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

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Sydney
2017

Background

- Synroc is a well known material for immobilization of different radionuclides

- Synroc can be synthesized using HIP (hot isostatic pressing), HUP (hot uniaxial pressing) or cold pressing followed with sintering in air

- The main difficulties of Synrock technology are related to precursor preparation

Preparation of starting precursor (simplified)

Evoparation
of liquid RW

⇩

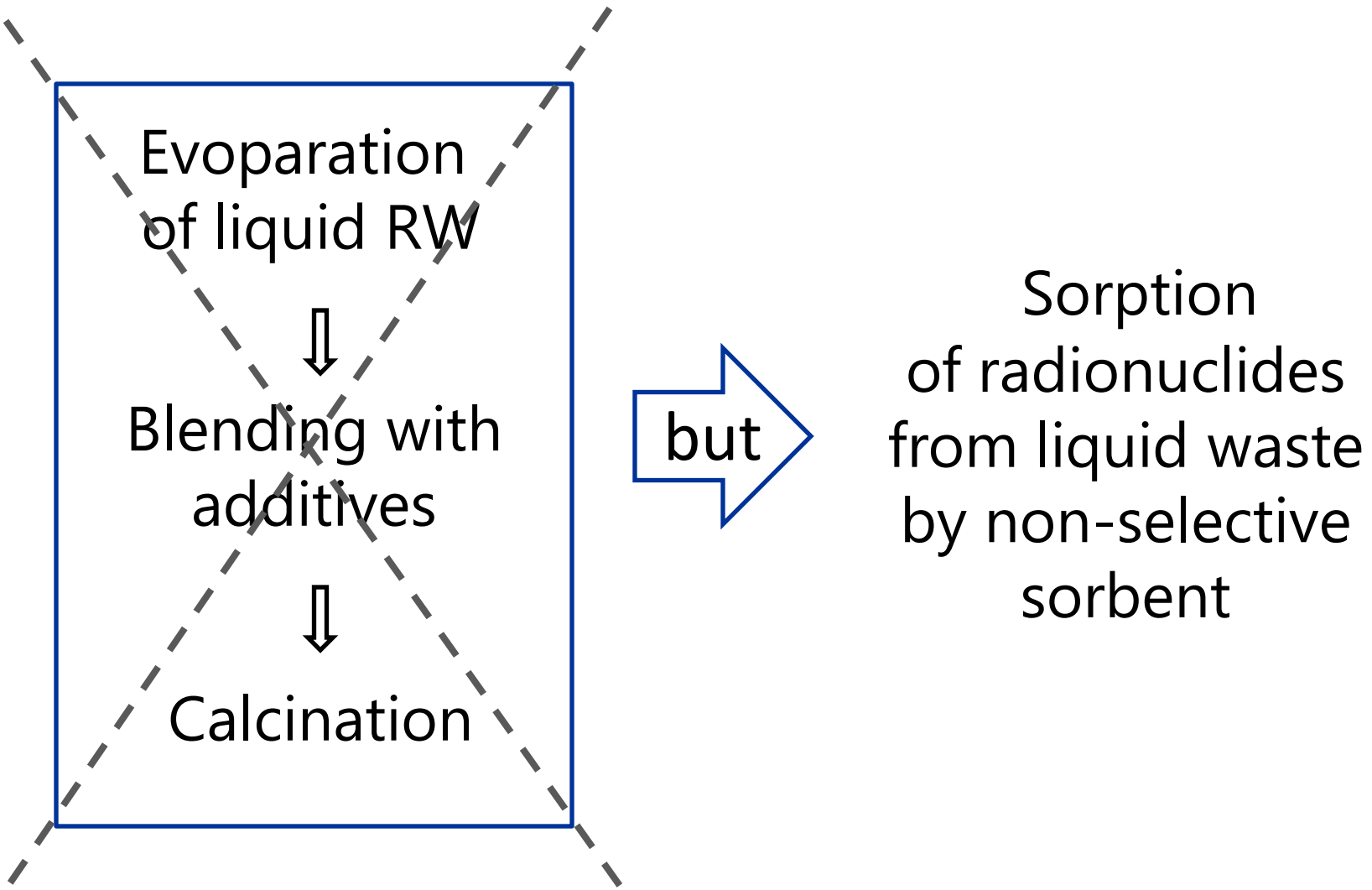
Blending with
additives

⇩

Calcination

Can we optimize this process?

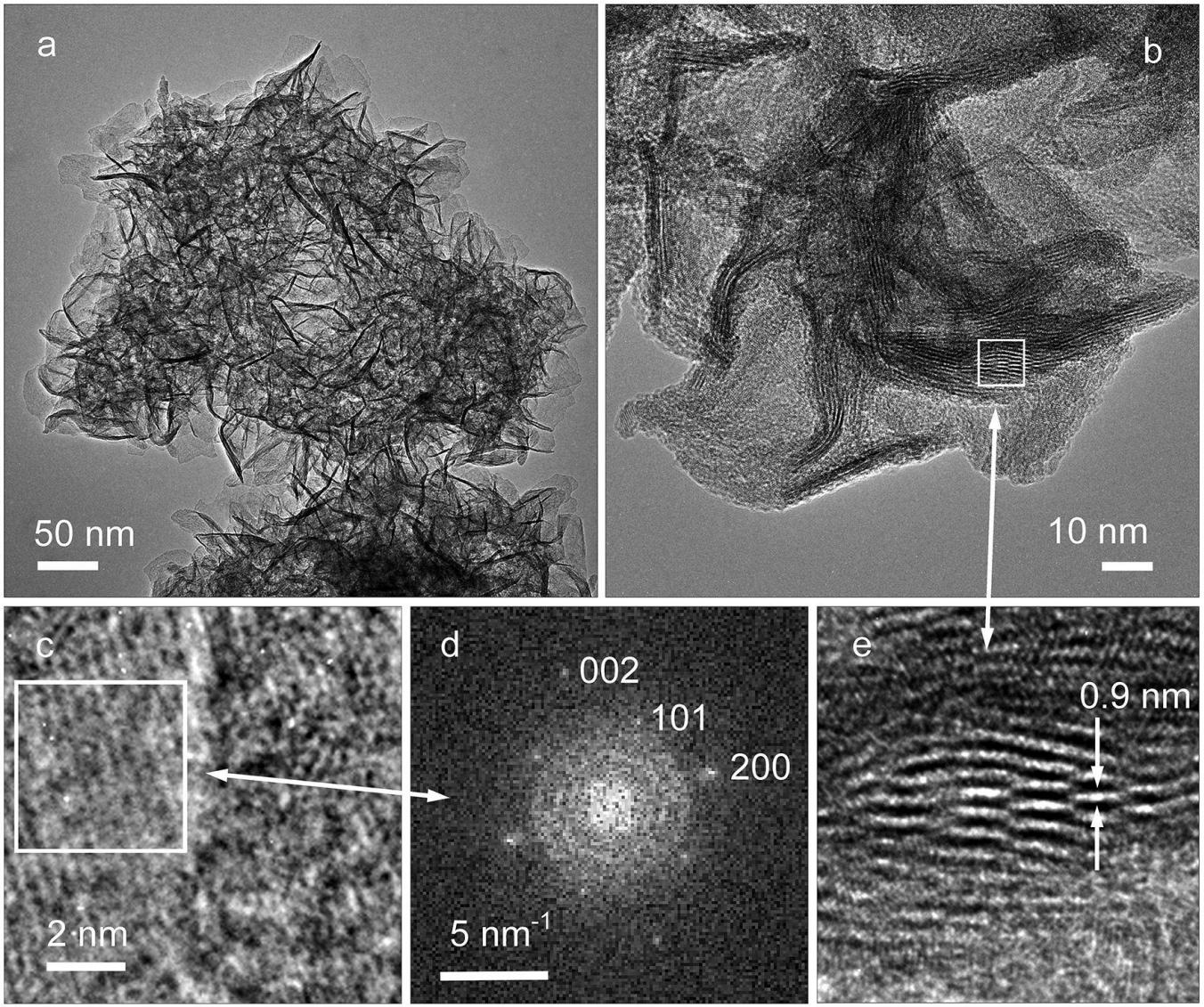
*Yes, if we have **non-selective titanate** sorbent*



Layered Hydrazinium Titanate (LHT-9)

$$(N_2H_5)_{0.5}Ti_{1.87}O_4$$

LHT-9: Layered Hydrazinium Titanate – 9 Å



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Layered Hydrazinium Titanate: Advanced Reductive Adsorbent and Chemical Toolkit for Design of Titanium Dioxide Nanomaterials

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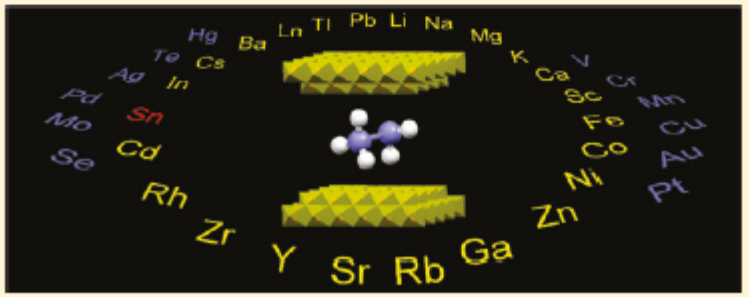
Supporting Information

ABSTRACT: LHT-9, a layered hydrazinium titanate with an interlayer spacing of ~9 Å, is a new nanohybrid compound combining the redox functionality of hydrazine, the ion-exchange properties of layered titanate, the large surface area of quasi-two-dimensional crystallites, surface Brønsted acidity, and the occurrence of surface titanyl bonds. LHT-9, ideally formulated as $(N_2H_5)_{1/2}Ti_{1.87}O_4$, relates to a family of lepidocrocite-type titanates. It possesses a high uptake capacity of ~50 elements of the periodic table. Irreversibility of reductive adsorption allows LHT-9 to be used for cumulative extraction of reducible moieties (noble metals, chromate, mercury, etc.) from industrial solutions and wastewaters. Unlike sodium titanates that do not tolerate an acidic environment, LHT-9 is capable of uptake of transition metals and lanthanides at pH > 3. Adsorption



Publications about LHT-9

- Britvin S.N., Lotnyk A., Kienle L., Krivovichev S.V., Depmeier W. **(2011)** Layered Hydrazinium Titanate: Advanced Reductive Adsorbent and Chemical Toolkit for Design of Titanium Dioxide Nanomaterials. *J. Am. Chem. Soc., Vol. 133, 9516–9525.*
- Britvin S.N., Korneyko Yu.I., Burakov B.E., Lotnyuk A., Kienle L., Depmeier W., Krivovichev S.V. **(2012)** Sorption of nuclear waste components by layered hydrazinium titanate: a straightforward route to durable ceramic forms. *Scientific Basis for Nuclear Waste Management XXXV*, *Materials Research Society Symposium Proceedings, Buenos-Aires, Argentina, Vol. 1475, 190-196.*
- Korneyko Yu.I, Britvin S.N., Burakov B.E., Lotnyuk A., Kienle L., Depmeier W., Krivovichev S.V. **(2012)** Crystalline titanate ceramic for immobilization of Tc-99. *Scientific Basis for Nuclear Waste Management XXXV*, *Materials Research Society Symposium Proceedings, St. Buenos-Aires, Argentina, Vol. 1475, 185-190.*

sorption

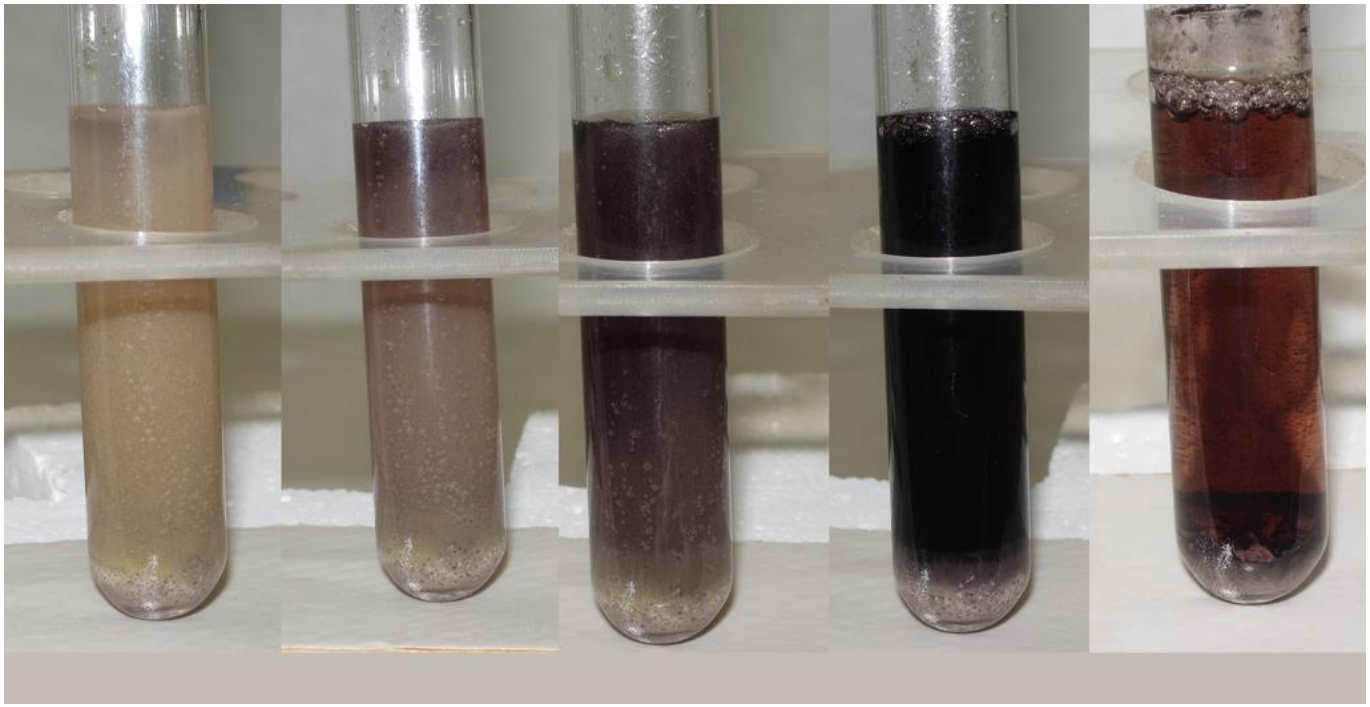
Sorption of real radionuclides in high amounts

(extra products after sorption are just water and nitrogen)

Nuclide, compound	Initial concentration	Duration (hours)	Removal, % of injected
^{99}Tc ($KTcO_4$, pH 7)	2 g/L ^{99}Tc	24	93
^{137}Cs ($CsNO_3$, pH 7)	87 MBq/L ^{137}Cs	1.5	94
^{90}Sr ($Sr(NO_3)_2$, pH 7)	10 MBq/L ^{90}Sr	1.5	90
^{239}Pu ($PuCl_3$, pH 3)	40 g/L ^{239}Pu	24	95
^{238}U ($UO_2(NO_3)_2$, pH 2)	50 g/L ^{238}U	24	97

Unique mechanism of Tc sorption accompanied with reduction of Tc^{7+} to Tc^{4+}

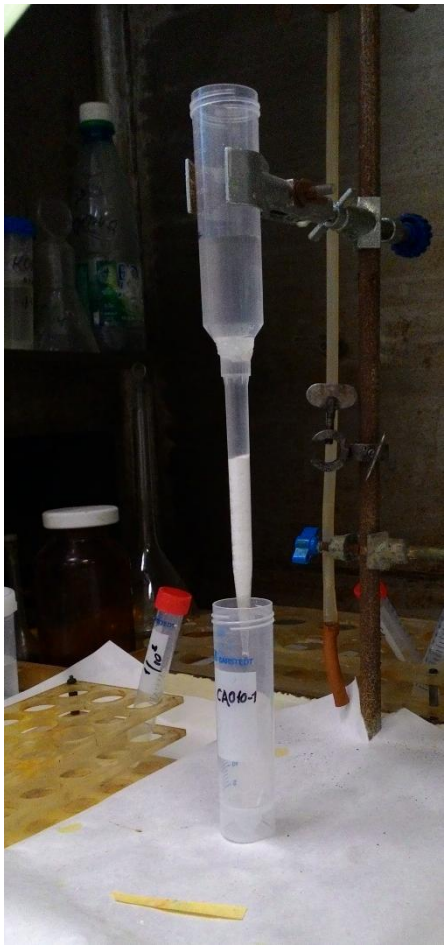
Fast (during 24 h) sorption of Tc from $KTcO_4$ solution:



Start **1 min** **3 min** **30 min** **1 day**

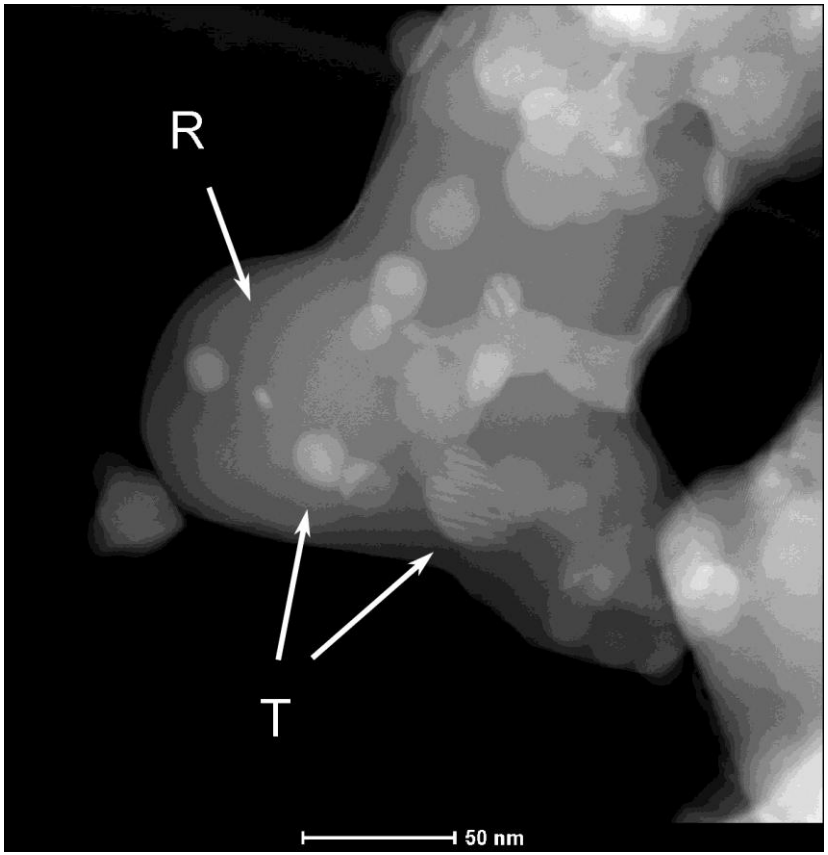
Dynamic sorption of liquid RW

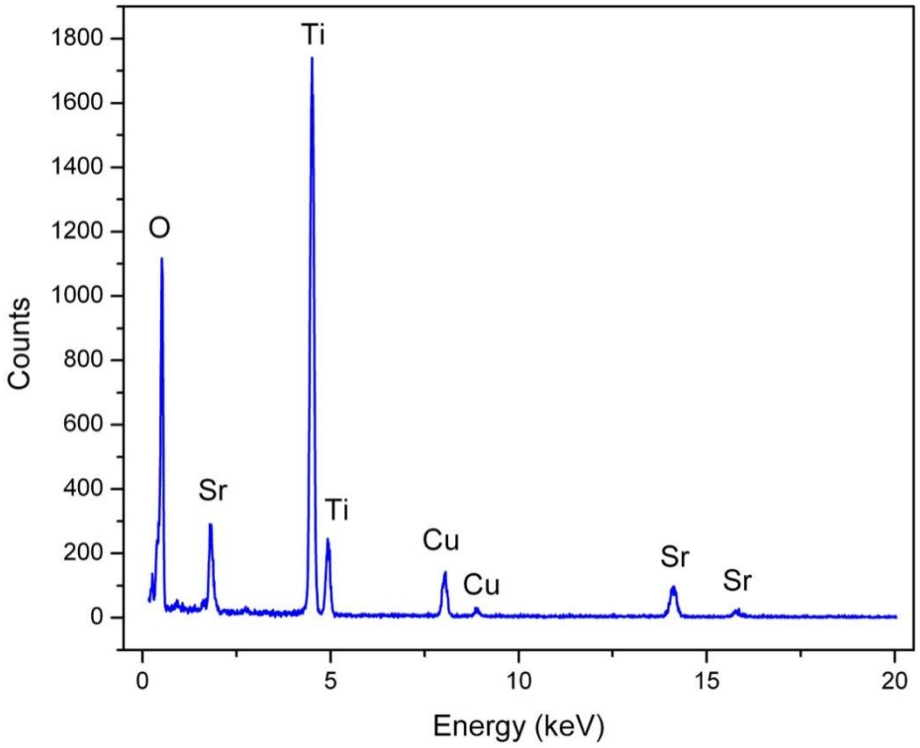
	Activity, Bq		
	^{137}Cs	^{154}Eu	^{241}Am
ILW **before** sorption V= 85,5 ml	$6{,}2\cdot10^{5}$	$3{,}0\cdot10^{5}$	$2{,}0\cdot10^{5}$
ILW **after** sorption V= 85,5 ml	~ 33	< 1	< 2
Purification	$1{,}9\cdot10^{4}$	$> 3\cdot10^{5}$	$> 10^{5}$
Total amount of RN on sorbent, Bq	$6{,}2\cdot10^{5}$	$3{,}0\cdot10^{5}$	$2{,}0\cdot10^{5}$
Concentration **in saturated area**, Bq/g LHT-9	$2{,}2\cdot10^{6}$	$2{,}1\cdot10^{6}$	$1{,}7\cdot10^{6}$



conversion of spent sorbent into ceramic waste form

Strontium





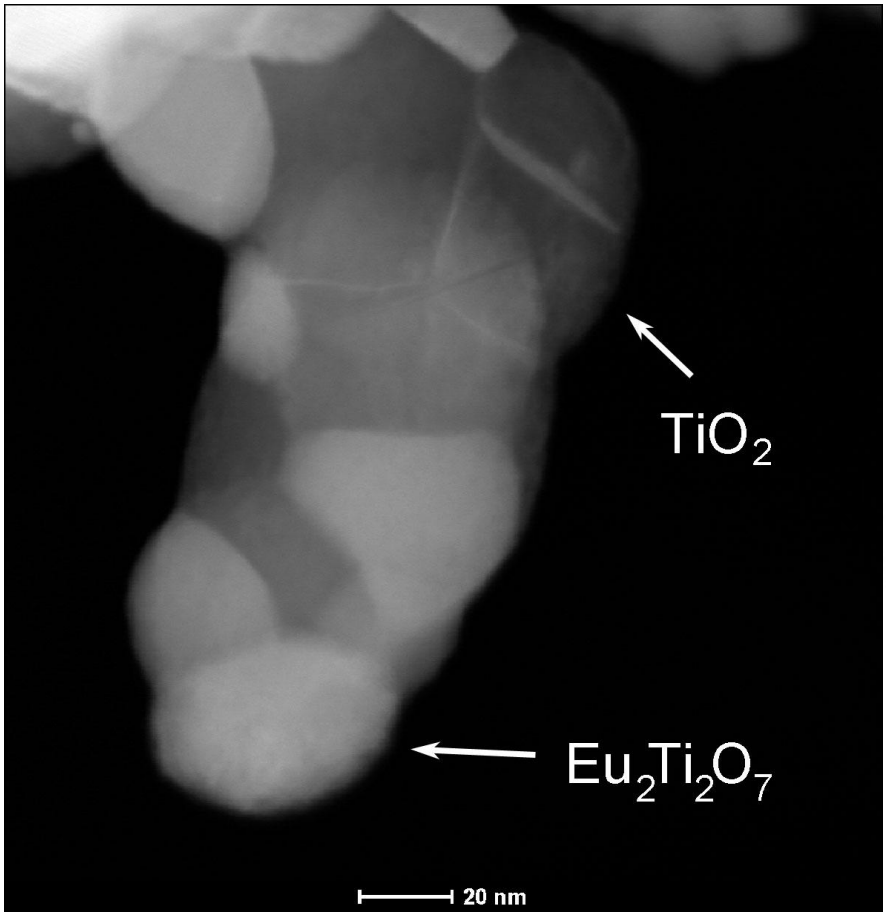
1000°C:

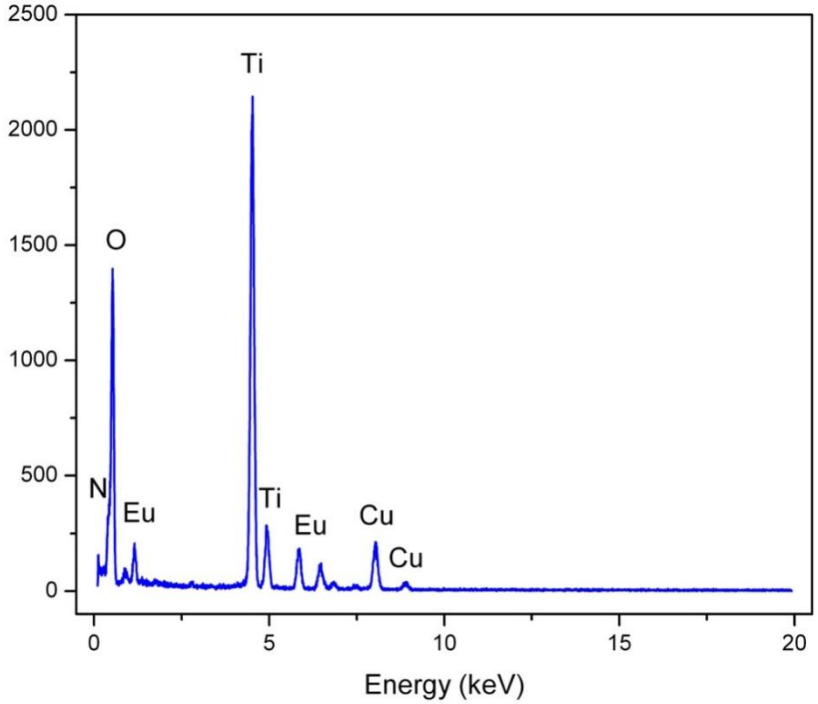
rutile TiO_2 + tausonite (perovskite)

$SrTiO_3$

~ 8 % Sr

Rare Earths



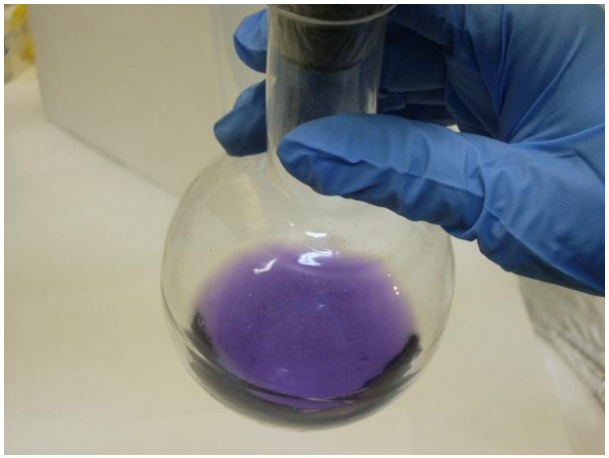


1000°C:

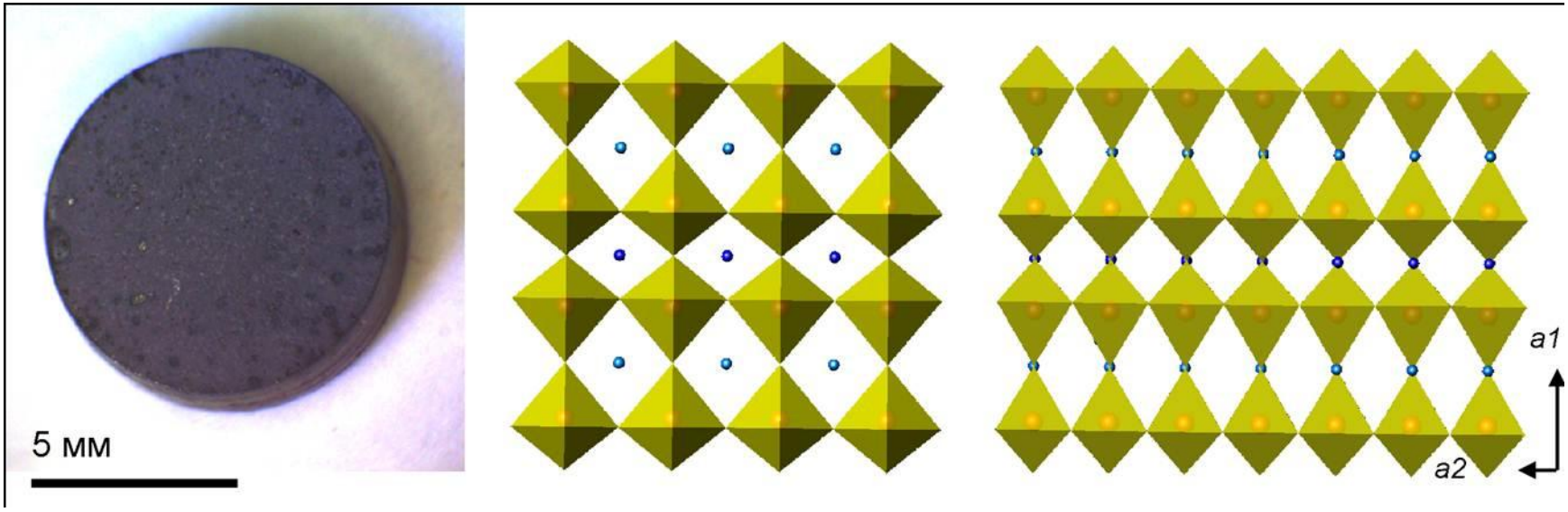
rutile TiO_2 + pyrochlore $Eu_2Ti_2O_7$

~ 12 % Eu

Double-phase Ti-ceramic
doped with 12 wt.% Pu-239
obtained after Pu-sorption on LHT-9
from concentrated Pu aqueous solution
(Pu content – 40 g/liter)



ceramic pellet and the structure of Pu-perovskite

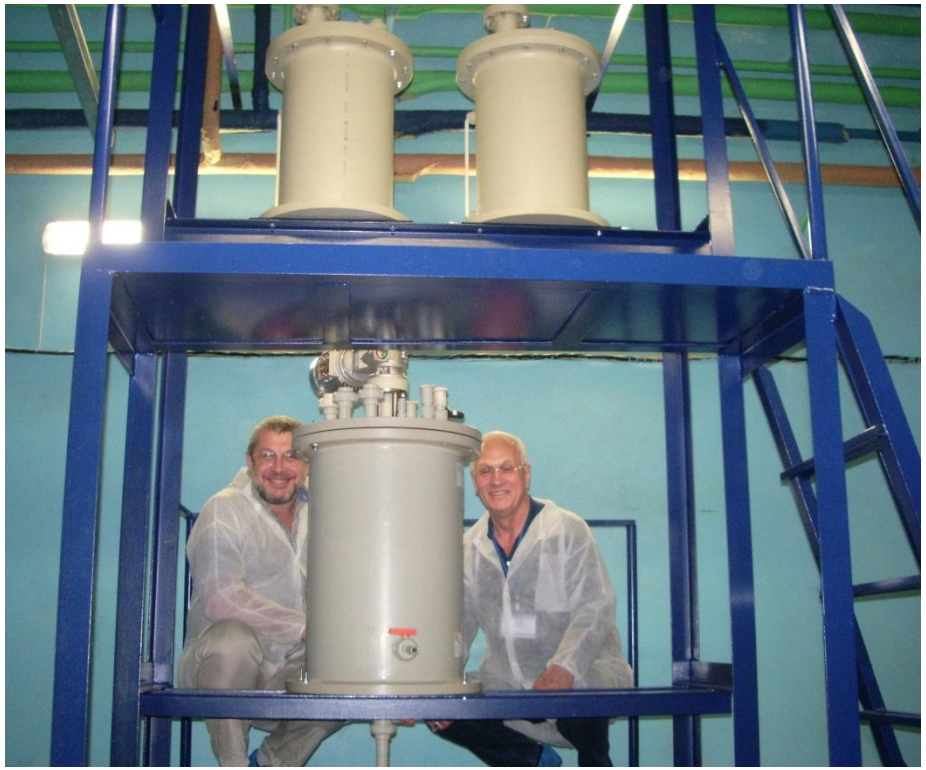


application of LHT-9: first steps

Pilot-scale device for synthesis of LHT-9

Developed and installed at KRI hot-cell facility, 2016

(in the framework of contract with Socium Ltd)

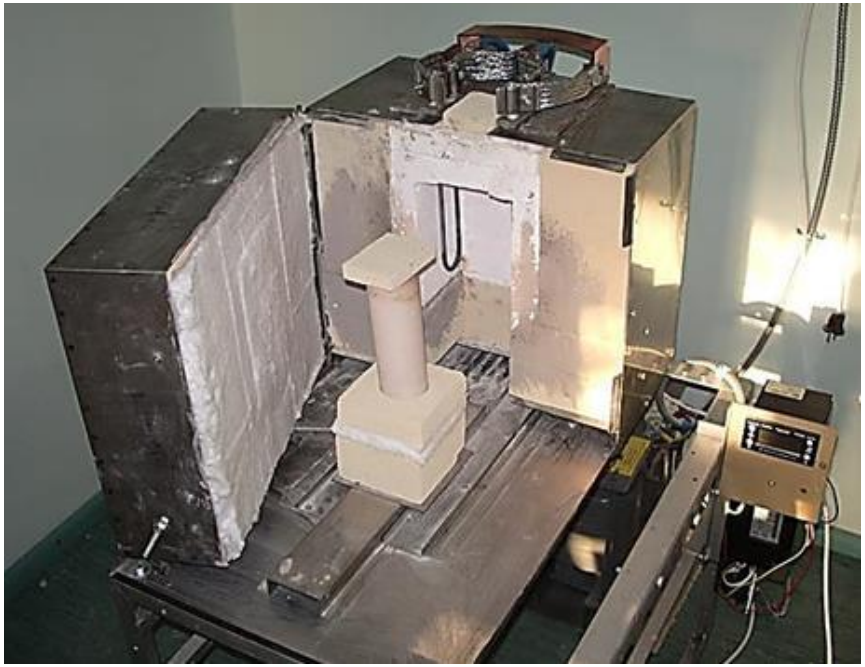


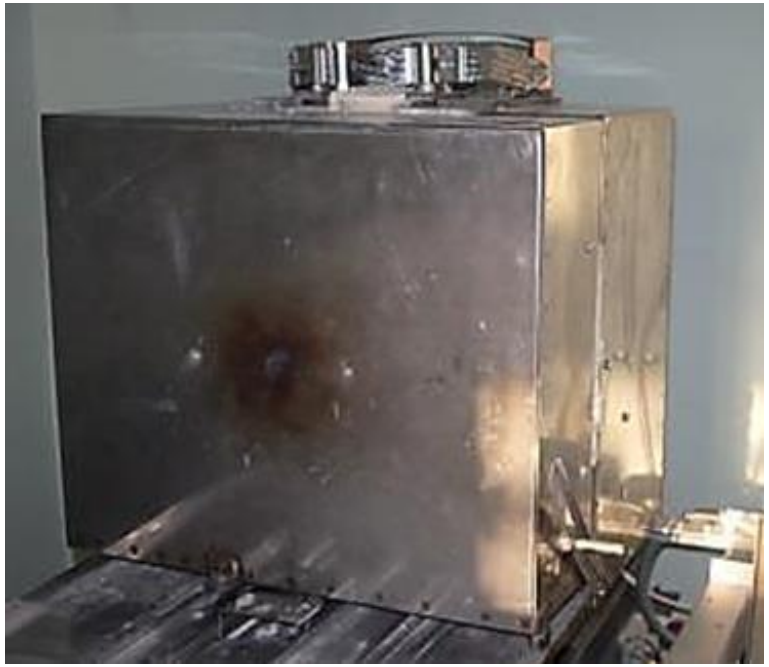
Final stage of installation

First production of sorbent LHT-9 synthesized at KRI

Mobile high-temperature furnace CUB-1

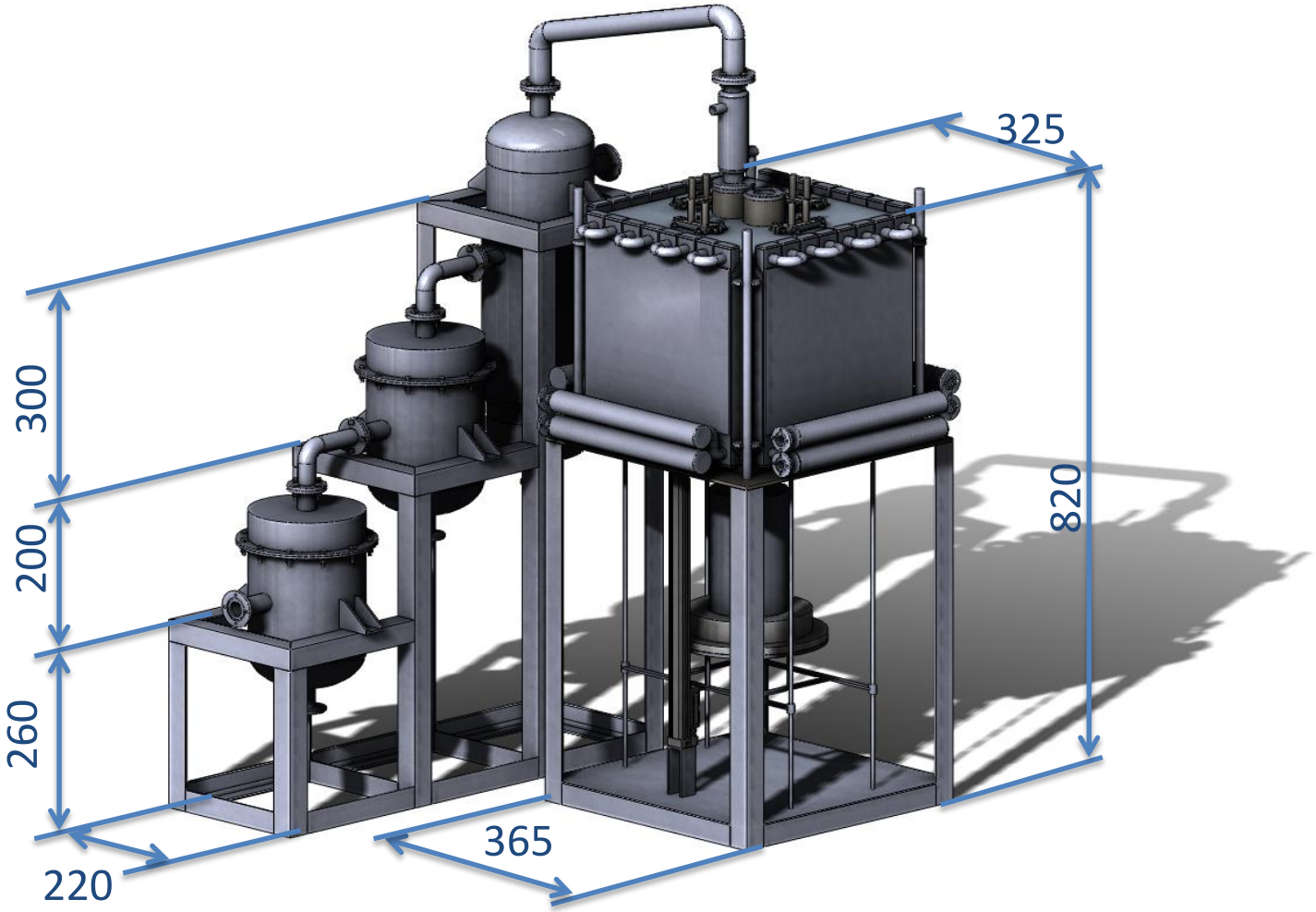
Patent № 146714





Modified project of CUB-1 furnace for HLW solidification

by "Sverdniichimmash", Ekaterinburg, Russia



KRI hot cell facility

- More than 40 years of safe operation
- Experience in processing about 150 kg of spent fuel of different types
- Performance 12000 Ci/year
- Unique equipment

The chain of 13 hot cells connected to the horizontal conveyor and 6 heavy boxes

Pellet of Synroc-like titanate ceramic doped with real HLW (after sorption of liquid wastes by LHT-9)

obtained at KRI hot-cell facility in 2016

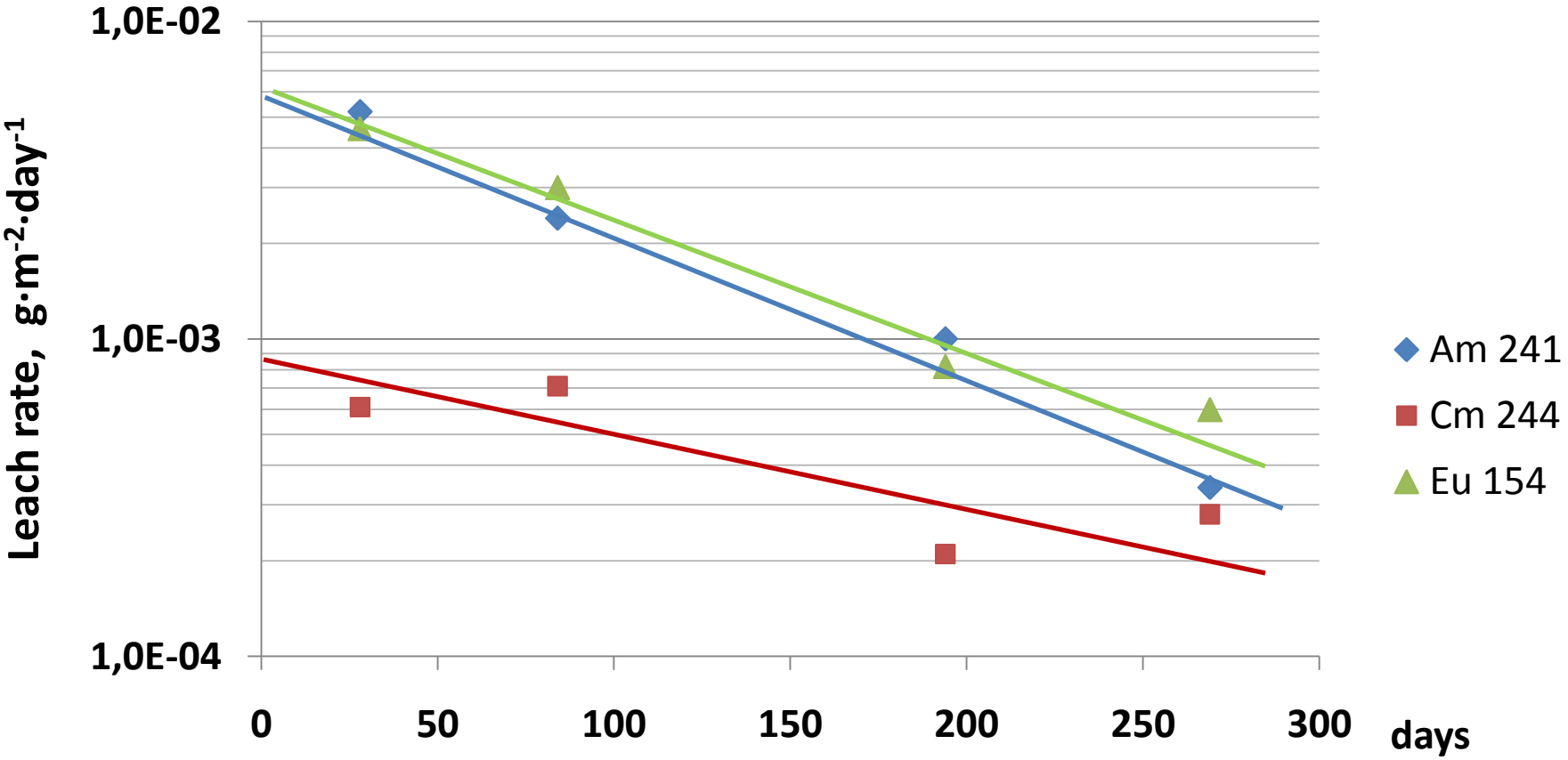
sintering in air at 1200°C for 2 hours

Nuclide	Activity, Bq/g
^{243}Am	1.5×10^{6}
^{241}Am	9.3×10^{7}
^{244}Cm	2.7×10^{8}
^{155}Eu	$1,5 \times 10^{6}$
^{154}Eu	$8,5 \times 10^{7}$
^{152}Eu	$1,2 \times 10^{5}$
^{144}Ce	$5,1 \times 10^{5}$
^{137}Cs	$2,4 \times 10^{5}$
^{90}Sr	$1,3 \times 10^{8}$

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

(for 10 month, dist. water, 90°C)

**calculated for geometrical surface area*



Conclusions

- LHT-9 is very efficient non-selective sorbent which is very prospective for nuclear waste management
- Spent LHT-9 (after sorption of liquid RW) can be directly converted into Synroc-like titanate ceramic by cold pressing followed with sintering in air at 1100-1200°C
- The use of LHT-9 can simplify essentially existing route of Synroc synthesis

Acknowledgement

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