U.S. DEPARTMENT OF ENERGY | Office of NUCLEAR ENERGY

Molten Salt Reactor PROGRAM

Thermochemical and Thermophysical Property Database Development at LANL

Marisa Monreal

Inorganic, Isotope, and Actinide Chemistry – Chemistry Division

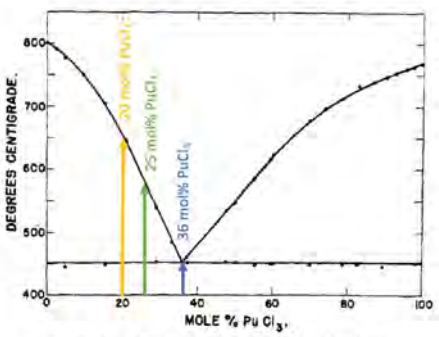
Los Alamos National Laboratory

LA-UR-23-24429

Annual MSR Campaign Review Meeting 2-4 May 2023

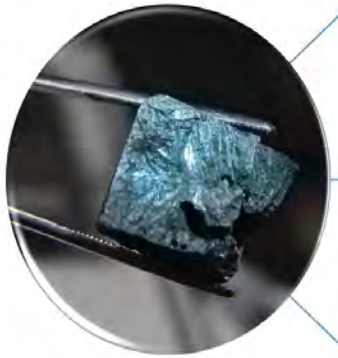
LANL MSR Campaign Work: $PuCl_3$-NaCl

- **LANL actinide-molten salt research program:**
  - Chemistry & thermophysical properties: experiment and modeling
  - Chlorides; expanding to fluorides, beryllium
  - Studies are across length scales
  - Pyroprocessing, nuclear energy, nonproliferation
  - **Sponsors:** MSR Campaign, LDRD, GAIN, Technology Commercialization Fund (TCF)
  - **Collaborations:** National Laboratories, universities, industry, NEAMS, SciDAC, FUTURE EFRC



Bjorklund, C. W., Reavis, J. G., Leary, J. A., Walsh, K. A. "Phase Equilibria in the Binary Systems $PuCl_3$-NaCl and $PuCl_3$-LiCl" 1959

MSR Campaign $PuCl_3$-NaCl Collaboration: INL, LANL, PNNL, ORNL



Experimental *INL, LANL*
- Investigate three compositions within binary
- Provide double verified, high fidelity results on thermophysical properties
- Focus: density, melting point, heat capacity

Modeling & Simulation *PNNL, ORNL*
- Ab initio molecular dynamics (AIMD) method used with solid state parameters
- Validate experimental results
- Extend knowledge into Pu-rich regions

Expected Outcomes
- Peer-reviewed journal article
- Validated data set on eutectic composition
  - Experimental – INL & LANL
  - Modeled – PNNL & ORNL
- To be added to the Molten Salt Thermophysical Property Database

$PuCl_3$-NaCl Shipment: INL→LANL

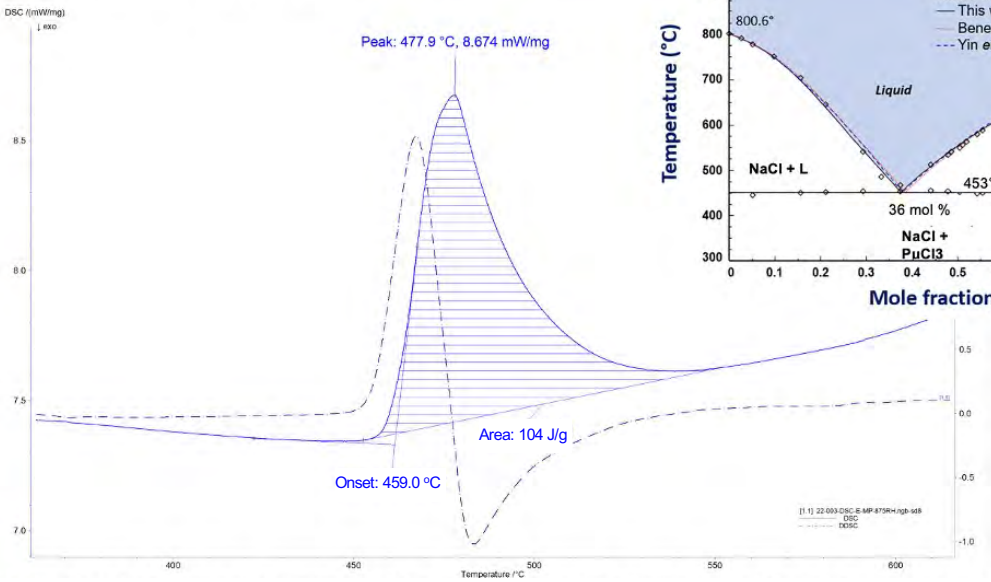
- ✓ INL and LANL measuring the same material: **INL-synthesized $PuCl_3$-NaCl eutectic**
- ✓ **INL shipped material to LANL:** 10g shipped and introduced into glovebox line in the Plutonium Facility at LANL (PF-4) in **September 2022**
- Upon receipt, material purity check, for inter-validation with INL data:
  - ✓ **Melting point** by differential scanning calorimeter (DSC)
  - Still pending: Powder X-ray diffractometry (**pXRD**)

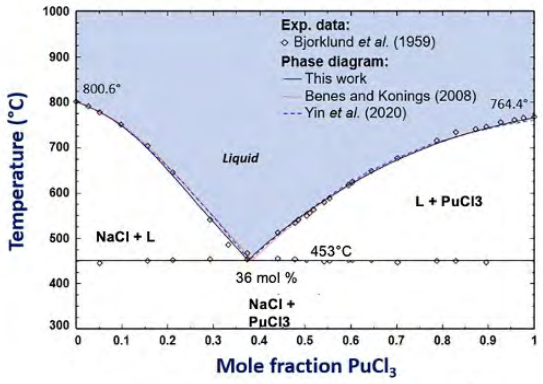
One of the fabricated capsules for shipping pelletized $PuCl_3$-NaCl eutectic from INL to LANL.

LANL Measurement of $PuCl_3$-NaCl Eutectic Melting Point

$PuCl_3$ + NaCl eutectic salt (INL)

Sample Stage





This work: $T_{melt,\ onset}$ = 459 +/-4 °C, $T_{melt,\ peak}$ = 478 +/-4 °C

(1) INL 2022: heating onset 451 +/-5 °C, peak 455 °C

For additional comparison:

(2) Bjorklund 1959: cooling onset 453 +/-8 °C

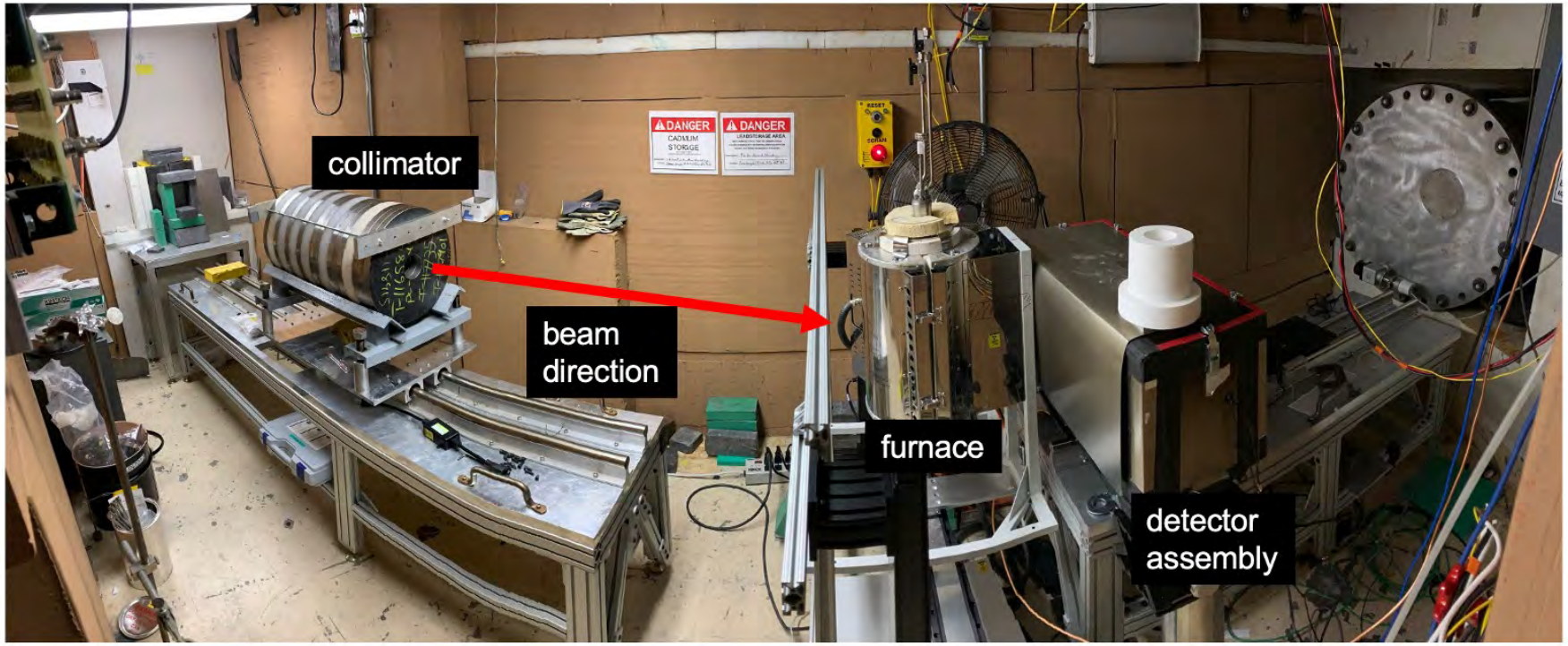
(3) ANL 2022: heating onset 456 +/-5 °C, peak 480 +/-3 °C

(1) INL/RPT-22-69181

(2) J. Phys. Chem., 1959, 63(10), 1774-1777

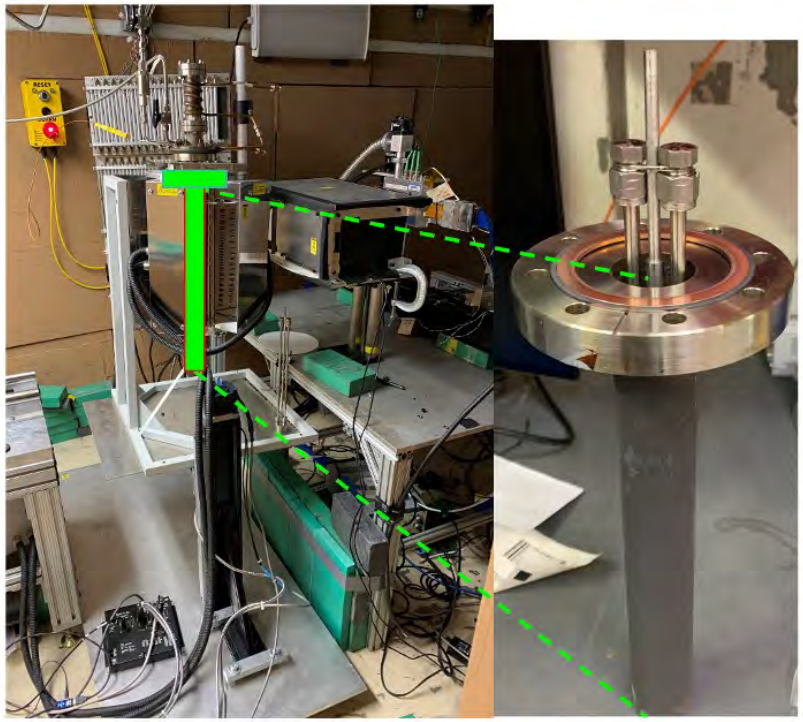
(3) ANL/CFCT-22/43(2022)

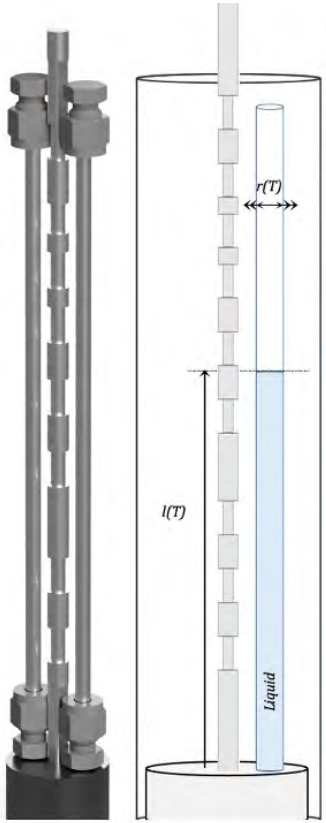
Density by Neutron Radiography at LANSCE



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

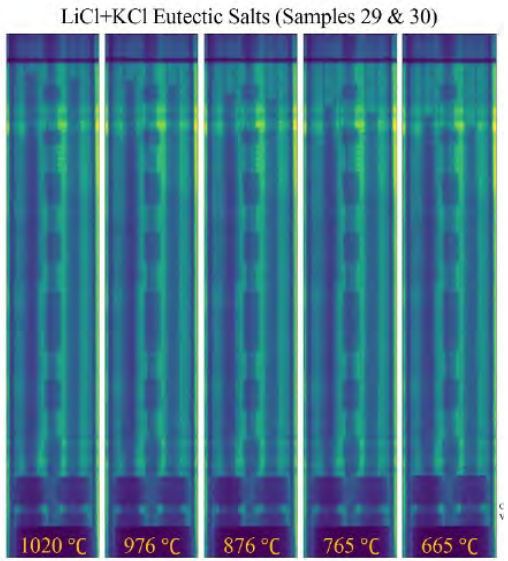
Density by Neutron Radiography at LANSCE





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

- Images stitched together
- Heights determined at different temperatures

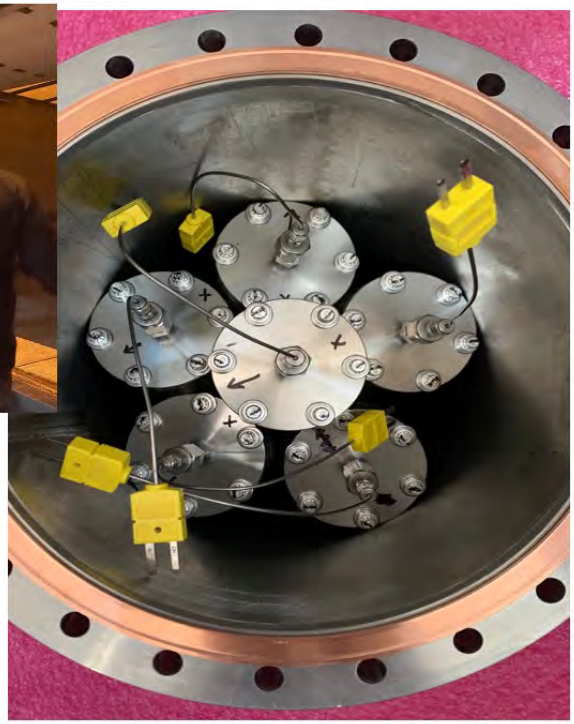


(1) Parker, S., Long, A., Lhermitte, C., Vogel, S., Monreal, M., Jackson, J. M., *J. Mol. Liq.,* **2022,** *346,* 118147

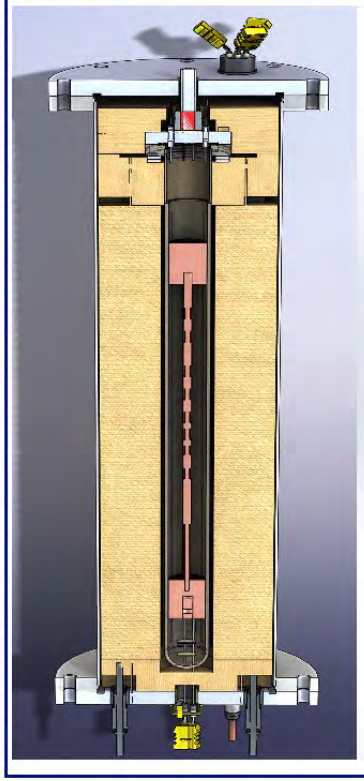
(2) Long, A., Parker, S., Carver, T. Jackson, J. M., Monreal, M., Newmark, D., Vogel, S., *J. Imaging,* **2021,** *7,* 88

Density by Neutron Radiography: $PuCl_3$-NaCl, December 2022

Sample move: PF-4 to LANSCE: December 9th, 2022



Required a New State-of-the-art Furnace

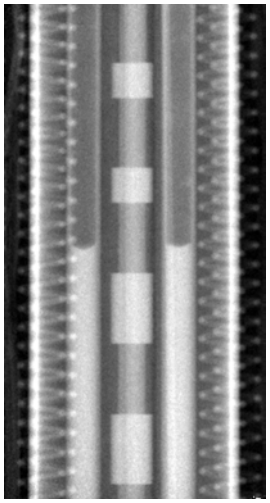


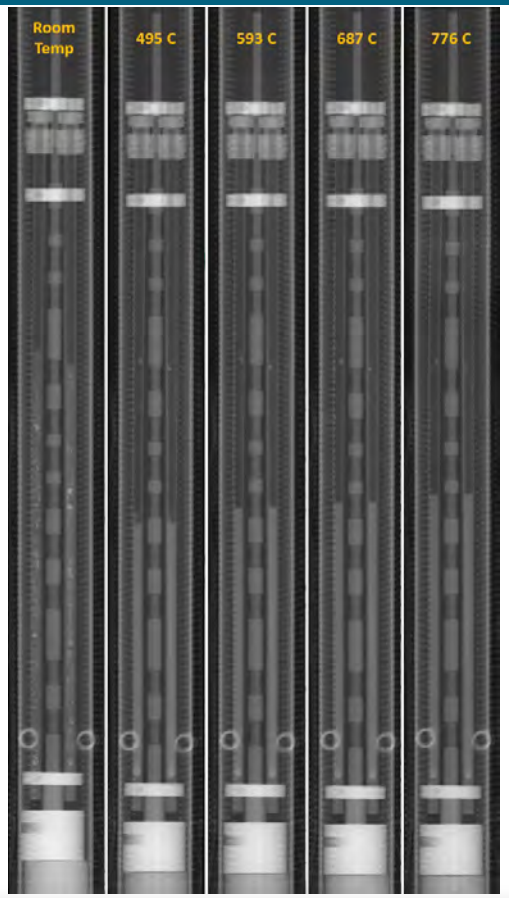
Furnace Design by Travis Carver

Density by Neutron Radiography: $PuCl_3$-NaCl, December 2022

Experimental Details:

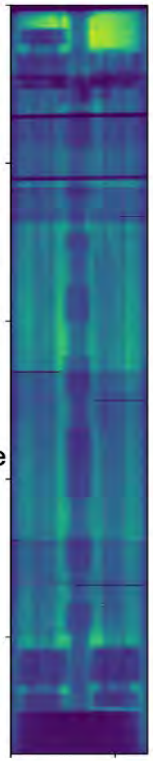
- Beam Time on FP5: Dec 10th – 20th, 2022
- Maximum Temperatures: ~950 °C
- Exposure Times: 1 min
- ~12- to 15-hour measurements per sample pair
- Each pair was measured once
- Used gantry to move sample through FOV
- 4-5 full sample scans were performed at elevated temperatures for each sample-pair; images of meniscus every ~5 °C





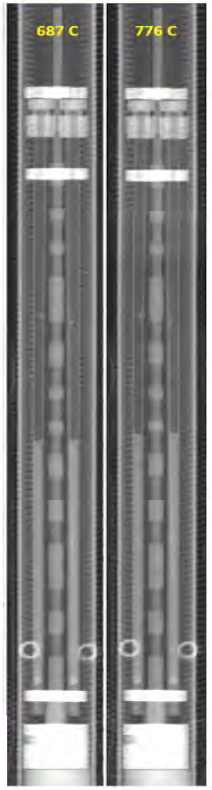
Density by Neutron Radiography: $PuCl_3$-NaCl, December 2022

Initial setup



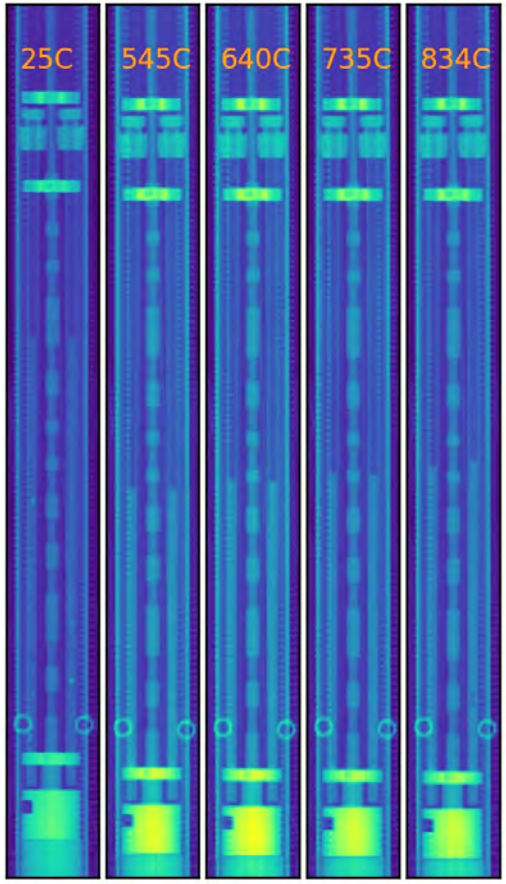
- CarboLite Gero Furnace
- Si-Flat Panel Detector
- 250um resolution
- 15-minute exposures
- NO automation
- NO Remote controls
- Just radiographs…

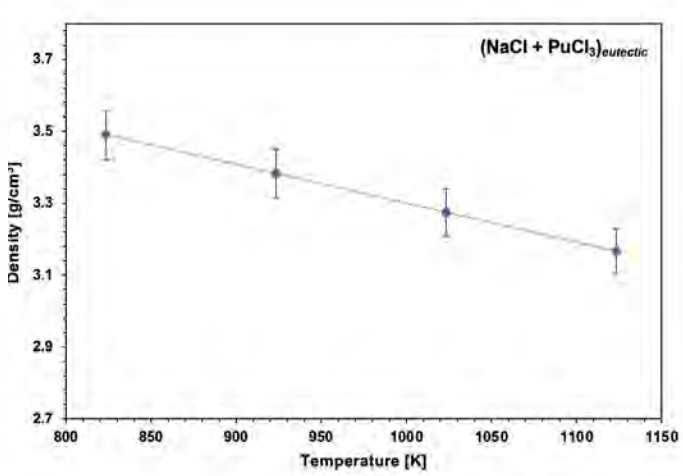
Current setup (Pu Measurements **December 2022**)

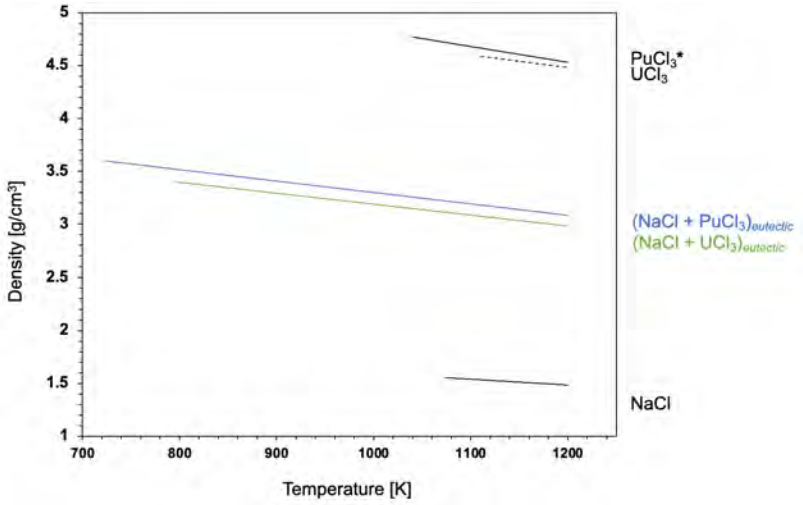


- State-of-the-art custom furnace that houses high-hazard samples
- New Imaging setup with ZWO-ASI cameras and ZEISS lenses.
  - < 1min exposures with ~50um resolution.
- Movies of melting and solidification process!
- Complete automation and remote control.
- Neutron Attenuation images instead of just radiographs
- **Image analysis underway; results will be published in joint manuscript with TerraPower**

Density by Neutron Radiography: $PuCl_3$-NaCl preliminary results







Temperature [°C]	Density [g/cm^3]
550	3.49
650	3.38
750	3.27
850	3.17

- Plotted results are from preliminary image analysis, error analysis (2% error bars shown)
- Pu > U density
- Next steps: complete analysis, comparison with INL, PNNL/ORNL

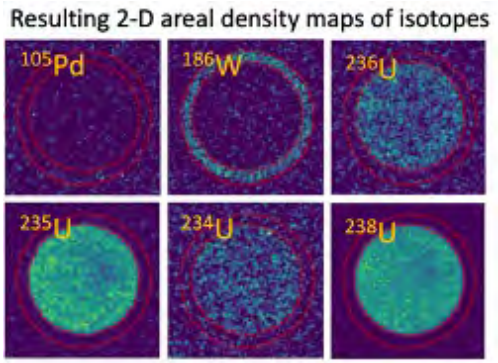
Scott Parker, Alex Long

**Pure $PuCl_3$ liquid density derived from measurements of salt mixtures of $PuCl_3$ with NaCl, $MgCl_2$, and UCl_3*

Density by Neutron Radiography at LANSCE

Density by neutron radiography general comments and features:

- Eyes on sample the whole time (watch out for bubbles!)
- Modular setup: multiple samples can be measured simultaneously, and samples can be swapped quickly (measurement times depend on furnace)
- Can measure same samples multiple times
- Suitable for Pu materials
- Potential to extract **additional information** with more advanced neutron imaging techniques:
  - Temps and actinide density can be measured in-situ with neutron resonances (i.e., ERNI)
  - Material compositions can be measured with diffraction



Energy-Resolved Neutron Imaging (ERNI) isotope mapping

Next steps: Drop Calorimetry for Integral Heat Capacities

A new methodology for measuring the ΔH_{mix} of molten salt systems has been developed using our Setaram AlexSYS-800 calorimeter.

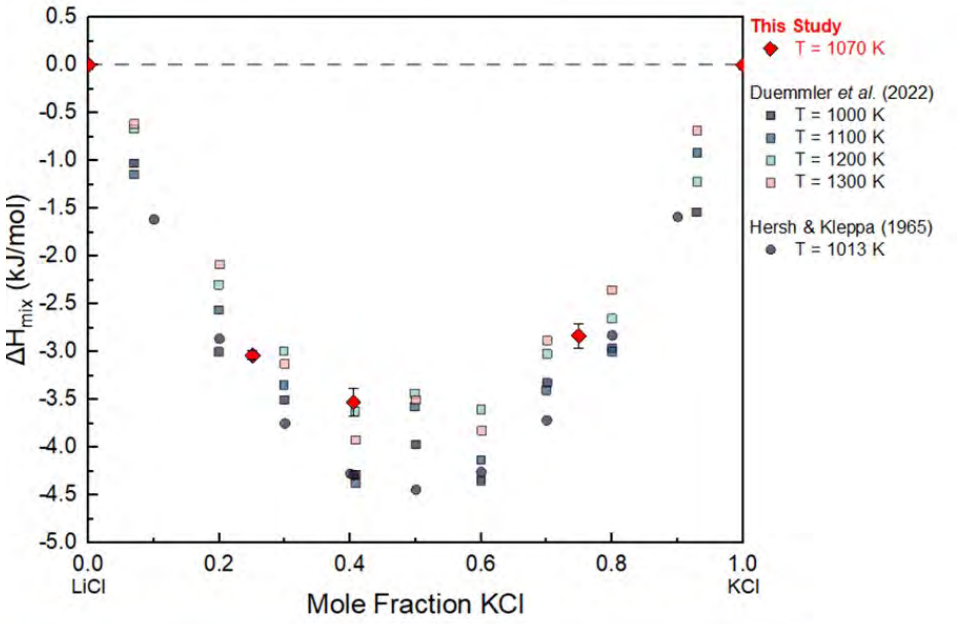
Advantages/improvements:

- Elimination of any effects arising from material-atmosphere interactions
- Minimal salt-crucible interactions
- No further mixing needed after being introduced into the calorimeter

- Will be employed in future calorimetric studies on other molten systems containing **actinides** or **fission products** of interest.

- Will be utilized for **integral heat capacities** for molten salts systems containing Pu in June 2023.

$$\Delta_{meas} = \Delta_{trans} = \int_{T_1}^{T_2} C_p dT + Thermal\ Event\ (i.e., Fusion\ or\ Mixing)$$



Sample	Temperature Room (K)	Temperature Calorimeter (K)	Experimental ΔH_{mix} (kJ/mol)
0.251KCl – 0.749LiCl	297.48 ± 0.11	1070.39 ± 0.01	-3.04 ± 0.05
KCl-LiCl eutectic	297.73 ± 0.15	1070.51 ± 0.00	-3.52 ± 0.15
0.749KCl – 0.251 LiCl	297.62 ± 0.27	1070.41 ± 0.01	-2.83 ± 0.13

Andrew Strzelecki, Hongwu Xu

Next steps: 2023 LANSCE Experiments

- **LANSCE 2023 beam cycle: June – December 2023**
  - New $PuCl_3$ compositions for density by neutron radiography
    - Lower concentrations; additional binary, ternary compositions (containing UCl_3, $MgCl_2$); **for MSR Campaign collaboration: 5%$PuCl_3$ in UCl_3-NaCl (thank you to Toni Karlsson @ INL and Hilary Fitzgerald @ TerraPower!)**
    - Note: Under LDRD DR project, also planning pair distribution function experiments for local structure studies at LANSCE in 2023 beam cycle
    - Supported by/coordinated with:
      - XAFS studies at SSRL
      - Continued electroanalytical studies (electromotive force measurements, corrosion rate determination)

Disseminating LANL Molten Salt Results

TMS Conference March 2023:

1. Hannah Patenaude (UNLV graduate student, currently working at LANL finishing dissertation work): "Electrochemical Characterization of Molten Salt Fuel Systems with Boron-Doped Diamond"
2. Scott Parker: "Thermophysical Properties of Liquid Halides"
3. Sven Vogel: "Characterization of UCl_3 and NaCl-0.352mol% UCl_3 Salts using Neutron Scattering"
4. LANL co-authored a Univ of Utah talk by Jacob Yankey of Mike Simpson's lab: "Chlorination of U Metal with $FeCl_2$ in LiCl-KCl and NaCl-$MgCl_2$"

Upcoming:

Presentations:

Actinide Separations - May 2023

ACS Conference - August 2023

AIChE Conference - November 2023

Papers:

Enthalpies of mixing by drop calorimetry (submitted February 2023)

Pu-NaCl density by neutron radiography (to be submitted Summer 2023)

Karla Erickson (Early Career Scientist)
New Capabilities to Access and Analyze Pure Inorganic Chlorides

Hannah Patenaude (Graduate Student)
Electrochemical Investigation of Uranium Redox Behavior in Molten Chloride Salts Using Boron-Doped Diamond

Looking Forward: LANL Molten Salt Research 2023+

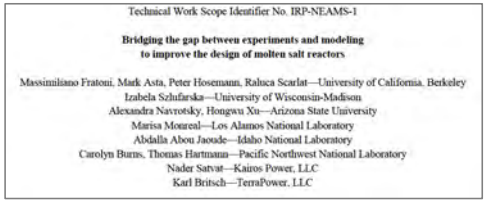
Properties	Experimental Techniques
Density	Neutron Radiography, Conventional (Push-rod) Dilatometry
Viscosity	Dynamic Neutron and X-ray Radiography
Melting Point/Phase Diagram, Heat Capacity	Differential Scanning Calorimetry (DSC)
Corrosivity	Electrochemistry, Exposure Tests
Heat of Dissolution, Enthalpy of Mixing, Heat Capacity	Drop Calorimetry
Thermal Diffusivity	Laser Flash Analysis (LFA)
Local Structure	Pair Distribution Function (PDF) Analysis, EXAFS, Raman Spectroscopy, Drop Calorimetry, Electrochemistry

Internal Collaborations:

- **New-start LDRD projects**
  - Nuclear magnetic resonance spectroscopy (actinide chlorides)
- **LANL-led SciDAC**
  - Scientific Discovery through Advanced Computing program to advance modeling behavior and properties of structural materials under molten salt conditions
- **Nuclear Energy Advanced Modeling and Simulation (NEAMS) – NTD Chris Stanek**
- **NA-22, Nonproliferation Stewardship Program**
- **LANL-led EFRC: FUTURE**
  - Studying corrosion under irradiation
- **Space Nuclear Propulsion**
  - Electrodeposition of fuel coatings in molten salt

LANL-University Collaborations:

- **University of Utah** (Simpson)
  - Electrochemistry, vapor pressure, student pipeline
- **MIT** (Khaykovich)
  - Pair distribution function analysis
- **UC Berkeley** (Scarlat, Fratoni)
  - Molten salt round robin, fluoride & beryllium salt expertise, student pipeline, IRP
- **Oregon State University, Texas A&M, UNLV**
  - Student pipeline—viscosity, materials corrosion, electrochemistry



Technical Work Scope Identifier No. IRP-NEAMS-1

Bridging the gap between experiments and modeling to improve the design of molten salt reactors

Massiniliano Fratoni, Mark Asta, Peter Hosemann, Raluca Scarlat—University of California, Berkeley
Izabela Szlufarska—University of Wisconsin-Madison
Alexandra Navrotsky, Hongwu Xu—Arizona State University
Marisa Monreal—Los Alamos National Laboratory
Abdalla Abou Jaoude—Idaho National Laboratory
Carolyn Burns, Thomas Hartmann—Pacific Northwest National Laboratory
Nader Satvat—Kairos Power, LLC
Karl Britsch—TerraPower, LLC

Acknowledgments

Actinide-molten salt team working on DSC, Density by Neutron Radiography, Drop Calorimetry:

Scott Parker (MST-16)
Alex Long (MST-8)
Matt Jackson (MST-DO)
Travis Carver (MST-8)
Alberto Gomez (MST-16)
Andrew Strzelecki (EES-16)
Hongwu Xu (EES-16)

Funding supporting DSC, Density by Neutron Radiography, Drop Calorimetry:

Molten Salt Reactor Campaign

LANL Laboratory Directed Research and Development (LDRD) Directed Research Project #20210113DR

Gateway for Accelerated Innovation in Nuclear (GAIN) #NE-21-25117

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

Thank you

Marisa Monreal
mmonreal@lanl.gov

U.S. DEPARTMENT OF ENERGY | Office of NUCLEAR ENERGY