Rolling Ball Viscometry for Molten Salts: Ensuring Measurement Accuracy, Quantifying Uncertainty

Workshop on Measurement and Analysis of Thermochemical & Thermophysical Properties of Molten Salts

July 17th, 2024

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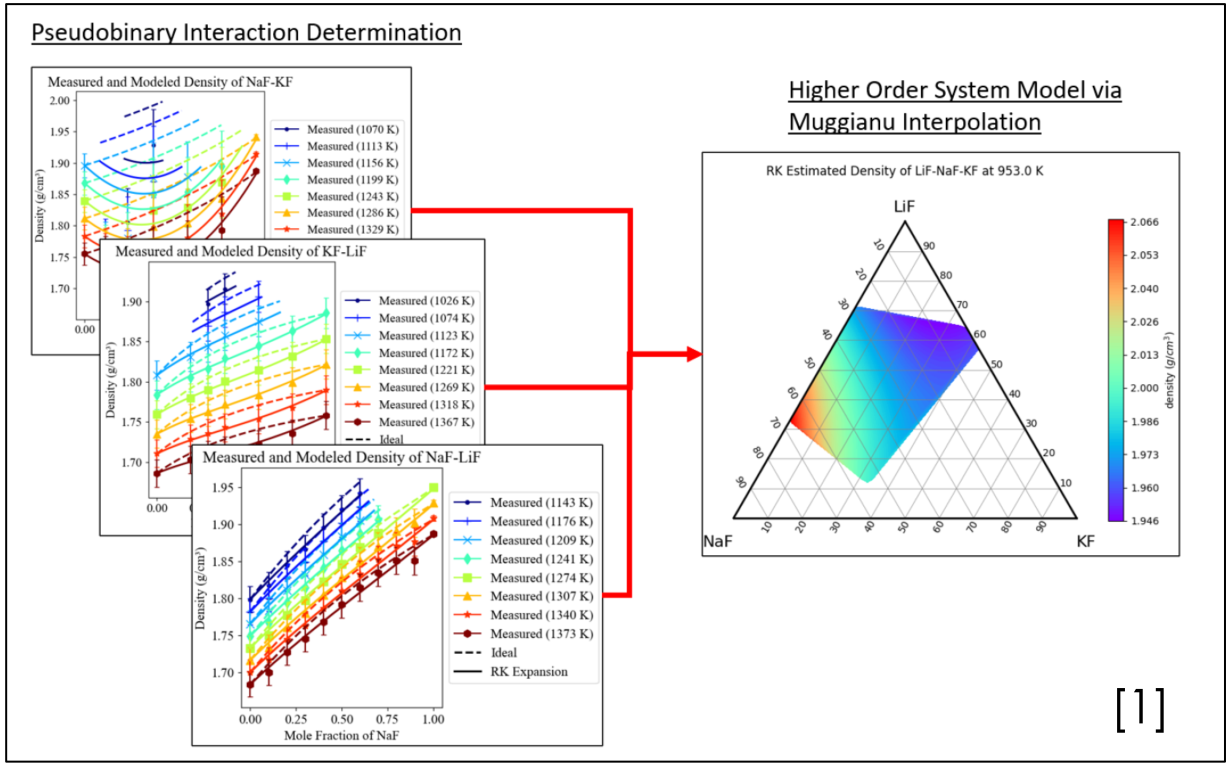
Overview of Thermophysical Characterization Efforts at ORNL

1. Experimental Measurements
2. Database Development
3. Predictive Modeling



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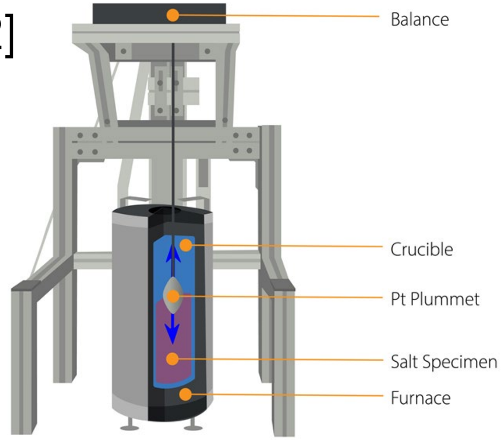

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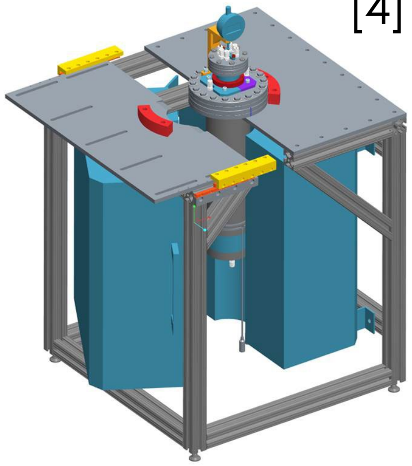

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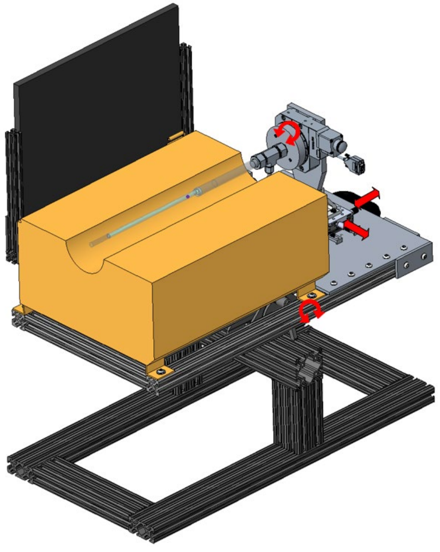
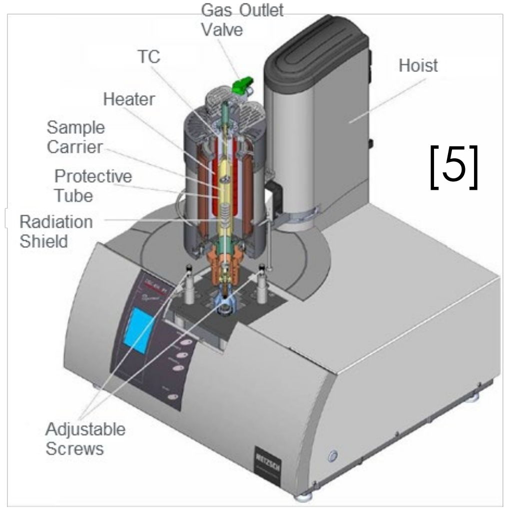




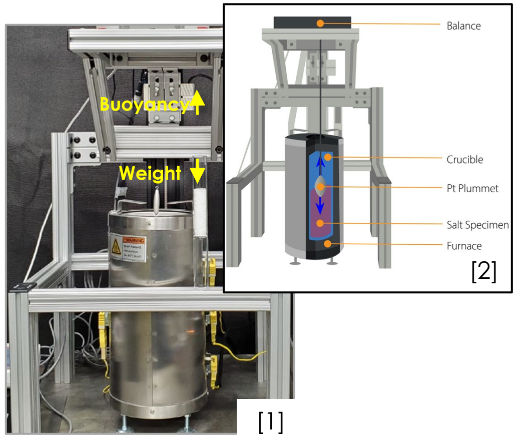
[5]

[1] ORNL/TM-2023/2955
[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] Netzch DSC 404 F3 Pegasus Manual

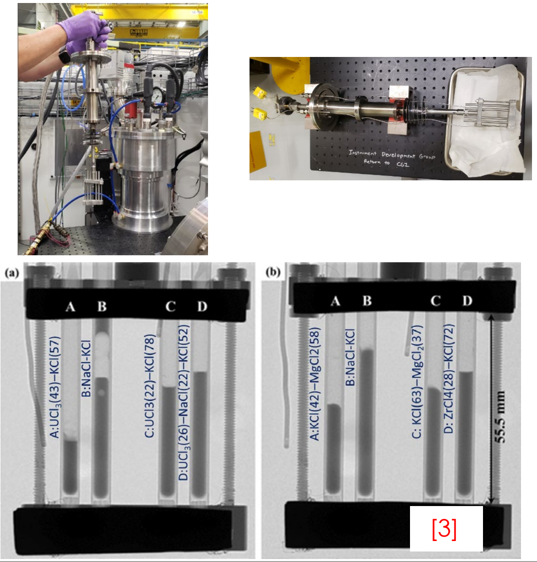
ORNL's Thermophysical Property Systems

Density

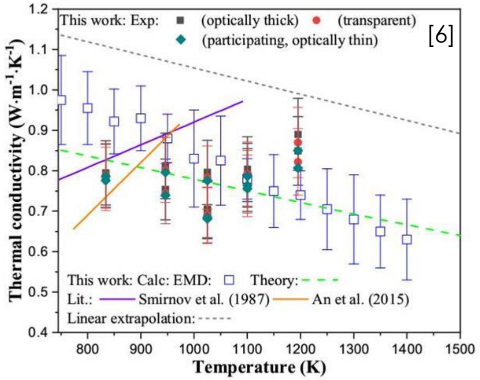
Archimedean Method

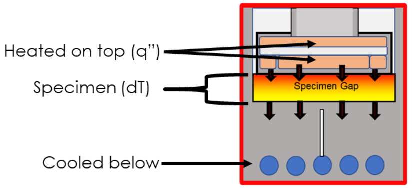


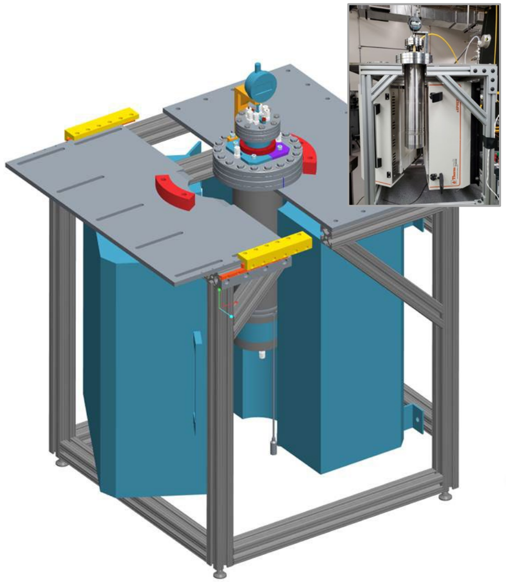
Neutron Radiography Method



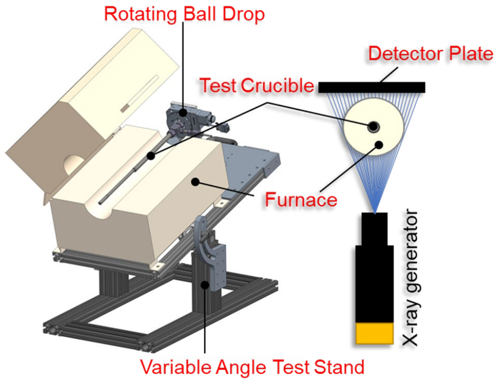
Thermal Conductivity







Viscosity



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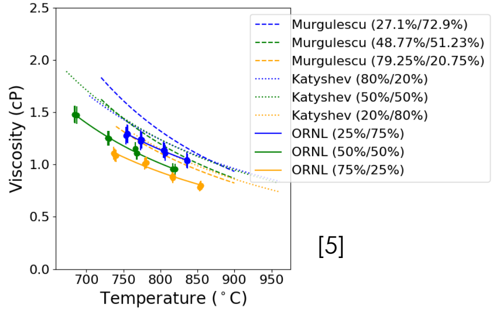
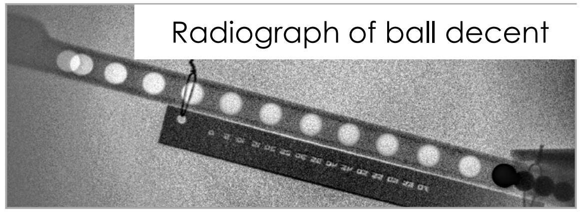
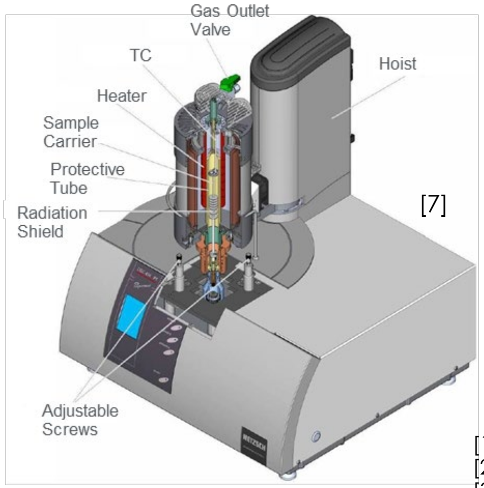
NaCl-KCl measurements



[5]

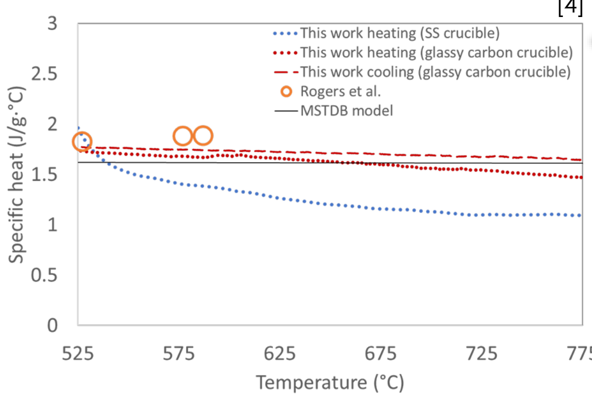
Radiograph of ball decent





[7]

Specific Heat

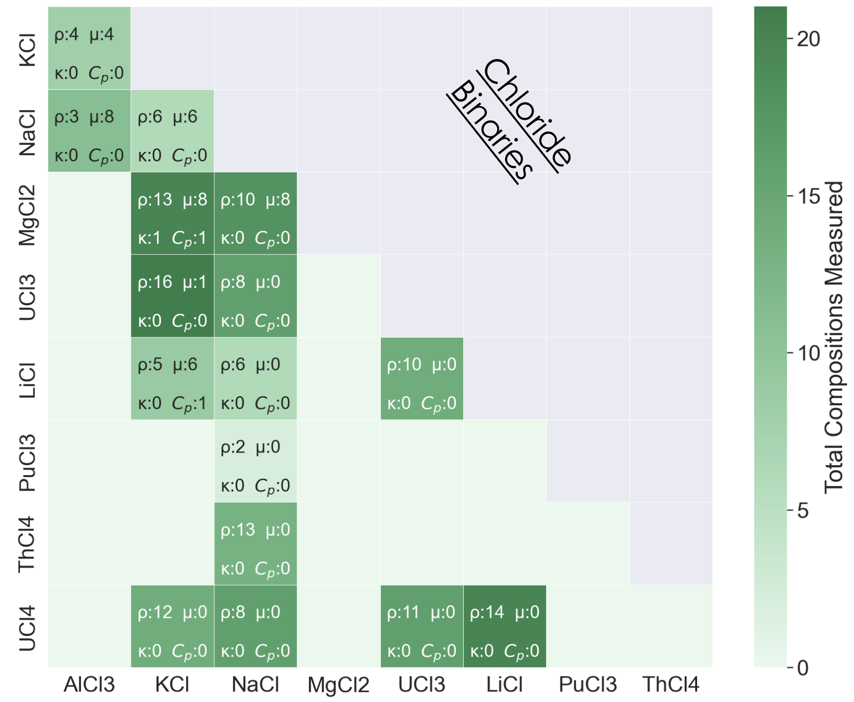


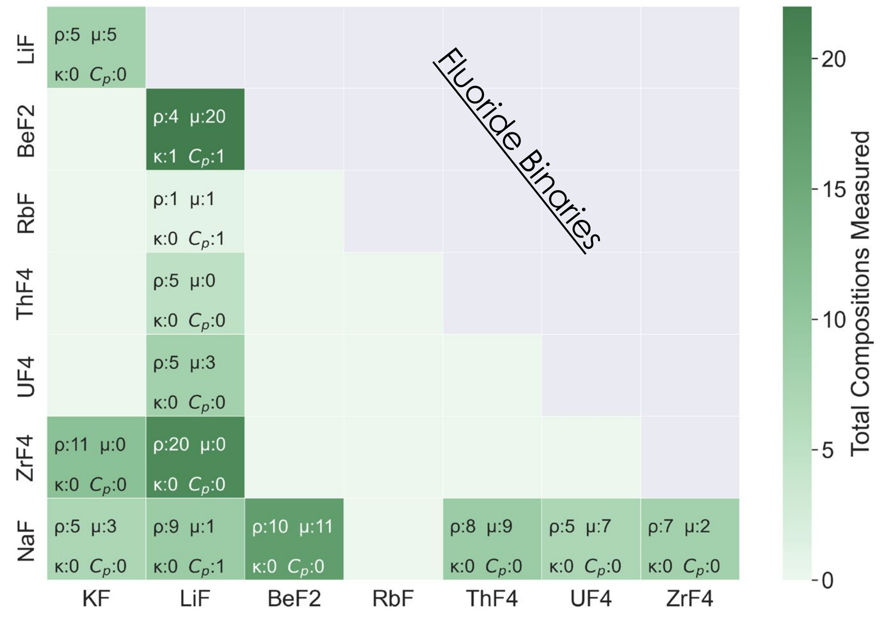
[4]

[1] ORNL/TM-2020/1633
[2] Gallagher et. al, J. Chem. Eng. Data 2022, 67, 6, 1406–1414
[3] Moon et al., Ind. Eng. Chem. Res. 2022, 61, 17665–17673
[4] ORNL/TM-2021/2216
[5] ORNL/TM-2023/3048
[6] Gallagher et al., J. Mol. Liq., 2022, 361, 119151
[7] Netzch DSC 404 F3 Pegasus Manual

Gaps in Viscosity Characterization

- Generally very few studies on actinide-bearing melt viscosity
  - For chlorides, limited to the data generated from a single group in Russia in the 70s through the 90s [1]
  - For fluorides, limited to a few studies by Blanke in the 50s [2, 3]
  - No duplicate studies to compare against
- No understanding of UF3-UF4, BeF2-UF3, BeF2-UF4, UF4-ZrF4, MgCl2-UCl3
  - However some higher order systems with these subsystems have been studied
- Nothing on PuCl3 bearing melts





[1] Katyshev, Sergey Filippovich. Properties of molten mixtures of alkali metal halides, zirconium, hafnium and uranium. Ural State Technical University, 2001.
[2] Blanke, B. C et al. Viscosity of Fused Mixtures of Sodium Fluoride, Beryllium Fluoride, and Uranium Fluoride. Mound Laboratory. 1958b.
[3] Blanke, B.C et al. Density and Viscosity of Fused Mixtures of Lithium, Beryllium, and Uranium Fluorides. Mound Laboratory. 1959

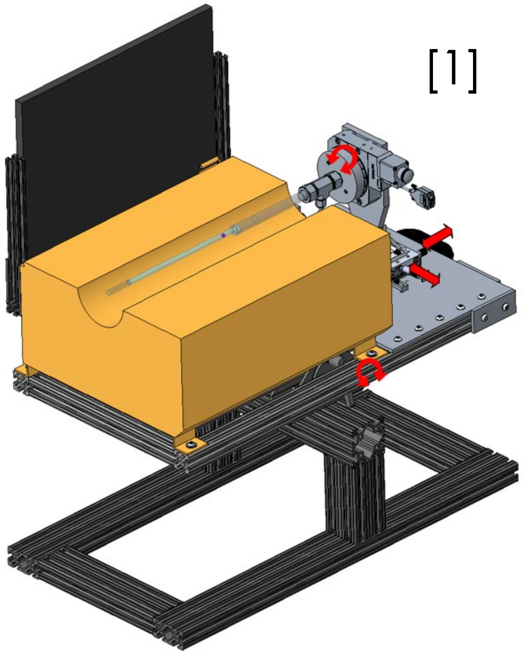
Overview of System

- Based on Rolling Ball Technique
  - Terminal velocity of ball corresponds with viscosity of fluids
  - Correlation determined based on calibration with NIST standard oils

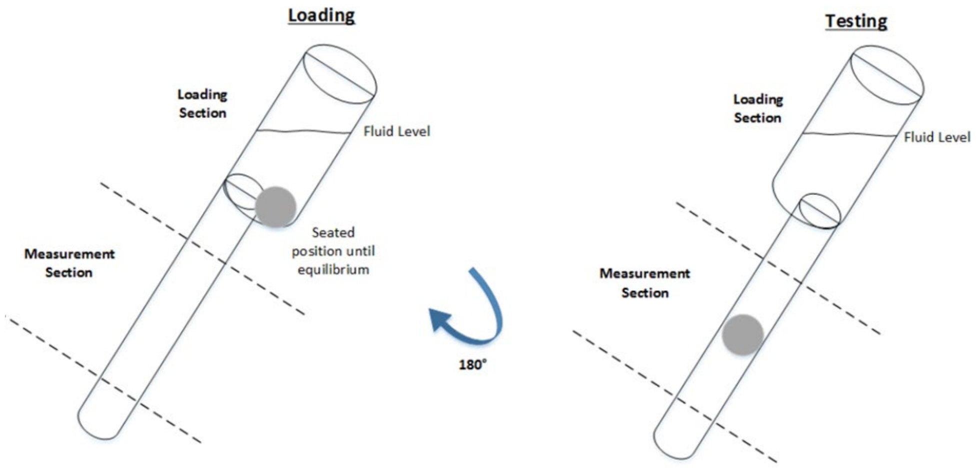
- Oxygen filter integrated (~ppb levels)

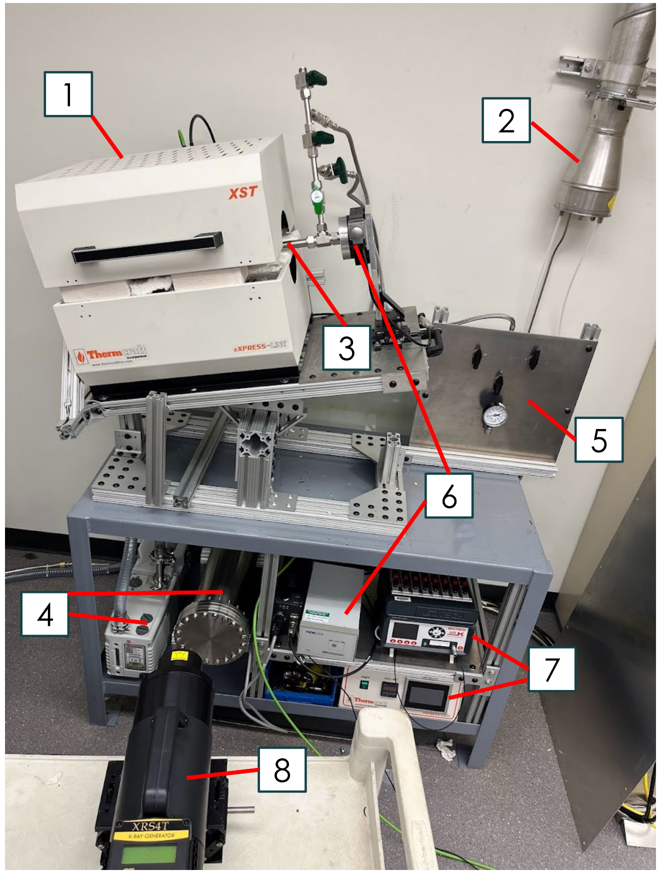
- Designated CA zone and ventilation to enable actinide salt measurements

- New x-ray system which requires minimal image processing
  - Used for stainless steel crucibles
  - For fluoride and actinide bearing salts which can't be contained in fused quartz



[1]



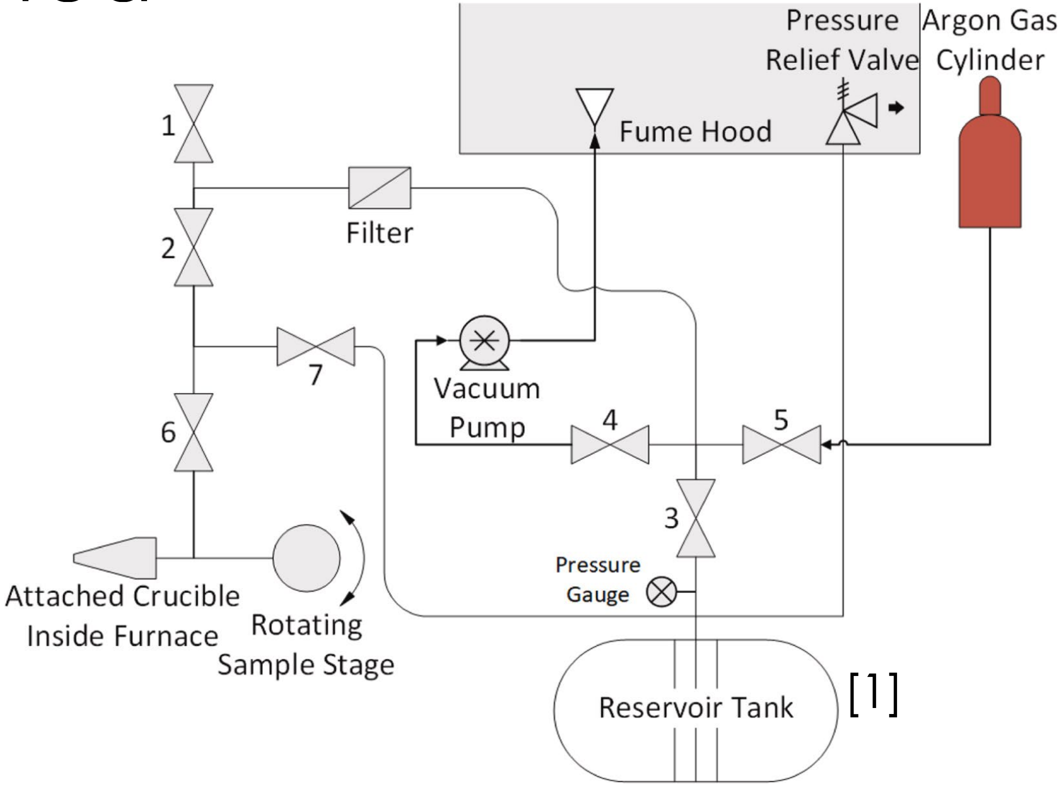


1. Furnace
2. Ventilation
3. Crucible
4. Backfill/pressure maintenance system
5. Gas control
6. Rotation control
7. Heating/temperature control
8. X-ray system (detector behind furnace

[1] Birri et al. (2023). TSEP, 44, 102029.
[2] ORNL/TM-2020/1633

How the Measurement is Conducted

1. The crucible is calibrated over a range of Re and d/D ratios with NIST standard oils
2. The crucible is loaded with purified salt in a glovebox and valved off
3. The entire system is backfilled with Ar
4. The crucible is attached to the system and control volumes are combined
5. The system is brought to desired temperature
6. Balls enter through load lock, terminal velocity is measured. Triplicate measurements at each temperature.



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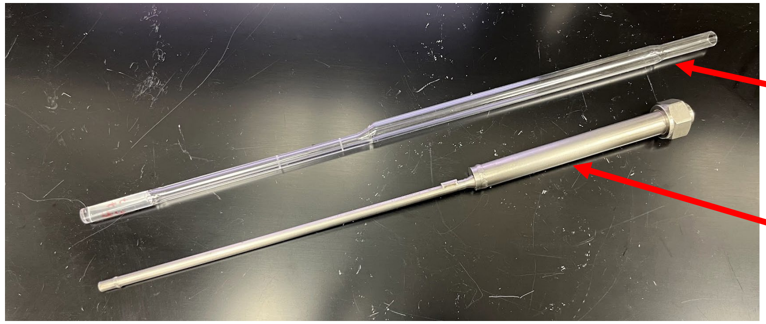


Fused quartz crucible

Stainless steel crucible

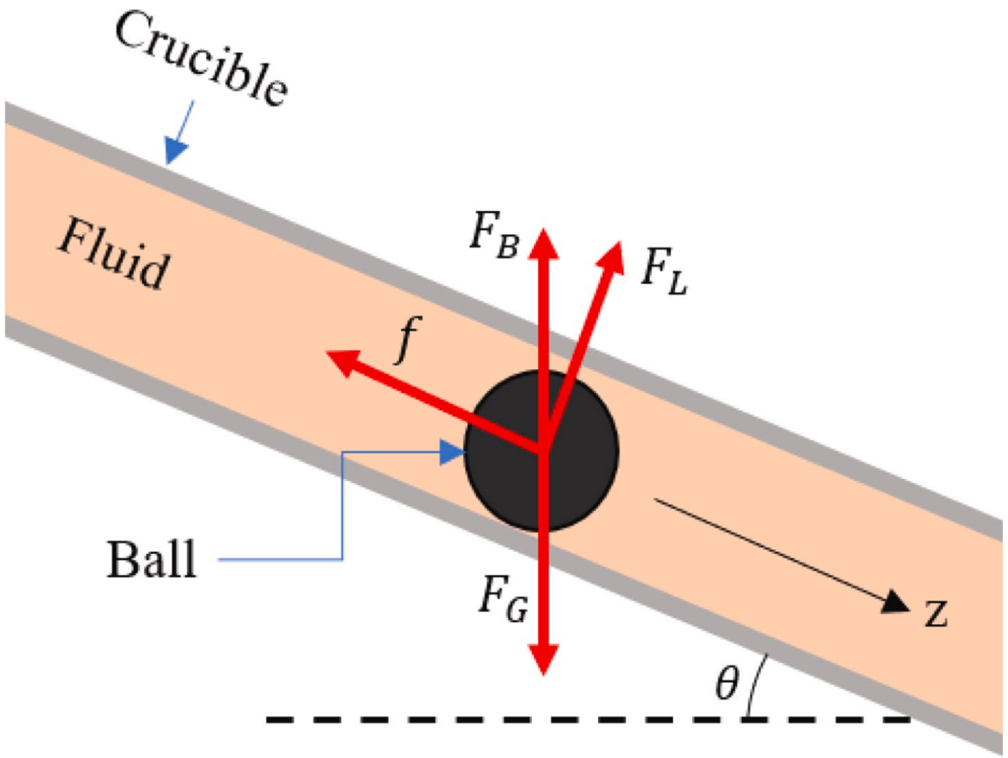
[1] Birri et al. (2023). TSEP. 44.

General Working Equation

- After balancing of forces [1], one arrives at:

$$\mu = \frac{K(\rho_b - \rho_f)tsin(\theta)}{L}$$

- K is a calibration factor, dependent on wall effects and flow conditions
- ρ_b is the density of the ball
- ρ_f is the density of the fluid
- t is the time to roll a specified distance
- θ is the angle of inclination
- L is the specified rolling distance



[1]

- F_B is the buoyancy force
- f is the opposing viscous force, involves K and μ
- F_L is the lift force
- F_G is the gravitational force

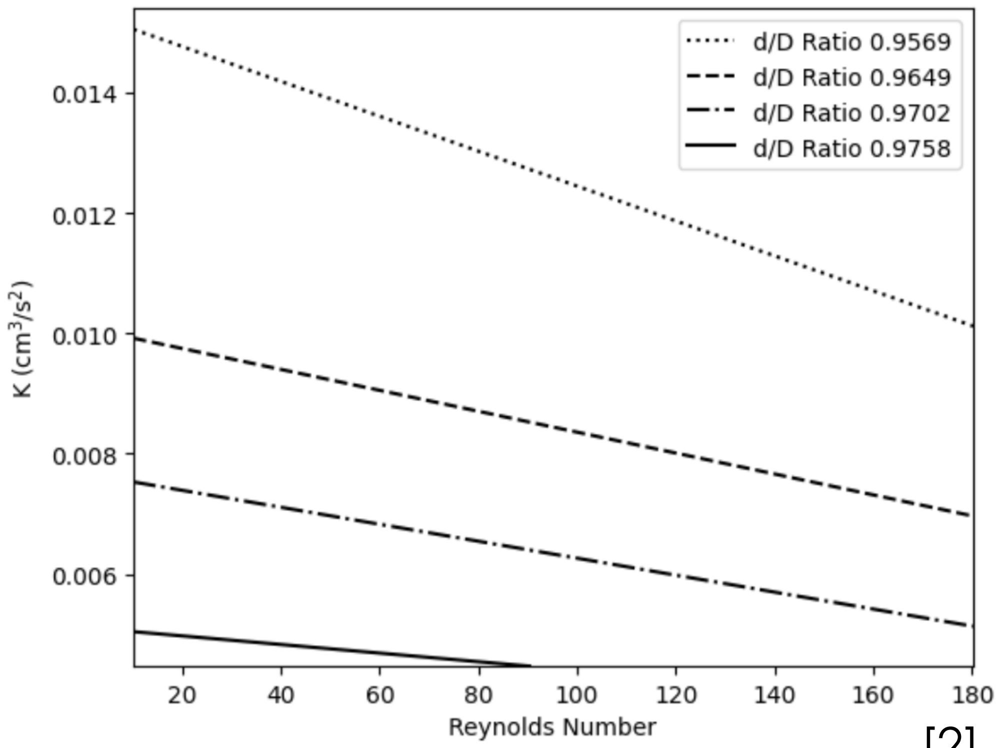
[1] Birri et al. (2023). TSEP. 44.

Determination of K

- There are several studies to describe K mathematically, but we have not found one which seems accurate based on oil experiments
  - This is likely a consequence of the difficulty to characterize Re >> 1 (our situation with low viscosity salts)

- Therefore, we must develop a calibration curve for $K\left(Re, \frac{d}{D}\right)$
  - From thermal expansion mismatch of ball and crucible, $\frac{d}{D}$ changes
  - If you know $d(T)$ and $D(T)$, you can get $K(Re, T)$

Example Calibration Curves



[2]

- Note that this linear functionality is ONLY observed for laminar regime
- For lower Re (Stokes flow, Re <1) and higher Re (formation of turbulent wake, Re>>100) things change

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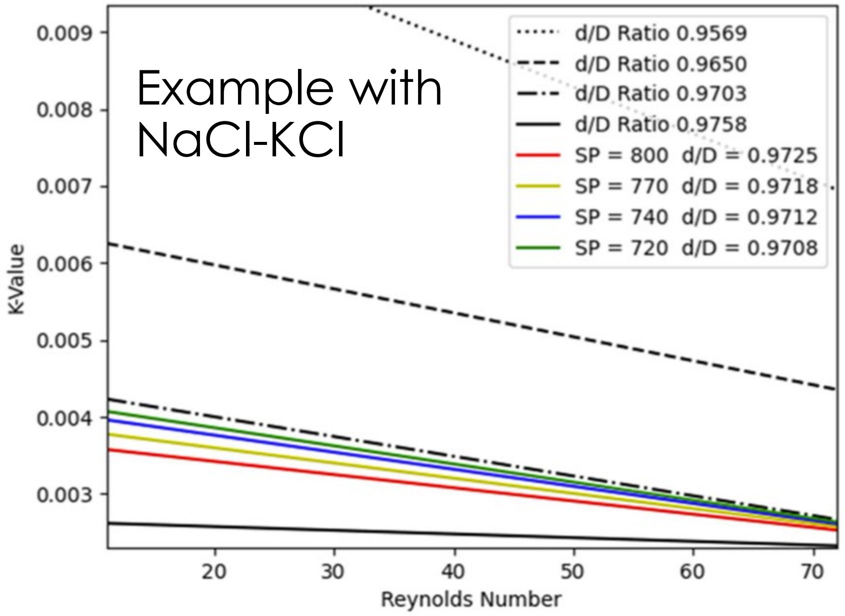
[2] ORNL/TM-2023/3048

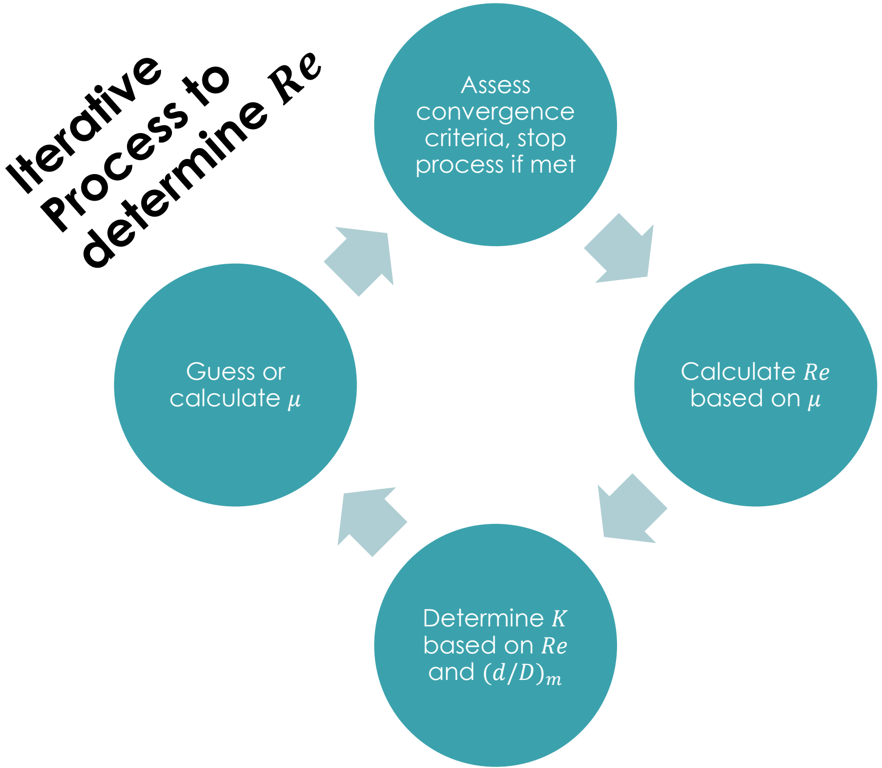
How we determine K for some arbitrary salt measurement

1. Measure a range of oils at different angles and ball sizes to measure K for a range of Re and d/D ratios
   - This yields a series of curves (with index i) defined by
     $K(d/D = (d/D)_i, Re) = a_i + b_i * Re$

2. Determine the measured salt $(d/D)_m$, and determine calibration curve for measurement
   - $K(d/D = (d/D)_m, Re) = a_m + b_m * Re$
   - a_m and b_m determined through interpolation

3. Iteratively determine Re based on calibration curve

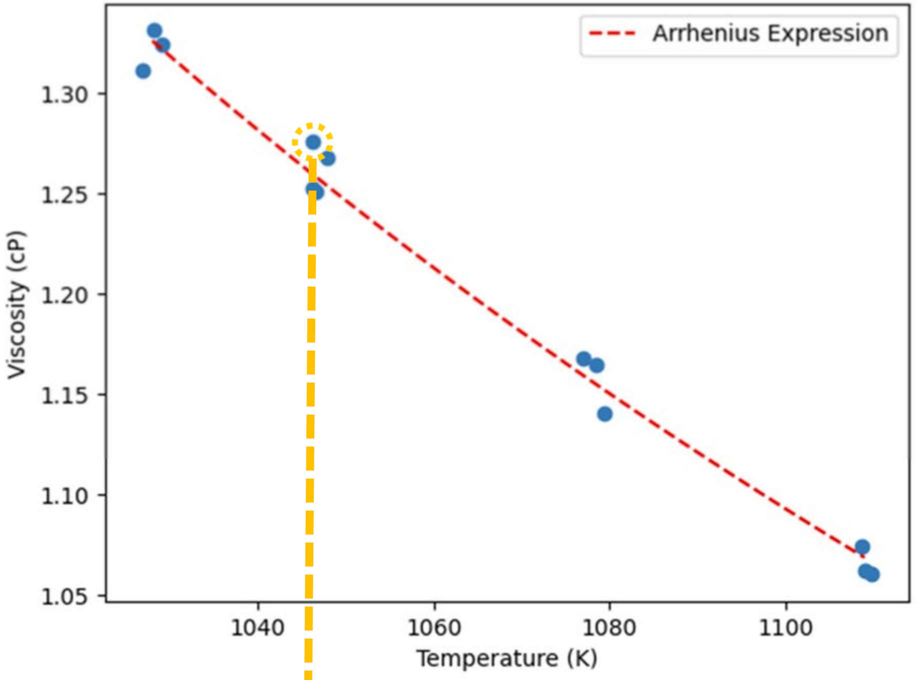




What the Data Ends up Looking Like

- After going through the complicated process of calibrating the crucible and determining K, we expect an Arrhenius relation with temperature
  - i.e. $\mu = Ae^{B/RT}$
  - This has generally been used for molten salts, assumes Newtonian fluid
- Typically 4 setpoints, 3+ datapoints at each setpoint
  - Triplicate measurements yield an understanding of measurement accuracy
- All calculations are automated in Python, we just need to supply angles, temperatures, and terminal velocities
  - True for calibration curve generation and salt measurement

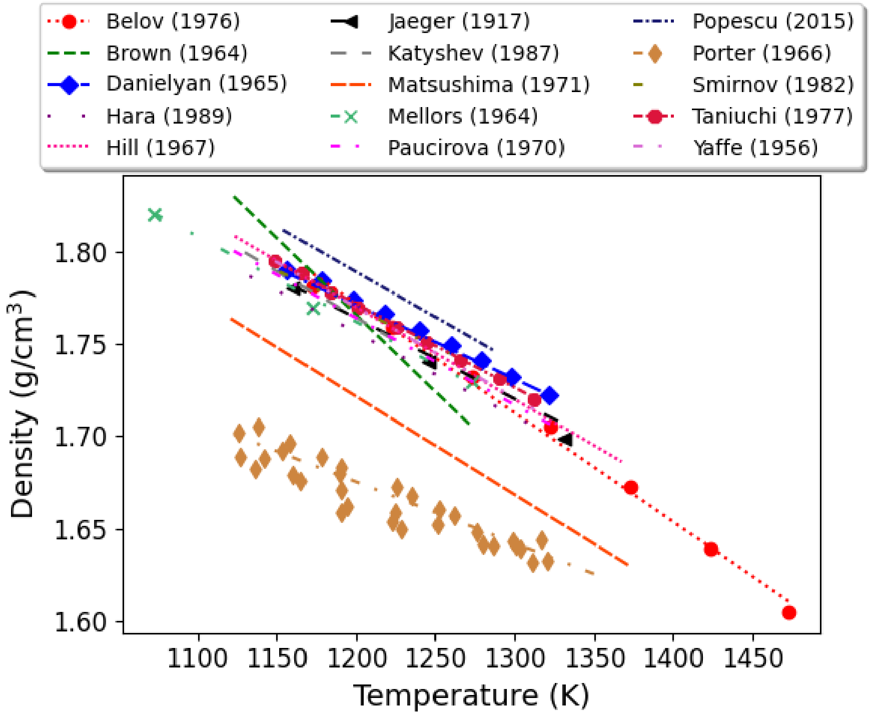
Example: NaCl-KCl (75/25)



Sources of Uncertainty

- Temperature
  - Both from thermocouples and difference in thermocouple/salt temperatures
- Salt density
  - Some salts are more well characterized than others
- Thermal expansion of ball and crucible
  - Glass thermal expansion is relatively uncertain
- Angle, distance, and time measurements subject to instrument precision limits

Example of LiF salt density spread



Fused Quartz Thermal Expansion [1]

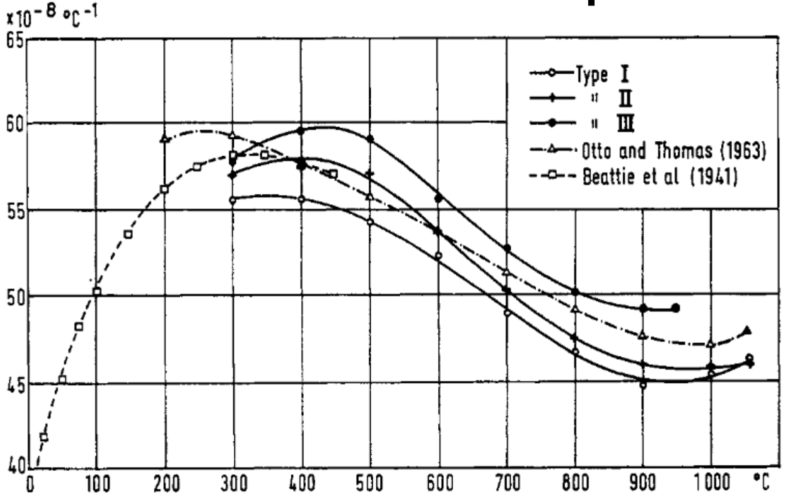


Fig. 7. Comparison of mean expansion coefficient $\bar{\alpha}_0^t$

[1] J. Oishi and T. Kimura. Thermal expansion of fused quartz. Metrologia, 5(2):50, 1969.

Uncertainty Propagation

- Use Gaussian error formalism for μ

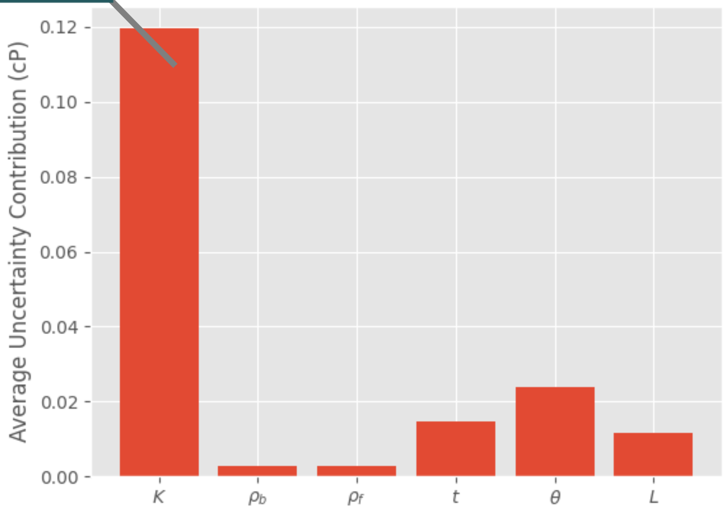
$$\sigma_\mu^2 = \left(\frac{\partial \mu}{\partial K}\sigma_K\right)^2 + \left(\frac{\partial \mu}{\partial \rho_b}\rho_b\right)^2 + \ldots$$

- For T, simply calculate $\mu(T+\sigma_T)$ and $\mu(T-\sigma_T)$ to get error bar on temperature axis

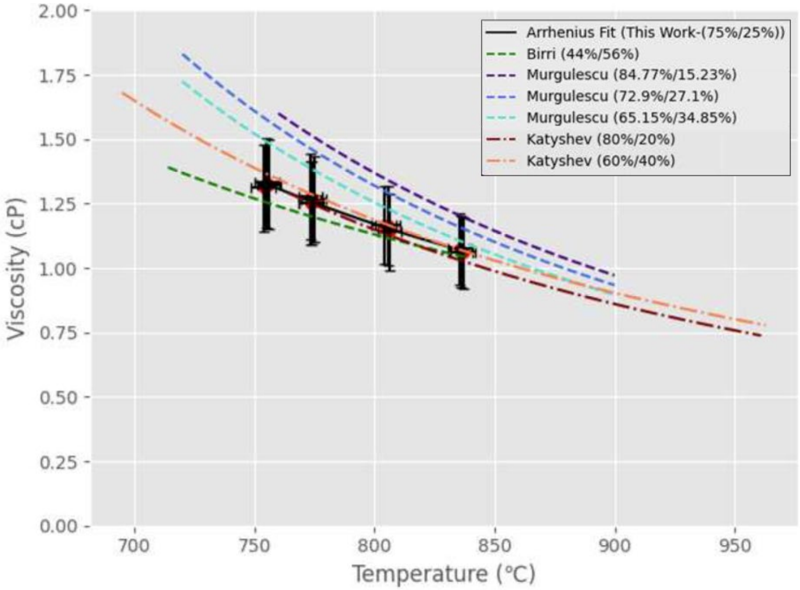
- Euclidian distance gives total uncertainty:
  - $\sigma_{tot}^2 = \sigma_\mu^2 + \sigma_T^2$

- K is the significant source of uncertainty
- This is primarily due to the sensitivity to d/D

From NaCl-KCl Measurements



These all contribute to vertical uncertainty margins



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X-ray Compatibility

- Fluoride salts and actinide salts need to be contained in steel crucibles
  - Fluorides etch glass
  - We need to eliminate risk of dispersing actinides
- We have an XRS4T X-ray source by Golden Engineering
  - 370 kV
  - Up to 9 pulses per second
- XRD 3025 Detector Plate by Varex Imaging
  - 3008 x 2512 pixel matrix (100 μm pixel pitch)
- Alkali halides have good x-ray transparency, actinides have higher attenuation leading to darker images
- These devices allow for rapid enough images collection for terminal velocity measurements

XRS4T

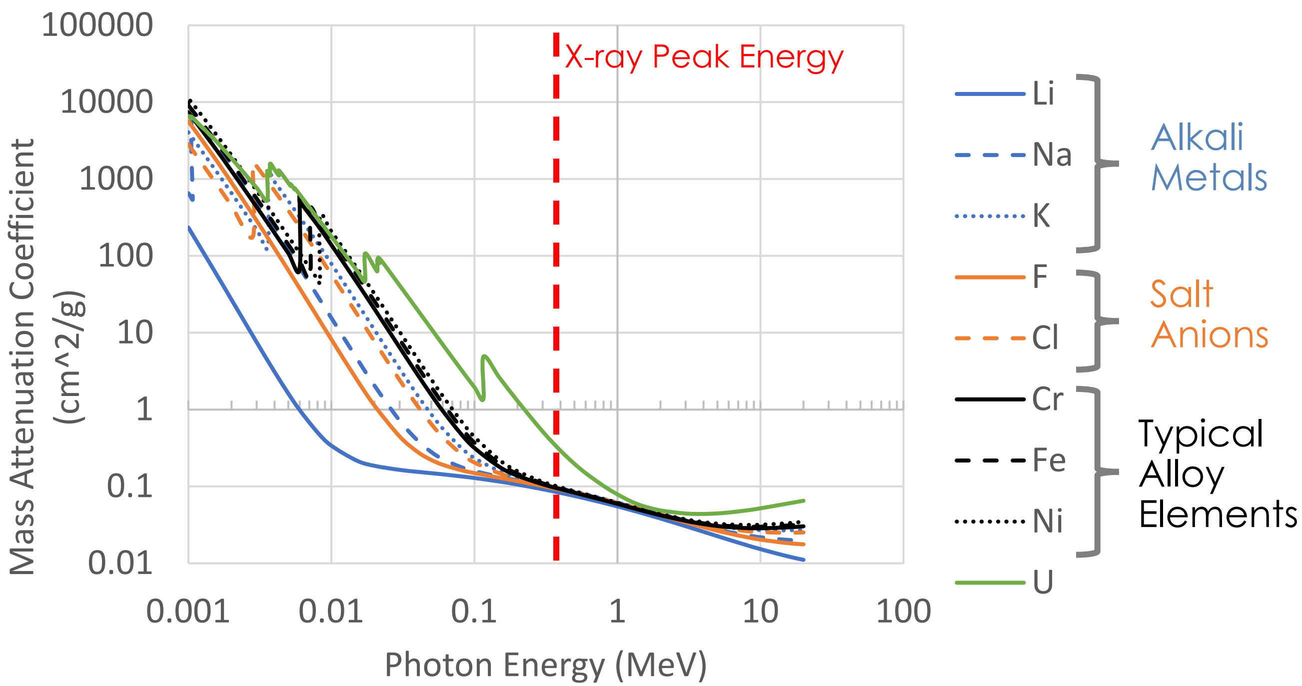
https://www.goldenengineering.com/products/xrs4/

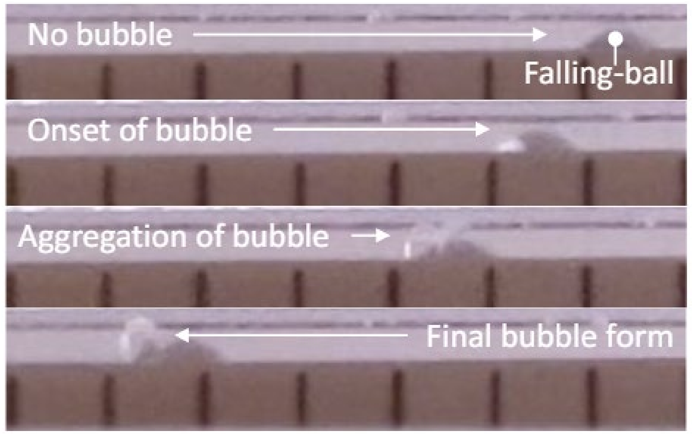
XRD 3025

https://www.x-innovations.co.uk/wp-content/uploads/2019/05/XRD-3025.pdf

X-ray Advantages and Disadvantages

- Advantages
  - Allows for measurement of a wider array of salts
  - Easier path for image processing automation with built in software
  - No real risk of crucible breaking
  - Thermal expansion matching→ BIG uncertainty reduction
- Disadvantages
  - Crucibles are challenging to manufacture and time consuming
  - May be harder to see bubbles (salt dependent)
  - Some salts may make seeing the ball a challenge





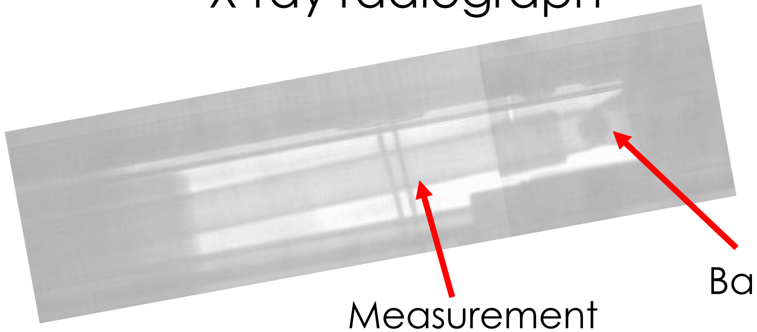
[1]

[1] ORNL/TM-2020/1633

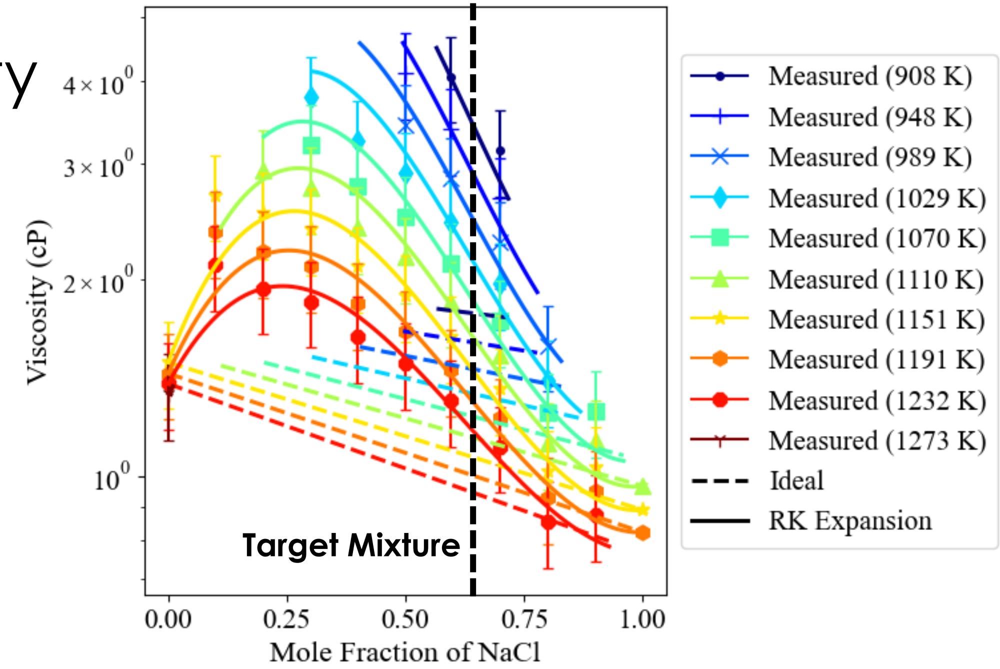
Plans to Measure NaCl-UCl3

- Planning to conduct actinide salt measurements in 2024
  - These will make use of stainless steel crucibles and x-ray radiography
- The target mixture to measure first is NaCl-UCl3
  - Synthesized at INL [1] (POC: Bill Phillips)
  - Already measured thermal conductivity
- We can compare our measurements to Russian literature on actinide chloride viscosity [2]

X-ray radiograph



NaCl-UCl3 synthesized at INL [1]



[1] INL/RPT-22-66727
[2] Katyshev, Sergey Filippovich. Properties of molten mixtures of alkali metal halides, zirconium, hafnium and uranium. Ural State Technical University, 2001.

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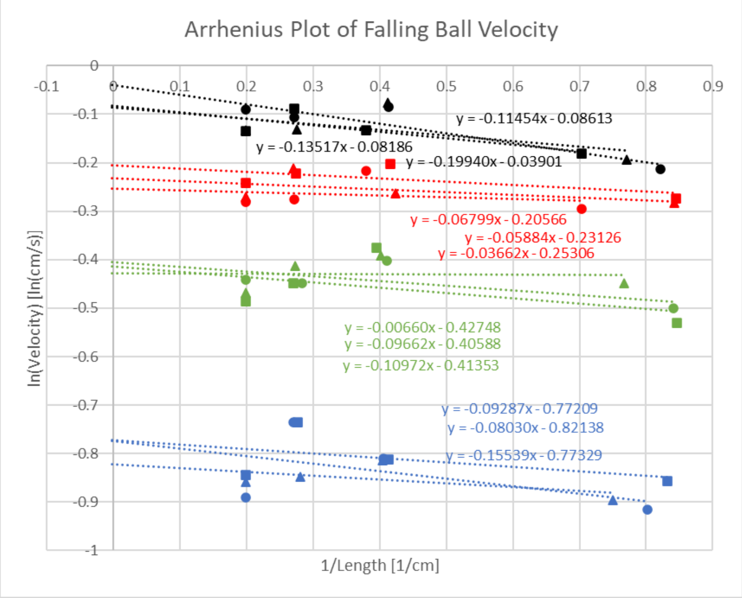
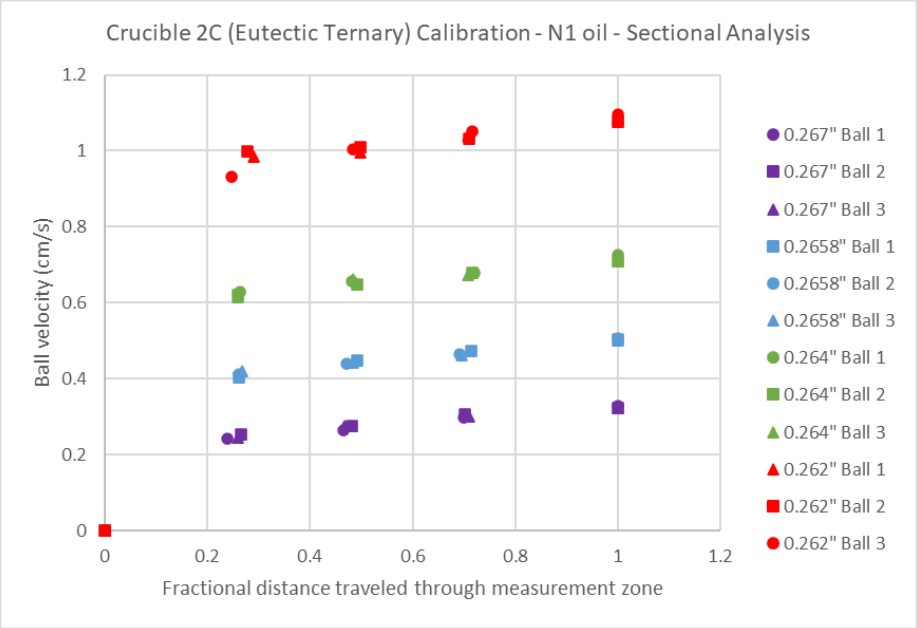
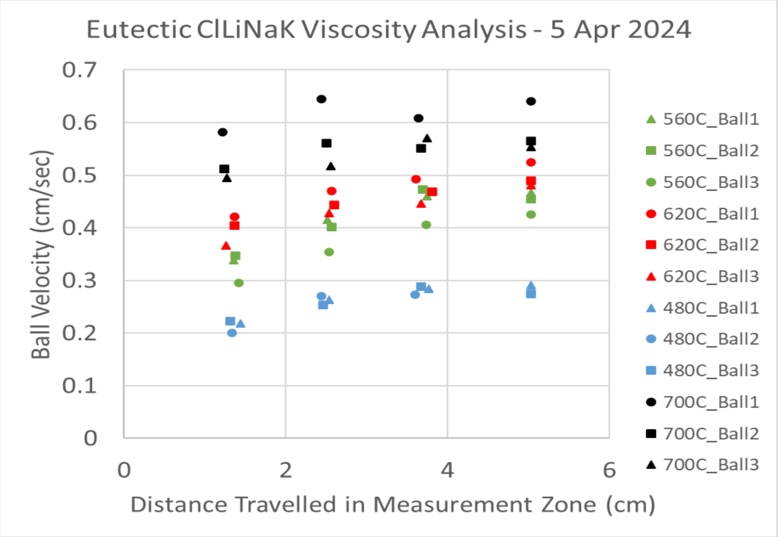
Terminal Velocity: Additional Source of Uncertainty?

- We are realizing that the ball is still speeding up in test section after more careful analysis
  - Assumptions about rapidly meeting terminal velocity may not be right
- Currently assessing if calibration data automatically captures this
- If not, we can exponentially extrapolate to get terminal velocity
- A longer distance before the measurement section could also solve this problem

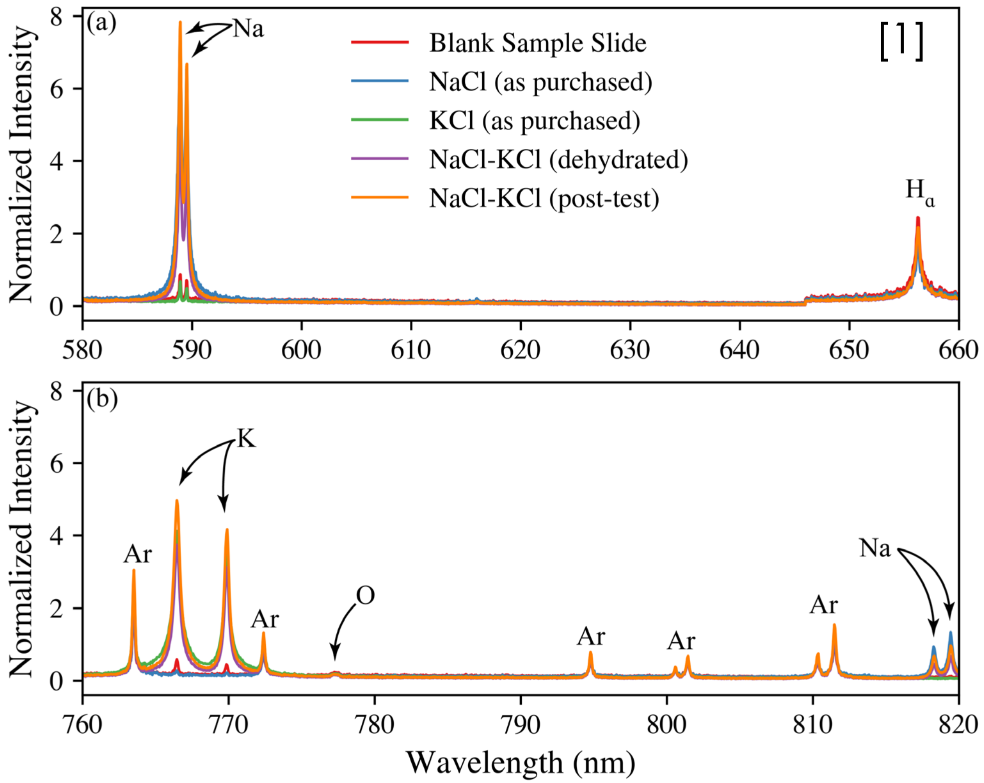


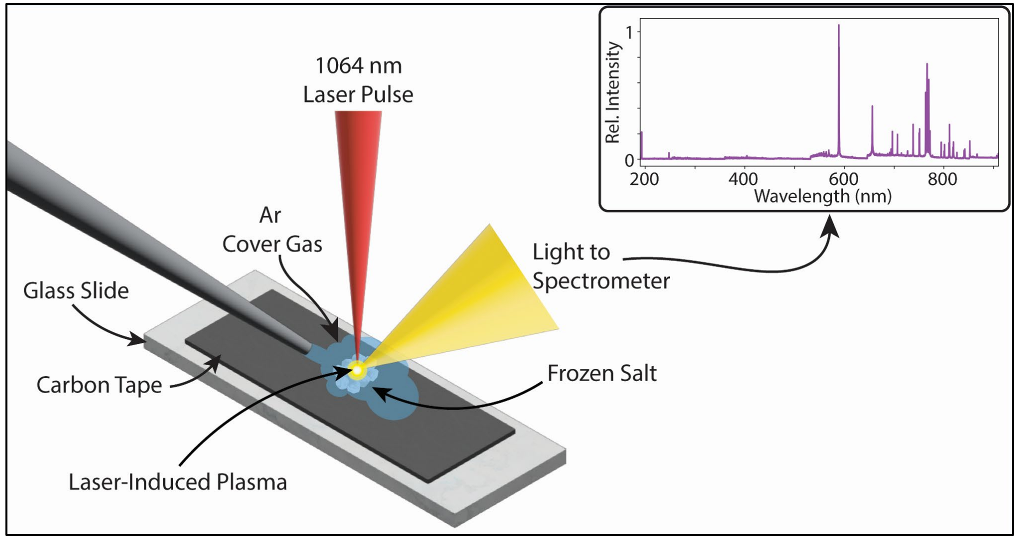




Ensuring Salt Purity

- Alkali Halides are always purchased with minimal possible trace metal basis (Sigma Aldrich)
- Lab synthesized salts assessed with ICP-OES, ICP-MS, or XRD
  - We work with synthesizers for analysis
  - Much credit to Bill Phillips (INL), Zach Huber and Bruce McNamara (PNNL), and Amanda Leong (VT)
- Pre and post test LIBS to check for O and H impurities (Hunter Andrews, ORNL)





[1] Birri et al. (2023). *TSEP*, *44*, 102029.

Summary

- Rolling ball viscometry is one method which can be used for measuring molten salt viscosity
- The working equation allows for full propagation of uncertainty
- Glass crucibles can be used which, thus far, have allowed for more rapid, inexpensive measurements
- Stainless steel crucibles can be used for salts which require this material, and they enable uncertainty reduction
- We have measured several alkali halide mixtures and a measurement of NaCl-UCl3 is upcoming

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The authors would like to acknowledge Joanna McFarlane and Kevin Robb for their molten salt expertise which has better informed decisions made in this work, Hunter Andrews for his collaboration on LIBS measurements of salt samples, and Callie Goetz on automation of the crucible rotation system.