SAND2019-11540C

Lanthanide precursors and materials as surrogates for actinide-containing wastes

Xavier J. Robinson, Timothy J Boyle, Joshua A. Hubbard, Fernando (NMI) Guerrero
Sandia National Laboratories, Advanced Materials Laboratory, 1001 University Blvd. SE, Albuquerque, New Mexico 87106

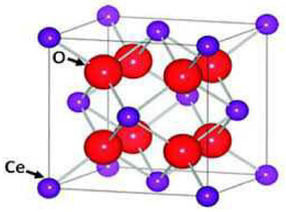
Sandia National Laboratories

Advanced Materials Laboratory

Introduction

It is estimated that 2,000-2,300 metric tons of uranium-bearing waste is generated every year by nuclear power plants. Fires at storage facilities are a large concern, as the resulting energy and air flow can spread radioactive particles. To simulate and model the spread of these particles, pyrolysis experiments have been performed on liquid- and solid-state dispersions of lanthanide nitrates and oxides by the DOE to find their airborne release fraction. These findings are compiled in a DOE handbook on airborne release fractions published in 1994 concerning all eventualities of nuclear power plants. Further research was performed to validate the findings of part of this handbook, specifically that of solid and liquid matrix fires.

Results of a fire at the Waste Isolation Pilot Plant



Unit cell of Ce_2O_3 , a commonly used actinide surrogate

Lanthanide (Ln) cations are often used as a surrogate to avoid the radioactivity and high cost of experimentation with actinide (An) species. However, the difference in properties of the Ln and An for aerosol applications are less studied. Therefore, in this study a variety of Ln and An oxide materials were prepared for pyrolysis to evaluate previously published release fractions and to determine the best Ln surrogate for further research.

"AIRBORNE RELEASE FRACTIONS/RATES AND RESPIRABLE FRACTIONS FOR NONREACTOR NUCLEAR FACILITIES," DOE-HDBK-3010-94, Dec, 1994. Washington, D.C.

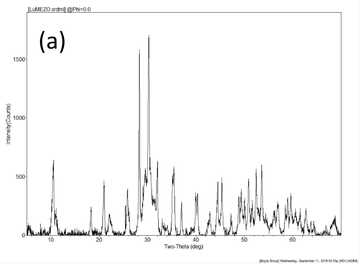
Lanthanide Materials

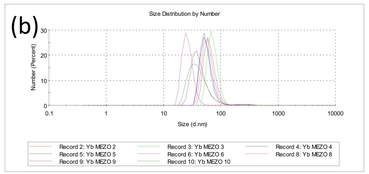
Commercially available lanthanide nitrate hydraes ($Ln(NO_3)_3 \bullet xH_2O$) were used as received, and lanthanum oxide (Ln_2O_3) was prepared by ammonium hydroxide (NH_4OH) precipitation. Upon addition of NH_4OH to an aqueous solution of $Ln(NO_3)_3 \bullet xH_2O$, a precipitate formed. The product was isolated via centrifugation and drying *en vacuo*. The dried powder was determined by Dynamic Light Scattering (DLS) to be approx. 200 nm in size. Late Ln derivatives (Yg and Lu) were chosen for U simulants after testing due to the higher density and their similarity their airborne release fractions to U.

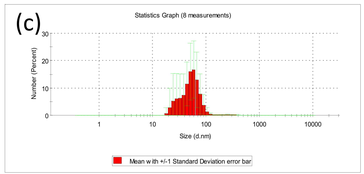
$$Ln(NO_3)_3 + NH_4OH \longrightarrow Ln_2(OH)_5(NO_3)$$

Ln = Yb, Lu

Lanthanide Oxide Characterization







(a) PXRD pattern matching $Lu_2(OH)_5(NO_3)$, (b) DLS of Yb particles and (c) statistical overview of DLS results

Actinide Materials

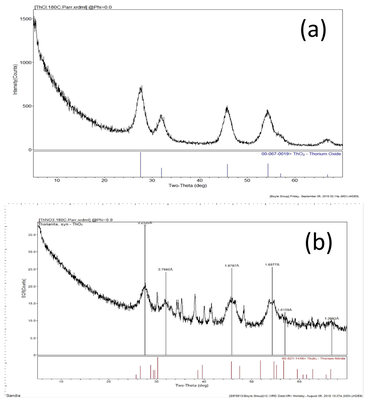
Chemical reductants such as lithium naphthalenide (LiNaph) were attempted for particle syntheses but, due to broad range of particle sizes generated, these were not considered useful. Thus, a variety of solvothermal methods were used to prepare actinide oxides with desirable size and dispersion qualities.

For each method, a Parr Digestion Bomb™ filled with solutions below were sealed and heated at 180°C for 12 h. Both methods have been used successfully for both U_2O_3 and Th_2O_3 production. Here, only uranium was used as a reference material for lanthanide surrogates.

Method 1: UCl_4 + trioctylamine + toluene

Method 2: $U(NO_3)_4$ + water + octylamine

PXRD Characterization



PXRD patterns of particles generated with (a) method 1 and (b) method 2.

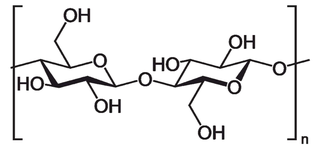
Solid Matrix Preparation

Phase 2 of pyrolysis experiments is focused on burning solid materials contaminated with uranium waste. For the solid matrix testing a matrix of cellulose shreds, approx. 0.5 x 1 cm in size was coated with $Ln(NO_3)_3 \bullet xH_2O$ where Ln = Yb and Lu. These were selected based on the liquid results (*vide infra*).

An XXX M solution of $Ln(NO_3)_3 \bullet xH_2O$ solution was made and added to the matrix at 10% mass loading of Ln metal. However, these samples were not ignitable. Thus, a mass loading of 1% equivalent Ln cation was chosen. This solution was soaked onto the cellulose fibers and then dried to leave only the residue from Ln or An materials on the cellulose matrix

The fibers were then packaged and burned in the pyrolysis test chamber for analysis of airborne release fractions

Structure of cellulose fibers used for solid-matrix pyrolysis sample.



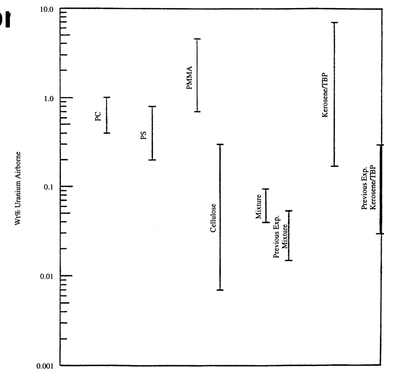
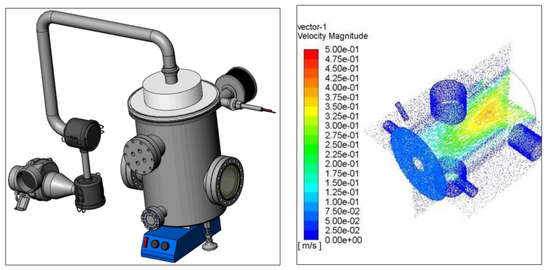


Figure 5-1. Results from Burning Contaminated Combustibles (Figure 2 - Halverson, Ballinger, and Dennis March 1987)

Figure from 1994 DOE Handbook on airborne release fractions with varying matrices

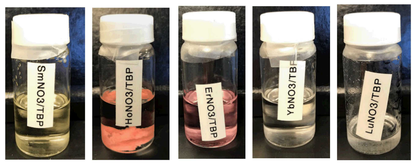
Pyrolysis Test Chamber



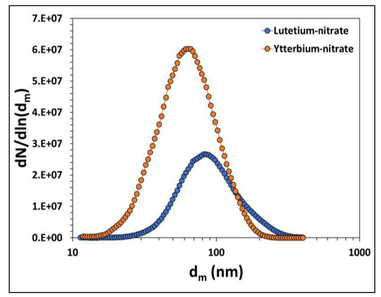
Custom test chamber used for solid- and liquid-matrix pyrolysis experimentation of surrogates

Liquid Matrix Preparation

For the first stage of pyrolysis, liquid-state tests, a 30% v/v matrix of tributyl phosphate (TBP) in kerosene was generated. To this solution, $Ln(NO_3)_3 \bullet xH_2O$ (1.0 g) or $UO_2(NO_3)_2 \bullet xH_2O$ material was added to 10 mL of the TBP solution. The resulting solutions are shown below.



Lanthanide nitrate solutions from pre-pyrolysis solubility tests



Release fraction data from liquid-matrix pyrolysis tests

Particulate analysis shows an airborne release fraction (ARF) of ~ 6×10^{-7} for $Yb(NO_3)_3 \bullet xH_2O$, with $Lu(NO_3)_3 \bullet xH_2O$ having an ARF = 2.5×10^{-7}. Compared against the ARF of $UO_2(NO_3)_2 \bullet xH_2O$ (~6×10^{-7}), the results are on the same scale and indicate these Ln cations are useful simulants. Because of this liquid matrix-based result, Yb and Lu were also chosen for solid matrix testing of ARF.

Summary

A series of Ln and An materials were successfully used to confirm the airborne release fractions of liquid and solid matrices. Pyrolysis testing confirmed for the liquid routes that the late Ln were useful surrogates. Solid waste testing is underway.

Results of liquid-matrix pyrolysis tests on lutetium nitrate

Surrogates for An materials are also being explored for further testing, with liquid matrix tests suggesting late Ln (e.g. Tm, Yb, Lu) have similar airborne release characteristics, making them better surrogates than industry standard Ce_2O_3.

Further testing with solid matrix pyrolysis is planned and ongoing, which will also provide more insight into Ln surrogates for An.

Acknowledgements

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Xavier J. Robinson
University of New Mexico Undergraduate
xjrobin@sandia.gov