

## Task 33

# Separation of Technetium from Uranium and Waste Form Synthesis

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## BACKGROUND

In the Advanced Fuel Cycle Research & Development (AFC R&D) activities, the uranium extraction (UREX+1) process is proposed as one of the most promising technique to separate transuranic elements (TRU) from light water reactor spent nuclear fuel in the years to come. The isotope  $^{99}\text{Tc}$  will be separated together with U within the first process steps. After the separation of U, Tc must be immobilized by their incorporation in a suitable storage and waste form.

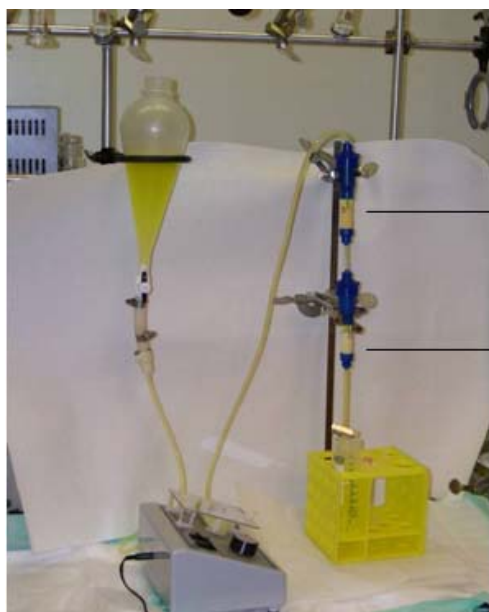
A candidate process to immobilize  $^{99}\text{Tc}$  is to alloy metallic Tc with excess metallic zirconium. This material has potential advantages in terms of the future reuse of  $^{99}\text{Tc}$  and its potential transmutation. Providing a Tc storage/waste form strongly promotes the AFC R&D and the separation of TRU elements using the UREX+1 process. However, little thermodynamic data in the binary technetium–zirconium metal system exist, and only few data are available on the synthesis of Tc-Zr alloys and on their potential performance under temporary or geological storage conditions.

In this project, systematic investigations on the Tc-Zr binary metal system will be evaluated for the first time. The synthesis of metallic Tc as well as its alloys with Zr will be evaluated. In order to provide valuable data to AFC R&D, the thermodynamic equilibrium phases, as well as their performance under repository conditions, will be examined.

## RESEARCH OBJECTIVES AND METHODS

The research objectives of this project are as follows:

- Evaluate anion exchange methods for achieving the separation of Tc from U.
- Synthesize metallic Tc from the separated product.
- Synthesize and characterize Tc alloys.



Separation process with two columns.

- Investigate Tc-corrosion and Tc-leaching of binary Tc-Zr phases under a range of conditions.

The following experimental techniques are used in the evaluation of the solutions and solids from the experiments: ultraviolet-visible spectroscopy, time-resolved laser fluorescence spectroscopy, X-ray Absorption Fine-Structure Spectroscopy (XAFS), and microscopy.

## RESEARCH ACCOMPLISHMENTS

### Separations

Static and dynamic experiments were performed to investigate the interaction of technetium with selected anion exchange resins. The kinetic static experiments showed Reillex resin had superior Tc sorption kinetics and was selected for further study. Reillex treated by nitric acid (Resin 6) was also used in the studies.

Dynamics experiments were performed on simulated UREX solution in order to determine the separation factor for uranium and technetium and to study the possibility of a Tc elution from the resin. The one column experimental set-up consisted of a reservoir of 250 mL, linked to a peristaltic pump, with a constant flux which can be between 1.2 to 8.4 mL/min. It is connected to a small column (length = 5 cm and diameter = 1 cm) and contained 1 g of resin (Reillex HP or Resin 6).

The process is divided into 3 steps: absorption, washing, and elution. For absorption, 150 mL of the UREX solution were placed in the reservoir and pumped with a peristaltic pump through the column at a constant flow rate (2, 4 or 8 mL/min). Samples were collected into centrifugation tubes (45 mL  $\pm$  0.5 mL for the first two and 10 mL  $\pm$  0.2 mL for the others). For each sample, 10  $\mu\text{L}$  of solution were removed and mixed with 10 mL of liquid scintillation fluid in a plastic vial, and  $^{99}\text{Tc}$  was counted by liquid scintillation. The samples were eluted with a 50 mL solution of  $\text{NH}_4\text{OH}$  (1M or 2 M) and were introduced in the reservoir and poured through the column with the same constant flow rate.

Samples were collected into centrifugation tubes of 10 mL  $\pm$  0.2 mL with 10  $\mu\text{L}$  of samples were removed and mixed with 10 mL of liquid scintillation fluid for  $^{99}\text{Tc}$  analysis. For samples containing a high amount of technetium, a dilution (1/100) was necessary for the liquid scintillation analysis in order to be able to use the calibration curve. To optimize U/Tc separation, treated and untreated resin were combined. The set-up is composed as before by a reservoir, a pump and two columns.

The absorption and washing steps were carried out with exactly the same conditions, as presented above.

Concerning the elution step, the columns are disconnected and only the first one containing the treated resin is eluted, whereas the second one is kept for a re-use and for an eventual Tc reprocessing by pyrolysis. A suitably pure Tc and U stream resulted from the experiment.



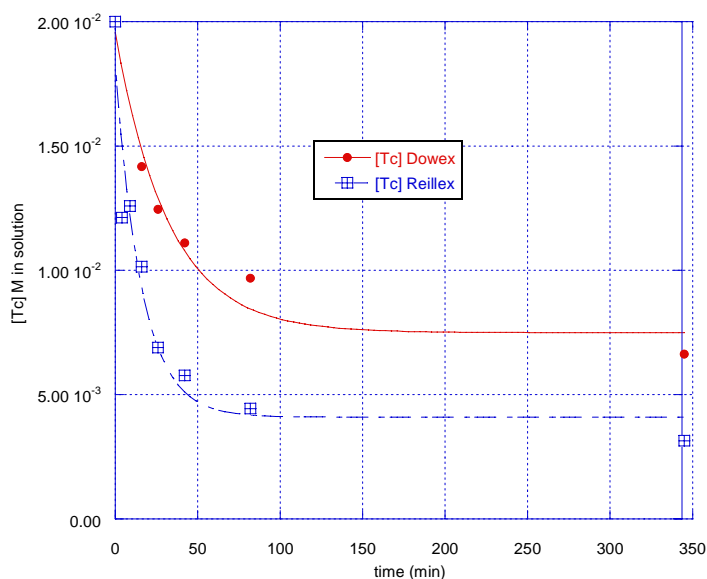
Tc/Zr sample before and after arc melting.

### Solid phase synthesis

Steam reforming of pertechnetate in the presence of carbon yielded Tc metal at 700°C under Ar or N<sub>2</sub>. Alloy samples were prepared by grinding Tc and Zr metal in different ratios, from 25 to 75 % Tc. Cylindrical pellets were obtained by pressing the powder and arc melting to produce the alloys. After arc melting, samples were analyzed by X-ray diffraction and optical microscopy.

### Other progress

- Sm<sub>2</sub>Tc<sub>2</sub>O<sub>7</sub> oxide was prepared. This was the first of a series for lanthanide-Tc oxide waste form.
- 2 % Tc electrode studies were completed and evaluated.
- Studies were conducted on Tc/Nd /Sm ternary oxide formations. The compounds targeted were (RE)<sub>2</sub>Tc<sub>2</sub>O<sub>7</sub> (RE = Nd, Sm). Mainly unreacted TcO<sub>2</sub> and Sm<sub>2</sub>O<sub>3</sub> was observed.



Kinetics of TcO<sub>4</sub><sup>-</sup> removal from solution with initial [TcO<sub>4</sub><sup>-</sup>]=0.02 M by Dowex Marathon and Reillex resins.

## ACADEMIC YEAR HIGHLIGHTS

- ◆ E.E. Rodriguez, F. Poineau, A. Llobet, K. Czerwinski, R. Seshadri, and A.K. Cheetham, "Preparation and Crystal Structures of Bismuth Technetates: A New Metal Oxide System," *Inorg. Chem.* 47(14), 6281-6288, 2008.
- ◆ F. Poineau, A.P. Sattelberger, and K.R. Czerwinski, "XAFS spectroscopic study of Tc<sub>2</sub>(O<sub>2</sub>CCH<sub>3</sub>)<sub>4</sub>X<sub>2</sub> (X = Cl, Br)," *J. Coord. Chem.*, 61(15), 2356-2370, 2008.
- ◆ F. Poineau, A.P. Sattelberger, S.D. Conradson, and K.R. Czerwinski, "Octachloro- and Octabromoditechnetate(III) and Their Rhenium(III) Congeners," *Inorganic Chemistry*, 47(6), 1991-1999, 2008.
- ◆ P.F. Weck, F. Poineau, T. Hartmann, E. Kim, G. Jarvinen, and K.R. Czerwinski, "Combined experimental and theoretical study of Tc-Zr alloys as possible waste form," European Research Materials Society, Strasbourg, France, May 2008.
- ◆ F. Poineau, E. Mausolf, and K.R. Czerwinski, "Electrochemical Behavior of Metallic Technetium in Aqueous Solution," Atlante 2008, Nuclear Fuel Cycles for a Sustainable Future, Montpellier, France, May 2008.
- ◆ E. Mausolf, C.S. Gong, J. du Bouchaud du Mazabrun, F. Poineau, D.K. Ford, G. Jarvinen, K.R. Czerwinski, "Elution of technetium from anion exchange resins," 235<sup>th</sup> ACS National Meeting, New Orleans, LA, April 2008.
- ◆ E.E. Rodriguez, F. Poineau, A. Llobet, K. Czerwinski, and A.K. Cheetham, "Synthesis of new ternary technetium oxides," 235<sup>th</sup> ACS National Meeting, New Orleans, LA, April 2008.
- ◆ F. Poineau, E.E. Rodriguez, A.P. Sattelberger, and K. Czerwinski, "Synthetic chemistry of high valence technetium oxides," 235<sup>th</sup> ACS National Meeting, New Orleans, LA, April 2008.
- ◆ F. Poineau, A.P. Sattelberger, and K. Czerwinski, "Technetium Chemistry: Fundamental Studies and Applications to the Fuel Cycle," Cadarache, France, September 2007.
- ◆ F. Poineau, G. Jarvinen, and K. Czerwinski, "Synthesis and Behavior of Metallic Technetium Waste Forms," MIGRATION 07, Munich, Germany, August 2007.
- ◆ F. Poineau, G. Jarvinen, and K. Czerwinski, "Synthesis and Characterization of Technetium Waste Forms," Idaho National Laboratory, June 2007.
- ◆ J. Du Mazabrun, F. Poineau, K. Czerwinski, G. Jarvinen, and D. Ford, "Separation uranium/technetium for the UREX process," 62<sup>nd</sup> Northwest Regional Meeting of the American Chemical Society, Boise, ID, June 2007.
- ◆ G. Jarvinen, D. Ford, K. Long, K. Czerwinski, F. Poineau, and J. Du Mazabrun, "Technetium Recovery and Conversion from the UREX Process Stream using Anion Exchange," Actinide Separations Conference, Las Vegas, NV, June 2007.
- ◆ J. Du Mazabrun, F. Poineau, K. Czerwinski, G. Jarvinen, D. Ford, and K. Long, "Separation and Recovery of Technetium in the UREX process," Actinide Separations Conference, Las Vegas, NV, June 2007.

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