

## **Fabrication and Properties of Advanced Ceramic Technetium Waste Forms – 17311**

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### **ABSTRACT**

Technetium-99 (Tc,  $t_{1/2} = 2.13 \times 10^5$  years) is a challenge from a nuclear waste perspective and is one of the most abundant, long-lived radioisotopes found in used nuclear fuel (UNF). Within the Hanford Tank Waste Treatment and Immobilization Plant, technetium volatilizes at typical glass melting temperature, is captured in the off-gas treatment system and recycled back into the feed to eventually increase Tc-loadings of the glass. In this research we are providing a technical solution for continuously depleting the Tc-content of the glass melter feed by precipitating Tc from the off-gas effluents and effectively immobilizing  $^{99}\text{Tc}$  as durable ceramic waste form. We have developed a wet-chemical coprecipitation-based synthesis route to fabricate gram-size Tc-based pyrochlores with the model composition  $\text{Sm}_2(\text{Tc}_{0.5-x}\text{Ru}_x\text{Ti}_{0.5})_2\text{O}_7$ . These ceramic Tc waste forms exhibit better technetium retention and corrosion resistance in ASTM C1220-10 based testing compared with technetium-containing LAWE4-type borosilicate glass, combined with optimal waste loading.

### **INTRODUCTION**

Technetium-99 is a major environmental concern due to its long half-life and high mobility of heptavalent Tc-species such as pertechnetate ion ( $\text{TcO}_4^-$ ) in groundwater. At the Hanford Site for example, Tc is found in both, the high level waste (HLW) solids and the Cs-137 containing low activity waste (LAW) feed, both of which will be converted to glass based waste forms. Tc is highly volatile at temperatures used in vitrification (1000-1200 °C) requiring off-gas capture and recycling systems. It has been determined that the solubility of Tc in glass ( $\sim 2000$  ppm) is orders of magnitude larger than the anticipated waste stream composition (10-100s ppm) and is therefore not limiting retention during processing [1]. Other factors influencing retention include Tc behavior in the cold cap, or surface layer of the glass melt, and the formation of high vapor pressure molten salt phases containing Tc. Compositional modifications of the glass and variation in processing conditions have resulted in increased single pass retention of Tc, however volatilization necessitates a recycle stream high in sulfur and halide content which impacts the melter feed composition and glass product [2]. An alternative solution is to capture the volatile Tc containing off-gas and incorporate into advanced waste forms such as crystalline ceramics which may be disposed of in a secondary waste stream [3], or potentially incorporated into existing waste streams aimed at Tc immobilization such as cements. The

environmental release mechanisms of Tc from heterogeneous waste forms are not understood to a large extent [4]. Factors including soil composition, groundwater pH, and the local structure of Tc in the glass/ceramic waste form impact the fate of radionuclides such as Tc in long-term disposal. During the vitrification process fission products such as Tc-99 along with Cs-137 show a tendency of volatilizing from the melter to accumulate in the off-gas stream. As the study of Vida [5] has demonstrated, substantial amounts of Tc do volatilize during laboratory-scale melter testing and the Tc content of the glass did decrease from 0.27 wt.% to less than 0.01 wt.% within 36 hours at 1200 °C, and without reaching equilibrium. This volatilization is a result of  $Tc_2O_7$  formation.  $Tc_2O_7$  has a boiling point of 311 °C and at first forms small gas bubbles within the glass melt [6] to finally accumulate in the off-gas stream and subsequently in the off-gas condensate tank. On the other hand, the presence of the cold cap might enhance Tc-99 retention and only little Tc loss from the DWPF production melter during the vitrification of Savannah River Site (SRS) HLW sludge slurries was observed [7]. In the LAW and HLW vitrification facilities, we can assume that within the residence time in the glass melter at 1150-1200 °C, less than 50 % of Tc will be incorporated into the HLW and LAW glasses, while more than 50 % of Tc due to its volatility, will leave the melter and will be captured in the submerged bed scrubbers and the wet electrostatic precipitators of the primary off-gas treatment system for each facility. The LAW condensate containing the captured Tc will be combined with fresh LAW and sent to the melter [8]. During operation, Tc retention in the glass melt might not be sufficient to provide at least steady-state conditions and the Tc inventory in the off-gas concentrate might constantly increase, especially under neutral or slightly oxidizing conditions required for glass forming. Therefore in this research, the development of effective methods to extract Tc from the off-gas condensates and to subsequently immobilize Tc as ternary/quaternary oxides (e.g. pyrochlores and perovskites) is addressed.

In the developed flowsheet of our research, we are reducing technetium from mock-up off-gas condensate to  $Tc^{IV}O_2$  which represents the feed stock for the synthesis of monolithic ceramic ternary or quaternary Tc-based oxides such as pyrochlores and perovskites. Pioneering research on the crystal chemistry of technetium-containing oxides was performed in the 1960s and a series of simple binary and ternary Tc-containing oxide structures were reported, including a variety of spinel, perovskite ( $SrTcO_3$ ) and pyrochlore compounds such as  $Sm_2Tc_2O_7$  [9]. Prior research includes some aspects of these studies by the systematic structural investigation of the incorporation of  $Tc^{IV}$  into pyrochlore oxide structures,  $Ln_2Tc_2O_7$ , where  $Ln$  represents trivalent lanthanide Pr, Nd, Sm, Gd, and Lu [10, 11] (Fig.1). In their research, phase-pure, high-crystalline Ln-Tc pyrochlores could be synthesized by annealing the stoichiometric powder mixtures at 1150 °C for 48 hours in vacuum-sealed Pt-envelopes. Even though the annealing temperature was high, Tc-volatilization and heptoxide formation could be avoided.



## METHODS

### Preparation on $\text{KTcO}_4$

Ammonium-pertechnetate ( $\text{NH}_4\text{TcO}_4$ ) was obtained from Oak Ridge National Laboratory and was purified by recrystallization. Crystalline  $\text{KTcO}_4$  was obtained by precipitation from an ammonium pertechnetate solution using potassium hydroxide.

### Wet Chemical Synthesis of $\text{Sm}_2(\text{Ru}_{0.5}\text{Ti}_{0.5})_2\text{O}_7$ Pyrochlore

Our overall strategy for a wet-chemical synthesis route to fabricate Tc-waste form pyrochlores, which as a consequence will provide the option of depletion and immobilization of part of the technetium inventory in a treatment plant for low and high level nuclear waste effluents, is summarized in Fig. 3.

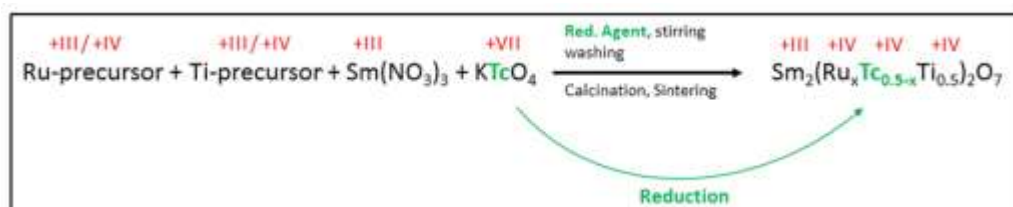


Fig. 3. Wet-chemical synthesis of Tc-pyrochlore to allow for depletion and immobilization of the technetium inventory in a treatment plant for low and high level nuclear waste effluents

For improved microstructure and mechanical properties of ceramic pyrochlore waste forms, and also to allow for up-scaling to a technical scale, a fabrication method for surrogate  $\text{Sm}_2(\text{Ru}_{0.5}\text{Ti}_{0.5})_2\text{O}_7$  by wet-chemical coprecipitation was developed. Hereby samarium(III) nitrate hexahydrate,  $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (99.9%, Sigma Aldrich®), ruthenium(III) chloride hydrate (99.9%, Alfa Aesar®), titanium(III) chloride solution (Merck), and titanium(VI) oxysulfate (Sigma Aldrich®) were used as source material and mass quantities were adjusted to fabricate ~2 grams of  $\text{Sm}_2(\text{Ru}_{0.5}\text{Ti}_{0.5})_2\text{O}_7$  pyrochlore.

The raw-materials are solubilized in water at pH 7 which produced a brown solution, caused by the Ru(III).  $\text{RuCl}_3$  was used as the raw material for ruthenium, Ru(III) has to be oxidized during the process to reach the tetravalent state.  $\text{Sm}(\text{NO}_3)_3$  was used as a precursor for the Sm(III), the oxidation state of the metal corresponds to the oxidation state of samarium in the pyrochlore. The introduction of Ti into the mixture was achieved by using two different raw materials.  $\text{TiCl}_3$ , which has to be oxidized to reach the tetravalent state, and  $\text{TiOSO}_4$  which already contains  $\text{Ti}^{4+}$ .

It is not really important in which order the raw materials are added to the mixture since no reaction between the chemicals is expected. Precipitation is then achieved by adding the precipitation agent, an oversaturated solution of  $(\text{NH}_4)_2(\text{C}_2\text{O}_4)$  (J.T. Baker/Life Science) in 14 M  $\text{NH}_4\text{OH}$  (Sigma Aldrich®) to the mixture. The combination of the insoluble metal oxalates and the very high pH value of around 14 initiate quantitative precipitation out of solution. The precipitate can be separated by filtration

using a Büchner-funnel and filter-paper (5-10  $\mu\text{m}$ ). The oxalates have to be dried in a furnace at 70  $^{\circ}\text{C}$  for about 10-12 hours and calcined at 550-600  $^{\circ}\text{C}$  for 10 hours converting the oxalates to oxides. The oxide mixture was pressed to “green” pellets at 400 MPa using uniaxial pressing without binder or lubricant. The pellets were sintered at 1400  $^{\circ}\text{C}$  for 3-5 days under inert argon atmosphere. The entire process is completed within 7 days and an overview is provided in the flowsheet in Fig. 4.

### **Incorporation of $^{99}\text{Tc}$ and Wet Chemical Synthesis of $\text{Sm}_2(\text{Ru}_{0.25}^{99}\text{Tc}_{0.25}\text{Ti}_{0.5})_2\text{O}_7$**

Technetium in the off-gas washer solution is present as heptoxide species  $\text{Tc}^{(\text{VII})}\text{O}_4^-$  and to allow for its incorporation into a pyrochlore structure, it has to be reduced by a suitable reducing agent to tetravalent  $\text{Tc}^{(\text{IV})}$ . In this study we tested the performance of the reducing agents tin(II) chloride dihydrate ( $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ , BDH-VWR analytical), iron(II) sulfate heptahydrate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , Amresco), sodium sulfite ( $\text{Na}_2\text{SO}_3$ , Amresco), and sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3$ , Wards Science). The ionic strength was adjusted with sodium perchlorate ( $\text{NaClO}_4$ , EMD Chemicals). To avoid re-oxidation from the tetravalent to the heptavalent state, all experiments were performed in a glove box and argon atmosphere. The required pH-measurements were made using a 781 pH/Ion meter from Metrohm and for LSC analyses a Liquid Scintillation Analyzer (Tri-Carb 3100TR, Perkin Elmer) was used. Some results of our studies to reduce pertechnetate to technetate are summarized in TABLE I. Among the tested reducing agents, tin(II) chloride is most effective in the pH range from 4.5 to 10, especially when used in excess. Using  $\text{SnCl}_2$  in a twofold excess at a neutral pH, we observed a complete reduction of  $\text{Tc}^{(\text{VII})}$  to  $\text{Tc}^{(\text{IV})}$  after 4 hours and after 2 hours using  $\text{SnCl}_2$  in 5-fold excess, which is in agreement with Le Chatelier’s principle. On the other hand, iron(II) sulfate heptahydrate shows better performance than  $\text{ZnCl}_2$  at high pH conditions. The sulfur-containing compounds  $\text{Na}_2\text{SO}_3$  and  $\text{Na}_2\text{S}_2\text{O}_3$  are not efficient reducing agents for pertechnetate under the tested parameters.

TABLE I. Efficiency of agents to reduce pertechnetate to technetate

Reducing Agent	pH	Stirring time (h)	Concentration (equilibrium)	Relative Tc-99 Residual (%)
$\text{SnCl}_2$	4.5	16	1	30.0
$\text{SnCl}_2$	5	16	1	24.8
$\text{SnCl}_2$	5.5	16	1	28.4
$\text{SnCl}_2$	6	16	1	30.0
$\text{SnCl}_2$	6.5	16	1	26.8
$\text{SnCl}_2$	7	16	1	27.3
$\text{SnCl}_2$	7	16	2	0.3
$\text{SnCl}_2$	7	16	5	0
$\text{SnCl}_2$	7	2	2	1.9
$\text{SnCl}_2$	7	4	2	2.2
$\text{SnCl}_2$	7	2	5	0
$\text{SnCl}_2$	7	4	5	0
$\text{SnCl}_2$	10	16	1	36.0
$\text{SnCl}_2$	10	16	2	2.9
$\text{SnCl}_2$	10	16	5	7.4
$\text{SnCl}_2$	10	2	2	5.2
$\text{SnCl}_2$	10	4	2	2.9
$\text{SnCl}_2$	10	2	5	4.1
$\text{SnCl}_2$	10	4	5	5.0

SnCl <sub>2</sub>	12	16	1	88.6
FeSO <sub>4</sub>	7	16	1	98.7
FeSO <sub>4</sub>	10	16	1	79.0
FeSO <sub>4</sub>	10	16	2	20.8
FeSO <sub>4</sub>	10	16	5	5.7
FeSO <sub>4</sub>	12	16	1	79.5
FeSO <sub>4</sub>	12	16	2	37.8
FeSO <sub>4</sub>	12	16	5	16.3
Na <sub>2</sub> SO <sub>3</sub>	7	16	1	99.7
Na <sub>2</sub> SO <sub>3</sub>	10	16	1	99.8
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	7	16	1	101.0
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	10	16	1	99.7

Based on the results of the reduction study we can provide a modified flowsheet for the fabrication of ternary or quaternary Tc-based pyrochlores, Ln<sub>2</sub>(Tc,Ti)<sub>2</sub>O<sub>7</sub> and Ln<sub>2</sub>(Tc,Ru,Ti)<sub>2</sub>O<sub>7</sub> (Fig. 5).

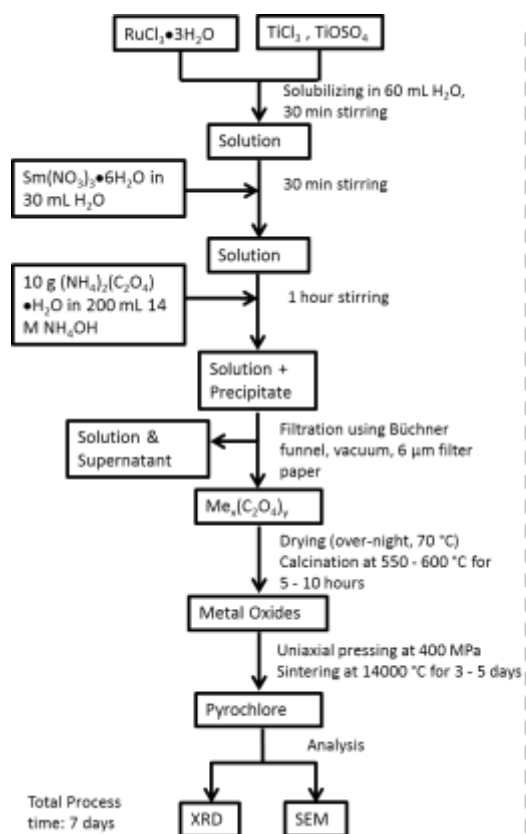


Fig. 4. Flowsheet for fabricating surrogate Ln<sub>2</sub>(Ru,Ti)<sub>2</sub>O<sub>7</sub> pyrochlore waste forms by a wet-chemical co-precipitation-based process route

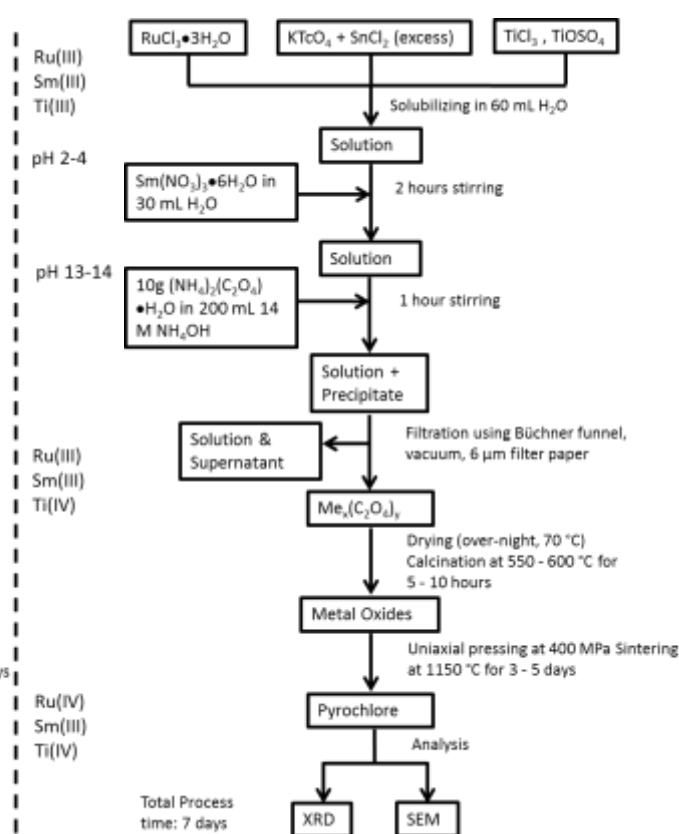


Fig. 5. Flowsheet for fabricating Ln<sub>2</sub>(Tc,Ru,Ti)<sub>2</sub>O<sub>7</sub> pyrochlore waste forms by a wet-chemical co-precipitation-based process route

## Characterization of Surrogate and Tc-Pyrochlore by X-ray Diffraction

Powder X-ray diffraction (XRD) and Rietveld structure refinement were used to quantify the crystalline phase content of the oxides. Hereby ~30 mg of specimens were ground and placed on an air-tight, low background sample holder. Powder XRD patterns were collected from 10° to 90° (step size 0.01°) 2θ. Measurements were performed using Cu Kα<sub>1</sub> emission (λ = 0.154063 nm) on a Bruker D8 Advance equipped with a Johansson-type monochromator (Ge) and a LynxEye® silicon strip detector. The data were analyzed using Rietveld structure refinement (Bruker AXS, Topas 4.2).

Surrogate pyrochlore waste forms, Sm<sub>2</sub>(Ru<sub>0.5</sub>Ti<sub>0.5</sub>)<sub>2</sub>O<sub>7</sub>, were synthesized following the flowsheet displayed in Fig. 4. Sintering at 1400 °C for 4 to 5 days induced increased average pellet density of 72 % (theoretical) starting from green pellet densities of 39 to 43 %. In addition, mechanical properties and fracture toughness was noticeably improved. High-temperature sintering is necessary to allow for interdiffusion of the metal oxides and to initiate densification, but it also induces the risk for partially reducing Ru<sup>[IV]</sup> to the metal. As consequence of this reduction, or if precipitation is incomplete and part of Ru and/or Ti remain in solution, the phase system shifts from the one phase field of pyrochlore to the two-phase stability field: pyrochlore + Sm<sub>2</sub>(Ti<sub>1-x</sub>Ru<sub>x</sub>)O<sub>5</sub>.

However, the synthesis of surrogate Sm<sub>2</sub>(Ru<sub>0.5</sub>Ti<sub>0.5</sub>)<sub>2</sub>O<sub>7</sub> and of quaternary Tc-based waste form was successful and the pyrochlore phases were obtained with high yield and high crystallinity (Fig. 6). Following the flowsheet in Fig. 5, phase-pure pyrochlore of the stoichiometry Sm<sub>2</sub>(Tc<sub>0.25</sub>Ru<sub>0.25</sub>Ti<sub>0.5</sub>)<sub>2</sub>O<sub>7</sub> was obtained.

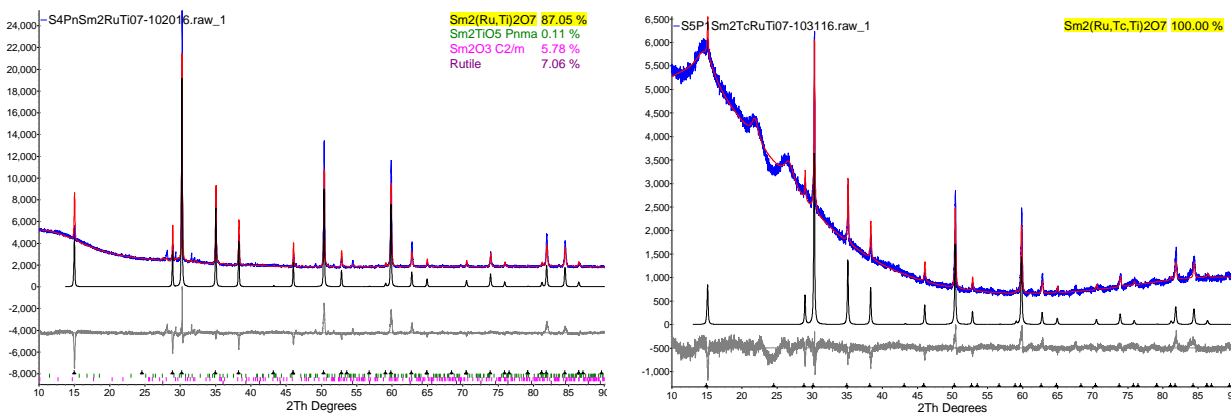


Fig.6. Phase characterization of Sm<sub>2</sub>(Ru<sub>0.5</sub>Ti<sub>0.5</sub>)<sub>2</sub>O<sub>7</sub> (left) and Sm<sub>2</sub>(Tc<sub>0.25</sub>Ru<sub>0.25</sub>Ti<sub>0.5</sub>)<sub>2</sub>O<sub>7</sub> (right) waste forms by X-ray diffraction and Rietveld structure refinement. The calculated peak intensities of the pyrochlore phases are highlighted (black patterns)

The Tc-pyrochlore phase was fabricated by sintering at 1150 °C for 3 days. To avoid volatilization of Tc, the samples were vacuum-sealed in fused silica ampoules. Under this rather low sintering temperature, compared with 1400 °C for the surrogate material, solid-state diffusivity and densification were insufficient and the mechanical properties of the ceramic Sm<sub>2</sub>(Tc<sub>0.25</sub>Ru<sub>0.25</sub>Ti<sub>0.5</sub>)<sub>2</sub>O<sub>7</sub> pellets are lacking. To improve the

mechanical strength, some samples were re-sintered at 1150 °C in fused silica ampoules for 4 more days. Additional sintering helped to improve mechanical properties, but the observed reduction of part of ruthenium shifted the phase system to the two-phase stability field: pyrochlore +  $\text{Sm}_2(\text{Me})\text{O}_5$  and in addition a lower crystallinity of the pyrochlore host phase was observed.

As a result, we have developed a successful flowsheet to allow for on-line depletion of pertechnetate from a generic off-gas treatment system to subsequently fabricate gram-size ceramic Tc-waste forms, even though more research work is needed to further enhance physical properties of Tc-based ceramics.

### Test Corrosion of Monolithic Surrogate Waste Forms and Microstructure

Subsequent to the fabrication of dense ceramic surrogate waste forms by co-precipitation and high-temperature sintering, corrosion tests of monolithic  $\text{Sm}_2(\text{Ru}_{0.5}\text{Ti}_{0.5})_2\text{O}_7$  specimens were performed following the ASTM C1220-10 test protocol. The specimen were placed in PTFE vessels with ASTM water (S/V ratio=  $10\text{m}^{-1}$ ) using Pt/Rh wire, and the vessels were sealed within stainless steel autoclaves. The corrosion vessels together with three blanks were kept in a convection furnace at 90 °C for 7 days and corrosion rates were determined based on the physical mass loss of the pellets (TABLE II). The hereby derived specific mass loss can be further compared with dissolution data of the dissolved metal content in the leachate as determined by ICP-MS elemental analysis. However, in our corrosion tests the dissolution data are not in compliance with the physical data and too low by orders of magnitude. The average specific mass loss for the surrogate waste form was determined to  $6.50 \text{ E-6 g/mm}^2 \cdot \text{days}$ , which is about four-fold of the specific mass loss determined for LAWE4 borosilicate and a factor of 45 higher than what was reported for monolithic  $\text{Nd}_2\text{Tc}_2\text{O}_7$  under similar conditions [10]. The rather high corrosion rates of the specimens could be explained by their phase constitution and the fact that the samples contain two phases:  $\text{Sm}_2(\text{Ru}_{0.5}\text{Ti}_{0.5})_2\text{O}_7$  and  $\text{Sm}_2(\text{Ti}_{1-x}\text{Ru}_x)\text{O}_5$  with about 50:50 in wt.%.

TABLE II. ASTM C1220-10 corrosion testing of  $\text{Sm}_2(\text{Ru}_{0.5}\text{Ti}_{0.5})_2\text{O}_7$

<b>Vessel Number</b>	<b>Mass (g)</b>	<b>Surface (mm<sup>2</sup>)</b>	<b>Volume of Leachate (mL)</b>	<b>Mass of Vessels incl. samples (g)</b>
4	0.2744	79.2	7.920	119.208
9	0.2710	78.5	7.850	119.356
10	0.3332	90.2	9.020	121.049
<b>Vessel Number</b>	<b>Mass Difference (g)</b>	<b>Specific Mass Loss (g/mm<sup>2</sup>•days)</b>	<b>Mass Loss from ICP data (g)</b>	<b>Specific Mass Loss from ICP data (g/mm<sup>2</sup>•days)</b>
4	0.00364	6.565 E-6	2.95E-07	5 E-10
9	0.00272	4.949 E-6	1.77E-06	3 E-9
10	0.00505	7.999 E-6	2.54 E-06	4 E-9

The microstructure of the ceramic pellets are rather complex and larger grains (20 to 50  $\mu\text{m}$ ) are embedded in a porous, microcrystalline matrix (Fig. 7). Microstructure of  $\text{Sm}_2(\text{Ru}_{0.5}\text{Ti}_{0.5})_2\text{O}_7$  were characterized using SEM-based imaging and EDS based microanalysis (JEOL JSM 5610).



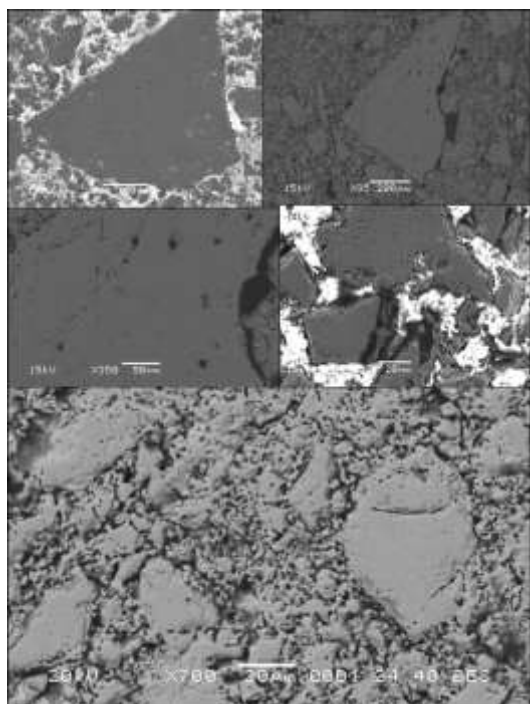


Fig. 7. SEM-based imaging of  $\text{Sm}_2(\text{Ru}_{0.5}\text{Ti}_{0.5})_2\text{O}_7$  using secondary (a, c) and backscattered electrons (b, d, and e). Dense grains (20 to 50  $\mu\text{m}$ ) are embedded in a porous, microcrystalline matrix.

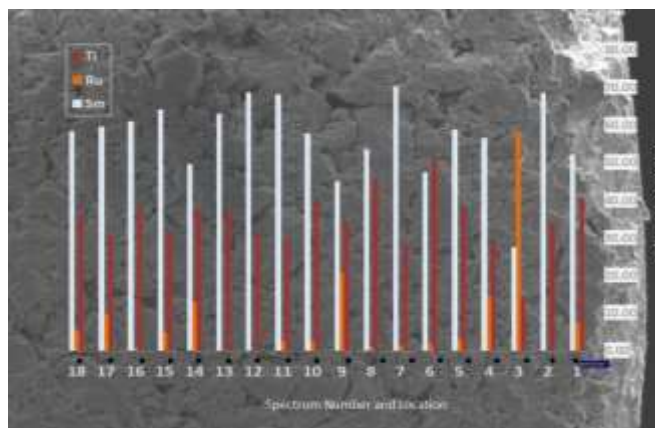


Fig. 8. SEM-based EDS analysis perpendicular to the pellet surface. Relative at.% for Ru, Ti, and Sm are overlaid with the corresponding location. The distance between spectrum 1 and 18 is about 0.5 mm (530  $\mu\text{m}$ ). The corrosion test did not induce noticeable changes and the microstructure and is virtually unchanged compared with the microstructure of the sample prior to corrosion testing.

To determine whether the corrosion is congruent or heterogeneous, a specimen of  $\text{Sm}_2(\text{Ru}_{0.5}\text{Ti}_{0.5})_2\text{O}_7$  was prepared for SEM-based EDS analysis in an orientation perpendicular to the surface formerly exposed to corrosion (Fig. 8). Hereby successive spectra were collected starting from the edge (former surface) and then moving inwards in 30  $\mu\text{m}$  steps. The specimen contains two crystallographic phases  $\text{Sm}_2(\text{Ru}_{0.5}\text{Ti}_{0.5})_2\text{O}_7$  and  $\text{Sm}_2(\text{Ti}_{1-x}\text{Ru}_x)\text{O}_5$ , therefore a low Ru-content might indicate the presence of the latter. Even though the point analysis show significant data scattering, probably as a result of small grain sizes, imperfect surface finish and insufficient absorption correction, the corrosion scenario can be described as congruent rather than heterogeneous since overall changes in the ratio trivalent/tetravalent cations ( $\text{Sm}^{3+}/(\text{Ru}^{4+} + \text{Ti}^{4+})$ ) as a function of distance to the corroded surface cannot be concluded.

## CONCLUSIONS

We have developed a promising technical solution for continuously depleting the Tc-content of the glass melter feed by precipitating Tc from the effluents of the off-gas capture and recycling systems and subsequently for effectively immobilizing Tc as durable ceramic waste form. This promising process is based on a wet-chemical

coprecipitation-based synthesis route to fabricate gram-size, phase-pure Tc-based pyrochlores with the model composition  $\text{Sm}_2(\text{Tc}_{0.5-x}\text{Ru}_x\text{Ti}_{0.5})_2\text{O}_7$ . In addition, this process is up-scalable to technical scale. Pertechnetate ( $\text{Tc}^{\text{VII}}\text{O}_4^-$ ), the dominant Tc-species in the off-gas washer solution, was successfully reduced to technetate ( $\text{Tc}^{\text{IV}}\text{O}_2$ ) within hours using tin(II) chloride in excess at pH 4.5 to 7 to subsequently allow for its immobilization and the fabrication of Tc-pyrochlore. Microstructure and mechanical properties of surrogate waste form  $\text{Sm}_2(\text{Ru}_{0.5}\text{Ti}_{0.5})_2\text{O}_7$  could be significantly improved compared with earlier studies and theoretical densities of 72 % can be reported. The Tc-pyrochlore  $\text{Sm}_2(\text{Tc}_{0.25}\text{Ru}_{0.25}\text{Ti}_{0.5})_2\text{O}_7$  is still lacking these properties and a more intense sintering regime has shown to induce volatilization and/or Tc-reduction to the metallic state.

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