IAEA-SM-358/36

ADVANCED FUEL CYCLE ON THE BASIS OF PYROELECTROCHEMICAL PROCESS FOR IRRADIATED FUEL REPROCESSING AND VIBROPACKING TECHNOLOGY

A.A. MAYORSHIN, O.V. SKIBA, V.A. TSYKANOV,
V.N. GOLOVANOV, A.V. BYCHKOV, V.A. KISLY, D.A. BOBROV
State Scientific Centre Research Institute of Atomic Reactors,
Dimitrovgrad, Russian Federation

Abstract

For advanced nuclear fuel cycle in SSC RIAR there are developed the pyroelectrochemical process to reprocess irradiated fuel and produce granulated oxide fuel UO_2, PuO_2 or $(U,Pu)O_2$ from chloride melts. The basic technological stage is the extraction of oxides as a crystal product with the methods either of the electrolysis (UO_2 and UO_2-PuO_2) or of the precipitating crystallization (PuO_2). After treating the granulated fuel is ready for direct use to manufacture vibropacking fuel pins. Electrochemical model for $(U,Pu)O_2$ coprecipitation is described. There are being developed new processes: electroprecipitation of mixed oxides - $(U,Np)O_2$, $(U,Pu,Np)O_2$, $(U,Am)O_2$ and $(U,Pu,Am)O_2$. Pyroelectrochemical production of mixed actinide oxides is used both for reprocessing spent fuel and for producing actinide fuel. There are estimated both the efficiency of pyroelectrochemical methods application for reprocessing nuclear fuel and of vibropac technology for plutonium recovery.

1.Introduction

The current stage of nuclear power is characterized by enhanced requirements to safety and influence of all the fuel cycle stages on the environment. Involving weapon grade nuclear material in the fuel cycle results in additive requirements both to its non-proliferation and to the systems of physical shield and MC&A (Material Control and Accounting). That's why the technology, that will enable to raise considerably potential possibilities of oxide fuel and to upgrade technicoeconomic characteristic of the fuel cycle as a whole with the allowance for modem requirements are of great interest.

The following directions of the efficiency growth for nuclear power are becoming the most important:

- closed advanced fuel cycle, i.e. the internal closeness of technologic processes with the object to reducing the release of the substances, which are harmful for the environment;
- optimization-of the technologic systems, which is aimed at achieving the necessary maximum results by means of the minimum number of the process stages;
- the highest level of the inherent safety, i.e. the use of the processes, the safety of which is based not only on the engineering principles but also on the own «natural» properties of the technologic system, creating maximum grade of ecological protection.

These principles influence both general safety and economics equally.

It should be taken into consideration, that the processes, concerning nuclear fuel recovery and preparation, were formed as early as 1950s and were developing as the military technologies continuation. That is why many processes haven't been optimized yet from the viewpoint of the real public needs.

At IAEA symposium in 1997 there was emphasized, that fuel cycle facilities of the next generation should provide:

- Maximum high levels of the safety;
- Minimum costs on the fuel cycle;
- Minimum effect on the environment, including minimum waste generation;
- Minimum usage of natural resources;

- Minimum risk of proliferation and maximum guarantees;
- Public support;
- Variety and safety of energy supplies.

Nonaqueous methods are considered as possible alternative technologies for the fuel cycle. Pyroelectrochemical reprocessing, using the molten salts, is applied to oxide fuel (SSC RF RIAR, Russia) and metal fuel (Argon National Laboratory, the USA) and exhibits the following advantages:

- High chemical stability of the medium;
- High concentration in fission elements (more than 30 %);
- Unavailability of neutron moderators;
- Implementing all the chemical processes in the same apparatus independently of the kind of initial products being reprocessed (metals, oxides, nitrides and etc.);
- Minimized volume of high-active waste;
- Batchwise production from the viewpoint of control and accounting of fission components distribution.

By the moment SSC RF RIAR has formulated and substantiated experimentally chief principles of the advanced closed fuel cycle, based on mutual compatibility of the technologies for recovering uranium-plutonium fuel and manufacturing fuel pins and SA. The principles are as follows:

- using “dry” pyroelectrochemical processes with the aim of recycling irradiated fuel and, as a result of recovery, obtaining the oxide granulated fuel of polydispersive composition with the particle density, that is close to the theoretical one. The granulate is ready for vibropacking in the pin cladding;
- applying vibropacking with the object to making fuel pins and SA from granulated fuel;
- employing remote-control automated equipment in reprocessing fuel, manufacturing fuel pins and SA.

“Dry” techniques make it possible to reprocess fuel of any burnup and exposure time in few technological stage. The media, the processes proceed in , don’t have moderator and therefore, the handling of fission and radioactive materials of high concentrations is possible. That is why «dry» processes are high productive, compact and result in small quantity of waste, which simplify considerably MC&A.

Remote-control processes are very important for fuel cycle, and extra charges, related to the transition from glove boxes to shielded cells, are substantiated due to the following reasons:

- there is an opportunity to optimize level of purification of FPs down to the one, meeting the requirements of reactor facility, followed by reducing charges for additional fuel purification and reprocessing of additional waste volume;
- rigorous restrictions on contents of high-toxic isotopes and transplutonium elements are removed;
- there are possibilities of working out new fuel cycle scenarios, for example:
  -it’s possible to reuse fuel after partial reprocessing with aim of releasing gas and high-volatile fission products;
  -it’s possible to use blanket zone fuel directly in BN Core;
  -it’s possible to burn out fuel of the reactor in the other one with lower enrichment through partial fuel reprocessing;
- undeep NM purification is “less attractive”, increases self-protectability level and enables to check easily NM movements, and therefore risk of their unauthorized usage decreases.

An experimental base for exercising the principles set forth above is Semi-Industrial Complex (SIC), including the Facility on granulated fuel production and the Facility of Fuel pin and SA manufacture. Tests of the fabricated fuel pins and SA take place in BOR 60 and BN 600.

2. Pyroelectrochemical technology of fuel reprocessing

Principal technologic flow-sheet of the pyroelectrochemical process of fuel reprocessing is given in Fig.2.1 .(a,b). Any kind of fuel (oxide, metal, carbide, nitride) can be an initial material for the process. At the first stage it is dissolved in the melt of salts, the most appropriate and investigated of which are chloride ones. Fuel is extracted from the melt either by electrolysis or by precipitating as crystalline oxides, for example UO_2, PuO_2 or $UPuO_2$. Upon separating the crystalline products from the salt-solvent and from other soluble impurities, the granulate of polydispersive composition, which is

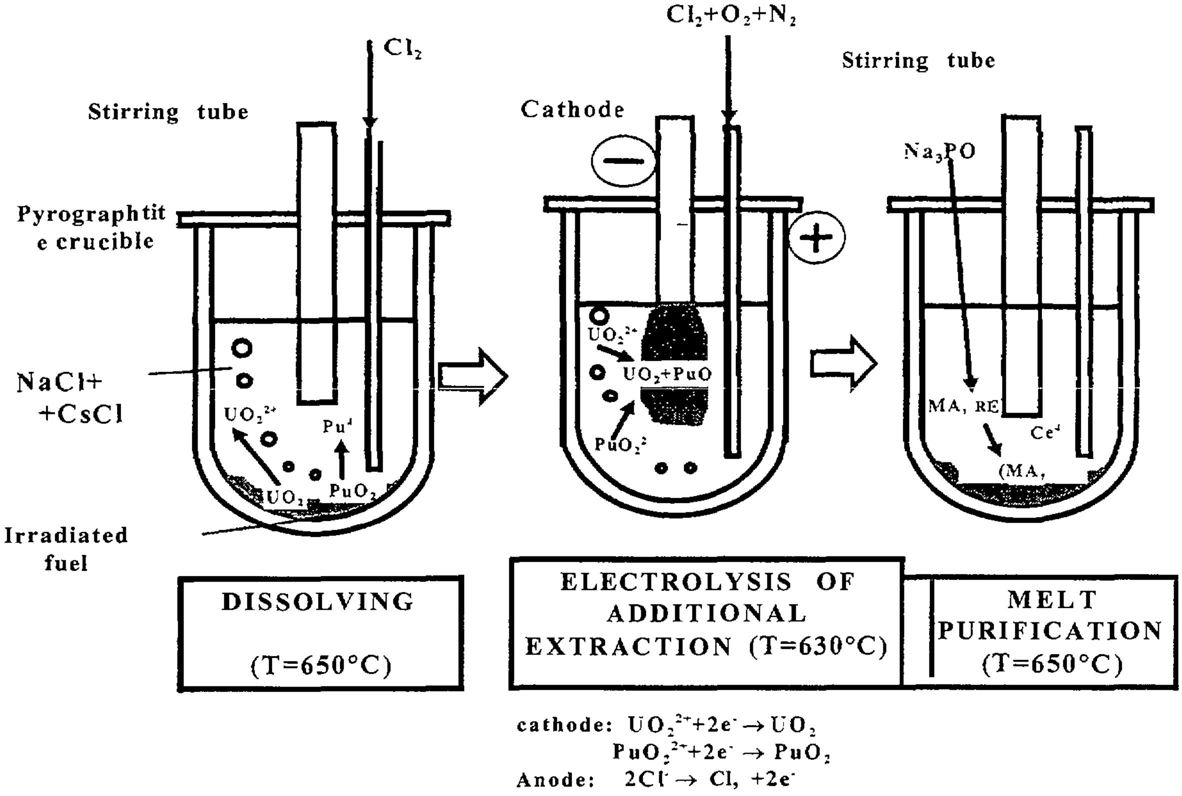

Fig.2.1.(a) Flow-sheet of pyroelectrochemical reprocessing of irradiated fuel under conditions of mixed fuel production

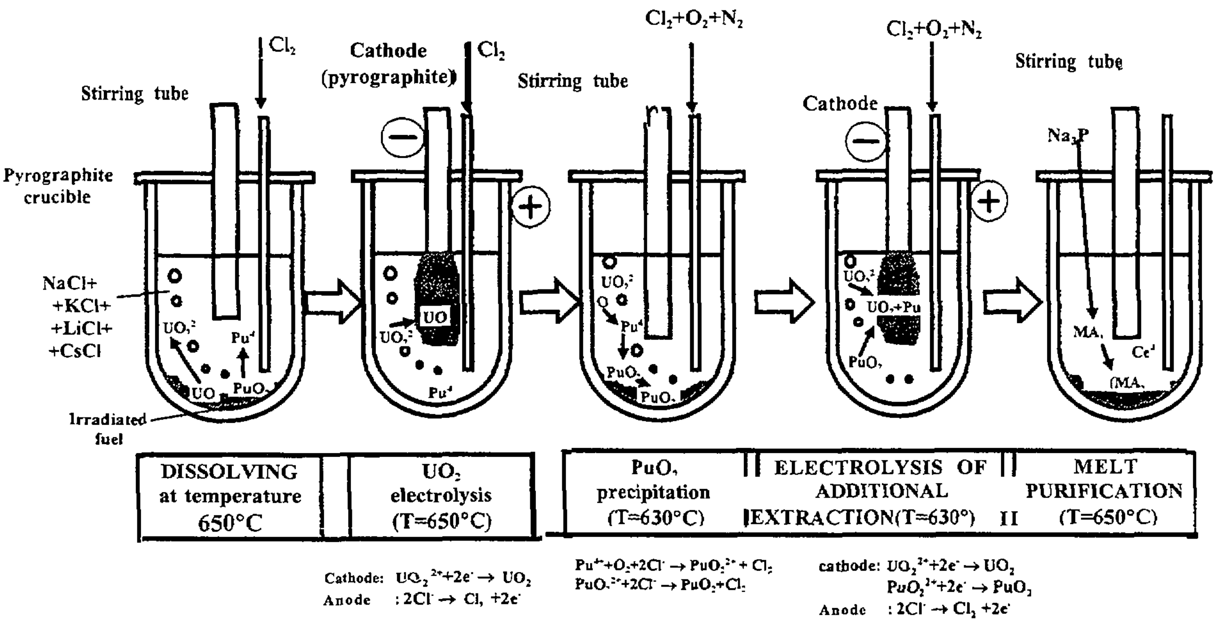

Fig.2.1 .(b) Flow-sheet of pyroelectrochemical reprocessing of irradiated fuel under conditions of plutonium dioxide production

suitable for vibropack fuel pin fabrication, is obtained. The particles have the density not less than 10,7 g&m' and their size is not more than 1,0 mm. Recovery of washing out solution is carried out by evaporating followed by returning the «dry» residue to the process beginning. Pyroelectrochemical process allows us to purify the fuel of FPs with total purification coefficient more than 100, which is sufficient from the viewpoint of reactor physics.

The waste volume is minimized, and a number of valuable elements (of ruthenium subgroup, for example) can be extracted from them. There are no rigorousrequirements to gas atmosphere for carrying out processes, so they are performed in the shielded cells under free air.

3. **Fuel pin and SA manufacture.**

Vibropacking technology is always considered as a way of fabricating the fuel column, enabling to reduce greatly the costs on the fabrication of fuel pins for nuclear reactor and to upgrade their performance. The principal merits of the vibropacking technology and vibropack fuel pins consist in

- simplicity and reliability of the production process related to the fewer number of technologic and check operations. This fact simplify automation and remote control of the process, therefore vibropacking technology can be employed to make pins of the recovered fuel in the shielded hot cells;
- the possibility of fabricating fuel column , having easily variable parameters, and on the basis of using multicomponent composition;
- the possibility of using any kind granulate: both of homogeneous composition and of mechanical mixture;
- less thermal-mechanical fuel effect on cladding in comparison with pellet fuel
- diminished requirements to inner diameter of fuel pin claddings.

The possibility of fabricating fuel pins by vibropacking is shown in two versions: hand - in the glove boxes and remote - in the shielded cells (Table2.1). Semi-industrial technology of fuel pin and SA manufacture for BOR-60, BN-3 50 and BN-600 reactors under remote conditions was implemented when working at «ORYOL» facility(1977 - 1986), SIC (1989-1997) and «Kolibry» mockup facility (1992-1997). At present there are operated two chains of glove boxes to fabricate fuel pins by vibropacking, which are used for carrying out different experimental programs and for producing fuel pins and SA of BOR-60 regular loading.

More than 25-year-old experience in manufacturing enabled to set forth the fundamental principles of the vibropack oxide fuel pin fabrication, to exercise the base technologic schedules, to choose the range of products and equipment performances. In sum there were manufactured about 30000 fuel pins, which became the base for mounting 730 fast reactor subassemblies.

During the pilot operation of the automatic line the yield of serviceable production was more than 98 %. In fabricating fuel pins manually at the technologic line, located in the shielded glove box (-1300 BN-350 fuel pins, -300 BN-600 fuel pins, -9000 BOR-60 fuel pins), the yield of serviceable fuel pins was 100 % almost in all quality parameters under check.

4.Waste handling.

Handling with waste and utilizable products, which are the result of granulated fuel, fuel pins and SA production technology can be divided into some processes:

- Reprocessing recycle products, arising from granulated fuel preparation and fuel pin fabrication.
- The processes of purifying gases being released of chlorine, high-volatile salts and radioactive aerosols.
- Purifying spent electrolyte (salt -solvant) of impurities.
- Burning and purifying combustible waste.

Besides there were developed the methods of extracting uranium and plutonium from the slime upon purifying the salt and the way of extracting U and Pu from the solutions after decontamination of high-radioactive equipment units.

All the NM content waste and utilizable products, arising from fuel and fuel pin fabrication, are placed into individual containers and sampled (if possibly) to analyze NM contents. Upon determining uranium and plutonium contents they are recycled in chlorator-electrolyzer followed by producing conditional fuel. Before starting the recovery, the waste are accumulated and stored in the shielded cell.

Evaluative data on waste amount are presented in table 4.1 and 4.2

Table 4. 1

Solid radioactive waste in fabricating MOX-fuel at SIC
(estimation at annual capacity 1000 kg of fuel)

Waste title	waste yield, kg/kg fuel	Waste amount, kg per year	Fission material content, g/kg of waste	
			Pu	U
High-active products, being sent to Storage (in increasing effective output almost 1000 kg will be re-processed to extract Pu)				
Concentrate upon purifying salt	0.0 13	13	0,02 %	0,08 %
Tatters, cleaning and packaging materials	0.02	20	0,033 %	0,040 %
High-active waste, being shipped to burial				
equipment made of pyrographite	0.2	200	0.4	1.6
Filters	0.13	130	0.7	1.5
Low-active solid waste, being shipped to burial				
Units of metal equipment, aids of check and remote operation (after decontamination).	0.7	700		

Table 4.2

Liquid radioactive at SIC
(estimation at annual capacity 1000 kg of fuel)

Waste title	Specific activity, Cu/l (Bk/l)	Quantity, l/per year	Product content, g/l	
			Pu	U
The solution after ÓÐÏÕ*	3.1×10^{-6} (1.15×10^{5})	2×10^{5}	5×10^{-5}	1.5×10^{-4}
Dissorbent solutions	$8.7 \times 10^{-9} - 1 \times 10^{-7}$ $(3.2\text{-}37) \times 10^{2}$	12×10^{5}	$1.4 \times 10^{-7} \div 1.6 \times 10^{-6}$	4.2×10^{-7} t4.8×10^{-6}

*ÓÐÏÕ - facility of recirculation and chlorine absorption.

S.Analysis of safety of fuel cycle processes on the basis of «dry» pyroelectrochemical fuel reprocessing and vibropacking technology.

The perspective direction of nuclear fuel cycle safety elevation is a transition to the technologies, which possess a high level of «inherent» safety. In other words, besides engineering barriers of safety in these technologies, the properties of the systems and processes themselves are natural barriers and minimize harmful effect on the environment both under normal and under extreme conditions. The process of nuclear oxide fuel pyrochemical recycling in the chlorides melt and the technology of remote fuel pin fabrication by vibropaking can be ascribed to the enhanced safety technologies.

5.1 Radiationsafety

Vibropacking and pyrochemical technologies have a number of features, which reduce the yield of active substances in movable phase (gas or liquid):

- Fuel of pyrochemical origin exists as a crystalline product. Crystalline PuO_2 (of energetic isotope composition) generates 1.5×10^3 as less aerosols, than analogous product does after oxalate precipitation and annealing. As a result, decontamination of the facilities and shielded cells after work with granulate takes less time than it does after handling of powder.
- In reprocessing there are used the molten mixture of alkaline metal chlorides (for example NaCl-KC1 or NaCl-2CsCl - ionic liquids). While dissolving all the fuel components pass into cloride form, but the properties of their solutions in ionic liquids are so that vapors volatility decreases by several orders of magnitude lower. This reason prevents radioactive elements from going out of chemical reactions zone (except for high-volatile substances $SbCl_3$, $TeCl_3$ and etc.). In an emergency the melt solidifies and transmutes into a salt monolith, which doesn't generate aerosols, and in contacting with water the melt slowly dissolves off the surface.
- As the systems deal with concentrated materials, liquid and solid medium-active and low-active waste are practically absence. High-active waste (HAW) has FP high concentration and leads to the necessity of diluting them. The dilution can be combined with HAW introduction in the stable matrix to be buried finally.

To estimate internal safety of the technologic processes there are used the criteria, characteristic of which are given in Table 5.1. The data are the results of

- large-scale experiments on uranium-plutonium oxide (with energetic plutonium) fuel production by pyroelectrochemical way and on pilot SA/fuel pin fabrication for BN type reactor by vibropacking,
- experimental recycling of irradiated uranium and uranium-plutonium oxide fuel at the pilot facilities.

The interval of numerical criteria values for waste are due to the differences in their compositions and in their reprocessing. A high radiological danger along with both energetic plutonium and actinides (Np, Am, Cm) toxicity demanded, that two level of the personnel and environmental protection should be envisaged when realizing the recycle.

- The first level includes the sealing of technologic equipment, transport and transfer containers, the usage of pneumo-mail.
- the second level includes - the sealing of boxes and cells; two-stage purification of the air, carried off out of them; usage of unfailed electromechanical manipulators; the system of shielded cell and equipment decontamination.

Employing technologic processes with high internal safety and additional safety barriers enabled to implement large-scale (-500 kg) plutonium recycle under minimum radiation effect on the personnel and the environment. Average joint personnel dose was 0.065 person*Zv/per year; and maximum dose of man-caused effect didn't exceed 0.2 % dose of natural background. It is shown, that the content of plutonium and transplutonium elements in the environmental objects hasn't increased and is at the global background level. For example, plutonium content in soils is 0.5 - 3.0 Bk/kg, in the free air - $(0.4 - 1\,1)*10^{-7}$ Bk/m^3.

Table 5.1

Criteria of estimation of internal safety for fuel cycle technologic processes

No	Criteria	Dimensionality	Value
1	Direct plutonium yield in ready product	- %	99,3 - 99,7
2	Plutonium ratio in the products, returned in technological cycle	%	0,2 - 0,6
3	Irretrievable loss	%	$\leq 0{,}015$
4	HAW yield	kg/kg of fuel	1,0
5	HAW radiation stability	$W/ñm^3$ gr	3,5 $3{,}5 \cdot 10^7$
6	HAW thermal stability (up to vitrification)	$^0Ñ$	500 - 900
7	HAW chemical stability (up to vitrification): • leachability in ^{137}Cs • pass in gas phase ^{137}Cs	 $g/(ñm^2 \cdot days)$ $g/(ñm^2 * days)$	 $1 \cdot 10^{-5} - 1 \cdot 10^{-4}$ $1 \cdot 10^{-11} - 4 \cdot 10^{-8}$
8	Activity outlet in aerosols (alpha-radiator)	% of fuel activity	$< 1 \cdot 10^{-3}$
9	Volume activity of alpha-nuclides under conditions of shielded cell and glove box atmosphere in handling energetic plutonium	Bk/l	< 37,0

These conclusions are verified with safety implementation of some experiments on the irradiated fuel reprocessing:

- with short exposure time - 6-7 months (1972 , UO_2-fuel of ÁÎÐ-60 reactor, burnup 7.7%),
- with high burnup - 21-24% (1995, ÌÎÕ-fuel of ÁÎ D60 reactor with the exposure time for 3.5 and 2.5 years).

5.2 *Nuclear safety underpyrochemical reprocessing*

Using the salt melts and unavailability of aqueous solutions excluded neutron moderators and reflectors from the technological system. The fact, that uranium and plutonium are only in two states - oxide and chloride enable to work in the same apparatus with large quantity of fission materials:

- up to 39 kg of uranium dioxide with 90% enrichment in U-235 before and after dissolving in chlorator-electrolyzer
- up to 30 kg of energetic grade plutonium dioxide before and after dissolving in the chlorator-electrolyzer.

Nuclear safety in operating is provided with the following technologic decisions:

- the solvent of fuel components - the salt melt exists in liquid state only under great apparatus heating, which excludes the possibility of solvent's random transfer to other crucibles, in which the conditions for FM accumulation and SCR (self-chain reaction) occurrence could be arisen;
- processes are carried out batch-by-batch and FM quantity control is performed by weighing without chemical analysis;
- the technology of recycling makes it possible to exclude completely water application, because the process of vacuum topping is developed to remove the salts from the products. (Sometimes the operation is carried out in the presence of limited water and spirit quantity, at that FMs are in crystalline state, they are not dissolved and dispersed, therefore there are no conditions to reduce FM critical mass.)

5.3 Technical and chemical safety of reprocessing

Technical and chemical safety are due to the technical decisions, worked out in studying high-temperature processes, using chlorine and salt melts, for a long time. The following decisions are the principal ones:

- Chemical medium (the melt of salts) neither is subjected to radiolysis, nor generates hydrogen and detonating gas.
- Low fire risk is provided with unavailability of appreciable quantity of organic substances and reagent-oxidizers in the technologic processes. The equipment is located in the rooms of limited volume and faced with metal coating. Local combustion of cables, rubber hoses within the cells can be easily eliminated either by inert gas or by dry salt.
- The process doesn't use explosive gases and substances, when blending there were no generated explosive mixtures.
- Drastic poison substance - chlorine - is employed restrictedly, is delivered in balloons of 60 l capacitance. Chlorine is supplied from the reservoir of reduced down to 0,2 Mpa gas pressure by batch. There have been carried experimental investigations to provide in future sharp volume reduction of the chlorine being used by recycling with cryogen technology.
- Applying dried air in the cells under much higher temperatures than dew point minimizes equipment corrosion due to chlorine gas. The conclusion is supported by long experience in working under shielded cell condition.

5.4 Safety from the viewpoint of non-proliferation criteria

Radiation characteristic of the product, obtained in reprocessing irradiated oxide fuel by pyrochemical way, diminish the probability of its unauthorized usage owing to low factors of purification and separation and, therefore, high radiation intensity.

Fig.3.1 shows comparative experimental data on oxide fuel activity of BOR-60 reactor before and after reprocessing. It is obvious, that recovered fuel remains in the limits of irradiated fuel standard on the radiation characteristic. Due to high fuel activity any fuel movements are easy to monitore, which decrease greatly the probability of its embezzlement.

The technologic cycle is defended against unauthorized interference with some barriers:

- The first, «engineering» barrier, is the technologic equipment itself, in which FMs are stored, and the shielded cells, the equipment is located in.
- Another specific barrier is chemical stability of the pyrochemical product. The experiment proves, that pyrochemical PuO_2 is almost insoluble in aqueous acid solution. In order to separate it either in PUREX-process or in an analogous system there is required special development of the method and the equipment to solve pyrochemical PuO_2.
- The third «barrier» is the chief principle of fuel handling - discreteness, which gives us two merits:
    - in technologic line there is carried out treating fuel batch and products, so simple check by weighing and monitoring facilitate all the inspection procedures.
    - unavailability of liquid flows in the system and reservoir-storage allows us to follow FM position at any point of technologic line at each instant time.

As for vibropacking technology it should be noted, that the process has fewer operations to control FMs in comparison with the technology of pellets and fuel pins fabrication. As a whole, the technologies, developed in SSC RF RIAR, not only facilitate and simplify FM control and accounting, but also make them (MC&A) much cheaper.

Thus, in terms of comprehensive safety, pyroelectrochemical recycling and vibropacking technologies enable to implement a new elevated level of fuel cycle safety in FM recycle field.

There is posed a reasonable question: whether these investigations are sufficient for commercial introduction? It can be answered positively. And in terms of historic analogies we have to state, that the gained experimental experience agrees with the investigation scope, which preceded commercial introduction of up-to-date fuel cycle technologies, such as PUREX-process, UOX-pellet technology, pellet MOX-fuel technology.

The work results of the last few years allow us to give a new look at the data massif, which is compiled in SSC RF RIAR and is realized at Semi-Industrial Complex. In our opinion, the Complex can serve as a flexible model of pilot plants on precommercial adaptation both of dry reprocessing technology and vibropacking one. One of the variants, using SIC model, is «nuclear island», including the facility of fuel recycle and 2 fast reactors. From primary estimations we can suppose, that this Complex will be competitive with VVER type reactors, and simultaneously the problem of radioactive waste will be solved.

6.CONCLUSIONS

Thus, complex of "dry" technologies and granulated fuel vibropacking in combination with unique properties of vibropack fuel pin enables to realize a new comprehensive approach to the fuel cycle problem, including the one of using different grade plutonium. Mass tests of vibropack uranium-plutonium oxide fuel pins in BOR-60 reactor, successful tests of experimental SA in BN-600, reliable operation of SIC facilities allow making a conclusion on a real possibility of developing safety, profitable uranium-plutonium fuel cycle on the basis of the set forth technologies, and recovering energetic and weapon grade plutonium in nuclear reactors under providing the reliable MC&A system as well.