Thermophysical Properties of Americium Chloride Salts

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Overview

- LLNL and Superblock – Who Are We?
- The LLNL Pyroprocess
- Work Package Milestones
- Task Breakdown and Status
- Expected Impact

LLNL and Superblock
Who are we?

- Superblock established in 1961 in Livermore, CA
- Currently 1 of 2 defense R&D facilities in the US
- Fundamental studies of plutonium, it's behavior in different environments, and how it interacts with other materials
- Impact Areas
  - Pyrochemistry
  - Aqueous
  - Analytical
  - Metallurgy and Casting
  - Engineering

https://str.llnl.gov/past-issues/aprilmay-2024/superblock-essential-facility-nuclear-operations

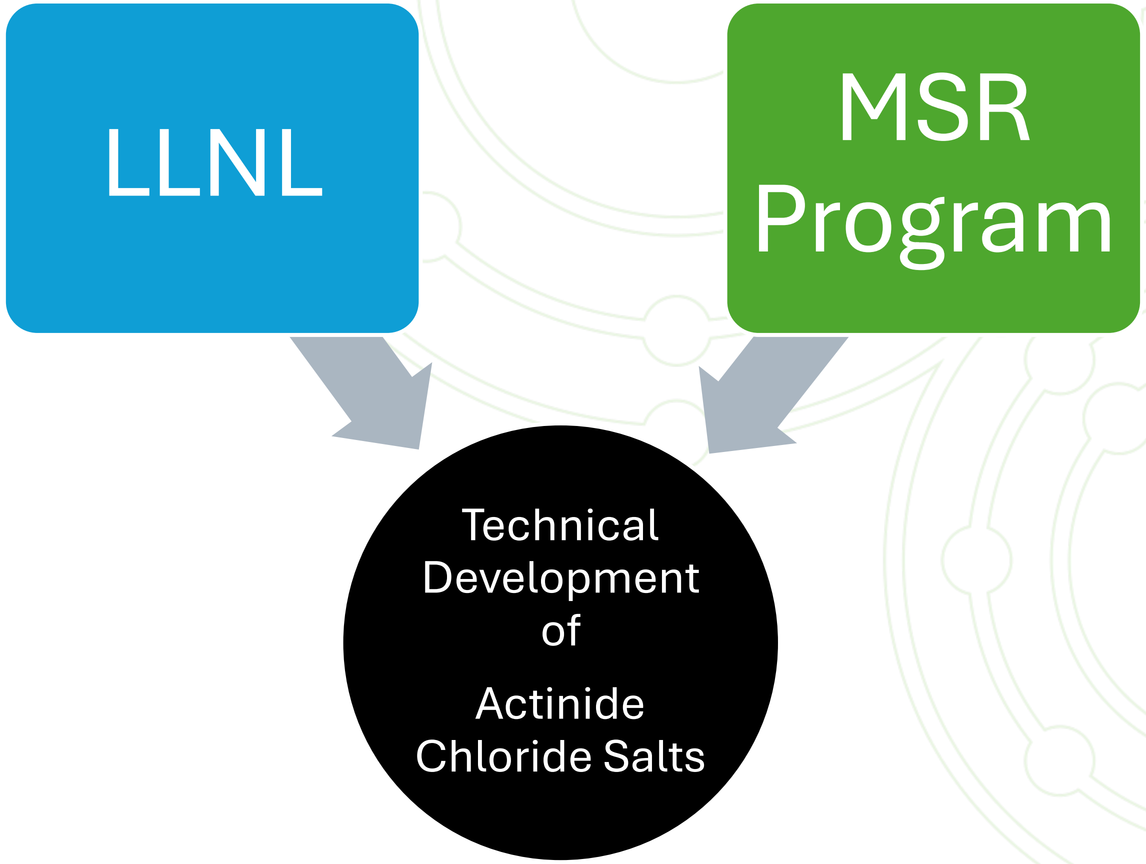
DOE/EIS-0547-S1: Supplemental EIS for Enhanced Plutonium Facility Utilization; Livermore, California

- NNSA deemed Superblock as "Underutilized" and working with DOE to increase R&D capabilities

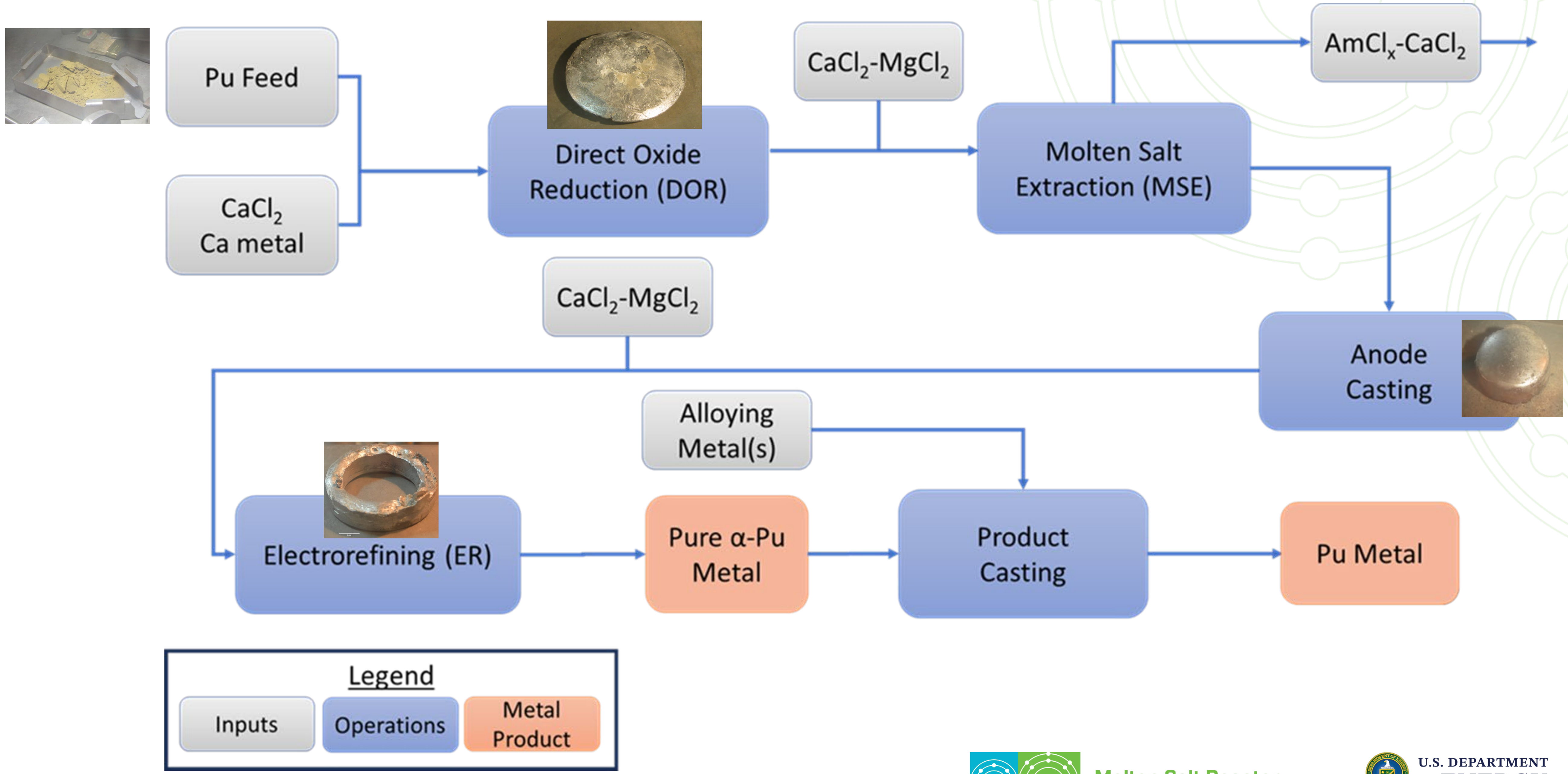
https://www.energy.gov/nepa/doeeis-0547-s1-supplemental-eis-enhanced-plutonium-facility-utilization-livermore-california

LLNL – How We Can Help

- FY26 is LLNL's first participation in MSR campaign
- Our salts are not that different…
  - LLNL uses chloride salt streams for pyrochemical purification of Pu
  - LLNL conducts heavy Pu loading experiments, so we routinely work with Am in large quantities
  - Am is a byproduct of Pu aging
- Interest in aqueous, pyrochemical, and oxide chemical behavior of Pu and Am
- **Goal:** Leverage LLNL facilities and expertise for joint LLNL/MSR technical challenges

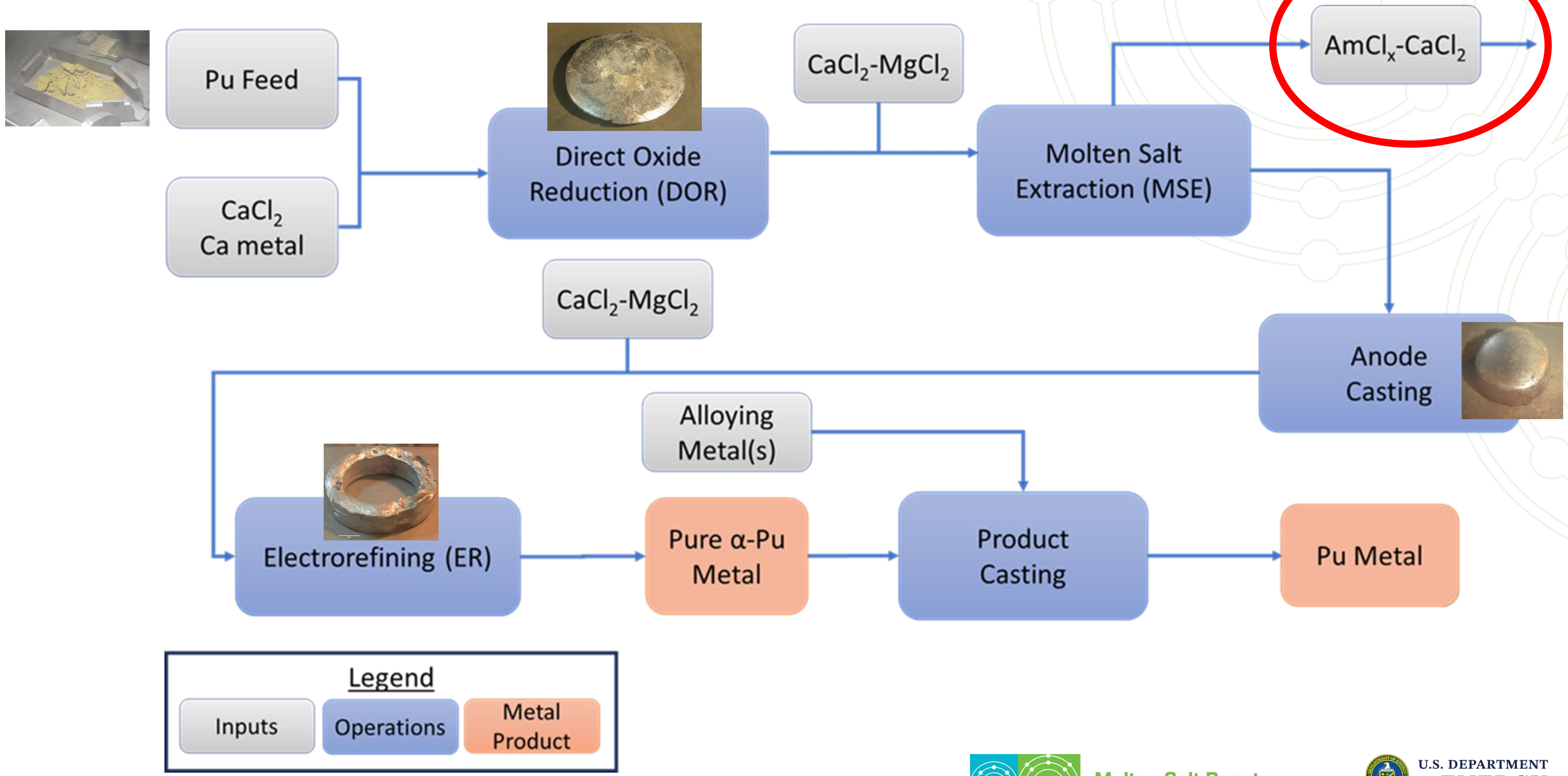


The LLNL Pyroprocess Flowsheet



The LLNL Pyroprocess Flowsheet

Source of $AmCl_x$ for LLNL Work



Molten Salt Reactor PROGRAM

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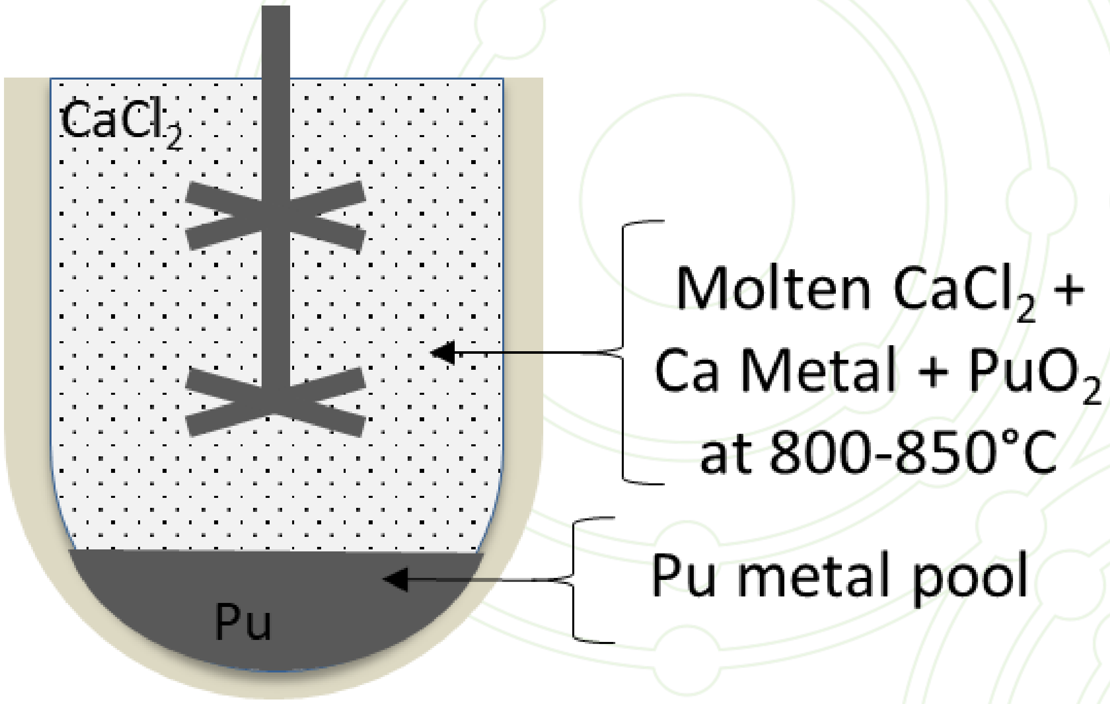
Direct Oxide Reduction

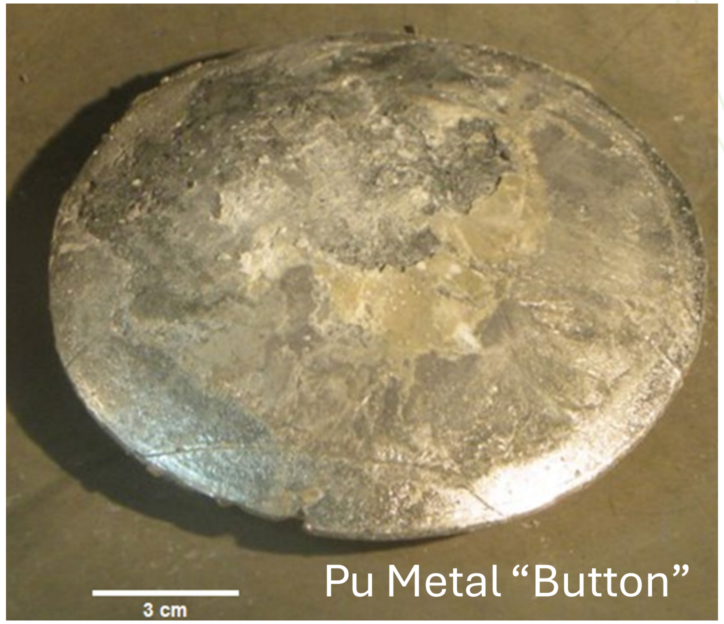
- Metal Reduction with Ca^0

$$PuO_2 + 2Ca \xrightarrow{CaCl_2} Pu + 2CaO$$

- No Pu purification with Am content retained in the metal button
- Separate metal button from salt and crucible
- Casted anhydrous $CaCl_2$ salt blocks prepared under vac heating*



MgO Crucible



Pu Metal "Button"

*Rappleye, D et al Development of Small-Scale Plutonium Electrorefining in Molten CaCl2. *J. Nucl. Mater.* **2021**, *552*, 152968. https://doi.org/10.1016/j.jnucmat.2021.152968

Molten Salt Extraction (MSE) for Am removal

- Am ingrowth removal from Pu via MSE

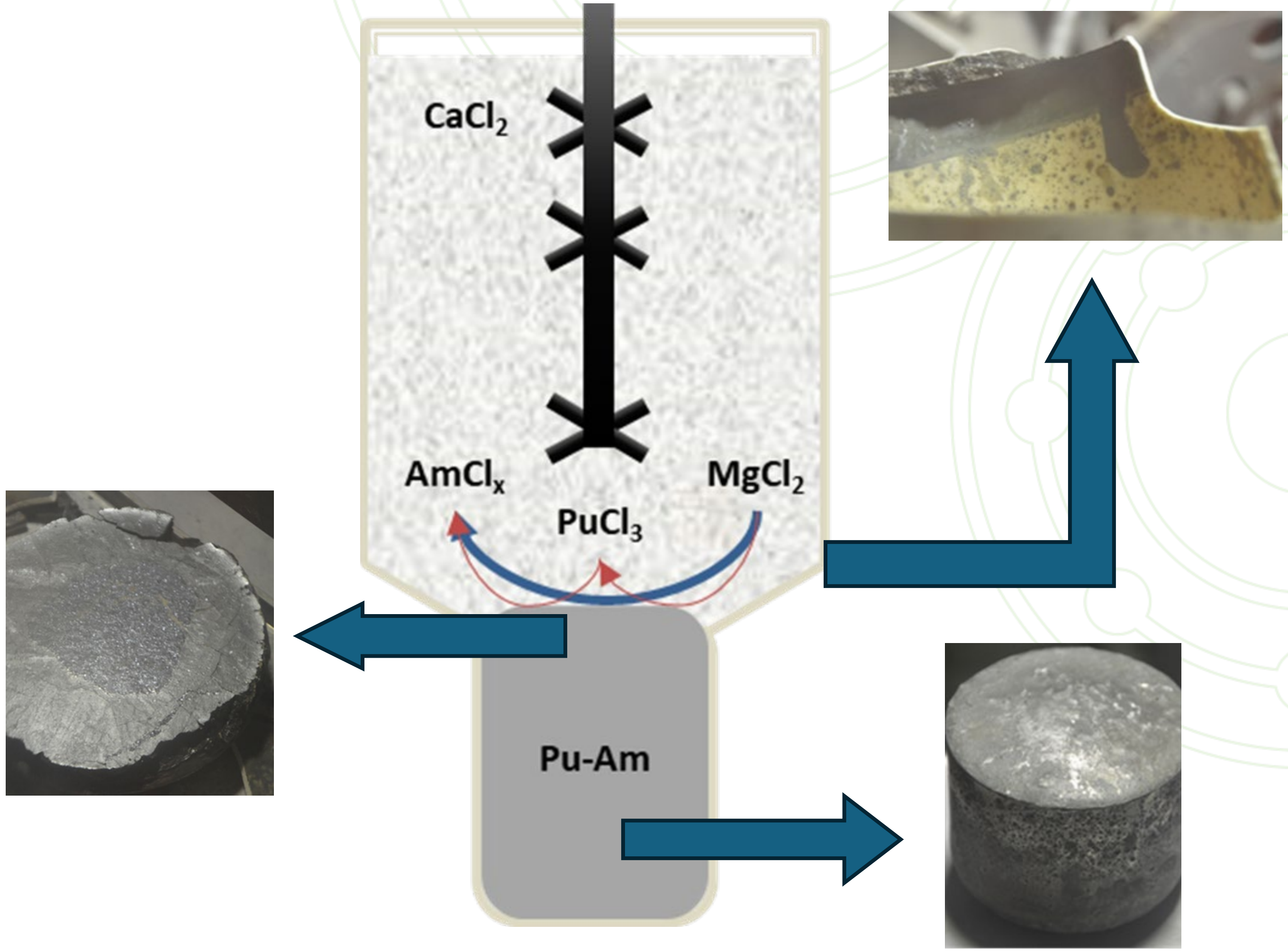
$$^{239}Pu \xrightarrow{n,\gamma} {}^{240}Pu \xrightarrow{n,\gamma} {}^{241}Pu \xrightarrow[t_{1/2} = 14.04\ yr]{\beta^-} {}^{241}Am$$

- Oxidation of Am^0 to $AmCl_x$ and back extracted into molten salt phase

$$\frac{3}{2}MgCl_2 + Pu^0 \overset{CaCl_2}{\Longrightarrow} PuCl_3 + \frac{3}{2}Mg^0$$

$$\frac{3}{2}MgCl_2 + Am^0 \overset{CaCl_2}{\Longrightarrow} AmCl_3 + \frac{3}{2}Mg^0$$

- Temperatures 850 – 950 °C



Molten Salt Reactor PROGRAM

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MSE (Cont.)

- Preferential formation of $AmCl_3$ over $PuCl_3$
- LLNL uses $MgCl_2$ as the oxidizing salt
- Other techniques use $PuCl_3$ as the oxidizing salt*

$$PuCl_3 + Am^0 \xrightarrow{CaCl_2} AmCl_3 + Pu^0$$

$$\frac{2}{3}PuCl_3 + Am^0 \xrightarrow{CaCl_2} AmCl_2 + \frac{2}{3}Pu$$

- Additions of $PuCl_3$ in feed - LLNL prioritizes Pu metal feeds for pyroprocessing
- Not currently authorized for *in-situ* chlorination to produce $PuCl_3$

Table: Free Energies of Formation at 727 °C of chloride

Chloride	$-\Delta G_f$ (kcal/g atom)
$BaCl_2$	83.7
KCl	81.6
LiCl	78.8
$CaCl_2$	76.8
NaCl	66.1
$LaCl_3$	66.1
$CeCl_3$	64.5
$AmCl_3$	60.0
$ErCl_3$	59.8
$PuCl_3$	58.6
$MgCl_3$	58.0

Possible Solvent Salts

Possible Oxidant Salts

*Paget, T., Mcneese, J., Fife. K., Jackson, M., Watson, R. Plutonium Handbook, 2nd ed. Chapter 21. (pp.201 - 286)

Material Challenges at LLNL: $AmCl_x$-$CaCl_2$

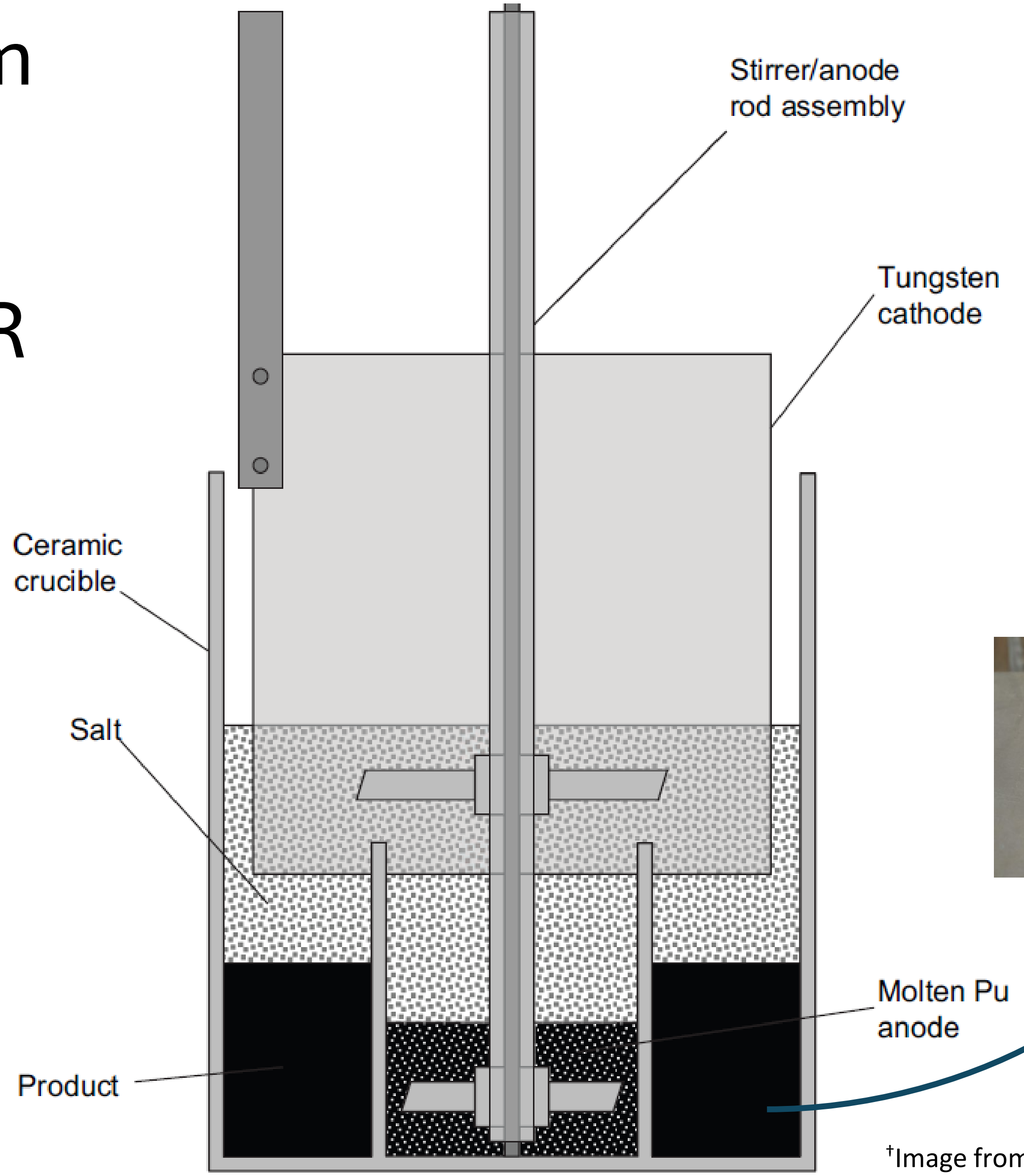
- High dose salts (Multiple Rem/hr)
  - Worker safety and dose monitoring (ALARA)
  - Glovebox work and complex sample movements between labs
- Material Control and Accountability (MC&A)
  - Part verification and procedural approval required
- Nuclear Facility Inventory
  - Mandatory regulatory pause for all sample handling in Superblock
  - Testing equipment and training staff during this time
- Competing projects and high staff demand constantly alter schedule

MSE breakout attire – modeled by Scott Simpson, LLNL

Electrorefining (ER) – Final impurity removal

- Remaining Am and other impurities removed in ER

Cast anode for ER feed†



ER cathode product ring

Chloride	ΔG° (kJ/mol Cl^-)*	
$TaCl_{2.5}$	-123	Anode
$SiCl_4$	-133	Anode
$CrCl_2$	-136	Anode
GaCl	-141	Anode
Al_2Cl_6	-175	Anode
$FeCl_2$	-187	Anode
UCl_3	-215	Anode
$NpCl_3$	-227	Anode
$PuCl_3$	-246	
$AmCl_3$	-249	Electrolyte
$AmCl_2$	-262	Electrolyte
$CeCl_3$	-271	Electrolyte
$CaCl_2$	-321	Electrolyte
ΔG° = Gibb's Free Energy		

$E = -nF\Delta G^o$

†Image from Christensen, Dana (1995). "The Future of Plutonium Technology." *Los Alamos Science* (23): 170

Work Package and Task Breakdown

- WP# AT-26LLA070404: (NEW) Salt Chemistry/LLNL- AT-26LL070404- Americium Thermophysical Property Measurement

Milestone #	Milestone/Deliverable	Due Date	Status
M3AT-26LL0704041	Measure density, heat capacity and melting point of $AmCl_x/CaCl_2$ salt system from LLNL pyrochemical salts	9/30/2026	On track – waiting for material release from inventory

- Task 1: Document thermal processing histories of LLNL Molten Salt Extraction (MSE) samples
- Task 2: Density, melting point, and heat capacity for $AmCl_x$-$CaCl_2$ MSE salts
- Task 3: MSTDB (Now MSD) buildout with LLNL experimental data and PNNL computational effort

Task 1: Document Thermal Processing Histories

- MSE is an established process at LLNL
- Incorporate LLNL pyroprocessing conditions of $AmCl_x$-$CaCl_2$ samples to understand formation conditions and chemical behavior of Am
- Combine with thermophysical measurement data for input into molten salt databases
- **Status:** Complete

Task 2: Density, melting point, and heat capacity measurements for $AmCl_x$-$CaCl_2$

- Glovebox environment
- Combined differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) of MSE salts
- Mass-spectrometry off-gas measurement
- Approved for use up to 1600 °C
- **Status:** Currently awaiting regulatory release of salts
  - Staff training in process
  - Equipment testing

Task 3: MSTDB* Buildout in collaboration with PNNL

- LLNL collects thermophysical property measurement data
- PNNL to run *ab-initio* molecular dynamic simulations of $AmCl_3$ and $AmCl_x$-$CaCl_2$ system
- PNNL collaborator: Manh Nguyen (manhthuong.nguyen@pnnl.gov)
- Collected data will populate the MSTDB-TC and support broader MSR technical goals
- Expected Deliverable: Joint journal publication on the experimental and computational measurements of $AmCl_x$-$CaCl_2$
- **Status:** on-hold until measurements complete

*New Name: Molten Salt Database (MSD)
(1) https://msd.ornl.gov/data-tp/
(2)https://msd.ornl.gov/data-tc/

Expected Impact

- Capabilities development
  - Highlight LLNL facility capability of performing R&D in high hazard facilities
  - Publishable thermal property investigations of Am containing pyrochemical salts
  - Contribute Am data to the MSTDB (MSD)
- Dual opportunities to leverage this work
  - Improvements to the LLNL plutonium flowsheet while supporting MSR technical challenges
    - Pyrochemistry of plutonium
    - Aqueous salt recovery
    - Am salt chemistry
  - Support LLNL's core energy security mission through nuclear reactor development
- Future work: Move to other Am salt systems with relevance to MSR development
  - $MgCl_2$
  - NaCl

Acknowledgments

- DOE-NE, NNSA, and entire MSR Program! We are excited to join you!
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  - Bradley Childs – Actinide Chemistry and Mass-Spec SME
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  - Jason Schnackenberg – Engineer and Metallurgy
- Pyrochemistry
  - Dave Roberts – Associate Program Leader for Pyrochemistry
  - Scott Simpson – Pyrochemistry lab lead
- Superblock Management - Jackie Meeker and Kiel Holliday
- E Program - Dan Flowers
- Admin staff (all programs)

DISCLAIMER

Thank You for Your Attention!

Questions?

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Connect with us at the MSR Review

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Backup Slides

Molten Salt Thermal Properties Databases (MSTDP)

- Consists of thermochemical(TC) and thermophysical(TP) databases for fluorides and chlorides
- Databases are for public use with technologies relevant to deployment of molten salt reactors
- MSTDP-TC: molten salt components and related systems of interest
- MSTDP-TP: Tabulated thermophysical properties and relations for computing properties as a function of temperature or composition

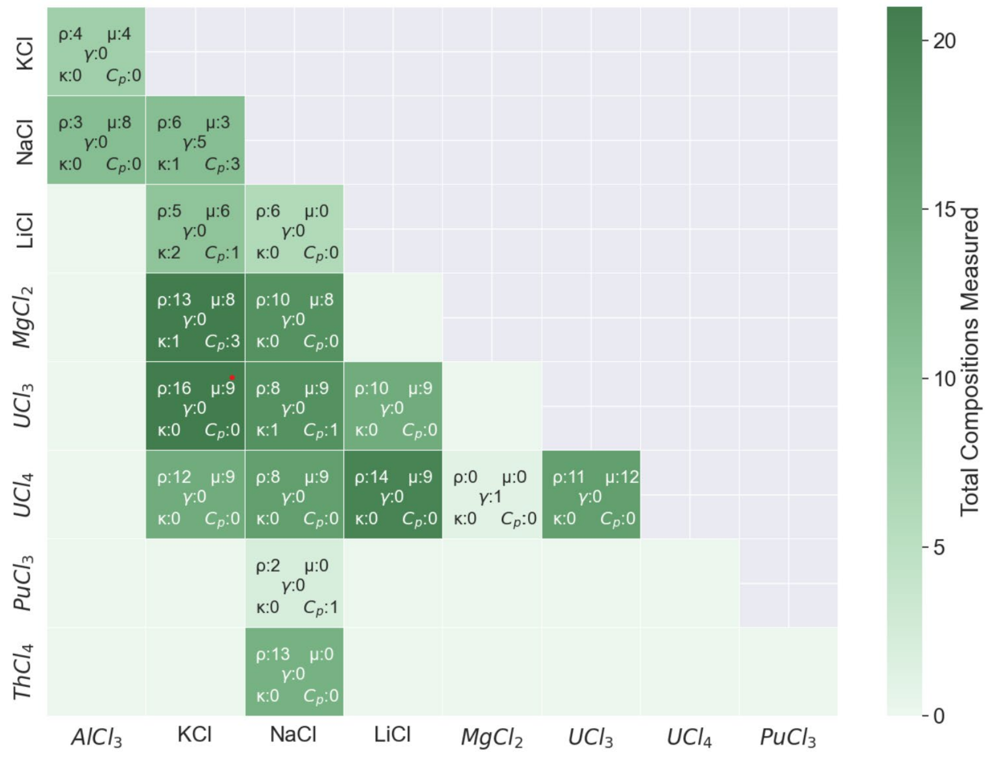
MSTDP-TP	MSTDP-TC
Melting and Boiling Points	Gibbs Free Energy Relations
Density	Computational Data
Viscosity	
Heat Capacity	
Thermal Conductivity	
Surface Tension	

Table. Properties of Interest in Thermal Property Databases
Note: MSRDP is undergoing a name change to Molten Salt Database (MSD)

(1) Termini, Nick, et al. "An Overview of the Molten Salt Thermal Properties Database–Thermophysical, Version 2.1.1 (MSTDB-TP v.2.1.1)." , Jul. 2023. https://doi.org/10.2172/1988348
(2) https://msd.ornl.gov/data-tp/
(3) https://msd.ornl.gov/data-tc/

Impact – LLNL can input 1st data on Am chlorides into MSTDP-TP

- Currently 976 unique entries in the MSTDP-TP database, none of which contain Am
- LLNL can be the first to contribute Am Chloride experimental data!
- Allow MSR developers to improve designs and account for Am chloride salts



Pseudo Binary Compounds in Chloride Database

Salt	ρ	μ	κ	c_p	γ
AlCl3	1	1	0	1	0
BeCl2	1	0	0	0	0
BeF2	1	1	1	1	0
CaCl2	1	1	1	1	1
CaF2	1	1	1	1	1
GdCl3	1	1	0	0	1
GdF3	0	0	0	0	0
KCl	1	1	1	1	1
KF	1	1	1	1	1
LaCl3	1	1	0	0	1
LaF3	1	0	0	1	0
LiCl	1	1	1	1	1
LiF	1	1	1	1	1
MgCl2	1	1	1	1	1
MgF2	1	1	1	0	1
NaCl	1	1	1	1	1
NaF	1	1	1	1	1
NdCl3	1	1	0	0	1
NdF3	0	0	0	1	0
NpCl3	0	0	0	0	0
NpF3	0	0	0	0	0
PuCl3	0	0	0	1	0
PuF3	0	0	0	1	0
SrCl2	1	1	1	0	1
SrF2	1	1	1	0	1
ThCl4	1	0	0	0	0
ThF4	1	0	0	0	1
UCl3	1	1	0	1	1
UCl4	1	1	0	0	1
UF3	0	0	0	1	0
UF4	1	1	0	1	1
ZrCl4	1	1	0	0	0
ZrF4	1	0	0	0	1
RbCl	0	0	0	0	1
CsCl	0	0	0	0	1
BaCl2	0	0	0	0	1
PrCl3	0	0	0	0	1
RbF	0	0	0	0	1
CsF	0	0	0	0	1
BaF2	0	0	0	0	1
UF6	0	0	0	0	1

Pure Compounds in Chloride Database

(1) Termini, Nick, et al. "An Overview of the Molten Salt Thermal Properties Database–Thermophysical, Version 2.1.1 (MSTDB-TP v.2.1.1)." , Jul. 2023. https://doi.org/10.2172/1988348
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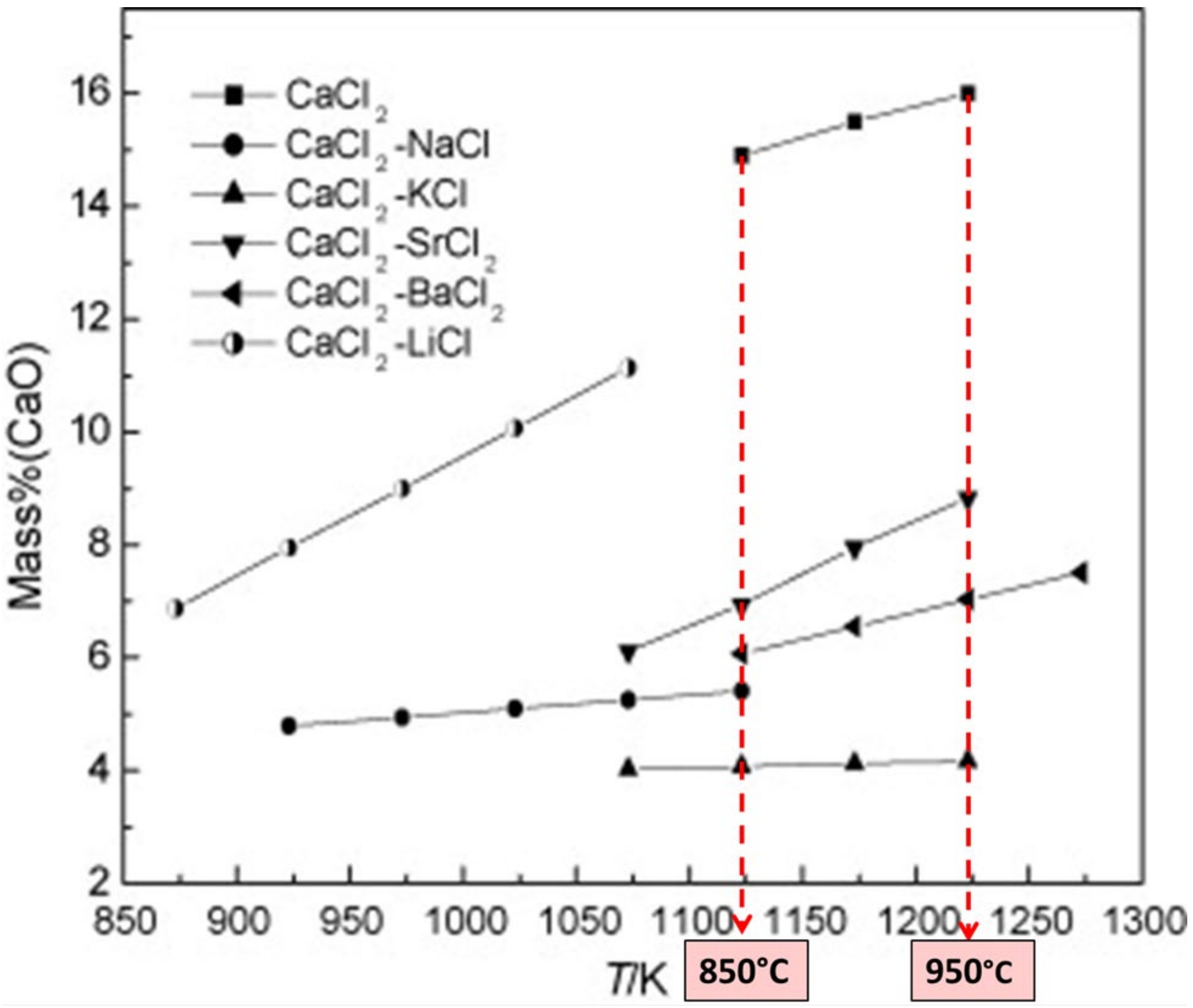
Material Melting Points and CaO Solubility



Material	Melting Point (°C)
Plutonium metal	640
$MgCl_2$	714
$PuCl_3$	767
$CaCl_2$	772
Calcium metal	842
PuO_2	2390
CaO	2572