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Argonne NATIONAL LABORATORY

Molten Salt Reactor PROGRAM

Effect of Impurities on Properties of Molten Salts

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Annual MSR Campaign Review Meeting 2-4 May 2023

Provide the data necessary to build a FOAK MSR by 2035

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

Thermophysical property data are needed to design, license and operate an MSR

No data exist for actual or simulated irradiated mixtures containing fission products, activation products, impurities, etc. for model validation

Actively engaging with industry, discussing their data and quality needs for MSR development

- **Coordinating GAIN, NEUP, and direct-funded activities with MSR developers**
- **Holding regular discussions to enhance collaboration between national labs and stakeholders.**
- **Coordinating with ORNL to incorporate new data and quality assessments into the Molten Salt Thermal Database**

FY23 Chemistry Activities

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

- Use of standardized methods
- Precision and accuracy of analyses determined based on measurements with reference salts
- Measured under a quality assurance program

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

High-quality measurements of chloride and fluoride salts with and without fission products

- Determine how fission product content changes molten salt properties

Properties being measured in FY23 include:

- Phase transition temperatures
- Specific heat
- Thermal diffusivity and thermal conductivity
- Compositional analysis including major and minor elements, and trace contamination including dissolved oxygen

Other Property Measurement Capabilities include:

- Viscosity
- Density
- Surface Tension
- Vapor Pressure
- Mass diffusion coefficients
- Activity measurements

Effect of Fission Products on Molten Salt Thermal Properties

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

- **Eutectic NaCl-UCl_3 with CsCl and CsI dopants**
- **Two doped FLiNaK salts were prepared representing high and low burn up**
  - **Inspired by depletion calculation results for MSRE**
  - **Same salts will be used in salt spill testing (S. Thomas on May 3rd, 2023)**
- **Will measure thermal behaviour, heat capacity and thermal diffusivity of all salts**

Doped NaCl-UCl_3 Composition

Compound	Concentration, mol %
NaCl	65
UCl_3	34
CsCl	0.9
CsI	0.01

Doped FLiNaK Compositions

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

Pure FLiNaK

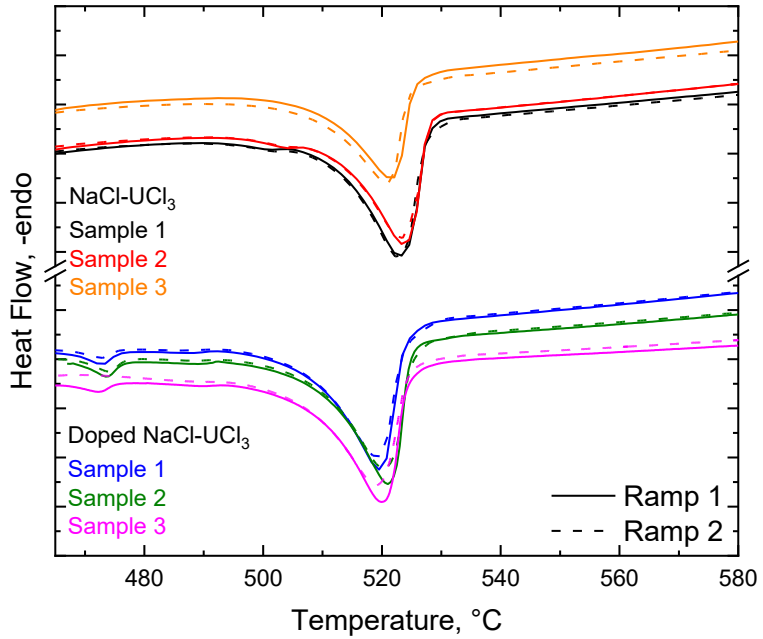
Doped FLiNaK (low burnup)

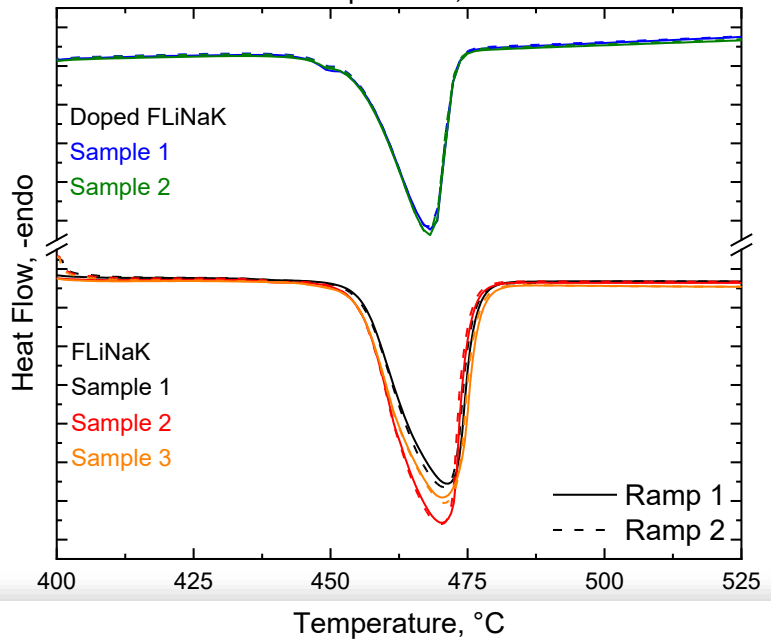
Doped FLiNaK (high burnup)

Thermal Behavior of Salts with Fission Products

- **Measured thermal behavior of salt samples encapsulated in sealed gold cells by differential scanning calorimetry (DSC)**
  - **Duplicate heating cycles of each sample at 5 °C/min are shown by solid and dashed curves**
  - **Accuracy of the measured temperature is ± 2 °C established through regular calibrations of the DSC using five reference metals**
- **Dopants shift the eutectic transition to slightly lower temperatures**
- **Additional transitions are observed in doped salt**

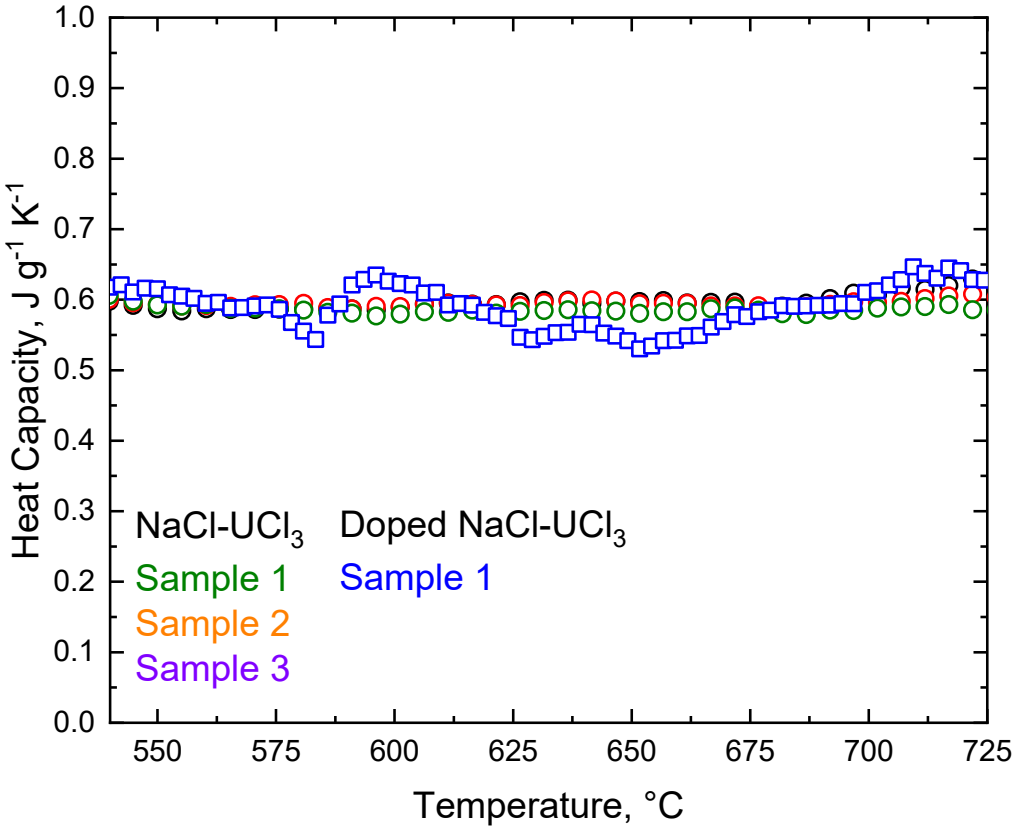
Salt		Transition 1, °C Onset	Transition 2, °C Onset	Eutectic, °C Onset
$NaCl\text{-}UCl_3$	average	-	-	510.7
	1 s			1.5
Doped $NaCl\text{-}UCl_3$	average	468.1	481.1	508.7
	1 s	0.9	1.7	1.3
FLiNaK	average	-	-	456.2
	1 s			0.6
Doped FLiNaK 1 (Low Burn-Up)	average	445.4	-	454.4
	1 s	0.1		0.1





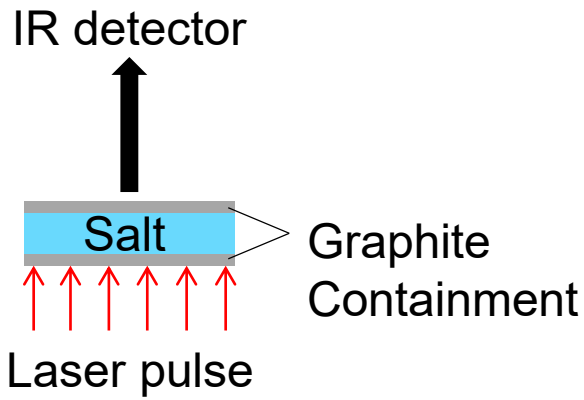
$NaCl\text{-}UCl_3$ Heat Capacity

- **Heat capacity measured according to ASTM E1269, the procedure consists of three analyses:**
  - **Instrumental baseline run using two empty weight-matched crucibles**
  - **Sapphire standard of known mass and heat capacity and an empty crucible**
  - **Salt sample and an empty crucible**
- **The three analyses are made using a linear ramp at 10 K min^{-1}**
- **Measured heat capacity precision is ~5%**
- **No detectable difference in heat capacity with doped salt**
  - **More measurements are being made to confirm**

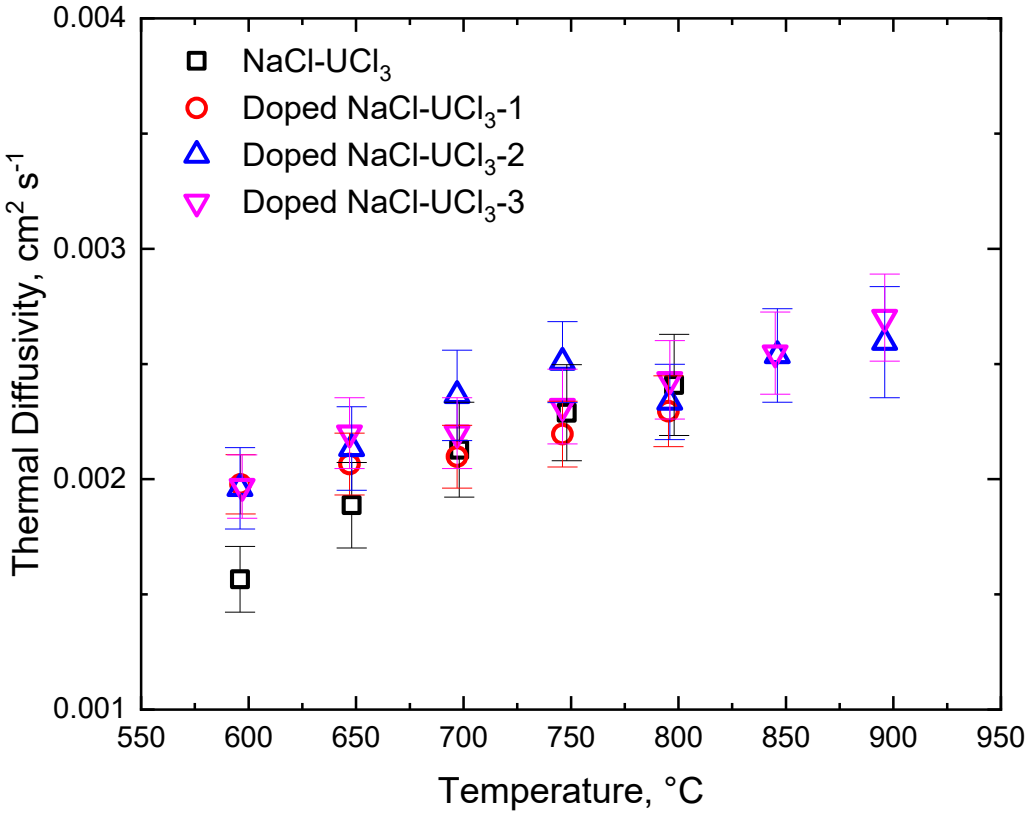


$NaCl\text{-}UCl_3$ Thermal Diffusivity

- **Measured thermal diffusivity by laser flash analysis**
  - **Samples of salt encapsulated in graphite cells**
  - **Three laser pulses fired at the underside of the sample at each temperature**
  - **Clark and Taylor model used to determine thermal diffusivity from measured thermal response**
    - **Corrects for radiative heat loss**

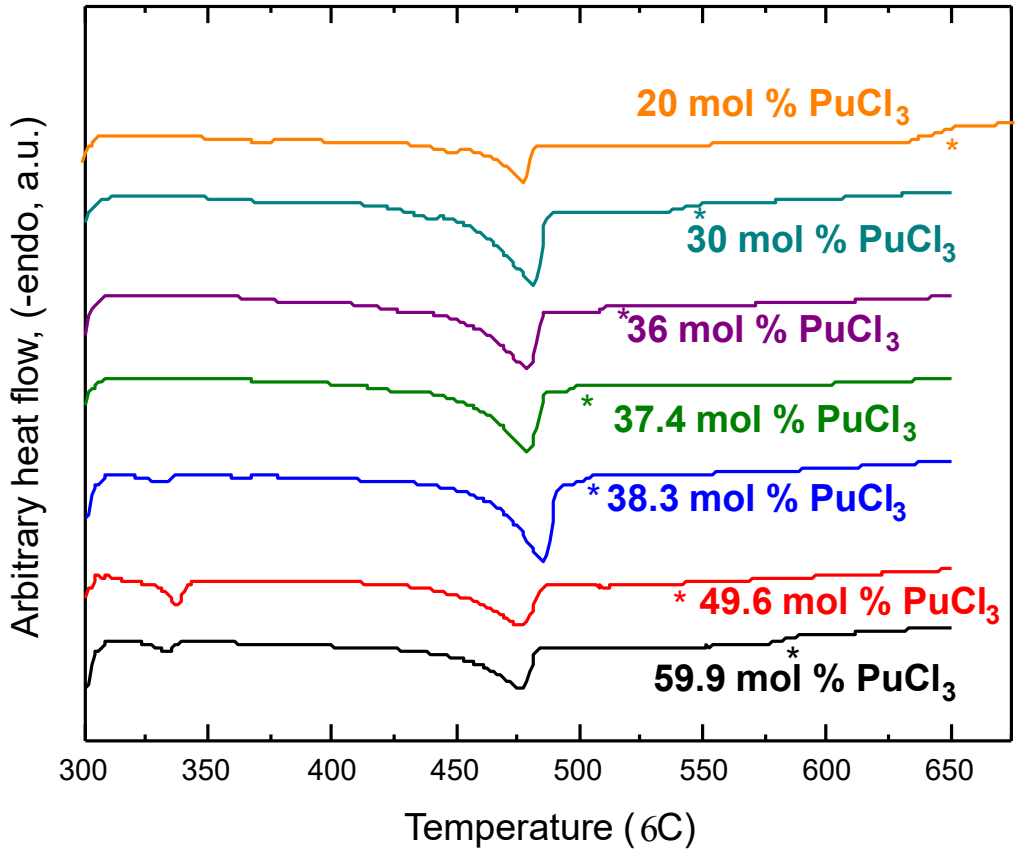


- **Uncertainties of three measurements of each sample at each temperature span 1.3-5.8% (error bars)**
- **Additional measurements of $NaCl\text{-}UCl_3$ without dopants at 850 and 900 °C will be made to determine effect of dopants on thermal diffusivity**



FY22 Work: NaCl-$PuCl_3$ Measurements

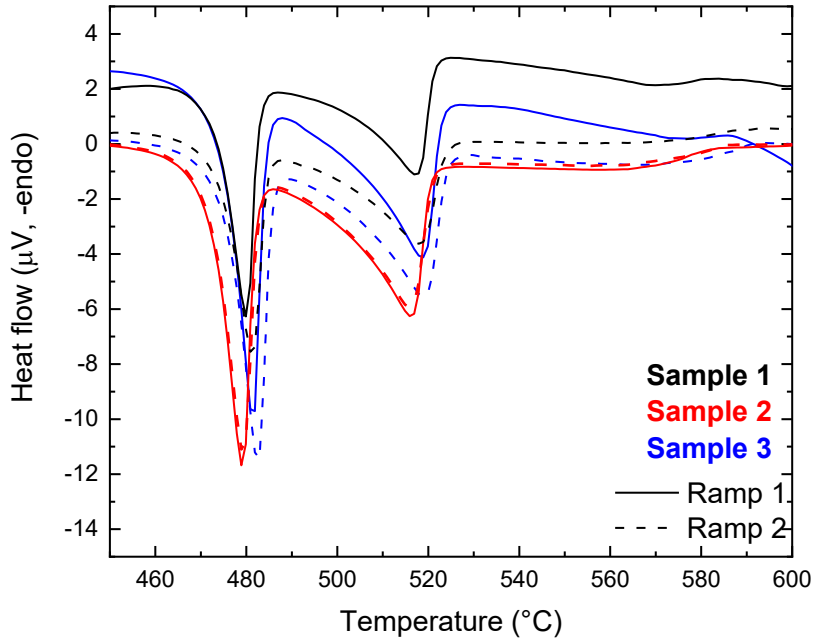
- **Seven compositions of NaCl-$PuCl_3$ between 20 and 60 mol %$PuCl_3$ were synthesized and measured for thermal behavior**
- **Eutectic composition between 37.4 and 38.3 mol %**
- **Low-temperature transitions were observed**
  - Analogous to other alkali chloride-$PuCl_3$ systems
- **XRD and compositional analyses are in progress**



Property Measurements of the NaCl-$PuCl_3$ Molten Salt System" Technical Report. ANL/CFCT-22/43

Measured Transition Temperatures of Off-Eutectic NaCl-KCl-UCl_3

- **Synthesized 50.9 mol % NaCl, 24.4 mol % KCl, 24.7 mol % UCl_3 – confirmed composition by ICP-OES**
- **Three samples of salt encapsulated in sealed gold cells analyzed by DSC for thermal behavior**
  - **Performed duplicate heating cycles of each sample at 5 °C/min (solid and dashed curves)**
- **Accuracy of the measured temperature is 2 °C established through regular calibrations of the DSC using five reference metals**



Sample No.	Mass, mg	Ramp	Temperature (°C)		
			Transition 1 Onset	Transition 2 Onset	Liquidus Endpoint
1	21.89	1	473.0	505.1	583.0
		2	473.9	503.1	587.1
2	22.04	1	472.1	504.6	586.9
		2	472.0	503.6	587.0
3	21.23	1	474.6	507.9	587.3
		2	475.1	505.3	590.7
		Average	474	505	587.0
		1 s	1	2	2

"Property Measurements of NaCl-UCl_3 and NaCl-KCl-UCl_3 Molten Salts" Technical Report ANL/CFCT-22/45

$NaCl\text{-}KCl\text{-}UCl_3$ Measurements vs Modeling

Comparison between transition temperatures measured at Argonne and calculated by different models for $NaCl\text{-}KCl\text{-}UCl_3$, delta T (measured-calculated) values listed in parentheses

Transition	Temp. (°C)				Phase transition reaction
	measured	MSTDB-TC V2.0	MSTDB-TC V1.2	Rose and Thomas (2021)	
T1	**474 ± 2**	361 (+112)	465 (+8)	460 (+13)	$(Na,K)Cl + K_2UCl_5 + UCl_3 \rightarrow Liquid + (Na,K)Cl + K_2UCl_5$
T2	**505 ± 2**	410 (+95)	478 (+27)	517 (-12)	$Liquid + (Na,K)Cl + K_2UCl_5 \rightarrow Liquid + (Na,K)Cl$
T3	**587 ± 2**	556 (+31)	500 (+87)	559 (+28)	$Liquid + (Na,K)Cl \rightarrow Liquid$
Total absolute deviation:		238	122	53	

- **Predictions of transition temperatures made using data from binary subsystems in Rose and Thomas (2021) and MSTDB-TC V1.2 are more accurate than predictions made using MSTDB-TC V2.0 which included new data.**
- **All data included in MSR campaign-managed databases need to undergo a transparent quality assessment process to build consensus.**
- **A data-based method to quantify the reliability of the model predictions is needed**

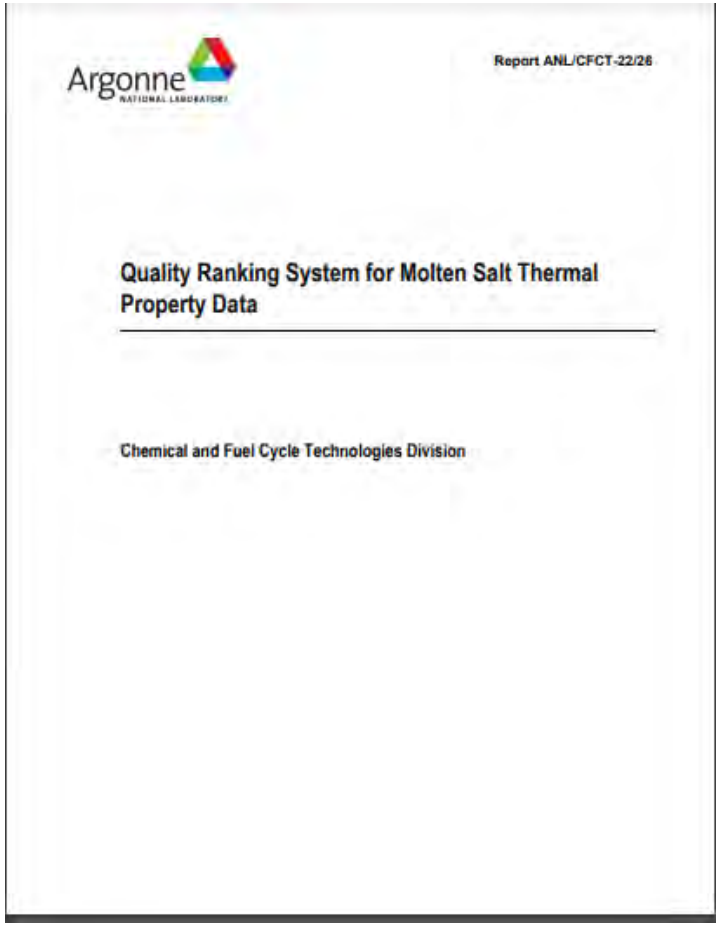
FY 23 Data Quality Tasks

- **Develop a quality ranking system for data in MSTDB-TC and –TP**
  - **Report ANL/CFCT-22/26 described a quality assessment process and ranking system for thermophysical data**
  - **Milestone M3AT-23AN070512 will describe an analogous process for thermochemical data**
- **Working closely with ORNL to support application of quality ranking system to MSTDB-TP**
- **Host a workshop on uncertainty in molten salt properties measurements and predictions**

Quality Assessment Process for Thermophysical Property Data

Recommend an assessment across six aspects for existing and new data for the MSTDB-TP:

1. **Method**
   - Appropriate and applied correctly, ideally a standardized method
2. **Calibrations**
   - Verified instrument performance with certified standard materials
3. **Salt Composition Analysis**
   - Replicate analyses including anion and impurity concentrations
4. **Environmental Controls**
   - Control and stability of temperature and atmosphere
5. **Measurement Precision**
   - Uncertainty quantified with at least three replicate measurements
6. **Verifiability of Property Determination- capstone criterion**
   - Value can be independently verified from the reported data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Report ANL/CFCT-22/26

Quality Ranking System for Molten Salt Thermal Property Data

Chemical and Fuel Cycle Technologies Division

Report on data quality assessment and ranking approach: ANL/CFCT-22/26

Quality Ranking System for Thermophysical Property Data

- **Datasets are ranked as either high quality (H), moderate quality (M) or incomplete (I) with regard to each of the six aspects.**

- **Overall Rankings for Data Entries then depend on these six aspect assessments:**

  Rank H: Data is ranked H or M for all quality aspects and property verification ranked H
  Rank M: Data ranked H or M for two or more quality aspects and property verification ranked H or M.
  Rank U: Data uncertainties do not warrant quantitative use of reported property value.

- **Notes on application to MSTDB:**
  - Should be applied to both new and existing data sets
  - Highest ranked data set can be identified in the database
  - Working closely with ORNL to apply system to data sets in MSTDB-TP

Upcoming milestone M3AT-23AN070512 for an analogous process for thermochemical data

Workshop on Uncertainty in Molten Salt Thermal Property Values and Predictions

July 2023

Identify best practices for quantifying confidence levels for property model predictions applied to multicomponent salts based on uncertainty in the models used to predict property values.

Best practices for taking the uncertainty in modeled property values into account in system model outputs.

Divided into 4 topic areas:

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

Will be inviting participants from national labs, universities and industry

Summary of Accomplishments and Milestones

All milestones are on schedule

Workshop is planned for July 2023

- Measuring properties of fission product doped salts to determine how fission product content changes salt properties
- Developing a quality ranking system for data in MSTDB
- Hosting a workshop on uncertainty in molten salt properties measurements and predictions
- Meeting bi-weekly with ORNL colleagues to support QA of MSTDB-TP

Milestone Number	Title	Due
M3AT-23AN070512	Quality Ranking System for TC data	6/30/23
M3AT-23AN0705011	Effect of Cs and I on TP Properties of MSs	9/15/23
M3AT-23AN0705013	Workshop Report	9/29/23
M3AT-23AN0705014	Support Application of quality ranking to MSTDBs	12/15/2023

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Thank you

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