Measurements of uranium-bearing salt properties

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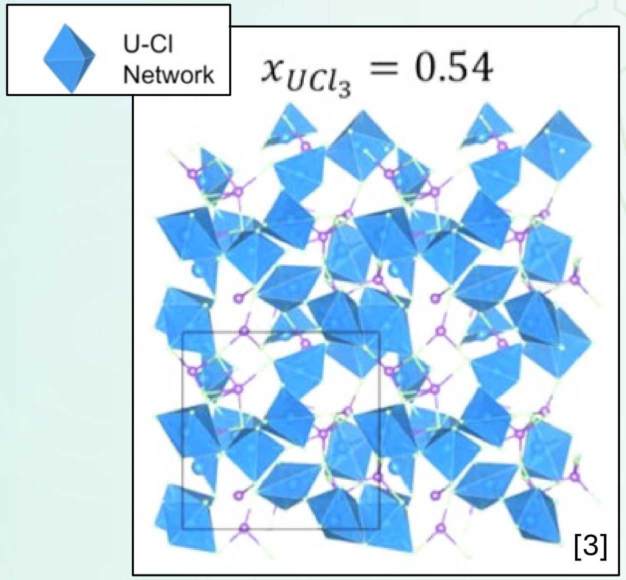
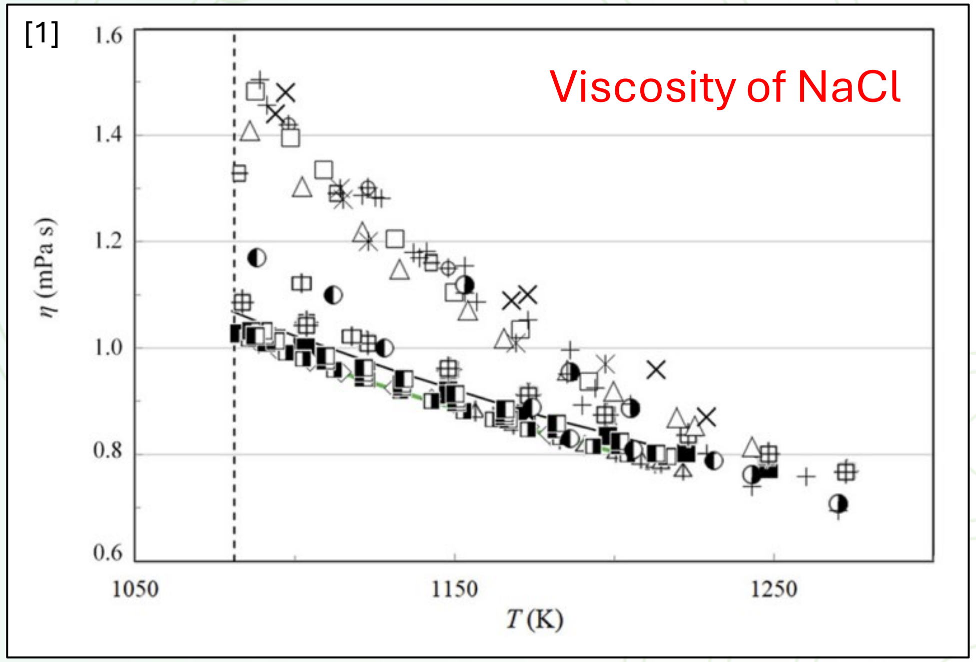
Molten Salt Reactor Program – Annual Review

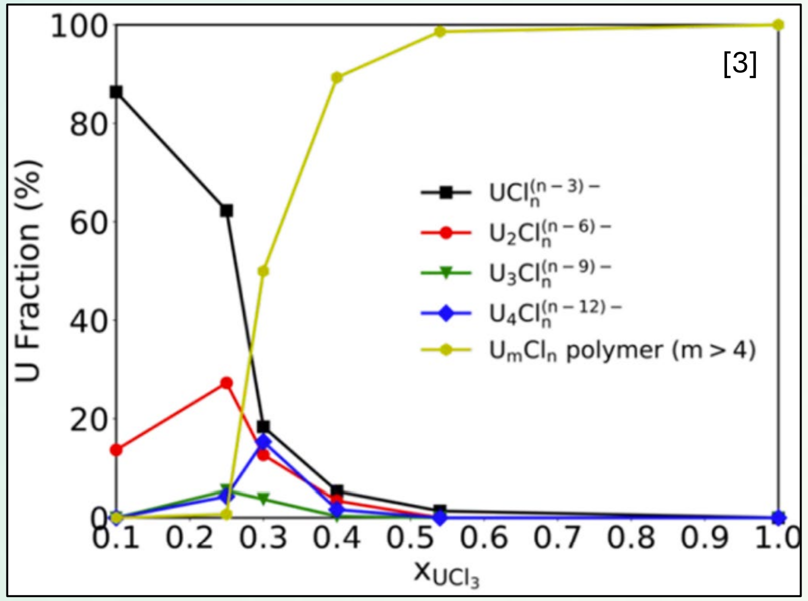
April 21

Motivation for transport property characterization

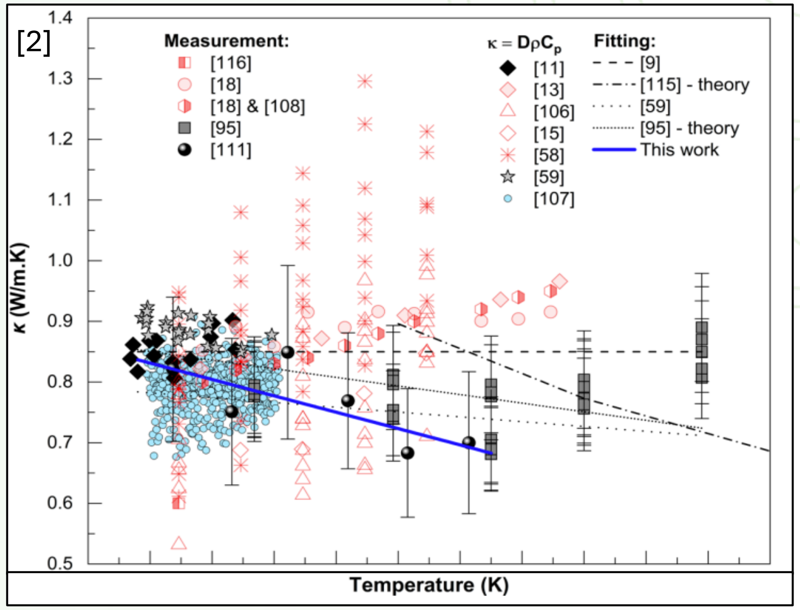
- Transport properties (i.e. viscosity, thermal conductivity) are notoriously challenging to measure
- Thermal conductivity data is super limited in MSD (formerly MSTDB)
- For U-bearing salts, we still have high uncertainty
  - Largely relying on datasets from USSR in the 70s and 80s
- We know that U-bearing salts exhibit unique structural phenomena
  - Can have a large impact on thermophysical properties
- Provides technical understanding for MSR fuel qualification







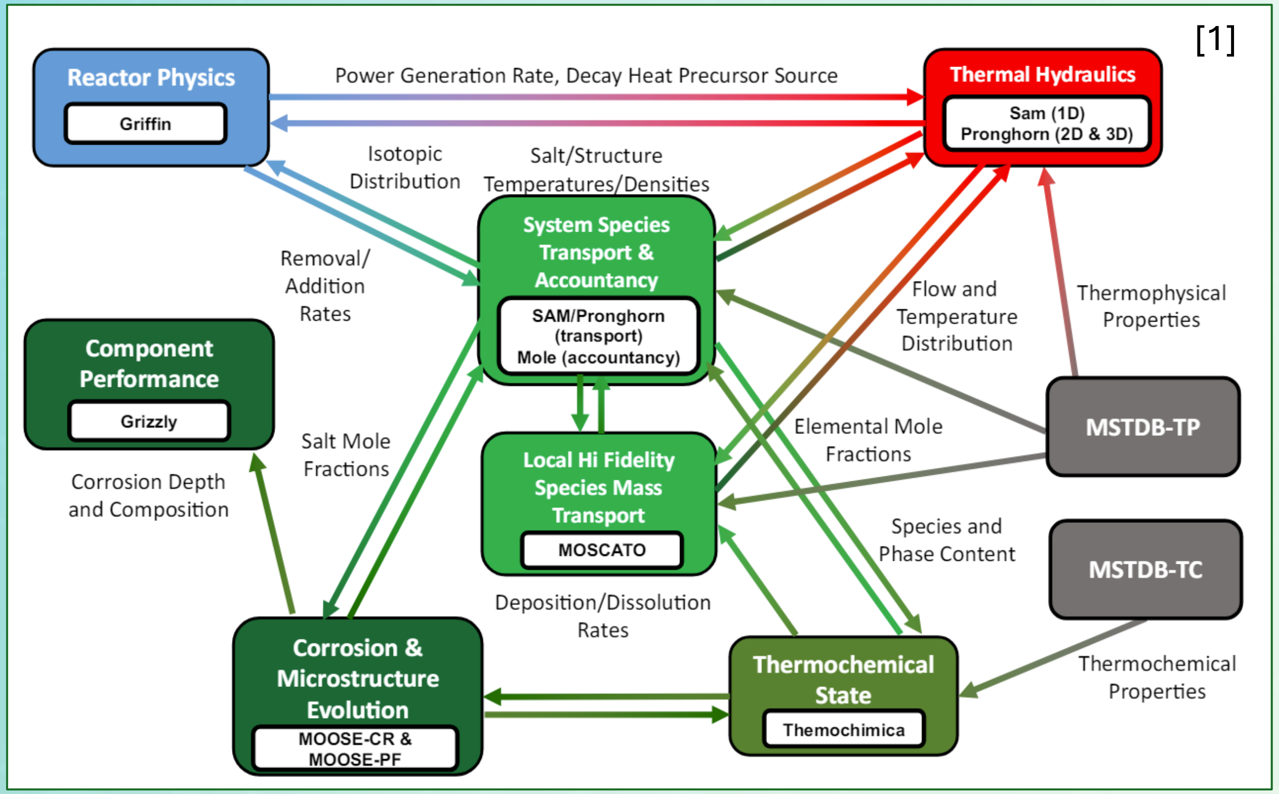
Thermal Cond. of FLiNaK

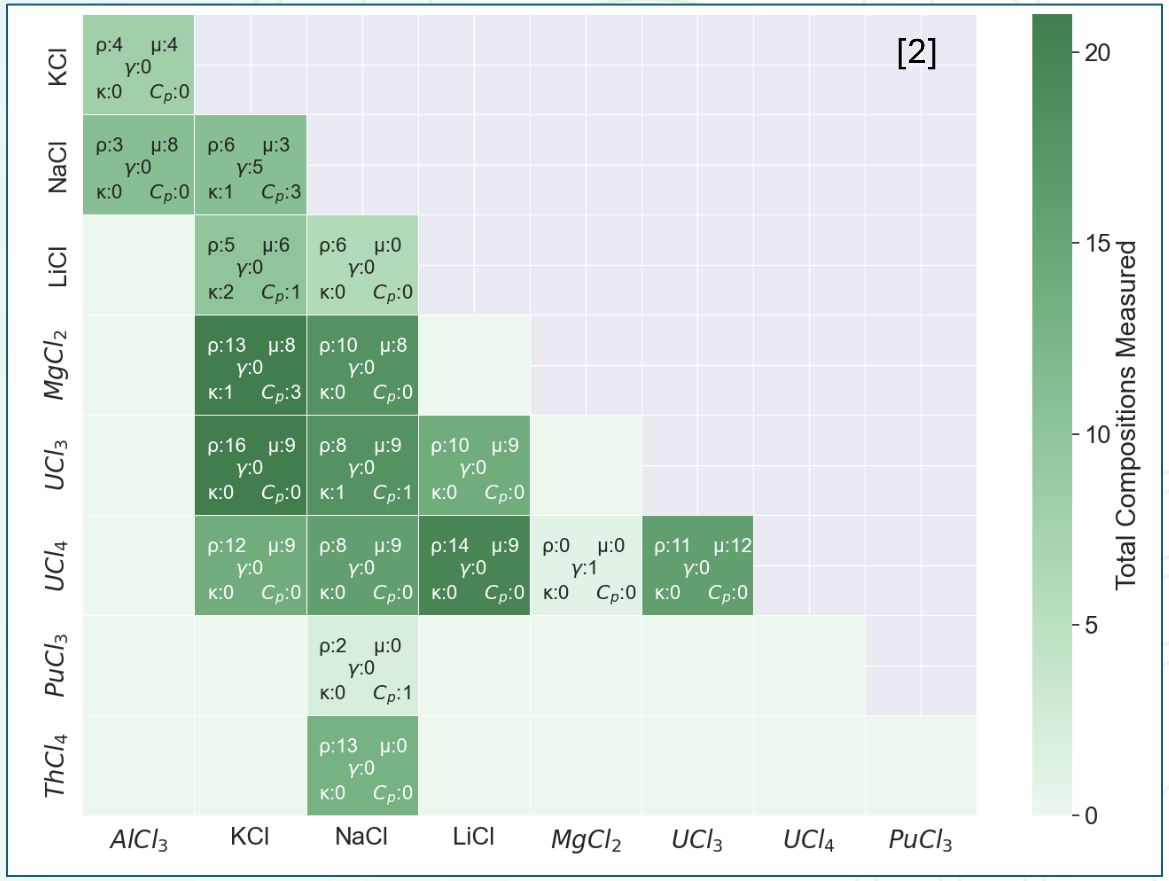


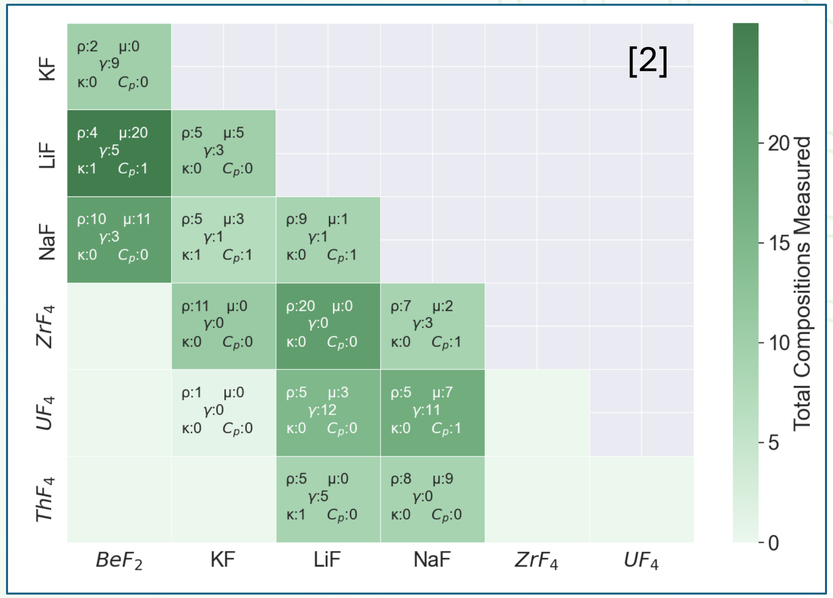
[1] Tasidou et al. *J. Phys. Chem. Ref. Data* 48, 013101 (2019)
[2] Shorne-Pinto et al. *ACS Appl. Energy Mater.* 2024, 7, 9, 4016–4029
[3] Li et al. *ACS Appl. Energy Mater*. 2019, 2, 2122−2128

The link to MSD-TP

- Very limited data on thermal conductivity for U-bearing salts
- We need to know more about:
  - Alkali fluorides mixed with UF_4
  - Alkali chlorides mixed with UCl_3
- Stretch goal: learn more about BeF_2-UF_4



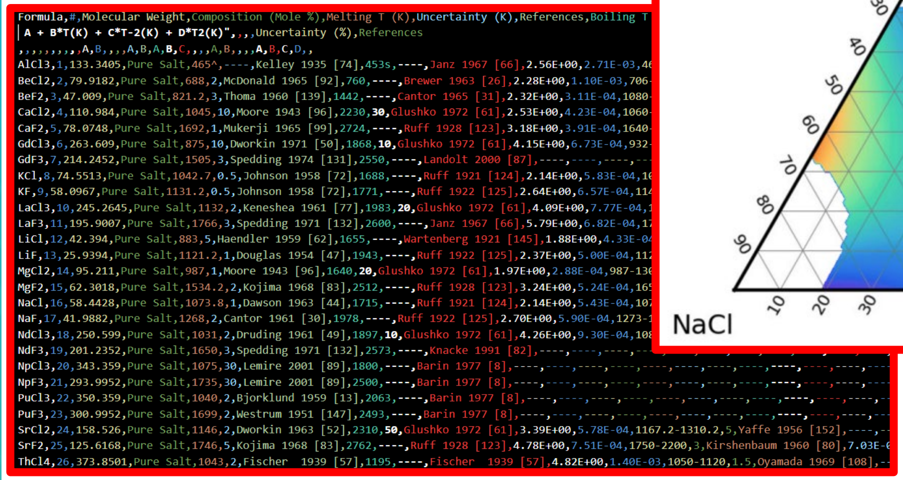




[1] INL/RPT-22-70694
[2] ORNL/TM-2025/4159

So, what are we doing at ORNL?

1. Experimental measurements of viscosity/ thermal conductivity
2. Ab initio molecular dynamics of U-bearing salts
3. MSD development and predictive modeling



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Formula,#,Molecular Weight,Composition (Mole %),Melting T (K),Uncertainty (K),References,Boiling T
 A + B*T(K) + C*T-2(K) + D*T2(K)",,,Uncertainty (%),References
,,,,,,,,,A,B,,,,A,B,A,B,C,,,,A,B,,,,A,B,C,D,,
AlCl3,1,133.3405,Pure Salt,465^,----,Kelley 1935 [74],453s,----,Janz 1967 [66],2.56E+00,2.71E-03,46
BeCl2,2,79.9182,Pure Salt,688,2,McDonald 1965 [92],760,----,Brewer 1963 [26],2.28E+00,1.10E-03,706-
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LiF,13,25.9394,Pure Salt,1121.2,1,Douglas 1954 [47],1943,----,Ruff 1922 [125],2.37E+00,5.00E-04,112
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NpF3,21,293.9952,Pure Salt,1735,30,Lemire 2001 [89],2500,----,Barin 1977 [8],----,----,----,----,----,----,----,----,----,----,----,---
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ThCl4,26,373.8501,Pure Salt,1043,2,Fischer  1939 [57],1195,----,Fischer  1939 [57],4.82E+00,1.40E-03,1050-1120,1.5,Oyamada 1969 [108],--
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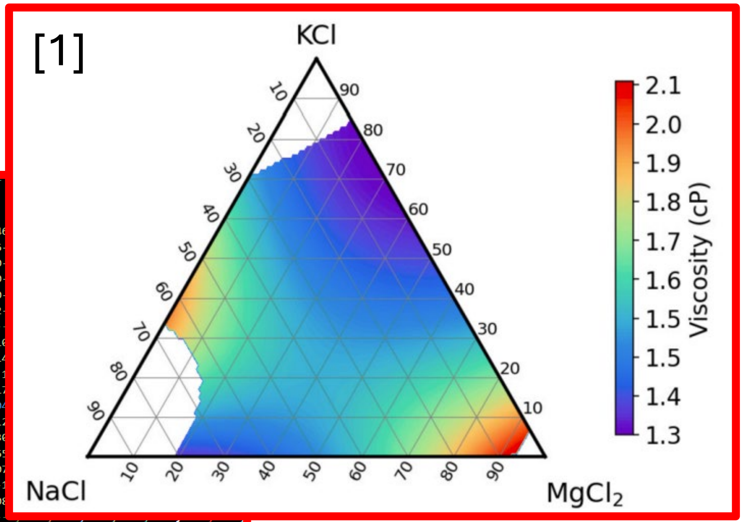
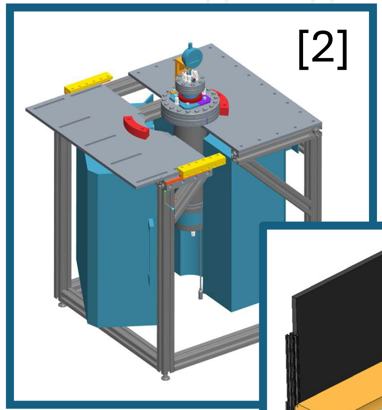
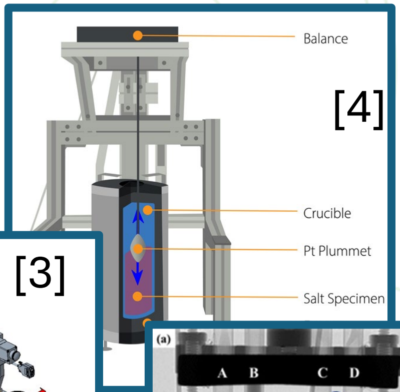
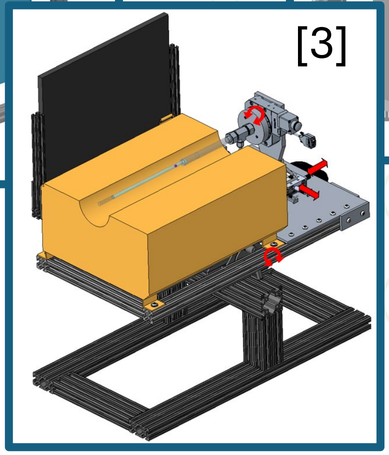
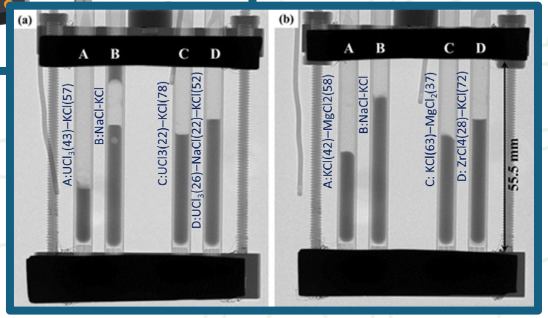
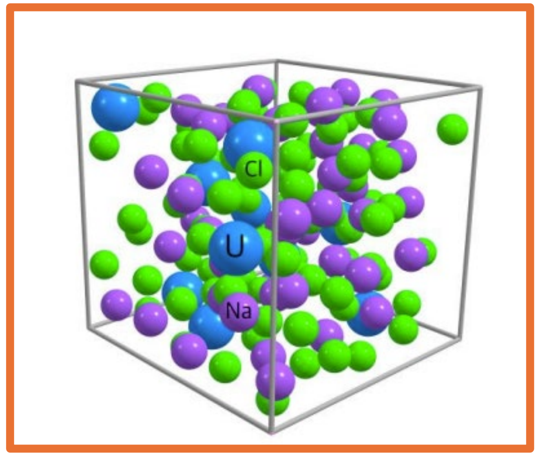


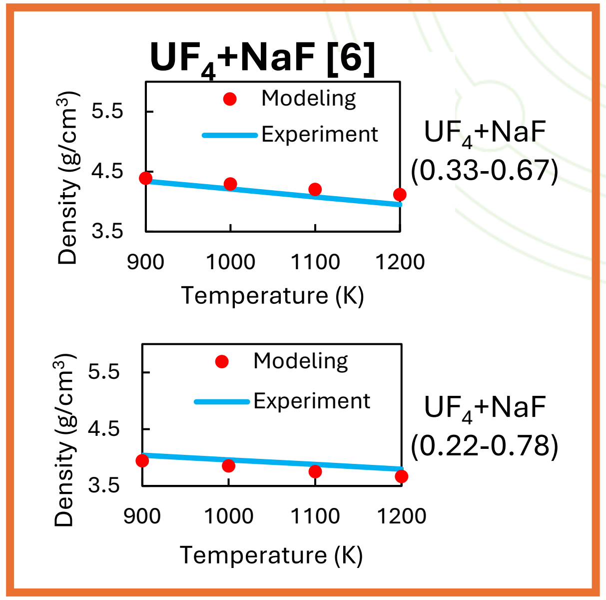










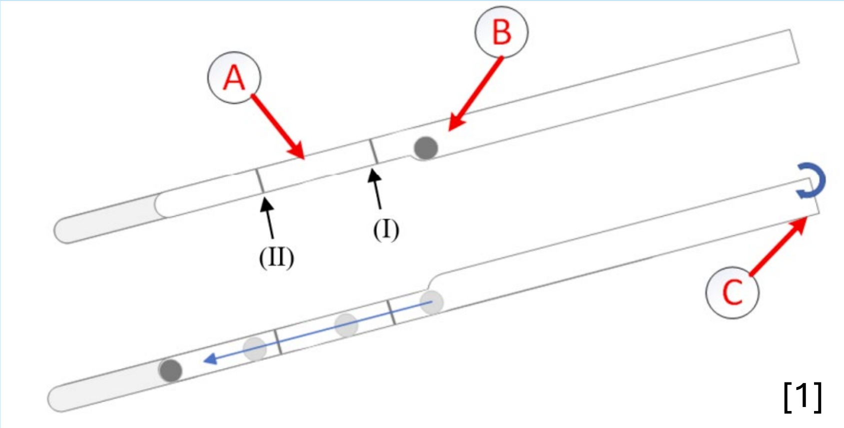


[1] Birri et al. Chem. Eng. Sci. 2024, 298, 120391
[2] Gallagher et. al, J. Chem. Eng. Data 2022, 67, 6, 1406–1414
[3] Birri et al. (2023). TSEP, 44, 102029.
[4] ORNL/TM-2020/1633
[5] Moon et al, Ind. Eng. Chem. Res. 2022, 61, 17665−17673
[6] Zhang, Glezakou MD properties and transport in NaF-UF4, NaF-KF-UF4, in preparation

How do we measure these properties?

- For viscosity we use a rolling ball viscometer
  - Ball tracking performed typically with x-ray radiography
  - Terminal velocity converts to viscosity after NIST oil calibration
- For thermal conductivity we use a variable gap apparatus
  - Heat flux driven across sample
  - Temperature change versus gap size corresponds to thermal resistance
  - Calibration with He accounts for losses
- All crucibles/containments loaded in inert glovebox
  - Gas maintenance system keeps samples inert during measurements

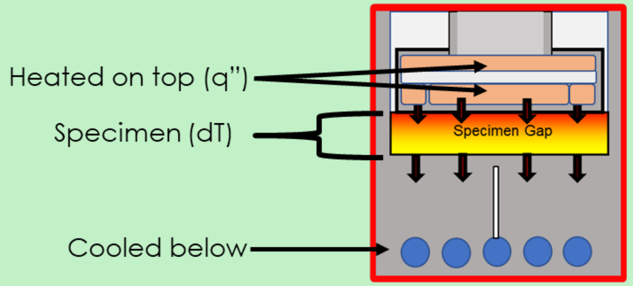
Rolling Ball Viscometer



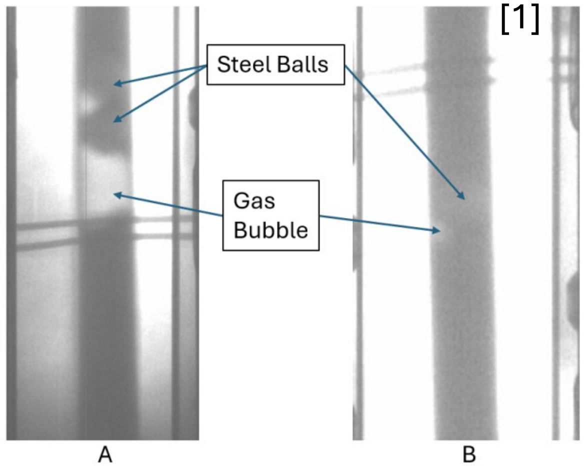
(A) The measurement section
(B) The loading section
(C) Connection to the rotational stage

[1] ORNL/TM-2024/3650

Variable Gap Apparatus



Sources of uncertainty/ error



Gas bubbles causing holdup/slowing

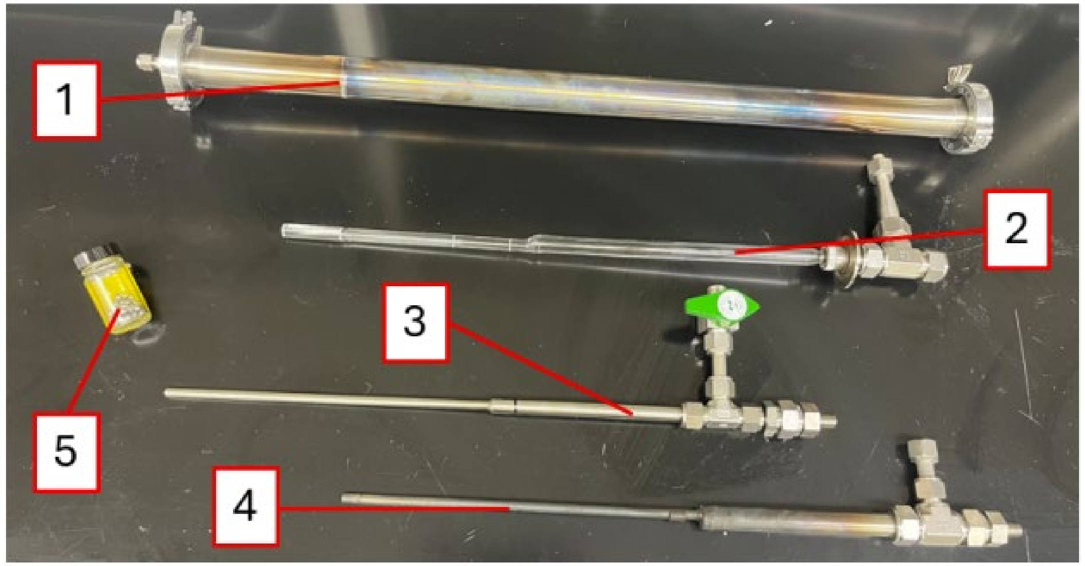


Figure 3. Photograph of the glass and stainless steel crucibles used in this study: (1) the outer containment for glass crucibles to enable actinide chloride measurements, (2) a glass crucible, (3) a new SS-316 crucible, (4) a used SS-316 crucible based on the old design from [31], and (5) SS-316 balls used for measurements.

- Variable gap apparatus
  - Temperature fluctuations
  - Inconsistencies between cal./exp.
  - Impurities introduced into the salt
  - Gap size uncertainty
  - Air cooling inconsistencies
  - Bubbles
- Rolling Ball Viscometer
  - Dimensional uncertainties
  - Angle uncertainty
  - Bubbles
  - Impurities introduced into the salt
  - Temperature gradient

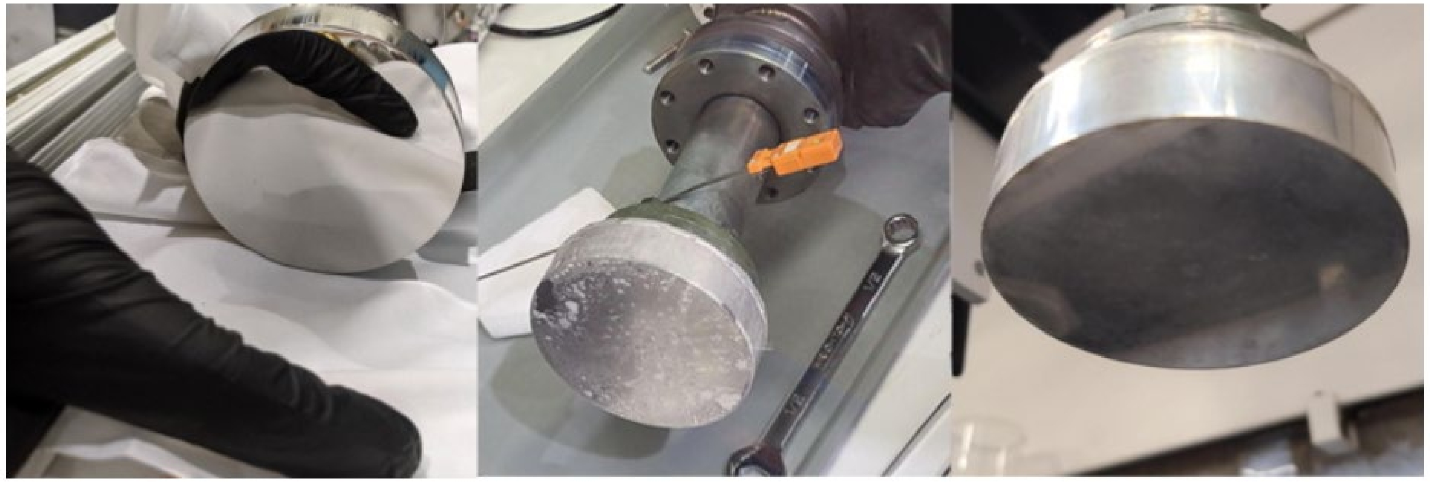
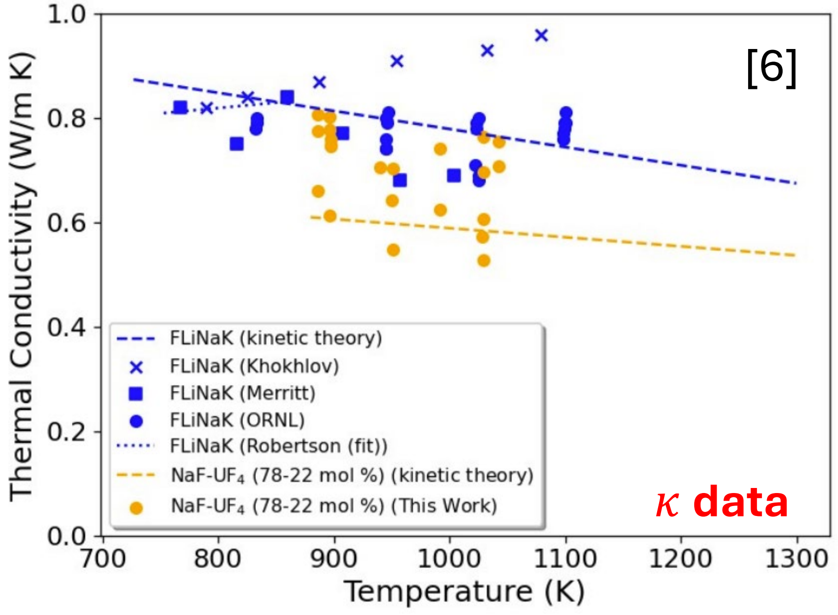


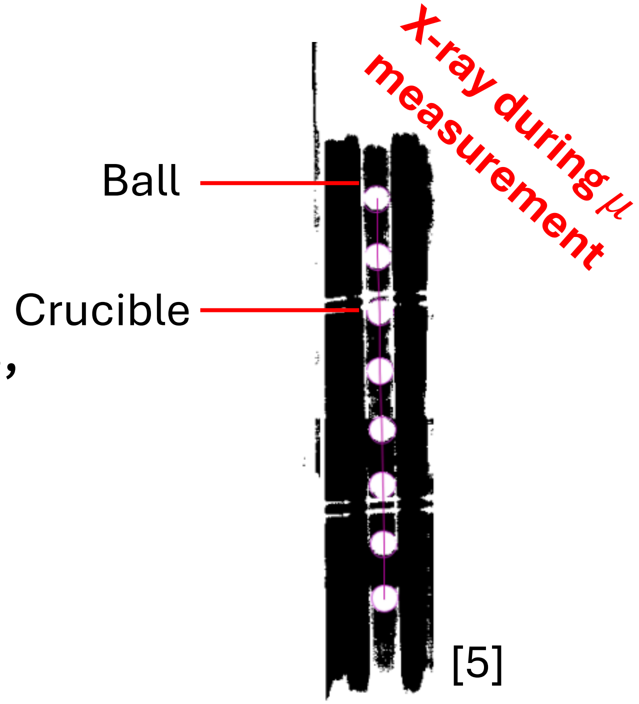
Fig. 6. The bottom surface of the heater cell before testing (left), directly after testing (middle), and after cleaning in an ultrasonic water bath (right). [2]

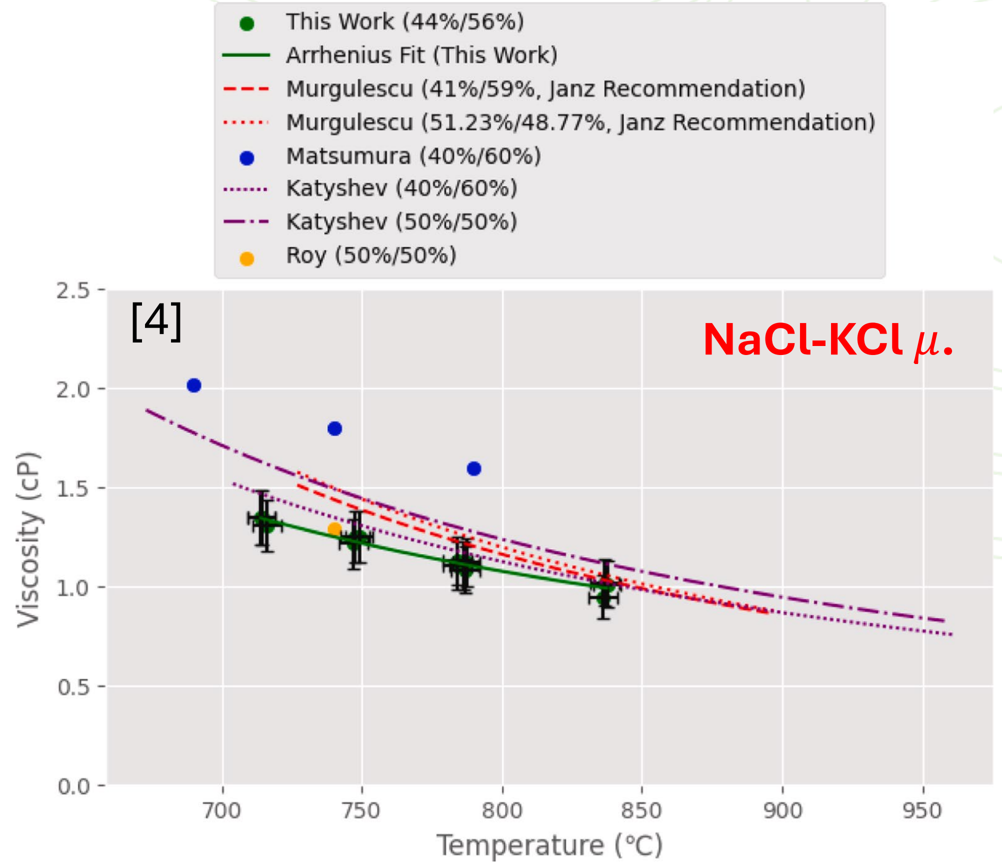
[1] ORNL/TM-2025/4057
[2] Gallagher et al. J. Mol Liq. 2022, 361, 119151

What have we measured so far?

- FLiNaK (ρ, C_p, κ) [1,2,3]
- NaCl-KCl (eut.) (μ, κ) [4,5]
- NaCl-LiCl, KCl-LiCl, NaCl-KCl-LiCl (various compositions) (μ) [5]
- NaF-UF_4 (78-22 mol%) (μ, κ) [6]
- FUNaK (μ) [6]
- $NaCl$-UCl_3 (63-37 mol%) (μ, κ) [5,7]
- $NaCl$-UCl_3 (63-37 mol%) +FPs (μ, κ) [5,7]
- *Other Programs:* LiF-BeF_2, LiF-BeF_2-LaF_3, $NaCl$-$MgCl_2$-UCl_3 (ρ) [8,9]



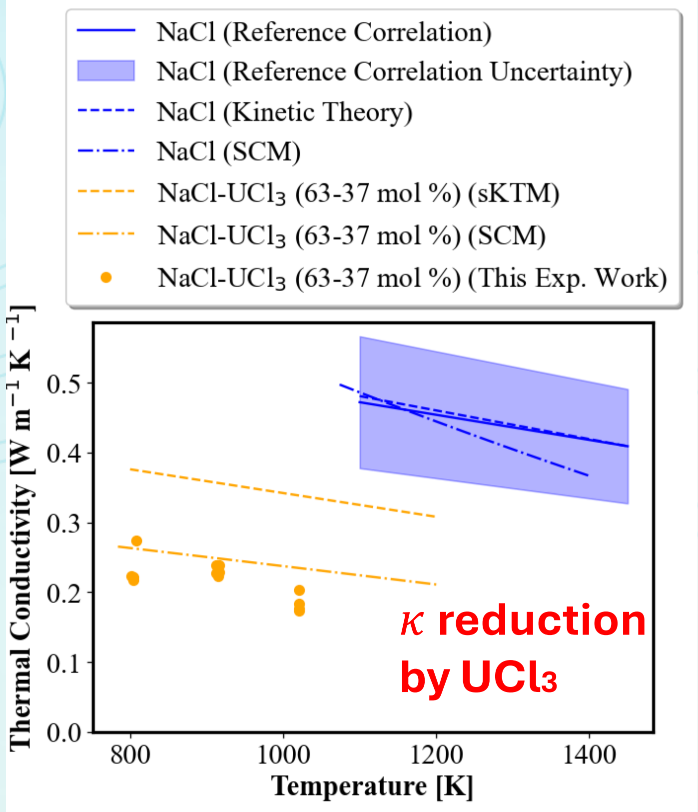


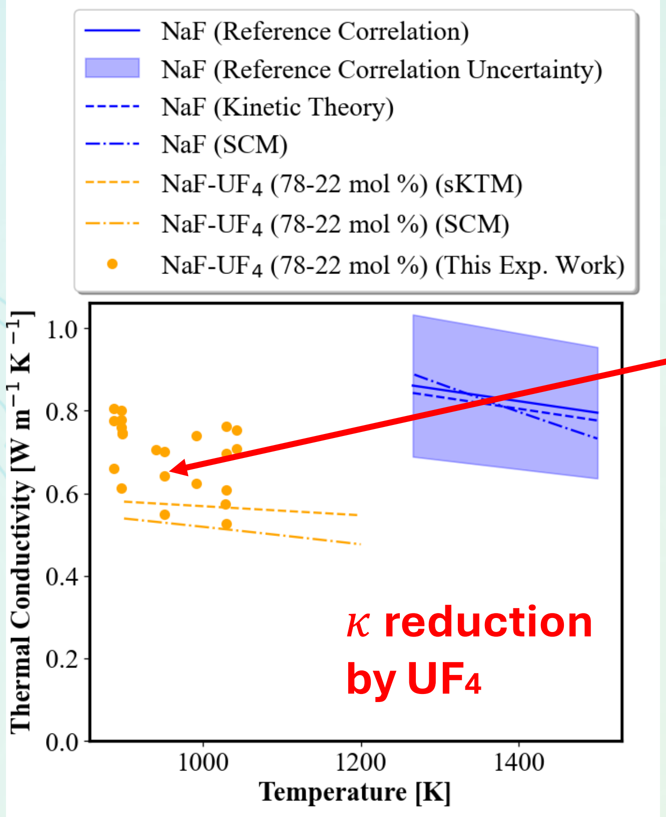


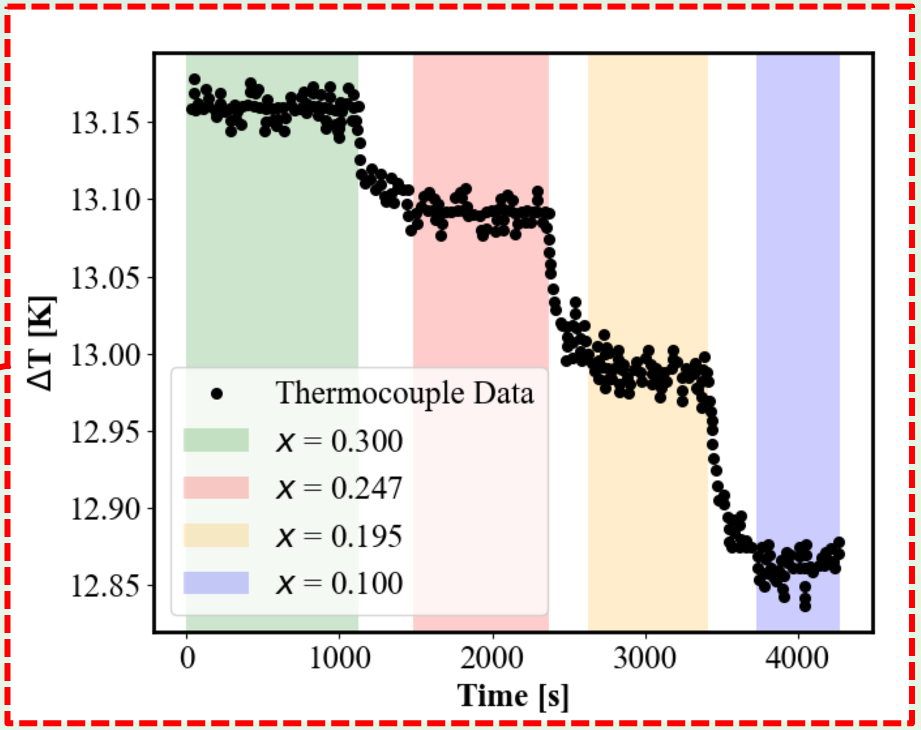
[1] Gallagher et al. *J. Chem. Eng. Data* 2022, 67, 6, 1406–1414
[2] ORNL/TM-2021/2216
[3] Gallagher et al. *J. Mol Liq*. 2022, 361, 119151
[4] Birri et al. *Therm. Sci. Eng. Prog*. 2023, 44, 102029
[5] ORNL/TM-2024/3650
[6] ORNL/TM-2025/4057
[7] ORNL/TM-2026/4487
[8] Moon et al. *Ind. Eng. Chem. Res*. 2022, 61, 48, 17665–17673
[9] Mool et al. *ACS Omega* 2024, 9, 25, 27204–27213

Recent thermal conductivity measurements

- Addition of uranium halides into your carrier salt will **decrease** thermal conductivity
  - Experimental measurements and theory confirm this
- In MSRE, UF_4 loading was small; negligible effect
- Currently, developers are interested in higher molar content of fuel like UF_4 and UCl_3

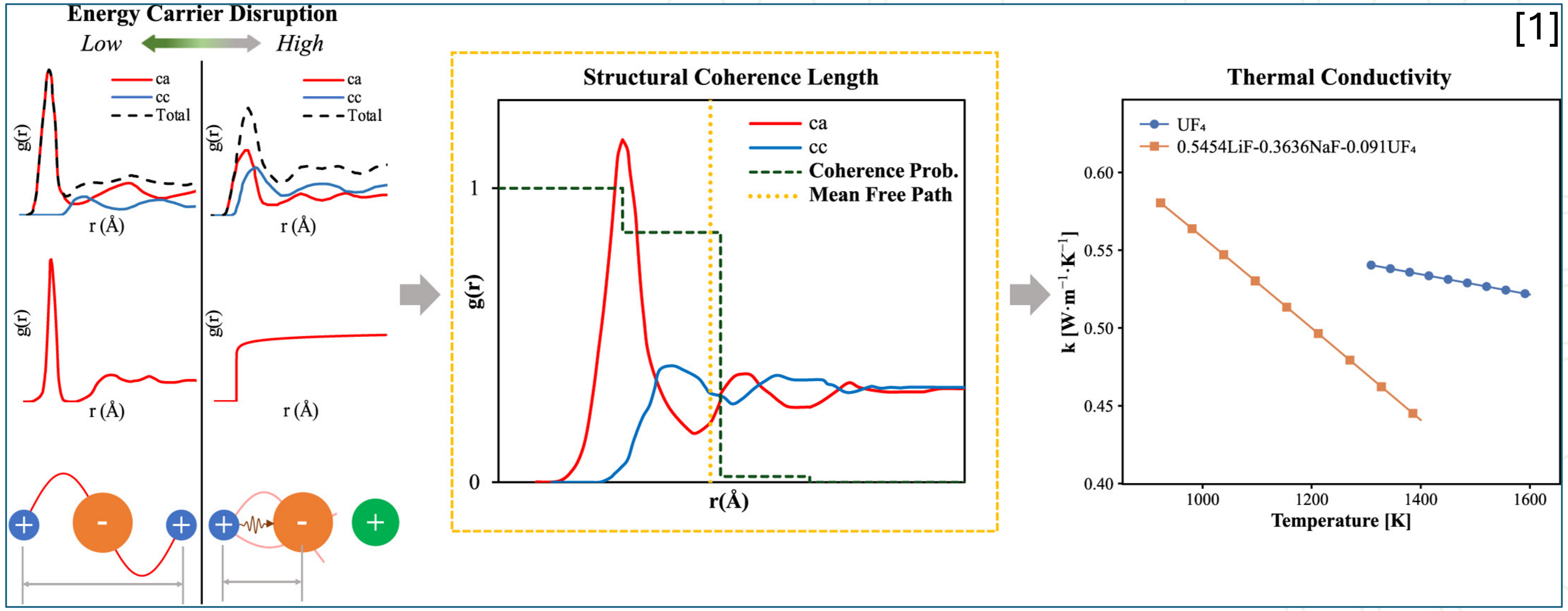


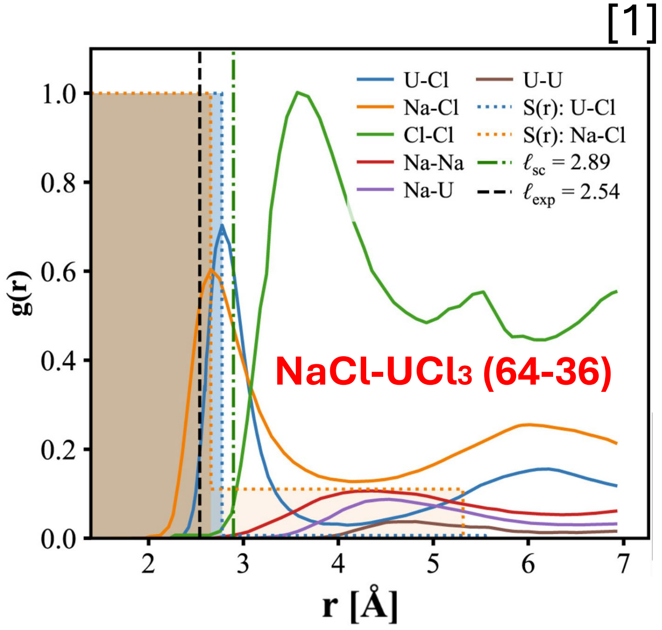


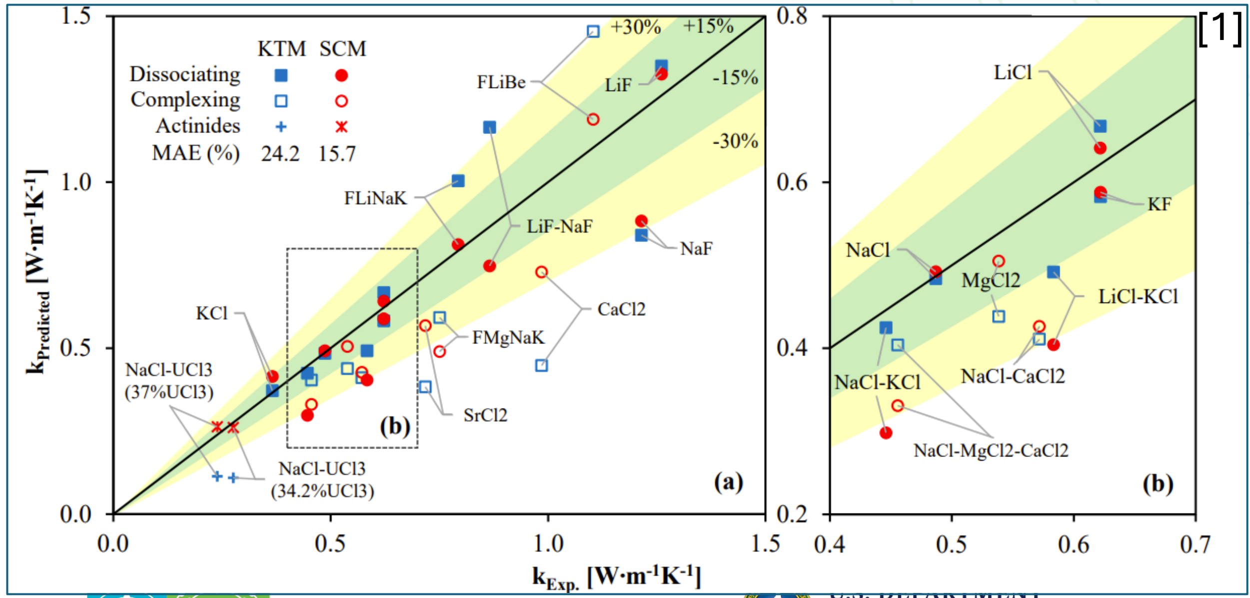


Why does uranium reduce thermal conductivity?

- A recent paper we've been collaborating with BYU on sheds light on this
- New structural coherence model to tie PDFs to thermal conductivity
  - Predict mean free path of energy carriers (i.e. phonons)
- We've learned two major consequences of actinide dissolution into the melt:
  1. Decrease in the energy carrier transport velocity
  2. Decreased likelihood of coherence after first coordination sphere
- This new model outperforms KTM when comparing against experiments in MSD-TP
- Follow-on paper in the works

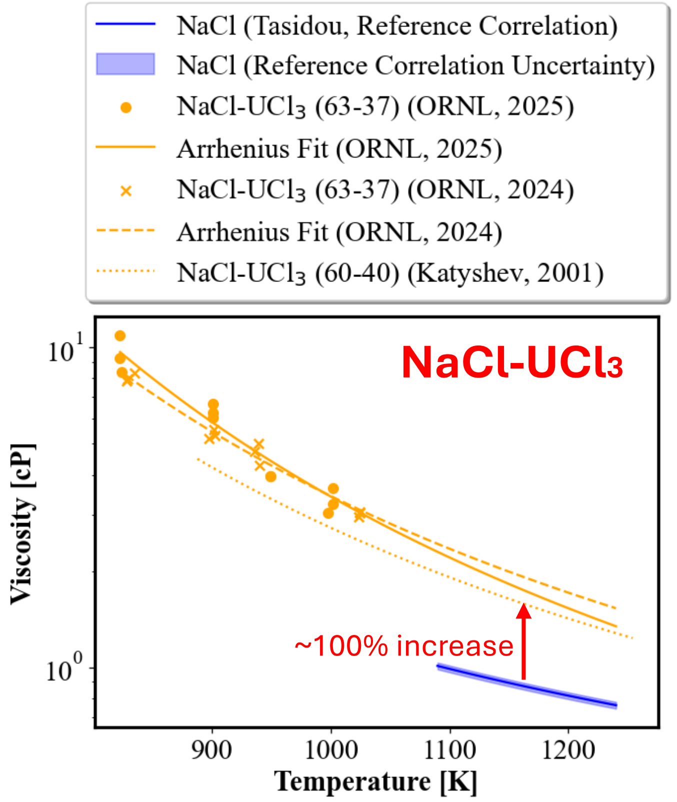


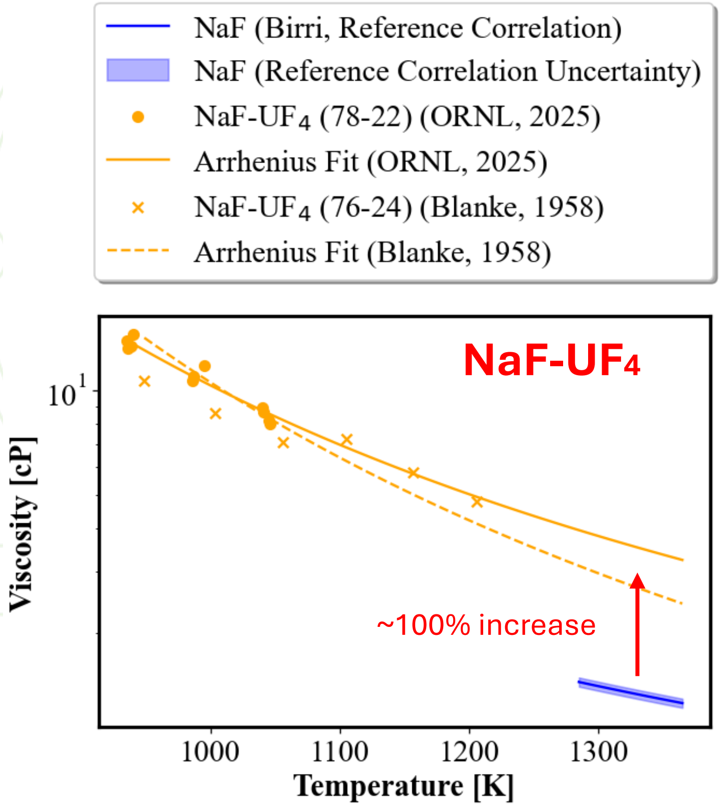


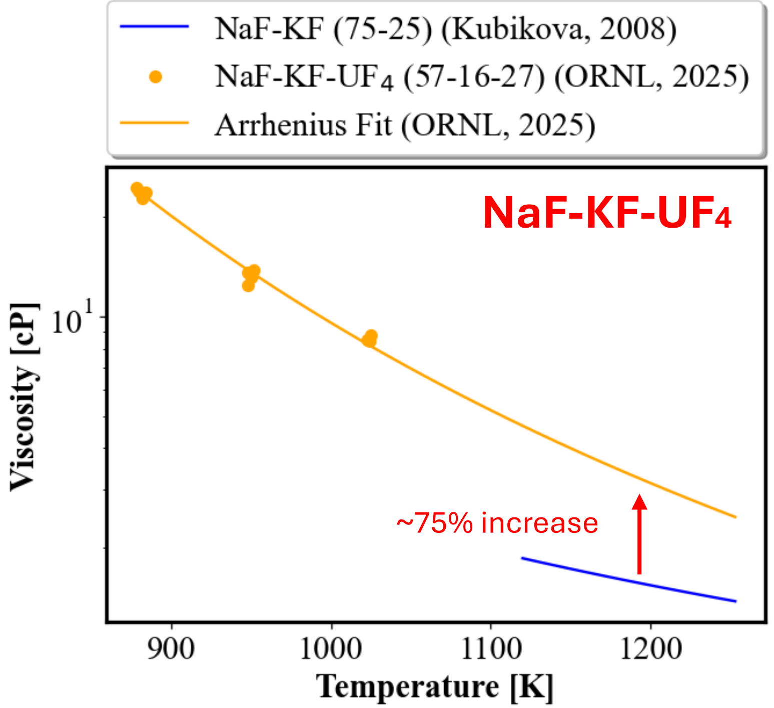


What we've learned about viscosity

- Addition of uranium halides into your carrier salt will tend to <u>**increase**</u> viscosity
  - The one main exception is high BeF_2 concentration carriers
- Carriers like NaCl, NaF, NaF-KF tend to be ~1cP
- Adding in substantial amount of UCl_3 or UF_4 can increase
  - Can double viscosity near eutectics







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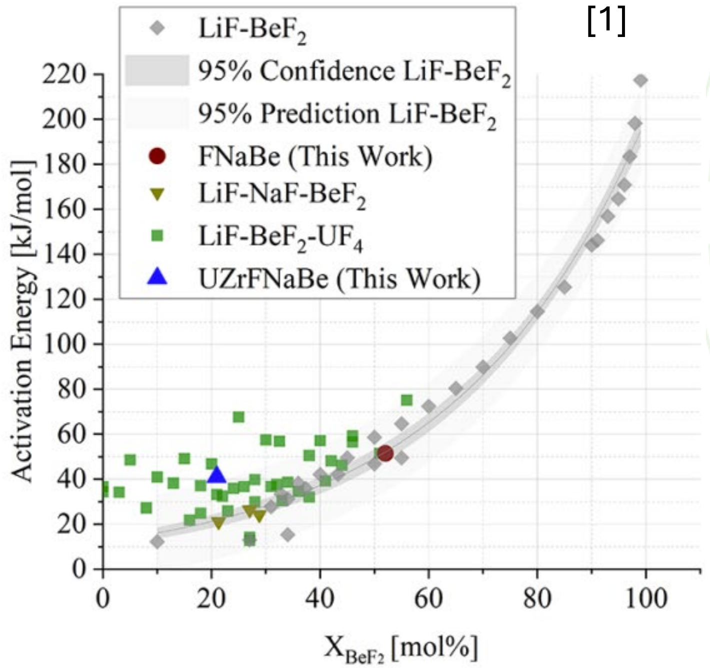
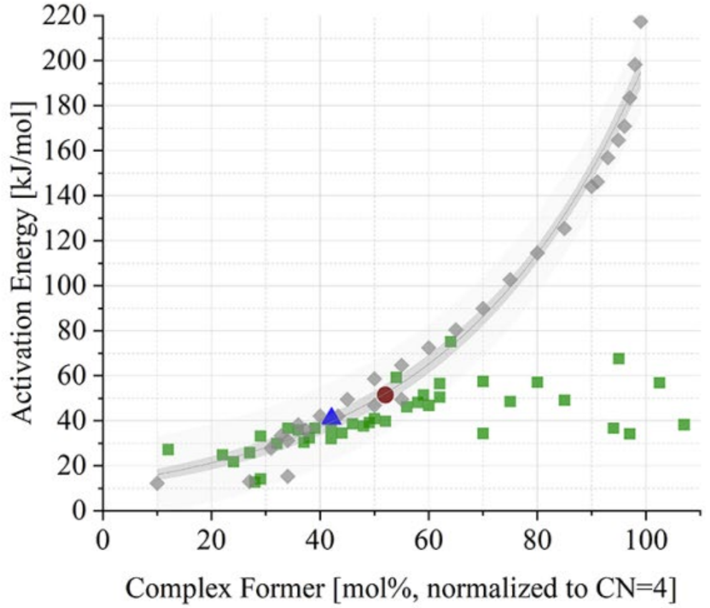
Why the increase in viscosity?

- Why?
  - Actinides form complexes (lower concentrations)
  - Networks (high concentrations)
  - These require higher activation energies for viscosity
    - Great work out of UC-Berkely on this [1]
- AIMD data shows diffusion coefficients of U > Na, K, Li
- Potential thermal hydraulic consequences
  - Required shaft power <u>increase</u>
  - Nusselt number <u>decrease</u>

[1]

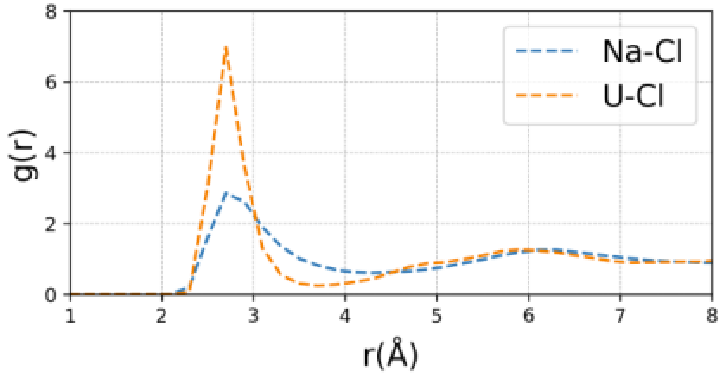


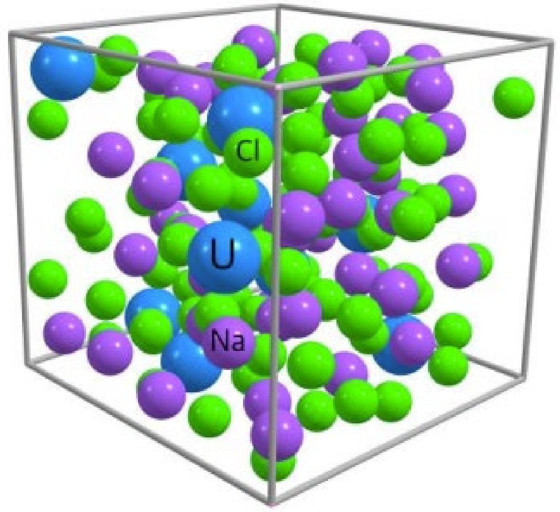


<u>NaCl-UCl3 calculations</u>

[2]

NaCl(0.66)-UCl3(0.34)





D_{Na} (10^{-5} cm^{2}s^{-1})	D_U (10^{-5} cm^{2}s^{-1})	D_{Cl} (10^{-5} cm^{2}s^{-1})
5.08	3.2	5.3

η_{mix}= 2.30 (cP, 987 K); Exp 3.0 (cP, 1025K) (Birri and co-workers); 2.29 (cP, 987K) (Desyatnik et al, 2020)

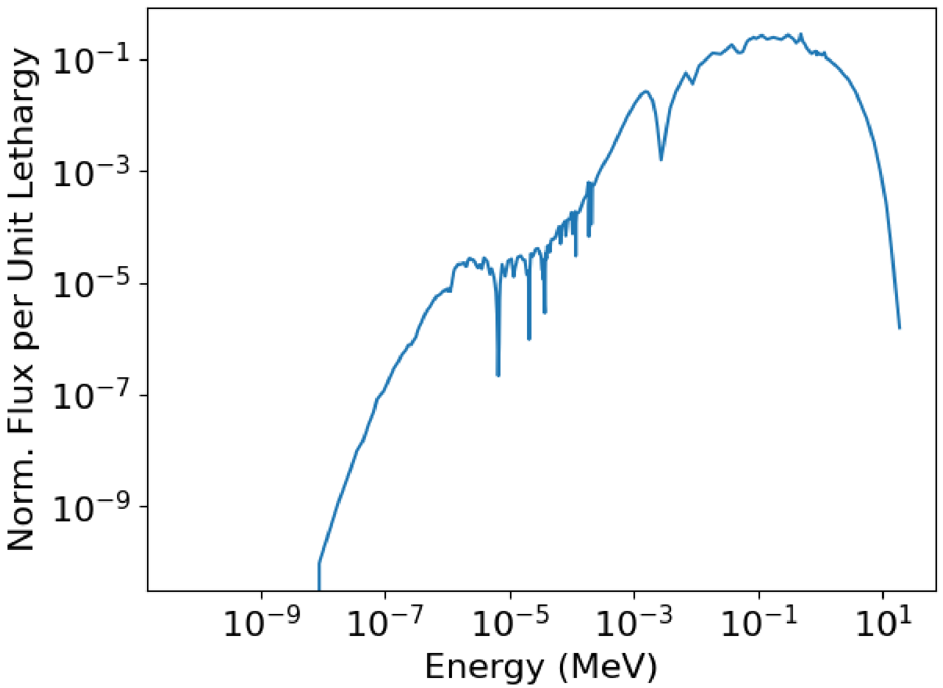
[1] Gardner et al. *ACS Phys. Chem Au* 2025, 5, 6, 579–588
[2] ORNL/TM-2024/3650

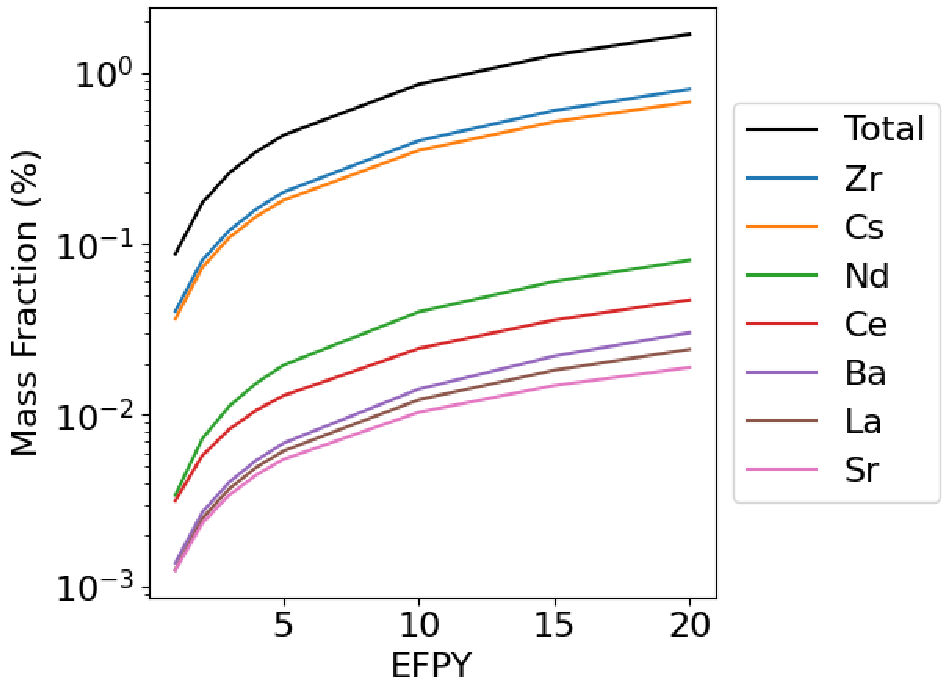
What about fission products?

- Over time, salt-seeking FPs will build into the salt
- The rate at which this happens is dependent on:
  - Neutron flux magnitude
  - Neutron flux distribution
  - Fuel enrichment
  - Core volume and residence time in-core
- We've run ORIGEN calculations to estimate quantity of salt-seekers
  - Details on our assumptions in the calc are reported [1]
  - Decent agreement with original chemistry roadmap [2]

Table 1. Composition of NaCl-UCl$_3$+FPs used in thermophysical property testing

Species	Mass (g)	mass %	Moles	mol %
NaCl	9.99816	21.800	0.17108	61.608
UCl$_3$	34.60174	75.447	0.10047	36.183
Total NaCl-UCl$_3$		**97.247**		**97.791**
ZrCl$_4$	0.68394	1.4913	0.00293	1.0569
CsCl	0.42934	0.93616	0.00255	0.91835
NdCl$_3$	0.06004	0.13091	0.00024	0.08628
CeCl$_3$	0.03447	0.07517	0.00014	0.05037
BaCl$_2$	0.02228	0.04858	0.00011	0.03853
LaCl$_3$	0.01853	0.04040	0.00008	0.02821
SrCl$_2$	0.01380	0.03009	0.00009	0.03135
Total FPs		**2.7526**		**2.2090**





[1] ORNL/TM-2026/4487
[2] ORNL/SPR-2020/1865

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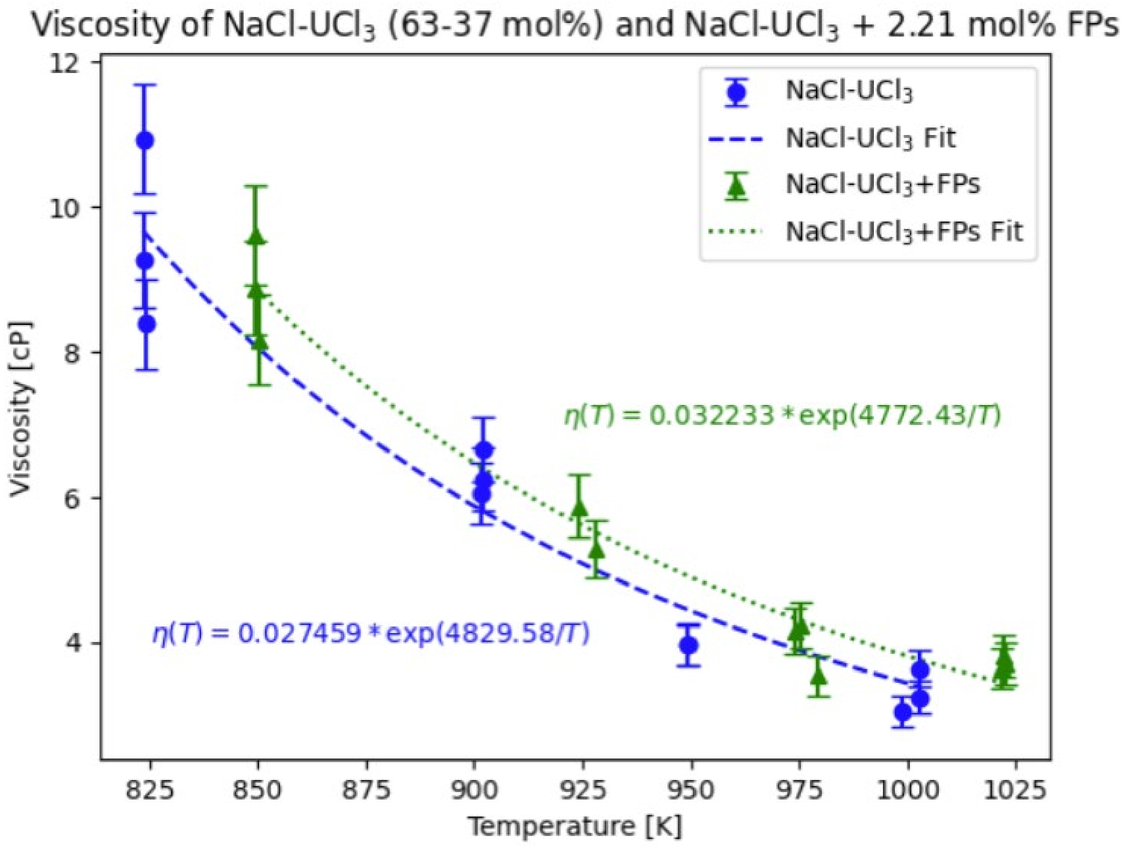
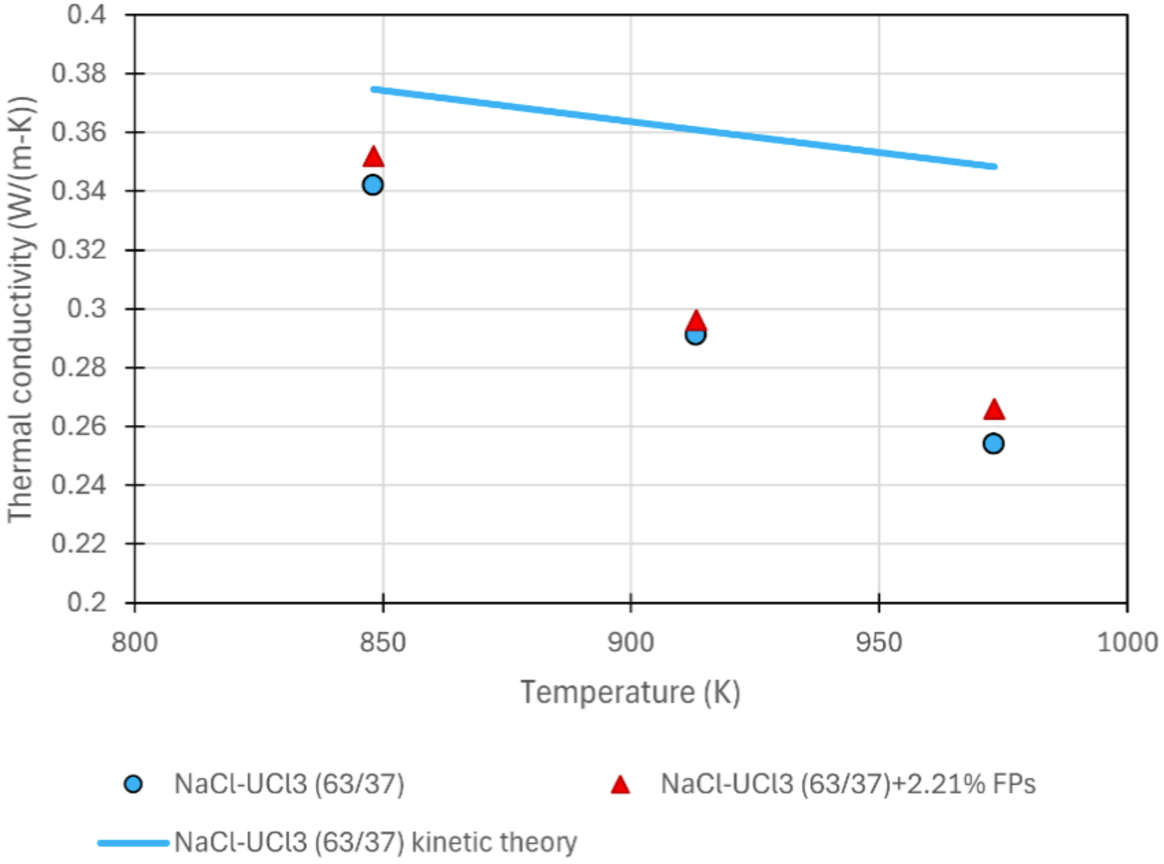
The effect of fission products on transport properties

- The data show generally minimal effects on viscosity and thermal conductivity





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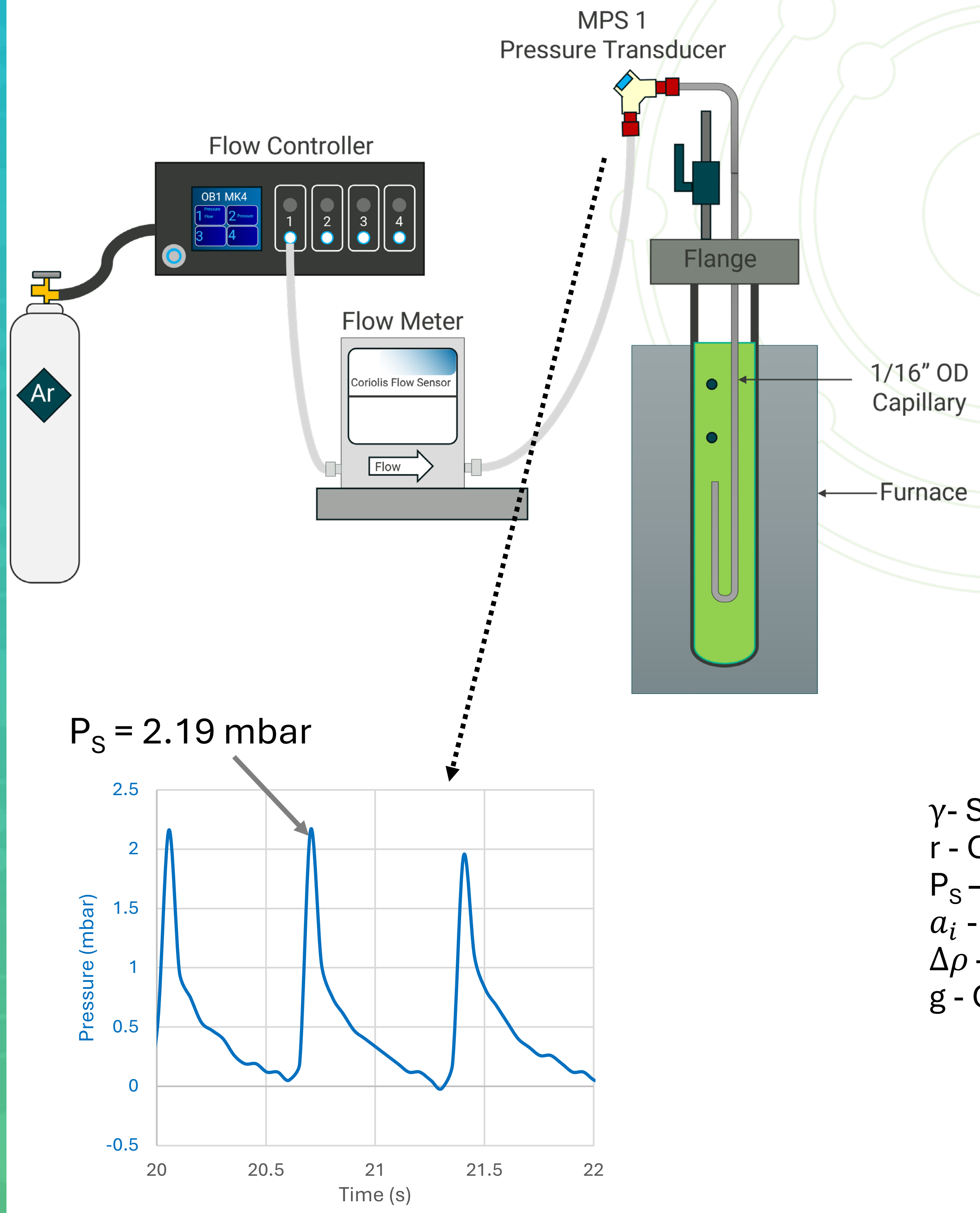
Ongoing effort: surface tension measurement

- The surface tension in a molten salt can be measured by the maximum pressure in bubble formation and separation
- A flow controller generates individual bubbles at a constant flow rate.
- A pressure transducer measures the bubble pressure over time to determine the maximum bubble pressure.



Surface tension

$$\gamma = f\frac{rP_S}{2}$$

Correction Factor

$$f = \sum a_i\left(\frac{r}{\sqrt{\frac{2\gamma}{\Delta\rho g}}}\right)^i$$

γ- Surface tension
r - Capillary radius
P_S – Maximum bubble pressure
a_i - Coefficient
$\Delta\rho$ – Fluid density difference
g - Gravity

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Okay, so what's next?

- Measure thermal conductivity of FUNaK
- Measure viscosity of:
  - Off-eutectic $NaCl\text{-}UCl_3$
  - $NaCl\text{-}KCl\text{-}UCl_3$
- Continue developing surface tension system
- Investigate new thermal conductivity measurement methods
- Investigate fluoride salts with fission products?

[1]

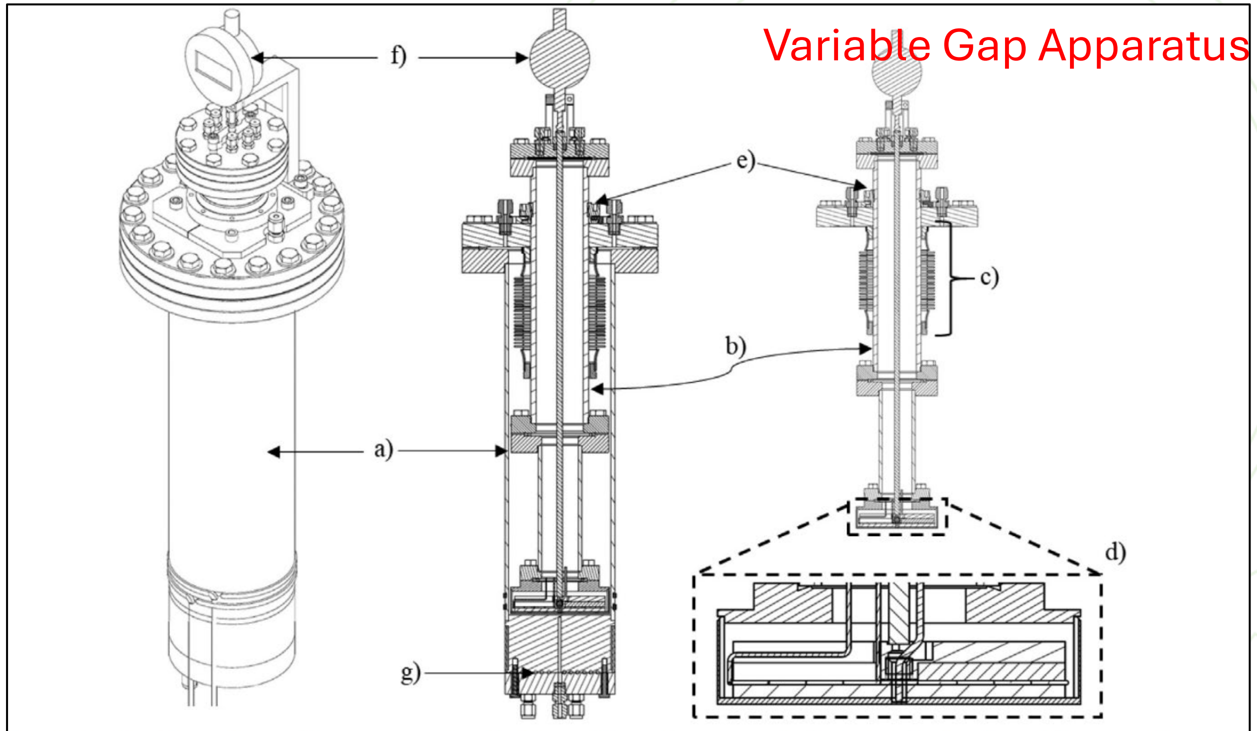


Fig. 3. Schematic and image of the variable gap system: a) external containment, b) internal containment, c) bellows feedthrough, d) heating module, e) jam nut, f) variance indicator, g) cooling channels.

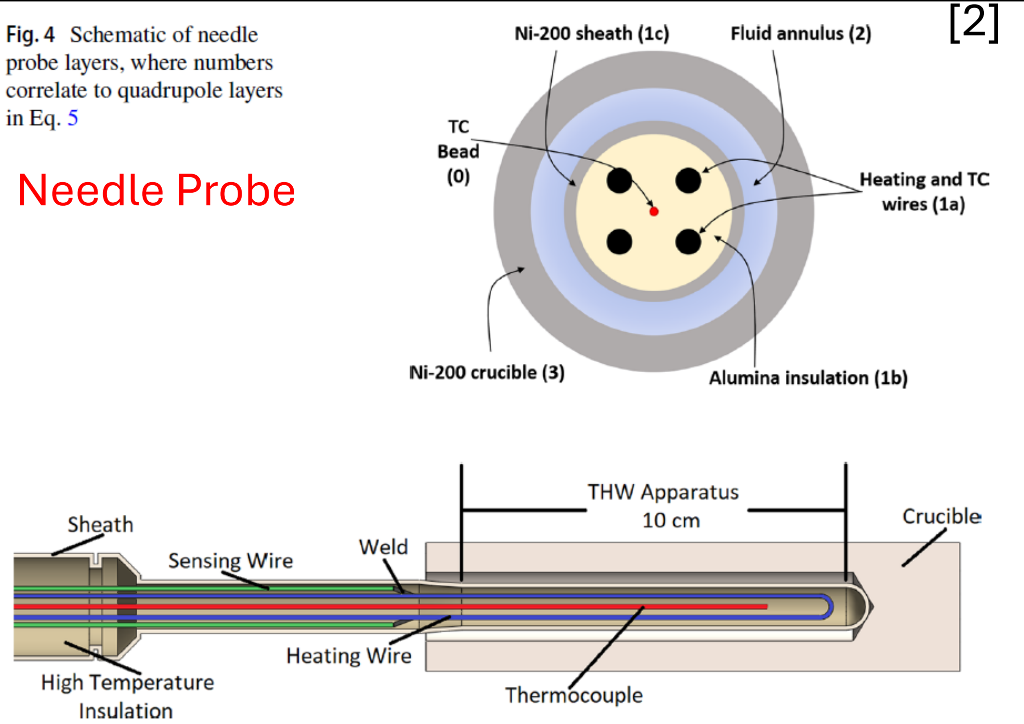
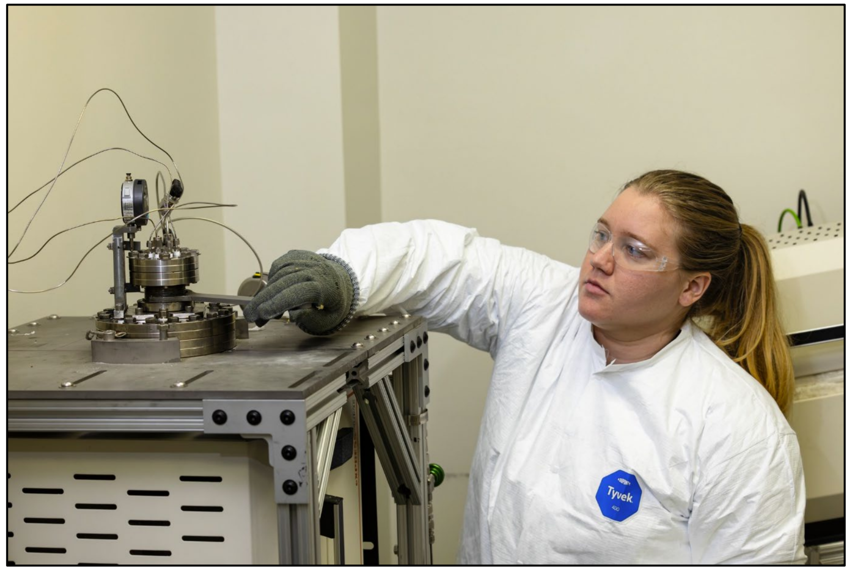


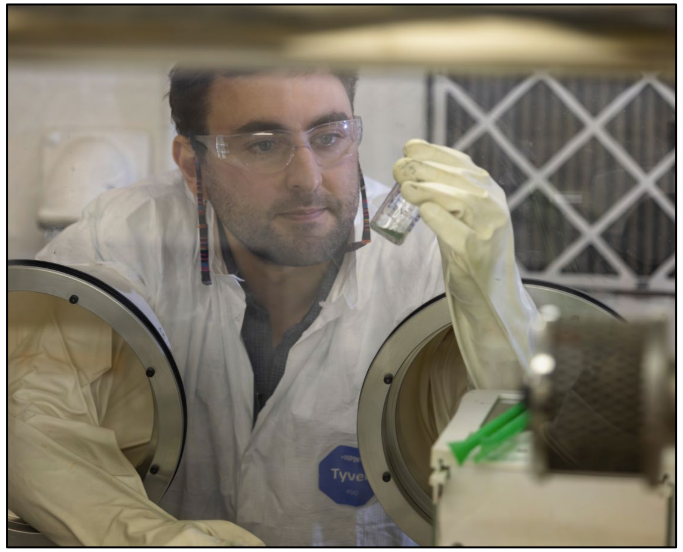
Fig. 4 Schematic of needle probe layers, where numbers correlate to quadrupole layers in Eq. 5

[1] Gallagher et al. *Int. J. Heat Mass Trans.* 2022, 192, 122763
[2] Ruth et al. *Int. J. Thermophys.* 2024, 45, 158

Conclusion

- Recent thermophysical property measurements have demonstrated to the following conclusions:
  1. Uranium halide dissolution in alkali halide solvents (carriers) will <u>decrease</u> thermal conductivity
  2. Uranium halide dissolution in alkali halide solvents (carriers) will <u>increase</u> viscosity
  3. Salt seeking fission products are expected to have <u>minimal effect</u> on transport properties
- These conclusions come from measurements at ORNL which have, in part, been validated by models





Acknowledgements

- Joanna McFarlane for guidance on experimental efforts
- Vanda Glezakou and Difan Zhang for MD collaborations
- RCTs: Ron Boyd, Tracy Pope, Corey Jones
- Machinists, manufacturing engineers, glass blowers
  - Andy Anderson, Jason Craig, Carlos Rodriguez Flores, Bob Sitterson
- Troy Munro and Jacob Numbers at BYU for thermal conductivity modeling collaborations
- Bruce McNamara at PNNL for synthesis of $NaF-UF_4$
- Bill Phillips and Jacob Yingling at INL for synthesis of $NaCl-UCl_3$
- Jinsuo Zhang and Amanda Leong at VT for synthesis of FUNaK

This work is directly funded by the Molten Salt Reactor Program under the Department of Energy, Office of Nuclear Energy.

Questions?

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