Molten Salt Reactor PROGRAM

# LANL Experimental Support of MSTDB Development

**Marisa Monreal**

Inorganic, Isotope, and Actinide Chemistry – Chemistry Division

Los Alamos National Laboratory

Molten Salt Reactor Campaign Annual Review, April 22-24, 2025

LA-UR-25-23739

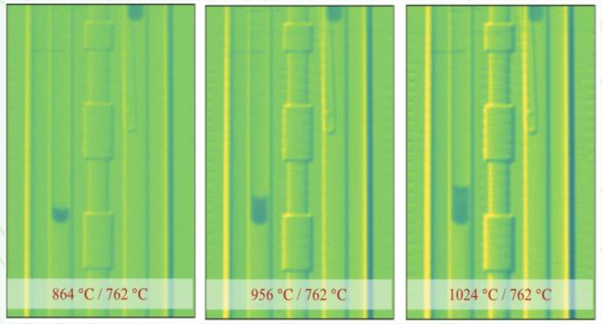
Argonne National Laboratory · INL Idaho National Laboratory · Los Alamos National Laboratory · Oak Ridge National Laboratory · Pacific Northwest National Laboratory · Sandia National Laboratories · U.S. Department of Energy Office of Nuclear Energy

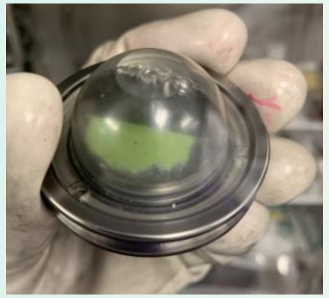
# LANL Actinide-Molten Salt Chemistry and Properties Research

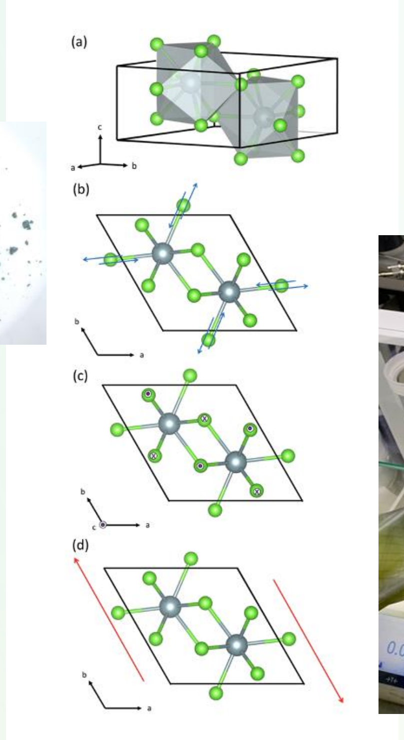
**Salt systems:**
- Actinides: uranium, thorium, plutonium
- Chlorides & fluorides

**Research:**
- Chemistry & thermophysical properties
- Both experiment and modeling
- Studies across length scales – local structure, macroscale properties

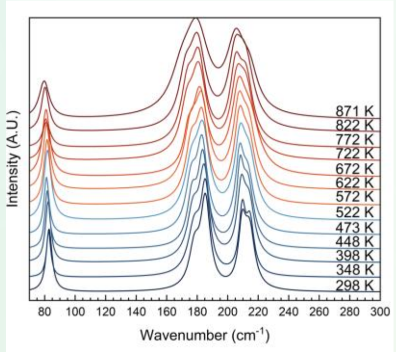
**Benefitting communities:**
- Pyroprocessing/recovery & purification of actinide materials, nuclear energy, fundamental actinide science, global security/non- and counter-proliferation







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# LANL Actinide-Molten Salt Chemistry and Properties Research

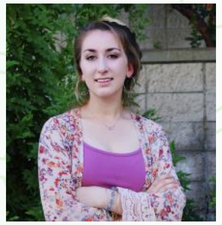
**Researchers:**
- Graduate students, post-docs, scientists, engineers
- Chemistry, materials science, earth and environmental science, theoretical/mod-sim

**Collaborations:**
- National Laboratories, universities, industry, NEAMS, SciDAC, FUTURE EFRC

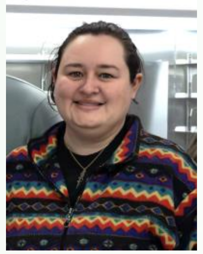
**Sponsors/Projects:**
- MSR Campaign, LDRD, GAIN, Technology Commercialization Fund (TCF), IRP, NEUP

**Scientists & Engineers**
Matt Jackson
Scott Parker
David Andersson
Alex Long
Hongwu Xu
Sven Vogel
Karla Erickson
Kristen Pace
Ping Yang
Gaoxue Wang
Harris Mason
Hakim Boulkhalfa
Travis Carver
*Research Technologist:*
Clare Hatfield

**Post-docs & Students**
Hannah Patenaude
Jarom Chamberlain
Olivia Dale
Dylan Tharp Eralie
**Summer 2025:**
Sean Peyres
Bryn Merrill


Hannah Patenaude


Jarom Chamberlain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Matt Jackson

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# LANL Actinide-Molten Salt Chemistry and Properties Research

| Properties | Experimental Techniques |
|---|---|
| Density | Neutron Radiography, Conventional (Push-rod) Dilatometry |
| Viscosity | Dynamic Neutron Radiography, Rotational Viscometry |
| Melting Point/Phase Diagram, Heat Capacity | Differential Scanning Calorimetry (DSC) |
| Corrosion | Electrochemistry |
| Heat of Dissolution, Enthalpy of Mixing, Heat Capacity | Drop Calorimetry |
| **Local Structure** | Pair Distribution Function (PDF) Analysis, Raman Spectroscopy, Electrochemistry |
| **Synthesis & Characterization** | Inorganic halide synthesis, SEM, Melting Point (DSC), pXRD, SS-NMR Spectroscopy |

**Experimental efforts & strategy:**

- Method development, uncertainty reduction
- Lower and higher throughput methods
- Non-rad → DU , Th → Pu
- Iterate with mod-sim

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# Actinide Halide Synthesis and Characterization

## Synthesis of pure, isolable actinide chlorides and fluorides to enable property research

- Both known & novel synthetic routes (e.g., for $UCl_3$, $UCl_4$, $ThCl_4$, $UF_4$)
- Characterization techniques to confirm purity (e.g., SS-NMR; pXRD; DSC)
    - Impurities: other actinide species; water; products of rxn with water

*FY25 work: scaling up*

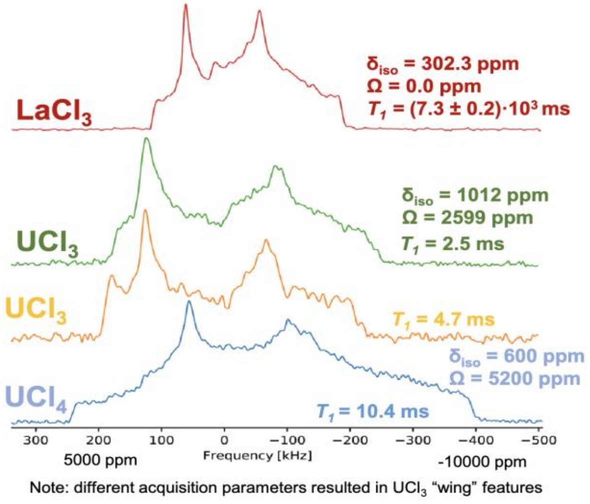
$UCl_3(py)_2$ —thermal elimination→ $UCl_3$

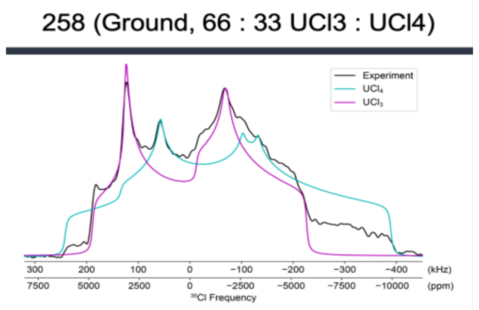
Erickson, K., Parker, S., Monreal, M. J. *Chem. Methods*, **2024**, e202300052.

*FY25 work: optimizing*

$UI_4(diox)_2$ —fluorination in organic solvent→ $UF_4$

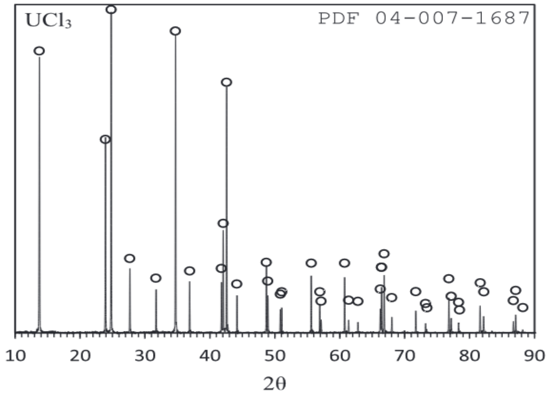
Erickson, K., Capra, N., Monreal, M., *in preparation*

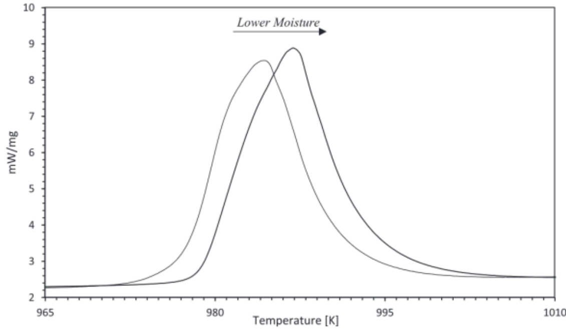


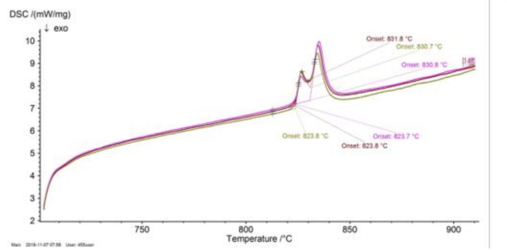




SS-NMR

Altenhof, Erickson, Rehn, Fetrow, Mattsson, Monreal, Mason, *in preparation*




pXRD, DSC

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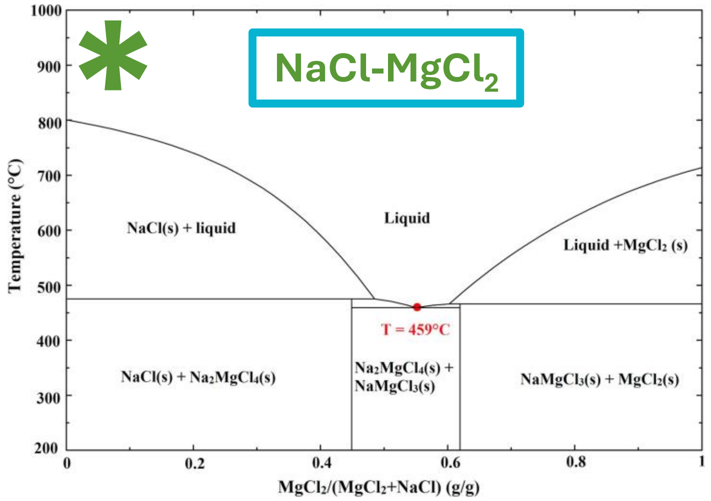
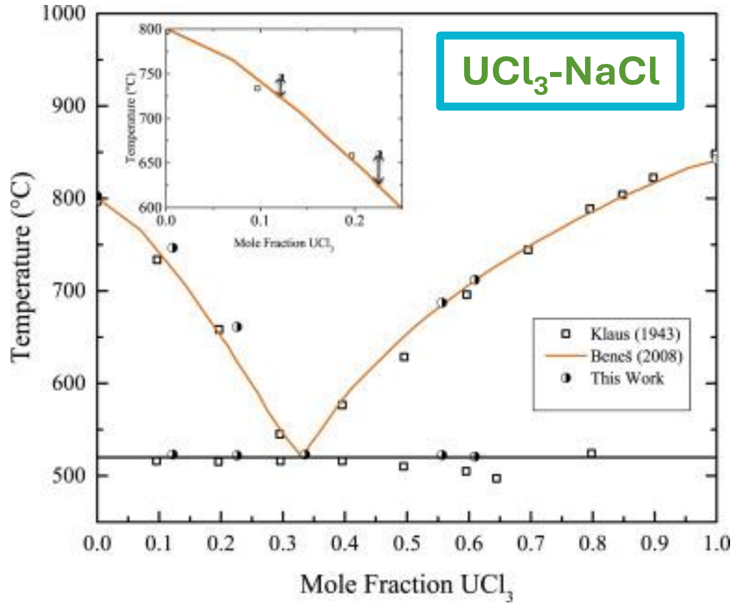
# $UCl_3$-NaCl-$MgCl_2$ Phase Transitions

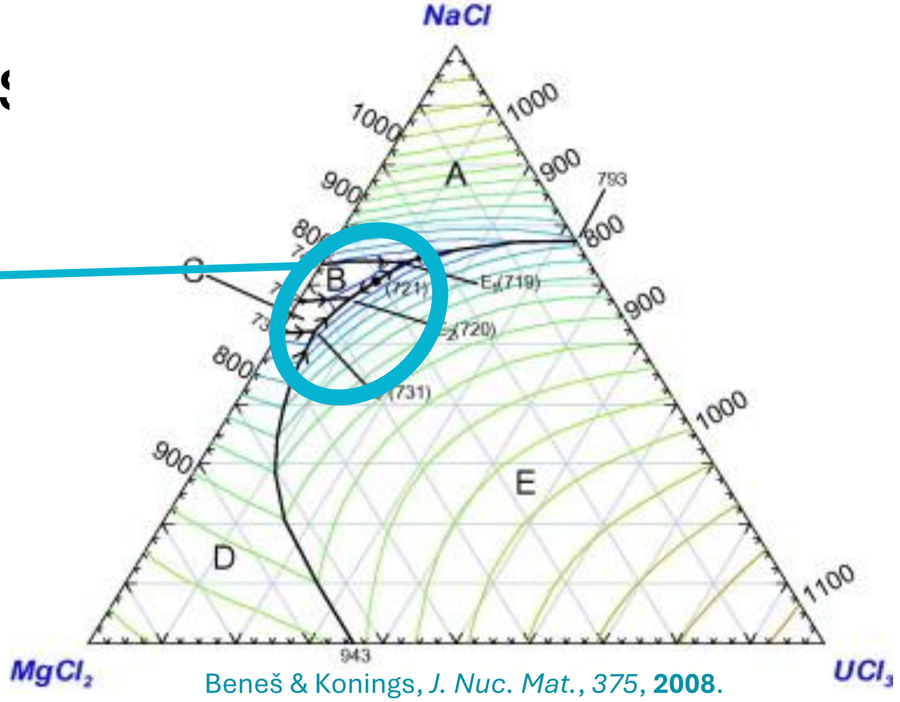
- Three pseudobinaries
  - ∗ **NaCl-$MgCl_2$**
  - $UCl_3$-NaCl
  - ∗ **$UCl_3$-$MgCl_2$**
- Four pseudoternary invariant points
  - 2 Eutectics
  - Quasi-Peritectic
  - Saddle Point
  - **Determined computationally!**



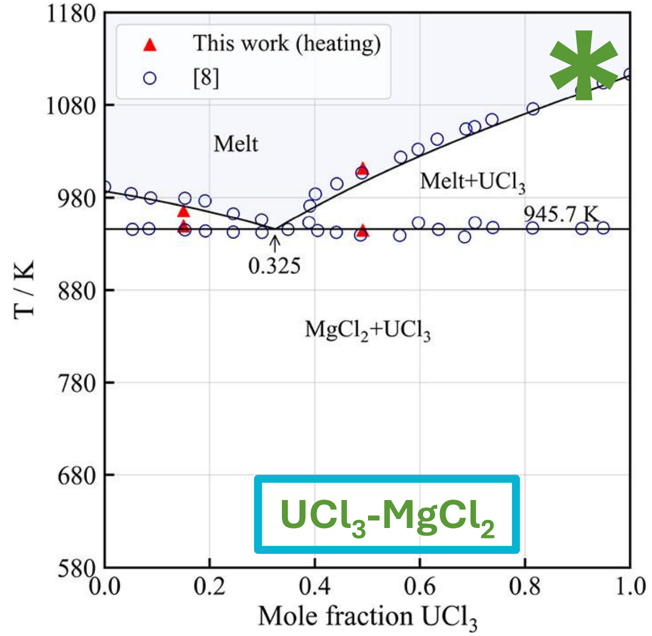

Mohan et al., *ECM*, *167*, **2018**.




Sooby et al., *J. Nuc. Mat.*, *466*, **2015**.



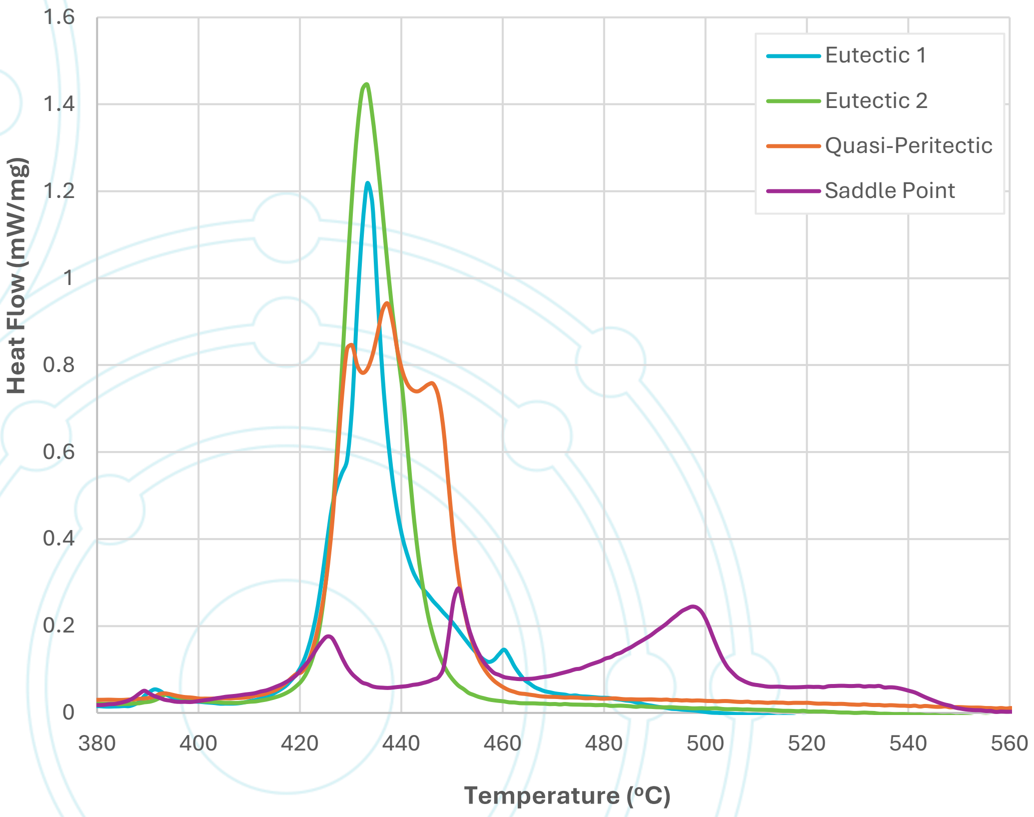

Beneš & Konings, *J. Nuc. Mat.*, *375*, **2008**.




Yingling et al., *ACS Appl. Energy Mater.*, *6*(11), **2023**.

# $UCl_3$-NaCl-$MgCl_2$ Phase Transitions

- Experimental plan (differential scanning calorimetry):
  - Various compositions around alleged eutectics of pseudobinaries
  - (In)Validate four calculated invariant points for pseudoternary
  - Manuscript in preparation




| Composition | $UCl_3$ (mol%) | NaCl (mol%) | $MgCl_2$ (mol%) | T (°C) | |
|---|---|---|---|---|---|
| **Pseudobinaries** | | | | | |
| NaCl-$MgCl_2$ | 0 | 65 | 35 | TBD | |
| | 0 | 60 | 40 | TBD | |
| | 0 | 58 | 42 | TBD | Alleged Eutectic |
| | 0 | 55 | 45 | TBD | |
| $UCl_3$-NaCl | 34 | 66 | 0 | TBD | Alleged Eutectic |
| $UCl_3$-$MgCl_2$ | 30 | 0 | 70 | TBD | |
| | 35 | 0 | 65 | TBD | Alleged Eutectic |
| | 40 | 0 | 60 | TBD | |
| **Pseudoternaries** | | | | | |
| Eutectic 1 | 11.2 | 63.7 | 25.1 | 446 | Alleged Transition Temperatures |
| Eutectic 2 | 6.6 | 57.8 | 35.6 | 447 | |
| Quasi-Peritectic | 4.7 | 52.0 | 43.3 | 458 | |
| Saddle Point | 30.4 | 60.7 | 8.9 | 448 | |

# $UCl_3$-NaCl-$MgCl_2$ Phase Transitions

- Experimental plan (differential scanning calorimetry):
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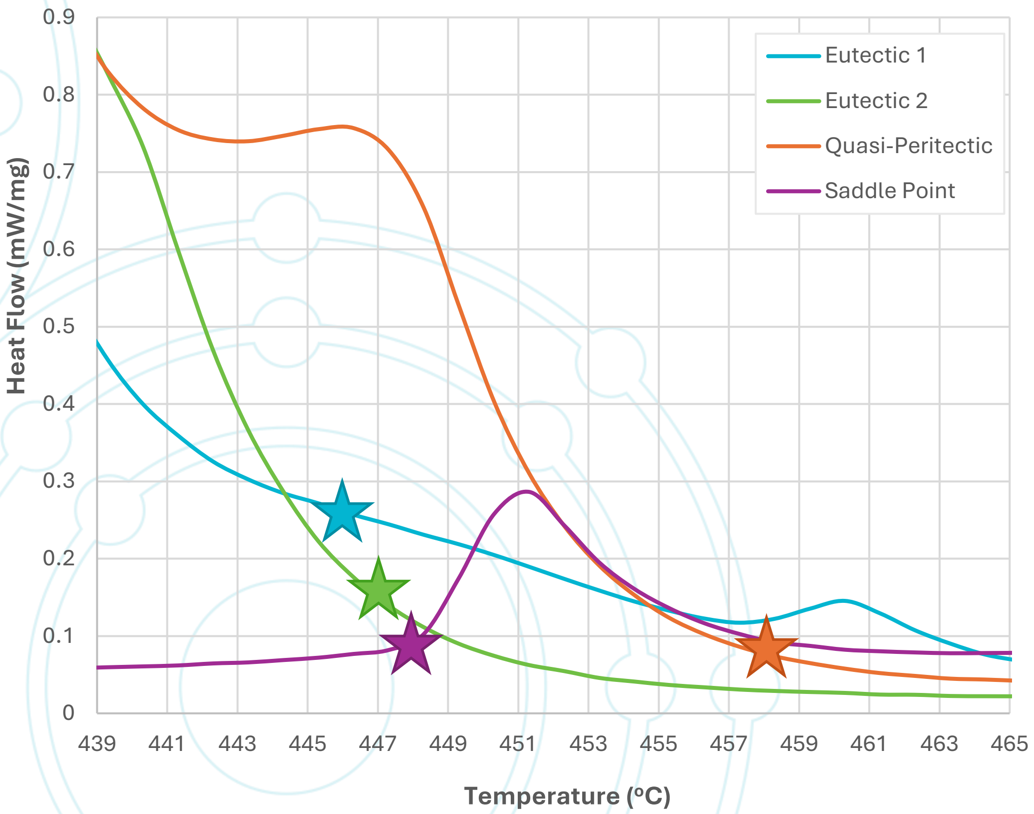


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| $UCl_3$-NaCl | 34 | 66 | 0 | TBD | Alleged Eutectic |
| $UCl_3$-$MgCl_2$ | 30 | 0 | 70 | TBD | |
| | 35 | 0 | 65 | TBD | Alleged Eutectic |
| | 40 | 0 | 60 | TBD | |
| **Pseudoternaries** | | | | | |
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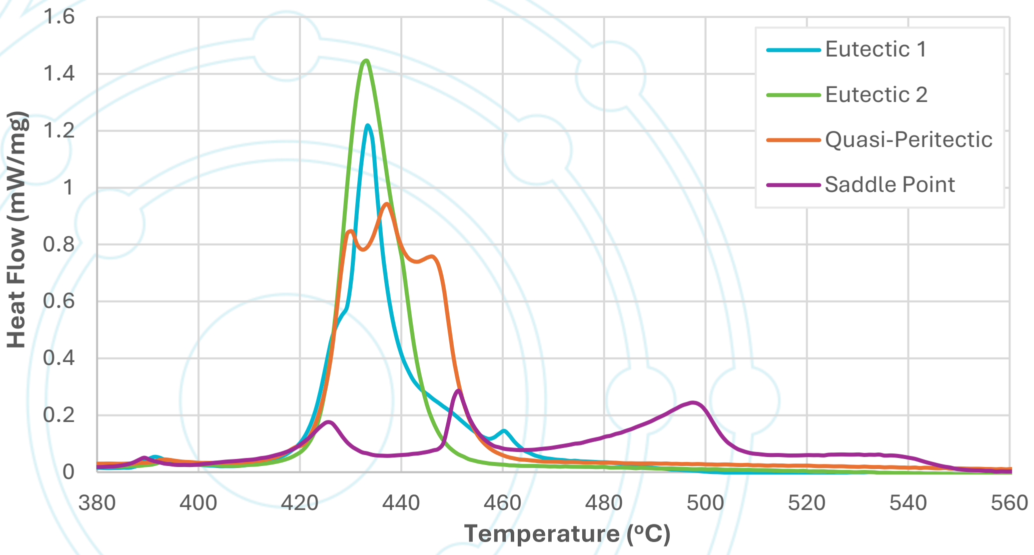
# $UCl_3$-NaCl-$MgCl_2$ Phase Transitions

- Experimental plan (differential scanning calorimetry):
  - Various compositions around alleged eutectics of pseudobinaries
  - (In)Validate four calculated invariant points for pseudoternary
  - Manuscript in preparation
- Collaboration with USC
  - Experimental comparisons
  - Computational validation

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|---|---|---|---|---|---|
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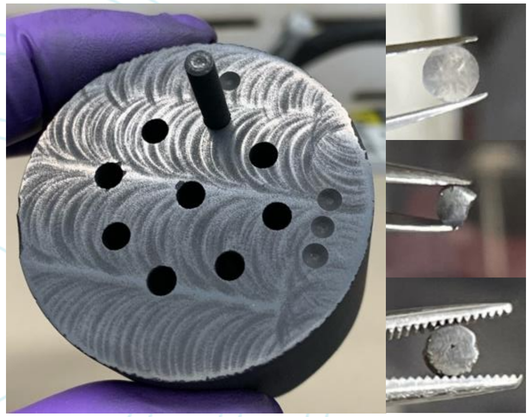
# Approach to $C_{p,liquid}$ via DSC:

Casting for $C_{p,solid}$

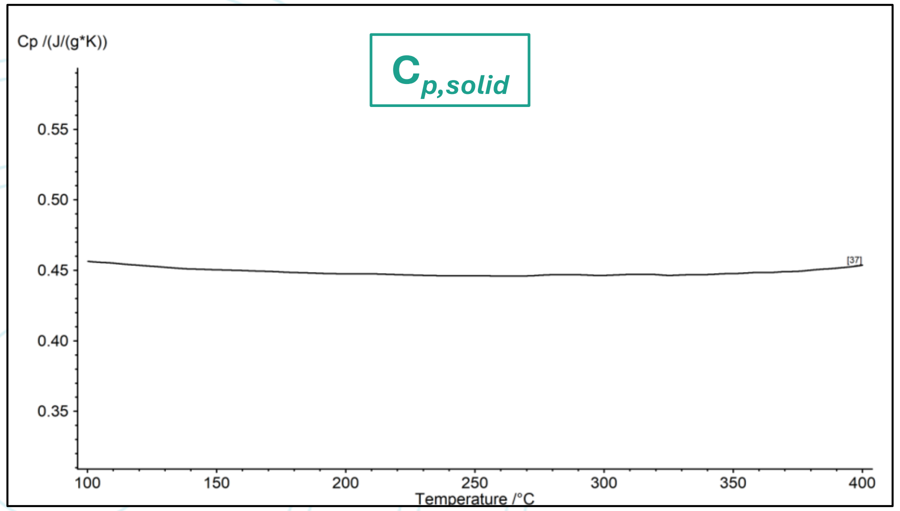


| Total Heat Energy | = | Solid Heat Capacity | + | Enthalpy of Fusion | + | Liquid Heat Capacity |
|---|---|---|---|---|---|---|
| $Q$ | = | $MC_{p,solid}\Delta T$ | + | $M\Delta H_{fus}$ | + | $MC_{p,liquid}\Delta T$ |

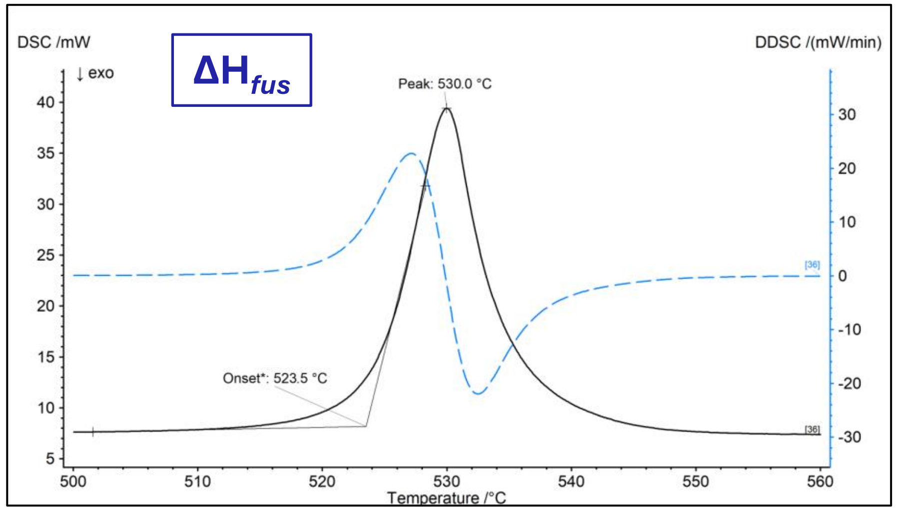
Need to eliminate assumptions required when measuring only liquid phase

## $UCl_3$-NaCl:

Q =




+




+ $C_{p,liquid}$ Liquid Heat Capacity

Solve for $C_{p,liquid}$

Measurement across full T range (25 °C → >$T_m$) to get total heat

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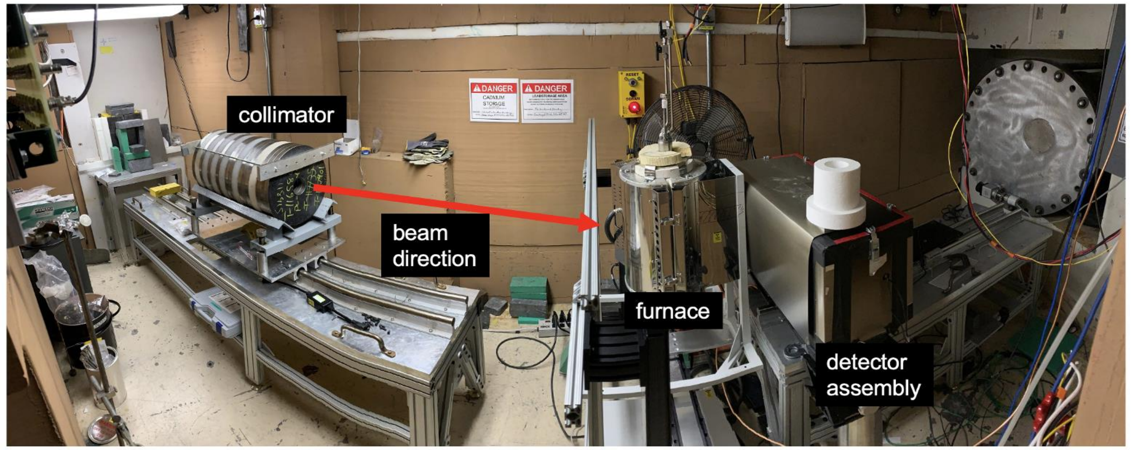
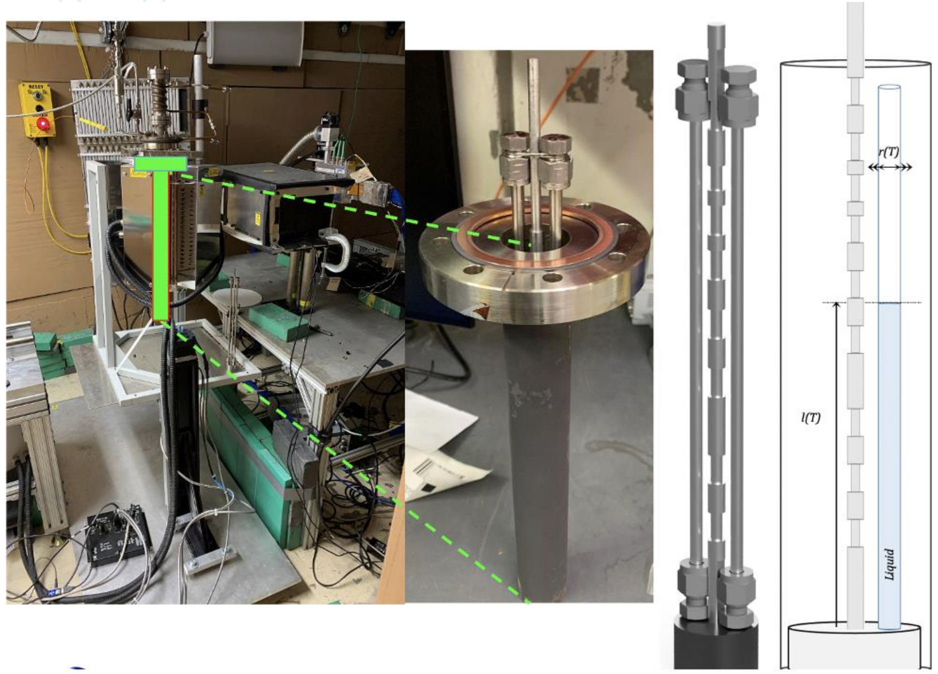
# Pu-Molten Salt Density by Neutron Radiography: Addressing Bubble Formation

- Density of molten U and Pu chloride salts has been determined via neutron radiography at LANSCE
- Bubbles were observed in some Pu chloride samples

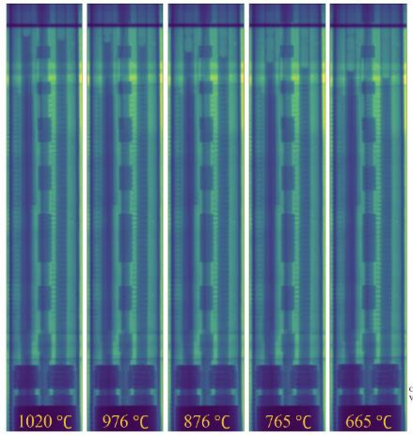

Flight Path 5 at Los Alamos Neutron Science Center (LANSCE)

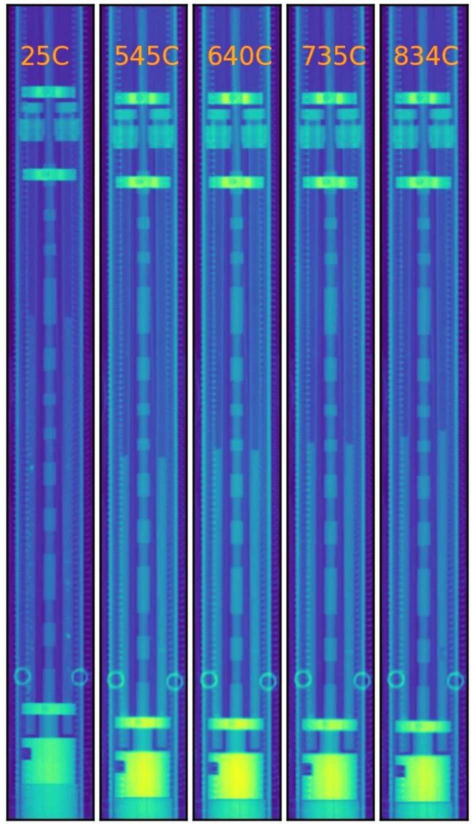


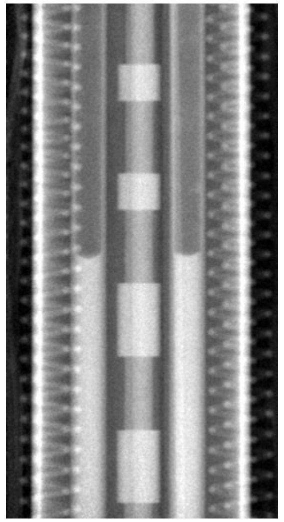

Fluid height is determined using the known height of a feature on our reference

- Images stitched together
- Heights determined at different temperatures

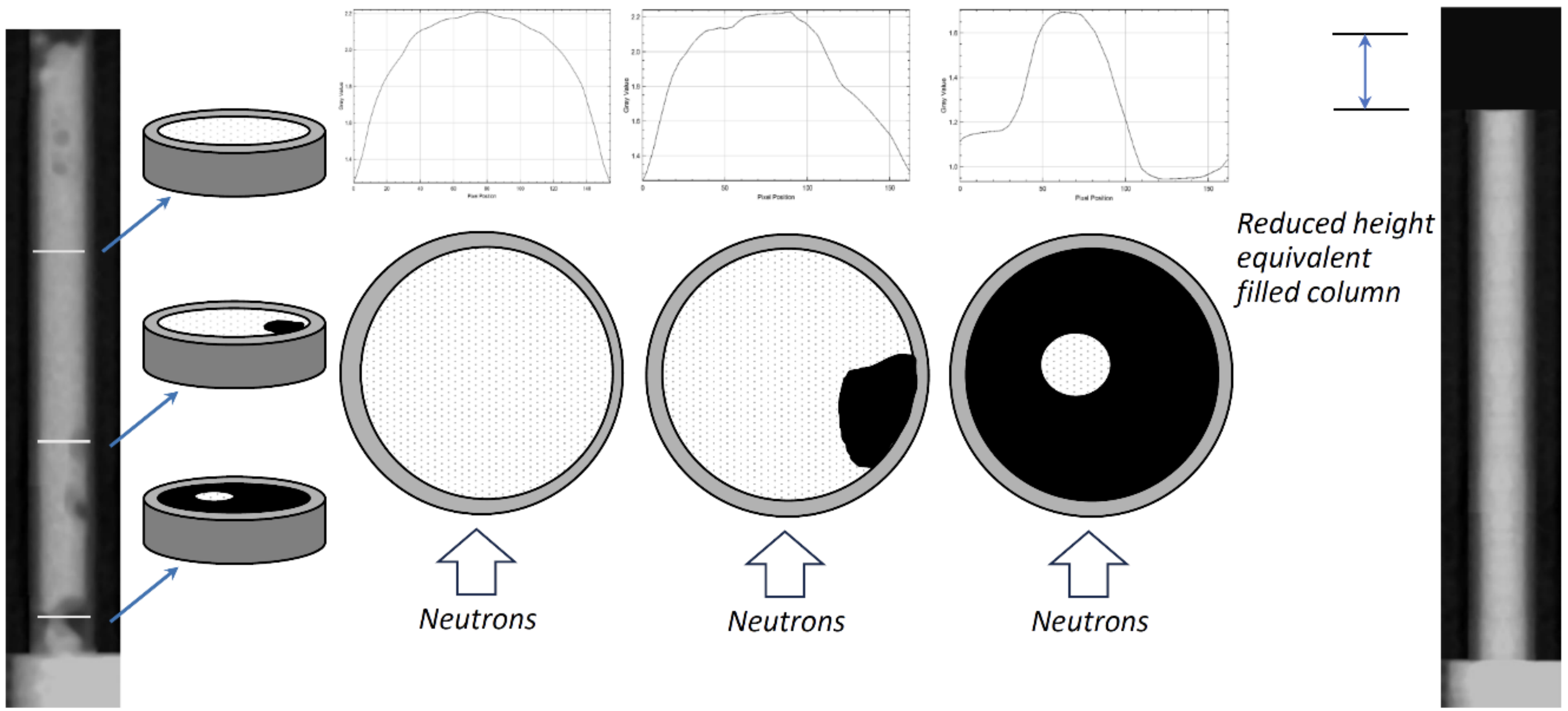
LiCl+KCl Eutectic Salts (Samples 29 & 30)

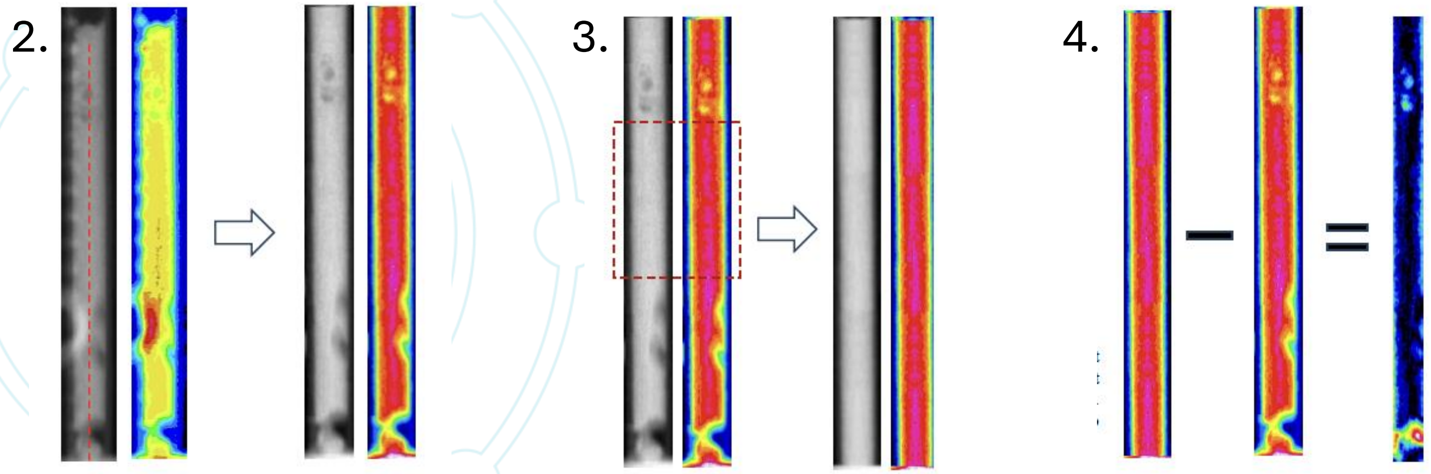


# Pu-Molten Salt Density by Neutron Radiography: Addressing Bubble Formation



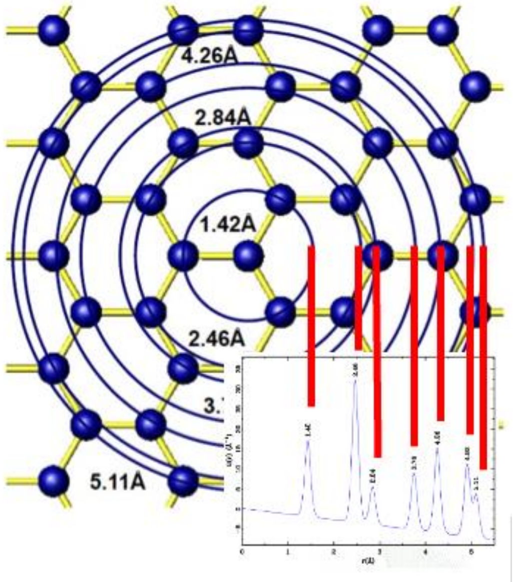




Developed a method in the image analysis to address the bubbles and determine densities

**Method:**

1. Create sample image stack
2. Perform artifact subtraction via radial symmetry
3. Create equivalent height reconstruction
4. Image subtraction of the artifact subtracted sample image from the equivalent height reconstruction

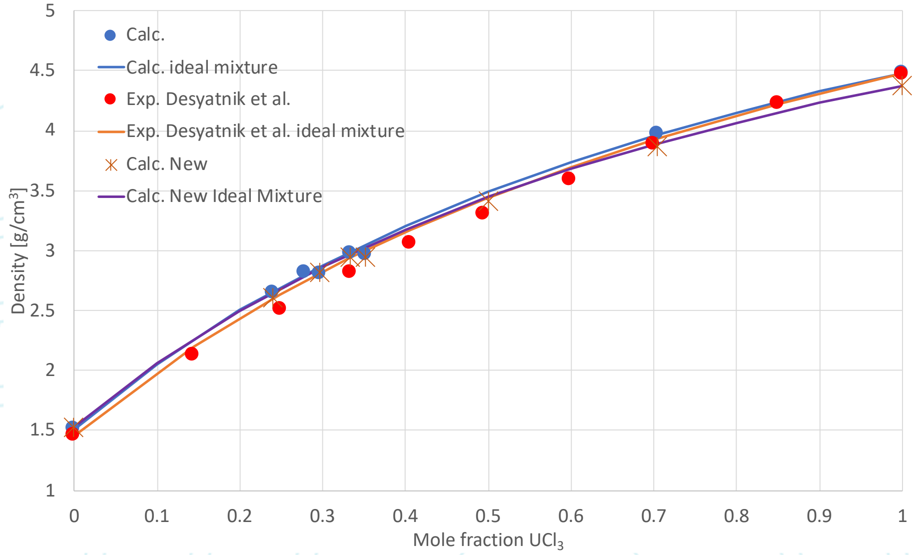
# Pair Distribution Function (PDF)

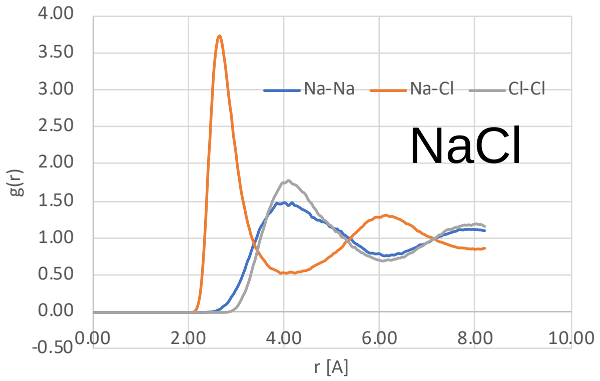


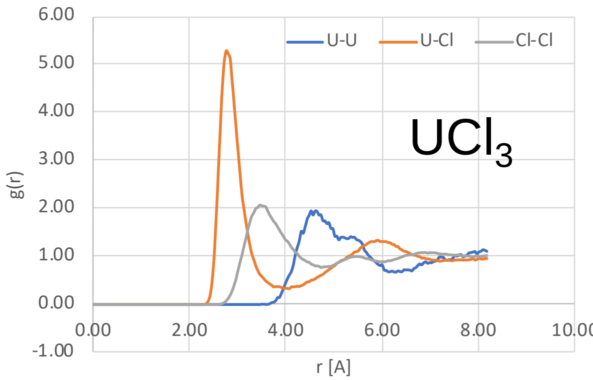

## Characterizing local structure

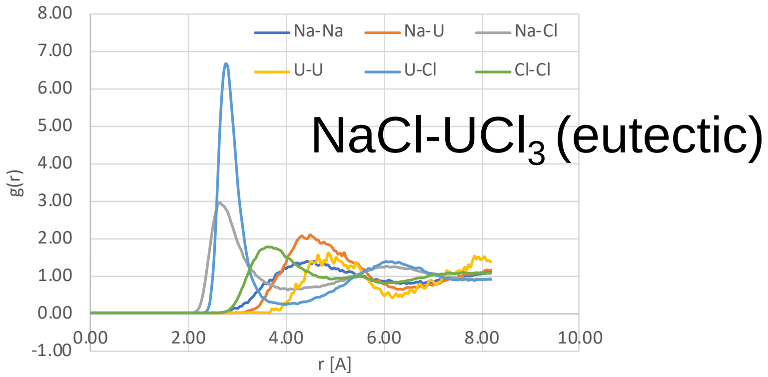
- **The pair distribution function (PDF), *g(r)*, gives the probability of finding an atom at a distance r from an atom at the origin**

### Mod-sim data, validated with data from density by neutron radiography experiment:



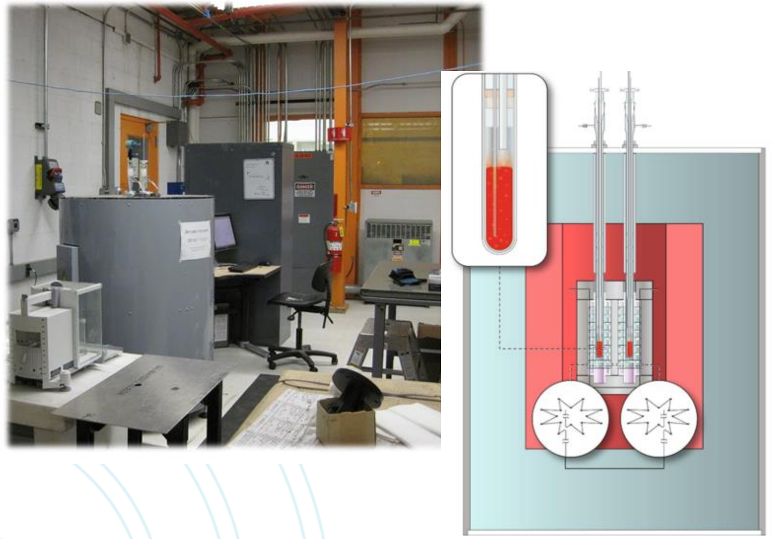



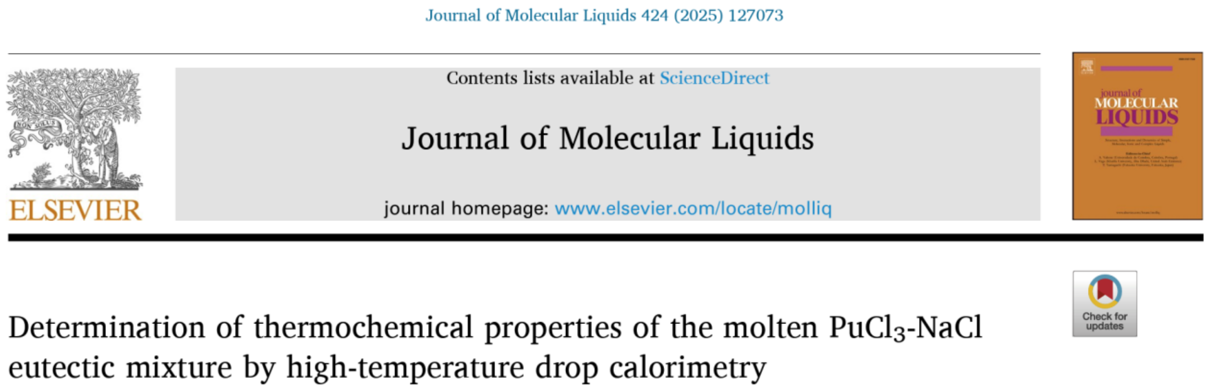

### Experimental data:

- Collected on pure $UCl_3$ and $UCl_3$-NaCl mixtures (LANSCE; **HFIR, Feb 2025**)
- Currently undergoing analysis—and comparison to/validation of mod-sim data
  - Fall 2025 ACS presentation

*Top center graphic credit: Kate Page's "Atomic Pair Distribution Function (PDF) Analysis", online as NXS_2018_PDF_KatePage.pdf*

# Drop Calorimetry




Journal of Molecular Liquids 424 (2025) 127073

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

ELSEVIER

Determination of thermochemical properties of the molten $PuCl_3$-NaCl eutectic mixture by high-temperature drop calorimetry

## MSR Campaign, Summer 2025:

**$UCl_3$-NaCl**

Hongwu Xu and Summer 2025 student Bryn Merrill

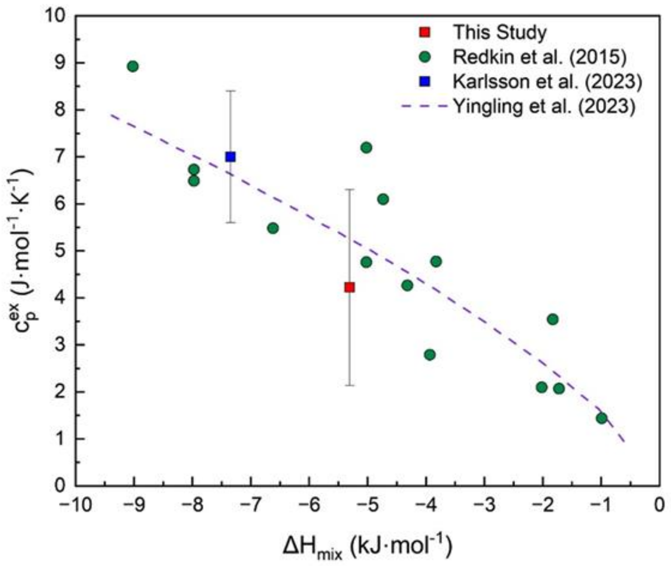
Developed methodology for actinide molten salt heat capacity ($C_p$), enthalpy of mixing, enthalpy of fusion

- Setaram AlexSys-800 calorimeter Isoperibol Calvet-type calorimeter
- T range: 400 to 800 °C
- Methodology developed using Setaram AlexSYS-800 calorimeter on **LiCl-KCl eutectic**

Strzelecki, A., Parker, S., Mann, S., Monreal, M. J., Jackson, Xu, H. et. al., *Rev. Sci. Inst.*, **2024**, *95*, 014103.

**$PuCl_3$-NaCl**

Strzelecki, A., Parker, S., Monreal, M., Xu, H., et. al., *J. Molec. Liq.*, **2025**, *424*,127073.




*Complementary research effort:*

**LDRD Exploratory Research Project, 2025-2027:**

**$UCl_3$-$UCl_4$-NaCl**

**$UCl_3$-$UCl_4$-$CrCl_2$-NaCl**

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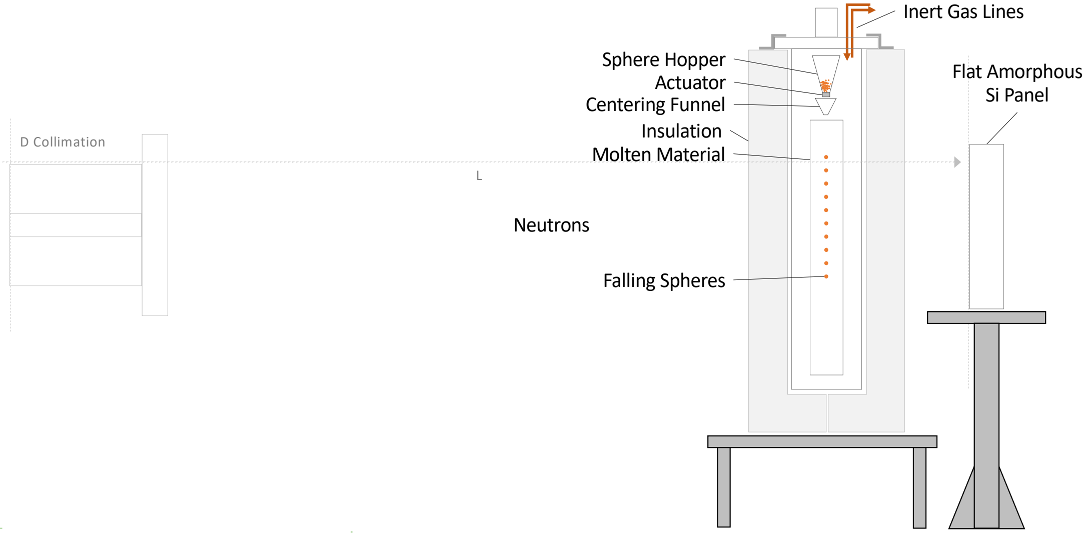
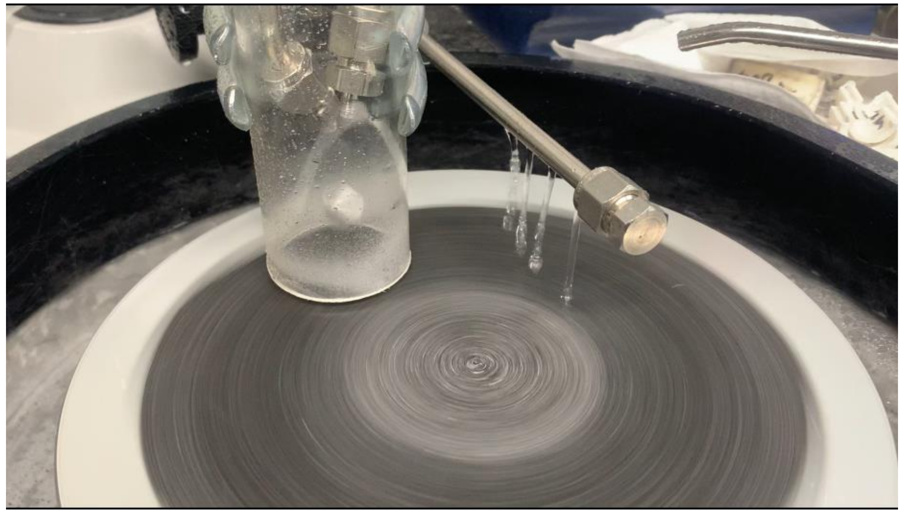
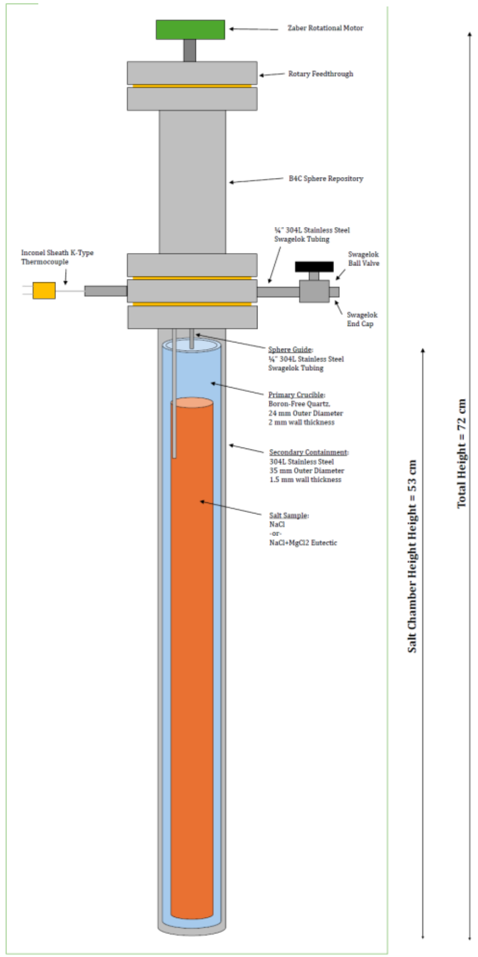
# Viscosity

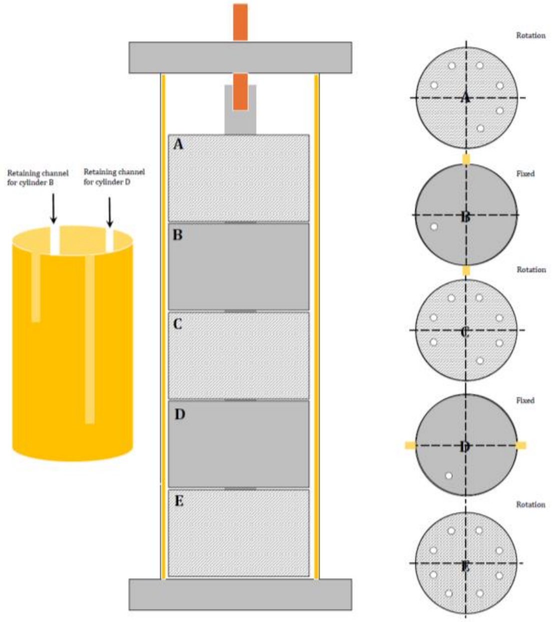
**Falling Sphere with Dynamic Neutron Radiography**

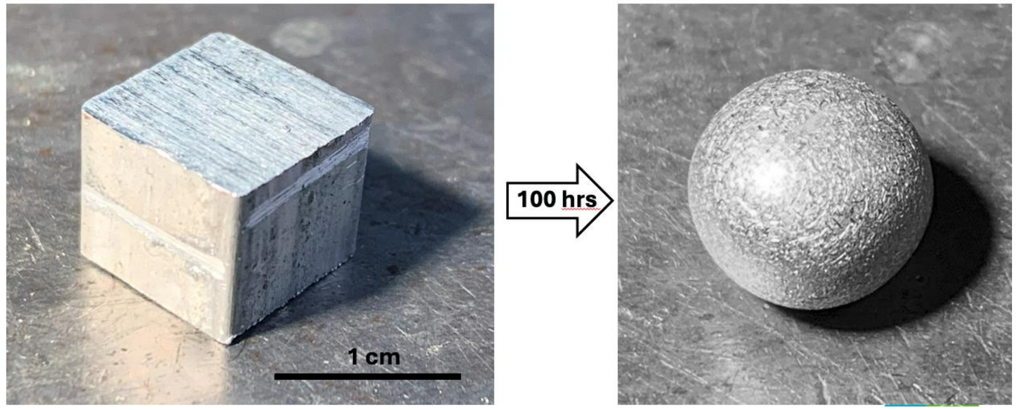
- New apparatus designed and built; testing at HFIR Fall 2024
- Sphere manufacture – $B_4C$
    - Developed a method to produce a sphere from an arbitrary shape
    - Tuned surface roughness and size to achieve 2 – 4 mm spheres
    - Characterized by laser profilometry, X-ray CT, immersion density

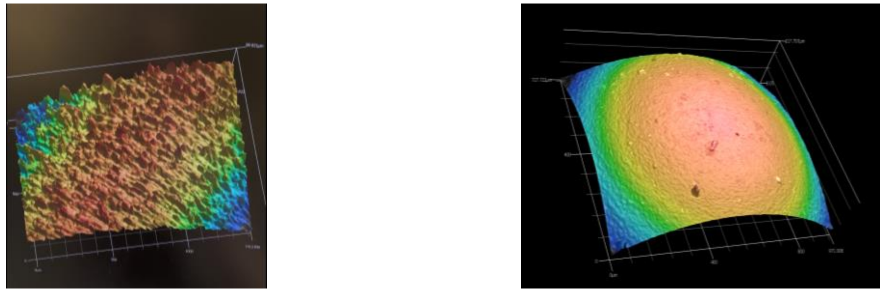






*Complementary research effort:*
**Compact Rotational Viscometer**

- Obtained FLiNaK preliminary results
- Further development this summer, towards actinide-bearing chlorides: 2025 DOE NNSA Stewardship Science Graduate Fellow Sean Peyres (Univ of Illinois, Urbana-Champaign)

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LANL Actinide-Molten Salt Research:

# Ongoing Efforts Complementary to MSR Campaign Activities

Los Alamos NATIONAL LABORATORY

LDRD

# Advancing the Prediction of Actinide-Molten Salt Behavior

- Ab initio molecular dynamics (AIMD) simulations; density functional tight binding (DFTB) modeling, machine-learning-augmented DFTB parameterization (MLTB)
- ***A grand challenge:*** lower computational costs to tackle vast chemical, compositional, and temperature space -- and complex properties (viscosity, corrosion)
    - New LDRD Exploratory Research Project (**2025-2027**): "Navigating Vast Chemical Space: Empowering Molten Salt Modeling with Universal Graph Neural Networks" (Wang and Monreal)

ELSEVIER Journal of Nuclear Materials Volume 568, September 2022, 153836

*Ab initio* molecular dynamics (AIMD) simulations of NaCl, $UCl_3$ and NaCl-$UCl_3$ molten salts

ELSEVIER Journal of Molecular Liquids Volume 385, 1 September 2023, 122347

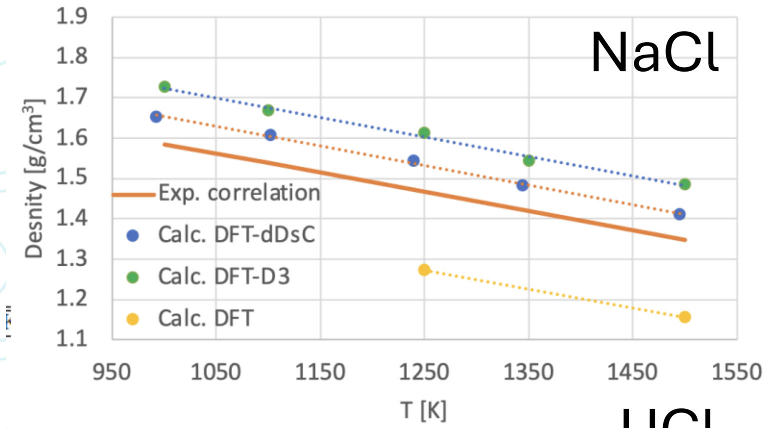
*Ab-Initio* molecular dynamics simulations of binary NaCl-$ThCl_4$ and ternary NaCl-$ThCl_4$-$UCl_3$ molten salts

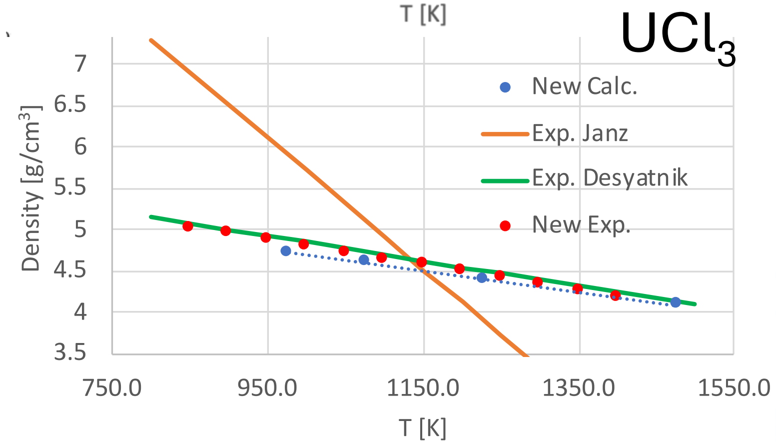
Gaoxue Wang [a], Bo Li [a], Ping Yang [a], David A. Andersson [b]

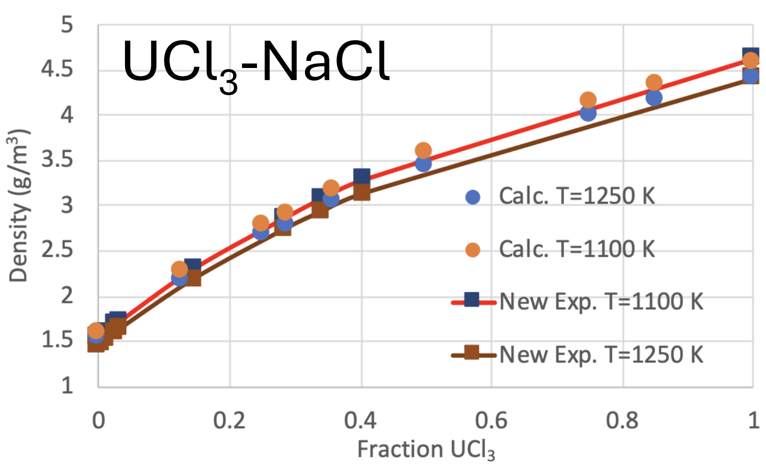
ELSEVIER Journal of Nuclear Materials Volume 591, 1 April 2024, 154902

First-principles investigation of the thermophysical properties of NaCl, $PuCl_3$, and NaCl-$PuCl_3$ Molten salts

Kai Duemmler [a], David Andersson [c], Benjamin Beeler [a b]




- Evaluated AIMD approaches; must include dispersion forces
- Reasonable agreement with our experimental data
- Interesting note: Small deviation from ideal solution <eutectic (<~37%$UCl_3$); correlates with calcd PDF: U-U network disruption (exptl data needed!)

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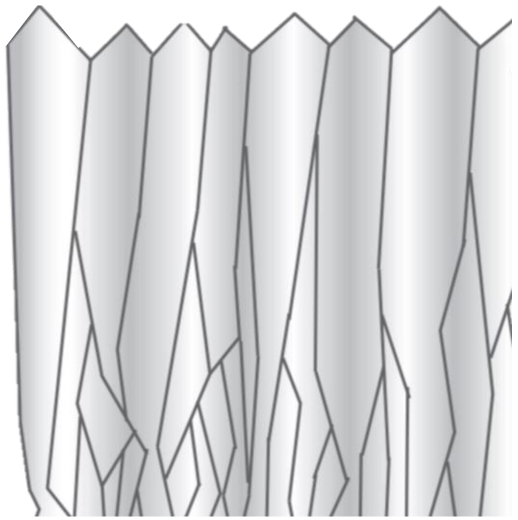
# Actinide-Molten Salt Electrochemistry

*Lead: Hannah Patenaude,*
*Director's Post-Doctoral Fellow*

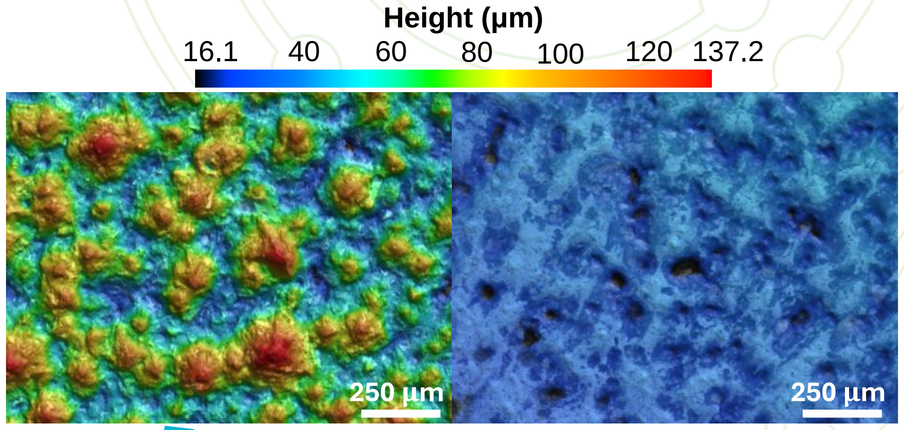
- Boron-doped diamond electrodes
  - Material customization
  - Measurement optimization
    - Geometry, topography, & surface chemistry
- Small-volume electrochemical cells
  - Minimize analyte (e.g., Pu)
  - Control surface area
- Example focus areas:
  - Cation influence on coordination & redox
  - Focus on actinides
- Integrated with Advanced Modeling and Simulation Expertise at LANL
  - SciDAC (*PI: Laurent Capolungo*): Scientific Discovery through Advanced Computing program to **advance modeling behavior and properties of structural materials under molten salt conditions**

**Boron-Doped Diamond**

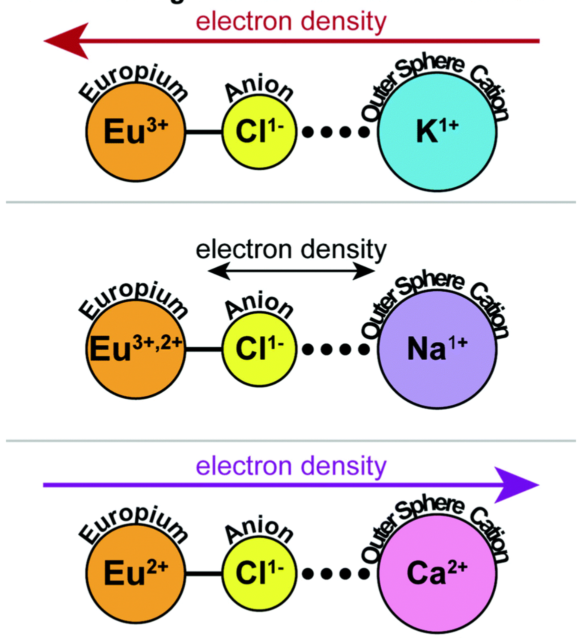


Adapted from Cobb et al., *Annu. Rev. Anal. Chem.*, **2018**.

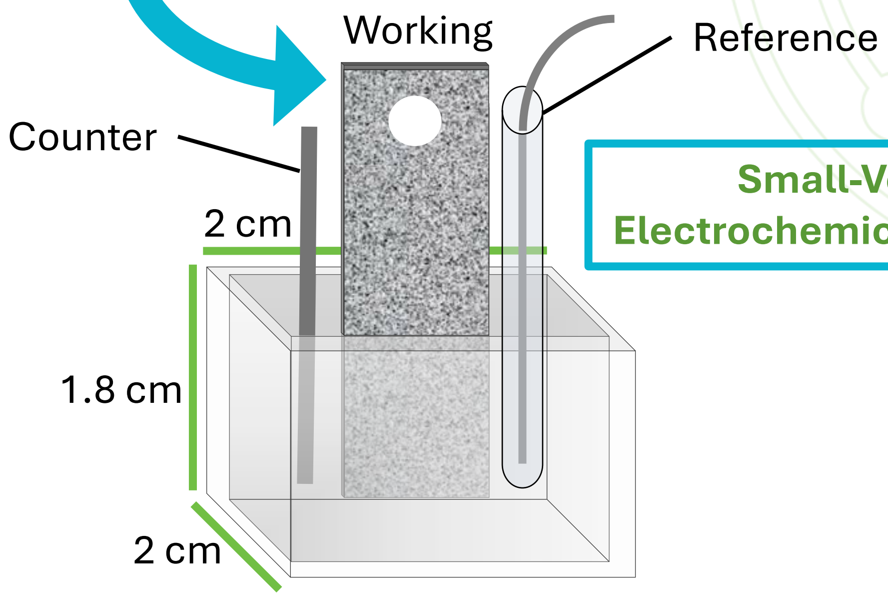
**Polishing & Surface Treatments**




**Cation Influence on Redox Chemistry**




MacInnes et al., *Dalt. Trans.*, *50*, **2021**.




**Small-Volume Electrochemical Cell**

Los Alamos NATIONAL LABORATORY

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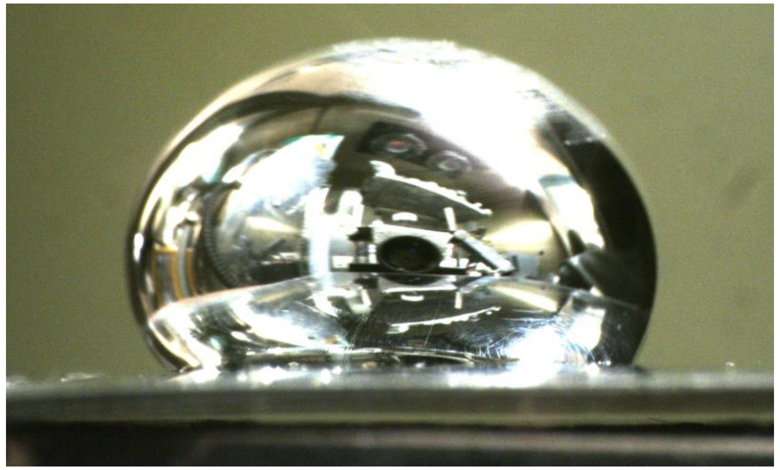
# Sessile Drop Experiments

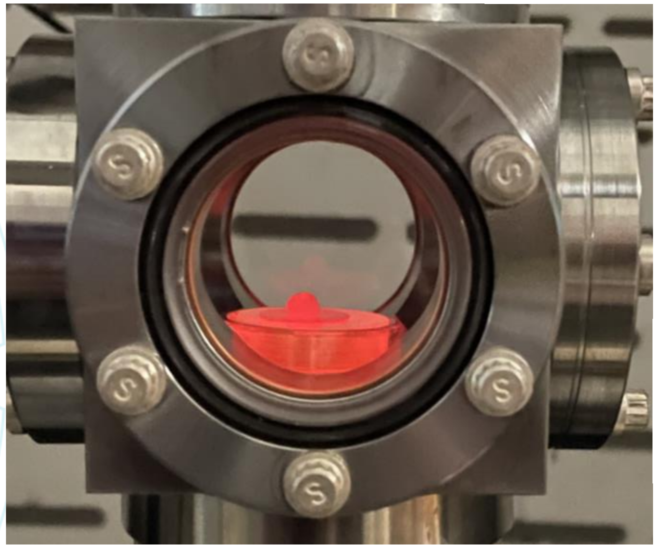

- Observing the shape of a liquid droplet resting on a solid surface (solid-liquid-gas/three-phase interface)
- Measure contact angles, surface energy, wettability

**Custom apparatus: compact modular furnace**

- Up to 100 mTorr, 1000 °C
- Continuous gas flow
- Compact, for use in glove box
- Very clear optical windows for imaging

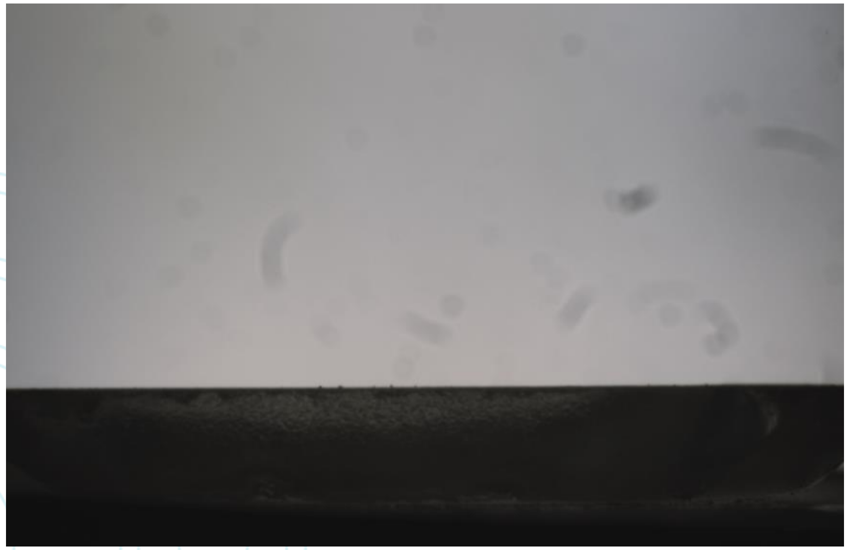
Tin on alumina, under argon at 300 °C



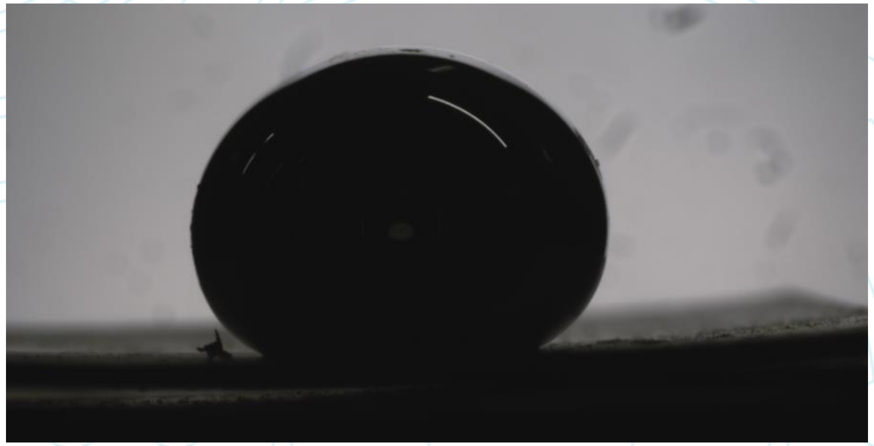


Gallium on alumina, under 2% $H_2$/Ar at 750.2°C

# Sessile Drop: Na

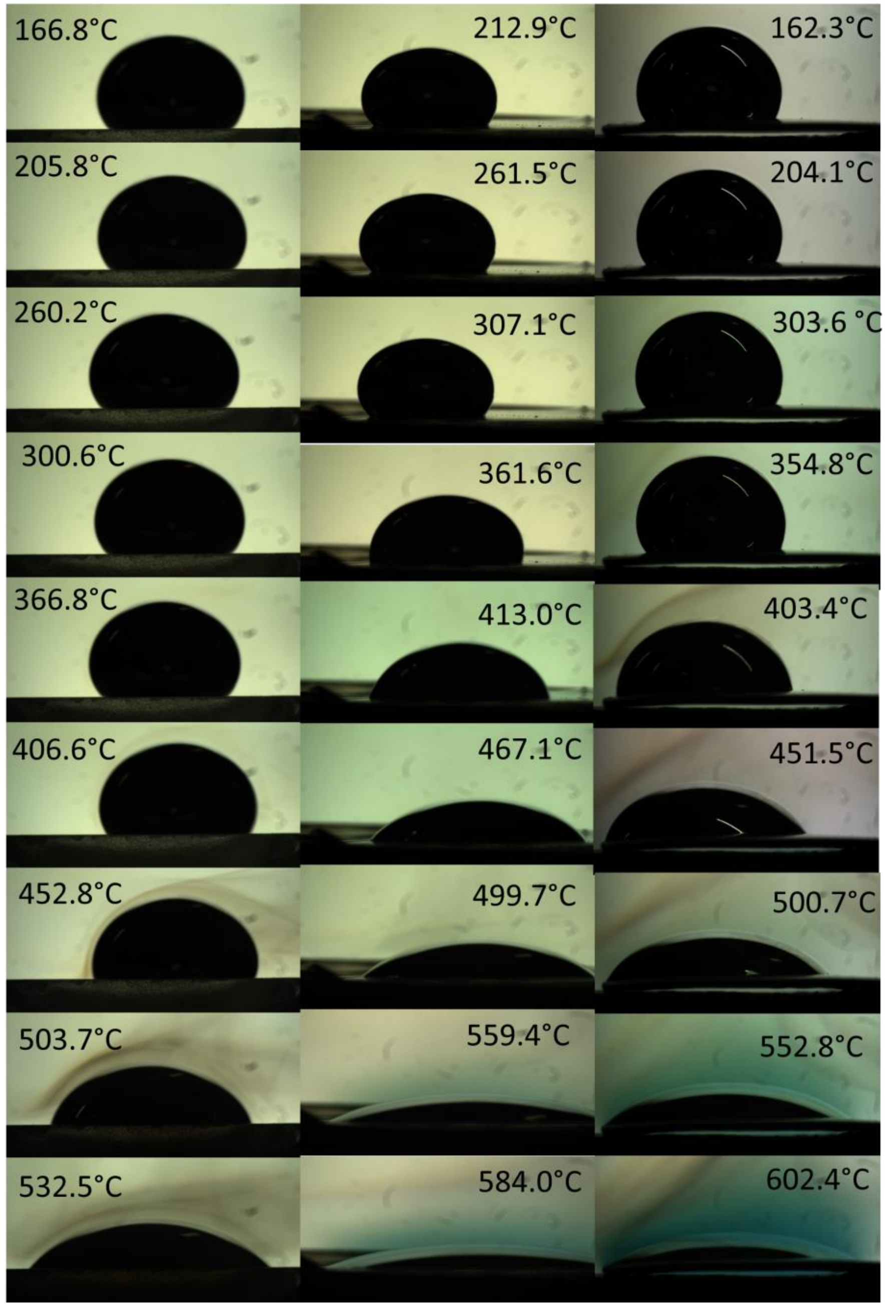


Pipetting Na on pyrex



Na on FeCrAl, 160 - 600 °C

- Na reaction with an FeCrAl alloy, 600°C under argon
- Exposure to 10 ppm $O_2$ begins reaction




Pyrex Mo Foil FeCrAl

***Actinide-molten salts are next up!***

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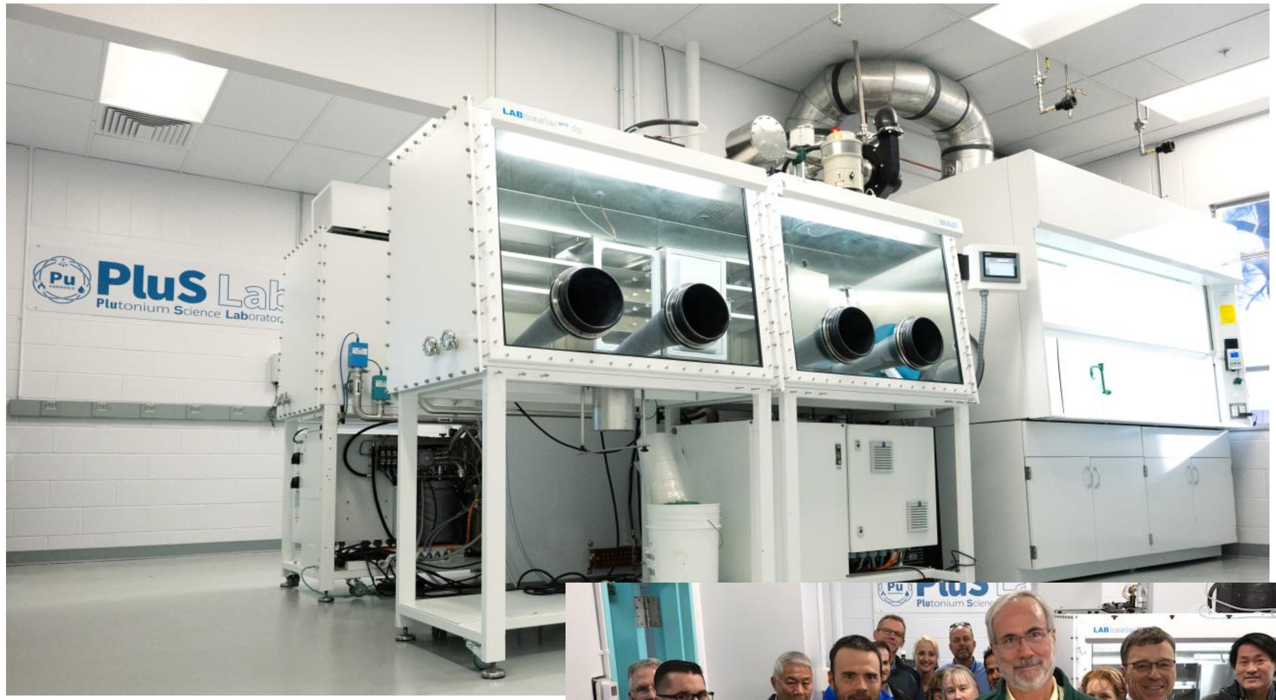
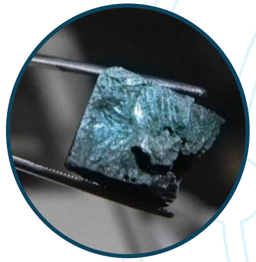
# The Plutonium Science Laboratory (PluS Lab)

The **PluS Lab** will **grow, sustain, and innovate workforce proficiency** to address **current and emerging nonproliferation challenges** through **targeted fundamental plutonium S&T**.

Gram-scale, non-irradiated Pu experiments • Unclassified • Flexible, agile



Molecular Chemistry & Materials Science

Aqueous Systems

Molten Salt Science

***Renovation and Commissioning: Completed***
***First Novel Pu Experiments: FY26***

# Acknowledgements

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Jarom Chamberlain
Dylan Tharpe Eralie
Olivia Dale
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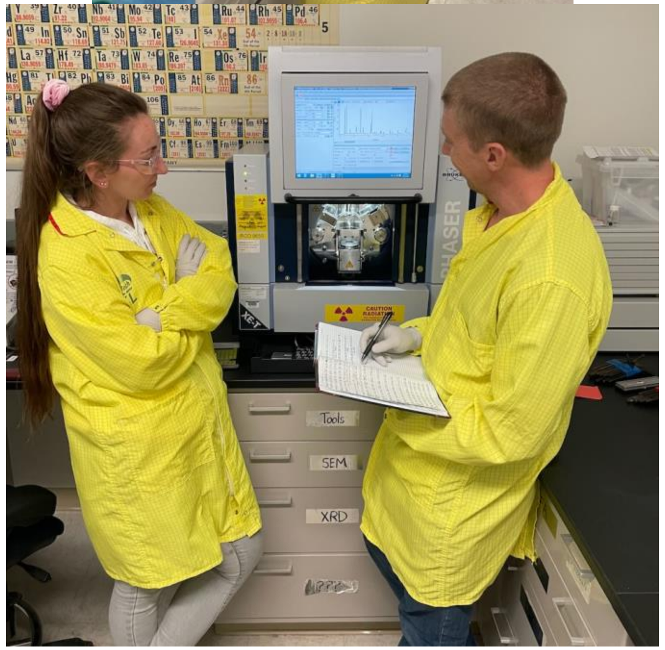

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Molten Salt Reactor Campaign

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Technology Commercialization Fund (TCF) with Kairos Power

Technology Commercialization Fund | OTT Office of Technology Transitions

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