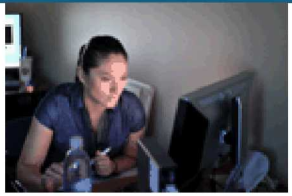
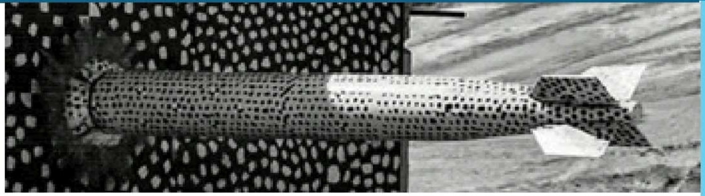
Dec 13-17 Pacific Rim Thermal Engineering Conference

Maui, Hawaii, USA

SAND2020-0480C

Passive Entrainment of Solid Contaminants from Pool Fires





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Outline

Objectives

Introduce EIE entrainment

- What it is, and why we care
- Historical work

Experimental Methods

Simulation Methods

Preliminary Experimental Results

Summary

Objectives

Broadly, we are interested in understanding safety for handling radionuclides

Our projects on this topic are based on four theses:

1. That limited datasets exist that are the basis for radionuclide release (as per DOE Handbook 3010); need additional data
2. Development and acceptance of surrogates for hazardous materials enables experimental testing without the hazard
3. Simulations can help bridge the gap between surrogate behavior and actual material tests reducing the need for the hazard testing
4. Simulations when appropriately developed and characterized can be credible representations of physical behavior

Narrowly, we are focused here on one entrainment mechanism for creating respirable radionuclides we are calling evaporation induced entrainment (EIE)

We seek to understand this behavior in order to make credible predictions with simulation tools

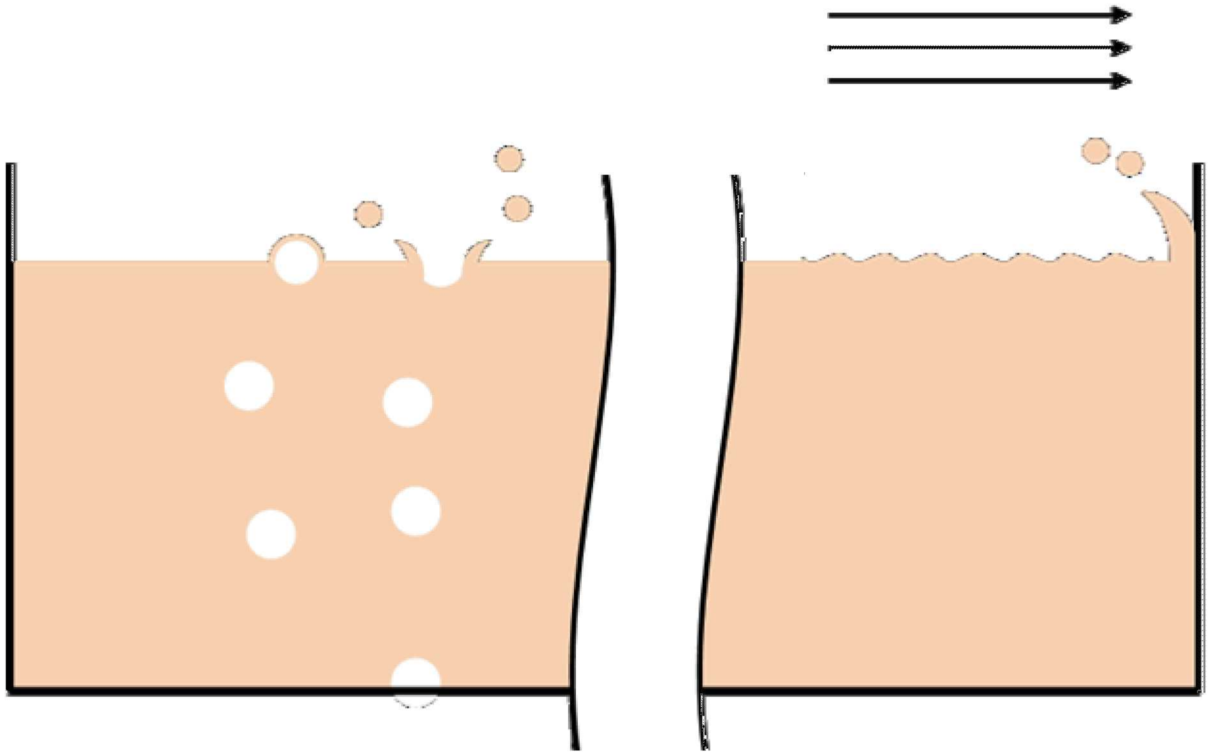
Entrainment Mechanisms

During Fire

After Fire

- Four natural mechanisms were identified
  - Evaporation Induced Entrainment
    - Particles ejected from pool by evaporating fluid
  - Surface Agitation by Wind
    - Strong winds create waves which suspend particles upon breaking
  - Surface Agitation by Boiling
    - Droplets become suspended as the gases rupture the liquid surface
  - Residue Entrainment (Resuspension)
    - After liquid has been consumed, remaining solid particles can erode by persisting flow conditions
- An external mechanism also exists
  - Impact Entrainment
    - Droplets (i.e. rain, water from suppression devices) can impact and disturb the fuel surface
    - Other such disturbance of the substrate (walking, collapsing structure, thermal stresses, etc.)

An Illustration of Two Mechanisms



<u>Surface Agitation by Boiling</u>
Involves pinch and rupture of bubbles

<u>Surface Agitation by Wind</u>
Involves waves created by flow

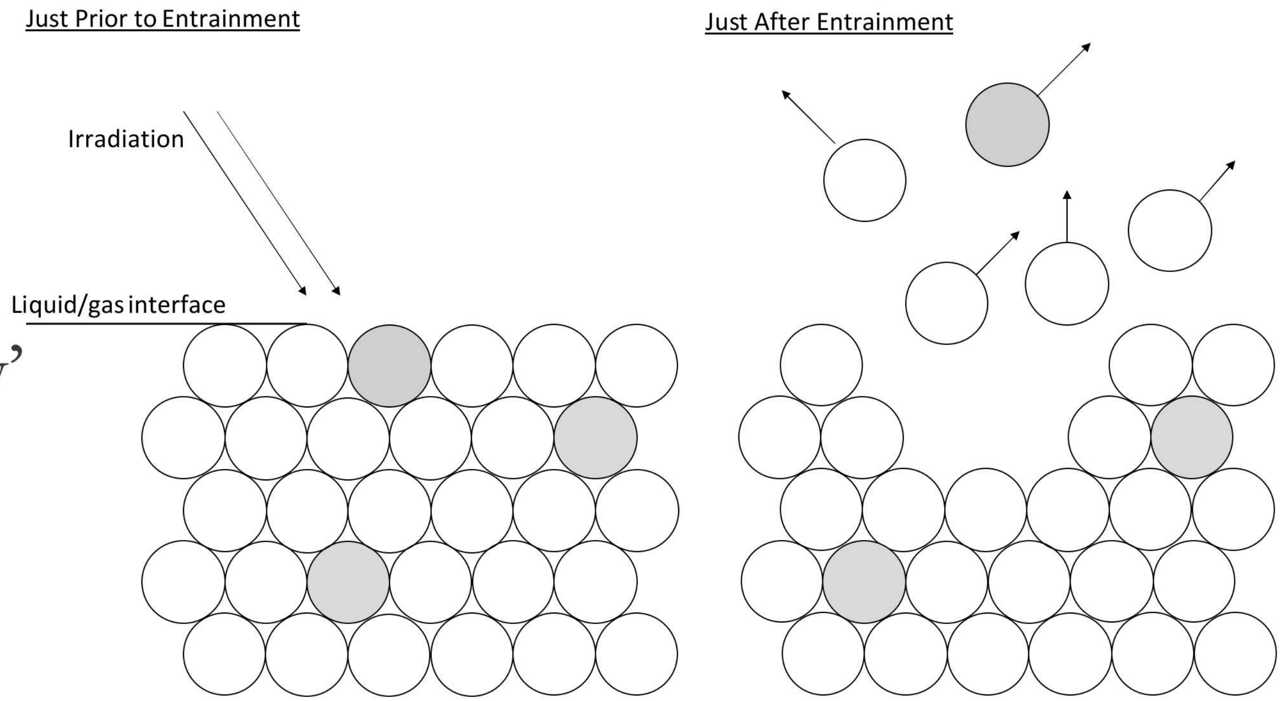
What is Evaporation Induced Entrainment (EIE)?

EIE requires no surface agitation

Particles entrained are well below their evaporation temperatures

Previous experiments have found that contaminants can release 'sympathetically' with an evaporating liquid well below the evaporation temperature of the contaminant

The schematic on the right represents our conceptual idea of the mechanism leading to EIE



Gray particles represent contaminants
White particles represent evaporating liquid

What indications do we have of EIE?

This is not a well studied field. It is a mix of colloquial evidence and testing that primarily goes back to a single report by Mishima et al. (1968)

- Using plutonium nitrate under air drying and forced drying (heated)
- Rates is generally low (non-zero) until surface agitates

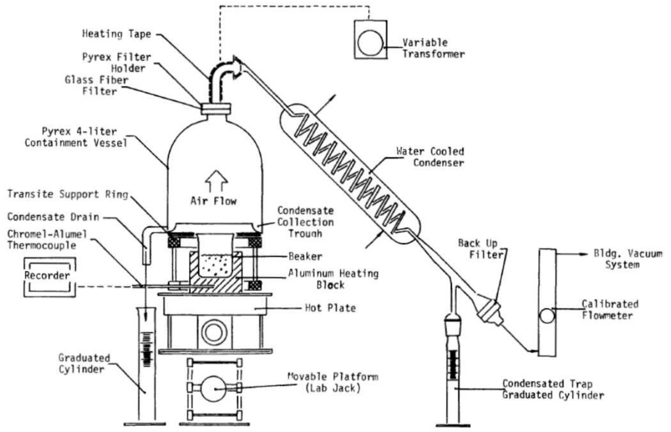
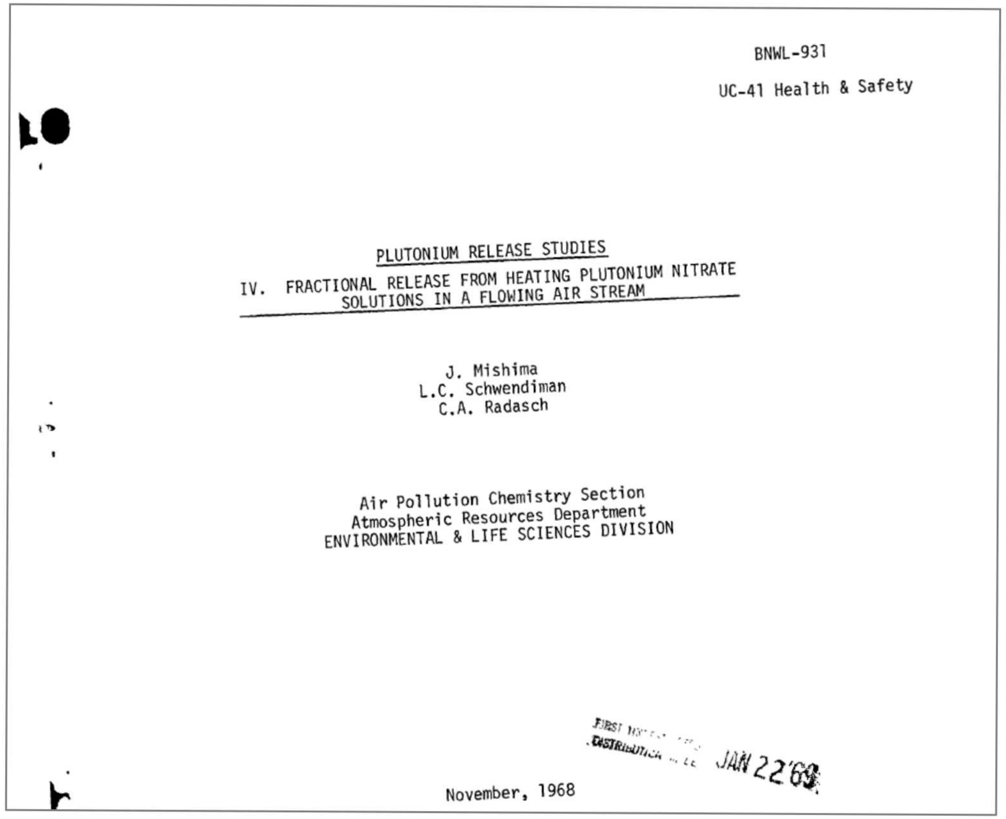


FIGURE 5

DIAGRAM OF APPARATUS USED TO DETERMINE FRACTIONAL RELEASES DURING THE HEATING OF POOLS OF PLUTONIUM NITRATE SOLUTIONS



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UC-41 Health & Safety

PLUTONIUM RELEASE STUDIES

IV. FRACTIONAL RELEASE FROM HEATING PLUTONIUM NITRATE SOLUTIONS IN A FLOWING AIR STREAM

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JAN 22 '69

November, 1968

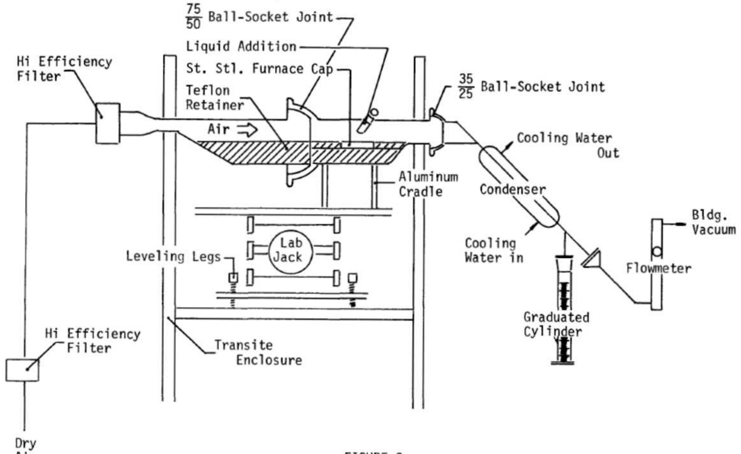


FIGURE 3

DIAGRAM OF APPARATUS USED IN AIR DRYING OF SHALLOW POOLS OF CONCENTRATED PLUTONIUM NITRATE SOLUTION

What is the liquid fuel source?

In historical work relating to the Plutonium Uranium Redox EXtraction (PUREX) process, we have TBP/Kerosene with nitrate and water

In Mishima et al. (1968) they used $Pu(NO_3)_6$ in dilute nitric acid

These are 'coordination complexes,' which are weakly or covalent bound liquid molecules

- My formal education did not include specific introduction to coordination complexes, only that weaker bonds than ionic and covalent exist
- Bond strength depends on atomic number

How these behave in evaporating conditions is not clear, but key to understanding historical EIE

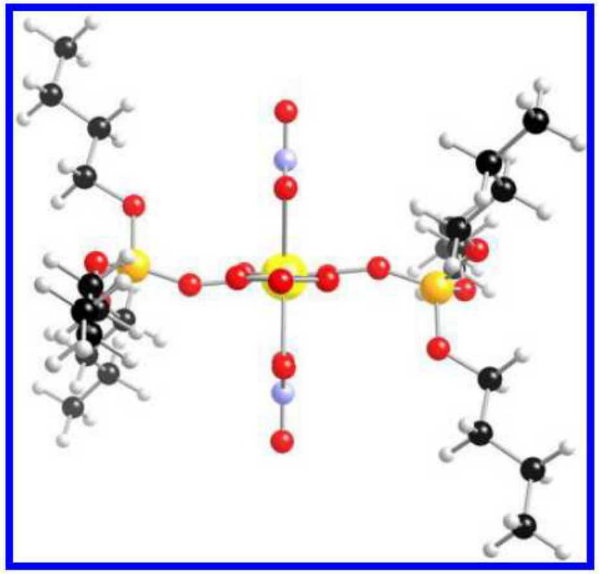


Figure 3. Structure of $Pu(NO_3)_4(TBP)_2$ complex.

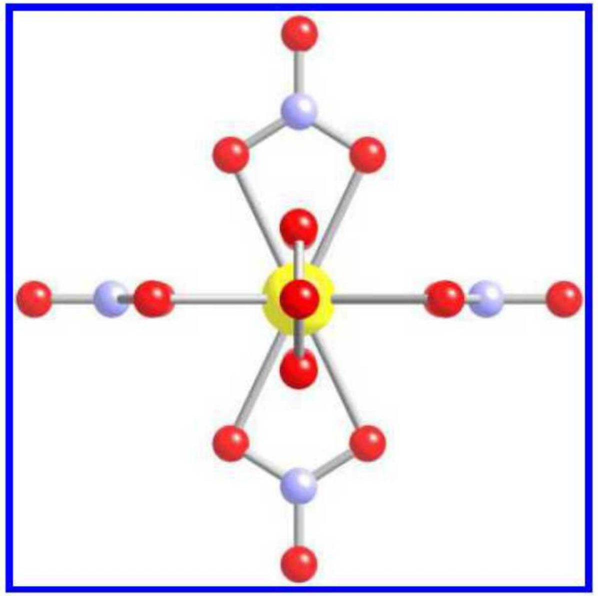


Figure 1. Perspective view of the $Pu(NO_3)_6^{2-}$ complex.

Šulka, M., Cantrel, L. and Vallet, V., 2014. Theoretical study of plutonium (IV) complexes formed within the PUREX process: A proposal of a plutonium surrogate in fire conditions. *The Journal of Physical Chemistry A*, *118*(43), pp.10073-10080.

Constituent Boiling points

Water boils at 100 ºC

Kerosene boils around 150-300 ºC (engineeringtoolbox.com)

TBP boils at 289 ºC (pubchem; nih.gov)

Nitrate boils at 493 ºC (chemspider.com)

Plutonium melts at 639, boils at 3228 ºC (wikipedia.org)

We are investigating what happens to coordination complexes

We find bond energies reported for PUREX related compounds in the literature, but don't have a good understanding of the relation between evaporation and coordination complex dissociation

Partial decomposition may be happening in the liquid phase, ionic behavior

Extrapolation to other sources

We are not uniquely focused on PUREX sources of contaminants

- Any contaminant that is part of processing and operations is within purview
- Interest extends to surrogates that are used for tests due to a lower hazard profile

Wastes generated during the handling of nuclear materials might not be acid dissolved, may involve larger particles (oxides), solvents, wipes, etc.

EIE may be unique to complex chemistry due to the atom/molecular scale requirements

On Surrogacy

Chemical surrogates are a challenging topic

Surrogates are often conditional for a given use case

- What may make a good surrogate for case A may make a bad one for case B
- The key is to identify the ways a surrogate is to be similar, and make sure those remain consistent

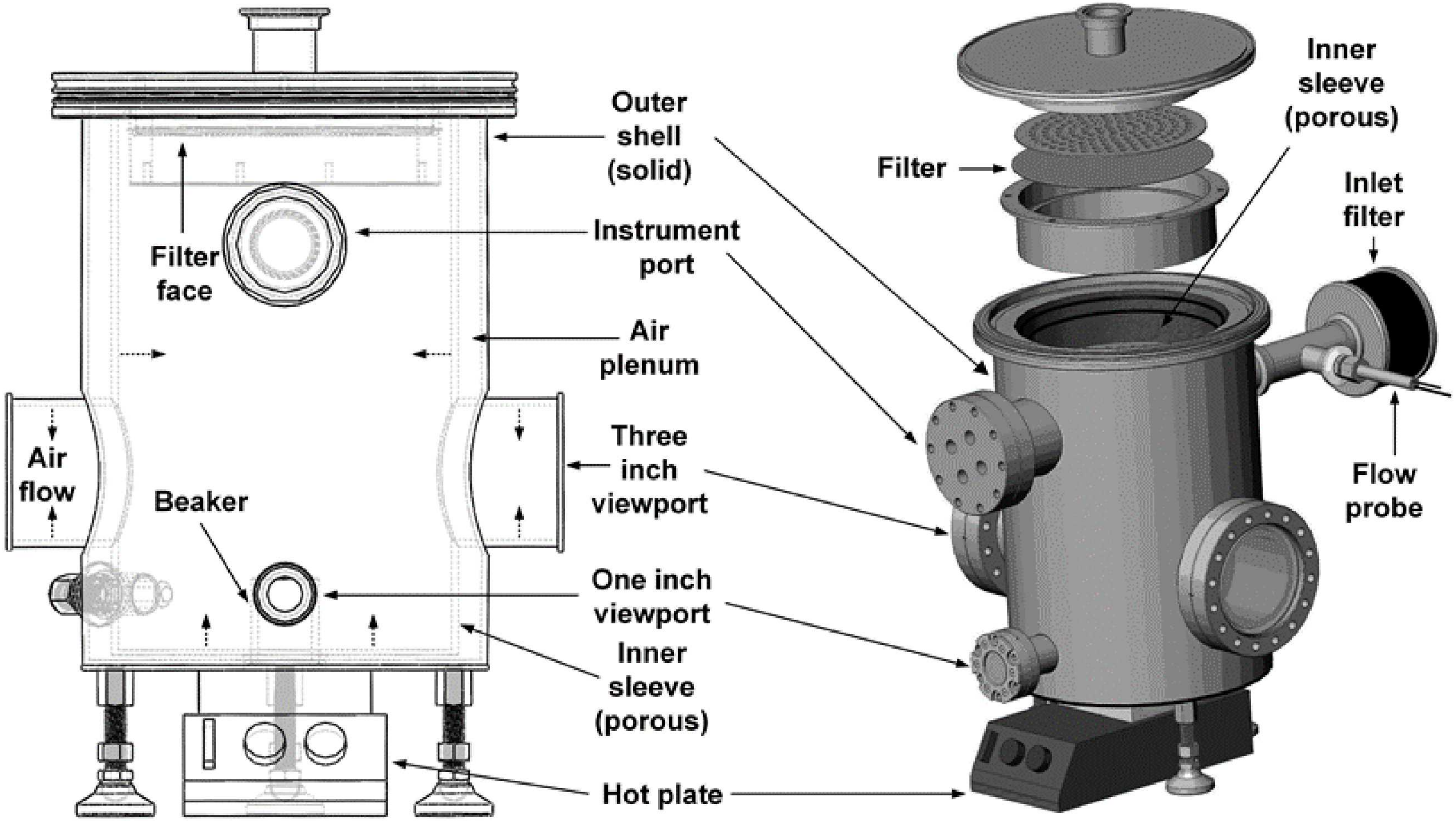
We are focused on surrogates. Two high-level aspects of concern:

- Liquid phase similarity (comparable evolution rates, similar solubility)
- Aerosol similarity (reactivity with soot, size density, aerodynamic behavior)

How will EIE results from limited data apply to other actinides/lanthanides?

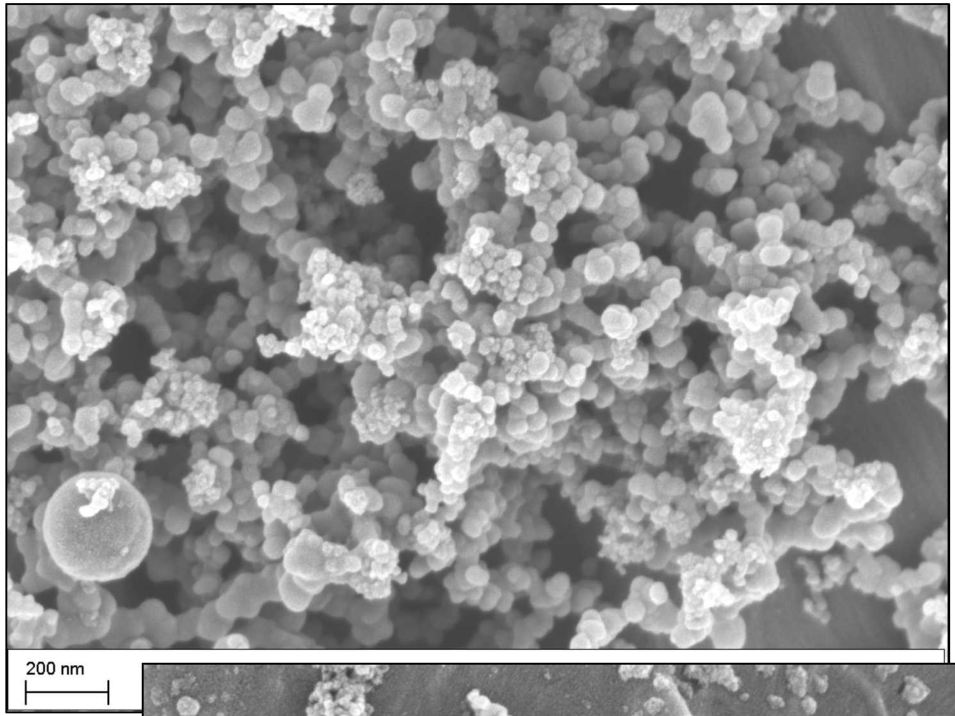
Experimental

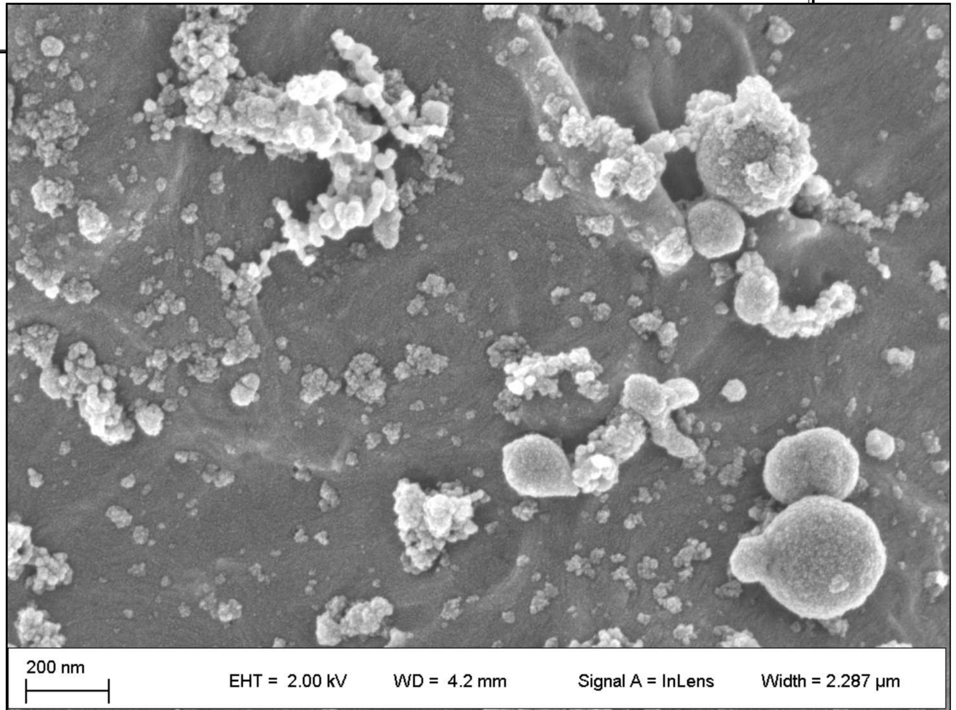
- We have designed a test enclosure to provide heating to a sample that off-gases or burns
- Heating from below or ignition through a side port
- Porous sleeve prevents wall deposition
- Particulates are collected for lab processing



Experimental Results

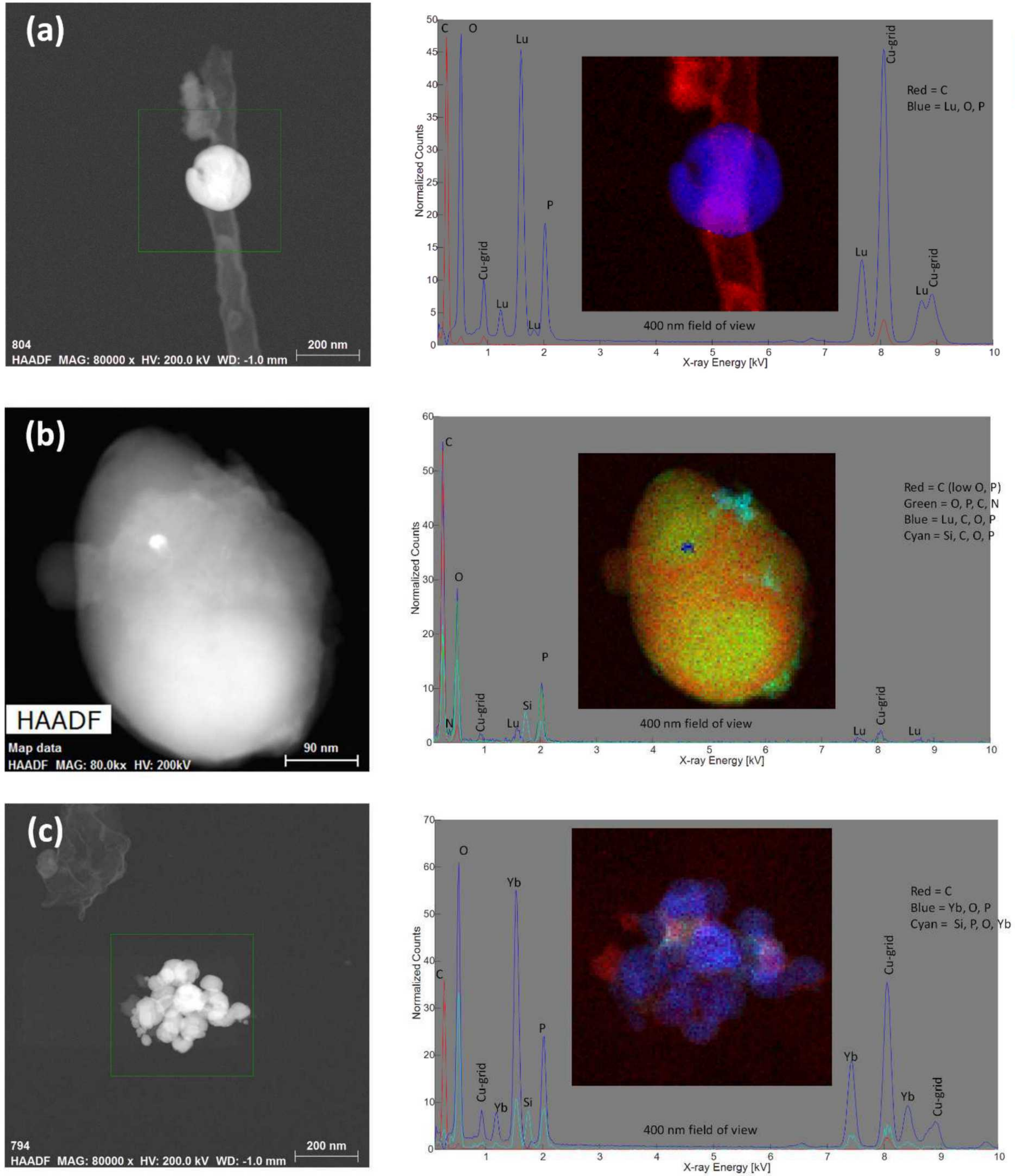
- Lutetium (Lu) and Ytterbium (Yb) were prepared as PUREX related samples
- Most tests involved burning
  - A few tests from heated evaporation only
  - All images shown here from burning tests
- SEM/TEM of collected samples from burn tests suggests:
  - 200 nm particles or aggregates
  - Variable carbon content in particles
  - Phosphorus, oxygen found with metals





Experimental Results

- Energy-dispersive X-ray spectroscopy provides speciation
- TEM imagery suggests the 200 nm particles are predominantly the contaminant as well as phosphorus and oxygen.
  - Suggests the P and the metal contaminant stay together, although the carbon from the ligands seems to be driven off
  - TBP is $(CH_3CH_2CH_2CH_2O)_3PO$



Modeling Methods

- At present we don't know enough about the chemical and evolutionary behavior of these metal contaminants for EIE
  - As a consequence we are using a simple model:

$$\dot{m}_{evap} \propto \dot{m}_{entrain}$$

- The model assumes the contaminant entrainment to be proportional to the evolution of the evaporating species
- We don't know when/how the aggregates or particles form
- Prior work on release from fire suggests similar mechanism (related to soot formation rate):

Ballinger, M.Y., Owczarski, P.C., Hashimoto, K., Nishio, G., Jordan, S. and Lindner, W., 1988. Aerosols released in accidents in reprocessing plants. *Nuclear Technology*, *81*(2), pp.278-292.

- For PUREX related emissions, we may assume metal contaminants with significant inorganic content based on test results
- For oxides, further evaluations are necessary
  - We suspect based on prior work that oxides may interact catalytically with the soot, while inorganic solids may not
  - Release by EIE may not be possible

Path Forward

- We are commissioning simulations using molecular dynamics to probe the evaporative behavior of complexes in relevant conditions
- We will be evaluating our test results for additional insight
- Modeling motivated by fire release experiments
- More emphasis will be placed on other mechanisms moving forward
  - Boiling mechanism is the most studied
  - Probably the most significant as well

Ballinger, M.Y., Owczarski, P.C., Hashimoto, K., Nishio, G., Jordan, S. and Lindner, W., 1988. Aerosols released in accidents in reprocessing plants. *Nuclear Technology*, *81*(2), pp.278-292.

Retrospective

- Coordination complexes apparently only exist in the liquid phase (solution)
  - How to simulate their gas-phase evolution is not clear
  - Test results suggest 200-1000 nm particles or aggregates form containing atoms from the source metals and ligands in fire tests
  - Mishima et al (1968) suggest ~20 μm particles from their experiments, no information on constituency
- Onus on simulation team or future data collection to provide/estimate release constant for modeling
- Even though complexes only exist in solution, it appears that the output particles contain ligand moieties from the solution complex in fire products
  - This suggests the metals may not undergo full dissociation with ligands in the process

Summary

- EIE is a less studied mechanism that results in particulate contaminant entrainment from liquids
  - New analytical techniques and literature data help improve the understanding of this entrainment mechanism
  - Recent tests are adding to the information available
  - Model approximations are being made with a simple relation, needs validation
- Ytterbium and Lutetium appear at first inspection to be reasonable surrogates for PUREX metals
- More information needed on oxide evolution

Extras