

New radiochemical technologies of spent nuclear fuel (SNF) reprocessing

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Abstract. The suggested new approach to reprocessing of SNF power reactors includes the following consecutively operations:

- alkaline voloxidation of fuel (oxidation at presence of NaOH by air or oxygen at 350-400 °C and localization of tritium in small volume of condensate);
- leaching of a oxide-salt mixture (removal of sediment formation compounds, molybdenum, first of all, primary partitioning of radionuclides);
- ¹³⁴Cs, ⁹⁹Tc and ¹²⁹I nuclides removing from alkaline solution;
- voloxidated fuel nitric acid dissolution ;
- solution evaporation and crystallization of hexahidrate of uranyl nitrate (HNU);
- uranium and plutonium extraction with simultaneous separation of transplutonium elements/rare earth elements (TPE/REE) fraction;
- recycling fractions (U, U+Pu, Pu) conditioning for transfer on fuel production;
- recycling fractions (Tc, I, Np, Am, Cm) conditioning for transmutation targets production;
- - Cs + Sr fraction conditioning for monitored stowage ;
- REE and fission products (FP) fractions conditioning for disposal.

According to the previously carried out estimations, such technology realization will reduce evaporating solutions volumes approximately in 10 times, reagents intake -in 2 times and basic process equipment dimensions - in 6 times.

1. Introduction

The earlier suggested concept [1, 2] assumes main uranium amounts separation by crystallization during SNF reprocessing. HNU crystallization has an important number of advantages before extraction methods, for example:

- High efficiency and compactness of the process;
- The absence of isomorphous impurities, that allows to achieve high uranium affintage coefficients during crystallization;
- Low melting temperature of HNU (59,60C), allowing to avoid high energy expenses during uranium recrystallization.

At first the operations of crystallization affintage were offered by the German researchers for replacement of second extractional cycle of uranium affintage on the simplified methods of HNU fusion cake crystallization [3-6].

This approach, but for conditions of thorium fuel cycle (main thorium mass separation), was used by the Russian researchers [7, 8] for head operations of reprocessing. In the considered case thorium was not a target product and was subject to storage within approximately 70 years before daughter radioisotope ^{232}Th decay, and did not require high FP affinity coefficients.

Later this approach was transferred on uranium - plutonium fuel cycle. Alkaline fuel voloxidation introduction allows to remove molybdenum, leaving sediments such as spinel during crystallization, which do not allow to achieve the necessary uranium regenerate refinement coefficients. This circumstance is not taken into account by the Japanese researchers [9-11], which actively study the similar approaches to process of SNF reprocessing.

The main idea of the Russian concept of SNF reprocessing is shown in fig. 1. This approach has received name REPA-process (REprocessing-PARTitioning), i.e. reprocessing with partitioning elements.

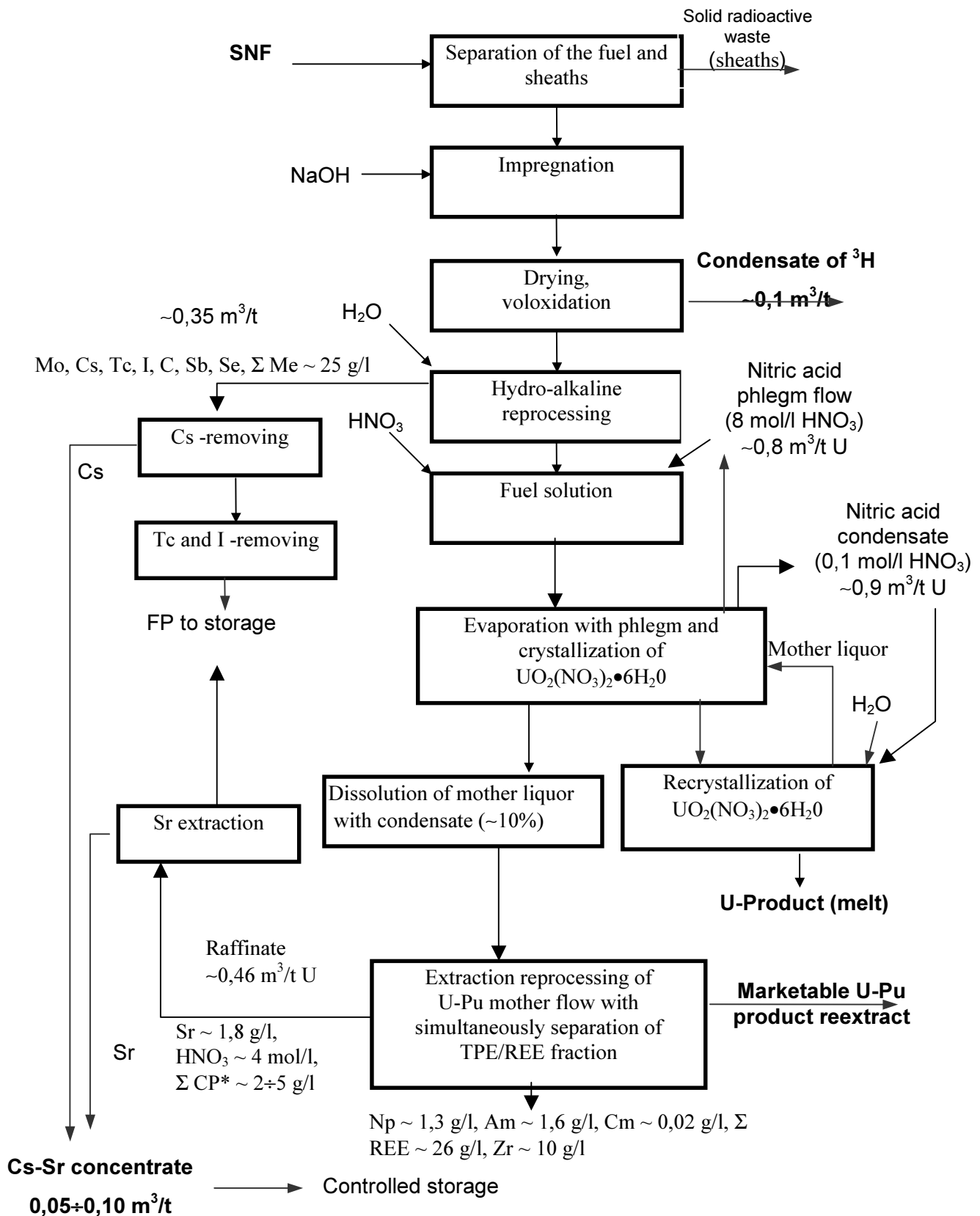


FIG. 1. The principle SNF reprocessing technology flowsheet .

2. Results and discussion

Parameters, shown at the scheme (fig. 1), require detailed experimental check and first of all on the samples of real fuel.

Two laboratory units for fuel alkaline voloxidation process investigation were created: one for this process investigation on simulators and second, placed in the hot chambers of Research-and-Production Association "Radium Institute", for testing of voloxidation mode of operation on real spent fuel samples. Both units had the approximately identical scheme and included the furnace with ohmic heating and transport container, the system of traps for inputting gases purification and system of traps for off-gases condensation and catching. The second unit was equipped with analytical devices allowing to carry out the control of Kr-85 and I-129 separation from fuel composition in real time in dynamics.

The main operations parameters were studied on simulators: there were the temperature and duration of process, expense of alkali, which selected at the estimate of only fuel decay products linkage and was about from 5 up to 25 mg of NaOH on 1g of fuel. The initial experiments have shown, that fuel sediment alkaline washing additional introduction is necessary for effective separation of anion-generative components.

It has allowed to remove molybdenum, antimony and carbon practically completely from the fuel mixture without any REE/TPE. The main part of Cs leaves at washing, while Sr in all cases remains in sediment. The experiments on real fuel have shown, that for realization of these processes the more large temperatures (about 600-700⁰C) are required, than for not irradiated uranium dioxide.

The second base element of REPA-process is the uranium purification by HNU crystallization.

The crystallization diagrams in systems $H_2O-UO_2(NO_3)_2-HNO_3-Me(NO_3)_n$, where Me is typical representatives of impurity elements groups in SNF, including receiving of missing experimental data, were carefully investigated for substantiation of this operation.

The model unit, which is shown in a fig. 2 was developed and produced as the prototype of continuous HNU melt crystallization apparatus design.

Initial HNU fusion cake is feeded from pressure vessel (1) through the regulation valve (2) to vertical hydro-cooling glass tube. The crystal phase, formed at cooling, mixed up by stirring rod (4) and fell on device ground part under gravitational forces action. From the ground part the crystals lifted by screw (7) to the top washing part of the device, to which washing solution is feeded as cross-current flow in relation to crystals.

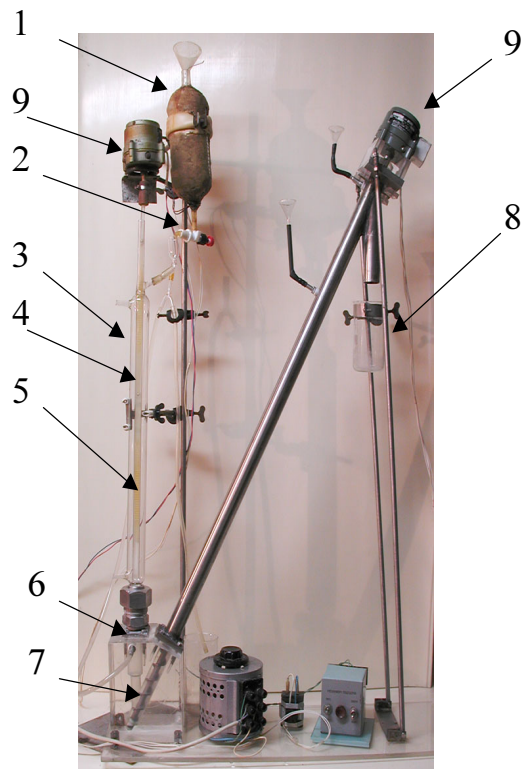
Spent washing solution was removed from its contact zone with mother solution through hydroseal. The washing solution and HNU melt inputs points provided hydrostatic replacement of mother solution from crystals washing zone.

Zr was chosen as impurity element label during the unit tests, as Pu imitator, one of the most significant by FD quantity and most hard-to-separate impurity on the data [5, 6].

Achieved for unitary cycle (crystallization - washing) purification coefficient was equal 10^3 (in first extraction cycle average purification coefficient was $10^5 - 10^6$). In crystal phase the U/Zr ratio logarithm is equal 4,9.

During the crystallization in static conditions, realization of repeating cycles of crystallization-washing, such ratio of U and Zr is reached only after two crystallization and two washings (Zr is not found out in uranium product after the third cycle).

Thus, there is experimentally shown, that crystallization affinage of uranium can be both successfully realized, and developed its effective apparatus design. The efficiency of crystallization process confirms the fact, that the unit with the diameter of crystallization zone equal to 7 mm, has productivity 2 t uranium / years.



- 1 - heated up vessel for melt feeding; 2 – regulation valve;
 3 - cooling jacket; 4 - mixer; 5 – crystallization zone; 6 - pocket;
 7 - screw; 8 - crystal phase reception vessel ; 9 - electric motors.

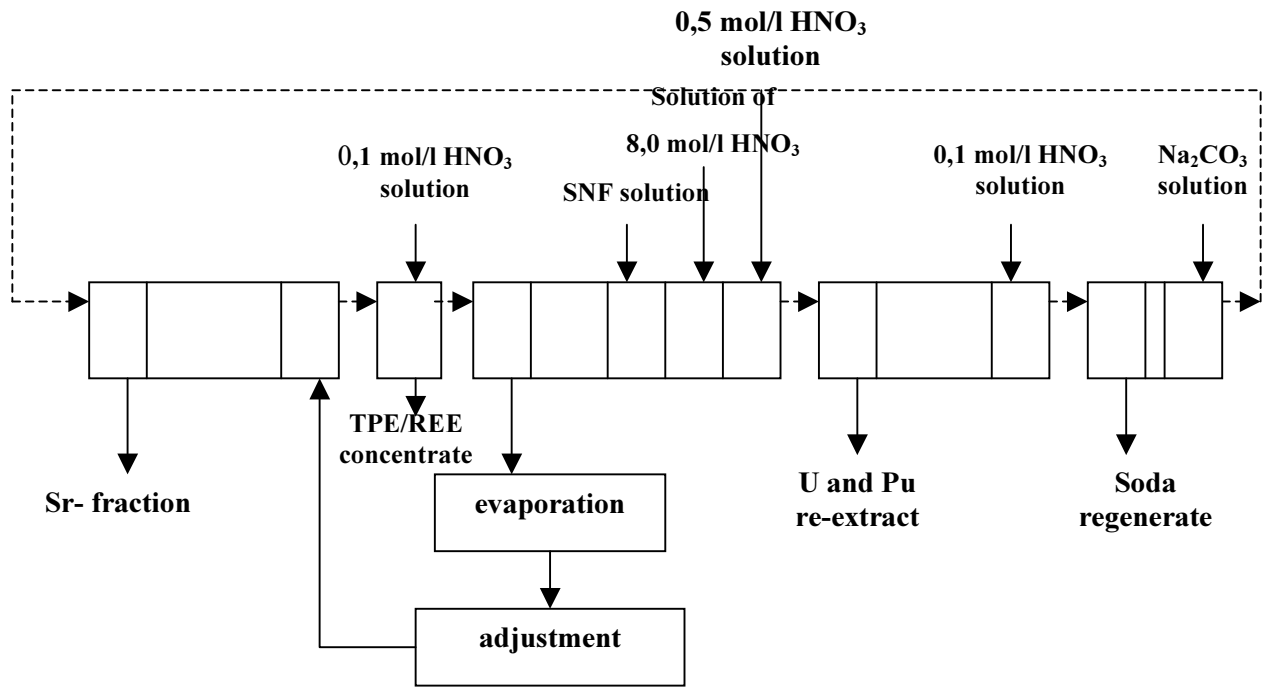
FIG. 2. HNU melt continuous crystallization investigation unit general view.

For an ecologically acceptable nuclear fuel cycle the SNF reprocessing should provide formation as minimum of two additional fractions: TPE/REE (TPE are long-lived radionuclide and require or deep controllable isolation, or transmutation on condition similar technologies development in the future) and Cs/Sr, which are middle-lived radionuclide, but determine mainly thermal flux from SNF FP.

Therefore, the working over scheme third essential element is the innovated uranium and plutonium affinage extraction cycle with simultaneous separation of TPE/REE fraction with uniform extractant (30 % TBP).

The principle scheme of such cycle is shown in a fig. 3. It includes extraction, two-zone extract washing from FP, joint re-extraction of uranium and plutonium (in order to maintenance technological support of non-proliferation mode), evaporation of intermediate raffinate, obtained solution adjustment and extraction of TPE/REE fraction from evaporated solution.

The such decision precondition is the circumstance, that trivalent f-elements (REE and minor-actinide (MA)) are moderate extracted by TBP from solutions containing significant amounts of salting-out agent (nitrate-ion) at the minimal contents of a nitric acid. Hence, if "to cut" head extraction block, to place evaporation operation "cut", to adjust the nitric acid contents in cube solution and to return the adjusted flow in the head block, than extraction zone and re-extraction zone of f-elements are realized in the block. Final block raffinate is the Cs - Sr fraction, organic flow selection - fraction REE-MA (after uranium and plutonium removal).



Dotted arrows - 30 % TBP organic solution in n-paraffin,

Continuous arrows - water solutions.

FIG. 3. The innovated extraction cycle principle scheme.

As show by preliminary calculations, practically all Zr amounts , present in SNF, will get in TPE/REE. The main part of other FP will be in Sr-concentrate.

The separated fractions further reprocessing is technological and technical-economic investigations matter taking into account possible technologies, which will be developed in a near future. Tc, I, Cs removing from fuel voloxidation alkaline solutions is necessary at transmutation technologies development . For first two nuclides, apparently, sorbtion methods are preferable for Cs allocation - precipitation as tetraphenylborate. The experiments have shown, that this operation allows to remove 99,9 % of Cs from an alkaline solution with coefficient of clearing not less than 10^3 .

For immobilization of other FP remaining in an alkaline solution and Cs - Sr concentrate, it is expedient to use borosilicate glasses admitting about 10 % FP inclusion in glass mass. Using of mineral-like compounds is preferable for others nuclides, including "Synroc" technology [12]. If it is necessary, the separation of TPE/REE fraction could be carried out with using of developing membrane-extraction processes [13], if it will be economically benefit, and REE fraction with impurity of Zr and others FP immobilized in mineral-like compositions. Using of pyro-chemical methods for TPE/REE fraction conditioning [14, 15] is possible, taking into account, that all subsequent operations (vitrification) are based on high-temperature processes.

However conditioning of fractions requires serious technical-economic investigations.

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