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Possibility of Various Types SNF Reprocessing at the PA Mayak exampled with AMB SNF

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Abstract

For the purpose of reprocessing of irradiated nuclear fuel from the water-cooled graphite-moderated pressure-tube reactor named AMB from decomissioned Russian "Atom Peaceful Big", modernization of the process flow-sheet of the RT-1 plant is being carried out at PA Mayak with participation of FSUE KRI and VNIINM. A particular AMB SNF feature is extremely broad range of fuel compounds with the main ones being the uranium-molybdenum metal, uranium oxide and uranium carbide compositions usually dispersed in magnesium or calcium. Wide range of fuel compositions required to amend SNF dissolution, extraction processing, evaporation of high-level radioactive wastes and vitrification of high-level radioactive wastes. The above set of laboratory research was completed with dynamic tests using samples of AMB from the water-cooled graphite-moderated pressure-tube reactor. Tests have shown the possibility of processing the entire range of AMB SNF at the radiochemical plant RT-1 plant of the PA Mayak. Thus, the ability of the RT-1 plant to process different fuel compositions, including the long-term research reactor fuel have been proved experimentally.

Keywords: SNF, uranium, molybdenum, processing, dissolving, extraction, vitrification, high-level radioactive waste

Introduction

In the Soviet Union, development of nuclear power was based on extensive use of research reactors and critical stands, which was associated with a wide range of used nuclear fuel. In addition, development of new

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types of nuclear fuel was conducted in parallel with full-scale research at the existing power units. An example is the large water-cooled graphite-moderated pressure-tube reactors (AMB) at the first stage of the Beloyarsk Nuclear Plant. The first reactor at the Beloyarsk Nuclear Plant AMB-100 was commissioned in 1964 and stopped in the 1981 after its lifetime was over. The second block with reactor AMB-200 was launched in 1967 and ceased generating electricity in 1989. Fuel assemblies (FAs) were used in reactors AMB-100 and AMB-200 with different fuel compositions, the main ones being uranium dioxide dispersed in Mg or Cu and U-Mo alloy with Mo content of 3 to 9%, dispersed in Mg, as well as uranium carbide dispersed in Ca. SNF from AMB and many types of SNF from the research reactors are classified as a deferred fuel solution, for which a long-term controlled storage outside the station is stipulated since such as spent fuel is not currently recycled. The final solution to the problem of AMB SNF handling at the Beloyarsk Nuclear Plant is its processing and subsequent localization of radioactive waste. The aim of this study was to develop and demonstrate the fundamental possibility of recycling previously un-recycled AMB SNF at the RT-1.

1. Processing of SNF from water-cooled graphite-moderated pressure-tube reactors

1.1. Dissolving of AMB SNF

Dissolution methods developed in the 60s have been tested using samples of different types of AMB SNF. Initially, the technology for processing of AMB uranium-molybdenum spent nuclear fuel involved entering of the complexing or chelating agents such as nitrate, iron, phosphoric acid, or trioxy glutaric acid to prevent introduction of sediment into unit-solvent [1,2]. It should be noted that presence of extraneous salts in the waste raffinate after extraction further complicates their treatment, so we developed a method of dissolution of AMB SNF without precipitation in the absence of complexing agents and determined the effect of temperature and pH on the dissolution of the phase stability of the obtained solutions (Figure 1).

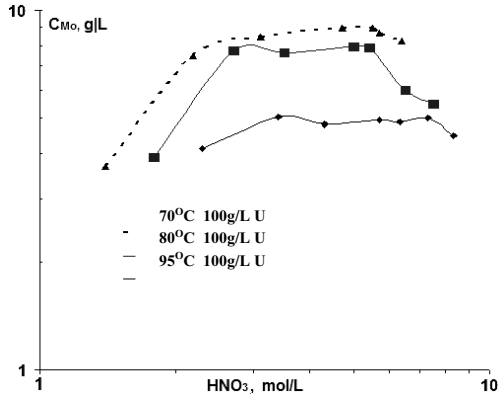

Figure 1 - Effect of temperature and concentration of nitric acid on the solubility of molybdenum in the presence of uranyl nitrate.

It is known [3] that in the absence of U solubility of Mo in the HNO_3 is of pronounced extreme character with a maximum in the range of 2.5 - 5.0 mol/L HNO_3, therefore, in the presence of U 150 g/L it is possible to get solutions containing Mo 12 g/L at the temperature of 70°C only when the residual content of HNO_3 is 2.5 – 3.5 mol/L, and at a higher temperature of 95°C solutions containing up to 60 g/L of U, and 5 g/L of Mo, and only a residual content of 3.0-5.0 mol/L HNO_3. If the specified contents of Mo and U are exceed solutions lose their aggregative stability. The resulting precipitate contains molybdic acid and uranyl molybdate. An average composition of the precipitate is formed with concentration of nitrate ions being less than 6 mol/L, which acceptably corresponds to the empirical compound $(UO_2)_2Mo_6O_{21}$, described in [4].

However, while carrying out preliminary experiments on extraction it was found that in contact to TBP solutions in hydrocarbon diluent solutions obtained at temperatures of 70 and 80^0C are unstable due to high content of Mo and with U extraction molybdic acid precipitation formed in raffinate. Secondary sedimentation caused us to lower the final concentration of Mo in the solution, limiting it to 5 g/L. In this case it was shown that the individual dissolution and extraction of uranium-molybdenum AMB SNF was possible. The use of complexing Mo additives that can increase the concentration of Mo, results in losses of plutonium in extraction.

A more detailed study of dissolution of the model and real R & D of oxide SNF containing 12% of Mg weight as a dock causing the crystallization of uranyl nitrate (Fig. 2.). For this reason, it is expedient to mix a solution of AMB SNF with solutions of SNF from the water-moderated power reactor AMB at a ratio of 1:3 to 2:3. The results of the dissolution of irradiated oxide AMB SNF are shown in Tables 1 and 2, along with other products of the extraction unit.

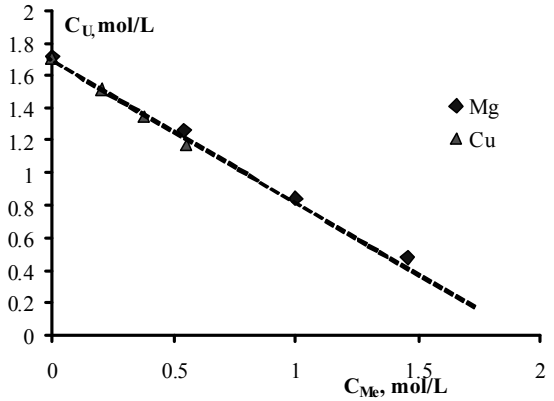

Figure 2. Solubility of uranyl nitrate in the presence of Cu and Mg. *Concentration HNO_3 2 mol/L*

Thus the conditions of dissolution have been identified (metal and oxide) for AMB SNF to obtain nitric acid solutions of uranyl nitrate containing no solid phase and suitable for further extraction.

In experiments with uranium-carbide AMB SNF, it was found that the dissolution process can be carried out in normal mode of the RT-1 PA Mayak both individually and in mixtures with normally recyclable spent fuel from water-moderated power reactor (VVER-440). In the event of AMB SNF dissolution with VVER-440 SNF no decrease of extractability of plutonium and plutonium retention in the organic phase due to the influence of water-soluble organic compounds were detected in conjunction with the AMB spent fuel.

1.2. Extraction of actinides from solution AMB SNF

The experiment was conducted at the stand of mixer-settlers in the *hot* chambers of KRI. The fuel solution was processed by the standard Purex flowsheet. Extraction of U, Pu, Np and Tc from the solution of the oxide SNF was performed using 30% TBP in a paraffinic fraction C13. The extract was scrubbed in the same block with strong and weak acidic flows, united with the feed. As striping agent for Pu, Np and Tc nitrate solutions of acetohydroxamic acid (AHA) with the addition of hydrazine nitrate. During the experiment, the head extractor target components were completely extracted, and Mo and Zr were withdrawn into the raffinate. The target radionuclides were successfully re-extracted into their strip liquor. The process parameters are shown in the Tables 1 and 2.

1.3. Management with HLW from AMB SNF reprocessing

Raffinate from reprocessing of AMB SNF are characterized with high content of molybdenum, calcium, magnesium, copper, which requires adjustment of liquid HLW vitrification. To do this, VNIINM developed a process of melting phosphate glass with inclusion of HLW components from the joint processing of oxide SNF from AMB and VVER-440.

Table 1 - Distribution of target and trace elements in the products of the technological flow-sheet for processing the real solution with a ratio of SNF from the AMB SNF from water-VVER-440 being 1:3

Description of solution	Solution composition							
	HNO_3, mg/L	U g/L	Pu g/L	Np mg/L	Tc mg/L	Zr mg/L	Mo mg/L	Mg^{-} g/L
Feed Solution	2.3	232	2.6	160	180	900	790	8.2
Raffinate	1.9	≤0.010	≤0.0004	≤5	13.3	760	680	5.6
U, Pu, Np, Tc extracts	-	92	-					
U, Pu, Np, Tc strip solutions	0.54	≤0.15	5.6	238	235	-	-	-
U extract	-	78	-	≤0.5	-	-	-	-
U strip solution	0.075	71	≤0.0005					
Waste carbonaceous solution	-	<0.005	-					
Recycled extractant	-	<0.005	-					

Table 2 – radiochemical composition of solution, for the table 1.

Description of solution	Σα MBq/L	α –spectrum, MBq/L			γ- spectrum, MBq/L				
		$^{239,240}Pu$	^{238}Pu+ ^{241}Am	^{244}Cm	^{137}Cs	^{134}Cs	^{154}Eu	^{241}Am	^{239}Np
Feed Solution	8.6×10^4	8.3×10^3	5.9×10^4	1.8×10^4	7.2×10^5	0.003	1.4×10^4	2.4×10^4	-
Raffinate	4.7×10^4	-	2.5×10^4	2.2×10^4	5.5×10^5	0.003	1.1×10^4	1.8×10^4	-
U, Pu, Np, Tc extracts	1.4×10^4	2.7×10^3	1.1×10^4	-	≤1.6	-	0.5	-	-
U, Pu, Np, Tc strip solutions	8.8×10^4	1.7×10^4	7.1×10^4	2.6×10^2	≤1.5	-	<0.8	4	170
U extract	1.6	-	-	-	2.8	-	-	-	-
U strip solution	0.5	-	-	-	<0.15	-	-	-	-
Waste carbonaceous solution	<0.2	-	-	-	<0.1	-	0.02	0.023	-
Recycled extractant	<0.1	-	-	-	≤0.02	-	0.02	0.085	-

During synthesis, homogeneous phosphate glass with no signs of crystallization was obtained. Research of thermal stability of phosphate glass samples showed that 100-hour exposure of phosphate glasses with the inclusion of 10 wt. % of HLW oxides from the AMB and VVER-440-440 SNF reprocessing does not change their structure. The glass resulting from HLW of joint processing of spent nuclear fuel from the AMB and VVER-440 are of the melt viscosity not exceeding ~ 10 dPa×c (Fig. 3).

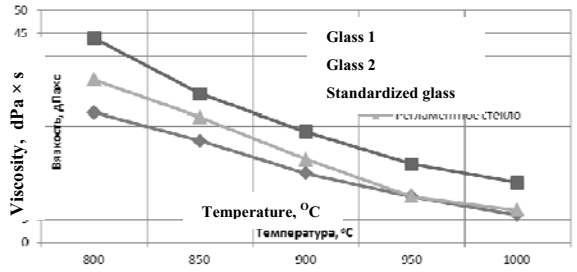

Figure 3 - Dependence of viscosity of phosphate glass with inclusion of HLW components on joint processing of oxide SNF from AMB and VVER-440.

The evaluation of hydrolytic stability of phosphate glasses containing waste from reprocessing of AMB SNF showed that the rate of sodium leaching does not exceed 5×10^{-5} g × cm^{-2} ×day^{-1}. The values obtained correspond to the requirements specified in the GOST 50926-96 [5] and NP-19-2000 [6] pertaining hardened forms of HLW. On the basis of complex research it was found that the main technological parameters of the HLW vitrification process during reprocessing of AMB SNF would mostly correspond to the Regulatory Parameters of the Vitrification Unit EP-500.

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Conclusion

We studied the processes of dissolution of AMB SNF based on U-Mo alloy and UO_2 in HNO_3 with due account for the influence of temperature, HNO_3 concentrations and nitrate ions to formation of precipitation. Due to the studies based on various types of model and real VVER-440 SNF the conditions of obtaining of acid solutions of uranyl nitrate containing no solid phase and suitable for further extraction have been identified.

The experiments with real AMB SNF demonstrated the possibility of extraction of valuable components with use of TBP solutions in hydrocarbon diluent out of solutions obtained by dissolving both individual AMB SNF and dissolving it in combination with the VVER-440 SNF.

It has been established that hardening solutions from reprocessing of AMB SNF in combination with VVER-440 SNF into phosphate glass can result in obtaining of composition, satisfying both the regulatory requirements of the furnace EP-500 and the requirements for high level waste.

Fuel compositions of metallic uranium-molybdenum alloy, uranium dioxide dispersed in a metallic Mg have been studied. The possibility of processing all of these compounds at the RT-1 plant has been demonstrated.

The conducted complex research allowed to carry out the RT-1 reprocessing of ~ 600 kg of oxide SNF from the research reactor named AM from Russian “Atom peaceful” in the end of 2011, which was the approbation of the developed technology on the pilot-industrial scale. The results achieved in conjunction with ongoing research convince us that there is an opportunity to recycle spent nuclear fuel from virtually any fuel compositions at the RT-1 in the future.

Development of the spent fuel technology will allow to solve the problem of accumulated spent fuel from the research reactors in Russia in 2020, then AMB SNF and all other "problematic" types of spent nuclear fuel.

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