

**PYROELECTROCHEMICAL REPROCESSING OF IRRADIATED MOX FAST REACTOR FUEL
TESTING OF THE REPROCESSING PROCESS WITH DIRECT MOX FUEL PRODUCTION**

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INTRODUCTION

Fast reactor fuel recycle can and must involve compact technologies that will improve its safety and reduce the fuel component cost. One of the advanced technologies is pyroelectrochemical molten salt technology. This particular technology is being developed at the SSC RIAR applicably to reprocessing of the irradiated MOX fuel followed by vibropac fabrication of fuel rods (1). A series of investigations carried out within 1985-1996 was aimed at testing the most simple reprocessing process that provided for extraction of plutonium dioxide from irradiated fast reactor fuel and its subsequent recycle in mixture with uranium dioxide (2-4). The demonstration reprocessing of the BOR-60 MOX fuel irradiated up to a high burnup (21 - 24% h.a.) verified the applicability of this approach and its feasibility for technological implementation. These data formed a basis for feasibility and process safety studies (5,6).

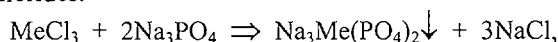
But that was a limited case and it excluded uranium from recycle and included extraction of plutonium dioxide. Taking into account the present stringent requirements to reprocessing technologies of irradiated nuclear fuel that should exclude uranium and plutonium separation, the next stage of the development should include optimization and testing of the pyroelectrochemical MOX fuel reprocessing process for MOX fuel production (process MOX→MOX).

PROPOSED FLOW-SHEET OF THE MOX TO MOX PYROCHEMICAL REPROCESSING

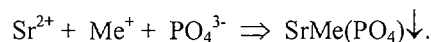
In 1998 we began to study the next phase of the irradiated oxide fuel reprocessing accordingly new process MOX→MOX which includes main operations:

- dissolution of irradiated fuel in molten alkaline metal chlorides
 - $UO_2(sol) + Cl_2(g) \rightarrow UO_2Cl_2(melt);$ (1)
 - $U_3O_8(sol) + Cl_2(g) \rightarrow UO_2Cl_2(melt) + UO_{2+x}Cl(melt);$ (2)
 - $PuO_2(sol) + Cl_2(g) \rightarrow PuO_2Cl_2(melt);$ (3)
 - $PuO_2Cl_2(melt) \leftrightarrow PuO_2Cl(melt) + 0,5 Cl_2(g);$ (4)
 - $PuO_2Cl_2(melt) + Cl_2(ras) \leftrightarrow PuCl_4(melt) + O_2(g);$ (5)
 - $PuCl_4(melt) \leftrightarrow PuCl_3(melt) + 0,5 Cl_2(g);$ (6)
- purification of melt from fission products that are co-deposited with uranium and plutonium oxides (preliminary electrolysis);
- electrochemical co-deposited of uranium and plutonium oxides under the controlled cathode potential
 - $UO_2^{2+}(melt) + e^- \rightarrow UO_2^+(melt);$ (7)
 - $UO_2^+(melt) + e^- \rightarrow UO_2(sol);$ (8)
 - $Pu^{4+}(melt) + e^- \rightarrow Pu^{3+}(melt);$ (9)
 - $PuO_2^{2+}(melt) + e^- \rightarrow PuO_2^+(melt);$ (10)
 - $PuO_2^+(melt) + e^- \rightarrow PuO_2(sol);$ (11)
- production of granulated MOX fuel following the process well developed at SSC RIAR (crushing, salt separation, sizing);
- purification of melt from FP impurities by phosphate precipitation.

Last procedure is based on the fact that practically all ions with oxidation state higher than (II) form double phosphates insoluble in molten chlorides:



precipitation of many elements having an oxidation rate (II), including alkaline earth elements, e.g. strontium, also takes place:



Such process allows for the arrangement of MOX fuel recycle in the form of MOX fuel.

The experimental research plan includes two basic stages:

- testing of the process on the enlarged laboratory scale using a simulator of the irradiated MOX fuel with minor-actinide and FP additives in order to test the validity of the main selected parameters and to determine the decontamination level from the main FP;
- actual experiments with the real irradiated BOR-60 MOX fuel using the pilot facility located inside the hot cell.

EXPERIMENTS WITH MOX FUEL SIMULATORS.

In 1998 a series of experiments was prepared and carried out using a special laboratory facility in the glove boxes line. This facility allows for the experiments with a single load of 400-800 g of mixed oxide fuel.

The purpose of the experiment is to simulate the real pyroelectrochemical MOX fuel reprocessing flow-sheet in molten chlorides and produce fuel decontaminated from the most of FP and minor-actinides that meet the requirements of the standard fast reactor fuel.

The experimental program had the following main operations:

- dissolution of fuel simulator in the melt;
- pyroelectrochemical deposition of cathode deposit of fuel oxides containing minor-actinides and partially decontaminated from FP;
- treatment of cathode deposits and assessment of the possibility to fabricate fuel rods by vibropacking;
- experimental verification of the "rough" separation of actinides and REEs by oxide precipitation that included two additional stages:
 - extraction of actinide and REE concentrate from the melt upon obtaining fuel;
 - reprocessing of the concentrate in the melt aimed at studying the separation process of REEs from actinides by fractional precipitation.

The main experimental conditions are:

- salt - solvent - NaCl-2CsCl eutectic;
- process temperature - 600-650°C;
- fuel dissolution in the melt - by gaseous chlorine;
- pyroelectrochemical deposition of cathode deposit of mixed fuel oxides (U,Pu)O₂ - by electrolysis in the potentiodynamic mode aimed at the complete extraction of Pu and Np from the melt;
- extraction of actinide and REE concentrate from the melt upon obtaining fuel by its precipitation as oxides, the precipitator is Na₂CO₃;
- treatment of cathode deposits - crushing, removal of salts, study of the physical-mechanical characteristics;
- studying the separation process of REE from actinides; procedure - fractional precipitation of oxides; two salt systems were studied - NaCl-KCl and NaCl-2CsCl.

Reprocessing of (U,Pu)O₂ fuel containing 10-15% of PuO₂ was simulated. The simulators of some FP (carrier+mark) were introduced with fuel components and their amount corresponded to a burnup of about 10% (h.a.).

Ce-144, Zr-95, Ru106, Eu-152,154, Cs-134 radionuclides were used as radioactive FP marks.

Two experiments were performed to simulate the irradiated MOX fuel reprocessing. The second experiment included the preliminary electrolysis of the reduced melt (see fig.2). The purpose was to purify the melt from noble FP and zirconium and to remove them from the system with a small amount of uranium dioxide similarly to the process developed before (4).

The plot in fig.1 shows the course of experiment No.1. In all, three cathode deposits were obtained in two experiments. Their characteristics are provided in table I.

Table I

Characteristics of cathode deposits

Experiment No.	Deposit	Deposit mass, g	Capture of salts, %	Content of basic components, % of initial quantity in system mass fraction in fuel, %						
				U	Pu	Np	Am	Ce	Zr	Ru
1	(U,Pu)O ₂	359,9	17,4	99,9 70,10	99,96 17,2	99,6 0,62	≈0	≈0	≥85	≥90
2	UO ₂ (preliminary electrolysis)	105,3	11,6	26,148 5,31	0,2 0,089	45,3 1,10	≈0	≈0	≥85	≥90
	(U,Pu)O ₂	337,4	14,8	73,857 5,17	99,75 12,4	54,3 0,41	≈0	≈0	≈0	≈0

The decontamination factors of the obtained MOX fuel from FP are as follows:

- for Cs - of the order of 1000;
- for REE (Ce, Eu) - more than 100;
- for Ru and Zr:
 - * without the preliminary electrolysis - of the order of 1;
 - * with the preliminary electrolysis - of the order of 10.

Thus, it was demonstrated that MOX fuel has a high decontamination from the REEs and Cs. The experiment verified the necessity to perform the preliminary decontamination of the melt from some FP (Ru, Zr and their analogs) prior to obtaining mixed fuel.

More than 99% of plutonium was deposited into (U,Pu)O₂ cathode deposit. Thus only 0.2% of plutonium was co-deposited at the stage of the preliminary electrolysis of uranium into the cathode deposit.

The physical-mechanical characteristics of the obtained MOX fuel granulate correspond to the quality of vibropac fuel.

Thus, the experiments verified the feasibility of the new "MOX to MOX" fuel reprocessing process.

MINOR-ACTINIDES BEHAVIOR

Minor-actinides (Np, Am Cm) were specially added to the experiment to study their behavior during reprocessing.

The behavior of neptunium corresponds to the regularities detected before (7) and it completely co-deposits with MOX fuel and uranium dioxide. In normal conditions americium and curium do not practically co-precipitate into the cathode deposit.

The experiments on fractional precipitation of americium and curium oxides from molten salts after fuel reprocessing were carried out. Precipitation was performed by sodium carbonate in molten NaCl-KCl and NaCl-2CsCl. Principally similar results were obtained for both systems in terms of the possible separation of actinides and REEs. The precipitation process in molten NaCl-2CsCl upon completion of electrolyses is given in fig.2. . The melt mass was about 2 kg and the mass component fractions at the beginning of the process were as follows: Pu-0.04%, Am-0.27%, Ce-0.08%, Eu-0.001%. Na₂CO₃ portions were introduced by 1.0 g.

The experiment demonstrated that the extraction of americium oxide into an individual phase is possible. Mixed precipitates of rare earth elements and americium oxides obtained by the carbonate precipitation and washed from salts are the free-flowing crystal powders of black color with the pronounced smooth sides of crystalline particles. The particle grain size is < 100 μm.

CONCLUSIONS:

- ◇ The proposed reprocessing flow-sheet of irradiated MOX fuel verified the feasibility of its decontamination from the most of FPs (REEs, caesium) and minor-actinides (americium, curium).
- ◇ A possibility to perform an additional decontamination from the noble metals and zirconium has been confirmed using the stage of the preliminary electrolysis of the reduced melt.
- ◇ It has been established that it is possible to perform the selective extraction of americium in the process of the fractional carbonate precipitation from molten NaCl-KCl and NaCl-2CsCl containing FPs (first of all, REEs), minor-actinides (americium and curium) and also uranium and plutonium traces into a certain fraction in the form of the crystalline oxide.

PLANS

The flow-sheet of the demonstration experiment for irradiated BOR-60 MOX fuel reprocessing in the shielded cell, which is scheduled for the middle of 2000 has been developed. Plane that about six irradiated BOR-60 MOX fuel assemblies will be reprocessed with the direct production of MOX fuel for recycle.

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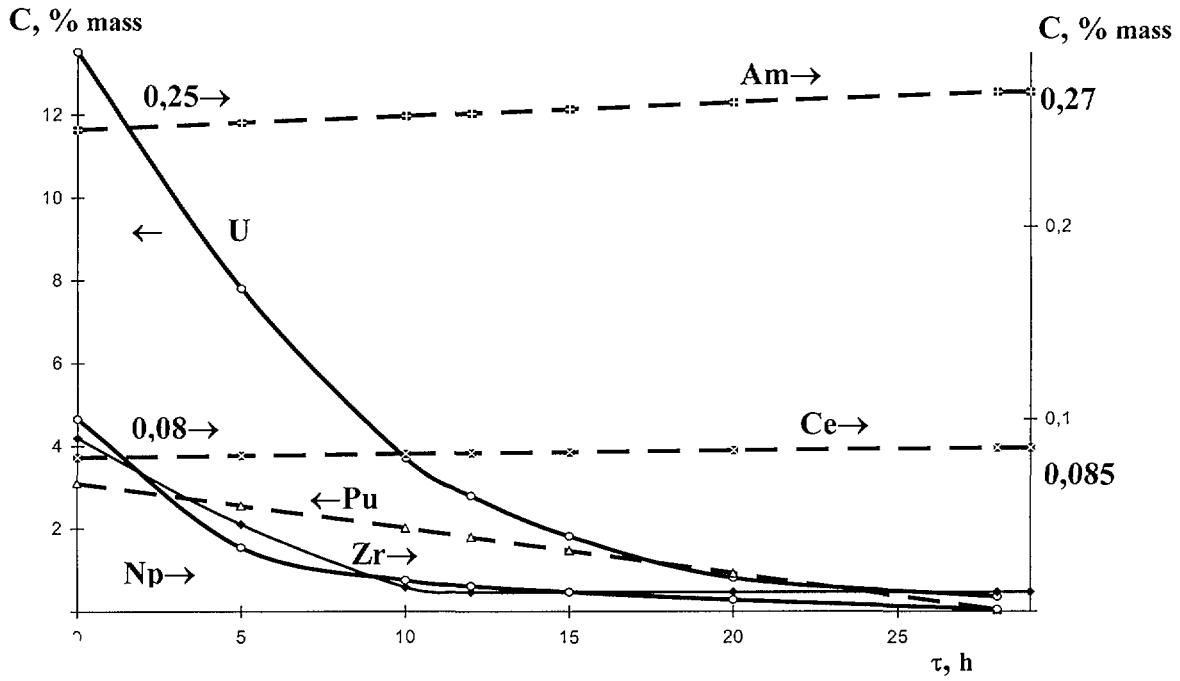


Fig. 1 The U, Pu, Np, Am, Ce, Zr contents change in the NaCl-2CsCl melt during MOX-fuel (U, Pu)O₂ electrodeposition (at 650°C)

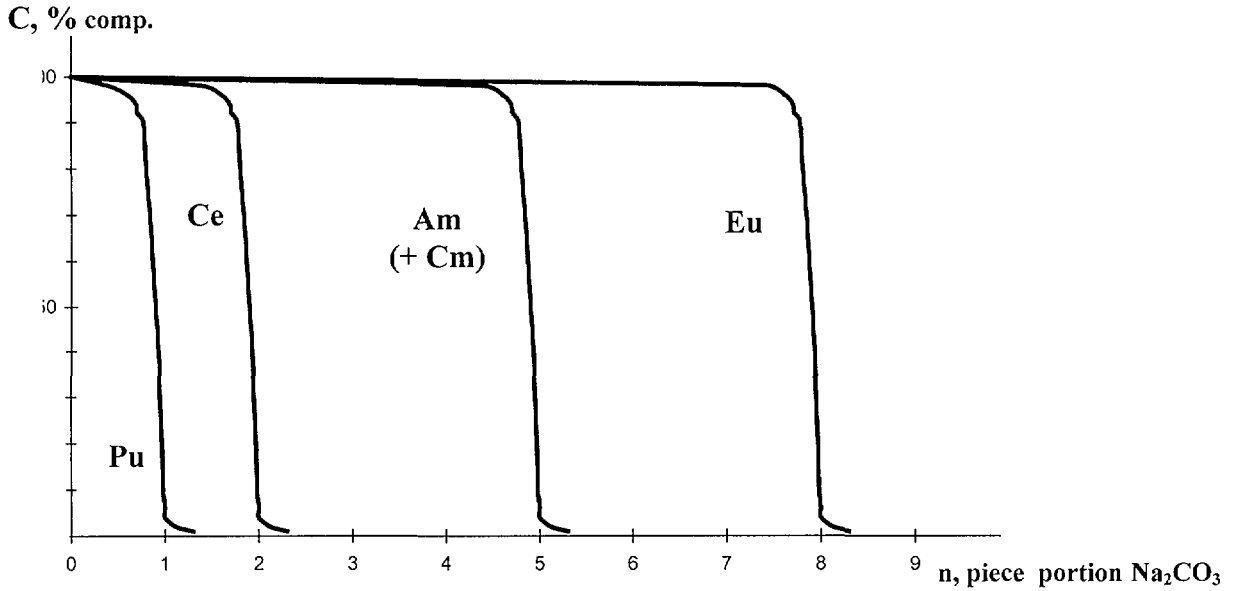


Fig. 2 The Pu, Am, Ce, Cm, Eu relative contents change in the NaCl-2CsCl melt during fractional carbonate precipitation after electrolysis.