

## Management of High-Level Waste Arisen from SNF Reprocessing by Non-Aqueous Methods

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**Abstract** - composition, properties and outputs of high-active products and waste have been studied after pyroelectrochemical reprocessing of BN-350 and BOR-60 reactor irradiated MOX fuel. The main amount of fission products, actinides and impurities is concentrated in a small volume of solid recycled products - uranium dioxides of two types and high-active waste - phosphate deposit and spent salt electrolyte. The phosphate deposit and electrolyte are subject to the final disposal but uranium dioxides are returned to the cycle after a certain period of storage. Based on the study of waste properties it was concluded that they can be kept in sealed stainless steel containers without treatment for a long time. Both types of waste may be immobilized in phosphate glass or in monazite-type and kosnarite-type (NZP) ceramics to make an additional safety barrier before the final disposal.

### INTRODUCTION

Since the middle of 1960s SSC RIAR has been involved into investigations and development to substantiate closed fuel cycle for fast neutron reactors consuming oxide uranium-plutonium fuel [1]. The fuel cycle involves pyroelectrochemical technology for oxide uranium-plutonium fuel reprocessing and granulation in chloride salt melts and fabrication of fuel rods by vibropacking.

At present the pyroelectrochemical technology for fuel reprocessing have been developed to compete with traditional aqueous methods. The advantage of the pyroelectrochemical technology is its high internal level of the process safety, compactness, high protection from the viewpoint of nuclear materials nonproliferation, and decreased amount of high-level waste [2].

The paper discusses SSC RF RIAR experience in various options of the recycle products reprocessing and methods for preparation of high-level solid waste (HLSW) produced at different stages of the fuel cycle for controlled storage.

### MAIN STAGES OF PROCESS AND WASTE TREATMENT

The objective of the process is to remove plutonium from the irradiated fuel for its recycling and to extract uranium, which is much less precious (since natural or depleted in U-235 uranium is used), from the cycle together with the most part of fission products and sent them for storage.

The fuel is mechanically de-cladded, crushed, and loaded into the chlorator-electrolyzer. The whole pyroelectrochemical part of the process is carried out in this apparatus. It includes the following operations:

- fuel chlorination in salt melts (NaCl-KCl, LiCl-NaCl-KCl-CsCl);
- electrodeposition of UO<sub>2</sub>-1 and a part of fission products;
- precipitating crystallization of PuO<sub>2</sub> purified from FP and other impurities;
- additional electrolytical extraction of UO<sub>2</sub>-2 together with FP and other impurities;
- phosphate purification of the melt.

The technological flow sheet rests on the principle of maximum recycling of the reversible products allowing us to remove 99.5-99.9% of PuO<sub>2</sub> and minimize the yield of high-level radioactive waste. UO<sub>2</sub>-1 and UO<sub>2</sub>-2 deposits, PuO<sub>2</sub>, phosphate precipitate are washed off from captured salts with water. Water solutions are boiled down to recycle solid salts and water condensate in the process. PuO<sub>2</sub> precipitate is planned to be used in fuel rods prefabrication, while uranium oxides should be sent for long-term storage with subsequent reprocessing and return of uranium into the cycle. The phosphate precipitate undergoes storage, immobilization, and disposal. The salts can be used in several technological cycles with subsequent removal from the process, storage and treatment prior to their storage.

In the process of operation of the fuel re-generation facility various combustible radioactive materials, such as polyethylene film, cleaning cloth, overalls, rubber, filters are accumulated. Experiments demonstrated that all these materials might be periodically burnt right in the salt melts. The main parameters of burning of pyrographite parts of the chlorator-electrolyzer with exhausted service life were determined and studied in laboratory. All the equipment units including fuel rod claddings are decontaminated prior to their removal from the process.

Decontaminating solutions are purified by ion-exchange resin to extract uranium and plutonium, and the resin is burnt in salt melts. Gaseous products from the chlorator-electrolyzer are run through a bulk filter to be purified from salt sublimates and then sent to a chlorine absorption column. Two ways of the released gas purification from chlorine were developed and tested: absorption in soda solution and freezing-out with subsequent recycling. The bulk filter is cleaned from the salt sublimates and regenerated, and the salts are put back into the chlorator. The air from the shielded cells housing the equipment is sent through the filters to capture radioactive aerosols.

The described methods for reversible products reprocessing were tested in the production of granulated mixed oxide fuel and included into the flow sheet for irradiated mixed fuel reprocessing. High-level solid wastes, i.e. phosphate precipitate and spent electrolyte are generated along with  $\text{PuO}_2$  and reversible products in the re-generation process.

### Properties of High-Level Waste

Certain amounts of high-level waste were accumulated as a result of experimental reprocessing of irradiated BN-350 and BOR-60 reactor fuel [3, 4]. Experimental and research work was done to study physical-chemical properties of the waste and determine possibilities and conditions for its long-term storage. The waste characteristics are given in table.

TABLE 1. Characteristics of solid high-active wastes (from BOR-60 fuel reprocessing)

Properties	Waste type	
	Phosphate deposit	Electrolyte
Output, kg/kg of fuel	0.14	2.5
Bulk density, kg/m <sup>3</sup>	600-700	-
Specific heat release, W/kg	14.8	0.95
Self-heating temperature, °C	40(180 g)	30(2000 g)

High-active products and wastes are powdery and solid (molten salt) materials. Its  $\gamma$ -activity is caused with  $^{144}\text{Ce}(\text{Pr})$  - 96% in phosphate deposit and  $^{137}\text{Cs}$  - 84.3% in electrolyte.

### Radionuclide Leaching

Leaching of Cs, Ru, Ce, Eu, Sb nuclides from phosphates was studied in distilled water at 25°C. In 28 days the rate of leaching for the main nuclide amount was  $1 \cdot 10^{-5} \div 1 \cdot 10^{-6}$  g/(cm<sup>2</sup>\*day) and for  $^{137}\text{Cs}$  it was somewhat higher. The rate of leaching  $1 \cdot 10^{-6}$  g/(cm<sup>2</sup>\*day) peculiar to the boro-silicate glass matrixes is taken as a conditional estimation of the chemical stability of solid radioactive waste. The presented data exceed this value. The increased release of the most toxic cesium-137 generates a need for waste storage in sealed containers.

### Radiation Gas Release

The phosphate deposit and electrolyte were studied. The discharge was recorded in both containers during tests for 2350 h and reaching integral dose  $\sim 9 \cdot 10^7$  Gy. The phosphate gamma-radiation stability at integral dose in the range  $1 \cdot 10^6 - 5 \cdot 10^8$  Gy has been demonstrated elsewhere [5]). The increment of pressure was absent during the SM-2 reactor irradiation of NaCl-KCl salts (integral dose  $3.5 \cdot 10^7$  Gy).

### Thermal Stability

The phosphate deposit has thermal stability in the range 20-800°C. The thermal analysis of spent electrolyte demonstrated the endothermal effect at 615°C due to the salt melting. The transformation of such type does not result to gas release but the temperature of waste storage should be less than that of transformations.

### Corrosion Resistance

Carbon steel (St.3) and stainless steel (12Cr18Ni10Ti) available a wide industrial application are chosen as structural materials of containers for waste storage. The compatibility of steel with phosphate deposit was studied at temperature of self-heating. No stainless steel corrosion was found in the medium of phosphate deposit. Its corrosion resistance is estimated by first number (perfectly resistant) according to ten scale. Under the same conditions the carbon steel (St.3) is estimated by second-fourth number. Steel corrosion resistance in the medium of molten electrolytes NaCl-KCl, LiCl-KCl-NaCl-CsCl was studied both at the moment of casting (650°C) and at temperature of waste self-heating (30-40°C). The main corrosion of samples was shown to take place at the moment of electrolyte casting and the rate of

St.3 corrosion is greater by an order of magnitude in comparison with 12Cr18Ni10Ti steel. The corrosion resistance of samples tested in electrolyte is estimated by number 4 (stable) for St.3 and by number 2 (very stable) for 12Cr18Ni10Ti steel. Thus, at self-heating temperature 30-40°C phosphates and electrolytes can be kept in St.3 containers but 12Cr18Ni10Ti steel containers are preferable. The studied properties showed that wastes can be kept in sealed St.3 and 12Cr18Ni10Ti steel containers without treatment. Taking into consideration the powdery state of phosphate deposit and high solubility of molten salt as well as outlook of their further storage an additional safety barrier is required to incorporate wastes in the stable matrix, for example glass and ceramics.

### High-Level Waste Vitrification

The real phosphate precipitate produced as a result of the BOR-60 fuel reprocessing contains 22.3% of REE and 14.7% of iron;  $^{144}\text{Ce}(\text{Pr})$  is responsible for 96% of the gamma-activity, and  $^{241}\text{Am}$  contributes 86% of the alpha-activity. X ray analysis showed the precipitate structure to be similar to monazite structure. Composition of the glass matrix and waste for a real experiment was selected: ( $\text{NaPO}_3$ -75 %,  $\text{AlF}_3$ -10%,  $\text{NaF}$ -5 %,  $\text{Al}_2\text{O}_3$ -10%)-85%, phosphate precipitate - 15 %. The rate of leaching of Na, Al, P, F and fission

products from the sample on the 28<sup>th</sup> day did not exceed  $1 \cdot 10^{-6} \text{ g}/(\text{cm}^2 \cdot \text{day})$  and decreased down to  $1 \cdot 10^{-7} - 1 \cdot 10^{-8} \text{ g}/(\text{cm}^2 \cdot \text{day})$  on the 118<sup>th</sup> day. Thermal analysis of glass specimens allowed determination of the de-vitrification temperature (570-580°C) and the storage temperature (no higher than 450°C).

It was found out that storage of the glass samples over 5 years (the integral dose of  $\beta$ -,  $\gamma$ -irradiation –  $9,4 \cdot 10^7 \text{ Gy}$ ,  $\alpha$ -irradiation –  $1,4 \cdot 10^{23} \text{ decay}/\text{m}^3$ ) did not worsen their hydrolytic resistance. To immobilize higher amounts of the phosphate precipitates a glass matrix based on lead and sodium metaphosphates was proposed and tested.

Experiments on vitrification of alkali metal chlorides showed that transparent glass-like specimens of high chemical resistance are produced, if up to 6% of chlorine-ion and 7-22% of chlorides depending on the alkali metal are included. The preliminary conversion of chlorides into metaphosphates allows vitrification of up to 46% of the waste. Thus, the proposed glass matrix can be used for immobilization of the waste. Co-vitrification of the phosphate precipitate and the salt waste was also studied. Table 2 briefly presents the main results of the experiments on vitrification of high-level waste from pyroelectrochemical processing of irradiated fuel.

TABLE 2. Vitrification of high-level waste from pyroelectrochemical process

Type of high-level waste	Type of glass matrix	Immobilization	Quantity of immobilized waste, %	Cs-137 leaching rate on the 7 <sup>th</sup> day, $\text{g}/\text{cm}^2 \cdot \text{day}$	Thermal stability, °C	Radiation resistance
Phosphate precipitate	$\text{Pb}(\text{PO}_3)_2$ , $\text{NaPO}_3$	Vitrification, T-950°C	28	$7 \cdot 10^{-6}$	400	$1 \cdot 10^7 \text{ Gy}$ ( $\gamma, \beta$ ), $1 \cdot 10^{18} \alpha$ -decay/g
Spent salt electrolyte	$\text{NaPO}_3$ , $\text{AlF}_3$ , $\text{Al}_2\text{O}_3$	Vitrification without chlorides conversion, T-950°C	20	$7 \cdot 10^{-6}$	400	
Phosphate precipitate + spent salt electrolyte	$\text{NaPO}_3$ , $\text{AlF}_3$ , $\text{Al}_2\text{O}_3$	Co-precipitation without chlorides conversion T-950°C	36	$4 \cdot 10^{-6}$	400	

### High-Level Waste Ceramization

Immobilization of the waste into matrices based on the monazite structure and sodium-zirconium phosphate  $\text{NaZr}_2(\text{PO}_4)_3$  (NZP) is studied as an alternative.

The phosphate powder can be compacted by pressing and sintering to make ceramic blocks

with the properties satisfying requirements of long-term controlled storage or disposal.

Systematic investigations of  $\text{NaZr}_2(\text{PO}_4)_3$  phosphates and their structural analogues in  $\gamma$ -irradiation fields and under the internal self-irradiation by  $\alpha$ -particles from  $\alpha$ -emitters making part of the phosphates gave an idea of the phosphates behavior under simulated conditions for storage of the high-level waste

immobilized into them. The capability of the NZP-structured phosphates to resist the internal self-irradiation was shown (by the example of Pu phosphates (IV) with inclusion of  $^{238}\text{Pu}$ ). The rates of cesium, sodium, and strontium leaching from double phosphates by different methods were studied (in the dynamic mode at  $95^{\circ}\text{C}$ , in the static mode at 25, 90, 200, 300,  $400^{\circ}\text{C}$ ).

Since such compounds can be formed right in the pyroelectrochemical process, the immobilization into the NZP ceramics can be a promising method.

Table 3 briefly presents the main results of ceramization of high-level waste from pyroelectrochemical reprocessing of irradiated fuel.

TABLE 3. Ceramization of high-level waste from pyroelectrochemical process

Type of high-level waste	Type of ceramics	Immobilization	Quantity of immobilized waste, %	Cs-137 leaching rate on the 7 <sup>th</sup> day, $\text{g}/\text{cm}^2 \cdot \text{day}$	Thermal stability, $^{\circ}\text{C}$	Radiation resistance
Phosphate precipitate	Monazite	Compacting, sintering, $T-850^{\circ}\text{C}$	100	$1 \cdot 10^{-6}$	850	$5 \cdot 10^8$ Gy ( $\gamma, \beta$ ), $1 \cdot 10^{19}$ $\alpha$ -decay/g
Spent salt electrolyte	Kosnarite (NZP)	Conversion from melt or water solution into NZP, compacting, sintering $T-1000^{\circ}\text{C}$	30-40	$3 \cdot 10^{-6}$	1000	

## CONCLUSIONS

Basing on the results of the investigations the following methods for the waste treatment can be recommended:

- co-vitrification of phosphate precipitate and spent electrolyte;
- ceramization of phosphate precipitate into monazite-like structure and conversion of spent electrolyte into kosnarite-structured ceramics.

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