ARGONNE'S MOLTEN SALT PROPERTY MEASUREMENTS

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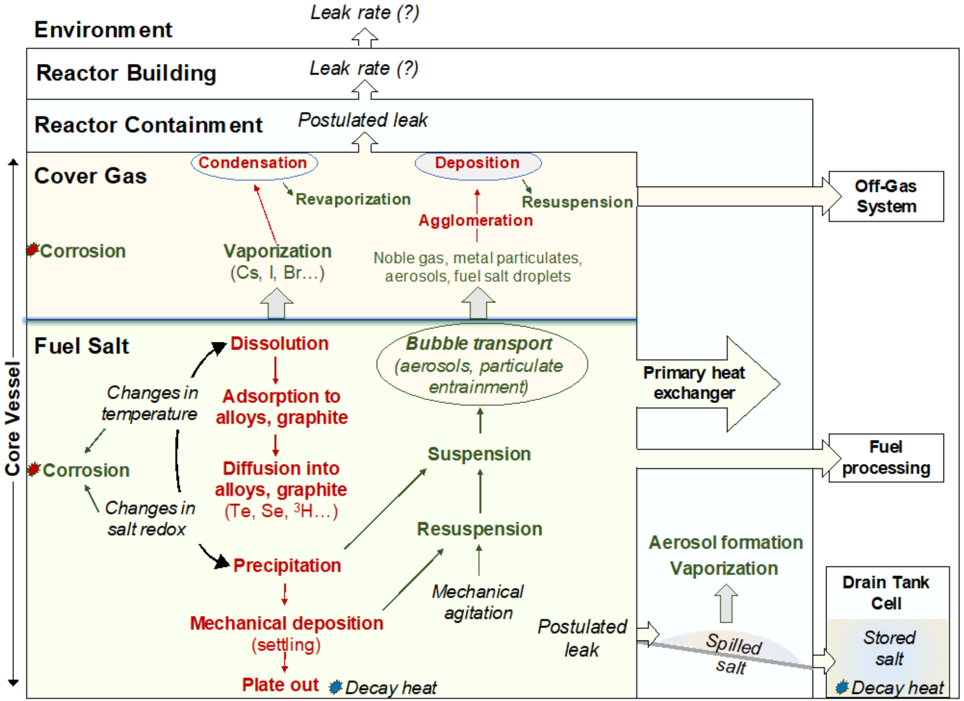
MODELING RADIONUCLIDE TRANSPORT AND BULK SALT BEHAVIOR FOR SOURCE TERM ASSESSMENTS

- Required thermochemical and thermophysical properties data
  - Viscosity
  - Thermal conductivity
  - Density
  - Heat capacities
  - Liquidus/solidus temperatures
  - Salt boiling temperatures
  - Volume expansion coefficients
  - Surface tension
  - Radiation emissivity

- Process contributions require experimental validation



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

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
- 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 $LiF-BeF_2-UF_4$ for which reliable property values must be measured
- Thermophysical property measurements in progress for FLiBe and eutectic FLiNaK
- Property measurements for $NaF-UF_4$, $NaCl-UCl_3$, and two compositions of $NaCl-KCl-UCl_3$ will be made in FY21

CHEMICAL & FUEL CYCLE TECHNOLOGIES DIVISION

- R&D activities spanning the range from fundamental property measurements to pilot-scale fuel cycle demonstrations
  - Milligram- to kilogram-scale tests with actinide halides in molten fluoride and chloride salts

- Radiological facility housing purpose-built inert atmosphere gloveboxes used for experiments with actinides and simulated fission products

- Expertise and capabilities in areas essential to advancing molten salt nuclear energy systems:
  - Thermophysical property measurements
  - Materials compatibility and corrosion studies
  - Electrochemical monitoring and control of salt chemistry and materials accountability
  - Fuel cycle research spanning fuel development and qualification to chemical separations to waste management
  - Nuclear chemical engineering from concept development to pilot-scale demonstrations

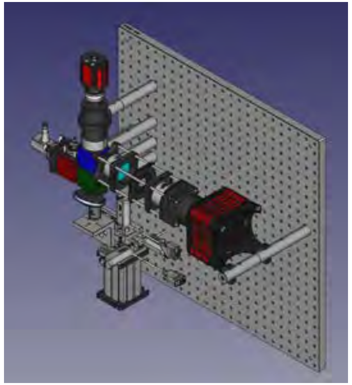
Thermophysics laboratory with equipment located in Ar-atmosphere radiological gloveboxes

MOLTEN SALT CHEMICAL ANALYSIS CAPABILITIES

- Approach for high quality data:
  - Using replicate analyses of salt composition and property values to quantify precision and determine effects of salt composition
  - Developing use of benchmark salts and standards to establish expected precision and accuracy of methods and measurements
  - Using DSC routinely to analyze and verify thermal stability of complex salt mixtures
  - Monitoring composition changes after measurements to detect preferential volatility

Measurement of oxide concentration in molten salts including beryllium salts by a LECO inert gas fusion analyzer

Method	Compositional Information
ICP-OES	Elemental analysis ppm level, accuracy of <0.2% with advanced methods
ICP-MS	Elemental analysis at ppb level, accuracy of <0.2% with advanced methods
XRD	Identification of crystalline phase composition
Alpha Spectroscopy	Identification and quantification of alpha-emitting isotopes
Gamma Spectroscopy	Identification and quantification of gamma-emitting isotopes
Liquid Scintillation Counting	Measurement of alpha/beta activity
Inert gas fusion (LECO)	Quantification of C, S, O, N contaminants at <1 mg/g levels



Raman spectroscopy of molten salts

- *Spectroscopy from ~15 to ~3500 cm^{-1}*
- *Portable and reconfigurable*
- *Microspectroscopy*

ELECTROCHEMICAL SENSORS FOR LONG-DURATION MOLTEN SALT MONITORING

Argonne is developing advanced electrochemical sensors to measure key molten salt properties and enable in situ monitoring of the salt composition and redox state within MSR-relevant flow loops. This work supports the design, licensing, and operation of MSRs.

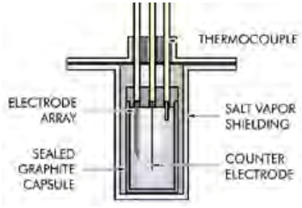
FUNDAMENTAL SALT PROPERTIES

The development of electroanalytical techniques for relevant MSR salts allows for the measurement of a variety of crucial fundamental properties including:

- Formal potentials
- Diffusion coefficients
- Kinetic constants
- Solubility limits

A sealed electrochemical cell has been developed for volatile fluoride salts.

Knowing these fundamental properties is essential to understand and quantify processes such as corrosion, mass transport, precipitation, and noble metal plate-out



BeF_2 compatible test cell for electrochemical measurements of fundamental fluoride properties

MOLTEN SALT LOOP MONITORING

Long-duration monitoring of the salt can occur when fundamental salt properties are known.

In situ capabilities for monitoring crucial salt attributes are being developed:

- Salt redox state
- Salt composition
- Extent of corrosion
- Salt impurities
- Oxygen and water ingressions
- Salt level

In situ monitoring of molten salt loops is essential to maintaining a balanced salt chemistry and successful long-duration operations

Argonne multielectrode sensor integrated into molten salt loop at ORNL for concentrating solar power applications

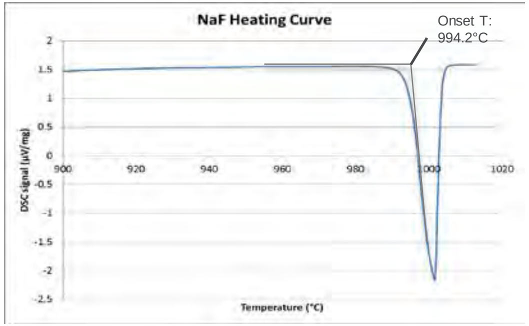
Argonne sensors will be installed into two flow loops at ORNL in FY21. Operations in vendor MSR loops are also being planned.

THERMOPHYSICAL PROPERTY MEASUREMENT CAPABILITIES

Property measurements available at Argonne for actinide-bearing fuel and coolant salts

Property	Method
Density, volumetric thermal expansion, surface tension	Archimedes method
Heat capacity, melting point, phase equilibria	Differential scanning calorimetry
Viscosity	Rotating spindle viscometer
Thermal diffusivity & thermal conductivity	Laser flash analysis system
Fission product & actinide solubility	Chemical analysis and DSC
Mass transfer diffusion coefficients	Restricted diffusion cells

Differential Scanning Calorimeter



Thermograph of NaF Showing Determination of On-Set Temperature of Salt Melting at 994.2 °C

SALT PREPARATION AND CHARACTERIZATION

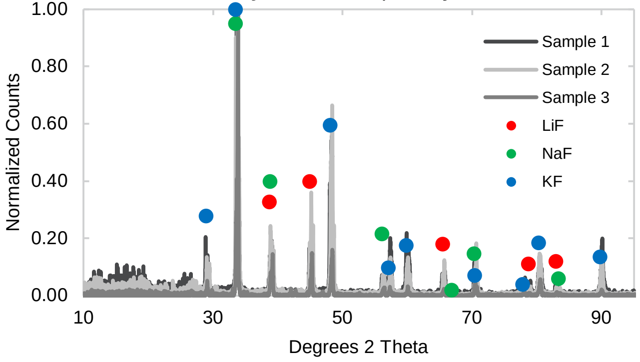
- Property values are sensitive to the salt composition and accurate batching using pure reagents is important

- All works occurs inside a glovebox (<10 ppm O_2, <1 ppm H_2O):
  - Reagent salts are heat treated to remove residual water
  - Dried salts are batched by mass (±0.0001 g)
  - Salt mixtures are heated to fuse

- Salt mixtures are analyzed prior to and post measurement by using a variety of techniques, including:
  - Inductively coupled plasma – mass spectroscopy or optical emission spectroscopy (ICP-MS or ICP-OES) for elemental composition
  - X-ray diffraction for phase identification
  - Differential scanning calorimetry for melting point determination
  - Analysis for dissolved oxygen and water using LECO's inert gas fusion analyzer

Photo of LiF-UF_4 Mixtures Prior To (left) and After (right) Fusing

XRD Patterns of Three Samples of FLiNaK Salt

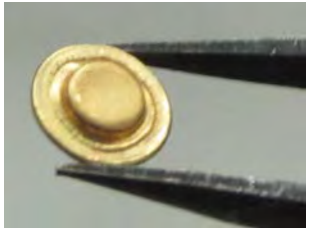


THERMAL ANALYSIS

Standard Thermal Analyzer (STA) with Thermogravimetric Analysis (TGA)- Differential Scanning Calorimeter (DSC)

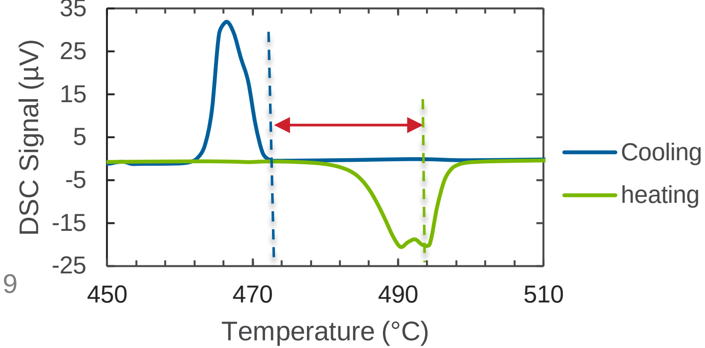
- Thermal calibration with five metal standards spanning temperature range 230 to 1065 °C (±1 °C uncertainty)
- Sealed gold cells are used to contain salts and provide good sensor contact
- Data are collected at the highest scan rate that yields reproducible results
- Heating data are used for analysis because significant super cooling may occur in molten salts that affects cooling data

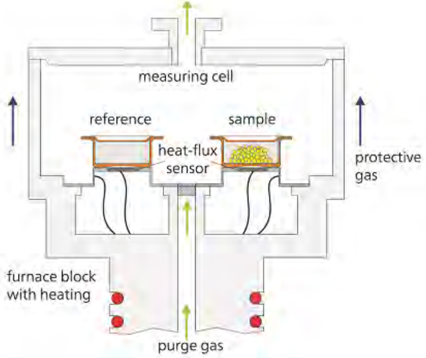
Netzsch Instrument Installed in Radiological Glovebox



Salt in Sealed Gold Sample Cell

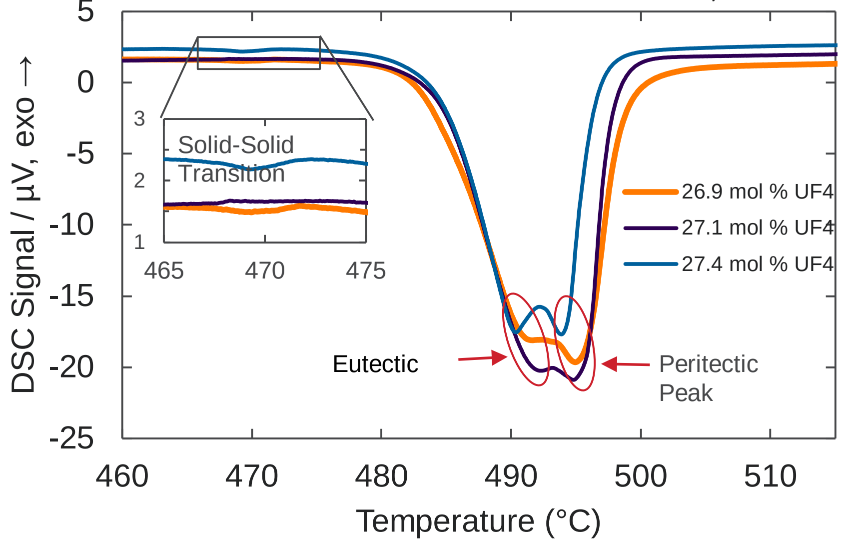
Melting Behavior of LiF-UF_4



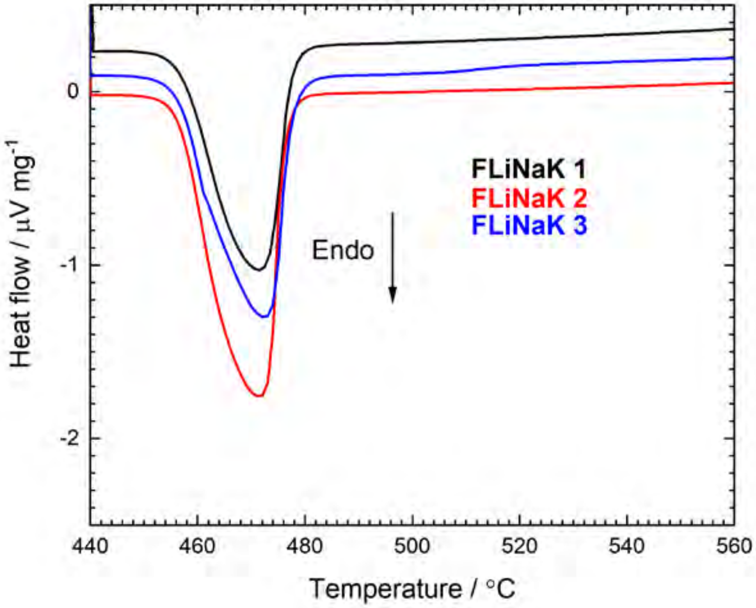


THERMAL ANALYSIS MEASUREMENTS

DSC Responses of 3 Mixtures LiF-UF$_4$



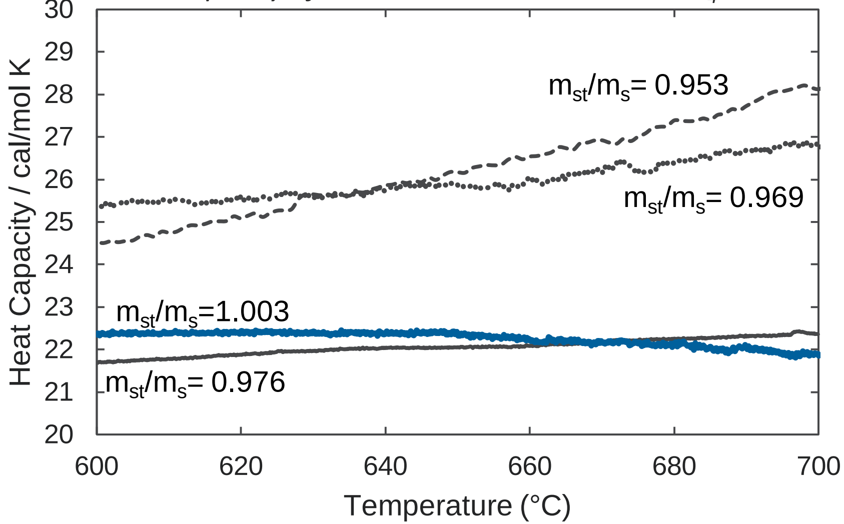
DSC Response of 3 Samples of Eutectic FLiNaK



The DSC response is highly sensitive to small differences in salt composition

HEAT CAPACITY MEASUREMENTS

Heat Capacity of 72.3 mol % LiF-27.7 mol % UF_4

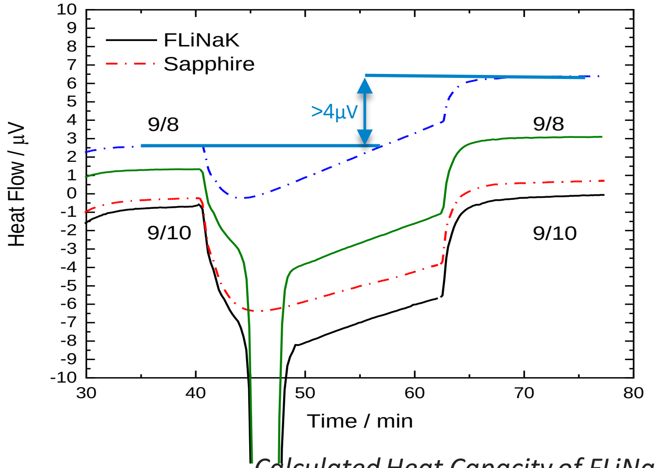


Temperature dependence in the measured C_p is due to differences between sample and standard masses

Ratio Method:

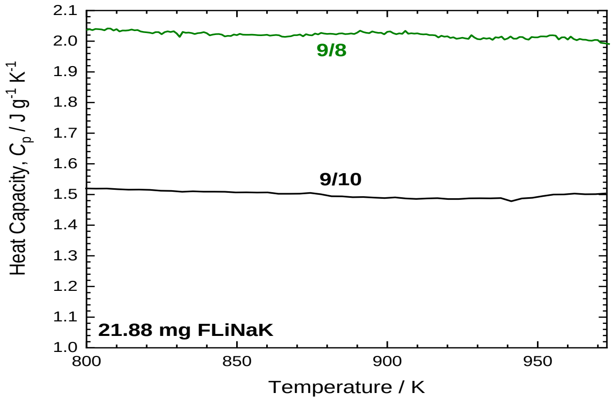
$$C_p^s = \frac{m_{st}}{m_s}\frac{\Delta\varphi_s}{\Delta\varphi_r}C_p^{st} + \frac{m_{cr}^{st} - m_{cr}^s}{m_s}C_p^{cr}$$

DSC Response of Two FLiNaK Cp Measurements

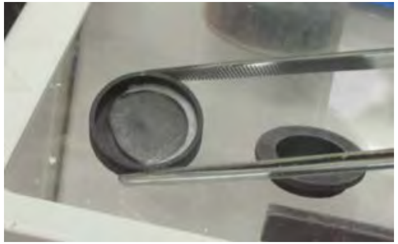


Data with isotherms which differ >2 µV yield inaccurate heat capacities

Calculated Heat Capacity of FLiNaK



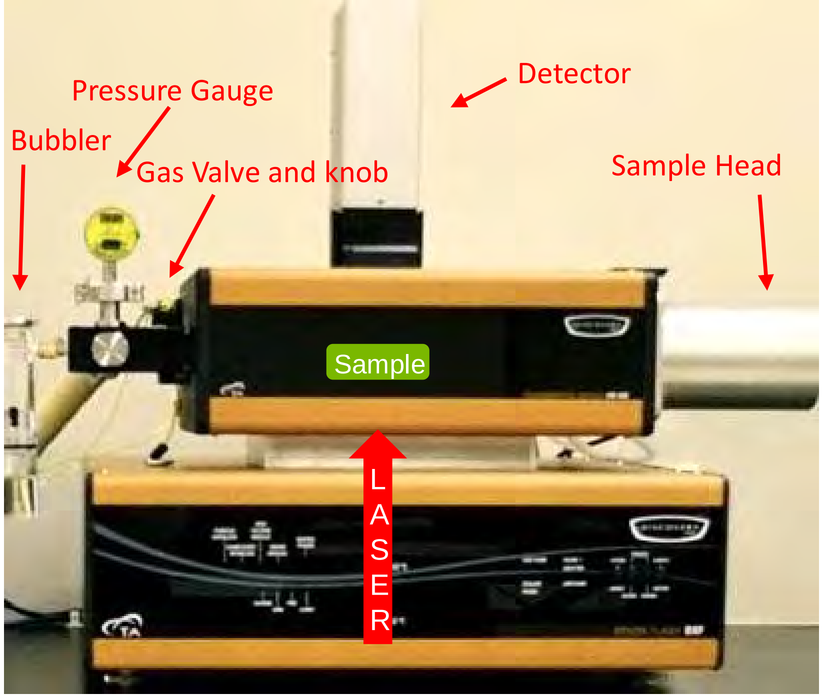
THERMAL DIFFUSIVITY MEASUREMENTS



Rejected Sample With a Void

Laser Flash Analyzer

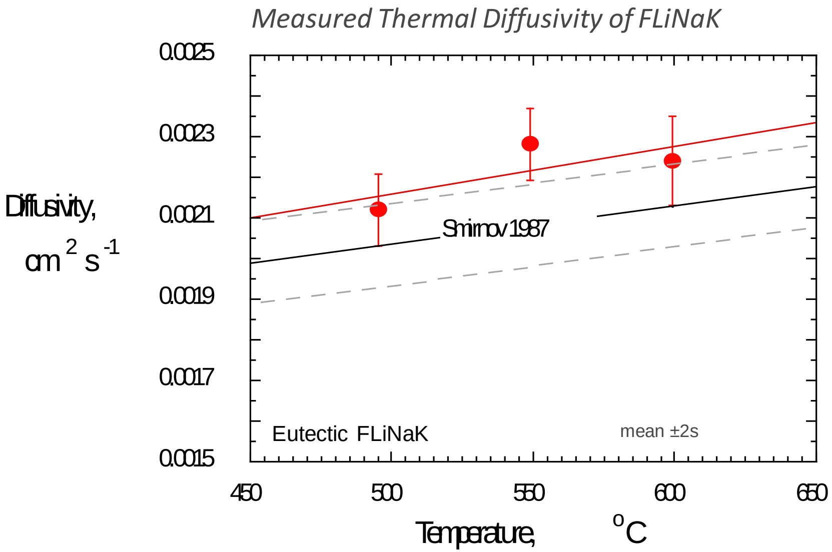
- Nd-glass laser instantaneously heats the bottom surface of crucible and an IR detector measures the temperature of the top surface of crucible vs. time after heating
- Eliminating voids and providing good sensor contact is necessary for accurate measurements
- Custom graphite crucible provides a thin, even layer of salt
- Measurements made under ultra high purity argon atmosphere to prevent contamination by oxygen or water

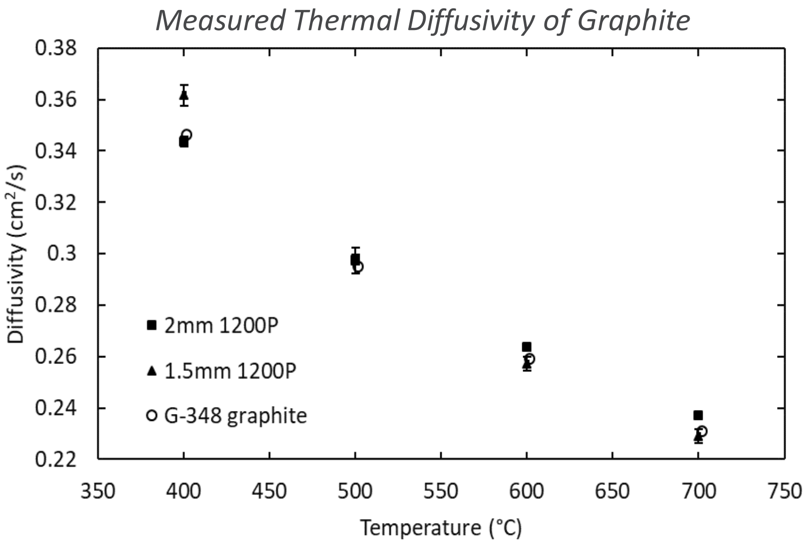


Photograph of LFA

THERMAL DIFFUSIVITY OF FLiNaK

- Measured FLiNaK diffusivities are similar to literature values
- Thermal diffusivity of graphite used for cell construction was verified to not affect the measured salt diffusivity (graphite 100-times more conductive)





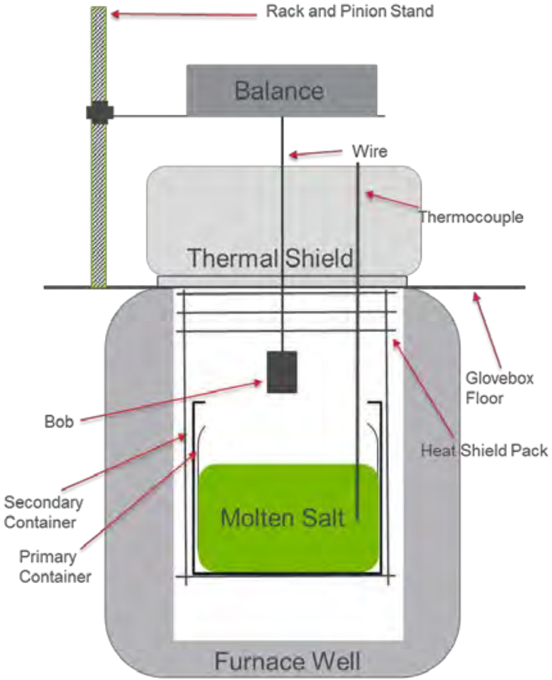
DENSITY MEASUREMENTS BY ARCHIMEDES METHOD

Archimedes Method

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

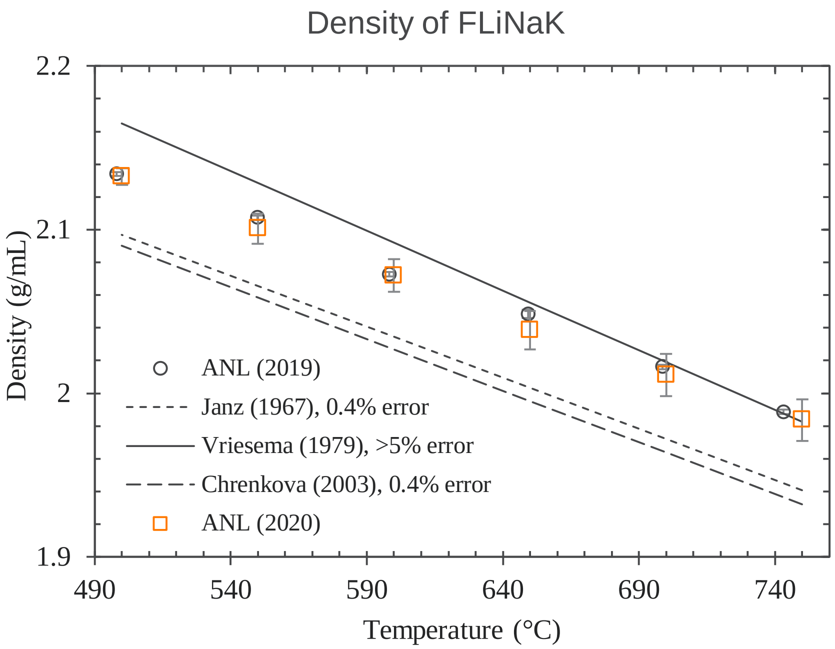
- Measure Δm due to immersion of bob to calculate density (ρ) of the fluid
- Use two bobs of different sizes to determine surface tension (σ) of the fluid

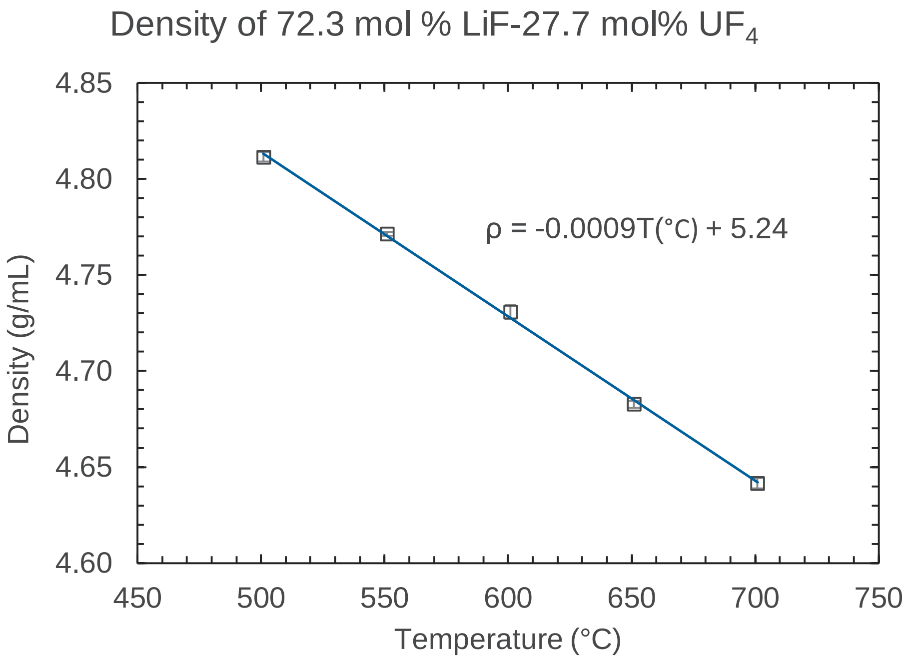
Photograph of Density Stand, Balance, Crucible and Bobs



Schematic of Densitometer Installed Over a Furnace Well

EXAMPLE DENSITY MEASUREMENTS



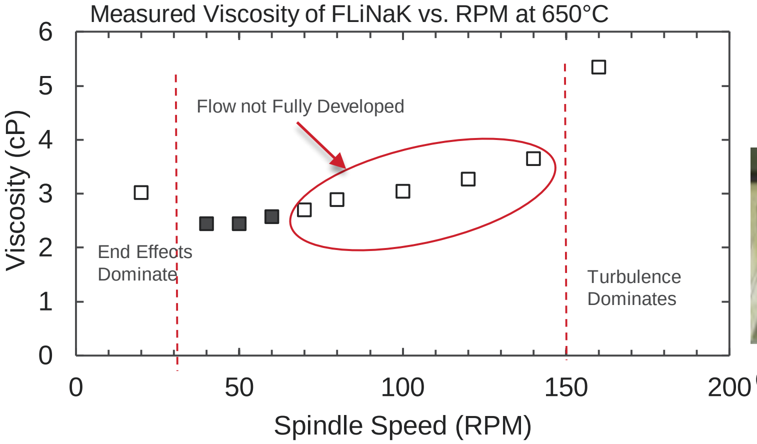


VISCOSITY MEASUREMENTS

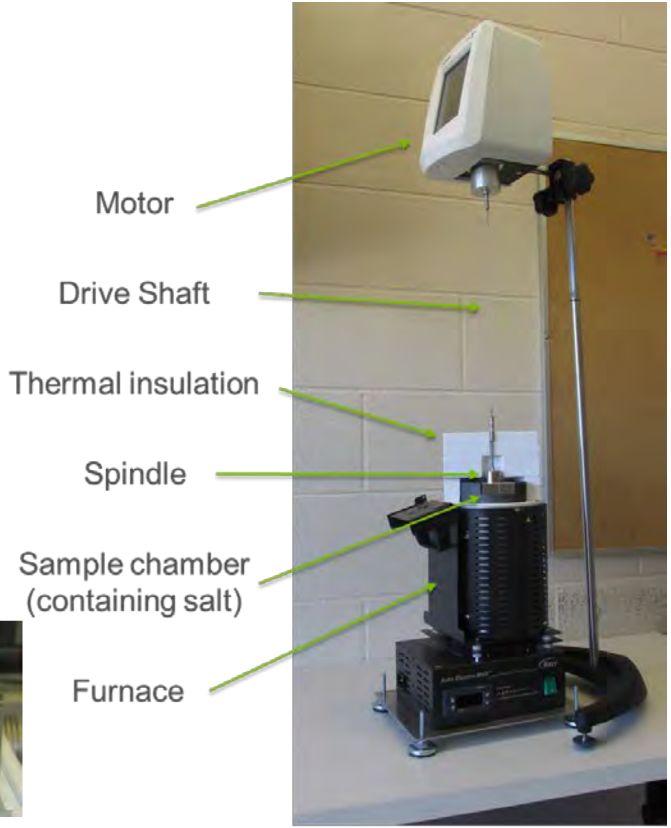
Rotational viscometer with a custom spindle

$$\eta = \frac{M\left(R_c^2 - R_b^2\right)}{8\pi^2 R_c^2 R_b^2 (L + L_0)\left(\frac{N}{60}\right)}$$

- Viscosity can be determined by measuring the torque (M) required to rotate a spindle at a specific speed (N)
- End effect, L_0, must be quantified by making measurements using spindles of different length



Custom Viscometer Spindles



X-Y positioning stage (Not shown)

SUMMARY

- Accurate measurements of these property values and the effects of salt composition are necessary to support design, licensing and operation of MSRs

- Measurements of FLiNaK and FLiBe property values are being used to standardize procedures and quantify expected precisions for measurements of:
  - Melting temperature and heat capacity
  - Thermal diffusivity and conductivity
  - Density, surface tension and volumetric thermal expansion
  - Viscosity

- Property measurements made for several salts systems of interest to developers
  - LiF – UF_4; NaF-BeF_2-UF_4-ThF_4

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Argonne Advanced Photon Source

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