

Data from Web Upload:

Project ID: **60118**

Project Title: **Fundamental Thermodynamics of Actinide-Bearing Mineral Waste Forms**

Lead Principal Investigator:

Dr. Mark A. Williamson
Technical Staff Member
Los Alamos National Laboratory
MS G730
P.O. Box 1663
Los Alamos, New Mexico 87545
Telephone: 505-667-4045
e-mail: maw@lanl.gov

Co Principal Investigators:

Dr. Bartley B. Ebbinghaus
Technical Staff Member
Lawrence Livermore National Laboratory
MS L394
P.O. Box 808
Livermore California 94550
Telephone: 510-422-8792
e-mail: ebbinghaus1@llnl.gov

Dr. Alexandria Navrotsky
Professor
Department of Chemical Engineering and Materials Science
University of California at Davis
Davis California 95616
Telephone: 916-752-3292
e-mail: anavrotsky@ucdavis.edu

Fundamental Thermodynamics of Actinide-Bearing Mineral Waste Forms

Mid-Year Progress Report

**Mark A Williamson
Los Alamos National Laboratory**

**Alexandra Navrotsky
University of California, Davis**

**Bartley Ebbinghaus
Lawrence Livermore National Laboratory**

June 1, 1999

Goals of Project:

The recent arms reduction treaties between the U.S. and Russia have resulted in inventories of plutonium in excess of current defense needs. Storage of this material poses significant, and unnecessary, risks of diversion, especially for Russia whose infrastructure for protecting these materials has been weakened since the collapse of the Soviet Union. Moreover, maintaining and protecting these materials in their current form is costly. The United States has about sixty metric tons of excess plutonium, half of which is high-purity weapon material. This high purity material will be converted into mixed oxide (MOX) fuel for use in nuclear reactors. The less pure excess plutonium does not meet the specifications for MOX fuel and will not be purified to meet the fuel specifications. Instead, it will be immobilized directly in a ceramic. The ceramic will be encased in a high level waste (HLW) glass monolith (i.e., the can-in-canister option) thus making a form that simulates the intrinsic security of spent nuclear fuel. The immobilized product will be placed in a HLW repository. To meet the repository requirements, the product must be shown to be durable for the intended storage time, the host matrix must be stable in the radiation environment, the solubility and leaching characteristics of the plutonium in the host material must be established, and optimum processing parameters must be determined for the entire compositional envelope of feed materials.

In order to provide technically sound solutions to these issues, thermodynamic data are essential in developing an understanding of the chemistry and phase equilibria of the actinide-bearing mineral waste forms proposed as immobilization matrices. However, the relevant thermodynamic data (e.g., enthalpy, entropy, and heat capacity) for the ceramic forms are severely lacking and this information gap directly affects the Energy Department's ability to license the disposal matrices and methods. High-temperature solution calorimetry is one of the most powerful techniques, sometimes the only technique, for providing the fundamental thermodynamic data needed to establish optimum material fabrication parameters, and more importantly, understand and predict

the behavior of the mineral materials in the environment. The purpose of this project is to experimentally determine the enthalpy of formation of actinide orthosilicates, the enthalpies of formation of actinide substituted zircon, zirconolite and pyrochlore, and develop an understanding of the bonding characteristics and stabilities of these materials.

Technical Description of Work:

Experimental conditions of the calorimeter, such as solubility limit and dissolution rate of actinide-bearing materials in an oxide melt solvent, optimum calorimeter temperature, sample encapsulation for contamination control, etc., were established using surrogate (i.e., Ce, Gd) waste form materials at UC-Davis (UCD). These conditions were further refined using U- and Th-bearing materials at UCD. Information and experience obtained from these preliminary experiments was transferred to Los Alamos National Laboratory (LANL), which will allow experiments to be carried out on transuranic-bearing materials. The high-temperature solution calorimeter was installed into refurbished laboratory space at LANL. Professor Navrotsky and her staff supervised modification and installation of the instrument at LANL.

UCD personnel established the thermodynamic properties of several surrogate waste forms. This thermodynamic data combined with chemical periodicity arguments relating the lanthanide and actinide series was used to estimate the behavior of transuranic elements in the mineral waste forms. These estimates are used to guide the synthesis procedures used to produce actinide-bearing minerals as well as provide insight into the calorimetry experiments.

Several mineral waste forms, for example CaMTi_2O_7 (zirconolite) where $M = \text{Zr}$ or Hf , $\text{CaCeTi}_2\text{O}_7$ (pyrochlore), and $\text{RE}_2\text{Ti}_2\text{O}_7$ (rare earth pyrochlore) were prepared by LLNL and LANL to develop the synthesis procedures required for actinide-bearing compounds.

Accomplishments to Date:

Table 1 provides a detailed list of the phases studied during the first 18 months of this research project. Each of the phases listed in the Table was synthesized at UCD, LLNL, or the Australian Nuclear Science and Technology Organization (ANSTO). A combination of low-temperature adiabatic calorimetry and high-temperature oxide-melt solution calorimetry were used to yield heat capacity and enthalpy of solution data. The low temperature adiabatic calorimetry experiments completed at Brigham Young University (BYU) were funded by LLNL and coordinated by UCD. The solution calorimetry experiments were completed at the UCD Thermochemistry Facility. A brief description of the sample synthesis techniques and the calorimetry experiments is given in the following paragraphs. A reference list is also supplied at the end of this section.

Zirconolite, perovskite, Gd-pyrochlore, and titanate samples were prepared by sintering pelletized mixtures of the binary oxides in air at 1573 K for 2 to 10 days. The U- and Th-brannerites were prepared at ANSTO by sintering mixtures of the binary oxides at 1623 K. The U-brannerite samples were sintered for 300 hours in a 5% CO / 95% CO_2

atmosphere. Cerium brannerite was prepared from the alcoxides by standard sol-gel methods. Samples containing Ce-pyrochlore were synthesized at UCD by sintering mixtures of oxide powders containing CaCO_3 and TiO_2 , or CaTiO_3 and TiO_2 , and CeO_2 at 1498 K in pure oxygen for 4 to 10 days. Results of the Ce-pyrochlore synthesis studies are being used by LANL to produce Pu-pyrochlore samples. Each sample, whether prepared at UCD, LANL, LLNL or ANSTO, is characterized by X-ray diffraction techniques that included Rietveld refinement of X-ray diffraction histograms, electron microprobe analysis, and scanning electron microscopy.

Calorimetry experiments were completed using two different instruments. The heat capacity of each sample was measured from about 4 to 400 K using an adiabatic calorimeter of the Westrum [2] design. The results of the measurements were fitted to the usual polynomial and extrapolated to 1500 K. The enthalpy of solution for each sample was measured using a twin-cell Calvet-type high-temperature oxide-melt solution calorimeter [1]. Small portions, 2-5 mg, of each sample were dissolved in the lead borate ($2\text{PbO}\cdot\text{B}_2\text{O}_3$) melt. The energetics of the dissolution reaction was monitored and the enthalpy of formation of each sample was calculated using a thermochemical cycle. The combination of heat capacity data up to 1500 K and formation energies allows the determination of the Gibbs energy and entropy for each sample.

Phase	Studies performed [reference]	Synthesis Site / Calorimetry Site
$\text{CaZrTi}_2\text{O}_7$ / Zr-zirconolite	Cp and ΔH_f° [1-3]	LLNL / UCD, BYU
$\text{CaHfTi}_2\text{O}_7$ / Hf-zirconolite	Cp and ΔH_f° [4-6]	UCD / UCD, BYU
Zr/Hf zirconolite solutions	Cp and ΔH_f° [5]	UCD / UCD, BYU
ZrTiO_4 / zirconium titanate	Cp and ΔH_f° [7]	UCD / UCD, BYU
HfTiO_4 / hafnium titanate	ΔH_f° [6]	UCD / UCD
CaTiO_3 / perovskite	Cp and ΔH_f° [1,8]	UCD / UCD
$\text{Gd}_2\text{Ti}_2\text{O}_7$ / Gd-pyrochlore	Cp and ΔH_f° [9]	LLNL / UCD, BYU
CeTi_2O_6 / Ce-brannerite	Cp and ΔH_f° [9]	ANSTO / UCD, BYU
$\text{CaCeTi}_2\text{O}_7$ / Ce-pyrochlore	S° and ΔH_f° * [9]	UCD / UCD
UTi_2O_6 / U-brannerite	S° and ΔH_f° * [9]	ANSTO / UCD
ThTi_2O_6 / Th-brannerite	S° and ΔH_f° * [9]	ANSTO / UCD
PuTi_2O_6 / Pu-brannerite	ΔH_f° * [9]	/UCD
CaUTi_2O_7 / U-pyrochlore	ΔH_f° * [9]	/UCD
$\text{CaPuTi}_2\text{O}_7$ / Pu-pyrochlore	ΔH_f° * [9]	/UCD

Table 1. Listing of the phases studied during the first 18 months of this project. Note that studies with an * are estimated data.

Table 1 also contains the actinide-bearing phases ThTi_2O_6 (Th-brannerite) and UTi_2O_6 (U-brannerite), which are currently being studied at UC-Davis. The table also indicates the actinide-bearing phases for which thermodynamic data has been estimated.

These estimates are based on thermochemical relationships that are being established from the studies of surrogate materials.

An experimental study of plutonium, americium, and perhaps neptunium bearing phases will be completed in the new solution calorimetry facility in the Chemistry - Metallurgy Research (CMR) building at LANL. Refurbishing the calorimeter laboratory space was completed in March of 1999. Installation of the calorimeter was completed in April 1999. This task is one of the first completed following the new CMR facility policies and procedures. Initial testing of the system is complete. Start-up of the furnace and control system will occur in the third quarter of this fiscal year.

References:

- [1] Putnam, R.L., Navrotsky, A., Woodfield, B.F., Boerio-Goates, J. and Shapiro, J.L., "Thermodynamics of Formation for Zirconolite, $\text{CaZrTi}_2\text{O}_7$, From $T = 298 \text{ K}$ to $T = 1500 \text{ K}$," *J. Chem. Thermodynamics* **31**(3), 229 (1999).
- [2] Woodfield, B.F., Boerio-Goates, J., Shapiro, J.L., Putnam, R.L. and Navrotsky, A., "Molar Heat Capacity and Thermodynamic Functions of Zirconolite, $\text{CaZrTi}_2\text{O}_7$," *J. Chem. Thermodynamics* **31**(3), 245 (1999).
- [3] Putnam, R.L., Navrotsky, A., Woodfield, B.F. and Boerio-Goates, J., "Heat Capacity, Third Law Entropy, and Formation Energetics of Zirconolite, $\text{CaZrTi}_2\text{O}_7$," *Environmental Issues and Waste Management Technologies in the Ceramic and Nuclear Industries IV*, *Ceramic Transactions Volume* **93**, 339 (1999).
- [4] Putnam, R.L., Navrotsky, A., Woodfield, B.F., Boerio-Goates, J., Stevens, R. and Shapiro, J.L., "Thermochemistry of Hf-Zirconolite, $\text{CaHfTi}_2\text{O}_7$," *Scientific Basis for Nuclear Waste Management*, Materials Research Society - Dec. 1998.
- [5] Putnam, R.L., Navrotsky, A., Woodfield, B.F., Boerio-Goates, J., and Shapiro, J.L., "Thermodynamics of Formation for Hf-Zirconolite, $\text{CaHfTi}_2\text{O}_7$, From $T = 298 \text{ K}$ to $T = 1500 \text{ K}$," to be submitted to *J. Chem. Thermodynamics* (1999).
- [6] Woodfield, B.F., Boerio-Goates, J., Shapiro, J.L., Putnam, R.L. and Navrotsky, A., "Molar Heat Capacity and Thermodynamic Functions of Hf-Zirconolite, $\text{CaHfTi}_2\text{O}_7$," to be submitted to *J. Chem. Thermodynamics* (1999).
- [7] Woodfield, B.F., Boerio-Goates, J., Shapiro, J.L., Putnam, R.L. and Navrotsky, A., "Heat capacity, Third Law Entropy, and Formation Energetics of Zirconium Titanate, ZrTiO_4 ," to be submitted to *J. Chem. Thermodynamics* (1999).
- [8] Woodfield, B.F., Shapiro, J.L., Stevens, R., Boerio-Goates, J., Putnam, R.L., Helean, K.B. and Navrotsky, A. "Molar Heat Capacity and Thermodynamic Functions for CaTiO_3 ," submitted and accepted, *J. Chem. Thermodynamics* (1999).

[9] Putnam, R.L., Ph.D. Dissertation, Department of Geosciences, Princeton University, to be submitted August 1999.