Hydrometallurgical and combined technologies fast reactor
MNUP and MOX UNF reprocessing

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Abstract. Russian Federation is developing the key technologies for closed nuclear fuel cycle with fast reactors used mixed uranium-plutonium nitride or oxide (MOX) fuel within the framework of the project “Proryv”. This is a new integrated comprehensive product for nuclear power, which provides in the future:
- no accumulation of spent nuclear fuel;
- radioactive waste management based on the principles of radiation-equivalent disposal;
- technological support for the non-proliferation treaty;
- competitiveness with other large-scale power technologies.

The experimental and demonstration energy complex is under construction now on the site of Siberian Chemical Combine for the industrial development of the closed nuclear fuel cycle. ODEC will include a fast reactor BREST-OD-300 with lead coolant, facility for fabricating/refabrication of nitride fuel and the spent nuclear fuel processing facility. Up today, the key technology elements were demonstrated using macro quantities U, Pu, Np, irradiated mixed nitride fuel and real high-level waste. Within the framework of the project "Proryv" a prototype of the fuel cycle of fast reactors is developing.

1. Introduction

Closed nuclear fuel cycle (CNFC) with the natural safety fast reactors (FR) is a new complex product ensuring in terms of radiochemical technologies:

- reduction of accumulated used nuclear fuel (UNF);
- move to RW handling based on the principles of radiation and equivalent RW filling;
- technological support non-proliferation regime;
- competitiveness with other large-scale energy technologies.

2. Hydrometallurgical and combined processing technologies for FR MNUP and MOX UNF

The development of hydrometallurgical and combined (pyro + hydro) reprocessing technology for fast reactors used mixed nitride and oxide irradiated uranium and plutonium (MNUP and MOX) is being currently completed \([1, 2, 3]\) and it will allow processing FR UNF with almost unlimited burn-up and cooling at the non-reactor storage area for less than 1 year. The
hydrometallurgical version ensures processing of FR UNF with the burn-up of 8% heavy atoms (h.a.) and more, with the non-reactor cooling time period of at least 2 years. Both versions rely on FR SNF processing without shift from heat neutron reactor SNF, provide for emission and refining the mixture of U-Pu-Np and obtaining as the target product of U-Pu-Np mixed oxides and excretion and separation of Am and Cm with obtaining of mixed U-Am and U-Cm oxides. Optionally, mixed U-Pu-Np-Am mixed oxides can be also obtained. The principal process of the combined (pyro + hydro) UNF processing technology is given at figure 1. Results of studies achieved by 2017 are given in [3,4], then the results obtained in 2107 are reviewed.

Figure 1. Principal Flowsheet of MNUP and MOX UNF Reprocessing Technology (PH-Process).

2.1. Trial industrial processing of FN-600 SNF MOX
Mixed oxide uranium-plutonium (MOX) used nuclear fuel (UNF) of BN-600 reactor was processed at RT-1 plant in 2012 and 2014 [4]. 8 assemblies with the burn-up of 73 to 89 GW/(d*day/t U) and the cooling time till the processing moment from 17 to 21 years were processed in total. Processing included stages of dissolution, clarification, extraction separation of uranium and plutonium with purification from fission product, and uranium and plutonium affinage at corresponding affinage cycles.

Due to the high plutonium content, extraction separation of plutonium was carried out sing nuclear safe equipment for UNF processing contains highly enriched uranium, and plutonium affinage - at the affinage set-up. Technological of extraction separation and affinage of fission products were carried out with no deviations from regular conditions.

Residue radiometric studies showed that main irradiating materials having an effect on the activity of deposit upon UNF dissolution are $^{137}$Cs, $^{106}$Ru and $^{125}$Sb. Inductive Coupled Plasma Mass-Spectrometry (ICP MS) was used to determine the composition if the undissolved residue. Main residue components (without carbon and silica) are Fe, Cr, Ru, Rh, Pd (figure 2). No increased plutonium losses were revealed resulted from BN-600 MOX UNF processing at RT-1 plant.

2.2. Main operations of the combined technology for FR SNF reprocessing

Main operations of the PH-process include disassembly of assembly, cutting of pins and oxidation (voloxidation) of MNUP and MOX UNF. Equipment of the both fuel types are the same. The operation is aimed at removal of tritium and volatile fission products (LFP) from UNF. In 2017, at RIAR, MNUP UNF with the burn-up of 5.45% h.a. was oxidized. It was showed that MNUP UNF can be fully oxidized in the air flow for 8 hours at the temperature of 450 °C, with the full fuel mass separation from the shell (see figure 3). Tritium was removed by more than 99.8%, $^{14}$C was removed by at least 98.4%.

For off-gas cleaning from great amounts of dust (emitted from cutting and oxidation) the bulk filter filled with shell fragments, metal-fabric filters and glass-fiber filters of fine cleaning were suggested to
be used. Molecular iodine and methyl iodide are recovered at the temperature of 200 °C with sorbent (silica gel or aluminum gamma-oxide) impregnated with the silver nitrate and reconstituted silver. RuO4 is recovered and degraded till non-volatile RuO2 on aluminum gamma-oxide at 110–150 °C. It has been experimentally showed that at the high-temperature these sorbents allow localizing up to 99.999 % of radioactive iodine. To recover 14СO2 it was suggested to use the adsorption column washed with the aqueous sodium hydroxide solution at the circulatory mode at 20 °C with further NaOH regeneration and its repeated use, deposition and separation of CaCO3, to be forwarded for conditioning, cementing and storage. It has been experimentally showed that recovery of CO2 at the circulatory washing mode ensures extraction of 99, 9% CO2 [5, 6, 7, 8].

2.3. Pyrochemical process stage of the Combined Technology for FR UNF Reprocessing

Pyrochemical technologies provide for processing of metal UNF (U-Pu-Zr alloys) [9] or MNUP and MOX SNF of various types of thermal and fast reactors [10]. For processing of metal UNF of EBR-I and EBR-II research reactors in the USA the pyrochemical pilot unit is used and makes it possible to process 100 - 150 kg of UNF. The unit placed in insulated chambers with the inert atmosphere maintained is used for R&D in the field of pyrochemical processing.

In the RF at the end of 2013, the demonstration experiment regarding the pyrochemical processing of MNUP UNF was carried out in air chamber of RIAR. However, this experiment did not take into account inhibition of MNUP UNF tablets through formation on their surface of the UNCl film having low dissolution ability in a salt electrolyte [11, 12], and a possibility of UN/U2N3 recharge, which leads to great uranium losses.

The pyrochemical processing development has been currently carried out at Institute of High-Temperature Electrochemistry of the Ural Branch of the Russian Academy of Sciences, under the supervision of Yu. P. Zaykov. In the process chart proposed, authors try to identify defects of previous works.

2.4. Hydrometallurgical process

Dissolution of oxidized MNUP UNF and the product of pyrochemical processing of MNUP UNF were verified several times with the application of plutonium-containing models. It was showed that insoluble residue contains 0.05-0.01 % of the quantity of nuclear materials used in the experiment [1]. Similar results were obtained upon dissolution of oxidized MNUP UNF at RIAR. Besides, experiments performed at Bochvar Institute and Radium Institute with the use of macro quantities of plutonium, verified variants of the chemical and electrochemical dissolution of simulated voloxidized MNUP UNF with the burn-up over 12 % h.a.. It was showed that Pu capture with the zirconium molybdate amounted to 0.008 % from plutonium mass delivered at the dissolution stage. UNF dissolution is accompanied with exhaust gases and, first of all, nitrogen oxides. The principal flowsheet of gas cleaning from NOx is given at figure 4. In case of a combined technology, there it almost no need in removal of FP from exhaust fumes, unlike purely hydro metallurgical variant.

As to the BREST reactor’s irradiated fuel reprocessing unit, gas claning at the dissolution stage the different filters were combined into one gas purifying unit. All types of filters are designed and tested for recovery of liquid and gaseous aerosols, for recovery of NO, NO2, absorption of CO2 (14С). It was showed that aerosol filters recover up to 70–80 % of NO2 in one operation, where main recovery accounts for filter devices gives an additional recovery of nitrogen dioxide up to 99.8 % [13,14].

To separate insoluble residue of UNF from the solution before extraction processing, it is suggested to use ceramic membranes with a membranous bend of the clarified solution used in the radiochemical industry to make LRW clear and the principal opportunity for SNF clarifying of which application is shown in [15]. The membranous filtration unit with GCVN-10/30-800 pump (figure 5) worked in the filtration mode for 205 hours with the use of SNF solution imitator (at several stages).
Maximum content of the solid phase in the suspension amounted to 103 g/L. The repeated regeneration of filtering components upon clarified solution with reverse current under the pressure of up to 2.7 atmospheres to maintain membranes permeability. The efficacy of this regeneration method has been confirmed. The clarified solution outflow through membranes during handling with the concentrate of the suspension, characterized with the solid phase, was stable and amounted to 192 to 209 L/h (with application of filtering components with the membrane pore size of 200 nm). Absence of deterioration of the clarified solution properties at repeated filter-cycles was confirmed. Solid phase content in the clarified solution amounted to less than 1.0 g/L throughout the whole period of operation of the unit - clarified solutions remained clear at all operation modes (figure 6).

The extraction and crystallization processes of PH process are used to solve the task of obtaining purified actinides. To check whether it is possible to use this process stage, the extraction and crystallization set-up was made at Siberian Chemical Combine (figures 7 and 8). The set-up is equipped with 6 units of centrifugal extractors, separators with the upper separation chamber to clarify extracts from the micro emulsion, two units of liquid chromatography, bulk-capacity and dispensing equipment. All equipment have nuclear safe design. The process equipment are 100% automated.

**Figure 4.** Principal chart of gas cleaning of exhaust fumes upon the dissolution process.
Figure 5. Full-Scale Stand of Dynamic Membranous Filtration Equipment

Figure 6. Clarification quality with the stand operating using the suspension with the solid phase concentration of 103 g/dm³.
At this set-up, it was experimentally showed that actinide recovery from the raffinate reached 99.97 %, which satisfies requirements of Proryv Project. Extraction technology indicators of combine reprocessing technology for MNUP UNF have been showed: recovery of U and Pu - 99.97 %, Pu purification coefficients for FP: for Cs – $10^6$, for Sr – $10^3$, for Zr and Mo – $10^3$, REE – $10^4$. In the course of elaboration of the crystallization cleaning of U and Pu, the possibility of their simultaneous excretion was confirmed, which serves as a technological barrier at proliferation of nuclear materials, with FP(REE) purification by factor 100-300.

To obtain mixed actinide oxides without generation of large amounts of mother solutions, the method of direct denitrification under the micro-wave was developed [16, 17, 18]. Actinide dioxides are obtained under the micro-wave is carried out at two stages. At the first stage, nitric-acid solution of actinides is
evaporated to the mixture of uranium trioxide and hydrated plutonium and neptunium oxides. The second stage is a calcination in Ar-H₂ medium. The dioxide obtained is ground finely by mechanical means in powder. Using tens of grams of actinides (30 to 95 g in each series of experiments), the possibility of obtaining homogenous powders of mixed actinide oxides has been demonstrated. At Siberian Chemical Combine the denitration unit was put into operation (figure 9). The works were carried out by Bochvar Institute and Vernadsky Institute. During performance of tests of the micro-wave denitration unit, process modes have been showed, during which mixed actinide oxides convert from solutions at one stage. 100 % denitration to U and Ce (Pu simulant) oxides was reached at one stage (to U₃O₈) per 7.5 kg of the load product (based on the capacity of 5 tons per year).

Under the lab conditions (Bochvar Institute and Vernadsky Institute) it has been shown that in the medium of 5% of hydrogen, UO₂ may be obtained directly at the denitration stage. UO₂ powders have given properties:

- ≥ 99 % U is in the oxidation state (IV);
- particle size - within the range of 25 to 400 mcm;
- bulk density – 2.0 - 2.2 g/cm³ and 2.3-2.5 g/cm³ with the powder shake down;
- relative density – 2.0-2.7 m²/g.

Obtaining U and Pu powders by means of direct micro-wave denitration will allow reducing amounts of liquid radwaste with high actinide content in 4.5 times.

Figure 9. General micro-wave denitration unit view.

In 2016, at RIAR, specialists of Frumkin Institute, Khlopin Institute and Bochvar Institute performed the test of the extraction system based on TODGA in the heavy polarized fluoridated solvent F-3 in order to recover transplutonium elements (TPE) from the raffinate of the first extraction cycle UNF hydrometallurgy reprocessing. Simulated raffinate solution containing 2 g/L of Am was used in the experiment. TPE mass values show that americium was efficiently extracted into the organic phase at the extraction stage, followed by separating from Mo, Zr and partially light lanthanides (La, Ce, Pr).
The possibility of Am separation from rare earth elements (REE) at the re-extraction stage was also demonstrated upon arrangement of the reverse flow process [19].

In 2017 specialists of Bochvar Institute, Khlopin Institute and RIAR carried out a series of experiments regarding study of the extraction system radiation resistance. These experiments demonstrated high radioactive resistance of the system and low output of fluoride-ion into solutions, which amounted to around 2 ions / 100 eV at α-irradiation and around 0.7 ions / 100 eV at γ- and β-irradiation [20].

In 2015 PA MAYAK using the laboratory extraction stand consisting of devices such as mixer-settler, a 140-hour dynamic experiment was carried out and covered verification of the process chart of americium extraction based on TOGDA extractant in F-3. During experiments, americium was more than by 99.99% extracted from the HLW imitator. Am losses with non-target products amounted to less than 0.1% [1]. In 2017 hot dynamics tests of the TOGDA-based technology of Am and Cm extraction from real HLW with the system. Americium extraction reached over 99.9 %.

The technology of americium and curium separation was demonstrated in 2016 at the trial and industrial unit of PA MAYAK. Around 14 g of 244Cm were recovered. The mixed americium-curium fraction contained around 4.6 g of 244Cm and around 40 g of 241,243Am. The enriched americium fraction the curium share was less than 0.8 % by mass, and the content of 154,155Eu was less than 0.1% by activity [4] and was about 60 g of Am.

3. Development of the HLW vitrification equipment

3.1. The full-scale make-up of the semi industrial vitrification unit based on the induction melter such as cold crucible (IMCC) for processing of highly-active waste obtained at the hydrometallurgical process stage and spent pyrochemistry electrolyte

To process HLW resulted from UNF processing (non-cycling pyrochemistry electrolyte and apparatus residue from hydrometallurgical raffinate) the unified vitrification unit based on the induction melter with the cold crucible was designed. Hydrometallurgy and pyrochemistry HLW processing units differ only by HLW dispensing conditions and vitrificating additives to the melter and the melter gas purifier systems. Processing of hydrometallurgy HLW results in production of the borosilicate glass. Processing of the non-cycling electrolyte at the pyrochemical process stage, taking into account the requirements to process temperature reduction and the chemical nature of the glass-making process, the borophosphate glass-like matrix is produced. Compositions of borosilicate and borophosphate matrices were developed and meet the requirements of normative documentation stated for HLW matrices. To elaborate the equipment operation modes, the full-scale make-up of the trial and industrial vitrification unit was manufactured and installed at the site of Bochvar Institute (figure 10). The make-up has a remote system of the unit nodes operation control and management. The structure of the make up has been developed based on the conditions of fast remote replacement of spent nodes using the power manipulator. In 2017, the make-up mentioned was used to test functional nodes and systems of the remote control under the blank operation mode and at melting of borosilicate glass, which confirmed the working capacity of the equipment manufactured.
3.2. The use of the method of dynamic membranous filtration for liquid radwaste cleaning

In order to evaluate the possibility of moving of radioactive waste of non-technological liquid radwaste from the category of medium-active to the low-active one, the experimental verification of their additional purification to remove uranium and trans-uranium elements - plutonium and americium (TUE) by means of dynamic membranous filtration has been performed. The pre-analysis of the non-technological liquid radwaste compositions shows that generated radwaste by TUE content are classified at Class 2 radwaste (TUE by its content (ILW containing trans-uranium elements). To reduce expenses for refilling of radwaste generated, it was decided to apply additional treatment of LLW solutions in order to reduce TUE concentration in the solutions to the values which allow referring end forms of radwaste generated to the 3rd or the 4th Class radwaste. The method of alkaline TUE deposition with further clarifying of solutions at membrane filters was used for additional removal of TUE from liquid radwaste. It was demonstrated that effective TUE deposition with the carrier (trivalent iron) is observed at the pH equal to 11. After clarifying at the unit for dynamic membranous filtration, permeates are clear colorless liquids corresponding to the LLW (10^2 - 10^3 Bq/dm³) with plutonium concentration of less than 1 mcg/dm³, americium less than 0.2 mcg/ dm³. This technology allows transferring radioactive wastes of Class 2 to Class 3 and reducing the cost of filling of radioactive wastes by around 450 thous. RUB/m³.

4. Conclusion

In 2019, it is planned to complete correction of initial data for engineering of the reprocessing model of the pilot demonstration energy complex with BREST-300-OD.

Under the technologies development:

- the stand of extraction and crystallization of U+Pu+Np affinage of un separated mixture with the full-scale crystallizer prototype was been made;
- the following has been experimentally certified and verified:
• modes and equipment of the extraction and crystallization affinage of U+Pu+Np mixture (the aggregate refinement ratio of $5 \times 10^6$ was confirmed);
• the technical achievability of the actinide extraction depth (over 99.99 %) for RW radiation equivalent filling;
• the mode and the full-scale unit of obtaining mixed oxides of U+Pu+Np, U-Am, U-Cm and pure U (checked on U and Ce);
• REE-TPE amounts extraction technologies and separation of Am and Cm;
• full-scale make-ups of trial and industrial equipment (dissolution, clarifying, off-gas cleaning, crystallization, micro-wave denitration, separation of Am and Cm) have been developed, manufactured and tested;
• technical projects of main and auxiliary equipment for hydrometallurgical processing of MNUP and MOX FR UNF have been developed;
• R&D have been completed;
• volume oxidation of UNF MNUP (UNF dry separation and fuel component shells, removal of over 99.99 % of tritium and over 98 % of $^{14}\text{C}$, were confirmed);
• clarifying of UNF solutions with membranous filtration;
• dissolution of SMF and the mixture of metal actinides;
• off-gas cleaning (established extraction of > 99.99 % I, 99 % $^3\text{H}$ and $^{14}\text{C}$).
• The technology of radwaste handling of combined and hydrometallurgical processing of MNUP and MOX UNF for reprocessing module have been developed:
• the use containing glass for hardening of chlorine-containing wastes with the cold crucible has been justified;
• pilot samples of main RW vitrification equipment have been created;
• using U-Pu-Am-containing solutions, the ability of transferring them into low-active RW (combination of deposition and membranous filtration) has been demonstrated.

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