Purification of Simulated Neptunium Filtrate Solution by Anion Exchange

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Why is Neptunium Important?

- ^{237}Np is the best feed source for production of ^{238}Pu
- ^{238}Pu is the ideal continuous energy source for deep-space missions
- ^{238}Pu was last produced in the U.S. for the 1996 Cassini mission
- The half-life of ^{238}Pu is 87.7 years.
- NASA’s projected ^{238}Pu needs exceed projected inventories
- ^{237}Np at SRS – about 300 kg – is a national asset

Outline

- Background
  - Program Status
  - Anion Exchange Process
- Description of Neptunium Filtrate Solution
- Characterization of Feed Solution
- Valence Adjustment
- Experimental Setup
- Experimental Results
- Conclusions

Background

- ^{237}Np was produced in SRS reactor fuels from neutron adsorption of ^{235}U

$$^{235}\text{U}\ (\text{n},\gamma)\ ^{236}\text{U}\ \rightarrow\ ^{236}\text{U}\ (\text{n},\gamma)\ ^{237}\text{U}$$

$$^{237}\text{U}\ \rightarrow\ ^{237}\text{Np} + \beta$$

- 250 kg of purified NpO_2 has been produced for improved transportation and storage safety
- SRS NpO_2 will provide future feed for ^{238}Pu production
- 60 kg of Np (impure solutions) still require stabilization
- Neptunium filtrate contains high Na, Mn, and elevated Pu

Background – Anion Exchange Process

- Reillex HPQ is current resin of choice
- In nitric acid, Np can exist as Np(IV), Np(V) or Np(VI)
- Only Np(IV) forms the hexa-nitrato complex needed for sorption onto Reillex HPQ
- Valence adjustment to Np(IV) required – typically by ferrous sulfamate [$Fe_2(SO_2NH_2)_2$ or FS]
- Np(IV) in 6-8M nitric acid loads onto resin
- Washing options available for greater purification
  - 8 M nitric acid “decontamination” wash
  - 6.4 M nitric acid with FS “reductive” or “partition” wash

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Description of Neptunium Filtrate Solution

- Neptunium oxalate precipitate is filtered
- Filtrate solution is combined with tank cleanouts
  - low Np concentration (~1-2 g/L)
  - appreciable oxalate
- To prevent post-precipitation, oxalate is destroyed by sodium permanganate
- Sodium nitrite is added to
  - destroy permanganate
  - solubilize manganese oxide (MnO_2) solids
- Trace Pu, Th are expected

Characterization of Feed Solutions

Analyte	Actual Filtrate	Simulant #1	Simulant #2	% Unc. (1-sigma)
Np-237, g/L	1.65	1.60	1.81	1-4 %
Pu-238, mg/L	0.28	0.44	0.29	5-10 %
Pu-239/240, mg/L	5.1	6.2	7.2	5-10 %
Acid, M	6.25	6.83	6.72	<1 %
Na, M	0.80	0.70	0.82	20 %
Mn, M	0.25	0.31	0.31	20 %

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Characterization of Feed Solutions

Analyte	Actual Filtrate	Simulants #1 & #2	% Unc. (1-sigma)
Nitrate, M	7.89	8.56	10%
Nitrite, M	<0.002	<0.002	10%
Oxalate, M	0.0005	<0.001	10%
Sulfate, M	0.020	0.045	10%

Valence Adjustment

- UV-visible diode array spectroscopy can detect Np(IV) or Np(V) but not Np(VI) [Low Np(VI) expected]
- As-received filtrate solution contained mostly Np(IV), some Np(V) [Np @ 1.6 g/L = ~0.007M Np]
- Ferrous Sulfamate (FS) added at 0.05 M
- Spectra 1 min after FS add'n – characteristic Np(V) peak at 615-617nm was gone.
- Characteristic Np(V) peak did not return after 24 hr
- No Np(V) peak after adjustment to 8 M HNO_3/0.02 M hydrazine (N_2H_4) [N_2H_4 protects Np(IV) and Fe(II)]

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Experimental Setup

- Column: 97 mL Reillex HPQ anion exchange resin
- For all column runs, Np feed was

$7\text{-}8\ M\ HNO_3\ /\ 0.05\ M\ FS\ /\ 0.02\ M\ N_2H_4$

- 2.5-L feed loaded in ~8 hr
- Wash steps varied
- Elution was always 3 bed volumes (BV) of

$0.17\ M\ HNO_3\ /\ 0.05\ M\ N_2H_4$

Experimental Setup - Np Column Elution

Np^{4+} Elution Band

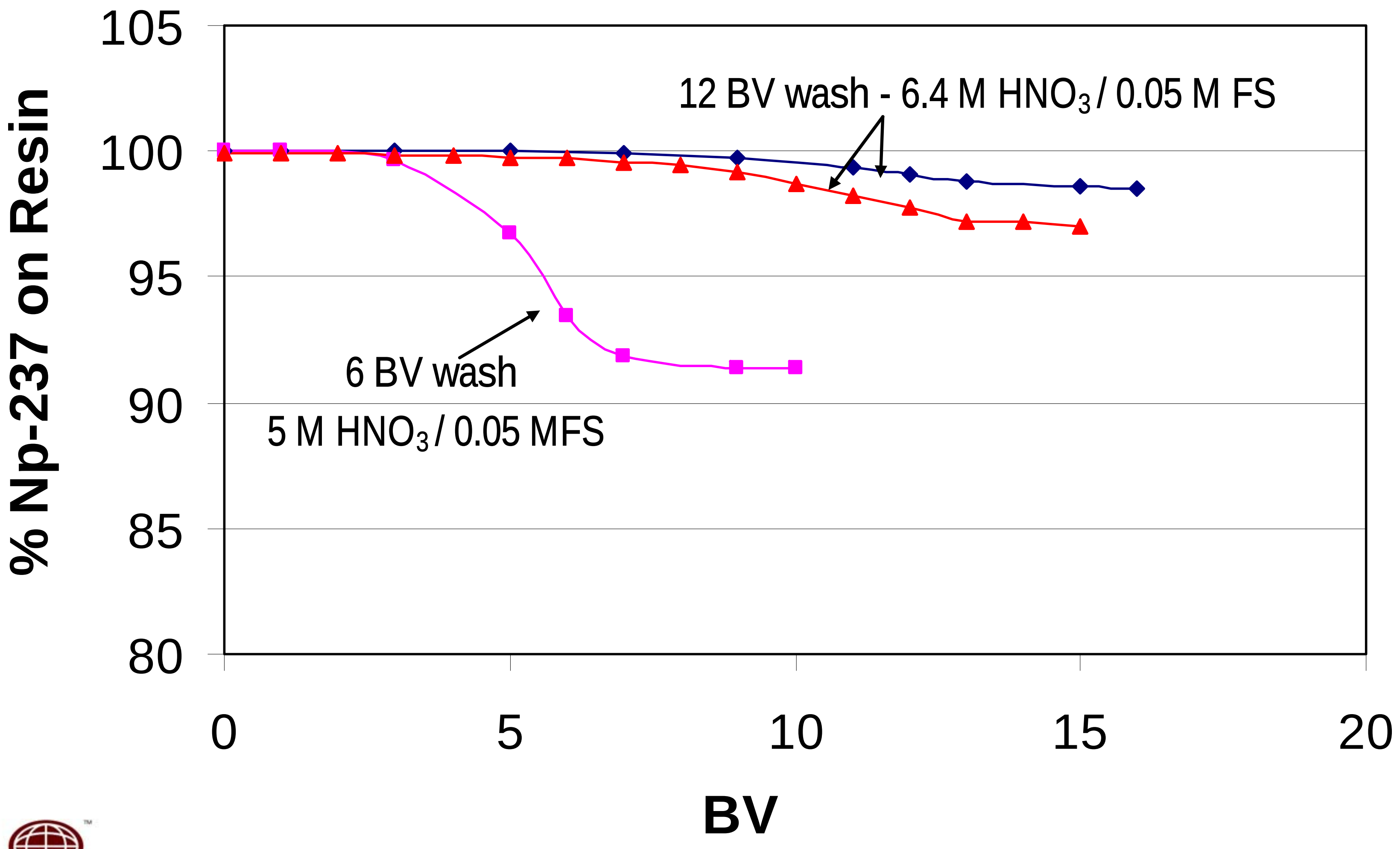
Np^{4+} in 8M HNO_3

Experimental Setup

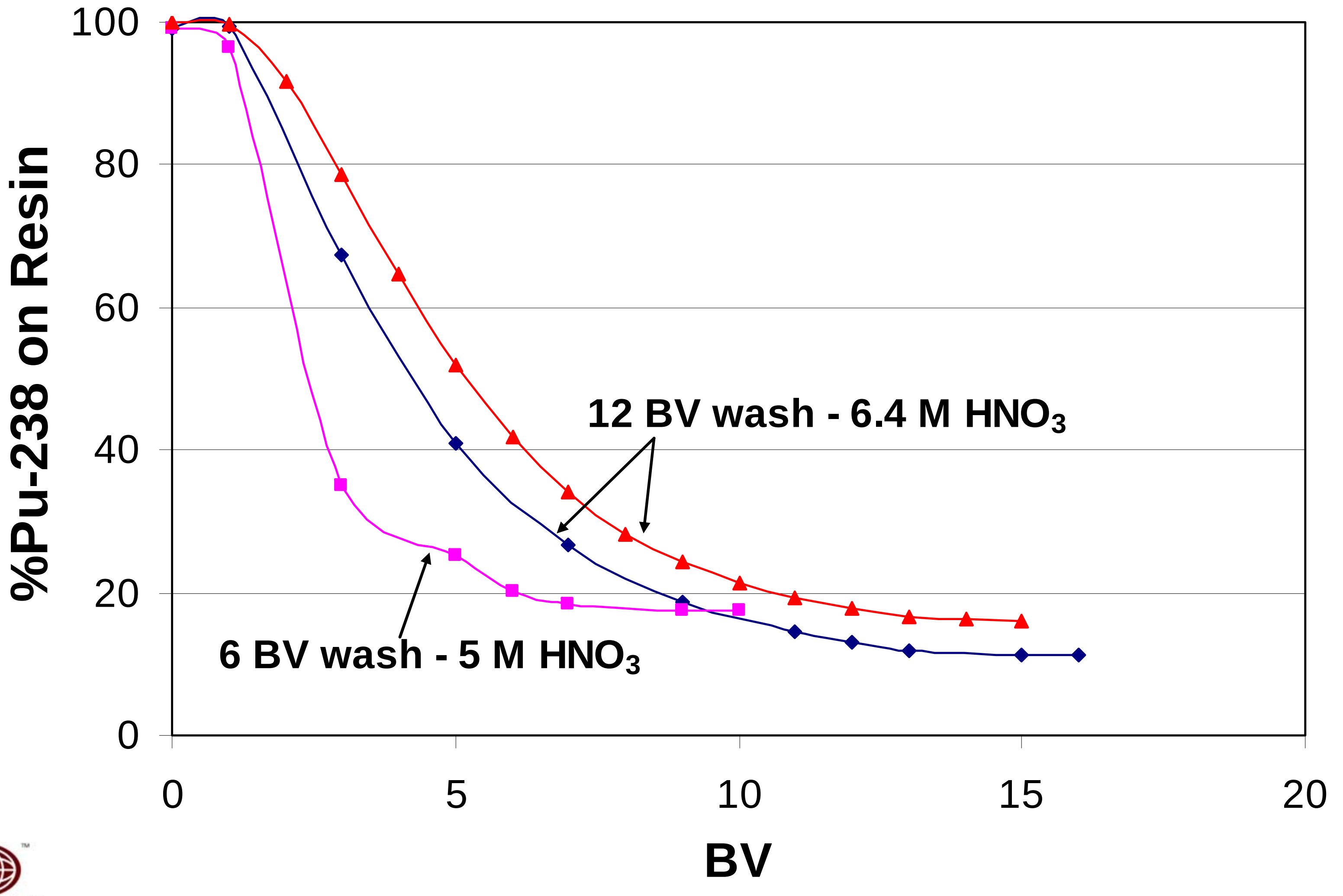
		Sim. #1	Sim. #2	Sim. #3*
Reductive Wash	FS, M Total Fe	0.0425 0.05	0.0474 0.05	0.06 0.06
	HNO_3, M	6.4	5	6.4
	BV	12	6	12
Decon Wash	HNO_3, M	8	8	8
	BV	3	3	3

*Sim. #3 did not contain Na or Mn

Experimental Results – Np Losses



^{238}Pu Rejection by Reductive Washing



Experimental Results - Mn

Mn and Np Analyses for Simulant #2

	Total Mn	Np	ppm Mn	Mn DF
	mg	g/L		
Feed	44,000	1.81	9,300,000	
Raffinate	46,000			
Heads	0.25	0.036		
Hearts	0.131	48.0	29	323,000

DF = Decontamination Factor = Feed/Product

Experimental Results – Na

Na and Np Analyses for Simulant #1

	Total Na	Np	ppm Na	Na DF
	mg	g/L		
Feed	41,000	1.4	12,000,000	
Raffinate	43,000			
Heads	3.0	0.04		
Hearts	2.7	45	620	19,000
Tails	2.6	0.7		

Elution Solution contained 2.2 mg Na before test.

Conclusions

- Valence adjustment with FS is adequate for Np filtrates
- Anion exchange process showed sufficient decontamination of Na and Mn
- Reductive washing with 12 BV of 6.4 M HNO_3/0.05 M FS removed 84-90 % Pu with only 2-4 % Np losses
- Reductive washing with 6 BV of 5 M HNO_3/0.05 M FS removed 83 % Pu with 9 % Np losses
- Reduced acid met goals of study – equivalent Pu rejection in less volume. Trade-off is higher Np losses.