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Fundamental Thermodynamics of Actinide-Bearing Mineral Waste Forms

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Research Objective

The end of the Cold War raised the need for the technical community to be concerned with the disposition of excess nuclear weapon material. The plutonium will either be converted into mixed-oxide fuel for use in nuclear reactors or immobilized in glass or ceramic waste forms and placed in a repository. 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. 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 form materials 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. The purpose of this project is to experimentally determine the enthalpy of formation of actinide orthosilicates, the enthalpy of formation of actinide substituted zircon, zirconolite and pyrochlore, and develop an understanding of the bonding characteristics and stability of these materials.

Research Progress and Implications

This report summarizes work after eight months of a three year project. 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. Solid state synthesis techniques are being investigated for the preparation of pyrochlore, $CaAnTi_2O_7$ where An is a actinide, plutonium-doped zircon, $ZrxPu_{1-x}SiO_4$, and plutonium silicate, $PuSiO_4$. X-ray diffraction analysis of the silicate samples revealed considerable sample - container interaction. Alternative container materials will be examined in future synthesis experiments so that high purity minerals can be produced for use in the calorimetry experiments.

Planned Activities

Research at UC Davis will continue with solution calorimetry experiments for $CaHfTi_2O_7$, $CaZr_{0.5}Hf_{0.5}Ti_2O_7$, $Gd_2Ti_2O_7$, and $CeTi_2O_6$. A model for predicting the solution energetics of the actinide(IV) oxides in the calorimetry solvent has been developed. Validation of the model with

ThO_2 is expected in the next six months which will allow for the extension of solution calorimetry to other actinide-bearing materials.

Research at Los Alamos will continue with the solid state synthesis of actinide-bearing pyrochlore and silicate minerals, preparation of the calorimetry laboratory, and a series of calorimetric experiments. The calorimetric experiments will include determining the enthalpy of solution of binary actinide oxides, actinide-bearing minerals, and solid solutions of minerals in the calorimetric solvent. Results from the solution calorimetry experiments will be used to calculate the enthalpy of formation of the actinide-bearing minerals (e.g., $CaPuTi_2O_7$) and the enthalpy of mixing in solid solution systems (e.g., $ZrxPu_{1-x}SiO_4$). The thermodynamic data will be used to establish the stability and bonding characteristics of the materials.

Other Access To Information

R.L. Putnam, A. Navrotsky, B.F. Woodfield, J. Boerio-Goates, and J.L. Shapiro, "Thermodynamics of Formation for Zirconolite, $CaZrTi_2O_7$, from T= 298 K to T= 1500 K," submitted to J. Chem. Thermodynamics (1998).

B.F. Woodfield, J. Boerio-Goates, J.L. Shapiro, R.L. Putnam, and A. Navrotsky "Molar Heat Capacity and Thermodynamic Functions of Zirconolite, $CaZrTi_2O_7$," submitted to J. Chem. Thermodynamics (1998).

R. L. Putnam, A. Navrotsky, B. F. Woodfield, J. L. Shapiro, and J. Boerio-Goates, "Heat Capacity, Third Law Entropy, and Formation Energetics of Zirconolite, $CaZrTi_2O_7$," submitted to Proceedings of the100th Annual Meeting of the American Ceramic Society: the International Symposium on Waste Management Technologies in Ceramic and Nuclear Industries (1998).