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RECYCLE OF SCRAP PLUTONIUM-238 OXIDE FUEL TO SUPPORT FUTURE RADIOISOTOPE APPLICATIONS

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Abstract

The Nuclear Materials Technology (NMT) Division of Los Alamos National Laboratory has initiated a development program to recover & purify plutonium-238 oxide from impure feed sources in a glove box environment. A glove box line has been designed and a chemistry flowsheet developed to perform this recovery task at large scale. The initial demonstration effort focused on purification of $^{238}PuO_2$ fuel by HNO_3/HF dissolution, followed by plutonium(III) oxalate precipitation and calcination to an oxide. Decontamination factors for most impurities of concern in the fuel were very good, producing $^{238}PuO_2$ fuel significantly better in purity than specified by General Purpose Heat Source (GPHS) fuel powder specifications. A sufficient quantity of purified $^{238}PuO_2$ fuel was recovered from the process to allow fabrication of a GPHS unit for testing. The results are encouraging for recycle of relatively impure plutonium-238 oxide and scrap residue items into fuel for useful applications. The high specific activity of plutonium-238 magnifies the consequences and concerns of radioactive waste generation. This work places an emphasis on development of waste minimization technologies to complement the aqueous processing operation. Results from experiments on neutralized solutions of plutonium-238 resulted in decontamination to about 1 millicurie/L. Combining ultrafiltration treatment with addition of a water-soluble polymer designed to coordinate Pu, allowed solutions to be decontaminated to about 1 microcurie/L. Efforts continue to develop a capability for efficient, safe, cost-effective, and environmentally acceptable methods to recover and purify $^{238}PuO_2$ fuel.

Recycle of Scrap Plutonium-238 Oxide Fuel to Support Future Radioisotope Applications.

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Why Do This???

Cassini fuel completed on time, mission launched.

Very large mission & payload.

Future missions will require heat sources in smaller quantities than Cassini.

SRS not producing or purifying $^{238}PuO_2$ fuel.

USA now without a future domestic supply of high purity $^{238}PuO_2$ fuel for future missions.

$^{238}PuO_2$ scrap and residue items exist, in forms that are useless without recovery, some of which may pose a hazard in storage.

LANL Near-Term Solution

Recycle existing $^{238}PuO_2$ fuel from scrap, residues, test pellets, failed fuel lots to produce high-purity feedstock for new heat source applications.

Utilize LANL Pu facility, experience and science capability.

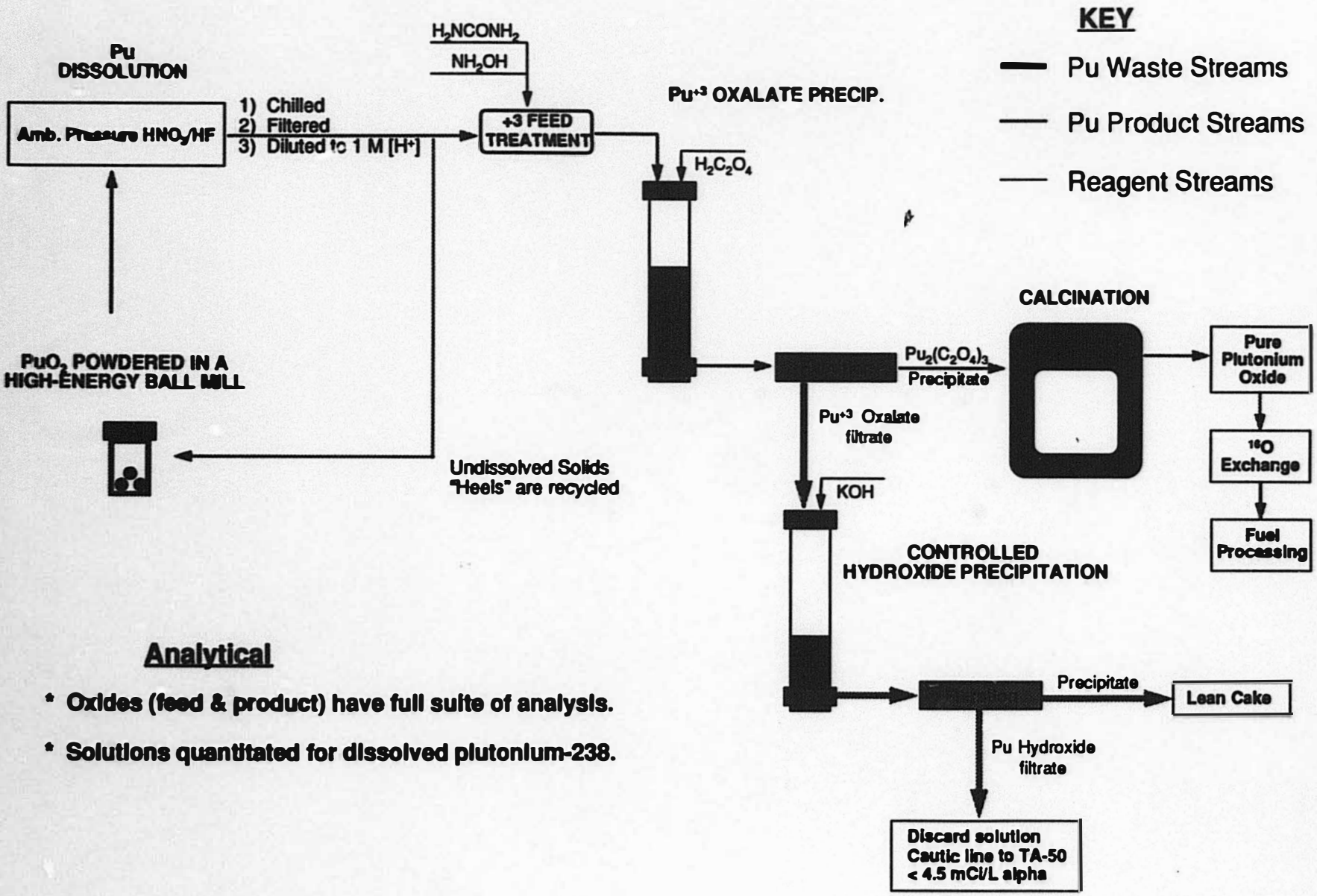
Non-Actinide Impurities (µg/g) in Plutonium-238 Fuel.

	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	2814
Feed #2	155	5	1	95	10	820	13	1500	10	18	20	50	455	20	20	850	5	23	3929
Feed #3	155	5	1	7	10	540	100	555	10	10	20	63	99	10		515	5	15	2051

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	350	978	1	14000	1600	16929
Feed #2	135	637	1	7000	530	8303

Current ^{238}Pu Process Flow Diagram



Analytical

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

Results for Actinide Impurities (µg/g).

Sample	Am-241	Np-237	Pu-236	U-234	Th	Sum 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

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	2814
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	246
Feed #2	155	5	1	95	10	820	13	1500	10	18	20	50	455	20	20	850	5	23	3929
Pdt. # 2A	185	5	3	40	10	15	20	39	10	2	20	50	8	10		7	5	5	313
Pdt. # 2B	155	5	3	40	10	19	18	78	10	3	20	50	14	10		5	5	5	329
Pdt. # 2C	55	5	2	450	10	23	100	62	10	6	20	50	18	10		23	5	5	741
Pdt. # 2D	62	5	2	>750	10	30	3	67	10	1	20	50	10	10		11	5	5	*
Pdt. # 2E	225	5	2	>750	10	56	3	145	10	1	20	50	25	10		91	5	5	*
Feed #3	155	5	1	7	10	540	100	555	10	10	20	63	99	10		515	5	15	2051
Pdt. # 3A	176	5	1	350	10	194	75	52	10	10	20	50	17	10		32	5	5	906
Pdt. # 3B	110	5	1	500	10	25	50	54	10	8	20	50	19	13		23	5	15	816
Pdt. # 3C	5	5	1	300	10	17	50	32	10	1	20	50	14	15		12	5	5	445
Pdt. # 3D	144	5	1	300	10	220	50	255	10	6	20	50	97	25		13	5	5	1109

$^{238}PuO_2$ Recovered

Mass name	Published designation	plutonium oxide recovered (g)
DISFLT-1AB	PUOXPDT-1A	9.03
	PUOXPDT-1B	7.79
DISFLT-2A	PUOXPDT-2A	16.99
DISFLT-2B	PUOXPDT-2B	9.40
DISFLT-2CD	PUOXPDT-2C	28.87
	PUOXPDT-2D	27.68
DISFLT-2E	PUOXPDT-2E	4.97
DISFLT-3AB	PUOXPDT-3A	14.35
	PUOXPDT-3B	13.36
DISFLT-3CD	PUOXPDT-3C	27.63
	PUOXPDT-3D	29.04
DISFLT-3EF	PUOXPDT-3E	28.78
	PUOXPDT-3F	31.81
DISFLT-3G	PUOXPDT-3G	25.11
DISFLT-3H	PUOXPDT-3H	34.03
DISFLT-3IJ	PUOXPDT-3I	22.82
	PUOXPDT-3J	13.67
DISFLT-3K	PUOXPDT-3K	70.59
12 Dissolutions	**18 precipitations**	**415.92**

Data for Plutonium-238 Oxalate Filtrate Solutions.

Sample	Volume (L)	[H+] (M)	Pu-238 (g/L)	alpha (mCi/L)	Actual Pu (g/L)	Soln. Pu % Recovered
OXFLT-1A	1.22	0.57	3.26E-02	558	4.09E-02	99.38
OXFLT-1B	1.05	1.04	2.87E-01	4913	3.60E-01	94.78
OXFLT-2A	1.90	1.33	2.51E+00	42964	3.05E+00	72.08
OXFLT-2B	1.74	1.39	6.28E-01	10749	7.64E-01	86.18
OXFLT-2C	1.90	1.14	1.72E-01	2944	2.09E-01	98.46
OXFLT-2D	1.90	1.14	1.73E-01	2961	2.10E-01	98.39
OXFLT-2E	0.86	1.19	2.25E-01	3851	2.74E-01	94.90
OXFLT-3A	2.80	0.98	1.64E-01	2810	2.00E-01	95.76
OXFLT-3B	2.35	1.10	5.74E-02	982	7.00E-02	98.62
OXFLT-3C	3.24	0.92	4.30E-02	736	5.24E-02	99.31
OXFLT-3D	3.00	1.05	4.76E-02	814	5.80E-02	99.33
OXFLT-3E	2.90	0.88	1.07E-01	1840	1.31E-01	98.52
OXFLT-3F	2.90	1.02	9.06E-02	1550	1.10E-01	98.87
OXFLT-3G	0.60	0.92	7.19E-02	1230	8.76E-02	99.76
OXFLT-3H	0.86	0.92	2.72E-01	4660	3.32E-01	99.06
OXFLT-3I	0.99	0.92	1.41E-01	2420	1.72E-01	99.16
OXFLT-3J	1.75	1.02	3.71E-01	6350	4.52E-01	93.84
OXFLT-3K	2.50	0.92	3.14E-01	5370	3.83E-01	98.49
Weighted avg.	**oxalate**	**recovery**				**97.1**

Data for Plutonium-238 Hydroxide Filtrate Solutions Sampled Immediately After Filtration.

Sample	Volume (L)	Pu-238 (g/L)	alpha (mCi/L)	Actual Pu (g/L)	OH ppt. Soln. Pu % Recovered	OX & OH ppt Overall Soln. Pu % Loss
OHFLT-1A	1.59	3.13E-04	5.36	3.93E-04	98.75	0.0078
OHFLT-1B	1.44	4.32E-04	7.39	5.42E-04	99.79	0.0108
OHFLT-2A	2.30	1.62E-04	2.77	1.97E-04	99.99	0.0022
OHFLT-2B	2.10	8.85E-04	15.15	1.08E-03	99.83	0.0235
OHFLT-2C	2.20	8.68E-04	14.86	1.06E-03	99.42	0.0090
OHFLT-2D	2.20	4.53E-04	7.75	5.51E-04	99.70	0.0049
OHFLT-2E	1.00	7.30E-04	12.50	8.88E-04	99.62	0.0192
OHFLT-3A	4.00	1.02E-02	173.80	1.24E-02	91.16	0.3749
OHFLT-3B	4.00	1.83E-03	31.35	2.23E-03	94.57	0.0748
OHFLT-3C	4.00	7.00E-03	119.90	8.54E-03	79.89	0.1393
OHFLT-3D	4.00	6.09E-03	104.28	7.43E-03	82.92	0.1153
OHFLT-3E	4.00	sampled	later			
OHFLT-3F	4.00	sampled	later			
OHFLT-3G	2.30	Awaiting	analysis			
OHFLT-3H	2.00	Awaiting	analysis			
OHFLT-3I	1.75	Awaiting	analysis			
OHFLT-3J	3.70	Awaiting	analysis			
OHFLT-3K	6.00	Awaiting	analysis			
Summation	**52.58**					

Data for Plutonium-238 Hydroxide Filtrate Solution Supernatant Sampled Weeks Later.

Sample	Volume (L)	Pu-238 (g/L)	alpha (mCi/L)	Actual Pu (g/L)	OH ppt. Soln. Pu % Recovered	OX & OH ppt Overall Soln. Pu % Loss
OHFLT-3AW	4.00	5.67E-05	0.97	6.92E-05	99.95	0.0021
OHFLT-3BW	4.00	5.50E-05	0.94	6.70E-05	99.84	0.0022
OHFLT-3CW	4.00	6.19E-06	0.11	7.55E-06	99.98	0.0001
OHFLT-3DW	4.00	1.32E-04	2.26	1.61E-04	99.63	0.0025
OHFLT-3EW	4.00	8.35E-04	14.30	1.02E-03	98.93	0.0158
OHFLT-3FW	4.00	4.06E-05	0.70	4.95E-05	99.94	0.0007

Removal of Alpha Activity from Hydroxide Filtrate Supernatent OHFLT-3BW by Polymer Filtration

Sample	wt % polymer	pH	Final alpha activity (mCi/L)	% alpha removal
3BW1	0.20	4.0	1.33E-02	44
3BW2	0.40	4.0	9.50E-03	59
3BW3	0.20	6.5	6.87E-04	97
3BW4	0.40	6.5	5.55E-04	98
3BW5	0.20	8.5	1.06E-03	95
3BW6	0.40	8.5	8.09E-04	96
3BW7	0.20	13.0	4.88E-03	79
3BW8	0.40	13.0	2.17E-03	91

"Waste Efficiency"

415.92 g $^{238}PuO_2$

52.6 L liquid waste "caustic" wasteline

7.91 g $^{238}PuO_2$ per L liquid waste

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 expected to be prohibitive with neutron shielding.

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

f. Preliminary results using Polymer Filtration demonstrated significant additional decontamination of neutralized effluent solutions .

Future

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

b. Develop additional corrosion resistant apparatus for solution storage and precipitation.

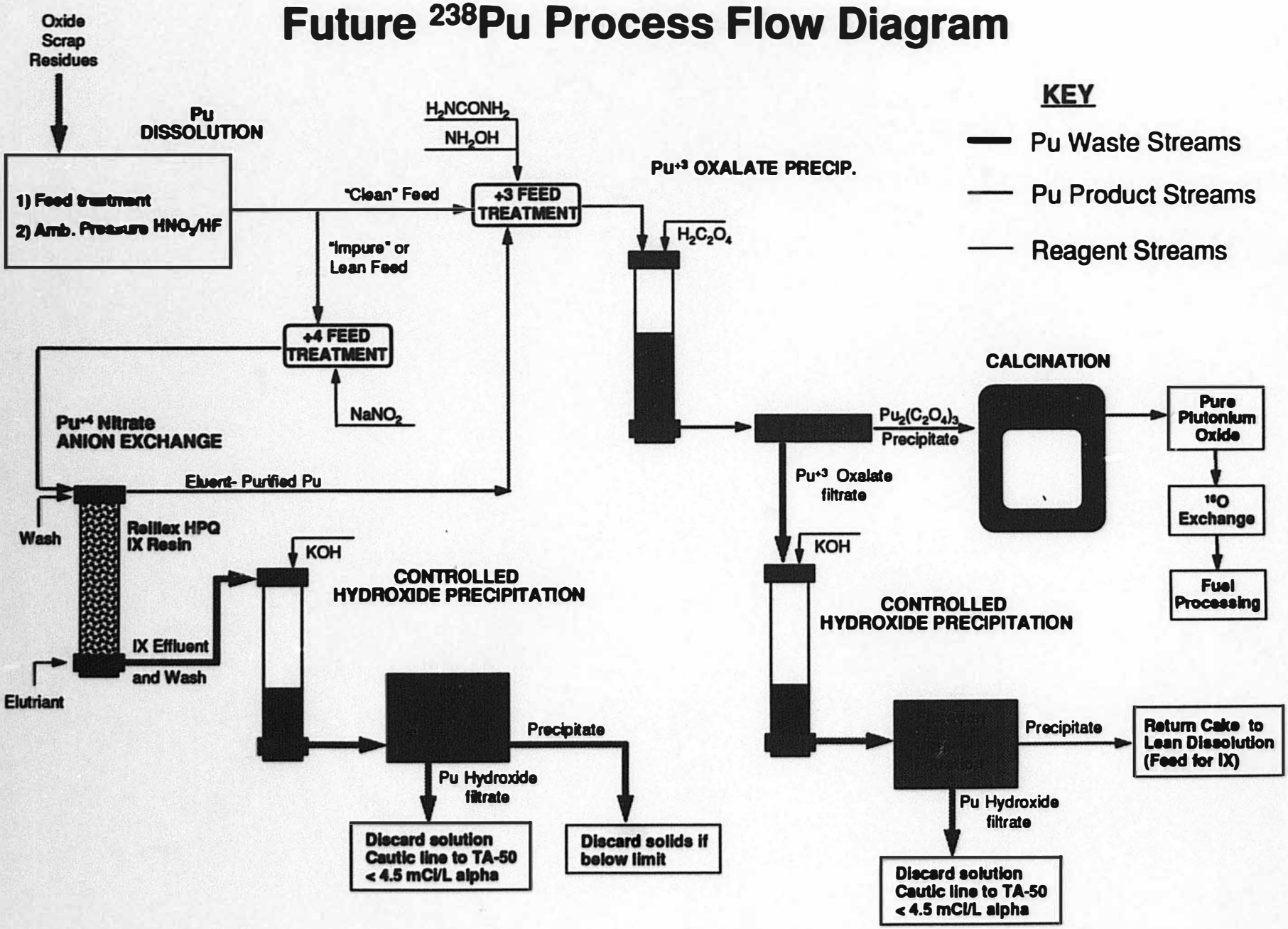
c. Expand dissolution & recovery operation to scrap & residue items lean in ^{238}Pu value.

d. 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.

e. Continue demonstration of waste minimization technologies including ultra-filtration and polymer-filtration of neutralized effluents and extraction chromatography of acidic effluents.

f. Install new glovebox line engineered for ^{238}Pu processes including better neutron shielding, on-line analytical capability, DI water delivery system.

Future ^{238}Pu Process Flow Diagram



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