U.S. DEPARTMENT OF ENERGY | Office of NUCLEAR ENERGY

Molten Salt Reactor PROGRAM

Thermochemical and Thermophysical Property Development for the Molten Salt Databases at LANL

Marisa Monreal

Inorganic, Isotope, and Actinide Chemistry – Chemistry Division

Los Alamos National Laboratory

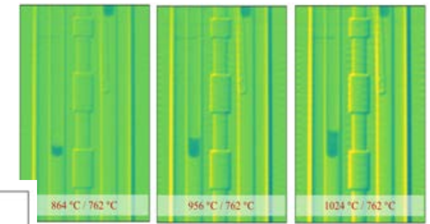
Los Alamos NATIONAL LABORATORY

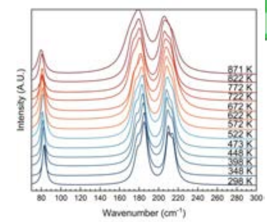
Annual MSR Campaign Review Meeting 16-18 April 2024

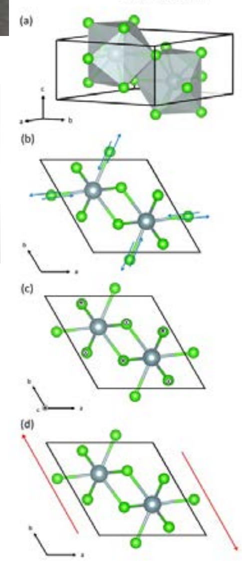
LA-UR-24-23405

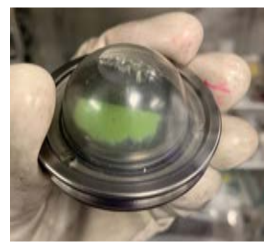
LANL Actinide-Molten Salt Chemistry and Properties Research

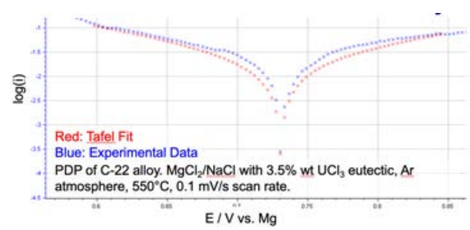
- **Salt systems:**
  - Actinides: uranium, thorium, plutonium
  - Chlorides; expanding to fluorides, beryllium
- **Research:**
  - Chemistry & thermophysical properties
  - Experiment and modeling
  - Studies across length scales
- **Benefitting communities:**
  - Pyroprocessing, nuclear energy, fundamental actinide science, global security/nonproliferation











LANL Actinide-Molten Salt Chemistry and Properties Research

- **Researchers:**
  - Graduate students, post-docs, scientists, and engineers
  - Chemistry, materials science, earth and environmental science, theoretical
- **Collaborations:**
  - National Laboratories, universities, industry, NEAMS, SciDAC, FUTURE EFRC
- **Sponsors/Projects:**
  - MSR Campaign, LDRD, GAIN, Technology Commercialization Fund (TCF), IRP, NEUP

Scientists & Engineers
Matt Jackson
Scott Parker
David Andersson
Alex Long
Hongwu Xu
Sven Vogel
Karla Erickson
Ping Yang
Gaoxue Wang
Sarah Hickam
Harris Mason
Hakim Boulkhalfa
Travis Carver
Brendt Wohlberg

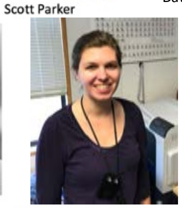
Post-docs & Students
Andrew Strzelecki*
Charles Lhermitte*
Hannah Patenaude
Jarom Chamberlain
Nicolas Capra
Adam Altenhof
Dylan Tharpe Eralie

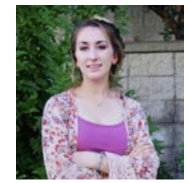

Matt Jackson


Scott Parker

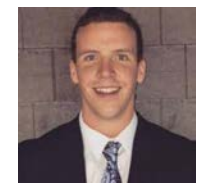

David Andersson

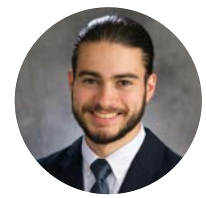

Alex Long

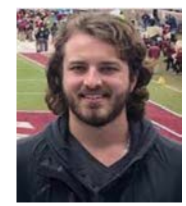

Karla Erickson


Hannah Patenaude


Jarom Chamberlain


Andrew Strzelecki

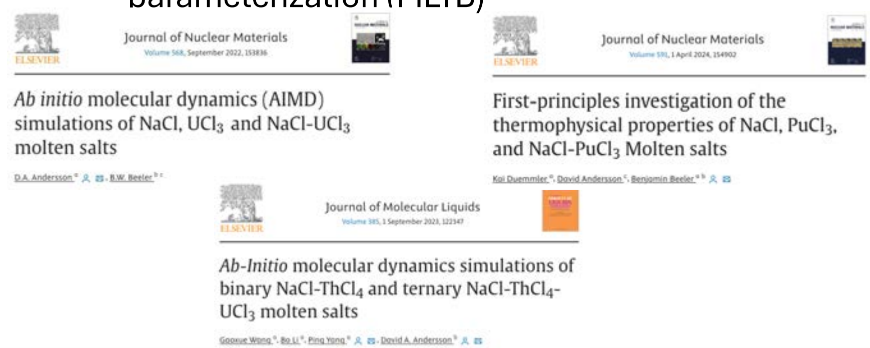

Nicolas Capra


Adam Altenhof

LANL Actinide-Molten Salt Chemistry and Properties Research

Properties	Experimental Techniques
Density	Neutron Radiography, Conventional (Push-rod) Dilatometry
Viscosity	Dynamic Neutron Radiography, Rotational Viscometry
Melting Point/Phase Diagram, Heat Capacity	Differential Scanning Calorimetry (DSC)
Corrosion	Electrochemistry, Exposure Tests
Heat of Dissolution, Enthalpy of Mixing, Heat Capacity	Drop Calorimetry
Local Structure	Pair Distribution Function (PDF) Analysis, Raman Spectroscopy, Electrochemistry
Synthesis & Characterization	Inorganic halide synthesis, SEM, Melting Point (DSC), pXRD, SS-NMR Spectroscopy

- **Experimental efforts & strategy:**
  - Method development, uncertainty reduction
  - Lower and higher throughput methods
  - Non-rad → U , Th → Pu
  - Iterate with mod-sim
- **Modeling and Simulation:**
  - David Andersson, Ping Yang, Gaoxue Wang
  - Ab initio molecular dynamics (AIMD) simulations; density functional tight binding (DFTB) modeling, machine-learning-augmented DFTB parameterization (MLTB)


Journal of Nuclear Materials
Volume 568, September 2022, 153836

Ab initio molecular dynamics (AIMD) simulations of NaCl, UCl_3 and NaCl-UCl_3 molten salts

D.A. Andersson, B.W. Beeler

Journal of Nuclear Materials
Volume 591, 1 April 2024, 154902

First-principles investigation of the thermophysical properties of NaCl, $PuCl_3$, and NaCl-$PuCl_3$ Molten salts

Kai Duemmler, David Andersson, Benjamin Beeler

Journal of Molecular Liquids
Volume 385, 1 September 2023, 122347

Ab-Initio molecular dynamics simulations of binary NaCl-$ThCl_4$ and ternary NaCl-$ThCl_4$-UCl_3 molten salts

Gaoxue Wang, Bo Li, Ping Yang, David A. Andersson

LANL MSR Campaign Work

1. **$PuCl_3$-NaCl salts (FY22-present)**
   - **Eutectic (36% $PuCl_3$ 64% NaCl)**
   - **Ternary: $PuCl_3$ in UCl_3-NaCl eutectic (<10% $PuCl_3$)**
     - **Density:** LANSCE neutron radiography method
     - **Heat capacity (C_p):** Drop calorimetry for integral C_p

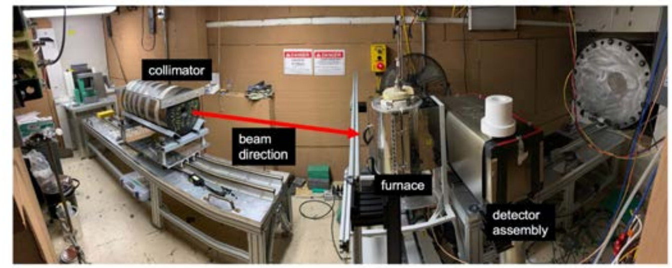
2. **Uranium-containing salts (FY24)**
   - **Synthesis & characterization of uranium halides**
     - **UCl_3, UF_4; UF_3, UI_3**
   - **LiF-NaF-KF-UF_4 :** ΔH_{fus}
   - **UF_4 :** C_p >350K to 1173K
   - **NaCl-$MgCl_2$-UCl_3 :** phase equilibria

   Ted Besmann-recommended / MSTDB

LANL MSR Campaign Work: $PuCl_3$-NaCl Salts

Density: LANSCE neutron radiography

- ✓ **Inter-lab collaboration:** INL and LANL measured the same material: INL-synthesized $PuCl_3$-NaCl eutectic
  - INL – Toni Karlsson: Shipped material to LANL: 10g shipped and introduced into glovebox line in the Plutonium Facility at LANL (PF-4)
- ✓ Upon receipt, material purity checked by melting point (DSC)

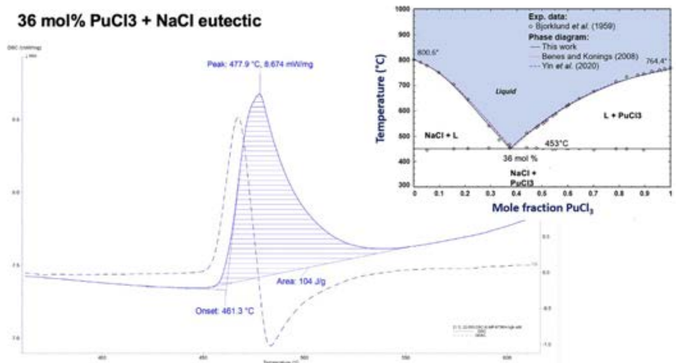


Flight Path 5 at Los Alamos Neutron Science Center (LANSCE)

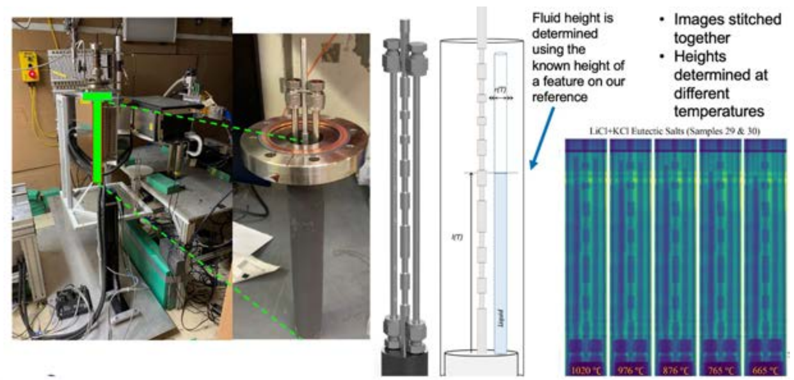
$PuCl_3$ + NaCl eutectic salt (INL)

Sample Stage

36 mol% PuCl3 + NaCl eutectic

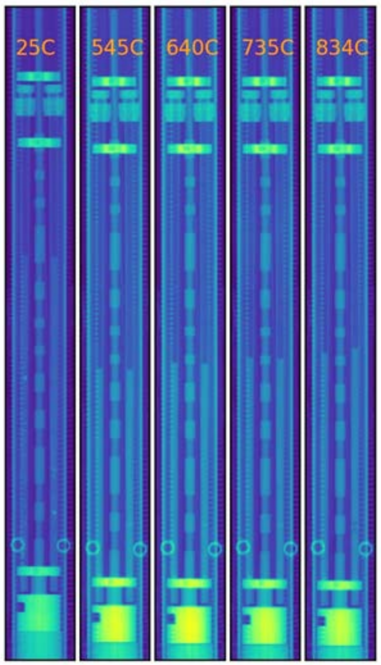


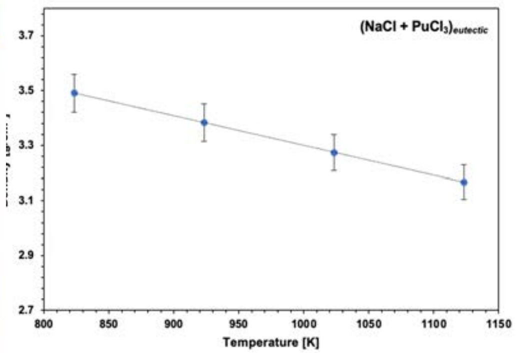
This work: $T_{melt,\ onset}$ = 461 +/- 2 °C, $T_{melt,\ peak}$ = 478 +/- 2 °C ΔH_{fusion} = 104 J/g



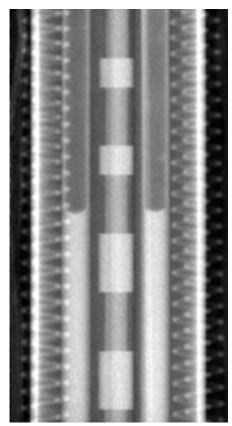
LANL MSR Campaign Work: $PuCl_3$-NaCl Salts

Density: LANSCE neutron radiography





Temperature [°C]	Density [g/cm³]
550	3.49
650	3.38
750	3.27
850	3.17



Alex Long, Scott Parker, Brendt Wohlberg

✓ Density by neutron radiography measurements completed on a set of $PuCl_3$-NaCl and $PuCl_3$-UCl_3-NaCl samples; preliminary image analysis and density values generated

- **Current work: Ensuring accuracy of volume measurement from images** → Accounting for filled and void spaces
  1. Modeler working on volume estimation, including modeling bubbles/voids
     - Potential future applications: analysis of volatiles in salt, surface tension
  2. Analyzing change in relative contrast
     - Average column intensity, compare to full intensity, any differences thus equal voids

- **Current work: Next steps for the LANSCE-measured samples**
  1. Post-mortem characterization (XRD)
  2. If pure, re-constituting into new compositions, making new measurements (more density, drop cal)

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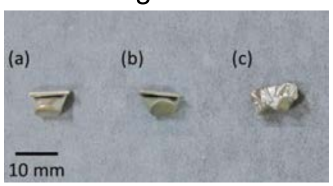
LANL MSR Campaign Work: $PuCl_3$-NaCl Salts

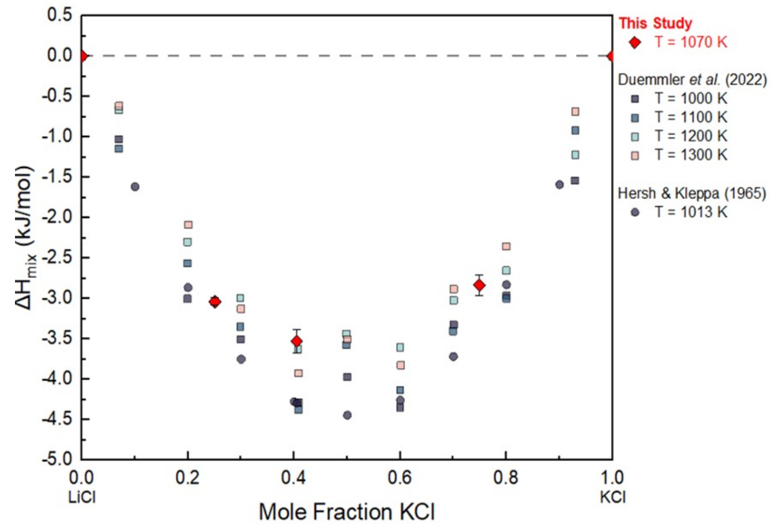
Integral Heat Capacity (Cp): Drop Calorimetry

- **En route to integral C_p:** with LDRD funding, a new methodology for measuring the ΔH_{mix} of molten salt systems was developed using Setaram AlexSYS-800 calorimeter.[1]

  Advantages/improvements:
  - Elimination of problems from material-atmosphere interactions
  - Minimal salt-crucible interactions
  - No further mixing needed after being introduced into the calorimeter



LiCl–KCl eutectic sample:
(a) before the calorimetric measurement
(b) after the measurement
(c) after sectioning



Sample	Temperature Room (K)	Temperature Calorimeter (K)	Experimental ΔH_{mix} (kJ/mol)
0.251KCl – 0.749LiCl	297.48 ± 0.11	1070.39 ± 0.01	-3.04 ± 0.05
KCl-LiCl eutectic	297.73 ± 0.15	1070.51 ± 0.00	-3.52 ± 0.15
0.749KCl – 0.251 LiCl	297.62 ± 0.27	1070.41 ± 0.01	-2.83 ± 0.13

- **Recent results: $PuCl_3$-NaCl eutectic integral C_p**
  - Used INL-synthesized material
  - **Good match with INL-measured C_p (by DSC); publication forthcoming**

Andrew Strzelecki (former LANL PD), Hongwu Xu

(1) Strzelecki, A., Cockreham, C., Parker, S., Mann, S., Lhermitte, C., Wu, D., Guo, X., Monreal, M. J., Jackson, J. M., Mitchell, J., Boukhalfa, H., Xu, H. "A New Methodology for Measuring the Enthalpies of Mixing of Molten Salts Using High Temperature Drop Calorimetry", Rev. Sci. Inst., 2024, 95, 014103.

LANL MSR Campaign Work: Uranium-containing salts

Synthesis of Uranium Halides (chlorides, fluorides, iodide)

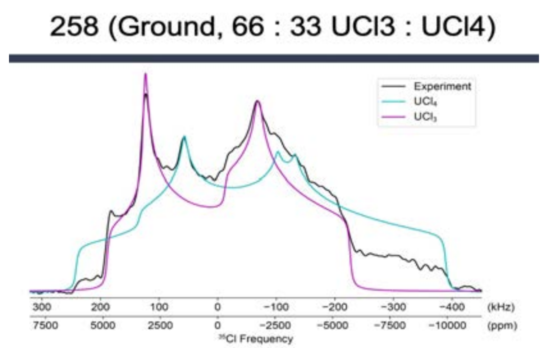
Current work: Synthesis of ***pure, isolable*** actinide chlorides and fluorides to enable property research

- Both conventional & novel synthetic routes
- Characterization techniques to confirm purity (e.g., SS-NMR; pXRD; DSC)
  - Impurities: other actinide species; water; products of rxn with water

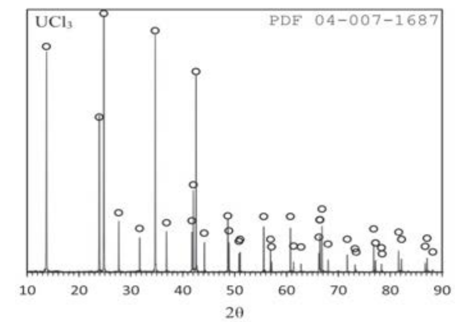
LDRD

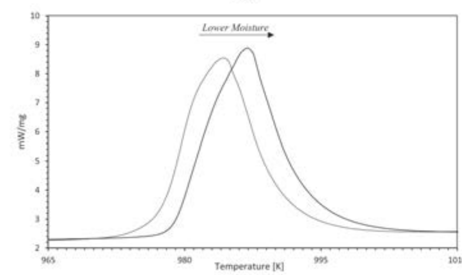
With LDRD funding, novel route to UCl_3 developed[2]:

$$UCl_3(py)_2 \xrightarrow{\text{thermal elimination}} UCl_3$$



SS-NMR: Adam Altenhof (PD), Harris Mason





XRD, melting point: Scott Parker (and more!)

***MSR Campaign work**: translate novel route learnings to other halides; execute conventional routes*

Molten Salt Reactor PROGRAM

(2) Erickson, K., Parker, S., Monreal, M. J. “Thermal Elimination of Pyridine from a Uranium Trichloride Precursor”, *Chem. Methods*, **2024**, e202300052.

LANL MSR Campaign Work: Uranium-containing salts

Synthesis of Uranium Halides (chlorides, fluorides, iodide)

Current work: New synthesis of UF_4 under development

UF_4

Scale: ≤1.5 g UF_4

- **Workup 1: wash**
  - Dry in desiccator → 2% organic, 1% iodine
  - Heat at 150 °C (hours) → 1-2% organic, <1% iodine
- **Workup 2: no wash**
  - Heat at 150 °C → 1-2% organic, <1% iodine
  - Heat at 250 °C → 1% organic, 0% iodine

Small amounts of organic and iodine byproduct

Nicolas Capra (PD), Karla Erickson

+ Incoming Seaborg 2024 Summer Student

Scott Parker, Hannah Patenaude
New addition: Kristen Pace

Current work:
- Completing workup refinement, scale up
- Collecting characterization data
  - [19]F Solid-State NMR Spectroscopy (first for UF_4!)
  - Others?
- Manuscript preparation: To be submitted by end of CY24
- Exploring other novel fluorination routes
- Next steps:
  - Synthetic efforts: UF_3, UI_3
  - Handoff to properties measurements
    - LiF-NaF-KF-UF_4 : ΔH_{fus}
    - UF_4 : Cp >350K to 1173K
    - NaCl-$MgCl_2$-UCl_3 : phase equilibria

Seed funding was provided by: LANL IMS RR (FY23)

Looking Forward: Collaborations and Building the Pipeline

Internal Collaborations:

- **LANL-led SciDAC**
  - Scientific Discovery through Advanced Computing program to advance modeling behavior and properties of structural materials under molten salt conditions
- **Nuclear Energy Advanced Modeling and Simulation (NEAMS)****
- **LANL Civilian Nuclear Program Director: Chris Stanek****
- **LANL-led EFRC: FUTURE**
  - Studying corrosion under irradiation

Upcoming 2024 presentations:

- MRS Spring Meeting
- Fall ACS
- Actinide Separations
- Plutonium Futures
- MSR Workshop

LANL-University Collaborations:

- **University of Utah** (Simpson)
  - Electrochemistry, vapor pressure, student pipeline
- **UC Berkeley** (Scarlat, Fratoni)
  - Molten salt round robin, fluoride & beryllium salt expertise, student pipeline, **IRP**
- **MIT** (Khaykovich)
  - Pair distribution function analysis, new **NEUP just announced**!
- **Oregon State University, Texas A&M, UNLV**
  - Student pipeline—viscosity, materials corrosion, electrochemistry

Technical Work Scope Identifier No. IRP-NEAMS-1

Bridging the gap between experiments and modeling to improve the design of molten salt reactors

Massimiliano Fratoni, Mark Asta, Peter Hosemann, Raluca Scarlat—University of California, Berkeley
Izabela Szlufarska—University of Wisconsin-Madison
Alexandra Navrotsky, Hongwu Xu—Arizona State University
Marisa Monreal—Los Alamos National Laboratory
Abdalla Abou Jaoude—Idaho National Laboratory
Carolyn Burns, Thomas Hartmann—Pacific Northwest National Lab
Nader Satvat—Kairos Power, LLC
Karl Britsch—TerraPower, LLC

NEUP Nuclear Energy University Program
U.S. Department of Energy

Redox potential, ionic speciation, and separation and recovery challenges from molten salts containing actinides and fission products

PI: Boris Khaykovich (MIT)

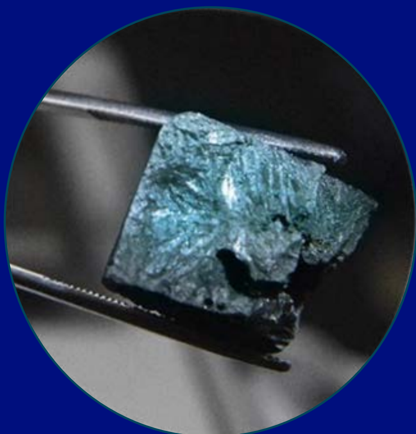
Program: Nuclear Fuel Recycle Technologies

Collaborators: Stephen Lam (University of Massachusetts), David Sprouster (Stony Brook University), Anatoly Frenkel (Brookhaven National Laboratory) Marisa Monreal (Los Alamos National Laboratory), and Joanna McFarlane (Oak Ridge National Laboratory)

New Plutonium R&D Capability:

Plutonium Science Laboratory (“PluS Lab”)

-- Gram-scale, non-irradiated materials --



PLUTONIUM CAPABILITY 1:
Molecular chemistry & materials science

ENVIRONMENT 1:
O_2- and H_2O-free

PLUTONIUM CAPABILITY 2:
Aqueous chemistry

ENVIRONMENT 2:
Water solutions

PLUTONIUM CAPABILITY 3:
Molten salt science

ENVIRONMENT 3:
High-temperature (400 °C-900°C), O_2- and H_2O-free

Leadership Team: Marisa Monreal and Karla Erickson
Sponsor: Nonproliferation Stewardship Program (NSP)

Acknowledgements

Scientists & Engineers
Matt Jackson
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Adam Altenhof
Dylan Tharpe Eralie

University Collaborators, Visiting Students
University of Utah, MIT, UC Berkeley, OSU, UNLV, Texas Tech

Funding:

Molten Salt Reactor Campaign

LANL Laboratory Directed Research and Development (LDRD) Directed Research Project #20210113DR

Gateway for Accelerated Innovation in Nuclear (GAIN) #NE-21-25117 with TerraPower

Technology Commercialization Fund (TCF) with Kairos Power

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Thank you

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