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Thermophysical Properties on NaCl-$PuCl_3$ salts

In collaboration with LANL & PNNL

INL/MIS-22-66948

MSR Campaign Review Meeting

26 & 27 April 2022

Presented by Toni Karlsson

Team: Michael Woods, Kevin Tolman, & Scott Middlemas

Molten Salt Reactor PROGRAM

Work Scope & INL Research Team

- Preparation of predetermined composition(s)
  - 36 mol% $PuCl_3$ (eutectic)
  - 25 mol% $PuCl_3$
- Verification of composition(s)
  - Elemental analysis of samples
- XRD analysis of samples
- Transition and melt temperatures
- Salt stability
- Heat capacity
  - Solid
  - Liquid (up to ~800^{o}C)
- Liquid density
- Peer-review journal article summarizing results


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Michael Woods


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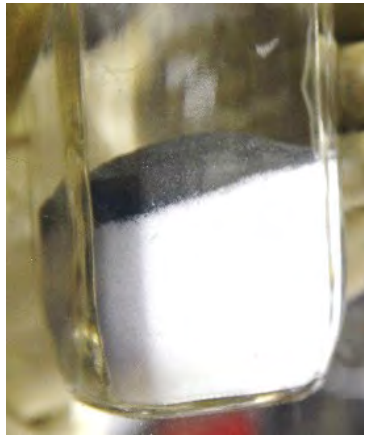
Kevin Tolman

Salt Synthesis & Blending

- Preparation of Starting Material
- Pu metal was corroded (hydride)
  - $Pu + H_2 = PuH_3$
- Then heated under vacuum (dehydride)
  - $PuH_3 \rightarrow Pu + H_2$
- NH_4Cl and NaCl were mixed with Pu
- Slow heating rate due to exothermic reaction
  - Solid : gas synthesis route



$$\boldsymbol{Pu_{(s)} + 3NH_4Cl_{(s)} \rightarrow PuCl_{3(s)} + 3NH_{3(g)} + 1.5H_{2(g)}} \quad \textbf{(1)}$$

$$NH_4Cl_{(s)} \rightarrow NH_{3(g)} + HCl_{(g)} \quad (2)$$

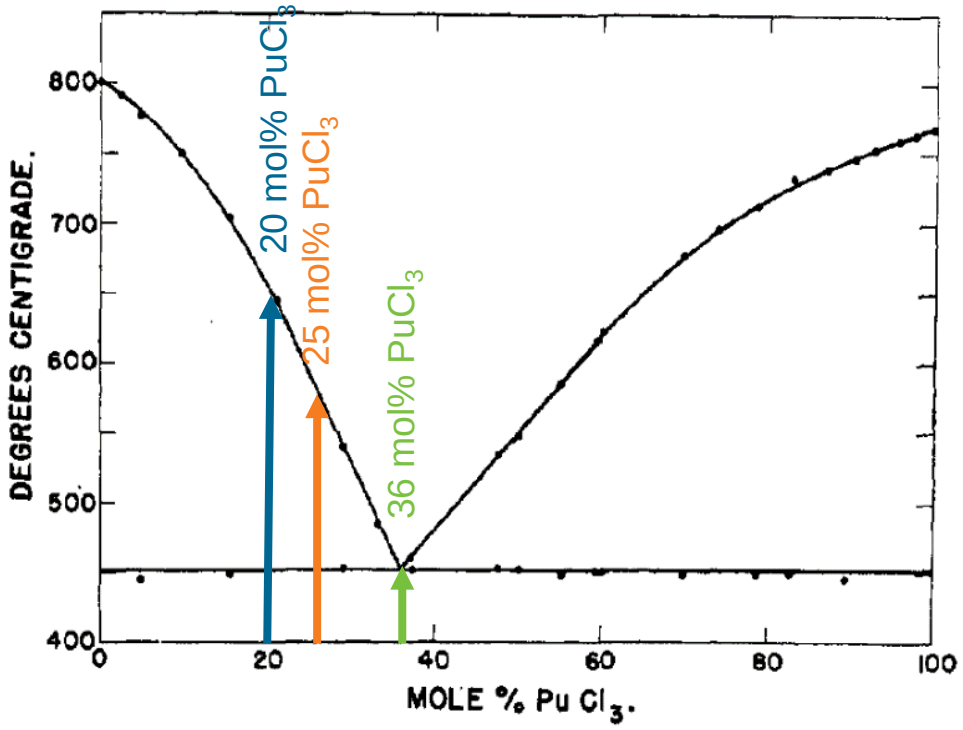
$$Pu_{(s)} + 3HCl_{(g)} \rightleftharpoons PuCl_{3(s)} + 1.5H_{2(g)} \quad (3)$$

$$\boldsymbol{Pu_{(s)} + 3NH_4Cl_{(s)} + NaCl_{(s)} \rightarrow PuCl_{3(s)} + NaCl_{(s)} + 3NH_{3(g)} + 1.5H_{2(g)}} \quad \textbf{(4)}$$

CRADA No. 18-CR-17, "Integrated Effects Testing for a Molten Chloride Fast Reactor."

Elemental/Isotopic Analysis

- Elemental analysis of starting material metal and salt
  - ICP-OES with TEVA separation
  - ICP-MS
  - Gamma Spec for Am^{241}
- Composition
  - 63.3 mol% NaCl (22.6 wt%)
  - 36.2 mol% $PuCl_3$ (76.4 wt%)
  - 0.5 mol% other (1.05 wt%)
    - ($FeCl_3$, UCl_3, $NpCl_3$, $AmCl_3$)
- Purity of salt is 99.5%
- Eutectic composition predicted from Bjorklund et al.
  - 64 mol% NaCl – 36 mol% $PuCl_3$

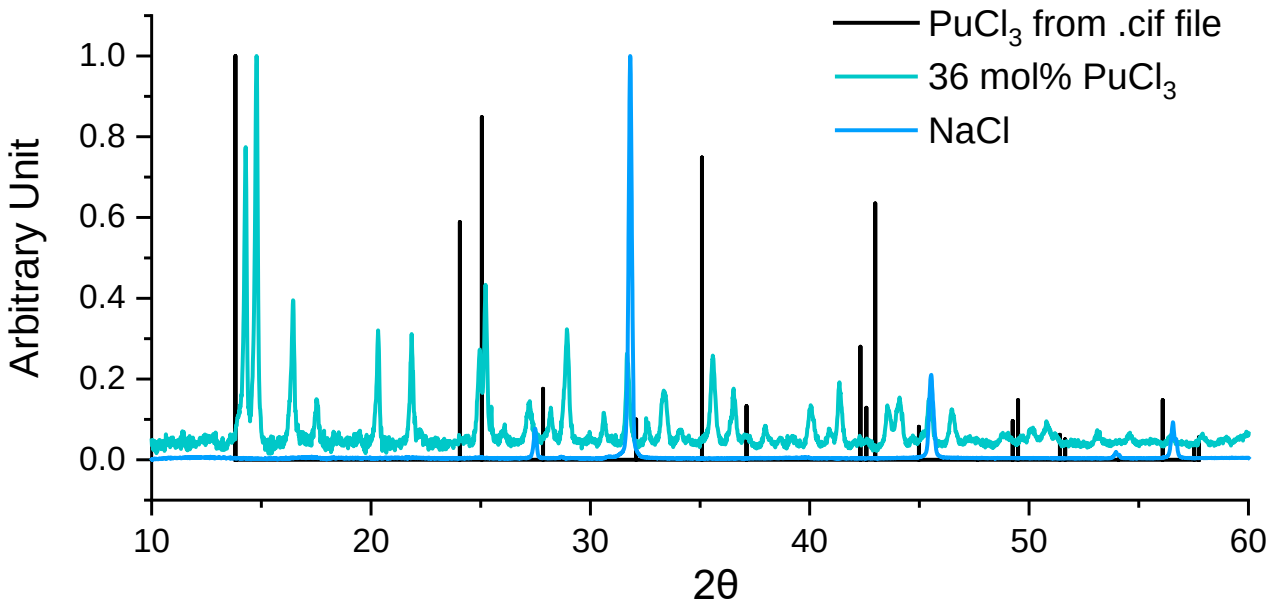


Bjorklund, C. W., Reavis, J. G., Leary, J. A., Walsh, K. A. "Phase Equilibria in the Binary Systems $PuCl_3$-NaCl and $PuCl_3$-LiCl" 1959

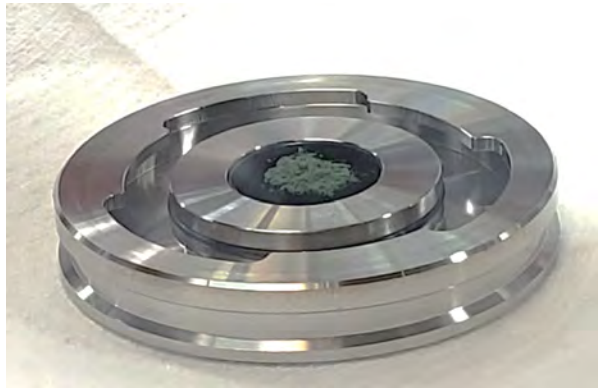
	Pu-metal		NaCl-$PuCl_3$ Eut. Salt	
Analyte	ug/g	% Error	ug/g	% Error
U-234	118	±10%	60.4	±10%
U-235	792	±5%	406	±5%
U-236	556	±5%	283	±5%
m/z-238	430	±5%	246	±5%
Np-237	390	±5%	212	±5%
Pu-239	807000	±5%	469000	±5%
Pu-240	157000	±5%	91600	±5%
m/z-241	10100	±5%	6040	±5%
m/z-242	3350	±5%	1960	±5%
Sr-88	<40	N/A	8.06	±15%
m/z-107	14.3	±30%	12.7	±15%
Ag-109	10.7	±20%	11.7	±20%
Fe	91.0	± 25 %	72.7	± 30 %
Na	<320	N/A	94900	±5%
Pr	<30	N/A	83.8	± 20 %
	Pu-metal		NaCl-$PuCl_3$ Salt	
Analyte	uCi/g	% Error	uCi/g	% Error
Am-241	2.51E+04	±3%	1.41E+04	±3%
Np-239	<7E-1	±3%	<3E-1	N/A

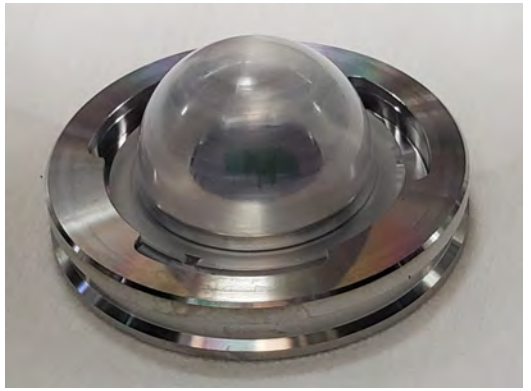
*Also looked for Ba, Cd, Ce, Eu, Fe, K, La, Li, Mn, Na, Nd, Ni, Pr, Sm, Sr, Y and many more but all were below detection limits of OES and MS

XRD – 36 mol% $PuCl_3$ in NaCl



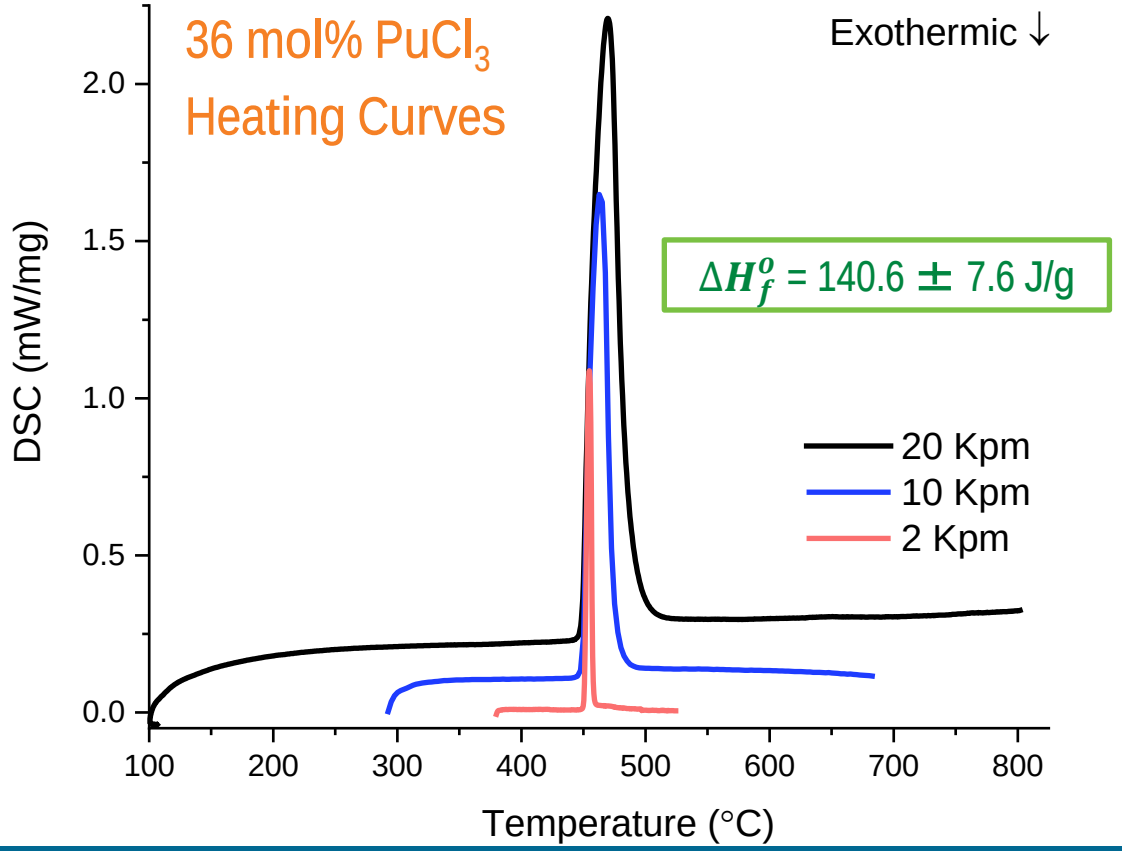
- PANalytical Empyrean X-ray Diffractometer
  - 45kV, 40mA Cu Ka X-ray beam
  - reflection-transmission spinner stage
  - PIXcel3D-Medipix3 detector.
  - step size = 0.013 degree, counting time = 600 sec/step
- Domed sample holder
  - top made of polycarbon, largely transparent to X-ray with a dome shaped background around 15-20 degree 2Θ
  - holder has gone through helium leak test to confirm its function as an airtight holder
- Loaded sample holder in Ar atmosphere
- No reference for mixtures of NaCl and $PuCl_3$



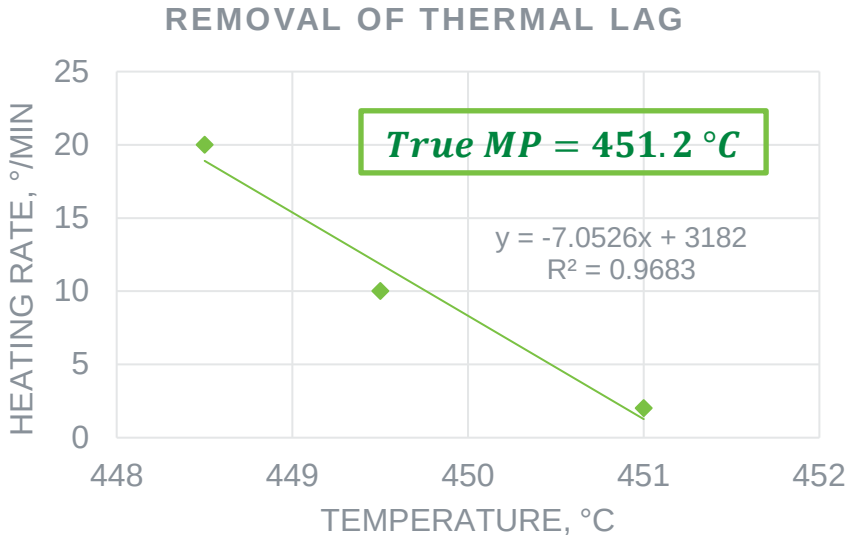


Melting Temperature & Enthalpy – 36 mol% $PuCl_3$ in NaCl

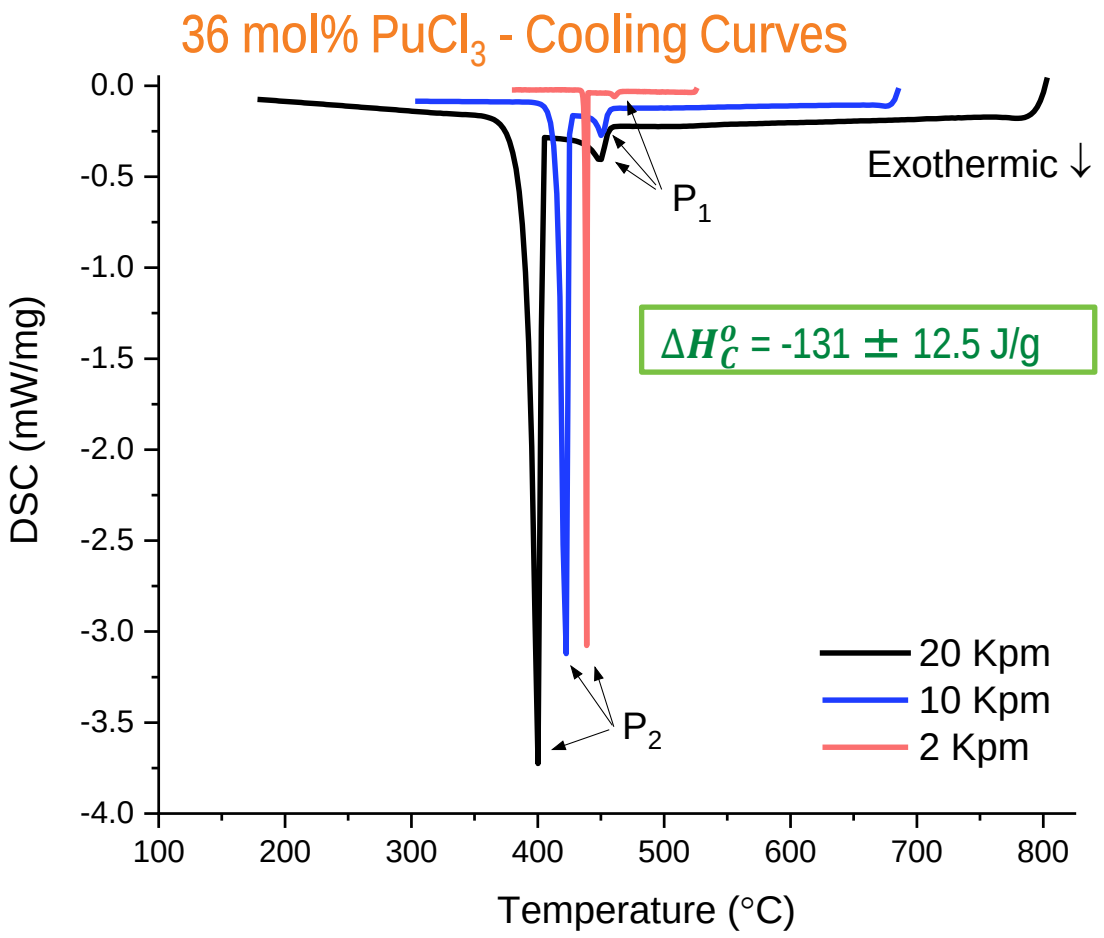
HR	Melt, °C	Peak, °C	Area, J/g
2	451.0	454.6	141.6
10	449.5	463.4	147.7
20	448.5	466.7	132.6
Average	449.7	461.6	140.6
Stdev	1.3	6.2	7.6
RSD, %	0.3	1.4	5.4



- STA in Ar glovebox
- UHP Ar cover and protective gas
- Calibration of STA with 5 standards
  - Verification of calibration with 2 standards
- Glassy Carbon sample/reference crucible
- Type S thermocouple
- 3 separate samples, one for each heating rate



Melting Temperature & Enthalpy – 36 mol% $PuCl_3$ in NaCl

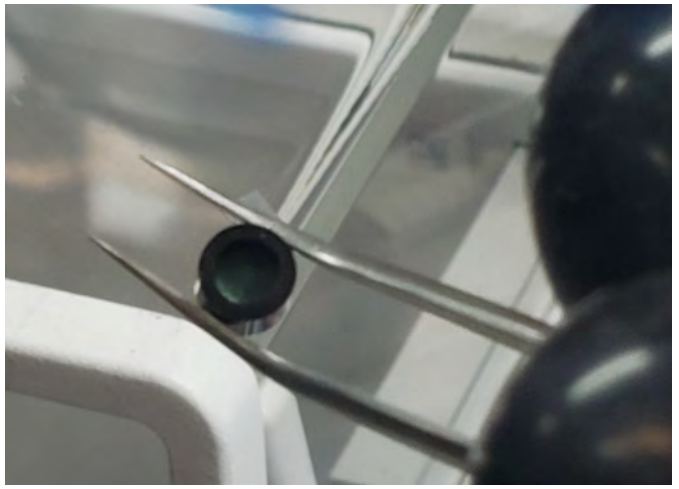


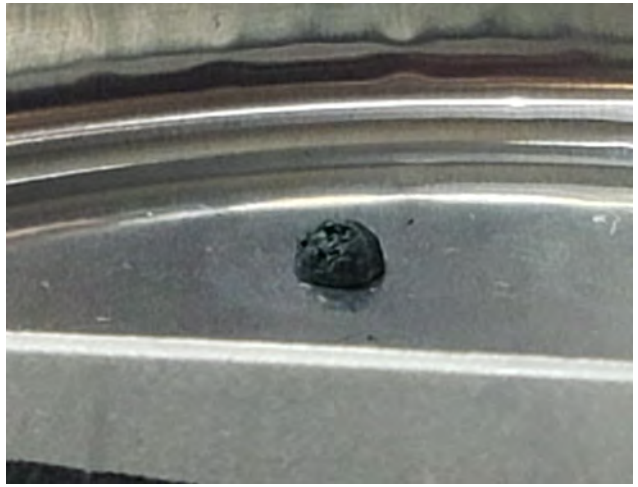
- Appearance of 2 peaks on cooling
- Don't know what peak 1 is
  - Possible Pu allotropic change energy?
- Higher deviations from cooling curve
- 2nd cooling curve from each cooling rate is shown

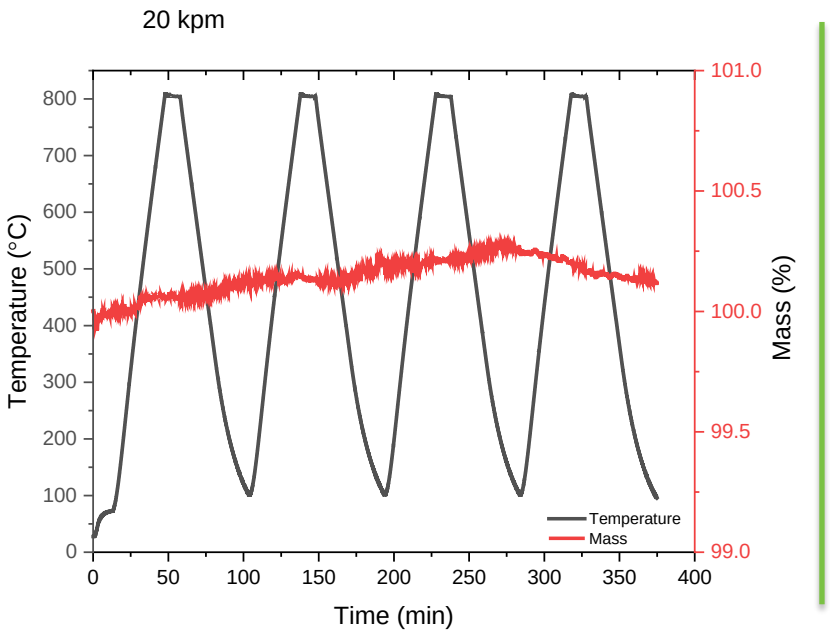
HR	Peak 1 – Onset, °C	Peak 2 – Onset, °C	Peak 2 – Peak, °C	Area, J/g
2	465.3	440.0	438.9	-137.6
10	456.1	415.4	413.4	-139.1
20	456.6	414.2	409.9	-116.7
Average	459.3	423.2	420.7	-131.2
Stdev	5.2	14.6	15.8	12.5
RSD, %	1.1	3.4	3.8	-9.6

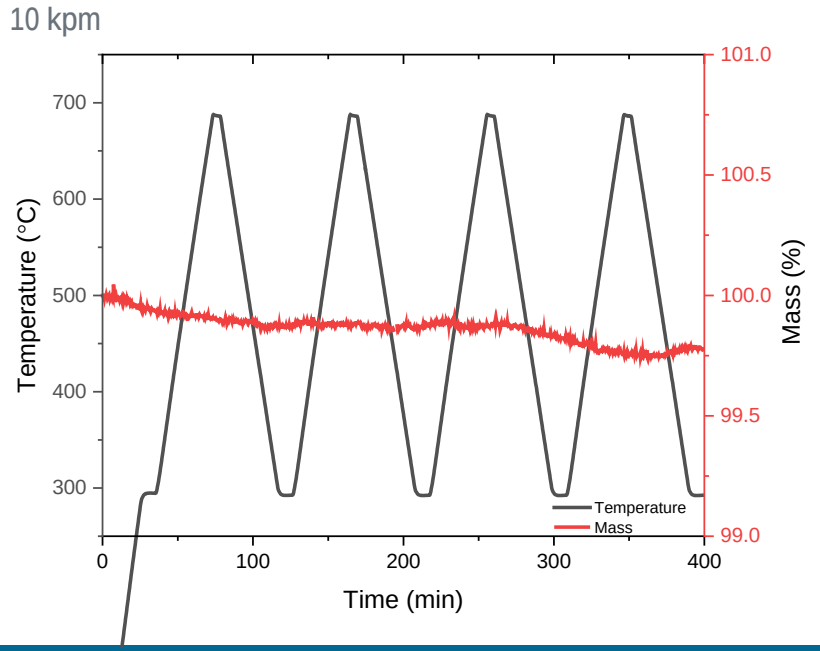
Salt Stability – 36 mol% $PuCl_3$ in NaCl

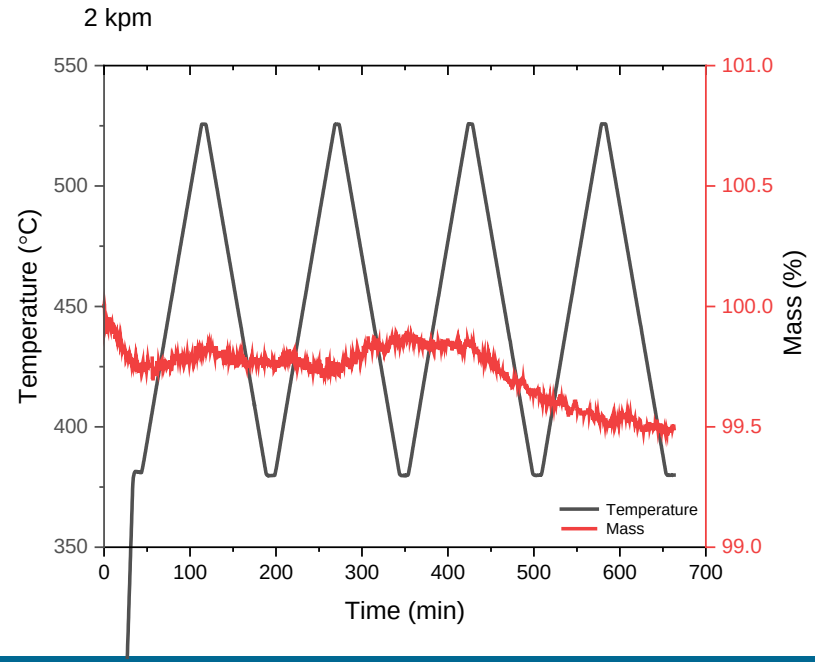
- STA in Ar glovebox
- UHP Ar cover and protective gas
- Glassy Carbon sample/reference crucible
- Run baseline to remove “buoyancy”
  - Longer runs harder for conditions to remain the same during run
- Less than 0.5 mass % change up to 800 ºC







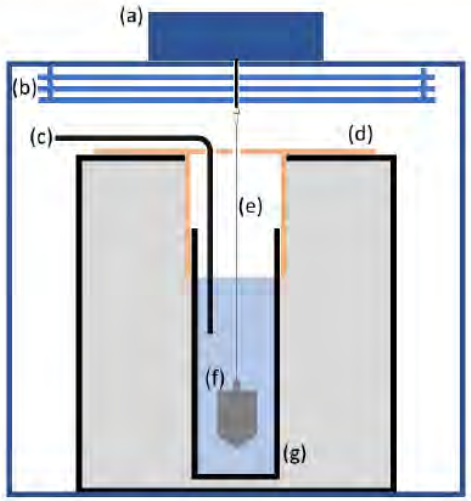


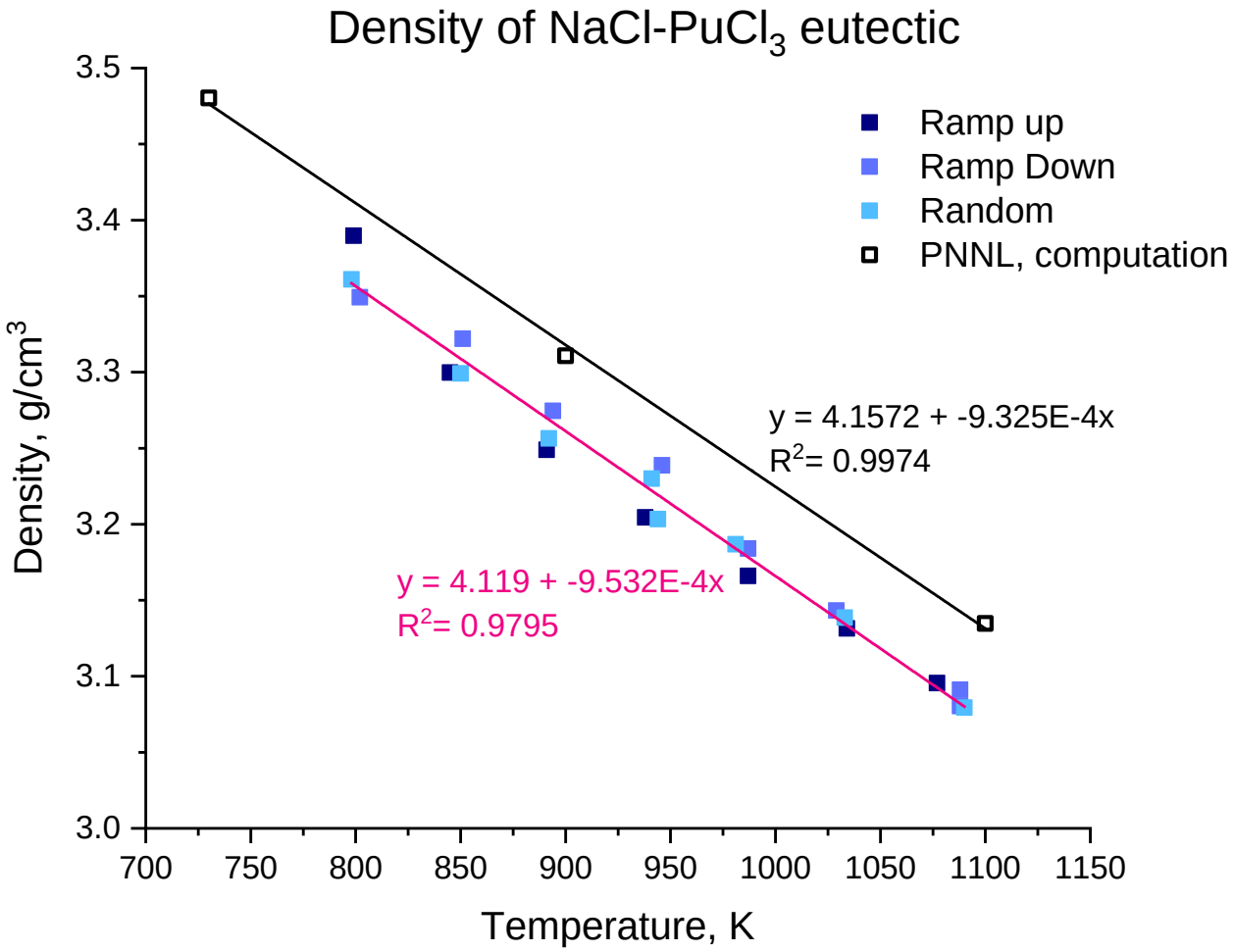


Density of 36 mol% $PuCl_3$ in NaCl

- Archimedes' hydrostatic method
- Calibrated, ~1cc bobber
- 0.1 mm wire
- 5 mass measurements per temp
- Heating, cooling, random cycles

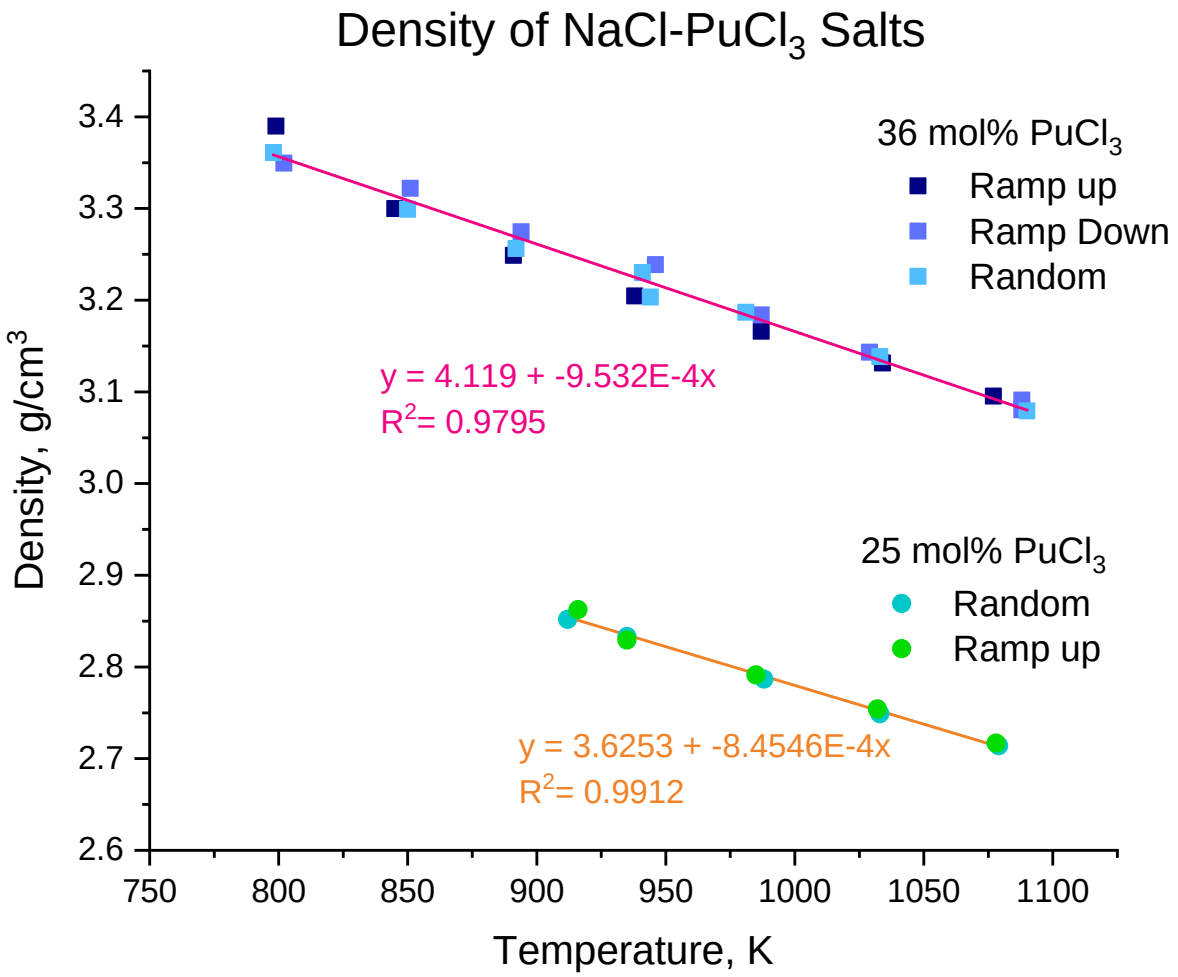
$$\rho_{salt} = \frac{M_{air} - W_{salt}}{V_0(1 + 3 \propto (T - T_0))}$$





Duemmler, K. et al. "Evaluation of thermophysical properties of the LiCl-KCl system via ab initio and experimental methods." Journal of Nuclear Materials (2021)

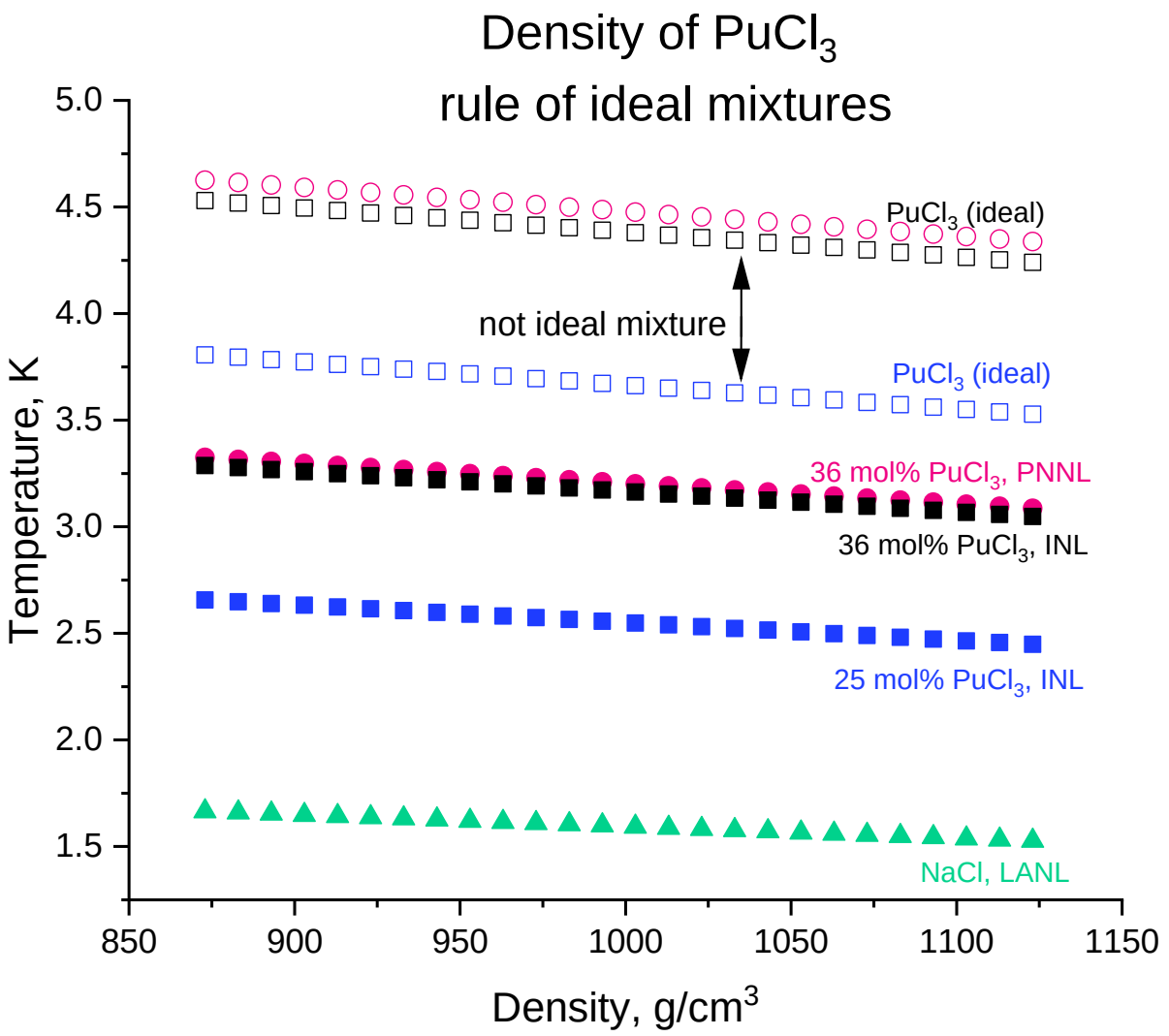
Density of 25 mol% $PuCl_3$ in NaCl



- 36 mol% $PuCl_3$ was down blended with NaCl to 25 mol% $PuCl_3$ in NaCl
  - Density measurements performed
  - Samples taken for
    - Elemental analysis
    - XRD analysis
    - Melt temperature
    - Enthalpy
    - Specific heat capacity

Is it possible to assume the NaCl-$PuCl_3$ system behaves ideally? …No

- To estimate the density of a $PuCl_3$
  - Use rule of additive volume
  - Assume 36 mol% $PuCl_3$ and 25 mol% $PuCl_3$ are ideal mixtures
- Calculate density of $PuCl_3$ from mixtures of NaCl-$PuCl_3$
- Rule of additive volumes
  - $\frac{1}{\rho_{mix}} = \frac{w_{NaCl}}{\rho_{NaCl}} + \frac{w_{UCl_3}}{\rho_{UCl_3}}$
- Density of NaCl* and $PuCl_3$**
  - $\rho_{NaCl} = 2.147 \frac{g}{cm^3} - 0.00055 \frac{g}{cm^3 * K} * T(K)$
  - $\rho_{PuCl_3} = \frac{w_{PuCl_3}}{\frac{1}{\rho_{mix}} - \frac{w_{NaCl}}{\rho_{NaCl}}}$
- Mixtures of NaCl-$PuCl_3$ in this study are not Ideal Mixtures

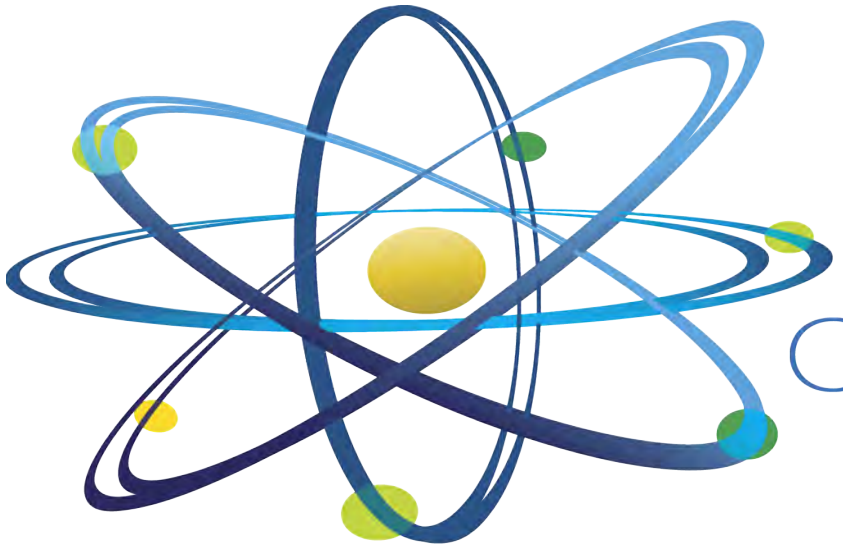


*Parker, S. Scott et al. "Thermophysical properties of liquid chlorides from 600 to 1600 K: Melt point, enthalpy of fusion, and volumetric expansion." *Journal of Molecular Liquids* (2022)
** assumed 36 mol% $PuCl_3$ and 25 mol% $PuCl_3$ were ideal mixtures

Next Steps

1. 36 mol% $PuCl_3$
   - Solid and liquid heat capacity experiments
   - 2nd attempt on XRD
   - Higher temp stability studies
2. 25 mol% $PuCl_3$
   - Elemental analysis
   - Melting temp and stability study
   - Solid and liquid heat capacity experiments
3. Synthesis of $PuCl_3$ for Pu-rich salt studies
4. Continue collaborations with LANL & PNNL
   - End goal is joint publication

Questions



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Molten Salt Reactor PROGRAM