V.G. Khlopin Radium Institute

Leach behavior of ceramics and glass doped with actinides

Bella ZUBEKHINA, Boris BURAKOV

ICTP, Trieste, 2018

HLW management in Russia

- More than 500 million m^3 of radioactive waste accumulated in Russian Federation
  (*according the data of National Operator of Radioactive Waste, 2017*)

LLW - 99,3% ILW - 0,67% **HLW - 0,03%**

- "Mayak" vitrification facility (Chelyabinsk region)

- 28560 m^3 of HLW were converted into glass (1987-2010)
- **6188 tones** of nuclear glass with total activity **643 000 000 Ci** *

** П.В. Козлов, М.Б. Ремизов. Сборник тезисов конференции «Зарождение радиоэкологии, её развитие и роль в обеспечении радиационной безопасности природной среды и человека», Озерск, 10-12 октября 2017.* ***(in Russian)***

how to study chemical durability

Leaching tests

Static

MCC1, PCT-A, PCT-B,…

Dynamic

SPFT, Soxlet test,…

Alteration tests

- Vapor hydration test (VHT) – to accelerate formation of secondary phases

Full scale and small scale experiments

- Sample interaction with groundwater, buffer and hostrock

radiation effects in solidified HLW

Confirmation chemical and mechanical durability

- Samples of ceramic and glass synthesized 30-40 years ago should be available for research

Prediction of future behavior

- Computer modelling
- Irradiation by heavy ions
- Accelerated radiation damage by ^{238}Pu or ^{244}Cm

synthesis of ^{238}Pu doped samples

- Only small samples 0.1 – 10 g
- Pu content up to 1 wt.% for glass
  up to 10 wt.% for ceramic
- All operations including high temperature sintering should be carry out in shielded conditions

Heavy box

Glow box

Right after synthesis

Checking contamination on the floor

synthesis and study of Pu-doped B-Si-glass

9/06/2016

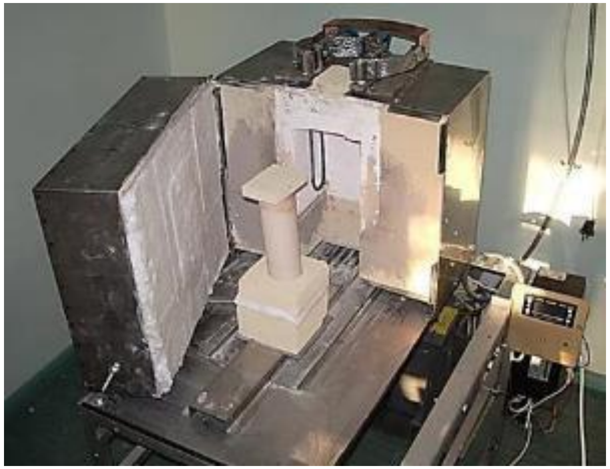
- **B-Si-glass (France)**
  - ✓ Well known material for HLW immobilization.
  - ✓ Commercial technology based on SON68 glass composition.

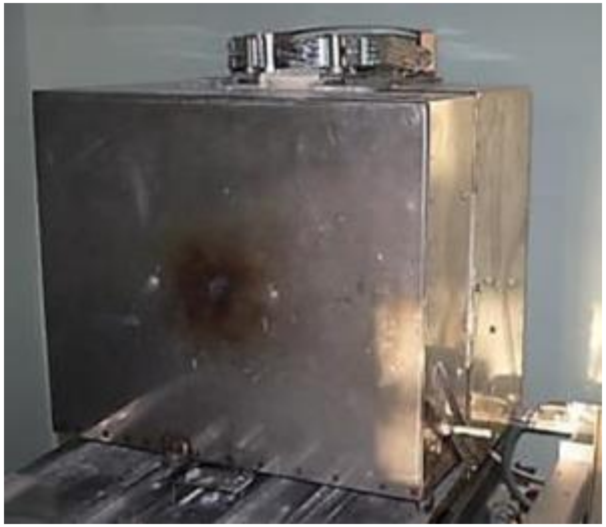
- **Sintering in air, 1400°C, 1 hour**

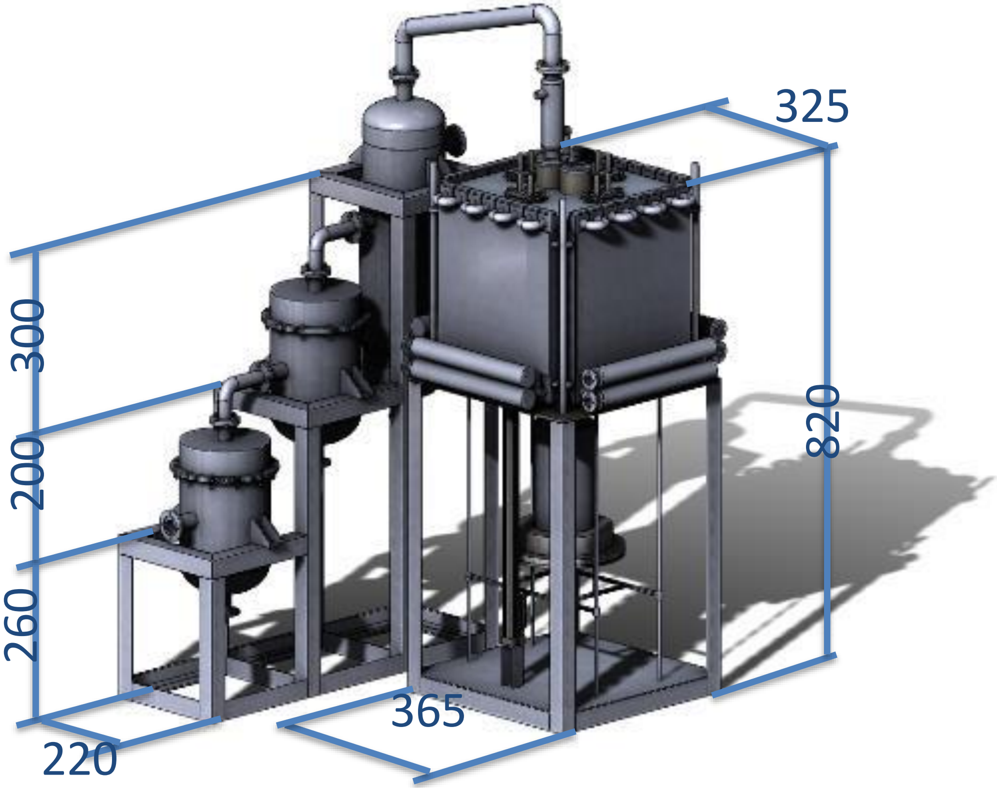
- **0,45 wt.% ^{238}Pu for acceleration of radiation damages** and nonradioactive (referent) sample with almost the same composition

- **3 wt.% Eu for trivalent lantanides simulation**

small high temperature furnace developed at KRI

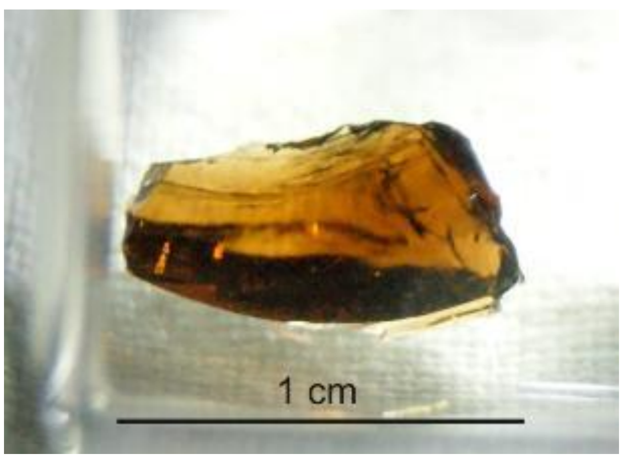


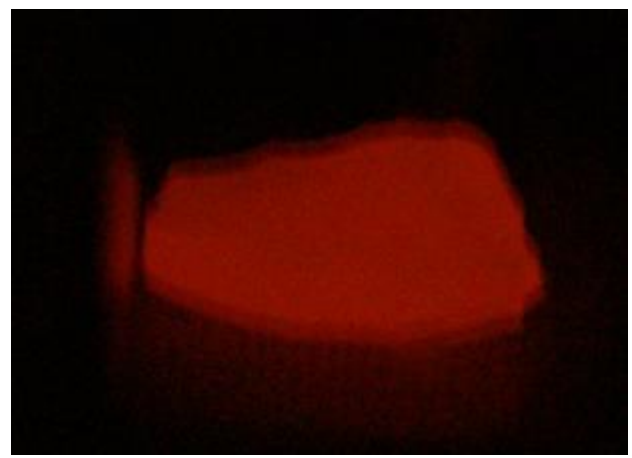




Patent №14714, Vol. №29, 20.10.2014

Sample of SON-68 glass doped with 0,4 масс.% ^{238}Pu right after synthesis





Self glowing in darkness

leaching test

Static leach test, 90°C

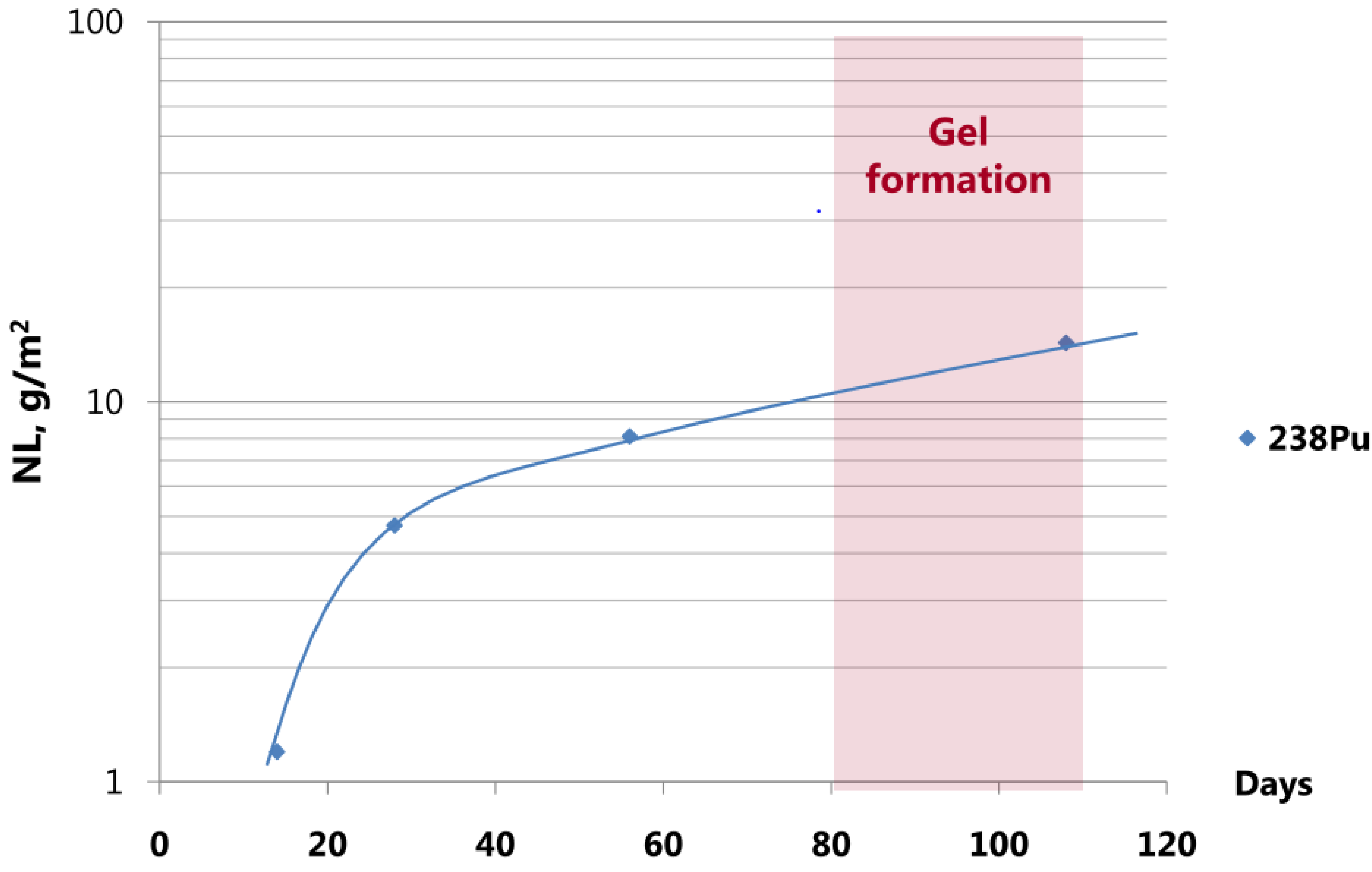
SA : V = 1 cm^2 : 80 cm^3

Accumulated dose (on 11.11.2017)

2,5·10^{23} α-decays/m^3

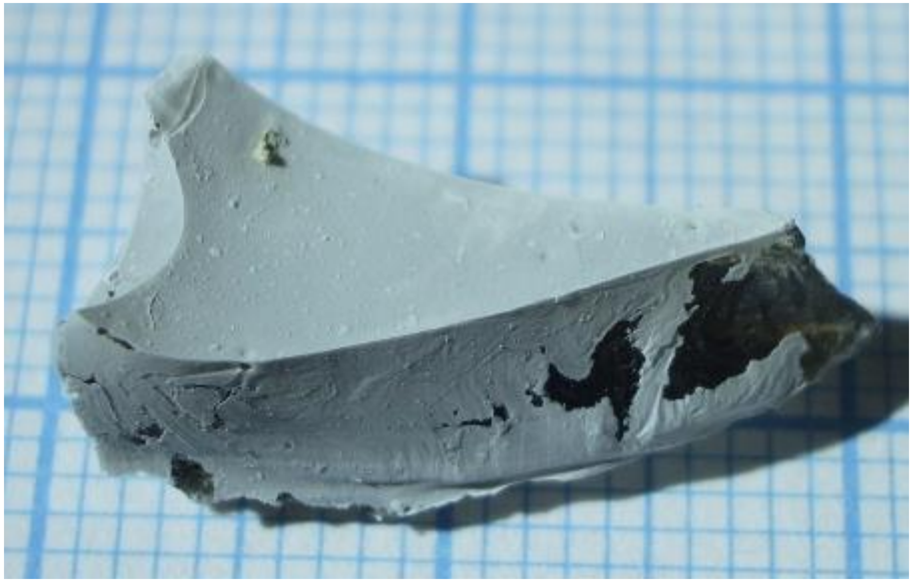
1,7·10^{16} α-decays/sample

Days	7	14	28	56	108
Pu leach rate, g/(m^2 day)	0.08	0.04	0.34	0.58	0.13



^{238}Pu normalized mass loss (90C, static, distilled water)

alteration at saturated conditions (1)

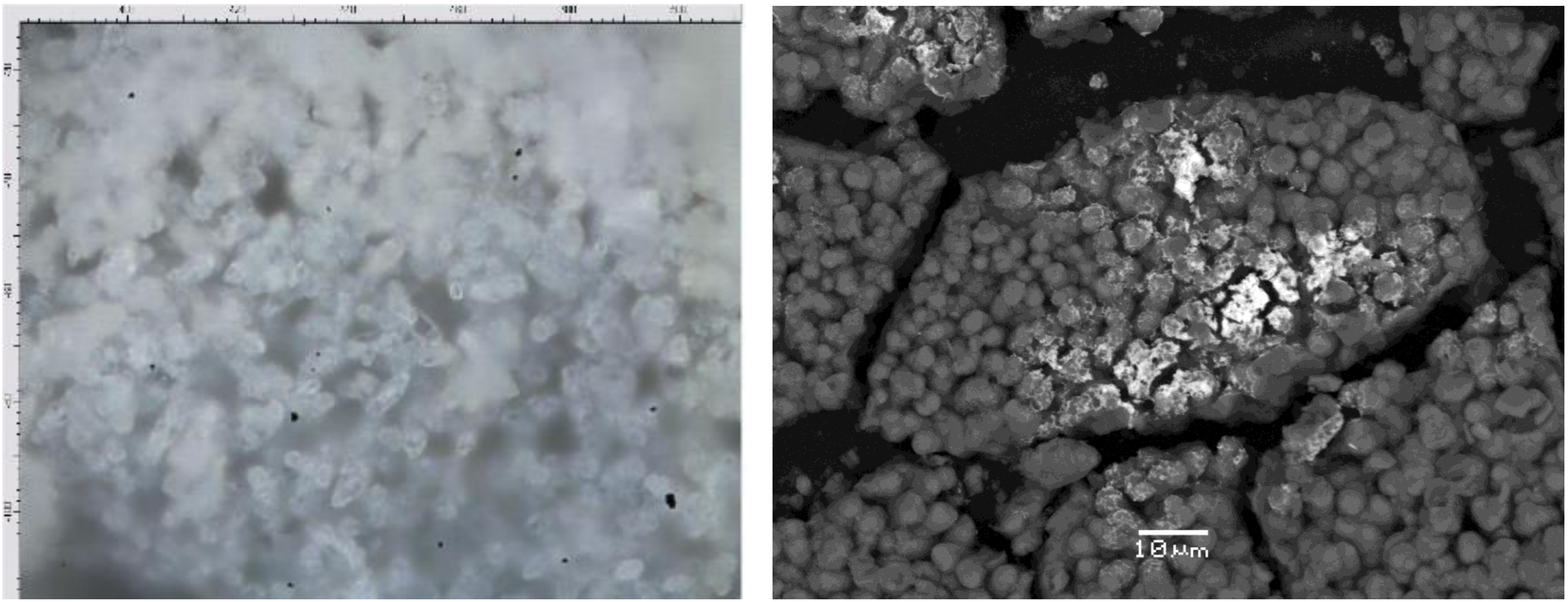


Sample doped with 0,4 wt. % ^{238}Pu (left) and non-radioactive sample with the same composition (right) after contact with water at saturated conditions

***static conditions, 4 month, 90°C,* SA : V= 1 cm^2 : 4 cm^3**

Self-destroying of the gel was observed in a week after gel formation!

alteration at saturated conditions (2)



left - optical image of the alteration xerogel detached from the bulk glass. Values of axes are in microns;
right – BSE images of carbon-coated xerogel detached from the glass. Whitish regions correspond to Pu-rich domains.

what kind of vessel material can be used for leaching test?

Stainess steel

Teflon

Gold

?

Platinum

Titanium

Quartz

Leaching of ceramics and single crystals doped with Pu based on cubic zirconia, monazite, zircon and plutonium oxide

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Leaching of Plutonium from "Old" Samples of Single Phase Ceramics Based on $Zr_{0.79}Gd_{0.14}Pu_{0.04}O_{1.93}$ and $La_{0.9}Pu_{0.1}PO_4$ Doped with ^{238}Pu

Bella Yu. Zubekhina and Boris E. Burakov
V.G. Khlopin Radium Institute, 28, 2-nd Murinskiy Ave., St. Petersburg, 194021, Russia

ABSTRACT

Samples of ^{238}Pu-doped single-phase ceramics based on cubic zirconia, $Zr_{0.79}Gd_{0.14}Pu_{0.07}O_{1.93}$, and monazite, $La_{0.9}Pu_{0.1}PO_4$, have been studied by static leach test in distilled water. Before leach test accumulated doses were (in alpha-decays/m^3 x 10^{26}): from 1.6 to 1.7 – for cubic zirconia; and 1.0 – for monazite. Despite high radiation damage both phases remained crystalline according to XRD analysis. The results of static leach tests demonstrate the following Pu normalized mass loss (in g/m^2, 90°C, 28 days): from 0.3 to 0.7 – for cubic zirconia; and 1.6 – for monazite. These data are discussed in comparison with results of previous leach tests carried out at lower accumulated doses.

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Bella Yu. Zubekhina* and Boris E. Burakov

Plutonium leaching from polycrystalline and monocrystalline PuO_2

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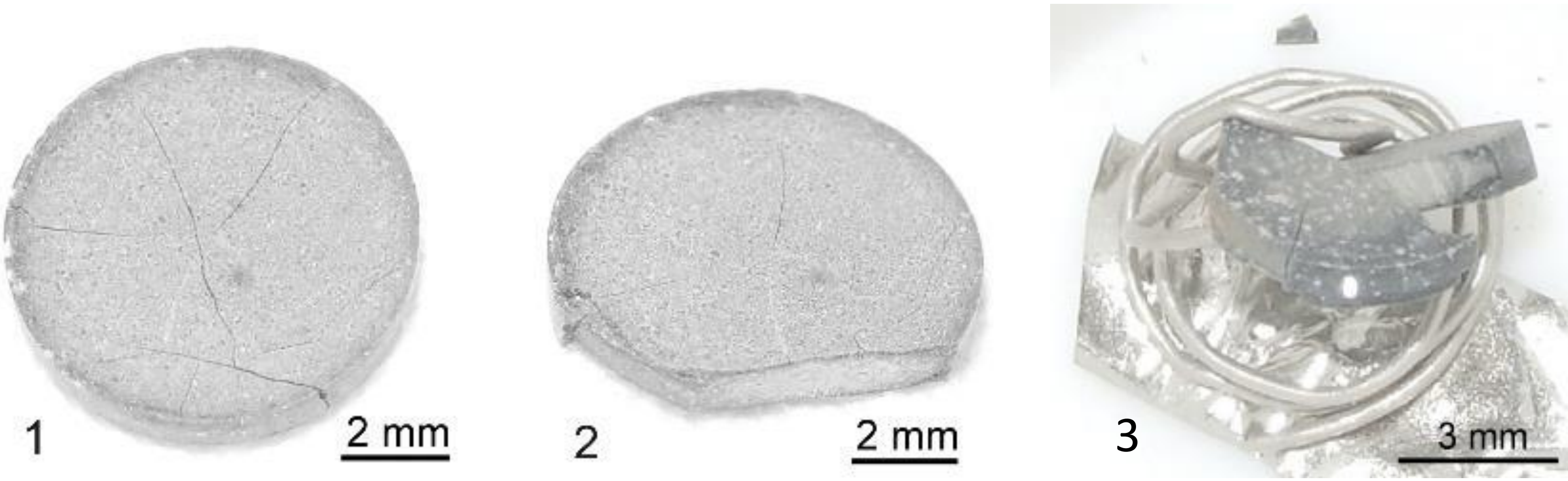
Abstract: Plutonium dioxide samples have been studied by static leach tests at a temperature of 25 and 90°C. A normalized Pu mass loss was observed from polycrystalline (without correction for matrix porosity) and monocrystalline $^{239}PuO_2$ samples occurring at a rate of 10^{-4}–10^{-3} g/m^2 in distilled water. This is comparable with some ceramic waste forms proposed for Pu immobilization. In contrast,

structure of the durable host-phase. There is some uncertainty, however, related to the acceptable level of Pu release from the ceramic waste form during interaction with aqueous solutions. A typical approach of characterizing of Pu loss in waste forms is based on static leach tests in distilled or deionized water at different temperatures, ranging from 25 to 90°C [4–10]. It is noteworthy to mention that similar to PuO_2 a much higher leaching rate of Pu from the ceramic matrix is observed for doping with ^{238}Pu compared to ^{239}Pu-doped samples [6, 8, 9].

Cubic zirconia $(Zr,Gd,Pu)O_2$ doped with **9.9 wt. % Pu-238**. Synthesized in 2000.

Cumulative dose **$1.2 \cdot 10^{26}$ α-decay/m^3**

self destruction of monazite ceramic sample



Pellet of single-phase ^{238}Pu-doped ceramic, $La_{0.9}Pu_{0.1}PO_4$, at accumulated dose approximately 10^{26} alpha-decays/m^3:

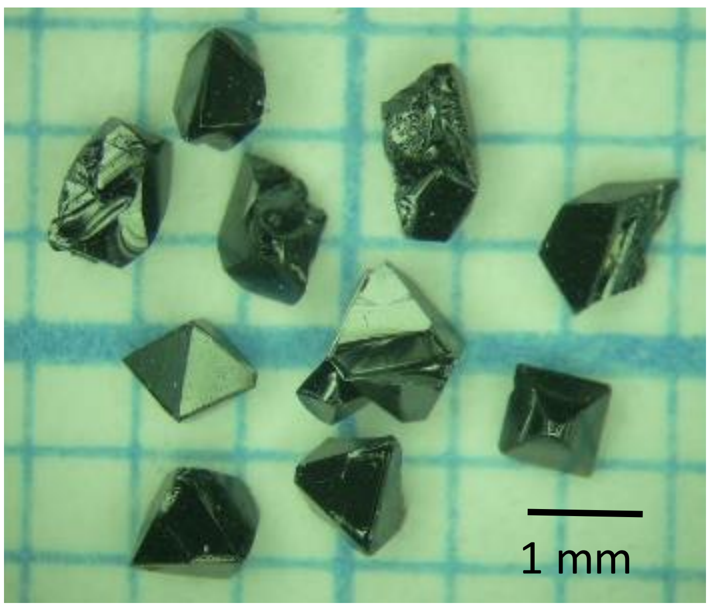
1) right after extraction from XRD sealed holder
2) piece used for leach test
3) pellet after leach test at 90˚C for 28 days

Normalized Pu mass loss from samples of single-phase Pu-doped ceramics after static leach tests in distilled water for 28 days. Correction for ceramic porosity was ignored

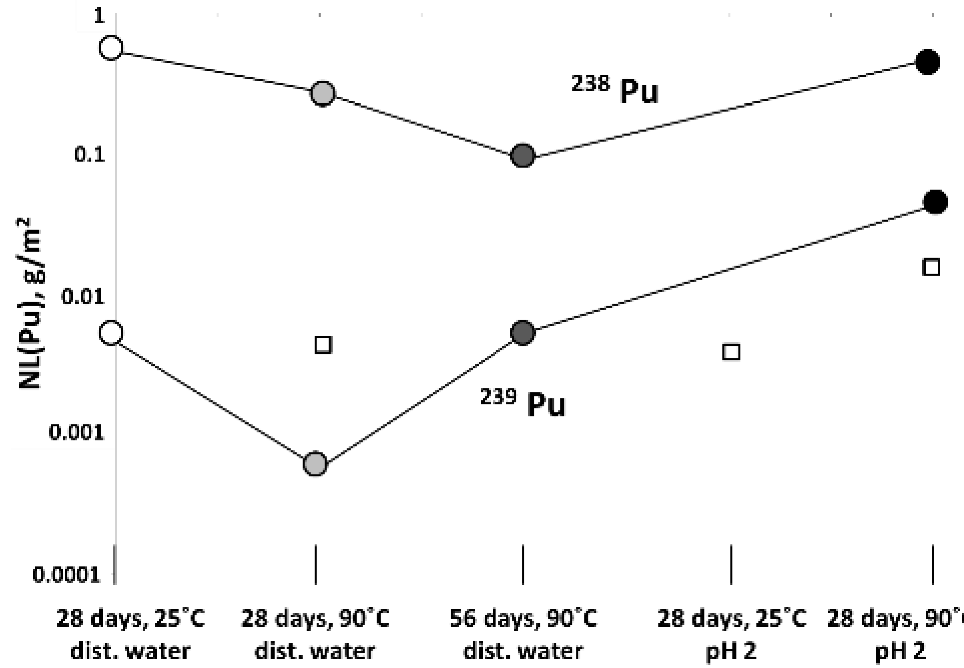
Sample	Cumulative dose, α-decay/m^3 x 10^{24}	NL, g/m^2, 28 days, 90 ˚C
Cubic zirconia $Zr_{0.79}Gd_{0.14}Pu_{0.04}O_{1.93}$ doped with 9.9 wt.% ^{238}Pu		
Previous data [1]	1	0.04
	6	0.4
	8	0.4
	13	0.2
Pellet #1	**163**	**0.3**
Pellet #2	**170**	**0.7**
Cubic zirconia $Zr_{0.75}Gd_{0.19}Pu_{0.06}O_{1.91}$ doped with 9.9 wt.% ^{239}Pu		
Previous data [2,3]	insignificant	0.04
Pellet #1	0.6	0.1
Pellet #2	0.6	0.1
Monazite $La_{0.9}Pu_{0.1}PO_4$ doped with 8.1 wt.% ^{238}Pu		
Pellet #1	1	0.4
Pellet #2	**100**	**1.6**

Leaching of plutonium from polycrystalline and monocrystalline PuO_2

Sample of polycrystalline $^{239-238}PuO_2$ contained 11% ^{238}Pu
Cumulative dose 3 x 10^{26} alpha-decay/m^3

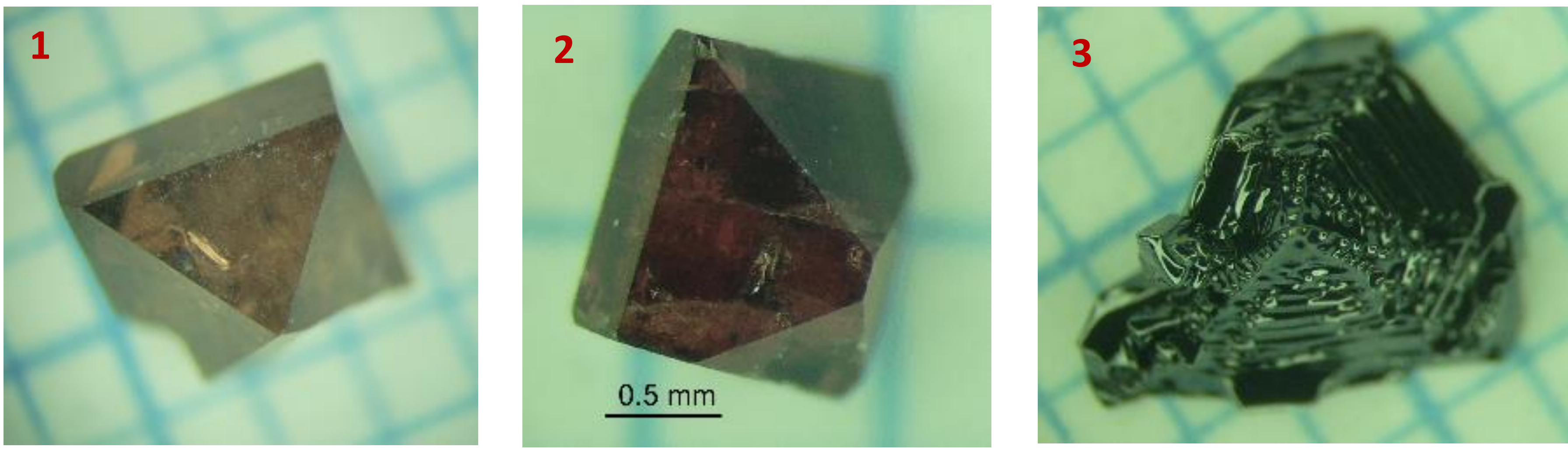


Single crystals of $^{238,239}PuO_2$



Results of PuO_2 static leach tests: ○ and ● – polycrystalline samples (the same pellet was used in different tests); □ – single crystals (only separate fresh samples for each test)

single crystalls to be studied



Single crystals of zircon doped with ^{237}Np (1) and ^{239}Pu (2).
Single crystal of neptunium oxide (3).

synthesis and study of Ti-ceramic with HLW

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New route for synthesis of Synroc-like ceramic using non-selective sorbent LHT-9

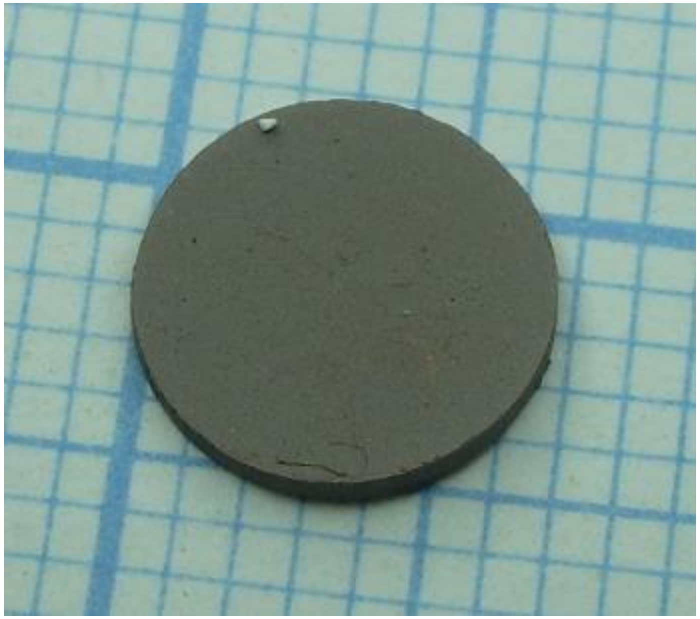
Zubekhina B.Yu.[1], Burakov B.E.[1], Petrov Yu.Yu.[1], Britvin S.N.[2-3], Mararitsa V.F.[4], Demidov Yu.T.[4], Nickolsky M.S.[5-6]

[1] *V.G. Khlopin Radium Institute (KRI), 28, 2-nd Murinskiy Ave., St-Petersburg, 194021, Russia*
[2] *Saint-Petersburg State University, 7/9, Universitetskaya Nab. St-Petersburg, 199034, Russia*
[3] *Nanomaterials Research Center, Kola Science Center, RAS, 14, Fersman St., Apatity, 184200, Russia*
[4] *Socium Ltd., St-Petersburg, Russia*
[5] *Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry RAS, 35, Staromonetniy per., Moscow, 119017, Russia*
[6] *A.N. Frumkin Institute of Physical Chemistry and Electrochemistry RAS, 31/4, Leninsky pr., Moscow, 119071, Russia*

All operations with liquid HLW were carried out in heavy box

Sintering in air inside glow box at temperature 1200ºC

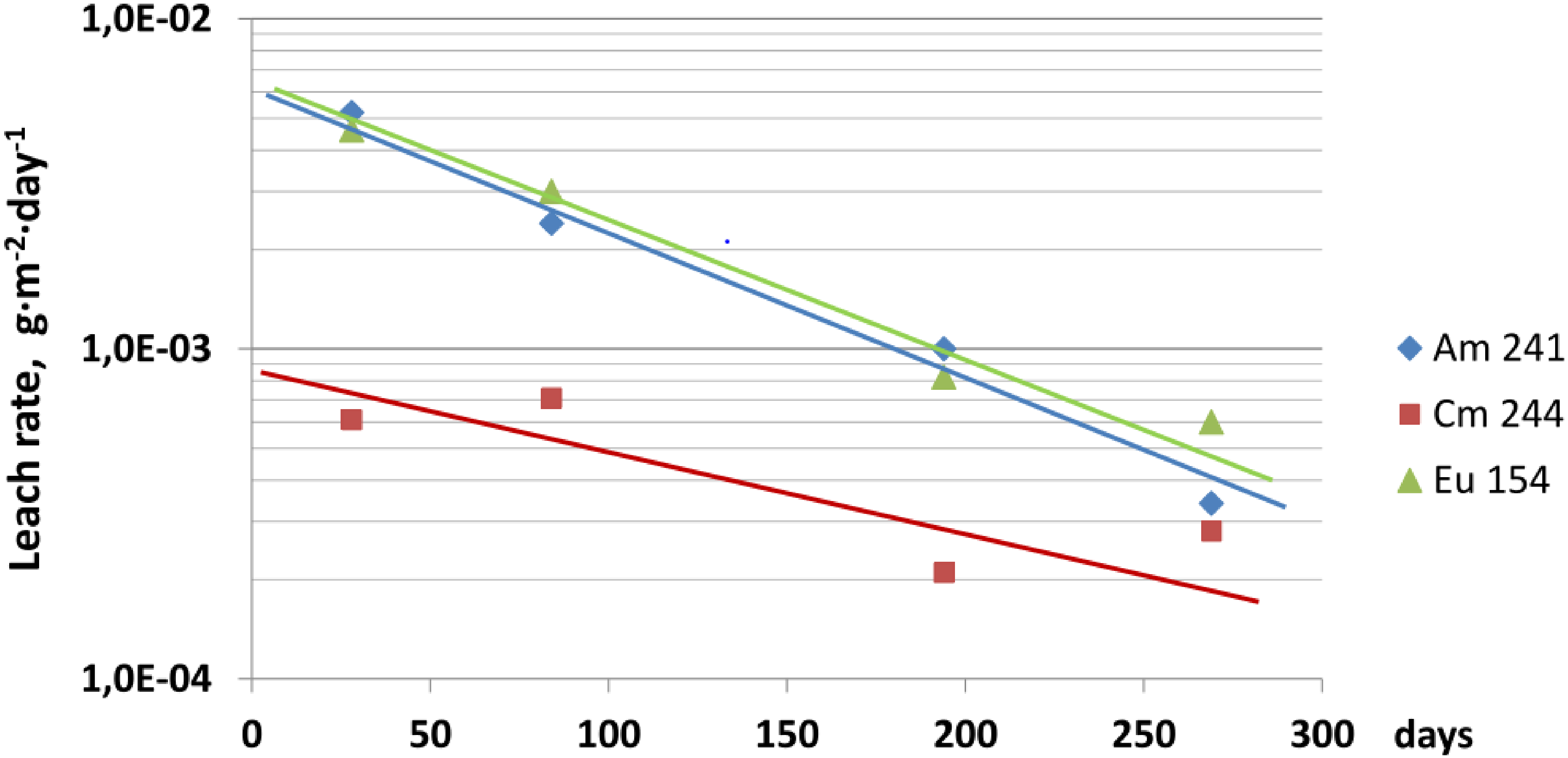
Pellet of Synroc-like polyphase titanate ceramic



Leach rates* of ^{154}Eu, ^{241}Am, ^{244}Cm

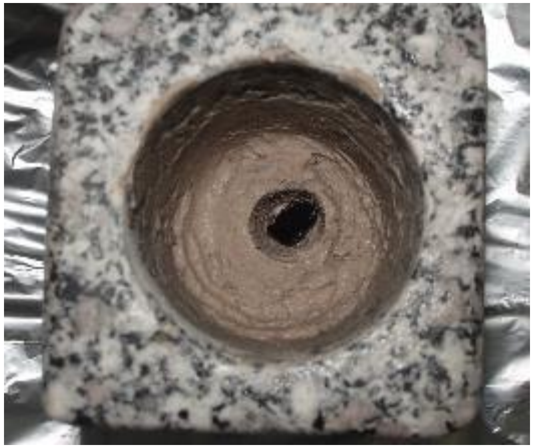
(for 10 month, dist. water, 90°C)

***calculated for geometrical surface area**

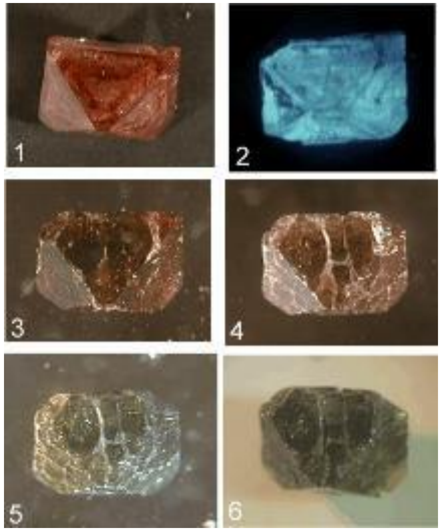


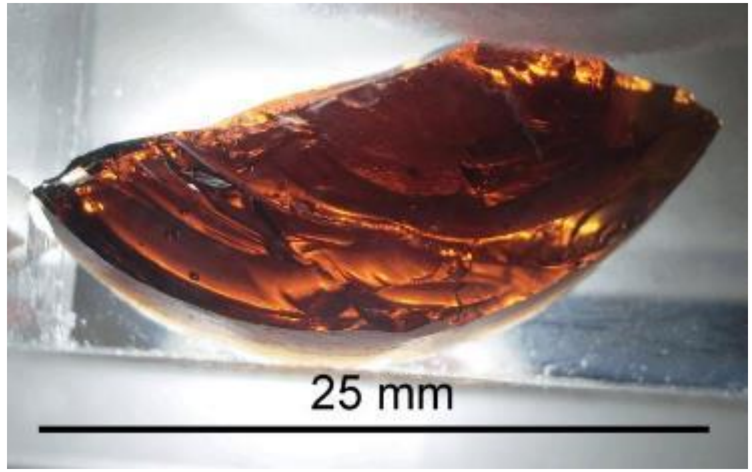
small scale experiment

with highly radioactive sample



Started in February 2018





Thanks for your attention!