Molten Salt Reactor PROGRAM

INL/MIS-26-91722

Examination of $PuCl_3$-$AmCl_3$-NaCl Salt

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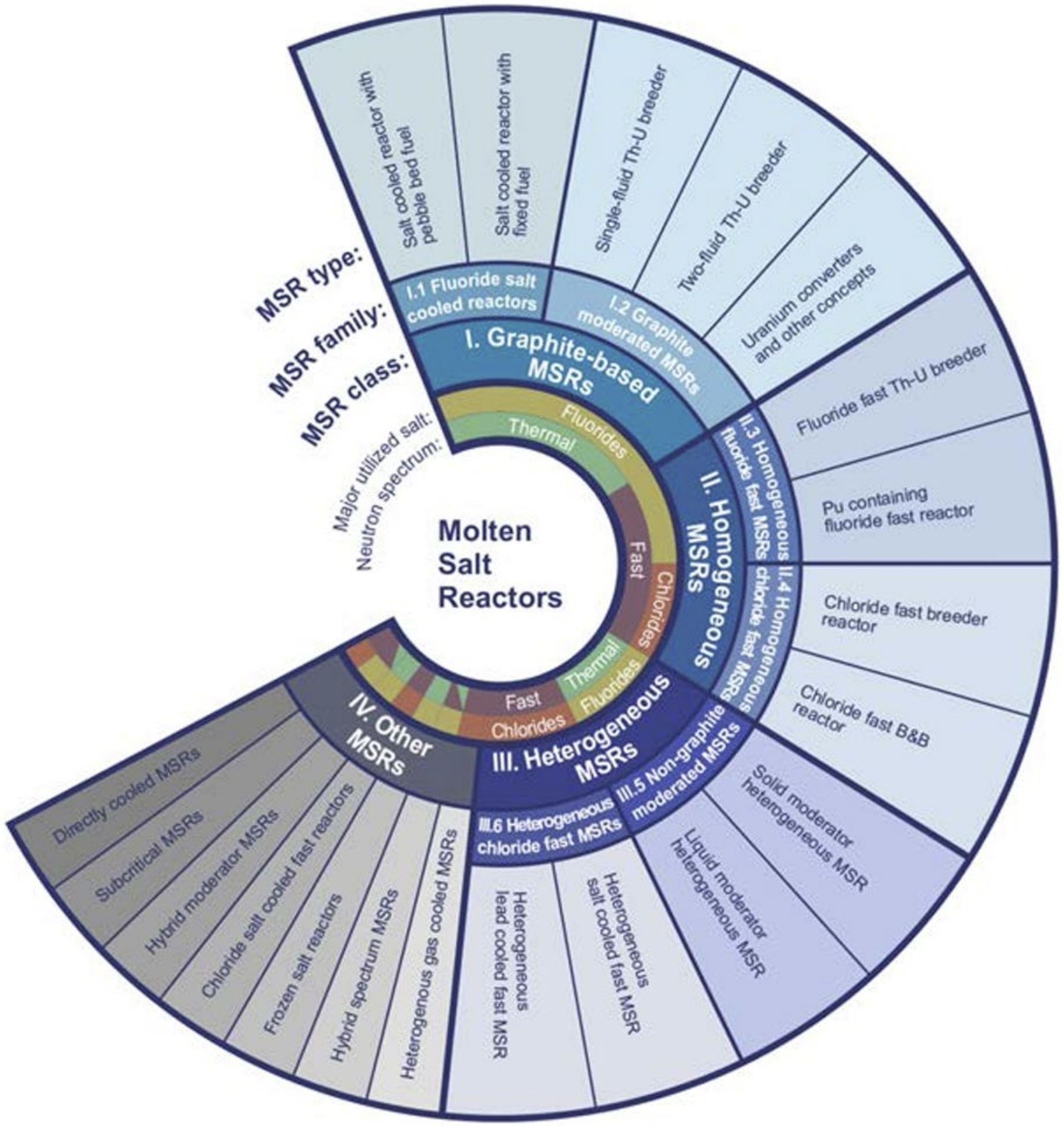
Outline & Milestones

- Outline
  - Background
  - Experimental Setup
  - Results
  - Conclusion
- Work Package Milestones
  - **M2AT-26IN0704025**: Complete Synthesis of Plutonium/Americium (Pu/Am) Metal to Chloride and Initiate Characterization of the Salt – on schedule
  - **M3AT-26IN0704026**: Complete Initial Thermal Property Measurements of $PuCl_3$-$AmCl_3$-NaCl Salt – on schedule

Status of Molten Salt Reactor Technology, Technical Reports Series No. 489, International Atomic Energy Agency, pg 37

Background

- Many advantages of MSRs
  - Safety
  - **Fuel Flexibility & Efficiency**
    - Can accommodate Th/U, U, Pu cycles, waste burner, high fuel utilization, online refueling and chemistry control
    - Can be efficient at "burning up" fuel, leaving behind far less long-lived radioactive waste
  - Waste Reduction
  - Economics & Practicality
  - Proliferation Resistance
  - Still many challenges!
- Waste Burner MSRs
  - Utilize U/TRU as fuel
  - Burn (i.e. transmutate) long lived fission products into shorter-lived fission products
  - Good for waste and disposal
  - Enables a closed fuel cycle



Hazards

- We have never performed a hydride run on Am containing material before!
  - Graded approach
  - 5g batch to start
  - Then 95g batch

Warning Energetic Reaction

- Use thermodynamic data to predict energy, compare U and Pu
- Follow previous procedure for UCl_3 and $PuCl_3$ synthesis
- Add NaCl carrier salt will absorb energy (heat) during synthesis
- Mix Pu-Am metal in slowly with NaCl + NH_4Cl
- Slow heating rate (10°C/hr) to limit energy introduced into chlorination reaction

Warning Gas from Synthesis

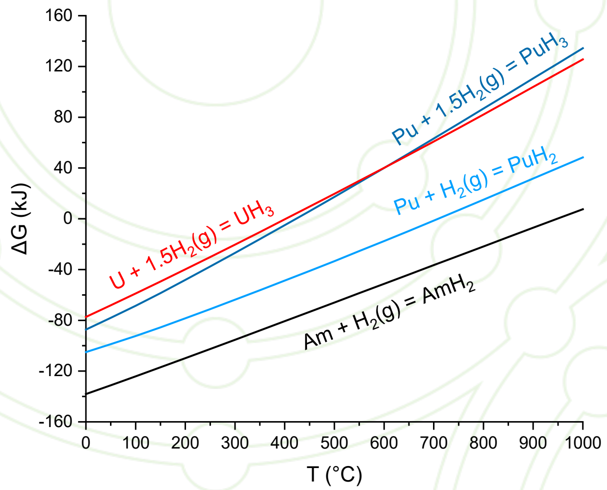
- Drager tubes in glovebox (detect NH_3)
- Steel wool on top of glassy crucible as indicator for HCl gas
- Run experiment with 1% excess NH_4Cl
- Quantities of off gases NH_3 = 26.7g/batch (~21,000 ppm if all HN3 was in GB at one time), H_2 = 1.567g/batch
- Bypass glovebox purification beds during synthesis

Warning Radiological

- High dose material
- Use graded approach for unknown processes
- Am and Pu powders are known to be "flighty"
- Reduce number of pours

Synthesis

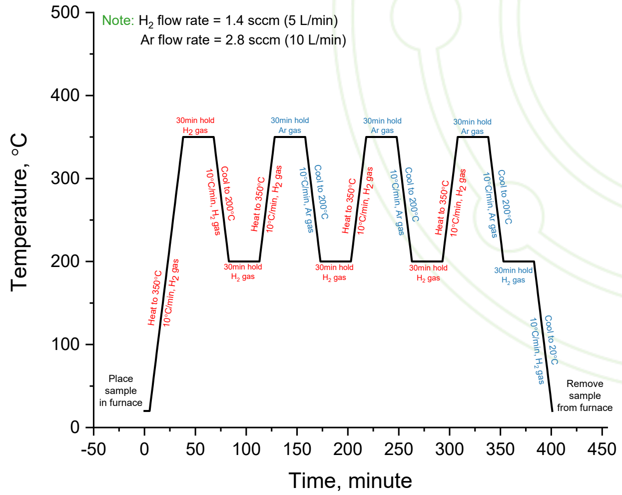
- Starting Material
  - Pu-Am alloy containing 80Pu-18Am-2U
  - Dried NaCl and NH_4Cl
- Perform hydride/de-hydride, <50 mesh
- Convert metal to chloride salt
- Salt composition (target)
  - 40$PuCl_3$-9$AmCl_3$-50NaCl (mol %)
- Verify elemental and isotopic composition of starting metal and salt
- Characterize salt to determine melting point, density, and heat capacity



Hydride:
$$Pu + H_2(g) \leftrightharpoons PuH_2,\quad Am + H_2(g) \leftrightharpoons AmH_2$$

Dehydride:
$$PuH_2 \leftrightharpoons Pu + H_2(g),\quad AmH_2 \leftrightharpoons Am + H_2(g)$$

Chlorination:
$$Pu + 3NH_4Cl \leftrightharpoons PuCl_3 + 3NH_3(g) + 1.5H_2$$
$$Am + 3NH_4Cl \leftrightharpoons AmCl_3 + 3NH_3(g) + 1.5H_2$$



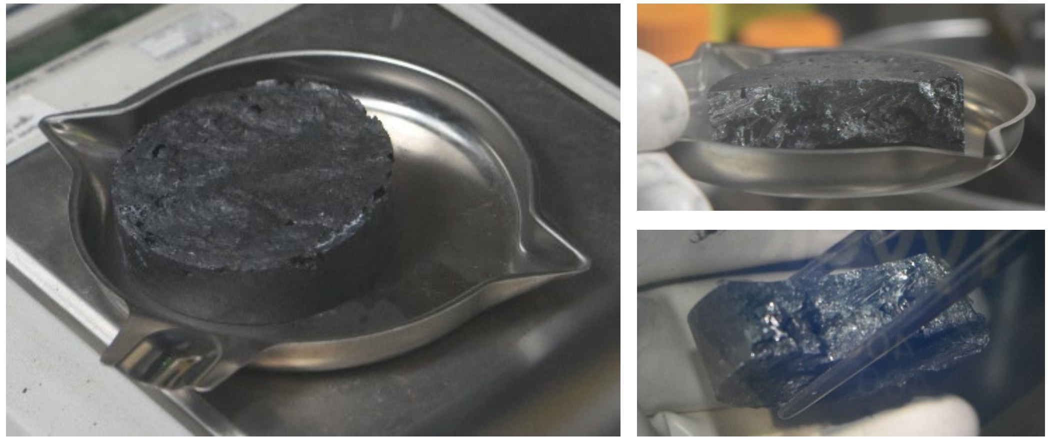
Pu-Am metal alloy that will be reduced in size and converted to a chloride salt (top, right). Gibb's free energy predictions for hydriding actinides (top, left). Chemical reactions for synthesis (bottom, left). Hydride/de-hydride run process (bottom, right).

Synthesis in pictures

Pu-Am metal material, ~350g (left), ~100g Pu-Am metal starting material (middle), Pu-Am powder after hydride/de-hydride (right)

NaCl and NH_4Cl in mixing container with fractions of Pu-Am metal being added (left) and NaCl, NH_4Cl, and Pu-Am metal mixed

Fuel Manufacturing Facility (FMF) operator assembling furnace for fuel salt synthesis

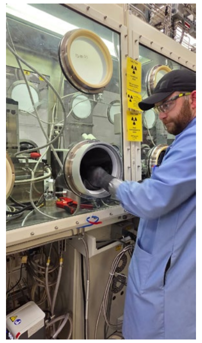


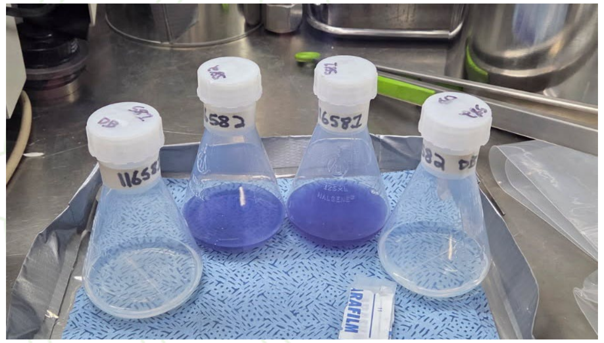
$40PuCl_3$-$9AmCl_3$-50NaCl (target) fuel salt puck (left) and broken up puck (right)

0.250g $PuCl_3$-$AmCl_3$-NaCl powder sample for analytical laboratory

2. Clow, J., et al., *Specific activities and DOE-STD-1027-92 hazard Category 2 thresholds, LANL fact sheet*. 1994: United States. p. Medium: ED; Size: 13 p.

Chemical Analysis






- *Data is preliminary*
- Pu/Am Starting Material
  - 80Pu-18Am-2U (assumed)
  - 80.2Pu-18.8Am-0.8Np-0.2U (preliminary)
- Salt
  - $40PuCl_3$-$9AmCl_3$-50NaCl (target)
  - $36.3PuCl_3$–$8.8AmCl_3$–$0.6NpCl_3$–$0.2UCl_3$–53NaCl (preliminary)
- Thoughts
  - Presence of Np was indicated from gamma spec
  - Am-241 data from gamma spec aligns well with M/Z-241 from ICP-MS data

ICP-MS Data - Preliminary

	Metal		Salt	
Isotope	µg/g	% Error	µg/g	% Error
Cr	**40.5**	**±20%**	**76.9**	**±20%**
Ga	<5	N/A	<5	N/A
Ge	<9	N/A	<10	N/A
Ni	**53.8**	**±25%**	**64.7**	**±10%**
Co-59	<20	N/A	13.2	±10%
Sr-86	<30	N/A	**18.9**	**±10%**
Sr-88	<300	N/A	**169**	**±5%**
Zr-91	<3	N/A	<3	N/A
Zr-94	5.7	±30%	7.12	±20%
Nb-93	<2	N/A	<2	N/A
M/Z-90	<20	N/A	9.53	±10%
M/Z-92	6.74	±20%	8.89	±20%
M/Z-96	5.71	±15%	8.09	±20%
Mo-95	4.33	±20%	6.38	±15%
Mo-97	2.73	±20%	4.11	±15%
Mo-98	6.78	±10%	9.75	±20%
Mo-100	2.8	±15%	3.98	±15%
Cs-133	<2	N/A	1.23	±30%
Cs-135	<20	N/A	12.4	±10%
Ba-136	<20	N/A	14.7	±10%
Ba-138	**131**	**±38%**	**139**	**±10%**
Ce-140	<8	N/A	6.86	±15%
Ce-142	2.23	±20%	2.56	±15%
M/Z-134	<6	N/A	<5	N/A
M/Z-137	<30	N/A	**21.6**	**±15%**
La-139	3.91	±35%	3.78	±15%
Pr-141	0.905	±25%	0.86	±15%
Nd-143	<0.8	N/A	0.652	±30%
Nd-144	1.21	±20%	1.38	±25%
Nd-145	0.419	±25%	<0.5	N/A
Nd-146	0.867	±30%	0.909	±20%

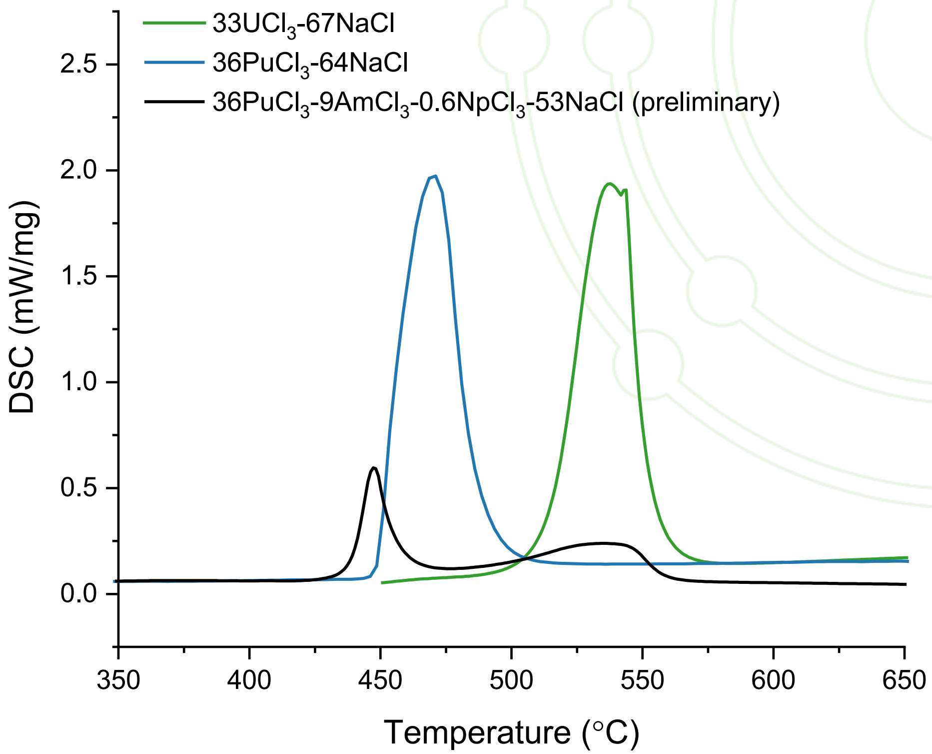
	Metal		Salt	
Isotope	µg/g	% Error	µg/g	% Error
Sm-147	<0.2	N/A	<0.2	N/A
Sm-149	<0.3	N/A	<0.3	N/A
Sm-152	<0.2	N/A	0.165	±35%
Eu-153	<0.2	N/A	<0.2	N/A
Gd-155	<0.3	N/A	<0.3	N/A
M/Z-134	<6	N/A	<5	N/A
M/Z-148	0.333	±30%	0.35	±30%
M/Z-150	0.308	±15%	0.319	±30%
M/Z-151	<0.2	N/A	<0.2	N/A
M/Z-154	<0.4	N/A	<0.4	N/A
Hf-178	<0.5	N/A	<0.5	N/A
Hf-180	<1	N/A	<1	N/A
Pt-194	<2	N/A	<2	N/A
Pt-195	<2	N/A	<2	N/A
Pb-206	**45.6**	**±20%**	**38.9**	**±10%**
Pb-207	**43**	**±20%**	**36.2**	**±10%**
Pb-208	**101**	**±20%**	**84.1**	**±10%**
Th-232	5.05	±15%	10.3	±10%
U-233	<0.2	N/A	0.164	±35%
U-234	**134**	**±5%**	**295**	**±5%**
U-235	**808**	**±5%**	**1780**	**±5%**
Np-237	**8140**	**±10%**	**7640**	**±5%**
Pu-239	**647000**	**±5%**	**379000**	**±5%**
Pu-240	**129000**	**±5%**	**74800**	**±5%**
M/Z-236	**581**	**±5%**	**1290**	**±5%**
M/Z-238	**490**	**±5%**	**543**	**±5%**
M/Z-241	**182000**	**±5%**	**111000**	**±5%**
M/Z-242	**2830**	**±15%**	**1630**	**±10%**
M/Z-243	<0.07	N/A	<0.08	N/A

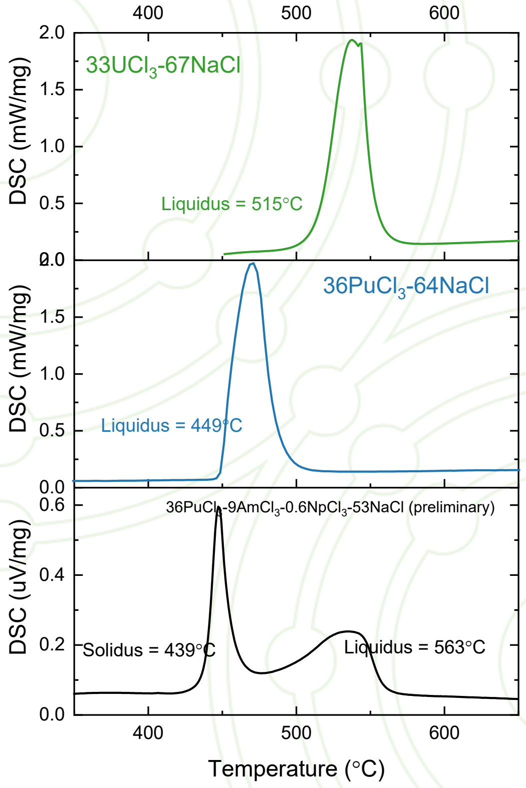
>15ppm = bold

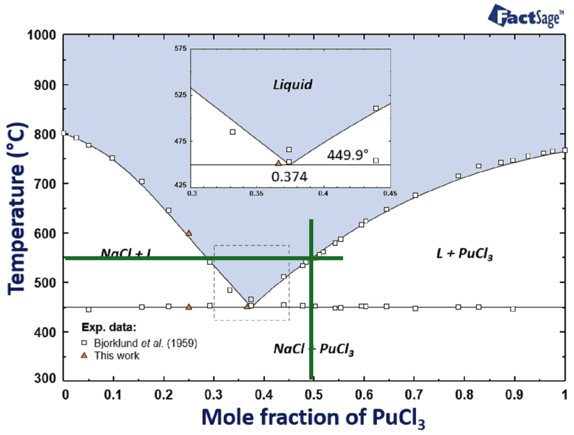
1. Karlsson, T.Y. and J.S. Pinto, M4AT-24IN0705022 - *Experimental Plan for Synthesis of an Americium and Plutonium Containing Salt*. 2024, Idaho National Laboratory (INL), Idaho Falls, ID (United States): United States.

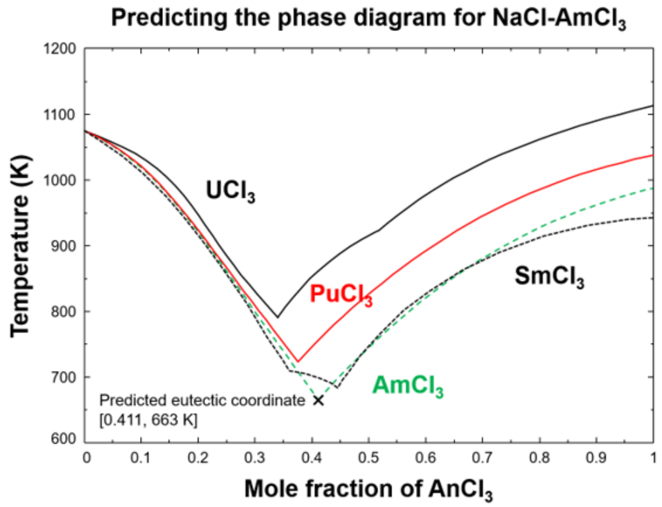
Phase Behavior

- Solidus: 438.8°C
- Liquidus: 562.9°C
- Indications from the thermogram
  - Binary eutectic system or close to?
  - Presence of $AmCl_3$ lowers solidus compared to NaCl-$PuCl_3$, 439 vs 450°C
    - Expected from models (Juliano Schorne-Pinto)
  - Can get a rough estimation of composition from NaCl-$PuCl_3$ phase diagram
  - Purposely did not aim for eutectic, can “dilute” salt for later studies







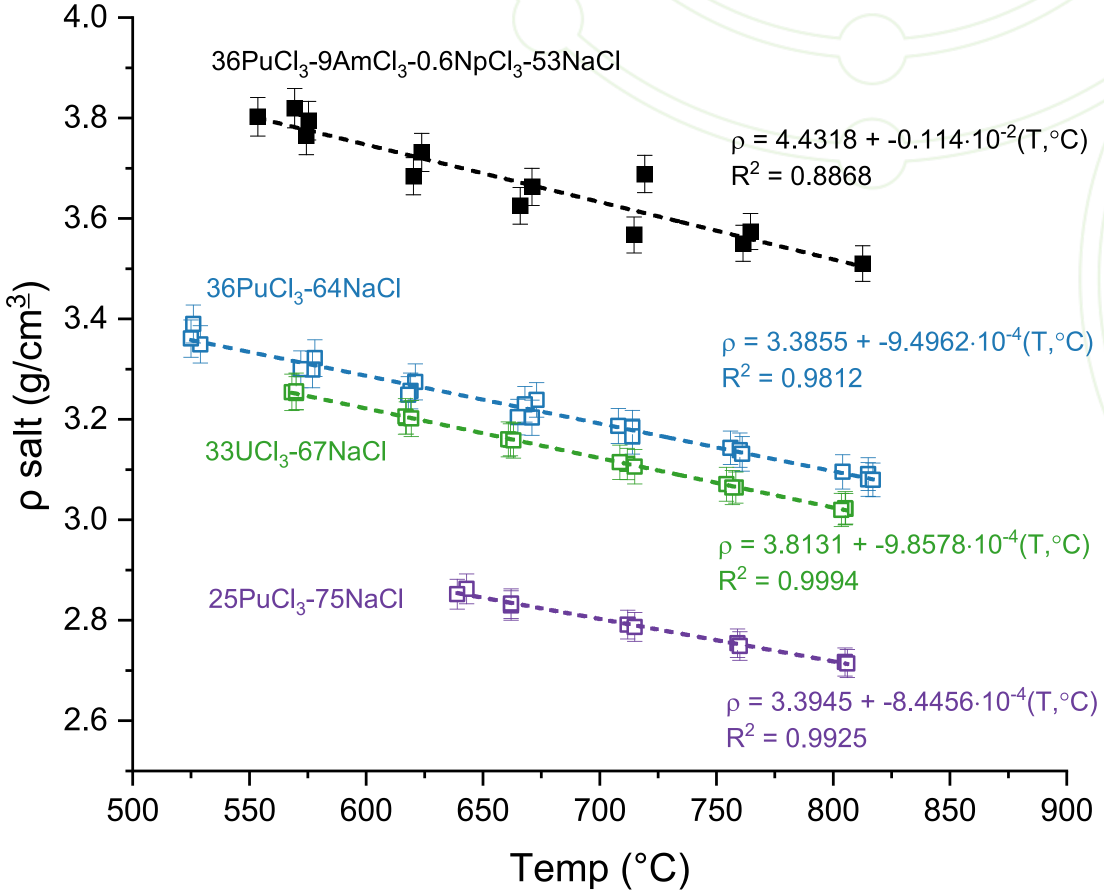


Density

- Archimedes' hydrostatic method
  - Calibrated 1cc bobber with 0.1mm wire
    - Each calibrated on a calibrated balance
    - Air, water, ethanol
  - 5 mass measurements per temp
  - Heating, cooling, random cycles
- Density
  - Validated between 550 to 800°C

Densitometer setup in FMF

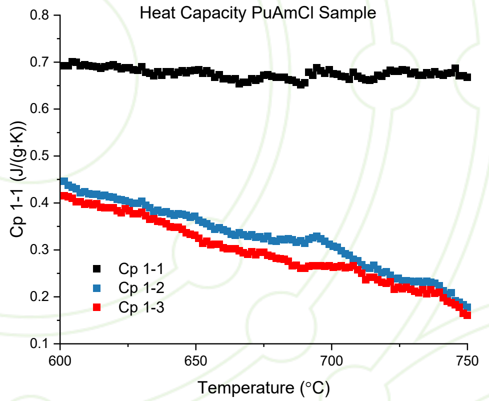
Equipment	Description
Furnace	Ventura electromelt with graphite crucible
Bobber	Ta, ESPI Metals 99.99%, 1.0408 ± 0.0006 cm^3
Wire	0.1 mm W, Alfa Aesar, 99.95% metals basis, Batch #10404 Lot #X28G043
Crucible	GAZA2, 25 mL Sigradur cylindrical crucible, HTW Germany
Balance, Bottom-loading	Mettler Toledo WXSS204, INL ID#525063 tolerance 0.8 mg
Thermocouple	Omega TJ36-CAIN-116U-8-SMPW-M, Inconel sheathed K-type ungrounded
Thermocouple Reader	Omega HH502, s/n 21000159, uncertainty 0.05% of reading + 0.3 K

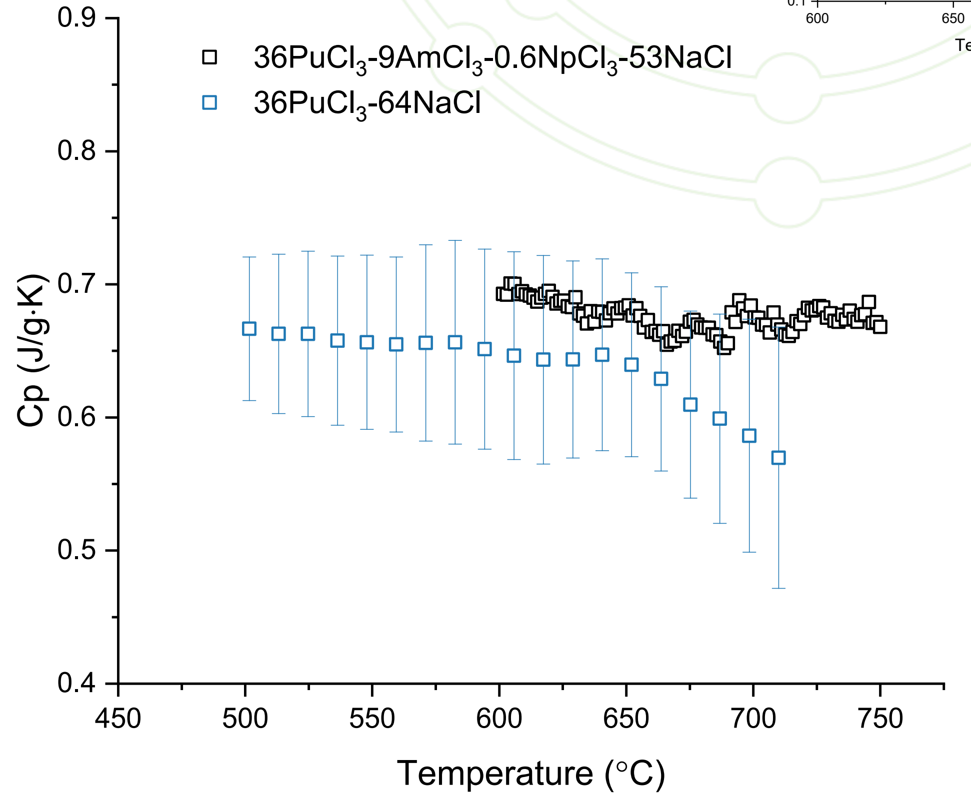


Karlsson, T.Y., et al., *Synthesis and thermophysical property determination of NaCl-PuCl3 salts*. Journal of Molecular Liquids, 2023. **387**: p. 122636.

Heat Capacity

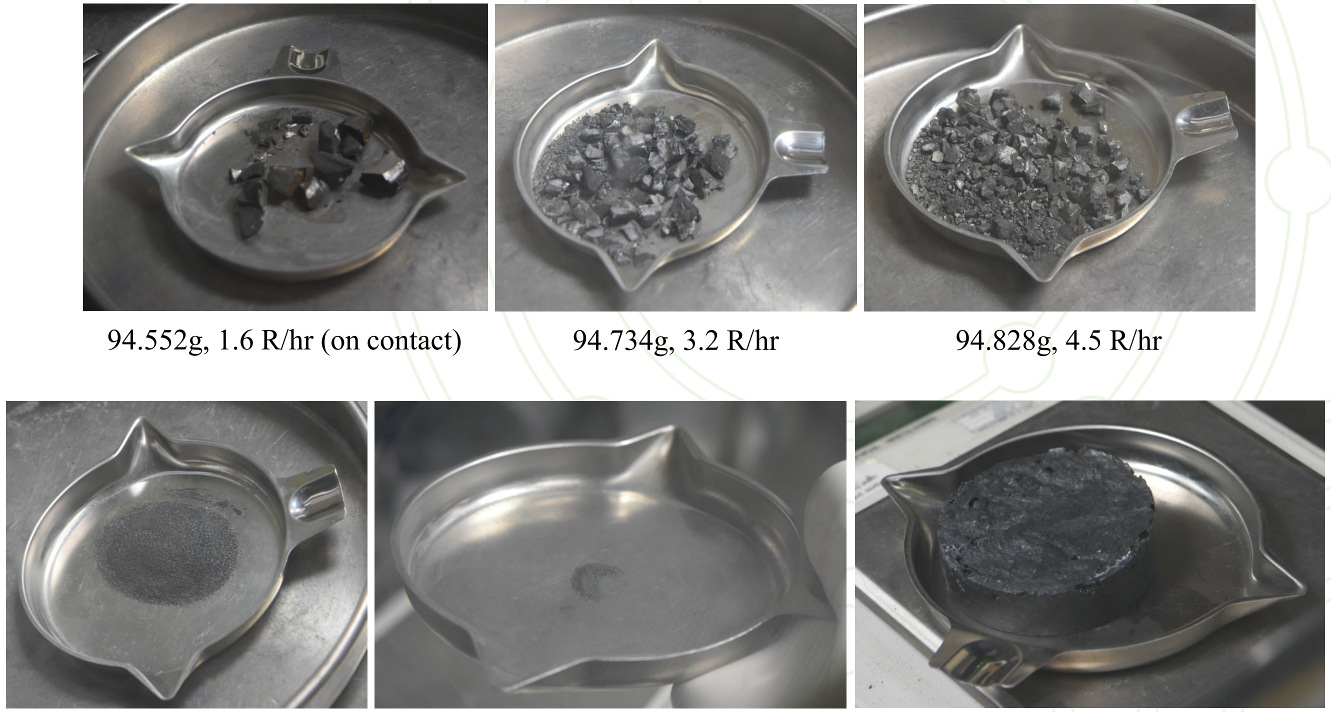
- Performed on DSC in glassy carbon crucibles at 5°C/min
- Difficult measurement for us this time around
  - New staff
  - Instrument availability
- One measurement inline with expectations…
  - But it was not reproducible after first heating





Dose Rate & Counting

- Passive Prompt Gamma-Ray Alpha Activation Analysis (PGAAA) for MSR Fresh Fuel Safeguards Verification
  - David Chichester Safeguards lead PI
  - Office of Defense Nuclear Nonproliferation Research and Development Project
- Assess the utility of PGAAA signatures as a complementary approach to traditional nondestructive assay (NDA) measurements for inferring U/Pu enrichment/isotopic content and mass within fresh molten salt reactor (MSR) fuel
- PGAAA emissions clearly seen in Am/Pu-bearing NaCl salt
- Relative intensity of observed Pu and Am gamma rays changed during melting
  - Indication of dynamic nonhomogeneity
  - Dynamic nonhomogeneity during melting suggests that Am/Pu are moving during the phase transition
  - Dynamic nonhomogeneity was different if the salt started as a powder vs. a solid monolith; evidence of change also seen as change in observed external dose rate



94.552g, 1.6 R/hr (on contact)

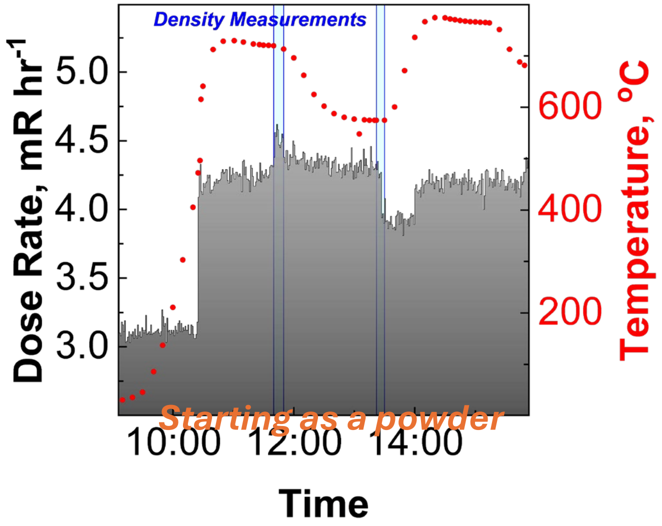
94.734g, 3.2 R/hr

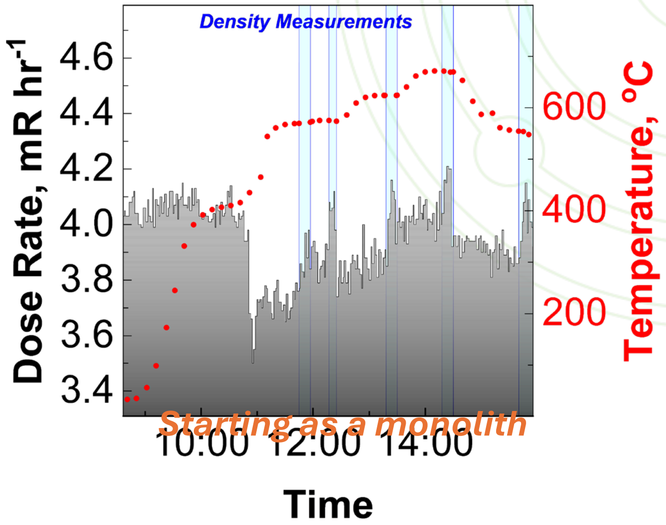
94.828g, 4.5 R/hr

30.881g, 1.2 R/hr

0.250g, 100 mR/hr

168.563g, 2.6 R/hr





This work is partially supported by the U.S. Department of Energy, National Nuclear Security Administration, Office of Proliferation Detection's Safeguards Portfolio."

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Conclusion

- Successfully synthesized a $PuCl_3$-$AmCl_3$-NaCl salt
- Salt could be diluted with carrier to further assess phase diagram and determine eutectic composition
- Preliminary elemental and isotopic data is available, will finish analysis in coming weeks
- Performed phase behavior, density, and heat capacity studies
    - Heat capacity needs further work
- Dose rate of material presented challenges and scientific opportunities
- Acknowledgements – FMF, ARL, the entire INL team, MSR Campaign, Juliano, US-DOE NNSA (Office of Proliferation Detection's Safeguards Portfolio)

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