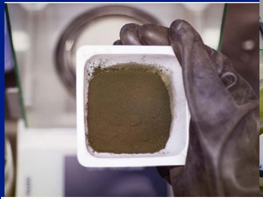
The LANL Molten Salt Research Capability: 2022 Status Update

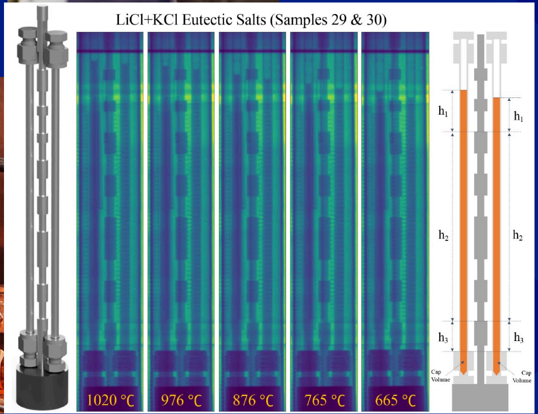
Marisa Monreal
Inorganic, Isotope, and Actinide Chemistry (C-IIAC)
Chemistry Division
Los Alamos National Laboratory
mmonreal@lanl.gov

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

FY21-23 LDRD Directed Research Project (#20210113DR):
"Advanced Characterization to Enable Prediction of Actinide-Molten Salt Behavior"

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

Main objectives:

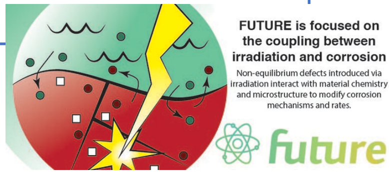
1. To integrate advanced characterization techniques in both experiment and modeling
2. To generate an experimentally validated predictive capability with quantified uncertainty for actinide-molten chloride salts (uranium, thorium, and plutonium)

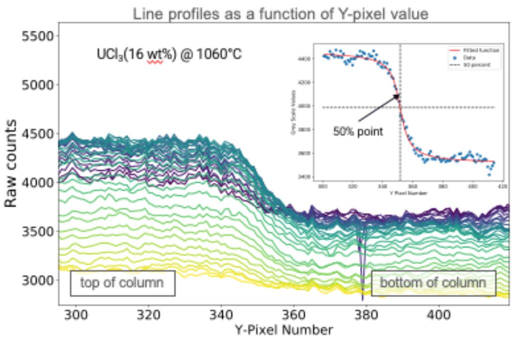
Technical goals:

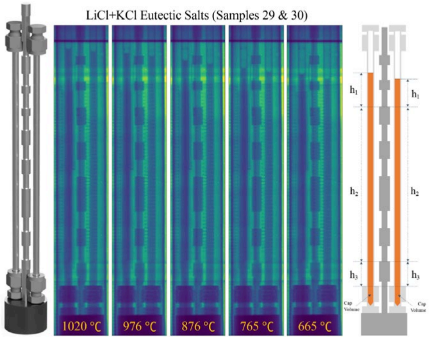
1. Develop atomic scale simulations of macroscale properties, then parametrized physics-based models with quantified uncertainty
   (Modeling and Simulation Thrust – Lead: David Andersson)
2. Synthesize and prepare pure materials: actinide chlorides and solvent salts; examine local structure
   (Chemistry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

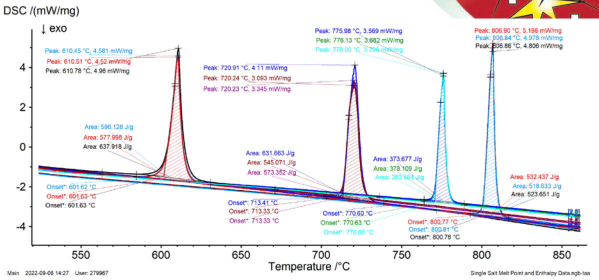
Properties Measurements at LANL

Properties	Experimental Techniques	2022+ Status, Plans
Density	Neutron Radiography*	Neutron Radiography Measurements on $PuCl_3$ X-ray Radiography Conventional (Push-rod) Dilatometry
Melt Point (T_m) Heat Capacity (C_p) Enthalpy of Fusion	Differential Scanning Calorimetry (DSC)*	DSC Measurements on $PuCl_3$
Corrosivity, redox potentials	Electrochemistry	Simultaneous ion-beam irradiation and corrosion experiments, with electrochemical monitoring (FUTURE EFRC)



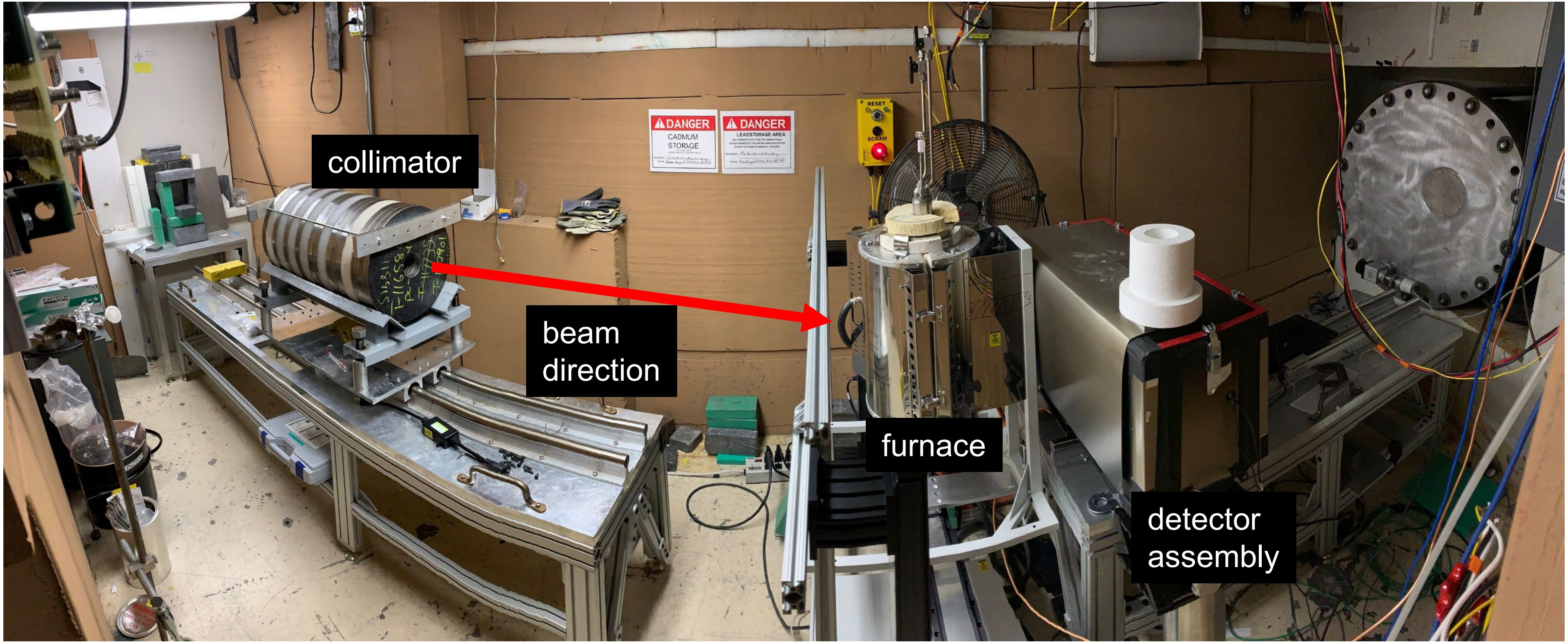






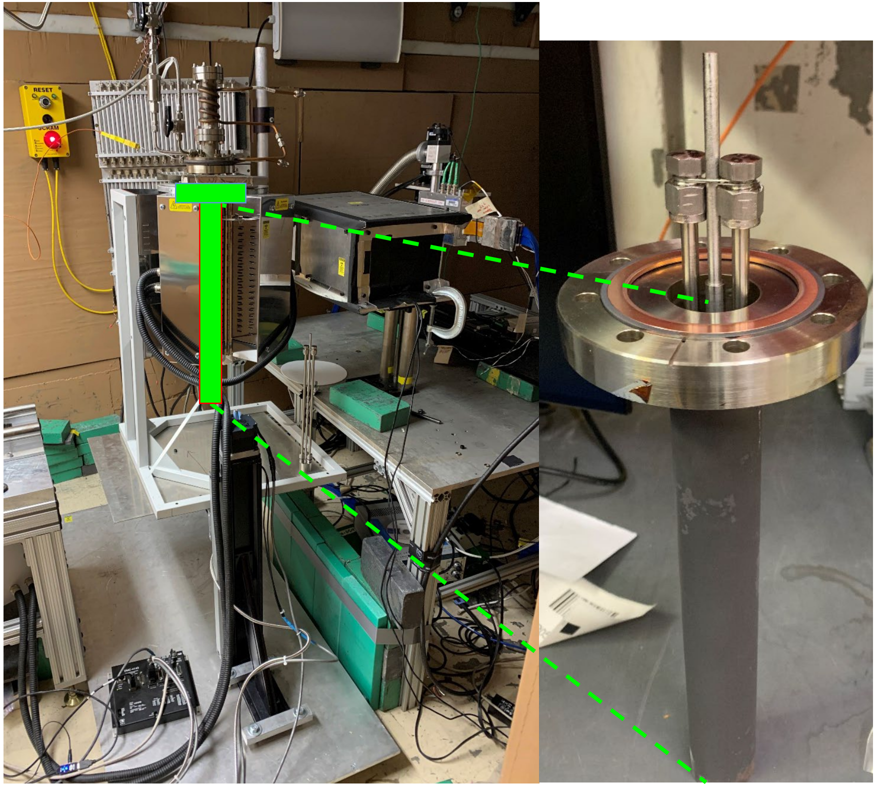
*can be performed on Pu-bearing salt

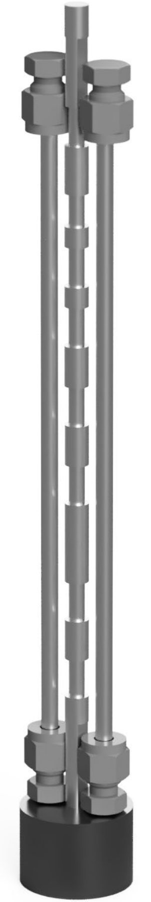
Density using Neutron Radiography: Experimental setup in flight path

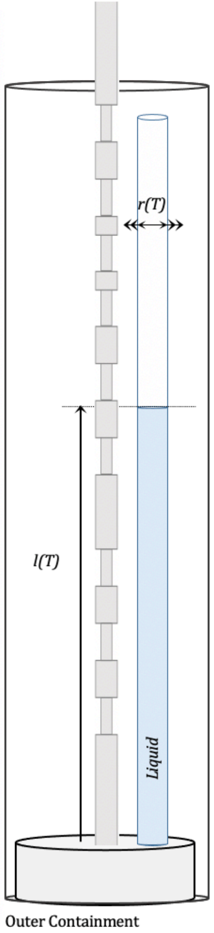


Flight Path 5 at Los Alamos Neutron Science Center (LANSCE)

Density using Neutron Radiography: Method ("Neutron Dilatometry")

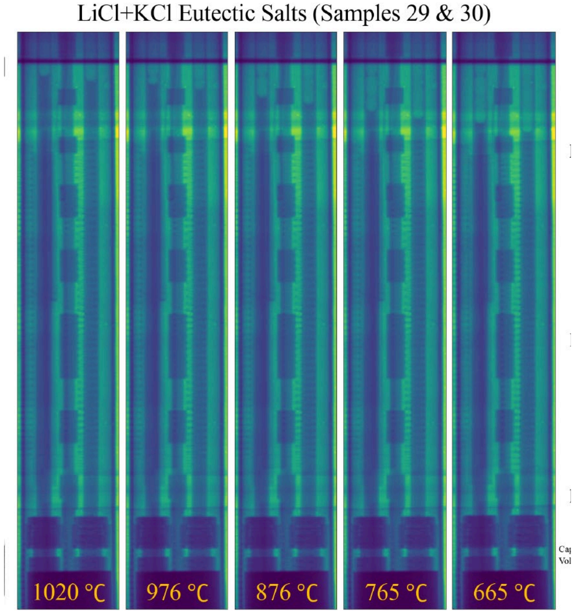






Fluid height is determined using the known height of a feature on our reference

- Images stitched together
- Heights determined at different temperatures



Density using Neutron Radiography: Uranium-molten chlorides

Binary Eutectic Mixtures	ρ_0 [g/cm³]	$\alpha \cdot 10^{-3}$	Uncertainty	Range [K]	Reference
0.595 LiCl + *0.405* KCl	2.0049	0.5148	±0.003	626-1300	This work
	2.0077	0.5302	±0.001	642-1150	[50]
	2.0183	0.5167	±0.003	740-860	[119]
	2.0286	0.5268	-	680-860	[76]
	2.0292	0.5275	±0.0002	668-866	[124]‡
	2.0183	0.5167	±0.008	720-1200	[94]
	2.1148	0.8700	-	-	[40]
0.431 $MgCl_2$ + *0.569* NaCl	2.1615	0.5169	±0.01	720-1300	This work
	2.1253	0.47419	±0.0006	1030-1100	[a]‡‡
	2.2971	0.5070	-	-	[40]
	2.002	0.48	-	1003-1173	[127]*
0.494 NaCl + *0.506* KCl	2.1064	0.5439	±0.01	927-1300	This work
	1.9764	0.5680	±0.0002	943-1182	[124]‡‡‡
	2.1314	0.5679	±0.008	945-1170	[94][119]*
0.328 $MgCl_2$ + *0.672* KCl	2.1187	0.5438	±0.02	710-1300	This work
	2.0007	0.4571	±0.025	1030-1140	[b]
	1.944	0.52	-	973-1173	[127]**
	1.896	0.47	-	923-1073	[136]
	1.904	0.552	±0.002	723-1073	[26]
	2.25458	0.4740		650-1050	[148]
0.66 NaCl + *0.34* UCl_3	4.2235	1.0347	±0.02	794-1300	This work
	4.2900	1.5903	±0.0009	973-1123	[149]***
	3.8604	0.8371	±0.001	892-1142	[99]**
0.81 KCl + *0.19* UCl_3 (E1)	3.1756	0.7645	±0.015	841-1300	This work
	3.981	1.3827	±0.0008	1230-1280	[129]†
0.43 KCl + *0.57* UCl_3 (E2)	4.6124	0.9531	±0.024	821-1300	This work
	8.405	4.1819	±0.0025	1180-1270	[129]††
(NaCl + KCl) + *0.034* UCl_3	2.0920	0.5014	-	970-1270	[149]
(NaCl + KCl) + *0.137* UCl_3	3.7985	1.4775	-	970-1270	[149]
(NaCl + KCl) + *0.195* UCl_3	3.4585	0.9492	-	970-1270	[149]
0.45 NaCl + *0.31* KCl + *0.24* UCl_3	2.5352	0.7010	±0.02	1000-1400	This work
(*0.505* NaCl + *0.130* KCl + 0.365 UCl_3)	3.4511	0.7432	±0.02	1000-1400	This work
0.494 NaCl + *0.462* KCl + *0.495* UCl_3	4.1241	0.9050	±0.02	1000-1400	This work
(NaCl + KCl) + *0.495* UCl_3	5.4813	2.0103	-	970-1270	[149]
(NaCl + KCl) + *0.718* UCl_3	5.9677	1.9953	-	970-1270	[149]
(LiCl + KCl) + *0.0085* UCl_3	2.0731	0.5290	±0.004	770-1300	This work
(LiCl + KCl) + *0.0177* UCl_3	2.1336	0.5311	±0.004	770-1300	This work

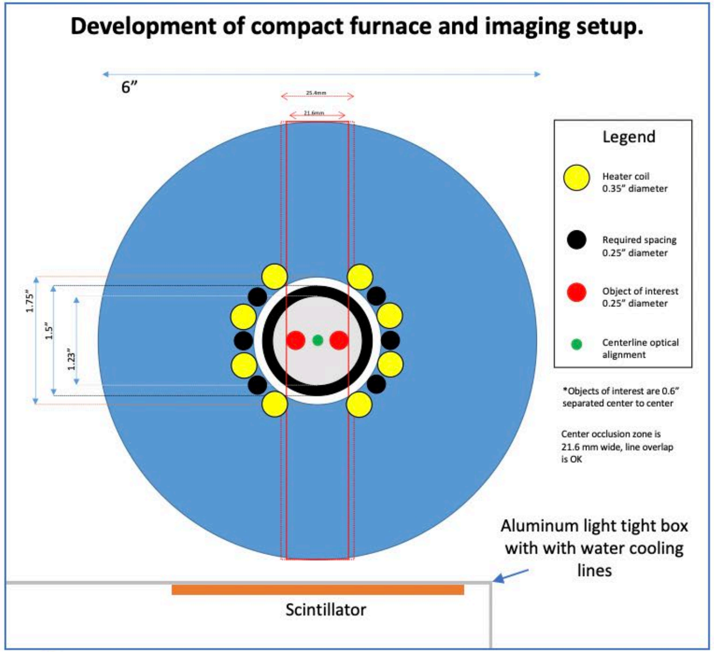
- ✓ We have determined a series of molten chloride salt densities, including with UCl_3
  - For more details, please see two journal publications—paper containing density data[1] and imaging technique paper[2]
- ✓ Have been working on improvements to reduce error:
  - **Mass**: Increase sample mass to 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...

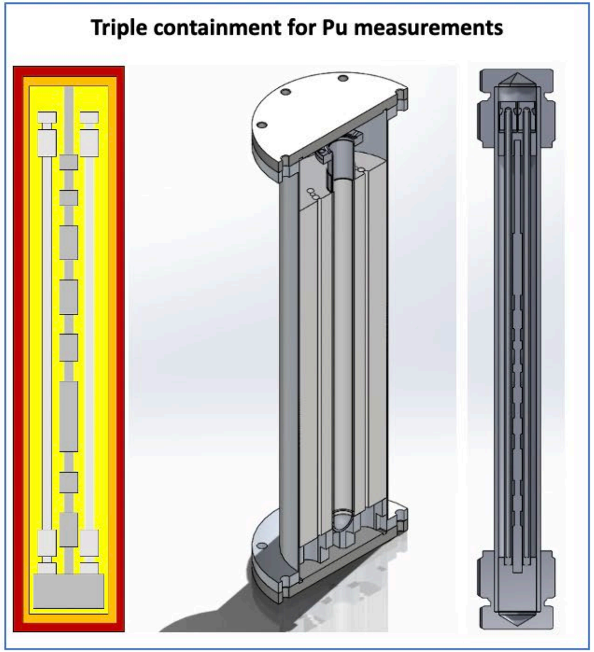
(1) Parker, S., Long, A., Lhermitte, C., Vogel, S., Monreal, M., Jackson, J. M., *J. Mol. Liq.*, **2022**, *346*, 118147
(2) Long, A., Parker, S., Carver, T. Jackson, J. M., Monreal, M., Newmark, D., Vogel, S., *J. Imaging*, **2021**, *7*, 88

Los Alamos NATIONAL LABORATORY

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**





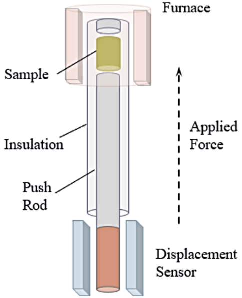
Los Alamos NATIONAL LABORATORY

Grateful acknowledgment to Toni Karlsson and team at INL for material!

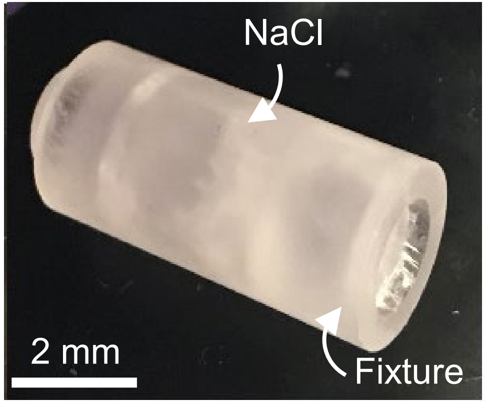
Density: Conventional (Push-Rod) Dilatometry

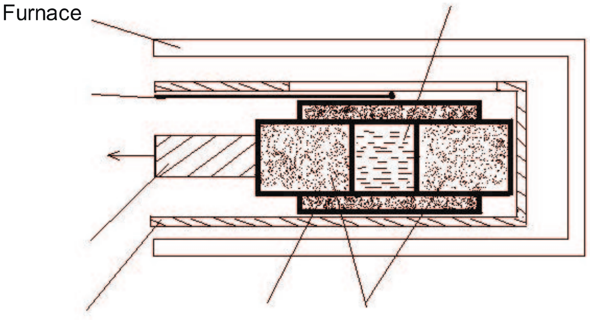
Dilatometer:

Coefficient of Thermal Expansion

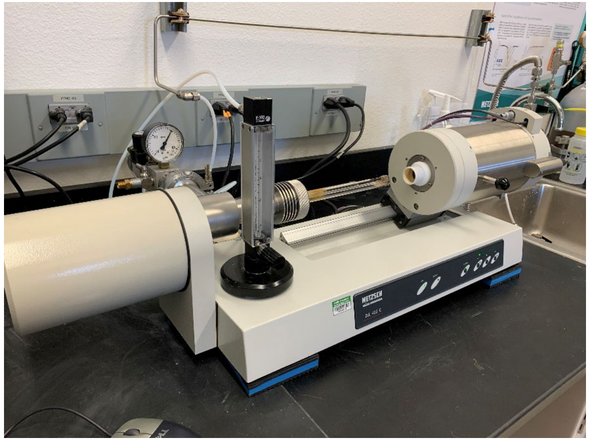


$$\frac{\Delta L}{L_0} = \alpha_L \left(\frac{1}{\Delta T}\right) \quad [^1/_K]$$





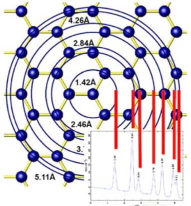
[Wang and Mei, *J Mater Sci and Technol*, **22**(4) (2006) 569-571]

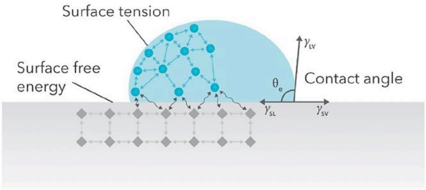


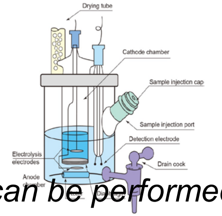
- ✓ Container-based dilatometry is viable up to 1000° C
- ✓ Loss of material during tests minimized by crucible design and manufacture
- ✓ New graphite crucibles, one-sided piston
- ✓ Salts measured include NaCl, KCl, LiCl, $MgCl_2$ and their associated eutectics
- ❑ Optimization: Minimization of sample loss will improve overall uncertainty

Properties Measurements at LANL *(cont.)*

Properties	Experimental Techniques	2022+ Status, Plans
Viscosity	Dynamic Neutron Radiography*	Dynamic X-ray Radiography* Rotational Viscometry (OSU)
Heat of Dissolution, Enthalpy of Mixing	Drop Calorimetry*	Uranium measurements 2023+: Thorium and plutonium measurements
Thermal Diffusivity	Laser Flash Analysis (LFA)	2023: Test custom sample chamber
Vapor Pressure	Transpiration	Collaboration continues (Univ. of Utah) 2023: Stand up at LANL
Surface Tension	Contact Angle Measurement (Optical method; neutron radiography*)	Optical method (OSU) 2023: Initial measurements during June-Dec beamtime at LANSCE
Local Structure	Pair Distribution Function (Neutron)	Pair Distribution Function (X-ray) (MIT) XAS (MIT) Raman & UV-vis Spectroscopy (UCBerkeley)
Characterization (purity)	pXRD*, DSC (T_m)*	Karl-Fisher Titration, Actinide SS-NMR*



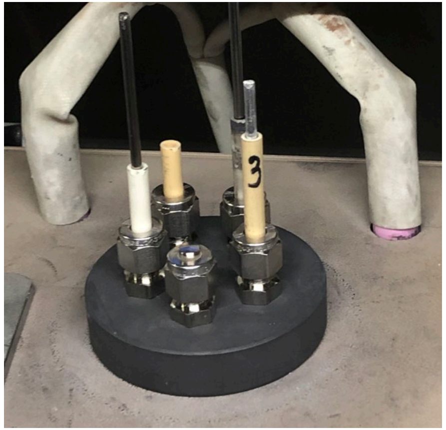




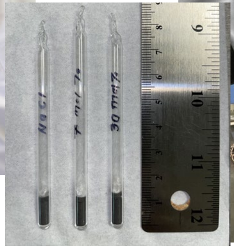
*can be performed on Pu-bearing salt

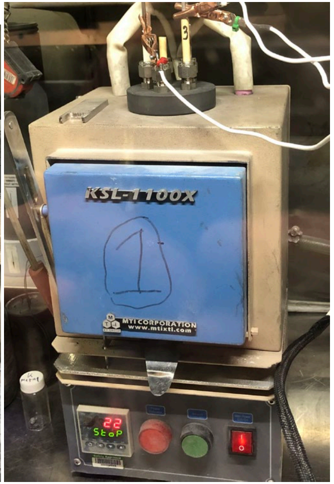
“Cold” Lab – Non-Radiological Molten Salt Lab

- Small- and large-scale furnaces
- Salt-drying glovebox (vac oven antechamber)
- Both pyrochemistry <u>and</u> MSR research activities, training
- **New 2022:** Improved electrochemistry setup



Molten salt research activities include: *Direct oxide reduction, electrolytic oxide reduction, salt drying; waste stream characterization; electrochemistry; sample prep*





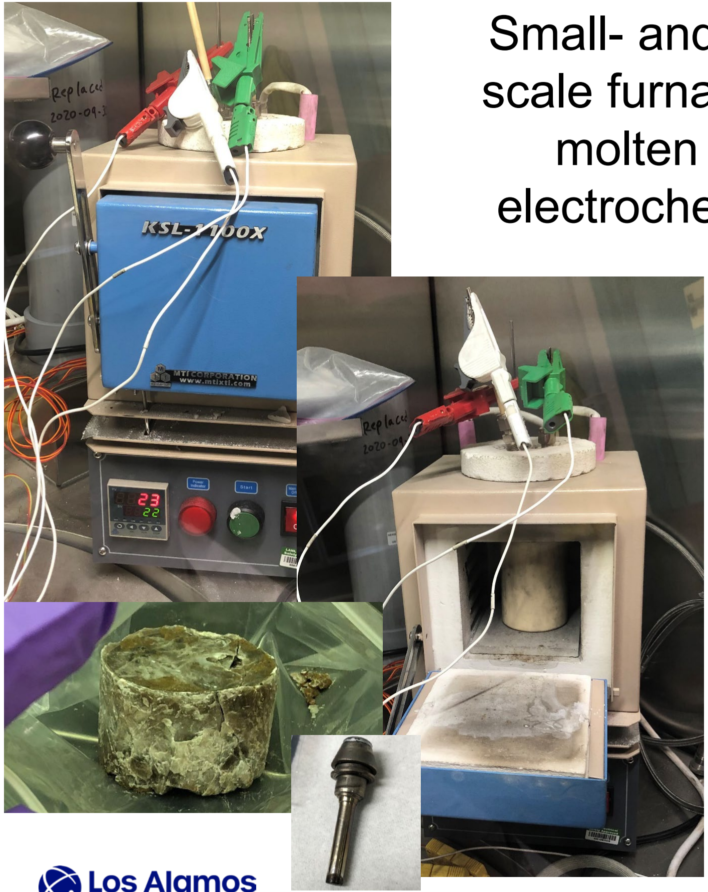
Los Alamos
NATIONAL LABORATORY

Depleted Uranium & Thorium Laboratories

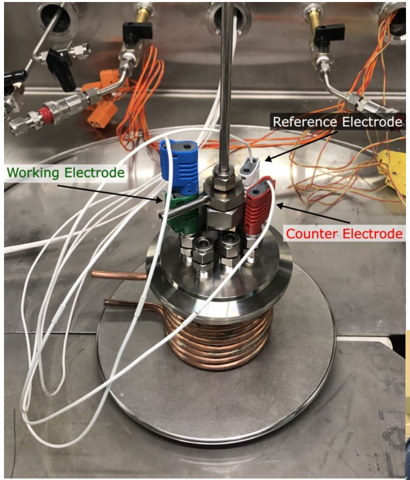
UCl_3-salt mixture loading for viscosity experiment

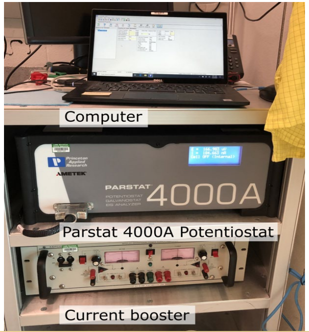
- Radiological control area with inert gloveboxes, hood, benchtop
- Large-scale furnace
- Several small-scale furnaces
- **Research activities:** electrochemistry, sample preparation for properties measurements (*see photo)*
- **New 2022**: actinide halide synthesis glovebox

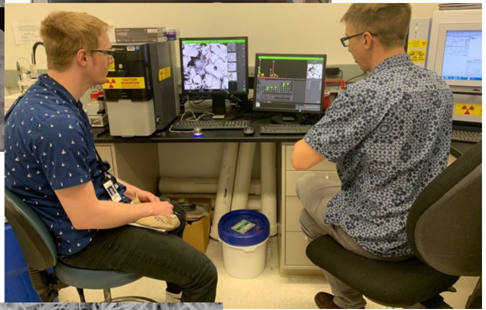
Depleted Uranium & Thorium Laboratories (*cont.*)



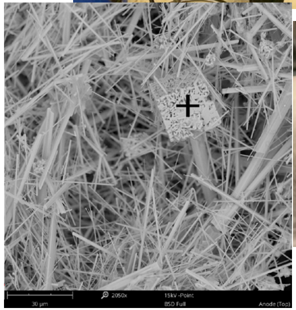
Small- and large-scale furnaces for molten salt electrochemistry

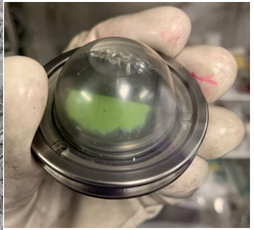






- **Electrochemistry:** Reference electrode development; corrosion studies; E^0 determination
- **Machining workspace** (metal and ceramic)
- **Characterization lab** (benchtop powder X-ray diffractometer--pXRD, benchtop scanning electron microscopy—SEM)





LANL Molten Salt Property Publications

Density via neutron radiography

Variable temp xtal structure... with neutrons

Technique: density via neutron radiography

Electrochemistry (ref electrode)

Mod-sim

Technique: conventional (push-rod) dilatometry

<u>2021-2022 Publications in Peer-Reviewed Journals</u>:

1. Parker, S., Long, A., Lhermitte, C., Vogel, S., Monreal, M., Jackson, J. M. "Thermophysical properties of liquid chlorides from 600 to 1600 K: Melt point, enthalpy of fusion, and volumetric expansion", *J. Mol. Liq.* **2022,** *346*, 118147.
2. Vogel, S., Andersson, D., Monreal, M., Jackson, M., Parker, S., Wang, G., Yang, P., and Zhang, J. "Crystal Structure Evolution of UCl_3 from Room Temperature to Melting." *JOM*, **2021**, 73, 3555-3563.
3. Vogel, S., Monreal, M., Shivprasad, A. "Materials for Small Nuclear Reactors and Micro Reactors, including Space Reactors." *JOM*, **2021**, 73, 3497-3498.
4. Long, A., Parker, S., Carver, T. Jackson, J. M., Monreal, M., Newmark, D., Vogel, S. "Remote Density Measurements of Molten Salts via Neutron Radiography", *J. Imaging*, **2021**, 7, 88.
5. Lhermitte, C., Parker, S., Jackson, J. M., Monreal, M. "$Mg^{2+/0}$ as a reliable reference electrode for molten chloride salts", *J. Electrochem. Soc.*, **2021**, 168, 066501.
6. Andersson, D. and Beeler, B. "Ab initio molecular dynamics (AIMD) simulations of NaCl, UCl_3 and NaCl-UCl_3 molten salts", *J. Nuc. Mat.,* **2022**, 568, 153836.
7. S. S. Parker, N. M. Abdul-Jabbar, M. Jackson, M. Monreal. *J. RadioAnal. Nucl. Chem.,* accepted **2022**.

<u>2022-2023 Publications: Selected Manuscripts In Preparation:</u>

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)

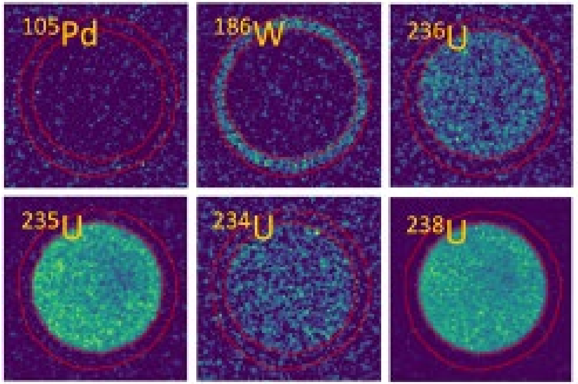
- **Broadening actinide-molten salt research scope**
  - Fluoride salts, beryllium salts
  - Adding techniques (just two examples: actinide Nuclear Magnetic Resonance Spectrocopy (NMR), rotational viscometry)
  - Broadening to other non-MSR molten salt research areas (two examples: hydrogen generation;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

Los Alamos
NATIONAL LABORATORY

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")

Resulting 2-D areal density maps of isotopes



ERNI isotope mapping

- **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))

Summary

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

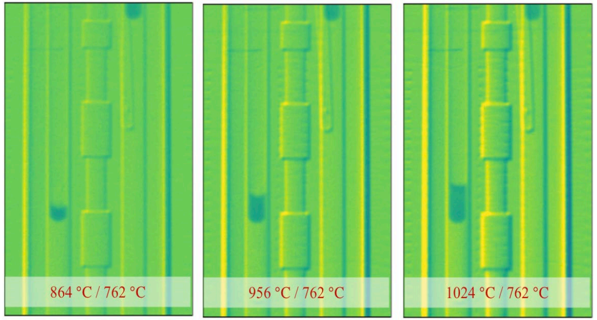
Funded TerraPower project (GAIN)

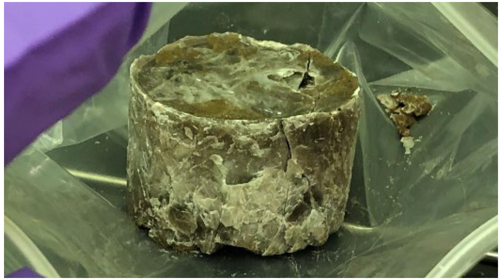
PluS Lab receives first sponsor funding

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 Boulkhalfa, 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)

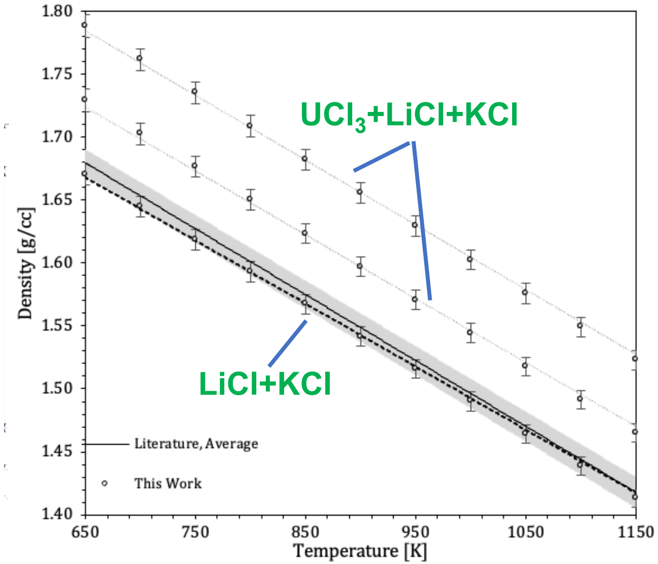
*This work was performed, in part, at the Los Alamos Neutron Science Center (**LANSCE**), a NNSA User Facility operated for the U.S. Department of Energy (DOE) by Los Alamos National Laboratory (Contract 89233218CNA000001).*

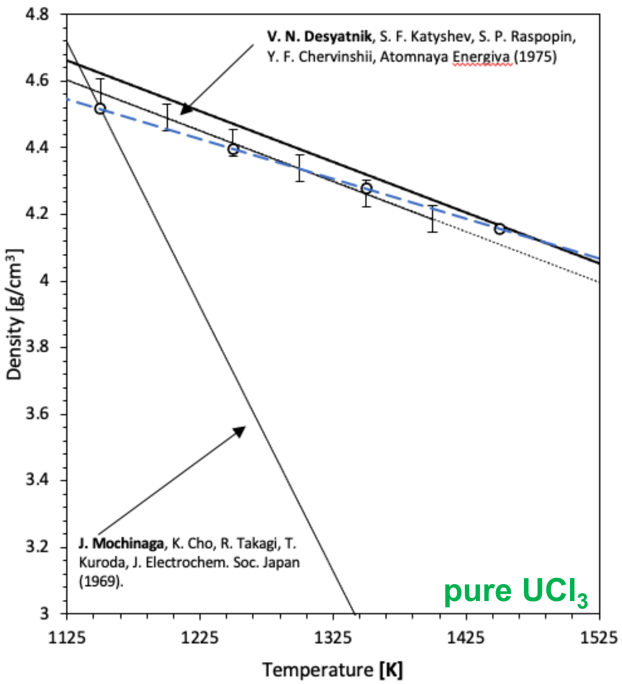
Questions?

Marisa Monreal
mmonreal@lanl.gov
Inorganic, Isotope, and Actinide Chemistry Group
Chemistry Division
(C-IIAC)
Los Alamos National Laboratory

Backup slides

Density using Neutron Radiography: Results





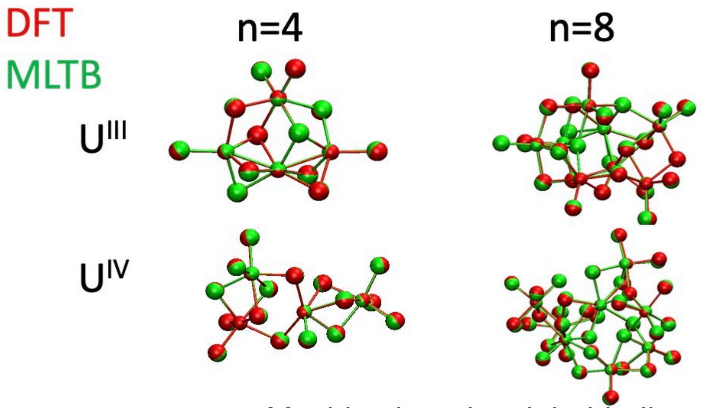
- ✓ Successful demonstration of novel, unique-to-LANL capability for **accurate measurement of liquid density of salts**, including uranium-bearing mixtures
- ✓ Two journal publications (imaging technique, and density data)

Next step: plutonium-bearing mixtures

(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

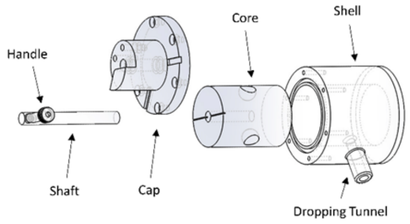
FY21-23 LDRD DR:
“Advanced Characterization to Enable Prediction of Actinide-Molten Salt Behavior”

- **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

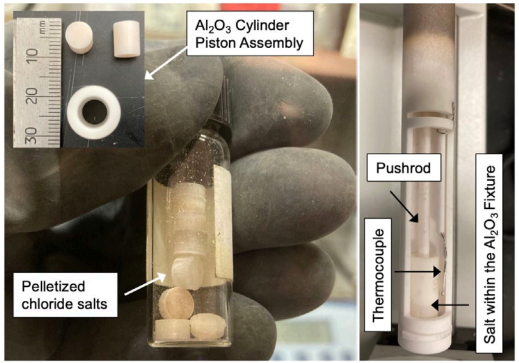


Machine learning tight binding

- **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!)

Drop calorimetry



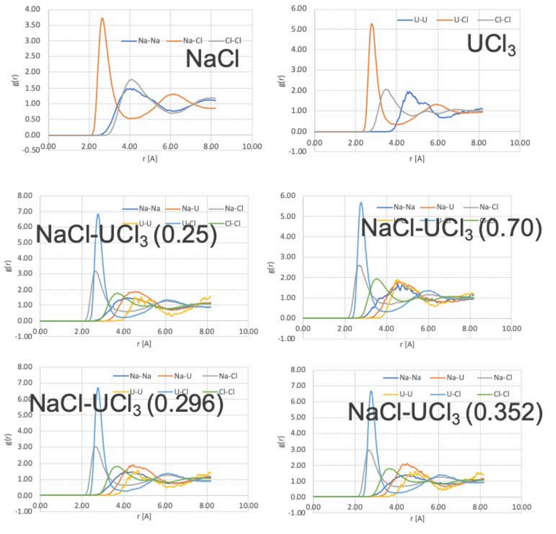
Dilatometry

FY21-23 LDRD DR:
“Advanced Characterization to Enable Prediction of Actinide-Molten Salt Behavior”

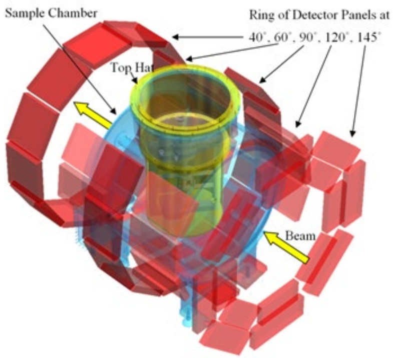
The pair distribution function (PDF) gives the probability of finding an atom at a distance *r* from an atom at the origin

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.



HIPPO @ LANSCE