Current Status to Reestablish a Reliable Supply of Pu-238

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

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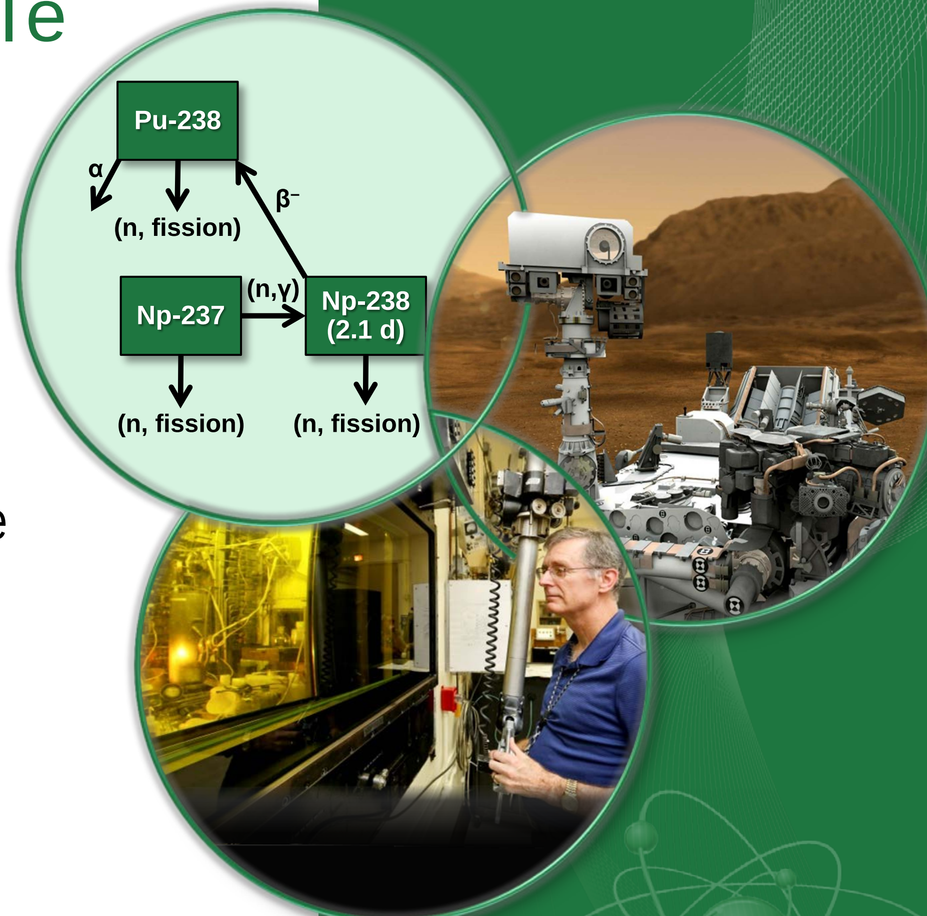
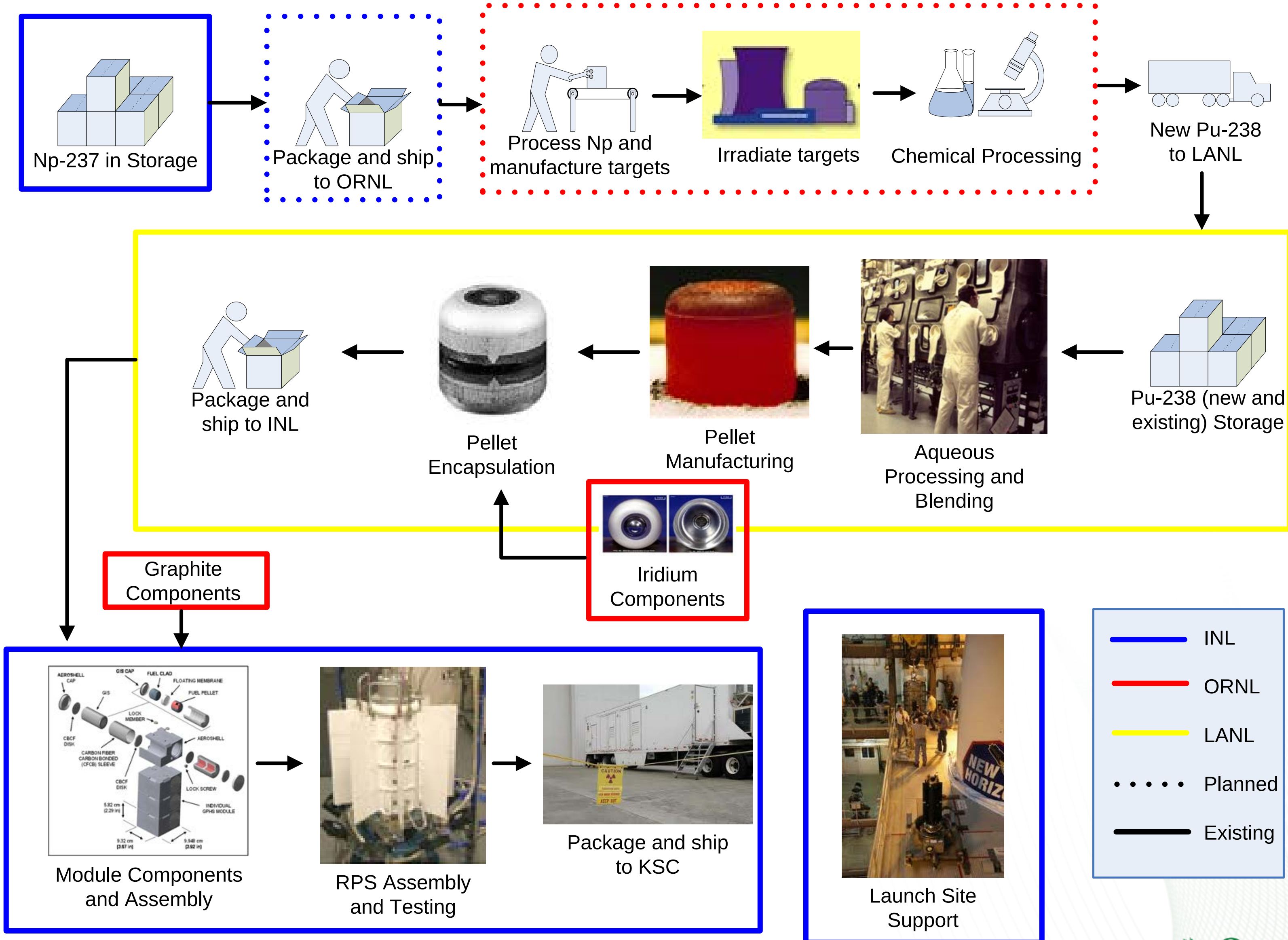
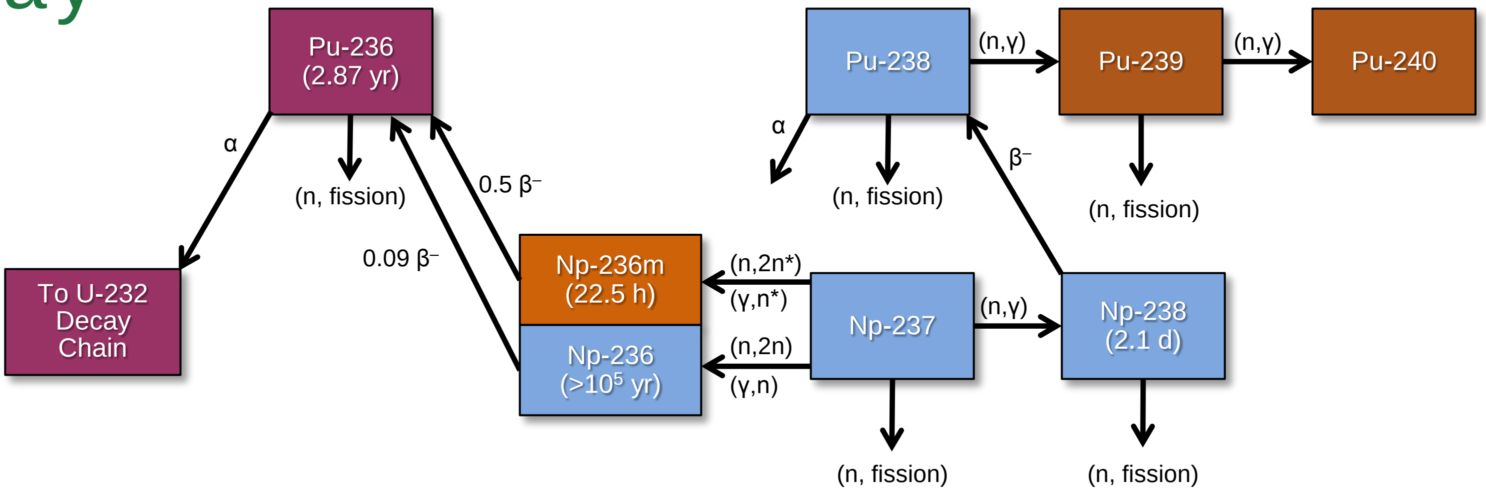


ORNL is managed by UT-Battelle for the US Department of Energy

Key Steps in Radioisotope Power System Production



Plutonium-238 is Produced in a Nuclear Reactor via Neutron Capture and Beta Decay



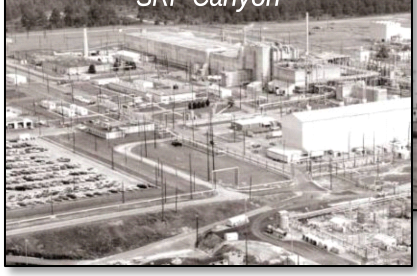
Reactor Characteristics Desired for Efficient ^{237}Np Conversion to ^{238}Pu

Characteristic	Desired to maximize ^{238}Pu	Desired to minimize ^{236}Pu impurity
Neutron spectrum	High thermal flux O(10^{14})	Minimize high energy flux (>7 MeV)
Photon spectrum	N/A	Minimize high energy flux (>7 MeV)
Target size	Large diameter	Small diameter
Neptunium loading	Maximize loading	Minimize loading

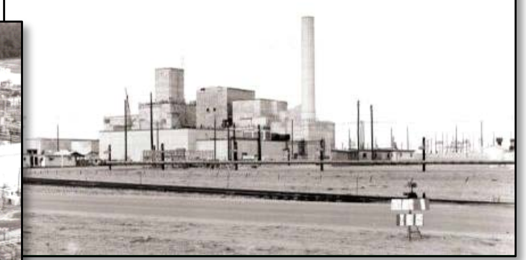
2012-016 RMW

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



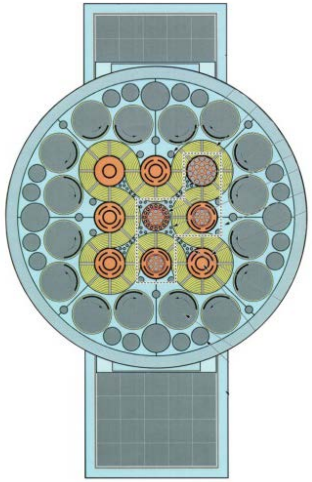
SRP Canyon



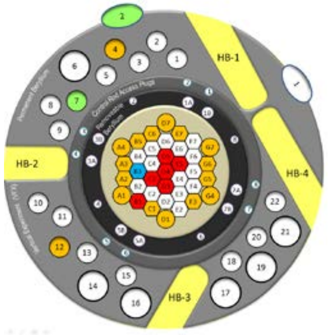
SRP Production Reactor

- Facilities and equipment available today much smaller

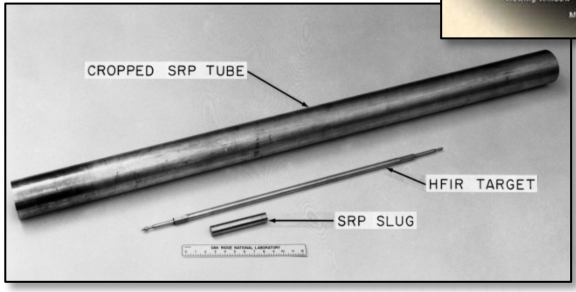
Advanced Test Reactor (ATR)

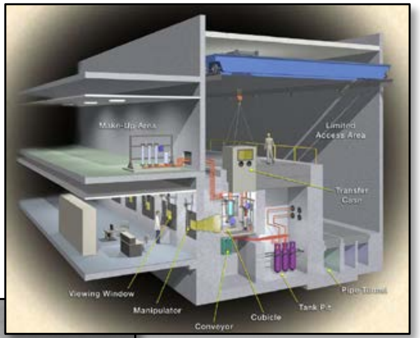


High Flux Isotope Reactor (HFIR)



Target Geometries



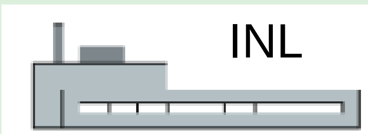


REDC

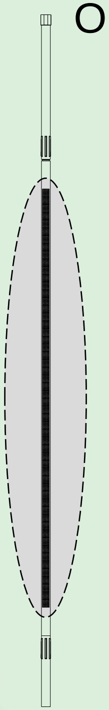
- SRS used annular target with 6 vol% NpO_2

The US DOE and NASA Have a Project Underway to Re-establish a Domestic ^{238}Pu Production

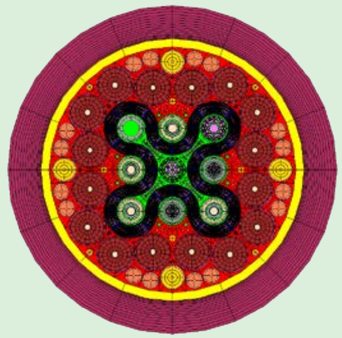
Storage of ^{237}Np

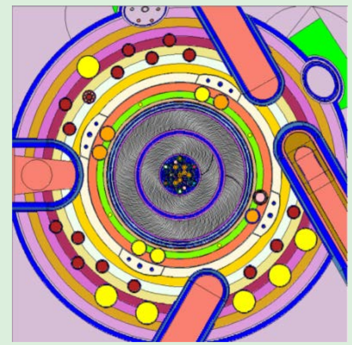


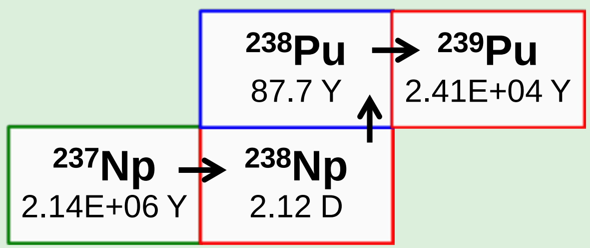
Target fabrication at ORNL REDC



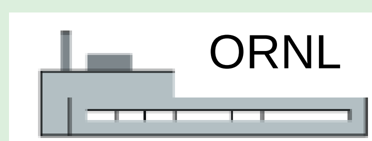
Irradiation of NpO_2/Al pellets ATR at INL and HFIR at ORNL







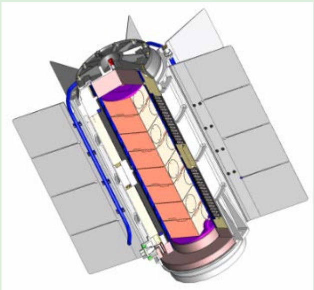
Chemical processing



Pu powder → PuO_2

LANL

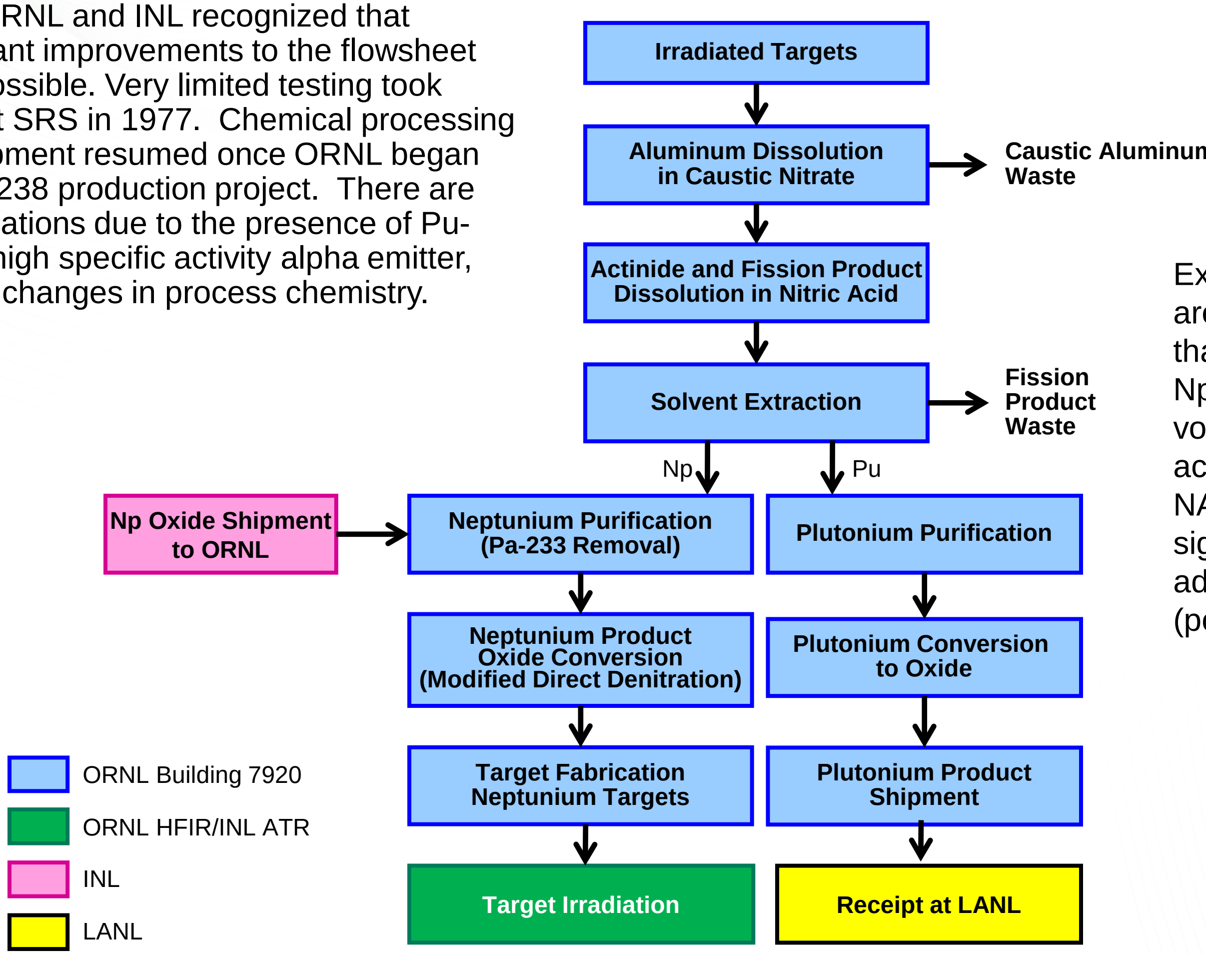
Power source (i.e., MMRTG)



Robotic rover (i.e., Curiosity)

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).

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2014-027 RMW

A Comparison to Existing Processes Shows Areas Requiring Validation and Scale Up

Process Step	Current Technology Using Existing Equipment	Proposed 1.5 kg/year	Issues to be Addressed During Development
Target Irradiation	< 50/year at ORNL SRS used long annular targets at ~ 6 vol%	~ 360/year; 20 vol% NpO_2	Target integrity – will not fail (breach) due to melting or excess pressure; excessive fission rate heating which requires high thermal conductivity
Target Fabrication	< 50/year (hot cell and glovebox)	~360/year (glovebox)	Production target design; material specifications; quality control; automation in a nuclear setting
Dissolution (caustic)	4 kg Al/batch (upper limit) , nearly pure aluminum	4 kg Al/batch , impurities introduced by 6061 alloy (required to qualify for ATR)	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
Dissolution (acid)	1-2 kg/batch heavy metal (HM) as used nuclear fuel (UNF)	~1 kg HM as irradiated Np/Pu per batch	Dissolution of actual irradiated target material (small batches); using concentrated nitric acid; no F^-
Solvent extraction	1-4 kg UNF – PUREX flowsheet sends Np to waste – UREX flowsheets are not well developed for high concentrations of Np	~3 Kg Np/Pu /batch	Np/Pu valence state adjustment; Np/Pu extraction behavior; effects of high specific activity ^{238}Pu on acid and solvents; kinetics of valence changes, extended the NNL model predicting Np behavior by increasing concentration 200X
Anion exchange	200 gm Pu/batch based on Reactor Grade Pu (very low Pu-238 content); Np anion exchange not used at REDC	~100 gm ^{238}Pu/batch ~500 g ^{237}Np/batch	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.

A Comparison to Existing Processes Shows Areas Requiring Validation and Scale Up (2)

Process Step	Current Technology Using Existing Equipment	Proposed 1.5 kg/year	Issues to be Addressed During Development
Cation Exchange	~ 20 g Cm is loaded on Dowex Resin and fired the resulting oxide also contains curium oxysulfate	~75 g ^{238}Pu per batch to be compatible with LANL aqueous process	Assess column hydraulics; chemistry changes with temperature and alpha decay; needs to meet low sulfur content, low actinide content (Th, Np) required by LANL.
Shipping	~ 5 gm ^{238}Pu/shipment	~ 200-600 gm ^{238}Pu/shipment	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.
Modified direct denitration	0.1 - 1.0 kg/hour based on U Np had not been tested except very low concentrations and combined with U, Pu	~100 gm/hour of Np	Demonstrate Np conversion chemistry. Scale to ~ full scale; characterize oxide product; set Np powder specifications.
Pa-233 removal	SRS relied on anion exchange for very large batches of Np. ORNL needed to develop technology suitable for existing facilities.	~ 15 kg Np/year	^{233}Pa removal occurred during anion exchange at SRS; new separation technique is needed.

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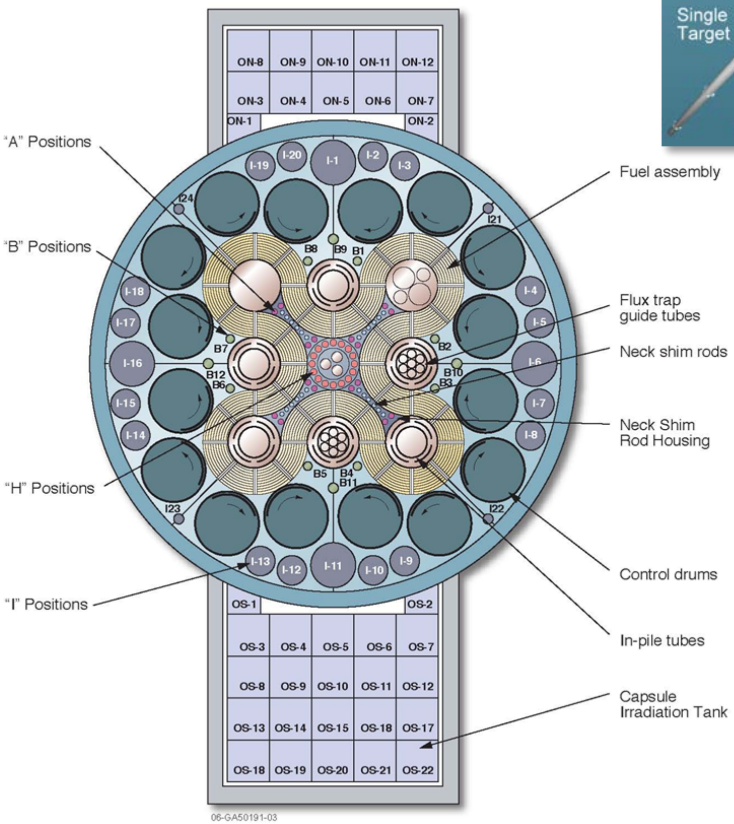
2012-039RMW

INL has Installed a Neptunium Oxide Repackaging Glovebox

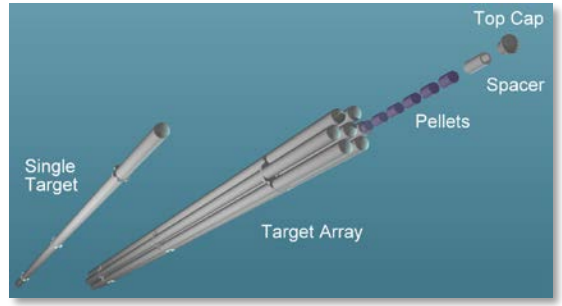
- Installation is complete
- The first shipment occurred in November, 2015
- The second shipment occurred in September, 2016

Both the Advanced Test Reactor and the High Flux Isotope Reactor Will Be Used to Produce ^{238}Pu

Advanced Test Reactor (ATR)

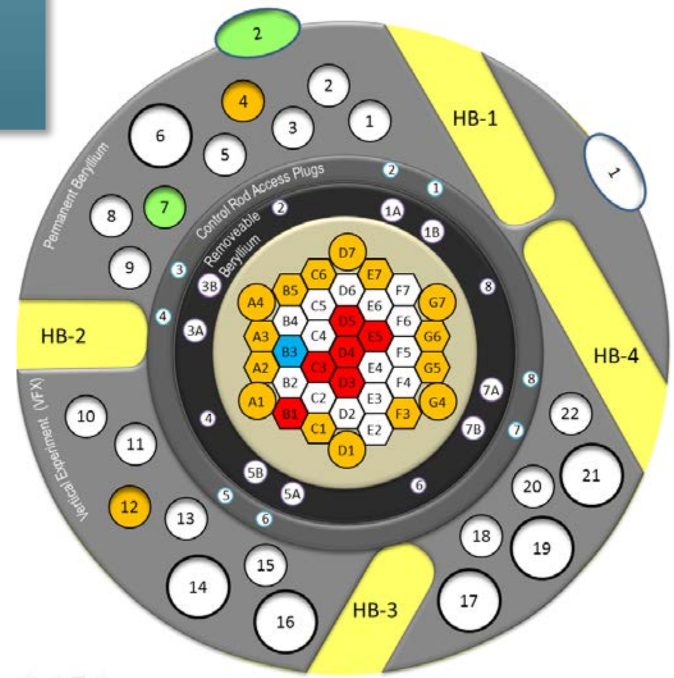


Reflector positions and flux traps can be used to irradiate NpO_2 at ATR



Target Bundle

High Flux Isotope Reactor (HFIR)



Reflector positions can be used to irradiate NpO_2 in the HFIR

Both Reactors Produce Radioisotopes for DOE

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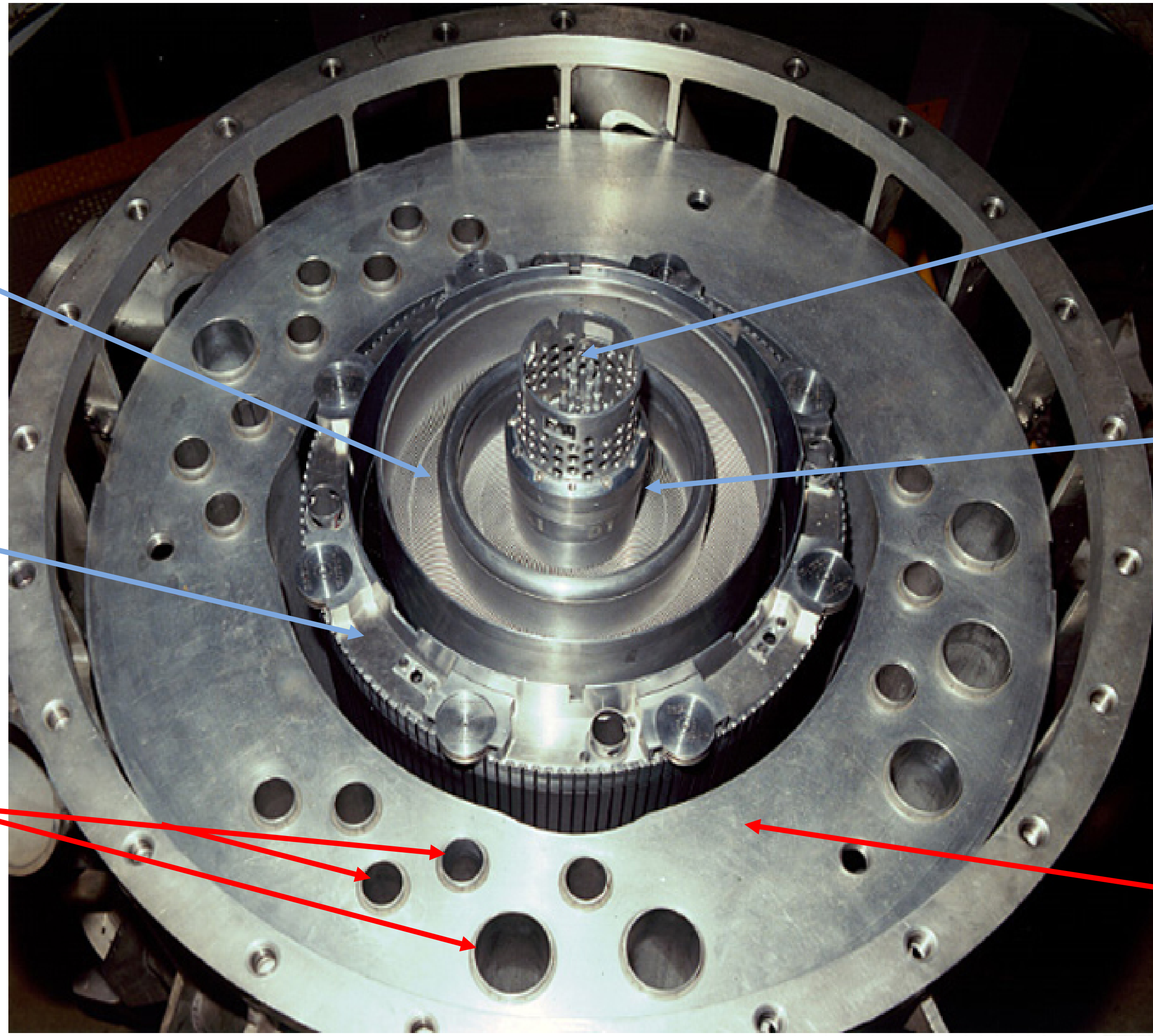
2012-015R1 RMW

Over View of HFIR Irradiation Sites



Pu-238 Production Will Utilize the Vertical Experiment Facility (VXF) Irradiation Positions Located in the Permanent Reflector

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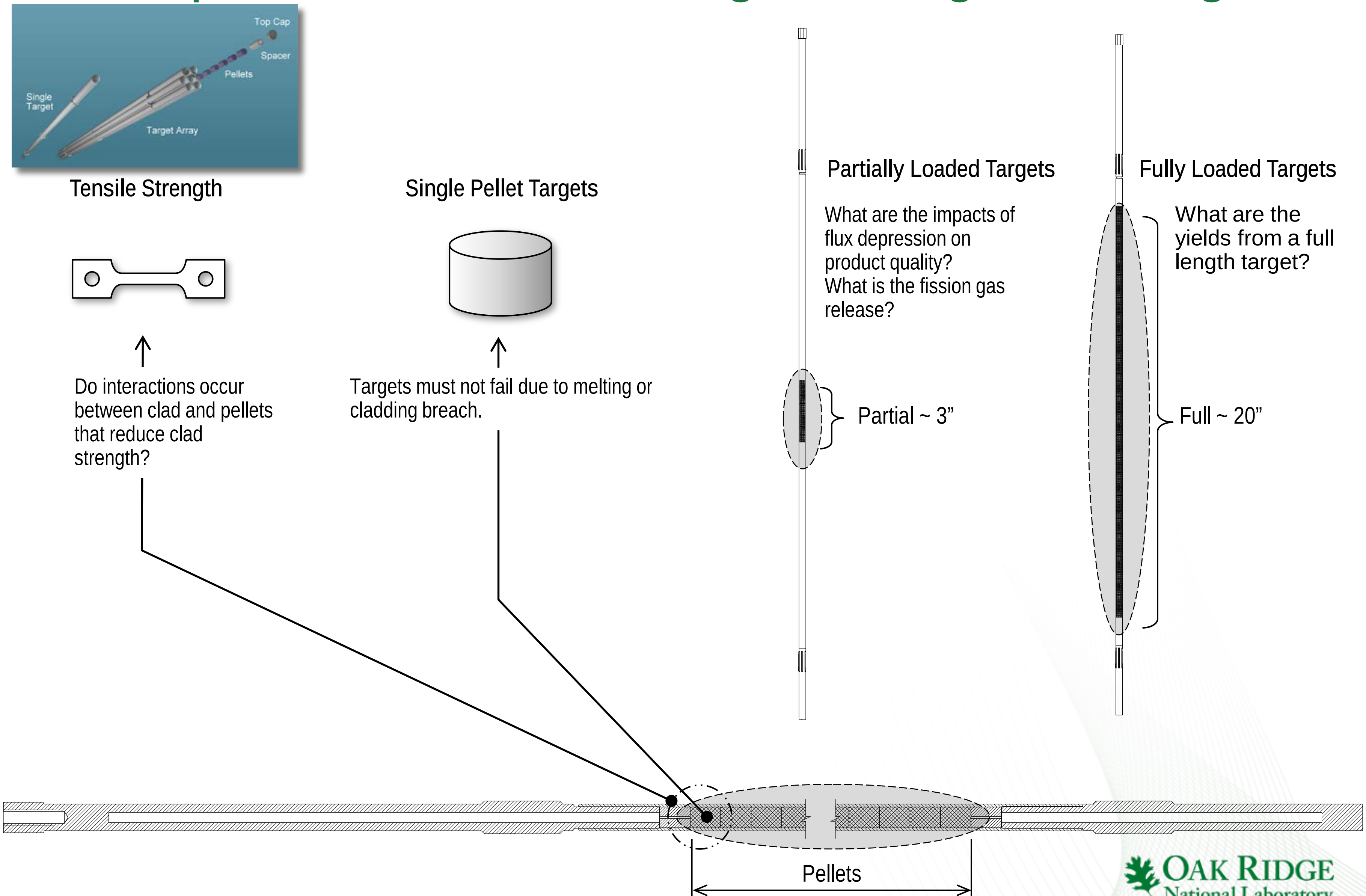
From R. Hobbs GAO slides

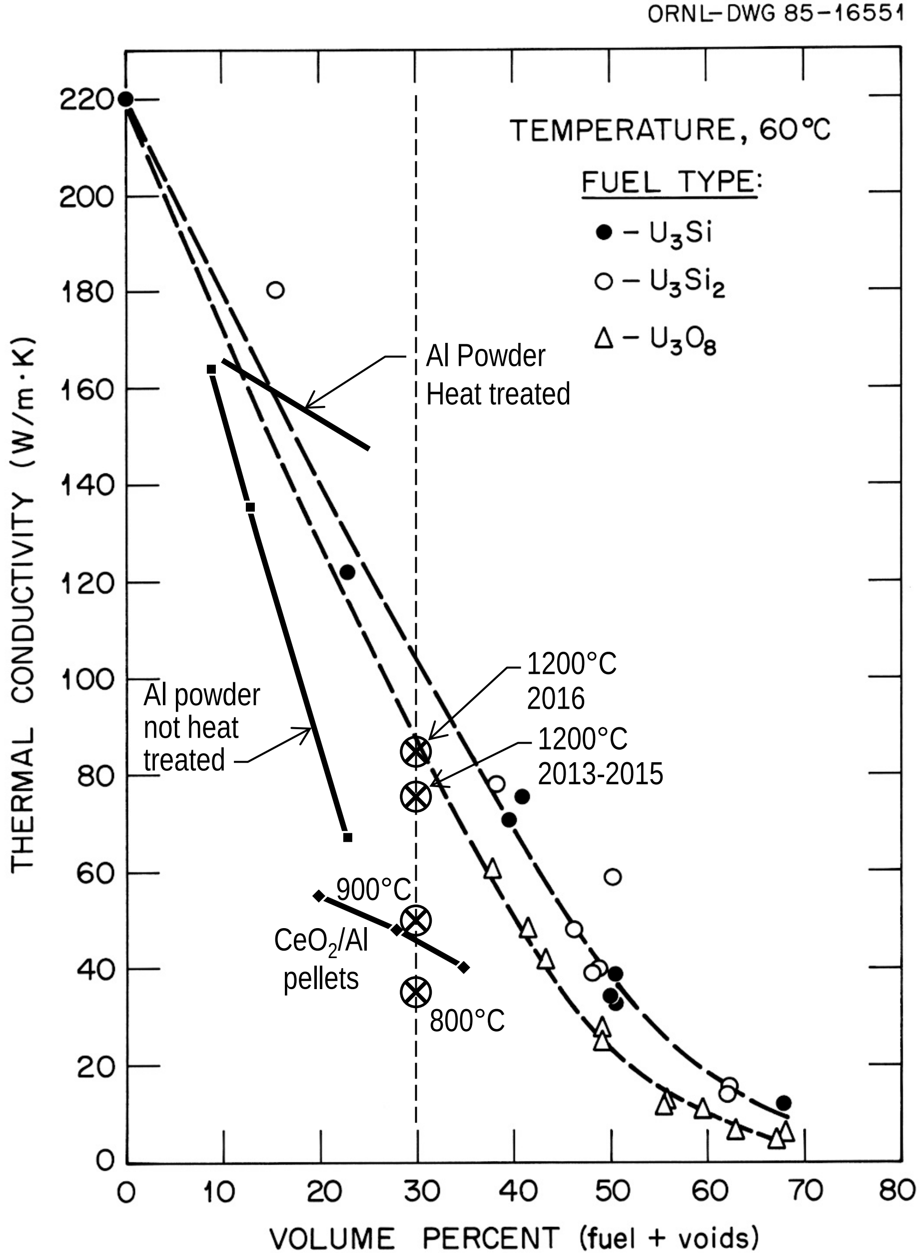
Target Design and Irradiation Focused on Development of Full Length Target Design



2012-037 RMW

Data from Thermal Conductivity Measurements for Cermet pellets are Compared to Data from IAEA Reactor Fuels Handbook

- First pellets with “as-is” NpO_2 did not survive
- Early pellets were made with NpO_2 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 NpO_2 to 1200°C increasing thermal conductivity



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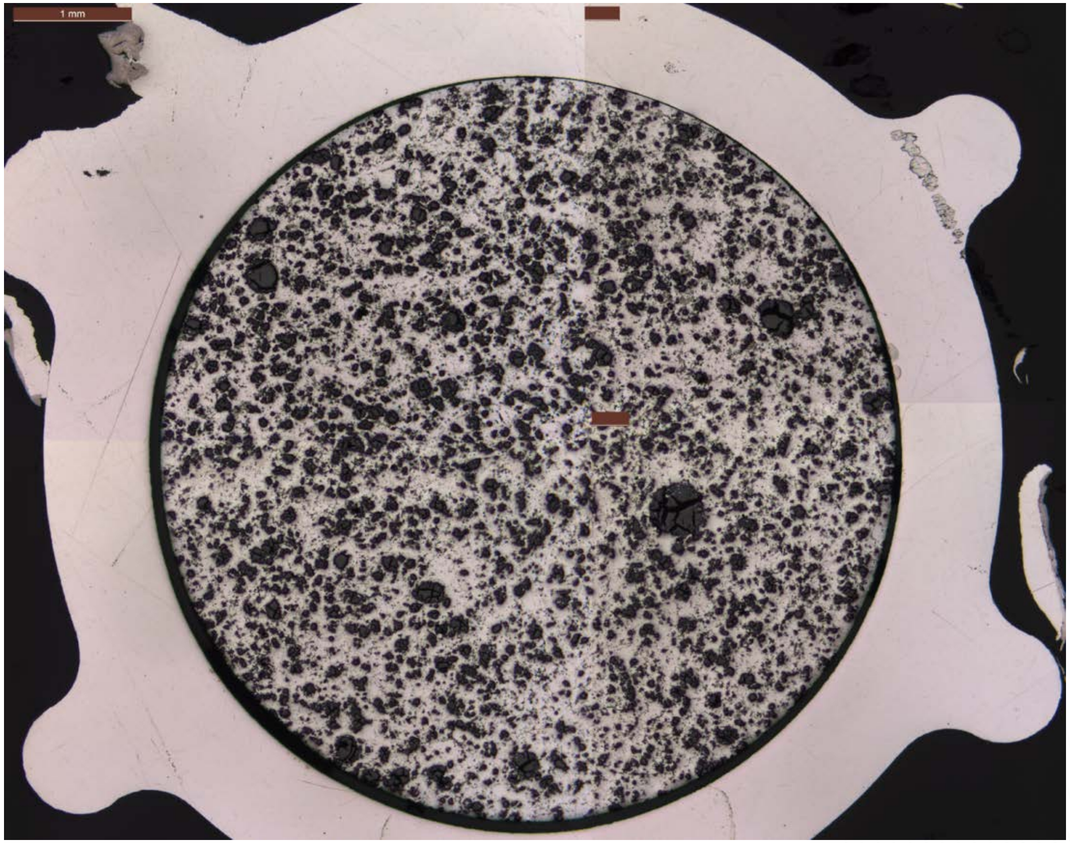
Metallurgical Mount of Pellet After Irradiation Showing Pellet Diameter Shrinkage



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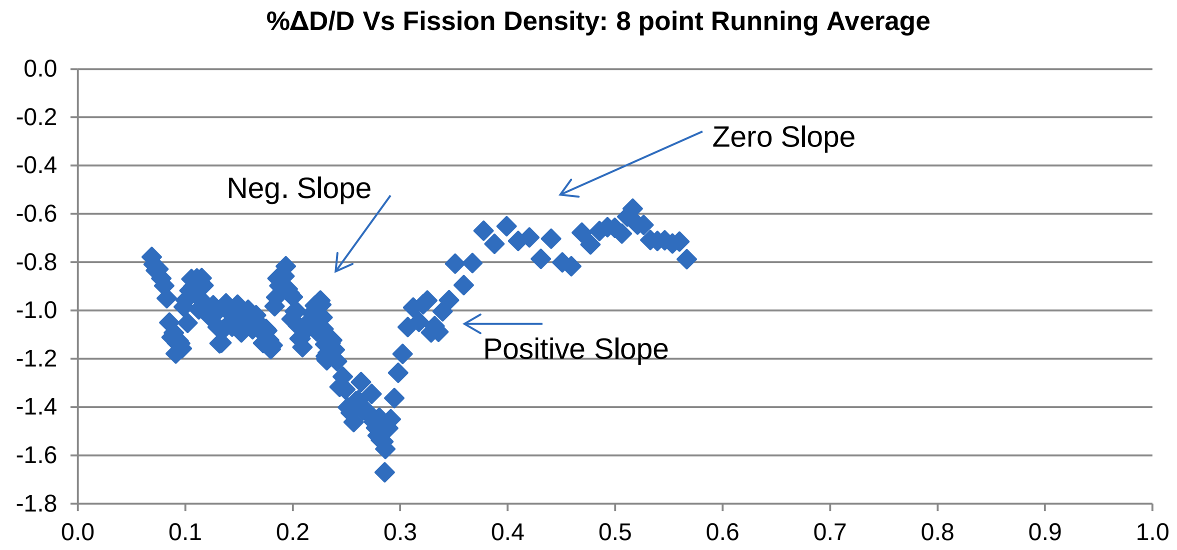
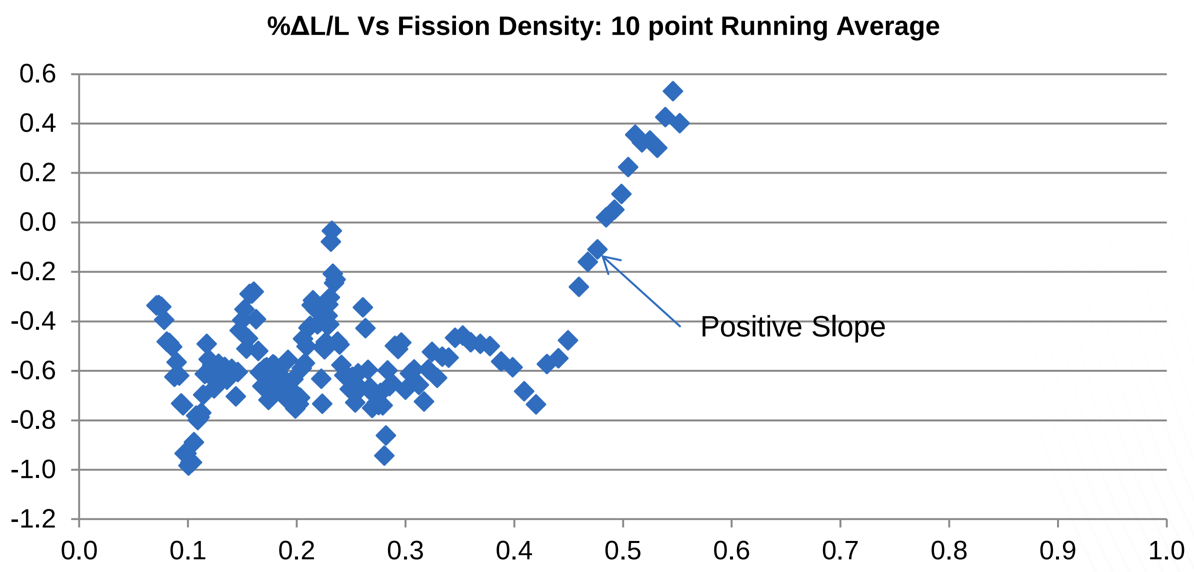
From R. Hobbs GAO slides

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

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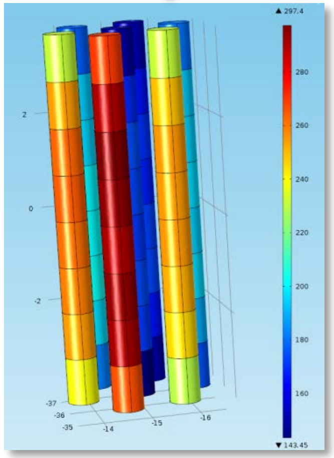
Target Irradiation Has Been Scaled Up By >100X

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

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2013-031 RMW

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

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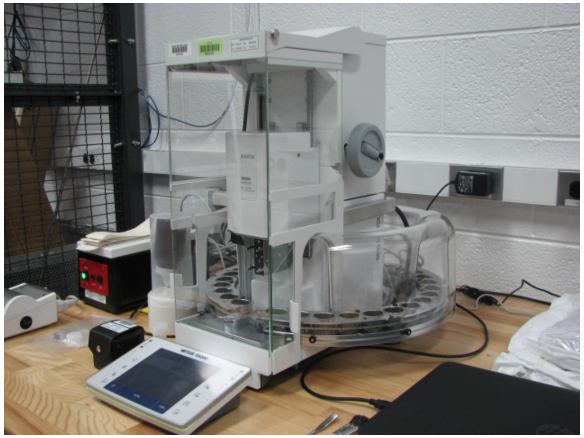
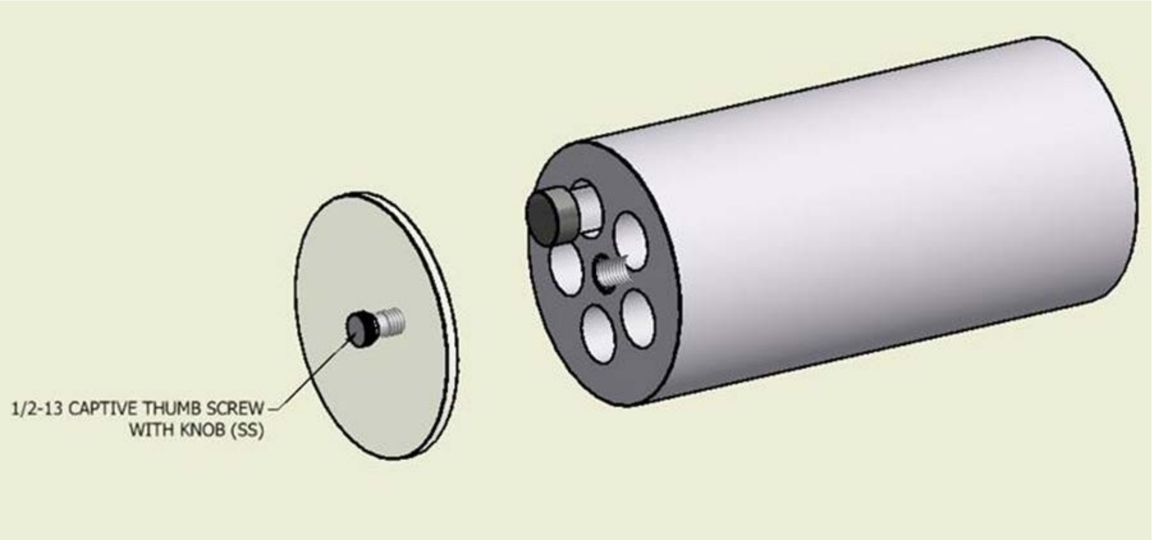
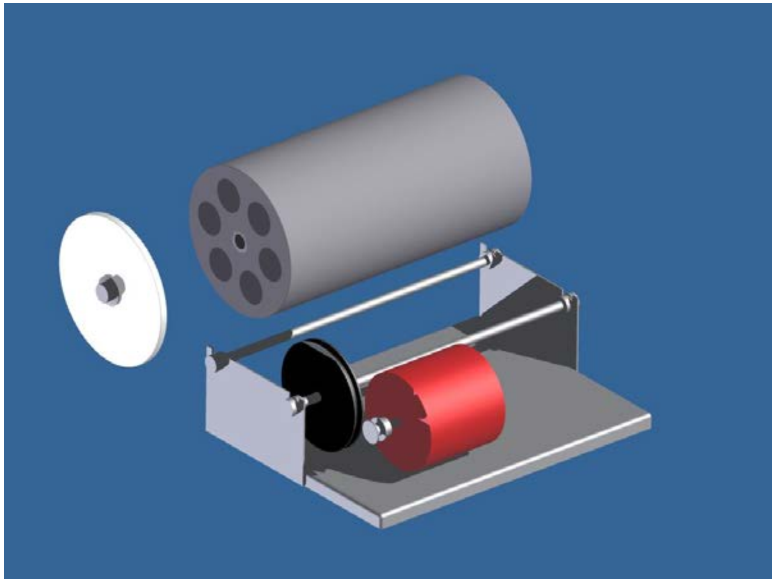
Powder Dispensing will be Carried out Using a Glovebox Mounted Commercial Powder Dispenser

- Automated commercial powder dispenser
- Automated mass-based powder charging of vials
- 30-vial carrousel
- One pellet charge per vial
- Aluminum and NpO_2 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

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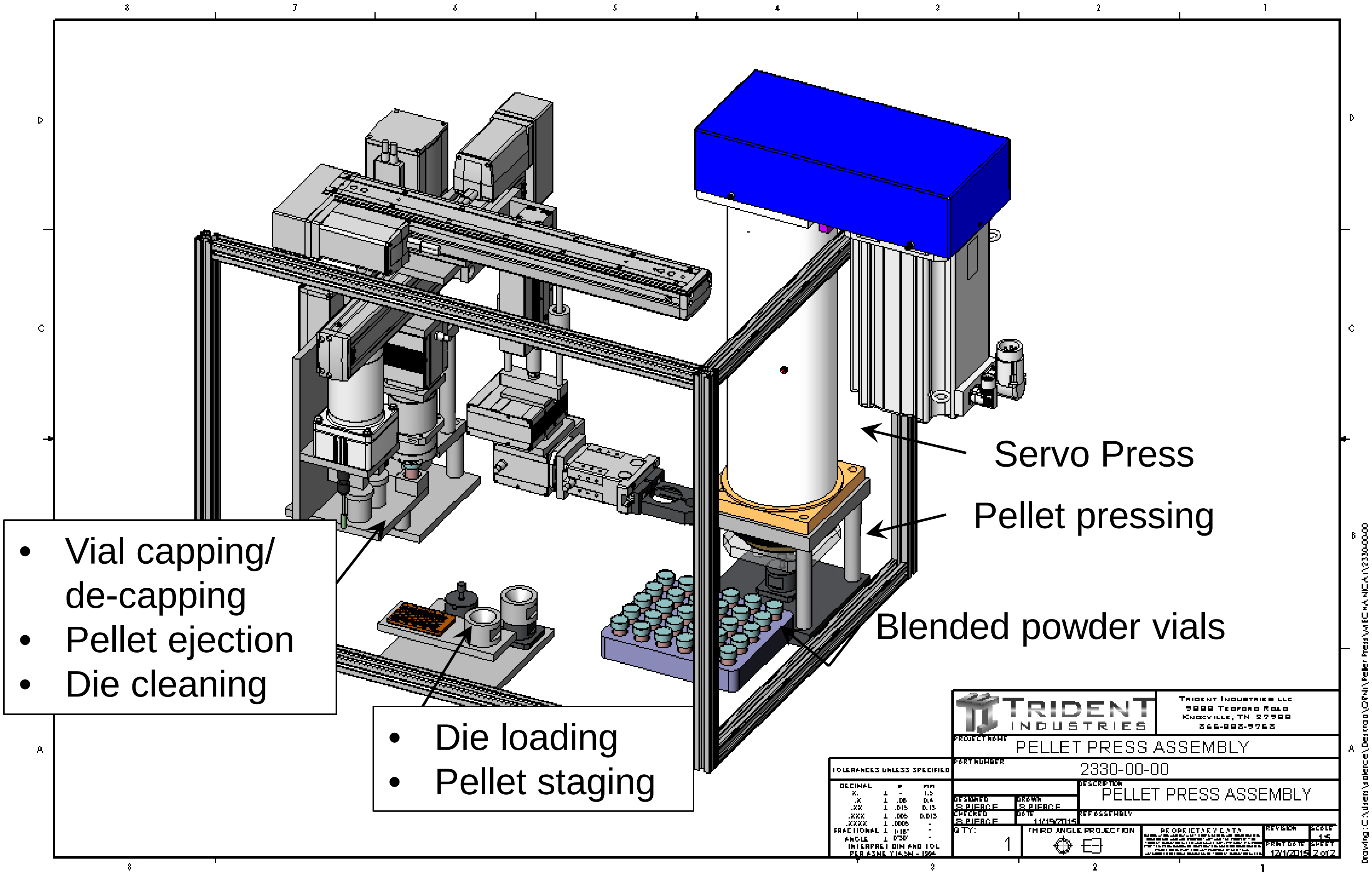
The Press System will Process 2 Pellets Every 8 Minutes



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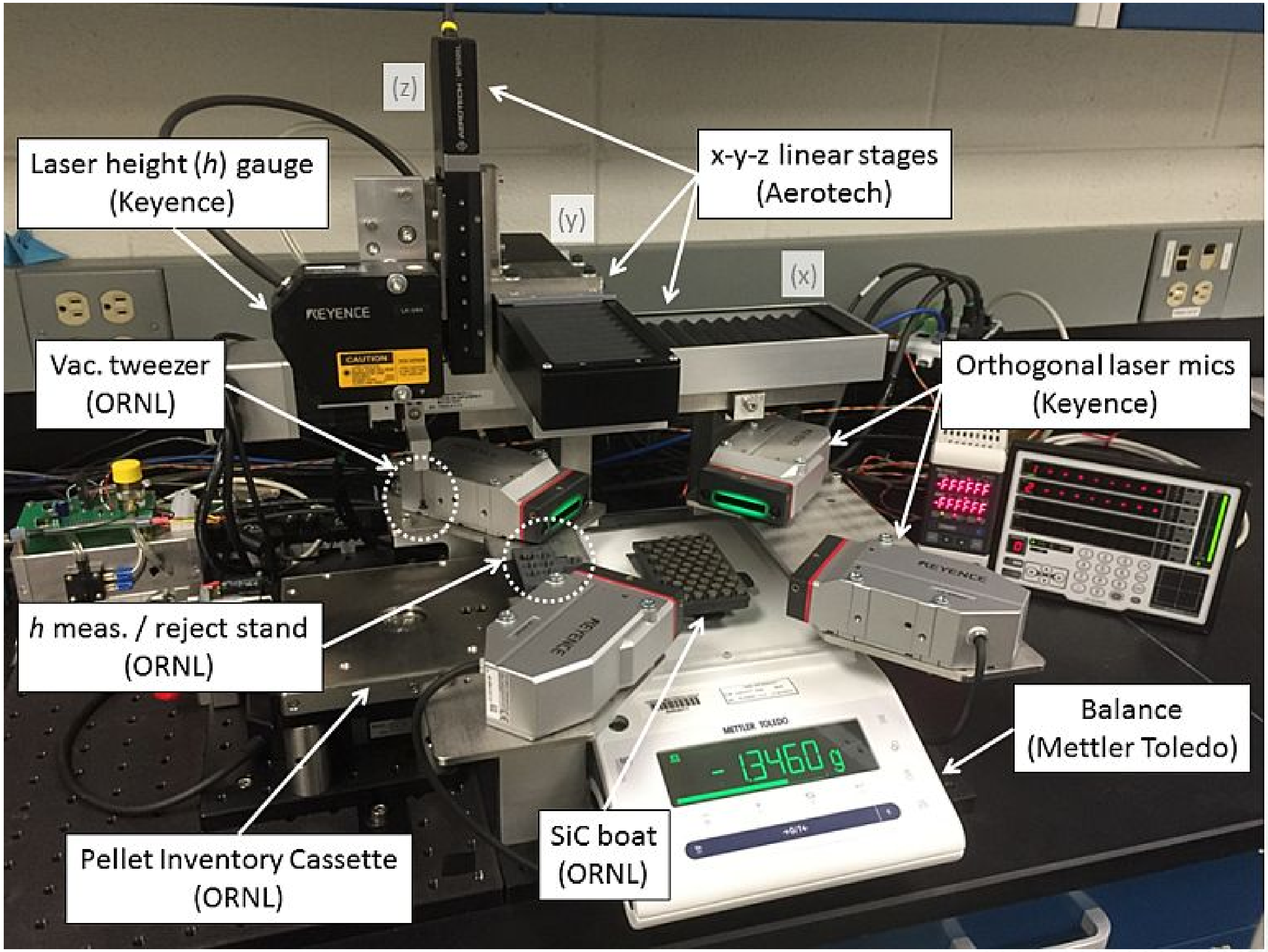
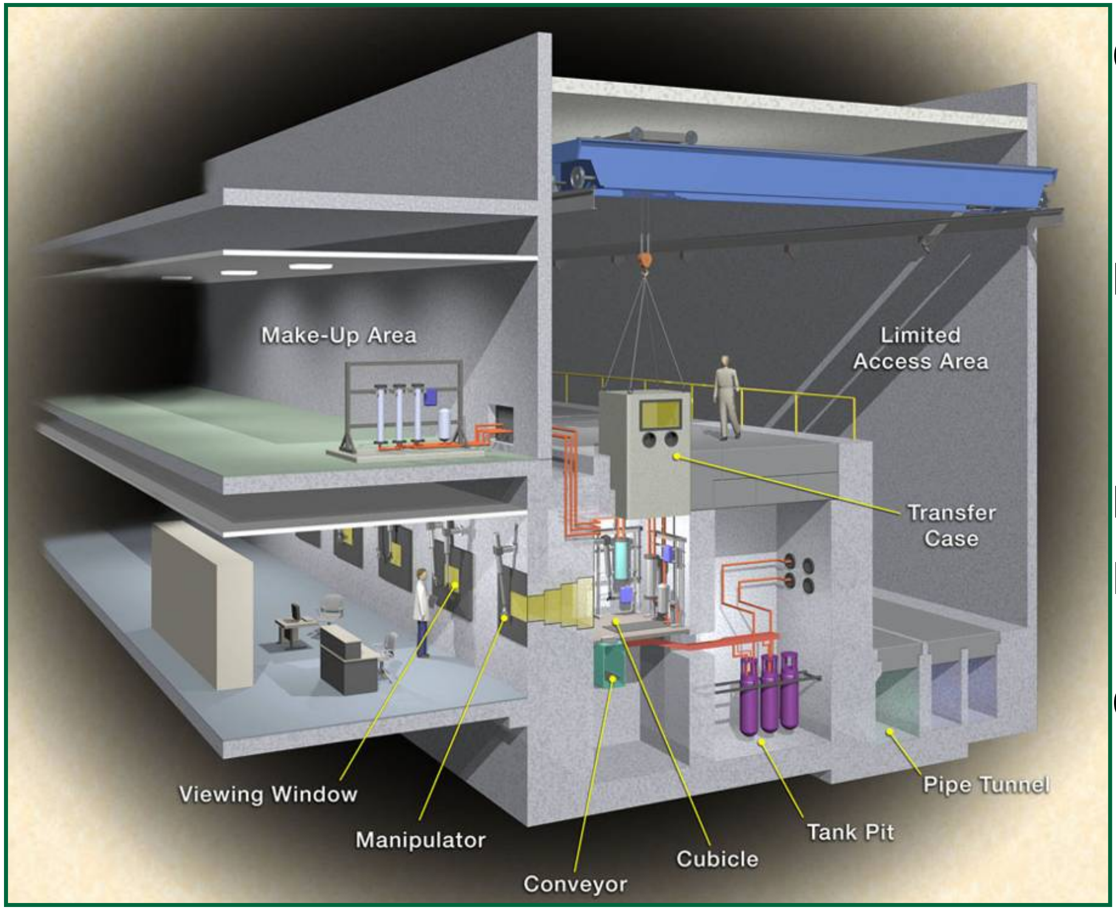
Commercial Laser Micrometers, Laser Triangulation Gage, and Mass Balance will be Used in a Custom Designed Metrology System



REDC Hot Cells Are Expected to Meet Current Projections for ^{238}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

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Transition of chemical processing operations from bench scale to full capacity

Bench Scale → Hot Cell Tests I → Hot Cell Tests II → Hot Cell Operations

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

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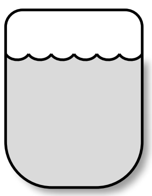
Current Tasks Focus on Chemical Processing to Recover Np/Pu

Dissolution

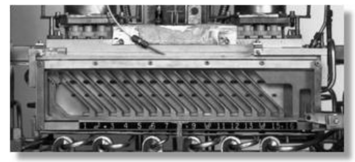
Target

Actinides in nitric acid solution



Can we dissolve with existing equipment?

Partitioning (using solvent extraction)

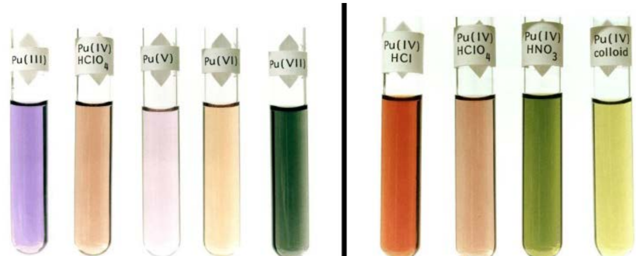


Np

Pu

Fission Products

Can we partition into components efficiently?



Pu Valence

Purity

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)

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2014-005 RMW

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):

$$NpO_2^{+} + \frac{3}{2}H^{+} \underset{k_r}{\overset{k_f}{\rightleftarrows}} NpO_2^{2+} + \frac{1}{2}HNO_2 + \frac{1}{2}H_2O$$

  - Complicated by
    - 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

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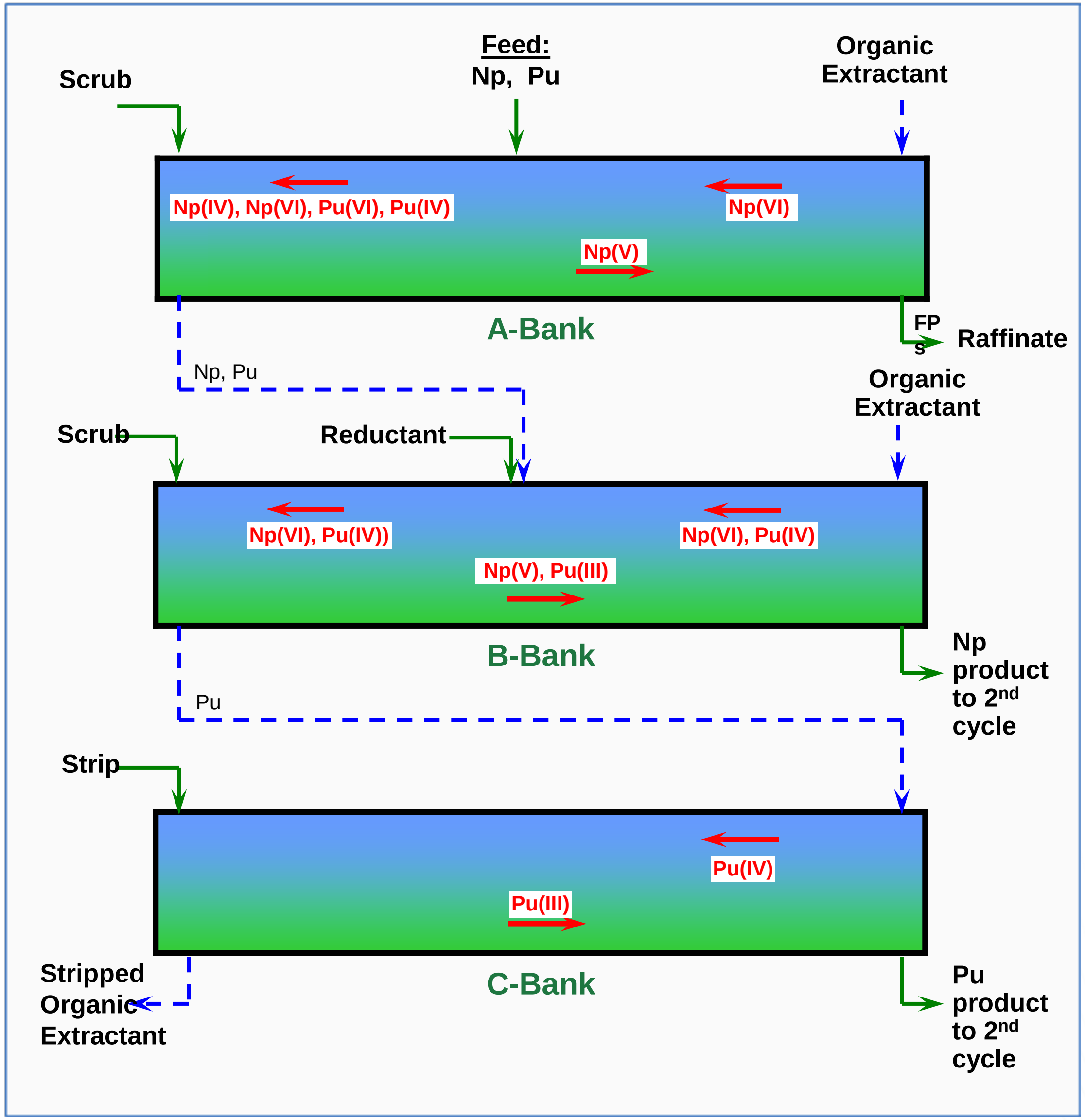
First-cycle Solvent Extraction Separations are Focused on Pu and Np Recovery



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

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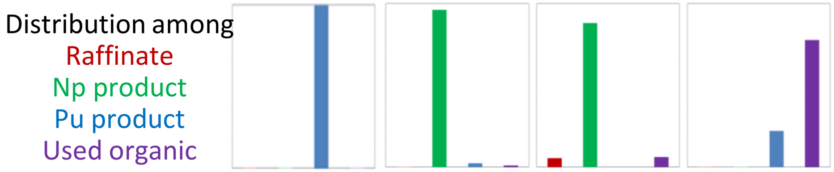
Solvent Extraction Test P1PX-1 with Material From Irradiated Targets was Run on October 27, 2015

Distribution of material in feed among outlet streams				
	Pu	Np	Zr	Th
Raffinate	0.004%	0.12%	5.6%	0.02%
Np product	0.029%	96.2%	88.2%	0.04%
Pu product	99.9%	2.54%	-	22.2%
Used organic	0.007%	1.13%	6.2%	77.8%



<u>Decontamination Factors</u>

Pu in Np product = 4000

Np in Pu product = 40

Zr in Np product = 7

Zr in Pu product = >790

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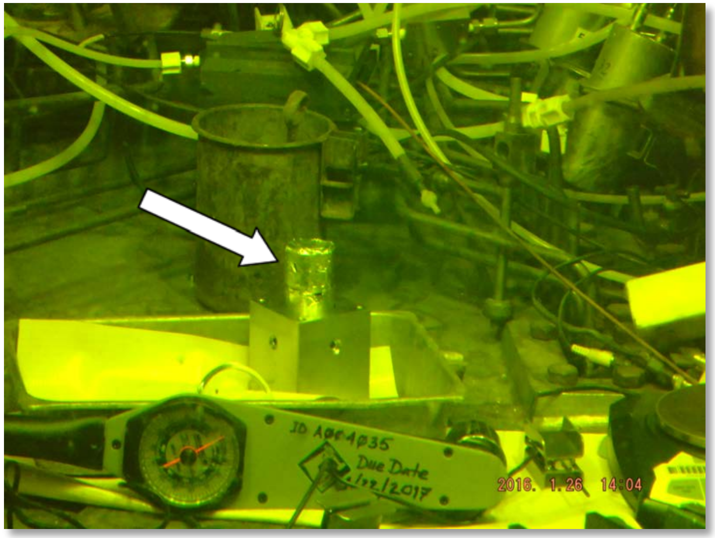
ORNL Packaged and Shipped a Small Sample of New PuO_2 to LANL in 1Q 2016



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

2016-003RMW

Comparison of Impurities is Good

- Total Pu assay - 88.1% is theoretical maximum

Sample ID	% Pu	ORNL
SN1008	85.0	
SN1009	83.7	87.0

- Percent Pu-238

Sample ID	g oxide	Measured Watts	LANL% Pu-238	ORNL %Pu-238
SN1008	1.9934	0.8487	88	87.9
SN1009	2.0141	0.8461	88	88.0

Actinide impurities are low as well

Sample	U-234 (ppm)*		Th-232 (ppm)		Np-237 (ppm)	
	LANL	ORNL	LANL	ORNL	LANL	ORNL
SN1008 PUP-084	2000	900	7800	6700		2300
SN1009 PUP-085	1500	600	11000	4900		800

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

Sample	Pu-236 (ppm)*	
	LANL	ORNL
SN1008	2	2.2
SN1009	2	

*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	<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	<10	<50	<50	<50
spec	500	20		5	500	50	500	200	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	<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	<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—$^{237}NpO_2$ Pellets Clad in Zircaloy

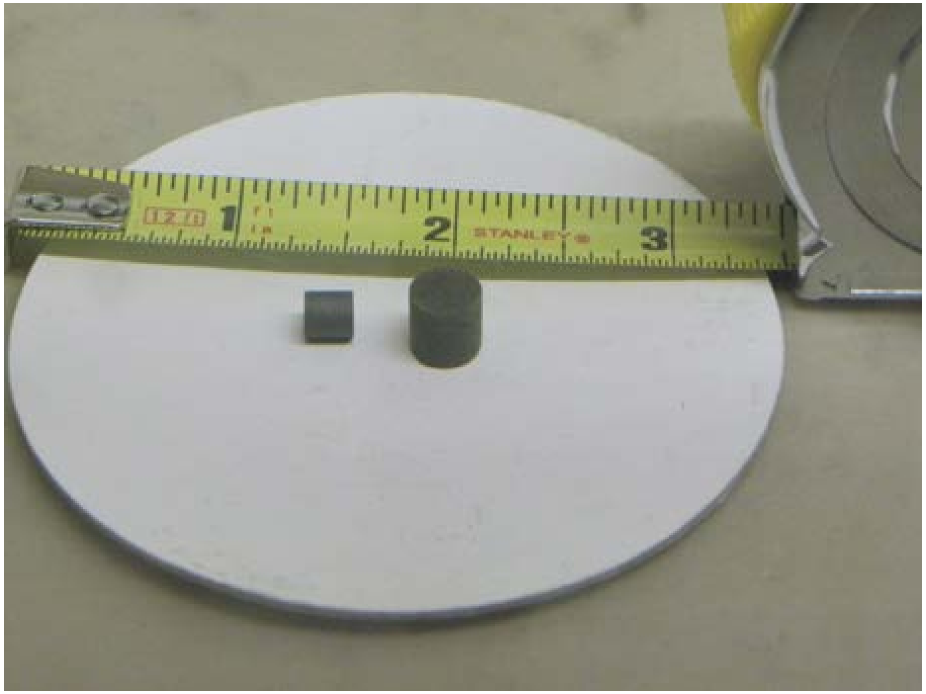
Benefits

- 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}Pu
- "Rich" product will enable "up blending" of ^{238}Pu concentration in low-purity ^{238}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 NpO_2 (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″)

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

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