U.S. DEPARTMENT OF ENERGY | Office of NUCLEAR ENERGY

Argonne NATIONAL LABORATORY

Molten Salt Reactor PROGRAM

Generating High-Quality Molten Salt Property Values

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Annual MSR Campaign Review Meeting 16-18 April 2024

Support a FOAK MSR by 2035

Goal: Provide developers and regulators with the information needed to design licenses and operate MSRs.

Argonne is supporting MSR developers by:

- **Generating high quality molten salt property data**
- **Standardizing measurement methods**
- **Providing assessment criteria for the quality of existing data**

Actively engaging with industry to address needs for MSR development

- **Supporting MSR developers though GAIN, NEUP, and direct-funded activities**
- **Hosting tri-weekly chemistry discussions to inform and enhance collaborations between national labs and stakeholders.**

FY24 Measurement Activities

Predicting molten salt behavior during normal and transient conditions requires knowledge of thermophysical property values over a range of temperatures and a range of compositions

Including the effect of fission products and contaminants

High-quality measurements of salts with and without fission products

- Determine how different fission product contents changes molten salt property values

Properties being measured in FY24 include:

- Viscosity
- Density
- Thermal conductivity

Other Property Measurement Capabilities include:

- Melting Point (measured doped salts in FY23)
- Heat Capacity (measured doped salts in FY23)
- Thermal Diffusivity (measured doped salts in FY23)
- Vapor Pressure
- Mass diffusion coefficients
- Activity measurements

Effect of Fission Products on Molten Salt Thermal Properties

Measuring thermal properties of salts doped with fission products for comparison with measurements of the same salts without dopants.

- **Two doped FLiNaK salts were prepared representing high and low burn up**
  - **Inspired by depletion calculation results for MSRE**
  - **Same salts were used in salt spill testing in FY23**
- **Measuring viscosity and density of salts**
- **Using FY23 measurements of heat capacity and thermal diffusivity and FY24 measurements of density to calculate thermal conductivity for salts.**

Pure FLiNaK

Doped FLiNaK (low burnup)

Doped FLiNaK (high burnup)

Doped FLiNaK Compositions (mol %)

Component	Composition 1 (low burnup)	Composition 2 (high burnup)
FLiNaK	99.65	98.23
ZrF_4	0.05	0.25
Mo	0.05	0.25
NdF_3	0.05	0.25
CeF_3	0.05	0.25
CsF	0.05	0.25
CsI	0.005	0.025
SrF_2	0.05	0.25
Ru	0.05	0.25
Te[a]	0.005	0.025

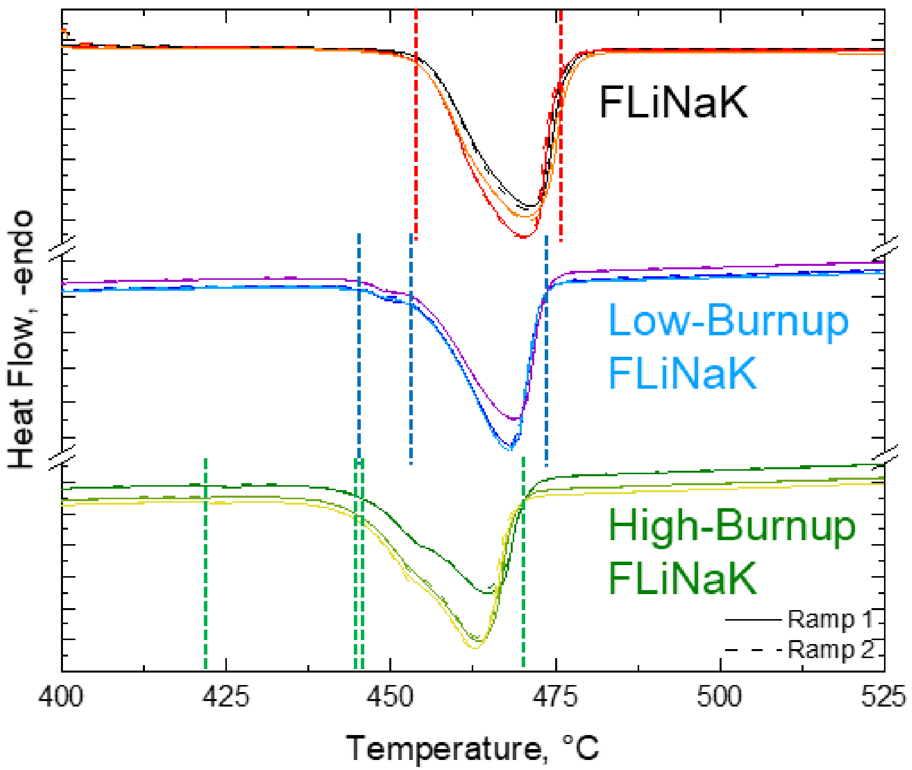
[a] Added as Na_2Te

M.A. Rose, L.D. Gardner, and T.T. Lichtenstein. Property Measurements of NaCl-UCl_3 and LiF-NaF-KF Molten Salts Doped with Surrogate Fission Products. ANL/CFCT-23/23. September 2023.

FY23 Melting Behavior Measurements

Melting behaviors of doped FLiNaK salts were measured by using differential scanning calorimetry (DSC).

- Three samples of each salt were measured to verify sample homogeneity.
- Replicate measurements of each sample were made to assess repeatability
- Vertical lines indicate average transition temperatures



The effects of fission products on melting behavior include:

- Depressed onset of melting and liquidus temperatures ΔT_{liq} = 3–6 °C
- Additional transitions observed at temperatures below the onset of melting
  - Pre peaks at ~419 °C and 445 °C

M.A. Rose, L.D. Gardner, and T.T. Lichtenstein. Property Measurements of NaCl-UCl_3 and LiF-NaF-KF Molten Salts Doped with Surrogate Fission Products. ANL/CFCT-23/23. September 2023.

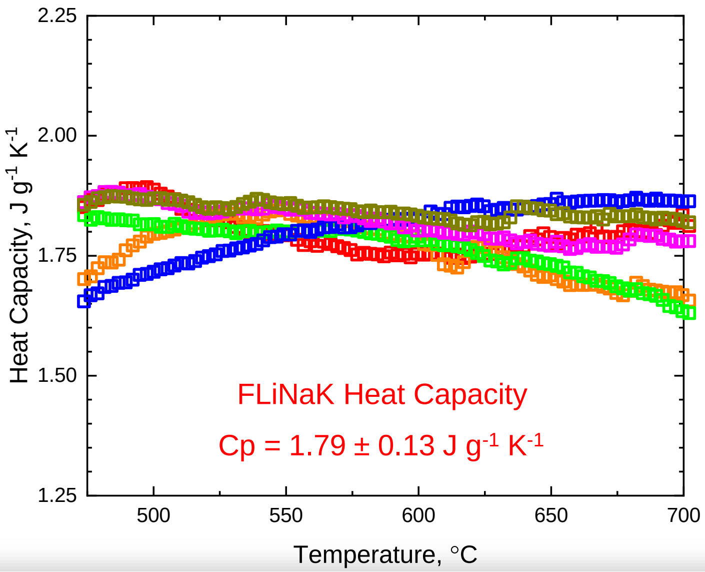
FY 23 Heat Capacity Measurements

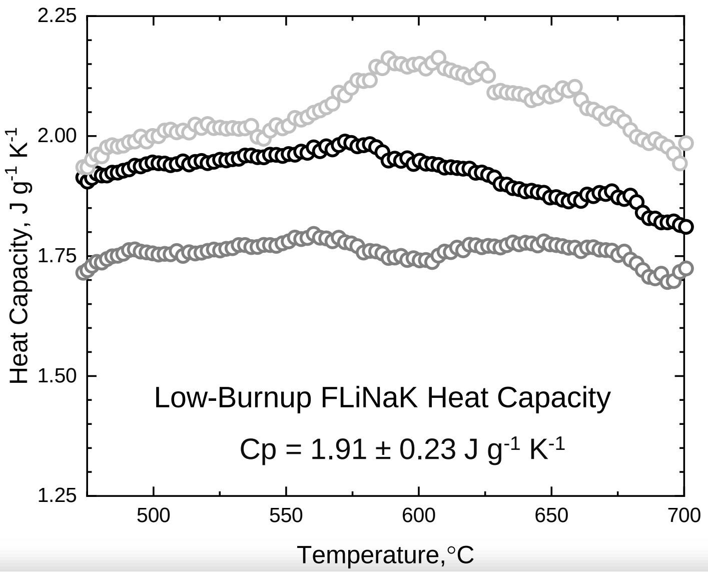
Heat capacity is measured by using differential scanning calorimetry

- **Three samples of low-burnup fission product doped FLiNaK salt were measured.**

The difference in average heat capacity of low-burnup FLiNaK and pure FLiNaK is within the measurement uncertainty.

- **Analyzing results to distinguish between measurement uncertainty and the effects of fission products.**
- **An approach to quantify uncertainty in heat capacity values determined using DSC was developed in FY24.**





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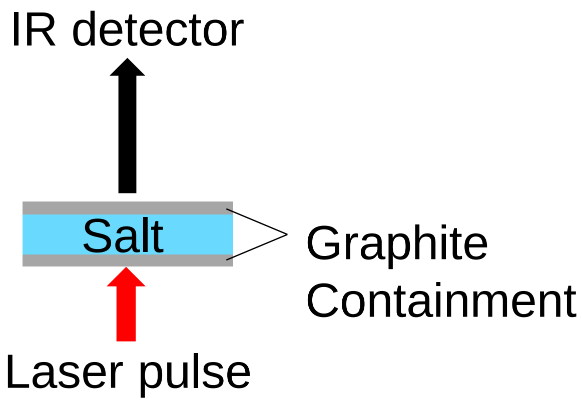
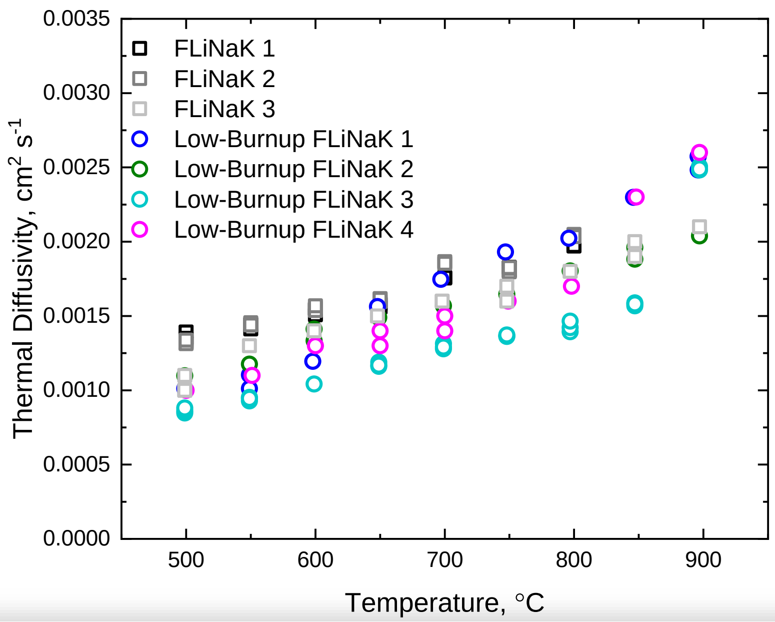
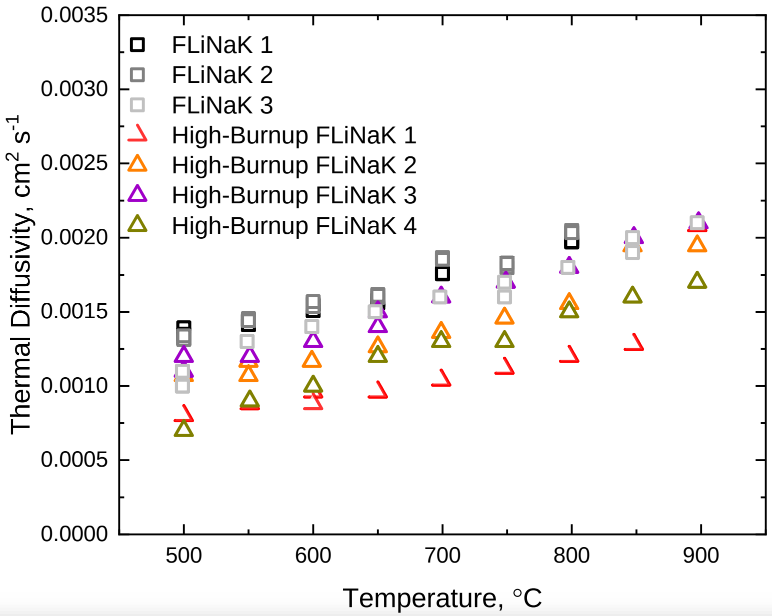
FY23 Thermal Diffusivity Measurements

- **Measured thermal diffusivity by laser flash analysis between 500 and 900 °C**
  - **Triplicate samples of each salt encapsulated in graphite cells were analyzed**
  - **Clark and Taylor model used to determine thermal diffusivity from measured thermal response**
    - **Corrects for radiative heat loss**
- **Using results to distinguish between measurement uncertainty and effects due to fission products in support of developing a standard measurement method**







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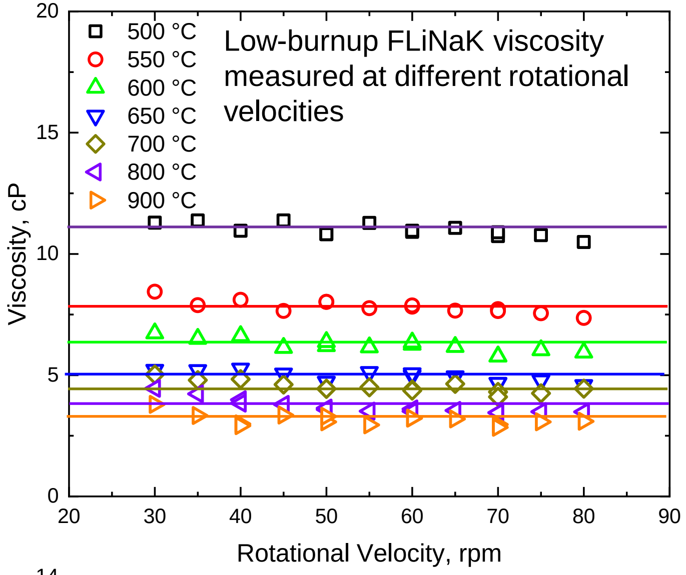
FY24 Viscosity Measurements

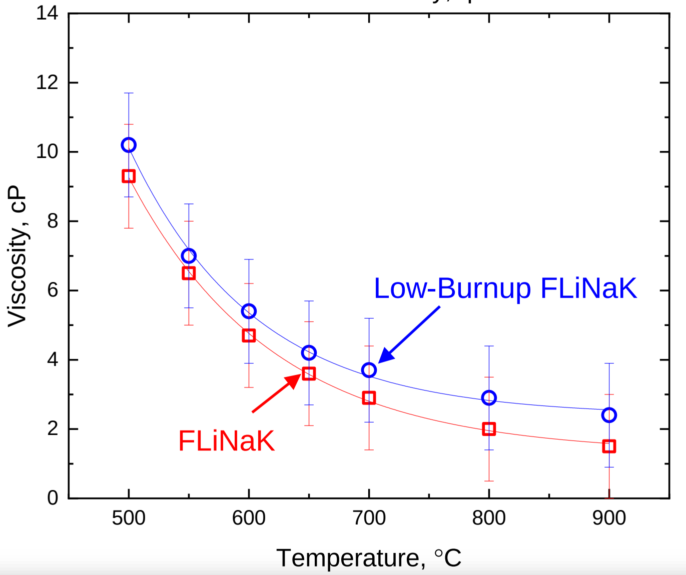
The viscosities of low-burnup FLiNaK salt were measured between 500 and 900 °C by using the rotating cylinder method.

- **Duplicate measurements at 40, 50, 60, and 70 rpm indicate measurements are repeatable.**
- **Measured viscosities are independent of rotational velocity between 40 and 70 rpm, as expected for Newtonian fluids.**
- **Error bars in plot represent ranges of replicate measurements**



The effects of fission products on viscosity

- **Viscosities of low-burnup FLiNaK are higher than those of FLiNaK at each temperature, but differences are within the range of the measurements.**
- **The temperature dependence of doped salt viscosity values is consistent with trends observed for FLiNaK and other salts.**

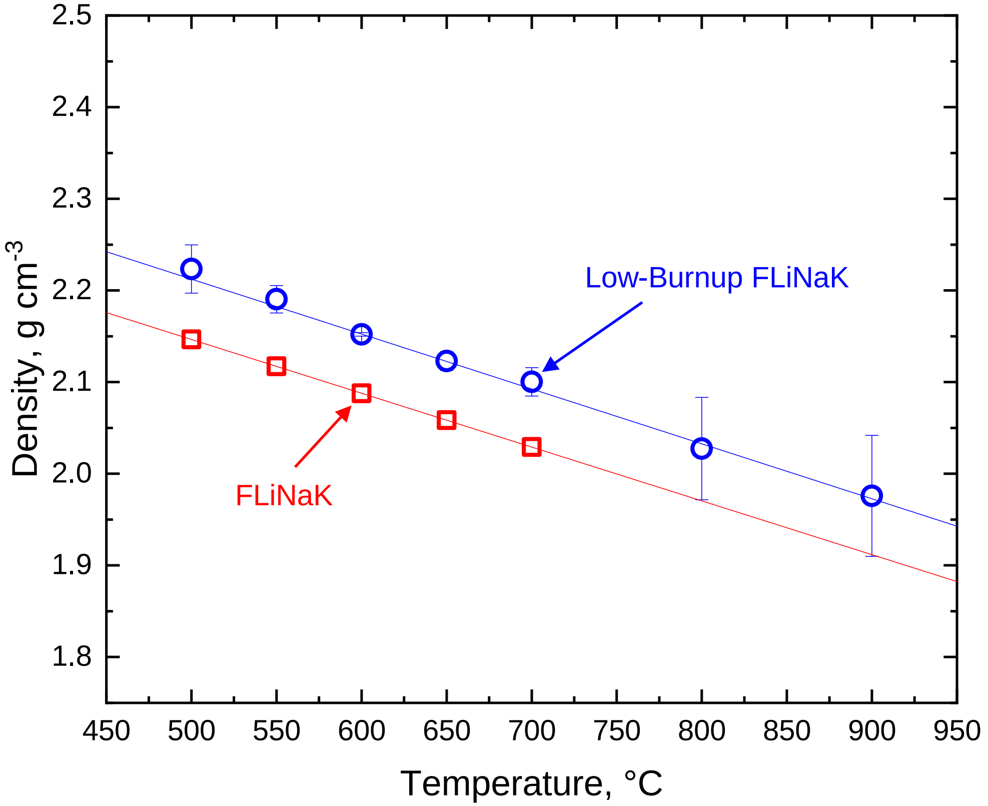


Milestone: M3AT-23AN0705011 – on schedule

FY 24 Density Measurements

The densities of doped FLiNaK salts were measured between 500 and 900 °C by the Archimedes method.

- Density measurements were made with two sets of inert metal bobs and wire with different diameters to take the effect of surface tension into account.
- Negative temperature dependence was observed for both salts, consistent with trends observed for other salts.
- Error bars in plot represent ranges of replicate measurements



The effect of fission products on density:

- The presence of surrogate fission products increases the density of FLiNaK.
- The presence of surrogate fission products does not change the temperature dependence of the density of FLiNaK.

Milestone: M3AT-23AN0705011 on schedule

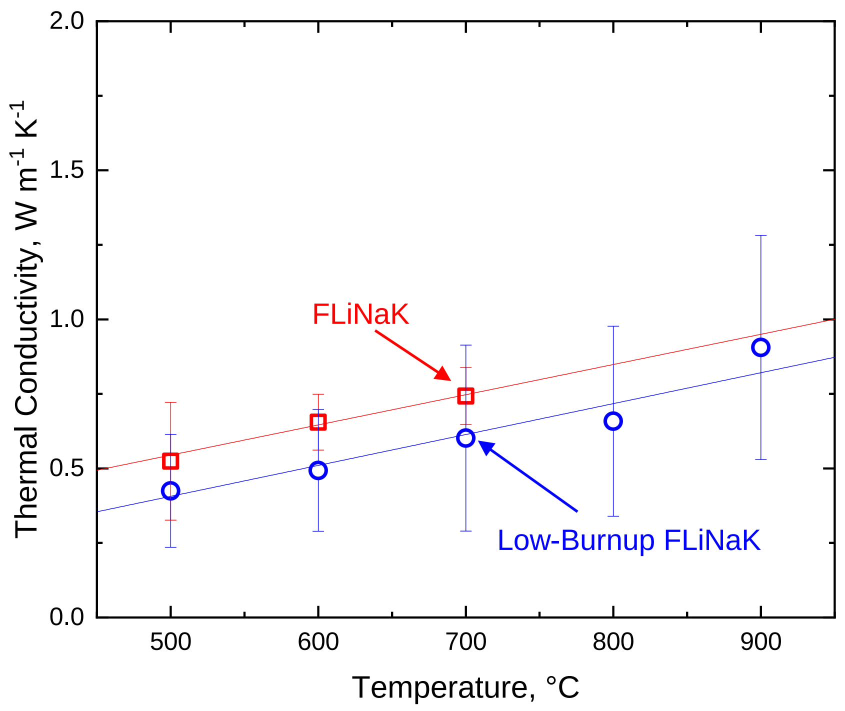
Thermal Conductivity of Fission Product Doped Salts

The thermal conductivities of doped FLiNaK salts were calculated as the products of the measured density, heat capacity, and thermal diffusivity values between 500 and 900 °C.

- **A slightly positive temperature dependence was observed in calculated values.**

The effect of fission products on thermal conductivity:

- **Differences between measurements of FLiNaK and doped salts are within precision of measurements**
- **Uncertainty in heat capacity and thermal diffusivity measurements both contribute significantly to uncertainty in thermal conductivity.**



Milestone: M3AT-23AN0705011 on schedule

FY24 Data Quality Activities

NQA-1 quality data will likely be necessary for licensing a reactor

- Use of standardized methods will add confidence to property values
- Precision and accuracy of analyses determined based on measurements with reference salts
- Measured under a quality assurance program

- Participating in international discussions on standardizing molten salt property measurement methods
- Leading task force on standardizing rotational viscometry for molten salts through ASTM
- Assessing existing property data in MSTDB-TP and providing quality rankings for users of the database
  - Using rubric from ANL/CFCT-23/48

Workshop Addressing Uncertainty in Molten Salt Thermal Property Values and Predictions

July 2023

Four sessions with presentations and discussions:

1. Quality Assessment of Measured Property Values
2. Quantifying Uncertainty in Property Models
3. Quantifying Consistency of Property Predictions with Measured Values
4. Quantifying Uncertainty in System Models

Recommendations from the workshop report:

- **Continue to apply transparent, thorough, and documented quality assessment processes to data in both MSTDB-TC and -TP.**
- **Quantify the uncertainty in model predictions where data gaps must be bridged by modeling; use of Bayesian statistics was recommended.**
- **Standardize methods for measuring the thermal properties of molten salts to enable the generation of high-quality property data.**
- **Identify and produce a standard reference material to enable researchers to quantify the accuracy of property measurement methods and compare results from different labs and using different methods.**
- **Promote regular interaction between modelers and those measuring properties of molten salts to communicate identified needs for specific data.**

Quality Assessments for MSTDB-TP

Assessed available thermophysical property data for unary fluoride salts

Applying a QA rubric to existing data in the MSTDB-TP in collaboration with ORNL.

Aspect	High Quality	Moderate Quality	Insufficient for Quantitative Use
Method	Standardized method	Well-established method	Documented procedure
Calibrations	Measured response using reference material ***and*** calibration of devices with certified pure standards	Measured response using reference material ***or*** calibration of devices with certified pure standards	Sufficient calibration results not provided
Composition	Replicate analyses for all constituents and impurities, or controlled batching	Replicate analysis for major salt constituents and impurities	No analyses or limited analyses prior to measurement
Environmental Control	Control and stability of temperature and atmosphere	Measured salt or furnace temperature and limited control of atmosphere	Environmental controls not reported
Measurement Precision	Quantified uncertainty based on replicate measurements	Propagated uncertainty based on individual measurements	No measured or estimated uncertainty are reported
Verifiability	Measured data and determined property value provided and verifiable	Both measured data and determined property value provided	Insufficient information available to verify reported value

M.A. Rose. Quality Ranking of Unary Fluoride Salt Property Data in MSTDB-TP. ANL/CFCT-23/48. December 2023.

Example Assessment: Unary Fluoride Thermal Conductivity Data

Assessed all available thermal conductivity measurements of unary fluoride salts in the MSTDB-TP

One B ranked data set

Three U ranked data sets

Two sets of property values determined solely through modeling ranked C

Variety of methods used - no standard method available

Author, Year	Salt Systems Studied	Overall Rank	Method	Calibrations	Composition Analysis	Environmental Controls	Measurement Precision	Verifiability
Sreenivasan, 1967 [32]	LiF	B	M - Transient Gap Analysis	M - Calibrated with sodium nitrate, microvolt amplifier ±0.4 µV and recorder ±0.5 µV	M - LiF purchased at 99.989% pure, no composition measurements	M - Under argon atmosphere, platinel thermocouples used but did not quantify stability	H - Replicate samples, quantified error for measurements of each sample. Uncertainty of the technique is estimated at 8.6%	H - Reports raw data and calculated values. Reports a correlation by least squares and its maximum deviation from measured values.
Powell, 1979 [33]	CaF_2	U	M - Hot Wire	M - calibrated with organic liquids at RT, current stabilized to 0.0001 amps	I - No information on source materials or analyses of salts.	I - No information reported.	I - Provided discussion of sources of error, 1024 data points are smoothed by averaging every 16 data points	I - No raw data provided. Reported two measured values in plot, and correlation generated by least squares.
Smirnov, 1987 [34]	LiF, NaF, KF, RbF, CsF	U	M - Coaxial cylinders	M - Maximum measurement error of 4%	I - Salts purified by zone melting - no composition analyses	M - Temperature controlled to 0.01 K, sealed in an air tight container- did not reported cover gas	I - no information reported	I - No raw data provided. Report measured conductivity and correlations which match the measured values within 5%.
Golyshev, 1992 [35]	LiF, MgF_2, BaF_2, CaF_2	U	M - Coaxial Cylinders	I - No information on calibrations.	I - No information on source materials or analyses of salts.	I - No information reported.	M - Measured 2–4 replicate cells. Error in averaging is estimated at 0.2%	I - No raw data provided. Reports measured diffusivity on a plot.
Nagaska, 1993 [36]	LiF, NaF, KF, RbF, CsF	C	I - Measured non-fluoride salts by Rayleigh scattering and predicted fluoride conductivity	I - n/a	I - n/a	I - n/a	I - n/a	I - Reported a correlation for fluorides based on measurements of non-fluoride salts
Gheribi, 2014 [37]	LiF, NaF, KF, RbF, CsF, MgF_2, CaF_2, BaF_2	C	I - Did not measure values- computational work only	I - n/a	I - n/a	I - n/a	I - n/a	I - generated correlations for fluorides based on modeling

Purity and composition are often not reported

Raw measurements are often not reported leaving assessors unable to verify property values and correlations

M.A. Rose. Quality Ranking of Unary Fluoride Salt Property Data in MSTDB-TP. ANL/CFCT-23/48. December 2023.

Drafting Standard Methods

Participated in the Putting Science into Standards Workshop held March 18-19, 2024 in Brussels.

- Delivered keynote address on standardizing molten salt property measurements
- Discussions focused on what standards are needed and prioritizing those standards.

Argonne is leading a task force through ASTM to standardize viscosity measurements of molten salts using a rotational viscometer

"A *set of standard methods* for measuring the thermal properties of molten salts will enable the generation of high-quality property data needed to qualify molten salt fuel and to design, license, and safely operate MSRs."

- from the MS properties uncertainty workshop report

Rotational Viscometer Installed in a Glovebox for Measuring Molten Salt Viscosity

M.A. Rose. *Molten Salt Thermal Property Uncertainty Workshop Report*. ANL/CFCT-23/32. September 2023.

FY24 Cross - Cutting Activities

Participating in workshops and discussions to identify and define research needs in the area of molten salt fuel cycle chemistry

Participated in the international discussion of this topic at the International Workshop on the Chemistry of Fuel Cycles for Molten Salt Reactor Technologies hosted by IAEA and NEA October 2023.

Deploying commercial molten salt reactors (MSRs) will require closing technological gaps associated with supplying fuel salt, maintaining fuel salt, and dispositioning used fuel salt

Working with NE-43 leadership to identify technologies needed to support a fuel cycle for MSRs

- Fuel supply chain including synthesis, purification, and qualification
- Back-end technologies including removal of insoluble or gaseous fission products, fuel purification and recycle

Molten Salt Reactor Fuel Cycle Chemistry Workshop

Held at Argonne National Laboratory

September 2023

Invited 46 experts in MSR Fuel Cycle Chemistry from National Labs, Universities, Industry, DOE, NRC and other R&D organizations

Workshop held to assist the Office of Material and Chemical Technologies (NE43) identify fuel cycle technologies needed for molten salt advanced reactors in advance of their deployment

Identified technological gaps in the molten salt fuel cycle and future research directions to close these gaps

Front End Topics:

- Synthesizing
- Purifying
- Scale-up of fuel synthesis
- Fuel Qualification

Back End Topics:

- Recovering and recycling actinides
- Purifying used salts
- Insoluble fission product removal
- Safeguards for molten salt fuel cycle facilities

Summary

Argonne is supporting MSR developers by:

- **Measuring high-quality molten salt property values**
- **Determining impact of fission products on property values**
- **Determining measurement precision for methods**
- **Assessing the quality of existing data in MSTDB-TP**
- **Standardizing methods for property measurements**

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Thank you

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