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Revision 0

Advanced Reactor Technologies

Experimental Plan for Synthesis of an Americium- and Plutonium-Containing Salt

M4AT-24IN0705022

AUGUST 2024

Toni Karlsson

Idaho National Laboratory

Juliano Schorne-Pinto

University of South Carolina

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Idaho National Laboratory
Advanced Reactor Technologies
Idaho Falls, Idaho 83415

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INL ART Program

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Technical Reviewer: (Confirmation of mathematical accuracy, and correctness of data and appropriateness of assumptions.)

Morgan Kropp

Morgan Kropp
Research Scientist

8/13/24
Date

Approved by:

Michael E. Davenport
ART Project Manager

8/13/2024
Date

Michelle T. Sharp
INL Quality Assurance

8/13/2024
Date

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FIGURES

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ACRONYMS

AFC	Advanced Fuels Campaign
FMF	Fuel Manufacturing Facility
MSR	Molten salt reactor

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Experimental Plan for Synthesis of an Americium- and Plutonium-Containing Salt

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1. BACKGROUND

In many molten salt reactor (MSR) concepts, the fuel cycle can also be closed for minor actinides [1] where the actinides from the spent fuel of existing reactors can be utilized by MSR breeders or burners in the closed cycle. Even in the open cycle, the utilization of resources in MSRs is higher than in solid fuel reactors. Excellent neutron economy, radiation stability of the carrier salt, and the possibility to continuously remove fission products and adjust the fuel composition allow for higher burnup and lower initial fissile fuel enrichment [2].

Some MSR concepts propose combining aqueous recycling to recover uranium and plutonium to use in light-water reactor or mixed oxide fuels. In this scenario, minor actinides, such as americium (Am), will be burned in an MSR to reduce the footprint of a geological repository. To study fuel salt compositions containing Am, salt must first be synthesized. Kersten et al. [3] synthesized americium trichloride ($AmCl_3$) by chlorination of americium oxide (Am_2O_3) with zirconium chloride ($ZrCl_4$) in a LiCl-KCl molten salt at 500°C. The formation of $AmCl_3$ was confirmed by cyclic voltammetry and gamma spectroscopy. Zirconium oxide (ZrO_2) is a byproduct that is not electrochemically active; however, the ZrO_2 product from this synthesis method would need to be removed prior to performing fuel salt property measurements as it affects the composition and properties of the salt.

Karlsson et al. [4] has previously used ammonium chloride (NH_4Cl) to chlorinate plutonium (Pu) metal in a sodium chloride (NaCl) carrier salt to form a high purity plutonium chloride – sodium chloride ($PuCl_3$-NaCl) fuel salt. Additionally, Herrmann et al. [5] used NH_4Cl as a chlorinating agent to form a high purity uranium chloride – sodium chloride (UCl_3-NaCl) fuel salt. In both studies, the salt was characterized to determine the completion of conversion of actinide metal (An) to actinide chloride ($AnCl_3$).

Therefore, NH_4Cl will be used to chlorinate an 80wt%Pu - 20wt%Am metal alloy at the Idaho National Laboratory in fiscal year 2025. Chlorination of the Pu-Am alloy will utilize a NaCl carrier salt. In this document, the experimental plan along with associated hazards are outlined. The major steps in the plan are preparation of salt and alloy, particle size reduction (increase surface area) of the Pu-Am alloy via the hydride-dehydride (H/dH) process, chlorination, and inspection. The large chunks of Pu-Am alloy that will be used for this synthesis is shown in Figure 1, left. Approximately 100g of the alloy will be separated from the bulk. The 100g will be manually broken up into pebble-sized particles prior to the H/dH process. Thermodynamic predictions using HSC Chemistry (version 9.9.2.3) show that U and Pu have very similar reaction enthalpies (see Figure 1, right) while hydriding Am is more thermodynamically favorable. Thus, our previous methods for size reduction (i.e., increase surface area for reactions to take place) will be used.

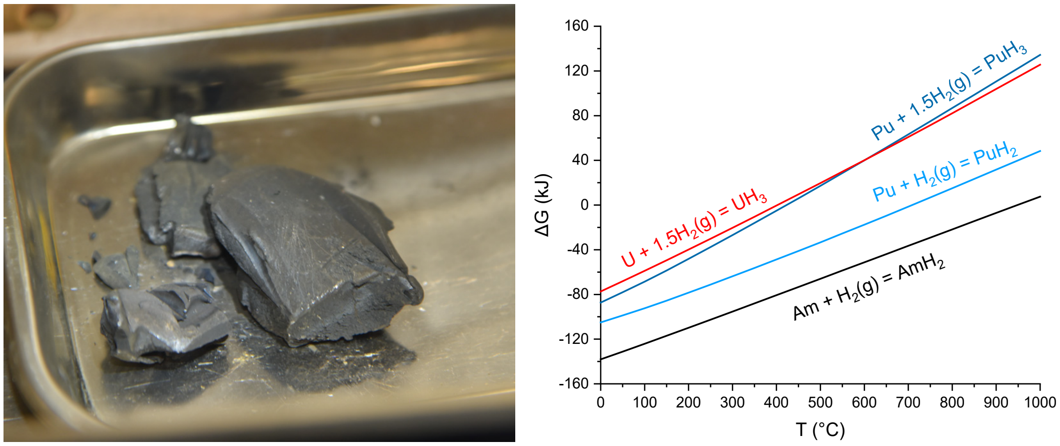

Figure 1. Pu-Am metal alloy that will be reduced in size and converted to a chloride salt (right) and Gibb's free energy predictions for hydriding actinides (left).

To date, these researchers are not aware of any available ternary $PuCl_3$-$AmCl_3$-NaCl phase diagrams to use as a guide in understanding melting temperature and phase formation. However, to make a baseline approach, phase diagram modeling by Professor Juliano Schorne-Pinto from the University of South Carolina was done to better understand the behavior of actinide mixtures/systems. Using the ionic radius of Am^{3+} with coordination number (CN) = 6 (r = 0.975 Å), a rough assumption can be made that Am^{3+} will behave similarly to Pm^{3+} (r = 0.97 Å) or Sm^{3+} (r = 0.958 Å). Moreover, $AmCl_3$ has a melting point of 988 K, which is close to $PmCl_3$ (1000 K) and somewhat close to $SmCl_3$ (941 K). Since the NaCl-$PmCl_3$ binary system is not readily available in literature, the NaCl-$SmCl_3$ system [6] was used for further approximations of the NaCl-$AmCl_3$ system.

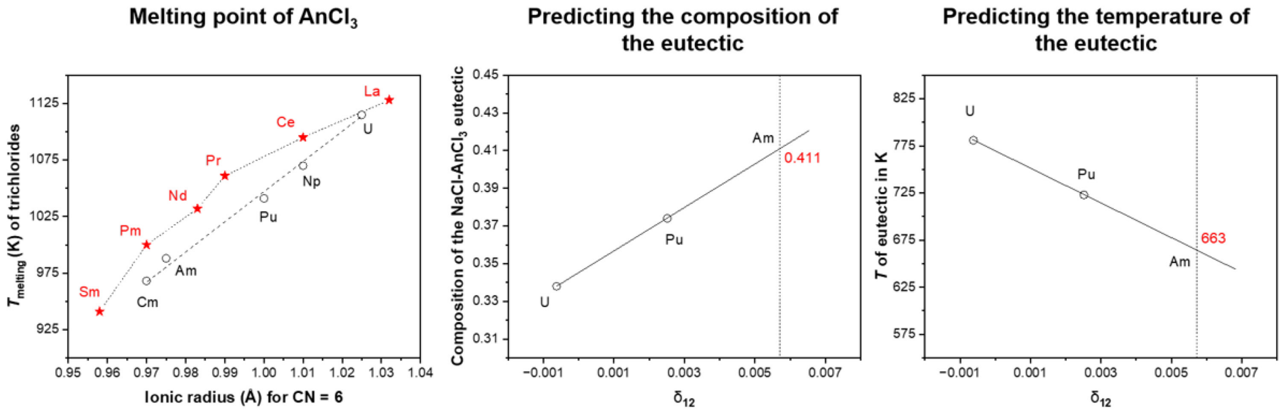

Figure 2. Comparison of melting temperatures of lanthanides and actinides (left), prediction of the eutectic composition of actinides (middle), and a prediction of the eutectic melting temperature for some NaCl-$AnCl_3$ (An = U, Pu, Am) (right).

Professor Schorne-Pinto then used correlation methods to validate the NaCl-$SmCl_3$ systems relevance in predicting the NaCl-$AmCl_3$ phase diagram. As seen in Figure 2 (left), the lanthanide chlorides ($LnCl_3$) correlate somewhat closely with the melting temperatures of the $AnCl_3$. The $AnCl_3$ (An = Cm, Am, Pu, Np, and U) melting points seems to follow a linear trend in function of the ionic radius. Then using the size parameter called $Sigma_{12}$ [7], Professor Schorne-Pinto predicted the composition of the eutectic point and melting temperature of the NaCl-$AmCl_3$ system seen in Figure 2 (middle, right). Finally, the NaCl-$SmCl_3$ and predicted NaCl-$AmCl_3$ systems were compared to known binaries of NaCl-UCl_3 and NaCl-$PuCl_3$. Figure 3 demonstrates that by using the NaCl-$SmCl_3$ as a proxy system and the correlation from the NaCl-$AnCl_3$ systems, the NaCl-$AmCl_3$ will have a proposed eutectic at $AmCl_3$ = 0.40–0.45mol%, and T = 650–700 K. It should be noted that the presence of intermediate phases for the NaCl-$SmCl_3$ (i.e., Na_2SmCl_5 and $Na_3Sm_5Cl_{18}$) [8] may indicate that NaCl-$AmCl_3$ will not be a simple eutectic.

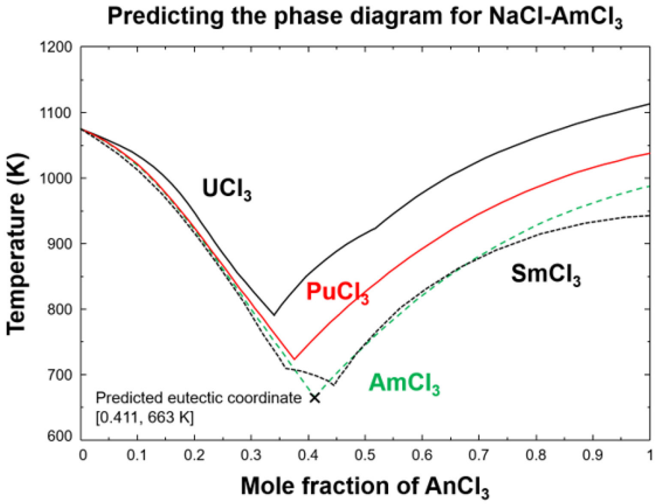

Figure 3. Predicted NaCl-$AmCl_3$ binary phase diagram alongside the NaCl-UCl_3, NaCl-$PuCl_3$, and NaCl-$SmCl_3$ systems

$AmCl_3$ has a low boiling point, 1253°C [9]. During synthesis (H/dH and chlorination), the vapor pressure of $AmCl_3$ must be considered. Concerning the volatility of $AmCl_3$, the pure salt only has relevant vapor pressures for T > 775–800°C. However, in mixtures with NaCl, the tendency is to have a negative enthalpy of mixing as predicted in Figure 4. $AmCl_3$ is 166 times more volatile than $PuCl_3$ at 1000 K, with a partial pressure of 7 Pa at its melting point (715°C/988 K). Behavior of the ternary mixture ($PuCl_3$-$AmCl_3$-NaCl) is not well understood, but having $AmCl_3$ in solution with $PuCl_3$ and NaCl will lower its volatility.

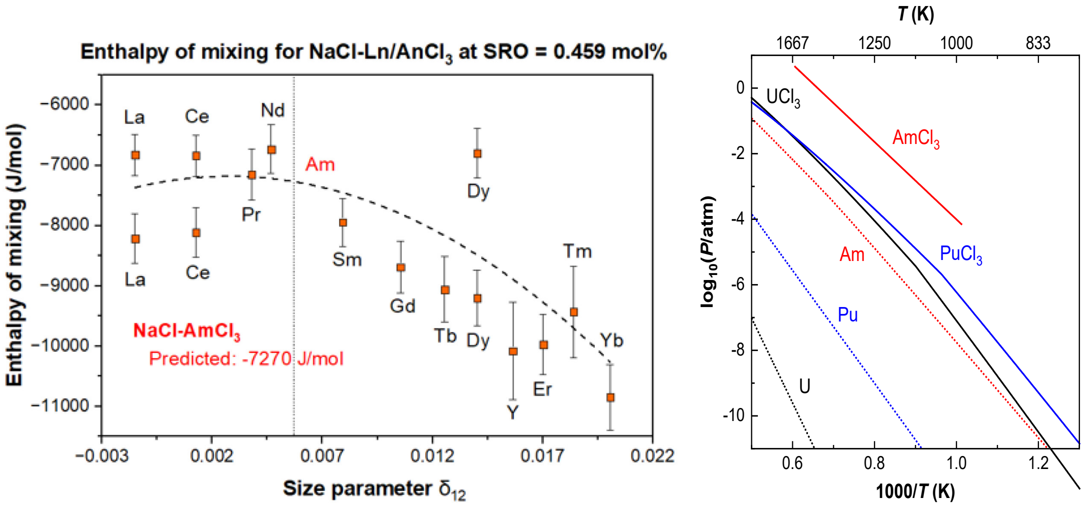

Figure 4. Predicted enthalpy of mixing for NaCl-AmCl$_3$ compared to other lanthanides (Ln) (left) and comparison of predicted vapor pressures of An metals and AnCl$_3$ (right).

Approximately 100g of the Pu-Am alloy will be used for the synthesis reaction. To make the salt having a composition of 0.40PuCl$_3$-0.09AmCl$_3$-0.50NaCl, 24.4g of NaCl, and 67.7g of NH$_4$Cl will be used. The NH$_4$Cl will be added in 1% excess. The synthesis reaction will take place following Equations 1–4.

$$Pu + H_2(g) \leftrightarrows PuH_2, \qquad Am + H_2(g) \leftrightarrows AmH_2 \qquad \text{Hydride} \qquad (1)$$

$$PuH_2 \leftrightarrows Pu + H_2(g), \qquad AmH_2 \leftrightarrows Am + H_2(g) \qquad \text{Dehydride} \qquad (2)$$

$$Pu + 3NH_4Cl \leftrightarrows PuCl_3 + 3NH_3(g) + 1.5H_2, \qquad (3)$$

$$\text{Chlorination}$$

$$Am + 3NH_4Cl \leftrightarrows AmCl_3 + 3NH_3(g) + 1.5H_2 \qquad (4)$$

To summarize the synthesis team will aim to synthesize a 0.40PuCl$_3$-0.09AmCl$_3$-0.50NaCl (mol fraction) salt from a Pu-Am alloy containing 0.79 Pu-0.18Am-0.03U. The salt composition was chosen since it is rich in PuCl$_3$ and AmCl$_3$ and can be diluted with carrier salt in future experiments. Modeling done by Professor Schorne-Pinto suggests NaCl-AmCl$_3$ mixtures will have a lower eutectic melting temperature compared to NaCl-PuCl$_3$, with a concentration of AmCl$_3$ = 0.40-0.45mol%, and T = 650-700K region. There is also the possibility of NaCl-AmCl$_3$ forming intermediate phases, such as Na$_2$AmCl$_5$ and Na$_3$Am$_5$Cl$_{18}$, similar to the NaCl-SmCl$_3$ analogue. Pure AmCl$_3$ is known to be volatile at low temperatures; mixing AmCl$_3$ in NaCl will make AmCl$_3$ more stable in the liquid phase, thus reducing its volatility.

2. EXPERIMENTAL PLAN

1. Materials and Equipment
    - Sintering furnace
    - Large Kerr furnace
    - Vacuum oven located in argon glovebox
    - Quartz crucible
    - Blending jar
    - Glassy carbon crucible
    - Steel wool
    - Modified Gavin Can (quality marked) containing 100g Pu/Am metal alloy
    - Ammonium chloride (NH_4Cl)
    - Sodium chloride (NaCl)
    - Mortar and pestle
    - 30 mesh sieve and pan
    - 50 mesh sieve and pan
    - Ammonia (NH_3) Drager sampling tubes
2. Experimental Setup and Preparations
    a. Preparing NaCl
        - Sodium chloride, AnhydroBeads, −10 mesh, 99.999%
        - Place the salt in an Inconel (or similar) crucible
        - Place NaCl in crucible in the vacuum oven
        - Heat to 350°C under vacuum
        - Hold for 48 hours
        - Cool vacuum oven
        - Remove the salt and collect four samples for moisture analysis
        - Reduce in size and sieve to −30 mesh (~600 µm)
        - Place in a poly bottle and transfer to the Fuel Manufacturing Facility (FMF)

    b. Preparing NH_4Cl
        - Use Ammonium chloride, 99.995% Suprapur
        - Place NH_4Cl on a metal tray
        - Place in the furnace and heat to 140°C
        - Hold for 24 hours and cool
        - Reduce in size and sieve to −30 mesh (~600 µm)

    c. Preparing Am/Pu Alloy and Particle Size Reduction
        - Break out 100 grams of material, place in the Advanced Fuels Campaign (AFC) glovebox
        - Remove the Pu/Am metal from the modified Gavin Can
        - Break Pu/Am alloy into smaller pieces place in a quartz crucible
        - Place the quartz crucible with Pu/Am alloy into the AFC furnace
        - Close the furnace and set program for the hydride/dihydride process

3. <u>H/dH Process</u>
   a. <u>Hydride</u>
      - Furnace prep (60 minutes)
         - Place the crucible and 100g Pu/Am in the AFC Sintering Furnace
         - Evacuate the chamber, ~23Torr = 23 mmHg
         - Purge 100% H_2, flow rate = 20 sccm
         - Heat the furnace to 250°C at a rate of 15°C/min
      - Cycle 1 (estimated time 90 minutes)
         - Dwell time (at 250°C) for 60 minutes while purging 100% H_2
         - Evacuate (vacuum), hold for 30 minutes (no flow of H_2 gas)
      - Cycle 2 (estimated time 90 minutes)
         - Purge (at 250°C) with 100% H_2 for 60 minutes, flow rate = 20 sccm
         - Evacuate (vacuum), hold for 30 minutes (no flow of H_2 gas)
      - Cycle 3 (estimated time 90 minutes)
         - Purge (at 250°C) with 100% H_2 for 60 minutes, flow rate = 20 sccm
         - Evacuate (vacuum), hold for 30 minutes (no flow of H_2 gas)
      - Cycle 4 (estimated time 90 minutes)
         - Purge (at 250°C) with 100% H_2 for 60 minutes, flow rate = 20 sccm
         - Evacuate (vacuum), hold for 30 minutes (no flow of H_2 gas)
      - Cool the furnace to room temperature, under vacuum
      - Overnight evacuation (vacuum), no flow of H_2 gas
   b. <u>Inspection</u>
      - Remove the sample from furnace and examine the product
         - If powder, then proceed to the dihydride step
         - If larger chunks remain, then try manual size reduction and restart hydriding procedure
   c. <u>Dehydride</u>
      - Heat the furnace to 375°C (15°C/min), **NO** hydrogen purge
      - Hold for 180 minutes
      - Cool the furnace to room temperature, under vacuum
      - Remove the sample and record weight (sample + crucible)
      - Sieve the material through 50 mesh sieve
         - > 50 mesh particle size (needs to be further reduced)
         - < 50 mesh particle size (good for synthesis)

4. Chlorination Process
    - Step performed in Kerr furnace
    - Reference FCF-NOP-9167D [10] for operating instructions
    - Reserve 0.5 grams of the Pu/Am material for elemental and isotopic analysis
    - In a glass container with lid, add the following material (+/− 0.005g)
        - Pu/Am = 100.0000g
        - NH_4Cl = 67.7188g
        - NaCl = 24.4184g
    - Mix the chemical in container with lid on
    - Add the mixed material to the glassy carbon crucible and place in the Kerr furnace
    - Place the glassy carbon lid on crucible
    - Place the steel wool on top of lid
    - Place the cover on the furnace
    - Ramp the Kerr Furnace to 450°C at 10°C/hr
    - Place NH_3 Drager tubes at several locations within the AFC glovebox
    - Turn on glovebox blowers
    - Heat the furnace to 700°C at 5°C/min
    - Hold at 700°C for 60 minutes
    - Turn off the furnace and cool to room temperature
    - Remove the glassy carbon crucible from furnace
5. Inspection of Synthesized Salt
    - Remove the lid from the glassy carbon crucible
    - Inspect the $PuCl_3$-$AmCl_3$-NaCl product
    - Weigh the $PuCl_3$-$AmCl_3$-NaCl product
    - Break material apart looking for a blue/green color
    - Reserve 0.5g of sample for elemental and isotopic analysis
    - Store material until needed for thermal property measurements.

3. EXPERIMENTAL HAZARDS

Warning Energetic Reaction

- Use thermodynamic data to predict energy, compare U and Pu
- Follow previous procedure for UCl_3 and $PuCl_3$ synthesis
- NaCl carrier salt will abosorb energy (heat) during synthesis
- Slow heating rate to limit energy introduced into reaction

Warning Off-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 HN_3 was in GB at one time), H_2 = 1.567g/batch
- Consider purification bed matierial (stailess steel, Cu, diatomaceous earth)

Warning Radiological

- Using Am and Pu, known to be flighty
- Reduce number of pours
- Once molten, this is less of a concern

4. NEXT STEPS

All materials and equipment needed to perform the synthesis have been ordered or are in place at the FMF in an argon glovebox, commonly referred to as the AFC glovebox. Once received, the NaCl and NH_4Cl will be prepared as described in the Experimental Plan section. H/dH experiments are expected to start in October 2024, and chlorination experiments will occur shortly thereafter. Salt synthesis is expected to be complete in early November 2024. Samples of the starting materials and the synthesized salt will be sent for elemental and isotopic analysis. Thermal property measurement such as density, meting point, enthalpy of fusion, enthalpy of crystallization, heat capacity, and thermal diffusivity are expected to be done as funding becomes available in fiscal year 2025.

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