

Reprocessing of Fast Reactors Mixed U-Pu Used Nuclear Fuel in Russian Federation: Studies and Industrial Test

A. Shadrin, Yu. Mochalov, K. Dvoeglazov, V. Kascheev

“Innovation and Technology Center by ”PRORYV” Project, State Atomic Energy Corporation “Rosatom”, Moscow, Russia

E-mail contact of main author: shau@proryv2020.ru

Abstract. Mixed U-Pu used fuel of fast reactors has a high Pu content, high burn-up (50 GW/days*ton and more), and short cooling time (not more than 3 years) as compared with the thermal reactor used fuel. Combined (pyro + hydro) and hydrometallurgy reprocessing technologies are developed in Russian Federation for the closed nuclear fuel cycle. These technologies provide reprocessing of used fuel with 1-3 years cooling time, 10-15 % of Pu content and burn-up up to 100 GW/days*ton.

The aim of reprocessing is production of purified mixture of actinide oxides. The purification power of actinides from fission products should be around 10^6 .

The dry reprocessing technology based on pyroelectrochemical refining is under development. This technology should be suitable for reprocessing of fast reactors used fuel with burn-up more than 100 GW/days*ton and 1 year cooling time.

The main results of the studies are being discussed in the current paper.

Within studying the analysis of products and operations of reprocessing 8 MOX irradiated assemblies from BN600 reactor unit having burn-up from 73 up to 89 GW/days*ton were performed at RT1 plant. The technology steps were made under standard conditions. The increase of Pu losses during MOX BN600 used fuel reprocessing as compared with thermal reactor unit used fuel reprocessing was not found.

The design of reprocessing facility for mixed U-Pu nitride fuel started in 2015. This facility is planned to be built at the Siberian Chemical Combine as part of experimental and demonstration energy complex with BREST-ED-300 reactor unit.

Key Words: mixed U-Pu fuel, used fuel reprocessing, hydrometallurgy.

1. Introduction

The combine (pyro + hydro) technology of reprocessing of fast reactor used nuclear mixed nitride and oxide U-Pu fuel (FR MNIT and MOX UNF) [1] and its hydrometallurgical version [2] were developed as a key element of closed nuclear fuel cycle (CNFC) technology within “PRORYV” project. Combined technology (PH-process) allows reprocessing FR UNF having non-limited burn-up and less than 1 year cooling time in off-reactor storage. Hydrometallurgical version of PH-process can be used for reprocessing of FR UNF with 6-8 % of heavy atoms burn-up and with more than 2 years cooling time. Both technologies were developed for FR UNF reprocessing without mixing with thermal reactor (TR) UNF. Both technologies can provide recovery and separation of americium and curium and production of uranium, plutonium and neptunium mixed oxides and mixtures of uranium – americium and uranium – curium oxides. There is a possibility to obtain a mixture of U – Pu – Np – Am oxides.

The intensive studies on FR MNIT and MOX UNF reprocessing have been performed over the past 5 years. The several processes were tested with simulated and real (irradiated) FR UNF, including MOX UNF of BN-600.

2. Studies and Industrial Test of Fast Reactors Mixed U-Pu Used Nuclear Fuel Reprocessing Technologies

2.1. Study on FR MNIT and MOX UNF reprocessing technology

The main requirements for modern FR UNF reprocessing technologies are the following: high safety; low influence on the environment; high proliferation resistance (no recovery of pure plutonium during the reprocessing); high resistance to external impact (earth shake, flood, airplane crash and etc.) [3, 4]. Combined technology of FR UNF reprocessing is under development for the reprocessing module (RM) of the experimental and demonstration energy complex (EDEC) and this technology, including the hydrometallurgical version, is satisfied to aforementioned requirements [1, 5]. A principal flowsheet of PH-process is shown in FIG. 1.

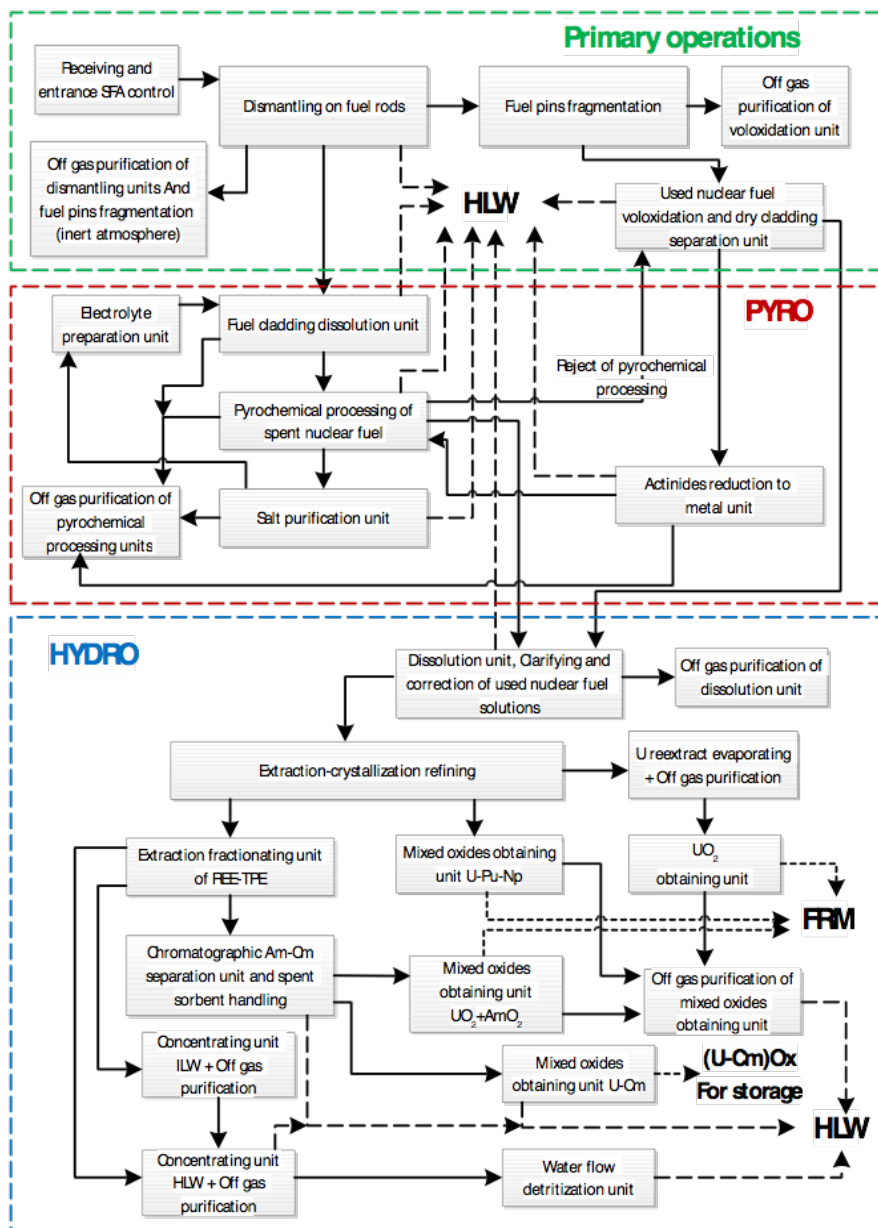


FIG. 1. Principal flowsheet of the combine technology for FR MNIT and MOX UNF reprocessing (PH-process).

The main version of PH-process is suitable for UNF after homogenous transmutation of neptunium and americium. However, there are insufficient experimental data on the implementation of technology for preparation of mixed nitride U, Pu, Np and Am fuel right now. Thus, as a first step the transmutation of Am can be heterogeneous using Am-pins contained around 10 % of americium oxide in uranium oxide. The hydrometallurgical version of PH-process should provide reprocessing of Am-pins as well. Removal of tritium by fuel voloxidation was added in flowsheet for reprocessing of Am-pins. Oxidized mixture of oxides can be sent to the dissolution stage and the following operations will be same for reprocessing of U-Pu-Np-pins and U-Am-pins.

Most of the developed pyrochemical technologies are suitable for reprocessing of metal UNF (different mixtures of U-Pu-Zr) [6] or MOX and MNIT UNF of TR and FR [7]. The pilot pyrochemical facility with capacity of 100-150 kg of UNF in one operation is used for reprocessing of metallic fuel of EBR-I and EBR-II in USA. This facility is placed in hot cells with inert atmosphere and is used for R&D on pyrochemical reprocessing.

There are a pilot facility for pyrochemical reprocessing of MOX fuel, and semi-industrial facility for vibropack mixed uranium and plutonium oxide fuel productions in RIAR (Russian Federation) [8]. RIAR in cooperation with other Rosatom RF and Russian Academy of Science institutes analyzed own and literature data and for "PRORYV" project proposed a new version of technology for MNIT UNF reprocessing. This technology was used as pyrochemical part of PH-process. The demonstration of pyrochemical operations with real (irradiated) MNIT was performed in air hot cells of RIAR in 2013. However the passivation of MNIT UNF pellets due to formation of low soluble in electrolyte UNCl surface layer [9, 10], and possibility of UN/U₂N₃ formation, also insoluble in electrolyte, could lead to losses of uranium. Due to these and some other reasons these experiments were not fully successful. The hydrometallurgical technologies were adapted for the FR UNF processing at 6 % h.a. burn-up (first 5 years of reactor operation) and the capacity of voloxidation was increased up to 5 tons per year and flowsheet of closed water and nitric acid recycle were changed.

The efficiency of main hydrometallurgical operations has been previously confirmed by experiments with simulated products, U and Pu, and with real (irradiated) UNF [1, 2, 5]. For example, the high efficiency of dissolution off-gases purification (more 99,9 %) from aerosols, nitrogen oxides, compounds of iodine, 14-carbon, tritium and ruthenium by system which consists of fiberglass rude purification filter (FyaS), aerosol regenerated fine purification filter (FARTOS), non-reagent collection with Al gamma-oxide apparatus (BRUNS) and silica gel – urea purification apparatus (SMOG) was demonstrated. The column apparatus with granulated Al gamma-oxide is proposed for recovery of RuO₄ by precipitation of RuO₂ at 150 °C. The Ag containing composite materials were used for iodine recovery. The absorptive packet-bed column with NaOH irrigation was used for ¹⁴CO₂ recovery at 20 °C. The precipitation and separation of CaCO₃ which can be sent for cementation and final storage were tested as well. Efficiency of CO₂ recovery was tested with real (irradiated) MNIT UNF [11-13].

Oxidation (voloxidation) of MNIT was tested with simulated (model) UNF [2] and real (irradiated) MNIT UNF. Oxidation was performed under 400-500 °C in the presence of water steam and CO₂. Obtained oxidized powder was dissolved in 10 M nitric acid under heating. More than 93-95 % of powder was dissolved. Insoluble residue contained 0,05-0,01 % of used plutonium and neptunium.

The cathode residue of PH-process pyrochemical operations (U - 84,5%; Pu – 15%; Np - 0,5%) was dissolved in 10 M nitric acid within 6 hours with 400 g/l actinides solution

formation. Insoluble residue was about 1,5 % mass. The presence of mixed U and Pu oxides ($(\text{Pu}_{0,89}\text{U}_{0,11})\text{O}_2$, $(\text{Pu}_{0,5}\text{U}_{0,5})\text{O}_2$) and metal phase were detected by X-ray analysis [1].

The ultrafiltration with ceramic membrane is planned to be used for clarification of UNF solution. The pilot set-up for testing of ultrafiltration was made at PA “Mayak” site. The filter is a multicanal cylinder from $\alpha\text{-Al}_2\text{O}_3$, with porosity from 1 to 2 micrometer, and ZrO_2 , with porosity 50 nanometre. This filter allows the pulp concentration up to 100 g/l. The light transmission coefficient of permeate was 98.9 % compared to distilled water.

The purification of recycled actinides is planned to be done by extraction and crystallization. These operations should allow to obtain purification coefficient $> 5 \cdot 10^4$ from γ -active fission products (FP) and $> 2 \cdot 10^5$ from the sum of Am and Cm. The set-up for extraction and crystallization tests was built at Siberian chemical combine (SCC) (FIG. 2, 3 and 4).



FIG. 2. Blocks and equipment of extraction set-up.

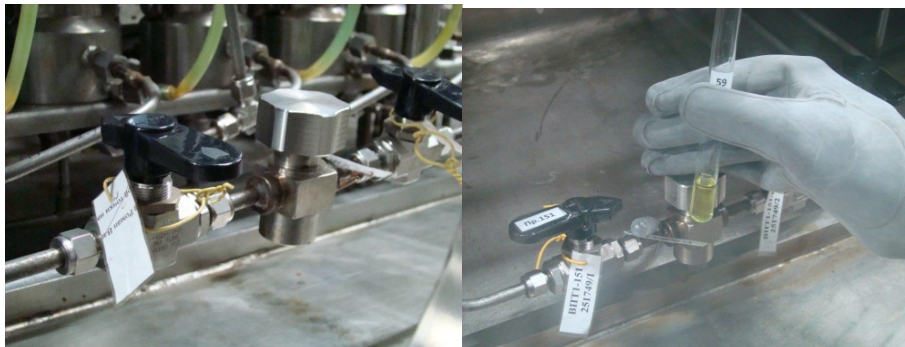


FIG. 3. Extraction set-up sample recovery system.

Extraction set-up includes 6 blocks of centrifugal contactors, separators with upper separation chamber, 2 liquid chromatography blocks, vessels and dosing pumps. All equipment is nuclear safe. The set-up is under automatic control. The set-up was tested with uranium and plutonium solution in 2016. The test with UNF dissolution simulated solutions (4,5 M nitric acid, U – 230-240 g/l, Pu - 25-30 g/l, Np – 0,08-0,1 g/l and several FP including Tc) showed that tested extraction flowsheet, developed by Bochvar Institute, allows to effectively extract U, Pu and Np from nitric acid solutions. The residues in raffinate of U, Pu and Np lower than 1, 0,6 and 0,2 mg/l, respectively, were obtained. The total recovery of Pu was also demonstrated. The Pu content in organic phase after stripping was $< 1,0$ mg/l.



FIG. 4. Full scale crystallisation set-up.

Set-up containing model of linear full scale crystallizer (capacity is 5 tons t.m. per year) was built by SCC and Bochvar institute for testing of $\text{UO}_2(\text{NO}_3)_2\text{-Pu}(\text{Np})\text{O}_2(\text{NO}_3)_2$ crystallisation (Figure 4). Set-up is under automatic control. The washing solution line is added in set-up flowsheet to increase the purification efficiency. The model was tested with velocity flow of 400-600 ml/hour of 800-910 g/l uranyl nitrate solution. The stability velocity flow, temperature of cooling and heating and other zones, level of water phase were demonstrated. The deviation during experiments was in a range of $\pm 5\%$. The direct recovery of uranium in crystals was estimated. The next experiments will be performed using $\text{UO}_2(\text{NO}_3)_2\text{-PuO}_2(\text{NO}_3)_2 - \text{HNO}_3 - \text{H}_2\text{O}$ system.

Method of direct denitration under microwave radiation was developed for mixed oxides preparation without formation of big volume of mother solution [14-16]. The process is performed in two stages. First one is evaporation of nitric acid actinides solution until the formation of mixture uranium trioxide and hydrated oxides of Pu and Np. The second stage is oxides reductions in Ar- H_2 mixture followed by mechanical milling of obtained dioxide. Several experiments with 30 - 95 g of actinides in each were performed and the mixture of U and Pu oxides were obtained. The full scale model of microwave denitration apparatus was made and planned to be tested in 2017.

Extraction system based on N,N,N',N'- tetraoctyldiglicole amid (TODGA) – metanitrobenzotrifluoride (F-3) is a base flowsheet for group separation of rare earth and transplutonium elements. The test of this flowsheet using simulated solutions spiked with americium and curium was made on settler – mixing set-up of PA “Mayak”. The test duration was 140 hours. Recovery $> 99,99\%$ of americium was achieved. The experiment demonstrated a high purification of americium from FP (La > 300000 ; Ce > 500 ; Pr > 20000 ; Nd > 4500 ; Sm > 600 ; Eu > 1000 ; Gd > 6000 ; Y > 30000 . Losses of Am were $< 0,1\%$ [1].

Complexing chromatography with strong acidic sulphogroups cationite were chosen for separation of americium and curium. This method for recovery and separation ^{244}Cm and $^{241,243}\text{Am}$ was tested at PA “Mayak” set-up using rafinate from reprocessing of VVER-440 UNF. The cationite Tokem-308 with 220 micrometers grains was used in this test. 14 g of ^{244}Cm were recovered and 9 g from this fraction contained $< 6\%$ of americium (activity). The

mixed Am and Cm fraction contained about 40 g $^{241,243}\text{Am}$ and 4,6 g of ^{244}Cm . Main Am fraction contained < 0,8 % mass of Cm and < 0,1 % activity of $^{154,155}\text{Eu}$.

High burn-up UNF contains high amount of FP. The proposed partitioning technology leads to high concentration of ammonium in solutions. The traditional flowsheets for high and intermedium level radioactive waste (HLW and ILW) were changed [1, 17, 18]. The method with destruction of nitric acid up to 2,3-3 M of nitric acid in bottom solution was proposed for HLW concentration. The process with joint destruction of ammonium nitrate and organic reagents by formalin in evaporated apparatus with circulation was proposed and tested for ILW treatment. The bottom solution from apparatus collected permanently in a vessel and from time to time sent to the ammonium destruction in autoclave.

2.2. Industrial Scale Reprocessing of MOX UNF BN-600

Reprocessing of the mixed uranium-plutonium spent nuclear fuel of the BN-600 reactor was performed at the RT-1 plant twice, in 2012 and 2014 [19]. In total, 8 fuel assemblies with a burn-up from 73 to 89 GW day/t and the cooling time from 17 to 21 years were reprocessed. The reprocessing included the stages of dissolution, clarification, extraction separation of U and Pu with purification from the fission products, refining of uranium and plutonium at the relevant refining cycles.

Compared to the regular operations, the UNF dissolution mode has been changed during the reprocessing of BN-600 MOX UNF. The operation of dissolution has been carried out in two or three stages. At the first stage (primary dissolution) the fuel has been exposed in 10 M nitric acid solution at a temperature below the boiling point of the solution in order to avoid the accumulation of hexavalent plutonium that has relatively low distribution coefficients at the extraction phase. After the primary dissolution, one or two steps of the control dissolution in nitric acid with 1 g/l fluoride ion took place. The process has been carried out at a similar temperature. One of the control dilution stages has been performed at the boiling point of the solution during certain reprocessing operations.

Due to the high content of plutonium, extraction reprocessing of UNF solution (first extraction cycle) has been carried out in the department of highly enriched fuel reprocessing, the refining of plutonium — in a specialized division of refining, and the refining of uranium — at the second (refining) extraction cycle of low enriched fuel reprocessing. HLW raffinates have been disposed in accordance to the HLW treatment scheme accepted at the RT-1 plant.

Radiometric studies of the residue have shown that the main activity is caused by ^{137}Cs , ^{106}Ru and ^{125}Sb . The elemental composition of the dissolved precipitate was determined by ICP MS method. The main components of the residue (excluding carbon and silicon) were found to be Fe, Cr, Ru, Rh, Pd (see FIG. 5).

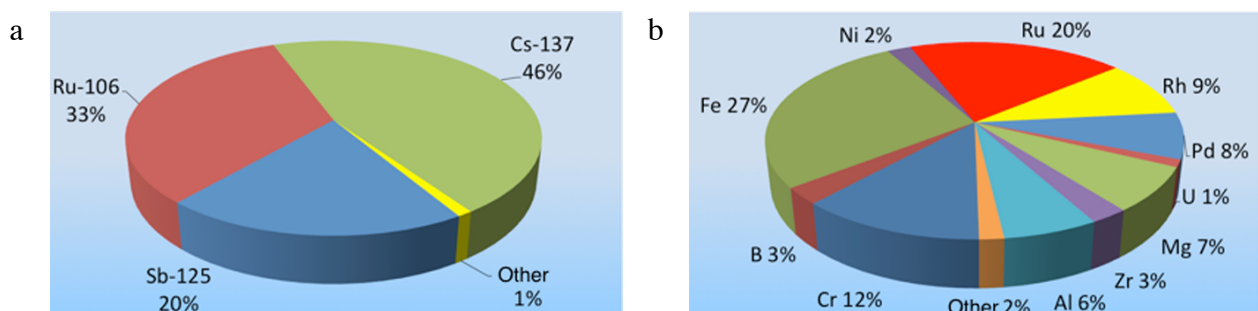


FIG. 5. Composition of the insoluble residue according to gamma-spectrometric (a) and element (b) analysis.

3. Conclusion

The combined technology of FR MNIT and MOX UNF reprocessing (PH-process) was developed under “PRORYV” project. PH-process allows to reprocess UNF with high amount (10-15 %) of fusible materials and to obtain a U-Pu-Np product with purification coefficient $\sim 10^6$. The hydrometallurgical version of PH-process is suitable for reprocessing of FR UNF with burn-up of 6-8 % h.a. and cooling time > 2 years.

The following technological operations were tested with simulated and real (irradiated) oxidation of MNIT UNF, dissolution of MNIT UNF and cathode product; preparation of actinide oxides; recovery and separation of rare earth and transplutonium elements. Apart from the technologies of evaporation, extraction and crystallisation affintage of U, Pu and Np, separation of Am and Cm and treatment of HLW and ILW were studied.

The reprocessing of the irradiated BN-600 reactor MOX fuel assemblies, which were prepared by the combined chemical precipitation of uranium and plutonium, has been successfully performed at the RT-1 plant. The dissolution of the mixed dioxide fuel composition in the solutions of nitric acid during the primary dissolution and using the control dissolutions in the presence of fluoride ion resulted in the full transfer of the target components into the solution. No deviations have been registered during the processes of MOX-fuel clarification and actinides extraction separation. The outflows of the extraction separation in their compositions complied with the regulatory requirements and remained at the levels of the flows compositions obtained during standard fuel types reprocessing at RT-1 plant. A mass balance has been calculated on uranium and plutonium technological refinement of BN-600 MOX UNF. No increased loss of uranium and plutonium into waste has been detected during reprocessing of BN-600 MOX UNF as compared with reprocessing of VVER-440 uranium oxide UNF.

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