Molten Salt Reactor
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Measurement Uncertainty and the Effect of Impurities on Molten Salt Properties

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FY25 Goals and Activities

Goal: Provide developers with high-quality data needed for use in design, licensing and deployment of MSRs

Evaluating and ensuring data quality

- Provide quality rankings of existing data in MSTDB-TP–unary chlorides[1]
- Support the development of draft standard property measurement methods for molten salts
  - In-depth analysis of uncertainty in measurement methods
  - Draft and submit a standard test method for rotational viscometry

Generating high-quality data

- Determine the impact of environmental contaminants on molten salt thermophysical properties
- Construct a custom apparatus for measuring vapor pressure of molten salts

[1] M.A. Rose, Quality Ranking of Unary Chloride Salt Property Data Included in MSTDB-TP. ANL/CFCT-24/34. December 2024.

Effects of Fission Products and Instrumental Error

Changes in fuel salt composition over time are expected due to:

- Fission reactions
- Periodic refueling
- Chemical adjustments for redox control
- Ingression of contaminants

[1] M.A. Rose, L.D. Gardner and T. Lichtenstein. Property Measurements of NaCl-UCl3 and LiF-NaF-KF Molten Salts Doped with Surrogate Fission Products. ANL/CFCT-23/23. September 2023

[2] L.D Gardner, K.A. Chamberlain and M.A. Rose. Property Measurements of LiF-NaF-KF Molten Salts Doped with Surrogate Fission Products. ANL/CFCT-24/23. September 2024.

FY23[1] and FY24[2] work at Argonne focused on the impact of fission product impurities on properties of molten FLiNaK

FY25 work at Argonne is focused on quantifying the uncertainties in derived property values based on principles outlined in the Guide to the Expression of Uncertainty in Measurement

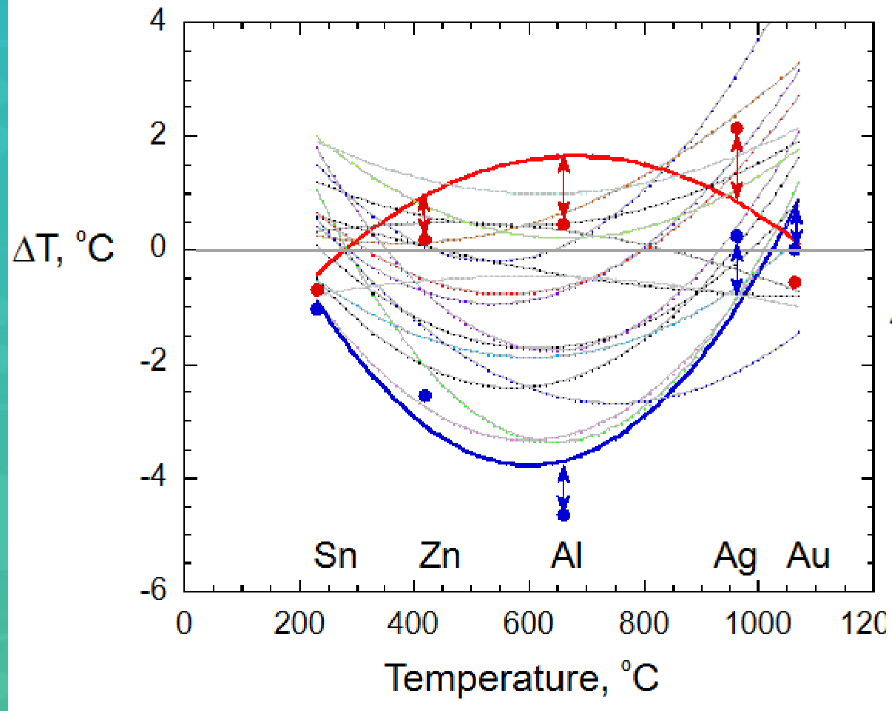
- Thermal transitions by differential scanning calorimetry (DSC)
- Density by the Archimedes method
- Thermal diffusivity by laser flash analysis (LFA)
- Viscosity by rotational cylinder method

The effects of composition on the measured values must be distinguished from instrumental and environmental effects to accurately quantify the salt properties

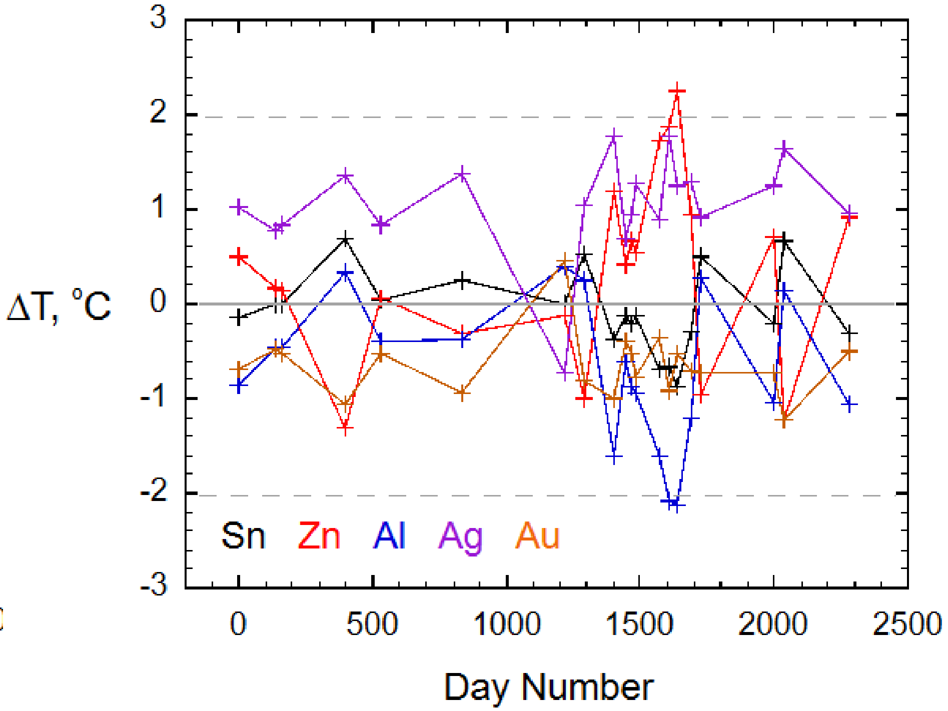
DSC Temperature Calibration

- DSC temperature calibrations were performed by using five reference metals (Sn, Zn, Al, Ag, and Au) to measure instrumental error under glovebox conditions
- Differences between measured and known melting temperatures of each reference material were used to generate a quadratic regression curve
  - Regression curve used to correct DSC responses during salt measurements
- Calibration data were tracked over a six-year period to detect instrumental drift, degradation of reference metals, and changes in environmental conditions

Regression curves for differences between measured onset and nominal melting temperatures of five reference materials for 20 sets of measurements



Residuals for known and fit temperatures for each reference material in calibrations spanning six years



Both the precision and accuracy of calibration curves are within 2 °C over this time span and temperature range

- Accuracy based on the pooled results for five reference metals
- Precision based on 100 calibrations

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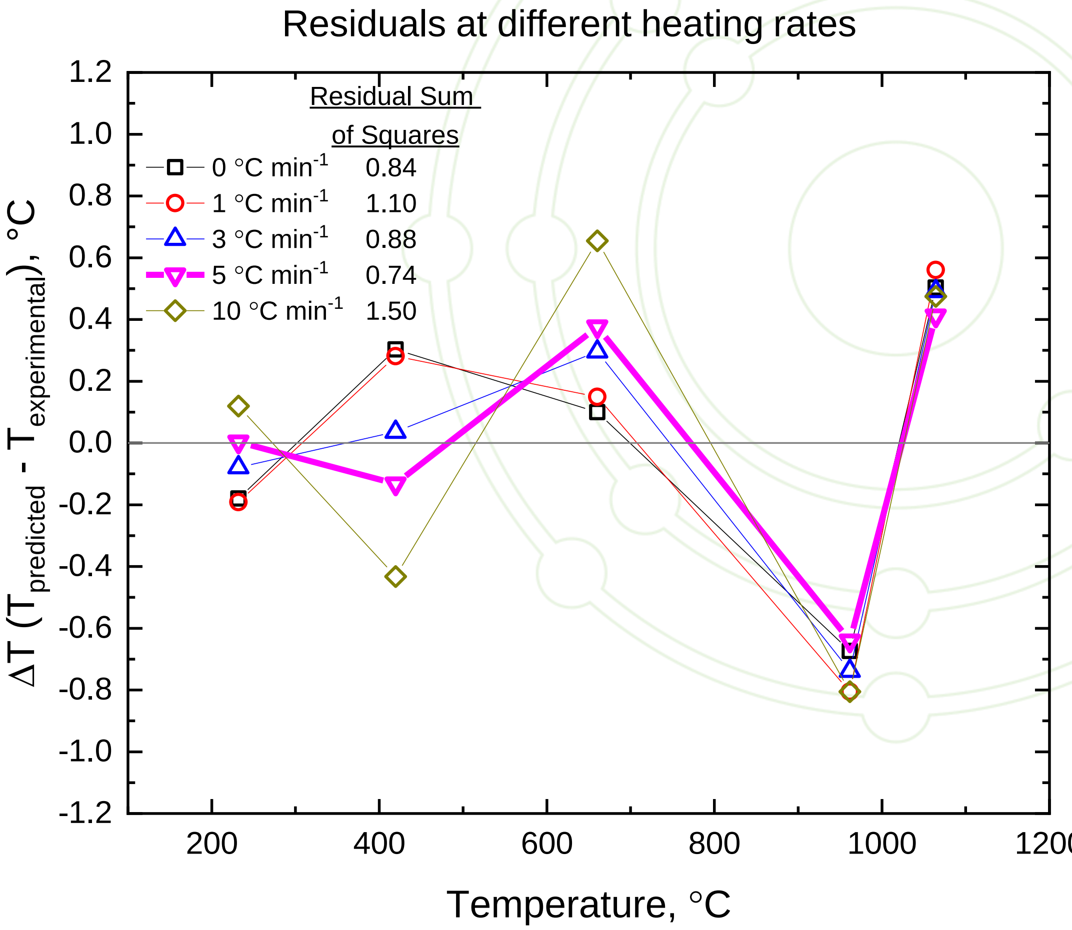
Effect of DSC Heating Rate

- Use of fast DSC heating rates causes thermal lag between the sample and the thermocouple.
- Use of slow heating rates lengthens the run time and increases effects of environmental and instrumental instabilities
- Performing temperature calibrations and salt measurements at a heating rate of 5 °C min^{-1} provides an appropriate compromise to decrease thermal lag and maintain system stability



Effect of heating rate was investigated by recording DSC responses of five reference metals at heating rates of 1, 3, 5, and 10 °C min^{-1} and extrapolating to 0 °C min^{-1}.

- The residuals of the parabolic fits over the temperature range used as calibration curves show the accuracy does not improve by decreasing the heating rate below 5 °C min^{-1}
- Differences between heating rates below 5 °C min^{-1} are within the measurement uncertainty

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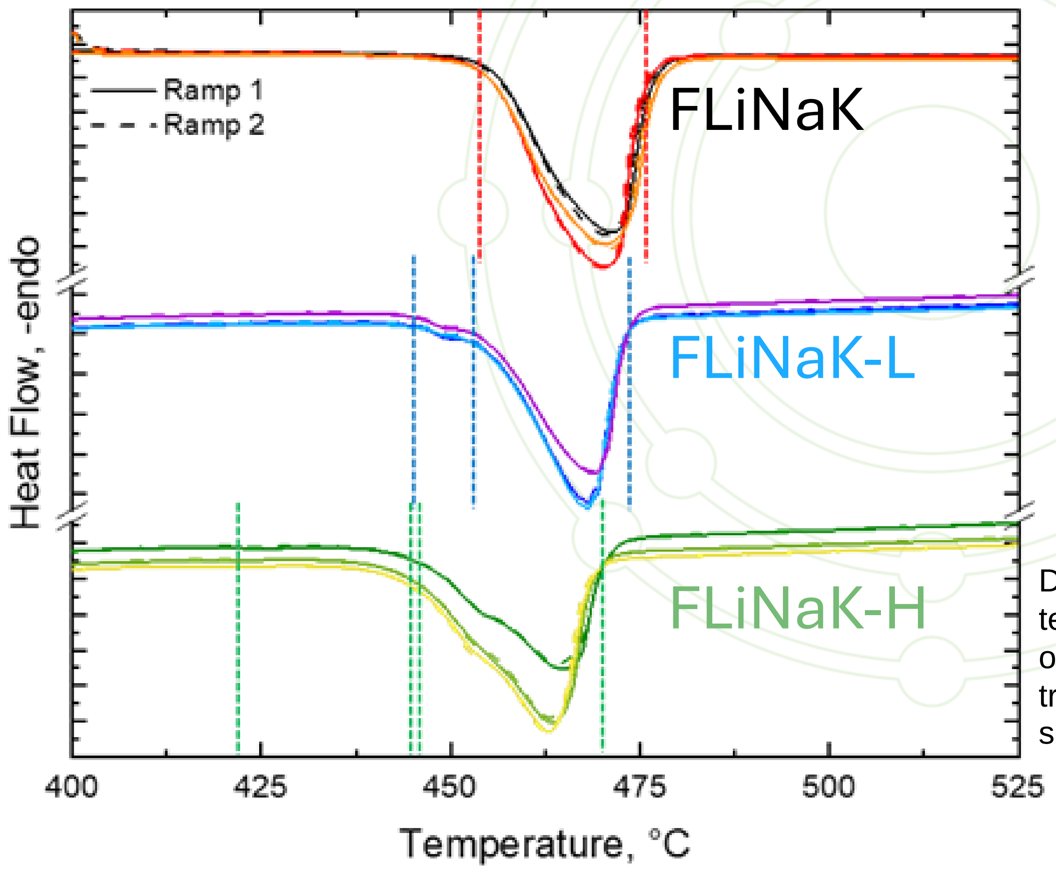
Thermal Analyses

- Thermal transitions of FLiNaK, FLiNaK-L, and FLiNaK-H were measured by using DSC
- Three samples of each salt mixture were measured
- Three heating cycles performed for each sample:
  - One 20 °C min^{-1} pre-melting ramp
  - Two 5 °C min^{-1} measurement ramps
- Consistency of transition temperatures measured in duplicate ramps of the same sample indicates measurement conditions were stable
- Consistency of the transition temperatures measured with different samples indicates compositional uniformity of salt mixtures



Decrease in melting temperatures and presence of low-temperature transitions due to addition of surrogate fission products

Lower onset of melting and liquidus point temperatures were measured for both low-burnup FLiNaK and high-burnup FLiNaK compared to those of pure FLiNaK, for which the onset of melting and liquidus point temperatures were 455 °C and 476 °C, respectively

- A small peak detected with an onset at 445 °C in analyses with both doped FLiNaK salts
- Additional pre-peak with an onset near 419 °C is observed in high-burnup FLiNaK measurements

Differences in melting onset temperatures are greater than the measurement uncertainty

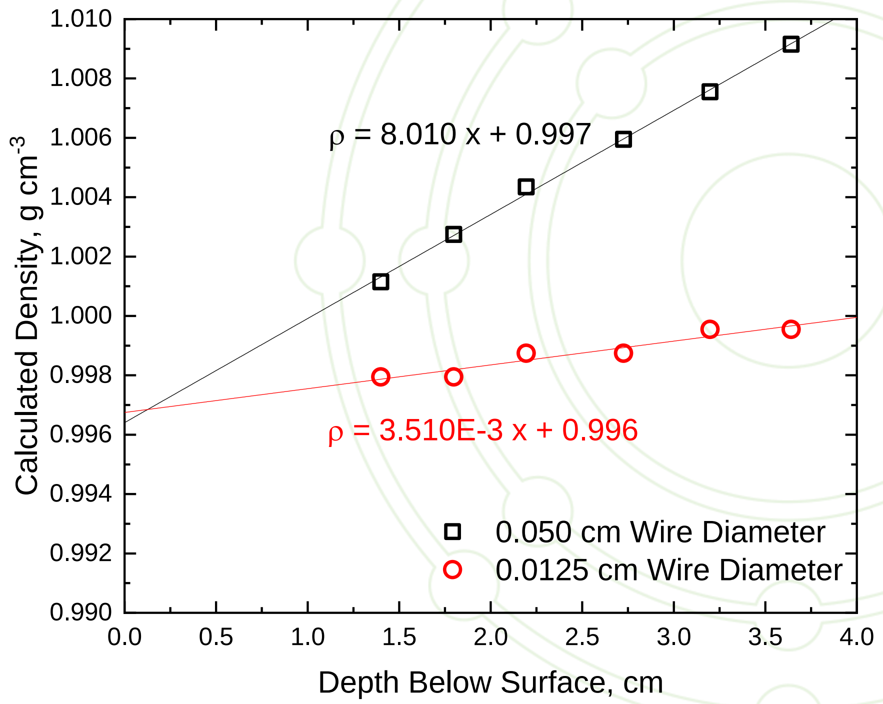
Density

Uncertainties in Archimedes density measurements are primarily due to:

- Balance resolution
- Variance in multiple measurements
- Thermocouple uncertainty
- Furnace controller resolution
- Uncertainties in properties of bob material (ρ,α)

Relative uncertainties at each temperature are < 2%

[1]L.D Gardner, K.A. Chamberlain and M.A. Rose. Property Measurements of LiF-NaF-KF Molten Salts Doped with Surrogate Fission Products. ANL/CFCT-24/23. September 2024.



Density of water measured with two different wires and the same bob at different immersion depths

Immersion of wire during measurement affects response of the balance

Effect of volume of immersed wire is greater than the effect of the surface tension term

The use of a thin wire is recommended for Archimedes density measurements

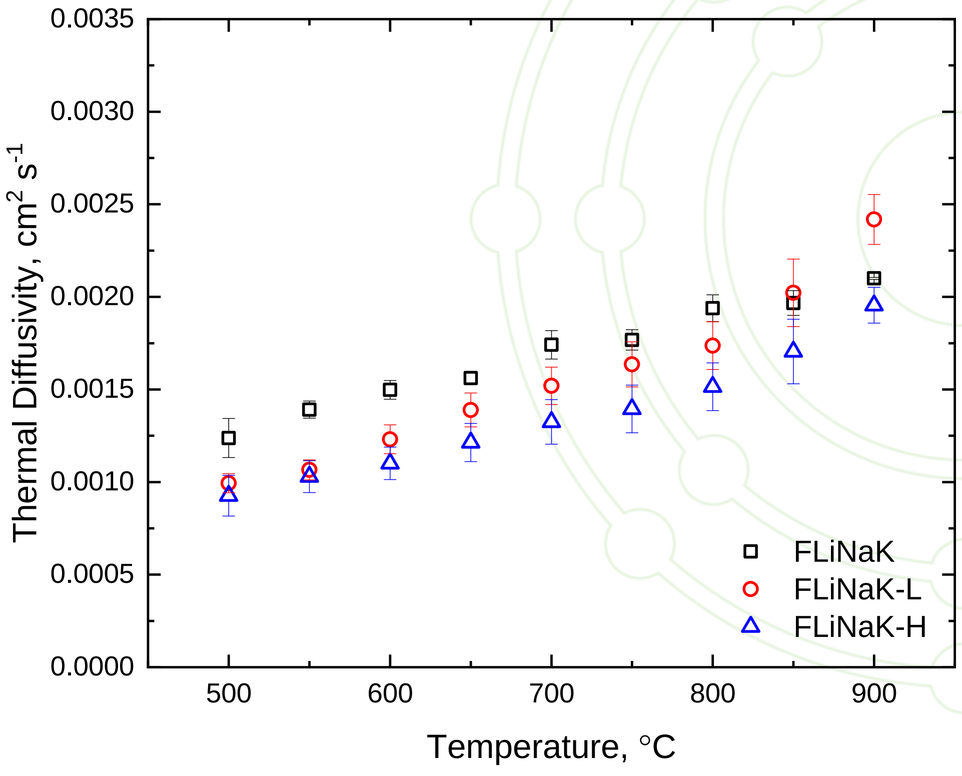
- Decreases the effect of immersing the wire
- Minimizes surface tension effects
- Decreases the likelihood of warping or contact between the wire and the crucible wall or furnace surfaces.

Thermal Diffusivity

Errors in thermal diffusivity measurements by laser flash analysis (LFA) are primarily due to:

- LFA timer resolution
- Variance in multiple measurements
  - Random error
  - Distortion in salt layer thickness
- Thermocouple uncertainty

Relative uncertainties at each temperature are on the order of 10%



Average thermal diffusivities and expanded uncertainties for FLiNaK, FLiNaK-L, and FLiNaK-H[1]

Graphite cells used to contain salt during measurements are designed to maintain a known uniform thickness of salt

Periodic instrument response checks with a certified reference material provide confidence that various instrument effects are controlled.

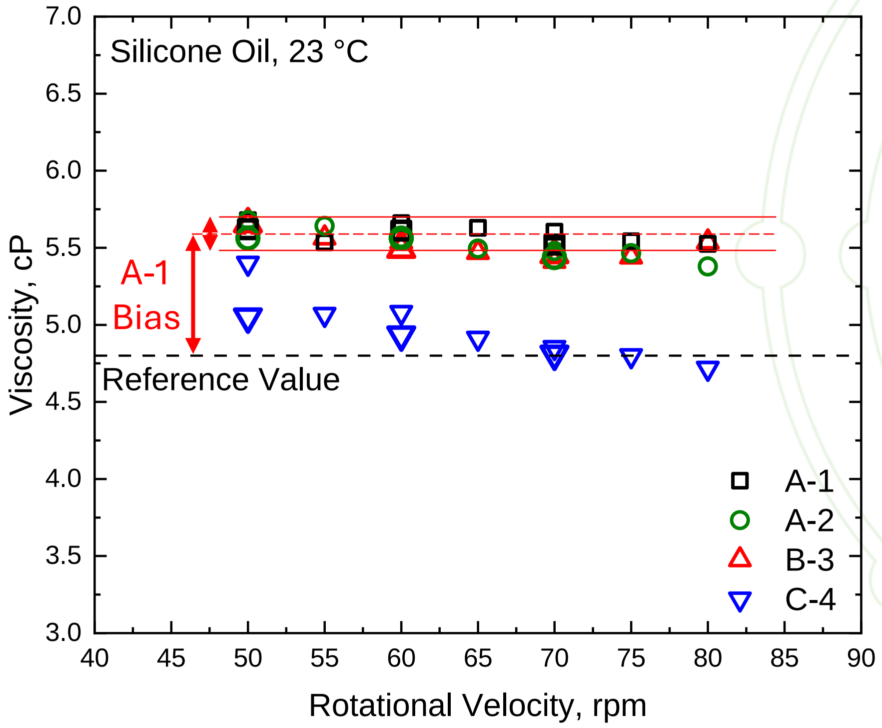
Differences in the responses of salts with and without dopants are greater than the measurement uncertainty

[1]L.D Gardner, K.A. Chamberlain and M.A. Rose. Property Measurements of LiF-NaF-KF Molten Salts Doped with Surrogate Fission Products. ANL/CFCT-24/23. September 2024.

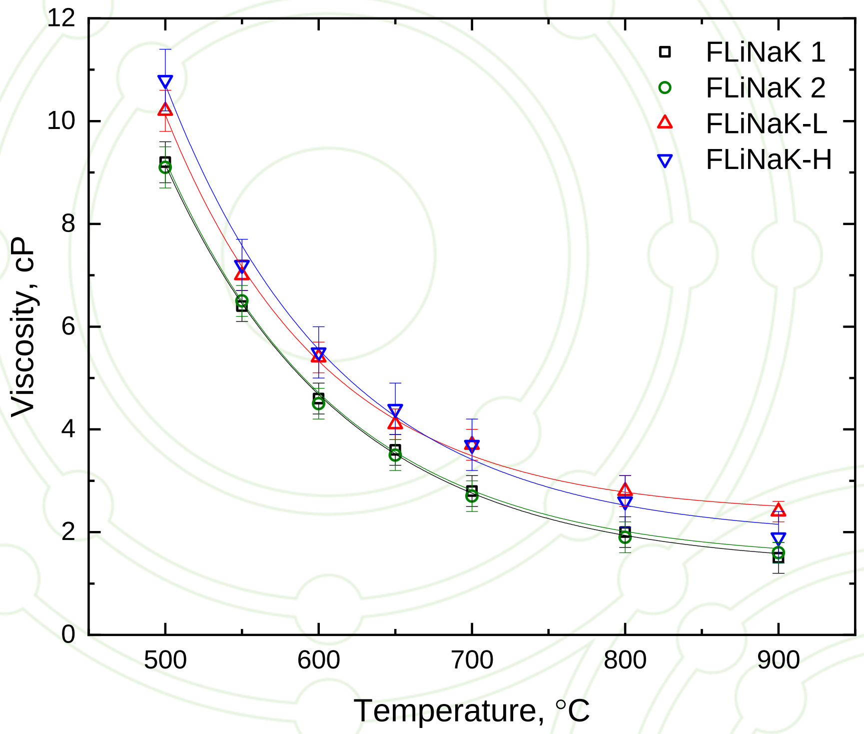
Viscosity

- Uncertainties in viscosity measurements are primarily due to:
  - Resolution of calipers, bore gauge
  - Viscometer torque calibration
  - Variance in multiple measurements
  - Uncertainty in salt temperature stability and control
- Relative uncertainties at each temperature are on the order of 10%

[1]L.D Gardner, K.A. Chamberlain and M.A. Rose. Property Measurements of LiF-NaF-KF Molten Salts Doped with Surrogate Fission Products. ANL/CFCT-24/23. September 2024.



Viscosities of silicone reference oil measured using three different viscometers (A, B, and C) at room temperature



Average viscosities and expanded uncertainties for FLiNaK 1, FLiNaK 2, FLiNaK-L, and FLiNaK-H[1]

A long drive shaft is needed to avoid heating the viscometer head, which increases gyration

Effects of gyration and bearing wear on measured values can be determined by performing measurements with a reference fluid using the same viscometer, drive shaft, and spindle size used for molten salts to determine a bias correction factor

- Viscometer calibration is performed by using a silicone reference oil
- The bias factor determined from measurements with silicone oil can be applied to measurements made in a molten salt

Differences in viscosities of salts with and without dopants are greater than the measurement uncertainty

Standardization of Property Measurements

Reliable molten salt property values are needed to design, license and operate MSRs

Standardized Property Measurement Methods

- Control variations in factors that affect measured property values
- Provide a method to quantify uncertainty in property values measured

No standardized test methods exist suitable for measuring properties of molten salts.

Modifications of existing standards are required to address unique aspects of measurements with molten salts.

- High temperature
- Air and moisture sensitivities
- Corrosivity and material compatibility
- Composition dependence of non-unary mixtures
- Incongruent volatility
- Solubility and stability
- Lack of established reference materials

A method for rotational viscosity measurements of molten salts has been prepared for standardization.

Effect of Environmental Contaminants

- Determining the effect of corrosion products and oxides on the properties of molten salt

Doping individual batches of FLiNaK salt with 1 wt % each of uranium oxide, nickel fluoride and chromium fluoride

- DSC is being used to measure the melting temperature and heat capacity of the molten salts between melting and 700 °C
- Laser flash analysis is being used to determine the thermal diffusivity of the molten salt at several temperatures

Measurements will be compared to previous measurements of FLiNaK synthesized with as low as achievable concentrations of contaminants to assess the impact of impurities

Vapor Pressure Measurements

- Developing instrument for measuring the vapor pressure of molten salt

Coupling a differential scanning calorimeter – thermogravimetric analyzer (DSC-TGA) and quadrupole mass spectrometer to measure vapor pressure by the transpiration method

- DSC-TGA is being used to record mass loss of molten salts during isothermal holds at selected temperatures
- Mass spec is being used to analyze evolved gases during heating

Vapor pressure measurements are being performed on reference materials and pure salts in preparation for measurements of salt mixtures

Summary

Molten salt properties research at Argonne supports the development of standard test methods suitable for generating high-quality data for MSR design, licensing, and deployment

Uncertainty analyses of molten salt property measurements were performed to:

- Add confidence that sources of measurement error have been identified and taken into account
- Recommend controls for use in draft standard test methods to distinguish effects of salt composition and environmental factors

Prominent factors affecting measurements were investigated separately to assess contributions to uncertainty:

- DSC temperature calibration
- Heating rate on thermal lag in DSC responses
- Wire thickness on density measurements
- Viscometer wear and shaft gyration on viscosity measurements

Summary of accomplishments and milestones

Task		Status
1	Complete quality assessment of unary chloride property data in MSTDB-TP	Complete
2	Complete a draft of a standard test method for rotational viscometry	Complete
3	Quantify the precision and bias in molten salt property measurements	Complete
4	Construct a custom apparatus for measuring the vapor pressure of molten salts by a transpiration method	In Progress
5	Measure effect of corrosion products and oxides on thermal properties of FLiNaK salt	In progress

Milestone Number	Title	Due
M3AT-25AN0705011	Complete quality assessment of unary chloride property data in MSTDB-TP	Complete
M3AT-25AN0705012	Quantify the precision and bias in molten salt property measurements	Complete
M3AT-25AN0705013	Construct a custom apparatus for measuring the vapor pressure of molten salts by a transpiration method	6/30/25 *on schedule*
M3AT-25AN0705014	Measure effect of corrosion products and oxides on thermal properties of FLiNaK salt	9/30/25 *On schedule*

Future work

- Determining the impact of corrosion products and oxides on molten salt thermophysical properties
  - Measuring melting point, heat capacity and thermal diffusivity of doped batches of FLiNaK
  - Comparing measurements of doped salts to FLiNaK synthesized with as low as achievable concentrations of contaminants to assess the impact of impurities
- Constructing a custom apparatus for measuring vapor pressure of molten salts.

Recent Reports

L.D Gardner, K.A. Chamberlain and M.A. Rose. Property Measurements of LiF-NaF-KF Molten Salts Doped with Surrogate Fission Products. ANL/CFCT-24/23. September 2024.

M.A. Rose, Quality Ranking of Unary Chloride Salt Property Data Included in MSTDB-TP. ANL/CFCT-24/34. December 2024.

L.D. Gardner and M.A. Rose. Uncertainty Analyses of Molten Salt Property Measurements. ANL/CFCT-25/5. March 2025

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- Government License Notice -the manuscript has been created by UChicagoArgonne, LLC, Operator of Argonne National Laboratory ("Argonne"). Argonne, a U.S. Department of Energy Office of Science laboratory, is operated under Contract No. DE-AC02-06CH11357.

Thank you

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Standard Test Method for Measurement of Viscosity of a Molten Salt using a Rotational Viscometer

1. Scope

1.1 This method can be used to determine the viscosity of a molten salt, including salt mixtures, contaminated salts, and radioactive salts, at high temperatures (e.g., 900 °C) in a controlled atmosphere by using a rotational viscometer. The torque generated by the resistance of a spindle rotated at a constant rotational speed due to the resistance of the salt is measured.

Controls necessary for accurate measurements are identified. These address the corrosive nature of molten salts, measurements of radioactive salts, elevated temperatures, and salt volatilization.

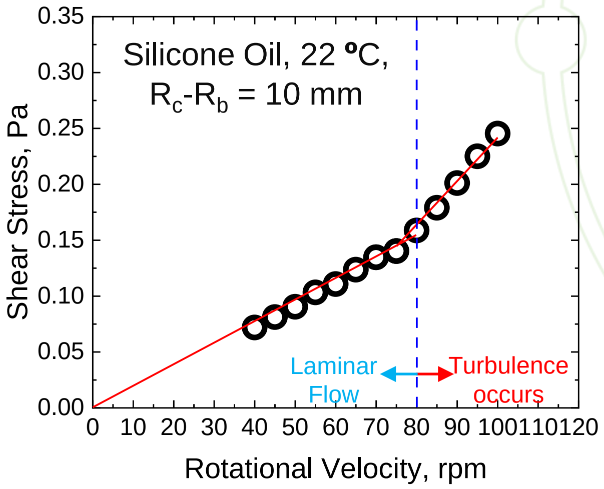
4. Summary of Method

4.1 A cylindrical spindle is immersed in a molten salt contained in a cylindrical container at a known temperature to a known depth and rotated at a known rotational speed. The viscous drag on the immersed spindle is measured as torque at several rotational speeds. Torque values measured at different speeds are used to determine the range of speeds resulting in non-turbulent flow. The viscosity is determined using torques measured under stable Couette flow conditions and the shear rate is determined based on the dimensions of the spindle and crucible.

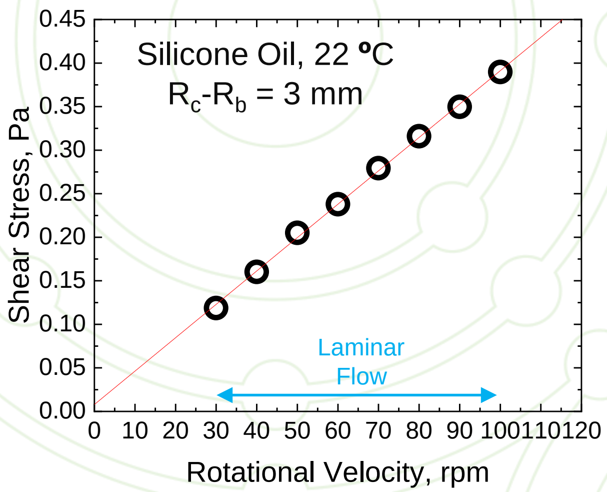
Controlled factors affecting viscosity measurements of molten salts

- Rotational velocities
- Spindle and crucible geometries
- Spindle depth and gyration
- Materials selection and engineering controls to minimize corrosion
- Temperature control

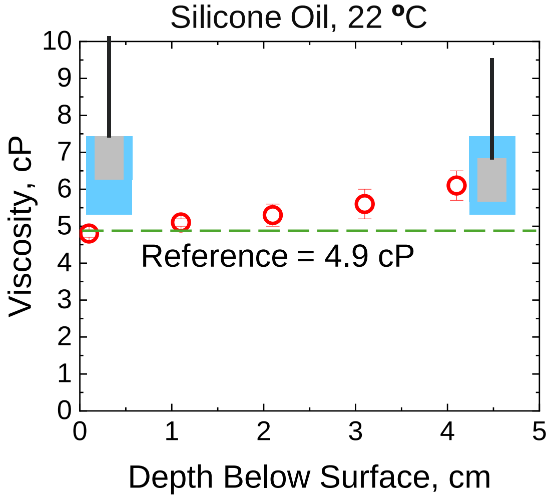
Turbulent flow is induced at high rotational velocity, exhibited as a sharp increase in shear stress.



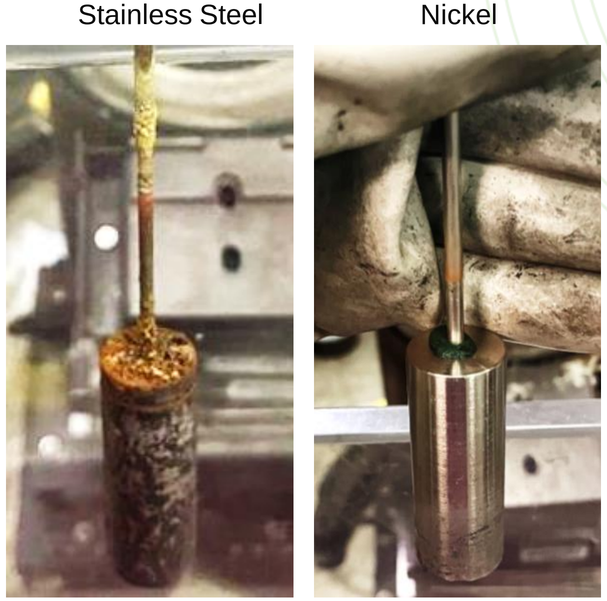
Laminar flow is maintained by using a cell having a narrow gap between spindle and crucible walls.



Increased spindle immersion depth increases the drag on the rotating shaft, which spuriously increases measured torque



Salt-facing materials should be selected to minimize corrosion



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