

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

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### ABSTRACT:

*Immobilization of bulk liquid high level radioactive waste (HLW) in Synroc ceramic is well-known reliable way for final isolation of dangerous long-lived radionuclides from biosphere. The alternative method of Synroc-like ceramic synthesis has been proposed. Radionuclide incorporation into crystalline titanate host-phases can be provided as a result of direct radionuclide sorption from liquid HLW using non-selective sorbent – layered hydrazinium titanate (LHT-9). Such an approach allows excluding expensive multi-stage procedure of precursor preparation. The precipitate obtained after sorption can be easily transformed into Synroc-like ceramic by cold pressing followed with sintering in air at 1000-1200°C. The highly radioactive samples of titanate ceramic loaded with real HLW have been synthesized and preliminary studied at KRI hot-cell facility. Chemical durability of this sample has been studied using static leach test in distilled water at 90°C and the leach rates for <sup>154</sup>Eu, <sup>241</sup>Am, <sup>244</sup>Cm were (in g·m<sup>-2</sup>·day<sup>-1</sup>) from 2·10<sup>-4</sup> to 5·10<sup>-3</sup>. Normalised <sup>137</sup>Cs mass loss was 0.3 g·m<sup>-2</sup> for 110 days at the same conditions.*

### INTRODUCTION

Ceramic waste forms for immobilization of actinides and HLW can be processed by three main well known methods: hot uniaxial or isostatic pressing (HUP and HIP); cold pressing followed with sintering and even melting [1]. The selection of optimal processing method for particular type of ceramic is based on many details including technological feasibility and national safety restrictions applied in different countries. For example ANSTO (Australian Nuclear Science and Technology Organization) encourages using HIP for making Synroc [2] but most R&D on development of ceramic waste forms in Russia consider mainly cold pressing followed with sintering in air as prospective synthesis method, which is justified enough for adoption by nuclear industry [1]. In any case total amount of radionuclides loaded into

ceramic waste forms synthesized through any methods should be incorporated into crystalline structures of durable host-phases. In order to avoid unreacted separate forms of radionuclides in the matrices of ceramic waste forms it is necessary to provide complete homogeneity and high chemical reactivity of starting precursors before ceramic synthesis. It is obvious that the use of simple mechanical oxide blend as starting precursor for ceramic waste form would cause high probability to face difficulties with complete reaction between all precursor's components and avoiding separate radionuclide phases in ceramic matrix. Although the use of oxide blend precursor for making Synroc and Ti-pyroxhlore ceramic for Pu immobilization was successfully demonstrated by ANSTO and Lawrence Livermore National Laboratory [2,3] other feasible but much more expensive types of starting precursors have been developed such as metal-organic compounds for Synroc [2]; sol-gel for zircon-based ceramic [1] and co-precipitated hydroxides or phosphates for zirconia and monazite ceramic, respectively [1]. The use of new non-selective sorbent LHT-9 (layered hydrazinium titanate,  $(\text{N}_2\text{H}_5)_{1/2}\text{Ti}_{1.87}\text{O}_4$ ) [4] for bulk simultaneous sorption of radionuclides and non-radioactive chemical elements from liquid radioactive wastes may optimize essentially the preparation of starting precursor and simplify synthesis conditions of titanate Synroc-like ceramic [5-7]. As a result of sorption by LHT-9 from aqueous solutions chemical elements including Sr, Pu, Am, Tc and rare earths form precipitate based on stable titanate compounds.  $\text{H}_2\text{O}$  and  $\text{N}_2$  are secondary products of sorption reaction. Cesium sorption by LHT-9 from solution of pure Cs-salt causes formation of Cs-bearing LHT-9, but in the presence of other chemical elements in common aqueous solution non-selective sorption by LHT-9 as assumed may be accompanied with formation of stable Cs-bearing titanate host-phases with hollandite, pollucite or leucite-type structures.

This paper presents first results on study of Synroc-type ceramic synthesized from precursor based on used LHT-9 after sorption from real liquid HLW. In order to understand mechanism of Cs incorporation into crystalline titanate phases one non-radioactive ceramic sample has been synthesized and studied using LHT-9 after sorption from Cs-nitrate solution in the presence of Si and Al admixtures.

## EXPERIMENTAL DETAILS

In order to test the alternative method of Synroc-like ceramic synthesis the real liquid HLW from KRI hot cell facility were used (Table I). The  $^{137}\text{Cs}$  content in this type of HLW was relatively low because main amount of Cs was previously extracted.

**Table I.** Composition of HLW from the 1-st cycle of PUREX-process

HNO <sub>3</sub> , mol/L	Mo, mg/L	Zr, mg/L	$\alpha$ -emitters, Bq/L		$\gamma$ -emitters, Bq/L				$^{90}\text{Sr}$
			$^{241}\text{Am}$	$^{244}\text{Cm}$	$^{137}\text{Cs}$	$^{144}\text{Ce}$	$^{154}\text{Eu}$	$^{243}\text{Am}$	
2.1	550	45	$1.7 \cdot 10^{10}$	$3.6 \cdot 10^{10}$	$6.1 \cdot 10^6$	$1.1 \cdot 10^9$	$1.5 \cdot 10^{10}$	$\sim 5.5 \cdot 10^8$	$3.2 \cdot 10^8$

Before sorption some amount of liquid HLW was dissolved in 15 times by distilled water. Then 100 ml of this solution has been placed into glass vessel and mixed with pulp of LHT-9 containing 1.5 g of sorbent (recalculated for dry powder). Static sorption during 3 days has been provided with repeated sampling and measurements by  $\alpha$ - and  $\gamma$ -spectroscopy. After sorption solid precipitate and liquid phase were separated. Precipitate of used sorbent has been dried at 600°C during 1 hour, ground in agate mortar with binder (0.3 wt.% of polyethylene glycol solution in water) and pressed into pellet at pressure 100 kg/cm<sup>2</sup>. The pellet obtained has been sintered in air at 1200°C during 2

hours. Precursor preparation, ceramic synthesis and leach test have been carried out under conditions of heavily shielded glove-box. Highly radioactive ceramic sample obtained is shown in Figure 1.



**Figure 1.** Pellet of highly radioactive Synroc-like titanate ceramic obtained after sorption of real liquid HLW on LHT-9 followed with cold pressing and sintering in air at 1200°C during 2 hours. Scale grid is 1 x 1 mm.

Radionuclide composition of ceramic obtained except  $^{244}\text{Cm}$  was measured by  $\gamma$ -spectroscopy (Table II). Content of  $^{244}\text{Cm}$  has been calculated using  $^{244}\text{Cm}$  concentrations in HLW before and after sorption.

**Table II.** Radionuclide content in Synroc-like ceramic sample

Activity of the entire sample, Bq (pellet weight = 0,0835 g)							
$^{243}\text{Am}$	$^{241}\text{Am}$	$^{155}\text{Eu}$	$^{154}\text{Eu}$	$^{152}\text{Eu}$	$^{144}\text{Ce}$	$^{137}\text{Cs}$	$^{244}\text{Cm}$
$1.3 \times 10^5$	$7.8 \times 10^6$	$1.3 \times 10^5$	$7.1 \times 10^6$	$1.0 \times 10^4$	$4.3 \times 10^4$	$2.0 \times 10^5$	$2.3 \times 10^7$

In order to understand Cs incorporation into titanate ceramic one non-radioactive sample has been synthesized after Cs sorption by LHT-9 from Cs-nitrate solution in the presence of some admixtures of Al and Si (simulating non-radioactive elements of HLW). Precursor preparation pressing pellet have been carried out by procedure, which was similar to the radioactive sample. Pressed pellet has been sintered in air at 1180°C for 2 hours. Polished piece of non-radioactive Cs-doped sample has been examined by SEM (JEOL JSM 5610lv) and semi-quantitative EMP analyses accompanied with X-ray powder diffraction analysis (using spectrometer STOE IPDS II, acceleration voltage – 45 kV and a beam current – 30 mA).

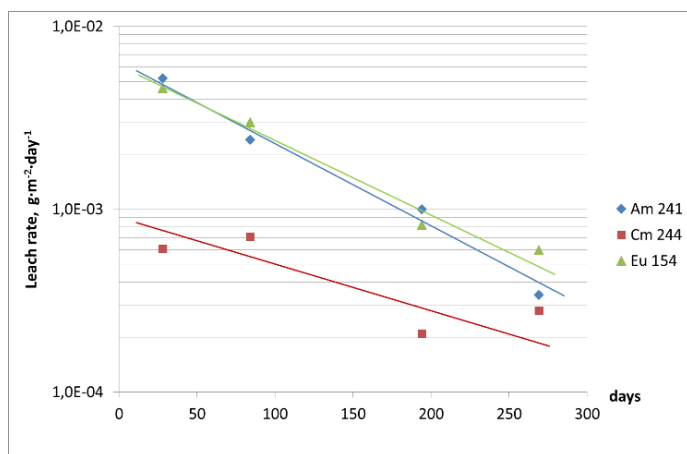
Static leach test was carried out using a modified MCC-1 method. In this procedure, the ceramic pellet was placed on a thin Pt-support at the bottom of a Teflon<sup>TM</sup> test vessel filled with distilled water. The temperature was adjusted to 90°C by keeping the leach apparatus in a furnace. Total duration of the test was 270 days with full replacing of water after 28, 84, 192 and 270 days from the beginning of the leach test. The ratio of water volume to surface area to was maintained at 10 cm<sup>3</sup> to 1 cm<sup>2</sup> throughout the entire experimental run. After final stage of leaching the surface of the sample has been examined using simple optical microscope and no cracks was observed.

The normalized Pu mass loss (NL) was calculated using the following equation:  $NL = A W/A_0 S$ , where  $A$  is the total activity (in Bq) of radionuclide in the water solution and absorbed on the walls of the test vessels after the leach test;  $A_0$  is the initial activity of radionuclide (in Bq) in the specimens;  $W$  is the initial mass of the samples (in g);  $S$  is the geometric sample surface area (in  $m^2$ ) not correcting for the porosity of the ceramics. The content of radionuclides in the leachate has been measured by alpha-spectrometry for  $^{241}\text{Am}$  and  $^{244}\text{Cm}$  using a Canberra-7401 spectrometer and by gamma-spectrometry for  $^{154}\text{Eu}$ ,  $^{241}\text{Am}$  and  $^{137}\text{Cs}$  using a Canberra spectrometer with a multi-canal analyzer DSA-1000 and a Ge-detector.

In order to evaluate roughly possible correction of polycrystalline sample's surface area for porosity one sample of titanate ceramic from spent LHT-9 with non-radioactive simulants, have been synthesized at the same conditions to the pellet with real HLW (to achieve average density approximately 90 % of theoretical value). Then non-radioactive ceramic sample has been studied by BET method [13] using AS-3012 BET Surface Area Analyzer.

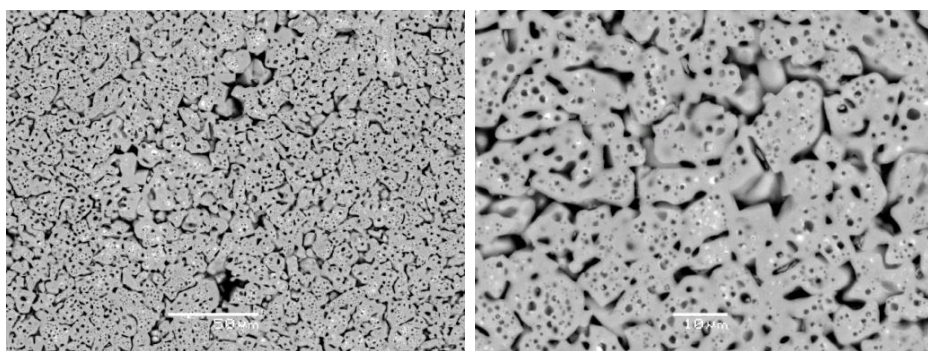
## RESULTS AND DISCUSSION

The leach rates for  $^{154}\text{Eu}$ ,  $^{241}\text{Am}$ ,  $^{244}\text{Cm}$  demonstrated tendency to decrease up to 10 times after 270 days (Figure 2). Content of  $^{137}\text{Cs}$  in leachate has been measured only for period between 84 and 194 days and normalized  $^{137}\text{Cs}$  mass loss was  $0.3 \text{ g}\cdot\text{m}^{-2}$  (for 110 days). The surface area expected from BET measurements of non-radioactive sample is  $3,7\cdot 10^{-2} \text{ m}^2$  while the geometrical surface area is  $9,0\cdot 10^{-5}$ . So the leach rates calculated for real surface (expected from BET) seems to be about three order of magnitude less.



**Figure 2.** Results of static leaching of titanate ceramic sample loaded with real HLW in distilled water at 90°C for 28, 84, 194 and 270 days. Geometrical surface of the sample has been used for calculation without correction for ceramic porosity.

SEM study of non-radioactive sample of ceramic obtained through sintering of used LHT-9 after static sorption from Cs-nitrate solution (with some small admixtures of Si and Al) demonstrated Cs incorporation into non-identified Cs-Al-Si-titanate phase (containing in wt.% el.: Al – 2-3; Si – 4-7; Cs – 15-18; Ti – 38-39) (Figure 3). Bulk content of inclusions of this phase in ceramic matrix was too low and XRD analysis identified rutile phase only. As assumed, in the presence of other chemical elements in common aqueous solution non-selective sorption by LHT-9 may be accompanied with formation of stable Cs-bearing titanate host-phases with hollandite, pollucite or leucite-type structures.



**Figure 3.** SEM-BSE images of non-radioactive Cs-doped titanate ceramic obtained by sintering in air (at 1180°C for 2 hours) of used LHT-9 powder after sorption from Cs-nitrate solution with admixtures of Si and Al. White inclusions are presented by non-identified Cs(Si,Al)-titanate phase; matrix of grey colour consists of rutile, TiO<sub>2</sub>; black colour is related to void space.

## CONCLUSIONS

The results obtained we consider as very preliminary data however they allow making already the following conclusions:

- 1) LHT-9 is a very prospective efficient non-selective sorbent, which after simultaneous sorption of radionuclides and non-radioactive elements from liquid wastes can be used as starting precursor for synthesis of titanate ceramic.
- 2) Ceramic waste form based on spent LHT-9 (after sorption) can be successfully synthesized by cold pressing followed with sintering in air at temperature 1100-1200°C. It was confirmed experimentally on highly radioactive ceramic sample loaded with real HLW. Chemical durability of this sample looks promising, because under static tests in distilled water at 90°C the leach rates (without correction for ceramic porosity) for <sup>154</sup>Eu, <sup>241</sup>Am, <sup>244</sup>Cm are from 2·10<sup>-4</sup> to 5·10<sup>-3</sup> g·m<sup>-2</sup>·day<sup>-1</sup>. Normalised <sup>137</sup>Cs mass loss was 0.3 g·m<sup>-2</sup> for 110 days at the same conditions.
- 3) The use of LHT-9 can simplify essentially existing route of Synroc synthesis.

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