The variants of Zirconium, Technetium and Neptunium Localization in the First Cycle of NPP High Burn-up Spent Fuel Reprocessing

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Introduction

NPP spent nuclear fuel (SNF) reprocessing should be environmentally and commercially admissible and lead to recycling of regenerated material as well as to minimization of the radioactive waste final volume. The goals of the reprocessing, originally developed for Pu and U recovery for weapons material production now changed considerably on passing to NPP SNF, as the fuel fraction to be utilized (U and Pu) dropped to 95-97%, while the amount of non-utilized elements increased from 0.05% to 3-5% of the total SNF mass **(Table 1)**. Only < 5% of these elements are hazardous long-lived radio-nuclides, namely, α-nuclides (TPE, Np) and Tc, of which Np, Tc and Zr are notably extractable by diluted TBP causing difficulties in the 1st cycle of the PUREX process.

Accumulation of ^{232}U generating the daughter radioactive series of powerful γ-emitters limits the time of regenerated U unshielded handling to 30 days, making pointless the deep U decontamination from FP to higher extent than the level of transportation to enrichment plant where it is subjected to required in-line purification. So, reprocessing flowsheet should be shrunk to a single more complicated extraction cycle in order to reduce the number and volume of process radwaste.

The classic structure of the PUREX reprocessing plant (**Fig. 1)** includes not only extraction cycles, but also a great number of bulky divisions for intermediate treatment of product or waste streams with HNO_3 and H_2O regeneration instead of their dropping to environment.

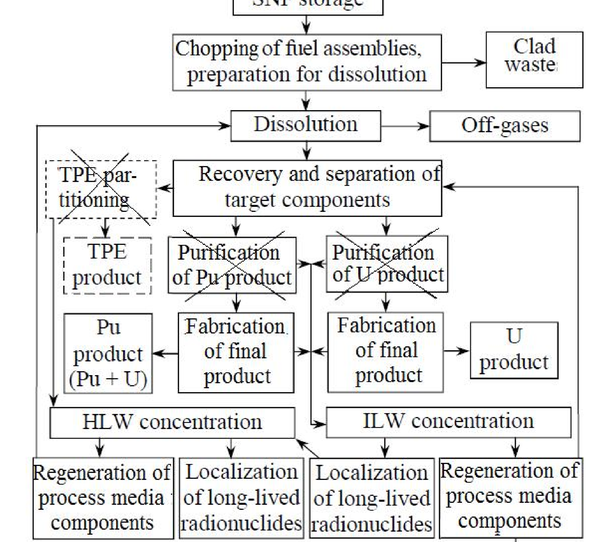

Fig. 1. Sketch of the classical Purex process structure . The units eliminated in the flowsheet of the PDC are crossed out.

Table 1. The influence of SNF burn-up on the content of actinides and multivalent fission products (5 year storage)

Element (isotope)	Element content at burn-up (GW*days/t HM)					
	Gramms per 1 tonne HM			Moles per 4,2 kmol (1 t HM)		
	0,5	50	70	0,5	50	70
^{232}U	-	0,0012	*0,0065*	-	-	-
^{235}U	*6550*	8800	*2640*	*27,5*	*37,5*	*11,2*
^{236}U	*270*	6170	*7530*	*1,15*	*26,1*	*31,9*
Np	0,5	720	*850*	0,002	3,0	3,6
Pu	500	12000	*13210*	2,1	50	54,5
Am	0,5	630	*810*	0,002	2,6	3,3
Sr	18	1 530	*2640*	0,20	17	30
Zr	66	5 380	*7200*	0,71	60	79
Mo	53	5035	*7100*	0,56	52	74
Tc	16	1 140	*1420*	0,16	11,5	14,3
I	5	330	*450*	0,035	2,6	3,5
Cs	68	3725	*5150*	0,50	28	39
Ba	31	2 505	*3490*	0,22	18	25
RE + Y	220	~15 000	*~21000*	1,3	103	145
SFP	*550*	*~50705*	*~71500*	*4,6*	*430*	*606*

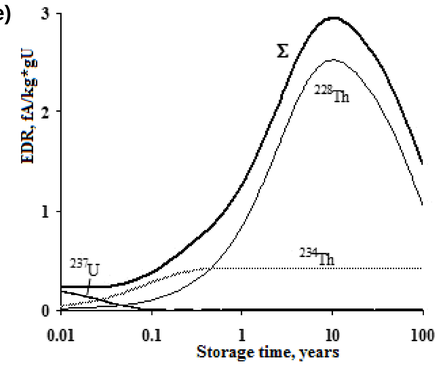

Fig. 2. EDR of U product during storage (NPP SNF burn-up 50 GW*d/t, 5 years cooling)

Table 2. Tested variants of 1st cycle flowsheet

Product	Flowsheet variant									
	RT-1 (PA "Mayak")			Test	RT-2	PDC at MCC		Superpurex		REMIX
	1	2	3			1	2	№ 1	№ 2	
	№ 1	2	3	4	5	6	7	8	9	10
Numb. of units	4	4	5	5	7	6	6	6	6	6
Raffinate	Zr	Zr, Tc	Zr	Np, Zr / Mo	-	-	-	-	-	-
Strip 1	-	-	-	Tc	Zr	Zr	Zr	Zr, Tc	Zr, Tc	Zr, Np
Strip 2	Pu, Np, Tc	Pu, Np	Pu, Tc	Pu	Pu	Pu, Np, Tc	Pu, Np	Pu (U)	Np	Pu (U)
Strip 3	-	-	Np	-	Np, Tc	Barrier	Tc	Np	Pu+U	Tc
U backwash	U	U	U	U	U	U	U	U	U(Pu)	U

Table 3. Product composition and purification factors for the flowsheet SuperPurex-1 (№8).
SNF burn-up 67 GW*d/t, 5 years cooling

Product	Product composition								Purification/decontamination factors from					
	HNO_3, mol/L	U, g/L	Pu, mg/L	Np, mg/L	Tc, mg/L	Zr, mg/L	Mo, mg/	b,g MBq/L	U	Pu	Np	Zr	Tc	b,g
Feed	1,8	424	5700	400	1560			$3,8*10^6$	-	-	-	-	-	-
Raffinate	0,8	<0,01	3	1	42	270	370	$3,7*10^6$	$>10^4$	$>10^3$	>100	~40	>30	-
Zr, Tc strip	4,5	<0,01	5	3	540	<10	220	9200	$>10^4$	$>10^3$	>100	106%	97%	800
Pu strip	1,3	<0,1	6100	<5	-	90	54	100	$>10^4$	99%	~100	$>10^3$	>200	10^3
Np strip	0,75	<0,01	10	490	-	<2	-	10	$>10^4$	$>10^3$	93%	-	-	10^4
U backwash	0,2	60	<0,1	0,1	-	<2	-	10 (^{237}U) 0.03	99%	$>10^4$	500	-	-	10^5(^{237}U) $3*10^6$

Table 4. Product composition for the flowsheet REMIX (№10)
Simulant feed solution

Product	Product composition					
	HNO_3, mol/L	U, g/L	Pu, mg/L	Np, mg/L	Tc, mg/L	Zr, mg/L
Feed	2,0	510	220	200	660	1200
Raffinate	1,0	<0,01	<0,1	0,3	20	120
Zr, Np strip	1,6	<0,01	0,1	410	80	1900
Pu strip	0,6	<0,01	312	0,5	1,2	<10
Tc strip	0,8	0,12	1,1	<0,1	630	-
U backwash	0,1	70	<0,01	<0,1	<1	-

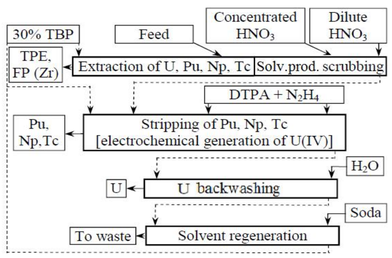

Fig. 3. Flowsheet of the 1st extraction cycle of RT-1 plant

The turn to "peaceful use of atomic energy" has lead to the change in reprocessing goals and therefore to that in flowsheets, especially in the head-end of the process, limited by behavior of precipitate-forming and multivalent elements, such as Zr, Tc and Np. The problem of their localization within the framework of the 1st extraction cycle of the Purex process could be solved by several ways. **Table 2** shows in which process product the problem element are going out from the cycle in commercial and/or tested project flowsheets. It can be either product (U, Pu) streams or selective strips. For example, Tc could be dropped to the raffinate in RT-1 process **(Fig. 3)**or to Zr&Tc strip in SuperPurex-1 (6-unit process, №8). The large volume of this strip made the flowsheet as a whole unsuitable for PDC project. The great expectations are connected with REMIX flowsheet (№10) since it makes possible to obtain U and Pu products free of Np and Tc as well as from each other providing the 2nd U cycle useless **(Fig. 4b)** It is the opposite approach to UP-3 flowsheet **(Fig. 4a)** where the 2nd U cycle is carried out only for purification from actinides (Pu traces and Np).

Results and discussion

Tables 3 and 4 confirm the possibility of Np localization before and after Pu stripping with the opposite Tc withdrawal. The data were obtained on KRI experimental rigs in "hot" chambers and boxes.

The last flowsheet (№10) is being implemented into PDC design for production of REMIX* fuel made of dioxides of regenerated Pu and enriched regenerated U, suitable for uploading of 100% WWER-1000 active zone. At the same time the process provides the HLW evaporation without Zr/Mo and $Ba(NO_3)_2$ precipitate formation **(Fig. 5)**. It is possible due to evaporation of Zr-containing waste strip separately from Mo-containing HLW as well as because of lower acidity of the latter. This regime is provided in turn by dissection of extraction and scrubbing zones of the head unit as well as by increase of U content in the warm feed solution.

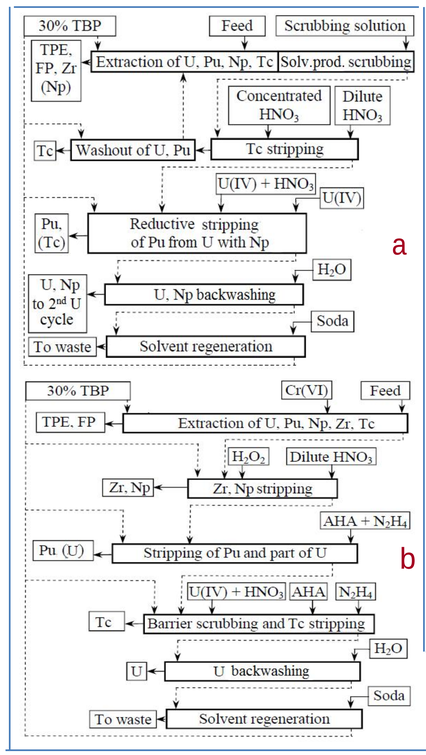

Fig. 4. Flowsheet of the 1st extraction cycle of UP-3 plant (a) and REMIX for PDC design (b)

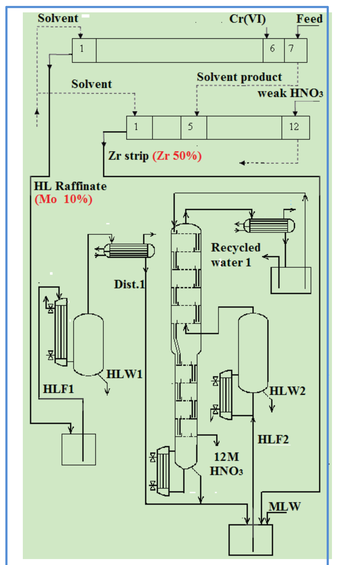

Fig. 5. The HLW management flowsheet at the PDC

It should be noted that no withdrawal of Np together with Tc, as well as Pu, Np, Zr and Tc separately to generally different products could be achieved in the frame of six-unit extraction flowsheet. Providing the precipitation-free HLW evaporation requires the hard multilevel structurization and optimization of process chain as a whole starting from the head-end process steps – carrying on traditions of the old ORNL and HW schools.

**REMIX is a fuel fabricated as a mixture of regenerated Pu and enriched regenerated U with some addition of natural enriched U, equipotential to standard PWR (BWR) fuel and suitable for uploading the full PWR (BWR) reactor zone to achieve maximal burn-up and disposal without reprocessing.*

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Patents RU:
2 249266 (2005); 2372279 (2009); 2454741 (2012); 2454740 (2012; 2454741 (2012); 2454742 (2012); 2473144(2012); 2535332 (2014); 22537013 (2012); 22561065 (2015); 2574036 (2016).