



Research Proposal under UNLV TRP

Title

Synthesis and Properties of Metallic Technetium and Technetium -
Zirconium Alloys as a Radioactive Storage Waste Form to Stabilize the
Technetium Waste Stream of the UREX+1 Process

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Technical Focus Area

Separation of TRU and Waste Storage Forms (Tc-99 waste storage form to stabilize Tc-99 waste stream from UREX+1)

Abstract

In the AFCI program the UREX+1 process is proposed as one of the most promising technique to separate TRU (transuranic elements) from LWR spent nuclear fuel in the years to come. The application of UREX+1 results in good separation of the 5f-transuranics from the 4f-lanthanides, reduced waste volumes by eliminating the uranium content, and reduced waste package costs. Technetium-99 will be separated together with uranium and iodine within the first process steps. After the separation of uranium, technetium and iodine must be immobilized by their incorporation in a suitable waste storage form. Based on recent activities within the AFCI community, a potential candidate as waste storage form to immobilize technetium-99 is to alloy metallic Tc-99 with excess metallic zirconium. Alloying metallic Tc-99 with zirconium has potential advantages in terms of the future reuse of Tc-99 and its potential transmutation, compare to the stabilization of Tc-99 in rock-forming mineral-type oxides. The synthesis of technetium[IV] based spinel-type oxides, and perovskite-type oxides as potential candidates for geological waste storage is known since 1969. However, Tc-99 is abundant in a variety of nuclear waste streams and has a long half-life, about 200,000



years. Released into the environment, Tc-99 is extremely damaging, traveling up the food chain, and causing cancer in humans. Due to the mobility of technetates it is believed that Tc-99 could cause long-term exposure problems for geological repositories to come, after the anticipated failure of engineered barriers in 10,000 to 100,000 years. Therefore, providing a waste storage form for Tc-99 waste streams which allows transmutation of Tc-99 into stable isotopes or less toxic radioisotopes strongly promotes the AFCI program and the future separation of TRU elements by applying the UREX+1 process. However, only few thermodynamic data in the binary metal system technetium–zirconium exist, and only few data are available on the synthesis of technetium-zirconium alloys and on their potential performance under temporary or geological storage conditions.

We intent to systematically investigate the binary metal system technetium-99 – zirconium for the first time. We propose to investigate the synthesis of metallic technetium as well as its alloys with zirconium. In order to provide valuable data to the AFCI program, we also propose to determine the thermodynamic equilibrium phases as well as their performance under the scenario of a geological repository. Therefore, we propose to address the following research tasks:

Task 1: Synthesis of metallic Tc[0]-99 applying up to three different procedures.

Task 2: Characterization of micro-structure, nano-structure and crystal structure of Tc-99 metal.

Task 3: Synthesis of alloys in the binary system technetium – zirconium.

Task 4: Determine thermodynamic equilibrium phases at 1000 °C to 1600 °C.

Task 5: Determine the binary phase constitution (phase diagram) of technetium and zirconium.

Task 6: Investigation of Tc-corrosion and Tc-leaching of binary Tc-Zr phases at elevated temperature (200 °C) and elevated pressure (20 MPa).

For now only alloys in the Tc-rich portion of the binary Tc-Zr system were investigated: Tc_2Zr (space group $P6_3/mmc$, $a = 5.129 \text{ \AA}$, $c = 8.655 \text{ \AA}$) and Tc_6Zr (space group $I4-3m$, $a = 9.637 \text{ \AA}$). Our first pretension is to (1) synthesize metallic technetium from a UREX+1 related waste stream and (2) to determine the impact of the applied synthesis procedure on the purity, crystallinity, structure modification, and the metallurgy (micro-structure, nano-structure). Furthermore, we will alloy metallic technetium with metallic zirconium by applying arc melting technology, and we will synthesize the



thermodynamic equilibrium phases for the individual isothermal sections in the temperature range of 1000 °C to 1600 °C by annealing platinum encapsulated samples in a high temperature furnace at controlled atmospheres. The phase constitution will be characterized by X-ray diffraction techniques, Least square and Rietveld analysis, and electron microprobe analysis (EPMA). The micro-structure of the pure metal and the alloys will be examined by optical polarization microscopy using polished and etched metallographic specimen, and by electron microscopy (SEM). We intent to analyze the nano-structure of the alloys, and we will determine real structure properties (grain boundaries, dislocations, point defects, mosaic structure, twinning defect, etc.) by high resolution electron microscopy (STEM) to a point resolution of 2.2 Å and to information limits of 1.4 Å. The proposed research will produce analytical data of great value with the overall purpose to understand the nature of alloys in the binary system technetium-zirconium as potential waste storage forms in order to stabilize and immobilize technetium from the UREX+1 waste stream.

Experimental Procedures

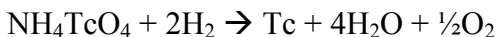
The following chapter provides background information to the experimental research work as proposed.

1) Synthesis of metallic Technetium-99

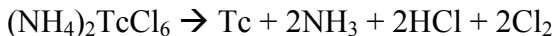
The proposed research work addresses the synthesis and the characterization of Tc metal applying two different synthesis routes. The comparison of the formation yields, crystallinity, and purity of Tc metal will provide information on the optimal process for synthesizing Tc metal as a precursor material to produce desired Tc waste storage forms as alloys in the binary system technetium - zirconium.

2) Literature research indicates that Tc metal can be obtained by the different routes as following:

(a) Reduction of pertechnetate by hydrogen at 500 °C,



(b) Thermal decomposition of $(\text{NH}_4)_2\text{TcCl}_6$ under inert atmosphere at 600 °C,



(c) Electrochemical reduction of TcCl_6^{2-} in ionic liquid or TcO_4^- in acid oxalate solution

(d) Chemical reduction of TcO_4^- by NaBH_4 in aqueous media



Among the routes presented, we have chosen to synthesize Tc metal by thermal decomposition of $(\text{NH}_4)_2\text{TcCl}_6$ and by chemical reduction of TcO_4^- using NaBH_4 . These two routes to synthesize metallic Tc are relatively simple, easy to perform, and safe in terms of radiological protection issues. The synthesis route by the reduction of pertechnetate using hydrogen might raise some safety concerns due to the risk of potential rabbit exothermal reactions (e.g. explosion). Furthermore, the chosen thermal decomposition of $(\text{NH}_4)_2\text{TcCl}_6$ does not produce any volatile product, and the syntheses can be performed by handling small technetium amounts of 10 mg to 1 g.

3) Preparation of Tc metal

In a first step, $(\text{NH}_4)_2\text{TcCl}_6$ and HTcO_4 will be produced as following:

- $(\text{NH}_4)_2\text{TcCl}_6$ (500 mg) will be synthesized by the reduction of $(\text{NH}_4)\text{TcO}_4$ using 12 M HCl.
- HTcO_4 will be synthesized by dissolving $(\text{NH}_4)\text{TcO}_4$ (500 mg) in 10 mL of water and passing through a ion-exchange column of DOWEX 50Wx8.

In a second step, Tc metal will be synthesized according the following procedure:

- $(\text{NH}_4)_2\text{TcCl}_6$ (50 mg) will be loaded in a silica (“quartz”) boat. The silica boat will be placed in a “quartz” tube which itself is placed in a tube furnace. The working tube will be heated up to 600 °C under protective Ar atmosphere. We could already collect experience performing this synthesis step in our laboratories by the recent synthesis of TcO_2 by thermal decomposition of $(\text{NH}_4)\text{TcO}_4$ under Ar



atmosphere.

- The chemical reduction of TcO_4^- by NaBH_4 will be performed in an atmosphere-controlled glove box (e.g. Ar atmosphere). A solution of HTcO_4 (0.01M) in NaOH 0.1M will be synthesized and NaBH_4 (10:1 $\text{BH}_4^-/\text{TcO}_4^-$) will be added. Metallic technetium will be separate by centrifugation in the glove box.

4) Synthesis of binary alloys in the system technetium – zirconium

Stoichiometric mixtures of metallic technetium and zirconium powder will be pressed to 1 g pellets at 500 MPa and fused at 4000 K applying arc melting technology (e.g. Centorr Model 5TA). The fused specimens will be annealed at the temperatures of the individual isothermal sections (1000 °C to 1600 °C) in order to achieve thermodynamic equilibrium conditions. The annealing aspect requires the encapsulation of the metals e.g. in sealed and welded Pt tubes to avoid oxidation or worse: Tc-volatilization as heptaoxide. Metallographic specimens of the annealed samples will be prepared and the phase constitution analyzed. As a result of the phase analysis, the binary phase diagram for the isothermal sections as well as for the investigated temperature range (1000 °C to 1600 °C) can be constructed.

5) Characterization

(a) The production yield will be determined for each synthesis:

- Using $(\text{NH}_4)_2\text{TcCl}_6$ as reactant, the yield can be determined by the fraction of unreacted $(\text{NH}_4)_2\text{TcCl}_6$. The amount of unreacted $(\text{NH}_4)_2\text{TcCl}_6$ will be quantified by washing the centrifuged technetium metal with 12 M HCl and by spectrophotometry (UV-Vis) of TcCl_6^{2-} in HCl solution.
- Using HTcO_4 as reactant, the yield will be determined by measuring the fraction of unreacted TcO_4^- by UV-Vis spectrophotometry or by liquid scintillation counting.

(b) The oxidation state will be determined by cerimetric titration.

(c) The phase constitution will be characterized by X-ray diffraction techniques, Least



square / Rietveld analysis, and electron microprobe analysis (EPMA). The purity of the metal will be controlled by XRD/Rietveld analysis and by X-ray spectroscopy (EDS/WDS). Based on XRD peak profile fitting using split Pearson VII functions, it will be possible to determine the level of crystallinity for each synthesis route applied (Debye-Scherrer equation). Phase impurities (> 0.2 wt.-% $(\text{NH}_4)_2\text{TcCl}_6$ or NaTcO_4) can be determined by XRD/Rietveld analysis and by X-ray spectroscopy (EDS/WDS).

(d) The micro-structure of the pure metal and the alloys will be examined by optical polarization microscopy using polished and etched metallographic specimen, and by electron microscopy (SEM).

(e) We intent to analyze the nano-structure of the alloys, and we will determine real structure properties (grain boundaries, dislocations, point defects, mosaic structure, twinning defect, etc.) by high resolution electron microscopy (STEM) to a point resolution of 2.2 \AA and information limits of 1.4 \AA .

(f) To investigate Tc-corrosion and Tc-leaching of binary Tc-Zr phases at elevated temperature ($200 \text{ }^\circ\text{C}$) and elevated pressure (20 MPa), experiments using a Parr stainless steel high pressure vessel will be applied. Therefore, binary Tc-Zr equilibrium phases will be corroded in G13-type synthetic groundwater at $200 \text{ }^\circ\text{C}$ and 20 MPa to adapt long-term conditions of radioactive high-level nuclear waste forms in geological repositories to come. The nature of corrosion in the binary Tc-Zr system and potential secondary phase formation will be characterized by metallographic optical microscopy, electron microscopy (SEM, EPMA) and XRD/Rietveld analysis. The Tc-leachability from binary Tc-Zr-phases will be determined by ICP-AES.

Our wet radiochemical laboratory can provide all necessary experimental equipment, experience, and materials needed for the synthesis and the characterization of Tc metal. We are well recognized for our capabilities in the synthesis of Tc-based solid phases as well as for our characterization capabilities on radioactive solid phases. We may have to request additional equipment to synthesize the binary refractory alloys as proposed her (e.g. Bench-top Arc melter e.g. Centorr Model 5TA, \$ 20,000) as well as additional analytical supply for high-resolution electron microscopy (one-tilt TEM sample holder for Tecnai F30, \$ 15,000). We wish to start our programmatic research work in July 2006 with the synthesis of $(\text{NH}_4)_2\text{TcCl}_6$ and HTcO_4 and we will complete



our research work in 2009 with the characterization of the repository-related performance of binary Tc-Zr alloys. The synthesis of technetium metal will be performed on a small scale (50 mg, ca. 50 MBq) in order to minimize the potential radiological hazards. This amount will be divided for the characterization study: XRD (10-20 mg), TEM (1-2 mg), cerimetric measurement (10 mg). Finally, synthesis on larger scale (500 mg) will be performed and the metal will be used for the synthesis of equilibrium phases in the binary Tc-Zr alloy system as described.

Proposed Scientific Investigation Plan

We are proposing the following experimental research work:

Academic year 2006

- 1) Synthesis of metallic Tc[0]-99 applying up to three different procedures.

Academic year 2007

- 1) Characterization of micro-structure, nano-structure and crystal structure of Tc-99 metal.
- 2) Synthesis of alloys in the binary system technetium – zirconium.

Academic year 2008

- 1) Determine thermodynamic equilibrium phases at 1000 °C to 1600 °C.
- 2) Determine the binary phase constitution of technetium and zirconium.

Academic year 2009

- 1) Investigation of Tc-corrosion and Tc-leaching of binary Tc-Zr phases at elevated temperature (200 °C) and elevated pressure (20 MPa).