Thermal Properties Measurements of Molten Salts At Argonne National Laboratory

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Objective: Provide the data necessary to build a FOAK MSR by 2035

Targeting molten salt reactor developer needs to support design, licensing and operation of molten salt reactors

- Thermochemical and thermophysical properties of molten salts
  - Generating quality data to predict the behavior of molten salts during normal and transient operations (Melissa Rose)

- Real-time chemistry monitoring and accountancy of materials in MSRs
  - Developing accurate sensors resistant to radiation damage and corrosive molten salt environments (Nathan Hoyt)

- Accident scenario analyses supporting the licensing process
  - Generating data needed to simulate salt spills, spreading behavior, and release of FPs as aerosols and vapor (Sara Thomas)
Generating Thermal Property Data

Predicting molten salt behavior during normal and transient conditions requires knowledge of property values over a range of temperatures and compositions

- Generating quality data for systems of interest to MSR developers for which limited or no data exists
  - Supporting development of the Molten Salt Thermal Database (MSTDB)

- Developing capabilities to measure salt property values under more extreme conditions relevant to MSRs (higher temperatures, more corrosive salts)

Measuring plutonium-bearing salts as well as binary and ternary uranium-bearing mixtures to expand the database of relevant mixtures available to developers
Laboratory Capabilities

- Radiological facility housing purpose-built inert atmosphere gloveboxes used for experiments with actinides, beryllium and simulated fission products
  - Glovebox furnace wells from six to thirty-six inches with furnace capability to 800°C
  - Induction and resistance furnaces for higher temperature applications

- Expertise and capabilities in areas essential to advancement of molten salt nuclear energy systems:
  - Thermophysical property measurements
  - Materials compatibility and corrosion studies
  - Electrochemical monitoring and control of salt chemistry and materials accountability
  - Linking understanding of fuel cycle chemistry and engineering

Thermophysics laboratory with equipment located in Ar-atmosphere radiological gloveboxes
Molten Salt Property Measurement capabilities at Argonne

<table>
<thead>
<tr>
<th>Property</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density, volumetric thermal expansion and surface tension</td>
<td>Archimedes method (in Ar-atmosphere rad glovebox)</td>
</tr>
<tr>
<td>Heat capacity, melting point, phase equilibria</td>
<td>Differential scanning calorimeter (DSC) (in Ar-atmosphere rad glovebox)</td>
</tr>
<tr>
<td>Viscosity</td>
<td>Rotating spindle viscometer (in Ar-atmosphere rad glovebox)</td>
</tr>
<tr>
<td>Thermal diffusivity &amp; thermal conductivity</td>
<td>Laser flash analysis system (in rad hood with Ar purge or under vacuum)</td>
</tr>
<tr>
<td>Fission product &amp; actinide solubility</td>
<td>Chemical analyses and DSC</td>
</tr>
<tr>
<td>Mass transfer diffusion coefficients</td>
<td>Restricted diffusion cells (in Ar-atmosphere rad glovebox)</td>
</tr>
<tr>
<td>Vapor Pressure</td>
<td>Coupled Thermogravimetric Analysis with Quadrupole Mass Spectrometry</td>
</tr>
</tbody>
</table>
Molten Salt Chemical Analysis Capabilities

On-site analytical chemistry laboratory provides rapid turn-around molten salt analyses

<table>
<thead>
<tr>
<th>Method</th>
<th>Compositional Information</th>
</tr>
</thead>
<tbody>
<tr>
<td>ICP-OES</td>
<td>Elemental analysis ppm level</td>
</tr>
<tr>
<td>ICP-MS</td>
<td>Elemental analysis at &lt;ppm level</td>
</tr>
<tr>
<td>XRD</td>
<td>Identification of crystalline phase composition</td>
</tr>
<tr>
<td>Alpha Spectroscopy</td>
<td>Identification and quantification of alpha-emitting isotopes</td>
</tr>
<tr>
<td>Gamma Spectroscopy</td>
<td>Identification and quantification of gamma-emitting isotopes</td>
</tr>
<tr>
<td>Liquid Scintillation Counting</td>
<td>Measurement of alpha/beta activity</td>
</tr>
<tr>
<td>Raman Spectroscopy</td>
<td>Measurement of speciation (vibrational modes of ionic clusters)</td>
</tr>
<tr>
<td>Inert gas fusion (LECO)</td>
<td>Quantification of C, S, O, N contaminants at &lt;1 mg/g level</td>
</tr>
</tbody>
</table>

LECO measurement of oxide concentration in molten salt including beryllium salts

Raman spectroscopy of molten salts
- Spectroscopy from ~15 to ~3500 cm⁻¹
- Portable and reconfigurable
- Microspectroscopy
NaCl-KCl-UCl₃ measurements vs. modeling

- Measured the thermal properties of (43.1-31.2-25.7 mol%) NaCl-KCl-UCl₃
- Use of values in MSTDB underpredicts liquidus temperature significantly

**DSC of (43.1-31.2-25.7 mol%) NaCl-KCl-UCl₃**

<table>
<thead>
<tr>
<th>DSC Feature</th>
<th>Reaction</th>
<th>Measured Temp.</th>
<th>Predicted Temp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Solid $\rightarrow$ Liquid + UK₂Cl₅ + (Na,K)Cl</td>
<td>474 ± 2 °C</td>
<td>465 °C</td>
</tr>
<tr>
<td>2</td>
<td>Melting (Na,K)Cl $\rightarrow$ Liquid + UK₂Cl₅</td>
<td>505 ± 2 °C</td>
<td>484 °C</td>
</tr>
<tr>
<td>3</td>
<td>Liquidus</td>
<td>587 ± 2 °C</td>
<td>502 °C</td>
</tr>
</tbody>
</table>
Sealable cells are required for high quality heat capacity measurements using DSC:

- Developing robust mechanically sealable cells for use above 750 °C
- Cells must be inert to a variety of molten salts and retain malleability to be sealable

- Ni and Mo of various thicknesses were tested for required shaping and sealing
- Different annealing procedures were attempted and Ni and Mo were not found to be satisfactory
- Next set of cells will be fabricated from Pt alloys
The binary NaCl-PuCl₃ system was examined to support developer needs

- Few empirical investigations into the phase equilibria of this system exist
- Eutectic composition is likely between 36 and 38.3 mol % PuCl₃ based on published studies
- Phase equilibria measured for series of near-eutectic compositions by using DSC
  - 59.9, 49.6 and 38.3 mol % PuCl₃
  - Still measuring 37.4, 36, 30 and 20 mol % PuCl₃
- Heat Capacity of 36, 37.4 and 38.3 mol % PuCl₃ are being measured by DSC for both the solid and liquid phases
Thermal Diffusivity Measurements of NaCl-KCl-UCl₃ System

- Thermal diffusivities of (43.1-31.2-25.7 mol%) NaCl-KCl-UCl₃ and (66-34 mol%) NaCl-UCl₃ measured using laser flash analyzer.
- A laser pulse is applied to one surface of a sample and the temperature response vs time at the other side is measured.
- Graphite sample cells are used to contain salts.

Graphical representation of thermal diffusivity measurements with error bars indicating average and standard deviation of three measurements at each temperature.
Viscosity Measurements Using a Rotational Viscometer

- A spindle is submerged in a molten salt and the torque required to maintain a constant rotational velocity is measured.

- Parameter values affecting measurements:
  - Temperature stability
  - Volume of fluid above spindle
  - Turbulence in fluid
  - Impurities (e.g., undissolved solids)

- Have measured viscosities of reference salts and actinide-bearing chloride and fluoride salts for private sponsors
  - Determined precision and accuracy using reference fluids

Viscosity measurements of FLiNaK compared to literature data. Measurements are average and one standard deviation of 15 measurements at each temperature.
Summary

Argonne is generating high quality property data to enable a FOAK MSR by 2035

- Generating high quality data for NaCl-UCl₃, NaCl-KCl-UCl₃ and NaCl-PuCl₃ systems to fill gaps in the MSTDB
- Developing high temperature mechanically sealable cells for use in thermal analysis by differential scanning calorimetry
- Comparing measured properties to model predictions using MSTDB data.
Acknowledgements

Financial support provided by U.S. Department of Energy, Office of Nuclear Energy

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