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

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Intro/work to be performed

- In this project, initiated in October 1997, we are performing detailed studies of the high-temperature behavior of actinide elements (U, Pu, Np, etc.) under conditions relevant to the thermal treatment of actinide-containing wastes and residues.

- The proposed work is in a combination of experimental measurements and thermodynamic modeling:
  - transpiration measurements to determine the extent of volatilization (vapor pressure) of Pu, Np, and possibly Am, when their respective oxides are heated to 600 – 1500 °C under oxidizing gases (O2, H2O) in the presence of chlorine (Cl2 or HCl).
  - thermal gradient transport experiments to determine the extent of volatilization of uranium oxide when it is heated to 500-1200 °C under simulated pyrolysis (reducing) conditions.
  - Other thermal processes:
    - determination of Pu volatility and volatilization of surplus Pu oxide

Intro/goals, objectives, and work plan

- The general objective of this work is to develop a basic understanding of the thermodynamics of actinide volatilization and partitioning/speciation behavior in the thermal processes that are central to DOE/EM’s mixed waste treatment program.

- For all of the actinides (An = Pu, Np, Am), the key thermodynamic parameters for the gaseous species AnO2Cl, AnO2F(OH), AnO2F, AnO2Cl(F,H)(OH), and AnO2(OF,H)2, where An = Np and Am, have been estimated.

Intro/relevance to DOE/EM problems

Problem: “Export-free destruction of organic (mixed) wastes”

Examples of MN thermal treatment processes presently under consideration:

- conventional incineration
- plasma arc technologies
- pyrolysis
- thermal description
- pyrolysis technologies (incl. Molten Metal)
- incineration technology (H20)
- non-thermal oxidation (N20)

Other thermal processes:

- transpiration measurement (vapor pressure) of Pu, Np, and possibly Am, when their respective oxides are heated to 600 – 1500 °C under oxidizing gases (O2, H2O) in the presence of chlorine (Cl2 or HCl).

- thermal gradient transport experiments to determine the extent of volatilization of uranium oxide when it is heated to 500-1200 °C under simulated pyrolysis (reducing) conditions.

- estimation of thermodynamic data for “unknown” vapor species

- pyrolysis, reducing conditions

- incineration technology (H20)

- non-thermal oxidation (N20)

Methods

- Determination of temperature and pressure conditions for the vapor pressure measurements (An = Pu, Np, Am)

Reactions, Species Responsible for Enhanced Actinide Volatility

Oxidizing atmospheres:

- PuO2(s) + 3/2O2(g) = PuO3(s) + 1/2O2(g)
- PuO2(s) + H2O(l) = PuO3(s) + 1/2O2(g) + H2(g)

Reducing atmospheres:

- UO2(s) + H2(g) = UO(s) + H2O(g)
- UO2Cl2(s) + H2(g) = UO2Cl(g) + H2O(g)
- UO2ClF(s) + H2O(g) = UO2ClF(g) + H2O(g)
- UO2F2(s) + H2O(g) = UO2F2(g) + H2O(g)
- UO2F2Cl(s) + H2(g) = UO2F2Cl(g) + H2(g)

Progress

- Apparatus for U transport studies under reducing conditions designed, built and currently being activated
- Simulated organic wastes containing U have been prepared
- An alternative location for conducting the planned Pu volatility experiments has been secured, and the necessary equipment (glove box, furnace, controllers, etc.) has been specified and ordered
- A post-doctoral position has been offered to a PhD chemist who has experience with transactinide element speciation
- Key thermodynamic parameters for the gaseous species AnO2Cl, AnO2F(OH), AnO2F, and AnO2Cl(F,H)(OH), where An = Np and Am, and UO2Cl2(s), UO2F2(s), and UO2F2Cl(s), have been estimated.

Two manuscripts are being prepared for the Journal of Nuclear Materials.