The LANL Molten Salt Research Capability: 2022 Status Update

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Physical Properties of Molten Salts Session
2022 Hybrid Molten Salt Reactor Workshop
Oak Ridge National Laboratory

October 12, 2022

LA-UR-22-30476
Outline

• “What we can do”
  - Describe LANL molten salt properties research capability; highlight 2022+ status & plans
    ▪ Include:
      - Types of materials we handle
      - Limitations
• “What we need to do as a community”
  - As prompts for discussion, describe growth areas, opportunities where we can continue to improve

PI: Marisa Monreal (C-IIAC); Co-PIs: David Andersson (MST-8), Matt Jackson (MST-16)

**Main objectives:**
1. To integrate advanced characterization techniques in both experiment and modeling
2. To generate an experimentally validated predictive capability with quantified uncertainty for actinide-molten chloride salts (uranium, thorium, and plutonium)

**Technical goals:**
1. Develop atomic scale simulations of macroscale properties, then parametrized physics-based models with quantified uncertainty *(Modeling and Simulation Thrust – Lead: David Andersson)*
2. Synthesize and prepare pure materials: actinide chlorides and solvent salts; examine local structure *(Chemistry Thrust – Lead: Marisa Monreal)*
3. Experimentally determine macroscale properties *(Thermophysical Properties Thrust – Lead: Matt Jackson)*
# Properties Measurements at LANL

<table>
<thead>
<tr>
<th>Properties</th>
<th>Experimental Techniques</th>
<th>2022+ Status, Plans</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>Neutron Radiography*</td>
<td>Neutron Radiography Measurements on PuCl₃</td>
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<tr>
<td></td>
<td></td>
<td>X-ray Radiography</td>
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<td></td>
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<td>Conventional (Push-rod) Dilatometry</td>
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<tr>
<td>Melt Point ($T_m$)</td>
<td>Differential Scanning Calorimetry (DSC)*</td>
<td>DSC Measurements on PuCl₃</td>
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<tr>
<td>Heat Capacity ($C_p$)</td>
<td></td>
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<tr>
<td>Enthalpy of Fusion</td>
<td></td>
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<tr>
<td>Corrosivity, redox potentials</td>
<td>Electrochemistry</td>
<td>Simultaneous ion-beam irradiation and corrosion experiments, with</td>
</tr>
<tr>
<td></td>
<td></td>
<td>electrochemical monitoring</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(FUTURE EFRC)</td>
</tr>
</tbody>
</table>

*can be performed on Pu-bearing salt
Density using Neutron Radiography: Experimental setup in flight path

Flight Path 5 at Los Alamos Neutron Science Center (LANSCE)
Density using Neutron Radiography: Method ("Neutron Dilatometry")

Fluid height is determined using the known height of a feature on our reference.

- Images stitched together
- Heights determined at different temperatures

LiCl+KCl Eutectic Salts (Samples 29 & 30):

- 1020 °C
- 976 °C
- 876 °C
- 765 °C
- 665 °C
Density using Neutron Radiography: Uranium-molten chlorides

We have determined a series of molten chloride salt densities, including with UCl₃:

- For more details, please see two journal publications—paper containing density data¹ and imaging technique paper².

Have been working on improvements to reduce error:

- Mass: Increase sample mass to 4-11 grams (Taller furnace, taller samples)
- Radius: Measure the radius with water prior to measurement with salt
- Height: Taller sample tubes (~30 cm)
- Pixel Resolution: higher quality camera, image stacking, image subtraction.

Developing a higher throughput pushrod dilatometry method—recent successes with liquid salt containment (custom graphite holder)

Prepped for plutonium...

<table>
<thead>
<tr>
<th>Binary Eutectic Mixtures</th>
<th>(\rho_0) [g/cm³]</th>
<th>(\alpha \cdot 10^{-3})</th>
<th>Uncertainty</th>
<th>Range (K)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.505 LiCl + 0.495 KCl</td>
<td>2.0049</td>
<td>0.5148</td>
<td>±0.003</td>
<td>626-1390</td>
<td>This work</td>
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<tr>
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<td>2.0077</td>
<td>0.5302</td>
<td>±0.001</td>
<td>642-1150</td>
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<td>2.0183</td>
<td>0.5167</td>
<td>±0.003</td>
<td>740-860</td>
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<td>2.0286</td>
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<td>2.0292</td>
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<td>2.0183</td>
<td>0.5167</td>
<td>±0.008</td>
<td>720-1200</td>
<td>[94]</td>
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<tr>
<td></td>
<td>2.1148</td>
<td>0.8700</td>
<td>-</td>
<td>-</td>
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<tr>
<td>0.431 MgCl₂ + 0.569 NaCl</td>
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<td>0.5169</td>
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<td>This work</td>
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<td>2.1253</td>
<td>0.47419</td>
<td>±0.0006</td>
<td>1630-1100</td>
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<td>2.2971</td>
<td>0.5070</td>
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<tr>
<td></td>
<td>2.002</td>
<td>0.48</td>
<td>-</td>
<td>1003-1173</td>
<td>[127]</td>
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<td>0.494 NaCl + 0.506 KCl</td>
<td>2.1064</td>
<td>0.5439</td>
<td>±0.01</td>
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<td>This work</td>
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<td>1.9764</td>
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<td>2.1314</td>
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<td>±0.008</td>
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<td>0.328 MgCl₂ + 0.672 KCl</td>
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<td>0.5438</td>
<td>±0.02</td>
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<td>0.552</td>
<td>±0.002</td>
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<td>2.2548</td>
<td>0.4740</td>
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<td>650-1056</td>
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<tr>
<td>0.66 NaCl + 0.34 UCl₃</td>
<td>4.2235</td>
<td>1.0347</td>
<td>±0.02</td>
<td>794-1390</td>
<td>This work</td>
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<tr>
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<td>4.2990</td>
<td>1.5903</td>
<td>±0.0009</td>
<td>973-1122</td>
<td>[149]²³²³</td>
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<td>3.8604</td>
<td>0.8371</td>
<td>±0.001</td>
<td>892-1142</td>
<td>[99]²²</td>
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<tr>
<td>0.81 KCl + 0.19 UCl₃ (El)</td>
<td>3.1756</td>
<td>0.7645</td>
<td>±0.015</td>
<td>841-1390</td>
<td>This work</td>
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<tr>
<td></td>
<td>3.3981</td>
<td>1.3827</td>
<td>±0.0008</td>
<td>1220-1280</td>
<td>[129]²²</td>
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<td>4.6124</td>
<td>0.9531</td>
<td>±0.024</td>
<td>821-1390</td>
<td>[129]²²</td>
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<tr>
<td>0.43 KCl + 0.57 UCl₃ (E2)</td>
<td>8.405</td>
<td>4.1819</td>
<td>±0.0025</td>
<td>1180-1270</td>
<td>[129]²²</td>
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<tr>
<td>(NaCl + KCl) + 0.04 UCl₃</td>
<td>2.9026</td>
<td>0.5014</td>
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<tr>
<td>(NaCl + KCl) + 0.137 UCl₃</td>
<td>3.7895</td>
<td>1.4775</td>
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<tr>
<td>(NaCl + KCl) + 0.193 UCl₃</td>
<td>3.4585</td>
<td>0.9492</td>
<td>-</td>
<td>970-1270</td>
<td>[149]</td>
</tr>
<tr>
<td>0.45 NaCl + 0.31 KCl + 0.24 UCl₃</td>
<td>2.5352</td>
<td>0.7010</td>
<td>±0.02</td>
<td>1600-1400</td>
<td>This work</td>
</tr>
<tr>
<td>(0.905 NaCl + 0.130 KCl + 0.965 UCl₃)</td>
<td>3.4511</td>
<td>0.7432</td>
<td>±0.02</td>
<td>1600-1400</td>
<td>This work</td>
</tr>
<tr>
<td>0.49 NaCl + 0.462 KCl + 0.048 UCl₃</td>
<td>4.1241</td>
<td>0.9650</td>
<td>±0.02</td>
<td>1600-1400</td>
<td>This work</td>
</tr>
<tr>
<td>(NaCl + KCl) + 0.493 UCl₃</td>
<td>5.4813</td>
<td>2.0013</td>
<td>-</td>
<td>970-1270</td>
<td>[149]</td>
</tr>
<tr>
<td>(NaCl + KCl) + 0.718 UCl₃</td>
<td>5.9677</td>
<td>1.9953</td>
<td>-</td>
<td>970-1270</td>
<td>[149]</td>
</tr>
<tr>
<td>(LiCl + KCl) + 0.0065 UCl₃</td>
<td>2.0731</td>
<td>0.5290</td>
<td>±0.004</td>
<td>770-1390</td>
<td>This work</td>
</tr>
<tr>
<td>(LiCl + KCl) + 0.0077 UCl₃</td>
<td>2.1336</td>
<td>0.5311</td>
<td>±0.004</td>
<td>770-1390</td>
<td>This work</td>
</tr>
</tbody>
</table>

Density using Neutron Radiography: Preparation for Plutonium*

- Developed compact furnace
  - Reduced insulation
  - Moved elements

- Changes for plutonium containment:
  - **Primary**: Special Ni tubes have been fabricated
  - **Secondary**: New gas-tight design
  - **Tertiary**: Received and tested
  - All three levels have passed certification for LANSCE

- **Our beam time starts end of October**

*Grateful acknowledgment to Toni Karlsson and team at INL for material!
Container-based dilatometry is viable up to 1000° C
- Loss of material during tests minimized by crucible design and manufacture
- New graphite crucibles, one-sided piston
- Salts measured include NaCl, KCl, LiCl, MgCl₂ and their associated eutectics

Optimization: Minimization of sample loss will improve overall uncertainty
## Properties Measurements at LANL (cont.)

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<tr>
<td>Viscosity</td>
<td>Dynamic Neutron Radiography*</td>
<td>Dynamic X-ray Radiography*&lt;sup&gt;*&lt;/sup&gt; Rotation Viscometry (OSU)</td>
</tr>
<tr>
<td>Heat of Dissolution, Enthalpy of Mixing</td>
<td>Drop Calorimetry*</td>
<td>Uranium measurements 2023+: Thorium and plutonium measurements</td>
</tr>
<tr>
<td>Thermal Diffusivity</td>
<td>Laser Flash Analysis (LFA)</td>
<td>2023: Test custom sample chamber</td>
</tr>
<tr>
<td>Vapor Pressure</td>
<td>Transpiration</td>
<td>Collaboration continues (&lt;span class=&quot;region&quot;&gt;Univ. of Utah&lt;/span&gt;) 2023: Stand up at LANL</td>
</tr>
<tr>
<td>Surface Tension</td>
<td>Contact Angle Measurement (Optical method; neutron radiography*)</td>
<td>Optical method (OSU) 2023: Initial measurements during June-Dec beamtime at LANSCE</td>
</tr>
<tr>
<td>Local Structure</td>
<td>Pair Distribution Function (Neutron)</td>
<td>Pair Distribution Function (X-ray) (MIT) XAS (MIT) Raman &amp; UV-vis Spectroscopy (UCBerkeley)</td>
</tr>
<tr>
<td>Characterization (purity)</td>
<td>pXRD*, DSC (T&lt;sub&gt;m&lt;/sub&gt;)*</td>
<td>Karl-Fisher Titration, Actinide SS-NMR*</td>
</tr>
</tbody>
</table>

*can be performed on Pu-bearing salt
Molten salt research activities include: Direct oxide reduction, electrolytic oxide reduction, salt drying; waste stream characterization; electrochemistry; sample prep
Depleted Uranium & Thorium Laboratories

- Radiological control area with inert gloveboxes, hood, benchtop
- Large-scale furnace
- Several small-scale furnaces
- **Research activities:** electrochemistry, sample preparation for properties measurements (see photo)
- **New 2022:** actinide halide synthesis glovebox
Small- and large-scale furnaces for molten salt electrochemistry

- **Electrochemistry**: Reference electrode development; corrosion studies; $E^0$ determination
- **Machining workspace** (metal and ceramic)
- **Characterization lab** (benchtop powder X-ray diffractometer—pXRD, benchtop scanning electron microscopy—SEM)
2021-2022 Publications in Peer-Reviewed Journals:


2022-2023 Publications: Selected Manuscripts In Preparation:

1. Electrochemistry (electromotive force measurements for standard reduction potentials)
2. Actinide halide synthesis
3. Heat capacity
4. Density by conventional (push-rod) dilatometry
5. Drop calorimetry--enthalpy of mixing
Next Steps at LANL

- **Expanding Pu research space**
  - Need to complement and leverage existing Pu capabilities (e.g., PF-4)
  - In development: Plutonium Science Laboratory (“PluS Lab”)
    - Plutonium R&D lab—flexible, unclassified, Sub-Haz-Cat-3
    - Opportunity for involving other programs (i.e., nonproliferation/safeguards)

- **Broadening actinide-molten salt research scope**
  - Fluoride salts, beryllium salts
  - Adding techniques (just two examples: actinide Nuclear Magnetic Resonance Spectroscopy (NMR), rotational viscometry)
  - Broadening to other non-MSR molten salt research areas (two examples: hydrogen generation; electrodeposition of coatings)
Next Steps at LANL (cont.)

• **Growing internal partnering**
  - Nonproliferation (integrate with other LANL global security/nonpro lines of research)
  - Sensors, in-situ monitoring (MSR health of salt + pyrochemistry process optimization)
  - Other LANSCE capabilities (for example: energy-resolved neutron imaging= “ERNI”)

• **Foster external collaborations**
  - Universities: University of Utah, MIT, UC Berkeley, OSU
  - Industrial partners, other funding mechanisms (GAIN/TerraPower, TCF/Kairos Power, MSR Campaign, Nuclear Energy Advanced Modeling and Simulation (NEAMS))
The LANL Actinide-Molten Salt Research Capability

- Successful growth from LDRD to programmatic and external investments
- Strong collaborations, both internal and external
- Growth areas identified, working to address
- Robust research capability established...and still growing!

2016
Start building molten salt lab in support of Plutonium Facility activities

2017
First molten salt LDRD projects

2019
Next-level Molten Salt LDRD projects
Initial interactions with industry (e.g., TerraPower)

2020
Three spin-off Molten Salt LDRD projects
C-Division program development funding

2021
*Molten Salt LDRD DR project*
Funded TerraPower project (GAIN)
PluS Lab receives first sponsor funding

2022
Funded Kairos Power project
Inclusion in MSR Campaign
PluS Lab reaches next step in funding & development
Discussion prompts: What do we need to do as a community?

As prompts for discussion, describe growth areas/opportunities where we can continue to improve, issues we’re facing as a whole

Need to increase the pipeline: students, postdocs, research technicians
- Need more skilled staff with molten salt experience
- Range of roles/levels, including permanent staff

Need stable, longer-term funding at level sufficient to sustain capabilities
- Keep advanced/specialized capabilities going, continue growing
- Enable more collaboration
- Increase pipeline
Acknowledgements

**Actinide-molten salt DR team:**
David Andersson, MST-8  
Matt Jackson, MST-DO  
Scott Parker, MST-16 (Thermophysical Properties)  
Karla Erickson, C-CDE (Synthetic Chemistry)  
Charles Lhermitte, Sigma-1 (Electrochemistry)  
Alex Long, MST-8 (LANSCE Beam Scientist)  
Ping Yang, T-1  
Bo Li, T-1  
Gaoxue Wang, T-1  
Sven Vogel, MST-8  
Josh White, MST-8  
Jeremy Mitchell, MST-16  
Najeb Abdul-Jabbar, MST-16  
Sarah Hickam, MST-16  
Arjen van Veelen, MST-8  
Hongwu Xu, EES-14  
Hakim Boulkhalifa, EES-14  
Andrew Strzelecki, EES-14

**Technicians & Engineers:**
Alberto Gonzalez, MST-16  
Shane Mann, MST-16  
Travis Carver, MST-8

**Funding:**
LDRD (FY17-24)  
TCF (FY22-24)  
MSR Campaign (FY22-23)  
GAIN (FY21-22)  
LANL C-Division (FY19-20)  
Civilian Nuclear Program (FY18-19)

This work was performed, in part, at the Los Alamos Neutron Science Center (LANSCE), a NNNSA User Facility operated for the U.S. Department of Energy (DOE) by Los Alamos National Laboratory (Contract 89233218CNA000001).
Questions?

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Backup slides
Density using Neutron Radiography: Results

- Successful demonstration of novel, unique-to-LANL capability for **accurate measurement of liquid density of salts, including uranium-bearing mixtures**
- Two journal publications (imaging technique, and density data)

Next step: plutonium-bearing mixtures

The application of experimental techniques to complex salt systems requires innovative approaches to contend with their harsh and challenging nature (high-temperature, radioactive, corrosive, hygroscopic, more!)

Modeling of \(d\) and \(f\) elements in a molten salt environment requires the use of innovative methods.

We must resolve strong electronic correlations, Van der Waals interactions, and multiple oxidation states – and also be sufficiently computationally efficient to use in molecular dynamics (MD) simulations.

Machine learning tight binding

Drop calorimetry

Dilatometry
**FY21-23 LDRD DR:**

**“Advanced Characterization to Enable Prediction of Actinide-Molten Salt Behavior”**

The pair distribution function (PDF) gives the probability of finding an atom at a distance $r$ from an atom at the origin.

Sven Vogel (MST-8, LANSCE), David Andersson (MST-8), and Boris Khaykovich (MIT)

- Technique characterizes crystalline, amorphous, and liquid materials
- Information on the local structure, local order of a material

*Latest data from mod-sim team: radial distribution functions from *ab initio* molecular dynamics simulations.*