



# System of Pyro Reprocessing

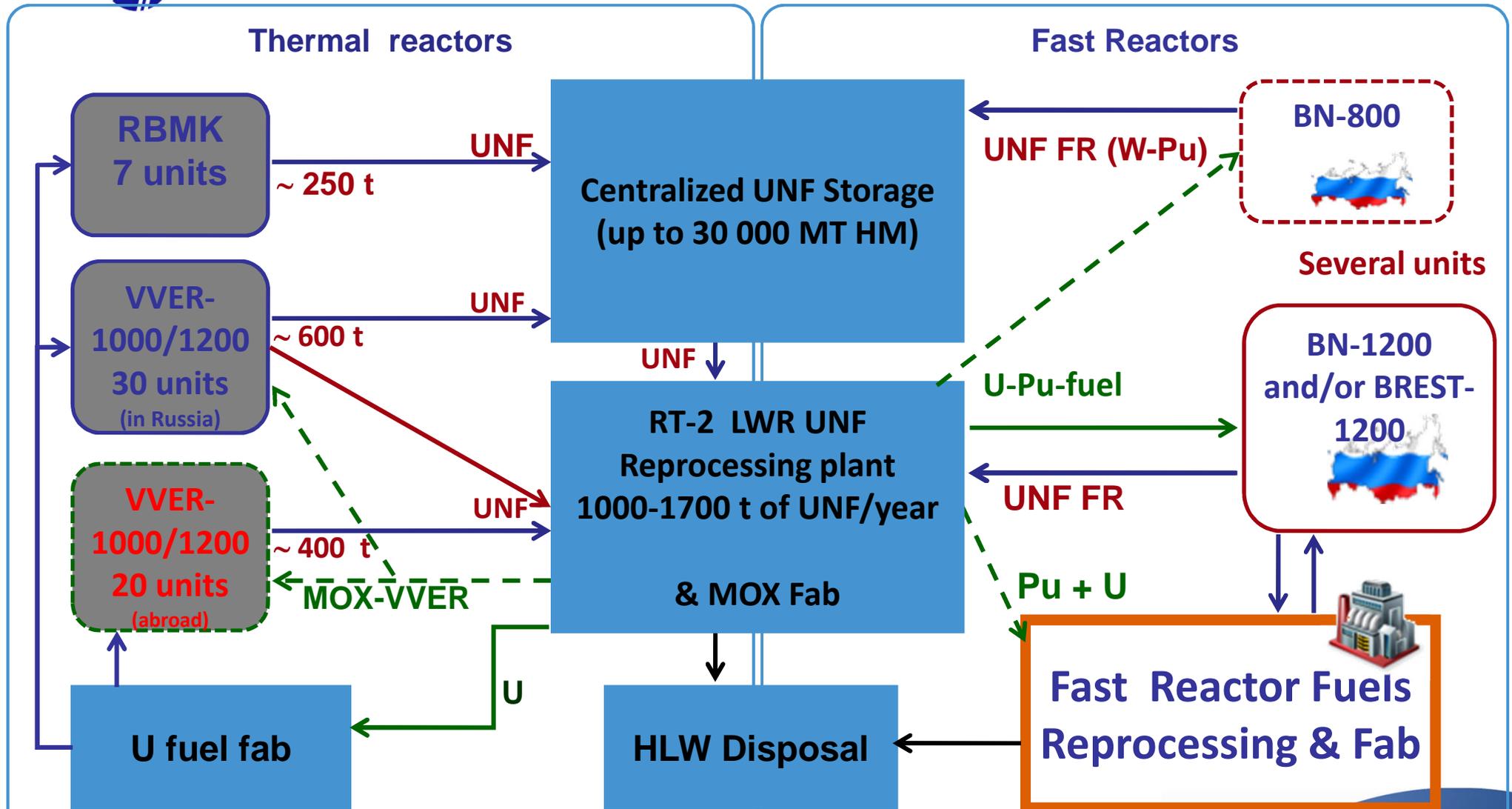
## RAW Treatment

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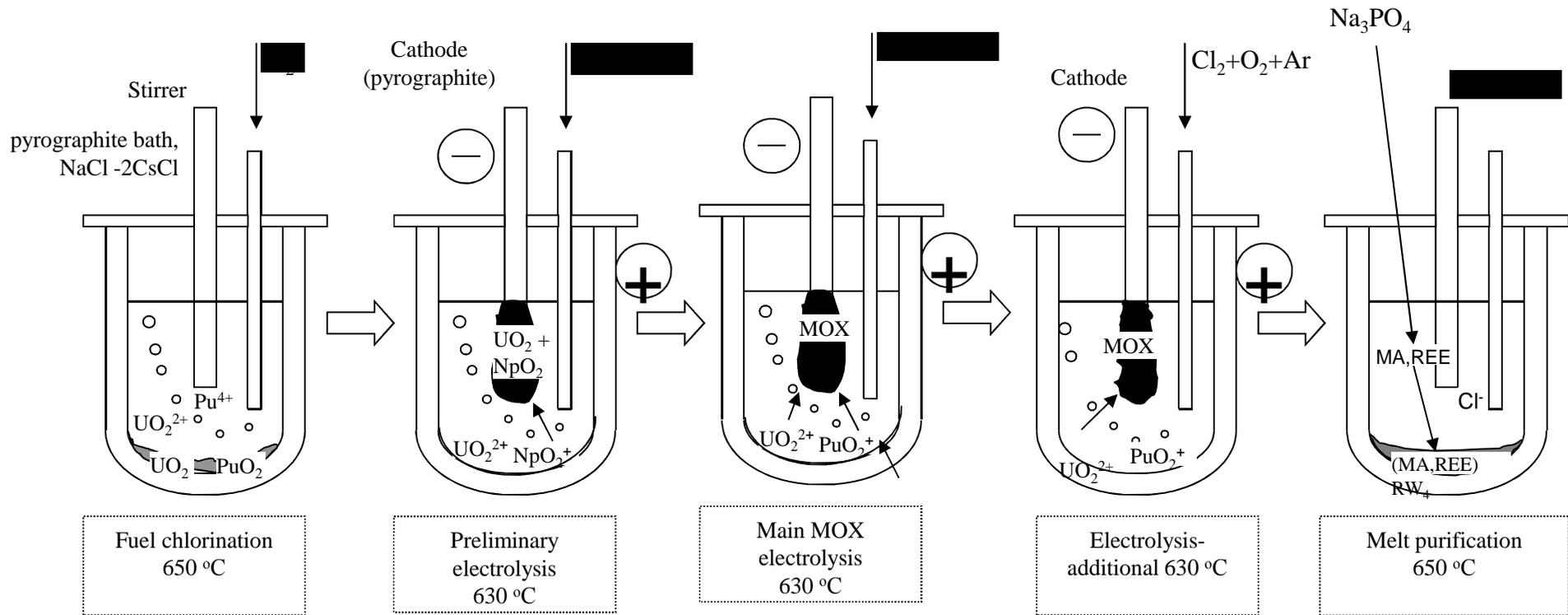


# INTERACTION OF THERMAL AND FAST REACTOR'S FUEL CYCLES



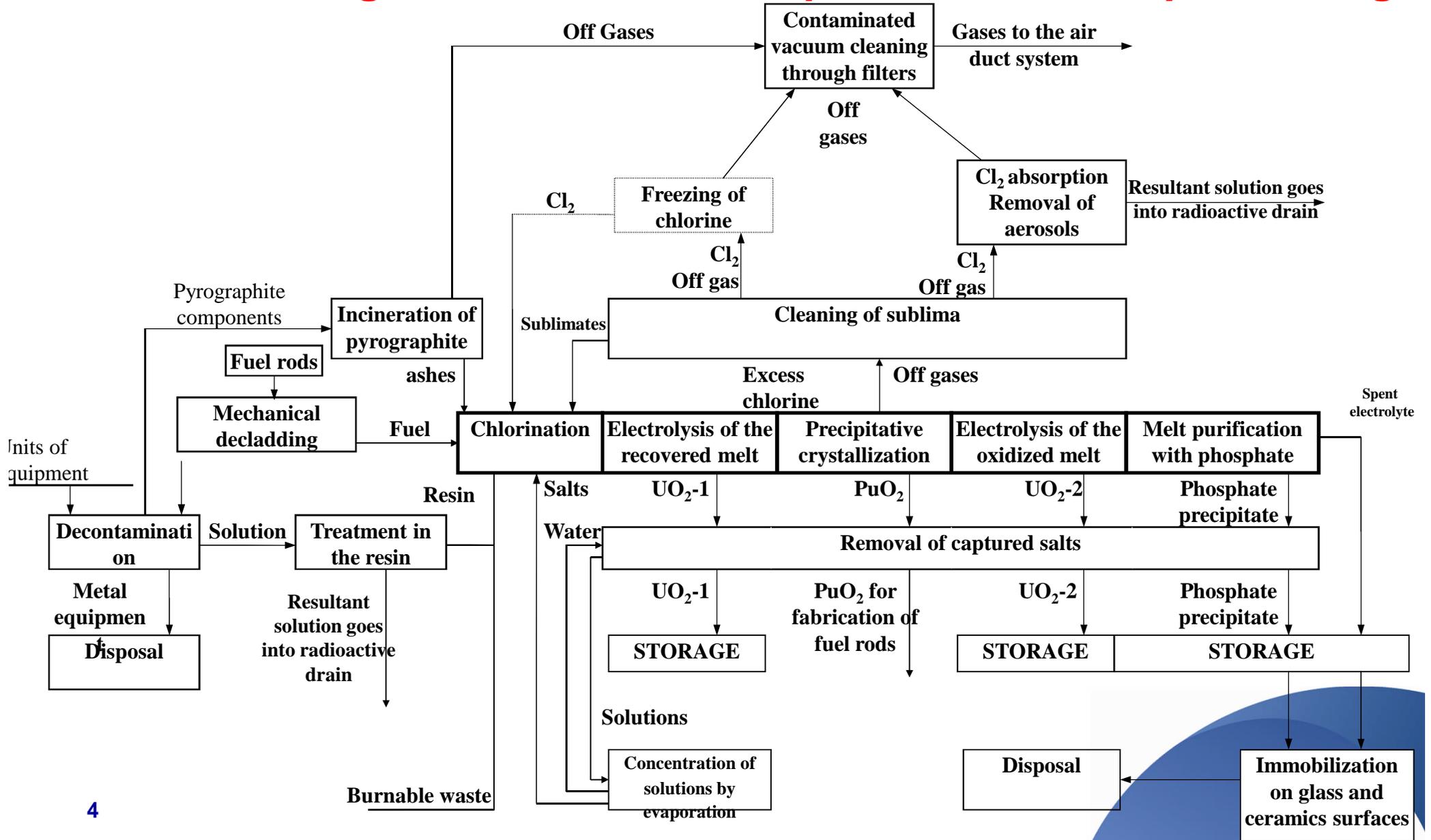
**Model of RUSSIAN Integrated UNF Management System for 2025-2030**

## Dimitrovgrad dry Process (DDP) MOX→MOX flow sheet





# Integrated flow sheet of spent MOX-fuel reprocessing



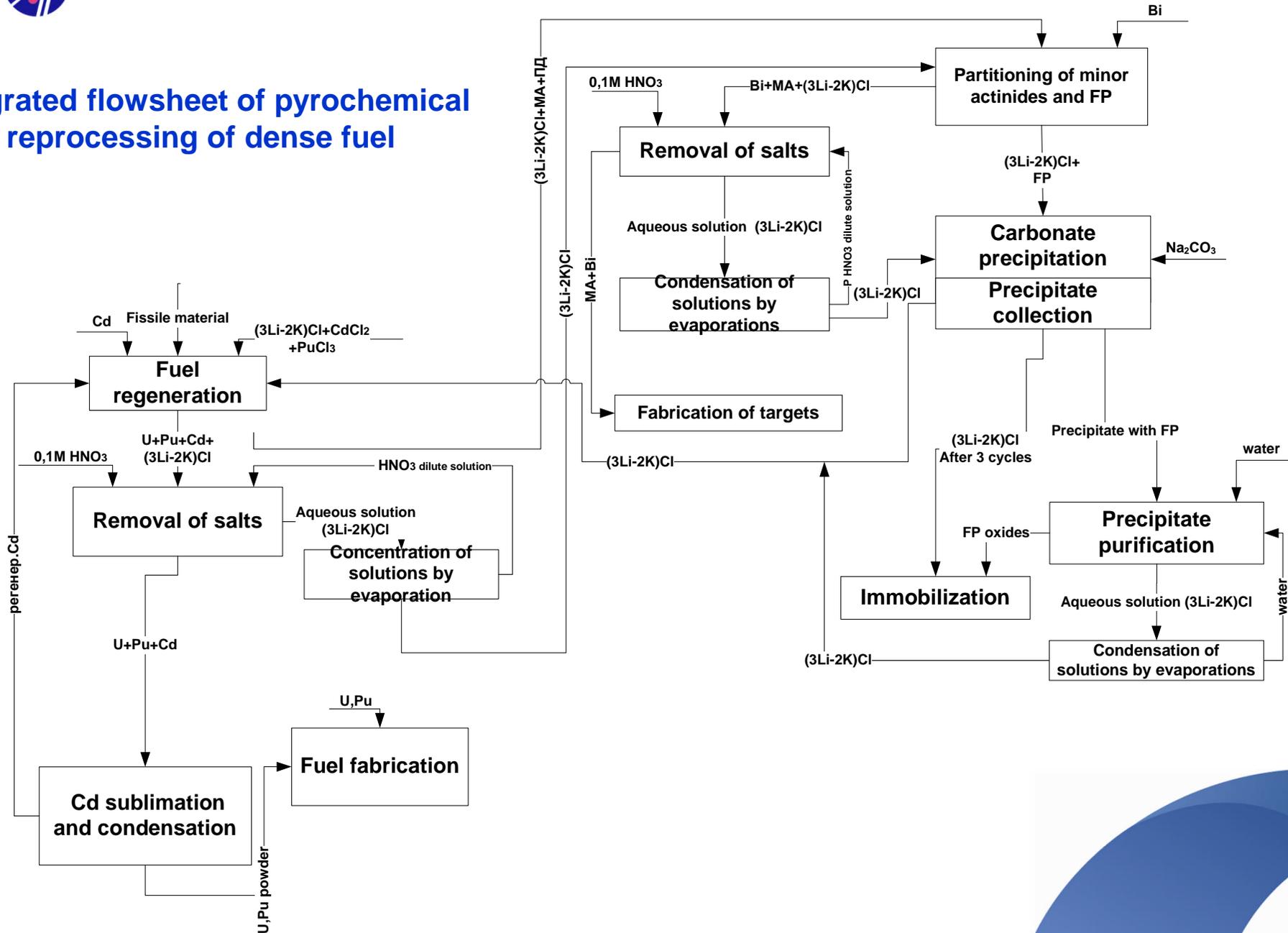


## Summary of the MOX-fuel reprocessing process and main types of radioactive waste

The MOX-fuel to be reprocessed is subjected to mechanical decladding, grinding to a powder and loaded into the head device- chlorator - electrolyser. All the operations of pyroelectrochemical reprocessing are carried out in the device. The sequence of operations is as follows:

- Fuel chlorination in molten NaCl-KCl; LiCl-NaCl-KCl-CsCl;
- Electrolysis for removal of  $UO_2-1$  with some fission products (FPs) captured by cathodic deposit;
- Precipitative crystallization of  $PuO_2$  decontaminated from FPs and other impurities;
- Additional electrolysis for removal of  $UO_2-2$  with deposited FPs and other impurities;
- Molten salt purification by introduction of phosphates into the melt.

## Integrated flowsheet of pyrochemical reprocessing of dense fuel





## Summary of the so called “dense” SNF (nitride, metal) reprocessing process and main types of radioactive waste

The basic processes include the following stages of the dense SNF reprocessing:

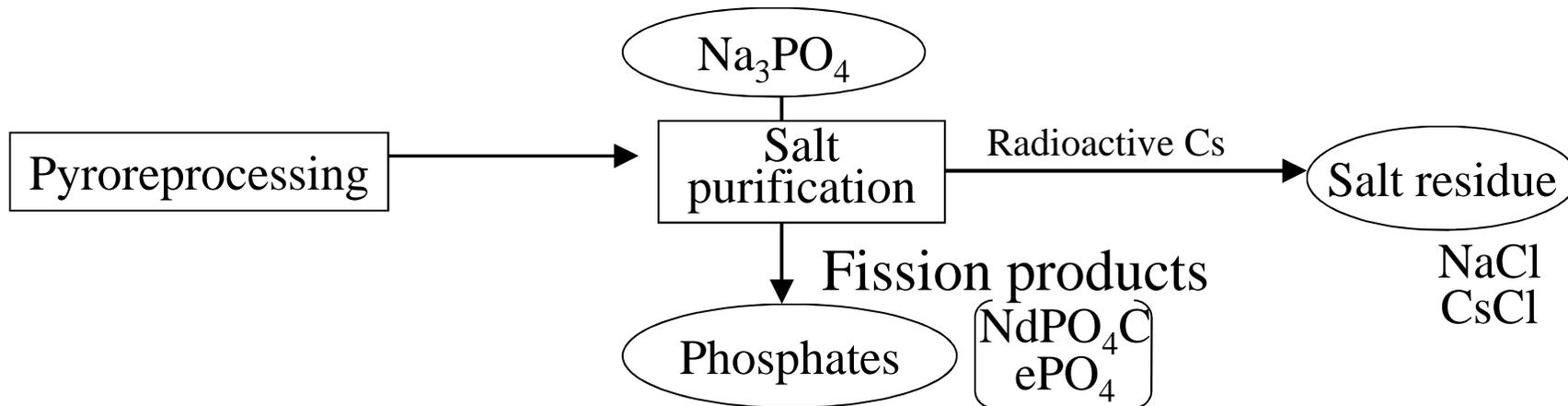
- Anodic dissolution with cadmium cathode in molten  $3\text{LiCl}-2\text{KCl}$
- Evaporation of liquid cadmium followed by separation fissile materials for further manufacturing of metallic and nitride fuel.
- MA partitioning from fission products in a liquid metallic cathode
- Precipitation of REE by  $\text{Li}_2\text{O}+\text{K}_2\text{O}$  through introduction of carbonate, collection and removal of salts
- Immobilization of the resultant oxide product and spent electrolyte (after repeated use).



## DDP Pyro HLW

HLW type	Phosphate or oxide concentrate	Spent electrolyte	Technological wastes	Pyrographite
Origin	Products after purification of molten salt	Spent Salts after accumulation of Cs and Sr	Fuel pin claddings, metallic equipment	Crucible structural materials
Characteristics	Crystalline fine powder containing REE and MA	Alkaline metals chlorides	Metallic wastes	Combustible wastes
Treatment procedures	Intermediate storage  <b>Vitrification or Ceramization</b>	Intermediate storage  <b>Vitrification or Ceramization</b>	Compactification  Disposal	Grinding, Flameless burning, Recycling of Ash into head of reprocessing

## DDP Pyro Wastes treatment



	Phosphates	
<b>Special features</b>	contain fission products	<b>Alkaline metal chlorides, high activity, significant heat release</b>
<b>Basic elements</b>	<b>11 wt.% Nd 4,4 wt.% Ce</b>	<b>81,96 wt.% CsCl 18,04 wt.% NaCl</b>
<b>Quantity*</b>	<b>&lt;0,15 kg/kg of fast reactor SNF</b>	<b>&lt;0,03 kg/kg of fast reactor SNF</b>

**\* Data by TOSHIBA estimation for DDP**

## HIGH LEVEL WASTE FROM PYROCHEMICAL PROCESSES AND THEIR SPECIFICATION

### Phosphate precipitates

As a result of the BOR-60 fuel reprocessing (an ultra high burn-up of 21-24% h.a) phosphate precipitate was obtained

#### Some characteristics of phosphate precipitate

Weight, g	Bulk density, g/cm <sup>3</sup>	Specific heat release, W/kg	Specific radioactivity, Ci/g	
			α-nuclides	γ-nuclides
442	0.6-0.7	9.5	9.3·10 <sup>-2</sup>	1.0

#### Radioactivity of nuclides in phosphate precipitate, Bq/g (%)

<sup>106</sup> Ru+ <sup>106</sup> Rh	1.7·10 <sup>7</sup>	<sup>154</sup> Eu	7.8·10 <sup>8</sup>	<sup>241</sup> Am	3.2·10 <sup>9</sup> (92.5)
<sup>144</sup> Ce+ <sup>144</sup> Pr	3.3·10 <sup>10</sup> (90)	<sup>155</sup> Eu	0.3·10 <sup>10</sup> (9)	<sup>242</sup> Cm	6.3·10 <sup>7</sup>
<sup>137</sup> Cs	1.6·10 <sup>7</sup>	<sup>54</sup> Mn	4.8·10 <sup>6</sup>	<sup>244</sup> Cm	2.1·10 <sup>8</sup>
<sup>125</sup> Sb	1.3·10 <sup>7</sup>	<sup>60</sup> Co	1·10 <sup>6</sup>		

## HIGH LEVEL WASTE FROM PYROCHEMICAL PROCESSES AND THEIR SPECIFICATION

### Phosphate precipitates

Hydrolysis tests on phosphate precipitate revealed that the  $^{134}\text{Cs}$  and  $^{137}\text{Cs}$  isotopes make for 55% to 88% of the solution activity, the  $^{144}\text{Ce}$  (Pr) isotopes make for 6.8% to 21% of activity and  $^{125}\text{Sb}$  produces from 4.5% to 16% of activity (see Table ).

Release rates of nuclides from phosphate precipitate  
(% as to the nuclide activity in the sample, distilled water, 20°C).

Nuclides	Duration of hydrolysis tests, days				
	1	3	7	28	100
$^{137}\text{Cs}$	2.2	1.0	0.7	0.2	0.06
$^{144}\text{Ce(Pr)}$	$3.9 \cdot 10^{-4}$	$1.6 \cdot 10^{-4}$	$8 \cdot 10^{-5}$	$4.7 \cdot 10^{-5}$	$3.5 \cdot 10^{-5}$
$^{125}\text{Sb}$	0.1	0.07	0.07	0.03	0.02
Total of $\gamma$ -nuclides	$5.3 \cdot 10^{-3}$	$2.3 \cdot 10^{-3}$	$1.7 \cdot 10^{-3}$	$5.3 \cdot 10^{-4}$	$2.1 \cdot 10^{-4}$
Total of $\alpha$ -nuclides	$2.9 \cdot 10^{-4}$	$7.2 \cdot 10^{-5}$	$5.5 \cdot 10^{-5}$	$2.5 \cdot 10^{-5}$	$2.1 \cdot 10^{-5}$

## HIGH LEVEL WASTE FROM PYROCHEMICAL PROCESSES AND THEIR SPECIFICATION

### Oxide precipitate

In Dec. 2010, 26 g of oxide concentrate were obtained as a result of dense fuel reprocessing

### Characteristics of real oxide precipitate

Precipitate weight, g	Content of some components and radionuclides				
	Pu, mass%	<sup>241</sup> Am, Bq/g	<sup>137</sup> Cs, Bq/g	<sup>154</sup> Eu, Bq/g	<sup>144</sup> Ce, Bq/g
26	<0.001	$5.4 \cdot 10^6$	$3.1 \cdot 10^4$	$1.0 \cdot 10^7$	$8.6 \cdot 10^6$





# HIGH LEVEL WASTE FROM PYROCHEMICAL PROCESSES AND THEIR SPECIFICATION

## Spent electrolytes

As an example, we refer to the spent electrolyte generated after high burnup fuel reprocessing of the BOR-60 reactor (1995).

As a result of reprocessing 8.1 kg of molten alkali chlorides remained. Their original composition was LiCl-4.53NaCl-4.88KCl-0.66CsCl.

### Chemical and radionuclide composition of spent electrolyte

U weight %	Pu weight %	Activity of α-nuclides GBq/kg	Activity of γ-nuclides, GBq/kg							
			<sup>106</sup> Ru (Rh)	<sup>125</sup> Sb	<sup>134</sup> Cs	<sup>137</sup> Cs	<sup>144</sup> Ce (Pr)	<sup>147</sup> Pm	<sup>154</sup> Eu	<sup>60</sup> Co
<0.001	<0.001	0.2	1.9	0.7	151.7	2024	200	33.3	5.9	0.1



# Vitrification of HLW from DDP pyro reprocessing

Characteristic	HLW type		
	Phosphate precipitate	Spent salt electrolyte	Phosphate precipitate + spent salt electrolyte
<b>Glass matrix type</b>	<b>Pb(PO<sub>3</sub>)<sub>2</sub> NaPO<sub>3</sub></b>	<b>NaPO<sub>3</sub>, AlF<sub>3</sub> Al<sub>2</sub>O<sub>3</sub></b>	<b>NaPO<sub>3</sub>, AlF<sub>3</sub> Al<sub>2</sub>O<sub>3</sub></b>
<b>Introduction method</b>	vitrification, T=950°C	vitrification without chloride conversion, T=950°C	vitrification without chloride conversion, T=950°C
<b>Introduced waste amount, %</b>	<b>28</b>	<b>20</b>	<b>36</b>
<b><sup>137</sup>Cs leaching rate</b> as of the 7 <sup>th</sup> day, g/cm <sup>2</sup> * day	<b>7*10<sup>-6</sup></b>	<b>7*10<sup>-6</sup></b>	<b>4*10<sup>-6</sup></b>
<b>Thermal resistance, °C</b>	<b>400</b>	<b>400</b>	<b>400</b>
<b>Radiation resistance</b>	<b>10<sup>7</sup> Gr</b> (for γ and β)		<b>10<sup>18</sup> α-decay/g</b>

## Vitrification of HLW after pyrochemical processes

### Vitrification of phosphate precipitates

A possibility is shown to embed the phosphate precipitate in the alumofluophosphate glass

The real phosphate precipitate generated after BOR-60 fuel reprocessing contains 22.3% of REE and 14.7% of iron; 96% of activity is given by  $^{144}\text{Ce}$  (Pr), while 86% of alpha-activity is given by  $^{241}\text{Am}$ .

A composition of glass matrix and waste was selected to carry out a real experiment: ( $\text{NaPO}_3$ -75 %,  $\text{AlF}_3$ -10%,  $\text{NaF}$ -5 %,  $\text{Al}_2\text{O}_3$ -10%)-85%, phosphate precipitation - 15%.

At the vitrification stage ( $T=1000^\circ\text{C}$ ), the release of activity into the gas phase made up  $2.8 \cdot 10^{-3}$  and  $1.0 \cdot 10^{-4}$  % of the initial phosphate precipitate activity for  $\gamma$  - and  $\alpha$  -emitters, respectively. Among the  $\gamma$  -emitters,  $^{125}\text{Sb}$  (51,6 %) and  $^{137}\text{Cs}$  (41,9 %) made the key contribution to the gas phase activity; as for the  $\alpha$ -emitters, it was  $^{241}\text{Am}$  (92 %). Thermal conductivity of the vitrified waste made up 0.8-1.1W/(m $\cdot$ °C) at 35-300°C that was an admissible level for the phosphate glass [10, 11].





## Vitrification of HLW after pyrochemical processes vitrification of phosphate precipitates

Rate of components leaching from radioactive glass sample P-1  
with phosphate precipitate at T=20-25°C, g/(cm<sup>2</sup>\*day).

Nuclides	Test duration							
	3 <sup>rd</sup> day	7 <sup>th</sup> day	14 <sup>th</sup> day	21 <sup>st</sup> day	28 <sup>th</sup> day	58 <sup>th</sup> day	88 <sup>th</sup> day	118 <sup>th</sup> day
Al	2.1·10 <sup>-6</sup>	2.2·10 <sup>-6</sup>	1.5·10 <sup>-6</sup>	2.3·10 <sup>-7</sup>	2.4·10 <sup>-7</sup>	2.7·10 <sup>-7</sup>	1.0·10 <sup>-7</sup>	8.9·10 <sup>-8</sup>
Na	1.2·10 <sup>-5</sup>	7.4·10 <sup>-6</sup>	7.2·10 <sup>-6</sup>	6.3·10 <sup>-6</sup>	4.5·10 <sup>-6</sup>	3.4·10 <sup>-6</sup>	1.1·10 <sup>-6</sup>	5.2·10 <sup>-7</sup>
P	3.0·10 <sup>-6</sup>	2.9·10 <sup>-6</sup>	8.4·10 <sup>-7</sup>	3.2·10 <sup>-7</sup>	3.5·10 <sup>-7</sup>	5.1·10 <sup>-7</sup>	2.7·10 <sup>-7</sup>	1.6·10 <sup>-7</sup>
F	7.0 ·10 <sup>-6</sup>	6.9·10 <sup>-6</sup>	5.1·10 <sup>-6</sup>	4.3·10 <sup>-6</sup>	2.4·10 <sup>-6</sup>	1.5·10 <sup>-6</sup>	7.9·10 <sup>-7</sup>	7.7·10 <sup>-7</sup>
<sup>125</sup> Sb	6.9·10 <sup>-6</sup>	2.4·10 <sup>-6</sup>	1.3·10 <sup>-6</sup>	8.1·10 <sup>-7</sup>	7.4·10 <sup>-7</sup>	2.4·10 <sup>-7</sup>	2.4·10 <sup>-7</sup>	2.2·10 <sup>-7</sup>
<sup>137</sup> Cs	2.2·10 <sup>-5</sup>	9.7·10 <sup>-6</sup>	5.6·10 <sup>-6</sup>	3.9·10 <sup>-6</sup>	2.8·10 <sup>-6</sup>	2.7·10 <sup>-6</sup>	1.6·10 <sup>-6</sup>	9·10 <sup>-7</sup>
<sup>144</sup> Ce( <sup>144</sup> Pr)	1.2·10 <sup>-6</sup>	1.2·10 <sup>-6</sup>	4.1·10 <sup>-7</sup>	3.6·10 <sup>-7</sup>	2.3·10 <sup>-7</sup>	6.4·10 <sup>-8</sup>	3.8·10 <sup>-8</sup>	2.4·10 <sup>-8</sup>
<sup>154,155</sup> Eu	1.6·10 <sup>-6</sup>	1.8·10 <sup>-6</sup>	6.3·10 <sup>-7</sup>	5.0·10 <sup>-7</sup>	4.6·10 <sup>-7</sup>	1.3·10 <sup>-7</sup>	7.8·10 <sup>-8</sup>	4.8·10 <sup>-8</sup>
<sup>241</sup> Am	1.1·10 <sup>-6</sup>	8.7·10 <sup>-7</sup>	6.6·10 <sup>-7</sup>	4.9·10 <sup>-7</sup>	3.3·10 <sup>-7</sup>	8.8·10 <sup>-8</sup>	5.9·10 <sup>-8</sup>	3.9·10 <sup>-8</sup>
<sup>242,244</sup> Cm	1.2·10 <sup>-6</sup>	8.5·10 <sup>-7</sup>	6.7·10 <sup>-7</sup>	5.0·10 <sup>-7</sup>	3.4·10 <sup>-7</sup>	9.3·10 <sup>-8</sup>	6.5·10 <sup>-8</sup>	4.4·10 <sup>-8</sup>



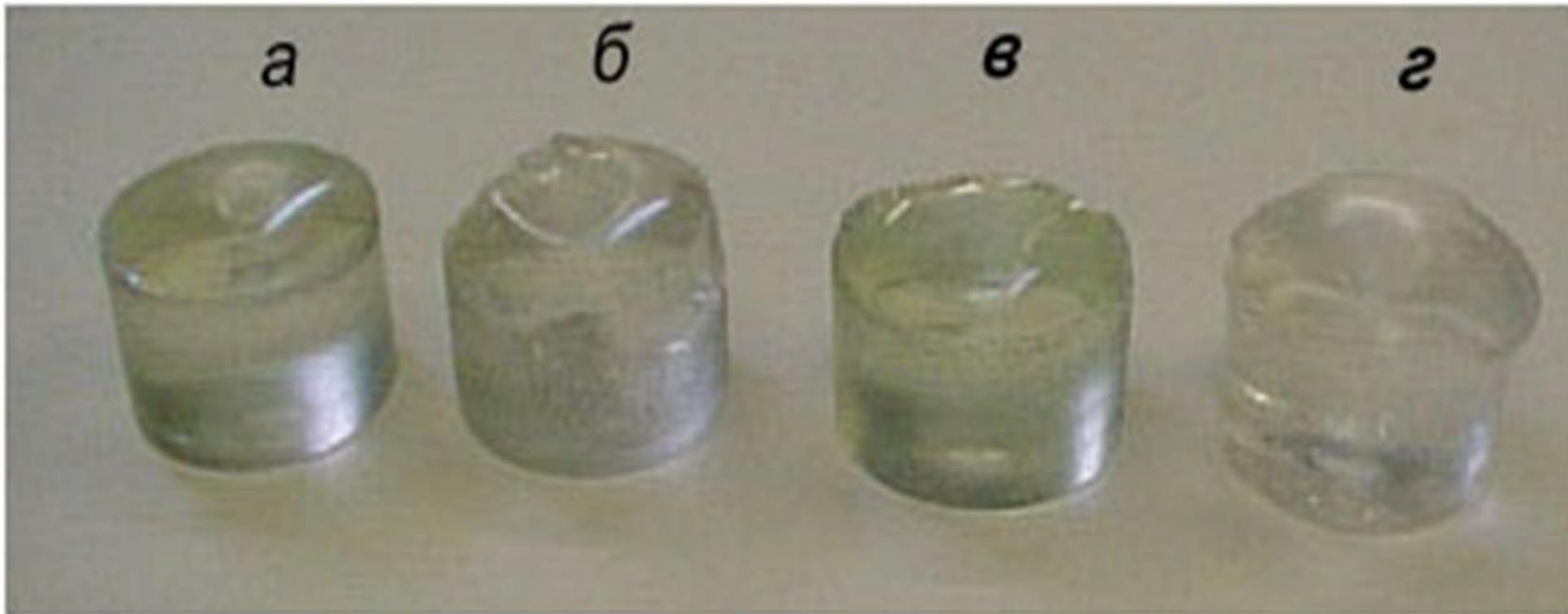
## Immobilization of spent electrolyte by vitrification (2010)

**Content of glass charge mixture, % wt.**

Sample No	NaPO <sub>3</sub>	AlF <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	BeO	3LiCl-2KCl	3LiPO <sub>3</sub> -KPO <sub>3</sub>
M - 1	67,5	17,1	-	5,4	10	-
M - 2	10	17	-	3	-	70
M - 3	10	17	3	-	-	70
M - 4	67,5	18	4,5	-	10	-
R - 1	67,5	18	4,5	-	10	-
R - 2	10	17	3	-	-	70

**Characteristics of samples**

Parameter	M-1	M-2	M-3	M-4	R-1	R-2
Weight, g	39,2	39,8	32,97	33,1	29,1	47,59
Diameter, mm	31,3	30,9	31,05	30,7	30,7	31
Surface, sm <sup>2</sup>	36,4	35,9	32,69	32,73	31,2	39,4
Density, g/ sm <sup>3</sup>	2,38	2,46	2,42	2,41	2,32	2,52
Radioactivity , Bk / g	-	-	-	-	7,1·10 <sup>6</sup>	2,4·10 <sup>7</sup>



Simulating samples: **M-4 (а)**, **M-5 (б)**, **M-6 (в)**, **M-7 (г)**



## Vitrification of HLW after pyrochemical processes

### Vitrification of spent electrolytes

Rate of glass components leaching from samples  
at 20-25°C, g/(cm<sup>2</sup>·day) (chlorides conversion)

Sample	Component	Test duration, days							
		3	7	14	21	28	58	88	118
M - 4	Na	$1.9 \cdot 10^{-5}$	$1.2 \cdot 10^{-5}$	$6.2 \cdot 10^{-6}$	$5.5 \cdot 10^{-6}$	$1.8 \cdot 10^{-6}$	$2.5 \cdot 10^{-7}$	$2.5 \cdot 10^{-7}$	$2.4 \cdot 10^{-7}$
	Al	$3.3 \cdot 10^{-6}$	$7.8 \cdot 10^{-7}$	$5.3 \cdot 10^{-7}$	$3.0 \cdot 10^{-7}$	$2.6 \cdot 10^{-7}$	$4.3 \cdot 10^{-8}$	$3.6 \cdot 10^{-8}$	$3.3 \cdot 10^{-8}$
	P	$2.3 \cdot 10^{-6}$	$1.1 \cdot 10^{-6}$	$7.0 \cdot 10^{-7}$	$2.6 \cdot 10^{-7}$	$1.7 \cdot 10^{-7}$	$5.5 \cdot 10^{-8}$	$4.6 \cdot 10^{-8}$	$4.0 \cdot 10^{-8}$
	F	$1.8 \cdot 10^{-6}$	$1.5 \cdot 10^{-6}$	$1.1 \cdot 10^{-6}$	$5.1 \cdot 10^{-7}$	$4.0 \cdot 10^{-7}$	$1.2 \cdot 10^{-7}$	$9.4 \cdot 10^{-8}$	$9.4 \cdot 10^{-8}$
M - 5	Na	$8.0 \cdot 10^{-6}$	$5.5 \cdot 10^{-6}$	$4.4 \cdot 10^{-6}$	$3.2 \cdot 10^{-6}$	$2.7 \cdot 10^{-6}$	$8.6 \cdot 10^{-7}$	$5.2 \cdot 10^{-7}$	$5.0 \cdot 10^{-7}$
	Al	$4.8 \cdot 10^{-6}$	$1.1 \cdot 10^{-6}$	$9.4 \cdot 10^{-7}$	$6.9 \cdot 10^{-7}$	$3.4 \cdot 10^{-7}$	$3.7 \cdot 10^{-8}$	$3.6 \cdot 10^{-8}$	$3.6 \cdot 10^{-8}$
	P	$2.5 \cdot 10^{-6}$	$1.2 \cdot 10^{-6}$	$8.5 \cdot 10^{-6}$	$3.6 \cdot 10^{-7}$	$2.6 \cdot 10^{-7}$	$4.9 \cdot 10^{-8}$	$4.9 \cdot 10^{-8}$	$4.3 \cdot 10^{-8}$
	F	$1.8 \cdot 10^{-6}$	$9.1 \cdot 10^{-7}$	$6.3 \cdot 10^{-7}$	$5.2 \cdot 10^{-7}$	$4.5 \cdot 10^{-7}$	$1.2 \cdot 10^{-7}$	$4.8 \cdot 10^{-8}$	$4.9 \cdot 10^{-8}$
P - 2	Na	$1.3 \cdot 10^{-5}$	$4.2 \cdot 10^{-6}$	$1.5 \cdot 10^{-6}$	$8.3 \cdot 10^{-7}$	$7.7 \cdot 10^{-7}$	$5.2 \cdot 10^{-7}$	$4.2 \cdot 10^{-7}$	$4.2 \cdot 10^{-7}$
	Al	$1.7 \cdot 10^{-5}$	$2.5 \cdot 10^{-6}$	$5.6 \cdot 10^{-7}$	$3.2 \cdot 10^{-7}$	$2.8 \cdot 10^{-7}$	$2.1 \cdot 10^{-7}$	$1.0 \cdot 10^{-7}$	$7.9 \cdot 10^{-8}$
	P	$8.3 \cdot 10^{-7}$	$7.1 \cdot 10^{-7}$	$6.3 \cdot 10^{-7}$	$5.0 \cdot 10^{-7}$	$6.2 \cdot 10^{-8}$	$5.0 \cdot 10^{-8}$	$5.5 \cdot 10^{-8}$	$5.3 \cdot 10^{-8}$
	F	$1.0 \cdot 10^{-5}$	$4.2 \cdot 10^{-6}$	$3.9 \cdot 10^{-6}$	$2.9 \cdot 10^{-6}$	$2.4 \cdot 10^{-6}$	$9.6 \cdot 10^{-7}$	$9.6 \cdot 10^{-7}$	$4.1 \cdot 10^{-7}$
	<sup>137</sup> Cs	$1.2 \cdot 10^{-5}$	$1.5 \cdot 10^{-6}$	$1.5 \cdot 10^{-6}$	$8.6 \cdot 10^{-7}$	$8.1 \cdot 10^{-7}$	$5.0 \cdot 10^{-7}$	$4.6 \cdot 10^{-7}$	$4.2 \cdot 10^{-7}$

# Ceramization of HLW from DDP pyro reprocessing

Characteristics	Type of high-level wastes	
	Phosphate concentrate	Spent salt electrolyte
Type of ceramics	monazite	Cosnarite (NZP)
Method of introduction into ceramics	pressing, calcination , T=850°C	Conversion to NZP from the melt or aqueous solution, pressing, calcination , T=1000°C
Quantity of waste introduced into ceramics, %	100	30..40
Leaching rate of <sup>137</sup> Cs on 7-th day, g/cm2 * day	1*10 <sup>-6</sup>	3*10 <sup>-6</sup>
Thermal stability, °C	850	1000
Radiation resistance	5*10 <sup>8</sup> Gy ( for γ and β)	10 <sup>19</sup> α- decay/g

## Cerimization of HLW after pyrochemical processes

### Cerimization of phosphate precipitates

A simulator of phosphate concentrate of pyroelectrochemical process  
is produced from NaCl-2CsCl melt

Element	Mass fraction, %						
La	2,74	Gd	0,1	Ti	0,19	Pb	0,14
Ce	4,11	Y	0,41	Mo	0,55	Ca	2,74
Pr	2,06	Al	0,20	Cu	0,14	Sr	2,80
Nd	10,27	Cr	2,03	Mn	0,27	P+O	54,17
Sm	1,37	Fe	13,70	Zn	0,21		
Eu	0,20	Ni	0,55	Mg	1,02		

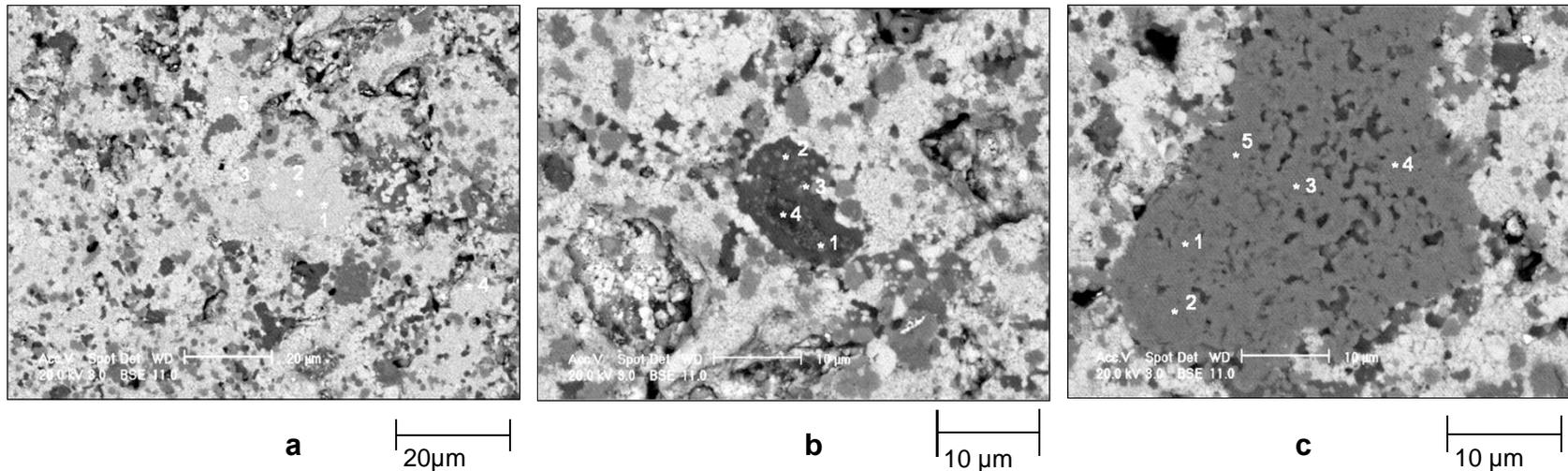
The produced powder was compacted into pellets annealed in air at 800-1400 0C for 10-12 hours. Phase composition of products was analyzed by X-raying. Chemical composition was identified by the emission spectrum analysis and X-ray spectrum microanalysis with the use of a scanning electronic microscope (SEM). The ceramics included the main monazite-like phase with the lattice parameters of  $a=6,773\pm0,003 \text{ \AA}$ ;  $b=6,987\pm0,002 \text{ \AA}$  ;  $c=6,435\pm0,002 \text{ \AA}$  ;  $\beta = 103,68\pm0,02$  degrees.

## Ceramization of HLW after pyrochemical processes

### Ceramization of phosphate precipitates

The SEM results showed the presence of three phases in its composition: light grey, grey and dark grey. Mass fractions of cations together with the X-ray diffraction analysis data are evident of the following:

1. light grey dominant phase – monazite incorporating lanthanides;
2. dark grey phase – ferrous orthophosphate  $\text{FePO}_4$  with isomorphous impurities - Al, Cr;
3. grey phase – Fe- and Cr-based oxide  $(\text{Fe, Cr})_2\text{O}_3$  with the hematite structure.

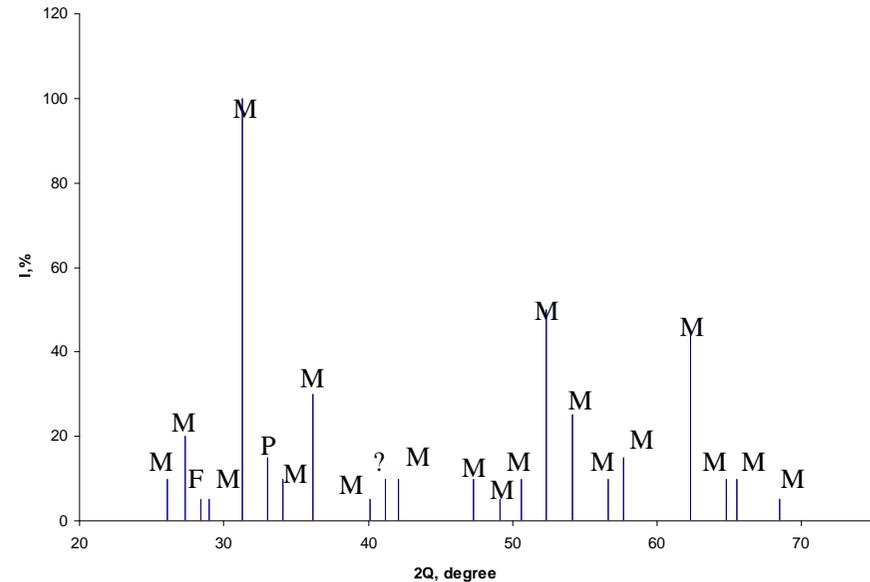


Images of microanalysis regions for ceramics on the basis of phosphate precipitate: light grey (a), dark grey (b) and grey (c) phases



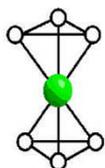
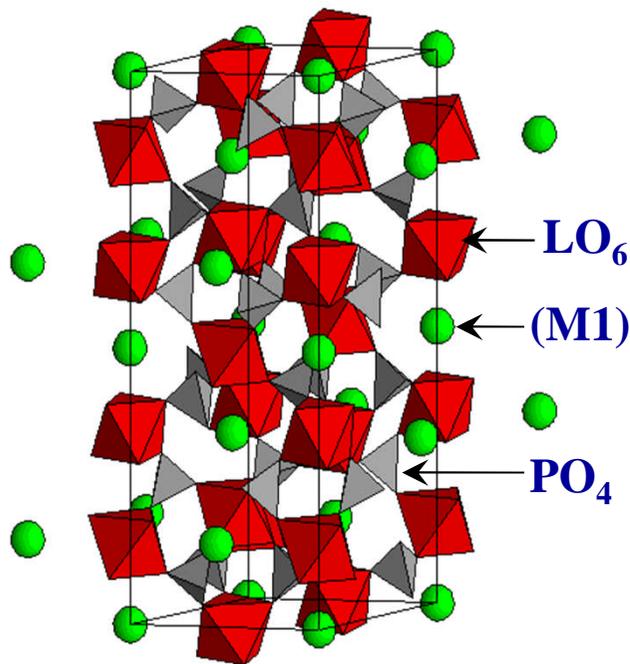
# Ceramization of oxide cocentate into Murataite type “fuse” ceramics (Y,Na)<sub>6</sub> Zn(Zn,Fe<sup>3+</sup>)<sub>4</sub>(Ti,Nb,Na)<sub>12</sub>O<sub>29</sub>(O,F,OH)<sub>10</sub>F<sub>4</sub>

Oxide	Components, mass. %	
	Composition 1	Composition 2
<b>Charge components</b>		
TiO <sub>2</sub>	55	55
MnO <sub>2</sub>	10	10
CaO	10	10
Al <sub>2</sub> O <sub>3</sub>	5	5
Fe <sub>2</sub> O <sub>3</sub>	5	5
ZrO <sub>2</sub>	5	5
<b>HLW simulators (or real oxide presipitate), 10 mass. %</b>		
SrO	0,3934	0,0426
MoO <sub>3</sub>	2,1930	0,2376
CeO <sub>2</sub>	2,7222	1,8680
Pr <sub>6</sub> O <sub>11</sub>	2,5452	0,2758
Nd <sub>2</sub> O <sub>3</sub>	0,5042	0,0546
Sm <sub>2</sub> O <sub>3</sub>	0,7812	0,0846
Eu <sub>2</sub> O <sub>3</sub>	0,5265	0,0570
UO <sub>2</sub>	0,3344	7,3800
<b>23</b>	<b>100,000</b>	<b>100,000</b>

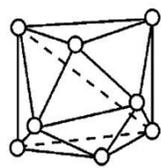


## Ceramization of spent electrolytes

### NZP (kosnarite)- structure

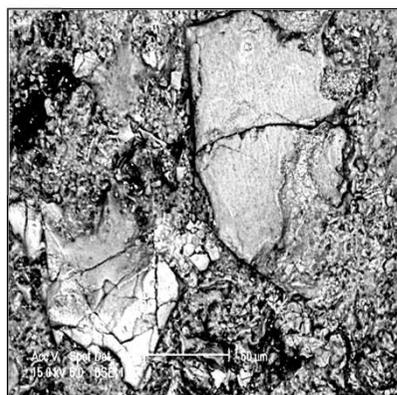


M1



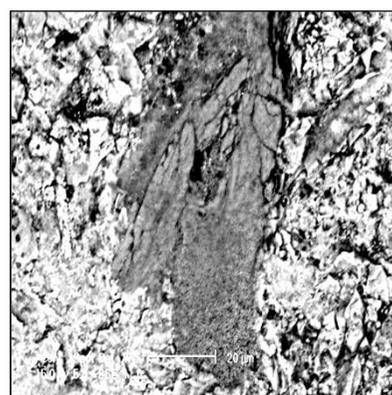
M2

Calculated composition	$Na_{0,5}K_{0,5}Zr_2(PO_4)_3$	$Na_{1/3}Cs_{2/3}Zr_2(PO_4)_3$	$(Li_{0,090}Na_{0,409}K_{0,441}Cs_{0,060})Zr_2(PO_4)_3$
Synthesis method	Impregnation with $H_3PO_4$ solution	Precipitation from solution	Precipitation from solution
Annealing	1000 °C, 3 h.	1200 °C, 5 h.	1000 °C, 4 h.
Lattice parameters of the NZP phases	$a = 8,737(4) \text{ \AA}$ $c = 23,71(2) \text{ \AA}$ $V = 1567(3) \text{ \AA}^3$	$a = 8,607(3) \text{ \AA}$ $c = 24,71(2) \text{ \AA}$ $V = 1585(2) \text{ \AA}^3$	$a = 8,746(1) \text{ \AA}$ $c = 23,54(1) \text{ \AA}$ $V = 1559(1) \text{ \AA}^3$



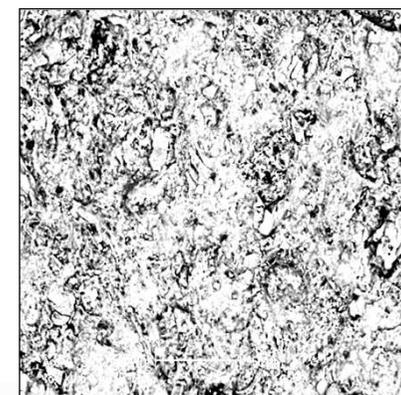
a

50 µm



b

20 µm



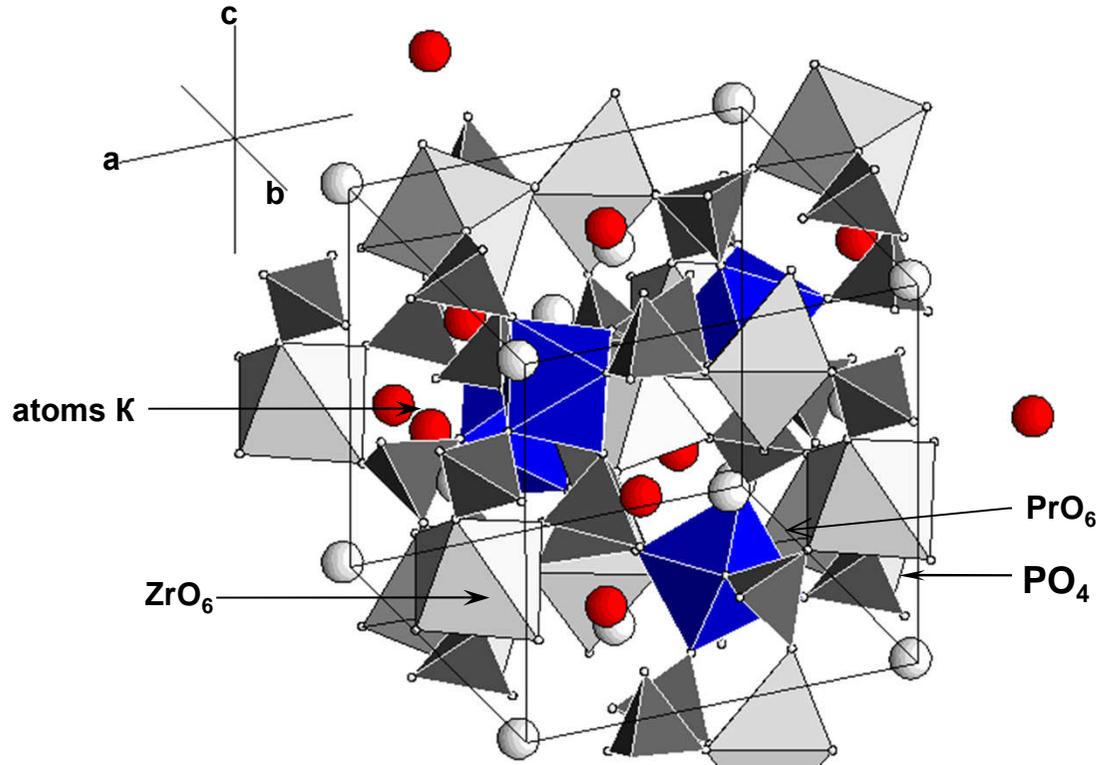
c

50 µm

SEM-images of ceramic particles with the composition  $Na_{1/3}Cs_{2/3}Zr_2(PO_4)_3$ :  
 a) light phase, b) dark phase, c) grey phase



### Ceramization of spent electrolytes - Langbeinite structure

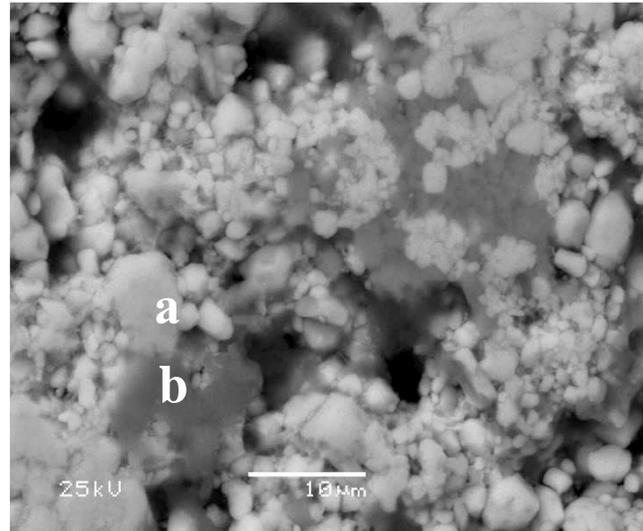


Initial electrolyte	Total composition of phosphate
NaCl-KCl	$\text{NaKFeZr(PO}_4)_3$
NaCl-2CsCl	$\text{Na}_{0,66}\text{Cs}_{1,33}\text{FeZr(PO}_4)_3$
LiCl-4,53NaCl-4,88KCl-0,66CsCl	$\text{Li}_{0,18}\text{Na}_{0,82}\text{K}_{0,88}\text{Cs}_{0,12}\text{FeZr(PO}_4)_3$
NaCl-2CsCl	$\text{Na}_{0,66}\text{Cs}_{1,33}\text{CrZr(PO}_4)_3$
3LiCl-2KCl+ NaCl-2CsCl	$\text{Li}_{0,6}\text{K}_{0,4}\text{Na}_{0,33}\text{Cs}_{0,67}\text{FeZr(PO}_4)_3$





### Ceramization of spent electrolytes - Langbeinite structure



SEM images of ceramic particles  $\text{Na}_{0,66}\text{Cs}_{1,33}\text{FeZr}(\text{PO}_4)_3$ ; a-light grey phase; b- dark grey phase.

Element	Mass fraction (calculation), %	Mass fraction (experiment), light grey phase, %	Mass fraction (experiment), dark grey phase, %
Na	2,45	2,06	3,59
Cs	28,37	29,52	21,13
Fe	8,94	7,04	6,87
Zr	14,61	16,47	20,19
P	14,87	14,63	16,08
O	30,74	30,16	32,14



## Ceramization of spent electrolytes

### Langbeinite structure

Element	Leaching period, days	Leaching rate, g/(cm <sup>2</sup> ·day)			
		Na <sub>0,66</sub> Cs <sub>1,33</sub> FeZr(PO <sub>4</sub> ) <sub>3</sub>	NaKFeZr(PO <sub>4</sub> ) <sub>3</sub>	Li <sub>0,18</sub> Na <sub>0,82</sub> K <sub>0,18</sub> Cs <sub>0,12</sub> FeZr(PO <sub>4</sub> ) <sub>3</sub>	Na <sub>0,66</sub> Cs <sub>1,33</sub> FeZr(PO <sub>4</sub> ) <sub>3</sub> with binding Bi <sub>2</sub> O <sub>3</sub> +NaF
Na	3 7	>1,1·10 <sup>-4</sup> 9,8·10 <sup>-6</sup>	2,3·10 <sup>-4</sup> 1,0·10 <sup>-4</sup>	2,9·10 <sup>-6</sup> 1,7·10 <sup>-6</sup>	
Cs	3 7	>1,1·10 <sup>-3</sup> 5,9·10 <sup>-4</sup>		2,3·10 <sup>-4</sup> 1,0·10 <sup>-4</sup>	1,4·10 <sup>-5</sup> <6,4·10 <sup>-6</sup>
Fe	3 7	3,5·10 <sup>-5</sup> 4,8·10 <sup>-6</sup>	3,1·10 <sup>-5</sup> 1,5·10 <sup>-5</sup>	3,1·10 <sup>-5</sup> 1,7·10 <sup>-5</sup>	6,3·10 <sup>-6</sup> 3,7·10 <sup>-6</sup>
Zr	3 7	<6,6·10 <sup>-7</sup> <9,9·10 <sup>-7</sup>	1,6·10 <sup>-6</sup> 5,1·10 <sup>-7</sup>	1,0·10 <sup>-6</sup> 1,8·10 <sup>-7</sup>	<7,2·10 <sup>-7</sup> <6,1·10 <sup>-7</sup>



# Conclusions

- **Pyro processes are characterized by a small spectrum and volume of the produced wastes, their high specific activity, absence of liquid high-level process wastes.**
- **The main types of solid process wastes are phosphate and oxide precipitates, as well as spent electrolytes**
- **The main waste forms of pyrochemical processes can be stored long-term in shielding containers without using any schemes of their chemical conversion and immobilization.**
- **If necessary, to enhance efficiency of the HLW shielding barrier for their long-term geological disposal, waste forms of pyroprocesses can be converted into more stable chemical forms.**





# Conclusions

- Alumofluophosphate glass and monazite-based matrix can be used for immobilization of phosphate precipitates
- Fuse ceramics on the basis of murataite mineral can be used for immobilization of oxide precipitates
- Alumofluophosphate glass and ceramics with the structures of kosnarite and langbeinite can be used for immobilization of salt electrolytes
- Further investigations on immobilization of salt systems can be aimed at a search of effective ways to prevent the formation of conversion and corrosion chlorine-containing gases, effective chemical bonding of chlorine-ion, research and development of hybrid glass-ceramic method of spent electrolytes fixation.