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Title:	Development Program for 238Pu Aqueous Recovery Process
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Los Alamos
NATIONAL LABORATORY

Development Program for ^{238}Pu Aqueous Recovery Process

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Power Source Technologies Group
Los Alamos National Laboratory

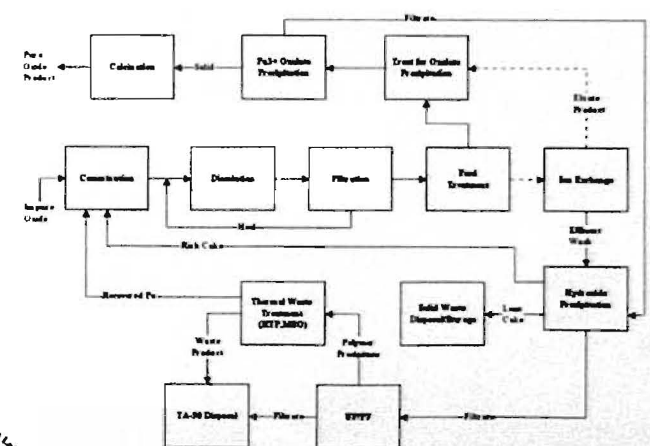
Background

- Los Alamos National Laboratory has fabricated Milliwatt Heat Sources for the nuclear weapons program and Low-Wattage Radioisotope Heater Units (LWRHUs) and General Purpose Heat Sources (GPHS) for space missions
- Plutonium-238 oxide ($^{238}PuO_2$) powder previously supplied from other Department of Energy sites
- Recently, Los Alamos National Laboratory tasked with the aqueous purification of scrap $^{238}PuO_2$

Goal

- To develop best process methodology for $^{238}PuO_2$ aqueous processing at bench scale level (100 gram $^{238}PuO_2$ batch-size).
- To demonstrate that process methodology produces $^{238}PuO_2$ oxide meeting GPHS impurity specifications thereby qualifying bench scale process for production purposes.
- To demonstrate that process methodology has high process efficiencies, while minimal waste volumes are generated.
- To apply process methodology to a full-scale aqueous processing line (5 kg ^{238}Pu annual throughput).

Plutonium-238 Aqueous Scrap Recovery Process



$^{238}PuO_2$ Dissolution Optimization

- Method used to dissolve $^{238}PuO_2$ from literature
- Feed included sintered radioisotope heat unit pellets, old milliwatt fuel and scrap GPHS fuel
- Milling of material using mortar and pestle and automatic SPEX milling
- Batch sizes kept small to maximize use of PTFE dissolution vessel, minimize waste generation, minimize thermal effects of $^{238}PuO_2$, and to minimize operator dose from (α,n) reactions

$^{238}PuO_2$ Dissolution Parameter

- Particle size analysis (PSA) on three different types of feed
  - hand-milled
  - SPEX milled
  - Heel

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$^{238}PuO_2$ Dissolution Parameter

- Comminution methods and feed materials studied and achievable mean particle sizes (PS)
  - Milling techniques (incoming feed)
    - Hand-milled (mortar and pestle) (0.78 μm PS)
    - SPEX milled (10-20 min.) (0.75 μm PS)
  - Material
    - Heel (15.33 μm PS)

Dissolution Efficiencies vs. Milling Technique

Method	Wt. Feed (g)	Wt. Product (g)	Dissolution Efficiency
No Milling	49.9	17.0	34
	11.9	9.4	81
Hand-Milling	17.7	16.8	95
SPEX Milling	64.6	56.6	88
	6.6	5.0	80
	39.0	27.7	71
	73.6	56.7	77
	76.0	60.6	80
	38.2	25.1	66
	38.2	34.1	90
	38.3	36.5	96
	76.3	70.6	93

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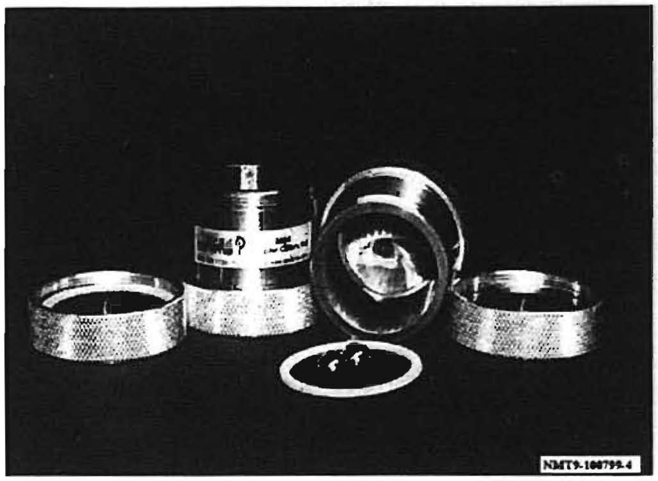
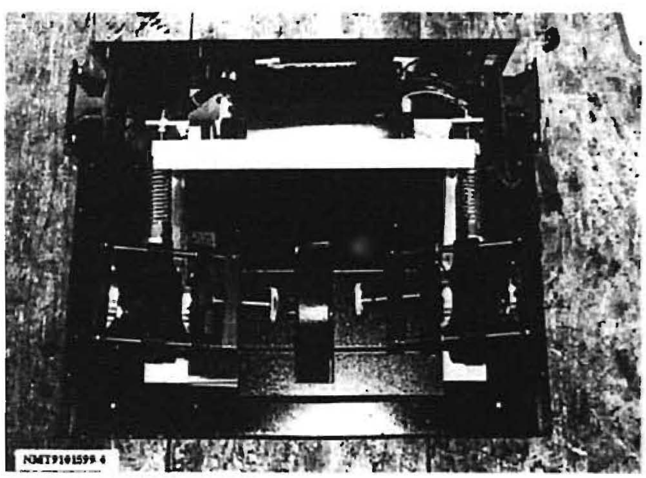
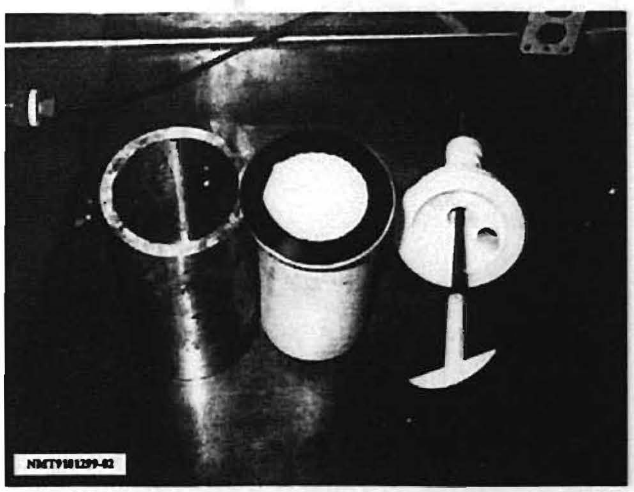


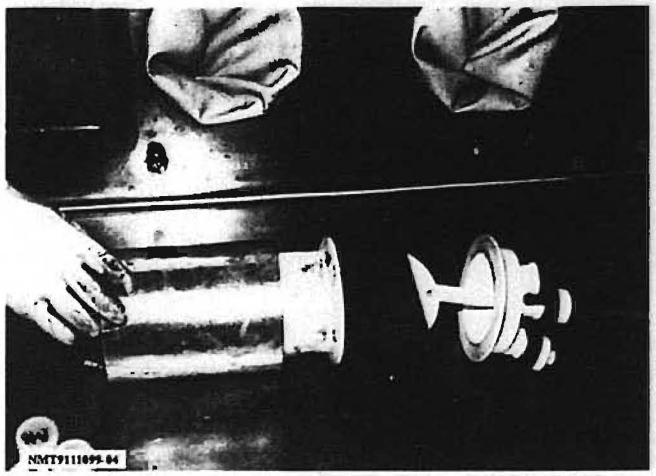


Dissolution

$$PuO_2 + 4HNO_3 \longrightarrow Pu(NO_3)_4 + 2H_2O$$

$$Pu^{+4} + HF \longrightarrow PuF^{+3} + H^+$$

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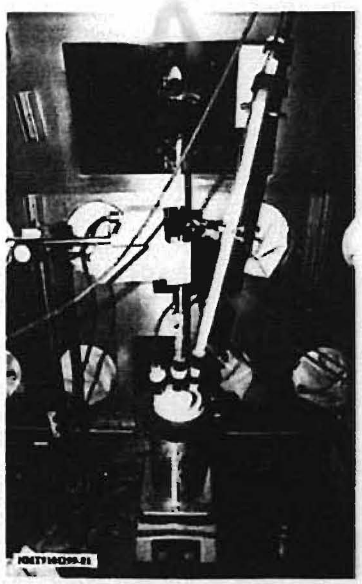
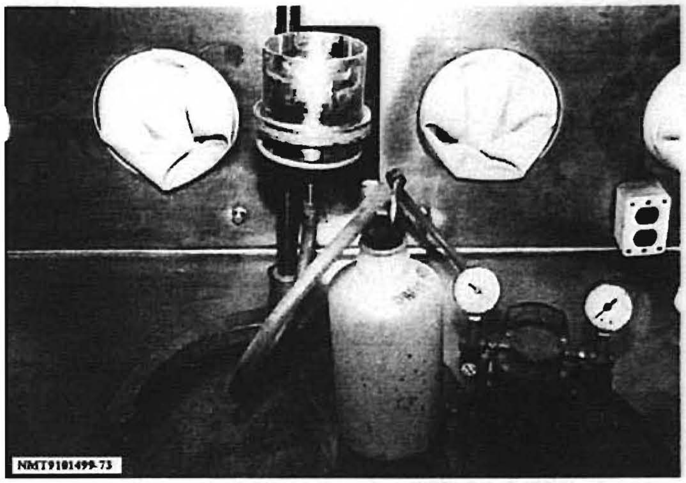




Oxalate Precipitation

- Scavenge Reaction

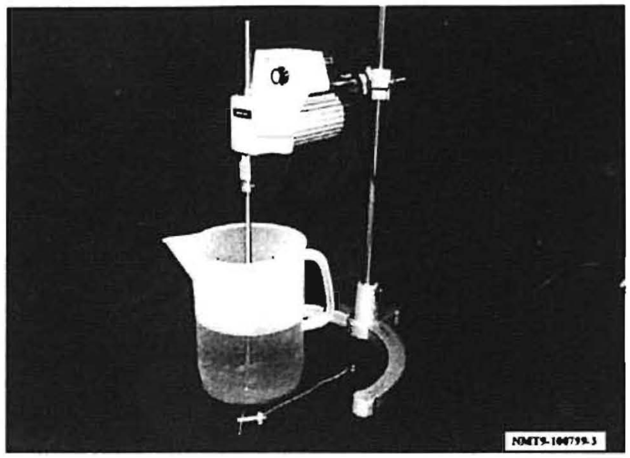
  $$2HNO_2 + CO(NH_2)_2 \longrightarrow 2N_2 + CO_2 + 3H_2O$$

- Pu Reduction

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

- Precipitation

  $$2Pu^{+3} + 3H_2C_2O4 \longrightarrow Pu_2(C_2O_4)_3 + 6H^+$$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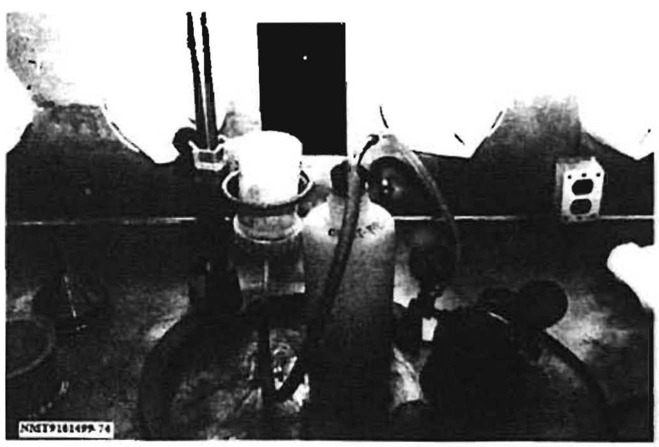
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Calcination

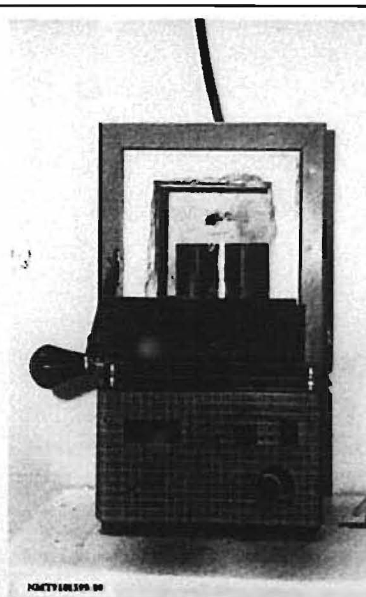
$$Pu_2(C_2O_4)_3 \longrightarrow 2PuO_2 + 2CO_2 + 4CO$$

Temperature:

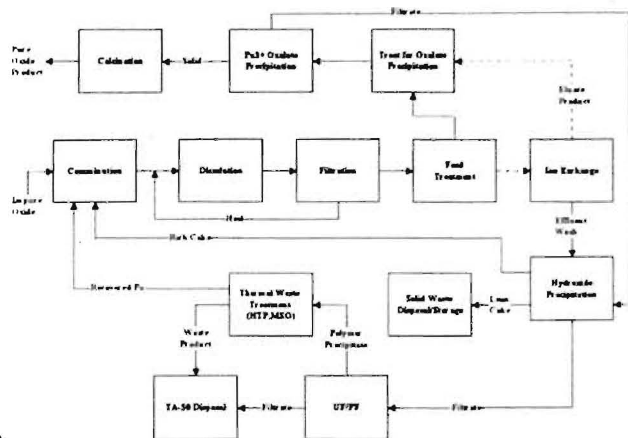
600°C Minimum. Calcination temperature > 600°C.

Time:

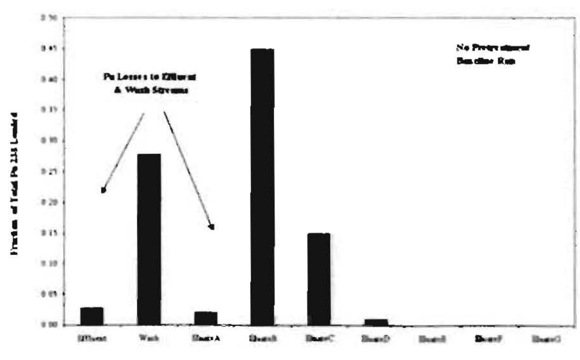
1 - 2 hours



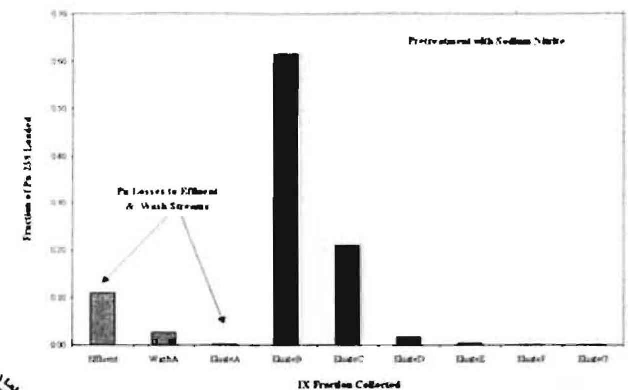
Plutonium-238 Aqueous Scrap Recovery Process



^{238}Pu Aqueous Scrap Recovery Process - Nitrate Anion Exchange Benchscale Experiments



^{238}Pu Aqueous Scrap Recovery Process - Nitrate Anion Exchange Benchscale Experiments



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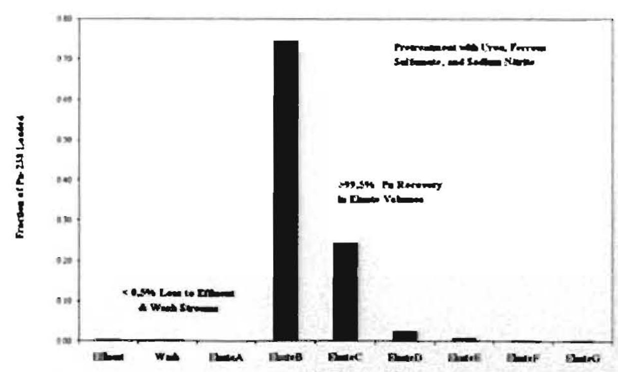

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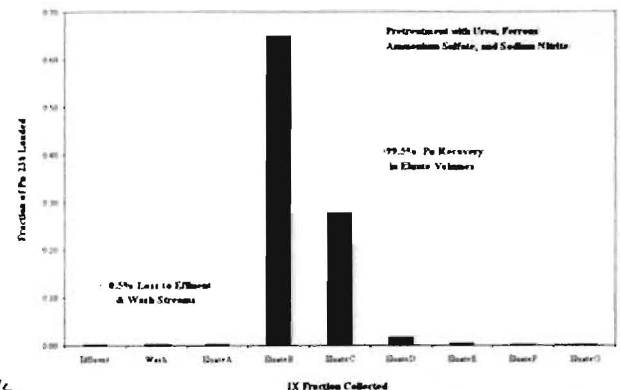
^{238}Pu Aqueous Scrap Recovery Process - Nitrate Anion Exchange Benchscale Experiments



Ion Exchange Optimization Results

- ^{238}Pu losses to effluent and wash streams when no pretreatment or only sodium nitrite used.
- Minimal losses occur when treatment with urea, ferrous salt, and sodium nitrite utilized.
- Ferrous salts:
  - ferrous sulfamate (problems with reagent availability and storage)
  - ferrous ammonium sulfate (optimal choice)

Ion Exchange - Chemical Treatment

- Acid adjustment to 3.0 M with 0.45 M HNO_3
- Scavenge Reaction:

  $$2HNO_2 + CO(NH_2)_2 \longrightarrow 2N_2 + CO_2 + 3H_2O$$

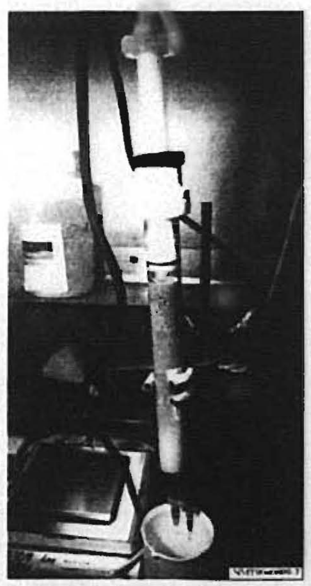
- Pu Reduction:

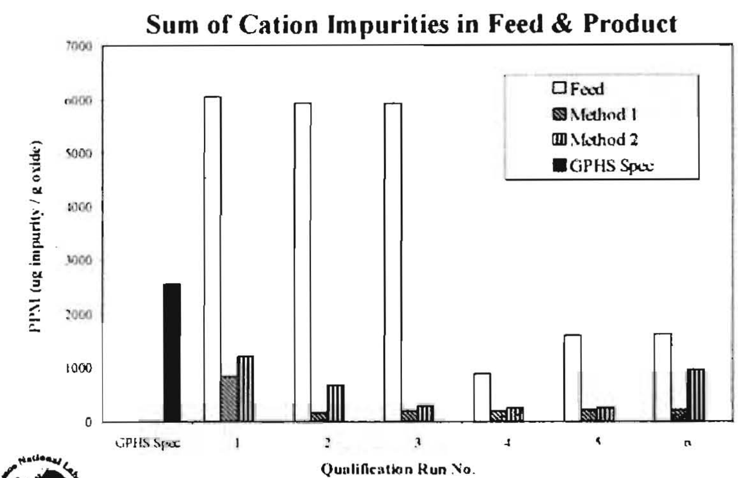
  $$Fe^{+2} + Pu^{+4,+6} \longrightarrow Fe^{+3} + Pu^{+3}$$

- Pu Oxidation:

  $$Pu^{+3} + H^{+} + HNO_2 \longrightarrow Pu^{+4} + NO + H_2O$$

- Acid Adjust to 7.0 M
- Wash column with 7.0 M; elute column with 0.45 M





Residue Treatment

- Sodium Hydroxide
  - Typically 50% NaOH solution used.
  - Adjust pH = 10-12 before sending to UF/PF
- Ultra Filtration / Polymer Filtration
  - Permeate @ <_ 4.5 mCi/L (for caustic discard)
    (4.5 mCi/L = 0.26 mg ^{238}Pu/L)

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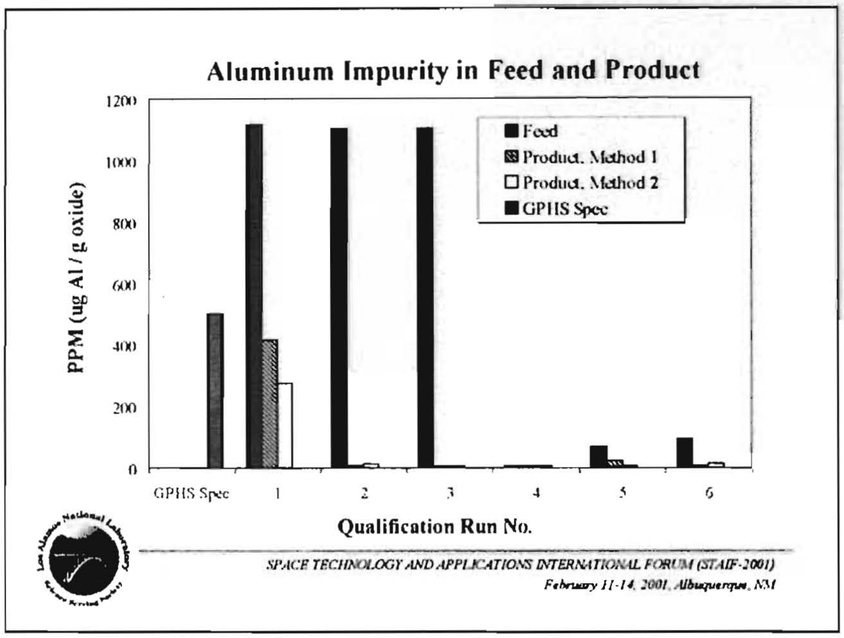
Aluminum Impurity in Feed and Product
PPM (ug Al / g oxide)
1200
1000
800
600
400
200
0
Feed
Product, Method 1
Product, Method 2
GPHS Spec
GPHS Spec
1
2
3
4
5
6
Qualification Run No.
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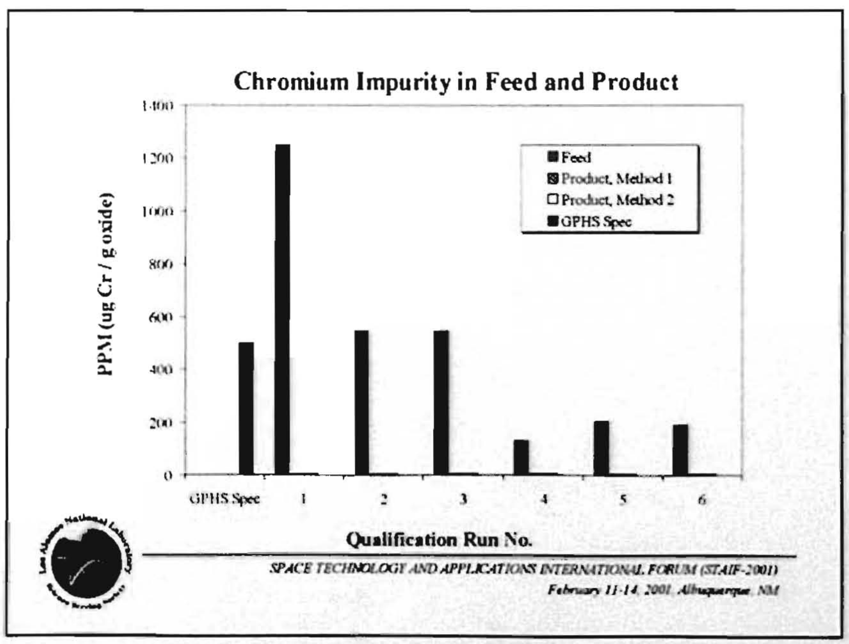
Chromium Impurity in Feed and Product
PPM (ug Cr / g oxide)
1400
1200
1000
800
600
400
200
0
Feed
Product, Method 1
Product, Method 2
GPHS Spec
GPHS Spec
1
2
3
4
5
6
Qualification Run No.
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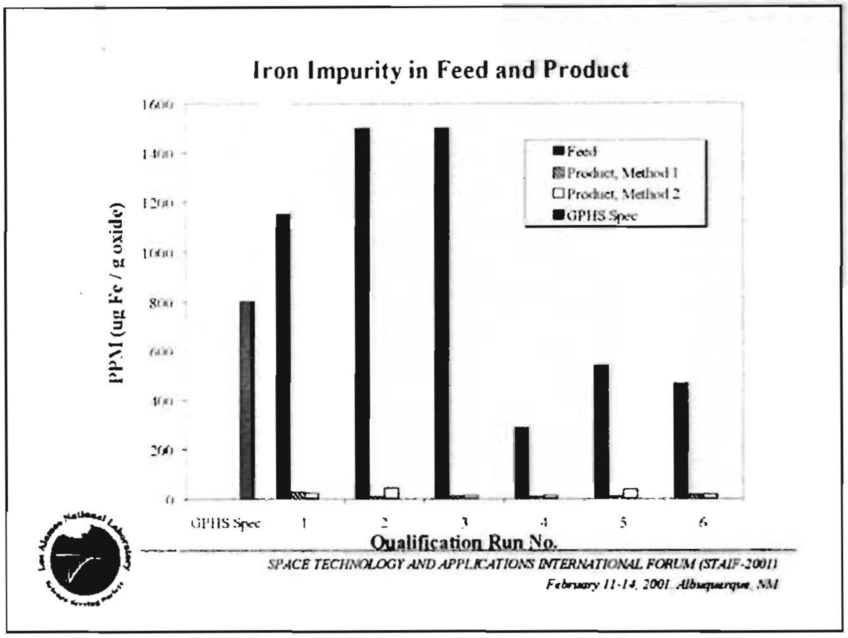
Iron Impurity in Feed and Product
PPM (ug Fe / g oxide)
Feed
Product, Method 1
Product, Method 2
GPHS Spec
GPHS Spec
Qualification Run No.
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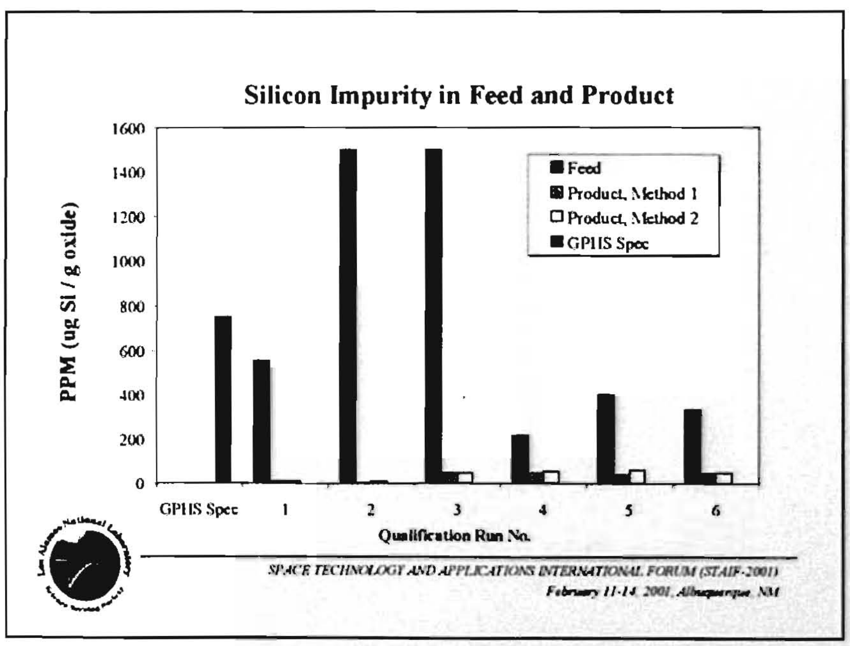
Silicon Impurity in Feed and Product
PPM (ug Si / g oxide)
Feed
Product, Method 1
Product, Method 2
GPHS Spec
GPHS Spec
Qualification Run No.
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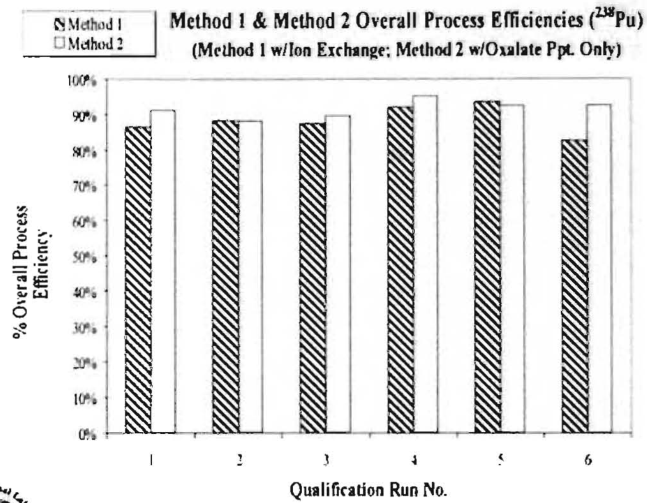

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Generated Process Solution Volumes

(Hydroxide Filtrates)

- With Ion Exchange
  - Calculated average volume generated per 100 g feed oxide: 30 L
  - Calculated volume at 5 kg ^{238}Pu annual throughput: 2022 L
- Without Ion Exchange (GPHS spec. met)
  - Calculated average volume generated per 100 g feed oxide: 7 L
  - Calculated volume at 5 kg ^{238}Pu annual throughput: 480 L
- Difference
  - Calculated difference in volume for 5 kg ^{238}Pu annual throughput: 1542 L

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Results

- Process methodology for $^{238}PuO_2$ aqueous processing at bench scale level developed (100 gm batch size).
- Process methodology produces $^{238}PuO_2$ oxide meeting GPHS impurity specifications thereby qualifying process for production purposes.
- High process efficiencies attained; best method provides generation of minimal waste volumes
- Process methodology to be applied to full-scale aqueous processing line (5 kg ^{238}Pu annual throughput)

Acknowledgement

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