LA-UR- 02-0562

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Title: Fundamental Thermodynamics of Actinide-Bearing Mineral Waste Forms

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Submitted to: 9th Biennial International Conference on Nuclear and Hazardous Waste Management
Aug 4-8, 2002
Reno, Nevada

Los Alamos
NATIONAL LABORATORY

9th Biennial International Conference on Nuclear and Hazardous Waste Management

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Summary Cover Sheet

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Presentation preference (indicate one): Poster

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Fundamental Thermodynamics of Actinide-Bearing Mineral Waste Forms

The end of the Cold War raised the need for the technical community to be concerned with the disposition of surplus nuclear weapon material. The United States Department of Energy has determined that of 50 tons of surplus weapons plutonium and clean metal; 17 tons will be incorporated into a ceramic material and then placed in a geologic repository. (US DOE ROD 2000) The form of that ceramic material is a solid solution between four end-member oxide phases: CaHfTi2O7, CaUTi2O7, CaPuTi2O7, and Gd2Ti2O7 (Ebbinghaus 2000). The stability and behavior of plutonium in the ceramic materials as well as the phase behavior and stability of the ceramic material in the environment is not well established. Recent studies into the fundamental thermodynamics of actinide substitution into surrogates of these phases have begun to provide a basis for technically sound solutions to the issue of a safe, secure, and environmentally acceptable waste material (Putnam 2001). However, the stability and behavior of plutonium in the proposed ceramic and end-member materials have only been estimated. With the recent installation at LANL (CMR wing 2) of the world's only high-temperature oxide-melt solution calorimeter work on actual plutonium-containing materials may be conducted.

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. Mineral materials of interest include zircon, zirconolite, and pyrochlore. 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 (Navrotsky 1997). The purpose of this project is to experimentally determine the enthalpy of formation of actinide-containing mineral phases and develop an understanding of the bonding characteristics and stability of these materials.

This report summarizes work after completion of a three-year project and our current ongoing efforts. Research efforts at UC Davis have focused on establishing the thermodynamic properties of zirconolite and pyrochlore, and the synthesis of other minerals relevant to storage of nuclear material. Heat capacity, entropy, enthalpy of formation, and free energy of formation data were established for zirconolite, $CaZrTi_2O_7$, in the range from 0 to 1500 K. The heat capacity, entropy, enthalpy of formation, and free energy of formation at 298 K for zirconolite are 211.9 J/K mol, 193.3 J/K mol, -3713.8 kJ/mol, and -3514.6 kJ/mol, respectively. Solution calorimetry experiments with cerium pyrochlore, $Ca_{0.8}Ce_{1.2}Ti_2O_7$, are complete. Heat capacity data and confirmation of the pyrochlore composition are required for final data analysis. Synthesis and characterization of $CaHfTi_2O_7$, $CaZr_{0.5}Hf_{0.5}Ti_2O_7$, $Gd_2Ti_2O_7$, and $CeTi_2O_6$ is complete.

Research efforts at Los Alamos have focused on establishing synthesis techniques for actinide-bearing minerals and preparation of the calorimetry laboratory. The preparation of Pu-pyrochlore, nominally $CaPuTi_2O_7$ has been achieved by Ebbinghaus at Lawrence Livermore National Laboratory. A sample of this material has been sent to Putnam at Los Alamos National Laboratory.

Future opportunity and Objectives:

Putnam et al. (Putnam 2001) recently completed a three year study of the formation energetics of phases related to the ceramic disposition form that has been suggested for surplus weapons plutonium, with the notable exception of plutonium-bearing materials. Because of radiological reasons, surrogates for the plutonium-bearing phases were used to estimate the thermodynamic stability of these key materials, specifically Pu-pyrochlore and Pu-zircon. The estimates are crude and contain large errors (Putnam 2001). Actual measured values would greatly enhance the models used to forecast the waste form performance in a waste repository as well as provide additional data for refining the models used to estimate the stabilities of other actinide-containing materials. Ebbinghaus at Lawrence Livermore National Laboratory has recently succeeded in synthesizing a nearly phase pure sample of $CaPuTi_2O_7$, Pu-pyrochlore. This sample is an excellent candidate for the determination of its thermodynamic stability using high-temperature oxide melt solution calorimetry. LANL is in the unique position to provide actual measured value of the formation enthalpy of $CaPuTi_2O_7$ because of the installation of a calorimeter capable of studying actinide-bearing materials. This high-temperature oxide-melt solution calorimeter is the world's first such instrument with actinide capabilities. This instrument provides all of the infrastructure needed to safely and accurately determine the fundamental thermodynamic quantities needed to certify proposed ceramic materials as technically sound solutions to the issue of a safe, secure, and environmentally acceptable waste material for surplus weapons plutonium pursuant to DOE's record of decision. (US DOE ROD 2000)

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