BRIDGING THE GAP BETWEEN EXPERIMENTS AND MODELING TO IMPROVE THE DESIGN OF MOLTEN SALT REACTORS

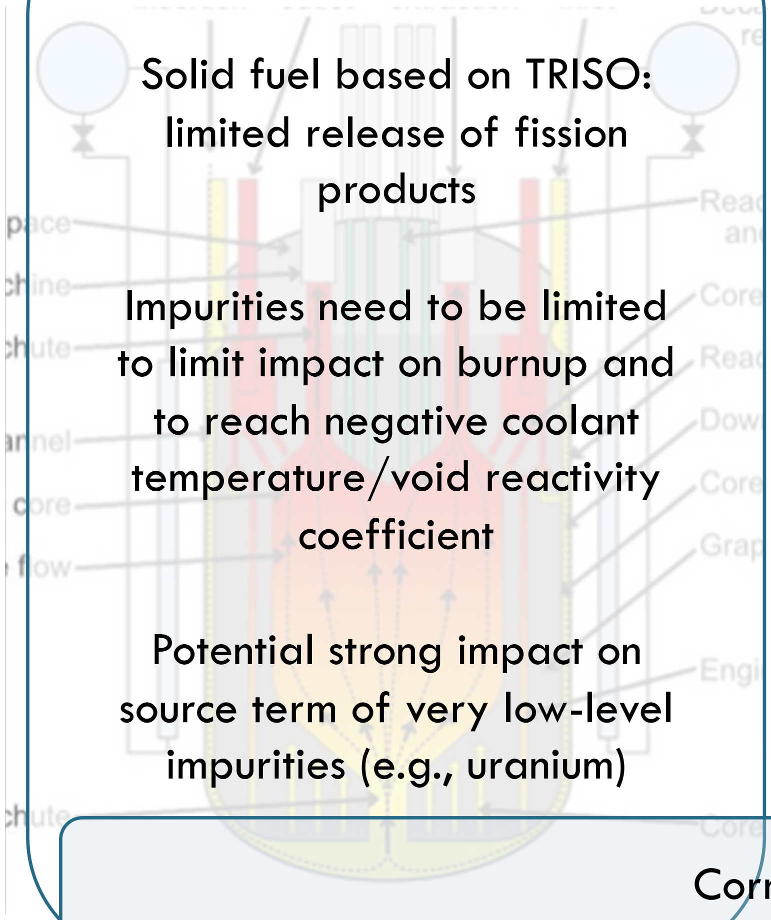
MSR Campaign Review Meeting
April 18, 2024

What is the impact of impurities and fission products in the salt on the performance of molten salt reactors?

Kairos Power

Fluoride-cooled High-temperature Reactor (FHR)

Solid fuel MSR



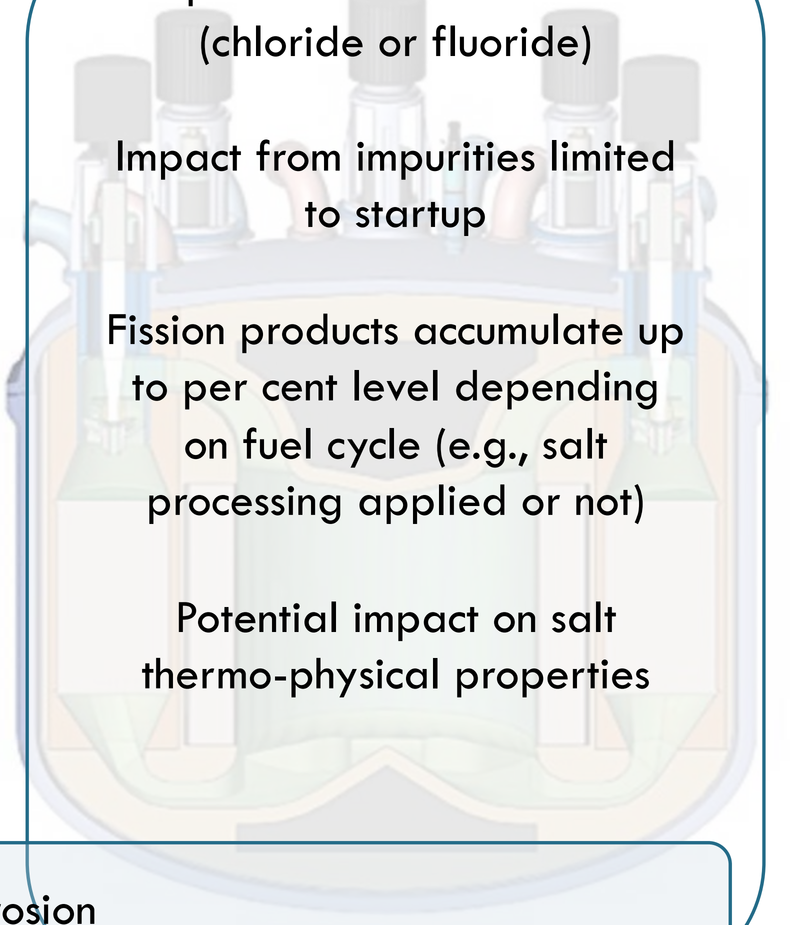
Molten salt coolant (fluoride)

Solid fuel based on TRISO: limited release of fission products

Impurities need to be limited to limit impact on burnup and to reach negative coolant temperature/void reactivity coefficient

Potential strong impact on source term of very low-level impurities (e.g., uranium)

Liquid fuel MSR



Liquid fuel dissolved in salt (chloride or fluoride)

Impact from impurities limited to startup

Fission products accumulate up to per cent level depending on fuel cycle (e.g., salt processing applied or not)

Potential impact on salt thermo-physical properties

Corrosion

TerraPower™

Molten Chloride Fast Reactor (MCFR)

Design	FHR	MCFR
Design Parameters	Burnup Reactivity coefficients	Peak temperatures during AOOs, DBAs, and BDBAs
Salt systems investigated	FLiBe + Activation products of impurities: 10-1000 ppm + Anionic impurities (e.g., O^{2-}, OH^-, CO_3^{2-}): 10 - 1000 ppm	UCl_3-NaCl eutectic + Fission products: 1-5 mol%
Properties	Volatility, activity coefficient, and ion diffusivity of transition activation products (e.g., Co, Pb) and their sensitivity to anionic impurities	Liquid density Thermal expansivity Viscosity Thermal diffusivity Heat capacity
Corrosion	Effect of anionic impurities on corrosion in flow loops, conditional upon effects of applied stress & manufacturing conditions	Effect of fission products on mechanical properties, conditional upon effects of applied stress & manufacturing conditions
Project output: Operational bounds/design guidelines for	Transition metal impurities (accumulated inventory, concentration) Different possible metrics for oxygen impurities (total O, OH- concentration, etc.).	Different possible metrics for FPs (groups of FPs, total inventory, total concentration)

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INL

Engineering scale modeling

Burnup/activation, sensitivity analysis, uncertainty quantification, multi-physics analysis of AOOs, DBEs and BDBAs, source term calculations

Experimental measurements

Experimental measurements of salt properties with fission products and of dilute species volatility and activity

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Los Alamos
NATIONAL LABORATORY
EST.1943

ASU

Molten Salt Reactors

TerraPower

Kairos Power

Atomistic scale modeling

Molecular dynamics with machine learning potentials (MLPs) to find features of the molecular structure correlated with properties of interest for high-throughput screening.

WISCONSIN
UNIVERSITY OF WISCONSIN–MADISON

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Corrosion

Corrosion kinetics of structural materials as a function of salt composition and localized corrosion under the influence of stress and environment.

Pacific Northwest
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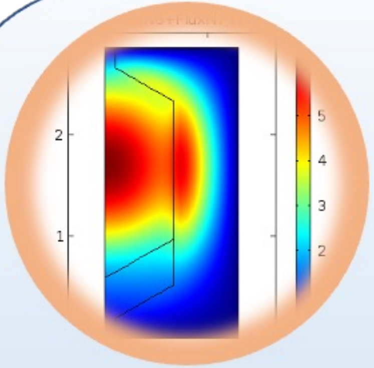
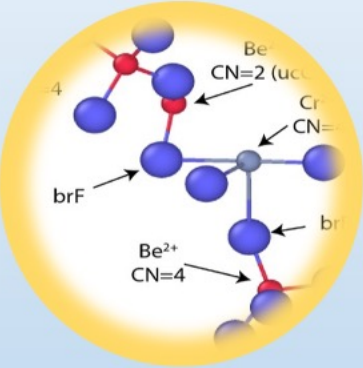
Phase 1 (12 months)



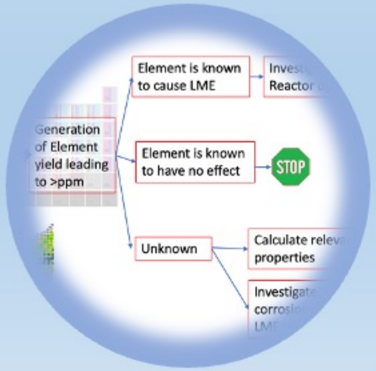
Task 1.1: burnup/activation, sensitivity to properties

Task 1.2: correlation of molecular structure and properties



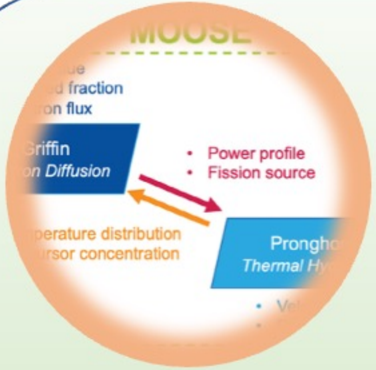
Task 1.3: screening experiments to identify trends

Task 1.4: screening of corrosion impact



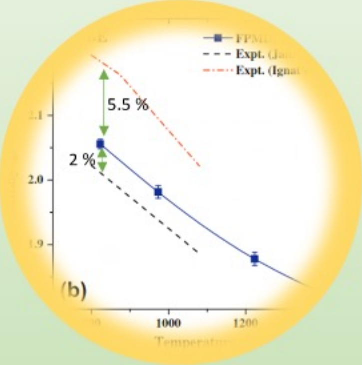
Elements and properties of main impact

Phase 2 (24 months)



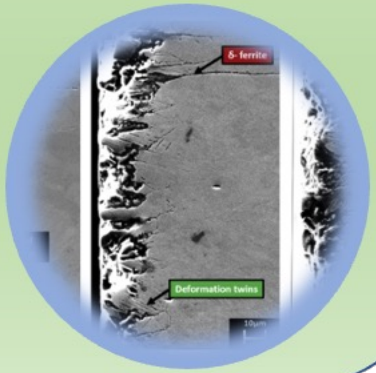
Task 2.1: multi-physics with composition dependent properties

Task 2.2: correlations for properties as a function of FP/solute concentration

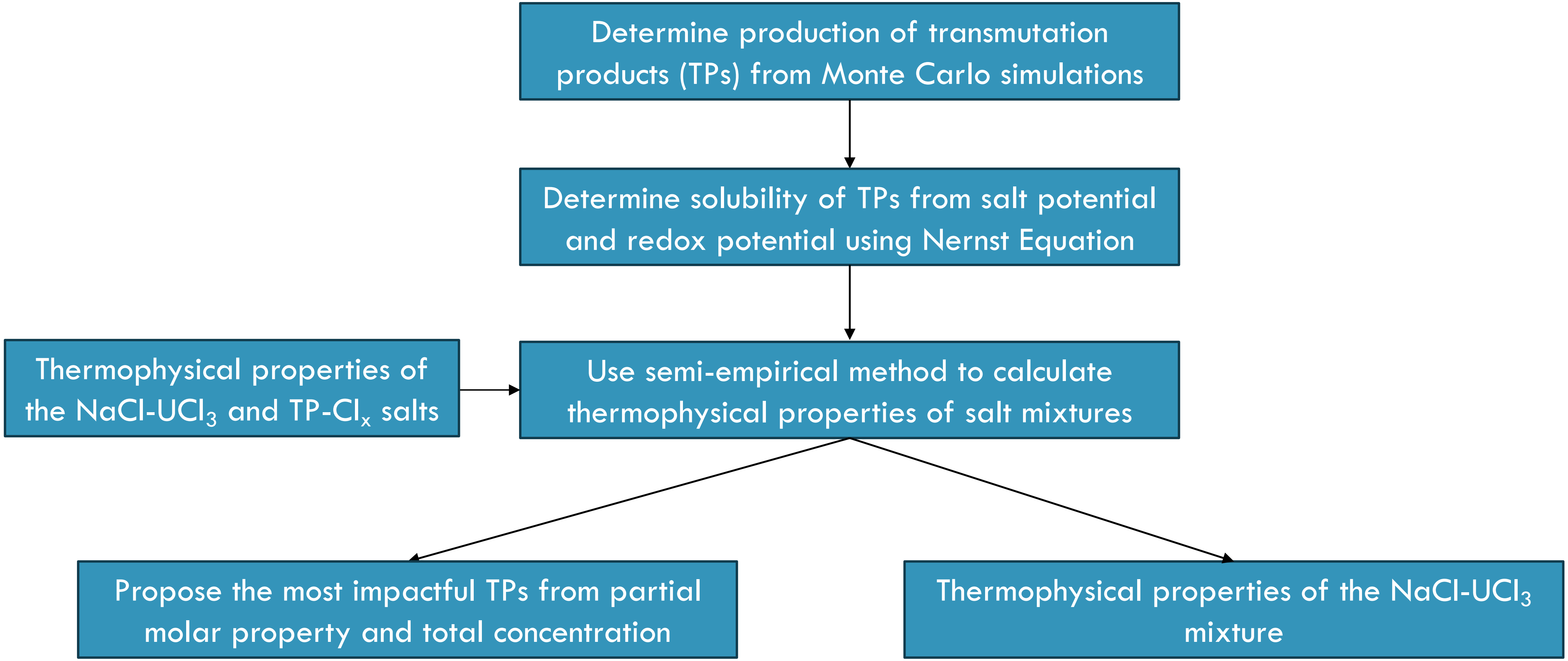


Task 2.3: properties measurements

Task 2.4: corrosion mechanisms; corrosion under stress



DOWN SELECTION PROCESS OF MOST RELEVANT ELEMENTS



Determine production of transmutation products (TPs) from Monte Carlo simulations

Determine solubility of TPs from salt potential and redox potential using Nernst Equation

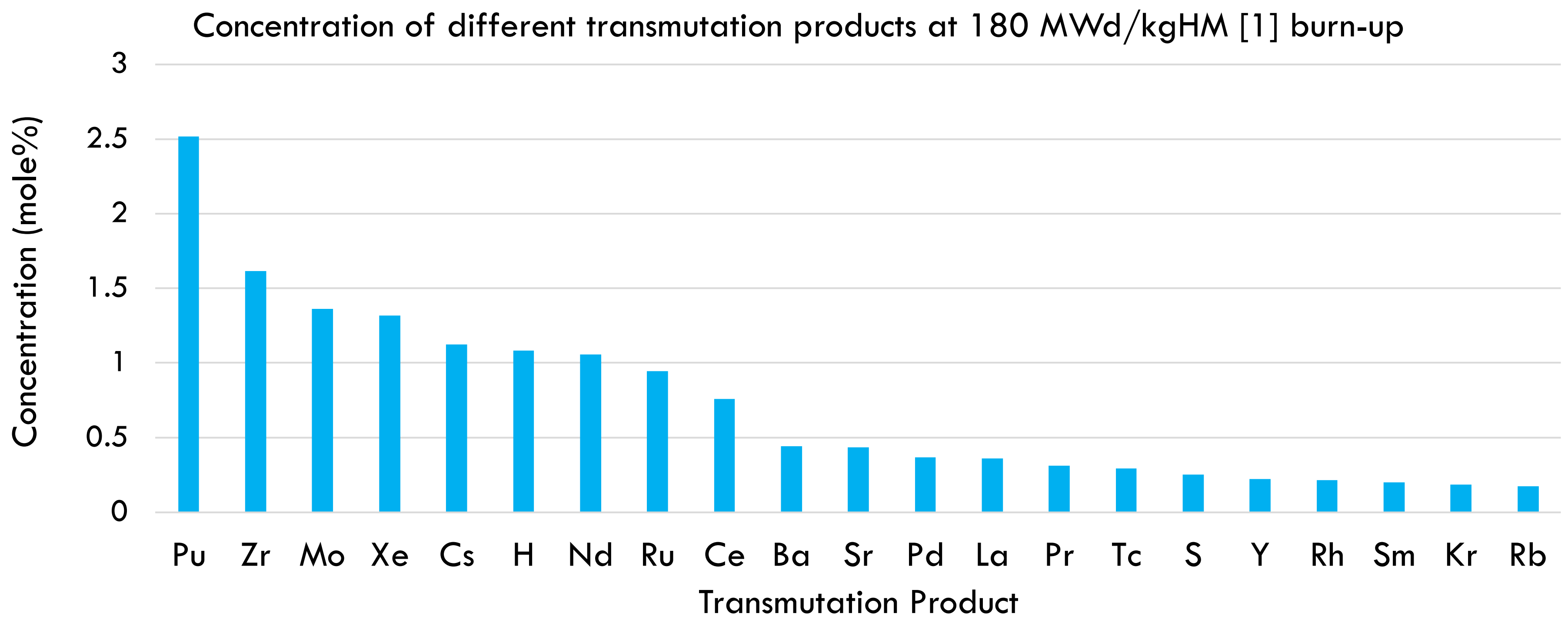
Thermophysical properties of the NaCl-UCl_3 and TP-Cl_x salts

Use semi-empirical method to calculate thermophysical properties of salt mixtures

Propose the most impactful TPs from partial molar property and total concentration

Thermophysical properties of the NaCl-UCl_3 mixture

CONCENTRATION OF DIFFERENT TRANSMUTATION PRODUCTS



- Initial salt composition — Eutectic NaCl-UCl_3 (0.67 NaCl-0.33 UCl_3)
- After 180 MWd/kgHM burn-up period, the salt composition — 0.74 NaCl-0.26 UCl_3 + TPs

[1] Molten Chloride Fast Reactor Technology - TerraPower

REDOX POTENTIAL AND SOLUBILITY

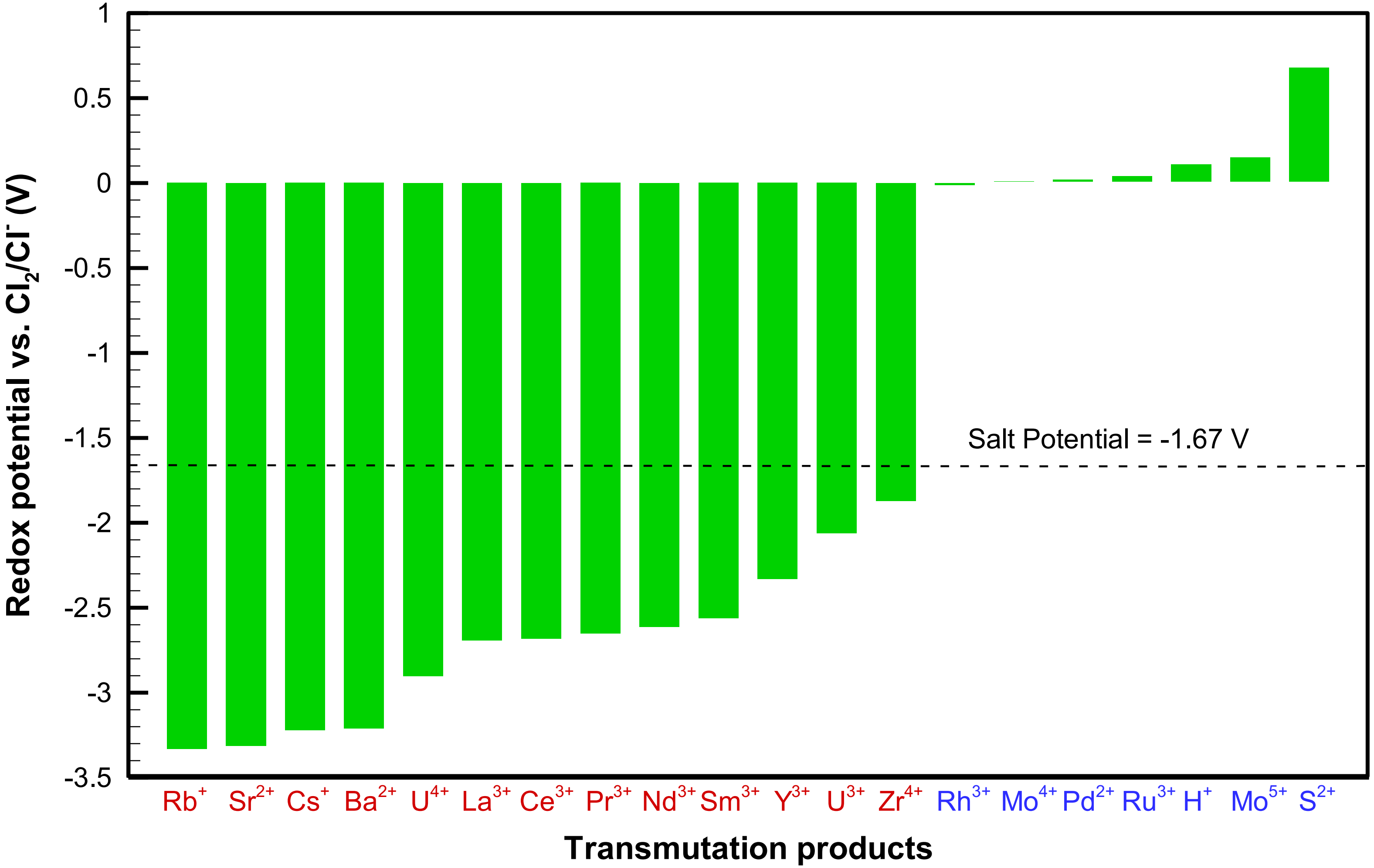
- The salt potential of the eutectic NaCl-UCl_3 system was calculated from thermodynamic relations and using the $\frac{[U^{4+}]}{[U^{3+}]}$ ratio suggested by TerraPower.
- The salt potential ranges from **-1.76 V to -1.67 V** for $4 \times 10^{-4} < \frac{[U^{4+}]}{[U^{3+}]} < 1 \times 10^{-3}$
- The redox potential of the TPs was calculated from standard state thermodynamic quantity.
- Nernst equation was followed to determine the solubility of the transmutation products.

$$[M] = \exp\left(\frac{n_e(V_S - V_{\mathrm{M}})}{k_B T}\right)$$

$[M]$ - solubility of any transmutation product M,
V_S – salt potential
V_{M} - redox potential.

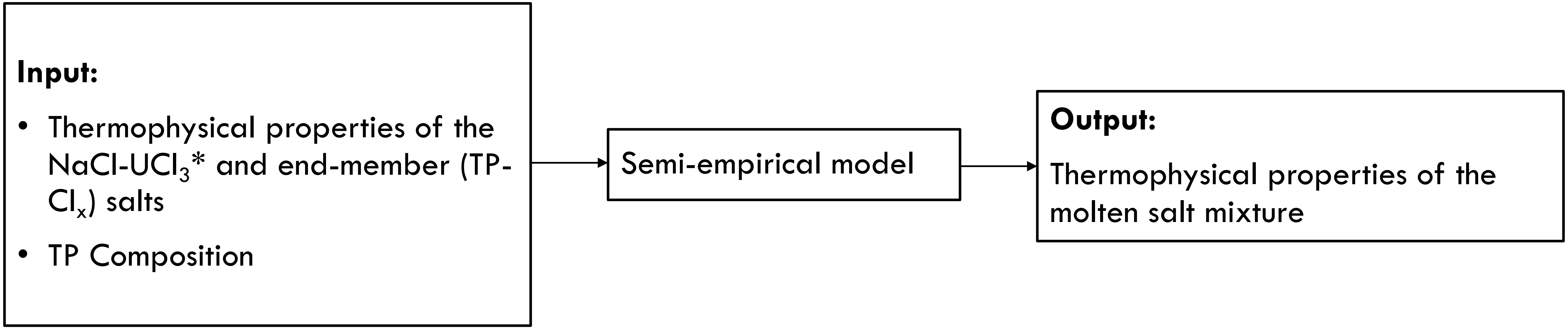
[2] NIST-JANAF Thermochemical Tables
[3] Barin, I., Knacke, O., & Kubaschewski, O. (2013). *Thermochemical properties of inorganic substances: supplement*. Springer Science & Business Media.

REDOX POTENTIAL AND OXIDATION OF TRANSMUTATION PRODUCTS



The elements in red and blue will be oxidized and non-oxidized thermodynamically

THERMOPHYSICAL PROPERTIES OF SALT MIXTURE FROM SEMI-EMPIRICAL MODELS



Input:

- Thermophysical properties of the NaCl-UCl_3* and end-member (TP-Cl_x) salts
- TP Composition

Semi-empirical model

Output:

Thermophysical properties of the molten salt mixture

Composition: 74% NaCl-26%UCl_3

[4] T. Bauer, and A. Bonk, Int. J. Thermophys. **39**(12), 134 (2018).
[5] G.P. Smith, and G.F. Petersen, J. Chem. Eng. Data **6**(4), 493–496 (1961).
[6] A. Saini, et al., RSC Adv. **6**(114), 113657–113662 (2016).
[7] A.A. Redkin, et al., J. Phys. Chem. B **119**(2), 509–512 (2015).
[8] H. Yang, et al., Sol. Energy **256,** 158–178 (2023).
[9] A.E. Gheribi, et al., Sol. Energy Mater. Sol. Cells **236,** 111478 (2022).

ESTIMATED CHANGES IN SALT PROPERTIES

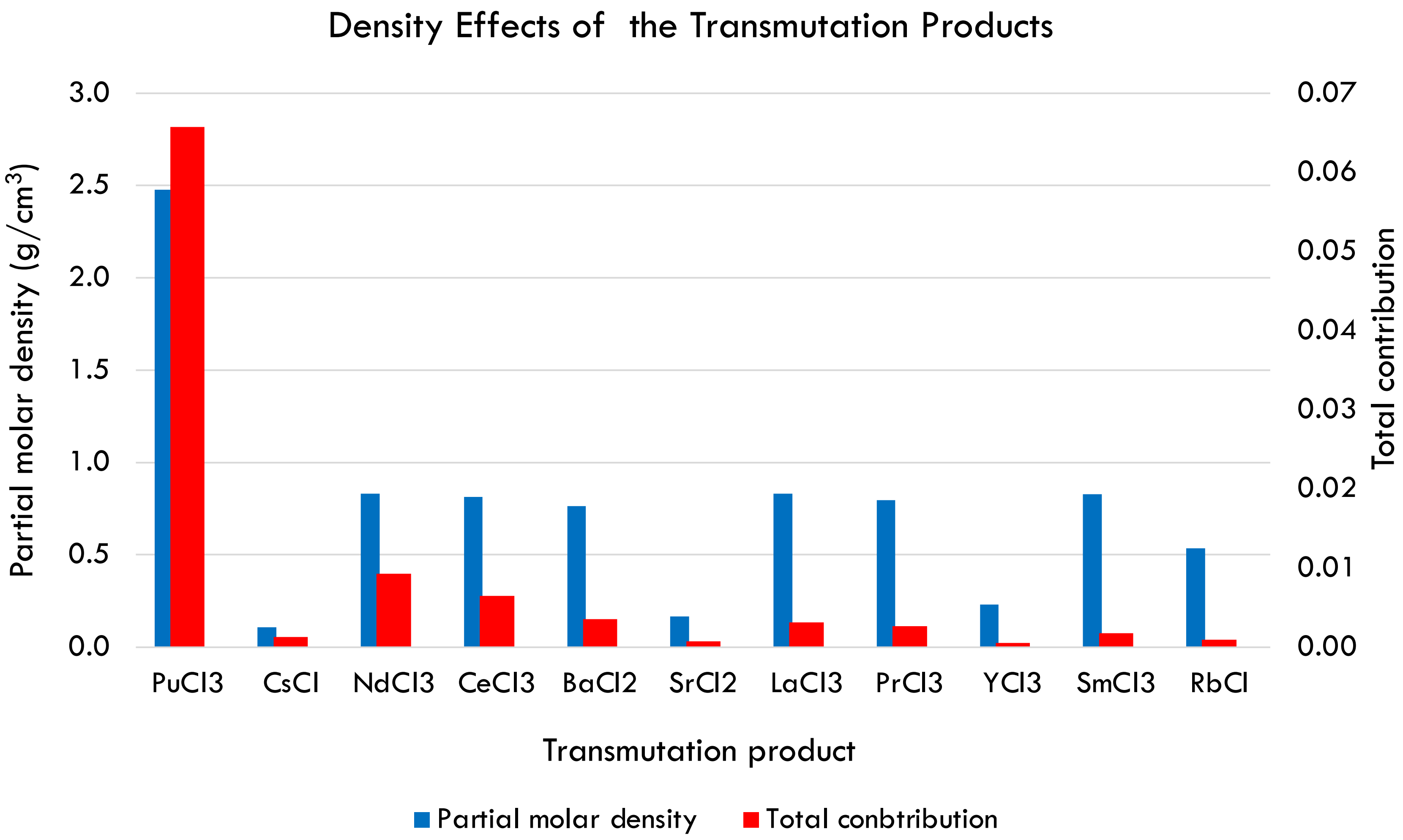
Properties**	Eutectic mixture	After burn-up time	% Change	74%NaCl-26%UCl_3
Density (g/cm^3)	2.930	2.588	-11.69%	2.503
Viscosity (mPa-s)	1.120	1.065	-4.91%*	0.978
Heat capacity (J/mol-K)	95.840	92.176	-3.82%	88.822
Thermal conductivity (W/m-K)	0.318	0.288	-9.46%	0.276

*Mean value of all the chloride salt viscosity data from ref [10] at 1250 K is used for $PuCl_3$. The total change in viscosity lies between -7.78% to -3.59% for viscosity of $PuCl_3$ equal to maximum and minimum viscosity of other chloride salts.

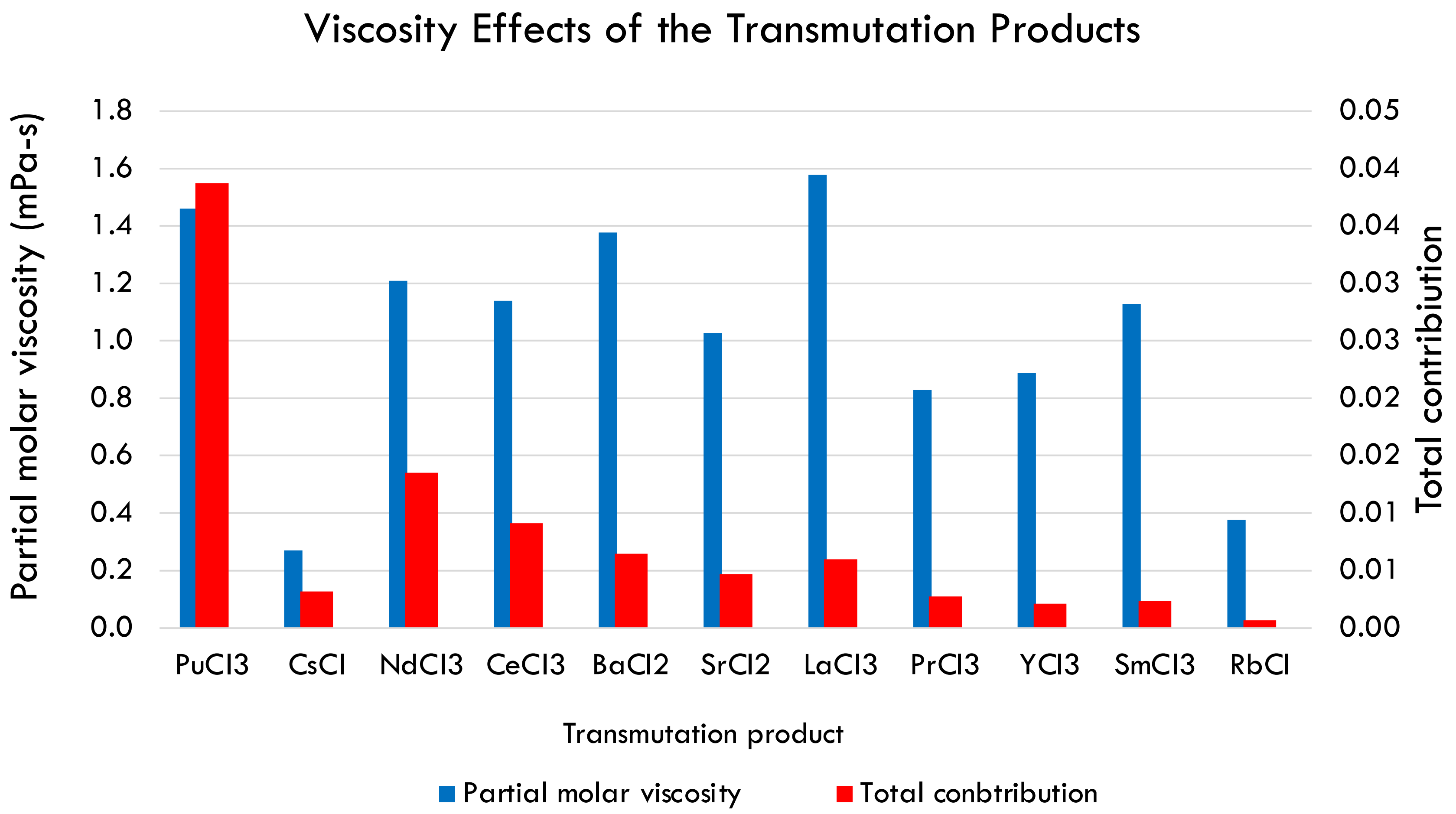
** $ZrCl_4$ was not included in our calculation (in progress, volatility very high).

[10] Janz, G. J. (1967). *Molten salts handbook*.

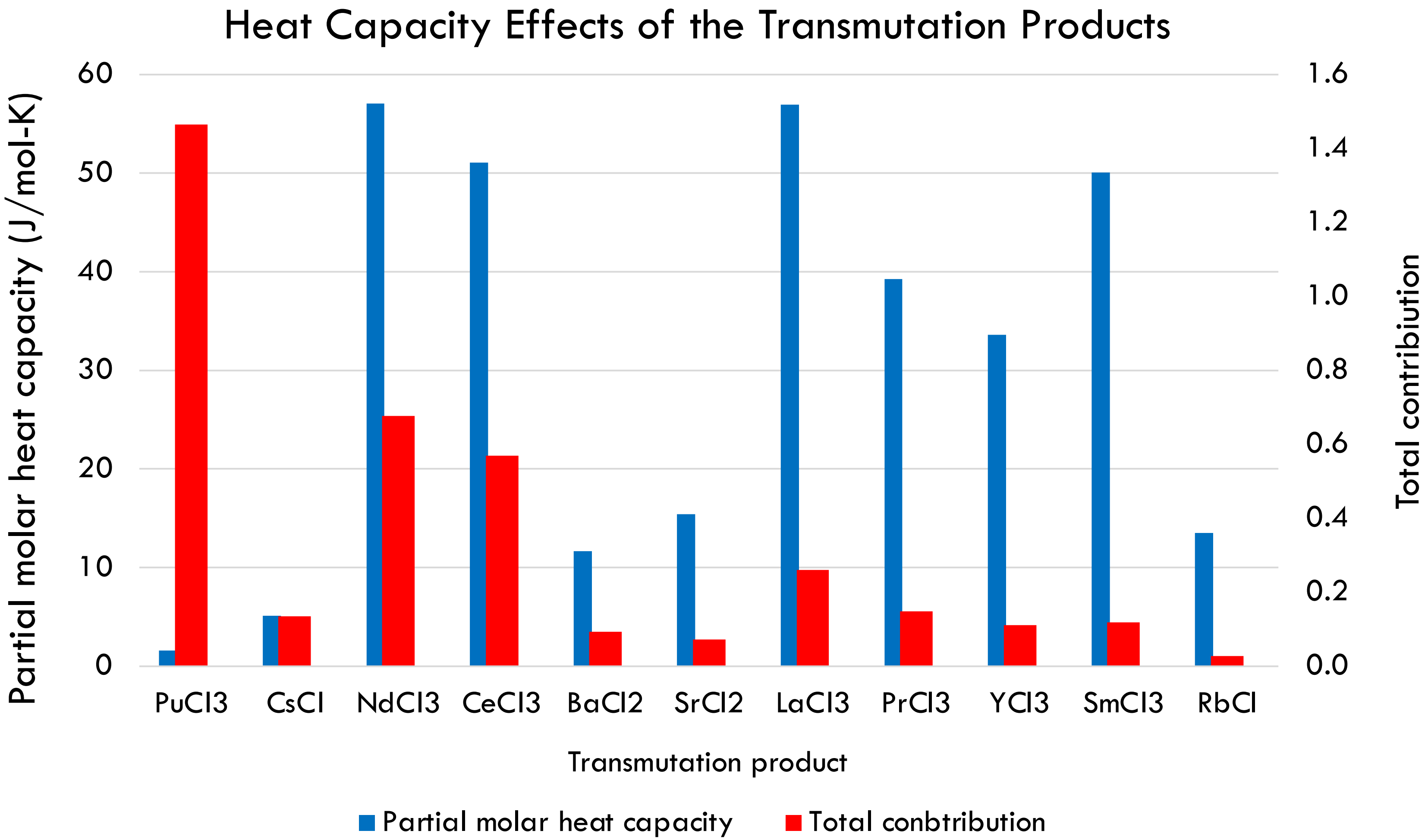
PARTIAL MOLAR DENSITY



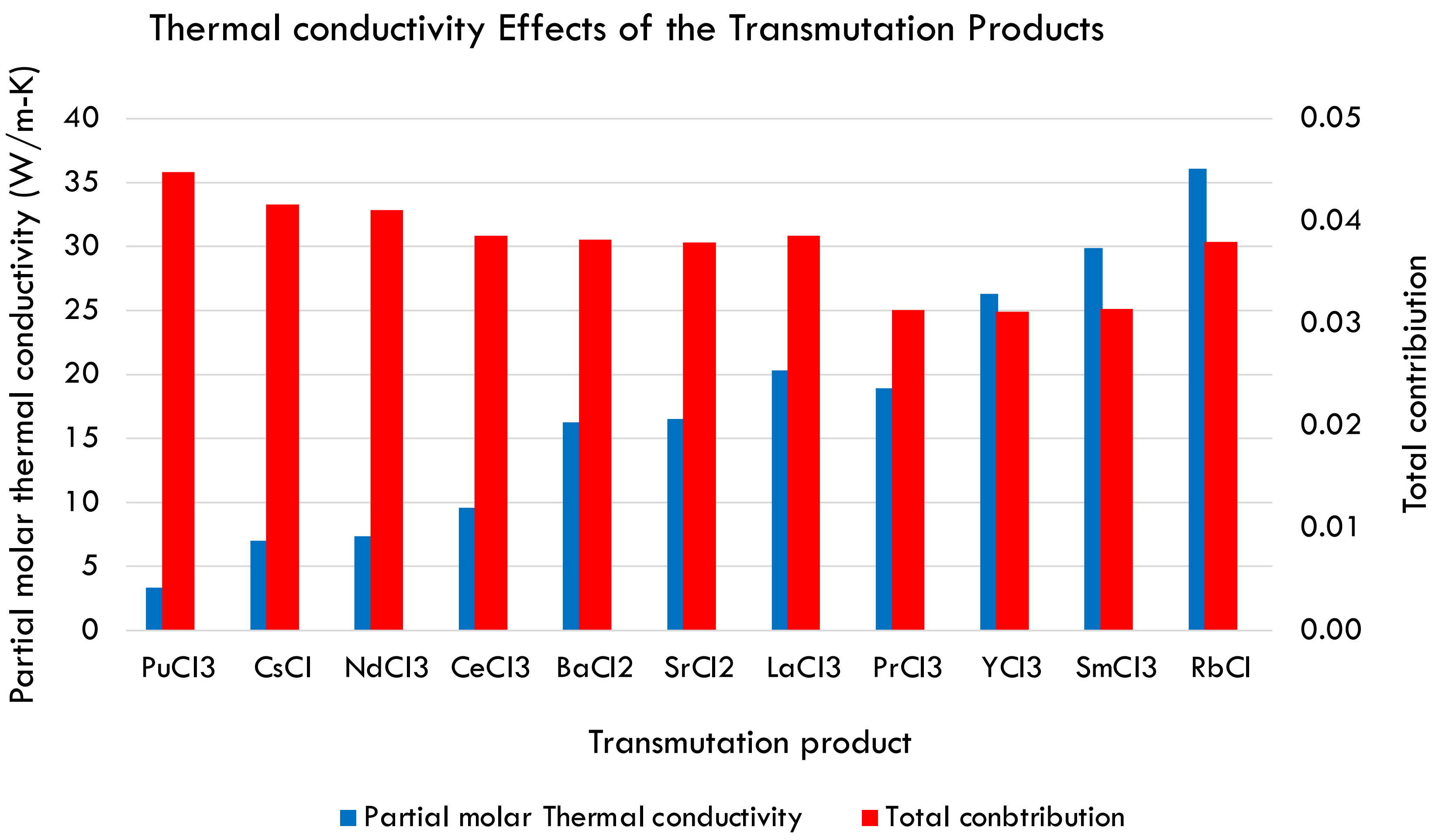
PARTIAL MOLAR VISCOSITY



PARTIAL MOLAR HEAT CAPACITY



PARTIAL MOLAR THERMAL CONDUCTIVITY



“MOST IMPACTFUL” TRANSMUTATION PRODUCTS

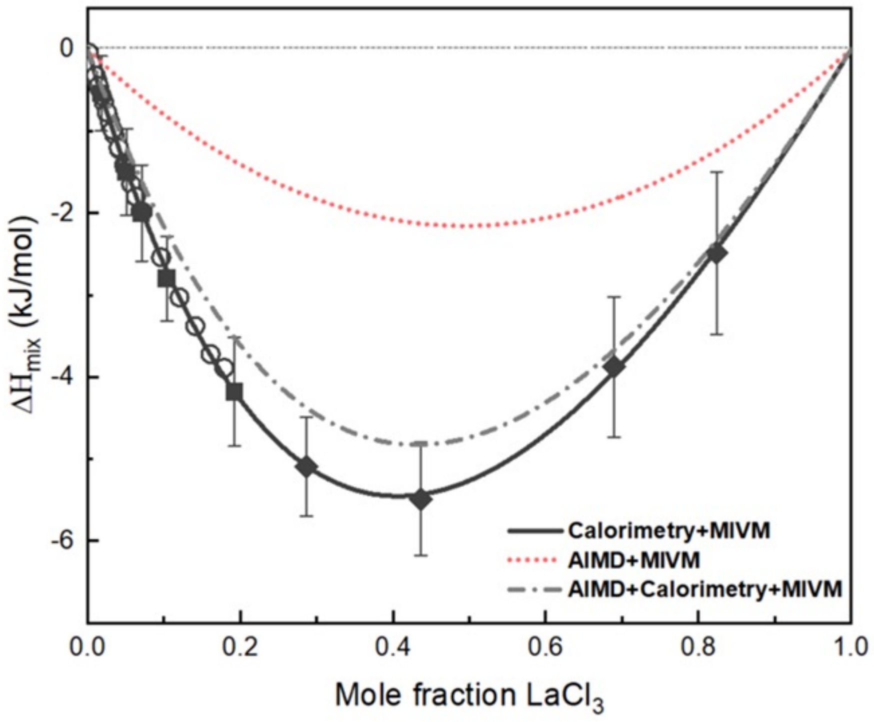
Group	Most impactful TP
Overall	La
Lanthanide	Nd, La
Actinide	Pu
4+ oxidation state	Zr
3+ oxidation state	Nd, La
2+ oxidation state	Ba
1+ oxidation state	Cs

MAJOR APPROXIMATIONS

- No unexpected physics in the salt environment was considered such as
  - No volatilization of TPs
  - No impactful polymerization, complexation, or compound formation
  - No change in salt potential during operation
- Approximate data of viscosity for $PuCl_3$ was used.

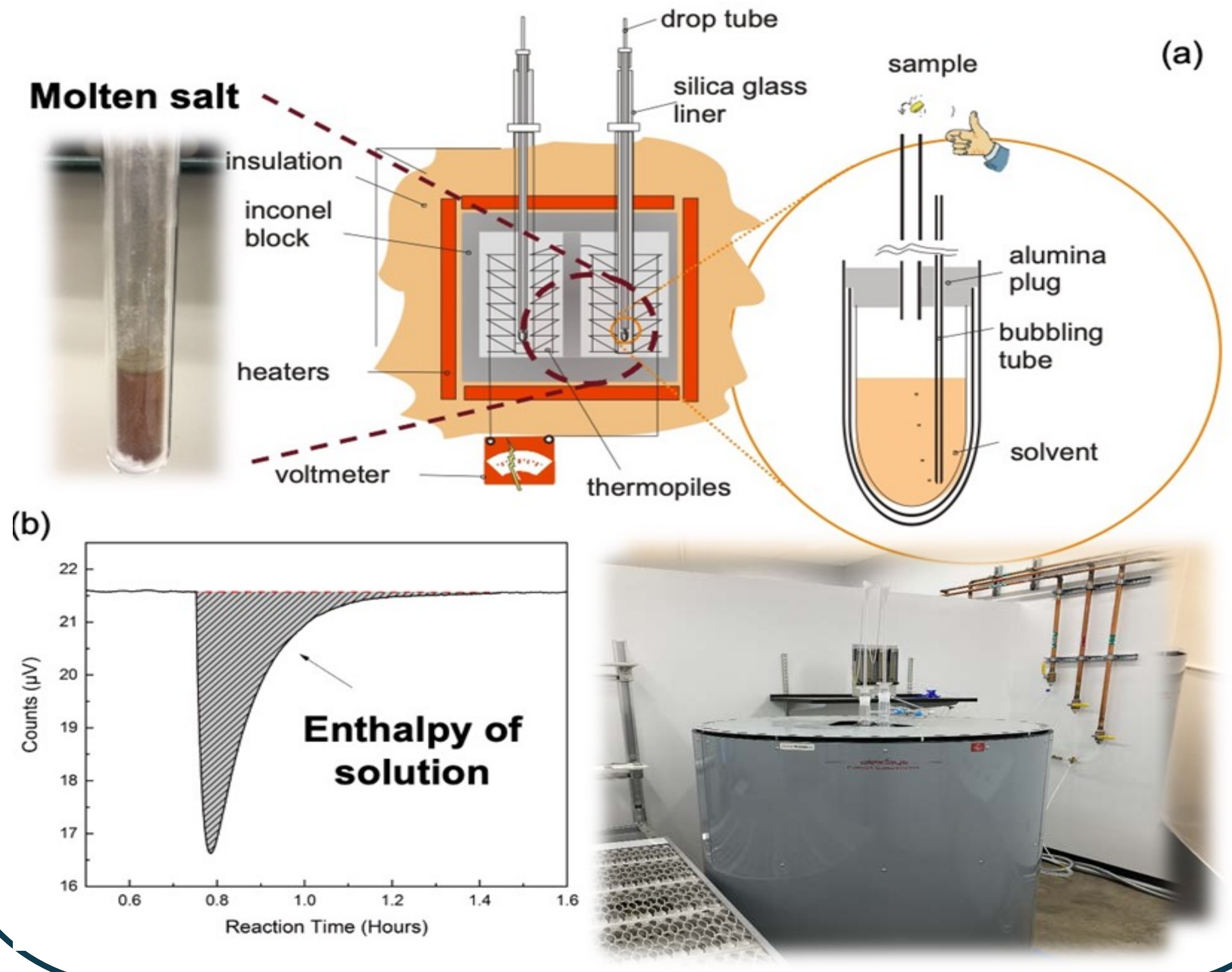
HIGH TEMPERATURE DROP CALORIMETRY OF MOLTEN CHLORIDE SALTS

Experiments constrain/benchmark modeling



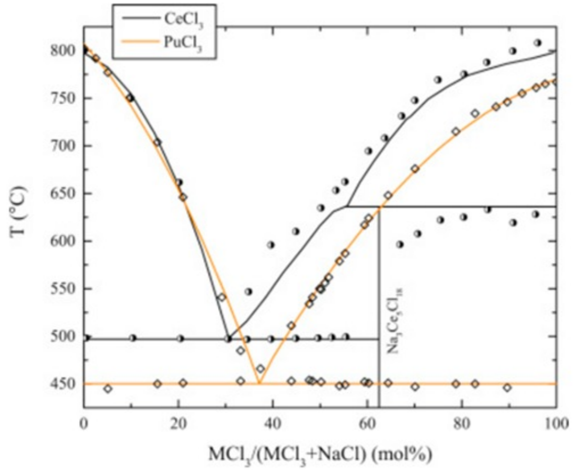
Goncharov et al., *J. Mol. Liq.* 2023 (in prep)

High Temperature Reaction Calorimetry



EXPERIMENTAL GOAL

CeCl$_3$ – NaCl Phase diagram



Sooby et al., *J Mol. Liq.*, 2015, 466, 280

Progress

1.

NaCl
+
CeCl$_3$

$\Delta H_{mix}(\mathrm{NaCl – CeCl_3})$

30mol%CeCl$_3$
70mol%NaCl

2.

$\Delta H_{mix}(\mathrm{CsCl – NaCl – CeCl_3})$ + $\Delta H_{mix}(\mathrm{SmCl_3 – NaCl – CeCl_3})$ + $H_{mix}(\mathrm{SrCl_2 – NaCl – CeCl_3})$

3.

NaCl
+
UCl$_3$

$\Delta H_{mix}(\mathrm{NaCl – UCl_3})$

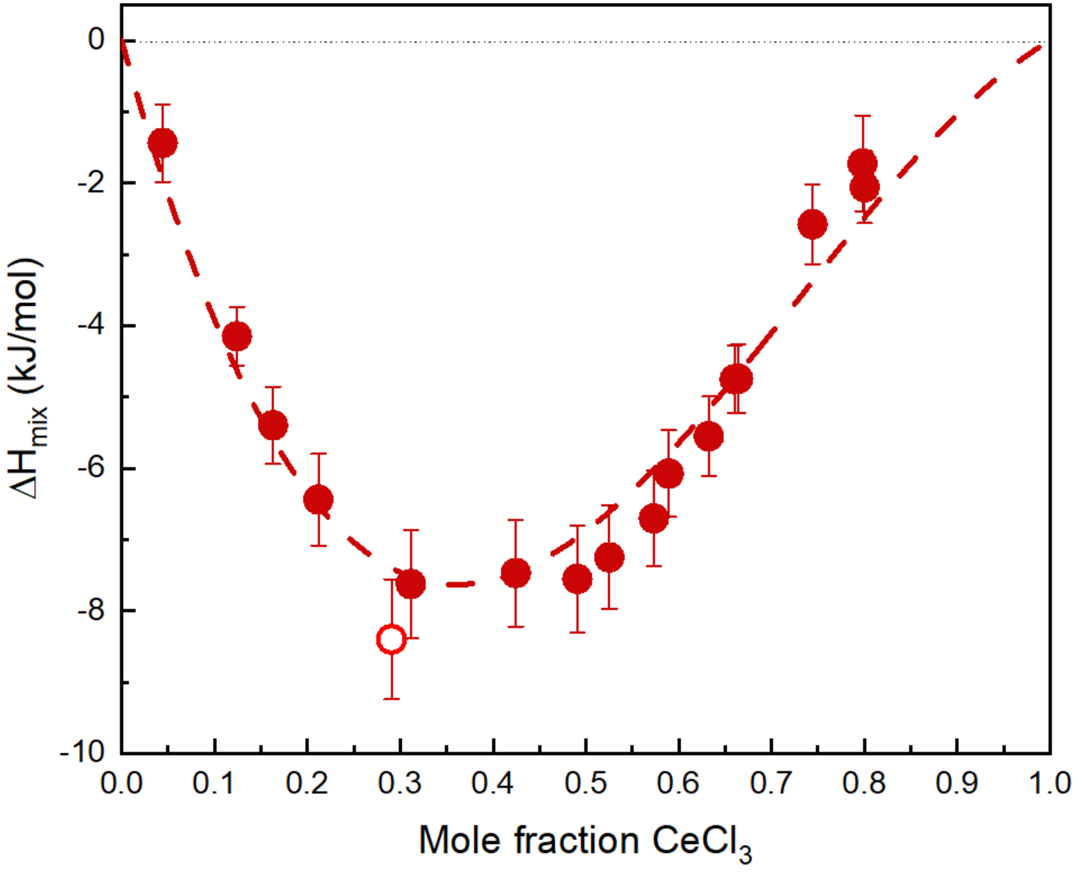
33mol%UCl$_3$
67mol%NaCl

$\Delta H_{mix}(\mathrm{CsCl – NaCl – UCl_3})$ + $\Delta H_{mix}(\mathrm{SmCl_3 – NaCl – UCl_3})$ + $H_{mix}(\mathrm{SrCl_2 – NaCl – UCl_3})$

4.

ENTHALPY OF MIXING OF THE NaCl-$CeCl_3$ SYSTEM

Experimental results



DFT

kJ/mol

-0.96

-1.93

-2.89

-3.85

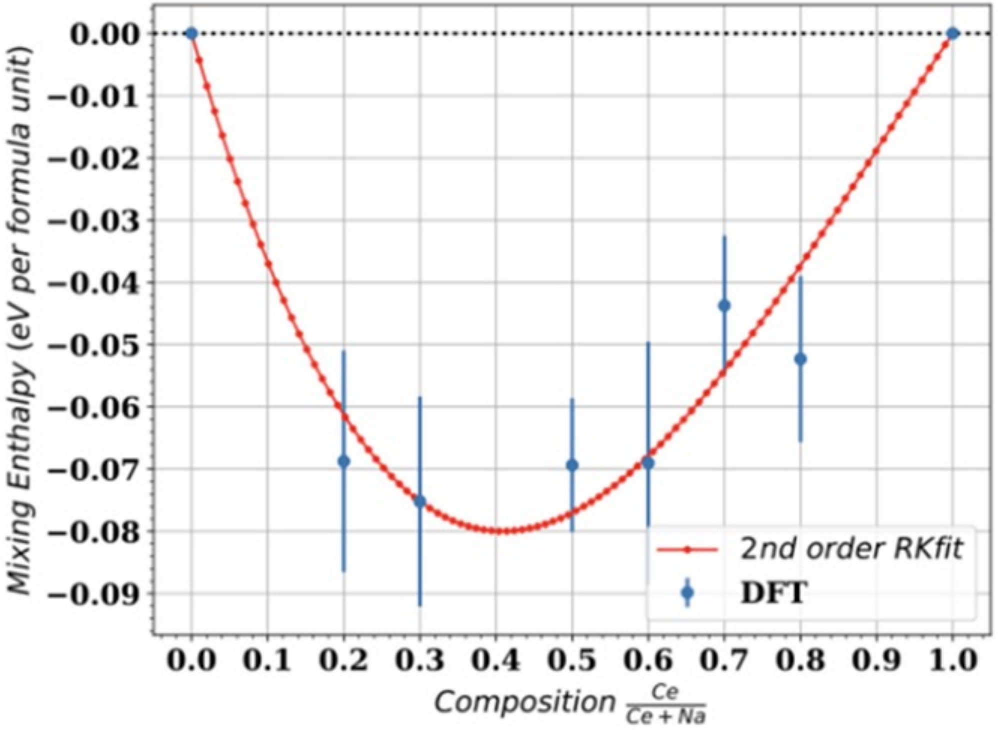
-4.82

-5.78

-6.75

-7.71

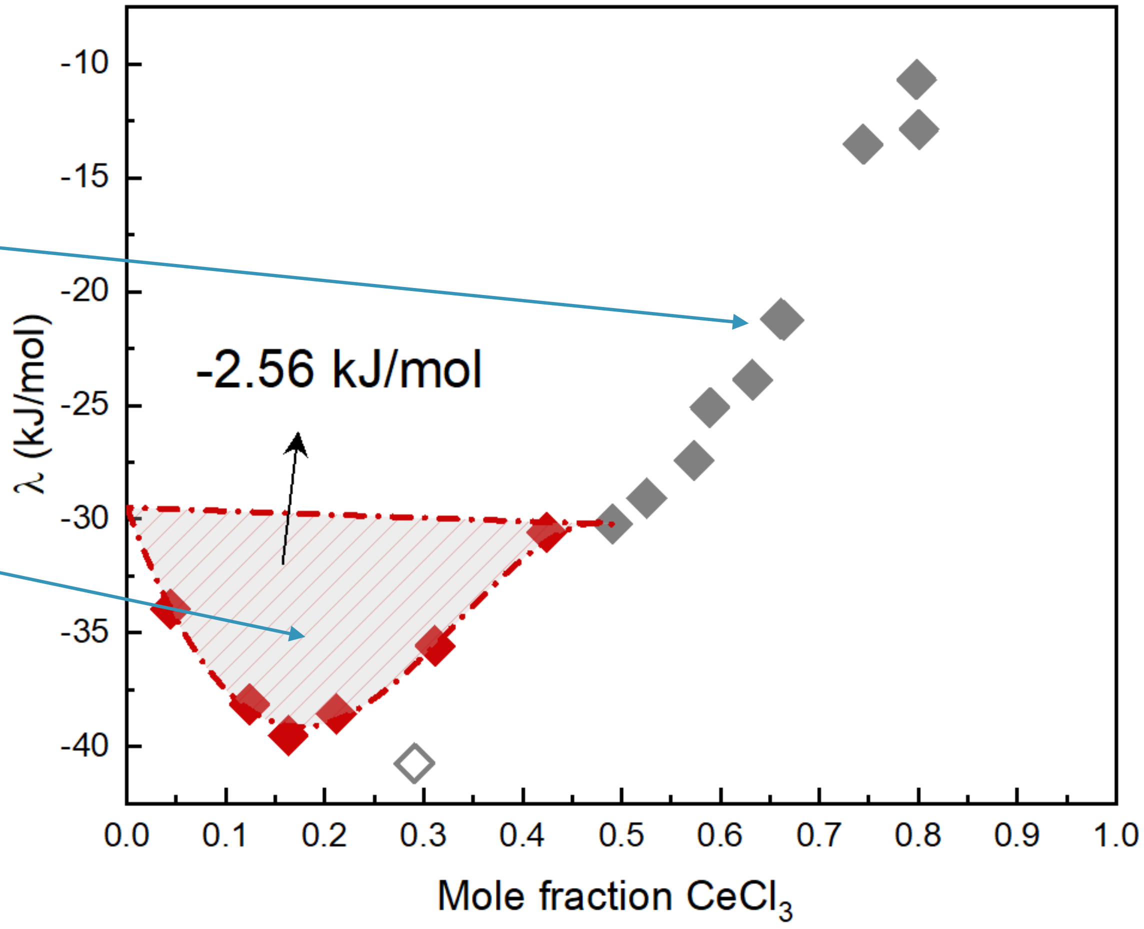
-8.67



COMPLEXATION IN THE NaCl-$CeCl_3$ SYSTEM

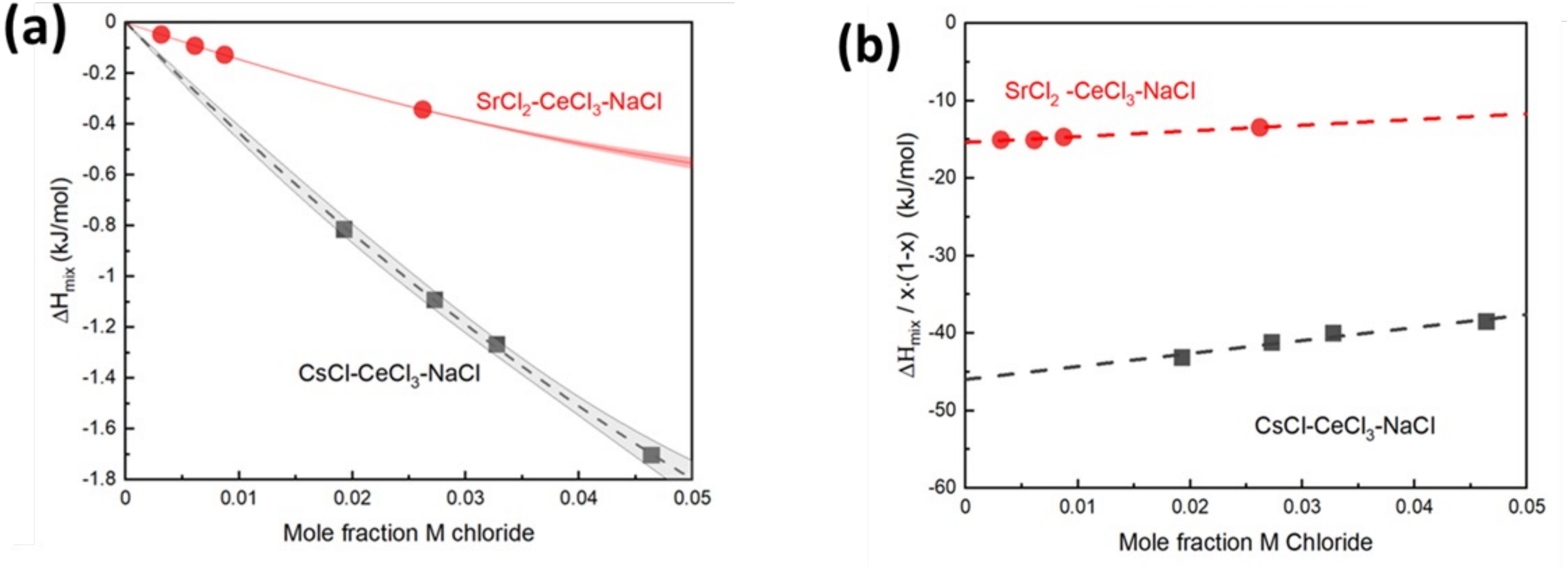
Linear slope = only coulombic interactions

Compositional range where complexation stabilizes the melt



EFFECT OF FISSION PRODUCTS IN MOCK NUCLEAR FUEL

$SrCl_2$ and CsCl added to the NaCl-$CeCl_3$ eutectic



COMPUTATIONAL STUDIES OF $NaCl\text{-}CeCl_3$ SALT MIXTURES

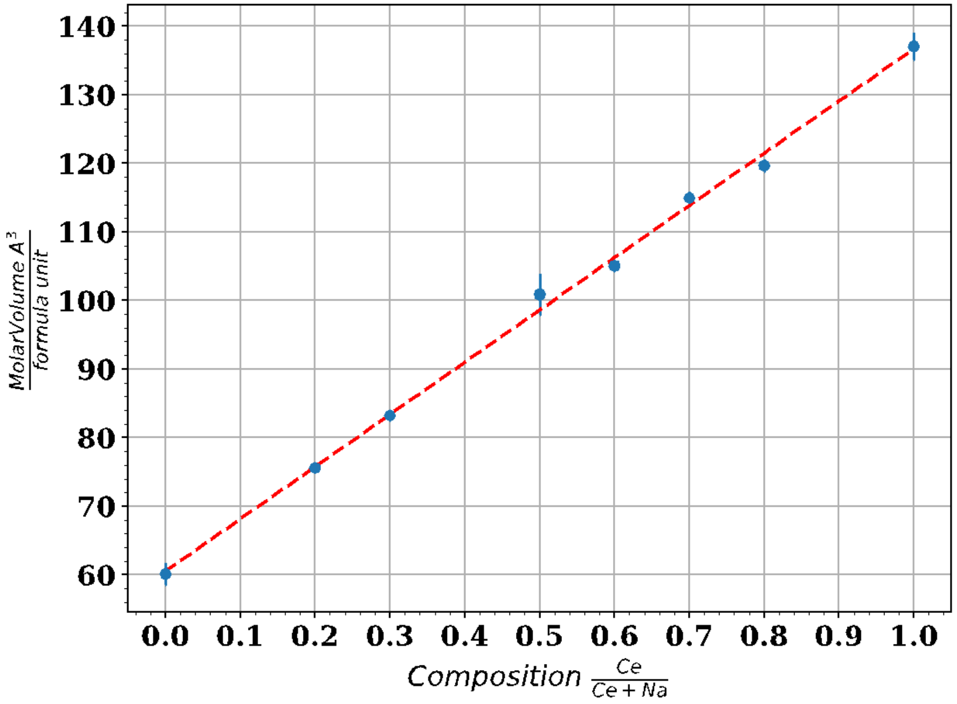
Motivation:

- Analysis of University of Wisconsin suggests the formation of $PuCl_3$ during burnup has significant effect on thermochemical and transport properties of $NaCl\text{-}UCl_3$ fuels
- Ce^{3+} is commonly used as a surrogate for Pu^{3+} in experimental investigations of nuclear fuels
- Ce^{3+} itself is a fission product and representative of family of trivalent lanthanides present during fuel burnup
- $NaCl\text{-}CeCl_3$ mixtures have been subject of thermochemical measurements by ASU, providing opportunities to validate the accuracy of the computational models

Present work:

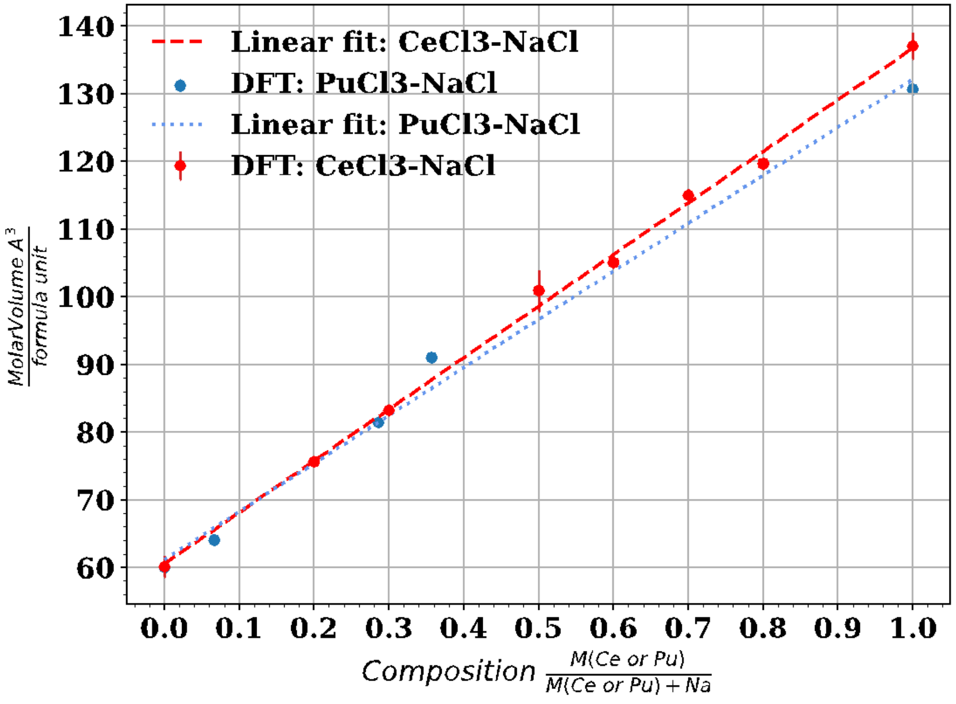
- Assess the reliability of CeC_{l3} as a surrogate for $PuCl_3$, through direct comparison of computed properties of $NaCl\text{-}CeCl_3$ mixtures with those of $NaCl\text{-}PuCl_3$ mixtures derived by same methods by collaborator David Andersson
- Assess the accuracy of computational methods for NaCl salts containing lanthanide fission products through comparisons with experimental measurements for $NaCl\text{-}CeCl_3$ by Navrotsky group
- Approach combines ab-initio molecular dynamics simulations and machine-learned interatomic potential methods

AIMD CALCULATED MOLAR VOLUMES OF NaCl-CeCl$_3$ VERSUS NaCl-PuCl$_3$



Molar Volume vs. Composition in NaCl-CeCl$_3$

T = 1250 K



Molar Volume for NaCl-CeCl$_3$ and NaCl-PuCl$_3$

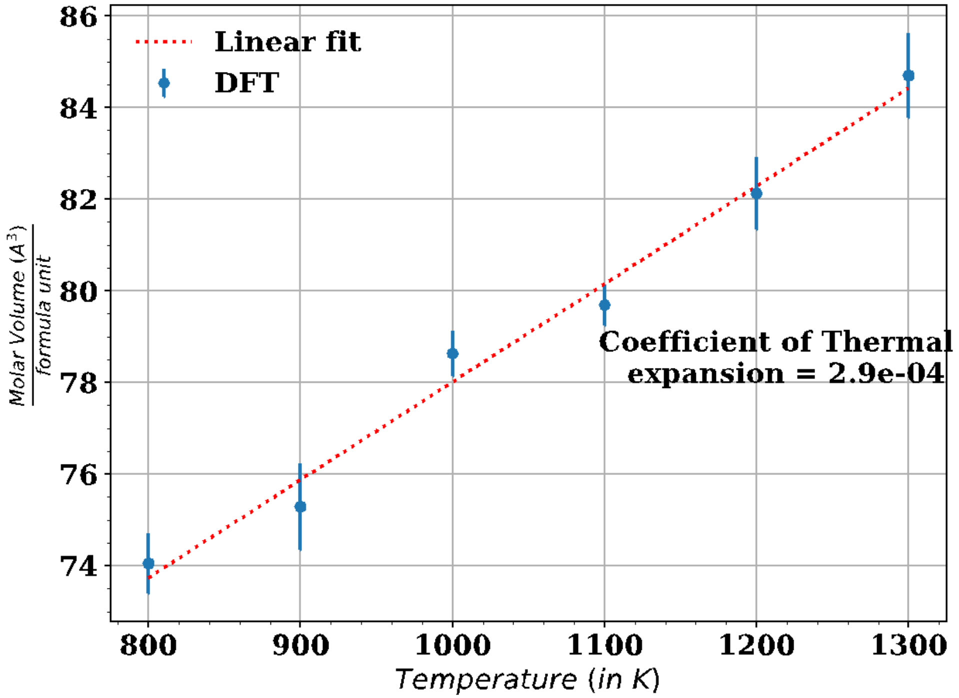
T = 1250 K

Both NaCl-CeCl$_3$ and NaCl-PuCl$_3$ show nearly ideal (linear) molar volume of mixing properties

AIMD CALCULATED THERMAL EXPANSIONS NaCl-CeCl$_3$ VERSUS NaCl-PuCl$_3$

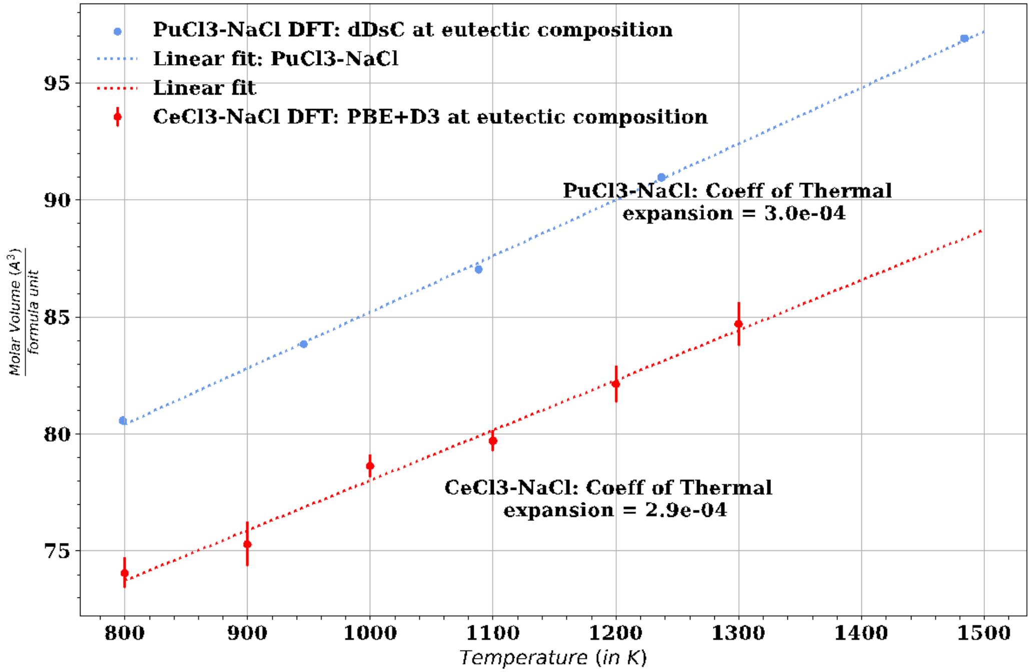
Molar Volume vs. Temperature

70% NaCl – 30% CeCl$_3$



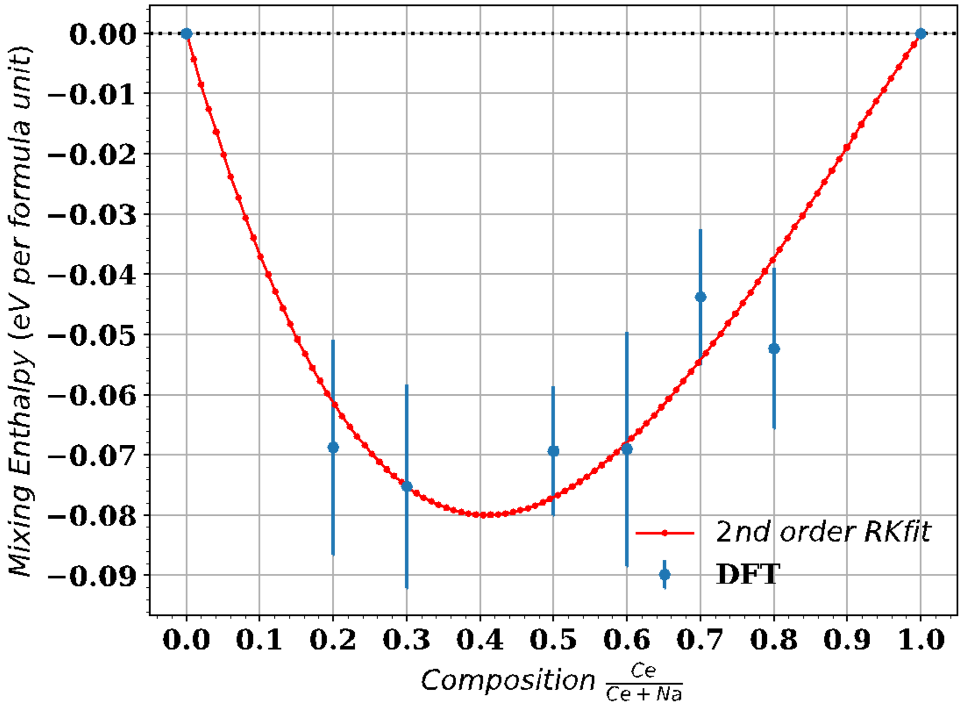
Molar Volume vs. Temperature

70% NaCl – 30% CeCl$_3$ vs. 64% NaCl – 33% PuCl$_3$



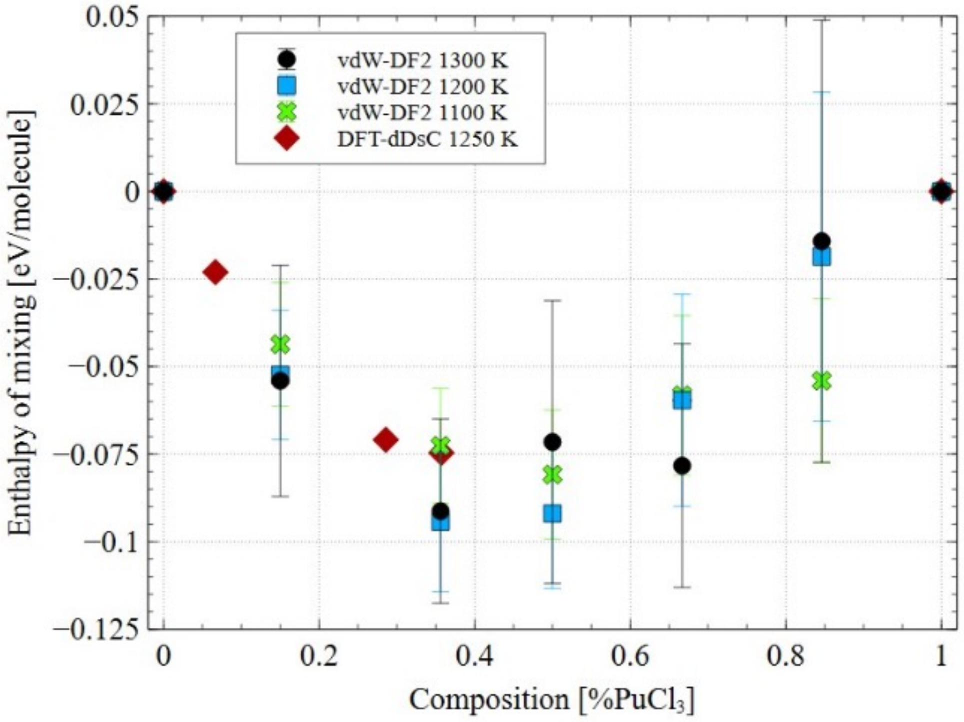
Thermal Expansions agree within a few percent

MIXING ENTHALPIES
NaCl-CeCl$_3$ VERSUS NaCl-PuCl$_3$



Enthalpy of Mixing

NaCl-CeCl$_3$ at T=1250 K



Enthalpy of Mixing

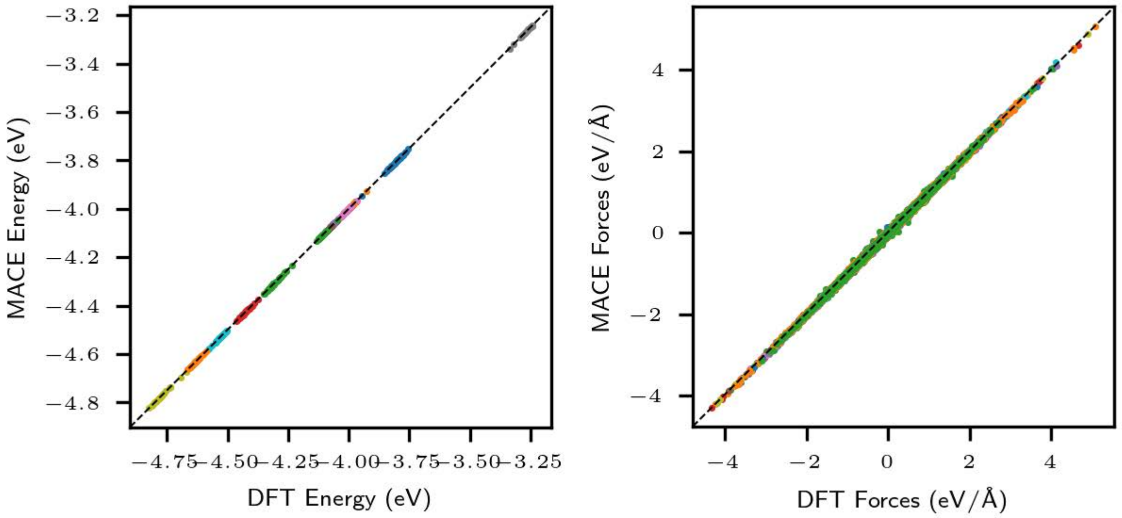
NaCl-PuCl$_3$ for T=1100 – 1300 K[1]

- Exothermic mixing enthalpies for both systems with very similar magnitudes
- Results for NaCl-CeCl$_3$ agree with experimental measurements by Navrotsky group to within better than 0.01 eV per formula unit

[1] K. Duemmler, D. Andersson and B. Beeler, J. Nucl. Mater. (2024)

MACHINE-LEARNED INTERATOMIC POTENTIAL MODELS

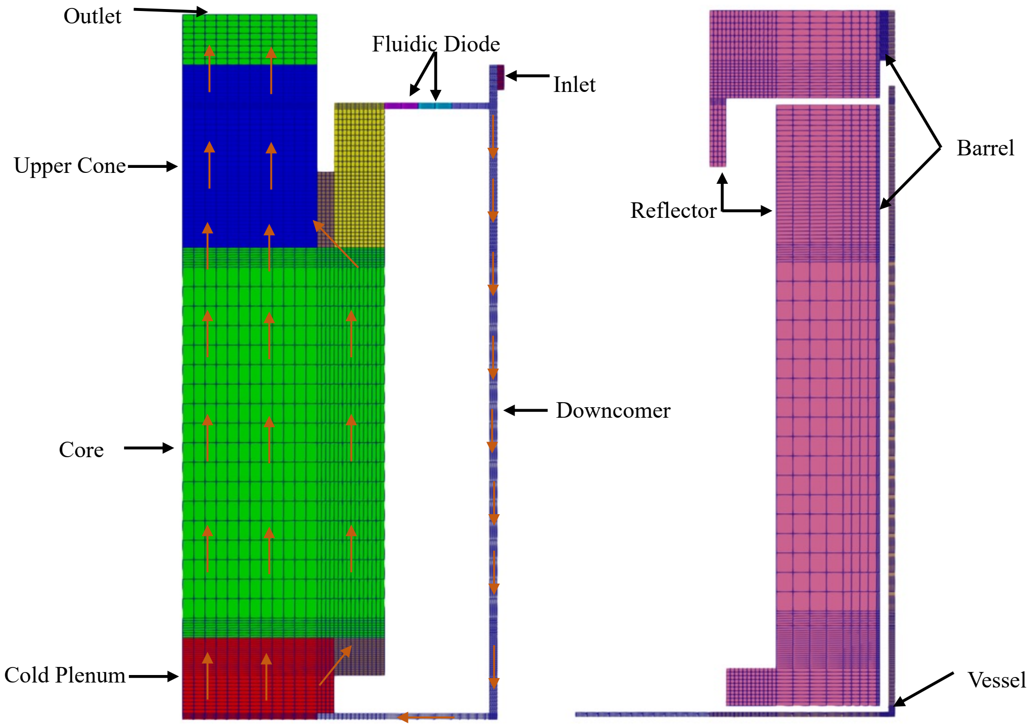
- Current Work
  - Machine-Learned interatomic potential models for both NaCl-$CeCl_3$ and NaCl-$PuCl_3$ to extend simulation length and time scales
  - Initial results for NaCl-$CeCl_3$ (below) show excellent reproduction of AIMD data using MACE potential formalism
  - Work will be extended to NaCl-$PuCl_3$ in coming months (in collaboration with D. Andersson, LANL)
- Goals
  - Longer simulation length and time scales enable calculations of transport properties (viscosity & thermal conductivity)
  - Opportunities for comparison to experimental data generated in IRP and for use in salt databases



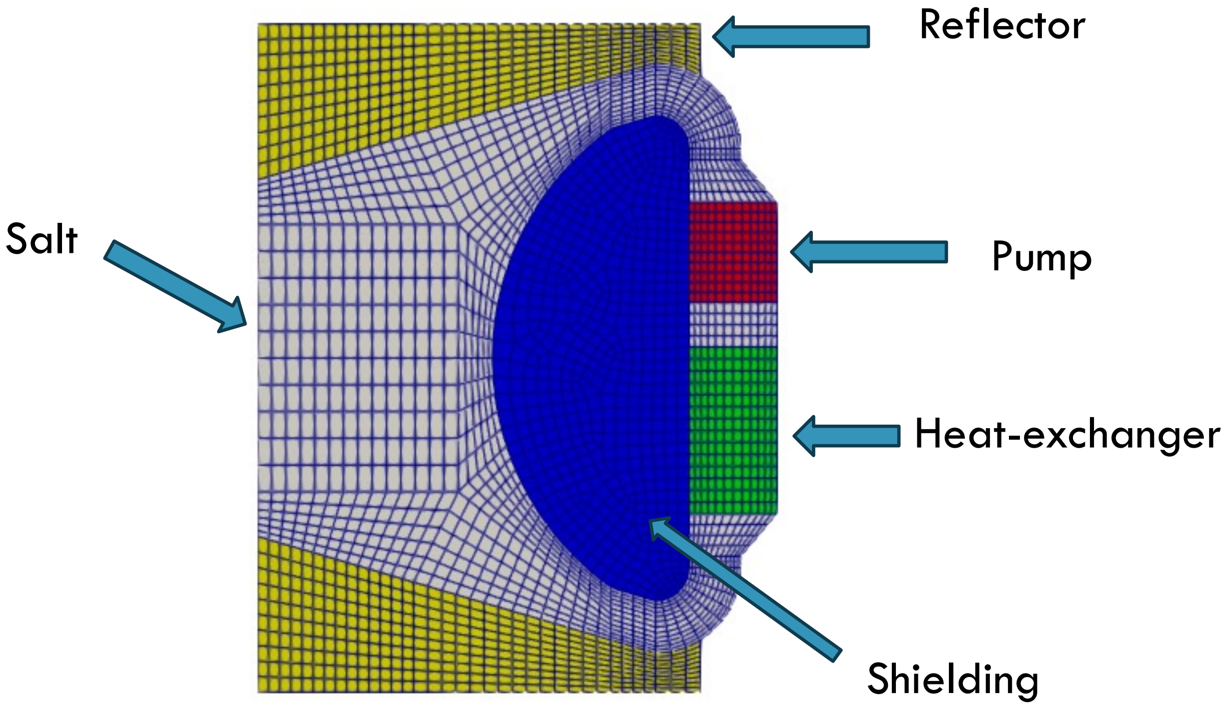
Parity plots comparing energy and forces from MACE potential fit to DFT data for NaCl-$CeCl_3$ across composition & temperature

SENSITIVITY ANALYSIS OF CORE OPERATIONAL PARAMETER TO SALT PROPERTIES

Coupled neutronics/TH calculations using MOOSE tools (Serpent for xs generation)



Pronghorn gFHR model (fluid part and solid part)

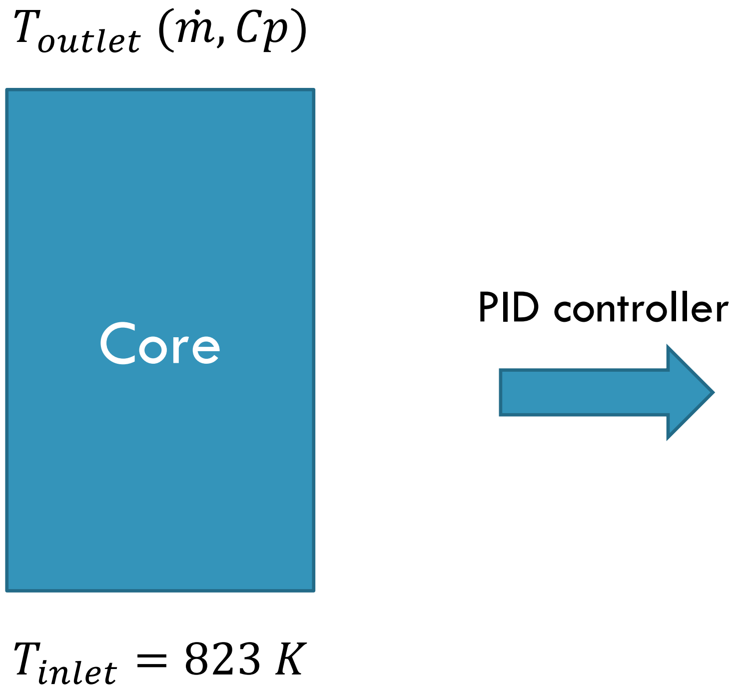


MOOSE MCFR model

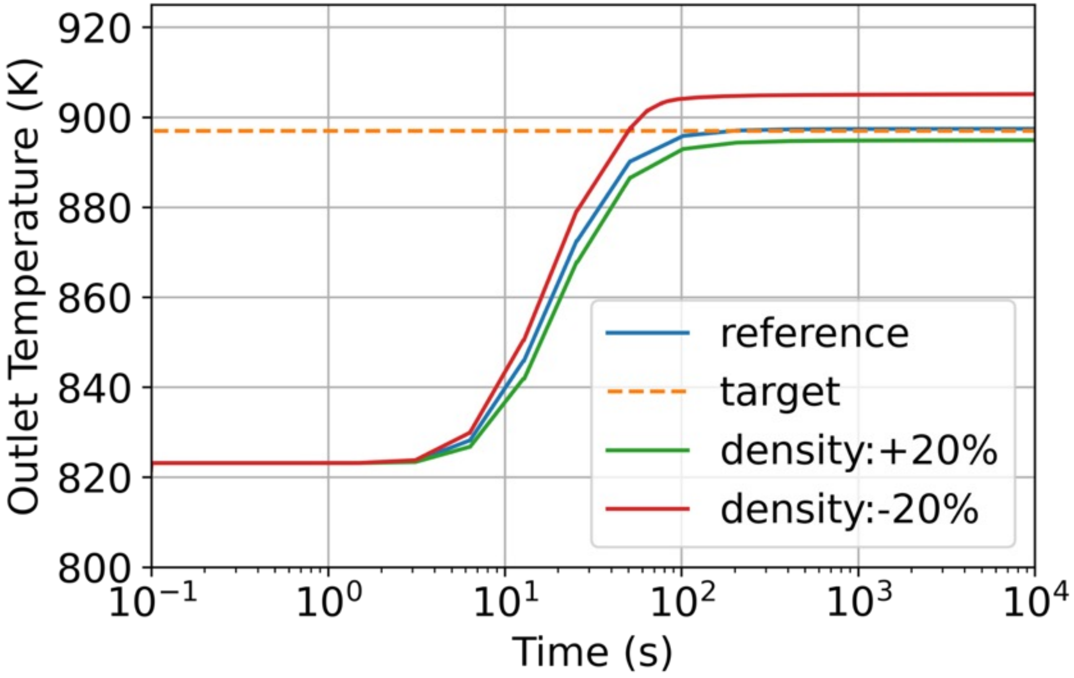
INLET TEMPERATURE AND CORE POWER ARE ASSUMED UNCHANGED

Changes to salt properties are assumed to not change boundary conditions

The mass flow rate is used to compensate any changes in salt properties



Core simplified scheme



PID response

SENSITIVITY RESULTS FOR FLUORIDE SALT

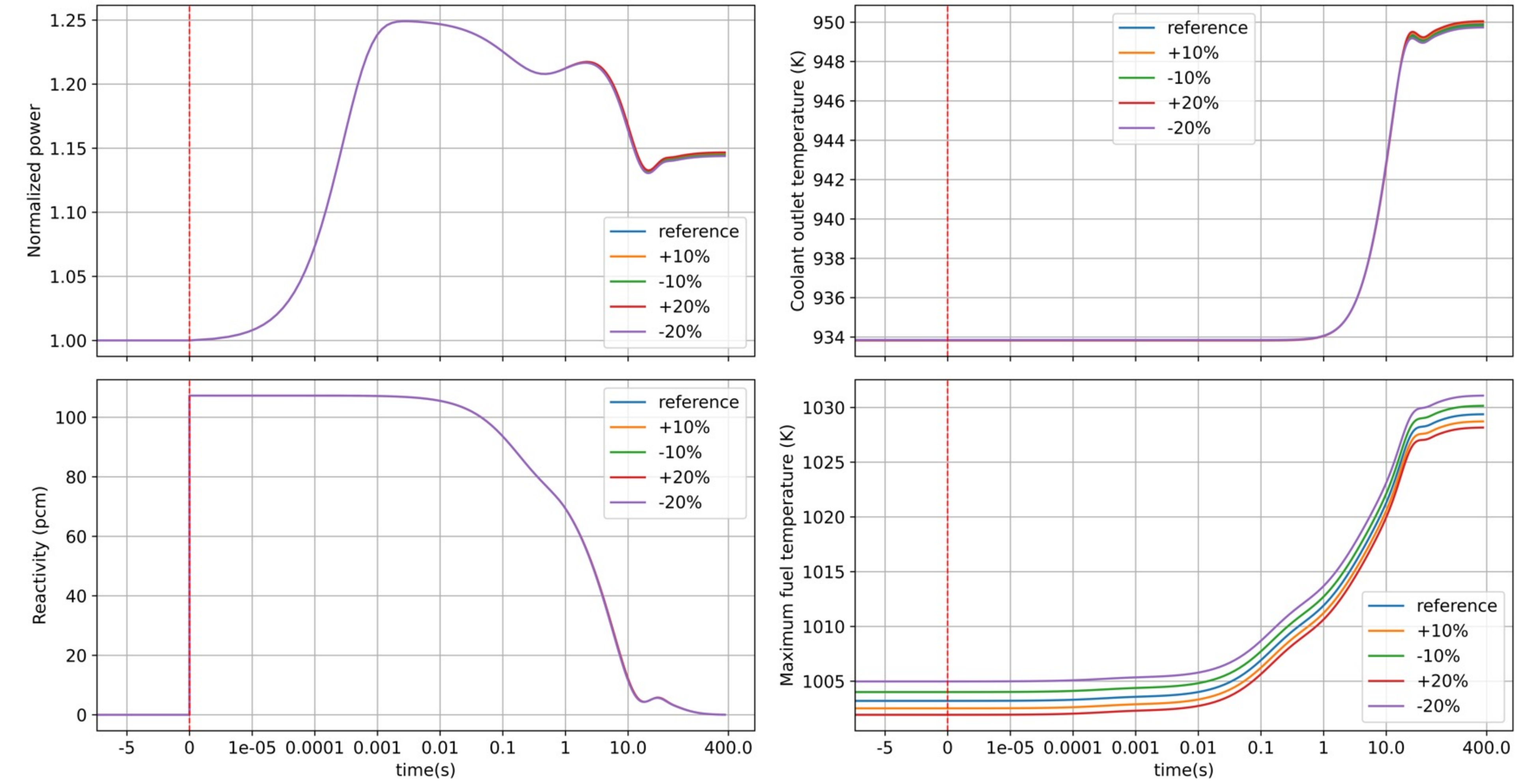
Fluid characteristics

Coolant properties and uncertainty (T=823 K)	
Mixture	FLiBe (Li_2BeF_4)
Density (g/cm^3)	2,019 ± 0.05 %
Viscosity $(mPa.s)$	11 ± 20 %
Thermal Conductivity $(W.K^{-1}.m^{-1})$	1.04 ± 15 %
Heat Capacity $(J.kg^{-1}.K^{-1})$	2416 ± 2%

Fractional dependency at steady-state

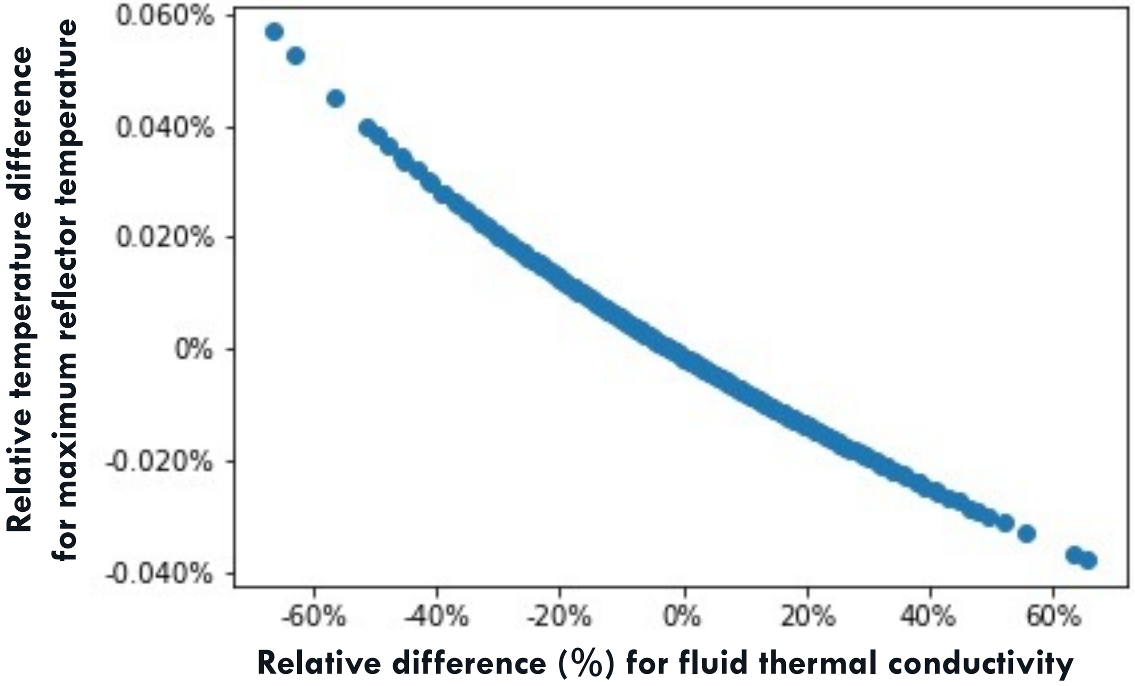
Coolant Property	Inlet Coolant Velocity	Outlet Coolant Temp.	Fuel Temp.	Reflector Temp.	Pressure Drop	Pump power
Density	-1.03	-	-	-	-0.76	-1.85
Thermal Conductivity	-	-	-0.07	-0.04	-	-
Viscosity	-	-	-	-	5e-4	-
Heat Capacity	-1.04	-	-	-	-0.76	-1.83

RESPONSE TO A REACTIVITY INSERTION IS NOT AFFECTED BY CHANGES IN THERMAL CONDUCTIVITY



Reactor Response to a reactivity insertion (0.2$) for different coolant thermal conductivities

THERMAL CONDUCTIVITY PERTURBATION EFFECT ON REFLECTOR TEMPERATURE



Thermal conductivity
Perturbation factor

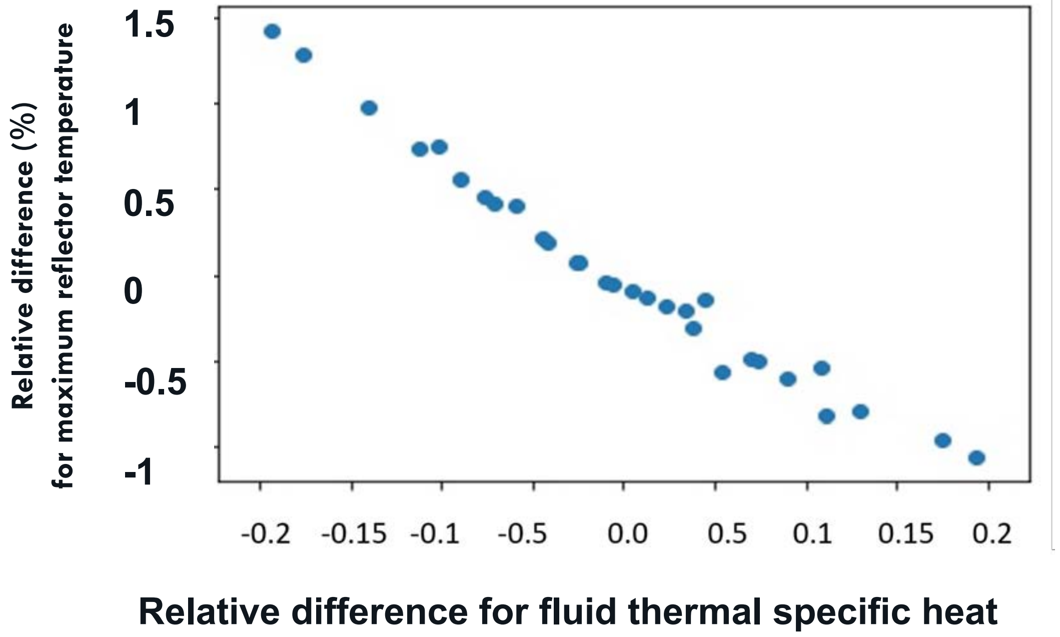
μ	σ
1	0.25

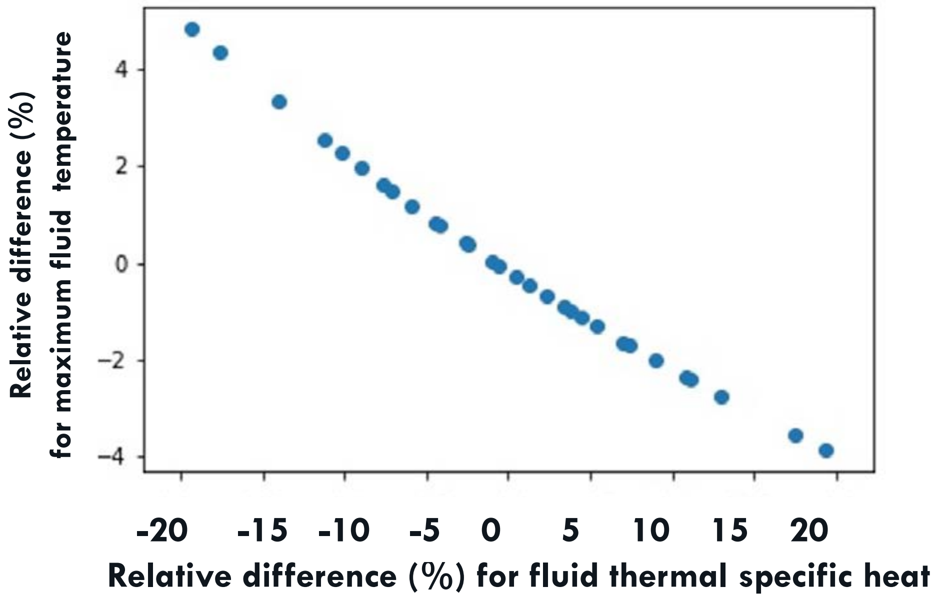
$$Nu \propto k^{-0.4}$$

SPECIFIC HEAT PERTURBATION EFFECT ON REFLECTOR TEMPERATURE

Thermal conductivity
Perturbation factor

μ	σ
1	0.1





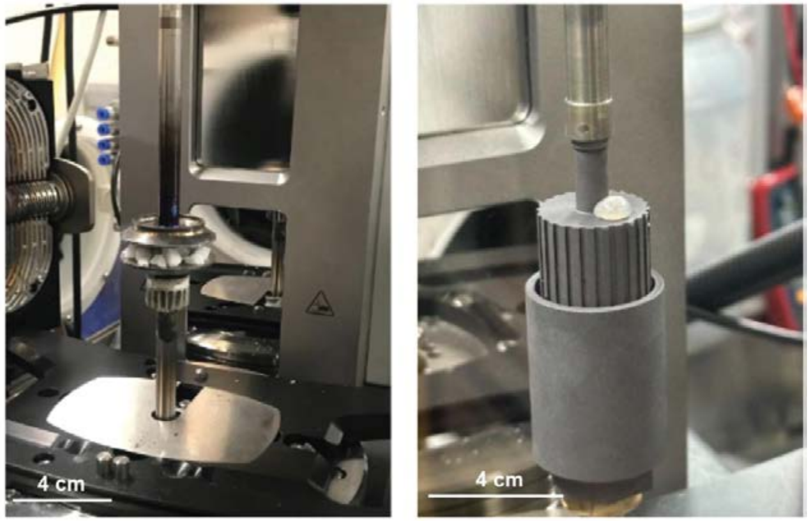
VISCOSITY METHODS & MATERIALS

Rotational Method (Parallel Plate, Cup & Bobber)

- *Measured Variable*
  - *Shear force of salt on rotating accessory measured as torque*
  - $Shear\ Stress(\tau) = \frac{Force\ (F)}{Area\ (A)}$
- *Controlled Variable*
  - *Angular velocity of rotating accessory preset by user*
  - $Shear\ Rate\ (\gamma) = \frac{Velocity\ (v)}{Height\ (h)}$
- *Measured Property*
  - $Viscosity\ (\eta) = \frac{Shear\ Stress\ (\tau)}{Shear\ Rate(\gamma)}$

Other methods…

Oscillatory, Drip, Falling/Rolling Sphere



(Left) Stainless steel parallel plate setup with frozen FLiNaK crystals loaded pre-measurement. (Right) Graphite measuring cup and cylinder (Cup and bobber) setup with frozen NaFBe droplet post measurement.

Viscosity fitting equations for activation energy extraction.

Arrhenius

$$\mu = A \times e^{\frac{E_a}{RT}}$$

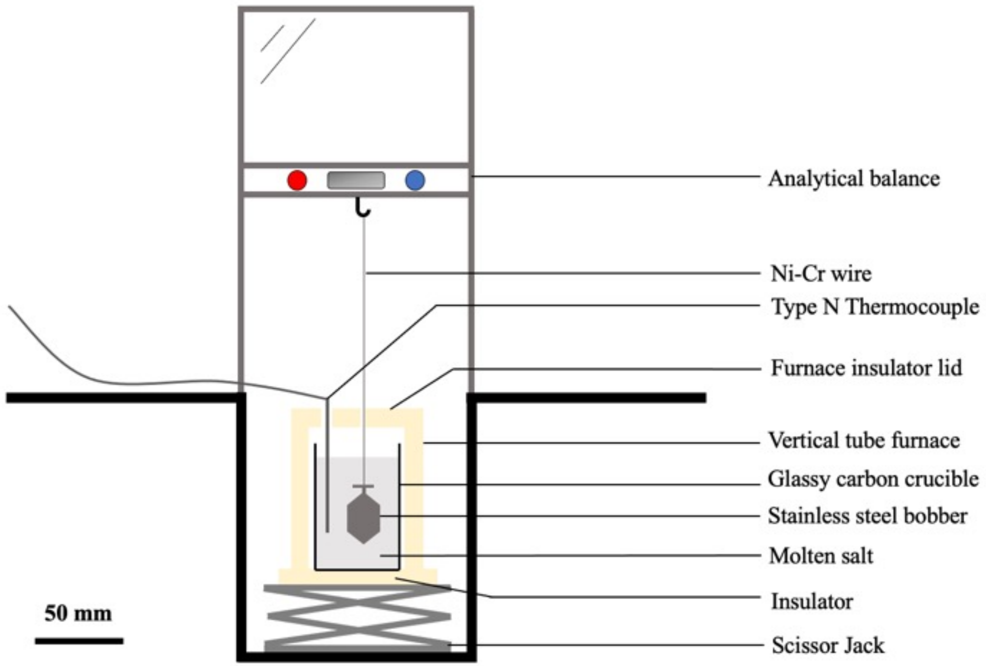
Volger-Fulcher-Tamman

$$\mu = A \times e^{\frac{Ea}{R(T-Tg)}}$$

DENSITY METHODS & MATERIALS

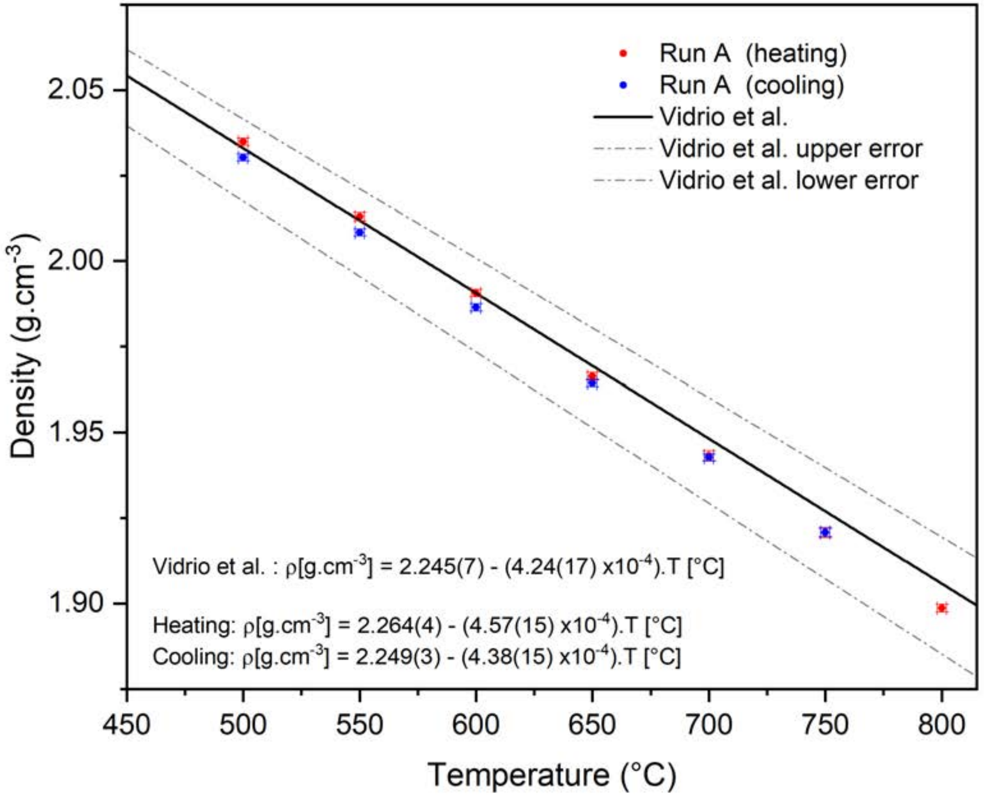
Hydrostatic Method

- Mass difference in fluid measured
  - $\Delta M = M_{Bobber} - M_{Bobber\ immersed}$
  - $M_{Bobber} = \rho_{316SS} \cdot g \cdot V_{Bobber}$
- Bobber volume calibrated using NIST standards
  - 0.8000 & 3.3100 (± 0.0005) g/cm^3
  - Two bobber sizes used
    - 12.612±0.005 cm^3
    - 1.622±0.005 cm^3
- Multiple bobber materials used for thermal expansion uncertainty
  - Stainless Steel, Brass, 80Ni-20Cr

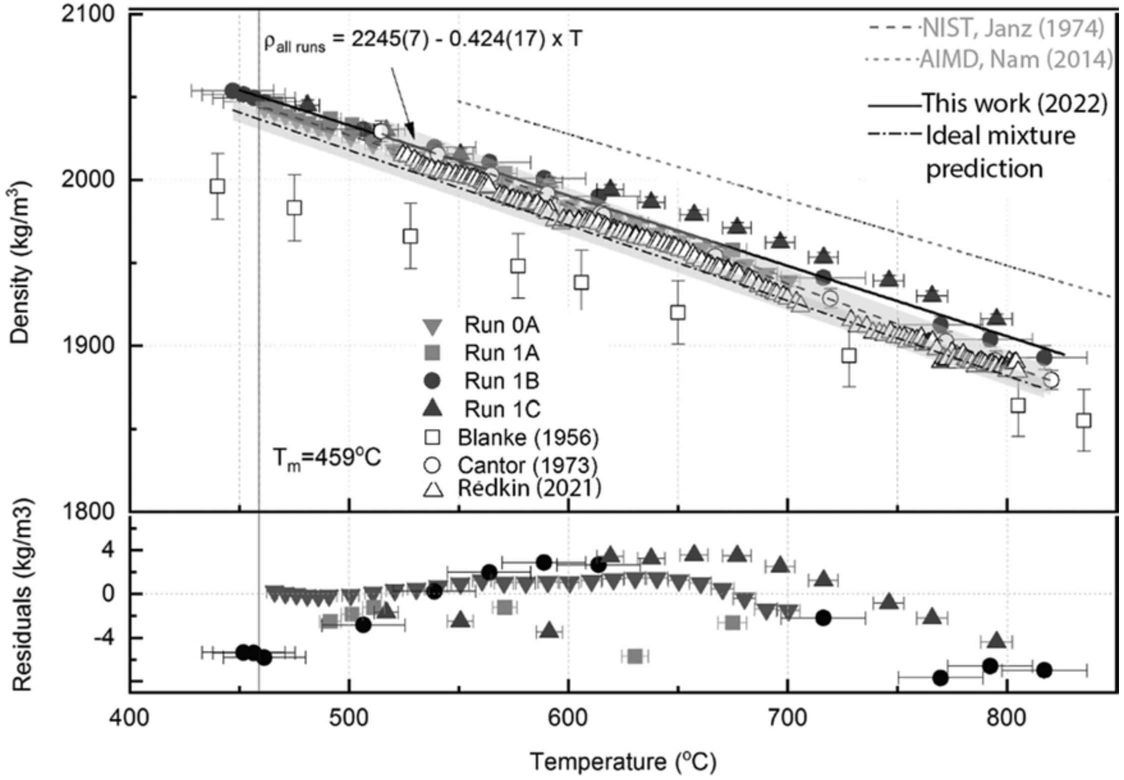


(Above) Scheme of the Hydrostatic method set-up.

METHOD BENCHMARKING



R. Vidrio, S. Mastromarino, E. Still, L. Chapdelaine, and R. O. Scarlat, “Density and Thermal Expansivity of Molten 2LiF-BeF2 (FLiBe): Measurements and Uncertainty Quantification,” J. Chem. Eng. Data, Nov. 2022,



SAMPLE DOWN-SELECTION

Fission Products in Chloride Fuel Salts

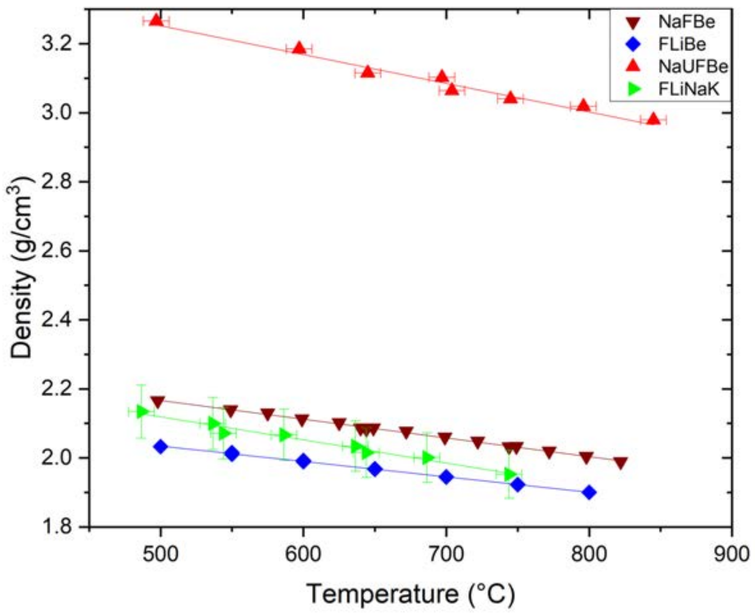
- Cerium as fission product and Plutonium surrogate as $CeCl_2$
- Zirconium, and Neodymium as chlorides
- Fission products Mo, Xe, Cs, Ru, H^3 are note expected to speciate as chlorides
- Initially added as “Kitchen Sink”

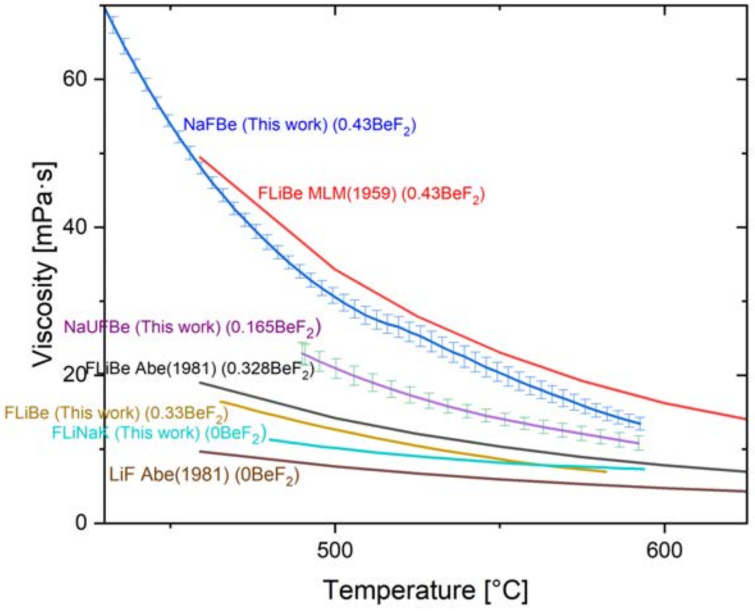
Solutes in FLiBe

- Graphite powder, Be metal, Cr metal

Oxides and Hydroxides in Chloride Salts

- Initially added as “Kitchen Sink”





(Right) Sample Density and Viscosity Baseline Data Collected

Salts utilized in the research were provided by the Nuclear Materials and Fuel Cycle Center at Virginia Tech. Salts also were provided by the University of Wisconsin Thermal Hydraulics Laboratory.

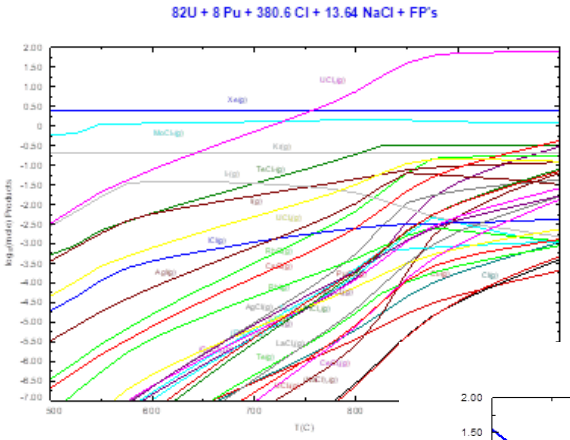
DENSITY EXPERIMENTAL MATRIX

Salt	Baseline	Titrations	Fission Products	Graphite	Redox Control	Oxides & Hydroxides
Fluorides						
$LiF\text{-}BeF_2$	○	○		○	○	
$NaF\text{-}BeF_2\text{-}UF_4$	○	○	○			
NaF-LiF-KF	○					
$LiF\text{-}AlF_3$	○				○	
BeF_2	○				○	
Chlorides						
$NaCl\text{-}UCl_3$	○	○	○			○
$MgCl_2\text{-}NaCl$	○	○				○
$NaCl\text{-}UCl_3\text{-}CeCl_3$	○		○			○
$MgCl_2\text{-}NaCl\text{-}UCl_3$	○					

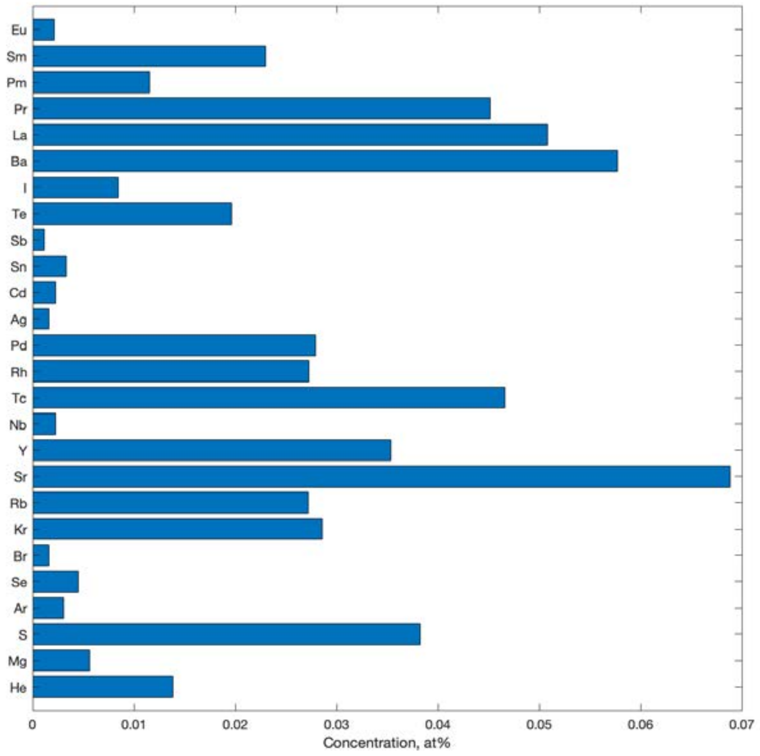
VISCOSITY EXPERIMENTAL MATRIX

Salt	Shear Rate	Baseline	Titrations	Relaxation Time	Fission Products	Graphite	Redox Control	Oxides & Hydroxides
Fluorides								
$LiF\text{-}BeF_2$	○	○	○	○		○	○	
$NaF\text{-}BeF_2\text{-}UF_4$	○	○	○	○	○			
NaF-LiF-KF	○	○		○				
$LiF\text{-}AlF_3$	○	○		○			○	
BeF_2	○	○		○			○	
Chlorides								
$NaCl\text{-}UCl_3$	○	○	○	○	○			○
$MgCl_2\text{-}NaCl$	○	○	○	○				○
$NaCl\text{-}UCl_3\text{-}CeCl_3$	○	○		○	○			○
$MgCl_2\text{-}NaCl\text{-}UCl_3$	○	○		○				

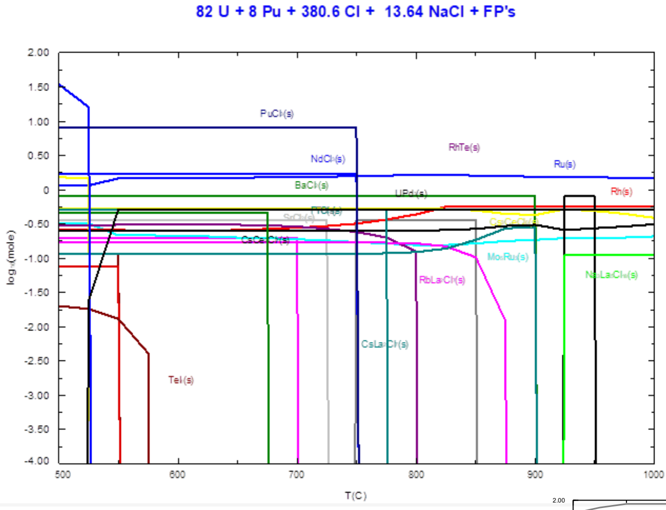
DOWN SELECT BASED ON THERMODYNAMIC CALCULATIONS



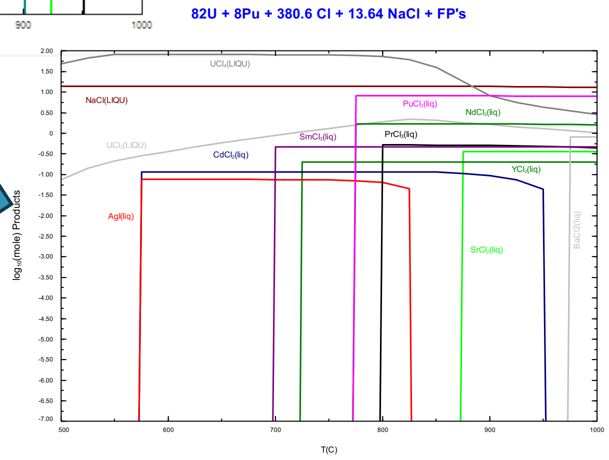
Gas Phase elements



Gas Phase elements



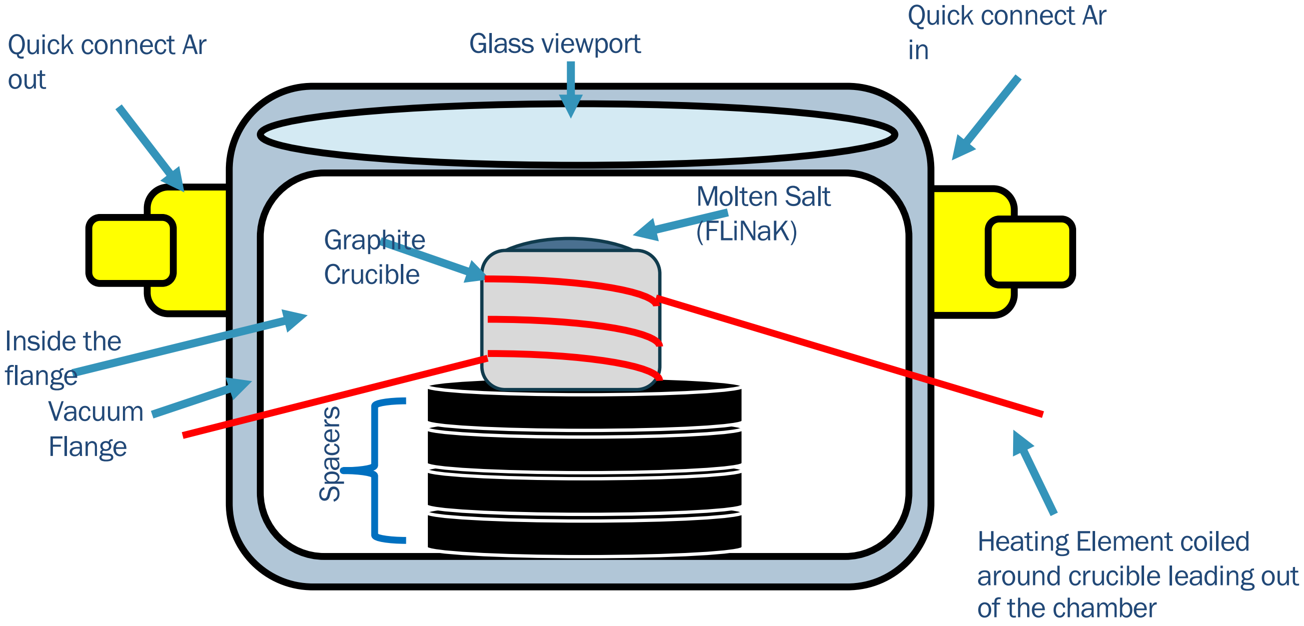
Solid Phase elements

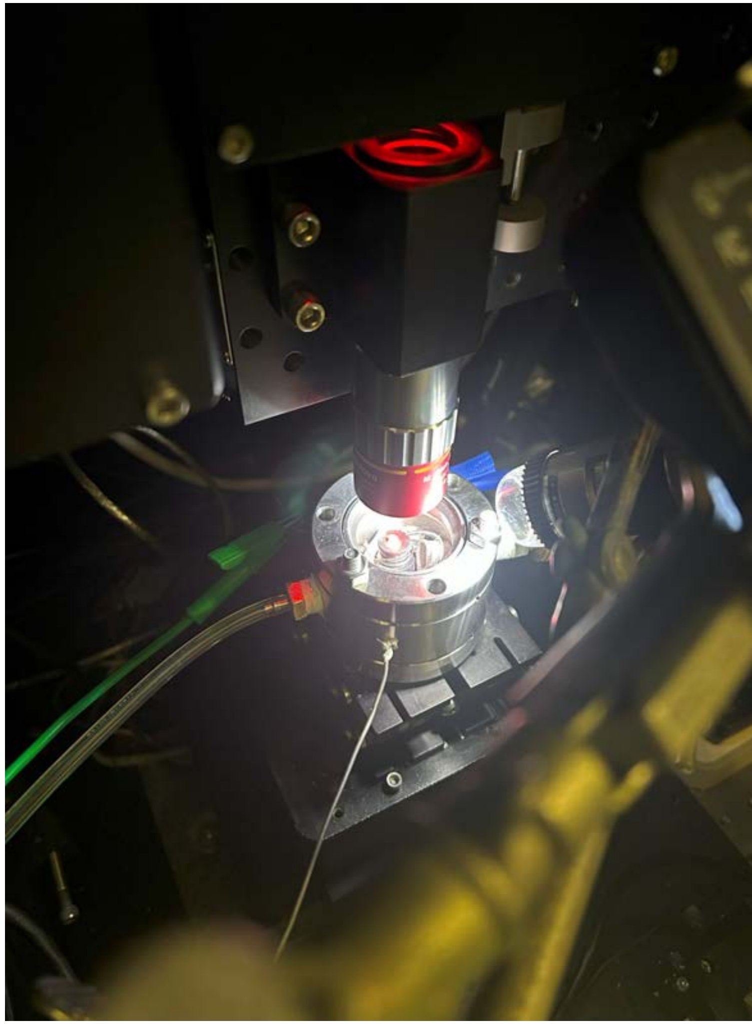


The initial assessment aims to understand which elements may remain in the salt in significant quantitates to potentially cause changes

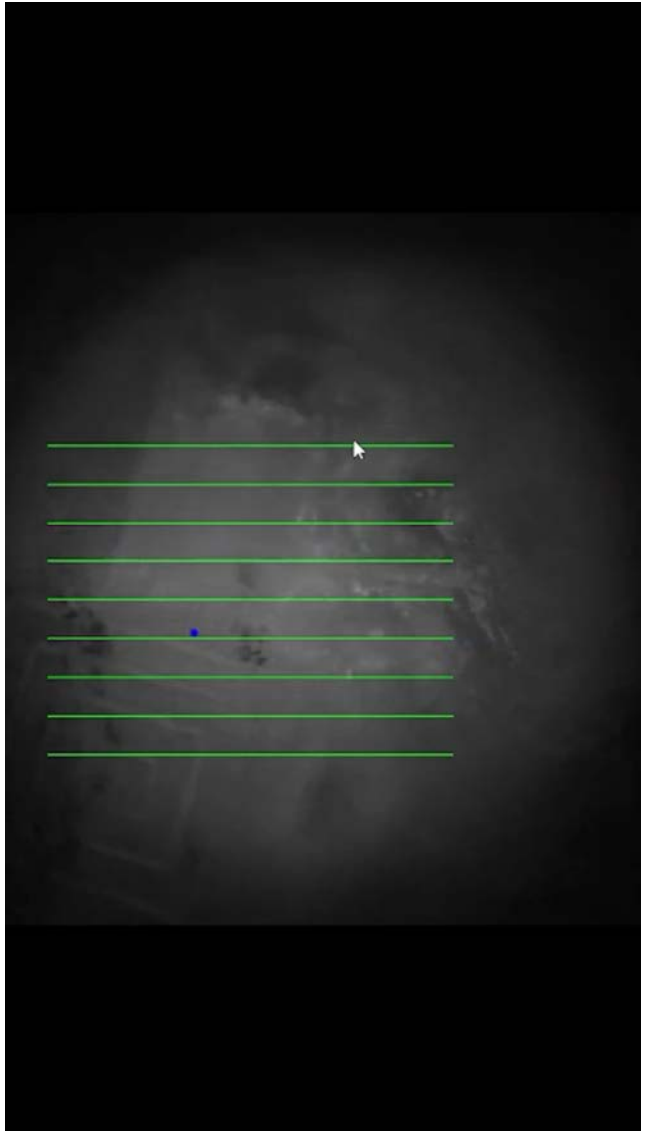
HOW TO QUANTIFY WHAT ELEMENTS STAY IN GAS PHASE? HOW DO WE KNOW THE SALT IN FACT CONTAINS THOSE ELEMENTS IN THE LIQUID PHASE?

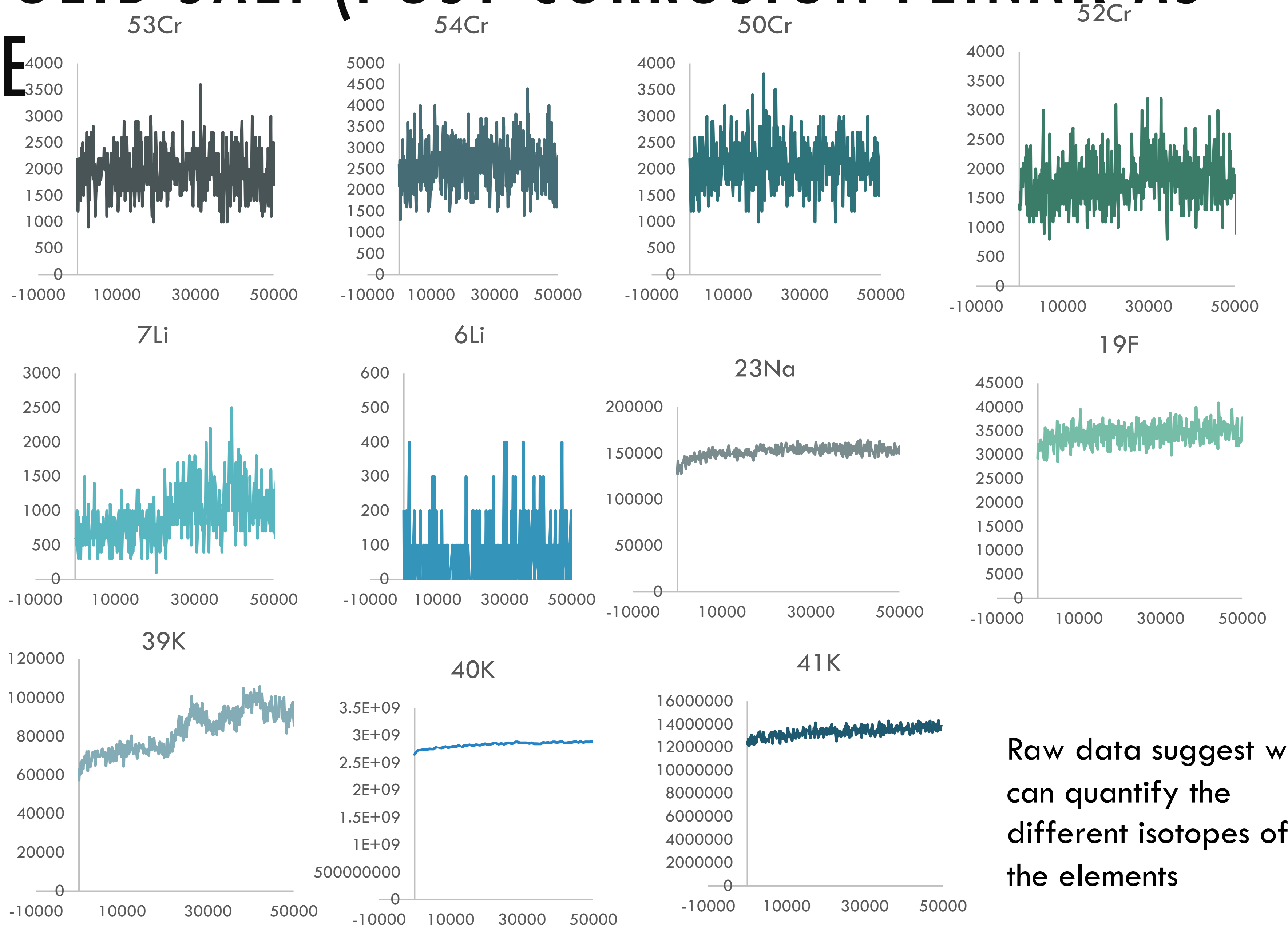
UCB developed in-situ Laser Ablation Inductively Coupled Plasma Mass Spectroscopy (I-LA-ICPMS).
This new technique allows to identify elements (and isotopes) directly in the molten salt





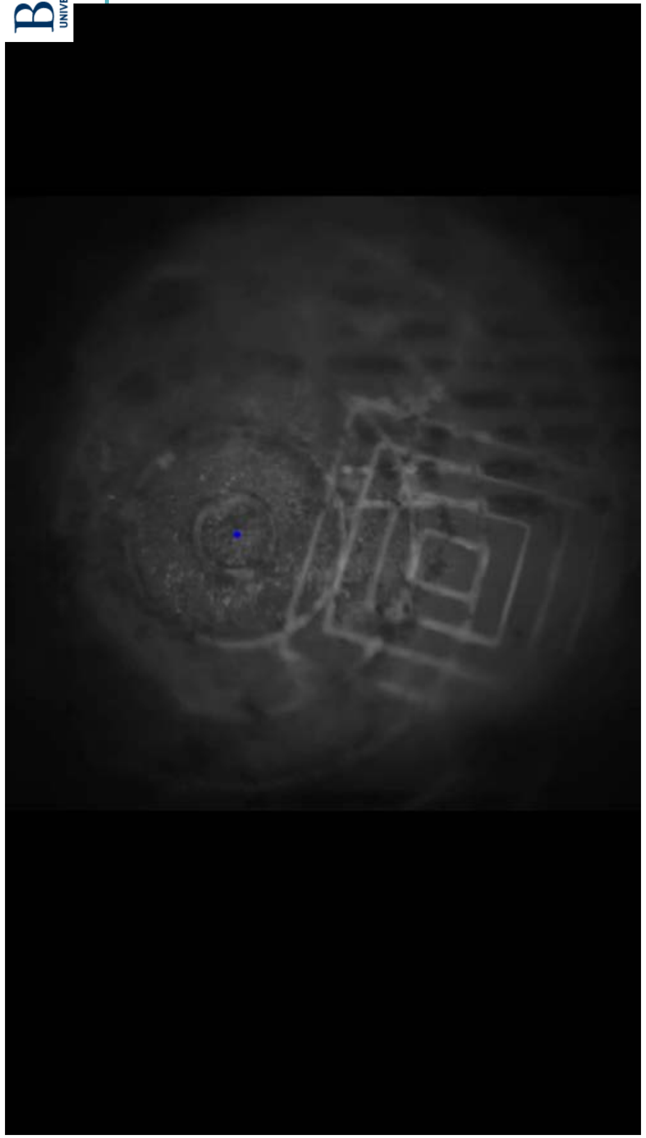
TEST CASE SOLID SALT (POST CORROSION FLINAK AS AN EXAMPLE

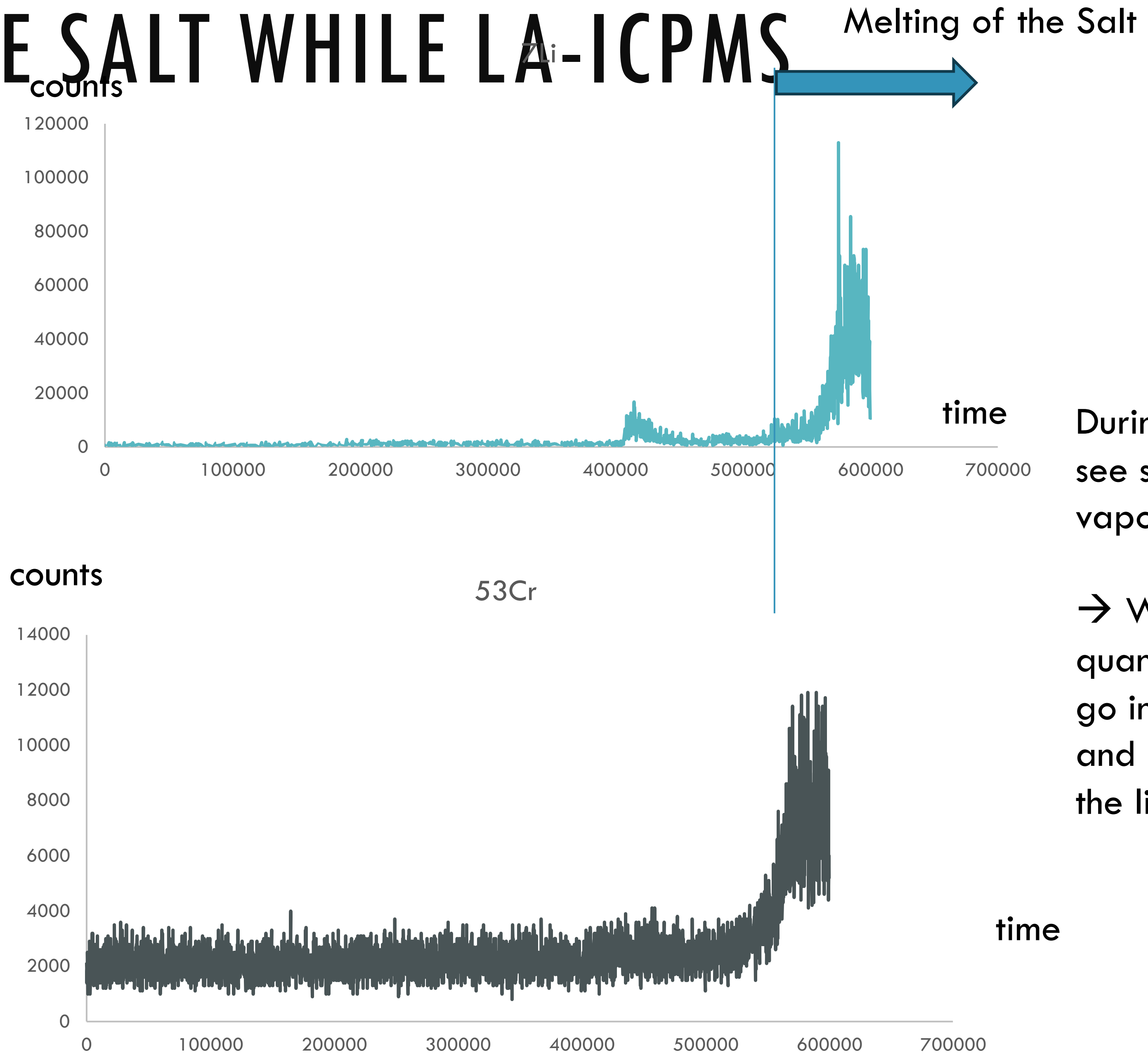




Raw data suggest we can quantify the different isotopes of the elements

MELTING THE SALT WHILE LA-ICPMS

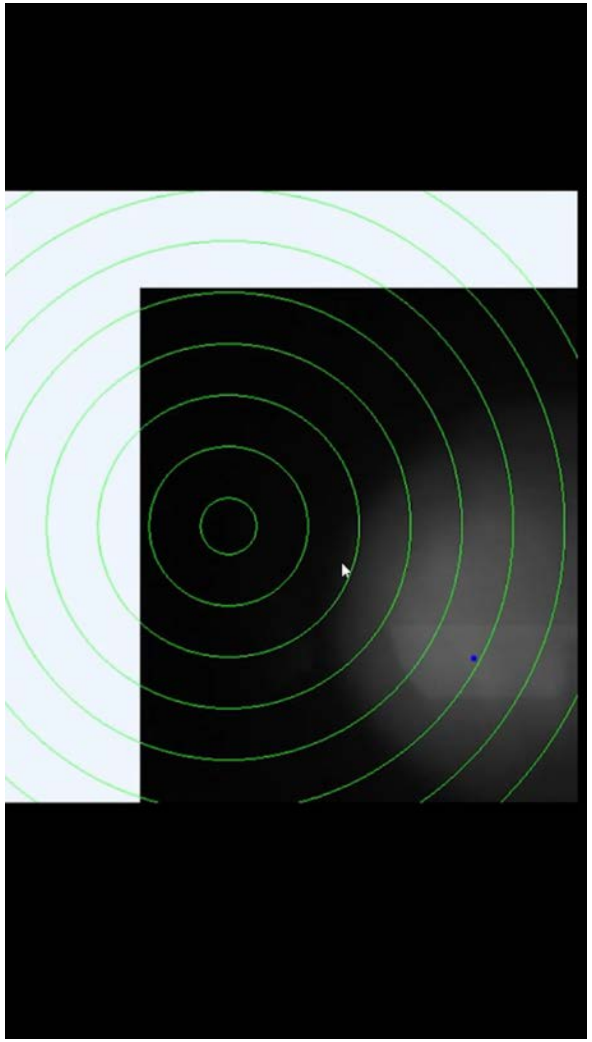


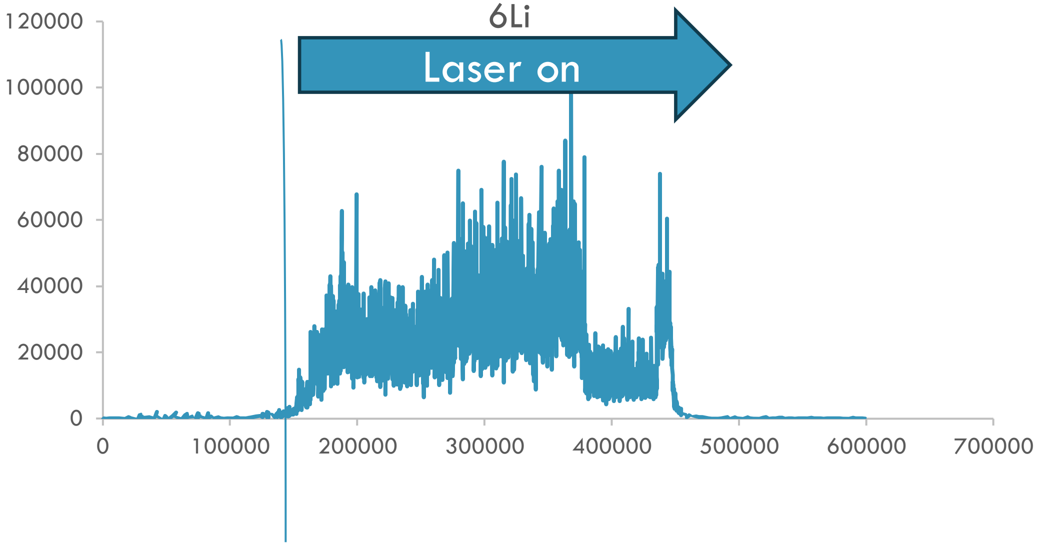


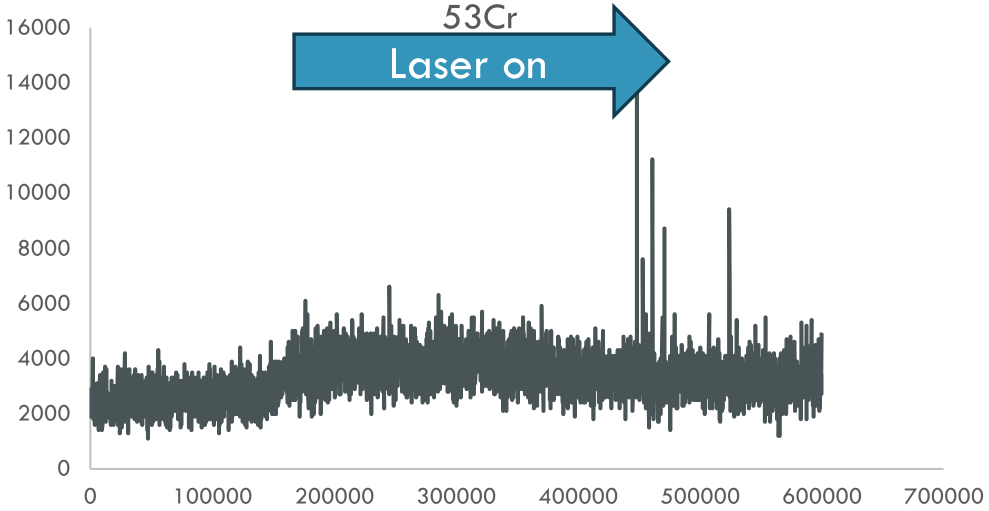
During melting we can see some species in the vapor phase.

→ We will be able to quantify what species go into the vapor phase and what will remain in the liquid

LA-ICPMS ON SALT IN THE MOLTEN STATE WILL ALLOW US TO ANSWER HOW MUCH CORROSION PRODUCT AND FISSION PRODUCTS ARE IN THE MOLTEN SALT.







DISCUSSION

Screening studies have concluded that Pu, La, Nd, Zr, Ba, Cs have potentially the most impact on chloride salts, with changes below 20%

Thermal-physical properties are being measured for Cs-bearing salts as surrogate of Pu

AIMD simulation have shown that Cs is viable surrogate for Pu

Engineering scale models show limited impact of 20% variations on reactor operational conditions

Jared Matteucci, Vitaliy Goncharov,
Hongwu Xu, Alex Navrotsky (ASU)
Yuan Chiang, Nathanael Gardner, Andrea Huang,
Ludovic Jantzen, Chai Pedetti, Davide Rotilio, Shivani
Srivastava, Mark Asta, Peter Hosemann, Raluca
Scarlat, Massimiliano Fratoni (UCB)
Sudipta Paul, Siamak Attarian, Dane Morgan, Izabela
Szlufarska (UW)
Abdalla Abou Jaoude (INL)
Thomas Hartmann (PNNL)
Marisa Monreal (LANL)
Nader Satvat (KAIROS POWER)
Karl Britsch (TERRAPOWER)

BRIDGING THE GAP BETWEEN EXPERIMENTS AND MODELING TO IMPROVE THE DESIGN OF MOLTEN SALT REACTORS

MSR Campaign Review Meeting
April 18, 2024