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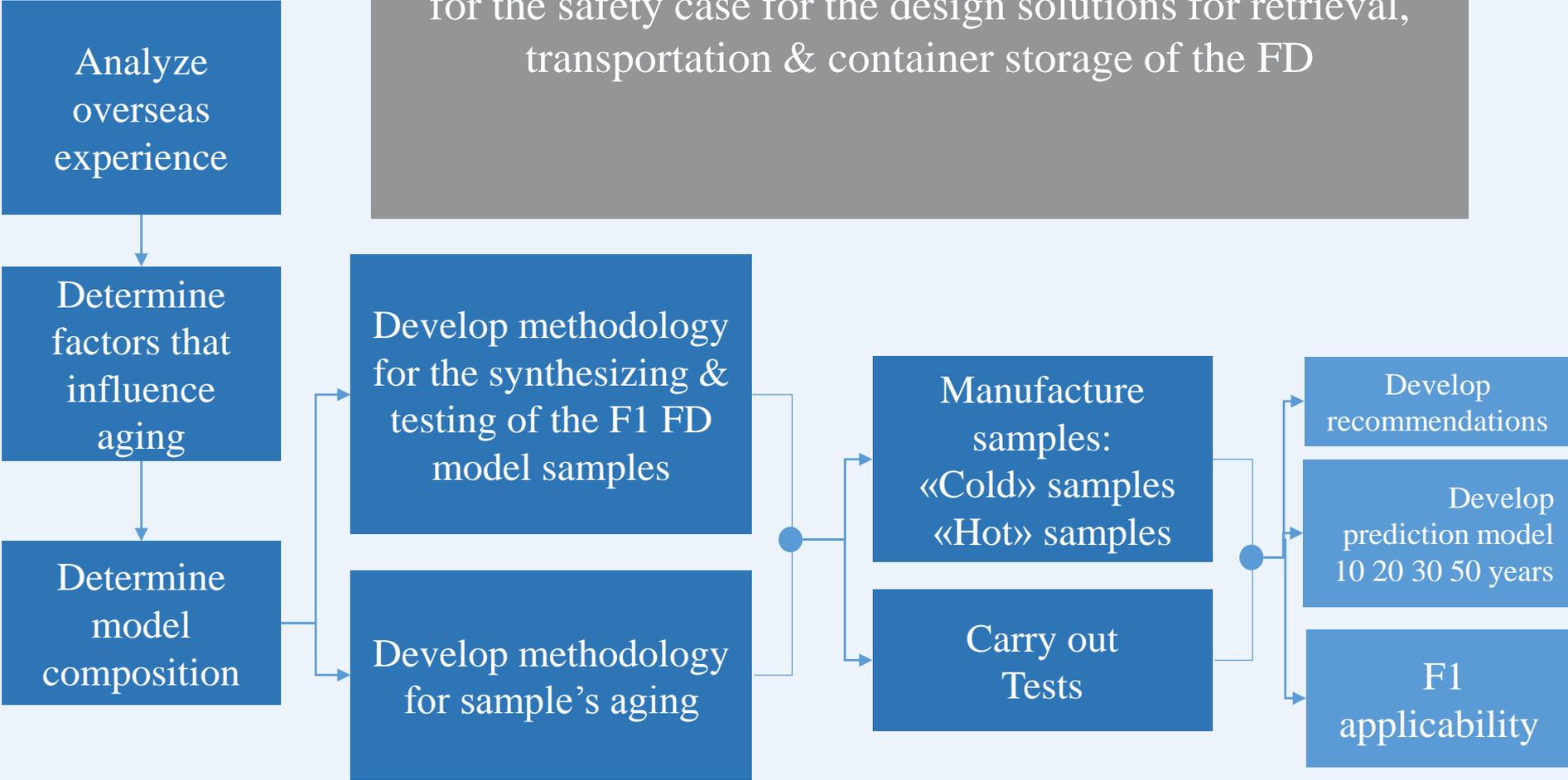
ROSATOM STATE CORPORATION COMPANY



# «Development of Technologies for Grasping and Analyzing Properties of Fuel Debris (Estimation of Aging Properties of Fuel Debris)»

# Project Background & Objectives

Forecast model of changing of Fuel Debris (FD) properties for the safety case for the design solutions for retrieval, transportation & container storage of the FD



# **Project Implementation Plan**

# Project Implementation Plan

## Manufacturing

- $H_2O + t^0$
- $\alpha$

## Aging

## Tests

- Phase composition
- Leaching rates
- Microstructure
- Mechanical strength
- Secondary Uranil phases

Experimental study of such processes of FD aging, as the change in mechanical strength, leaching of different radionuclides, the change in the phase composition, the appearance of secondary phases wrangling etc. needed to develop predictive models of changes over time of the properties of the Fukushima samples and to develop safety recommendations retrieving and container storage of FD.

## Analysis of the tests results

verification

Input data for prediction model

Develop forecast model of FD behavior for safety justification during extraction, packing, storage & transportation

## Algorithm of Manufacturing & Investigating

- 1 Synthesis of a fuel composition with inclusion of oxides (carbonates) of fission product simulators
- 2 Study of the behavior of concrete during heating
- 3 Preparation of the metallic phase
- 4 Preparation of the silicate phase
- 5 Accelerated degradation of samples
- 6 Leaching test during the aging of samples
- 7 Compression test: mechanical strength
- 8 Analysis of the obtained sample fragments: phase composition, microstructure

## RIAR/KRI Model Samples Composition (Metallic\oxide phase)

Component	Mass Content	Remarks
UO <sub>2</sub>	56.6%	The basis of nuclear fuel
ZrO <sub>2</sub>	13.1%	Zirconium is represented as two compounds to simulate its partial oxidation, it is assumed that 50% zirconium is oxidized
Zr	10%	
Fe	12.6%	Simulates the steel body and sub-shell devices, can be replaced by stainless steel
PuO <sub>2</sub>	3,0%	
SrCO <sub>3</sub>	1.6%	Multiply increased to study the effect on aging of fuel debris
Cs <sub>2</sub> CO <sub>3</sub>	2.5%	Multiply increased to study the effect on aging of fuel debris
Nd <sub>2</sub> O <sub>3</sub>	0.3%	
La <sub>2</sub> O <sub>3</sub>	0.3%	

# Sample's Manufacturing



Box with high-temperature furnace Xerion XVAC2300, hydraulic press Retsch PP25 and weighing device

Mixer «drunk barrel»

Laboratory scales

Grinding of the components of the working mixture

Mixing of the components of the working mixture

Prepared working mixture divides into two parts: for metallic phase with & without Cm

calculated part of the samples dissolve in concrete to obtain the silicate phase, both with & without Cm

sintering tablets in an oven

Calculated amounts of required reagents weighed on Sartorius brand analytical balance with an accuracy of 0.001 g.



Machine for preparing billets

# Preparation of the Metallic Phase

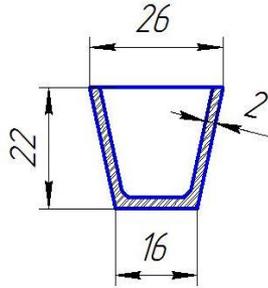
$V_{\text{heat,cool}} = 500 \text{ }^{\circ}\text{C/h}$

$T_{\text{cool}} = 20 \text{ }^{\circ}\text{C}$

$T = 1800 \text{ }^{\circ}\text{C}$

3 hours

- $\text{ZrO}_2$  crucible
- $\text{ZrO}_2$  lid
- Ar
- Cs carbonate



Calcined zirconia crucible

$P_{\text{Ar}} = + 15 \text{ mbar}$   
 $Q = 0,3-0,4 \text{ l/sec}$

26 Moist Tablets

(13+13):

$M1 = 2,36 \text{ g}$

$M2 = 1,38 \text{ g}$

26 Tablets

(13+13):

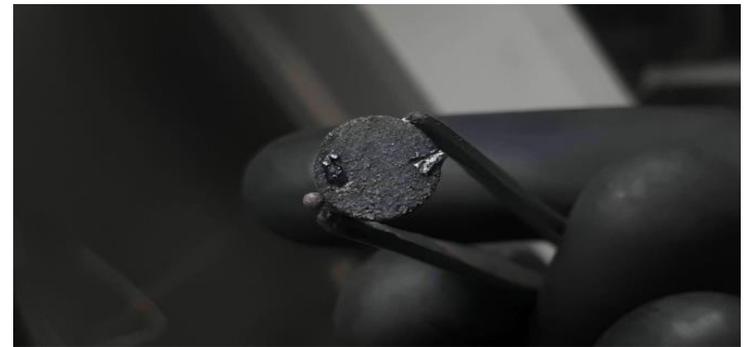
$D_{\text{med}} = 9,5 \text{ mm}$

$M1 = 2,36 \text{ g}$

$M2 = 1,38 \text{ g}$

$H1 = 7,5 \text{ mm}$

$H2 = 4,3 \text{ mm}$



# Preparation of the Metallic Phase with Cm

$$V_{\text{heat,cool}} = 500 \text{ }^{\circ}\text{C/h}$$

$$T_{\text{cool}} = 20 \text{ }^{\circ}\text{C}$$

$$T = 1800 \text{ }^{\circ}\text{C}$$

3 hours

- ZrO<sub>2</sub> crucible
- ZrO<sub>2</sub> lid
- Ar
- Cs carbonate

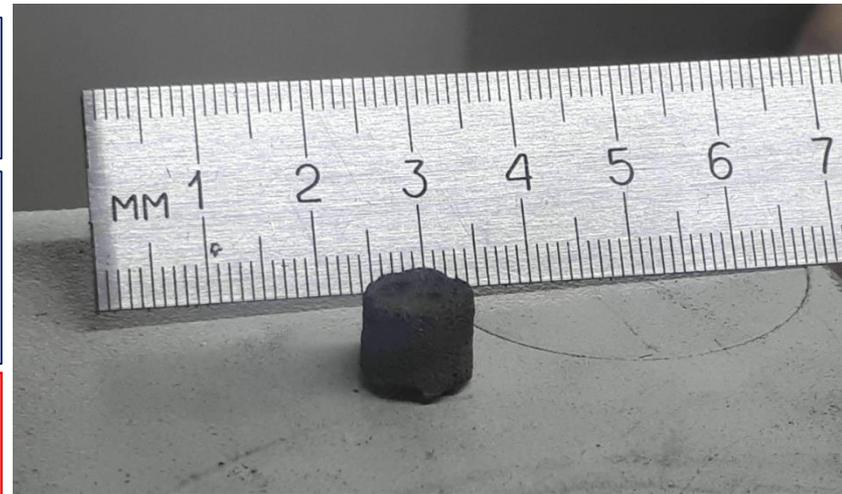
$$P_{\text{Ar}} = + 15 \text{ mbar}$$

$$Q = 0,3-0,4 \text{ l/sec}$$

$$D_{\text{med}} = 7,4 \text{ mm}$$

$$M1 = 2,16 \text{ g}$$

$$H1 = 6,5 \text{ mm}$$



## Calculation of the amount of Curium introduced into the metallic phase samples

Specific activity of SNF =  $2,7 \times 10^8 \text{ Bq/g}$ .

To accelerate aging ~180 times (10 years in 20 days) => introduce into the sample the activity of  $^{244}\text{Cm} = 4.3 \times 10^{10} \text{ Bq/g}$  or  $^{244}\text{Cm} = 16.5 \text{ mg/g}$  (1.6% wt.).

Metallic phase (MP) contains ~60% of SNF => alpha-activity of the MP:

$$4.3 \times 10^{10} \times 0.6 = 2.85 \times \frac{10^{10} \text{ Bq}}{\text{g}}$$

Silicate phase (SP) contains ~30% of SNF => alpha-activity of the SP:

$$4.3 \times 10^{10} \times 0.3 = 1.29 \times \frac{10^{10} \text{ Bq}}{\text{g}}$$

The specific activity of  $^{244}\text{Cm}$  is  $3 \times 10^{12} \text{ Bq/g}$  => MP:

$$\frac{2,58 \times 10^{10}}{3 \times 10^{12}} \times 100\% = 0,86\%$$

$$\frac{1,29 \times 10^{10}}{3 \times 10^{12}} \times 100\% = 0,43\%$$

Mass of sample ~ 3 grams (before sintering)

Mass of Cm of MP =  $0.86 \times 3 = 0.0258 \text{ g}$ .

Mass of Cm of SP =  $0.43 \times 3 = 0.01229 \text{ g}$ .

The total amount of Cm(per 22 samples):

For the MP:  $11 \times 0.0258 = 0.2838 \text{ g}$ .

For SP:  $11 \times 0.0129 = 0.1419 \text{ g}$ .

Total Cm =  $0.2838 + 0.1419 = 0.4257 \text{ g}$ .

The total activity of Cm =  $0,4257 \times (3 \times 10^{12}) = 1,28 \times 10^{12} \text{ Bq} = 34,52 \text{ Curie}$

# Preparation of the Silicate Phase

$T_{\text{cool}} = 20 \text{ }^{\circ}\text{C}$

$T = 1500 \text{ }^{\circ}\text{C}$

$P_{\text{Ar}} = + 15 \text{ mbar}$

3 hours

$V_{\text{heat,cool}} = 400 \text{ }^{\circ}\text{C/h}$

ZrO<sub>2</sub> crucible

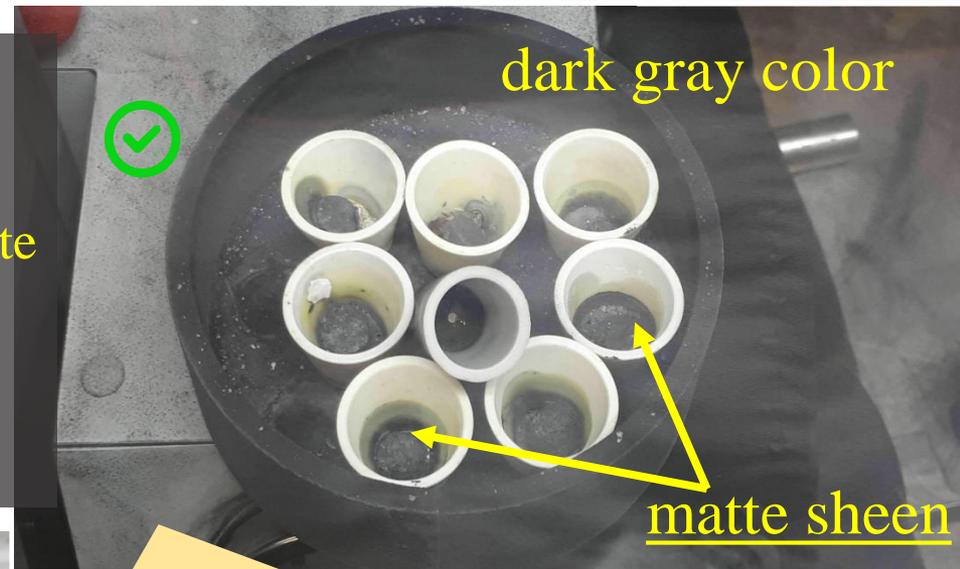
ZrO<sub>2</sub> lid

Metallic Phase + Concrete

$M_{\text{sample}} = 1,5 \text{ g}$

$M_{\text{concrete}} = 1,7 \text{ g}$

placed in a furnace



**The result:  $M_{\text{sample}} = 21,7 \text{ g.}$ ,  $M_{\text{crucible}} = 16,1 \text{ g.}$   
The glass phase of silicate samples with Pu has a dark gray color and a matte sheen due to the complete fragmentation of the metallic FD**



**Porous chip with sharp edges**

## Concrete:

cement - 17.62 %

crushed stone from dense rocks - 49.28%

river sand - 24.69 %

chemical additives - 0.21 %

water - 8.20%

# Preparation of the Silicate Phase with Cm

$V_{\text{heat,cool}} = 400 \text{ } ^\circ\text{C/h}$

$T = 1500 \text{ } ^\circ\text{C}$

3 hours

$P_{\text{Ar}} = + 15 \text{ mbar}$

$T_{\text{cool}} = 20 \text{ } ^\circ\text{C}$

ZrO<sub>2</sub> crucible

ZrO<sub>2</sub> lid

Metallic Phase + Concrete

$M_{\text{sample}} = 2,16 \text{ g}$

$M_{\text{concrete}} = 2,74 \text{ g}$

placed in a furnace



In three crucibles, the metallic phase samples with curium did not dissolve completely, possibly due to the difference in the composition of the concrete loaded into each crucible (the amount of rubble in the concrete in different crucibles was not the same).

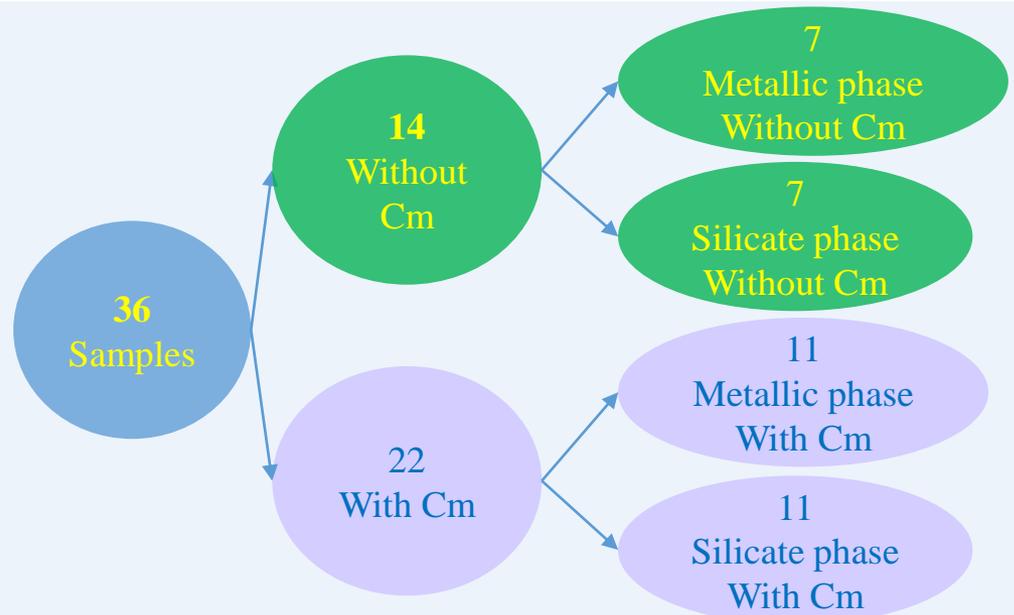
The bulk of the concrete evaporated, 0.14 g of concrete “entered” into the tablet. Several grains of a light brown color are visible on the graphite cup

The result: 11 brown tablets

$M_{\text{sample}} = 20,4 \text{ g.}$ ,  $M_{\text{crucible}} = 16,1 \text{ g.}$  The glass phase of silicate samples with Pu has a dark gray color and a matte sheen due to the complete fragmentation of the metallic FD

# Matrix of Prepared Samples

Sample №	Metallic Phase without Cm			
	Height, mm	Diameter, mm	Mass, kg	S open geometric surface of sample, sm <sup>2</sup>
K-3 – K-7	7,40 – 7,60	9,55 – 9,70	0,00214 – 0,00220	3,63 – 3,78
	Metallic Phase with Cm			
K-15 – K-24	8,80 – 9,10	6,90 – 7,05	0,00212 – 0,00220	2,69 – 2,80
	Silicate Phase without Cm			
K-10 – K-14	–	15,80 – 16,20	0,00421 – 0,00438	1,97 – 2,05
	Silicate Phase with Cm			
K-26 – K-35	–	15,80 – 16,20	0,00421 – 0,00438	1,97 – 2,05



# Samples & Tests: Basic Set of 24 Samples

Parameters		Water 10 years	Water 20 years	Water 30 years	Water 50 years
FD without silicate phase	without <sup>244</sup> Cm	▶ ▼ ●	▶ ▼ ●	▶ ▼ ●	▶ ▼ ●
	I I 10 years	▶ ▼ ■ ●			
		▶ ▼ ◆			
	I I 20 years	▶ ▼	▶ ▼ ■ ●		
		▶ ▼	▶ ▼ ◆		
	I I 30 years	▶ ▼	▶ ▼	▶ ▼ ■ ●	
		▶ ▼	▶ ▼	▶ ▼ ◆	
	I I 50 years	▶ ▼	▶ ▼	▶ ▼	▶ ▼ ■ ●
▶ ▼		▶ ▼	▶ ▼	▶ ▼ ◆	
FD with silicate phase	without <sup>244</sup> Cm	▶ ▼ ●	▶ ▼ ●	▶ ▼ ●	▶ ▼ ●
	I I 10 years	▶ ▼ ■ ●			
		▶ ▼ ◆			
	I I 20 years	▶ ▼	▶ ▼ ■ ●		
		▶ ▼	▶ ▼ ◆		
	I I 30 years	▶ ▼	▶ ▼	▶ ▼ ■ ●	
		▶ ▼	▶ ▼	▶ ▼ ◆	
	I I 50 years	▶ ▼	▶ ▼	▶ ▼	▶ ▼ ■ ●
▶ ▼		▶ ▼	▶ ▼	▶ ▼ ◆	

▶ Inspection (Uox) ▼ leaching ● Compression test ■ XRD ◆ SEM I I = internal irradiation

## Complementary Samples. Total: 36 Samples

In addition to the samples initially specified in the Research program, manufactured and investigated:

1

Initial samples before impact of degrading factors with & without silicate phase - on compressive strength, phase composition and microstructure

4  
samples

2

Samples with & without a silicate phase, with  $^{244}\text{Cm}$  added, which will remain in the air environment - with XRD to determine the evolution of the phase composition without the influence of chemical reactions

2  
samples

3

Three extra samples with & without a silicate phase for leaching

6  
samples

# Accelerated Aging Mechanism

Metallic & Silicate  
Phase with Cm

aging accelerated ~180 times

1 year  $\equiv$  2 days  
10 year  $\equiv$  20 days  
50 year  $\equiv$  100 days

**Cm**

## Leaching

In solution imitation seawater  
(93% of resemblance)

T = 95 °C

Each 1st, 3rd & 7th day of the exposition until the sample undergo damage equivalent to 10, 20, 30 & 50 years the concentrations of U, Pu, Cs, Sr, Zr, Fe, La, Nd, Cm measured

The change of the leaching rate shows the evolution of the surface layer and the whole sample.

Equipment for leaching with stable temperature

The technique of "accelerated aging":

- accelerated dose collection from  $\alpha$ -decays for a shorter time interval due to addition of a powerful  $\alpha$ -radiation source to the simulated material;
- creation of more stringent conditions (in comparison with available in PCV / RPV) in terms of concentrations of chemical elements affecting the degradation process;
- acceleration of the course of chemical reactions under the influence of an increase in the soaking temperature.

# Test Results

# Experimental Leaching Results

Data on leaching rates were obtained and treated in two ways:

- 1) **Traditional method.** Graphic images which show dependences of leaching rates to the sample area per day of the experiment prepared in accordance with MCCI.
- 2) **Dynamic method.** Obtained results used to analyze summarized leaching rate of the revised nuclides excluding the influence of solutions uniting, as for each time replacement solution prepared. Data from dynamic method switched into the real time (conversion rate = 180) and averaged over time range.

Transfer rates of U into the contact solution for samples with and without Cm change in the similar way – no impact of self-irradiation on the behavior of U. At the initial stage, the leaching rates change to an order of magnitude, during the later period – two orders of magnitude

Pu leaching from Cm samples has the rate to an order of magnitude higher than leaching from samples without Cm. Pu leaching rate decreases by an order of magnitude in the first 20 years, the minimum Pu release rate is expected by 22-24 years. After that, the leaching rate increases again and returns to its initial values approximately

Release of Zr from fuel debris is low and allows to conclude that the structure will stay stable and main properties of the zirconate phase of the debris will not change during long period

The transfer of Cs to contact solution takes place only during the first day of the test, after that cesium is found at the level equal to detection threshold of the analytical methodic

Sr demonstrate high leaching rates, release for curium samples is two orders of magnitude higher than for samples without curium

La and Nd demonstrate low leaching rates

Cm is being released during the first days of the tests

Fe release occurs predominantly from the curium samples and release rate increases during the whole test period

The U leaching rate is almost constant during the period of 3-5 years, and only after that, the rate decreases

Pu leaching rate increases in the course of degradation, passing its minimum in the period of 6-7 years

Zr leaching rate is low and remains stable

Cs leaching rate is low and remains stable

The release of Sr from the products of interaction of fuel debris with concrete is very high and remains at a high level almost during all the period: by 6-8 year the decrease of the leaching rate is over

La and Nd demonstrate similar behavior of low leaching rate to contact solution

Fe release from silicate samples differs from metallic phase: it is similar to release of other elements, mostly decreases to 10-12 years, no difference between Cm samples and samples without Cm observed. At the later stages red suspensions on the crucible (inside and outside) can be observed

**Metallic  
Phase**

**Silicate  
Phase**

# Expected Leaching Rates

## Metallic Phase

## Silicate Phase

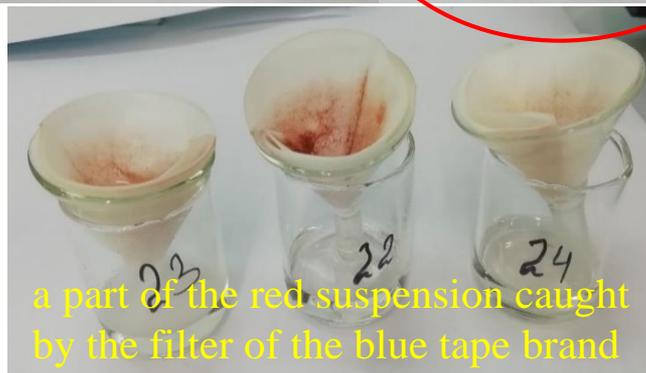
Leaching rate, g/m <sup>2</sup> ·day	Duration of «aging» in accelerated mode, days				
	Calculated duration of «aging» in real time mode, years				
<b>U</b>	<u>0-20</u> 0-10	<u>20-40</u> 10-20	<u>40-60</u> 20-30	<u>60-100</u> 30-50	<u>0-100</u> 0-50
Metallic phase (MP) w/o Cm	4,38·10 <sup>-5</sup>	1,5·10 <sup>-5</sup>	0,3·10 <sup>-5</sup>	2,2·10 <sup>-5</sup>	2,1·10 <sup>-5</sup>
Metallic phase with curium	3·10 <sup>-5</sup>	0,8·10 <sup>-5</sup>	0,7·10 <sup>-5</sup>	0,6·10 <sup>-5</sup>	1,3·10 <sup>-5</sup>
<b>Pu</b>	<u>0-20</u> 0-10	<u>20-40</u> 10-20	<u>40-60</u> 20-30	<u>60-100</u> 30-50	<u>0-100</u> 0-50
MP w/o curium	10 <sup>-5</sup>	0,2·10 <sup>-5</sup>	0,2·10 <sup>-5</sup>	1,4·10 <sup>-5</sup>	10 <sup>-5</sup>
MP with curium	12,8·10 <sup>-5</sup>	3,4·10 <sup>-5</sup>	3,4·10 <sup>-5</sup>	7,4·10 <sup>-5</sup>	5,6·10 <sup>-5</sup>
<b>Zr</b>	<u>0-20</u> 0-10	<u>20-40</u> 10-20	<u>40-50</u> 20-30	<u>0-30</u> 30-50	0-50
MP w/o curium	0,4·10 <sup>-5</sup>	0,1·10 <sup>-5</sup>	0,1·10 <sup>-5</sup>	0,2·10 <sup>-5</sup>	0,2·10 <sup>-5</sup>
MP with curium	0,5·10 <sup>-5</sup>	0,2·10 <sup>-5</sup>	0,2·10 <sup>-5</sup>	0,2·10 <sup>-5</sup>	0,3·10 <sup>-5</sup>
<b>Cs</b>	<u>0-20</u> 0-10	<u>20-40</u> 10-20	<u>40-60</u> 20-30	<u>60-100</u> 30-50	<u>0-100</u> 0-50
MP w/o curium	5,2·10 <sup>-5</sup>	0,1·10 <sup>-5</sup>	0,1·10 <sup>-5</sup>	0,2·10 <sup>-5</sup>	1,5·10 <sup>-5</sup>
MP with curium	1,3·10 <sup>-5</sup>	0,2·10 <sup>-5</sup>	0,2·10 <sup>-5</sup>	0,2·10 <sup>-5</sup>	0,5·10 <sup>-5</sup>
<b>Sr</b>	<u>0-20</u> 0-10	<u>20-40</u> 10-20	<u>40-60</u> 20-30	<u>60-100</u> 30-50	<u>0-100</u> 0-50
MP w/o curium	4,8·10 <sup>-5</sup>	0,3·10 <sup>-5</sup>	0,4·10 <sup>-5</sup>	0,5·10 <sup>-5</sup>	1,5·10 <sup>-5</sup>
MP with curium	22·10 <sup>-5</sup>	12·10 <sup>-5</sup>	4,9·10 <sup>-5</sup>	3·10 <sup>-5</sup>	6,7·10 <sup>-5</sup>
<b>La</b>	<u>0-20</u> 0-10	<u>20-40</u> 10-20	<u>40-60</u> 20-30	<u>60-100</u> 30-50	<u>0-100</u> 0-50
MP w/o curium	1,2·10 <sup>-5</sup>	0,5·10 <sup>-5</sup>	0,5·10 <sup>-5</sup>	0,6·10 <sup>-5</sup>	0,7·10 <sup>-5</sup>
MP with curium	1,4·10 <sup>-5</sup>	0,6·10 <sup>-5</sup>	0,6·10 <sup>-5</sup>	0,8·10 <sup>-5</sup>	0,9·10 <sup>-5</sup>
<b>Nd</b>	<u>0-20</u> 0-10	<u>20-40</u> 10-20	<u>40-60</u> 20-30	<u>60-100</u> 30-50	<u>0-100</u> 0-50
MP w/o curium	11·10 <sup>-5</sup>	0,5·10 <sup>-5</sup>	0,5·10 <sup>-5</sup>	0,7·10 <sup>-5</sup>	3,7·10 <sup>-5</sup>
MP with curium	12,6·10 <sup>-5</sup>	0,6·10 <sup>-5</sup>	0,6·10 <sup>-5</sup>	0,9·10 <sup>-5</sup>	3,3·10 <sup>-5</sup>
<b>Cm</b>	<u>0-20</u> 0-10	<u>20-40</u> 10-20	<u>40-60</u> 20-30	<u>60-100</u> 30-50	<u>0-100</u> 0-50
MP w/o curium	-	-	-	-	-
MP with curium	10 <sup>-5</sup>	3,7·10 <sup>-7</sup>	3,5·10 <sup>-7</sup>	3,6·10 <sup>-7</sup>	6,4·10 <sup>-7</sup>
<b>Fe</b>	<u>0-20</u> 0-10	<u>20-40</u> 10-20	<u>40-60</u> 20-30	<u>60-100</u> 30-50	<u>0-100</u> 0-50
MP w/o curium	4,2·10 <sup>-5</sup>	3,7·10 <sup>-5</sup>	2·10 <sup>-5</sup>	7,3·10 <sup>-5</sup>	5,3·10 <sup>-5</sup>
MP with curium	27,5·10 <sup>-5</sup>	28,4·10 <sup>-5</sup>	43,6·10 <sup>-5</sup>	37,3·10 <sup>-5</sup>	31,7·10 <sup>-5</sup>

Leaching rate, g/m <sup>2</sup> ·day	Duration of «aging» in accelerated mode, days				
	Calculated duration of «aging» in real time mode, years				
<b>U</b>	<u>0-20</u> 0-10	<u>20-40</u> 10-20	<u>40-60</u> 20-30	<u>60-100</u> 30-50	<u>0-100</u> 0-50
Silicate phase (SP) w/o curium	6,5·10 <sup>-5</sup>	4,4·10 <sup>-5</sup>	1·10 <sup>-5</sup>	1·10 <sup>-5</sup>	2,9·10 <sup>-5</sup>
Silicate phase with curium	4·10 <sup>-5</sup>	1,7·10 <sup>-5</sup>	1,4·10 <sup>-5</sup>	2·10 <sup>-5</sup>	1,8·10 <sup>-5</sup>
<b>Pu</b>	<u>0-20</u> 0-10	<u>20-40</u> 10-20	<u>40-60</u> 20-30	<u>60-100</u> 30-50	<u>0-100</u> 0-50
SP w/o curium	0,6·10 <sup>-5</sup>	0,4·10 <sup>-5</sup>	0,2·10 <sup>-5</sup>	0,8·10 <sup>-5</sup>	0,5·10 <sup>-5</sup>
SP with curium	0,8·10 <sup>-5</sup>	1,2·10 <sup>-5</sup>	3·10 <sup>-5</sup>	7,4·10 <sup>-5</sup>	1,5·10 <sup>-5</sup>
<b>Zr</b>	<u>0-20</u> 0-10	<u>20-40</u> 10-20	<u>40-50</u> 20-30	<u>0-30</u> 30-50	0-50
SP w/o curium	0,7·10 <sup>-5</sup>	0,3·10 <sup>-5</sup>	0,3·10 <sup>-5</sup>	1,5·10 <sup>-5</sup>	0,9·10 <sup>-5</sup>
SP with curium	0,7·10 <sup>-5</sup>	0,8·10 <sup>-5</sup>	1·10 <sup>-5</sup>	0,4·10 <sup>-5</sup>	1·10 <sup>-5</sup>
<b>Cs</b>	<u>0-20</u> 0-10	<u>20-40</u> 10-20	<u>40-60</u> 20-30	<u>60-100</u> 30-50	<u>0-100</u> 0-50
SP w/o curium	2,1·10 <sup>-5</sup>	0,3·10 <sup>-5</sup>	0,3·10 <sup>-5</sup>	0,3·10 <sup>-5</sup>	0,5·10 <sup>-5</sup>
SP with curium	2,5·10 <sup>-5</sup>	0,3·10 <sup>-5</sup>	0,3·10 <sup>-5</sup>	0,3·10 <sup>-5</sup>	2,1·10 <sup>-5</sup>
<b>Sr</b>	<u>0-20</u> 0-10	<u>20-40</u> 10-20	<u>40-60</u> 20-30	<u>60-100</u> 30-50	<u>0-100</u> 0-50
SP w/o curium	1,8·10 <sup>-4</sup>	3,3·10 <sup>-5</sup>	1,9·10 <sup>-5</sup>	3,4·10 <sup>-5</sup>	8,5·10 <sup>-5</sup>
SP with curium	1,3·10 <sup>-4</sup>	6,5·10 <sup>-5</sup>	8·10 <sup>-5</sup>	9,1·10 <sup>-5</sup>	7,7·10 <sup>-5</sup>
<b>La</b>	<u>0-20</u> 0-10	<u>20-40</u> 10-20	<u>40-60</u> 20-30	<u>60-100</u> 30-50	<u>0-100</u> 0-50
SP w/o curium	3,5·10 <sup>-5</sup>	0,8·10 <sup>-6</sup>	0,9·10 <sup>-6</sup>	1·10 <sup>-5</sup>	1,3·10 <sup>-5</sup>
SP with curium	2,2·10 <sup>-5</sup>	0,9·10 <sup>-5</sup>	1·10 <sup>-5</sup>	1·10 <sup>-5</sup>	1,3·10 <sup>-5</sup>
<b>Nd</b>	<u>0-20</u> 0-10	<u>20-40</u> 10-20	<u>40-60</u> 20-30	<u>60-100</u> 30-50	<u>0-100</u> 0-50
SP w/o curium	1,3·10 <sup>-4</sup>	0,8·10 <sup>-5</sup>	0,8·10 <sup>-5</sup>	1,1·10 <sup>-5</sup>	2,7·10 <sup>-5</sup>
SP with curium	1·10 <sup>-4</sup>	0,9·10 <sup>-5</sup>	1·10 <sup>-5</sup>	1·10 <sup>-5</sup>	3,1·10 <sup>-5</sup>
<b>Cm</b>	<u>0-20</u> 0-10	<u>20-40</u> 10-20	<u>40-60</u> 20-30	<u>60-100</u> 30-50	<u>0-100</u> 0-50
SP w/o curium	-	-	-	-	-
SP with curium	3,2·10 <sup>-8</sup>	5,6·10 <sup>-7</sup>	2,1·10 <sup>-7</sup>	3·10 <sup>-7</sup>	3,7·10 <sup>-7</sup>
<b>Fe</b>	<u>0-20</u> 0-10	<u>20-40</u> 10-20	<u>40-60</u> 20-30	<u>60-100</u> 30-50	<u>0-100</u> 0-50
SP w/o curium	7,4·10 <sup>-5</sup>	1·10 <sup>-4</sup>	1·10 <sup>-5</sup>	3,6·10 <sup>-5</sup>	4,6·10 <sup>-5</sup>
SP with curium	7,7·10 <sup>-5</sup>	4·10 <sup>-5</sup>	4,8·10 <sup>-5</sup>	6·10 <sup>-5</sup>	5,2·10 <sup>-5</sup>

# Formation of Red Suspensions & Sludges

A mass output of a fine solid red-colored suspensions into a contact solution was detected in samples with Cm

Silicate samples with Cm



## mechanism of red suspensions formation

- irradiation of a contact solution with the formation of peroxide ions and reactive oxygen species in the surface layer
- catalytic decomposition of peroxide near the exit to the surface of metallic inclusions containing iron and chromium
- corrosion of metallic inclusions and transition to the solution of fine particles of iron oxides
- sorption by pores of iron oxide particles of various heavy metals and radionuclides from solution
- Heavy metals hydrolyze and co-precipitating of red suspensions with iron
- the formation of films on the surfaces



# Weakening of Metal Samples

	<u>Duration of «aging» in accelerated mode, days</u>			
	<u>Calculated duration of «aging» in real time mode, years</u>			
	<u>0-20</u> 0-10	<u>20-40</u> 10-20	<u>40-60</u> 20-30	<u>60-100</u> 30-50
The state of the external surface of the sample	“Smoothing” of the external surface, the protruding parts are removed, part of the pores is closed	Noticeable change in geometry of the external surface of the sample, erosion by inclusions of iron	Macroscopic changes (cracks, caverns)	External surface of the samples is damaged significantly. The damage is more noticeable for curium samples
Corrosive damage	Corrosive destruction of iron particles at the sample/ contact solution boundary	Inclusion of particles of iron to the corrosions processes to a depth of more than 300 μm from the sample boundary	Destruction of particles of iron by the sample volume (1000 μm and more from the boundary), penetration of contact solution into the depth of the sample	
Structure integrity	The beginning of the formation of ring cracks around iron containing inclusions	Development of ring cracks, the appearance of first cracks crossing the grain	Covering the entire field of the sample with cracks	

1. The “metallic” samples at the initial stage have **high porosity, heterogeneity and developed external surface**.
2. Samples after manufacturing have large amount of **isolated iron-containing inclusions** (similar to steel “globules” in Chernobyl lava).
3. Development of internal defects and corrosion of certain elements will lead to the destruction of the sample as these internal defects accumulate. The **rate of destruction** process depends on the **state of metallic (especially iron-containing) inclusions**. The completion of the mass destruction of samples is associated with the exhaustion of the stock of elements included in the corrosion processes.
4. The resulting products of corrosion of metallic inclusions serve as additional “accelerator” of the destruction due to the loss of main structure-forming elements of the sample as well as due to the increase of internal stresses inside the sample, caused by the increase of the corrosion products as compared to the volumes of initial inclusions.

## Weakening of Silicate Samples

	<u>Duration of «aging» in accelerated mode, days</u> <u>Calculated duration of «aging» in real time mode, years</u>			
	<u>0-20</u> <u>0-10</u>	<u>20-40</u> <u>10-20</u>	<u>40-60</u> <u>20-30</u>	<u>60-100</u> <u>30-50</u>
The state of the external surface of the sample	Smooth, glossy surface for samples with curium, matt surface for samples without curium. No deposits.	No noticeable change in geometry of external surface	Selective leaching out of concrete matrix from the surface of the sample (up to 200 μm), start of surface degradation	
Corrosive damage	Corrosion destruction of particles of iron was not found even at the boundary “sample/contact solution”	Corrosion destruction of particles of iron was not found	Corrosion of metallic inclusions appear	Products of corrosions appear at the surface of sample and crucible
Structure integrity	Structural integrity, high level of penetration of secondary uranium-plutonium phases into silicate matrix	The structure is integral, the boundary zones are “strengthened” by (U, Zr, O) phases	The surface is cracking	
1. “Silicate” samples in their initial state have <b>smooth, glass-like surface, lower porosity</b> (as compared to “metallic” samples). 2. Samples after manufacturing contain <b>large quantity of isolated iron-containing inclusions</b> (similar to steel “globules” in Chernobyl lava)				

## XRD. Microstructure of Metallic Samples

	<u>Duration of «aging» in accelerated mode, days</u>			
	<u>Calculated duration of «aging» in real time mode, years</u>			
	<u>0-20</u>	<u>20-40</u>	<u>40-60</u>	<u>60-100</u>
	0-10	10-20	20-30	30-50
Dominant phase	ZrO			
Minor phase	UO <sub>2</sub> , ZrO <sub>2</sub> – monoclinic,		UO <sub>2</sub> , U <sub>0.5</sub> Zr <sub>0.5</sub> O <sub>2</sub> , cub.	
Trace phases in samples w/o curium	(U, Zr)O <sub>x</sub> – orthorhombic, (U <sub>x</sub> Zr <sub>y</sub> )O <sub>2</sub> , cub.	PuO <sub>2</sub> , U <sub>0.5</sub> Zr <sub>0.5</sub> O <sub>2</sub> , cub.	γ-Fe – cub.; FeZr <sub>2</sub> , cub.	γ-Fe – cub.; FeZr <sub>2</sub> , cub.; Na <sub>2</sub> ZrO <sub>3</sub> , cub.,
Trace phases in samples with curium	(U, Zr)O <sub>x</sub> – orthorhombic, (U <sub>x</sub> Zr <sub>y</sub> )O <sub>2</sub> , cub	γ-Fe – cub.; β-Zr – cub.	α-, γ-Fe – cub. β-Zr cub.,	γ-Fe – cub.; β-Zr – cub. CmO <sub>2</sub> and Nd <sub>2</sub> Zr <sub>2</sub> O <sub>7</sub> , - NaPu(x)O(z).
Microstructure of samples is stable, the changes in phase composition are minor during the observed time periods				

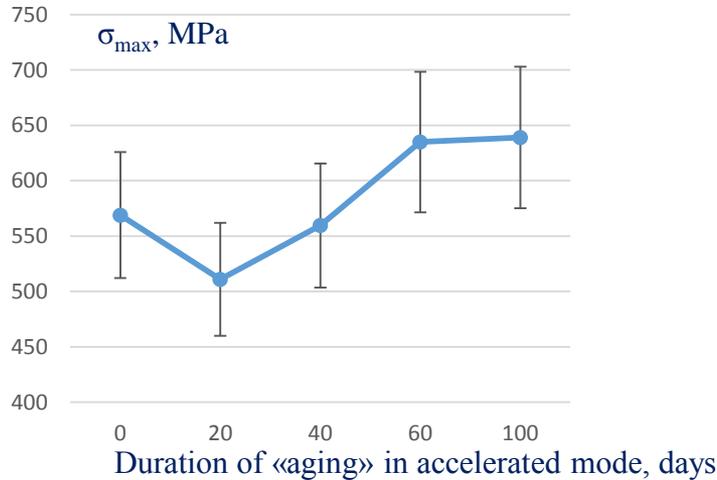
## XRD. Microstructure of Silicate Samples

	<u>Duration of «aging» in accelerated mode, days</u>			
	<u>Calculated duration of «aging» in real time mode, years</u>			
	<u>0-20</u> 0-10	<u>20-40</u> 10-20	<u>40-60</u> 20-30	<u>60-100</u> 30-50
Dominant phase	$\text{UO}_2$ – cub.			
Minor phase	Pyrochlore type phase, close to $\text{Eu}_2\text{Zr}_2\text{O}_7$ – cub., $\text{La}_2\text{Zr}_2\text{O}_7$ – cub.			
Trace phases	$\text{SiO}_2$ – tetragonal; $(\text{U}, \text{Zr})\text{O}_x$ – orthorhombic; $\text{U}_3\text{O}_7$ – tetragonal 4 reflexes of unknown phase, close to $\text{UO}_x$			
Microstructure of samples is stable; the changes in phase composition are minimum during the observed periods.				
The samples contain the traces of possible additional oxidation of uranium.				

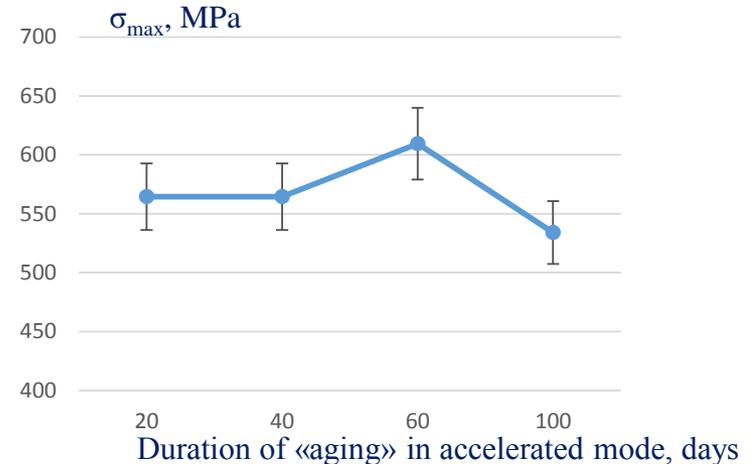
# Mechanical strength

For the mechanical tests, samples were selected that simulate 0, 10, 20, 30 and 50 years of fuel debris aging ( $\sigma_{\max}$ /days of experiment, MPa)

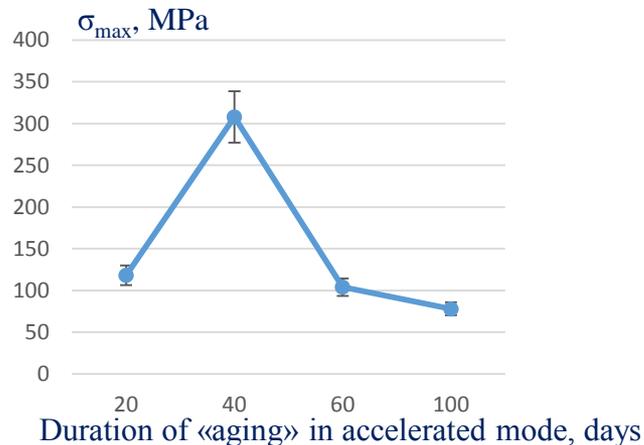
Hardening of metallic samples without Cm



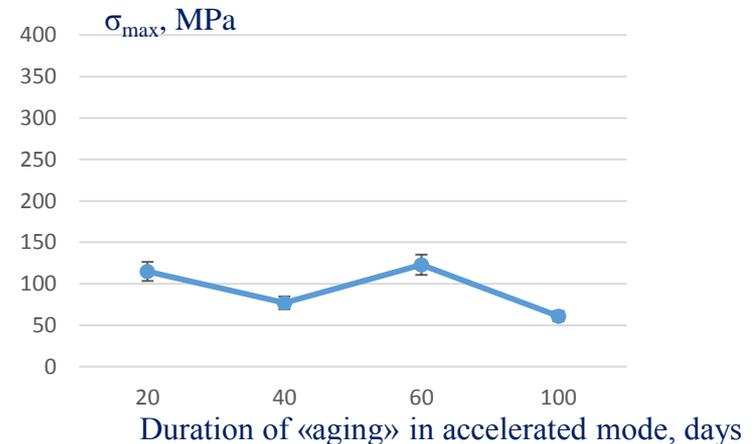
Weakening of metallic samples with Cm



Silicate samples without Cm



Silicate samples with Cm



# Expected compression force

Compression force, MPa	Duration of «aging» in accelerated mode, days				
	Calculated duration of «aging» in real time mode, years				
	<u>0-20</u> 0-10	<u>20-40</u> 10-20	<u>40-60</u> 20-30	<u>60-100</u> 30-50	<u>0-100</u> 0-50
Metallic phase w/o Cm	511	560	635	639	586 (+ <sup>53</sup> - <sub>75</sub> )
Metallic phase with Cm	565*	564*	610	534	568 (+ <sup>42</sup> - <sub>34</sub> )

## Metallic samples

- Compression force has changed little over time, actually within 10-15% of statistical error
- The samples demonstrated fragile destruction, which corresponds to their structure
- For samples without Cm certain increase of compression force over time can be observed, and for Cm samples, to the opposite, the decrease of strength on the last time period can be observed

\* *The samples of this type have been tested for compression force without additional crucible, that's why all maximum values of the chart were used for averaging.*

Compression force, MPa	Duration of «aging» in accelerated mode, days				
	Calculated duration of «aging» in real time mode, years				
	<u>0-20</u> 0-10	<u>20-40</u> 10-20	<u>40-60</u> 20-30	<u>60-100</u> 30-50	<u>0-100</u> 0-50
Silicate phase w/o Cm	118	(150-308)**	104	78	100 (+ <sup>18</sup> - <sub>22</sub> )
Silicate phase with Cm	115	77	123	61	94 (+ <sup>29</sup> - <sub>33</sub> )

## Silicate samples

- More heterogeneous structure
- Fragile destruction
- Much lower values of compression force
- Decrease of strength on the latest test period can be observed (the minimum value of compression force corresponds to curium sample at the final stage).

\*\* *This sample has abnormal characteristic of destruction due to its heterogeneity – excluded from the averaging*

\*\*\**The averaging was made for maximum values of chart describing the destruction of the sample not taking into account the more vertical part of the chart, which refers to the strength characteristics of the crucible.*

# Damage to the structure of Metallic samples

	Duration of «aging» in accelerated mode, days			
	Calculated duration of «aging» in real time mode, years			
	0-20 0-10	20-40 10-20	40-60 20-30	60-100 30-50
The state of the external surface of the sample	“Smoothing” of the external surface, the protruding parts are removed, part of the pores is closed	Noticeable change in geometry of the external surface of the sample, erosion by inclusions of iron	Macroscopic changes (cracks, caverns)	External surface of the samples is damaged significantly. The damage is more noticeable for Cm samples
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Structure integrity	The beginning of the formation of ring cracks around iron containing inclusions	Development of ring cracks, the appearance of first cracks crossing the grain	Covering the entire field of the sample with cracks	

## Metallic samples

- High porosity, heterogeneity, developed external surface
- Large amount of isolated iron-containing inclusions (similar to steel “globules” in Chernobyl lava)
- Development of internal defects and corrosion of certain elements lead to the destruction of the sample as these internal defect accumulate. The rate of destruction process depends on the state of metallic inclusions
- The resulting products of corrosion of metallic inclusions serve as additional “accelerator” of the destruction

## Damage to the structure Silicate samples

	Duration of «aging» in accelerated mode, days			
	Calculated duration of «aging» in real time mode, years			
	<u>0-20</u> 0-10	<u>20-40</u> 10-20	<u>40-60</u> 20-30	<u>60-100</u> 30-50
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Structure integrity	Structural integrity, high level of penetration of secondary uranium-plutonium phases into silicate matrix	The structure is integral, the boundary zones are “strengthened” by (U, Zr, O) phases	The surface is cracking	

## Silicate samples

- Smooth, glass-like surface, lower porosity
- Large quantity of isolated iron-containing inclusions (similar to steel “globules” in Chernobyl lava)
- The stability of silicate samples during the test period depends on the integrity of protective glass-like layer, and in case of destruction of this layer (due to chemical, mechanical or any other factors) the destruction rate may increase significantly

# Conclusions and Recommendations

# Conclusions & Recommendations

## Metallic Phase

- **Cumulative** radiation-chemical damage leads to **greater degradation** of fuel fragments, than total radiation and chemical effect
- **Fe is corrodible**
- **Ferrous hydroxide** is a good coagulant of Pu and U and other elements, except for Cs, it will lead to formation of larger quantities of small particles and **hazardous fine dust**. Delay in removal of fuel fragments after 20-25 years after an accident can lead to complication of dose and radiation environment, because of increased emission of plutonium, its further transit into colloidal forms and solid particles of submicrometer dimension
- Despite the fact that most of Cs emitted during high-temperature processes, but approximately 10-20% of it is left in the form of cesium plutonate
- In the FD mass areas of reduced sponginess can exist, in these areas speed of degradation processes will be lower
- For handling FD of “metallic” phase, the following requirements should be taken into account:
  - to develop **instruments**, which let work with ceramics
  - to estimate **reduction of FD strength properties in course of time**
  - to estimate **increase of dust formation** with  $\alpha$ -active and dose-producing components
  - prolonged removal operations will lead to activation of degradation processes, after the works are started and “covering” layers are opened

## Conclusions & Recommendations

### Silicate Phase

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- Low integral strength of matrixes and local involvement into silicate matrixes give high values of local strength.
- **Time delay of degradation** processes start related to protection of PCV water from intense alpha-irradiation from the MCCI surface.
- In the course of scanning electron microscopy of silicate phase, formation of **secondary crystallization areas for U and Pu compounds**, significantly distant from the place of fuel fragment and molten contact, in stratum of melted concrete was revealed.
- **Mechanical strength** of silicate samples is commensurate with strength of **vitrified HLW matrixes**.
- **Leaching rate** of controlled radionuclides of silicate samples is commensurate with leaching rates of the same radionuclides of **vitrified HLW matrixes**.
- **Chemical stability** of silicate stage in simulation water is **slightly lower**, than chemical stability of **borosilicate glass**.
- Prolonged removal operations will lead to activation of degradation processes, after the works are started and “covering” layers are opened.

## Definitions

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- **Fuel debris (FD)** – solidified melt of nuclear fuel containing materials formed in PCVs during accident at 1F, usually consist of fuel, fissile materials, fission products and structure materials (stainless steel, Zr cladding, control rod materials, concrete etc)