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Thermodynamics of the Volatilization of Actinide Metals in the High-Temperature Treatment of Radioactive Wastes

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Research Objective

In this project, we will perform a detailed study of the volatilization behavior of U, Pu and possibly Am and Np under conditions relevant to the thermal treatment (destruction) of actinide-containing organic-based mixed and radioactive wastes. The primary scientific goal of the proposed work is to develop a basic thermochemical understanding of actinide volatilization and partitioning/speciation behavior in the thermal processes that are central to DOE/EM's mixed waste treatment program. This subject addresses several technical needs/problem areas recently identified by DOE/EM's Office of Science and Technology. In the Low-Level and Mixed Low-Level Waste problem area, emission-free destruction of organic wastes is listed as the first exemplary science need. In the TRU Waste, Plutonium Materials, and Spent Nuclear Fuel problem areas, interactions between actinides and organic residues and materials stabilization are listed as exemplary science needs. Both of these needs require high-temperature thermodynamic studies of actinides and actinide-organic interactions.

A sound basis for designing safe and effective thermal treatment systems and the ability to allay public concerns about radioactive fugitive emissions are the principal benefits of the project. The proposed work is a combination of experimental studies and thermodynamic modeling. Vapor pressure measurements will be made to determine U, Pu and possibly Am volatile species and the extent of their volatilization when $\text{UO}_2/\text{U}_3\text{O}_8$, PuO_2 and AmO_2 solids are heated to temperatures of 500 to 1500°C under pyrolyzing (reducing) conditions or under oxidizing conditions (i.e. $\text{O}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$ mixtures) in the presence of chlorine ($\text{Cl}_2(\text{g})$ or $\text{HCl}(\text{g})$). Work on uranium volatilization under reducing conditions will be performed in a laboratory at U. C. Berkeley in a collaboration with Professor D. R. Olander. In parallel with the experimental effort, a complete thermodynamic database for expected actinide gaseous species will be developed from literature data, from the proposed measurements, and from data predictions using bond energy correlation and statistical thermodynamics estimation methods.

Research Progress and Implications

This report summarizes work performed since October 1, 1997 in the first year of a 3-year project.

In December 1997, we put in place a small sub-contract at UC Berkeley to allow Professor D.R.Olander and a graduate student to begin work on uranium volatilization under reducing/gasification conditions. During this time a transport apparatus has been designed and built, and it is currently being activated. A method for the determination of small quantities of uranium on collection foils using neutron activation has been selected, and several methods for preparing organic chars containing uranium oxide have been evaluated. The most promising char preparation approaches involve as first steps (i) incorporating dry uranium compounds into epoxy cements and (ii) loading uranyl ions onto suitable ion exchange resins. We are also trying to obtain small quantities of a uranium porphyrin compound such as bis(phthalocyaninato) uranium(IV) to serve as a model transportable specie.

Preparations for the planned plutonium volatility measurements have been somewhat slower than originally planned due to the need to change the facility in which the measurements will be conducted (the main Pu facility at LLNL has been shut down for several months) and the slow process of hiring the scientist identified for this project. To date we have identified and secured a

location for this work in a suitable facility (B-151), we have prepared the necessary work plans and are well along in the approval process, and we have ordered the necessary equipment for the Pu transpiration experiments (glovebox, furnace, controllers, gas flowmeters, etc). A job offer has been made to a PhD chemist who has experience with transactinide element thermochromatographic behavior.

We initiated our effort to compile a complete thermodynamic database for potential actinide vapor species by estimating key thermodynamic parameters for species such as $\text{AnO}_3(\text{g})$, $\text{AnO}_2(\text{OH})_2(\text{g})$, $\text{AnO}_2\text{Cl}_2(\text{g})$ and $\text{AnO}_2\text{F}_2(\text{g})$, where $\text{An}=\text{Np}$ and Am , and $\text{UO}_2\text{Cl}(\text{OH})(\text{g})$, $\text{UO}_2\text{F}(\text{OH})(\text{g})$ and $\text{UO}_2\text{FCl}(\text{g})$. These estimations extend previous thermodynamic predictions we have made for uranium and plutonium vapor species. Two papers that describe this and related work are being prepared for publication in the Journal of Nuclear Materials.

Planned Activities

During the remainder of the current fiscal year (June - September 1998), we will initiate and conduct several of the experiments designed to characterize uranium volatility under reducing conditions. The principal objective of these tests will be to determine whether there is any evidence for enhanced uranium volatilization due to the formation of organouranium compounds in chars at elevated temperatures. If such evidence is obtained, these experiments will be continued through FY99 with the aim of identifying the responsible specie(s). Equipment for the planned plutonium volatility experiments will also be assembled and commissioned during the remainder of FY98, and we are aiming to begin activation of the equipment (with uranium compounds) in September 1998. Transpiration experiments with Pu, Am, and possibly Np, compounds will be conducted through FY99 and FY2000. Throughout the remaining period of this project we will continue to estimate key thermodynamic parameters for actinide vapor species of interest and to develop the database that will be used in thermochemical prediction models.