

Reprocessing of spent mixed nitride U-Pu fuel from BREST-OD-300 reactor

Shadrin A. Yu., Dvoeglazov K.N., Ivanov V.B.

Bochvar Institute (VNIINM)

123060, 5a, Rogova str., Moscow, Russia, shau@proryv2020.ru

Abstract. BREST-OD-300 is pilot demonstration lead-cooled fast reactor fuelled with mixed nitride uranium-plutonium fuel (MNIT). Nuclear fuel cycle with BREST reactors concept implies that the fuel has an burn-up about 10 % h.a. “Equilibrium” isotopic composition of fissile materials (FM) fuel is used in the nuclear fuel cycle and the duration of the external fuel cycle does not exceed one year. Combined (pyro+hydro) technology (PH-process) is proposed for reprocessing of MNIT BREST SNF. PH-process consists of a combination of pyrochemical, including pyroelectrochemical, head operations and hydrometallurgical operations for refining of end product (U-Pu-Np-Am) and waste treatment. Development of PH-process has been run since 2011 by RIAR, Bochvar Institute, and Khlopin Radium Institute. In 2014 manufacturing of experimental setups to test engineering solutions for equipment for pyroelectrochemical operations was started and installation for study of innovative systems for hydrometallurgical operations was completed. In 2015 engineering of reprocessing MNIT SNF and waste treatment unit was started. Reprocessing unit will be located at the same site with the pilot demonstration power complex with BREST-OD-300 reactor on the territory of SCC (Seversk).

INTRODUCTION

BREST-OD-300 is pilot demonstration lead-cooled fast reactor (FR) fuelled with mixed nitride uranium-plutonium fuel (MNIT). Nuclear fuel cycle with BREST reactors concept implies that the fuel has an burn-up about 10 % h.a.. “Equilibrium” isotopic composition of fissile materials (FM) fuel is used in the nuclear fuel cycle and the duration of the external fuel cycle does not exceed one year. It means that within one year spent nuclear fuel (SNF) should be reprocessed and fresh MNIT-fuel should be fabricated from the products of the reprocessing. At the present time a carbothermic synthesis technology is chosen as a basic process for the fabrication of mixed uranium-plutonium powders and pellet technology – for fuel fabrication. Thus manufacture on reprocessing of MNIT SNF from BREST reactor should provide reprocessing of fuel with cooling time not exceeding one year, FM content of 10-15%, burnup about 10% h.a. and obtain a mixture of actinides with coefficients of purification about 1000000. In our opinion PH-process (combined (pyro+hydro) technology) of reprocessing SNF can meet all these requirements. PH-process consists of a combination of pyrochemical, including pyroelectrochemical, head operations and hydrometallurgical operations for refining of end product (U-Pu-Np-Am) and waste treatment. Development of PH-process has been run since 2011 by RIAR, Bochvar Institute, and Khlopin Radium Institute.

COMBINED (PYRO + HYDRO) REPROCESSING OF MNIT SNF (PH-PROCESS)

The proposed combined pyro + hydro flowsheet of SNF FR reprocessing, which had got the name PH-process [1,2] is based on the use of non-aqueous head end operations, assigned achieve the purification of fissile materials from fission products with a purification factor 100, followed by a row of aqueous processes to get the starting material for new fuel fabrication (Figure 1).

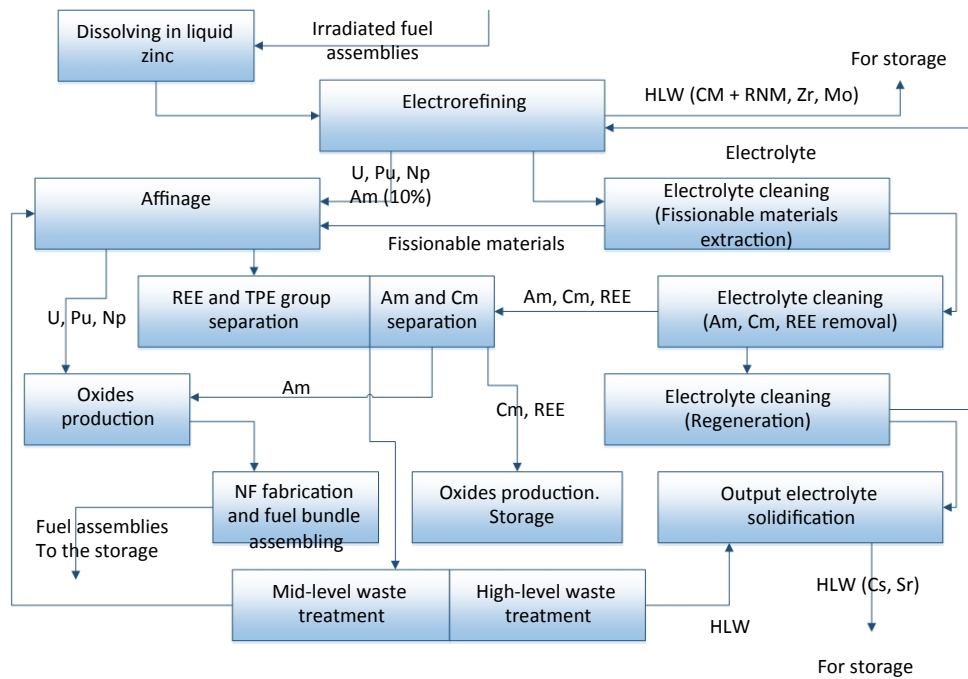


Figure 1. PH-process principal flowsheet

The pyrochemical head end of PH-process comprises the following operations: fuel decladding by liquid zinc; preliminary MOX reduction to metal state with lithium vapors in $\text{Li}_2\text{O} - \text{LiCl}$ melt; electrorefining of any dense (including MNIT, metal or metallized MOX) fuel with liquid cadmium electrodes; local gas purification system for pyrochemical head end for trapping Cs, Sb, Te, Se, radioactive noble gases and ^3H); vacuum distillation of cadmium metal and salt electrolyte; oxide precipitation of U, Pu, Am, Cm and REE oxides from salt electrolyte; alkaline and alkaline earth selective crystallization from electrolyte followed by the vitrification of the product and return of the purified salt to the process.

The aqueous part of PH-reprocessing of SNF FR includes the following operations: dissolution of all products containing uranium, plutonium, neptunium, americium and curium in nitric acid; solutions clarification; separation of fission products from U-Pu-Np using extraction – crystallization scheme; extraction recovery of minor actinides; Am-Cm separation; evaporation of high and medium level liquid wastes; preparation of U, Pu, Np and Am oxides; preparation of curium oxides for long-term storage; medium level waste management; high level waste solidification.

DEVELOPMENT OF SOME OPERATION OF PH-PROCESS

First stage of hydrometallurgy part of PH-process is dissolution. A metal ingot consists of U - 84,5%; Pu – 15%; Np - 0,5% was prepared for dissolution test. This ingot with mass 66,3 g was separated on three parts (Figure 2). Dissolution was tested under following conditions:

- 8 M HNO_3 , 4 hours and concentration of actinides in final solution – 450 g/l, $T_{\text{max}} = 132\text{ }^\circ\text{C}$;
- 10 M HNO_3 , 6 hours and concentration of actinides in final solution – 400 g/l; $T_{\text{max}} = 105\text{ }^\circ\text{C}$

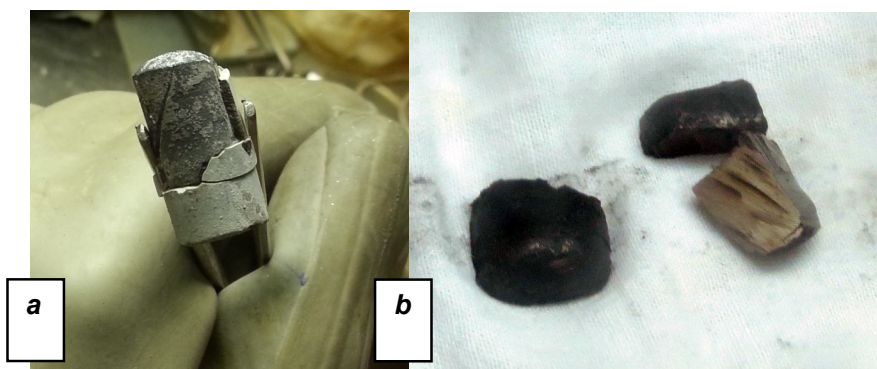


Figure 2 – Initial (a) and separated (b) U-Pu-Np ingot

Weight of insoluble residue after dissolution under first and second condition set were 16,5 and 1,5 % from initial metal weight, respectively. The residues contain mixed 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.

The extraction and crystallization affnige is a main operation of aqueous part of pH-process. This technology is developed jointly by Bochvar Institute and Siberian Chemical combine. The crystallization experiments were performed the solutions obtained by purification of U and Pu using trybutylphosphate (TBP) solutions extraction (first serial of tests) or by mixture of $\text{UO}_2(\text{NO}_3)_2$ with Pu purified by sorption with anion exchange resin (RH-1) (second serial of tests). Before the starts of crystallization study Pu in all initial solutions was oxidized to Pu (VI). Composition of initial solutions for first serial of tests are given in Table 1.

Table 1 – Composition of initial solutions (firs serial of tests)

Test	[Pu], g/l	Contain of Pu(VI), %	[U], g/l	[HNO ₃], M	T, °C
1	143	69,8	363,4	1,7	0
2	130	44,0	330,3	1,55	- 17
3	95,3	63,1	242,3	6,5	- 17
4	130	69,8	330,4	1,64	- 17

All tests were performed using 5 ml glass tubes. The closed tubes were kept under needed temperature with periodical shaking for 1 hour. The mother solutions were sampled from any tubes after crystallization. The co-crystallization coefficients were calculated using eq. (1). The results are given in table 2. It should be noted that increase of Pu co-crystallization coefficient was observed for high content (44 %) of Pu(IV). The explanation of this fact needs additional study.

$$K_{\text{Me}} = \frac{G_{\text{MeKr}}/G_{\text{MeSum}}}{G_{\text{UKr}}/G_{\text{USum}}}, \quad (1)$$

Were G_{MeKr} and G_{MeSum} – amount of component in crystal and total amount.

Table 2 – Pu co-crystallization coefficients (first serial of tests)

Test #	Solution composition, M		T, °C	Pu co-crystallization coefficient	Initial U/Pu ratio
	HNO ₃	Pu+U			
1	1,7	2,13	0	0,65	2,87
2	1,55	1,93	- 17	1,03	2,74
3	6,5	1,42	- 17	0,68	2,67
4	1,63	1,93	- 17	0,53	2,81

Second serial of tests mixture of Pu after sorption purification and U after extraction purification were evaporated. Evaporated residue was kept under boiling temperature for 2 hours. 77,4 % of Pu were oxidized to Pu(VI). Composition of initial solutions for second serial of tests are given in Table 3. Experimental data are given in Table 4.

Table 3 – Composition of initial solutions (firs serial of tests)

Test #	[U], g/l	[Pu],g/l	[HNO ₃], M
5	356,8	202,6	5,9
6	356,8	202,6	5,9
7	317,1	180,1	7,7
8	277,5	157,6	9,5
9	396,4	225,2	7,5
10	365,9	207,8	7,5
11	339,8	193,0	7,5
12	339,8	193,0	7,5

Table 4 – Pu co-crystallization coefficients (second serial of tests)

Test #	Solution composition, M		T, °C	Pu co-crystallization coefficient	Initial U/Pu ratio
	HNO ₃	Pu+U			
5	5,9	2,35	- 5	0,86	1,62
6	5,9	2,35	- 20	0,96	1,10
7	7,7	2,09	- 20	0,74	1,47
8	9,5	1,83	- 20	0,71	1,71
9	7,5	2,61	- 5	0,76	1,57
10	7,5	2,41	- 5	0,67	1,82
11	7,5	2,24	- 5	0,73	1,58
12	7,5	2,24	- 20	0,80	1,76

The obtained data show that there is an enrichment of crystals with uranium. Pu co–crystallization coefficients are < 1 for all experiments. It should be noted that increasing of [HNO₃] from 5,9 M to 9,5 M leads to decreasing of Pu co–crystallization coefficients from 0,96 to 0,71 at – 20 °C, and decreasing of temperature from -5 to -20 °C leads to increasing of Pu co–crystallization coefficient.

The next important operation of PH-process is recovery and separation of Am and Cm. This operation is need for transmutation of MA. The extraction method of transplutonium (TPE) and rare earth elements (REE) intragroup separation based on well known CMPO (carbamoymethilenephosphine oxide) extarctant and novel diluent formale-H2 (octafluoropentane, [H(CF₂)₄CH₂OCH₂OCH₂(CF₂)₄H]) was tested for PH-process [3]. The test flowsheet is given on Figure 3. Dynamic tests of this flowsheet using simulated solution (Table 5) and real raffinate of PUREX process of VVER-1000 SNF with burnup 60 GVt*day/t show the high efficiency of this method for TPE and REE intragroup separation. Thus novel extraction mixture (0,2 M CMPO in mixture 30 % vol. TBP – 70 % vol. formale-H2) effectively recovers Am and other actinides.

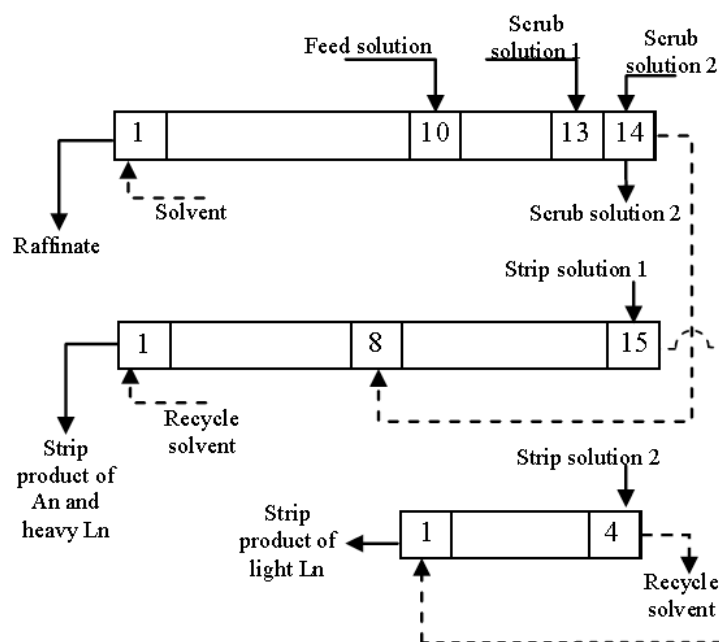


Figure 3 – Principal flowsheet of intragroup REE and TPE separation by extraction mixture - 0,2 M CMPO in mixture 30 % vol. TBP – 70 % vol. formale-H2 (from [3])

Table 5 – Distribution of components during intragroup REE and TPE separation by extraction mixture - 0,2M CMPO in mixture 30 % vol. TBP – 70 % vol. formale-H2 from simulated solution (from [3])

Element	Distribution of elements, % from initial		
	Raffinate	Am and heavy REE strip solution	Light REE strip solution
Ce	0,04	0,6	100
Eu	0,04	95	11
Fe	0,01	1	3
La	0,005	0,01	100
Nd	0,3	1	100
Pm	0,3	1	100
Sm	0,2	90	10
U	0,01	0,8	100
Am	0,01	98	4

A part from the technology of actinides mixed oxides preparation was studied. Traditional technology actinides mixed oxides preparation is precipitation from ammonia solution and calcination of precipitate at $\sim 800^\circ\text{C}$ in Ar-H₂ atmosphere. It is a multistage technology with rather big volumes of mother solution. The actinides mixed oxides preparation from nitric acid solution in the presence of hydrazine hydrate described in [4,5,6] were proposed for PH-process. It was shown that thermal treatment at $\sim 90^\circ\text{C}$ solutions of U, Np and Pu ($^\circ\text{C}$) in the presence of hydrazine hydrate leads to form of hydrated oxides of actinides, which performs to crystalline dioxides at 300°C . The thermalize of hydrated oxides of actinides U, Np и Pu under same conditions allows to obtain firstly (in solution) hydrated U,Np,Pu)O₂·nH₂O, which performs under calcination (air, 800°C) in crystal. This method allows to obtained the solid solutions of actinides with uncertain composition. It was shown that prepared by this technique U-Np-Pu oxide is X-ray amorphous compound [4,5]. X-ray analysis identified or (U,Pu,Np)O₂ phase or homogenous mixture of three dioxides in calcinated under 800°C oxides mixture (Figure 4).

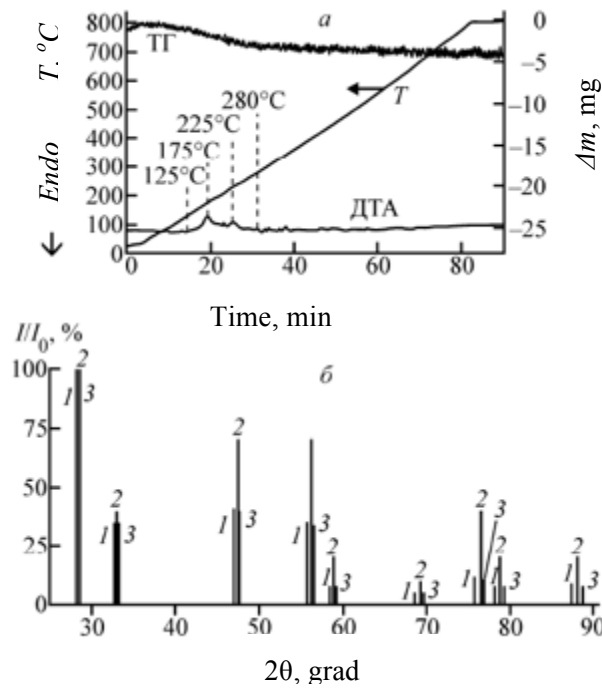


Figure 4 – Thermal analysis of hydrated oxides of U, Pu and Np (a) and X-ray analysis of this mixture after calcination (air, 800 °C) (from [5])

ELABORATOION OF PILOT SCALE FACILITIES FOR THE PH REPROCESSING TEST

At the present time two Russian enterprises including for RIAR and “SOSNY” are engaged to the development of the inert hot cell with simultaneous mounting of the principal apparatus of pyro-branch for the pilot scale test of PH reprocessing. (Figure. 5).

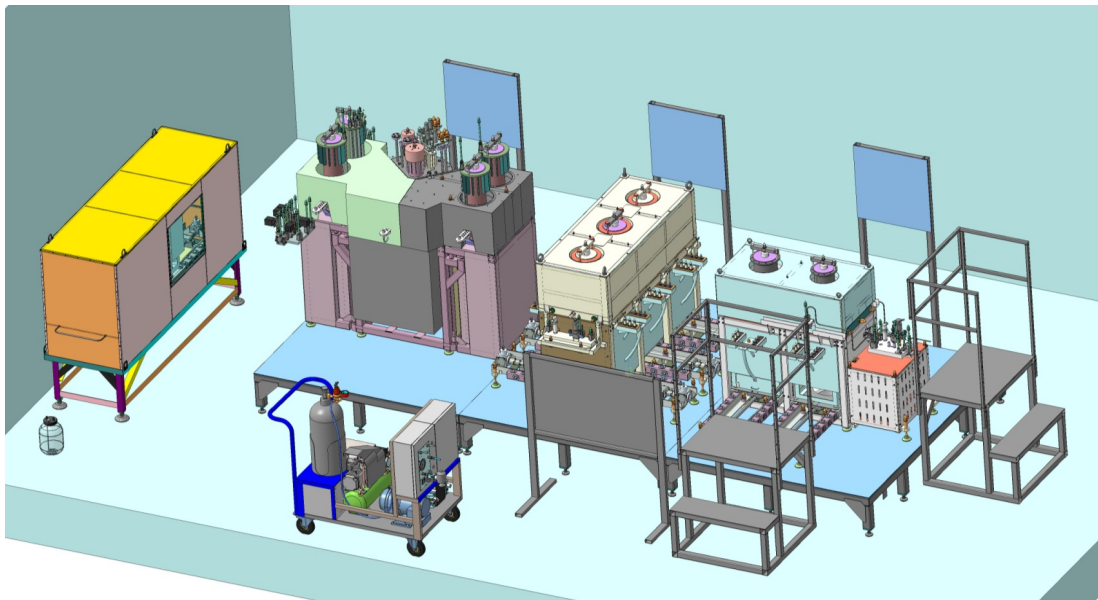


Figure 5. Placement of the PH reprocessing pyrochemical facility in the inert hot cell.

Bochvar Institute finished the mounting of a facility for pilot scale gas purification system, steps of dissolution, partitioning and actinide oxide preparation (Figure 6).



Figure 6. Dissolution, extraction, gas purification and actinide oxides preparation facilities

At the same time, Bochvar Institute in co-operation with Siberian Chemical Combine is mounting scale-up facility of extraction-crystallizing to evaluate the technology of extraction and extraction-crystallizing refining (Figure 7a). Joint R&D work of Bochvar Institute, Khlopin Radium Institute and SverdNIChimMash resulted in the finishing of the equipment scale-up and in the start of the experiments testing the processes of nitric acid solutions evaporation and ammonium nitrate (and/or) organics thermal decomposition (Figure 7b).

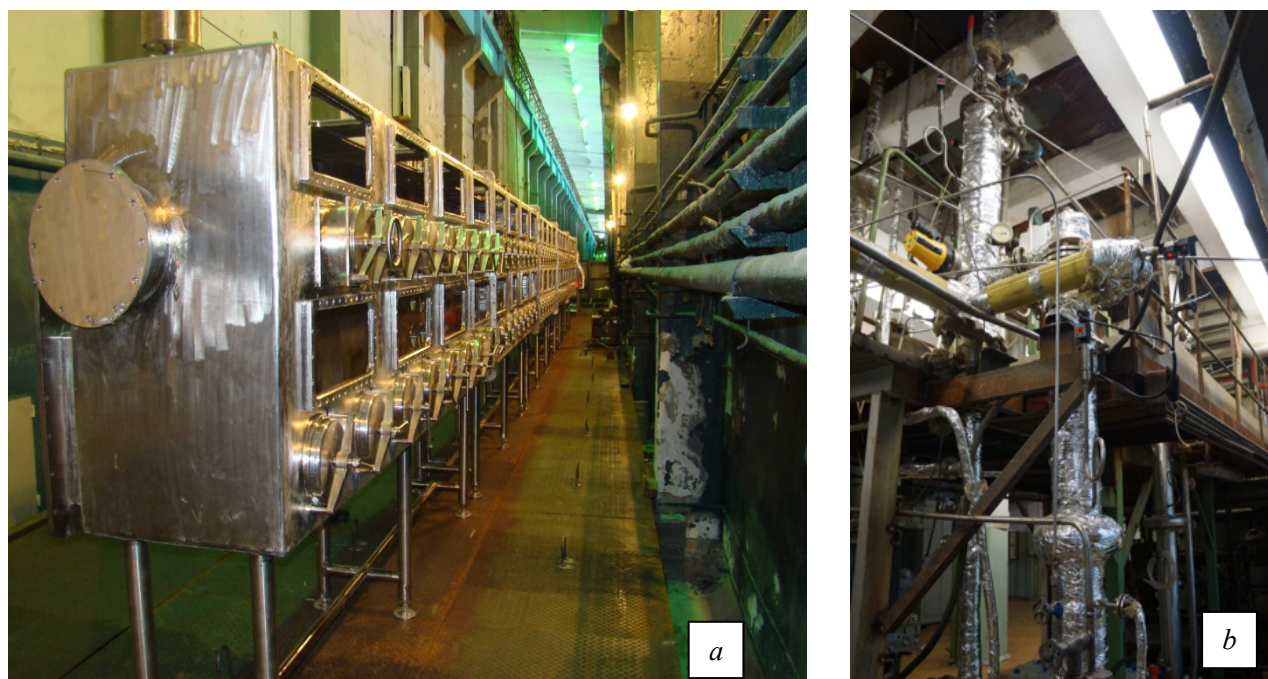


Figure 7 6. Extraction – crystallization (a) and evaporation – thermal decomposition facilities (b) (Siberian Chemical Combine).

The R&D with the mentioned facilities directed to check a number of operations involved to PH process, including gas purification system [7,8,9], dissolution, partitioning [3,10] and actinide oxides preparation [4,5,6] is planned to be carried out in 2015-2017.

MODELLING OF SNF REPROCESSING

A pilot software “Balance model” has been created earlier [11]. It allows to execute express updating of calculation model and to balance settlement all over the PH-process flowsheet of SNF reprocessing, fuel refabrication and waste management. A block library, containing the modules for the material balance calculation for separate processes, involved to the reprocessing, written in C#, was created as a part of developed software. Work on integration “Balance models” in a software system on the basis of platform ATEK that perform a number of different tasks on modeling of chemical and physical processes and operations was started.

The work on integration of “Balance models” into “WizArt” software system simultaneously with carrying out of balance models improvement was completed. The inclusion of “Balance model” in the software system structure allowed to implement the visualization of calculation model plotting in design mode, to simplify the task of input of compositions of incoming products, of input of operation parameters, of output of calculation data using the means of user interface. In addition, the studies directed to the implementation of functional on dynamic balance modeling of the flowsheet taking into account productivity of equipment, of transport lines and storage containers capacity are carried out. This development will allow to provide the calculations of the equipment functioning cyclograms, using the blocks of integrated balance model and calculation scheme variant.

CONCLUSION

Combine (pyro + hydro) technology for MNIT BREST SNF reprocessing (PH-process) is under development. PH-process would allow: reprocessing of FR SNF with high burn up and low cooling time; decrease the volume and time of SNF storage; to reprocess any type of SNF; to prepare the final uranium – neptunium – plutonium product running the requirements for fabrication of the final pelleted mixed MNIT fuel.

By now following basic technological operations have been tested in laboratory conditions on real products: steel cladding removal by dissolution in molten zinc; pyroelectrochemical recovery of uranium, plutonium, and neptunium; extraction refining of uranium, plutonium, and neptunium; separation of rare earth elements and transplutonium elements.

In 2014 manufacturing of experimental setups to test engineering solutions for equipment for pyroelectrochemical operations was started and installation for inspection innovative systems for hydrometallurgical operations was completed. In 2015 engineering of reprocessing MNIT SNF and waste treatment unit was started. Reprocessing unit will be located at the same site with the pilot demonstration power complex with BREST-OD-300 reactor on the territory of SCC (Seversk).

ACKNOWLEDGEMENTS

The present work was financially supported by The State Atomic Energy Corporation ROSATOM of Russian Federation.

LITERATURE

- [1] V. VOLK, V. “Combined (Pyro+Hydro) Technology of FNR SNF Reprocessing”, Proc. Int. Conf. Global 2011, Makuhari, Japan, 386756, (2011),
- [2] V. VOLK, “Combined (Pyro+Hydro) technology for FR SNF reprocessing”, *Proc. Int. confFR13*, Paris, 4-7 March 2013, CN-199-339
- [3] V. BABAIN, “Dynamic tests for actinide/lanthanide separation by CMPO solvent in fluorinated diluents”, *Proc. Int. conf. Global 2013*, September 29 – October 3, 2013, Salt Lake City, Utah, USA, CD, #8201
- [4] Yu. KULYAKO “Preparation of uranium oxides in nitric acid solutions by the reaction of uranyl nitrate and hydrazine hydrate”, *Radiochemistry*, 55, 6, 481 (2013)
- [5] B. MYASOEDOV “Preparation of U, Pu and Np dioxides in nitric solutions in the presence of hydrazine nitrate”, *Radiochemistry*, 55, 6, 487 (2013)
- [6] Y. KULYAKO, “UO₂, NpO₂ and PuO₂ preparation in aqueous nitrate solutions in the presence of hydrazine hydrate”, *Journal of Radioanalytical and Nuclear Chemistry* Vol. 299, № 3, p. 1293 (2013)
- [7] O. USTINOV, “Study of dissolubility carbon dioxide (CO₂) in nitric acid and nitric acid solutions with view to estimate the distribution of product division carbon-14 between the gas phase and the regeneration solution”, *Proc. 17-th Radiochemical Conference (RadChem)*, 11-17 May, 2014, Czech Republic. <http://www.radchem.cz/babstr/Babstr14.pdf> C. 391 (Id:98)
- [8] S. KULYUHIN, “A study of nitrogen oxides released into the gas phase during uranium nitride dissolution in nitric acid”, *Journal of Radioanalytical and Nuclear Chemistry* 1, 415 (2014).
- [9] Y. Voskresenskaya “RuO₄ Capture on Solid Adsorbents”, *Atomnaya Energiya*, 117, 1, 42, (2014).
- [10] V. BABAIN, “Actinide-lanthanide separation with solvents on the base of amides of heterocyclic diacids”, *Proc. Int. conf. Global 2013*, Salt Lake City, Utah, USA, September 29 – October 3, 7783.
- [11] S. TRETYAKOVA, “Spent nuclear fuel reprocessing and nuclear fuel fabrication technological process modeling // *Proc. Int. conf. Global 2013* Salt Lake City, Utah, USA, September 29 – October 3, 2013, #7513 .