Development of Analysis and Estimation Technology for Characterization of Fuel Debris

(Development of Estimation Technology of Aging Properties of Fuel Debris)

Final report for FY 2019 and 2020

Project Background & Objectives

POCATOM

Data on degradation of Chernobyl NPP and TMI-2 debris & vitrified HLW

conduct experiments in parallel on cold & hot samples

Zr / Fe / Si variations

SNF composition

Exposure conditions
- amount of oxygen in the gas phase above the contact solution,
- dissolved oxygen
- pH, temperature, etc

Evaluating data on physical and chemical phenomena that may contribute to aging of FD

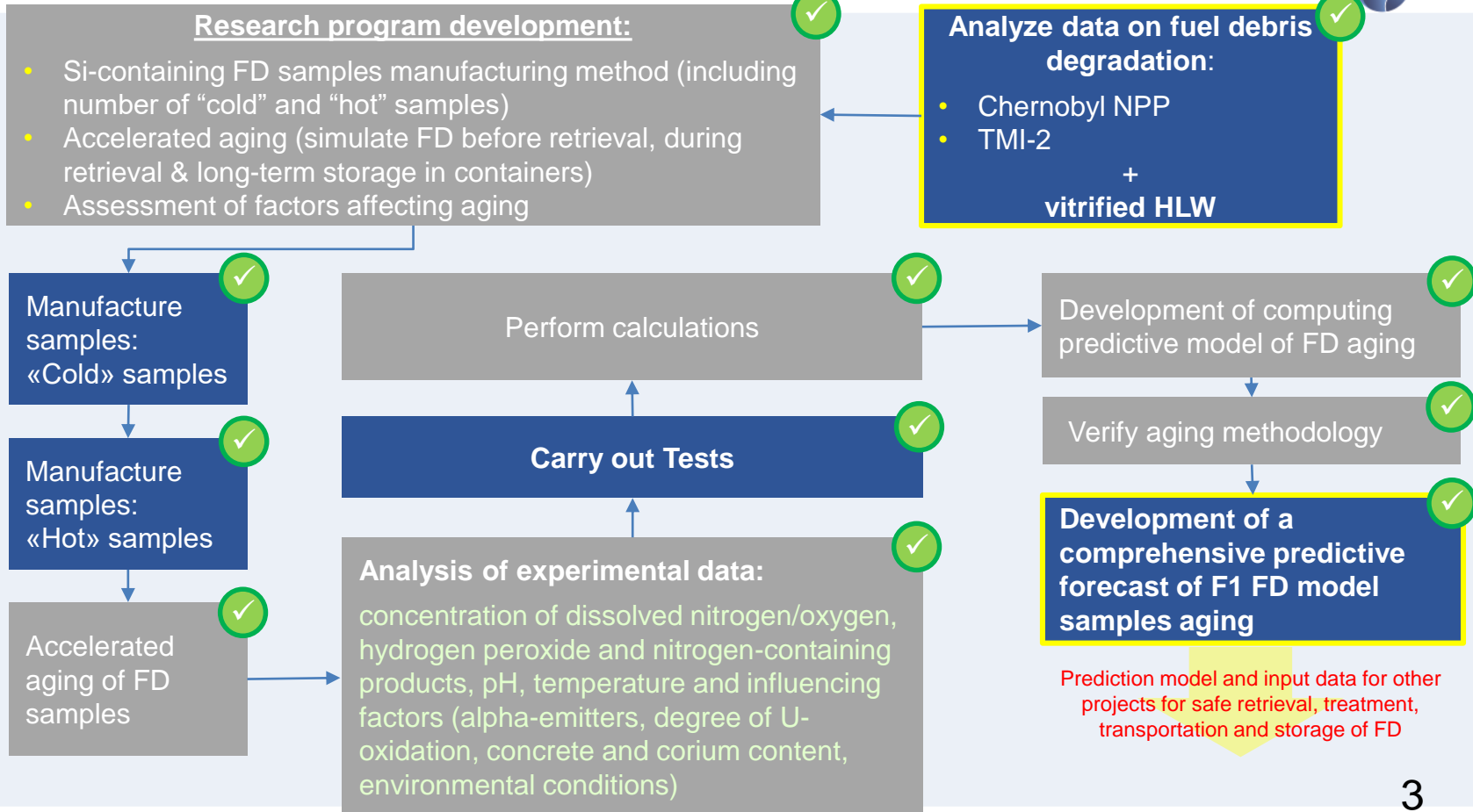knowledge about changing of FD properties caused by the aging

knowledge about FD particles release into water/air environment
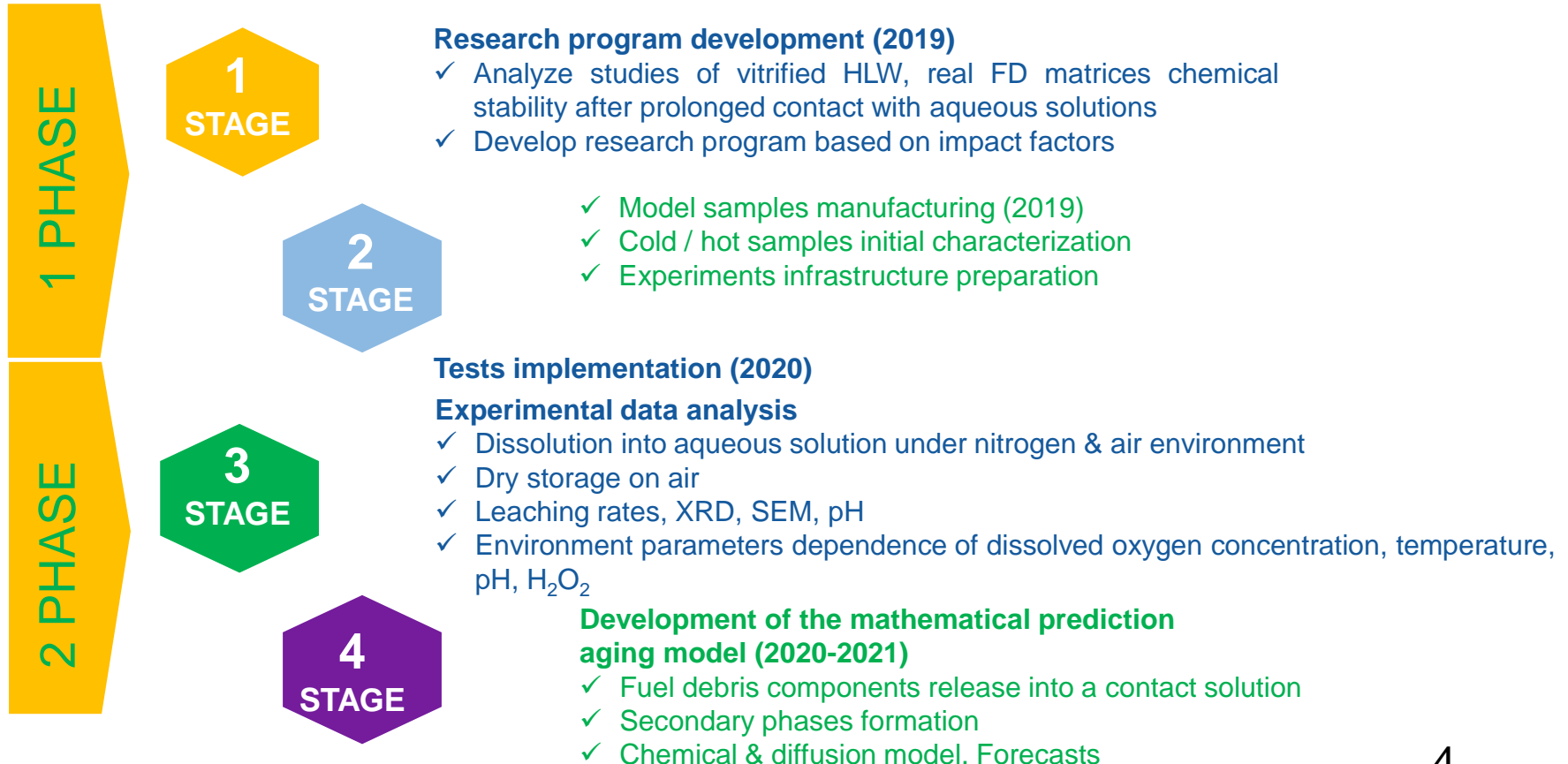
prediction of FD properties in the long term

develop comprehensive aging forecast of F1 FD

The results obtained in this work can be used for subsequent retrieval of FD from PCV/RPV of F1 NPS units, design and development of equipment for retrieval, treatment, transportation and storage of FD. Predicted effects of aged FD could be used for safety assessment and radioactive waste treatment for related research and development projects of the Mid-and-Long-Term Roadmap

Project Scope

POCATOM

Research program development:

- Si-containing FD samples manufacturing method (including number of "cold" and "hot" samples)
- Accelerated aging (simulate FD before retrieval, during retrieval & long-term storage in containers)
- Assessment of factors affecting aging

Analyze data on fuel debris degradation:

- Chernobyl NPP
- TMI-2

+

vitrified HLW

Manufacture samples: «Cold» samples

Perform calculations

Development of computing predictive model of FD aging

Manufacture samples: «Hot» samples

Carry out Tests

Verify aging methodology

Accelerated aging of FD samples

Analysis of experimental data:

concentration of dissolved nitrogen/oxygen, hydrogen peroxide and nitrogen-containing products, pH, temperature and influencing factors (alpha-emitters, degree of U-oxidation, concrete and corium content, environmental conditions)

Development of a comprehensive predictive forecast of F1 FD model samples aging

Prediction model and input data for other projects for safe retrieval, treatment, transportation and storage of FD

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Project Schedule 2019-2021

РОСATOM

1 PHASE

1 STAGE

Research program development (2019)
- ✓ Analyze studies of vitrified HLW, real FD matrices chemical stability after prolonged contact with aqueous solutions
- ✓ Develop research program based on impact factors

2 STAGE

- ✓ Model samples manufacturing (2019)
- ✓ Cold / hot samples initial characterization
- ✓ Experiments infrastructure preparation

2 PHASE

3 STAGE

Tests implementation (2020)

Experimental data analysis
- ✓ Dissolution into aqueous solution under nitrogen & air environment
- ✓ Dry storage on air
- ✓ Leaching rates, XRD, SEM, pH
- ✓ Environment parameters dependence of dissolved oxygen concentration, temperature, pH, H_2O_2

4 STAGE

Development of the mathematical prediction aging model (2020-2021)
- ✓ Fuel debris components release into a contact solution
- ✓ Secondary phases formation
- ✓ Chemical & diffusion model. Forecasts

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Corium model samples manufacturing

Samples Manufacturing

6 types of compositions of large-sized U-containing cold samples manufactured (> 300 g) ✓

Large-sized cold samples fragmented into small-sized "cold" samples ✓

Sample characterization by SEM / EDX, XRD, XRF methods and chemical analysis ✓

Set of 45 "hot" samples manufactured by doping cold samples with ^{238}Pu 4% wt proportional to U content of composition ✓

Party of "cold' small-sized samples transported to RIAR ✓

✓ **790+ Cold samples manufactured (containing ^{238}U)**

chemical simulation of accelerated oxidation (by adding appropriate amount of H_2O_2 and nitriding a contact solution) & leaching (accelerating dissolution mechanism by increasing temperature and SA/V)

✓ **Set of 45 "hot" samples manufactured**
(containing ^{238}U and ^{238}Pu)
to verify the chosen method of aging for chemical similarity of aging processes and to estimate the radiation factor impact

C5

C4

C3

C2

C1

C6

C2«hot»

C3 «hot»
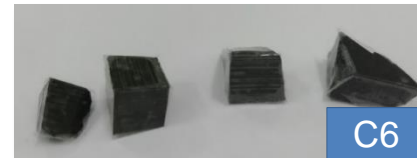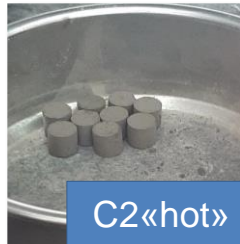
C1 means **Composition 1**
C2…**C6** means
Composition 2…Composition 6 etc

Compositions & preparation

In elements

	Composition 1	Composition 2	Composition 3	Composition 4	Composition 5	Composition 6
Simulated plant	Fukushima Daiichi NPS (Chemical content changes gradually)					TMI-2
U	16.0	25.5	30.8	36.0	36.0	65
Zr	5.6	7.7	8.8	9.9	9.9	15
Fe	2.7	3.0	3.4	3.8	3.8	7
Cr	0.7	0.8	0.9	1.0	1.0	
Ni	0.4	0.5	0.6	0.6	0.6	
Si	22.4	17.9	15.3	12.6	12.6	-
Ca	6.4	5.1	4.3	3.6	3.6	
Al	6.4	5.1	4.3	3.6	3.6	
O	39.4	34.4	31.6	28.9	28.9	13
Quench rate	rapid	rapid	rapid	slow	rapid	rapid
Melt date	14/12/2019	17/12/2019	23/12/2019	12/11/2019	23/10/2019	26/12/2019
Facility	RASPLAV-4	RASPLAV-4	RASPLAV-4	RASPLAV-2	RASPLAV-2	RASPLAV-3

Composition 5

Melting conditions. Temperature, °C vs Time, s. $\sim T_{liq}+100°C$
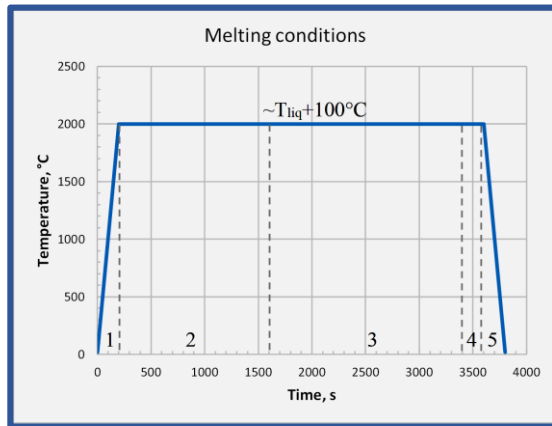
① **Heating and melting** the charge material at a rate of 10 °C/s

② **Refilling the remaining charge material**, adjusting the parameters of the inductor and the position of the crucible (slight overheating over the liquidus T)

③ **Homogenizing** isothermal exposure of the melt (30 min)

④ **Measurement** of the depth of the molten pool, sampling

⑤ **Cooling** by switching off power of high-frequency generator (rate of 10 °C/s)

Samples compositions
Total composition analysis

	Composition 1	Composition 2	Composition 3	Composition 4	Composition 5
Corium: concrete mass ratio	30 : 70	44 : 56	52 : 48	60 : 40	60 : 40
Actual corium: concrete mass ratio	26.4±1.3 : 73.6±4.0	37.1±0.8 : 62.9±2.0	43.7±0.5 : 56.3±0.9	50.5±6.8 : 49.5±7.4	49.0±1.5 : 51.0±5.2
Cooling rate, °C/s	15 ± 8 (quenching)	12 ± 5 (quenching)	10 ± 4 (quenching)	0.1 → 1.5 (slow cooling)	12 ± 2 (quenching)
Pycnometric density, g/cm³	3.77	3.95	4.78	4.89	4.90

Mass, %

Composition 1 / Composition 2 / Composition 3 / Composition 4 / Composition 5 / Composition 6

Amorphous part SiO_2, Al_2O_3, CaO

Reactor elements FeO, Cr_2O_3, NiO

Fuel elements UO_2, ZrO_2, PuO_2

Composition 3

End surface of the sample

Amorphous silicate phase (dark grey)

$(U,Zr)O_2$ dendrites (light)

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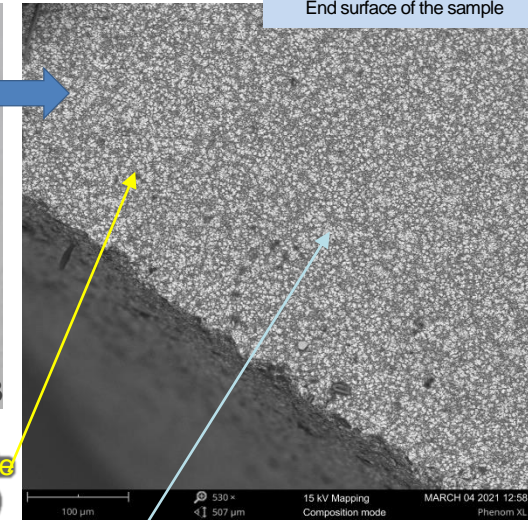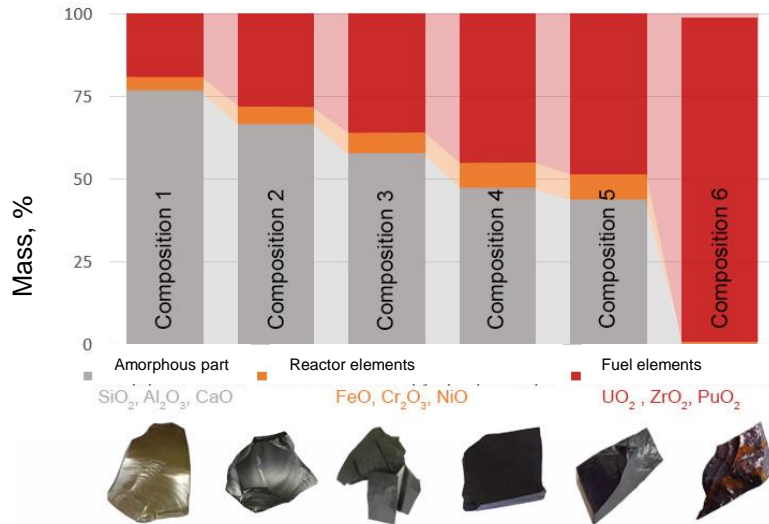
SEM/EDX analysis

Oxidic silicate-enriched sample specific microstructure (Composition 3)
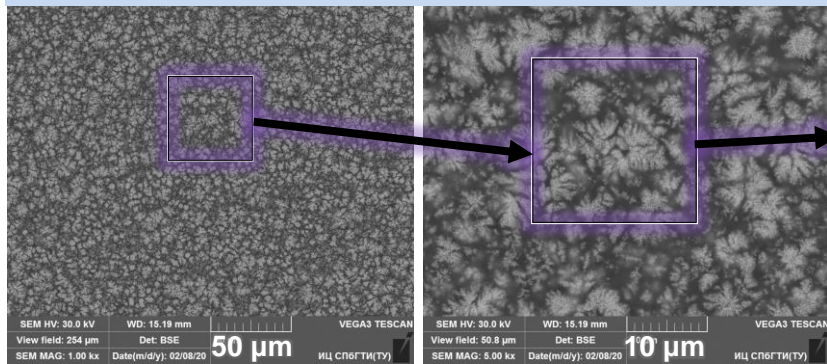
Amorphous silicate phase

$(U,Zr)O_2$ dendrites

50 µm   10 µm   5 µm   5 µm

BSE
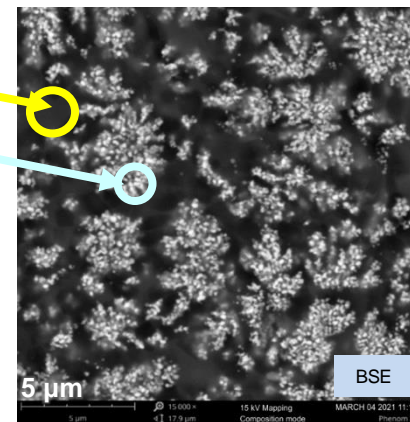
Composition 3

Oxidic-metallic sample specific microstructure (Composition 6)
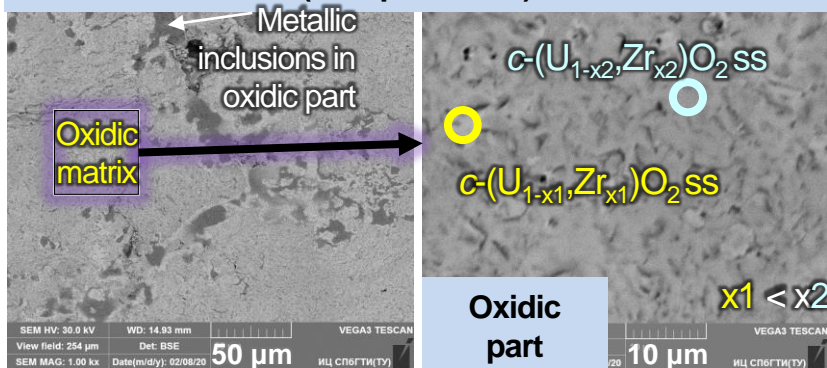
Metallic inclusions in oxidic part

Oxidic matrix

c-$(U_{1-x2},Zr_{x2})O_2$ ss

c-$(U_{1-x1},Zr_{x1})O_2$ ss

$x1 < x2$

Oxidic part

Metallic part

Fe

$Zr(U)Fe_{2+x}$

$U(Zr)Fe_{2+x}$

50 µm   10 µm   20 µm
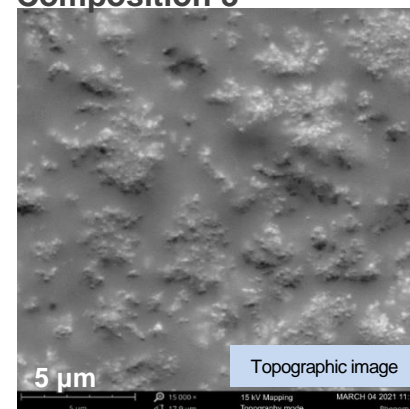
5 µm   Topographic image

РОСАТОМ

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Cold Samples Manufacturing Results

Corium : Concrete ratio change

POCATOM

Composition 1

Composition 2

Composition 3

Composition 4

Composition 5
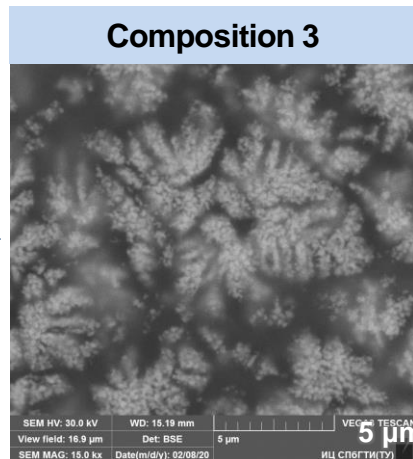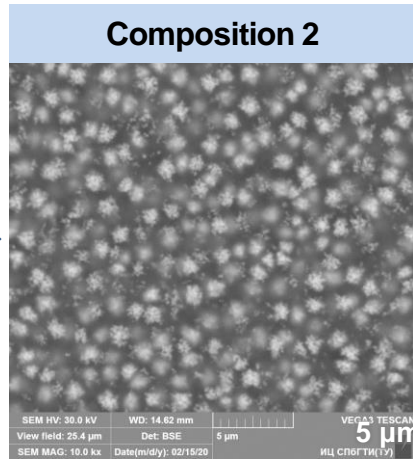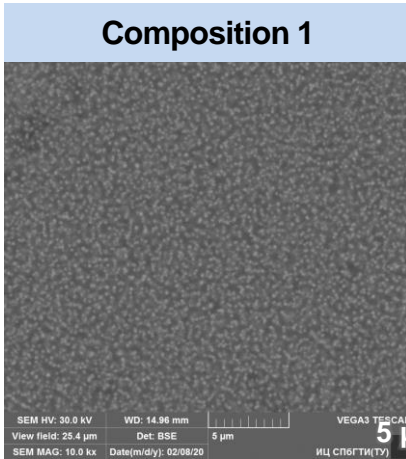
Increasing of corium : concrete ratio leads to increase size and quantity of $(U,Zr)O_2$ inclusions:
- In No. 1 - 100 nm spherical nanoinclusions
- In No. 2 – 1 µm spheroidal dendrites
- In No. 3 – 10 µm length dendrites
- In No. 5 – 100 µm length dendrites
- In No. 4 unhomogeneous ingot with good crystallized phases

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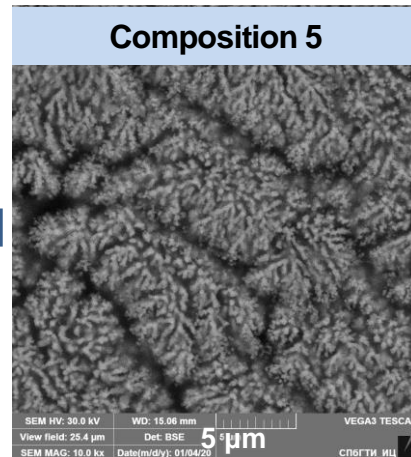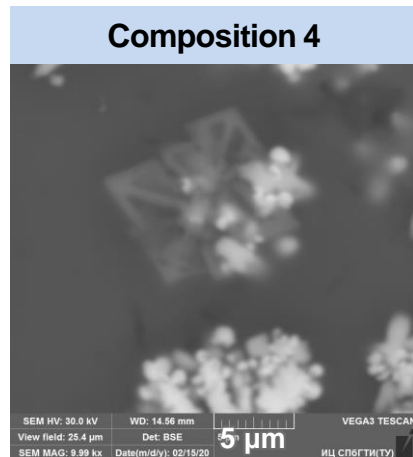
Hot samples

Phase study. Composition №3

SE

BSE

Pores filled with abrasive

Pores filled with Wood's Alloy (used for microsection preparation)
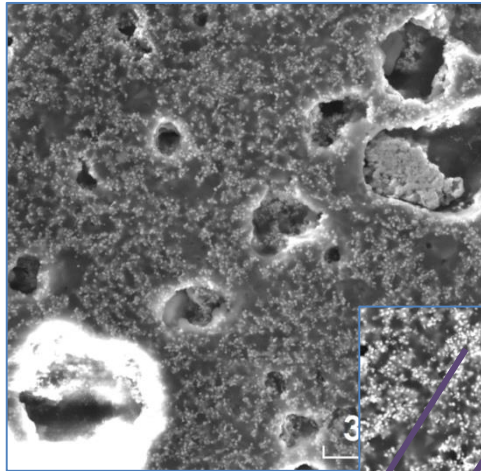
$(U,Pu,Zr)O2$

Amorphous phase based on SiO_2

SE	BSE	Zr
U	Pu	Fe
Si	Ca	Cr

Zone 3

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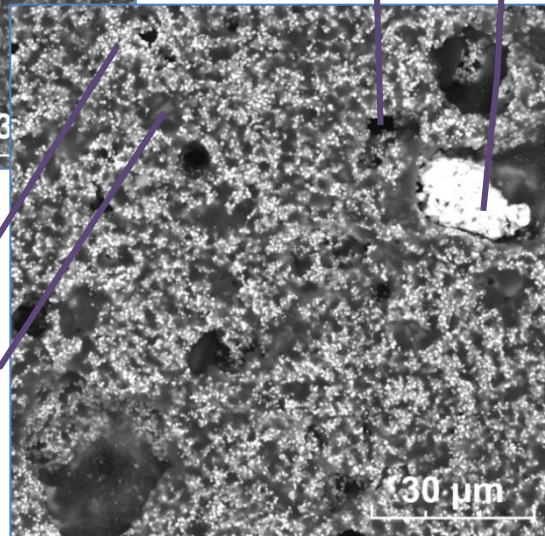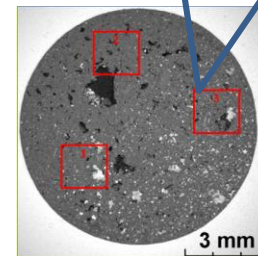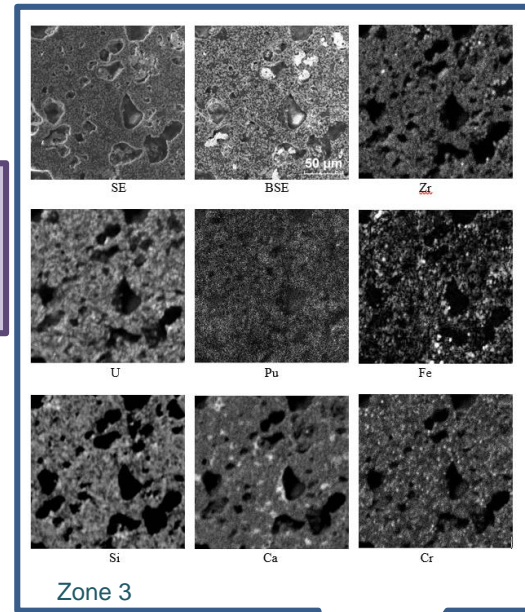
Aging Experiments

Accelerated Aging Methodology

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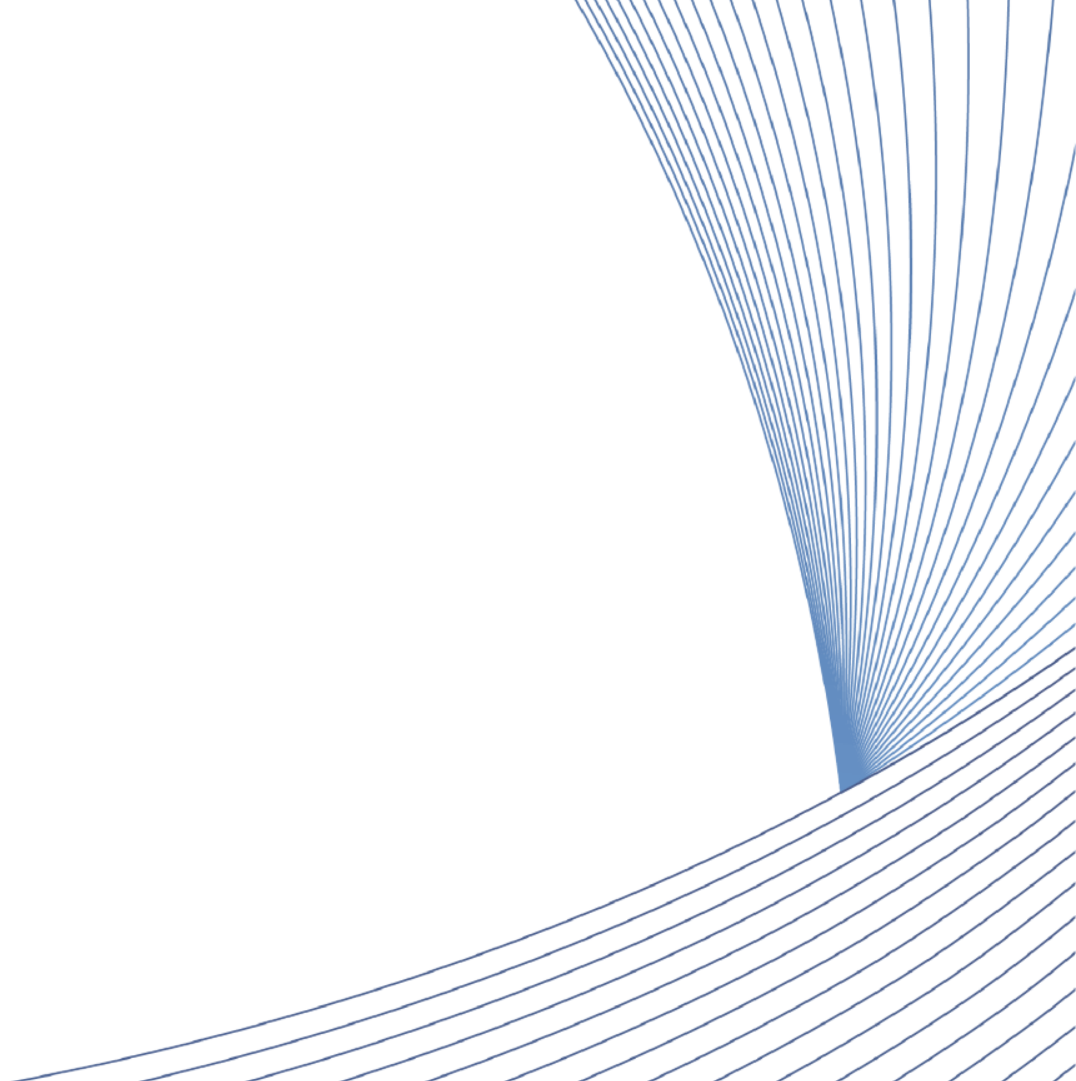
AGING:
- Factor of model FD elements release into a contact media
- Secondary phases and dust particles generation
- Phase content change
- Factor of oxidation of U (IV) → U (VI)

Studies of 1F model samples in 3 different environments :

(I) **Storage inside PCV** — FD water cooling, nitrogen atmosphere (ratio $N_2:O_2=100/1$)

(II) **Retrieval —** water cooling and purge of nitrogen (ratio $N_2:O_2=82/18$)

(III) **Long-term container storage of extracted FD** — dry condition and atmosphere

(I) **(II)** **(III)**

N_2
T=25/50/90 °C
t=1,5-672 hours

H_2O

Air
T=25/50/90/120 °C
t=1,5-2016 hours

H_2O

Air

T=150 °C
t=2200 hours

Monolith

Powdered
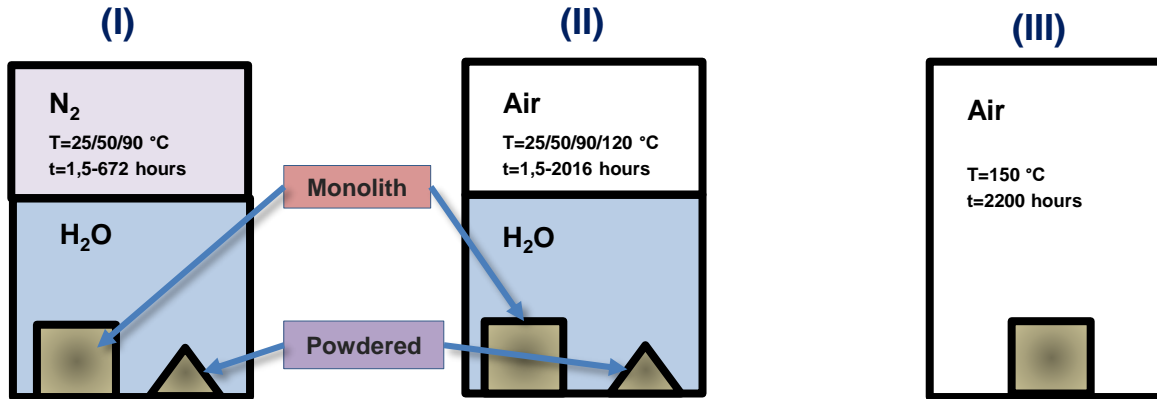
Accelerated Aging Methodology

Dissolution experiment implementation scheme

(I) Storage in water + N$_2$ atmosphere

(II) Storage in water + air atmosphere

Nitrated water

Deionized water

Initial characterization

- Ox-Red state (Mossbauer Method)
- Density
- Porosity
- Microhardness
- Chemical elements distribution (SEM/EPMA)
- Phase composition (XRD)

Monolith samples
Sampling on 3, 7, 14, 21, 28 days
T=25, 50, 90 °C
SA/V = 3 cm^{-1}
Extended tests: dissolution 56, 84 days with T=90, 120 °C

Powdered samples

Sampling: 0.5, 1.5, 4, 24, 168, 672 hrs
25, 50 °C
SA/V =10 and 100 cm^{-1}

H$_2$O preparation

- Demineralization
- Deaeration (CO$_2$↑)
- Sealing
- Cooling
- N$_2$ saturation (for (I))
- Storage

pH			H$_2$O$_2$ mmol/l	
4,1	7	9,18	0,1	0,3

H$_2$O characterization

Samples/Solution characterization:
- Element composition (ICP-AES, ICP-OES);
- Chemical elements distribution (SEM/EPMA);
- Phase composition (XRD)

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Accelerated Aging Methodology

Dry storage experiment implementation scheme

POCATOM

(III) Storage air atmosphere

Small-sized samples → Initial Characterization

Dry storage
Stainless steel sealed container

Output Characterization

- Chemical composition
- Phase composition
- Surface area
- Micro hardness
- Morphology of the surface
- Porosity
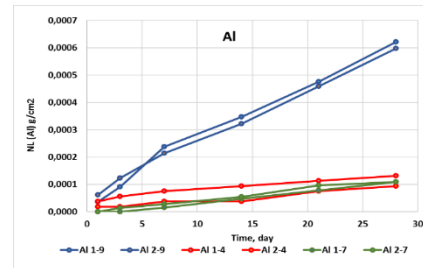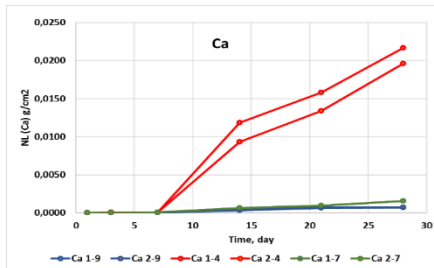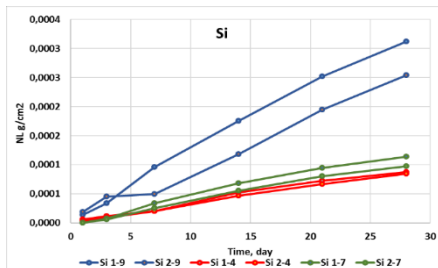- Density
- U(IV)/U(VI) ratio
- Fe(II)/Fe(III) ratio

Air

T: 150° C
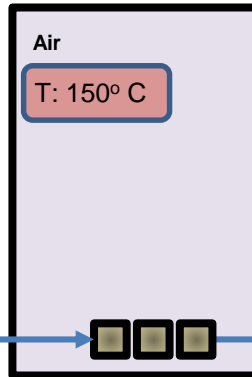
- Chemical composition
- Phase composition
- Surface area
- Micro hardness
- Morphology of the surface
- Porosity
- Density
- U(IV)/U(VI) ratio
- Fe(II)/Fe(III) ratio

Sampling: 500, 800, 1200 and 2200 hours
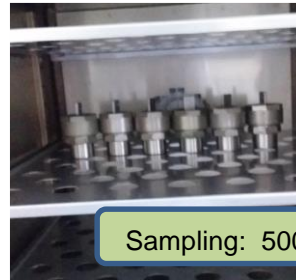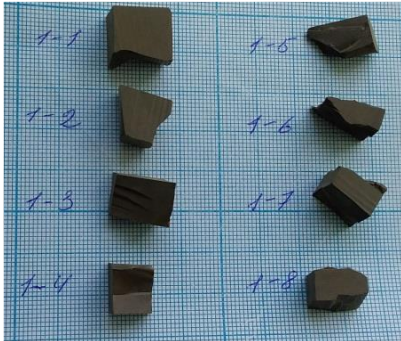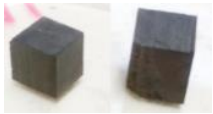
Accelerated Aging
Leaching tests, mass loss

POCATOM

Composition 1. Deionized water, 28 days, T=90°

Composition 3. Deionized water, 28 days, T=90°
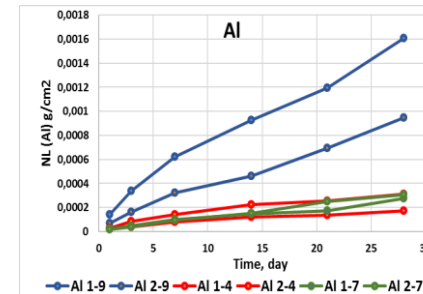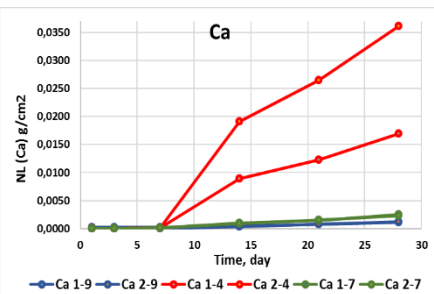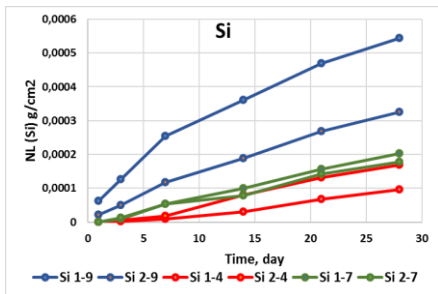
- The normalized mass losses of spinel components, solid solutions of uranium and zirconium (U, Zr, Fe, Cr, Ni) at elevated temperatures (90°C) are very small, as well as the yield of concrete components at temperatures of 25 and 50°C

- For 1-5 compositions in an acidic environment (pH = 4), the maximum mass loss is observed for alkaline-earth Ca; in an alkaline environment (pH = 9), the maximum mass loss of Si and Al

- Normalized losses of the elements of two parallel samples have similar values

Figures show graphs of the dependence of the normalized mass losses from time of the glass phase components (Si, Ca, Al) during leaching (T=90 °C) for two parallel samples (for pH 9 (blue), pH 4 (red), pH 7 (green)).

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Accelerated Aging
Leaching tests, pH, results

POCATOM

Composition 3. Deionized and nitrided water, 28 days, pH=4,7,9 T=25, 50,90º

Composition No.3

Nitrided water — Deionized water

Si

Ca

Al
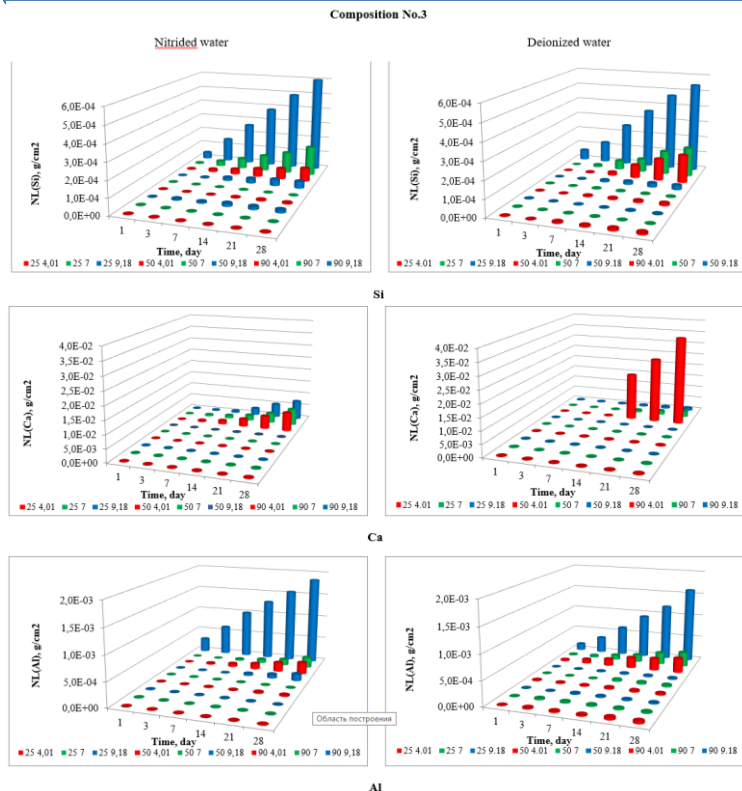
- During the leaching of monolithic samples of 1-5 compositions in all the studied conditions of the aqueous medium, the amorphous component dissolves and passes into contact solutions of Si, Ca, Al. Normalized losses of the glass phase elements, i.e., Si, Al, and Ca have the same tendency for all compositions

- **Si** is acidic by nature has large normalized losses in an alkaline environment, **Ca** is an alkaline-earth element and leaches well in an acidic environment, **Al** is an amphoteric element and, according to our observations, leaches better in an alkaline environment than in an acidic one.

- The effect of nitriding of water during leaching does not appear, the expected decrease in the yield of all elements in the solution under all conditions does not occur.

- Normalized losses increases with an increase in the concentration of H_2O_2 for all elements. The highest value of normalized Ca mass loss.

- In nitrided water, the concentrations of Si and Al were below the detection limit, and the normalized loss of Ca increased by 1 order of magnitude

- Concentrations of U, Zr, Fe, Ni, and Cr in the contact solutions under all leaching conditions (up to 28 days) were low

- No new crystal phases were detected on the surface of the samples after leaching at 90 °C

- Phase content of samples of compositions 1-5 after leaching in all media for 28 days at a temperature of 50 ° C did not change

Graphs show the dependence of the normalized mass losses from time (days 1-28) of the glass phase components (Si, Ca, Al) during leaching (T= 25, 50 and 90 °C) for (for pH 9 (blue), pH 4 (red), pH 7 (green).
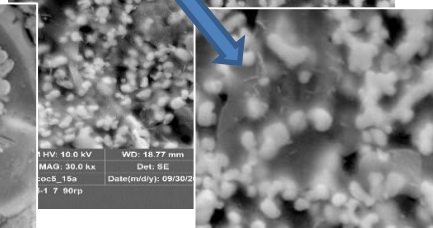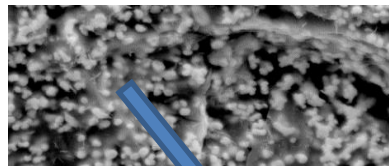
Accelerated Aging
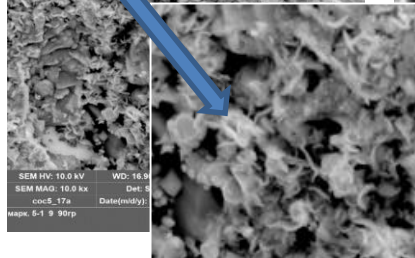
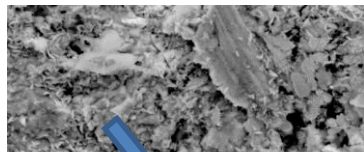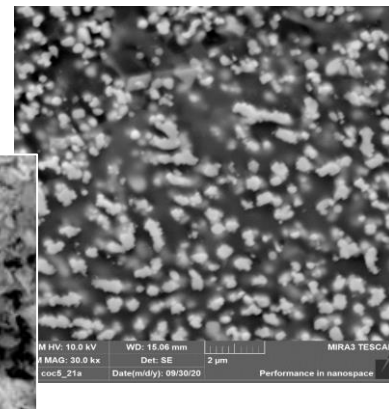Surface   analysis. Composition 5, 28 days

pH=4, T=90ºC
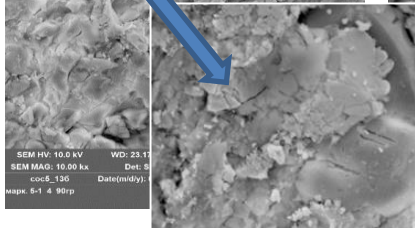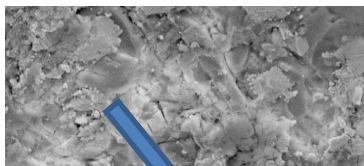
pH=7, T=90ºC

pH=9, T=90ºC

CH2O2=0,3 mmol/l, T=50ºC

Conditions T, °C, pH, Concentration of H_2O_2, mmol/L	Al_2O_3	SiO_2	CaO	Cr_2O_3	FeO	NiO	Total
90°C, pH4	12	73	8	2	5	0	100.0
90°C, pH7	16	56	7	4	16	0	100.0
90°C, pH9	7	28	5	2	54	4	100.0
50°C, 0.3 mmol/L	13	69	8	3	8	0	100.0
Initial	13	65	9	3	10	1	100.0

- With pH=4.01 the Si content increases; the formation of a hydrolyzed silicate layer is possible

- When leaching in contact solutions with H_2O_2, no surface changes are detected after leaching

- When leaching in contact solutions with pH=7 and 9.18, the iron content increases, and the formation of iron-containing phases may occur.

- Processes of formation of surface layers during leaching of monolithic samples for 28 days at different pH values in samples of compositions 1-5 are the same.
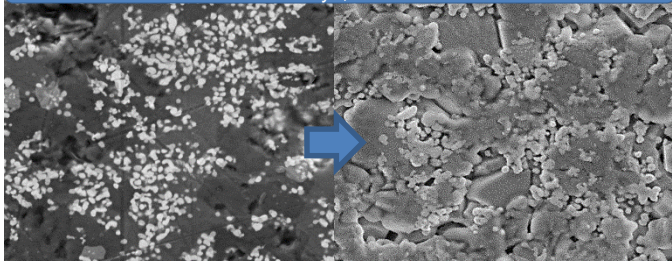
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Accelerated Aging

Dissolution experiments results, T=90°C

Composition 1. Deionized water, C_{H2O2}=0,3 mmol/l 18 days, T=90°
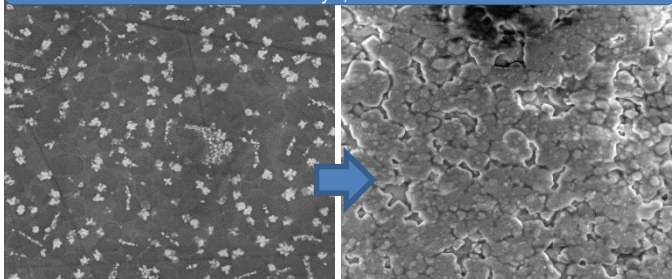
Mass,%	Al2O3	SiO2	CaO	Cr2O3	FeO	NiO	ZrO2	UO2	∑
initial	8,7	64,5	5,6	0,0	2,6	0,0	5,5	13,2	100
after	5,0	65,0	3,1	0,0	3,5	0,0	7,3	16,1	100

Composition 3. Deionized water, C_{H2O2}=0,3 mmol/l 18 days, T=90°

Mass,%	Al2O3	SiO2	CaO	Cr2O3	FeO	NiO	ZrO2	UO2	∑
initial	6,7	47,3	4,5	1,2	4,2	0,0	9,5	26,7	99,6
after	4,0	44,3	2,4	0,0	6,0	0,0	11,9	31,4	100

- **Sample composition** influence on dissolution results is **insignificant** and could be averaged

- Observed changes in the surfaces of all samples

- **Formation of a layer** is observed, which covers the surface of the sample with crusts on samples of Compositions 1 and 2, formed by poorly soluble Si and Fe compounds

- On the surfaces of samples of Compositions 3 to 5, a decrease in continuous layers is observed, it covers only specific areas

- Blockage of further leaching processes, which is explained by clogging of the pores of the surface layer by **reprecipitated Si**

- Composition 6 after leaching in some spectra is completely covered with a layer of iron hydroxide, in other spectra only uranium and zirconium oxides are present. This confirms the heterogeneity of the phase distribution in the Composition 6, and may also indicate that iron is re-deposited on the surface of the sample forming a porous surface layer that does not prevent the further release of the components into the solution

Accelerated Aging

Extended dissolution tests. Composition 1

Composition 1. Deionized water, $C_{H2O2}=0,3$ mml/l
56 days, T=90°

Ferruginous Chlorite
$Fe_4Al[Si_3AlO_{10}][OH]_8\ nH_2O$

Hydrated Silica (opal)
$SiO_2 \cdot nH_2O$
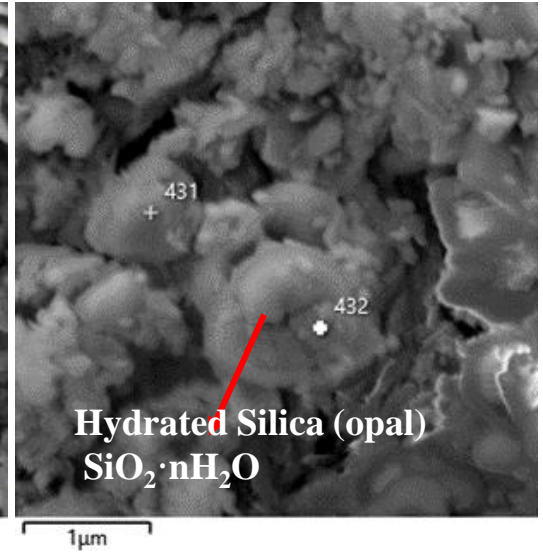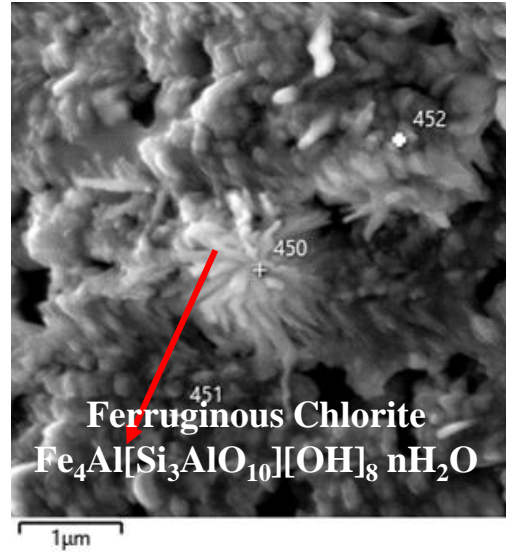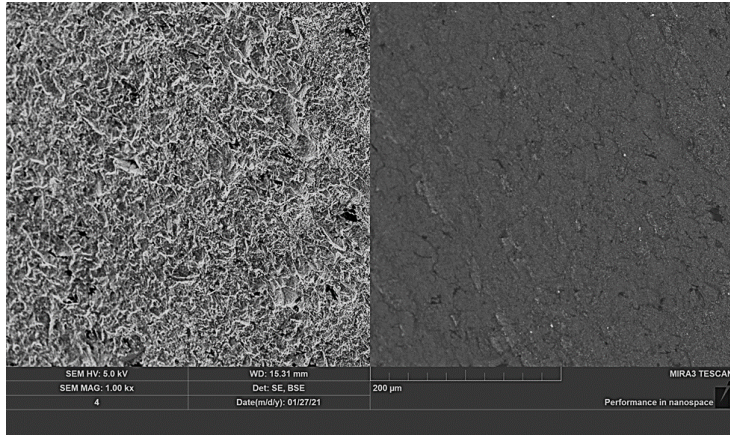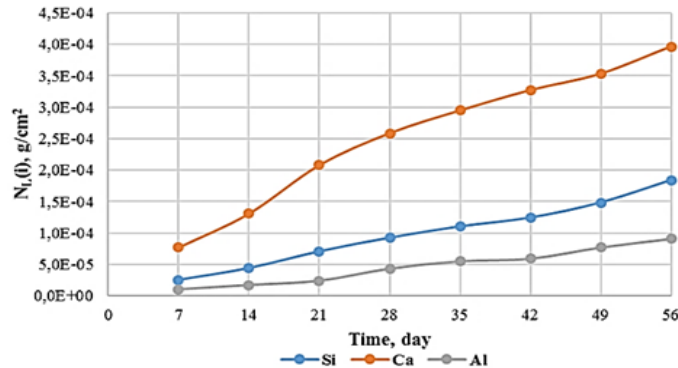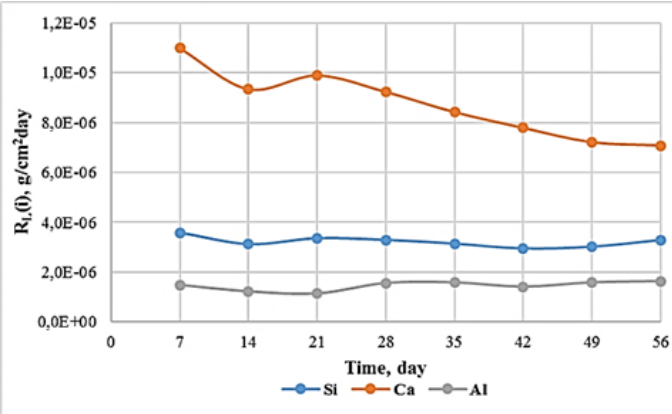
- Secondary phases layer depth ~0,5 µm
- Ca, Zr, U are not detected in secondary phases
- Secondary phases are hydrated Fe-containing aluminosilicates

20

Accelerated Aging

Extended dissolution tests. Composition 5

POCATOM

Composition 5. Deionized water, $C_{H2O2}=0.3$ mml/l
56 days, T=90°


- Dissolution rates decreases and in balance on day 28 for all glass phase components

- Secondary layer depth ~0,2 µm are zeolites (Fe-containing aluminosilicates)

- The phases containing U and Zr are observed. Hypothesis: the silicate-containing re-precipitated phases cover the crystals of solid solutions $(U,Zr)O_2$ of variable composition

- The surface of the sample has become loose, there are shells that are presumably formed as a result of the dissolution of the glass phase (such as an etched surface)
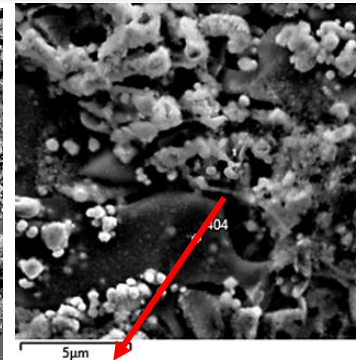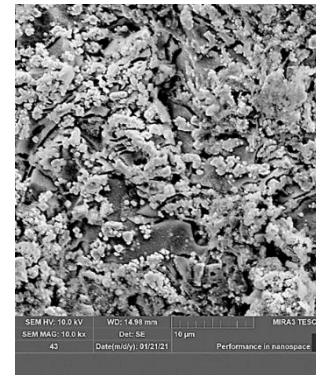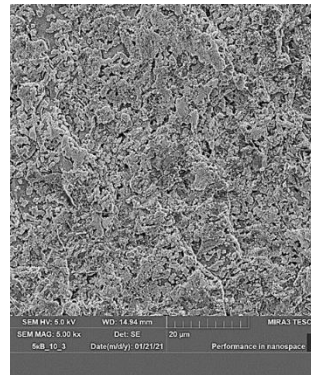
Glass phase

Accelerated Aging

**Extended dissolution tests. Secondary phases**
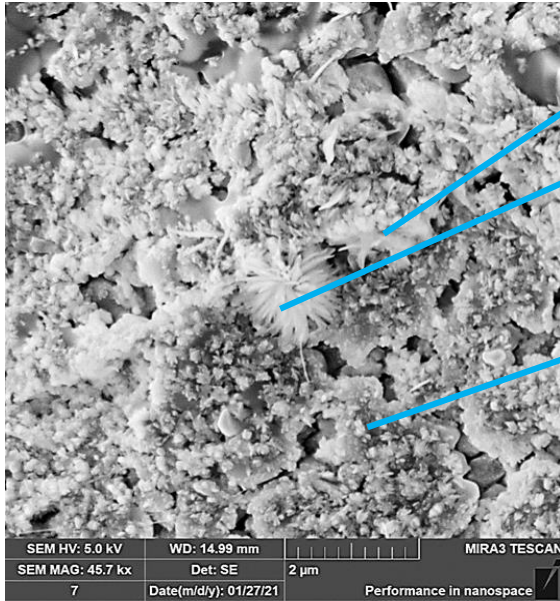
Chlorite

Al, Fe enriched crystals

$SiO_2 \cdot H_2O$

- Surface layer change occurs mainly due to the dissolution of the amorphous glass phase and the formation of new secondary phases

- Transition to the liquid phase of the most soluble components (Ca, Si, Al, Fe) leads to the appearance of a porous layer formed by poorly soluble compounds of the solid solution $(U,Zr)O_2$

- Secondary phases are formed by oxide compounds of Al, Si and Fe with a small amount of Ni, Zr and Cr. Ca, U, and Zr were not found in the secondary phases

- Main secondary phases are: hydrolyzed silicon oxide $SiO_2{}^*H_2O$, compounds of variable composition – ferruginous chlorite groups, bertierine, crystals with a high content of Al and Fe - $(Al_xFe_{1-x})O(OH)$.

- The thickness of the surface layer in the samples is proportional to the amount of glass phase in the initial compositions. up to 500 nm (in different areas) in composition1, ≈300 nm for Composition 3

- Surface of composition 5 is changed due to the dissolution of the glass phase (by the type of etching), the secondary phases layer is minimal
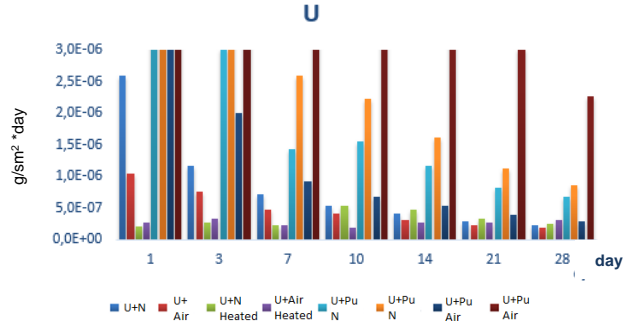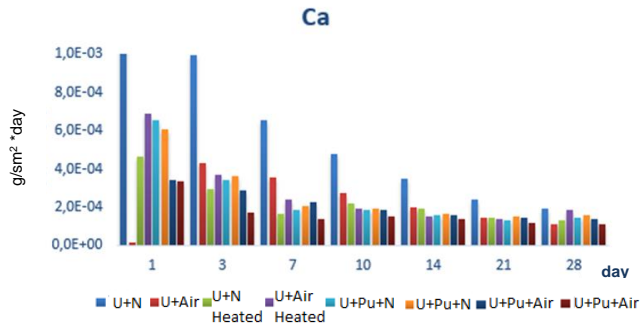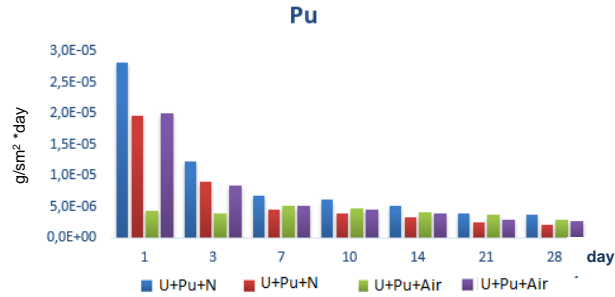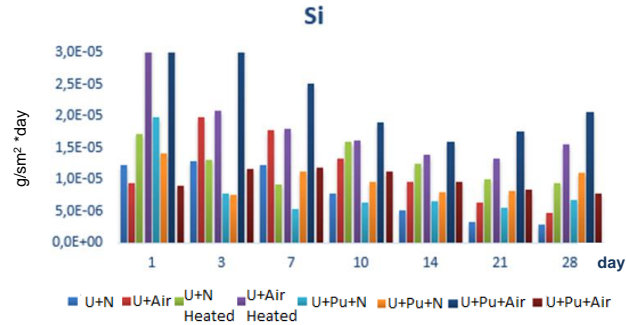
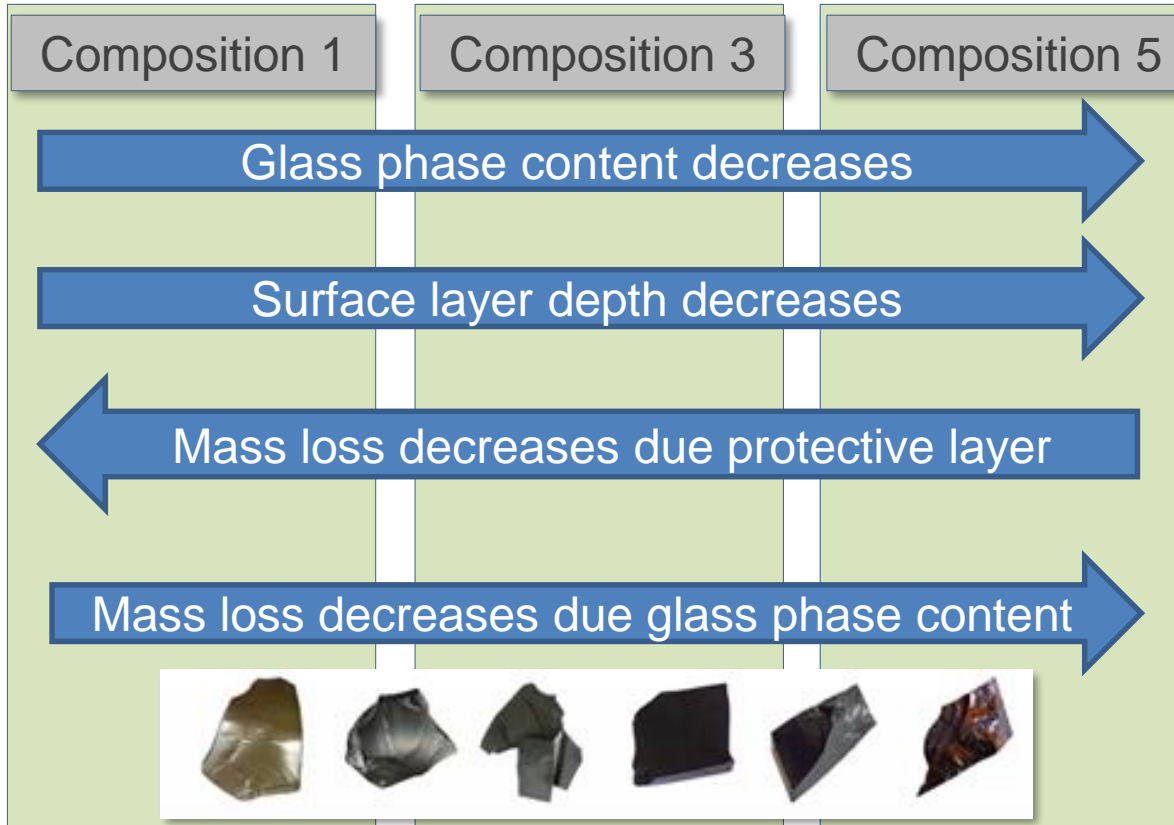22
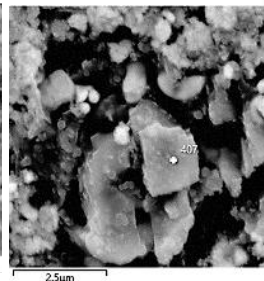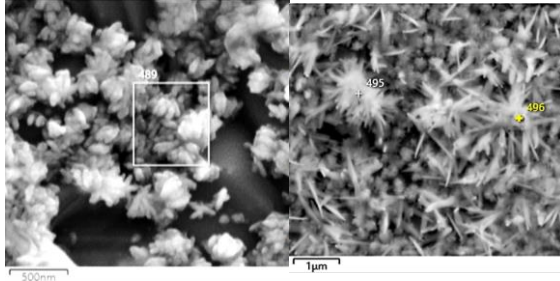
Accelerated Aging

Dissolution experiments results. Hot samples

Composition 3. Deionized water, C_{H2O2}=0,3 mml/l
28 days, T=90°

- Dissolution rates decrease for all components of hot samples. U, Zr, Si, Fe release rates of Pu-samples are higher than U-samples

- Ca, Al, Si release from amorphous phase of 'hot' Pu-samples is comparative to corresponding components of 'cold' U-samples

- Hot samples has higher leaching rates of Fe, Cr, Ni, U, Zr, Pu, Am but doesn't depend on Pu concentrations. Hypothesis: it is the result of thermal treatment (doping) and higher porosity

- No secondary phases detected (28 days)

- Surface remains unchanged, no significate phase change (XRD)

Accelerated Aging
Dissolution experiments. General conclusions

Composition 1	Composition 3	Composition 5

Glass phase content decreases →

Surface layer depth decreases →

← Mass loss decreases due protective layer

Mass loss decreases due glass phase content →

- Mass loss of all compositions are within similar ranges
- Composition 3 has higher mass loss
- Glass phase dissolves with Si and Al re-precipitates on surface and Ca releases into solution
- Fe, Ni and Cr supposedly dissolve because found in surface secondary phase layers
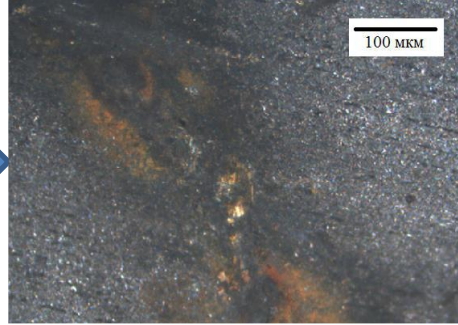- U and Zr not found in secondary phase but in solutions only

10µm

24
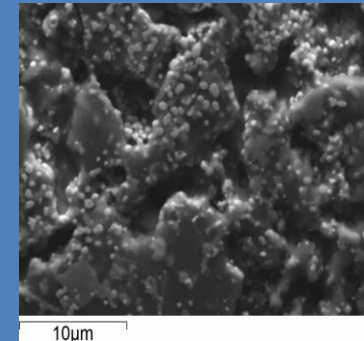
Accelerated Aging

Dry storage experiments results

Composition 6. Dry storage 2200 h, T=150°

Composition 6. Dry storage 2200 h, T=150° Brown rust generation

100 мкм

Composition 6. Dry storage 500h. T=150°

2.5μm

- Fe(OH)$_3$, Fe$_2$O$_3$ brown rust generation
- Impurities of UO$_2$, ZrO$_2$
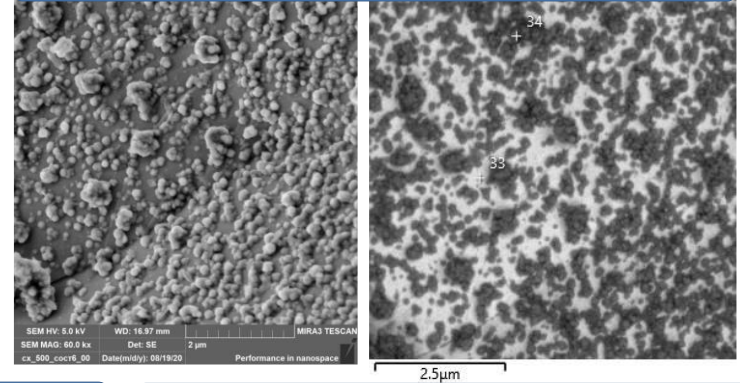
Composition 6. Dry storage 500h. T=150° Dust generation

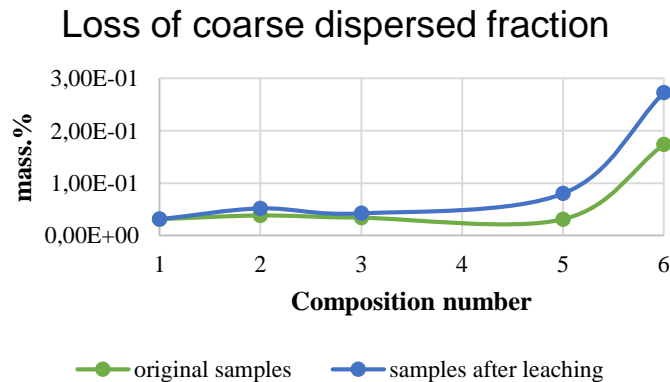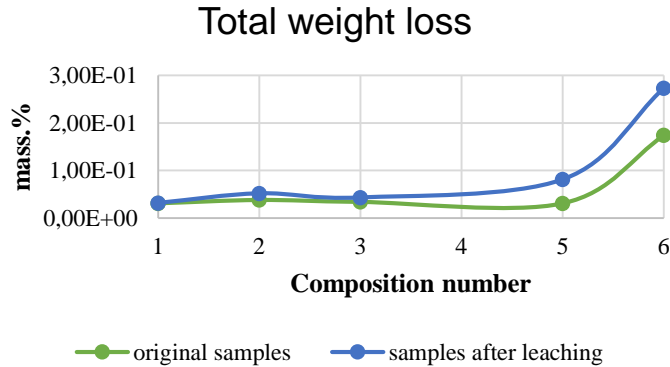Composition 6. Dry storage 1200h. T=150°

25
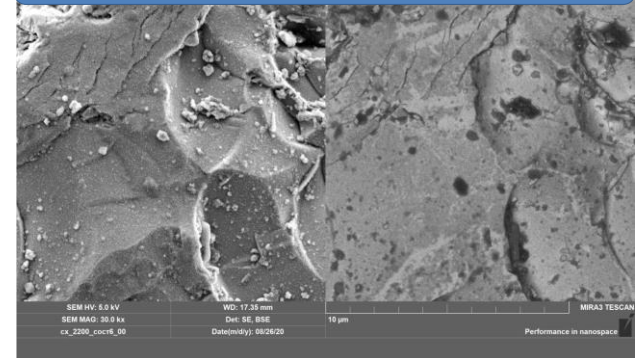
Accelerated Aging

Dry storage results. Dust formation

POCATOM

Dry storage 2200h, T=150°

Total weight loss

original samples — samples after leaching

Loss of coarse dispersed fraction

original samples — samples after leaching

- Dust fraction formation is less than 0.016% mass
- Fine fraction is less than 1% of total mass loss
- Fragments, initially exposed to contact with water, were dried, particles of **secondary phases** were observed out of the samples. Hypothesis: the source of dust can be the secondary phases formed during contact between debris and an aqueous solution

Loss of fine dispersed fraction

original samples — samples after leaching
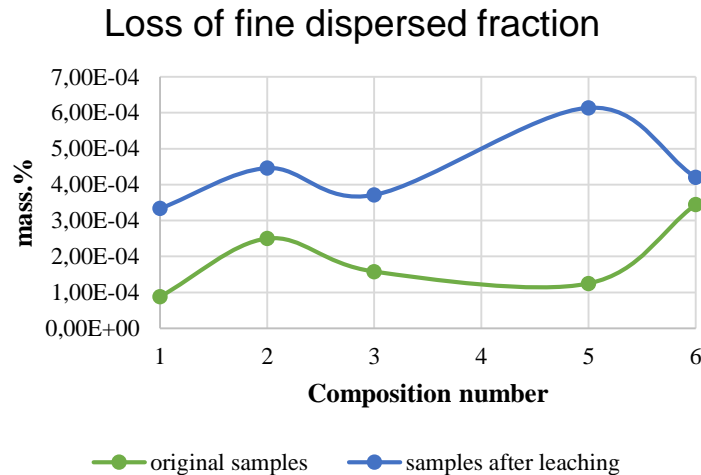
Accelerated Aging
Dry storage conclusions

- The process of dry storage at a temperature of 150 ° C for 2200 h of corium samples did not lead to significant changes in their properties

- No external changes in the surface of the MCCI samples were found. On the surfaces of composition 6, the presence of "brown rust" was observed.

- No changes in the elemental and phase composition were found

- Fragments, initially exposed to contact with water, were dried, particles of **secondary phases** separated from the samples. Thus the source of dust can be the secondary phase formed upon contact between debris and an aqueous solution

- **The entire volume of the hydrated layer formed during wet storage is potential volume of dust formation during further treatment and dry storage (considered as prediction model assumption)**

Dry storage fine fraction release prediction **with** and **without** preliminary dissolution

27
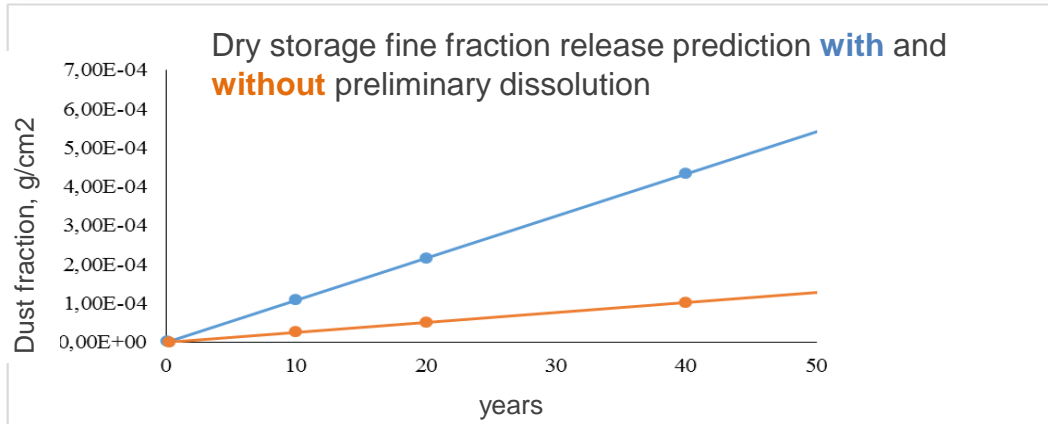
Prediction model development

Development of prediction model
Basic assumptions

FD properties change:

1) Estimation of the degradation (leaching) depth of the sample surface
2) Calculation of the volume of formation of secondary mineral phases on the surface

When the sample comes into contact with an aqueous solution, the process of leaching of components from the matrix is activated. Sample properties change only in the near-surface layer
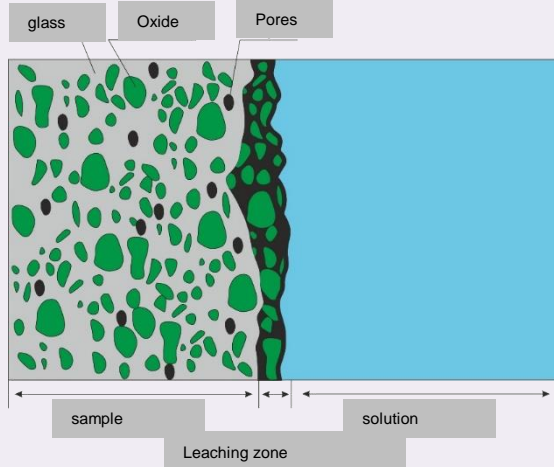
Secondary mineral phases – potential source of dust formation

glass   Oxide   Pores

sample   solution

Leaching zone

Prediction model
Experimental program summary assumptions

1. Influence of the composition with the rate of release of the components into the solution

No effect of compositions 1-5 on the rate of release of the components into the solution was found.

Experimental estimates of the rate of exit of components from compositions 1-5 can be averaged.

Composition 6 was considered separately from the others, since it consists exclusively of hardly soluble oxides.

2. What components are leached from the samples into the solution?

The components of the amorphous component **(Ca, Si, Al)** intensively pass into the aqueous solution. At the same time, the oxide (crystal) does not actually dissolve even at higher temperatures.

The behavior of compositions 1-5 on contact with an aqueous solution can be considered as the behavior of a two - phase system (highly-and low-soluble phases) .

Only **Fe** and **U** pass from composition 6 to the aqueous solution.
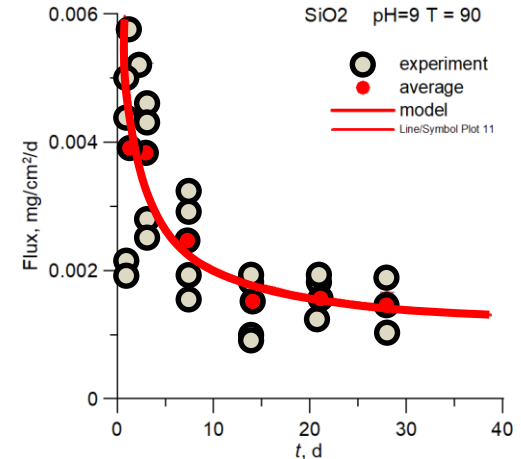
Prediction model

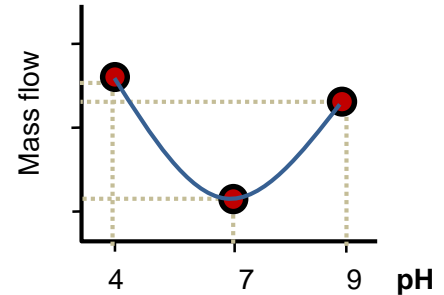**Experimental program summary assumptions**

3. pH influence on the leaching rate

The total flow of the components into the aqueous solution increases at pH = 4 and pH = 9, compared to pH = 7.

Acid-base conditions determine the composition of the dissolved components: at pH = 9, Al and Si are released into the solution, at pH = 4, Ca is dissolved.

Under different acid-base conditions, different secondary phases and different volumes of the dusty fraction can be expected to form.

4. Temperature influence on the leaching rate

The total flow of components into the solution increases non-linearly with increasing temperature.

The acceleration of aging was estimated by interpreting laboratory experiments and using analytical dependencies. Acceleration: from **25 to 50 °C – 8 times**; from **25 to 90 °C - 150 times**, from **25 to 120 °C - 900** times.

31
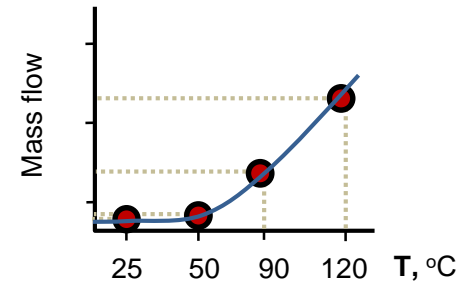
Prediction model

Experimental program summary assumptions

5. Air atmosphere influence on the leaching rate

In experiments on the interaction of fuel-containing samples with aqueous solutions, it was found that the yield of components in nitrided solutions is slightly higher than in deoinized solutions.

A higher flow in a nitrided environment is formed by **Ca.** In this case, the **Si** and **Al** fluxes into the aqueous solution are the same in the nitrided and deonized environment.

6. Secondary phases

On the surface of fuel-containing samples of compositions 1-5 exposed to aqueous solutions, the formation of a thin (several microns) layer of secondary phases was recorded.

According to the results of thermodynamic calculations and SEM analysis, the secondary phases are represented by zeolites and mica minerals.

A rapid formation of a brown secondary phase was recorded on the surface of the sample of composition 6. According to the calculated and SEM data, the phases are represented by iron oxides.
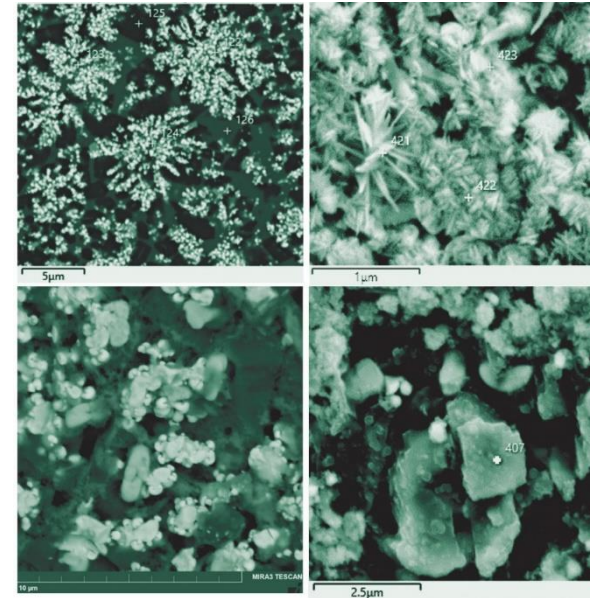
Prediction model

Experimental program summary assumptions

7. Aging of "cold" and "hot" samples: comparison

The rate of release of components (Ca, Al, Si) from the amorphous component of "hot" samples into an aqueous solution is comparable to the flow of these components from non-draped ("cold") samples.

From the Hot samples there is an intensive release into the solution of **Fe, Cr, Ni, U, Zr, Pu, Am**. Due to this, the total rate of dissolution of the hot samples is significantly higher than that of the cold.

It is assumed that the intensive dissolution of the hot samples occurs due to the peculiarities of their structure and preparation modes.

Composition 5

"cold"   "hot"

33

Prediction model

Experimental program summary assumptions

8. Dissolution of powdered samples

The features of leaching of powdered samples and monoliths are similar. (Composition of leachable components, relation to pH and temperature). Experiments with powders allowed us to observe the leaching process at normal temperatures (in experiments with monoliths at normal temperature, the yield of the components was absent).

9. Dry storage

During dry storage, no changes were recorded on the surface of the original monolithic samples with compositions 1-5. When drying the fragments initially exposed to contact with the aqueous medium, the particles represented by the secondary phases were separated from the samples. Thus, the source of dust can be a secondary phase formed during the contact of the debris-aqueous solution.

A brown coating (probably iron hydroxides) appears on the surface of composition 6.

Prediction model approach

Model 1: Thermodynamics+Kinetics (Chemical)

Multicomponent thermodynamic model of surface dissolution

solution

glass | oxide | leaching zone

experiment duration
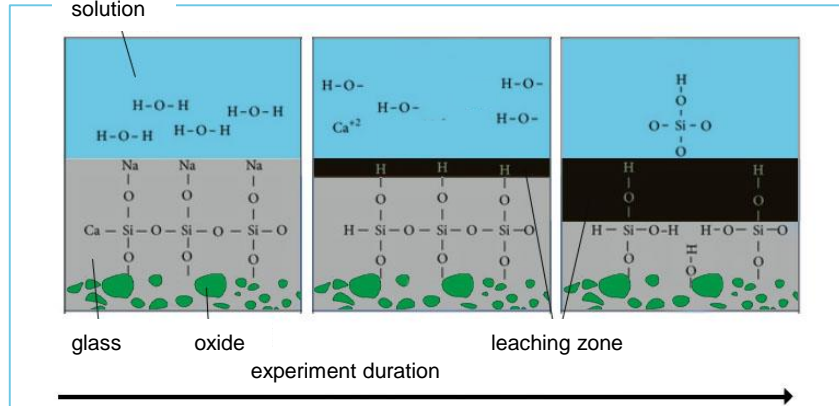
Purpose: Processing laboratory experiments. Consideration of the influence of external factors (T, pH, composition, etc.). Calculation of the formation of secondary phases on the sample surface
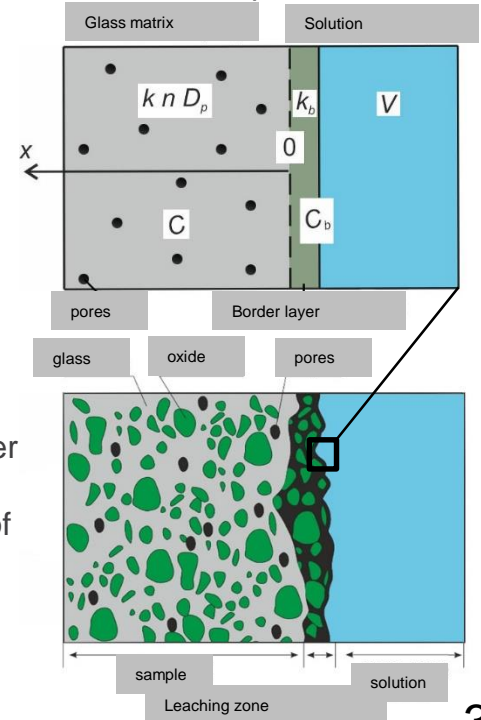
Model 2: Physical

One-component balance model of surface dissolution and solution diffusion into the sample

Lab Scale

Purpose:
Processing laboratory experiments and selection of parameters for prediction

Long Term Scale

Purpose:
Predicting the leaching layer thickness of the sample surface over long periods of time

Glass matrix | Solution

$k\,n\,D_p$ | k_b

V

0

x

C | C_b

pores | Border layer

glass | oxide | pores

sample | solution

Leaching zone

35

Multi-component layer dissolution model

Compositions 1-6

I. Kinetics of dissolution of oxides and spinel

$$r = S_A \sum_j A_j \cdot e^{-E_{a,j}/RT} \prod_i a_{i,j}^{n_i} (1-\Omega^{p_j})^{q_j}$$

j - mechanisms corresponding to dissolution in acidic, neutral and alkaline conditions;
S_A - specific surface area of the phase per unit mass of water (m^2/kg);
A_j - pre-exponential factor in the Arrhenius equation ($mol/m^2 \cdot s$);
E_a- energy activation during the j-th reaction (J/mol);
R - universal gas constant (8,31446 J/mol·K);
T - temperature (degrees Kelvin);
a_i - activity of the i-th water ion;
Ω – phase saturation ration фазы (the degree of deviation of the phase from the state of equilibrium in a specific period of time - includes the equilibrium constant of dissolution)
n, p, q - empirical coefficients.

II. Kinetics of dissolution of amorphous part

$$R = S_A \cdot k \cdot k_{inh} \cdot e^{(-E_a/RT)} \cdot (1-\Omega) \qquad k_{inh} = \frac{1}{(1+k_1 \cdot \sum_i M_i)^{k_2}}$$

k - reaction rate constant; k_{inh} – deceleration ratio;
k_1, k_2 – selectable parameters; M – number of secondary phases formed;

III. Kinetics of dissolution of PuO$_2$

$$R = k \cdot S_A^{0.33} \cdot T_c^{-1}$$

k - reaction speed constant; S_A – specific surface;
T_c – grain sze;

IV. Kinetics of dissolution of Fe

$$R = S_A \cdot k \cdot (1-\Omega)$$

k - reaction speed constant; S_A – specific surface;

Analytical model of dissolution from the surface and diffusion deep into the sample

POCATOM

Asymptotic solution for concentration in solution

$$C_b = \sqrt{\frac{4Dn}{\pi}} C_e f_i S_s \sqrt{t} + C_e f_i S_s k_b t$$

responsible for the **diffusion** from the surface

responsible for **dissolving** from the surface

At **the initial moments** of time, the main contribution to the removal of components into the solution is played by **diffusion**.
Over time, the contribution of diffusion to the total rate of dissolution decreases. The process of **dissolution** begins to prevail.
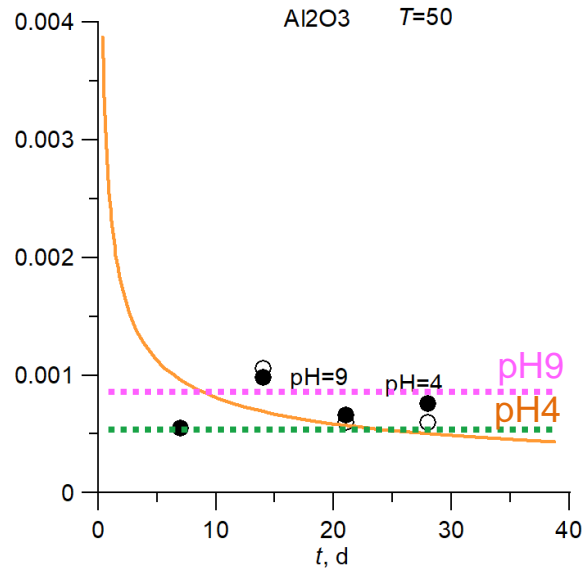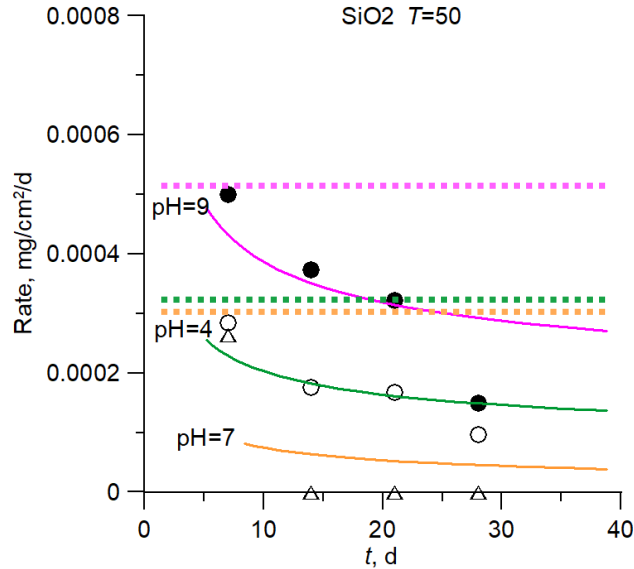
Change in flow rate over time

Diffusion + dissolution
Diffusion only
Dissolution only

Rate, mg/d cm²

Time, d
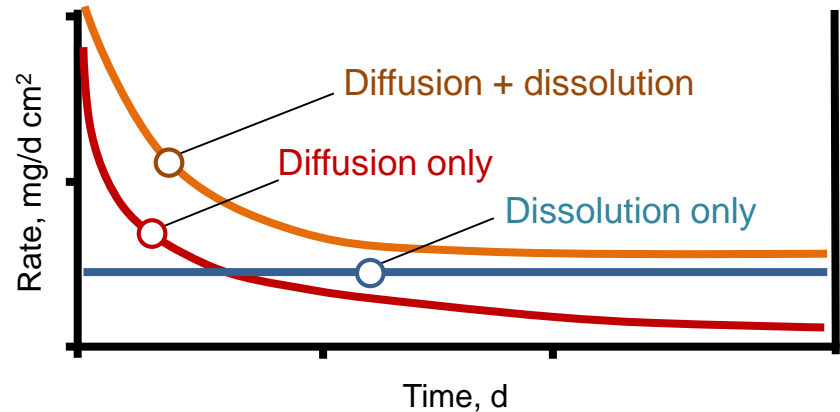
Calculation of the equilibrium concentrations of components

T, °C	pH								
	9			7			4		
	Si	Ca	Al	Si	Ca	Al	Si	Ca	Al
90	458.9	108.1	111.1	443.8	102.6	107.4	442.1	102.2	107.1
50	202.0	48.6	49.2	199.5	48.1	48.6	199.0	47.9	48.5
25	109.2	26.4	26.6	108.7	26.3	26.5	108.6	26.2	26.5

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Interpretation of experiments T=50°C

Monolith samples

Compositions 1-5

Hot sample No. 3 pH 7, T90°C

The rate of release of the components (**Ca, Al, Si**) from the amorphous component of the "hot" samples into the aqueous solution is comparable to the flow of these components from the "cold" samples.

However, unlike" cold " samples, **Fe, Cr, Ni, U, Zr, Pu, and Am** are intensively released into the solution. But no significant **Pu** concentration impact observed between different «hot» compositions

So, it is assumed that the intensive dissolution of the hot samples occurs due to the peculiarities of their structure and preparation modes.


SiO$_2$ pH7 T90

CaO pH7 T90

Al$_2$O$_3$ pH7 T90

······ Model 1 "Chemical" (multicomponent kinetics and dissolution on the sample surface)
—— Model 2 "Physical " (kinetics and dissolution on the surface + diffusion into the sample)
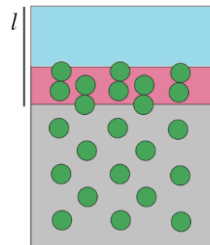● Experimental
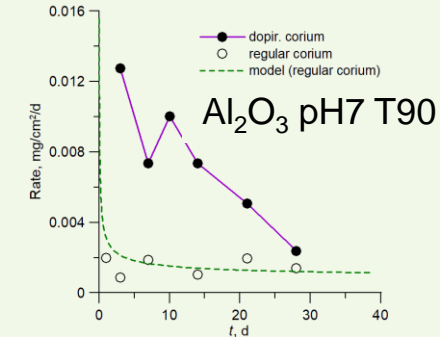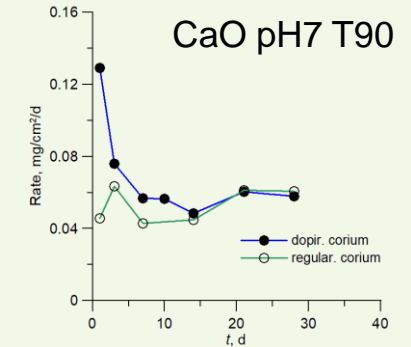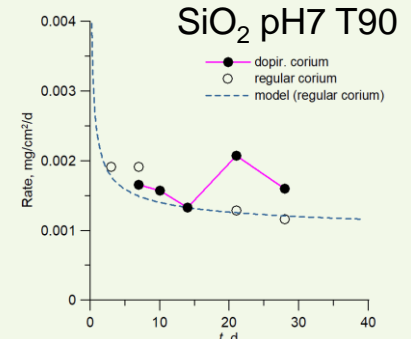
Development of prediction model

FD aging: change of FD properties leading to radionuclide release from matrix to environment

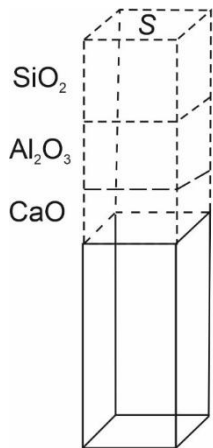**FD considering as 2-phase system with different solubility**

Leaching time: 0, 10 yr, 50 yr
solution / solution / poorly soluble phase
glass
debris
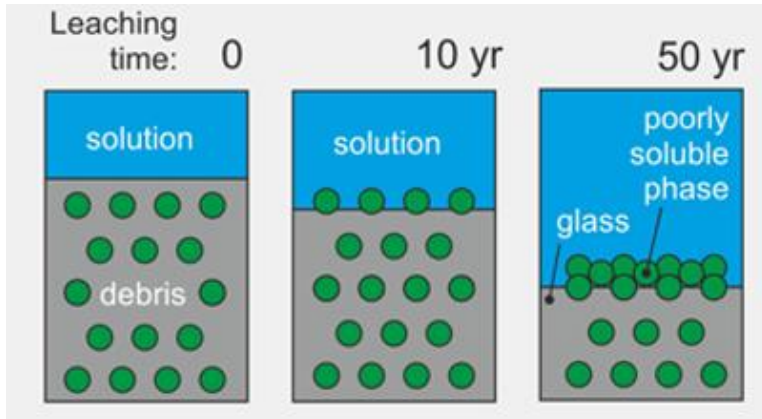
- Soluble amorphous phase
- Low soluble oxide phase
- Secondary phase

3 processes lead to FD aging and radionuclide release:

1. Radionuclide release from **amorphous phase** because its dissolution

2. Accumulation on the surface of hardly soluble dispersed aggregates consisting of **(U,Zr,Pu)O$_2$ oxides and spinel**;

3. Deposition of **secondary phases** and generation of dust fine fraction which is risk factor for safe FD treatment;

40

$$P_{UZr} = \rho_{UZr}\varepsilon\Delta V$$

$$\Delta V = \sum_{i=1}^{M}\Delta V_i \approx S\Delta l = S\sum_{i=1}^{M}\Delta l_i$$

$$N_{UZr} = P_{UZr}/S = \rho_{UZr}\varepsilon\sum_{i=1}^{M}\Delta l_i$$

$$-\frac{dl_i}{dt} = \frac{M_i f_i k_{bi}}{\rho_{gl}}([C_{ei}]-[C_i])$$

$$\Delta l_i(t) = l_0 - l_i(t) = \frac{M_i[C_{ei}]}{S_s\rho_{gl}}[1-\exp(-k_{bi}f_iS_st)]$$
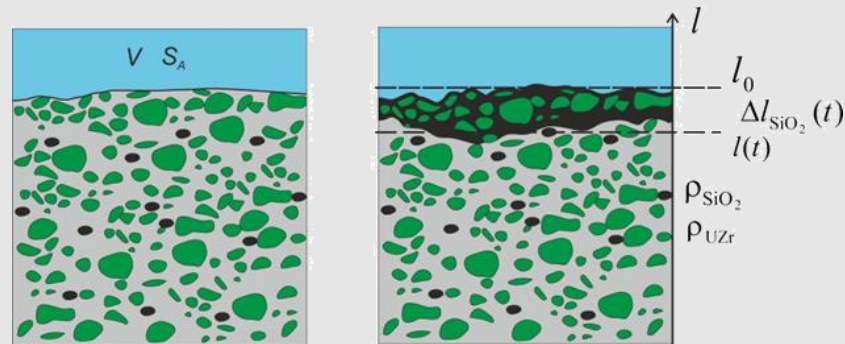
$$f_{SiO2}=0.46, \quad f_{Al2O3}=0.07, \quad f_{CaO}=0.05$$

Accumulation of (U, Zr, Pu)O$_2$ phase on the surface

$$N_{UZr} = \rho_{UZr}\varepsilon\sum_{i=1}^{3}\Delta l_i = \frac{\varepsilon\rho_{UZr}}{S_s\rho_{gl}}\sum_{i=1}^{3}M_i[C_{ei}]\{1-\exp(-k_{bi}f_iS_st)\}$$

Leaching depth

$$\Delta l = \frac{N_{UZr}}{\rho_{UZr}\varepsilon}$$

Prediction model

The surface transformation is characterized by the leaching of an amorphous glass phase (an alloy of Si, Al, and Ca oxides), including insoluble agglomerations of the uranium-zirconium alloy (U, Zr)O$_2$.

The loss of the glass phase mass during the transition of Si, Al, and Ca compounds from the solid phase to the solution leads to the formation of a mobile dissolution front l(t) on which insoluble particles (U, Zr)O$_2$ accumulate

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Long term prediction results

(U, Zr)O$_2$ phase accumulation speed on surface

$$N_{UZr} = \rho_{UZr}\varepsilon\sum_{i=1}^{3}\Delta l_i = \frac{\varepsilon\rho_{UZr}}{S_s\rho_{gl}}\sum_{i=1}^{3}M_i[C_{ei}]\{1-\exp(-k_{bi}f_iS_st)\}$$

Leaching depth

$$\Delta l = \frac{N_{UZr}}{\rho_{UZr}\varepsilon}$$

Prediction model parameters

T °C	Component	fi	pH			
			9.0	7.0	9.0	7.0
			K_{bi}, cm/d		C_{ei}, mol/cm^3	
90	Si	0.46	7.93E-03	2.89E-03	1.63E-05 1.58E-05 1.63E-05	
	Al	0.07	8.99E-02	7.98E-03	2.13E-06 2.05E-06 2.13E-06	
	Ca	0.05	1.83E-01	3.86E-02	2.69E-06 2.57E-06 2.69E-06	
50	Si	0.46	1.06E-03	3.78E-04	7.19E-06 7.12E-06 7.19E-06	
	Al	0.07	4.47E-03	3.89E-04	9.39E-07 9.39E-07 9.39E-07	
	Ca	0.05	3.46E-02	7.02E-03	1.22E-06 1.2E-06 1.22E-06	
25	Si	0.46	2.26E-04	8.01E-05	3.88E-06 3.88E-06 3.88E-06	
	Al	0.07	4.52E-04	3.90E-05	5.17E-07 5.17E-07 5.17E-07	
	Ca	0.05	9.77E-03	1.97E-03	6.49E-07 6.49E-07 6.49E-07	

Physical properties
Density (U, Zr)O$_2$ 8 g/sm^3;
Amorphous phase density 2.5 g/sm^3;
(U, Zr)O$_2$ Content
30%
Average volume fraction of components in the sample: SiO$_2$ – 46%; Al$_2$O$_3$ – 7%; CaO – 5%
External factors
Temperature: 90, 50, 25 °C;
 pH: 7 и 9
Water flow scenario
   I. Closed system: S_A/V = 0.1 см$^{-1}$;
   II. Flow systeS_A/V = 1E-04 см$^{-1}$

RESULTS

The maximum accumulation of (U, Zr)O$_2$ over 50 years will be observed in the conditions of the **flow system** at T=90°C and pH=9.

Under these conditions, the glass matrix leaching layer is 0.3 mm over 50 years. At the same time, up to 70 mg/cm2 (U, Zr)O$_2$ accumulates on the surface.

The chemical model shows that no secondary phase is formed under dynamic conditions.

For **static conditions** at T=90°C and pH=9, the etching depth will not exceed 0.03 mm in 50 years. The amount of (U, Zr)O$_2$ phase will be 7 mg/cm^2. In addition, according to calculations based on the chemical model, up to 360 mg / cm^2 of the secondary phase can be formed on the surface.

Closed system   **Flow system**
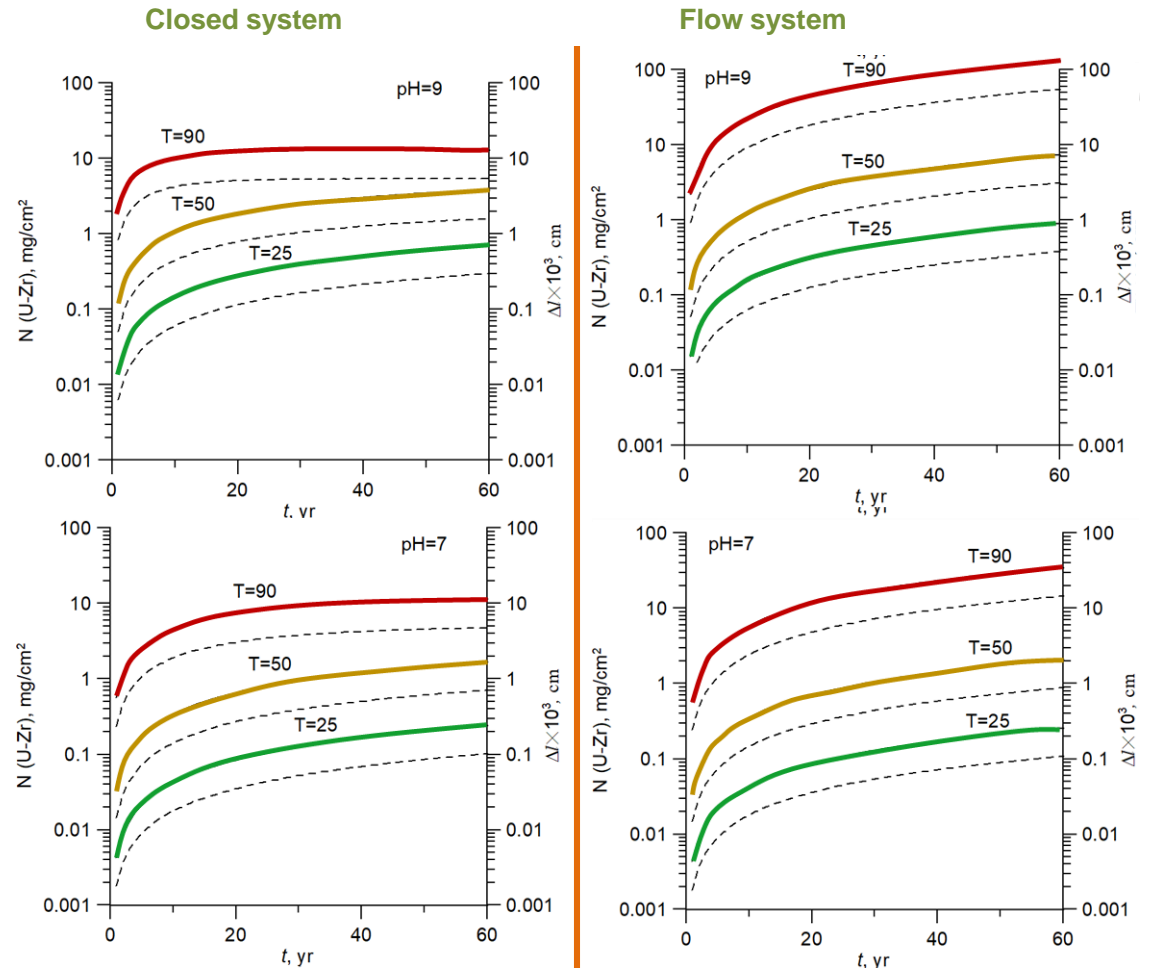
(U,Zr)O$_2$ accumulation on corium surface (solid curve)
Layer depth (dotted curve) depending on time
Refer to the equations shown on pages 41 and 42

Program code

Based on the proposed physical model and conducted laboratory experiments, a program code was developed that allows to calculate the change in the properties of corium over time at different phase ratios in the pH range of 7-9 and T = 25-120 °C

On step 1
The compositions of the phases and their ratio in corium are set. The sources of the radioactive output are also indicated.

Fukushima Debris Evolution Model

| 1. Debris composition | 2. Leaching parameters (LAB) | 3. Forecast |

70 30 Percentage of soluble and poorly soluble phases

Soluble phase — Number of oxides: 3

Oxide	fm, %	Mox, g/mole	f, %
SiO2	79	60.08	55.3
Al2O3	12	101.96	8.4
CaO	9	50.077	6.3

100 %   2.5   Density of soluble phase, g/cm^3

Poorly soluble phase — Number of oxides: 2

R	Oxide	fm, %	Mox, g/mole	f, %
☐	[U,Zr]O2	96	270	28.8
☑	PuO2	4	276	1.2

100 %   8.0   Density of poorly soluble phase, g/cm^3

fm - mass fraction of a component in the soluble phase
f - mass fraction of the component of the total mass of the composition (soluble + insoluble phases)
Mox - molar mass of the oxide
R - check the box next to the oxide if you want to calculate its activity on the debris surface during leaching

<< Previous   Next >>   Reset to default Fukushima data   Save...   Load...   Close

Fuel debris initial composition settings menu

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Program code

On step 2

According to the results of laboratory experiments, the relationship between the rate of release of individual components into the solution with pH and Temperature is determined.

In addition, based on the data of thermodynamic modeling, the relationship between the temperature and the equilibrium concentration is set.

Leaching parameters and activity adjustment menu

Program code

On step 3

The external conditions (pH, T) and forecast time are set.

The conditions of water circulation are also determined: static or dynamic.

Based on these parameters, the program calculates:

1. The accumulated mass of the poorly soluble phase on the surface of the debris, N [mg/cm^2];

2. Accumulated mass loss during glass dissolution, M [mg/cm^2];

3. The thickness of the leaching layer, L [cm];

4. Accumulated activity in the dispersed fraction on the surface of the debris, A [Bq/cm^2].
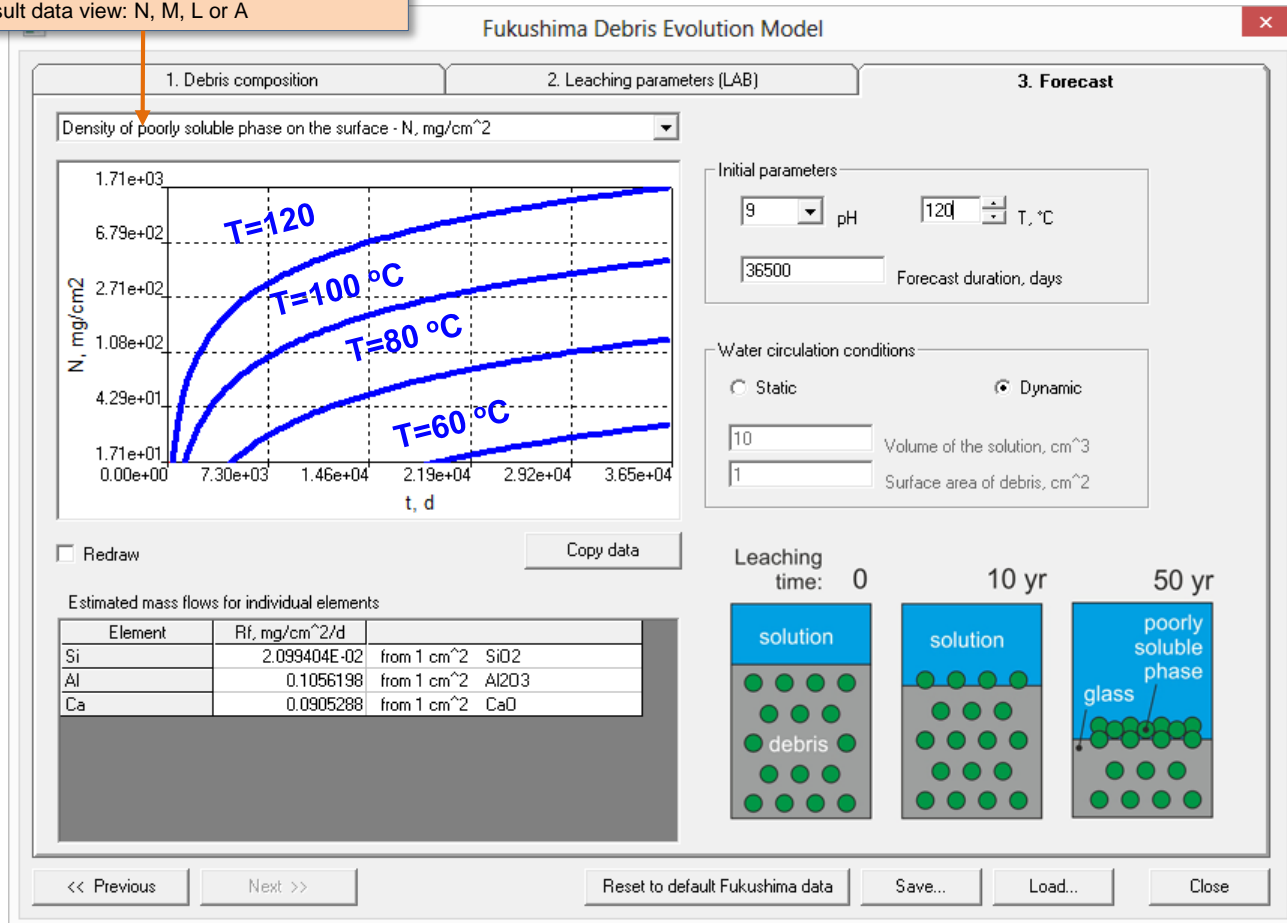
Prediction model parameters and calculation results view