Isolation of Metals from Liquid Wastes: Reactive Scavenging by Sorbents in Turbulent Thermal Reactors

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Project Overview

Abstract

A large portion of the Department of Energy (DOE) radioactive waste inventory is composed of metal-bearing liquid wastes. These wastes contain a variety of metals and organic species. It is highly desirable to concentrate the metals in order to reduce the volume of these wastes and to render them into an environmentally benign form. One method for doing this is the high-temperature reactive capture of the metals by sorbents. High-temperature scavenging by sorbents has been demonstrated for a variety of toxic metals. This method not only captures the metals, but also destroys almost all of the organic species present in the wastes. The current work focuses on two particular metals, which are present in the DOE inventory as radioactive isotopes: cesium and strontium.

The Problem

- To dispose radioactive wastes in an environmentally benign manner.
- To isolate the semi-volatile and non-volatile radioactive wastes within the DOE liquid mixed waste inventory from the environment.
- To simultaneously destroy any organic compounds present.

A Possible Solution

- Employ thermal treatment in turbulent flow reactors to destroy organic components and isolate radioactive metals.
- Exploit the application of high-temperature sorbents which will chemically combine with radioactive metals to form glassy melts.

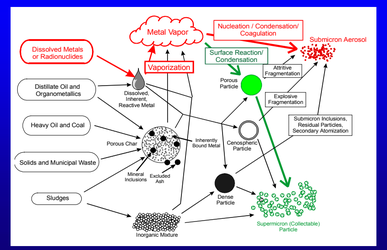


Figure 1: Partitioning mechanisms on combustion systems

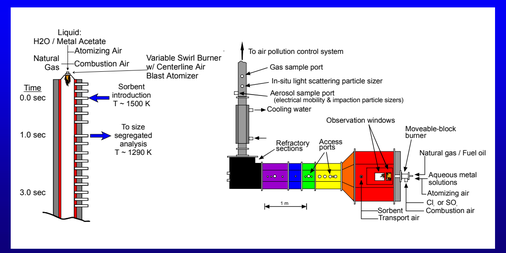


Figure 2: Laboratory combustors at the University of Arizona and at the US EPA's Research Triangle Park laboratory

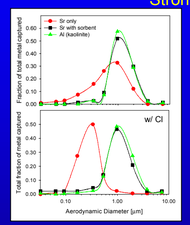
Overall Approach

- Interdisciplinary, collaborative research involving five senior scientists at the University of Arizona, the University of Illinois, Sandia National Laboratories at Livermore, and the EPA National Risk Management Research Laboratory at Research Triangle Park.
- **Validation of the overall solution concept**
  - Screening experiments on capture of cesium and strontium by sorbents, such as kaolinite, hydrated lime, and a commercially available combination of the two (University of Arizona)
- **Predictive modeling to ensure performance and environmental safety**
  - Droplet trajectories in turbulent flows using the One Dimensional Turbulence Model (University of Arizona/Sandia National Laboratories) with improved estimation of droplet drag coefficients (University of Illinois).
- **Experimental determination of kinetic parameters and model calibration**
  - Laser sheet diagnostics to find 'rogue' droplet positions and measure droplet destruction rates(University of Illinois).
  - Laser beam diagnostics for *in-situ* multi-element assays(University of Illinois).
  - Apply to laminar (University of Arizona) and turbulent (US EPA) flow reactors

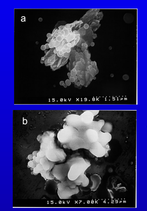
Solution Concept Validation

- Focus on two metals, cesium and strontium, which are present at DOE waste sites.
- Screening test performed to examine sorbent/metal interactions for these waste metals and to explore the effect of other chemical species (Cl and S) on capture.
- Aqueous solutions injected into flame of downflow reactor (Fig2) with sorbent particle introduce in the post flame
- Particle size distributions (PSDs) are examined to determine the effect of sorbent on partitioning of metal
- Sorbent examined were lime, kaolinite and a commercially available mixture of the two.
- Results for kaolinite/metal tests shown here for brevity.
- All experiments were conducted with Sr conc. = 100ppm Kaolinite = ~2g/min, Molar Ratio (sorbent/metal) ~3, Residence time=~0.6s and 1000ppm Cl where appropriate.

Strontium Interaction with Kaolinite

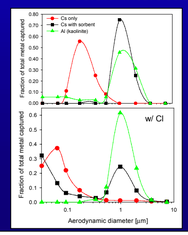


- Without Cl in system, Sr does not appear to vaporize.
- Interactions may be result of coagulation processes.
- With Cl, Sr vaporizes and appears to be captured by kaolinite



- Panel (a) is SEM picture of Sr particles agglomerated to larger kaolinite particles for No Cl case.
- Significant melting of kaolinite particles in Panel (b) indicates Sr/kaolinite reaction.

Cesium Interaction with Kaolinite



- Kaolinite reactively captures cesium vapor
- Presence of Cl, causes reduction of kaolinite ability to capture cesium

Conclusion

- High temperature injection of kaolinite reactively captures strontium and cesium.
- When injected without chlorine, Sr does not vaporize and subsequently cannot react with kaolinite particles.
- Presence of chlorine allows Sr to vaporize and react with kaolinite sorbent particles.
- Sr is nearly entirely captured by kaolinite in presence of chlorine
- Cesium is effectively captured by kaolinite.
- For a given sorbent feed rate, the presence of chlorine reduces, but does not eliminate, the effectiveness of kaolinite at capturing cesium.
- Kaolinite shows promise at controlling cesium and strontium

Performance and Safety Model

Objective

PRIMARY OBJECTIVE: Construct an accurate model of turbulent flow reactor to ensure the performance and safety of proposed treatment alternative

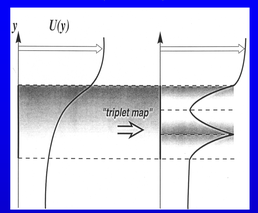
Introduction

- "Rogue" droplets, 10x the mean diameter have been observed in thermal treatment processes
- For example, one rogue droplet will fail the 99.99% conversion criteria.
- Experiments by Mulholland et.al. (1991) injected uniform diameter drops with uniform spacing and identical injection angle into a combustion chamber. They found a wide spread in the trajectory end points (or burn out points).
- Initial model development is validated against the experimental data reported by Mulholland.

One Dimensional Turbulence / Droplet Model

One Dimensional Turbulence Model (Sandia/UA)

- Simulates the evolution of the transverse velocity and temperature profiles.
- Uses conventional transport equations omitting advection and pressure terms.
- Implements triplet maps to account for missing terms which represent turbulent 'eddies'.
- Varies droplet (velocity and position) according to a droplet drag law.

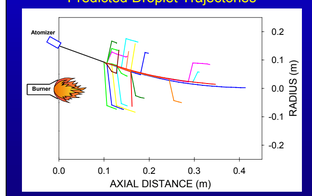


Droplet Drag Coefficient Model (UIUC)

- In this work, we are developing techniques to assess the extent to which drop trajectories deviate from streamlines of the surrounding gas flow.
- Large drops have significant deformation and inertial effects
- The drag coefficient and projected area are computed using a free-surface finite-element code that computes solutions of the full Navier-Stokes solutions, including the drop shape.
- The code is steady, which requires that the dynamics of the drop be fast compared to the time scale on which changes.
- For drops no larger than a few mm, this is an excellent approximation
- For water drops moving through air, over a wide range of drop sizes and relative velocities. Significant deformation is predicted for drops on the order of 1 mm at relative velocities typical of spray systems.

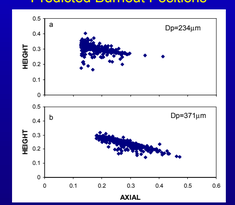
Results

Predicted Droplet Trajectories



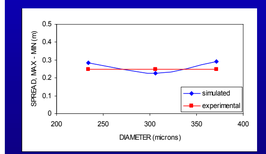
- Predictions from ODT-droplet model for select cases
- Demonstrates random trajectories generated by interactions with eddies
- Appears to 'realistically' represent droplet behavior

Predicted Burnout Positions



- Predicted trajectory endpoints represent 'rogue' droplet burnout positions.
- Larger droplets persist at further axial distances in reactor.

Droplet Spread: Predicted vs. Experimental



- Droplet spread = difference between closest and furthest axial burnout positions.
- Predicted droplet spread shows excellent agreement with reported experimental data

Conclusions

- An ODT-droplet trajectory model was developed to examine the performance and safety of a thermal treatment process for metal containing wastes.
- The ODT model is able to predict experimentally measured mean velocity and temperature fields in a turbulent flow combustor.
- The model accurately predicts existing experimental data on the effect of droplet diameter on the *spread* of droplet burnout points (due to turbulence) without the cost and effort of a 3-dimensional, DNS calculation.
- The model also predicts experimental data on effects of droplet velocity, and angle of injection (not shown here) although it failed at predicting effects of droplet spacing, since this was not included so far.
- Advanced computed droplet drag models predict significant deformation for drop diameters greater than 1mm.

References

1. Mulholland, J.A., Srivasta, R.K., Wendt, J.O.L., Agrawal, S.R., and Lanier, W.S., *Trajectory and Incineration of Rogue Droplets in a Turbulent Diffusion Flame*, Combust. Flame, 86: 297-310 (1991).
2. Kerstein, Alan R., *One-dimensional turbulence: Model formulation and application to homogeneous turbulence, shear flows, and buoyant stratified flows*, J. Fluid Mech. (1999)

In-situ Diagnostics

Mie/Rayleigh scattering measurements

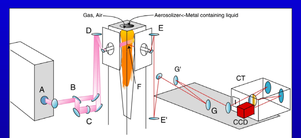
- XeCl excimer laser (=308 nm, labeled "A") light focused into a thin sheet by a cylindrical mirror (D) illuminates the experimental volume.
- Mie/Rayleigh Scattered light is collected for images that contain size and spatial information of particles.
- The images will be wavelength resolved by passing them through a Czerny-Turner spectrograph (CT).
- Alternatively, the simultaneous collection of PLIF images and the measurement of Mie/Rayleigh scattering at the laser focus (F) are possible, using only a bandpass filter, parabolic mirrors, and an ungated detector.

Planar-Laser-Induced-Fluorescence (PLIF) spectroscopy

- The spatial distribution of vaporized metal species can be imaged using fluorescence of vaporized metal species.
- Initial experiments will involve aluminum containing drops (Al absorbs 308 nm light, and emits at 396 nm).
- Exciplex fluorescence from organic species dissolved in the liquid stream will allow measurement of drop temperature, in the manner of Melton et al.

Laser Induced Plasma Breakdown Spectroscopy (LIBS)

- Detection of metal species that do not absorb 308 nm light can be accomplished by recording spontaneous emission.
- Sufficient laser power densities for plasma excitation will be accomplished by splitting (B) off a portion of the laser beam and focusing it to a spot with a lens (C).



A	XeCl Excimer Laser (λ = 308 nm)	E,E'	Parabolic Mirrors (1st Pair)
B	50% Beamsplitter	G,G'	Parabolic Mirrors (2nd Pair)
C	Lens (LIBS Experiment)	CT	Czerny-Turner Spectrograph
D	Cylindrical Focusing Mirror	CCD	CCD Camera
F	Laser Focus, center of the combustor		

Conclusions

- Thermal treatment of metal containing liquid wastes in turbulent flow reactors appears to be a promising option for the safe environmentally benign disposal of these wastes. This process reduces the waste volume, and provides for isolation of the radioactive metal components contained therein. It also destroys any toxic organic matter present in the wastes.
- Proof of concepts tests show that cesium and strontium can be reactively scavenged at high temperatures by kaolinite which is present in the disperse phase.
- Theoretical results suggest that one can predict possible failure modes inherent in this process.
- More work is needed on model development, model validation and experimental determination of parameters necessary for the design of a fail-safe system.

Future Work

- Extend ODT/Droplet model to include
  - improvements in sub-models for drag coefficients and droplet/eddy interactions.
  - effects of droplet spacing and droplet combustion chemistry
  - more accurate simulation of three velocity components
- Complete systematic experiments for verification and calibration of the ODT/Droplet model, using laminar flow furnace and both cold flow and hot flow turbulent furnaces.
- Finish construction of laser diagnostic system and complete *in-situ* measurements in laminar and turbulent flow reactors

Publications

- Davis, S.B., Amos, J.M., Gale, T.K., Wendt, J.O.L., Biermann, J.J.B. and Voogt, N., "Use of Sorbents from Paper recycling Wastes for the High Temperature Capture of Multiple Metals in the Presence of Chlorine" presented at 4th International Symposium & Exhibition on Gas Cleaning at High Temperatures, , University of Karlsruhe (TH),Sep 22-24, 1999.
- Amos, J.M. and J.O.L.Wendt, "High Temperature Scavenging of Cesium and Strontium by Sorbents", Poster presented at Joint Meeting of the US Sections of the Combustion Institute, George Washington University, Washington, DC March 1999
- Schmidt J.R., Kerstein, A.R., and J.O.L. Wendt, "Trajectories of Evaporating Droplets in Highly Turbulent Flows using the One Dimensional Turbulence Model" presented at the Fall Meeting of the Western States Section of the Combustion Institute, Colorado Springs, Colorado, March 13-14, 2000, to be submitted for publication in Combust. Flame
- Amos J.M., Davis, S.B., and J.O.L. Wendt, "Evaluation of Sorbent to Reduce Radionuclide Emissions from Mixed Waste Incineration", to be submitted for publication to Environ. Sci. and Technol., March 2000

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