Current Status to Reestablish a Reliable Supply of Pu-238

Robert Wham, Ph.D.
Oak Ridge National Laboratory

Presented to
National Academy of Sciences—Committee on Astrobiology and Planetary Science

September 15, 2016
Key Steps in Radioisotope Power System Production

1. Np-237 in Storage
   → Package and ship to ORNL
   → Process Np and manufacture targets
   → Irradiate targets
   → Chemical Processing
   → New Pu-238 to LANL

2. Chemical Processing
   → Process Np and manufacture targets
   → Irradiate targets
   → Chemical Processing
   → New Pu-238 to LANL

3. Pellet Manufacturing
   → Pellet Manufacturing
   → Aqueous Processing and Blending

4. Module Components and Assembly
   → Package and ship to KSC
   → RPS Assembly and Testing
   → Package and ship to KSC
   → Launch Site Support

5. Graphite Components
   → Pellet Encapsulation
   → Pellet Manufacturing

6. Iridium Components
   → Pellet Manufacturing
   → Aqueous Processing and Blending

7. INL
   → New Pu-238 to LANL

8. ORNL
   → New Pu-238 to LANL

9. LANL
   → New Pu-238 to LANL

10. Planned
    → New Pu-238 to LANL

11. Existing
    → New Pu-238 to LANL
Plutonium-238 is Produced in a Nuclear Reactor via Neutron Capture and Beta Decay

Pu-236
(2.87 yr)

Pu-238
(>10^2 yr)

Np-236m
(22.5 h)

Np-236
(>10^5 yr)

Pu-239
(n, fission)

Pu-240
(n, fission)

Np-237
(n, fission)

Np-238
(2.1 d)

Reactor Characteristics Desired for Efficient $^{237}$Np Conversion to $^{238}$Pu

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Desired to maximize $^{238}$Pu</th>
<th>Desired to minimize $^{236}$Pu impurity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neutron spectrum</td>
<td>High thermal flux O($10^{14}$)</td>
<td>Minimize high energy flux (&gt;7 MeV)</td>
</tr>
<tr>
<td>Photon spectrum</td>
<td>N/A</td>
<td>Minimize high energy flux (&gt;7 MeV)</td>
</tr>
<tr>
<td>Target size</td>
<td>Large diameter</td>
<td>Small diameter</td>
</tr>
<tr>
<td>Neptunium loading</td>
<td>Maximize loading</td>
<td>Minimize loading</td>
</tr>
</tbody>
</table>
Comparison with Previous Experience at Savannah River Plant – Early 1960s to Late 1980s

• SRP production process used as guideline to plan new production at ORNL/INL

• Facilities and equipment available today much smaller

• SRS used annular target with 6 vol% NpO₂
The US DOE and NASA Have a Project Underway to Re-establish a Domestic $^{238}$Pu Production

Storage of $^{237}$Np
INL

Target fabrication at ORNL REDC

Irradiation of NpO$_2$/Al pellets
ATR at INL and HFIR at ORNL

Chemical processing

Pu powder $\rightarrow$ PuO$_2$
LANL

Power source (i.e., MMRTG)

Robotic rover (i.e., Curiosity)

$^{237}$Np $\rightarrow$ $^{238}$Np
2.14E+06 Y $\rightarrow$ 2.12 D

$^{238}$Pu $\rightarrow$ $^{239}$Pu
87.7 Y $\rightarrow$ 2.41E+04 Y
Development Efforts Underway to Recover Np, $^{238}$Pu is Based on Enhancing Previous Flowsheet as well as Using Existing Infrastructure

SRS, ORNL and INL recognized that significant improvements to the flowsheet were possible. Very limited testing took place at SRS in 1977. Chemical processing development resumed once ORNL began the Pu-238 production project. There are complications due to the presence of Pu-238, a high specific activity alpha emitter, causes changes in process chemistry.

Existing DOE research reactors are considerably smaller volume than the SRS production reactor. NpO$_2$ density increased from 6 vol % to 20 vol % in order to achieve production rate for NASA. Targets required significant redesign and testing to address reactor safety issues (potential to breach targets).
### A Comparison to Existing Processes Shows Areas Requiring Validation and Scale Up

<table>
<thead>
<tr>
<th>Process Step</th>
<th>Current Technology Using Existing Equipment</th>
<th>Proposed 1.5 kg/year</th>
<th>Issues to be Addressed During Development</th>
</tr>
</thead>
<tbody>
<tr>
<td>Target Irradiation</td>
<td>&lt; 50/year at ORNL SRS used long annular targets at ~ 6 vol%</td>
<td>~360/year; 20 vol% NpO₂</td>
<td>Target integrity – will not fail (breach) due to melting or excess pressure; excessive fission rate heating which requires high thermal conductivity</td>
</tr>
<tr>
<td>Target Fabrication</td>
<td>&lt; 50/year (hot cell and glovebox)</td>
<td>~360/year (glovebox)</td>
<td>Production target design; material specifications; quality control; automation in a nuclear setting</td>
</tr>
<tr>
<td>Dissolution (caustic)</td>
<td>4 kg Al/batch (upper limit), nearly pure aluminum</td>
<td>4 kg Al/batch, impurities introduced by 6061 alloy (required to qualify for ATR)</td>
<td>Aluminum dissolution is exothermic; process controls are needed to ensure safe operation at maximum throughput; minimal solids since caustic waste is filtered to retain actinides</td>
</tr>
<tr>
<td>Dissolution (acid)</td>
<td>1-2 kg/batch heavy metal (HM) as used nuclear fuel (UNF)</td>
<td>~1 kg HM as irradiated Np/Pu per batch</td>
<td>Dissolution of actual irradiated target material (small batches); using concentrated nitric acid; no F⁻</td>
</tr>
<tr>
<td>Solvent extraction</td>
<td>1-4 kg UNF – PUREX flowsheet sends Np to waste – UREX flowsheets are not well developed for high concentrations of Np</td>
<td>~3 Kg Np/Pu /batch</td>
<td>Np/Pu valence state adjustment; Np/Pu extraction behavior; effects of high specific activity ²³⁸Pu on acid and solvents; kinetics of valence changes, extended the NNL model predicting Np behavior by increasing concentration 200X</td>
</tr>
<tr>
<td>Anion exchange</td>
<td>200 gm Pu/batch based on Reactor Grade Pu (very low Pu-238 content); Np anion exchange not used at REDC</td>
<td>~100 gm ²³⁸Pu/batch</td>
<td>Assess column thermal hydraulics, chemistry changes with temperature and alpha radioactive decay. Test with improved resins. Determine yields, losses, product purity, outgassing, hydraulic behavior, adapt as necessary.</td>
</tr>
</tbody>
</table>
### A Comparison to Existing Processes Shows Areas Requiring Validation and Scale Up (2)

<table>
<thead>
<tr>
<th>Process Step</th>
<th>Current Technology Using Existing Equipment</th>
<th>Proposed 1.5 kg/year</th>
<th>Issues to be Addressed During Development</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cation Exchange</td>
<td>~ 20 g Cm is loaded on Dowex Resin and fired the resulting oxide also contains curium oxysulfate</td>
<td>~75 g $^{238}$Pu per batch to be compatible with LANL aqueous process</td>
<td>Assess column hydraulics; chemistry changes with temperature and alpha decay; needs to meet low sulfur content, low actinide content (Th, Np) required by LANL.</td>
</tr>
<tr>
<td>Shipping</td>
<td>~ 5 gm $^{238}$Pu/shipment</td>
<td>~ 200-600 gm $^{238}$Pu/shipment</td>
<td>Increase capacity per shipment for $^{238}$Pu shipments by adding load out capability and updating safety documents. Handling large quantities of $^{238}$Pu product without incident. Send small amount of “surrogate” $^{238}$Pu to LANL to exercise shipping methods and evaluate product impurities.</td>
</tr>
<tr>
<td>Modified direct denitration</td>
<td>0.1 - 1.0 kg/hour based on U Np had not been tested except very low concentrations and combined with U, Pu</td>
<td>~100 gm/hour of Np</td>
<td>Demonstrate Np conversion chemistry. Scale to ~ full scale; characterize oxide product; set Np powder specifications.</td>
</tr>
<tr>
<td>Pa-233 removal</td>
<td>SRS relied on anion exchange for very large batches of Np. ORNL needed to develop technology suitable for existing facilities.</td>
<td>~ 15 kg Np/year</td>
<td>$^{233}$Pa removal occurred during anion exchange at SRS; new separation technique is needed.</td>
</tr>
</tbody>
</table>
INL has Installed a Neptunium Oxide Repackaging Glovebox

- Installation is complete
- The first shipment occurred in November, 2015
- The second shipment occurred in September, 2016
Both the Advanced Test Reactor and the High Flux Isotope Reactor Will Be Used to Produce $^{238}\text{Pu}$

Reflector positions and flux traps can be used to irradiate NpO$_2$ at ATR

Both Reactors Produce Radioisotopes for DOE
Over View of HFIR Irradiation Sites

Pu-238 Production Will Utilize the Vertical Experiment Facility (VXF) Irradiation Positions Located in the Permanent Reflector
Target Design and Irradiation Focused on Development of Full Length Target Design

- **Single Pellet Targets**
  - Tensile Strength
  - Do interactions occur between clad and pellets that reduce clad strength?
  - Targets must not fail due to melting or cladding breach.

- **Partially Loaded Targets**
  - Partial ~ 3”

- **Fully Loaded Targets**
  - Full ~ 20”

- What are the impacts of flux depression on product quality?
- What is the fission gas release?
- What are the yields from a full length target?
Data from Thermal Conductivity Measurements for Cermet pellets are Compared to Data from IAEA Reactor Fuels Handbook

- First pellets with “as-is” NpO₂ did not survive

- Early pellets were made with NpO₂ heat treated to 800°C – thermal conductivity was too low to survive 2 cycles of irradiation

- A series of tests led us to heat treat NpO₂ to 1200°C increasing thermal conductivity
Metallurgical Mount of Pellet After Irradiation Showing Pellet Diameter Shrinkage
Post Irradiation Data was needed to Characterize Fully Loaded Target Pellet Dimensional Changes

Averaging of Diameter Data to Reduce Scatter Shows 3 Distinct Slopes:
Negative for FD<0.28
Positive for 0.28<FD<0.41
Zero for 0.41

Averaging of Length Data to Reduce Scatter Shows:
Considerable Scatter for FD<0.41
Positive Slope for FD>0.41
Target Irradiation Has Been Scaled Up By >100X

Starting with NpO$_2$

Single pellets were irradiated in FY2012 (~ 0.6 g NpO$_2$)

Multi pellet test targets were irradiated and analyzed

Leading to fully loaded test targets

About 2.7 kg of NpO$_2$ will have been irradiated at the conclusion of the next irradiation cycle
Summary of Target Design/Irradiation

• Single pellet targets were irradiated in 2012
• Through a combination of irradiation and post irradiation analysis, target irradiation was scaled up by a factor of 200x in 2013
• Pu-238 production per target has increased by ~40% due to an increase in length (number of cycles) of irradiation (2016)
• Design of an improved target body to ease target handling complications underway (2017)
• Scale up testing is underway to increase to ~ 150 targets/yr. (from 40 targets/yr.—full scale is ~ 360 targets/yr.)
Scale Up: Target Automation Steps

• Powder dispensing
• Powder blending
• Pellet pressing
• Pellet metrology
• Loading pellets in targets
Powder Dispensing will be Carried out Using a Glovebox Mounted Commercial Powder Dispenser

- Automated commercial powder dispenser
- Automated mass-based powder charging of vials
- 30-vial carrousel
- One pellet charge per vial
- Aluminum and NpO₂ dispensed separately
NpO$_2$/Al Powder is Accomplished by Blending via Rotating Drum

- Commercial tumbler
- Custom drum holds 30 vials
- Each vial contains a single pellet powder charge
- Drum loaded by hand after automated powder dispensing
- After blending the vials are placed in a tray compatible with the press system
The Press System will Process 2 Pellets Every 8 Minutes

- Vial capping/de-capping
- Pellet ejection
- Die cleaning
- Die loading
- Pellet staging
Commercial Laser Micrometers, Laser Triangulation Gage, and Mass Balance will be Used in a Custom Designed Metrology System
REDC Hot Cells Are Expected to Meet Current Projections for $^{238}\text{Pu}$ Production

Currently operating with approved DOE Category 2 Safety Basis – Pu-238 production requires SAR update with similar safety envelope

Process equipment in place to dissolve, separate, recover and purify Np/Pu products and dispose of fission product wastes

Fully remotely operated and maintained

In-house analytical chemistry to support initial R&D activities

Optimization studies should be conducted to determine opportunities to enhance operations
Transition of chemical processing operations from bench scale to full capacity

Bench Scale

- ~ 100 milligrams $^{238}$Pu
- ~ 20 grams Np
- Glovebox
- RSS
- USQD
- Test proposed flowsheets (feed adjustment conditions, expected separation efficiency or other outcomes)

Hot Cell Tests I

- Few grams $^{238}$Pu
- 100's of grams Np
- Research Staff direction
- USQD
- Identify specific equipment
- Identify equipment modifications (if any)
- Modify flowsheet as necessary
- Covered by SAR

Hot Cell Tests II

- 10-100 grams $^{238}$Pu depending on availability
- Kg Np
- Work plans and shift instructions for hot cell shift operations
- Modify existing Hot Cell Procedures
- Modify equipment if needed
- Strive to match expected batch rate
- Maintenance Plan

Hot Cell Operations

- Covered by SAR/TSR
- Hot Cell Procedures
- “Routine operations”
- Match expected mass flow rate
- Existing hot cell equipment
- Numerous tank pit tanks
- Installation of new equipment as needed

Proof of concept → Process optimization and scale-up → Production
Current Tasks Focus on Chemical Processing to Recover Np/Pu

Dissolution

Partitioning (using solvent extraction)

Purity

Can we dissolve with existing equipment?

Actinides in nitric acid solution

Target

Can we partition into components efficiently?

Np

Pu

Fission Products

How ORNL ensures that LANL can use new $^{238}$Pu in their existing process line (product purity, neutron emission rate)

How do we recycle Np into additional targets? (decontamination from Pu, Fission products)

Pu Valence

Pu Valence
Neptunium Control with Nitrite

- Extractability of Np depends on oxidation state; for tri-n-butyl phosphate (TBP): Np(VI)>Np(IV)>>Np(V)

- Nitrite has been used for Np valence control in solvent extraction (Poe et al 1964; Schulz and Benedict 1972).
  - Np(V) in nitric acid solution is reversibly oxidized to Np(VI):
    - $\text{Complicated by } \text{NpO}_2^+ + \frac{3}{2} \text{H}^+ \xrightleftharpoons[k_r]{k_f} \text{NpO}^2_2^+ + \frac{1}{2} \text{HNO}_2 + \frac{1}{2} \text{H}_2\text{O}$
    - Radiolysis
    - Complex role of nitrous acid as catalyst for oxidation and reactant for reduction

- Taylor and coworkers (2013) demonstrated >99% Np recovery
  - This is promising, but there were unproven aspects for our application:
    - Np concentration in feed >100X higher
      - Need to demonstrate sufficient Np oxidation rate
      - Nitrous and nitric acid concentrations will vary more significantly with reaction
    - No Pu or FPs in previously reported tests
      - Need to demonstrate Pu recovery and FP removal
      - Evaluate Pu-238 radiolysis effects on chemistry
First-cycle Solvent Extraction Separations are Focused on Pu and Np Recovery

1. Coextraction
   - Remove fission products (FPs)
   - Oxidize Np(V)
   - Recover Np and Pu

2. Partitioning
   - Reduce Np and strip in aqueous phase
   - Retain Pu in organic phase

3. Stripping
   - Reduce Pu and recover in aqueous phase
Solvent Extraction Test P1PX-1 with Material From Irradiated Targets was Run on October 27, 2015

<table>
<thead>
<tr>
<th>Distribution of material in feed among outlet streams</th>
<th>Pu</th>
<th>Np</th>
<th>Zr</th>
<th>Th</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raffinate</td>
<td>0.004%</td>
<td>0.12%</td>
<td>5.6%</td>
<td>0.02%</td>
</tr>
<tr>
<td>Np product</td>
<td>0.029%</td>
<td>96.2%</td>
<td>88.2%</td>
<td>0.04%</td>
</tr>
<tr>
<td>Pu product</td>
<td>99.9%</td>
<td>2.54%</td>
<td>-</td>
<td>22.2%</td>
</tr>
<tr>
<td>Used organic</td>
<td>0.007%</td>
<td>1.13%</td>
<td>6.2%</td>
<td>77.8%</td>
</tr>
</tbody>
</table>

Decontamination Factors
Pu in Np product = 4000
Np in Pu product = 40
Zr in Np product = 7
Zr in Pu product = >790
ORNL Packaged and Shipped a Small Sample of New PuO$_2$ to LANL in 1Q 2016

Inner container which holds ~ 5g PuO$_2$

ORNL Staff close the middle package using a torque wrench

LANL Staff observed loading and packaging of the PuO$_2$
Comparison of Impurities is Good

- Total Pu assay - 88.1% is theoretical maximum

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>% Pu</th>
<th>ORNL</th>
</tr>
</thead>
<tbody>
<tr>
<td>SN1008</td>
<td>85.0</td>
<td></td>
</tr>
<tr>
<td>SN1009</td>
<td>83.7</td>
<td>87.0</td>
</tr>
</tbody>
</table>

- Percent Pu-238

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>g oxide</th>
<th>Measured Watts</th>
<th>LANL% Pu-238</th>
<th>ORNL %Pu-238</th>
</tr>
</thead>
<tbody>
<tr>
<td>SN1008</td>
<td>1.9934</td>
<td>0.8487</td>
<td>88</td>
<td>87.9</td>
</tr>
<tr>
<td>SN1009</td>
<td>2.0141</td>
<td>0.8461</td>
<td>88</td>
<td>88.0</td>
</tr>
</tbody>
</table>
Actinide impurities are low as well

<table>
<thead>
<tr>
<th>Sample</th>
<th>U-234 (ppm)*</th>
<th>Th-232 (ppm)</th>
<th>Np-237 (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LANL</td>
<td>ORNL</td>
<td>LANL</td>
</tr>
<tr>
<td>SN1008</td>
<td>2000</td>
<td>900</td>
<td>7800</td>
</tr>
<tr>
<td>PUP-084</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SN1009</td>
<td>1500</td>
<td>600</td>
<td>11000</td>
</tr>
<tr>
<td>PUP-085</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

LANL and ORNL resolved the U-234 numbers (decay)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pu-236 (ppm)*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LANL</td>
</tr>
<tr>
<td>SN1008</td>
<td>2</td>
</tr>
<tr>
<td>SN1009</td>
<td>2</td>
</tr>
</tbody>
</table>

*ug of actinide per gram of oxide
### Trace Elements

Phosphorus needs additional review; ORNL and LANL will discuss additional details of analysis.

#### Comparing LANL measurements* against LANL GPHS spec:

|     | Al | B  | Bi | Be | Ca | Cd | Cr | Cu | Fe | Mg | Mn | Mo | Na | Ni | Pb | Si | Sn | Zn | P  | Ba | Co | V  | Ti | Zr | Ta | Y  |
|-----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| SN-1008 | 40 | <5 | 2.7 | <1 | 210 | <10 | 25 | 4.7 | 20 | <10 | <10 | 35 | 150 | 45 | 80 | 230 | 60 | <20 | >1100 | <10 | <5 | <10 | <50 | <50 | <50 |
| SN-1009 | 80 | <5 | 6.1 | <1 | 140 | <10 | 55 | 140 | 70 | 15.6 | <10 | 20 | 260 | 30 | <10 | 300 | 35 | <20 | >1100 | <10 | <5 | <10 | <50 | <50 | <50 |
| spec   | 500 | 20 | 5   | 500 | 50 | 1000 | 100 | 50 | 250 | 400 | 500 | 100 | 750 | 50 | 50 | 25 |
| Min. Method 2 DF† | 1 | 1 | 1 | 0.2 | 1 | 26 | 10 | 14 | 2.5 | 10 | 1 | 1 | 8 | 0.6 | 4 | 1 | 0.1 |

#### Comparing LANL and ORNL measurements:

|     | Al | B  | Bi | Be | Ca | Cd | Cr | Cu | Fe | Mg | Mn | Mo | Na | Ni | Pb | Si | Sn | Zn | P  | Ba | Co | V  | Ti | Zr | Ta | Y  |
|-----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| SN-1008 | 40 | <5 | 2.7 | <1 | 210 | <10 | 25 | 4.7 | 20 | <10 | <10 | 35 | 150 | 45 | 80 | 230 | 60 | <20 | >1100 | <10 | <5 | <10 | <50 | <50 | <50 |
| ORNL PUP-084 | 33 | 107 | <0.04 | 80 | 0.1 | 21 | 6.6 | 68 | 17 | 1 | 41 | 90 | 40 | 150 | 116 | 22 | <4200 | 0.8 | 60 | 0.8 |
| SN-1009 | 80 | <5 | 6.1 | <1 | 140 | <10 | 55 | 140 | 70 | 15.6 | <10 | 20 | 260 | 30 | <10 | 300 | 35 | <20 | >1100 | <10 | <5 | <10 | <50 | <50 | <50 |
| ORNL PUP-085 | 304 | 108 | <0.1 | 2175 | <9 | 77 | 10 | <610 | <176 | <8 | 13 | <500 | 13 | 26 | 72 | <1800 | <4200 | <12 | 230 | 14 |

* ug per gram of oxide
† from LA-UR-00-418
An Opportunity to Increase Yield has been Integrated into the Baseline—\(^{237}\text{NpO}_2\) Pellets Clad in Zircaloy

**Benefits**

- Improved production yield per unit reactor volume
- Reduces number of targets required to be fabricated, irradiated, and processed to ~100 targets per year
- Pu product assay is projected to be 92% \(^{238}\text{Pu}\)
- “Rich” product will enable “up blending” of \(^{238}\text{Pu}\) concentration in low-purity \(^{238}\text{Pu}\) currently in the inventory
- Will eliminate aluminum from liquid waste (zircaloy cladding will become solid waste)

**Concerns**

- Heat generation limits
- Modifications to target fabrication line (minimal)
The Alternate Target Design Uses a Pure Neptunium Dioxide Pellet Clad in Zircaloy

- The same process is used to convert aqueous neptunium nitrate solution to oxide (modified direct denitration)
- Pellets are pure NpO₂ (no aluminum)
- Pellet density of ~ 85% of theoretical density has been obtained to date (goal is 90% or greater)
- Neutronics calculations are underway which will be followed by thermal hydraulic analysis
- Two pellet sizes are currently under evaluation (~ 0.325” and ~ 0.25”)

[Image of pellets and measuring tape]
Summary

• Automation of target fabrication is underway – with first stage expected to be complete in FY17

• Good results have been obtained in hot testing with prototypic materials

• Development of chemical processing steps to recover additional Pu(low Th content) and recycle Np back to target fabrication is underway

• Potential improvements to target design will be evaluated during FY17
Acknowledgments

• NASA, Science Mission Directorate
• DOE Office of Nuclear Energy, NE-75

• Multiple contributors at ORNL, including:
  – Chris Bryan, Emory Collins, Dave DePaoli, Randy Hobbs, Chris Jensen, Joanna McFarlane, Bob Morris, Ken Wilson
  – Nuclear Analytical Chemistry and Isotopics Laboratory
  – Hot Cell Operations staff
  – Eight Research Divisions