitivity of system to presence of Al^{3+} ions, but at the same time efficiency of molybdenum sorption significantly depends from acidity of solution and rate of passing solution through layer of sorbent.

The method for extraction recovery of Mo-99 from irradiated highly enriched uranium-aluminum composite, according to patent [30], consists in its dissolving in nitric acid at presence of mercury. Then precipitation of mercury iodide at presence of reducing agent carried out and then iron (III) is reduced to iron (II) in a flow. Further joint extraction of molybdenum and uranium in continuous mode using synergetic (equimolar) mixture of TBP and D2EHPA carried out. Obtained extract is washed by concentrated nitric acid. Then molybdenum and uranium are separated by highly acidic solution of hydrogen peroxide with washing of reextract from uranium by reverse extracting agent. Further uranium is reextracted by solution of mixture of DTPA and methylamine carbonate. Process is carried out in centrifugal extractors in cyclic mode with returning reextract of molybdenum in extraction zone and breaking cycle when initial solution ends. As technical result, recovery of molybdenum in total is more then 90 % and purification ratio of molybdenum from radionuclides is more than 10^5.

During production of Mo-99 solid uranium-containing waste is generated. To recover uranium, in work [31] such waste was dissolved in nitric acid then obtained UO_2^{2+} was extracted by TBP whereby acetohydroxamic acid was added in the water phase to prevent extraction of plutonium and fission products. Approximately 99% UO_2^{2+} was reextracted from organic phase by 0.5 M water solution of ammonium carbonate. At low concentrations of UO_2^{2+} in solution just one extraction stage is enough whereas at high ones two and more stages are needed.

CONCLUSIONS

From spent products and waste of atomic industry (materials and solutions) radioactive and other metals can be obtained. At reprocessing spent nuclear fuel and other kinds of waste to recover from them of uranium, thorium, plutonium, technetium, americium, rare earth elements, cesium, zirconium, and rhenium hydrometallurgical technologies are used, mainly liquid extraction as well as acid dissolution, chemical precipitation, sorption on ion-exchange resins and electrolysis in molten salts. To obtain radionuclide molybdenum-99 from uranium-containing nitrate solutions sorption on aluminum oxide and extraction (jointly with uranium) are used.

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ВТОРИЧНОЕ СЫРЬЕ РАДИОАКТИВНЫХ МЕТАЛЛОВ

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Приведены основные виды вторичного сырья радиоактивных металлов. Рассмотрены технологии переработки отработанного ядерного топлива и некоторых видов отходов атомного производства, включая процессы получения из них радионуклида молибден-99.

ВТОРИННА СИРОВИНА РАДІОАКТИВНИХ МЕТАЛІВ

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Наведено основні різновиди вторинної сировини радіоактивних металів. Розглянуто технології переробки відпрацьованого ядерного палива і деяких видів відходів атомного виробництва, включаючи процеси отримання із них радіонукліду молібден-99.