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Development Program to Recycle and Purify $^{238}PuO_2$ Fuel from Scrap

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Nuclear Materials Technology (NMT) Division has initiated a development program to recover & purify plutonium-238 oxide from impure feed sources. A glove box line has been designed and a chemistry flowsheet developed to perform this recovery task at large scale. Our initial effort has focused on purification of $^{238}PuO_2$ fuel associated with Radioisotope Thermoelectric Generators (RTG) slated for the Cassini space mission, but which failed to meet General Purpose Heat Source (GPHS) specifications due to impurities. The most notable non-actinide impurities were silicon and phosphorus, but aluminum, chromium, iron and nickel also were near or in excess of thresholds specified by GPHS fuel powder specifications. Among actinide impurities uranium is of paramount concern, as ^{234}U is the daughter product of ^{238}Pu alpha decay, and the largest impurity observed.

An aqueous method based on nitric acid was selected for purification of the $^{238}PuO_2$ fuel. All aqueous processing used high purity reagents, and was performed in PTFE apparatus to minimize introduction of new contaminants. Impure $^{238}PuO_2$ was first dissolved in refluxing HNO_3/HF and then filtered. The dissolved ^{238}Pu was adjusted to the trivalent state by an excess of reducing reagents to compensate for radiolytic effects, precipitated as plutonium(III) oxalate, and recovered by filtration. The plutonium(III) oxalate was subsequently calcined to convert the plutonium to oxide form.

Decontamination factors for silicon, phosphorus and uranium attained by the described purification scheme were excellent. Decontamination factors for aluminum, chromium, iron and nickel were also very good. The purity of the $^{238}PuO_2$ recovered from this operation was significantly better than that specified by GPHS fuel powder specifications.

Efforts continue on this project to develop the capability for efficient, safe, cost-effective, and environmentally acceptable methods to recover and purify $^{238}PuO_2$ fuel in a glovebox environment. Sources of $^{238}PuO_2$ feed targeted for recovery include relatively impure oxide and scrap residue items that are more lean in ^{238}Pu values.

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Non-Actinide Impurities (µg/g) in Plutonium-238 Fuel.

	Al	B	Be	Ca	Cd	Cr	Cu	Fe	Mg	Mn	Mo	Na	Ni	Pb	P	Si	Sn	Zn	Sum non-Actinides
GPHS Rev A	500	5	5	300	50	500	200	800	100	50	250	250	500	100	25	750	50	50	2550
Feed #1	**145**	*5*	*1*	**9**	*10*	**390**	*1*	**830**	**18**	**13**	*20*	*50*	**120**	**20**	**710**	**560**	*5*	*5*	**2203**
Feed #2	**155**	*5*	*1*	**95**	*10*	**820**	**13**	**1500**	*10*	**18**	*20*	*50*	**455**	**20**	*20*	**850**	*5*	**23**	**4051**

Actinide Impurities (µg/g) in Plutonium-238 Fuel.

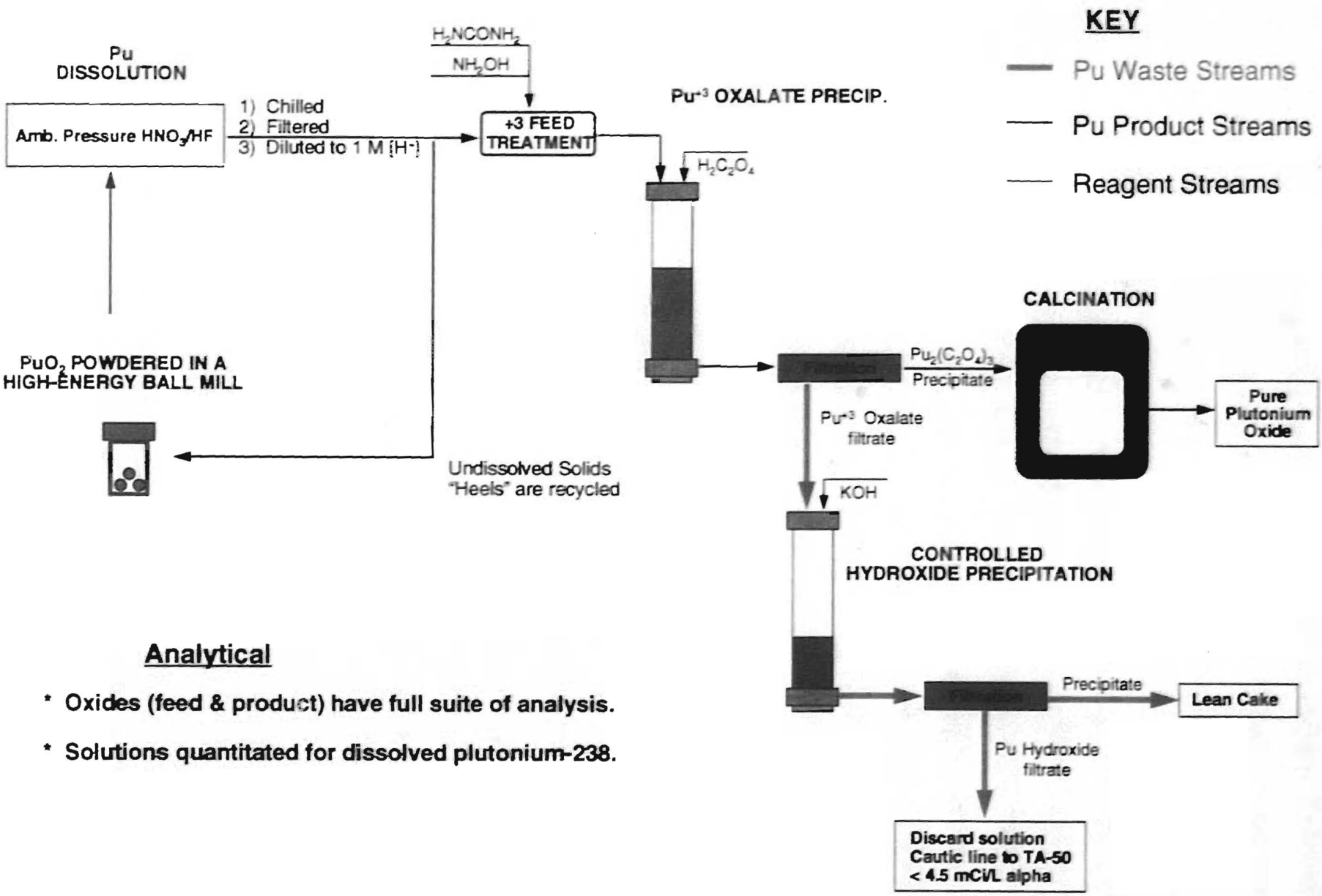
Sample	Am-241	Np-237	Pu-236	U-234	Th	Sum of Actinides
GPHS Rev A	5000	5000	2	5000	5000	10,000
Feed #1	**373**	**978**	*1*	**14000**	**1600**	**16952**
Feed #2	**103**	**637**	*1*	**6960**	**530**	**8231**

1. Approaches to Pu-238 purification- HNO_3/HF dissolution
   a. Pu(III)/Pu(IV) oxalate ppt
   b. Pu hydroxide
   c. Pu peroxide
   d. IX followed by ppt

2. Pu(III) oxalate ppt
   a. High purity reagents
   b. All PTFE or PE apparatus

3. REDOX control of Pu-238 a challenge
   a. Mound: sulfamic acid/ascorbic acid.
   b. SRS: sulfamic acid or hydrazine/ascorbic acid.
   c. LANL: hydroxylamine alone is insufficient.
   d. Katz & Seaborg: discussion of radiolytic effects on Pu REDOX control of Pu-238.

Present Pu-238 Process Flow Diagram



Analytical

* **Oxides (feed & product) have full suite of analysis.**
* **Solutions quantitated for dissolved plutonium-238.**

Dissolution Results

	Feed	Treatment	Pu-238 % Dissolved	Comments
DIS-1	RHU's	Hand Crushed	<1%	Reflux stopped after minutes
DIS-2	RHU's	Hand Crushed	95%	Heel from DIS-1
DIS-3	GPHS	None	34%	
DIS-4	GPHS	SPEX	99% +	Heel from DIS-3
DIS-5	GPHS	SPEX	90%	SPEX "overloaded" with 65 g PuO_2
DIS-6	GPHS	SPEX	99% +	Heel from DIS-5

Dissolution Conditions
15.8 M HNO_3
0.05 – 0.50 M HF
Ambient pressure reflux with stirring (~110 °C)
7–8 hours of reflux

^{238}Pu Chemistry Equations:

1. Dissolution.

$$^{238}PuO_2 + HNO_3/HF \longrightarrow Pu(NO_3)_x$$

2. Dilution to 1 M $[H^+]$.

3. REDOX adjustment.

$$Pu^{+6} + 2\,H_2NSO_3H + 2\,NH_2OH \cdot HNO_3 \rightleftharpoons Pu^{+3}$$

4. Plutonium (III) oxalate precipitation.

$$Pu^{+3} + 3\,H_2C_2O_4 \rightleftharpoons Pu_2(C_2O_4)_3 \cdot 10H_2O(s)$$

5. Plutonium (III) oxalate calcination.

$$Pu_2(C_2O_4)_3 \cdot 10H_2O(s) \longrightarrow {}^{238}PuO_2 + CO_2 + CO$$

6. Treatment of plutonium (III) oxalate filtrate.

$$Pu^{+3} + KOH \rightleftharpoons Pu(OH)_x$$

Autoradiolysis of ^{238}Pu HNO_3 Solutions:

The observed behavior of Pu in HNO_3 with significant alpha radiolysis is that it moves to a higher valence steady-state condition (predominately Pu^{+6}). Observed for ^{238}Pu and also for ^{239}Pu in the presence of ^{244}Cm.

1. Reducing agents.

$$4\,Pu^{+6} + 6\,NH_2OH \longrightarrow 4\,Pu^{+3} + 3\,N_2O + 12\,H^+ + 3\,H_2O$$

$$4\,Pu^{+4} + 2\,NH_2OH \longrightarrow 4\,Pu^{+3} + N_2O + 4\,H^+ + H_2O$$

HI
H_2O_2

Ascorbic acid
$NH_2OH \cdot HNO_3$

2. Valence Stabilizers/Holding Agents.

Function by reactiing quickly with nitrous acid (and presumably with other oxidizing NO_x compounds & radicals generated).

$$3\,Pu^{+3} + 4\,H^+ + NO_3^- \longrightarrow 3\,Pu^{+4} + NO + 2\,H_2O$$

SLOW

$$2\,NO + H_2O + HNO_3 \longrightarrow 3\,HNO_2$$

$$6\,Pu^{+3} + 2\,NO_2^- + 8\,H^+ \longrightarrow 6\,Pu^{+4} + 4\,H_2O + N_2$$

RAPID oxidation of Pu^{+3}

NH_2CONH_2 (urea)
H_2NSO_3H

amines, imides, imines, amides
N_2H_4

Non-Actinide Impurities (µg/g) in Plutonium-238 Fuel.

	Al	B	Be	Ca	Cd	Cr	Cu	Fe	Mg	Mn	Mo	Na	Ni	Pb	P	Si	Sn	Zn	Sum non-Actinides
GPHS Rev A	500	5	5	300	50	500	200	800	100	50	250	250	500	100	25	750	50	50	2550
Feed #1	**145**	*5*	*1*	**9**	*10*	**390**	*1*	**830**	**18**	**13**	*20*	*50*	**120**	**20**	**710**	**560**	*5*	*5*	**2203**
Pdt. # 1A	**200**	*5*	*1*	**4**	*10*	**285**	*1*	**335**	*10*	**9**	*20*		**5**	*10*	*20*	*5*	*5*	*5*	
Pdt. # 1B	**34**	*5*	*1*	**65**	*10*	**19**	*1*	**67**	*10*	**2**	*20*	*50*	**9**	*10*	*20*	**53**	*5*	*5*	**377**
Feed #2	**155**	*5*	*1*	**95**	*10*	**820**	**13**	**1500**	*10*	**18**	*20*	*50*	**455**	**20**	*20*	**850**	*5*	**23**	**4051**
Pdt. # 2A	**185**	*5*	*3*	**40**	*10*	**15**	**20**	**39**	*10*	**2**	*20*	*50*	**8**	*10*	*20*	**7**	*5*	*5*	**436**
Pdt. # 2B	**155**	*5*	*3*	**40**	*10*	**19**	**18**	**78**	*10*	**3**	*20*	*50*	**14**	*10*	*20*	*5*	*5*	*5*	**453**

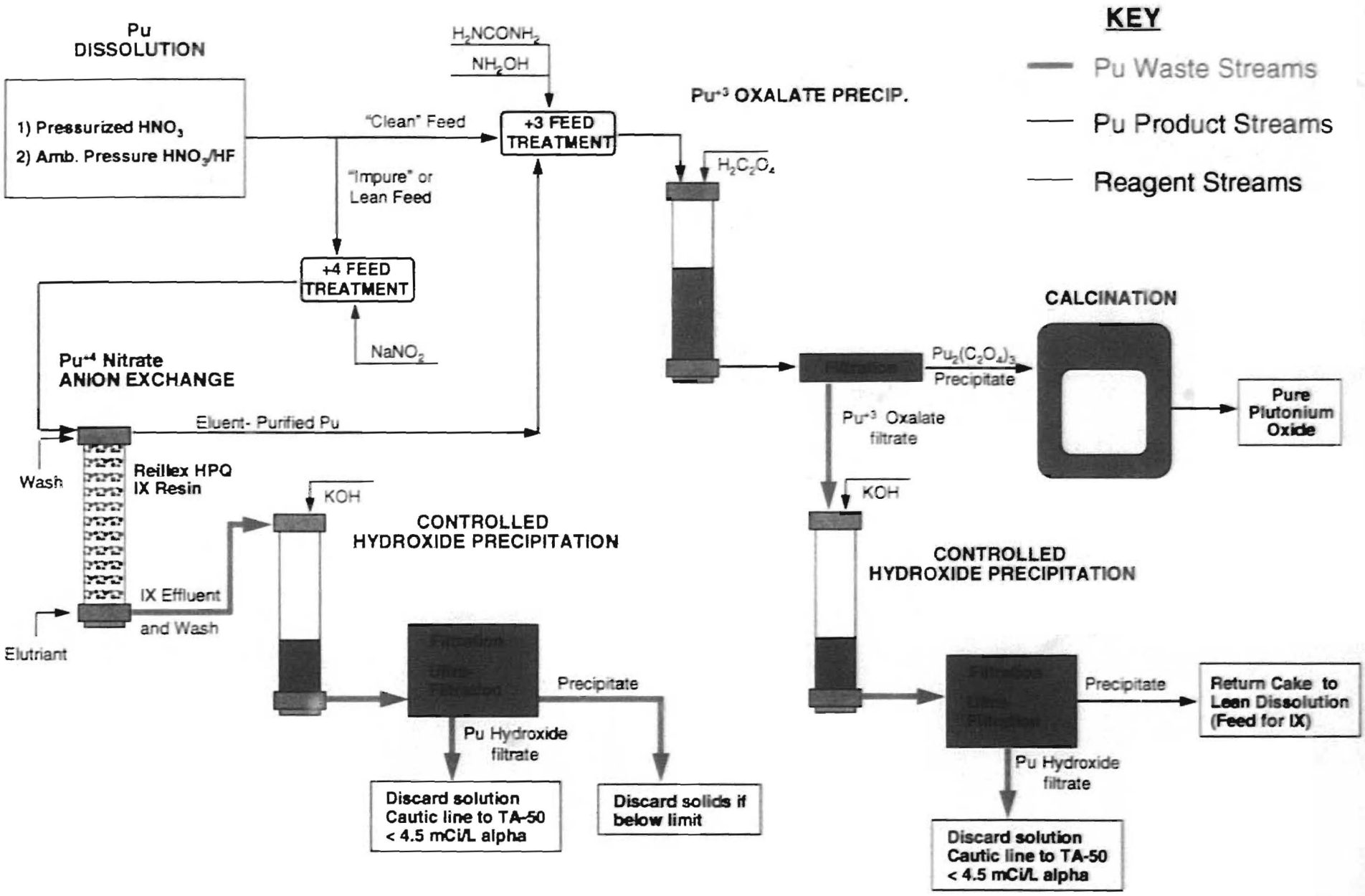
Actinide Impurities (μg/g) in Plutonium-238 Fuel.

Sample	Am-241	Np-237	Pu-236	U-234	Th	Sum of Actinides
GPHS Rev A	5000	5000	2	5000	5000	10,000
Feed #1	**373**	**978**	*1*	**14000**	**1600**	**16952**
Pdt # 1A	**342**	**936**	*1*	**2460**	**1600**	**5339**
Pdt # 1B	**351**	**237**	*1*	**580**	**1700**	**2869**
Feed #2	**103**	**637**	*1*	**6960**	**530**	**8231**
Pdt. # 2A	**65**	**891**	*1*	**540**	**560**	**2057**
Pdt. # 2B	**98**	**603**	*1*	**500**	**530**	**1732**

					These columns corrected for the isotopic purity of the parent lot of Pu-238			
	Volume (L)	[H+] (M)	Pu-238 (g/L)	alpha (mCi/L)	Actual Pu (g/L)	Actual Pu total (g)	Process Recovered %	Overall Recovered %
DISFLT-1	0.40		8.96E-02	1574.1	1.12E-01	4.50E-02		
DISFLT-2	1.40		6.67E+00	117175.9	8.37E+00	1.17E+01		
OXFLT-2A	1.22	0.57	3.26E-02	572.7	4.09E-02	4.99E-02	99.15	
HXYFLT-2A	1.59		3.13E-04	5.5	3.93E-04	6.25E-04	98.75	99.989
OXFLT-2B	1.05	1.04	2.87E-01	5041.9	3.60E-01	3.78E-01	93.55	
HXYFLT-2B	1.44		4.32E-04	7.6	5.42E-04	7.81E-04	99.79	99.987
DISFLT-3	1.80		7.68E+00	134919.2	9.59E+00	1.73E+01		
OXFLT-3	1.90	1.33	2.51E+00	44094.7	3.05E+00	5.80E+00	66.40	
HXYFLT-3	2.30		1.62E-04	2.8	1.97E-04	4.53E-04	99.99	99.997
DISFLT-4	0.96		8.00E+00	140540.8	9.73E+00	9.34E+00		
OXFLT-4	1.74	1.39	6.28E-01	11032.5	7.64E-01	1.33E+00	85.77	
HXYFLT-4	2.10		8.85E-04	15.5	1.08E-03	2.26E-03	99.83	99.976
DISFLT-5	1.68		2.35E+01	412838.6	2.86E+01	4.80E+01		
OXFLT-5A	1.90	1.14	1.72E-01	3021.6	2.09E-01	3.98E-01	98.34	
HXYFLT-5A	2.20		8.68E-04	15.2	1.06E-03	2.32E-03	99.42	99.990
OXFLT-5B	1.90	1.14	1.73E-01	3039.2	2.10E-01	4.00E-01	98.33	
HXYFLT-5B	2.20		4.53E-04	8.0	5.51E-04	1.21E-03	99.70	99.995
DISFLT-6	0.73		2.61E+00	45851.4	3.18E+00	2.30E+00		
OXFLT-6	0.86	1.19	2.25E-01	3952.7	2.74E-01	2.35E-01	89.77	
HXYFLT-6	1.00		7.30E-04	12.8	8.88E-04	8.88E-04	99.62	99.961
						OXFLT Average	90.19	
						HXYFLT Average	99.59	99.985

"Waste Efficiency"		
		"Waste Efficiency"
	PuO2	Waste Sol.	PuO2/L waste
	(g)	(L)	(g/L)
PuOXPDT-2A	9.0	1.59	5.7
PuOXPDT-2B	7.8	1.44	5.4
PuOXPDT-3	17.0	2.30	7.4
PuOXPDT-4	9.4	2.10	4.5
PuOXPDT-5A	28.9	2.20	13.1
PuOXPDT-5B	27.7	2.20	12.6
PuOXPDT-6	5.0	1.00	5.0
Summation	**104.8**	**12.83**	**8.2**

Pu-238 Process Flow Diagram



Worker exposure rates

Pu-238 (g)	Distance in inches from scource pt	Neut./s/g Pu-238	Neut./s	Neut. Flux in N/cm2/hr	4 MeV Neut. Dosimitry REM/N/cm2	mREM/hr of Exposure (no shielding)	Inches of shielding	BISCO shielding coefficient	mREM/hr of Exposure at shield contact (w/ shielding)
108	20	25000	2.70E+06	3.00E+05	3.63E-08	10.8802	0	0.400	10.8802
108	20	25000	2.70E+06	3.00E+05	3.63E-08	10.8802	2	0.400	4.8888
108	20	25000	2.70E+06	3.00E+05	3.63E-08	10.8802	4	0.400	2.1967
108	**20**	**25000**	**2.70E+06**	**3.00E+05**	**3.63E-08**	**10.8802**	**5**	**0.400**	**1.4725**
108	20	25000	2.70E+06	3.00E+05	3.63E-08	10.8802	8	0.400	0.4435
108	40	25000	2.70E+06	7.49E+04	3.63E-08	2.7200	0	0.400	2.7200
108	40	25000	2.70E+06	7.49E+04	3.63E-08	2.7200	2	0.400	1.2222
108	40	25000	2.70E+06	7.49E+04	3.63E-08	2.7200	4	0.400	0.5492
108	**40**	**25000**	**2.70E+06**	**7.49E+04**	**3.63E-08**	**2.7200**	**5**	**0.400**	**0.3681**
108	40	25000	2.70E+06	7.49E+04	3.63E-08	2.7200	8	0.400	0.1109
108	60	25000	2.70E+06	3.33E+04	3.63E-08	1.2089	0	0.400	1.2089
108	60	25000	2.70E+06	3.33E+04	3.63E-08	1.2089	2	0.400	0.5432
108	60	25000	2.70E+06	3.33E+04	3.63E-08	1.2089	4	0.400	0.2441
108	**60**	**25000**	**2.70E+06**	**3.33E+04**	**3.63E-08**	**1.2089**	**5**	**0.400**	**0.1636**
108	60	25000	2.70E+06	3.33E+04	3.63E-08	1.2089	8	0.400	0.0493

4" Shielding

	hrs/day at distance	Exposure mR/day	Assume 170 days
20"	2	4.39	747
40"	2	1.10	187
60"	4	0.98	166
Sum		6.47	1100

5" Shielding

	hrs/day at distance	Exposure mR/day	Assume 170 days
20"	2	2.94	501
40"	2	0.74	125
60"	4	0.65	111
Sum		4.34	737

Conclusions

a. Good dissolution efficiencies of high-fired PuO_2 with milling of feeds.

b. Pu(III) oxalate ppt purification adequate for this feed.

c. Other feeds may require other methods.

d. Worker exposure not prohibitive.

e. Good efficiency in regards to liquid waste generated per gram processed.

Future

a. Repeat experiments & increase scale in G251.

b. Demo IX capability for lean residues.

c. Additional SPEX Mill demo in the glovebox.

d. Elevated pressure HNO_3 dissolution. Avoids HF. Even better efficiency.

e. Waste treatment technologies. Actinide extractants. Ultra-filtration. Polymer Filtration. Organics destruction.

f. New glovebox line designed. LANL aqueous GB specifically engineered for Pu-238 processes. New Materials. Better N Shielding. Fiber optic UV-vis for process control. DI water delivery system.