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DEVELOPMENT PROGRAM TO RECYCLE $^{238}PuO_2$ SCRAP IN A GLOVEBOX

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Mounting Instructions

1. Trim all of this material to 1/2" margin of white space around text, then mount on poster board in standard format selected for Actinide Separations. I assume rounded corners and 1/2" colored board margin
2. Call (Jake Espinoza) if there is a problem. Office 7-2370.

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Abstract:

Nuclear Materials Technology (NMT) Division has initiated a program to recover & purify plutonium-238 oxide from impure feed sources. The initial effort has focused on purification of $^{238}PuO_2$ fuel which failed to meet General Purpose Heat Source (GPHS) specifications due to impurities. The most notable non-actinide impurities were silicon, aluminum, chromium, iron and nickel. Among actinide impurities, uranium is of paramount concern as ^{234}U is the daughter product of ^{238}Pu alpha decay, and the largest actinide impurity observed.

All aqueous processing used high purity reagents, and was performed in PTFE apparatus to minimize introduction of new contaminants. Impure $^{238}PuO_2$ was dissolved in refluxing HNO_3/HF and 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.

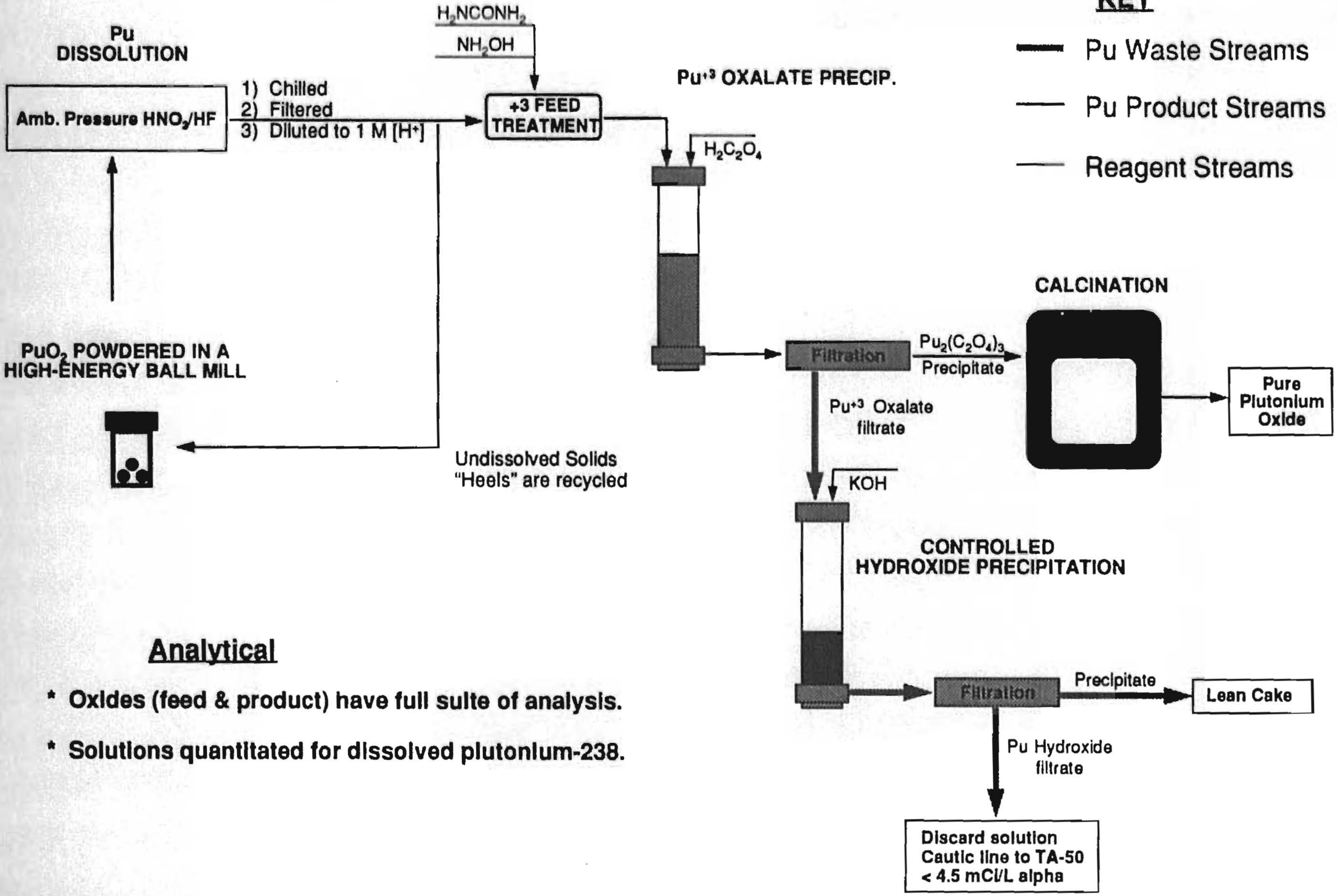
Decontamination factors for uranium, aluminum, chromium, iron, nickel and silicon were very good. The purity of the $^{238}PuO_2$ recovered from this operation was significantly better than that specified by GPHS fuel powder specifications. Efforts continue on this project to develop the capability for efficient, safe, cost-effective, and environmentally acceptable methods to recover $^{238}PuO_2$ scrap in a glovebox environment.

Introduction:

Plutonium-238 is an excellent radioisotope for heat source applications in space because of availability, power density, useful lifetime, minimal shielding requirements, and oxide stability. LANL experience with the plutonium-238 isotope goes back many years to pioneering efforts associated with pacemaker development (Mullins 1972 and Shupe 1970). Several rooms containing dozens of glove boxes in our facility are dedicated to processing plutonium-238. Processing capability includes production-scale operations for oxygen-16 isotope exchange of plutonium-238 oxide fuel (to reduce neutron emission from alpha-N reactions), pellet fabrication, fuel cladding, and testing. Over 300 General Purpose Heat Source (GPHS) units containing ~150 g $^{238}PuO_2$ each have been fabricated over the last three years for Radioisotope Thermoelectric Generator (RTG) units. At the same time, approximately 200 smaller heat sources have been produced for use as Radioisotopic Heater Units (RHU). The majority of these heat sources are to support the Cassini mission to Saturn.

Fuel received at LANL for the most recent production campaign has exhibited impurity levels in excess of historical values. While feed stock plutonium-238 has traditionally been primarily fresh from reactors, feed for this campaign was primarily recycled from other heat sources, the most likely source for future missions. This effort is focused on developing the capability in a glove box to produce high purity $^{238}PuO_2$ from relatively impure returns.

Present Pu-238 Process Flow Diagram



Pu DISSOLUTION

Amb. Pressure HNO_3/HF

1) Chilled
2) Filtered
3) Diluted to 1 M $[H^+]$

H_2NCONH_2

NH_2OH

+3 FEED TREATMENT

Pu^{+3} OXALATE PRECIP.

$H_2C_2O_4$

Filtration

$Pu_2(C_2O_4)_3$ Precipitate

CALCINATION

Pure Plutonium Oxide

Pu^{+3} Oxalate filtrate

KOH

CONTROLLED HYDROXIDE PRECIPITATION

Filtration

Precipitate

Lean Cake

Pu Hydroxide filtrate

Discard solution
Caustic line to TA-50
< 4.5 mCi/L alpha

PuO_2 POWDERED IN A HIGH-ENERGY BALL MILL

Undissolved Solids "Heels" are recycled

KEY

▬	Pu Waste Streams
—	Pu Product Streams
—	Reagent Streams

Analytical

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

Chemical Processing Information:

The plutonium-238 oxide fuel used as feed for this study was fired at temperatures up to 1600 °C. Dissolution of plutonium oxide fired to these temperatures is very slow and often incomplete in refluxing nitric acid (Cleveland 1979). Addition of a small amount of hydrofluoric acid aids oxide dissolution, but was too slow for our purposes. Our best dissolution results to date incorporated an initial milling of the $^{238}PuO_2$ feed in a high-energy ball mill. The milled oxide was stirred in a mixture of nitric and hydrofluoric acids refluxing at ambient pressure. This provided good dissolution efficiency after 7-8 hours at reflux.

Reagent grade chemicals were used to minimize introduction of contaminant elements. Teflon or polypropylene apparatus was used for handling ^{238}Pu solutions to avoid leaching silicates from glassware.

Plutonium (III) oxalate precipitation was selected over other possible purification methods because of simplicity, speed, and adequacy of purification. In particular, plutonium (III) oxalate precipitation requires no temperature control, shows little detrimental effect from excess oxalic acid, and has a rapid reaction, precipitation, and filtration time.

The large amount of radiolysis associated with plutonium-238 complicates control of the Pu oxidation state in nitric acid. In general, the radiolysis of nitric acid produces a more oxidizing environment, and a larger proportion of Pu(VI) (Katz 1986). The presence of additional oxidizing agents in the nitric acid increase the amount of reducing agents required to effect complete reduction to Pu(III). Others have observed that ^{238}Pu is best reduced to Pu(III) by combinations of "holding reagents" and "reducing agents" (Greinetz 1980 and Burney 1984). Holding agents react quickly with nitrite and other oxidizing species, reducing the rate of Pu(III) reoxidation, while the reducing agent rapidly reduces Pu(VI) and Pu(IV) in solution to Pu(III). Hydroxylamine nitrate was used as the primary reducing agent, while either sulfamic acid or urea was the holding agent. One precipitation using only hydroxylamine nitrate as a reducing agent gave poor results. All steps were performed as rapidly as possible to minimize the effects of radiolysis. Precipitations varied from 9 to 30 g of PuO_2 per batch.

For this study, recovered plutonium(III) oxalate was air-dried and then heated to dull red heat in a stainless steel, slip-top can on a hot plate for about 60 minutes to convert the material to the oxide. Heating for longer time produced no significant weight loss.

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TABLE 1: Results for Non-Actinide Impurities (µg/g).

	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*	**3.5**	*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*	**1.5**	*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**
Pdt. # 2C	*5*	*5*	*2*	*	*10*	**10**	**15**	**50**	*10*	**1**	*20*	*50*	**9**	*10*	*20*	**17**	*5*	*5*	*
Pdt. # 2D	**62**	*5*	*2*	*	*10*	**30**	**3**	**77**	*10*	**1**	*20*	*50*	**10**	*10*	*20*	**11**	*5*	*5*	*
Pdt. # 2E	**225**	*5*	*2*	*	*10*	**56**	**3**	**145**	*10*	**1**	*20*	*50*	**25**	*10*	*20*	**91**	*5*	*5*	*

The first row in Table 1 lists the element limits in µg/g that are specified in the GPHS standard (Los Alamos 1996). Two different sources of plutonium-238 oxide fuel, as designated by Feed #1 and Feed #2, were utilized for the experiments. Analytical data from several plutonium(III) oxalate precipitation experiments are also shown. Good decontamination was achieved in all cases for silicon, chromium, iron and nickel, with mixed results for aluminum. The entries marked "*" showed an indeterminate, but large amount of that impurity. In the case of the Ca values of 2C, 2D & 2E, an analytical error is suspected and samples been submitted for reanalysis.

TABLE 2: Results for Actinide Impurities (µg/g).

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	**350**	**978**	*1*	**14000**	**1600**	16929
Pdt # 1A	**331**	**936**	*1*	**1900**	**1600**	4768
Pdt # 1B	**340**	**237**	*1*	**60**	**1700**	2338
Feed #2	**135**	**637**	*1*	**7000**	**530**	8303
Pdt. # 2A	**57**	**891**	*1*	**60**	**560**	1569
Pdt. # 2B	**91**	**603**	*1*	**70**	**530**	1295
Pdt. # 2C	**132**	**517**	*1*	**130**	**350**	1130
Pdt. # 2D	**136**	**577**	*1*	**280**	**410**	1404
Pdt. # 2E	**108**	**315**	*1*	**0**	**290**	714

The first row in Table 2 lists the actinide impurities in µg/g as specified by the GPHS standard. The numbers in boldface type in Table 2 represent values (µg/g) observed for the actinide impurities. Those numbers presented in italics indicate results that are at or below the indicated detection limits. ^{234}U was by far the largest actinide impurity observed in the feed material because it is the daughter product of ^{238}Pu by alpha decay. Good decontamination was achieved for U. Little or no decontamination of Np, Am and Th was observed under the conditions of plutonium (III) oxalate precipitation, but as these actinides were already well below the GPHS standard, they were not a major concern. Values listed in the table for U-234 and Am-241 are decay corrected for the time interval between precipitation and analysis. The rapid ingrowth of U-234 adds significantly to the uncertainty in these values.

TABLE 3: Process Effluent Activity.

	Volume (L)	[H+] (M)	Pu-238 (g/L)	alpha (mCi/L)	Pu-238 Recovered %	Pu-238 Process Loss %
DISFLT-1AB	1.40		6.67E+00	117175.9		
OXFLT-1A	1.22	0.57	3.26E-02	572.7	99.15	
HYXFLT-1A	1.59		3.13E-04	5.5	98.75	0.011
OXFLT-1B	1.05	1.04	2.87E-01	5041.9	93.55	
HYXFLT -1B	1.44		4.32E-04	7.6	99.79	0.013
DISFLT-2A	1.80		7.68E+00	134919.2		
OXFLT-2A	1.90	1.33	2.51E+00	44094.7	66.40	
HYXFLT -2A	2.30		1.62E-04	2.8	99.99	0.003
DISFLT-2B	0.96		8.00E+00	140540.8		
OXFLT-2B	1.74	1.39	6.28E-01	11032.5	85.77	
HYXFLT -2B	2.10		8.85E-04	15.5	99.83	0.024
DISFLT-2CD	1.68		2.35E+01	412838.6		
OXFLT-2C	1.90	1.14	1.72E-01	3021.6	98.34	
HYXFLT -2C	2.20		8.68E-04	15.2	99.42	0.010
OXFLT-2D	1.90	1.14	1.73E-01	3039.2	98.33	
HYXFLT -2D	2.20		4.53E-04	8.0	99.70	0.005
DISFLT-2E	0.73		2.61E+00	45851.4		
OXFLT-2E	0.86	1.19	2.25E-01	3952.7	89.77	
HYXFLT-2E	1.00		7.30E-04	12.8	99.62	0.039

Table 3 lists the measured plutonium-238 content of the process solutions in this work including dissolved feed solutions (DISFLT), oxalate filtrate solutions (OXFLT), and hydroxide filtrate solutions (HYXFLT). An acid-base titration was performed on solutions prior to oxalate precipitation to measure free acid in solution. Dissolved Pu-238 solutions were adjusted to the trivalent state, precipitated with oxalic acid followed by filtration, then the filtered solution from oxalate precipitation was neutralized with KOH and again filtered. Data for OXFLT and HYXFLT solutions list the percent of Pu-238 recovered from solution in each filtration step. The column entitled "Pu-238 Process Loss %" shows the total loss of dissolved Pu-238 to effluent streams following the sequential precipitation and filtration steps. Dissolved feed solutions containing two letters (DISFLT-1AB and DISFLT-2CD) were split prior to further processing.

Future Work:

a. Test new Ta container for solution storage and precipitation.

b. Complete fabrication and testing of pressed Pt filter in an Inconel 625 filter boat body. Direct calcination of plutonium(III) oxalate with less powder handling..

c. Demo anion exchange capability for lean residues using LANL-developed resins. Capture SRS expertise in regards to ^{238}Pu(IV) anion exchange authorization basis and experience.

d. Fabricate & test a GPHS from LANL-purified fuel.

e. Obtain additional data on dissolution of PuO_2 feed that has been finely powdered using the SPEX Mill.

f. Demonstrate waste minimization technologies including ultra-filtration of neutralized effluents and extraction chromatography of acidic effluents.

g. Additional SPEX Mill demo in the glovebox.

Conclusions:

a. Good dissolution efficiencies of high-fired $^{238}PuO_2$ with milling of feeds.

b. Pu(III) oxalate ppt purification adequate for these items.

c. Very small ^{238}Pu losses to liquid effluent streams.

d. Worker exposure not prohibitive.

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

f. A new glovebox line has been designed, building upon LANL aqueous glovebox experience but specifically engineered for Pu-238 processes. Design includes better neutron shielding, fiber optic UV-vis capability, DI water delivery system.

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Dissolution Results

	Feed	Treatment	Pu-238 % Dissolved	Comments
DIS-0	RHU's	Hand Crushed	<1%	Reflux stopped after minutes
DIS-1AB	RHU's	Hand Crushed	95%	Heel from DIS-0
DIS-2A	GPHS	None	34%	
DIS-2B	GPHS	SPEX	99% +	Heel from DIS-2A
DIS-2CD	GPHS	SPEX	90%	SPEX "overloaded" with 65 g PuO_2
DIS-2E	GPHS	SPEX	99% +	Heel from DIS-2CD

<u>Dissolution Conditions</u>

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

"Waste Efficiency"

	PuO2 (g)	Waste Sol. (L)	"Waste Efficiency" PuO2/L waste (g/L)
PuOXPDT-1A	9.0	1.59	5.7
PuOXPDT-1B	7.8	1.44	5.4
PuOXPDT-2A	17.0	2.30	7.4
PuOXPDT-2B	9.4	2.10	4.5
PuOXPDT-2C	28.9	2.20	13.1
PuOXPDT-2D	27.7	2.20	12.6
PuOXPDT-2E	5.0	1.00	5.0
Summation	**104.8**	**12.83**	**8.2**