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Leaching and chemical alteration of ^{238}Pu-doped borosilicate glass

ICTP, Trieste, Italy *6-11 November, 2017*

Background

- Chemical durability and radiation effects in waste forms
- How to study radiation effects?
- Accelerated radiation damages (by ^{238}Pu or ^{244}Cm): challenges at every step!

Samples

Synthesis of Pu-doped B-Si-glass **9/06/2016**

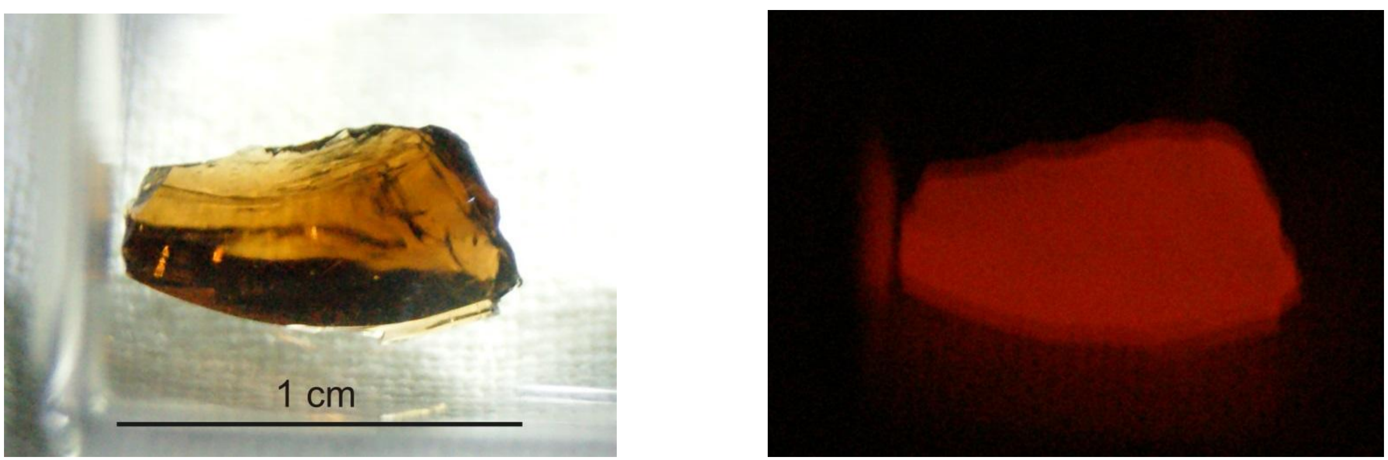
- **B-Si-glass SON68 (France)**
  - ✓ Well known material for HLW immobilization.
  - ✓ Commercial technology based on SON68 glass composition.

- **Sintering in air, 1400°C, 1 hour**
  at high temperature furnace developed at KRI (Patent №14714,
  Vol. №29, 20.10.2014)

- **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**

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



Self glowing in darkness

Leach tests in static conditions

Leaching of plutonium
(unsaturated conditions)

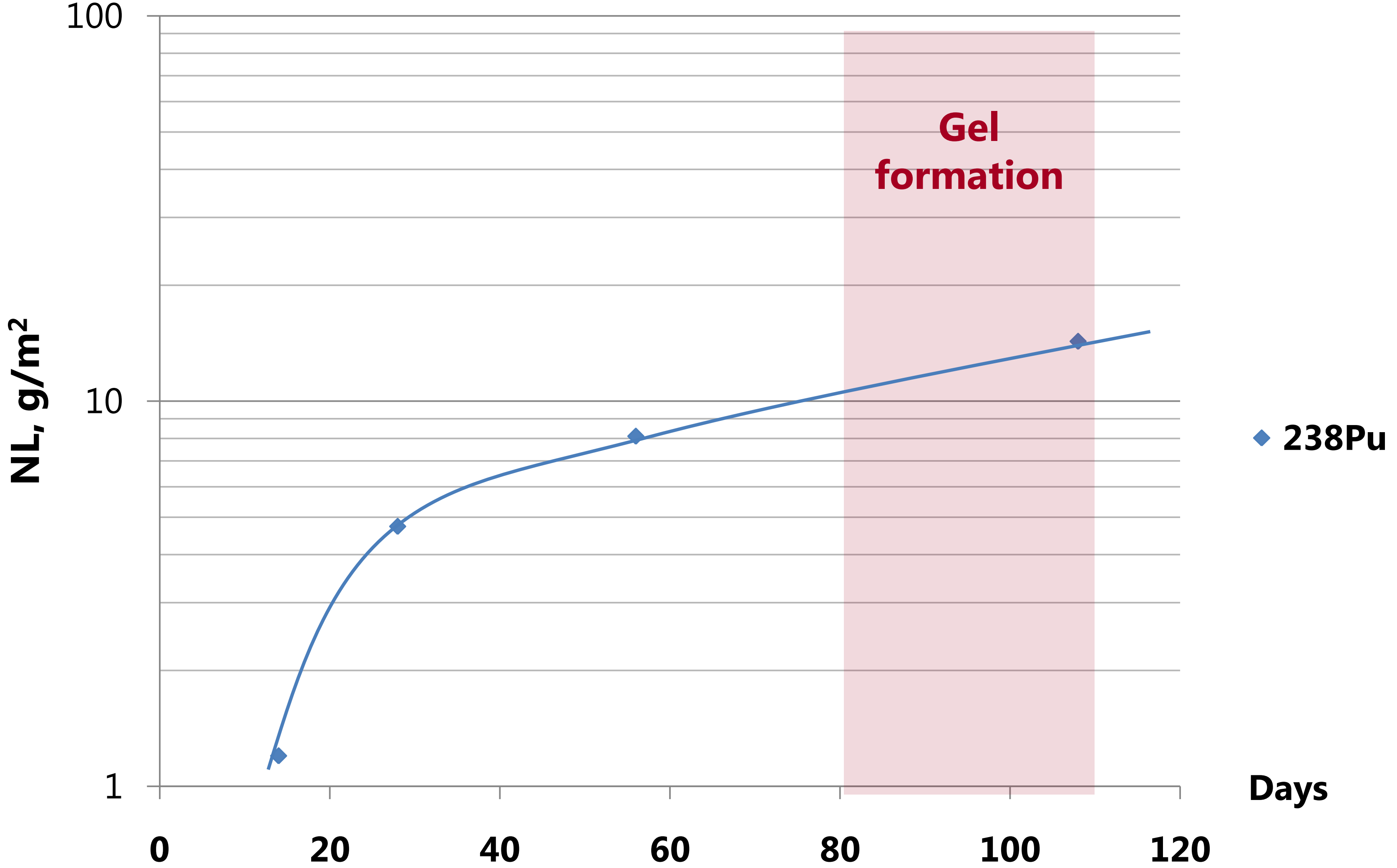
Static leach test, 90°C

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

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

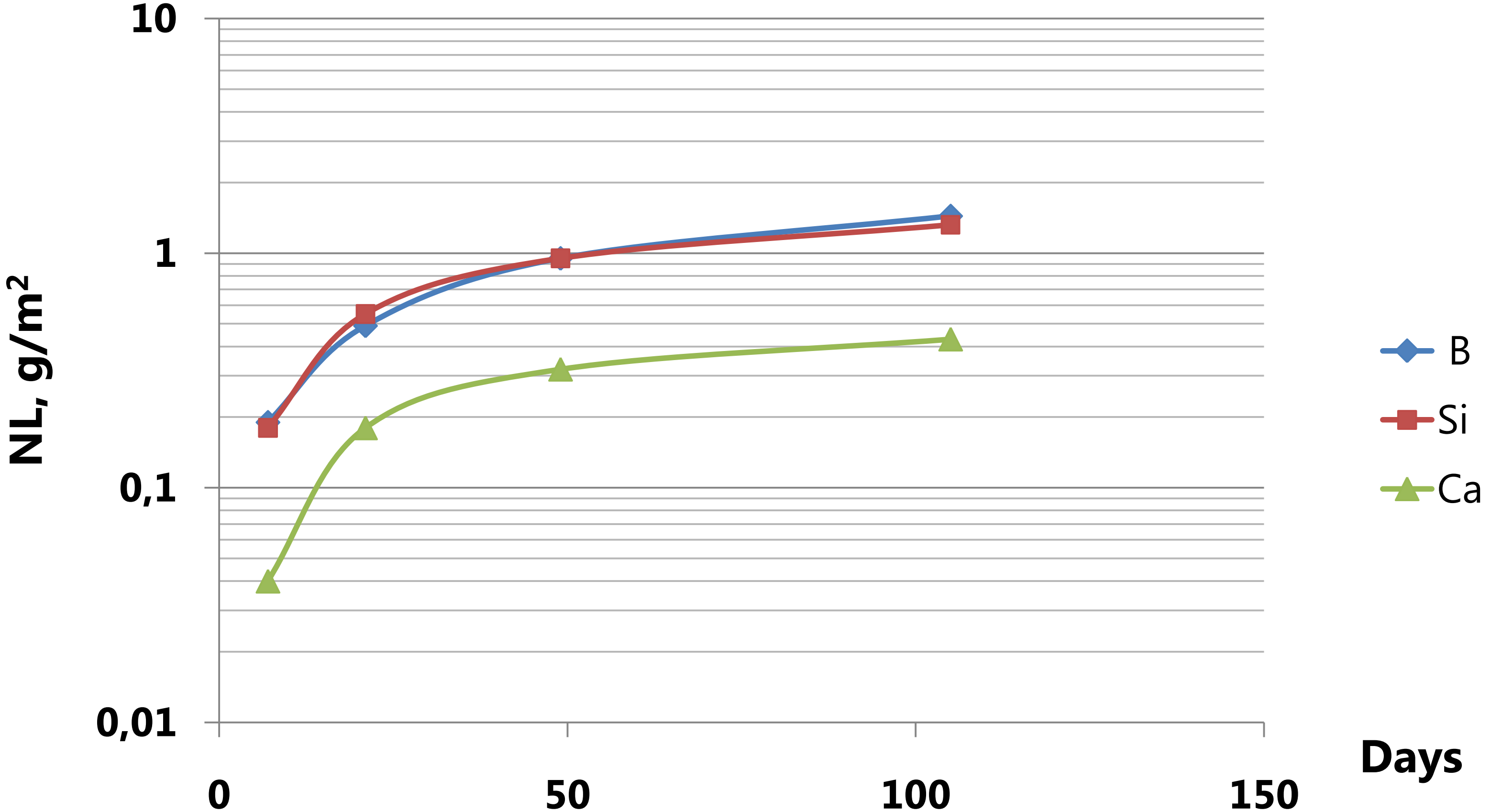
Accumulated dose (on 11.11.2017)

$2{,}5 \cdot 10^{23}$ α-decays/m^3 or $1{,}7 \cdot 10^{16}$ α-decays/sample



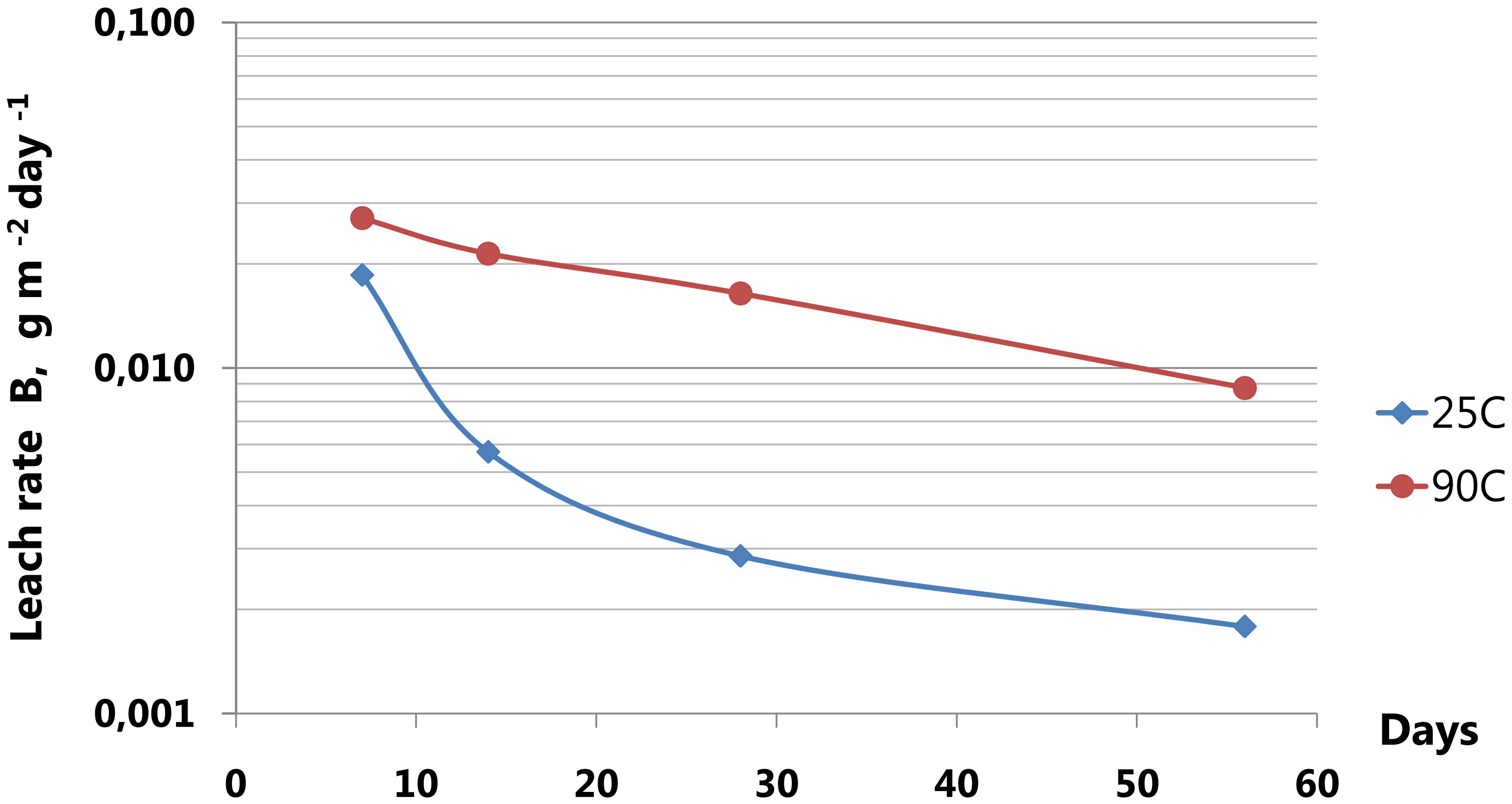
^{238}Pu normalized mass loss (90C, static, distilled water)

Corrosion of glass matrix (for non-radioactive sample)



Static leach test at 90°C, distilled water

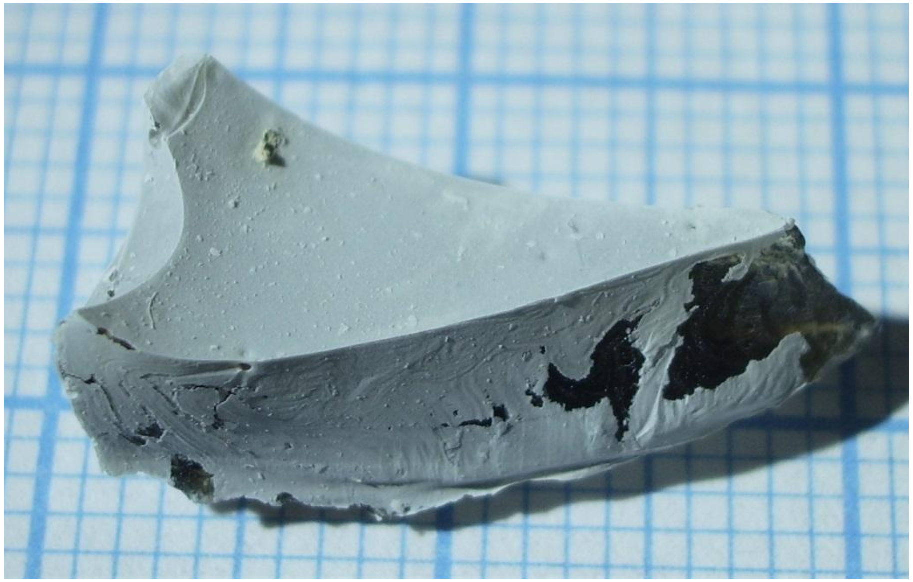
Effect of temperature on boron leaching



Static leaching at 25 and 90°C

Alteration

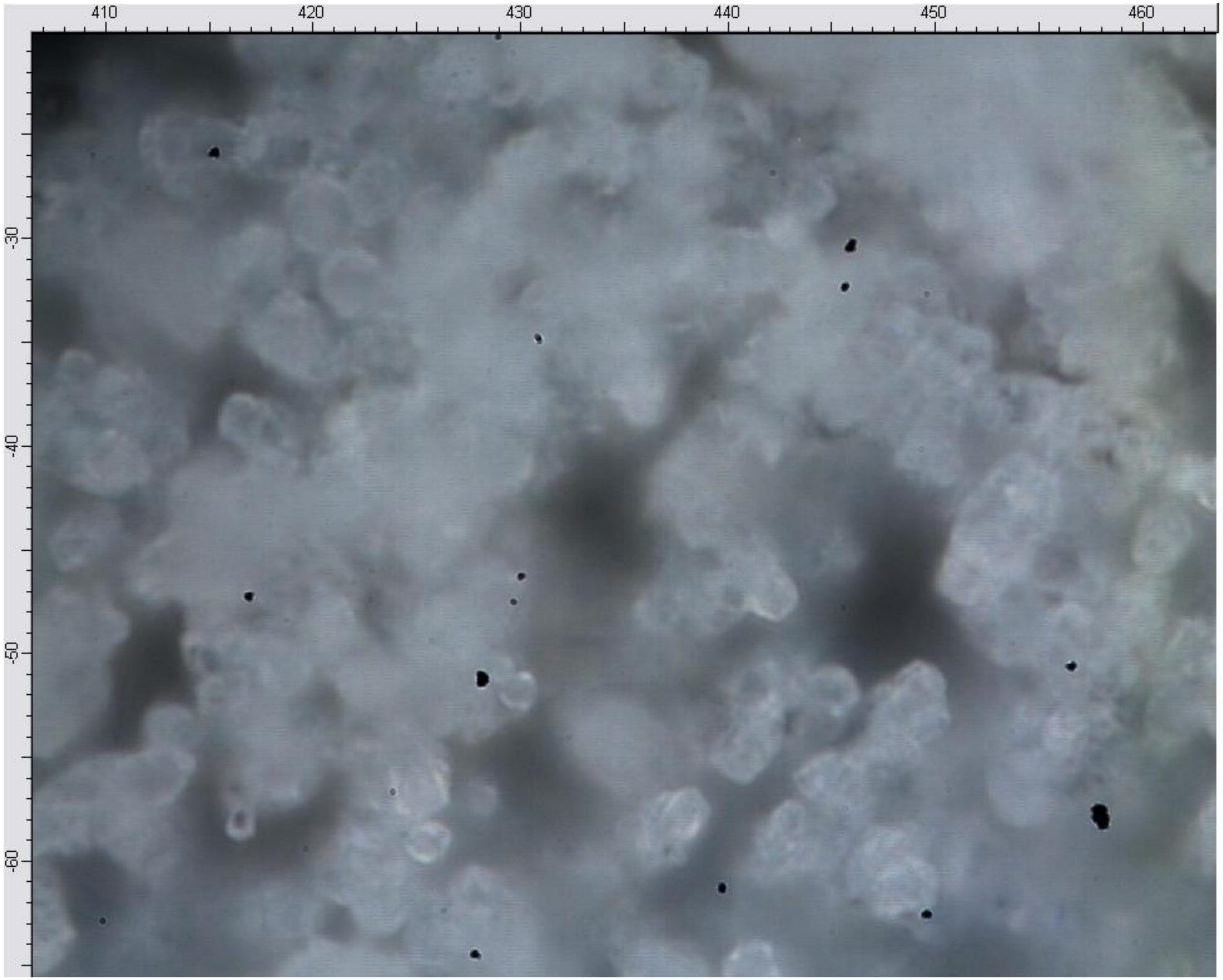
Alteration at saturated conditions



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!



Optical microscopy of «gel» fragment
(scale in microns)

Summary

- After about 4 month Pu leach rate decrease and gel formation was observed at the same time. Glass sample remains monolith, visually homogeneous, no cracks were observed.

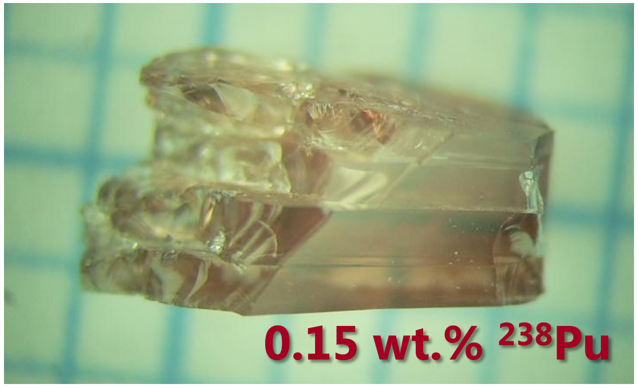
- Different behavior of ^{238}Pu-doped glass at different ratio SA : V Strong fixation of the gel in unsaturated conditions and self destroying of the gel at less amount of water. What about VHT?

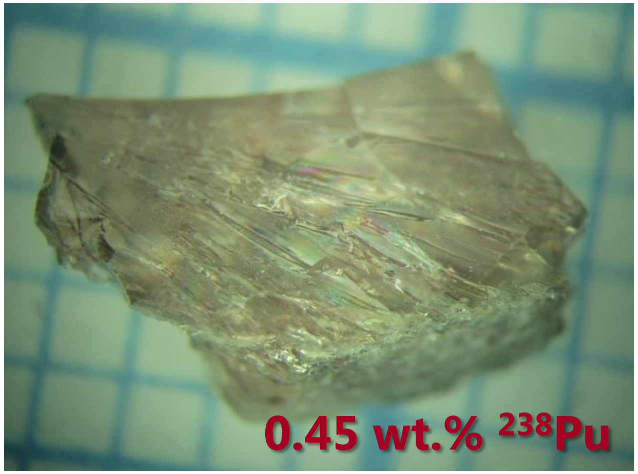
- Different alteration behavior of non-radioactive and ^{238}Pu-doped glass. What is the key factor affecting this process – radiolysis, radiation damage…?

- Further research in needed to study secondary phases and altered glass surface

Other research activities

- Study of Na-Al-P glass doped with ^{238}Pu





- Study of artificial glass-like material – Chernobyl “lava”

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Leaching of actinides and other radionuclides from matrices of Chernobyl “lava” as analogues of vitrified HLW

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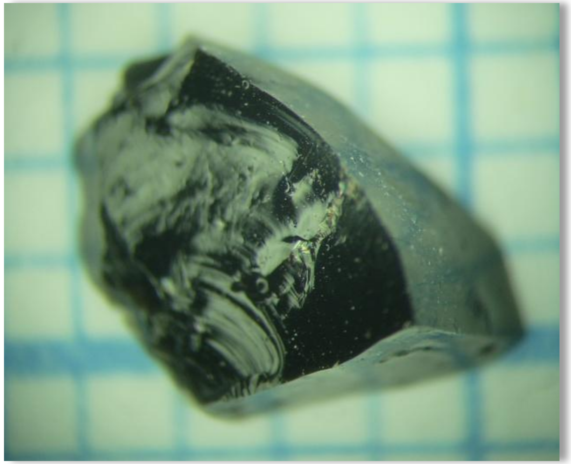

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IAEA and **ICTP**

St-Petersburg 2017 – a year of anniversaries

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100 years
of October Revolution

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Khlopin Radium Institute

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80 years of first cyclotron in Europe

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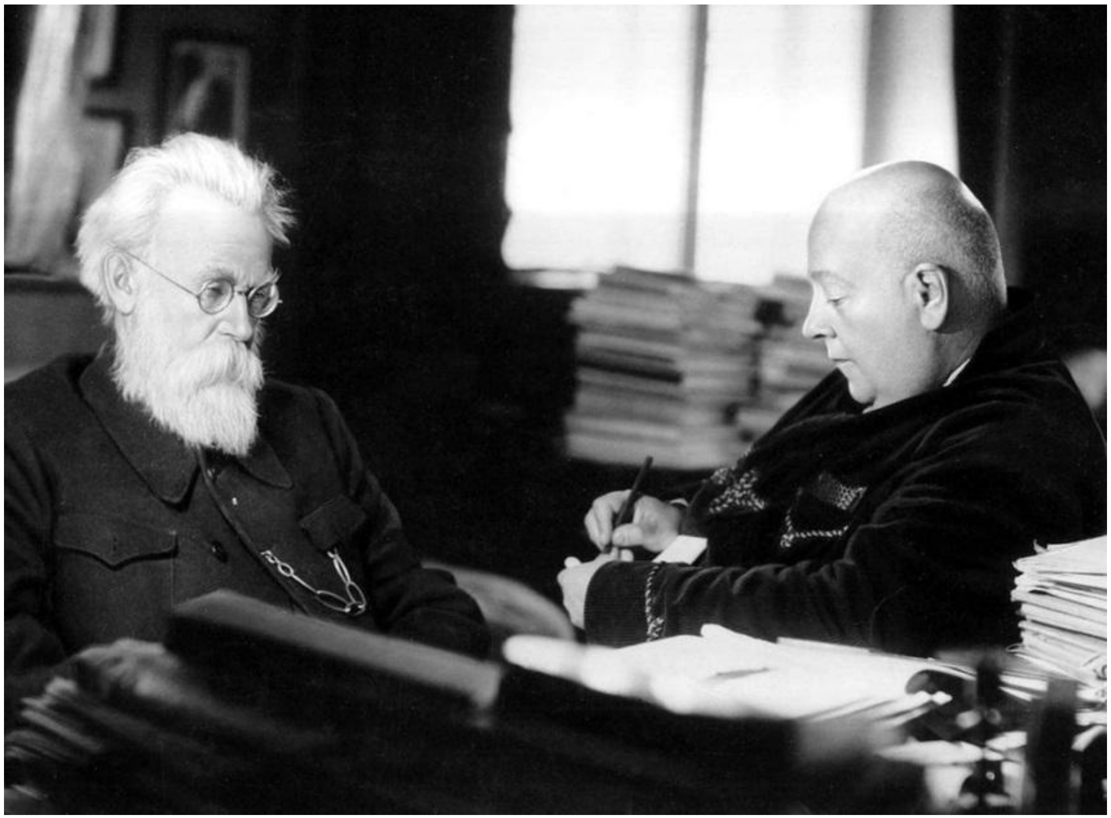
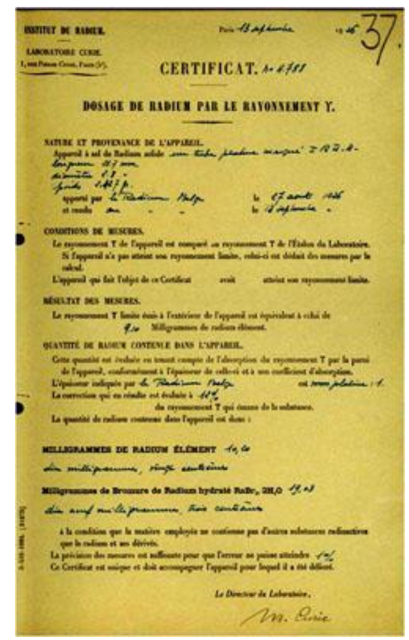
from geochemistry to radiochemistry





INSTITUT DU RADIUM.
LABORATOIRE CURIE.
1, rue Pierre Curie, Paris (5e).

Paris [illegible] 19[illegible] 37.

CERTIFICAT. N° [illegible]

DOSAGE DE RADIUM PAR LE RAYONNEMENT γ.

NATURE ET PROVENANCE DE L'APPAREIL.
Appareil à sel de Radium solide [illegible]
apporté par [illegible] le [illegible]
et rendu [illegible] le [illegible]

CONDITIONS DE MESURES.
Le rayonnement γ de l'appareil est comparé au rayonnement γ de l'Étalon du Laboratoire.
Si l'appareil n'a pas atteint son rayonnement limite, celui-ci est déduit des mesures par le calcul.
L'appareil qui fait l'objet de ce Certificat avait atteint son rayonnement limite.

RÉSULTAT DES MESURES.
Le rayonnement γ limite émis à l'extérieur de l'appareil est équivalent à celui de [illegible] Milligrammes de radium élément.

QUANTITÉ DE RADIUM CONTENUE DANS L'APPAREIL.
Cette quantité est évaluée en tenant compte de l'absorption du rayonnement γ par la paroi de l'appareil, conformément à l'épaisseur de celle-ci et à son coefficient d'absorption.
L'épaisseur indiquée par [illegible] est [illegible]
La correction qui en résulte est évaluée à [illegible] du rayonnement γ qui émane de la substance.
La quantité de radium contenue dans l'appareil est donc :

MILLIGRAMMES DE RADIUM ÉLÉMENT 10,10
[illegible]

Milligrammes de Bromure de Radium hydraté $RaBr_2, 2H_2O$ 19,03
[illegible]

à la condition que la matière employée ne contienne pas d'autres substances radioactives que le radium et ses dérivés.
La précision des mesures est suffisante pour que l'erreur ne puisse atteindre 1%
Ce Certificat est unique et doit accompagner l'appareil pour lequel il a été délivré.

Le Directeur du Laboratoire,
M. Curie

The only hot cell facility…

The only hot cell facility…

… located in 3 km distance from Emperor Palace

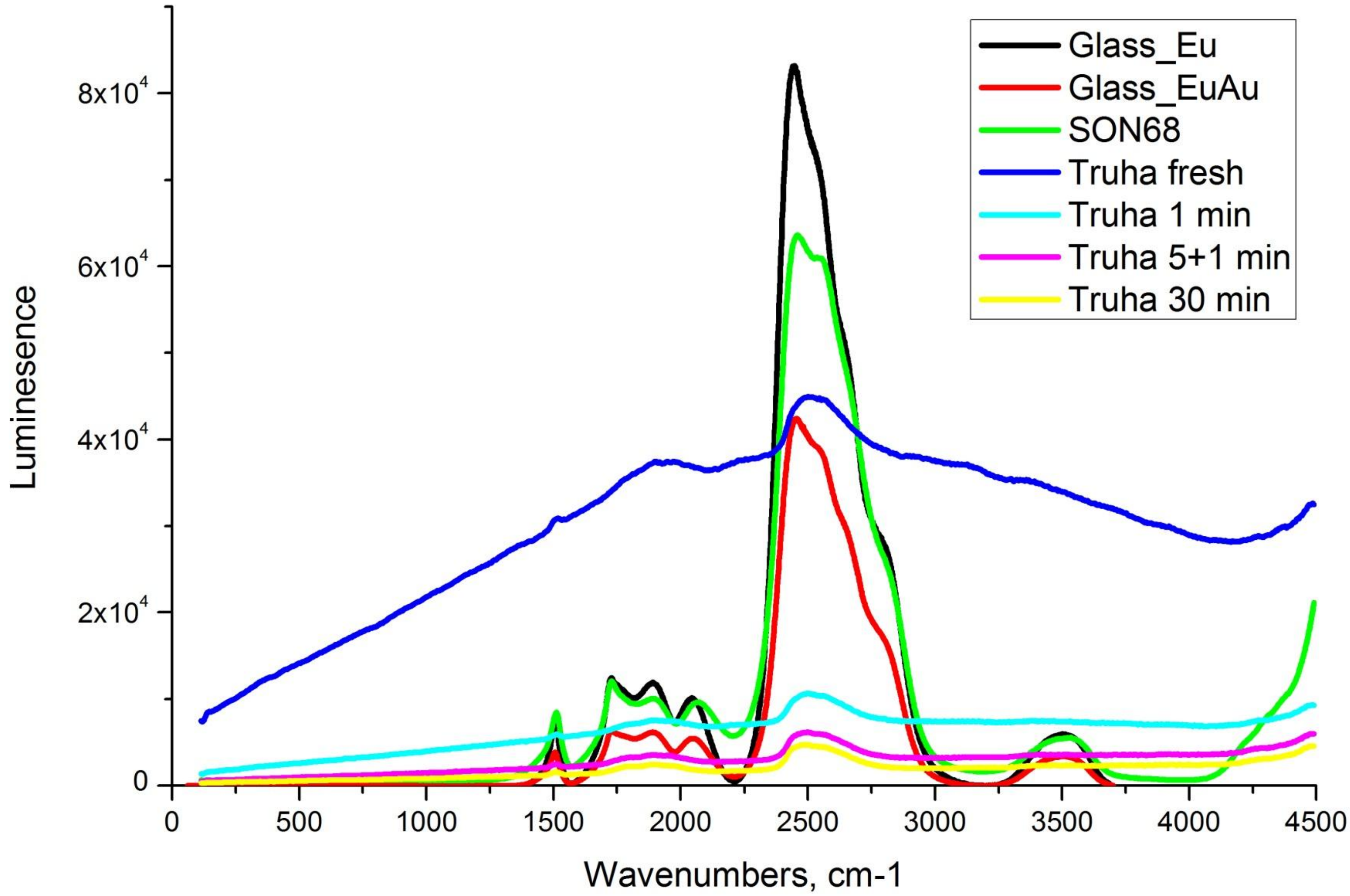
Practical workshops at KRI and abroad

Thank you for your attention!

Glass composition

элемент / оксид	масс.%	
	Стекло с ^{238}Pu	Нерадиоактивное стекло
SiO_2	47.84-47.87	47.71
Na_2O	14.59-14.60	14.52
B_2O_3	21.19-21.21	21.13
Al_2O_3	6.84-6.85	6.96
Eu_2O_3	3.02	3.84
CaO	5.87	5.84
PuO_2 (81.3 wt. % ^{238}Pu)	0.65-0.58	-
$^{238}PuO_2$	0.53-0.47	-
^{238}Pu	0.45-0.42	-

Спектры фотолюминесценции исходных образцов стекла SON68 и новообразованной фазы («Truha»)



Synthesis of Pu-doped Na-Al-P glass

- **Na-Al-P glass (Russia)**
  - ✓ Uses for vitrification of HLW only in Russia
  - ✓ Vitrified legacy waste for disposing in deep geological disposal

- **Sintering in air, 1200°C, 2 hours**
  at high temperature furnace developed at KRI (Patent №14714, Vol. №29, 20.10.2014)

- **0,43 wt.% ^{238}Pu for acceleration of radiation damages**
  and nonradioactive (referent) sample with almost the same composition

- **HLW simulation for both samples, including 2,5 wt.% of lantanides (La, Nd) and fission products (Ba, Cs, Sr, Mo)**

Leaching

NL – normalized mass loss, g/m^2

for radioactive samples

$$NL = \frac{a}{a_0} W_0 \frac{1}{SA}$$

a – activity of isotope in leachate, Bq
a_0 – initial activity of isotope in the sample, Bq
W_0 – initial weight of the sample, g
SA - surface area, m^2

for non-radioactive samples

$$NL = \frac{m}{f \cdot SA}$$

m – weight of element in leachate, g
f – mass fraction of element in the sample before leaching
SA - surface area, m^2