OVERVIEW OF THE MSR CAMPAIGN: EXPERIMENTAL DETERMINATION OF MOLTEN SALT PROPERTIES

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RELIABLE PROPERTY DATA REQUIRED FOR MSR DESIGN, LICENSING, AND OPERATION

- Predicting molten salt behavior during normal and transient conditions requires knowledge of property values over a range of temperatures and salt compositions, including contaminants and accumulating fission products

- Licensing a reactor requires quality data collected using standardized methods with known precision and accuracy

- Available data are not sufficient or of suitable quality as most developers are considering salt mixtures other than $LiF\text{-}BeF_2\text{-}UF_4$ for which reliable property values must be measured

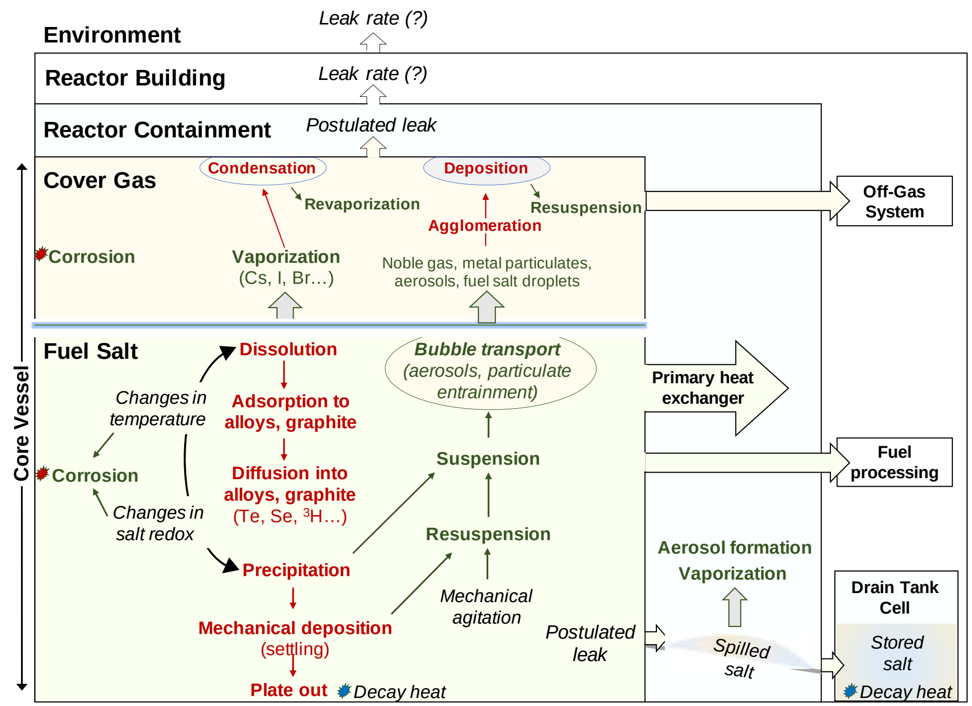
OBJECTIVES OF THE MSR CAMPAIGN MOLTEN SALT PROPERTY MEASUREMENTS

Generate high quality measurements of property values of fuel-bearing molten salts to assist developers in designing, licensing and operating MSRs

1. Identify quality-affecting aspects of property measurement techniques, sensitivities, and measurement controls to achieve NQA-1 data quality
   - Assess the precision of measurements
   - Distinguish effects of uncertainty in salt composition and in the measurement
2. Determine property values of reference salts that can be used to compare methods and determine within-lab repeatability, lab-to-lab reproducibility, and bias in measurements
   - Develop consensus standard practices issued through ASTM-International
   - Identify and generate database for an approved reference material salt (ARM-salt)
   - Round Robin effort is supporting these tasks
3. Measure fuel-bearing systems using consensus standard practices controlled at the highest quality level
   - This data will be populated into the Molten Salt Thermal Properties Database (MSTDB) for developers to access

REQUIRED THERMOCHEMICAL AND THERMOPHYSICAL PROPERTIES

- Liquidus/solidus temperatures
- Salt boiling temperatures
- Solubility of FPs and impurities
- Heat capacities
- Density
- Volume expansion coefficients
- Surface tension
- Viscosity
- Thermal conductivity/diffusivity
- Emissivity



Radionuclide transport and retention processes considered in source term models for generic MSR

SALTS BEING MEASURED

- Gaps in the MSTDB are being targeted by measurements of uranium and plutonium bearing fuel salts
- Reference Salts – FLiNaK, FLiBe, and NaCl-KCl
  – Confirming composition, impurity content and the impact of both on property values
  – Perfecting measurement methods
  – Quantifying data quality
- Round Robin – National labs and Universities are measuring aliquots of the same batch of FLiNaK, and NaCl-KCl to quantify reproducibility of several methods

NATIONAL LABORATORY PARTICIPANTS

Property	Argonne	Oak Ridge	Los Alamos	Idaho
Phase Transition Temperatures	**DSC**	DSC	DSC	DSC
Heat Capacity	**DSC**	DSC	DSC	DSC
Solubility of FPs	Saturation Method	Press. Drop Method		
Vapor Pressure	Transpiration	Transpiration		
Density / Volume Expansion Coefficients	**Hydrostatic Method**	Hydrostatic Method & X-ray dilatometer	Neutron Radiography & Push Rod Dilatometry	Pycnometer & Hydrostatic Method
Viscosity	**Rotating Spindle**	**X-ray Falling Ball**	Dynamic Neutron Radiography	Rheometer
Thermal Conductivity/ Diffusivity	Laser Flash Analysis	Variable Gap	Laser Flash Analysis	Laser Flash Analysis
Emissivity	Under Development			
Surface Tension	**Hydrostatic Method**			Contact Angle

QUALITY OF PROPERTY DATA

- Affected by
  - Salt composition
  - Environmental factors
  - Instrumental uncertainties
  - Analytical limitations
  - Calculation method

- Data quality assured by
  - Reagent purity and controlled batching
  - Controlled & monitored glovebox atmosphere
  - Reliable measurement procedures and device calibrations
  - Reliable reference and standard materials
  - Fundamental understanding

APPROACH TO QUALITY

- Salt composition
  - Use batched compositions to determine composition effects rather than measured compositions when possible
- Environmental factors
  - Require low and constant oxygen and humidity levels during data collection
  - Identify and quantify instrumental artifacts and uncertainties
  - Routine calibration checks of devices and instruments
  - Routine checks of measured responses of reference materials
  - Control chart calibrations and checks to detect long-term instability
- Analytical limitations
  - Replicate samples and replicate analyses
  - Reference materials
- Calculation method
  - Identify quality-affecting parameter values subjected to calibration checks
  - Use reference materials and standards for each parameter used for property determination

DENSITOMETER DATA QUALITY

- Calculate molten salt density (ρ) from measured mass difference of Ni bob in the gas space and immersed in molten salt (Δm)

$$\rho = \frac{\Delta m + \frac{\pi D \sigma}{g}}{V_0[1+\alpha T]^3}$$

D = diameter of hanging wire

σ = surface tension of salt

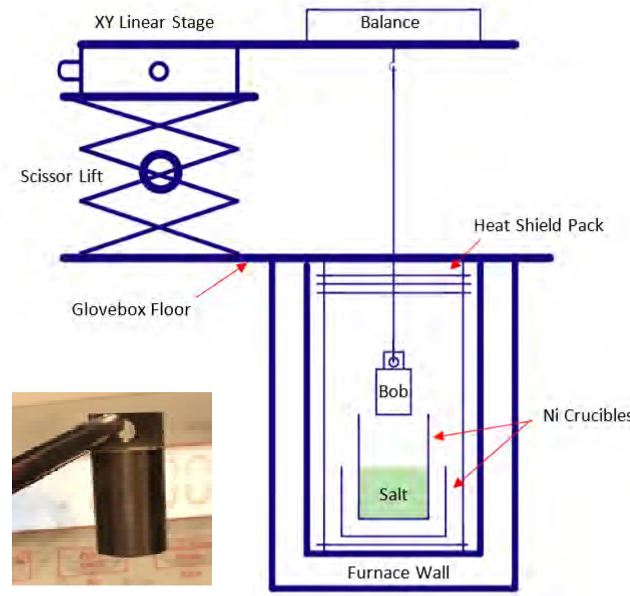
g = gravitational acceleration

V_0 = volume of bob

α = thermal expansion of bob

T = temperature

- Balance for mass
- Calipers for wire diameter
- Calibrated thermocouple for molten salt temperature
- Reference values for π, *g*, thermal expansion and density of Ni
- Determine *σ* from densities measured with different bobs



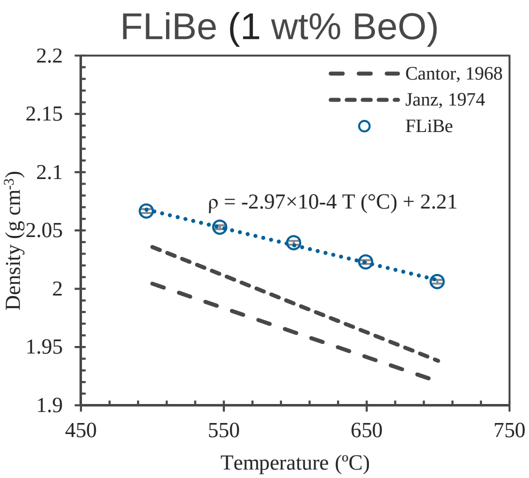
DENSITY MEASUREMENT BY HYDROSTATIC METHOD

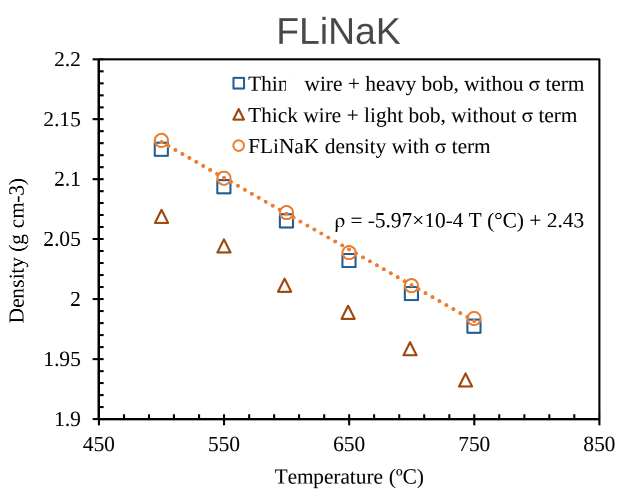
Measured density values affected by:

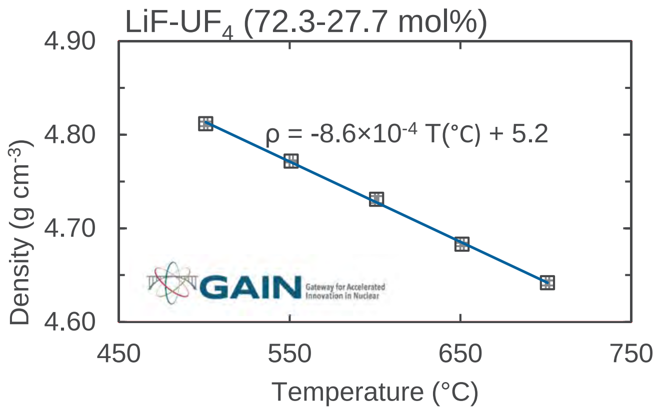
- Surface tension
  - Surface tension (σ) at each temperature is calculated from density measurements made using two bobs of different mass and volume with support wires of different diameter.
  - Often not included in literature
- Preferential volatilization
  - Causes change in salt composition
  - Salt condensing on the suspension wire affects measurement
- Impurities (BeO)

$$\rho = \frac{\Delta m + \frac{\pi D \sigma}{g}}{V_0[1+\alpha T]^3}$$

surface tension term



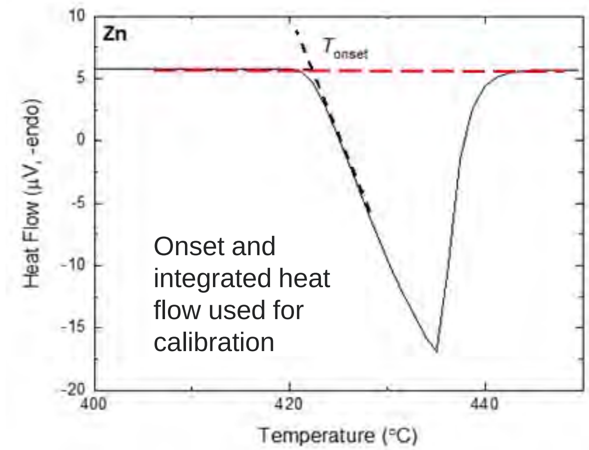




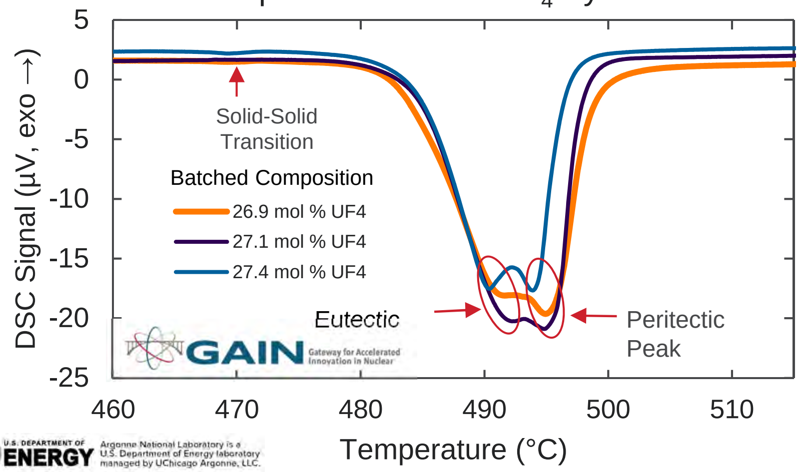
DIFFERENTIAL SCANNING CALORIMETRY (DSC)

- Ramp temperature at constant rate and measure difference in heat flow through salt sample and empty crucible
- Temperature and heat flow read out are calibrated with metal standards
- Significant super cooling can occur, so only use heating data
- Three samples analyzed to check composition homogeneity
- Two analyses run with each sample to check system stability

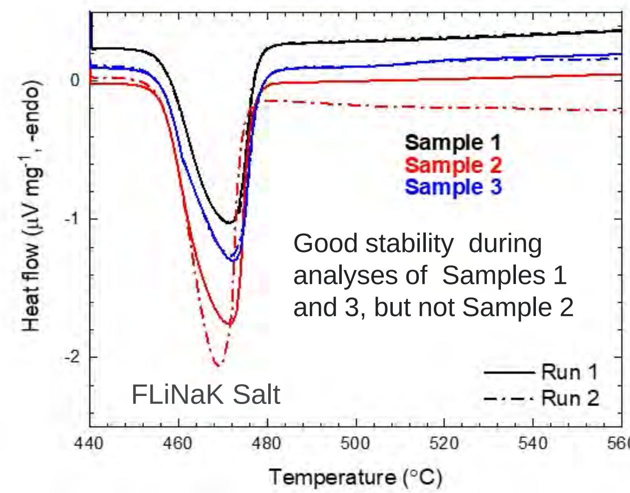
Zn Reference Heat Flow



DSC Response of the LiF-UF_4 System



Salt mixtures can be batched more accurately than they can be analyzed:
10% Uncertainty
→ 2.7 mol%



HEAT CAPACITY DATA QUALITY

Using reference salts to optimize method and minimize uncertainty.

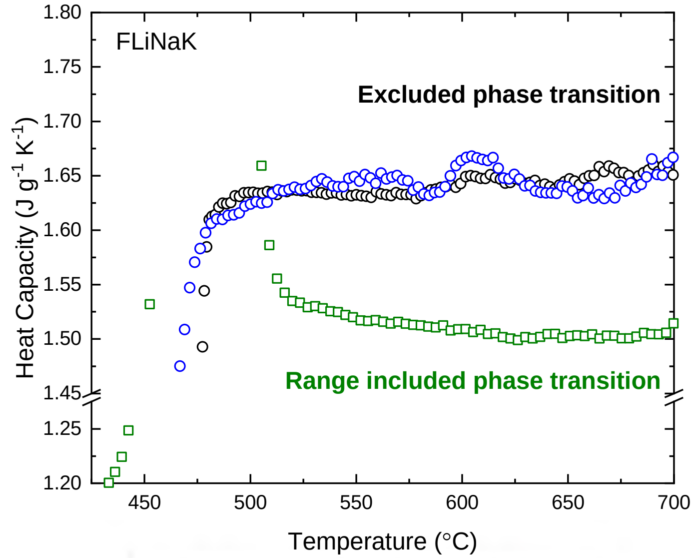
Ratio Method:

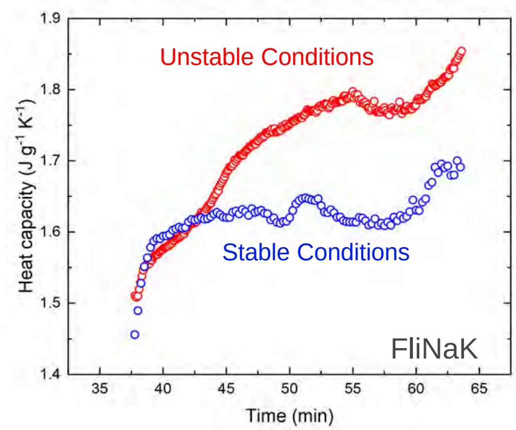
$$C_p^s = \cancelto{1}{\frac{m_{st}}{m_s}} \frac{\Delta\varphi_s}{\Delta\varphi_{st}} C_p^{st} + \cancelto{0}{\frac{m_{cr}^{st} - m_{cr}^{s}}{m_s}} C_p^{cr}$$

st = sapphire reference with known C_p; *s* = salt; *cr* = gold crucible

Measured C_p is affected by:

- Differences between masses of sample and sapphire
- Differences between masses of crucibles
- Melt transition occurring within the temperature range scanned
- Stability of conditions in the DSC

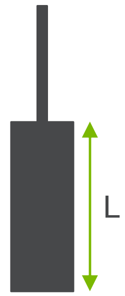




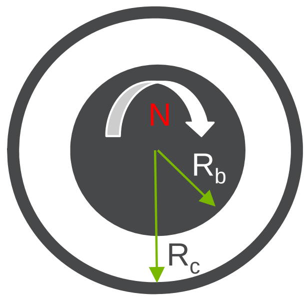
VISCOSITY BY ROTATING CYLINDER METHOD

- A hanging spindle is rotated at a speed N and the torque M required to maintain rotation is measured
- Method is applicable for laminar fully developed Newtonian Couette flow
- Dimensions are measured using calibrated devices
- Measurements with a reference fluid confirm proper operation

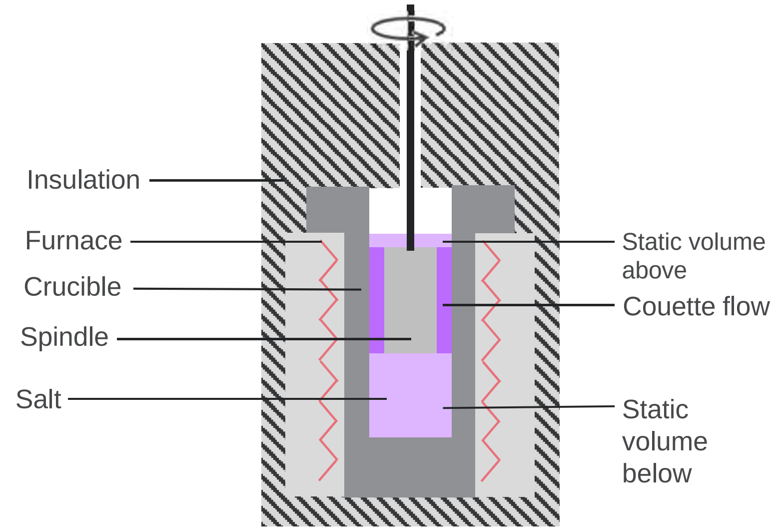
$$Viscosity = \frac{M\left(R_c^2 - R_b^2\right)}{8\pi^2 R_c^2 R_b^2 L\left(\frac{N}{60}\right)}$$



Side View of Spindle



Top View of Spindle in Crucible

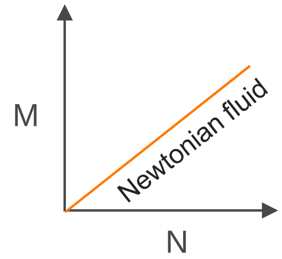


VISCOSITY DATA QUALITY

Silicone reference fluid measurements

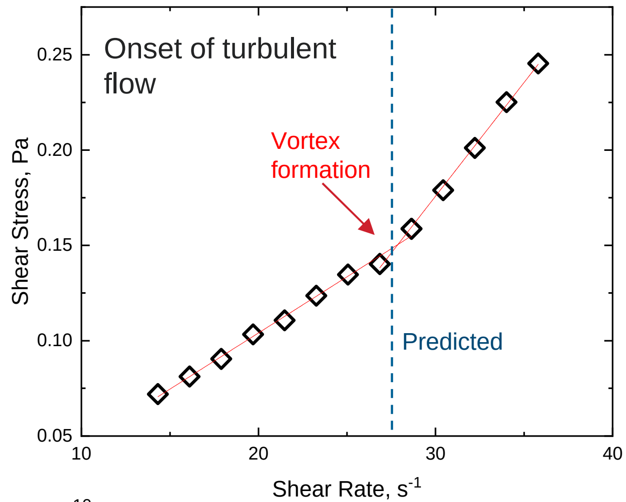
Operation of the viscometer must ensure laminar fully developed Newtonian flow

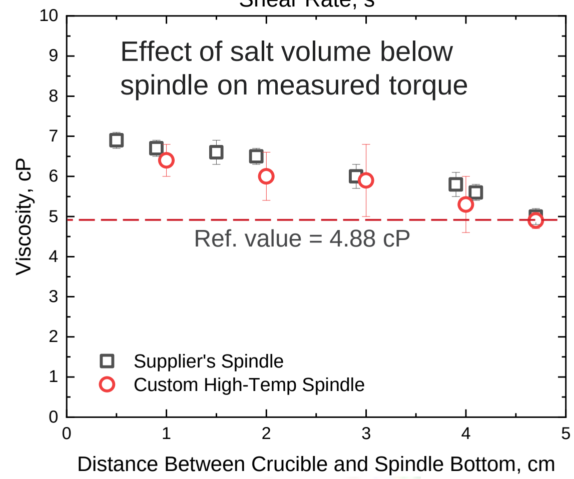
- Torque measurements are collected at multiple speeds to confirm Newtonian (linear) fluid flow



Calculated viscosity is affected by:

- Volume of fluid below and above spindle
- Turbulence
- Impurities (e.g., undissolved solids)





DYNAMIC X-RAY VISCOSITY MEASUREMENT

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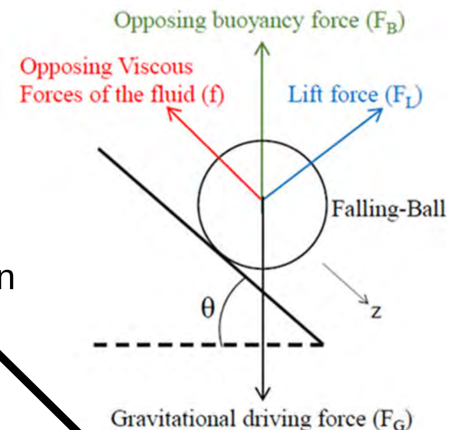
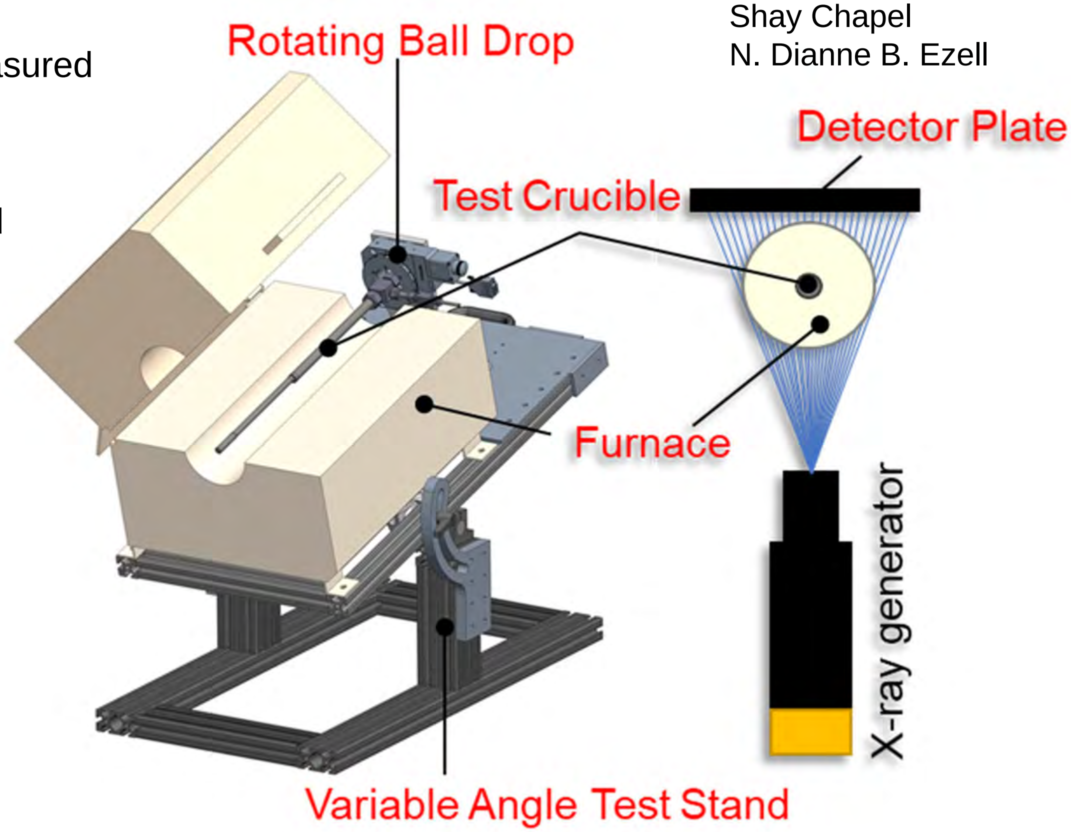
- Ball is dropped into a fluid filled tube/crucible
- Terminal velocity, t, of falling/rolling ball is measured with x-ray radiography
- Viscosity, μ, can be determined with known densities (ρ_b and ρ_f) and measured fall speed



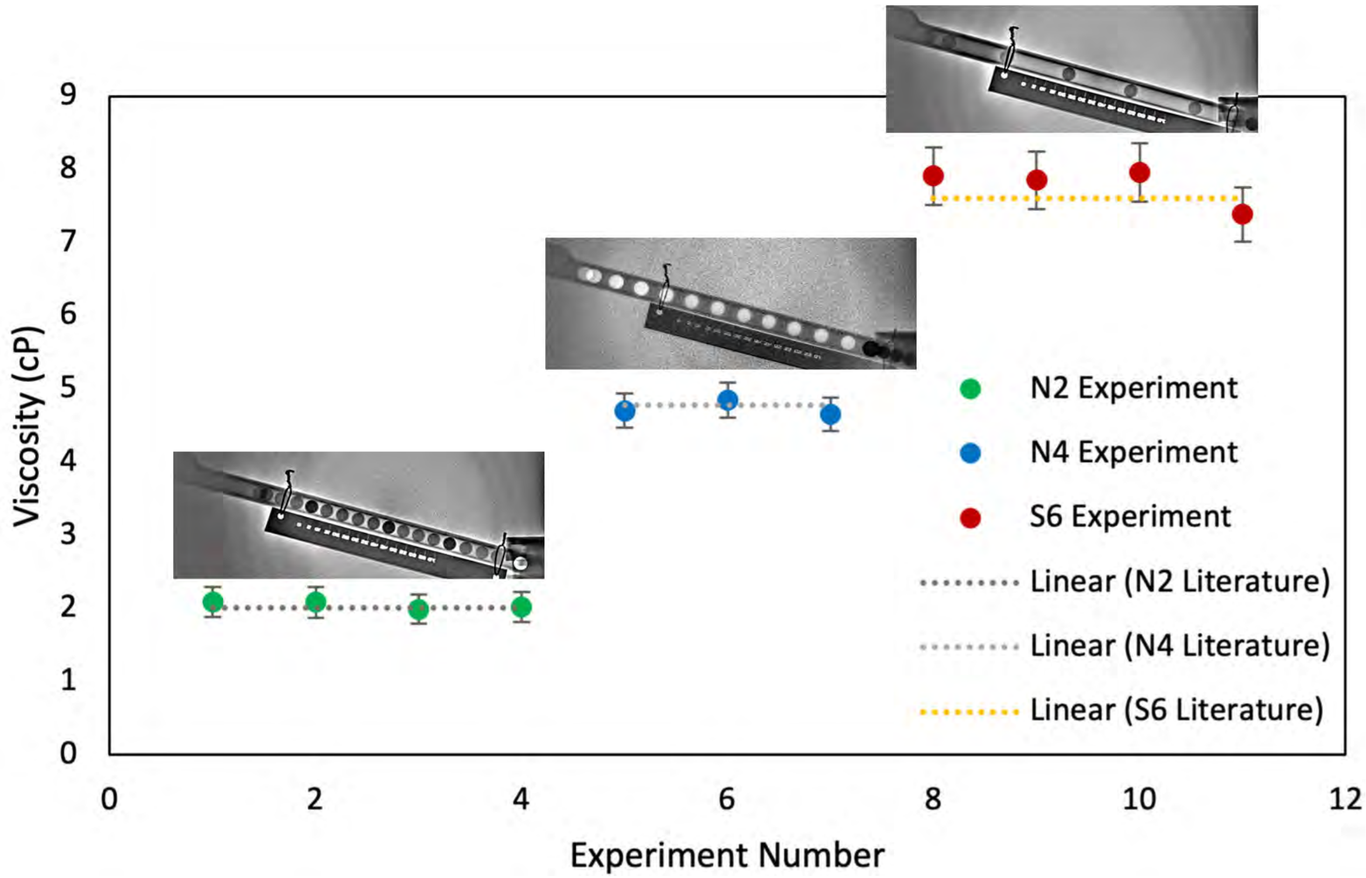
calibration factor

$$\boxed{\mu = K(\rho_b - \rho_f)t * g * \sin(\theta)}$$



VISCOSITY RESULTS ON NIST CALIBRATION STANDARDS

- Each crucible/ball combination is calibrated with NIST traceable standards to get unique calibration factors "K"
- K is used to correct for factors that may influence the measurement, but are difficult to correct for individually:
    - Crucible roughness
    - Straightness
    - Ball roundness
- Replicate measurements demonstrate repeatability of technique



SUMMARY

MSR Campaign Molten Salt Property Measurements

- Generating high quality measurements of property values of fuel-bearing molten salts to assist developers in designing, licensing and operating MSRs
- Identifying quality-affecting aspects of property measurement techniques, sensitivities, and measurement controls to achieve NQA-1 data quality
- Determining property values of reference salts that can be used to compare methods and determine within-lab repeatability, lab-to-lab reproducibility, and bias in measurements
- Developing consensus standard practices issued through ASTM-International

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- Portions of this work were conducted by Oak Ridge National Laboratory which is managed by UT-Battelle LLC for the US Department of Energy

GAIN Gateway for Accelerated Innovation in Nuclear

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