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Author(s): Mark A. Williamson

Submitted to: Mark Gilbertson
Roland Hirsch
U.S. Department of Energy

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Fundamental Thermodynamics of Actinide-Bearing Mineral Waste Forms

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Mark A. Williamson, Argonne National Laboratory
Alexandra Navrotsky, University of California at Davis
Bartley B. Ebbinghaus, Lawrence Livermore National Laboratory
John Huang, Los Alamos National Laboratory
Robert L. Putnam, Los Alamos National Laboratory, post-doctoral fellow
Sergey V. Ushakov, University of California at Davis, post-doctoral fellow
Katheryn B. Helean, University of California at Davis, graduate student

Research Objective: The landmark record of decision in January 2000 by the US Department of Energy stated that at least 17 tons of surplus weapons plutonium will be converted to a mineral waste material and disposed of in a geological repository similar to the proposed Yucca Mountain nuclear waste site in Nevada. The need for fundamental thermodynamic properties (e.g., entropy, enthalpy and free energy of formation) of specific actinide-bearing mineral phases, related non-actinide phases, and potential decomposition phases is vital to waste material formulation, fabrication process optimization, environmental modeling, and licensing a proposed mineral waste material. Two and one half years ago we began a study designed to obtain the first measured values for the formation energetics of phases related to the disposal of this surplus weapons plutonium.

Research Progress: A combination of calorimetric techniques is being used to establish the thermodynamic properties of the mineral waste forms. High-temperature oxide-melt solution calorimetry is being used to establish the enthalpy of formation of the minerals while adiabatic calorimetry is being used to establish the heat capacity and entropy of the minerals. The enthalpy and entropy data are combined to calculate the free energy of formation of the phase. Thermodynamic data are available for (1) CaMTi_2O_7 where $\text{M}=\text{Zr}$, Hf , and Ce ; (2) AnTi_2O_6 where $\text{An}=\text{Ce}$, Th , U ; (3) REPO_4 where $\text{RE}=\text{La}$, Ce , Nd , Eu , Yb , and Lu ; (4) $\text{Gd}_2\text{Ti}_2\text{O}_7$; (5) CaTiO_3 ; and (6) MTiO_4 where $\text{M}=\text{Zr}$ or Hf . The enthalpy of formation of $\text{CaPuTi}_2\text{O}_7$, PuTi_2O_6 , UPO_4 , PuPO_4 , and AmPO_4 was estimated from the systematic trends observed in the measured values of the appropriate aforementioned phases. These trends are only approximations, which result in large error margins on the predicted values. The remaining resources and our efforts are targeting the synthesis, characterization, and measurement of the formation energetics of the Pu-bearing phases.

A high-temperature solution calorimeter has been installed at Los Alamos National Laboratory (LANL) to allow the study of high-activity actinide-bearing materials. Uranium and thorium containing materials were studied at the University of California at Davis (UCD). Optimal experimental conditions, techniques, and solvents have been determined at UCD and this information has been transferred to LANL. Heat capacity data were obtained at Brigham Young University (BYU) on some of the phases of interest. Funding for the BYU studies was through an outside contract from Lawrence Livermore National Laboratory (LLNL).

Planned Activities: We plan to complete the revised 1997 scope of the project. The original scope of work was downsized in 1997 because LANL, UCD, and LLNL received less funding

than originally requested. LLNL has synthesized but not fully characterized PuTi_2O_6 . Precursor material for Pu-pyrochlore, $\text{CaPuTi}_2\text{O}_7$, has been prepared but no pyrochlore sample has been synthesized. When synthesis and characterization of these phases is completed, the samples will be transported to LANL where calorimetric studies will be performed.

Additional funding will be sought to fully characterize the thermodynamics of other actinide-bearing mineral waste forms and to establish the energetics of mixing of waste form materials. The energetics of mixing data are needed in modeling the behavior of a multi-component waste material such as the solid solution ($\text{CaHfTi}_2\text{O}_7 + \text{Gd}_2\text{Ti}_2\text{O}_7 + \text{CaUTi}_2\text{O}_7 + \text{CaPuTi}_2\text{O}_7$) proposed as the waste material for surplus weapons plutonium.

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Contact Information:

Mark A. Williamson, Argonne National Laboratory, Chemical Technology Division, 9700 S. Cass Ave., Argonne, IL 60439-4837 phone: 630-252-9627 email: williamson@cmt.anl.gov

Alexandra Navrotsky, University of California at Davis, Department of Chemical Engineering and Materials Science, Davis, CA 95616 phone: 530-752-3292 email: navrotsky@ucdavis.edu

Bartley B. Ebbinghaus, Lawrence Livermore National Laboratory, MS L394, P.O. Box 808, Livermore, CA 94550 phone: 510-422-8792 email: ebbinghaus1@llnl.gov

John Huang, Los Alamos National Laboratory, Nuclear Materials Technology Division, MS E506, P.O. Box 1663, Los Alamos, NM 87545 phone: 505-665-1440 email: jhuang@lanl.gov

Robert L. Putnam, Los Alamos National Laboratory, Nuclear Materials Technology Division, MS K762, P.O. Box 1663, Los Alamos, NM 87545 phone: 505-667-6825 email: rputnam@lanl.gov

Sergey V. Ushakov, University of California at Davis, Department of Chemical Engineering and Materials Science, Davis CA 95616 phone: 530-754-2133 email: svushakov@ucdavis.edu

Katheryn B. Helean, University of California at Davis, Department of Chemical engineering and Materials Science, Davis, CA 95616 phone: 530-754-2133 email: kbhelean@ucdavis.edu