Project ID: **60319**

Project Title: **Thermodynamics of the Volatilization of Actinide Metals in the High-Temperature Treatment of Radioactive Wastes**

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EMSP SUMMARY/PROGRESS REPORT

Project No. 60319

RESEARCH OBJECTIVE

We are performing 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 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 at least two key technical needs/problem areas recently identified by DOE/EM's Office of Science & Technology: emission-free destruction of organic wastes, and interactions between actinides and organic residues in materials stabilization.

A sound basis for designing safe and effective treatment systems, and the ability to allay public concerns about radioactive fugitive emissions, will be 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 UO2/U3O8, PuO2 and AmO2 solids are heated to temperatures of 500 to1200 C under pyrolyzing (reducing) conditions or under oxidizing conditions in the presence of chlorine. Work on uranium volatilization under reducing conditions is being performed in a laboratory at UC 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 June 1 1998 in the second year of a 3-year project.

At UC Berkeley, Professor D.R.Olander and a graduate student (J.C.Cole) continued work on uranium oxide volatilization under reducing/gasification conditions. They have used the thermal transport furnace built during the first year to conduct two series of vaporization experiments on UO2-containing organic specimens in flowing Ar-H2-H2O-CO-CO2 atmospheres. The simulated waste specimens comprised (i) epoxy pellets filled with U3O8 powder and (ii) a dry Amberlite cation-exchange resin previously loaded with uranyl ions. Using a very sensitive neutron activation analysis technique and the TRIGA reactor at Oregon State University, they have been able to detect nanogram quantities of uranium on downstream deposition tabs, and hence show that some uranium transport has occurred at specimen temperatures as low as 600C. Currently, using high temperature filters, efforts are being made to understand the mechanism of uranium transport, and to characterize the suspected aerosol particles collected on the deposition tabs using electron microscopy. After unsuccessfully trying to obtain small quantities of bis(phthalocyaninato) uranium(IV) or superphthalocyaninine uranium(VI) commercially,

we ended up synthesizing 50 mg of the latter compound at LLNL. Anhydrous uranium chloride starting compounds were kindly provided by Dr Carol Burns at LANL. It is intended to use this material as a model organouranium transportable specie in imminent transport experiments.

Preparations for the planned transuranium (Pu, Np, Am) volatility measurements using the transpiration technique have proceeded slowly, mainly due to unexpected B151 facility requirements to upgrade the ventilation system for the chosen room and glovebox from the category of Workplace Type 2 to Workplace Type 3. This necessitates the installation of additional ducting, blowers and HEPA filters, and has required numerous ES&H reviews and approvals. A postdoctoral fellow, Dr Nadia Hakem, was hired to work on this project in September 1998. Assembly of the glovebox in which the experiments will be performed, and associated equipment such as the furnace and controller, gas distribution and control circuits and the toxic gas cabinet, etc, is about 90% complete. The furnace has been tested to its maximum operating temperature (1200C), and the temperature profile of the transpiration tube has been determined.

In support of our thermodynamic database compilation effort, we have acquired, and are in the process of installing, the latest stand-alone version of the FACT/EQUILIBRIUM computer code (V3.0). Like other FACT users, we have encountered difficulty running this software under Windows NT 4.0. Dr Hakem is trying to resolve this problem, and, in the process, is becoming familiar with the FACT/EQUILIBRIUM program and its ability to make speciation predictions.

PLANNED ACTIVITIES

During the remainder of the current fiscal year (June – September 1999), we expect to complete both the B-151 room modification and installation of the glovebox and related transpiration system equipment. A new series of uranium volatility experiments will be conducted at UC Berkeley. Having recently obtained evidence of uranium migration, these experiments will be designed to characterize the mechanism of transport of uranium under gasification conditions, and possibly to identify the responsible specie(s). Provided continued good progress is made, it is expected that these experiments will be continued through FY2000. We expect to conduct the planned transpiration experiments on Pu, Am, and possibly Np oxides in chlorine-containing atmospheres in the newly installed glovebox during FY2000. Before this, the glovebox will be activated using uranium oxide as a surrogate for plutonia. Also during FY2000, as time and funding allow, 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.

INFORMATION ACCESS (PUBLICATIONS)

Two manuscripts dealing with thermodynamic data estimations for uranium and plutonium vapor species are in preparation.

June 14, 1999