Molten Salt Thermophysical Property Measurement and Modeling Efforts at ORNL

Molten Salt Reactor Workshop, October 11th 2022

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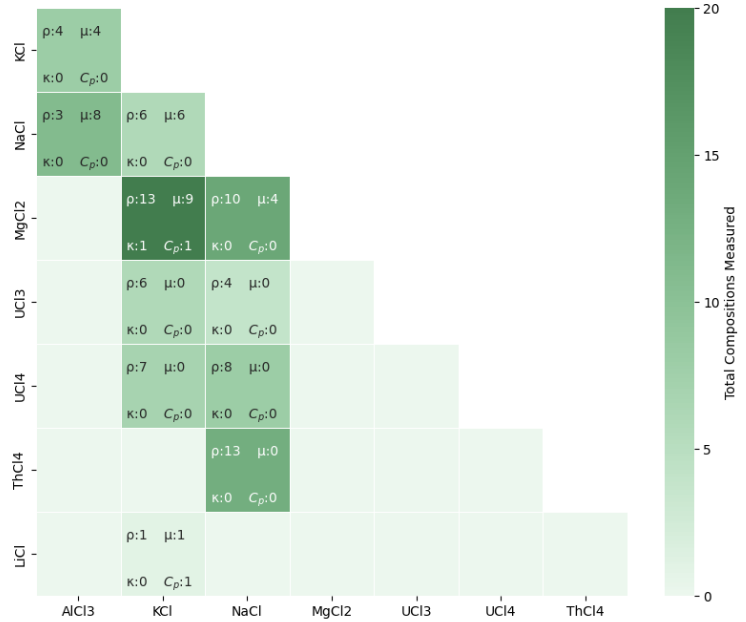
ORNL is managed by UT-Battelle, LLC for the US Department of Energy

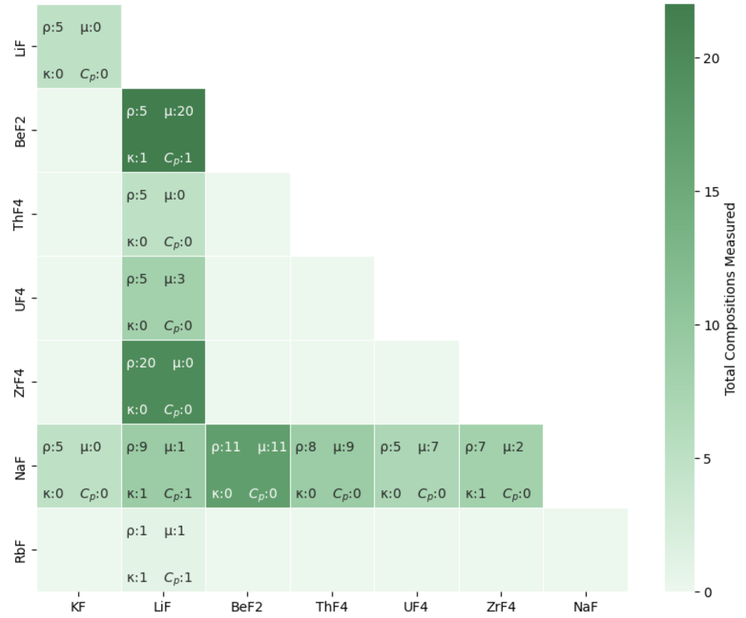
Motivation

- A precise understanding of thermophysical properties of molten salts in MSRs is necessary for developing an accurate understanding of nuclear reactor thermal hydraulics
  - Necessary for understanding the steady-state temperature distribution, thermal response to transient conditions, expected pressure conditions, thermal efficiency of the reactor, etc.
- Developing this understanding for MSR relevant salts is challenging, because:
  - MSRs are typically interested in pseudo-ternary+ mixtures
  - These salts may bear U, Th, and Be
  - Corrosion and fission products may be introduced over the core/reactor lifetime

Chloride Pseudo-Binary Characterizations



Fluoride Pseudo-Binary Characterizations

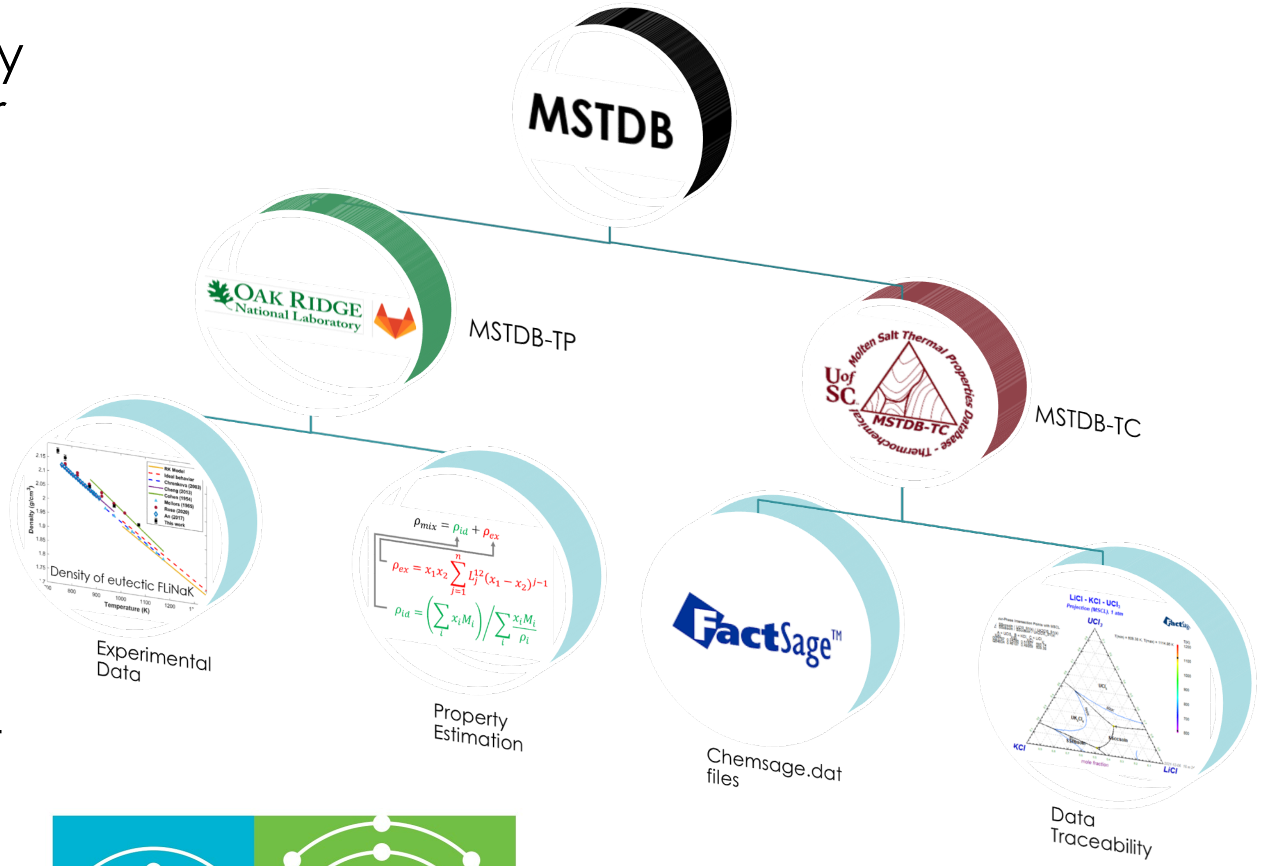


Main Driver for Property Characterization: MSTDB

- The Molten Salt Thermal Property Database (MSTDB) is an effort funded by the DOE-NE funded Molten Salt Reactor (MSR) Campaign and the Nuclear Energy Advanced Modeling and Simulation (NEAMS) program.

- The goal of the MSTDB is to provide thermochemical and thermophysical characterizations of molten salt compounds and mixtures which are relevant to the nuclear industry

- MSTDB-TC is managed by UoSC, MSTDB-TP is managed by ORNL.



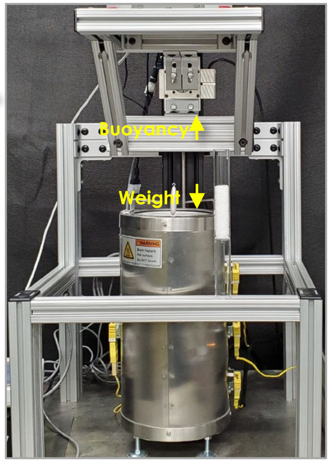
NEAMS
Nuclear Energy Advanced Modeling and Simulation

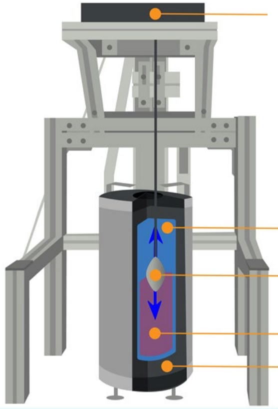
Molten Salt Reactor
PROGRAM

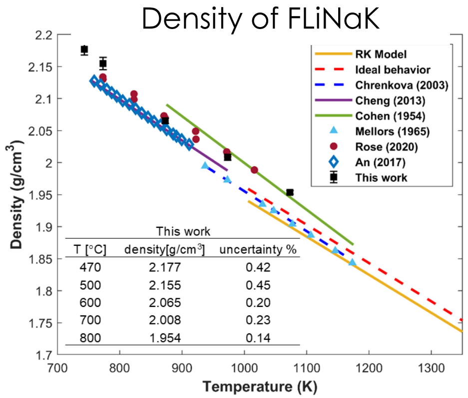
ORNL's Thermophysical Property Systems

FY22 measurement focus – driven by MSTDB-TP

Density



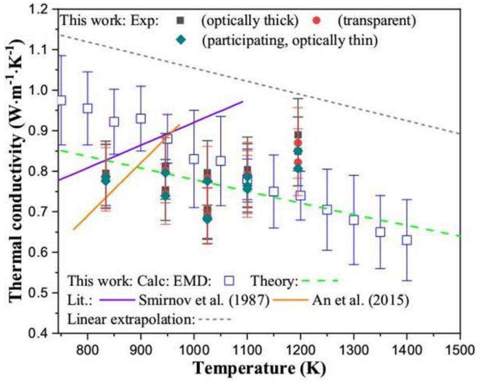


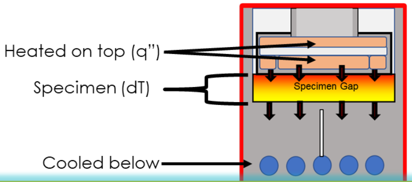


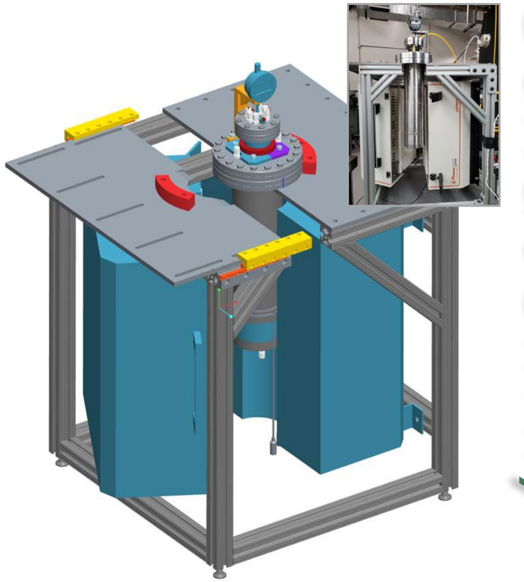
This work

T [°C]	density[g/cm³]	uncertainty %
470	2.177	0.42
500	2.155	0.45
600	2.065	0.20
700	2.008	0.23
800	1.954	0.14

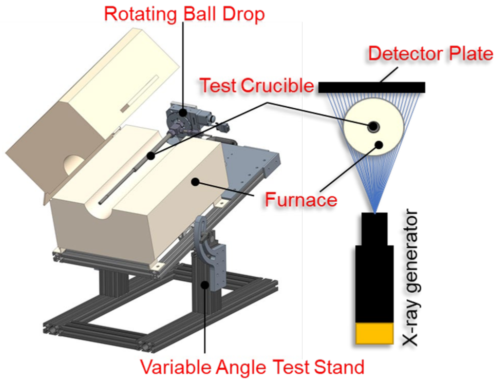
Thermal Conductivity

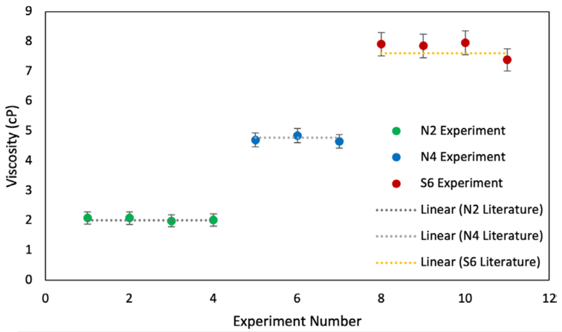




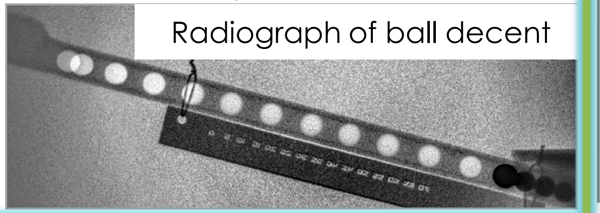


Viscosity

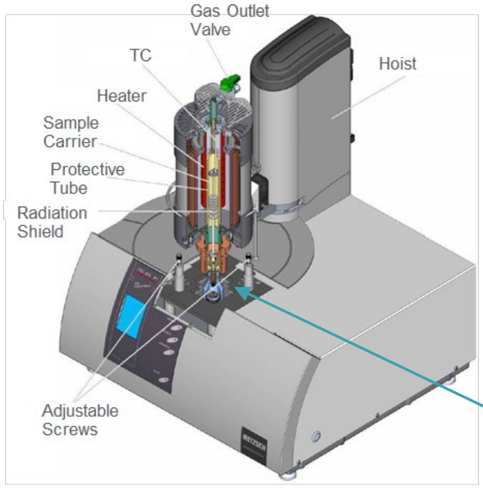


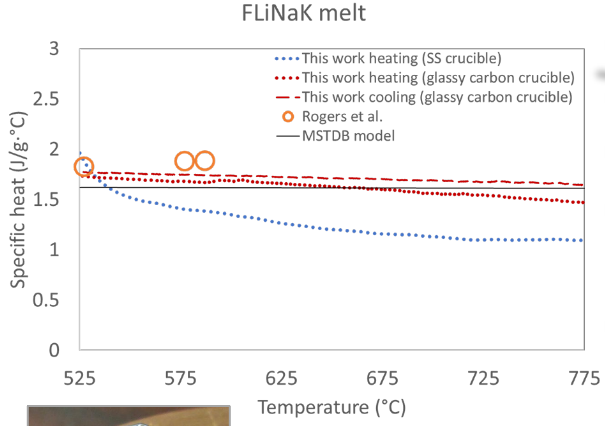


Radiograph of ball decent



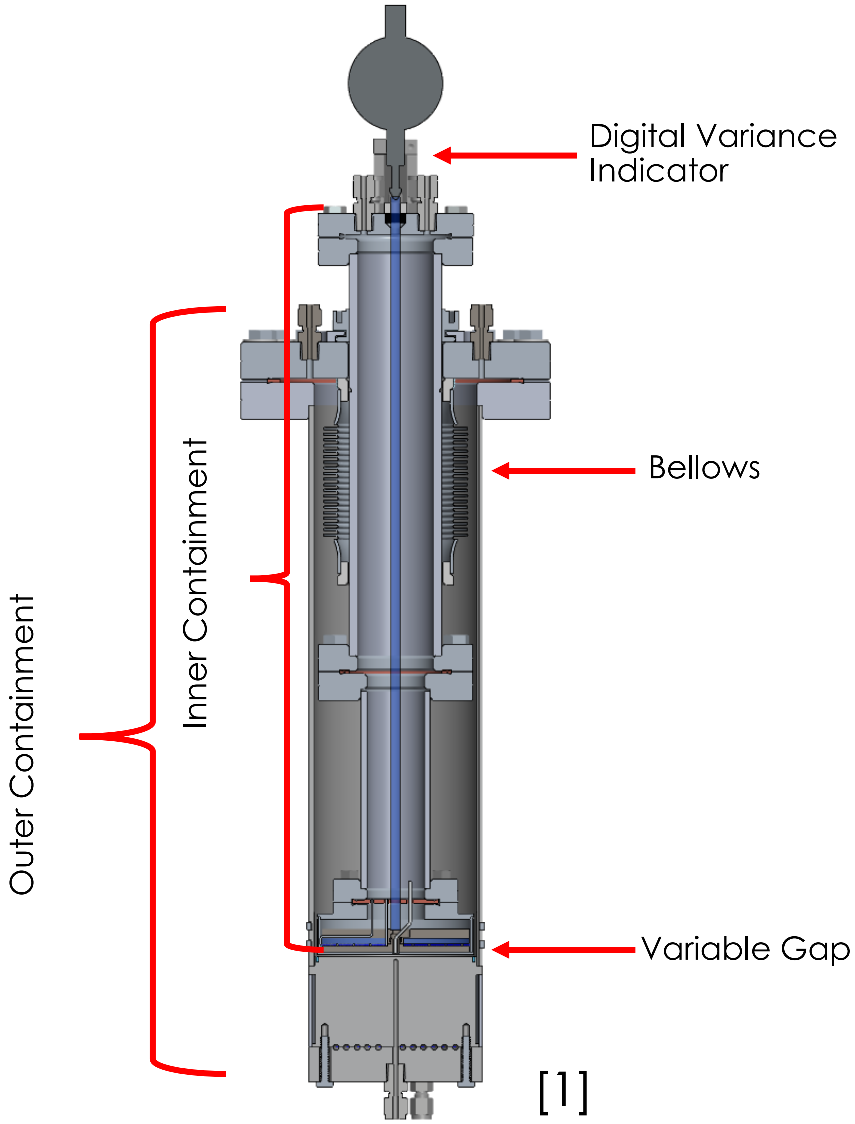
Specific Heat



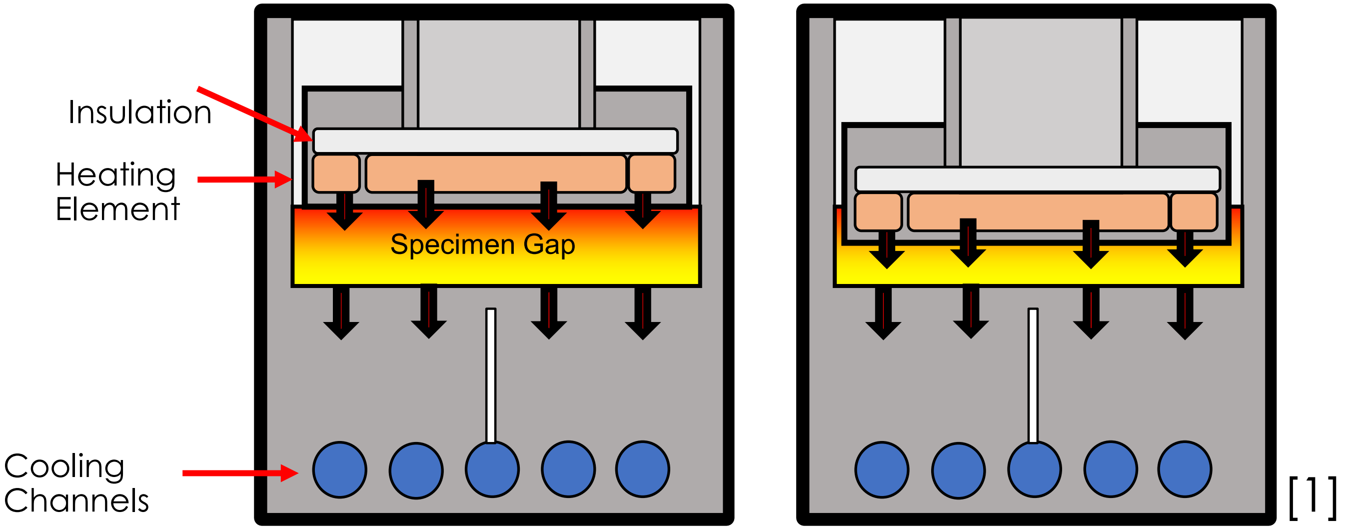


E-beam welded crucibles

FY2022 System Focus 1: Thermal Conductivity



- This system is based on the variable gap technique
- There is an inner and outer containment
  - Specimen is stored within the outer containment
  - Heating elements are within the inner containment
- A temperature difference is driven across the specimen gap, and based on 1D heat transfer we can back out thermal conductivity
- Equations are modified to account for radiant heat transfer
- Gap is <0.3 mm, making convective heat transfer negligible
- Since this is a differential approach, extra thermal resistances which affect the temperature difference can be effectively canceled out



[1] DOI: 10.1016/j.ijheatmasstransfer.2022.122763

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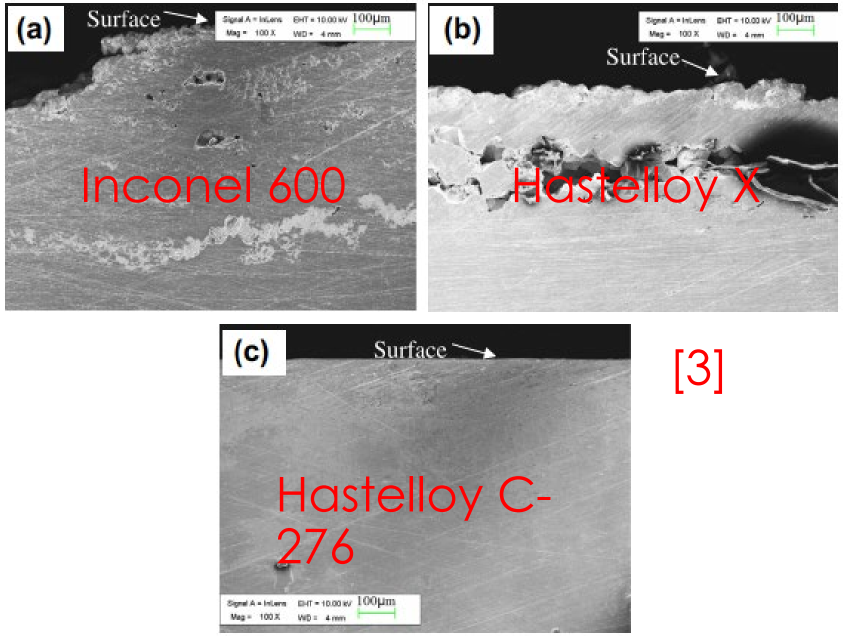
Thermal Conductivity System Improvements

- The inner and outer containments have been fabricated out of C-276 instead of SS316 due to superior corrosion resistance
  - Liu et. al have demonstrated superior corrosion resistance afte a 320 h FLiNaK bath at 750 C [3]

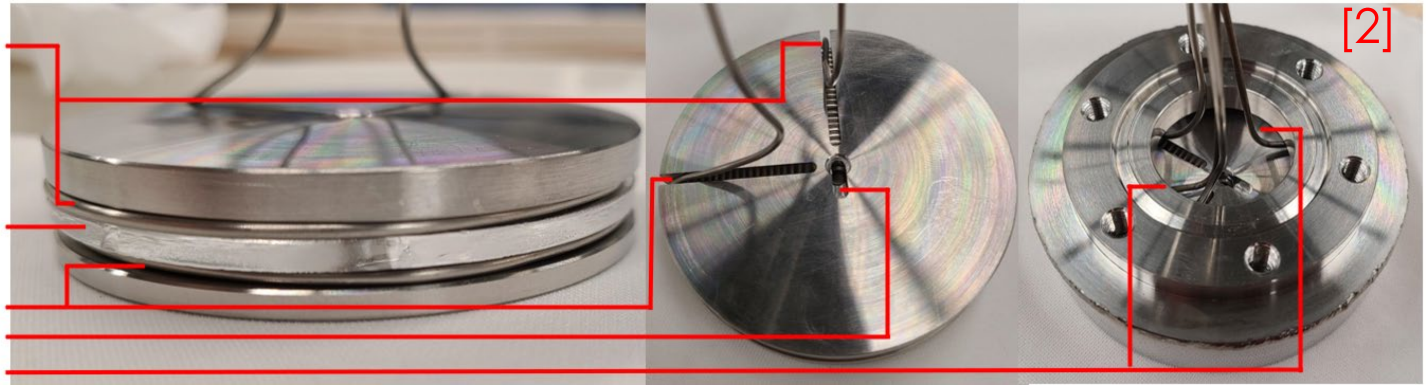
- An axial guard heater had been added to minimize heatir losses in the upward direction

C-276 outer containment (post-testing)



[3]

A
B
C
D
E



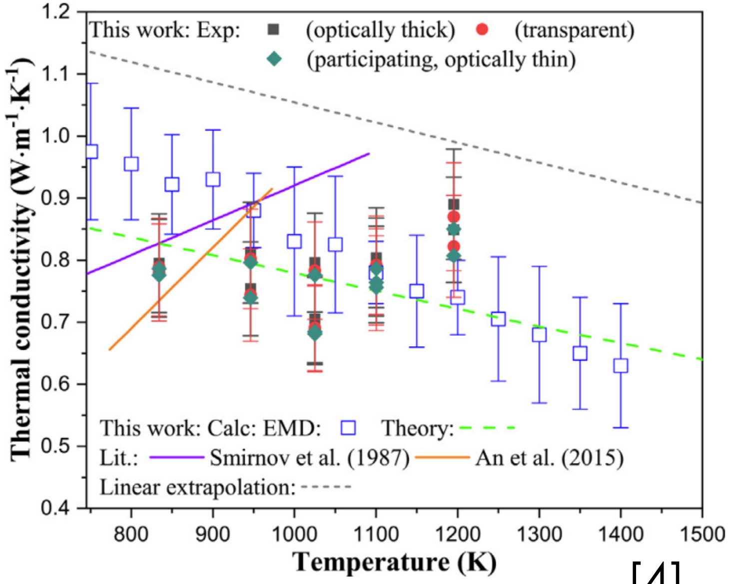
(A) axial guard heater, (B) quartz insulator, (C) main heater,(D) center thermocouple slot, and (E) side thermocouples placed in welded heater assembly cup

[2] DOI: 10.2172/1887678
[3] DOI: 10.1016/j.jnucmat.2013.04.056

Thermal Conductivity System Measurements

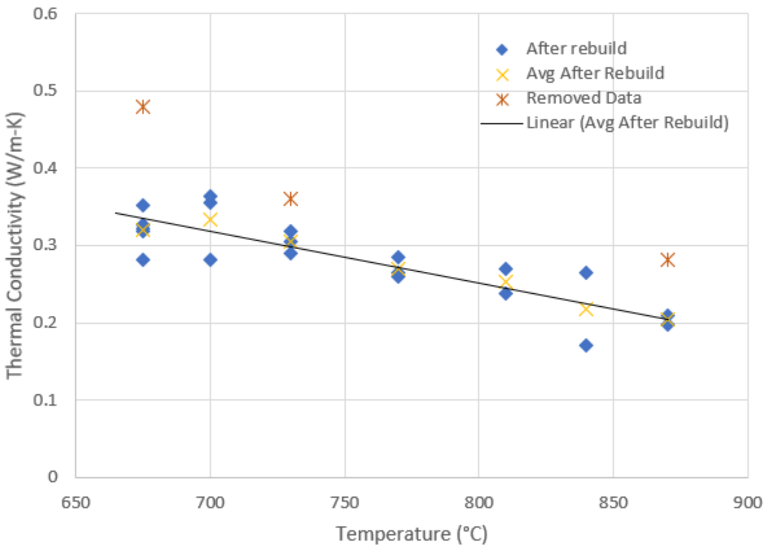
- Measurements have been made with FLiNaK and with NaCl-KCl
- Impact of heating losses potentially seen in FLiNaK measurements (high temperature deviation)
- In general guard heating shows negative dependence with temperature (expected)
- Comparing NaCl-KCl data to kinetic theory and published ab-initio models is a current effort

FLiNaK Measurements



[4]

NaCl-KCl (44/56) Measurements



[4] DOI: 10.1016/j.molliq.2022.119151

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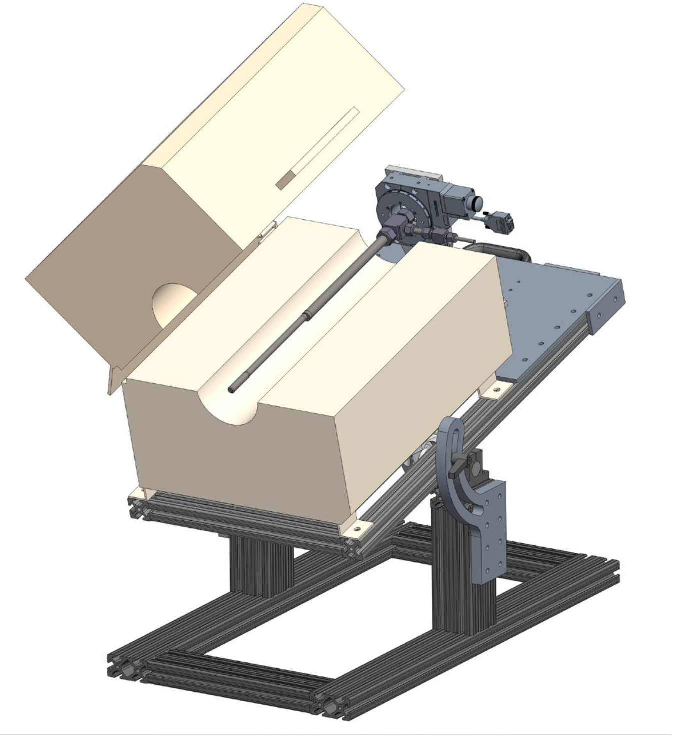
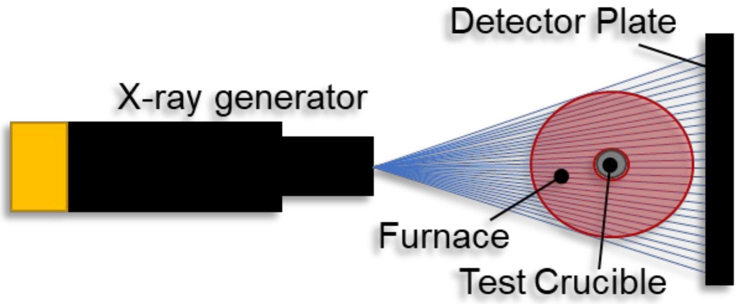
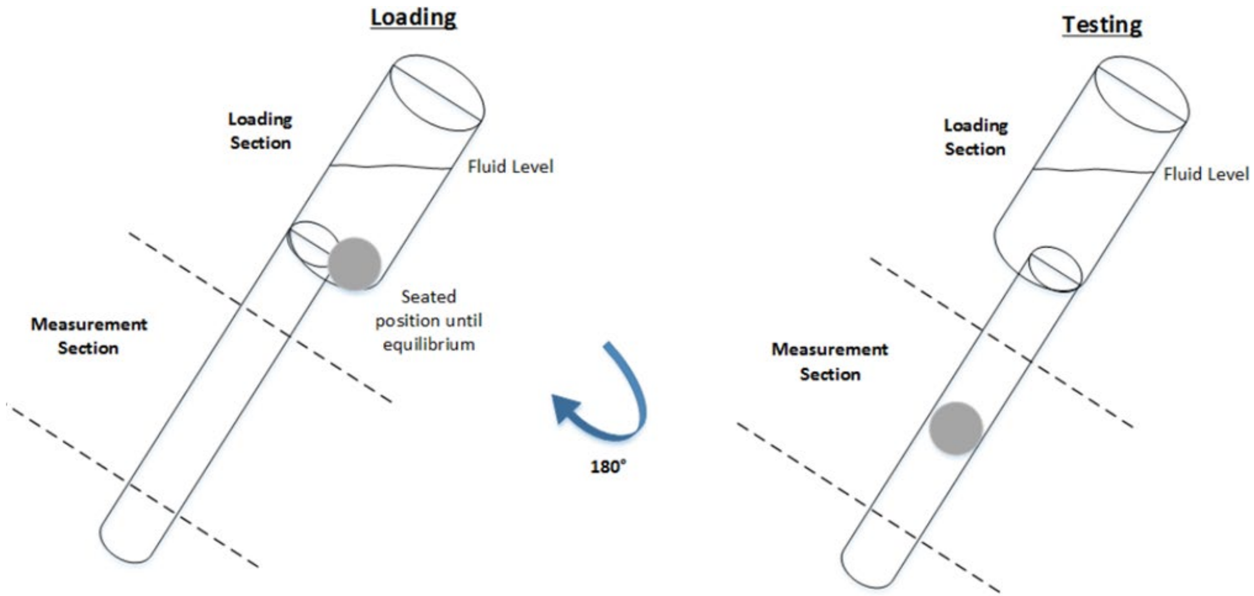
FY2022 System Focus 2: Viscosity

- Technique: Falling Ball
- The viscosity of a fluid can be determined based on the terminal velocity of the ball going through that fluid in a tube
- Can track the ball using radiography if a non-transparent crucible is used
- Crucibles are maintained under inert environment
- NIST standard oils with well known viscosities used to calibrate the system

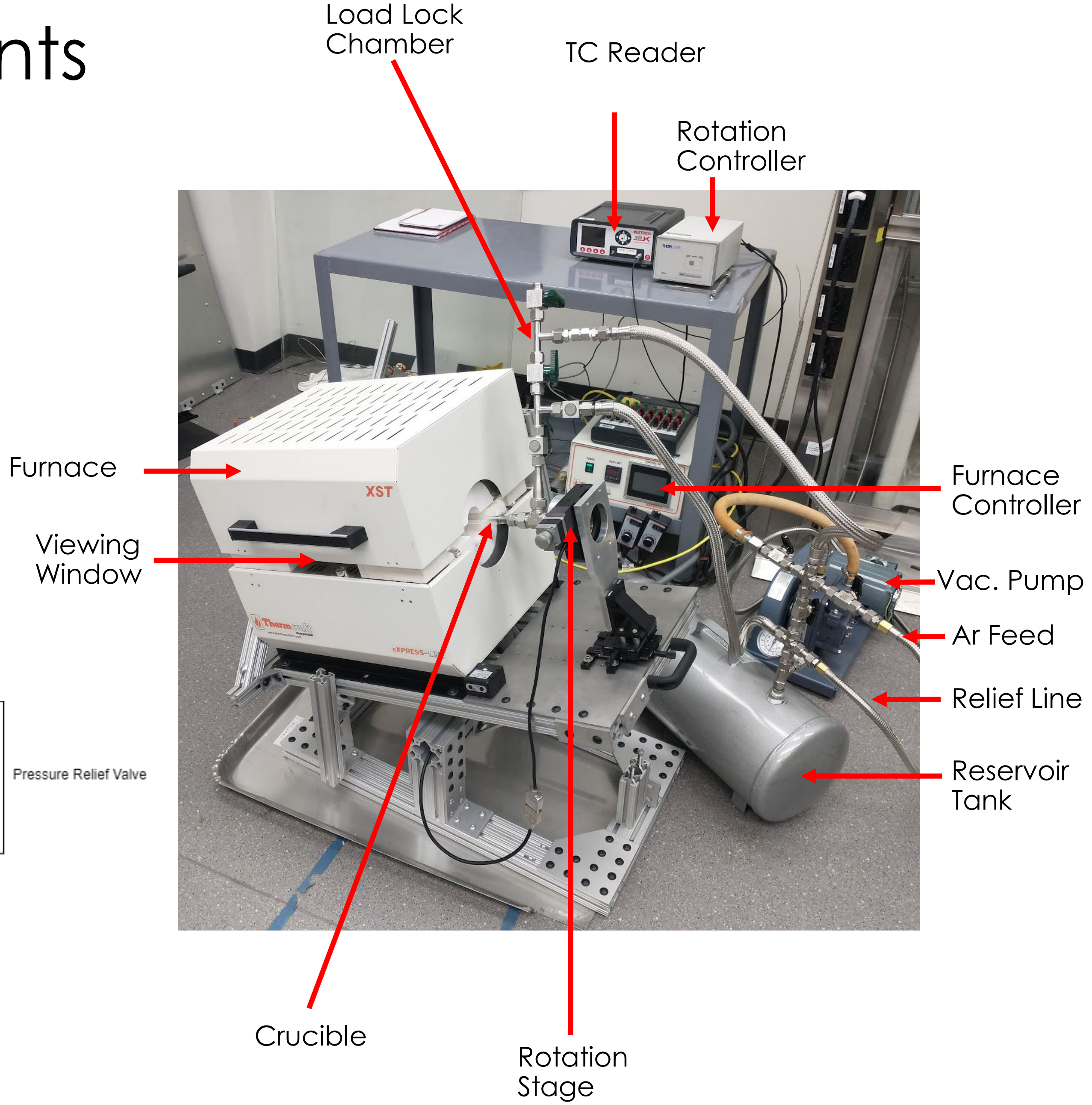


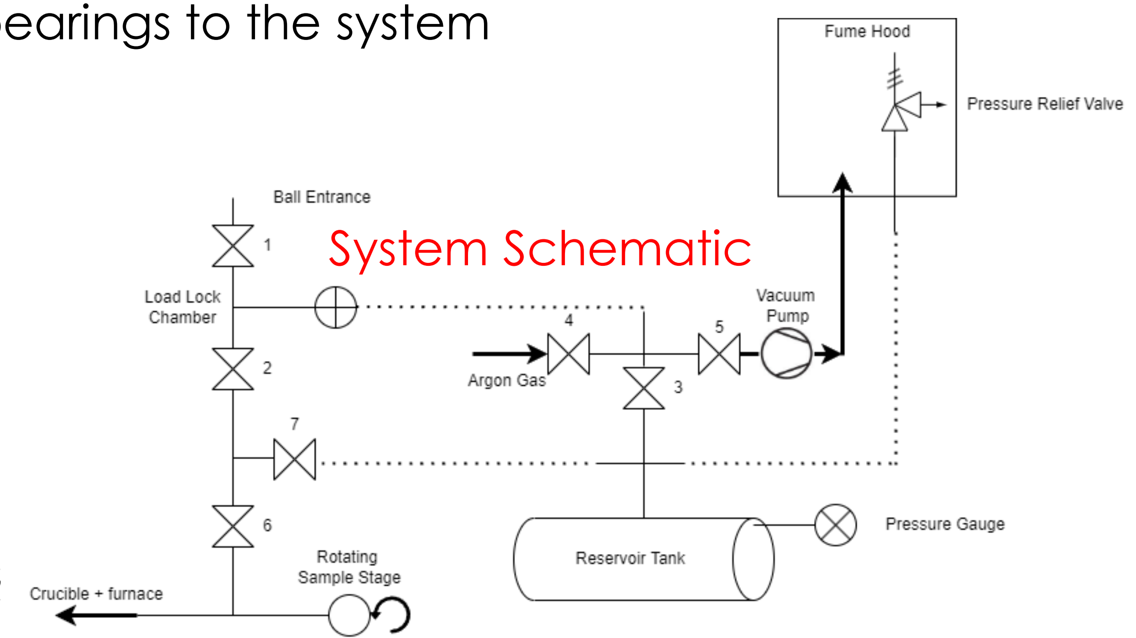




Viscosity System Improvements

- System now has an integrated Vacuum/Argon tubing infrastructure that improves system versatility
- Reservoir tank prevents over-pressurization due to heating/off-gassing
- Vacuum pump can be used to pull bubbles out of the specimen
- System can use steel/Inconel or glass crucibles
  - Steel necessary for particularly corrosive salts, glass is good for troubleshooting/understanding
- Load-lock chamber allows for continual insertion of ball-bearings to the system



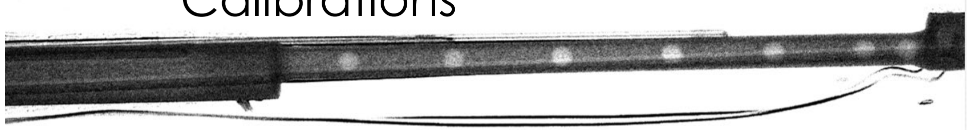


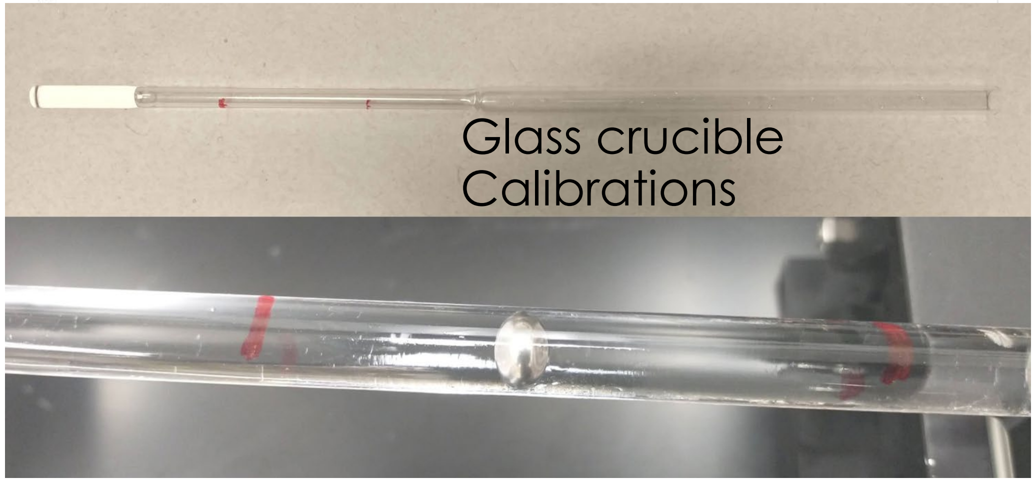
System Schematic

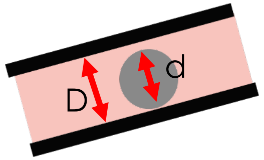
Viscosity System Measurements

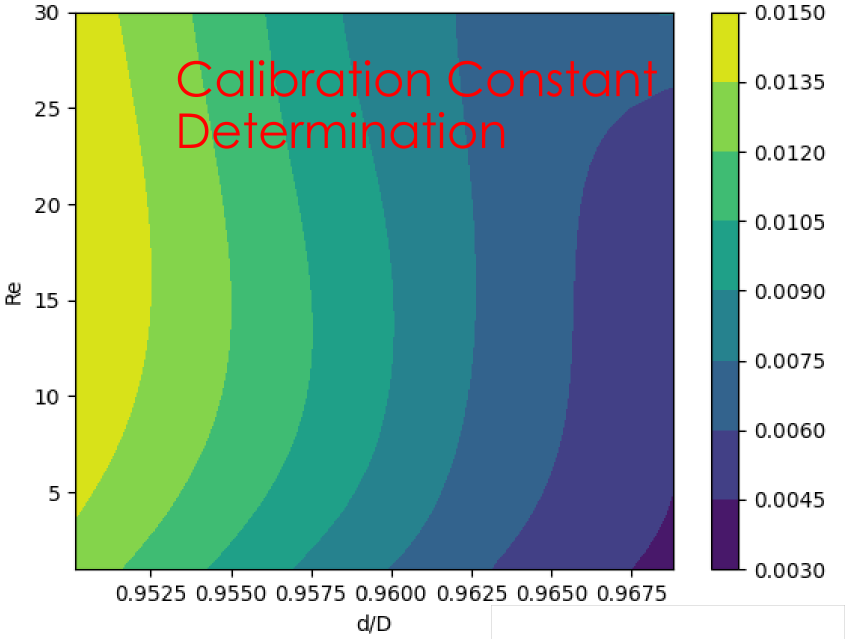
- Measurements have been made with NIST standard oils for a range of d/D ratios and tube angles (impacting Re) in order to calibrate for a wide range of conditions
  - This allows for the thermal expansion corrections
  - This also allows for adjusting to different flow regimes
- Measurements have been made with NaCl-$MgCl_2$
  - Issues with salt purity. Going to try NaCl-KCl next to avoid hydrolysis issues.

Stainless steel crucible Calibrations







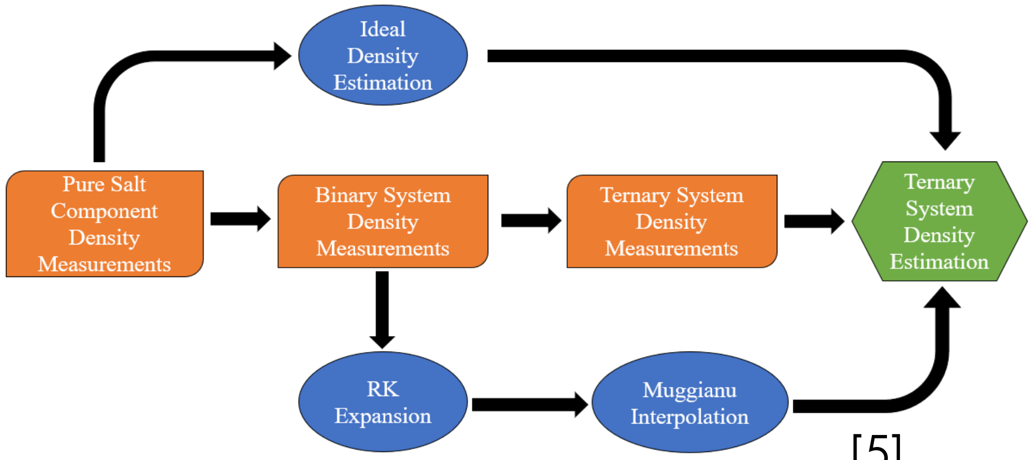


Where the data ends… what can we do?

- We can only make measurements across the national laboratories so fast
  - Time and funding is finite
  - There are countless possible pseudo-ternary+ systems which may be of interest, we cannot measure them all
- We can use modeling techniques to fill in the gaps initially, for experimental validation later on for select systems
- A number of possible techniques: Ab-initio, Modified Quasi-Chemical, Redlich-Kister…
- ORNL is focusing on Redlich-Kister, for a couple reasons:
  - It has its basis in experimental measurements (pure and pseudo-binary data)
  - It is relatively simple to set up
  - It allows for modeling over an entire compositional space of any higher order system for which pseudo-binary subsystem data exists

Redlich-Kister Technique

- Redlich-Kister technique takes pure and pseudo-binary data as input, and can spit out interaction parameters for estimation of higher order systems
- We have been investigating this RK technique with density data
  - Mainly looking at Fluorides because there is more higher-order system data for validation
- Oftentimes, people assume ideality when estimating properties of liquid mixtures.
  - For many molten salts, this is not accurate
  - Using an RK technique will account for non-idealities
- Two Main Assumptions:
  - The underlying data is accurate
  - Ternary interaction is negligible



[5]

$$\rho_{mix} = \rho_{id} + \rho_{ex}$$

$$\rho_{ex} = x_1 x_2 \sum_{j=1}^{n} L_j^{12} (x_1 - x_2)^{j-1}$$

Excess Mixing Term (Comes from pseudo-binary data)

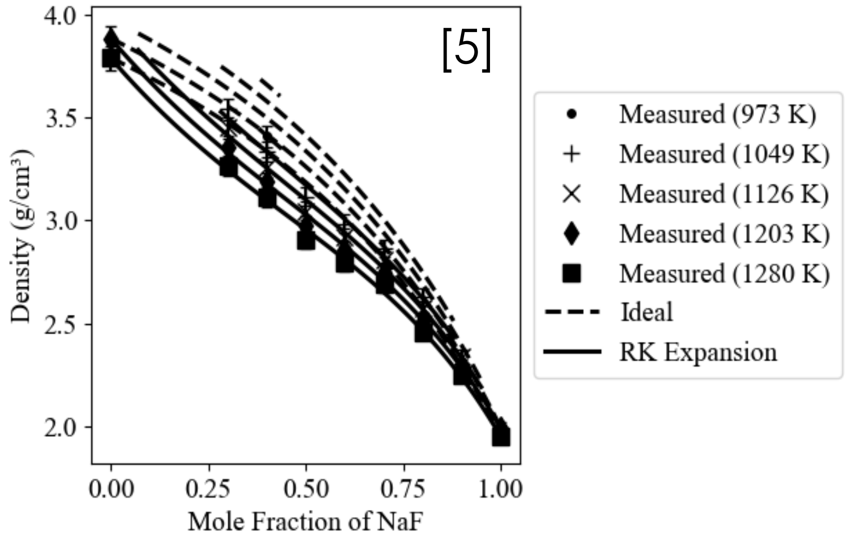
$$\rho_{id} = \left(\sum_i x_i M_i\right) \Big/ \sum_i \frac{x_i M_i}{\rho_i}$$

Ideal Mixing Term (Comes from pure component data)

Binary Interaction Calculations

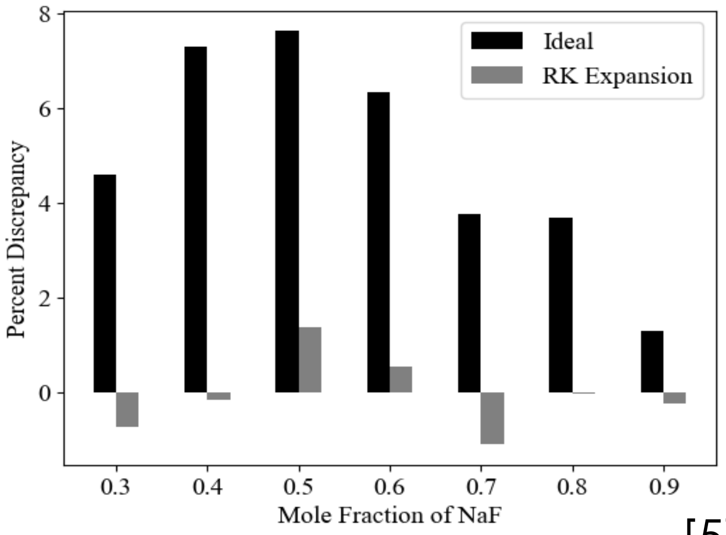
- We've calculated the binary interaction parameters for several fluoride molten salts of nuclear interest
- These molten salts include compounds such as BeF2, ThF4, ZrF4, UF4
- The interaction parameters can then be used to estimate higher order systems via Muggianu interpolation

RK Expansion fitted to NaF-ZrF4 data



System	R^2 (ideal)	R^2 (RK expan.)	ε_{avg} (ideal)	ε_{avg} (RK expan.)	ε_{max} (ideal)	ε_{max} (RK expan.)
NaF-LiF	0.96	0.995	0.59%	0.18%	0.89%	0.56%
NaF-KF	0.58	0.71	1.2%	1.0%	5.9%	5.3%
$NaF-ZrF_4$	0.84	0.997	5.4%	0.69%	9.6%	1.8%
$LiF-ZrF_4$	0.68	0.994	7.8%	1.1%	18.4%	7.8%
$NaF-BeF_2$	0.77	0.94	1.5%	0.67%	5.5%	4.4%
$LiF-BeF_2$	0.75	0.997	1.5%	0.15%	3.9%	0.59%
$LiF-ThF_4$	0.998	0.9992	0.89%	0.70%	2.3%	1.9%
$NaF-ThF_4$	0.98	0.9997	3.0%	0.30%	5.9%	1.2%
$NaF-UF_4$	0.97	0.995	3.6%	1.2%	10.4%	4.5%

[5]



[5]

[5] DOI: 10.1016/j.ces.2022.117954

Ternary Density Estimation

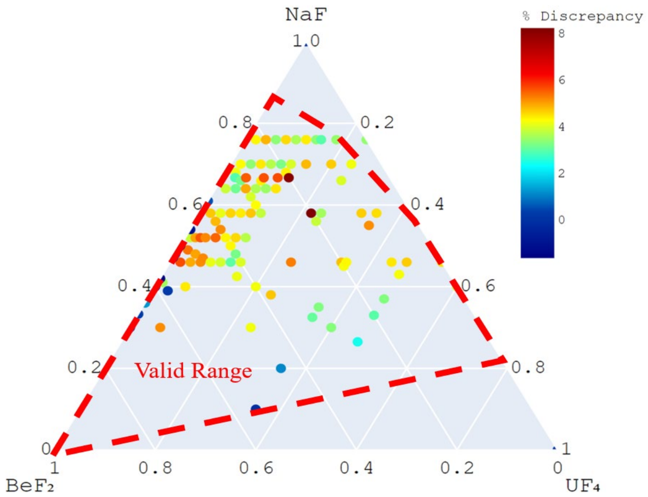
- We've used RK expansion to estimate higher order system densities, showing general improvement over ideal assumption
- In some cases, we've applied ternary interaction terms to add more accuracy to the model
  - Only possible if sufficient ternary data exists

System	Estimate with higher R^2	ε_{avg} (Ideal)	ε_{avg} (RK expan.)	ε_{max} (Ideal)	ε_{max} (RK expan.)
NaF-LiF-ZrF_4	RK estimation	3.9%	3.8%	8.3%	5.9%
LiF-BeF_2-ZrF_4*	RK estimation	0.79%	0.79%	1.7%	0.98%
LiF-BeF_2-ThF_4*	RK estimation	1.5%	0.85%	2.6%	1.6%
NaF-LiF-BeF_2	RK estimation	2.6%	1.7%	3.6%	4.0%
NaF-KF-BeF_2	RK estimation	4.6%	3.6%	4.9%	5.0%
NaF-ZrF_4-UF_4*	RK estimation	20%	13%	22%	14%
NaF-BeF_2-UF_4*	RK estimation	3.7%	2.0%	8.2%	5.6%

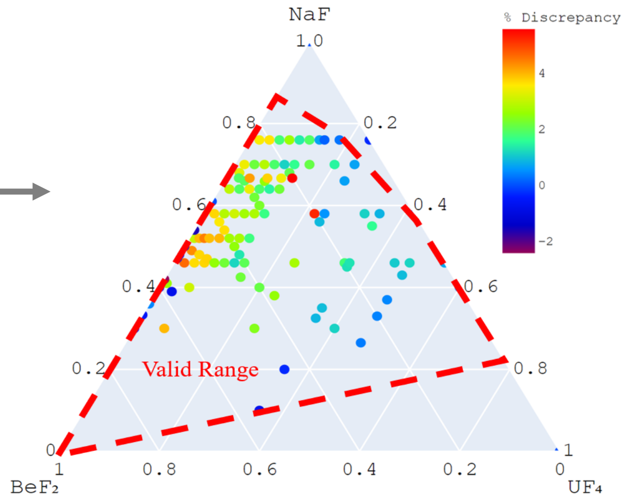
*Only 2/3 binary interactions considered

[5]

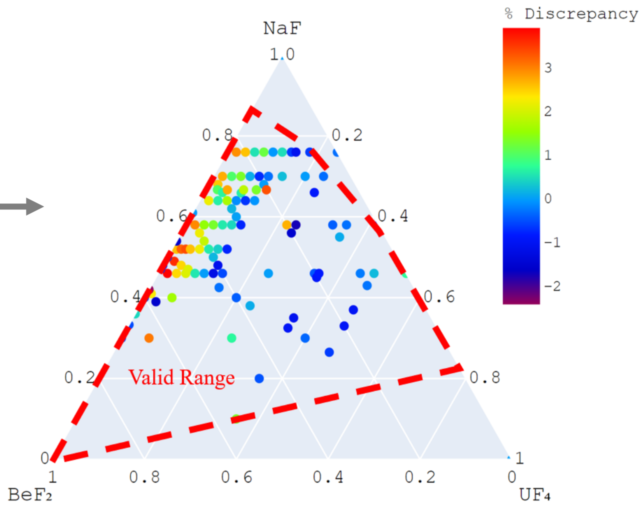
Ideal Assumption



Binary Interaction Considered



Ternary Interaction Considered



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Note: All at 1073 K

[5] DOI: 10.1016/j.ces.2022.117954

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Summary

- MSR developers need to know thermophysical properties of their molten salts with a high degree of accuracy to have confidence in modeling the thermal performance of a reactor
- The MSTDB highlights data needs for relevant pure, pseudo-binary, and higher order systems
- ORNL has the ability to measure density, viscosity, thermal conductivity, and heat capacity: FY22 focuses were on viscosity and thermal conductivity
- ORNL's thermal conductivity and viscosity systems have been improved to obtain more accurate data and be more versatile. However, further improvements of error reduction are required
- ORNL is also focusing on demonstrating Redlich-Kister for thermophysical property estimation, for gap closure purposes

Acknowledgments

References:

1) Ryan C. Gallagher, Anthony Birri, Nick Russell, N. Dianne B. Ezell, International Journal of Heat and Mass Transfer, Volume 192, 2022,122763

2) Anthony Birri, Ryan Gallagher, Nicholas Russell, Nicholas Termini, Paul Rose Jr., N. Dianne Bull Ezell, ORNL/TM-2022/2573, 2022

3) Min Liu, Junyi Zheng, Yanling Lu, Zhijun Li, Yang Zou, Xiaohan Yu, Xingtai Zhou, Journal of Nuclear Materials, Volume 440, Issues 1–3, 2013, pp. 124-128

4) Ryan C. Gallagher, Anthony Birri, Nick G. Russell, Anh-Thu Phan, Aïmen E. Gheribi, Journal of Molecular Liquids, Volume 361, 2022,119151

5) Anthony Birri, Ryan Gallagher, Can Agca, Jake McMurray, N. Dianne Bull Ezell, Chemical Engineering Science, Volume 260, 2022,117954

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