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

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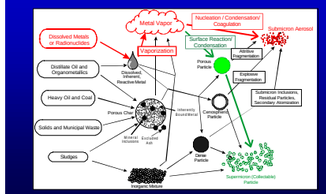
Research Objectives

- Understand high-temperature reaction kinetics between sorbent substrates and certain volatile and semi-volatile metals in the DOE liquid waste inventory (e.g., Cs and Sr), using a laminar-flow reactor for which extraction of kinetic data is not complicated by turbulence;
- Develop models to predict both trajectories of individual droplets in turbulent high temperature reactors, and rates of metal evolution from droplets, and compare model predictions with experimental data from a pilot scale turbulent thermal reactor;
- Connect the reaction kinetic models with the droplet trajectory/mass evolution models, in order to predict and optimize metal scavenging processes in turbulent flow reactors, and to test these combined models against data taken from a turbulent high temperature reactor.

Metal Partitioning Mechanisms



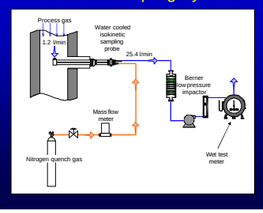
Approach

- Conduct 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.
- Perform screening experiments on a 17 kW University of Arizona (UA) laminar flow reactor with:
  1. *ex-situ* analysis of extracted size segregated particulate samples
  2. both aqueous salt solutions *and* organometallic liquids as metal inputs
  3. kaolinite injected in disperse phase in the post flame as sorbent substrates
  4. chlorine and SO_2 injection
- Design and construct a unique laser *in-situ* diagnostic system for drop position and size measurement, and for analysis of metallic species in solid and vapor phases (UIUC), to be used for both UA laminar flow and EPA turbulent flow reactors.
- Test laser diagnostic system on UA laminar flow reactor.
- Measure drop trajectories and metal species in UA laminar flow reactor using UIUC diagnostic system.
- Model kinetics of interaction between metal vapor and dispersed phase sorbent substrates

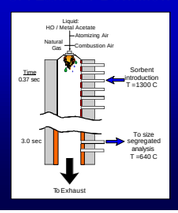
Approach (continued)

- Model drag forces of large and small evaporating drops and compare model with drop trajectory data in UA laminar flow reactor.
- Develop model to predict *distributions* of trajectories of drops in turbulent flow, using Kerstein's One Dimensional Turbulence model.
  1. Incorporate droplet trajectory model into existing 1-D Turbulence code at Sandia Laboratories.
  2. Qualitatively check out code with existing droplet trajectory data in turbulent flows.
  3. Incorporate various drag models for large evaporating drops.
  4. Verify model with droplet imaging data obtained from EPA turbulent flow reactor.
- Connect the reaction kinetic models with the drop trajectory/mass evolution models for turbulent flow reactors.
- Move laser diagnostic system to EPA turbulent flow reactor to measure drop position and size, and metal speciation.
- Conduct metal scavenging experiments with turbulent flow reactor at EPA, using *both* available particulate sizing and speciation analysis tools *and* newly installed laser imaging instrumentation.
- Compare turbulent flow metal scavenging data with predictions.
- Use model to optimize process and eliminate escape of waste products into the atmosphere.

Particulate Sampling System



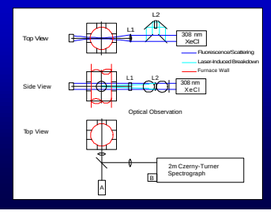
UA Laminar Downflow Combustor



Residence times and temperature profile are similar to practical systems.

Inner diameter	.15 cm
Height	6 m
Heat Load	< 22 kW

UIUC Laser Diagnostic System



Optical Diagnostics

A sheet of laser light from a 5-10 Hz XeCl pulsed laser (308 nm) excites fluorescence, scattering, and laser-induced incandescence in the flame. This is observed by a video camera through filters (to monitor flame stability and gross features) and by a spectrograph with intensified, gated charge-coupled array detector (ICCD). Figures schematically represent mechanical and optical details.

Furnace Illumination

The laser beam is split into two, 200 MW peak power beams. One (dark blue) is focused by a cylindrical optic (L1) to a sheet of illumination viewed face-on by the observation optics. The other (light blue) is focused by two cylindrical optics (L2, followed by L1) to a ~ 300 μm focus, producing laser-induced breakdown. All observations must contend with a 1500 K blackbody background from the furnace wall (red). Actual geometry avoids the Mach-Zehnder interferometer geometry apparent in the sketch.

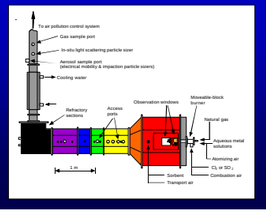
Optical Observation

One camera (A) is an ordinary camcorder, viewing the flame for unanticipated activity and (in 5-10 of its 30 frames per second) for the spatial/spectral integral of the effect of laser illumination. The other (B) is on the focal plane of a high-dispersion spectrograph. With judicious choice of intermediate optics (not shown), a spectrally-resolved image of a 5 cm by 10 cm section of the flame can be observed by the gated detector. Gating prevents saturation of the detector by the blackbody continuum.

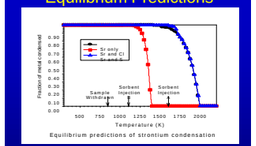
Feasible Experiments

- Rayleigh scattering from soot; laser-induced incandescence
- Mie scattering from drops; direct optical size measurement for ≥75μm.
- Temperature measurement from liquid-phase exciplex fluorescence
- Temperature measurement from OH fluorescence
- Point-wise elemental composition by laser-induced breakdown
- Spatially-resolved spontaneous emission by metal atoms and molecular radicals
- Drop trajectory mapping
- Vaporization and condensation rate measurement

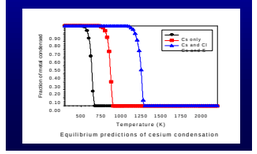
U.S. EPA Turbulent Flow Combustor



Equilibrium Predictions



Equilibrium predictions of strontium condensation



Equilibrium predictions of cesium condensation

Screening Tests Completed

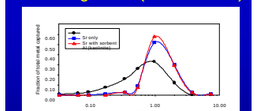
I. Strontium interactions with kaolinite sorbent in the absence of sulfur and chlorine

II. Effect of sulfur on strontium capture

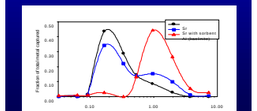
III. Effect of chlorine on strontium capture

IV. Effect of sorbent injection temperature, above and below the metal dewpoint, in presence of chlorine

Screening Tests (Sr / Kaolinite)

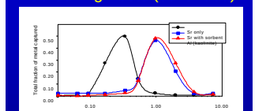


I. Size distribution of strontium with and without sorbent, no S, no Cl

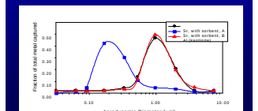


II. Size distribution of strontium with 1000 ppm sulfur, with and without sorbent

Screening Tests (continued)



III. Size distribution of strontium with 2000 ppm chlorine, with and without sorbent



IV. Temperature dependence of strontium capture with 2000 ppm chlorine. A denotes kaolinite injection at 1580 K; B denotes kaolinite injection at 1100 K.

Interim Conclusions

- Strontium alone does not appear to vaporize at combustion temperatures and appears to be only *minimally* captured by commercial kaolinite sorbent, in the post-flame, possibly through physical coagulation processes, rather than through chemical scavenging processes.
- In contrast to equilibrium predictions, sulfur appeared to enhance strontium vaporization in the flame. The strontium subsequently nucleated to form small particles. However, sulfur did not significantly enhance strontium capture by the kaolinite.
- Chlorine enhances vaporization of strontium and, without a sorbent present, causes the strontium to be sampled as very small particles in the condensed nuclei particle size mode.
- The presence of chlorine allows strontium to be *almost completely reactively* scavenged by kaolinite powder, provided the powder is injected into the reactor at a temperature above the predicted dew point of the strontium compounds present.
- When sorbent injection occurs below the predicted dew point of the strontium compounds, almost no capture occurs.
- Chlorine can be used to enable nonvolatile metals like strontium to be reactively scavenged by dispersed commercial sorbents, at high temperatures. In this respect, strontium behaves similarly to nickel.
- Equilibrium predictions suggest that cesium is easily vaporized and hence it may be conjectured that commercial kaolinite might be an effective sorbent for this metal. Experimental work is currently underway to test this.