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Effect of Fe^{2+} Oxidation on the Removal of ^{238}Pu from Neptunium Solution By Anion Exchange

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June 2004

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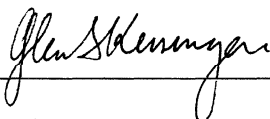
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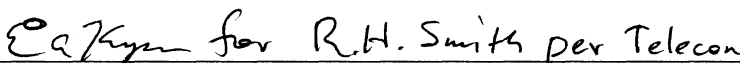
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Acronyms and Terminology:

- A – Cross sectional area of a resin bed in the column
- ADS – Analytical Development Section of Savannah River National Laboratory: Provided analytical services in support of this work.
- Alpha PHA – Alpha plate counting method with Pulse Height Analysis to discriminate by alpha energy.
- BV – (Bed Volume), Volume occupied by the bed of resin in a column. Includes both resin volume and void space volume.
- CLAB – Central Laboratories Facility
- Composite Sample – Solution collected for a relatively long period of time. Represents solution collected over a significant portion of a step of the process. Normally used for material balance calculations.
- DF – Decontamination Factor: A measure of the ability of the process to remove a specific impurity. Calculated by dividing the concentration of the impurity (on a Np basis) in the feed solution by the concentration of the impurity (on a Np basis) in the product solution.
- Down-Flow – Refers to the flow direction of the process stream as being the same direction as gravity through the column.
- Effluent – Solution that is discharged from the column after transfer through the resin bed to either absorb the Np onto the resin or wash impurities from the resin bed.
- Elution – The process step where dilute acid is passed through the resin bed to remove the absorbed Np and collect it as a product solution.
- Free Acid – Acid titration method using metal ion complexant in an attempt to determine hydrolysable H⁺ only.
- FS – Ferrous sulfamate is the primary reducing agent used to adjust Pu and Np valence states in the separation processes.
- Gamma Scan – Gamma emitting isotope counting method by gamma energy.
- Grab Sample – Sample collected over a relatively short period of time. Approximates an instantaneous sample.
- H – Height of the resin bed in the column
- Heads Cut – Initial portion of elution solution that has passed through the column. This solution consists of the displacement of the 8 M HNO₃ contained within the resin bed and column from the loading/wash steps and contains minimal Np at 4 to 6 M HNO₃.
- Hearts Cut – High concentration product Np solution taken from the middle portion of the elution step. Often will be cut off at the point the Np concentration drops to a low level, but prior to complete elution of the column.
- HN₃ – Hydrazoic acid: Reaction product from hydrazine and nitrous acid.
- HNO₂ – Nitrous acid
- HNO₃ – Nitric acid
- Linear Velocity – (Q/A): The volumetric flowrate divided by the cross sectional area of a resin column. Reflects the velocity of the solution flowing through a column (ignoring the space occupied by the resin beds).
- Load – The process step where 6-9 M HNO₃ containing Np is passed through the resin bed to absorb the Np onto the resin.
- N₂H₄ – Hydrazine: purchased as hydrazine mono-nitrate that is commonly prepared by neutralizing the strongly basic hydrazine mono-hydrate with HNO₃.
- NaI – Sodium iodide: Type of detector used to measure column inventory by gamma rays.
- NaNO₃ – Sodium nitrate
- Q – Volumetric flowrate
- Raffinate – Solution that is discharged from the column after flowing through the resin bed to absorb the Np
- SO₄²⁻ – Sulfate ion: Reaction product from sulfamate in the ferrous sulfamate.
- SRNL – Savannah River National Laboratory (formerly Savannah River Technology Center, SRTC):
- Tails Cut – Last portion of elution step that contains dilute HNO₃ and minimal Np. Generated when excess elution acid is used to ensure complete elution of Np from the column.
- Total Acid – Acid titration method measures base required to titrate both free acid and metal ions.
- Up-Flow – Refers to the flow direction of the process stream as being the opposite direction as gravity through the column.
- Visual Break-through – Point during the loading cycle where Np can be visually observed in the effluent from the column by its pale green color. Concentration where this occurs in laboratory sized equipment is in the range of 0.2 to 1 g Np/L.

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From Neptunium Solution
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Summary:

The effect of ferrous sulfamate (FS) oxidation and variation in nitric acid concentration on the removal of ²³⁸Pu contamination from Np by the HB-Line anion exchange flowsheet has been tested. Significant rejection of ²³⁸Pu was observed by washing with a reductive wash solution containing 6.0 to 6.8 M nitric acid (HNO₃) with as little as 30% of the Fe²⁺ from the FS remaining in its reduced form. To achieve the desired 30% removal of ²³⁸Pu from the process, conditions should be controlled to maintain the Fe²⁺/Fe³⁺ ratio in the reductive wash to be greater than 60%/40% (or 1.5). Since Fe²⁺ oxidation is strongly affected by temperature and nitric acid concentration, these parameters (as well as time after FS addition) need to be controlled to ensure predictable results. A shortened-height column was utilized in these tests to match changes in the plant equipment. Lab experiments scaled to plant batch sizes of 2000 g Np were observed with modest losses for “up-flow” washing. The following are recommended conditions for removing ²³⁸Pu from Np solutions by anion exchange in HB-Line.

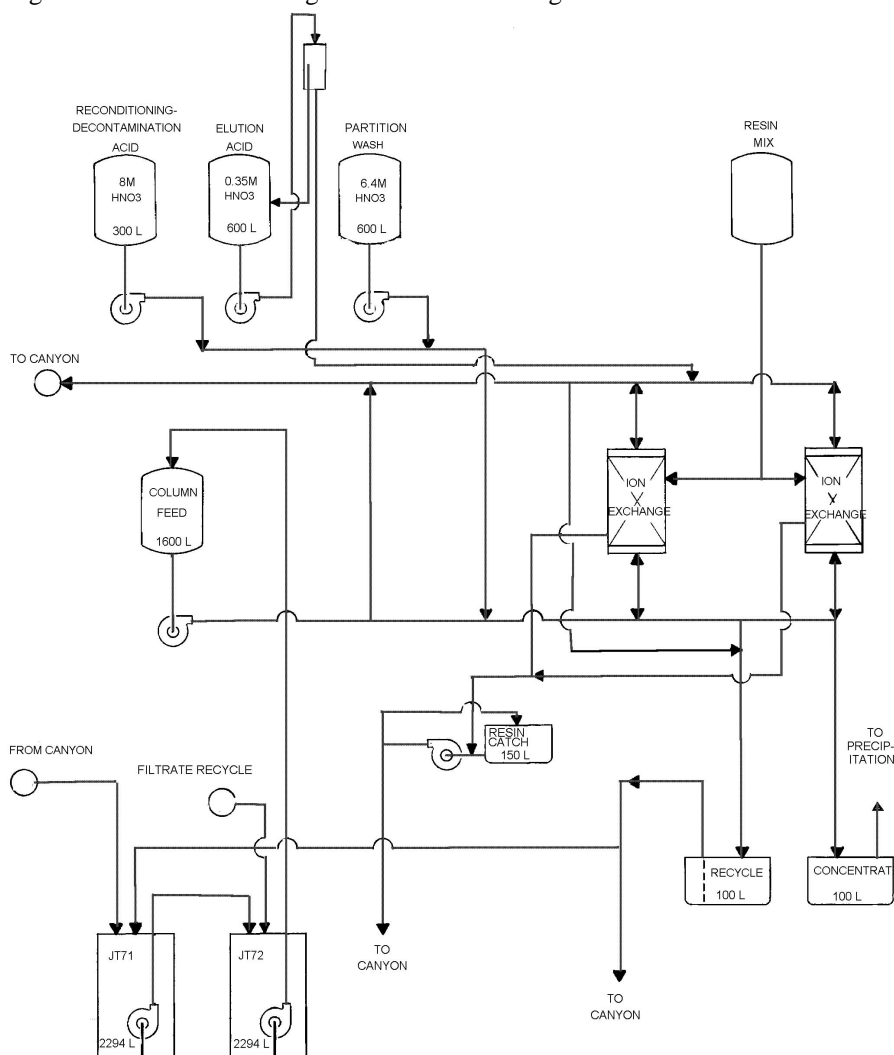
- Feed conditions: “Up-flow” 6.4-8.0 M HNO₃, 0.02 M hydrazine (N₂H₄), 0.05 M excess FS,
- Reductive Wash conditions: “Up-flow” 6 Bed volumes (BV) of 6.4 M HNO₃, 0.05 M FS (minimum 0.03M Fe²⁺ during wash cycle), 0.05 M hydrazine, less than 1.8 mL/min/cm² flowrate.
- Decontamination Wash conditions: “Up-flow” 1-2 BV of 6.4-8.0 M HNO₃, no FS, no hydrazine, less than 1.8 mL/min/cm² flowrate.
- Elution conditions: “Down-flow” 0.17 M HNO₃, 0.05 M hydrazine, no FS

Background:

The new HB-Line facility was designed and built in the early to mid 1980's. Phase II of HB-Line was started up to stabilize Pu solutions in 2001. This facility was designed to receive Pu or Np nitrate solutions from H-Canyon and convert them into oxides for storage or shipment. Currently preparations are being made to process Np nitrate solutions stored in H-Canyon. After receipt of the Np solution, anion exchange columns will be operated to both purify and concentrate the Np nitrate solution, after which the purified concentrated Np solution will be converted to an oxide via oxalate precipitation, filtration, and calcination. The existing tanks and interconnecting piping associated with anion exchange (1) are shown in Figure 1.

Np solution will be received from H-Canyon as a moderately concentrated Np nitrate solution (15-20 g Np/L, 6-7 M HNO₃). The valence state and acid concentration will be adjusted in a feed adjustment tank (JT72) via the addition of FS, N₂H₄ and 64% HNO₃ solutions. In the past, Np valence adjustment

Figure 1. Process Flow Diagram of Anion Exchange Process in HB-Line.



was performed by adding sufficient FS and N₂H₄ to make the solution 0.05 M FS and 0.02 M N₂H₄. The FS was added to reduce all Np⁵⁺, 6⁺ to Np⁴⁺ and all Pu⁴⁺, 5⁺, 6⁺ to Pu³⁺. Np⁴⁺ is the only oxidation state of Np that forms the anionic nitrate complex that significantly loads onto anion resin. The high nitrate concentration and radiolysis of HNO₃ will produce sufficient HNO₂ to oxidize both the Fe²⁺ and Pu³⁺ after several days to several weeks. N₂H₄ is added to react with HNO₂ produced via radiolysis and to protect the Fe²⁺ and Np⁴⁺ from oxidation. During past Pu processing, either a nitrite addition step or a “heat-kill” step was included to rapidly oxidize the Pu³⁺ to the absorbable Pu⁴⁺ valence state. For Np, a “heat-kill” that oxidized the Pu³⁺ and Fe²⁺ but did not destroy all the sulfamate was used to produce a Np⁴⁺ and Pu⁴⁺ feed

solution. In the current Np process, Np⁴⁺ is the preferred species and it is desirable to reject Pu to the raffinate stream. However in high nitrate solution, Pu³⁺ tends to oxidize to the Pu⁴⁺ valence state, which binds to anion exchange resin more strongly than Np⁴⁺. In the historical process for Np purification, the nitrate concentration was lowered to 5.4-6.5 M HNO₃ in the presence of FS during the wash step, to suppress the formation of the absorbable Pu(NO₃)₆²⁻ complex, so that Pu could be rejected to the raffinate stream.

The anion column will be prepared for a Np run by “reconditioning” the resin bed with a quantity of 8 M HNO₃ passed through the piping and the bed to flush dilute HNO₃ from the system. The adjusted feed will be transferred from the receipt/feed adjustment tanks to a column feed tank. The feed solution

Table I. Comparison of SRNL Conditions to HB-Line Standard Flowsheet (1,2,3)

	Recon- dition	Feed	Reductive Wash	Decon Wash	Elution	
Np (g/batch)		2000	4.56	13		
Np (g/L)		10.7	0.02	0.2		
HNO ₃ (M)	8	8	6.4	8	0.17	Assumptions
HB-Line	up	up	up	up	down	Col ID 14.75 in Column area = 1102 cm ²
Flow (L/min)	2.7	1.5	1.6	1.6	1.6	Resin Bed Height 13.5 in
v (mL/min/cm ²)	2.4	1.4	1.5	1.5	1.5	Resin Bed Volume 39.5 L
Volume (L)	40	188	228	66	90	Volumes from Flowsheet
Time (min)	15	125	143	41	56	
BV	1	4.8	5.8	1.7	2.3	
mgs Np/min/cm ²		14.5				Assume 10.65 g Np/L
SRTC Np	up	up	up	up	down	Col ID 19 mm Column area = 2.835 cm ²
Flow (mL/min)	5	5	5	5	5	Resin Bed Volume measured as 97 cc
v (mL/min/cm ²)	1.8	1.8	1.8	1.8	1.8	Resin Bed Height 13.5 in (34.2 cm)
Volume (mL)	100	570	1200	200	250	Plant to Lab Column Scale
Time (min)	20	114	240	40	50	407 Resin Volume Ratio
BV	1.0	5.9	12.4	2.1	2.6	389 Cross-sectional Area Ratio
mgs Np/min/cm ²		15.9				9 g Np/L in Feed

will then be pumped “up-flow” through the column, with the anionic $\text{Np}(\text{NO}_3)_6^{2-}$ complex absorbing onto the resin bed. The column raffinate (which contains the cationic metal impurities and is normally waste) will be transferred directly to an H-Canyon tank. After a full batch of Np feed solution has been loaded onto the column (using 70 to 100% of the resin bed’s physical capacity), the bed will be washed “up-flow” with both a reductive wash and a decontamination wash. In the historical flowsheet, a reductive wash step (referred to as a “partition wash”) was used to wash out additional ^{238}Pu cross-contamination. This wash used a lower HNO_3 concentration (5.5-6.4 M), in addition to N_2H_4 (to scavenge the HNO_2) and FS (to reduce the Pu). In old HB-Line this step was typically performed when additional ^{238}Pu removal was desired.

The proposed reductive wash step for the current flowsheet is very similar to the historical partition wash performed in old HB-Line and will be performed to remove ^{238}Pu contamination. The decontamination wash provides improved decontamination from impurities by displacing residual impure solution from the column and piping prior to elution. The Np will then be eluted with 0.17 M HNO_3 by gravity feed from a head tank “down-flow” through the column. The elution stream passes through a sight-glass that is connected with fiber optics to a colorimeter that determines the point to start collecting Np into the product concentrate tank. The initial effluent from the column collected during elution is commonly referred to as the “heads cut”. The high Np concentration solution collected next is referred to as the “hearts” or product cut. Any dilute acid concentration, dilute Np concentration solution collected near the end of the elution is referred to as the “tails” cut. At the end of a column run, the column is left in a dilute acid concentration state with little or no Np heel. The resin is considered to be in a safe condition for storage until the next run. Interference from the ^{233}Pa daughter from ^{237}Np decay and partial separation of the Pa from the Np makes the use of installed NaI detectors to monitor holdup impractical.

Normally an anion exchange column would be operated less than fully loaded, leaving a large amount of excess capacity. This excess capacity results in minimal losses to the raffinate stream. The capacity of the resin must be known under normal process conditions to determine the batch size. If loading is continued, the concentration of Np in the raffinate stream will gradually rise until visual “break-through” occurs. Higher loading produces higher product concentration in the “hearts” cut. Under normal conditions, it is desirable to produce a raffinate stream that has only discardable amounts Np or Pu. Low production losses require a reasonable knowledge of the capacity of the resin under processing conditions.

The anion exchange resin proposed for use in HB-Line is Reillex™ HPQ. Fred Marsh of Los Alamos National Laboratory and Reilly Industries jointly developed this resin based on another polypyridine-based resin, Permutitt SK, which was used in Pu and Np processes in the late 1950’s (4,5,6). Superior resistance to radiolytic and chemical damage has been attributed to both of these resins due to the use of a pyridine ring “N” functional group compared to the quaternary amine function group used in the conventional divinylbenzene anion resins. Marsh also found this resin attractive due to its relatively high

Table II. Capacity of Reillex™ HPQ for Np.

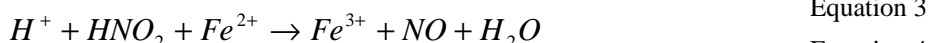
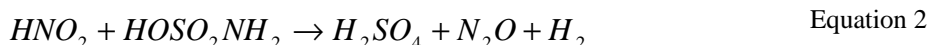
[HNO ₃] Feed M	Resin Loading Breakthru gm Np /L resin	Np Losses Loaded % of Feed
6.4	~40	74
6.4	44	76
6.4		46
7.6	71	80
7.4		61
5.7	36	45
8.2		51

loading for Pu and its excellent elution behavior (4). In 2000, Crooks (7) and Kyser (8) studied the loading of the current version of Reillex™ HPQ for use in the Pu columns in HB-Line.

In a previous study, Kyser (9) measured the capacity of Reillex™ HPQ for Np under various process conditions (see Table II). From ~6 M HNO₃, 40 g Np/L was loaded prior to breakthrough, with a saturation capacity of 75 g Np/L. When the HNO₃ concentration was 7-8 M, the breakthrough capacity of the resin was observed to increase to greater than 50 g Np/L. In that study the concentrations of FS and N₂H₄ in the feed for the HB-Line flowsheet were set to 0.02

M N₂H₄ and 0.05 M FS. In a later study, Kyser (10) developed a modified flowsheet to accomplish a nominal 30 percent ²³⁸Pu removal via reductive washing (sometimes referred to as partition). Based on previous work of Kyser (9) and also Burney (11), reductive wash conditions were proposed and tested. The recommended approach was to wash with 6 BV's of 6.4 M HNO₃ -0.05 M FS -0.05 M N₂H₄. The current work is a follow-up to recommendations from that previous study.

The FS quality was recognized to strongly influence the effectiveness of the ²³⁸Pu removal. Early work by Dukes (12) established that HNO₃ oxidizes Fe²⁺ to Fe³⁺ in the presence of sulfamic acid according to the following reactions:



Historical data have demonstrated that the oxidation of Fe²⁺ to Fe³⁺ in HNO₃ is first order with respect to Fe²⁺ (12,13). The data further indicate that as the HNO₃ concentration increases the oxidation rate of the Fe²⁺ also increases. The first order rate constant (*k*, min⁻¹) for the oxidation of Fe²⁺ in HNO₃ can be calculated using the following equation developed by Dukes (12).

$$\log k = 4.56 \log [HNO_3] - 5140 \left(\frac{1}{T \text{ } ^\circ K} \right) + 10.4 \quad \text{Equation 5}$$

The concentration of Fe²⁺ at any time (*t*, min) can be calculated from:

$$[Fe^{2+}] = [Fe^{2+}]_0 \cdot e^{-kt} \quad \text{Equation 6}$$

where [Fe²⁺]₀ is the initial concentration. Equation 5 is derived from experimental data taken at temperatures of 23 to 55 °C and HNO₃ concentrations of 5 to 8 M. Based on this equation, Fe²⁺ is oxidized relatively quickly in 6.4 M HNO₃ (reaction half-time of approximately 34 hours at 20 °C and approximately 5 hours at 35 °C). Assuming that this equation applies to the reductive wash solution, then the temperature and the storage time of this solution (starting after FS addition) must be carefully controlled to ensure that enough Fe²⁺ is present to provide adequate Pu removal. Several studies, including those by Thompson (14) and Thompson (15), have indicated that the amount of total Fe present cannot be ignored in the reduction of Pu. From basic electrochemistry the reduction potential is controlled by the ratio of [Fe²⁺]/[Fe³⁺] rather than just the [Fe²⁺].

Conditions are further complicated by the presence of N₂H₄ in the wash solution. N₂H₄ is added to scavenge HNO₂ and protect the Fe²⁺ from other oxidation reactions. N₂H₄ is also known to reduce Fe³⁺ to Fe²⁺ in HNO₃; however, this reaction is expected to be relatively slow at ambient temperature [16,17,18]. Most of the available data for this reaction were taken at higher temperatures. In the current study, experimental work was performed to determine the effect of 0.05M N₂H₄ on the Fe²⁺ concentration in the reductive wash solution over time. In parallel with those experiments, Np column runs were per-

formed at known $[\text{Fe}^{2+}]/[\text{Fe}^{3+}]$ ratios in the reductive wash to determine the requirements to meet the goal of removing 30% of the ^{238}Pu with the anion exchange process.

Experimental

Cold FS Studies:

Experimental work was performed to verify the model presented by Dukes and Wallace (12) and to determine if N_2H_4 has a significant impact on the concentration of Fe^{2+} . Two solutions were prepared to simulate the HB-Line reductive wash solution. These two solutions contained 6.4 M HNO_3 , 0.05 M FS, and 0.05 M N_2H_4 . Two other similar solutions (6.4 M HNO_3 and 0.05 M FS) without N_2H_4 were also prepared. Two of the solutions (with and without N_2H_4) were maintained at 20°C using a controlled temperature bath. The other two solutions were maintained at 35°C using a controlled temperature bath. Samples of each solution were taken at 0, 4, and 24 hours and analyzed immediately for Fe^{2+} concentration.

The Fe^{2+} concentration was measured by titrating with 0.01 N ceric ammonium sulfate standard prepared from a traceable 0.1N ceric ammonium sulfate purchased from Fisher Scientific. An aliquant of sample was added to a 1 M sulfuric acid matrix containing ferroin (1, 10 phenanthroline iron(II) sulfate solution) indicator. This solution was then titrated from orange to colorless or light blue using the ceric solution. Due to the time sensitive nature of the experiment, the samples were analyzed immediately after sampling.

Column Studies:

Figure 2. Assembled Column

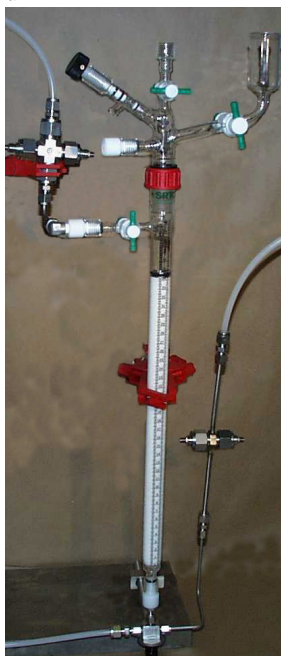


Figure 3. Screen used to Retain Resin Bed.



Process Flowrate Scaling: Plant scale anion exchange equipment is typically 100 to 1000 times larger than laboratory equipment. Normally the process is scaled based on the linear velocity (Q/A , $\text{mL}/\text{min}/\text{cm}^2 \equiv \text{cm}/\text{min}$) through the resin bed (which is related to residence time in the bed) and the loading profile of the resin. If a laboratory column contains resin at the same depth as the plant equipment, then the scaling problem is primarily reduced to one of linear velocity. However, higher Np concentrations in the feed solution will produce a higher Np resin loading. Slower flowrates would also tend to increase the effective loading by increasing the time for mass transfer. The baseline flowsheet feed rate was based on $14.5 \text{ mg}/\text{min}/\text{cm}^2$ (1, 3, 9, 10). Hill (19) recommended a loading rate of $5\text{-}10 \text{ mg}/\text{min}/\text{cm}^2$, which is somewhat lower than the baseline rate. Table I shows a comparison between the baseline design flowsheet and current SRNL test conditions.

The original columns were designed for operation with a 15.5 inch resin bed depth that retained 45 liters of resin. However, plant modifications to the Np columns for installation of rupture disks for pressure relief have changed the effective resin capacity. The current study was based on calculations that showed the two Np columns to hold 13.48 inch (39.05 liters) and 13.86 inch (40.13 liters) respectively (20). More recent calculations have slightly increased the resin capacity of each column by repositioning the piston. For the present experimental work, a new laboratory column was prepared with a 34.2 cm (13.5 inch) resin depth. For these experiments, a resin volume of 97 cm^3 of settled resin was used in a 19 mm inside diameter glass column (cross sectional area of 2.835 cm^2). An assembled column is shown in Figure 3.

Resin Pretreatment: Like the earlier Np work (9, 10), no resin pretreatment was performed to eliminate the low temperature exotherm. All resin that was tested came from the same 1998 manufacturer's lot (#80302MA) that was purchased by SRNL for Pu flowsheet work. All resin was initially converted from the chloride form (as-shipped) to the nitrate form by washing with 1 M NaNO_3 (10 BV in a column was the preferred method, but other methods are acceptable).

Column Preparation: A sufficient quantity of resin was converted into the nitrate form prior to loading the column. The resin was slurried into

Figure 4. Up-flow Load/Wash Experimental Setup.

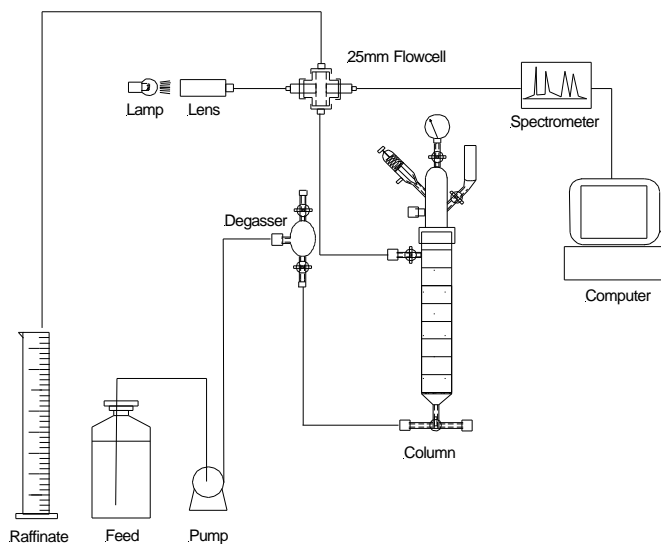
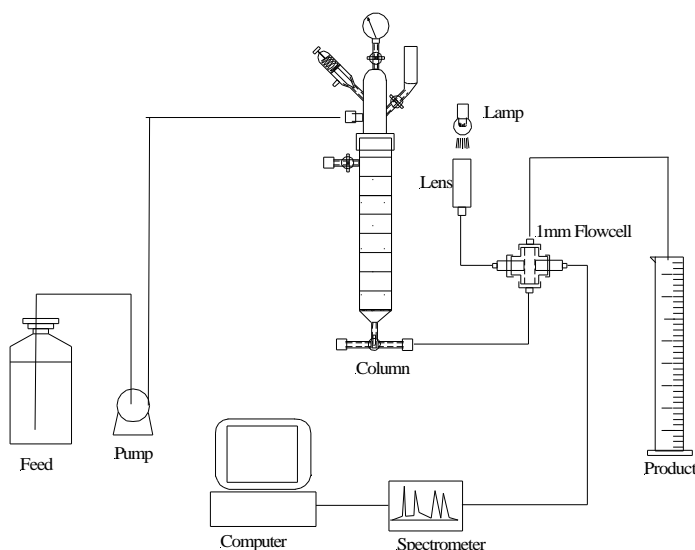


Figure 5. Elution Experimental Setup.



the column with distilled water. The resin bed was settled by running water/dilute HNO_3 “down-flow” through the resin bed to fill the excess void spaces until all apparent gaps were filled. The final resin bed volume was adjusted by adding a small amount of resin or removing excess resin with a slurry pipette. A 100 mesh 304L screen (see Figures 2 and 3) was installed to retain the resin bed and allow for “up-flow” operation. This screen was installed tightly within the column body and did not allow the resin bed to expand significantly. It also prevented upward flow from fluidizing the resin bed. Actual volume changes of the resin beads are insignificant, but retained gas bubbles would cause the resin bed to expand without the screen installed. Gas bubbles trapped within the moist bed are often very difficult to remove and will cause channeling of the flow through the bed. A tightly held resin bed does not readily allow channeling to occur. Gas pumped “up-flow” through such a retained bed in the lab has been observed to pass the gas up through the resin bed in finely divided bubbles without the appearance of a major liquid displacement.

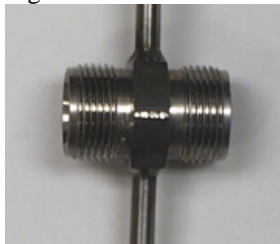
Lab Equipment: A picture of a column is shown in Figure 2. The column utilized #7 Teflon™ bushings for connecting 1/4 inch polypropylene tubing to the upper part of the column. The column consists of a 19 mm ID glass body to retain the resin bed and a head-piece. The headpiece is attached to the column body with a Rodaviss™ joint to allow the column to retain a larger pressure head than that allowed solely by a ground glass joint. As a safety precaution, the head also had an Ace glass pressure-relief valve. An additional arm with a stopcock and funnel allowed the column to be vented. A modification was made to the bottom of the column over that used in past designs. The 3-way stopcock used to change flow direction was replaced with a 3-way 1/8 inch Swagelok™ valve. Replacing the stopcock was done to eliminate an apparent flow dead-zone that held up Np solution and appeared to cause tailing in the elution profile. With the use of 100 mesh screen held into place with an o-ring (Figure 3), this column was operated load-wash “up-flow” and elution down-flow. A sketch of the experimental setup for the “up-flow” load/wash steps is shown as Figure 4. A separate sketch of “down-flow” elution experimental setup is shown as Figure 5. “Down-flow” wash was performed with the same setup as “down-flow” elution.

A standard FMI piston pump was used to pump feed, wash, or elution acid through the column. A 1/2-inch Swagelok™ cross and two 1/2 inch optic lenses were used to fabricate a flowcell with a 25.4 mm path-length that was used to observe dilute Np solution from the column during the load/wash steps. A 1 mm flowcell for use during the elution step was fabricated by welding 3/16-inch tubing into a 1/2-inch

Table III. Spectrophotometer System Component Description.

- Spectrometer: Diode array spectrometer based on the Zeiss MCS module (190-1024 nm range, approximately 0.8 nm/pixel). Interfaced to computer through Hamamatsu C4070 driver/amplifier board. Power supply: Condor D.C. Power supplies model MTL-5W-A.
- Fiber optic cable: Ceramoptec or Polymicro, IR grade, 400 micron low-OH core with SMA fittings each end
- Computer: Texas Micro industrial PC, IPC-6806P.233MHz, Windows NT
- Data acquisition card: National Instruments AT-AI-16XE-10 Multiple I/O Board (16-bit resolution, 16 analog and 8 digital inputs).
- Flowcell: Swaglock ½ " Union Cross (SS-810-4) for body, Swaglock ¼" to ½ " Reducer (SS-400-R-2) 2 each to attach ¼" poly tubing, Fiber optic Lens: Equitech CL-UV-K. Stainless steel body, 1/2" diameter. Quartz lens. Kalrez o-ring seal. Stainless SMA connector, 2 required
- Light Source: Ocean Optics Tungsten Halogen LampHousing, LS-1
- Variable Attenuator Oz Optics Part # BB-200-55-300 600-SP to adjust light levels
- Cuvette Blocks: SRTC fabricated plexiglass cuvette holders each with 2 lenses similar to flowcell, 1 unit for light reference and 1 for glovebox standards

Figure 6. 1 mm Flowcell



Swagelok™ union and milling out the union to allow two ½-inch optic lenses to slide to the center. An unassembled 1-mm cell without lenses is shown in Figure 6. Two pairs of fiber optic lines previously installed through the ceiling of the glovebox allowed a light signal to be brought into the glovebox, passed through the flowcell and carried out to a Zeiss spectrometer controlled by an NT-based computer. A detailed list for the complete spectrophotometer system used is given in Table III. The multiplexer used in past work proved unsuitable for this work as it used UV grade fibers, which absorbed significant light in the 950 nm wavelength range. Np^{4+} and Np^{5+} absorption peaks at 960 nm and 980 nm were not useable if UV grade fibers

were used in the system. Therefore, the multiplexer was bypassed and reference and measurement spectra were taken on the same pair of IR grade fibers. Light references were taken prior to the beginning of the experiment and stored. Fibers were switched at the lamp and spectrometer after the wash step.

Feedstock Preparation and Valence Adjustment: Np solution was prepared as a feedstock by adjusting to 8 M HNO_3 and performing a valence adjustment with N_2H_4 and FS. For these runs a change from past practice was made. Instead of adding the N_2H_4 first and the FS just prior to the column run, the order was reversed. A day or more prior to the column run, sufficient FS was added to make the solution 0.05 M excess FS over that required to reduce all the Np from Np^{5+} to Np^{4+} . The FS also reduces all Pu^{4+} , $^{5+}$, $^{6+}$ to Pu^{3+} . The high nitrate concentration gradually produces sufficient HNO_2 to oxidize both the Fe^{2+} and Pu^{3+} . In Pu solutions at 8 M HNO_3 at 50°C, the half-life for Fe^{2+} is on the order of 10 minutes compared with 1 hour at 35°C and 10 hours at 25°C (21). Fe^{2+} is expected to persist for longer periods due to the reduced alpha activity in the Np feed solutions. FS degrades to Fe^{3+} and SO_4^{2-} . Increased Fe^{3+} hinders the effectiveness of Fe^{2+} in the reduction and stabilization of Np as Np^{4+} . Repeated additions of FS will result in increased levels of $[\text{SO}_4^{2-}]$ in the feed and will both increase the raffinate losses due to SO_4^{2-} complexation with Np^{4+} and reduce the resin capacity for Np. The effect of SO_4^{2-} on anion resin capacity was studied by Burney (22). In 8 M HNO_3 , he observed a 30 percent reduction in resin capacity for Np with 0.1 M SO_4^{2-} present and a 70 percent reduction in resin capacity for Np with 0.5 M SO_4^{2-} present. Due to tank heels in the feed tanks, some concentration buildup of SO_4^{2-} is inevitable and may have a negative effect on resin capacity. In Np past studies, the FS was added just prior to the start of the column run (within 1 hour) to improve the opportunity to reject Pu during the feed step by keeping it as Pu^{3+} and thus not loading it onto the resin. The addition of FS at least 16 hrs prior to the column run allowed for time for Fe^{2+} and Pu^{3+} to oxidize with the intention of reducing the gassing observed during loading. Adding the N_2H_4 within an hour prior to loading would convert some radiolysis induced gases (from HNO_2) into HN_3 and would reduce gas generation within the resin bed.

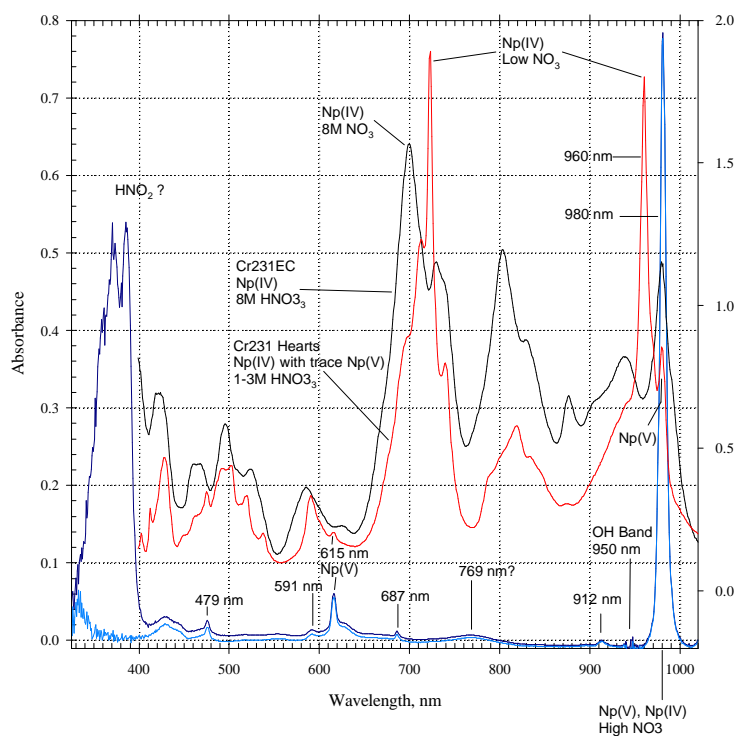
Np Loading: Sufficient Np feedstock was prepared for the column run. A sample was taken and analyzed for total alpha by alpha PHA and gamma scan. Feed acidity was not measured but calculated based on previous free acid analyses of the Np solution and the addition of 70% reagent grade HNO_3 and distilled water. At the beginning of the column run, ~1 BV of 8 M HNO_3 was fed “up-flow” to the column to displace the dilute HNO_3 in the resin bed from the previous run. At this point in the experiment, the spectrophotometer was checked for proper operation and a new “zero” spectrum was stored for the 25-mm

flowcell (background with no Np in the flow cell). The Np feed was then pumped “up-flow” through the column at approximately the desired flowrate, with the raffinate passing through the flow cell and being collected and measured in one of several graduated cylinders. The amount of Np in the raffinate was monitored by both visual inspection and by periodic spectra. The entire feed raffinate was collected and analyzed for Np content by alpha and gamma counting. The spectra were stored along with the time and volume of raffinate collected. The feed flowrate was periodically checked with a 10 mL graduated cylinder and a stopwatch. The instantaneous flowrates were somewhat variable (sometimes $\pm 50\%$ of the targeted value), but the average flowrate could generally be regulated within 15% of the desired value.

The Np loaded onto the resin was also visually monitored. Visual monitoring of the Np loaded onto the resin was more difficult than the previous observations with Pu. The appearance of Np proved difficult to recognize until after break-through had occurred. Flow abnormalities within the resin bed sometimes caused “tailing” of the loaded Np (e.g. Np loaded non-uniformly on the resin where the Np interface is further down the resin bed on one side of the column than on the other). Tailing is not visually detectable during studies with Np due to the subtle color of Np loaded onto the resin bed. In past Pu work, tailing has been observed to vary from column to column and even from run to run on the same column. Tailing could cause higher than expected losses to the raffinate stream during either the loading or the reductive wash steps. Tailing problems could also prove to be more of a problem with a large diameter resin bed such as that used in HB-Line. The ability of the column design to uniformly distribute the flow of the feed solution across the entire area of the column is not known.

Analytical: Samples were taken of feed, composite raffinate and product solutions, as well as grab samples of the raffinate stream. These samples were routinely analyzed by alpha PHA and gamma scan analyses to determine the activity from ^{238}Pu , ^{239}Pu , ^{237}Np and ^{233}Pa . ^{237}Np (2.2e6 yr half-life) and ^{233}Pa (27.4 day half-life) would approach secular equilibrium after three to six months. The anion exchange process separates Np from Pa and the raffinate and wash samples often have a high $^{233}\text{Pa}/^{237}\text{Np}$ activity ratio. When the $^{233}\text{Pa}/^{237}\text{Np}$ activity ratio was greater than ~ 10 , gamma counting was not able to provide good ^{237}Np results due to interference from the ^{233}Pa . When ^{238}Pu activity was greater than 50 times the ^{237}Np activity, the precision of the ^{237}Np counting was also reduced. For samples with both high ^{233}Pa and ^{238}Pu activity levels relative to ^{237}Np , no satisfactory means of determining the ^{237}Np concentrations was available.

Figure 7. Absorbance Spectra of Np^{4+} and Np^{5+} in HNO_3 .

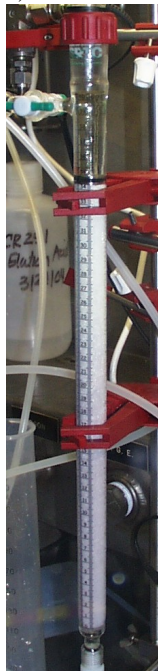


Calibration of Spectrophotometer: The absorbance spectra of Np solutions are highly dependent on acid concentration. Efforts to calibrate the spectrometer system for Np^{4+} and/or Np^{5+} were too time-consuming for the scope of this program. Instead, the spectrometer was used to provide qualitative results on the presence of Np^{4+} and Np^{5+} .

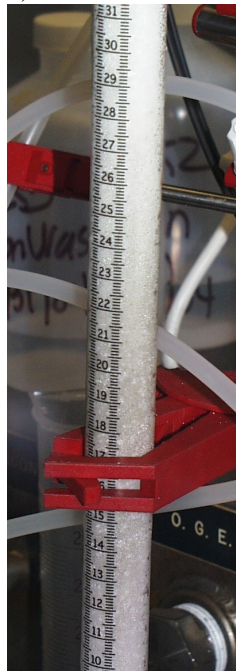
Literature references for Np absorbance spectra in HNO_3 are limited. Johnson and Shepard (23) measured spectra of Np^{4+} , $^{5+}$, $^{6+}$ in 1 to 10 M HNO_3 . They found a strong nitrate dependence in the spectra between 5 and 10 M HNO_3 . They also reported disproportionation of Np^{5+} above 3 M HNO_3 along with a strong acid dependence for the disproportionation reaction. The Np^{5+} spectra that they published clearly show Np^{4+} absorption peaks, but interestingly do not show the Np^{6+} peaks. Friedman and Toth (24) reported

Figure 8. Np Columns During Load and Elution Steps.

a) Load



b) Elution



(Cr255). Otherwise no Np^{5+} was observed during the loading or wash steps of any of the experiments in the current study.

Np spectra in up to 4 M HNO_3 . They reported difficulty in obtaining pure Np^{4+} in low HNO_3 concentrations due to oxidation to Np^{5+} . They also observed no indication of Np^{4+} hydrolysis at 0.1 M or greater HNO_3 concentrations. Figure 7 shows Np^{4+} spectra in both low and high HNO_3 compared with reference Np^{5+} spectra (9). Note that the major Np^{4+} peak at 960 nm at low acid is shifted to 980 nm in 8 M HNO_3 . This spectral shift precludes the use of the 980 nm peak to determine the success of valence adjustment and oxidation in anion feed solutions. Also, note the appearance of characteristic Np^{5+} peaks at 615 and 980 nm in low HNO_3 . While relatively small, the 615 nm Np^{5+} peak has been used in past work to identify the presence of Np^{5+} in 8 M HNO_3 (9). Np^{5+} was clearly observed in the raffinate of column run # 255

Results and Discussion:

Cold FS Studies: Initial studies attempted to validate the applicability of the Dukes and Wallace model (12) to the current process conditions for storage of the reductive wash solution. The main difference is the presence of N₂H₄ to the current reductive wash solution. Experimental results and predicted Fe²⁺ concentrations are shown in Table IV. The predicted Fe²⁺ concentrations are from the Dukes and Wallace model. Where duplicate titrations were performed, a 2σ uncertainty was calculated. Analytical uncertainties of < 5% were observed for samples of 0.03 M Fe²⁺ or higher. Samples with < 0.005M Fe²⁺ had

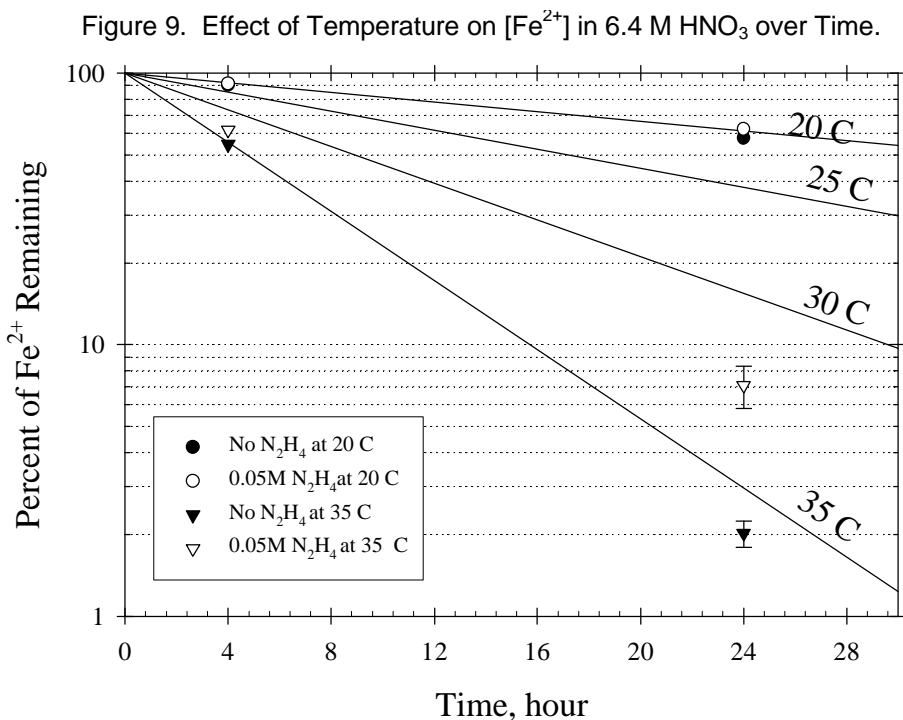
Table IV. Measured vs Predicted Fe²⁺ Concentrations

Sample	Time hr	[N ₂ H ₄] M	Temp °C	[Fe ²⁺] M		Std Error
				Predicted	Measured	2σ Confidence
1	0	0	35	---	0.051	NA
	4	0	35	0.028	0.028	NA
	24	0	35	0.0015	0.001	± 13.9%
2	0	0.05	35	---	0.052	NA
	4	0.05	35	0.028	0.032	NA
	24	0.05	35	0.0015	0.0037	± 21.8%
3	0	0	20	---	0.052	NA
	4	0	20	0.048	0.047	± 3.7%
	24	0	20	0.032	0.03	± 2.7%
4	0	0.05	20	---	0.052	NA
	4	0.05	20	0.048	0.047	± 1.3%
	24	0.05	20	0.032	0.032	± 2.0%

observed analytical uncertainties of up to 22%. The higher uncertainties at the lower concentrations appear to be due to the small volume of titrant required for the analysis.

Figure 9 is a graph of the percentage of the total Fe²⁺ remaining over time in 6.4 M HNO₃. The lines on the graph are predicted from the Dukes and Wallace model (12) for various temperatures. The data points represent experimental data from the current study. Data from samples without N₂H₄ show excellent agreement

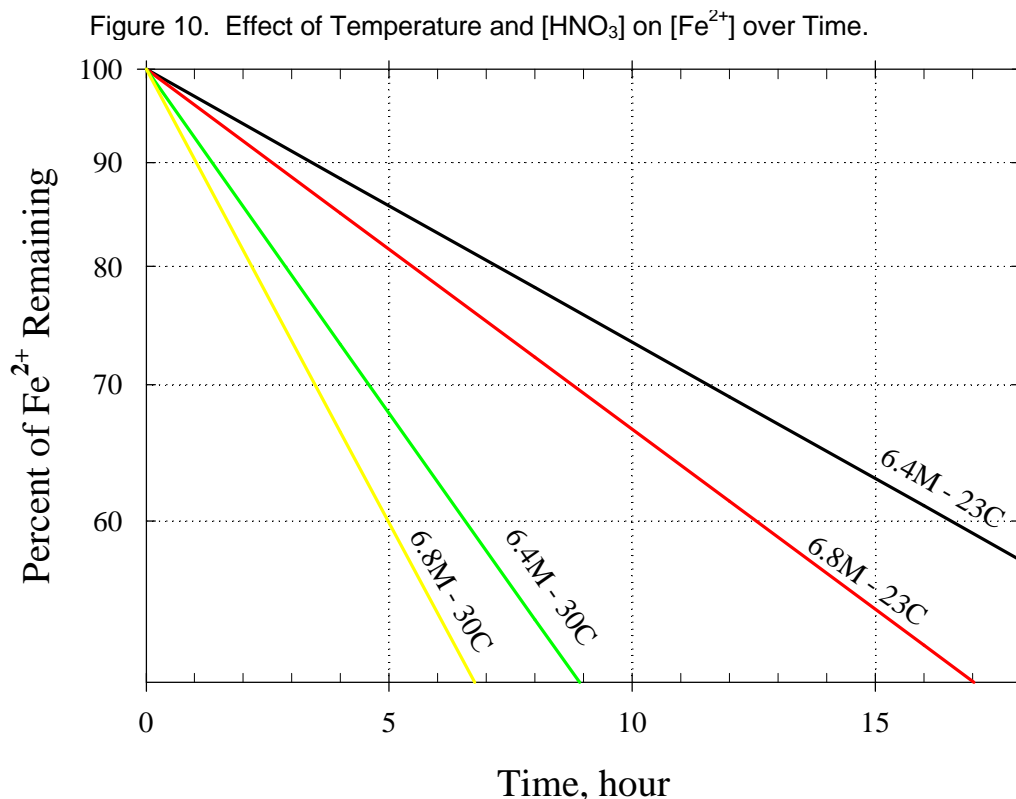
with values predicted by the model. The sample with N₂H₄ at 20 °C also matches the model closely. Error bars (2σ) are shown for the two 35 °C samples taken at 24 hours. The sample at 35 °C with N₂H₄ contained a higher concentration Fe²⁺ than predicted by the model. This result suggests that some of the Fe³⁺ may have been reduced back to Fe²⁺ by the N₂H₄. More Fe³⁺ would be expected to be reduced for the 35 °C case with N₂H₄ than for the 20 °C case with N₂H₄ because a) the temperature is higher which increases



the reaction rate of Fe³⁺ with N₂H₄ and b) more Fe³⁺ is present which also increases the reaction rate. Although there is evidence that Fe³⁺ is being reduced by N₂H₄, the rate of this reaction in the temperature range of interest appears to be too low to provide a significant increase in the Fe²⁺ concentration.

The rate of oxidation of Fe²⁺ is strongly dependent on the concentration of HNO₃. Figure 10 shows the effect of increasing the HNO₃ concentration from 6.4 to

6.8 M. While the HNO_3 concentration is not expected to vary this much during plant processing, it is important to realize that significantly higher than the planned HNO_3 concentration will reduce the effective shelf-life of the reductive wash solution. A 2% increase in HNO_3 concentration will reduce the shelf life of Fe^{2+} by 10%.



Np Column Studies: A series of three column runs followed by a pair of demonstration column runs was performed with the 1998 batch of Reillex™ HPQ purchased for development of the previous Pu flowsheet. For each experiment, composite samples of the feed, raffinate, wash, and product solutions were analyzed. The results from those analyses and the volume of each solution were used to calculate a material balance for each experiment. The amount of Np absorbed (or loaded) onto the resin was calculated as the difference between the cumulative amount in the feed solutions and the amount found in the raffinate solutions. Detailed results from each of the column runs and some sample calculations for the individual runs are shown in the appendix as Tables IX, X, XI, XII and XIII.

In Cr251-3, a series of 10 - 2BV reductive wash steps of the loaded Np was performed and the fraction of ^{238}Pu removed was determined. A common Np feedstock bottle was prepared for all 3 runs complete with FS adjustment. The N_2H_4 was added to the portion of the feed for that run just prior to the start of the column run (within 30 min). The effect of acid concentration variation on the effectiveness of the reductive wash was tested at 6.8, 6.4 and 6.0 M HNO_3 . In each of the runs, a progressive reductive wash was performed by varying the Fe^{2+} from 10 to 100% of the total Fe present. In all three experiments, a 2BV-8 M HNO_3 decontamination wash (Decon Wash) was performed after the reductive wash to displace the FS remaining in the lines and in the resin bed. All three experiments used 0.17 M HNO_3 and 0.05 M N_2H_4 for the elution of the resin bed. Process parameters for these experiments are detailed in Table IV. The reductive wash solutions were prepared from a separate stock acid solution for each run. Stock acid solution (200 mL) was combined with ferric nitrate salt and FS to prepare each concentration of reductive wash solution in 2BV portions. Ten separate wash solutions were prepared for each column run by a procedure that kept the HNO_3 and total Fe concentrations essentially constant. For Cr251, these wash solutions were all prepared at once during the initial loading step. For Cr252-5, everything but the FS was added in advance and the FS was added no earlier than one hr prior to use to limit the oxidation of the Fe^{2+}

Table V. Process Parameters for the Reductive Wash Experiments.

		Cr251	Cr252	Cr253	Cr254	Cr255
Feed	FS, M	0.043	0.043	0.043	0.049	0.049
	N ₂ H ₄ , M	0.022	0.022	0.022	0.023	0.023
	HNO ₃ , M	7.9	7.9	7.9	8.1	8.1
	Np, g/l	10.7 ⁽¹⁾	9.9	9.9	11.3 ⁽²⁾	10.3
Wash	FS, M	0.05	0.05	0.05	0.05	0.05
	Fe ²⁺ ⁽⁴⁾	9-63% ⁽³⁾	10-97%	11-98%	49%	58%
	N ₂ H ₄ , M	0.05	0.05	0.05	0.05	0.05
	HNO ₃ , M	6.8	6.4	6	6.4	6.4
	T, °C	25	21.6	20.5	23.2-24.2	23.5-23.9
	BV	20	20	20	6	6
Decon	HNO ₃ , M	8	8	8	8	8
Wash	BV	2	2	2	1	1
Elution	N ₂ H ₄ , M	0.05	0.05	0.05	0.05	0.05
	HNO ₃ , M	0.17	0.17	0.17	0.17	0.17
	BV	0.9	0.9	0.8	0.8	0.8

- (1) Feed solutions for Cr251-3 are identical, Cr251 analysis value is high
- (2) Feed solutions for Cr254-5 are identical, Cr254 analysis value appears to be high
- (3) Reductive wash solutions for Cr251 were prepared at beginning of run. Values reported are corrected for time at laboratory temperature
- (4) Reductive wash solutions for Cr252-5 were prepared no more than 1 hr prior to use. Values reported are corrected for time at laboratory temperature

column are shown in Figures 8a and 8b. The Np loaded resin is characterized by the lavender-gray color on the lower 75 percent of the bed in Figure 8a. In Figure 8b, there is white eluted resin at the top of the column, a dirty section of resin with a plug flow section of eluted Np below, and an uneluted section of lavender colored resin that is still loaded with Np.

The principal objective of this work was to demonstrate the capability of a modified process to reject ²³⁸Pu from ²³⁷Np while still keeping Np losses at acceptable levels. . An unstated but important aspect of this work was to determine what effect the flowsheet changes would have on the batch size for anion exchange. Other process phenomena were observed while performing the experiments. Specific results for several aspects of these experiments are discussed in detail in the following discussion.

Table VI. Summary of Results from Reductive Wash Experiments.

	Cr251	Cr252	Cr253	Cr254	Cr255
Loading, g Np/l	60.9	50.4	50.3	49.6	50.0
g Np/l	54.0	46.3	38.2	44.8	42.9
Load 38.4L Resin, g Np	2072	1779	1469	1721	1649
Product Conc, g Np/l	62	60	54	60	56
Loading Loss ¹	0.19%	0.31%	0.38%	0.05%	2.51%
6 BV Wash Loss ¹	0.0%	0.1%	0.3%	0.1%	0.2%
Wash Loss ¹	2.8%	4.7%	7.0%	0.1%	0.3%
Heads Loss ¹	0.0%	0.1%	0.1%	2.4%	0.3%
Tails Loss ¹	1.0%	0.9%	1.0%	1.2%	0.9%
Np Matl Balance ¹	-8.6%	-3.4%	-16.9%	-9.6%	-13.5%
²³⁸ Pu Matl Balance ²	-5.4%	-9.7%	-3.3%	2.8%	-3.5%
Np Prod Eff ³	96%	94%	92%	96%	96%
Feed ²³⁸ Pu, ppm	437	453	454	432	463
Product ²³⁸ Pu, ppm	63	23	21	356	302
Product Pu, ppm	294	23	172	356	302
Wash	Up-flow	Up-flow	Up-flow	Up-flow	Up-flow

¹ % of Np in feed, ² % of ²³⁸Pu in feed, ³ % of Np in product relative to feed corrected for material balance differences by subtracting Np material balance %

prior to use. The laboratory temperature was measured several times during each run and these temperatures and time estimates were used to correct the target Fe²⁺ percentage. These corrections as well as estimated corrections for Np runs in the previous study are included as Table V.

A summary of results, which includes a material balance for each experiment, is included as Table VI. Generally, calculations of the material balances for Np and ²³⁸Pu were closed to within of 5 to 15 percent for each run. The uncertainties in the material balance are of similar magnitude to the uncertainty of an individual analysis. For this series of column runs, all five Np material balances came up short.

Glovebox photos of a partially loaded Np column and the elution of hearts cut of a Np column are shown in Figures 8a and 8b. The Np loaded resin is characterized by the lavender-gray color on the lower 75 percent of the bed in Figure 8a. In Figure 8b, there is white eluted resin at the top of the column, a dirty section of resin with a plug flow section of eluted Np below, and an uneluted section of lavender colored resin that is still loaded with Np.

Pu Rejection: The effectiveness of a reductive wash at removing ²³⁸Pu from Np is shown in Figure 11, a plot of the fraction of ²³⁸Pu remaining on the column during the wash for the three progressive wash experiments (Cr251-3). This fraction was determined by difference from the material balance for each column run. For ease of illustration

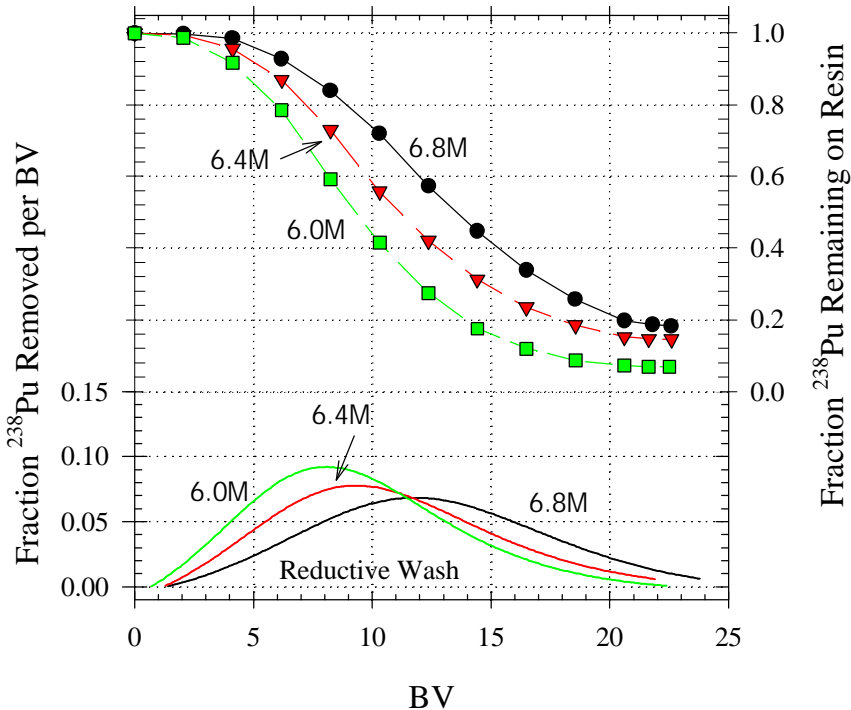
Table VII. Calculated Fe²⁺ Corrections for Reductive Wash Solutions

	Cr246-8*	Cr251	Cr252	Cr253	Cr254	Cr255
RW1	86%	9%	10%	11%	49%	58%
RW2	84%	18%	21%	21%	49%	58%
RW3	82%	26%	31%	31%	49%	58%
RW4	81%	32%	40%	41%	49%	58%
RW5	79%	39%	50%	51%	49%	58%
RW6	78%	45%	60%	61%	49%	58%
RW7		51%	70%	71%		
RW8		55%	80%	80%		
RW9		59%	89%	89%		
RW10		63%	97%	98%		
Fe ²⁺ Correction	11 to 22%	1 to 37%	0.3 to 3%	0.2% to 2%	1.6 to 2%	2 to 2.1%

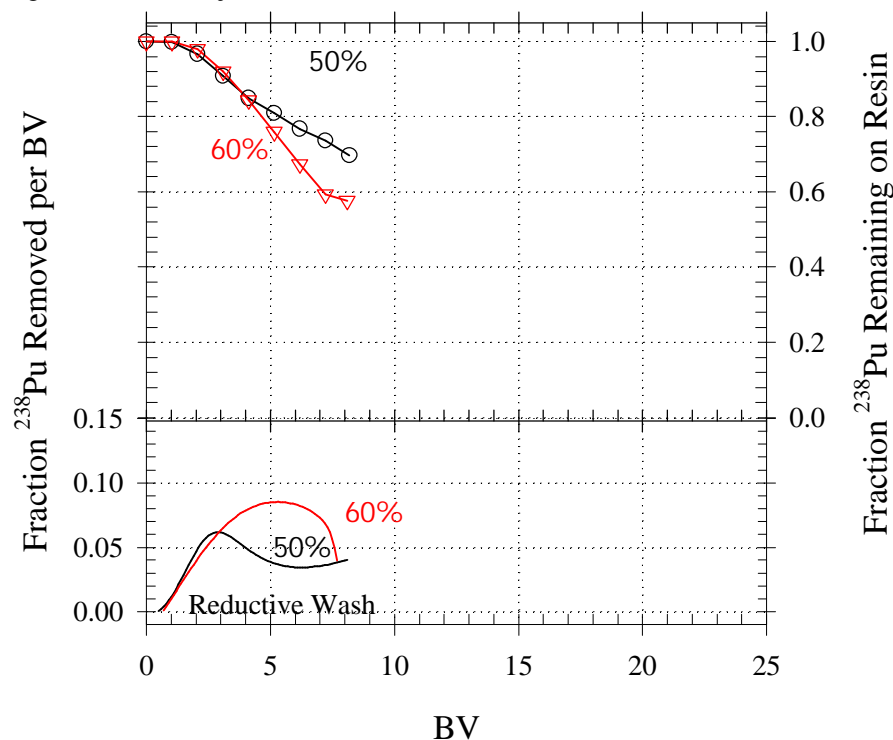
* Estimated

figures in this report have the feed raffinate value plotted at 0 BV the analyzed feed value (when shown) plotted at -1 BV. For these three runs only, the first BV of each wash solution was placed into the previous cut. This method of collection reflects the reality of displacement of solution on the resin bed, but complicates discussion and comparison of these results with other runs. These ²³⁸Pu plots stop after the elution displacement cuts are taken. These data were modeled with a 5-parameter rational function fit in Sigmaplot[®] 8.0. The models provided a mathematical means of calculating the rate of change of removal ²³⁸Pu by taking the derivative of those functions. This rate was plotted on the graph. The maximum rate of removal of 7 to 9% per BV was reached after 8 to 12 BV of reductive washing on the progressive wash experiments and was a function of HNO₃ concentration in the wash. After the rate peaked, ²³⁸Pu removal continued at a declining rate but never stopped. Examination of the Figure 11 for ²³⁸Pu removal and then looking up the corresponding % Fe²⁺ data in Table VII shows that the BV of maximum ²³⁸Pu removal corresponds to ~40% removal in all three runs. An explanation for this observation could be that 40% may be the point at which the readily accessible ²³⁸Pu has been removed. Reillex HPQ is a highly cross-linked macroporous resin and the removal of the remaining ²³⁸Pu may be limited more by diffusion processes.

Figure 11. ²³⁸Pu Rejection during Progressive Reductive Wash Column Runs.



The point of the progressive wash experiments was to identify the minimum Fe²⁺/Fe³⁺ ratio where efficient ²³⁸Pu removal was possible. The expectation was that 70 to 90% Fe²⁺ might be required, but these experiments show significant removal with as little as 30% Fe²⁺. The problem is that the first 1-2 BV do not accomplish much removal and tank space will limit the reductive wash to no more than 6 BV. To achieve the 30% ²³⁸Pu removal target in 5 BV requires an average rate of 6% per BV. With 6.4 M HNO₃, it appears that 40% Fe²⁺ might be sufficient, but due

Figure 12. ^{238}Pu Rejection in Flowsheet Demonstration Column Runs

number of data points involved, so the models must be used with care. For the 60% Fe^{2+} wash (Cr255), the ^{238}Pu removal increased until it appears to plateau at 6% per BV at 6 BV. This corresponds to ~40% removal just as was observed in Cr251-3. Since only 6 BV of washing was performed, the removal of ^{238}Pu for additional wash volume can only be speculatively observed to be similar to that in the extended washing performed in Cr251-3. The run at 50% Fe^{2+} (Cr254) showed very similar removal to the 60% Fe^{2+} run for the first 4 BV. After this point, the ^{238}Pu removal declined somewhat, but the removal rate was still fairly significant at ~4% per BV. This result does not support the hypothesis that only 40% of the ^{238}Pu is easily removed, but since the washing was stopped prior to removing 40% of the ^{238}Pu , it does not necessarily disprove it either. This particular run resulted in slightly less than the targeted 30% removal, directing the recommended conditions to a minimum of 60% Fe^{2+} .

Figure 13 shows the reanalysis of the existing data from the previous scoping tests of Kyser (10). The same five parameter rational function fits were performed as for Cr251-3, and the same sort of plots were obtained. Cr248 exceeded 20% per BV removal, but in that experiment the wash direction was reversed to “down-flow” and resulted in unacceptable Np losses. The other two runs reached maximum ^{238}Pu removal rates of 9 to 13% per BV. These rates were higher than what was observed in the current study due to the use of fresher FS (higher percent Fe^{2+}). Interestingly, on these runs the maximum rates for all three runs were observed to occur at ~30% ^{238}Pu removal.

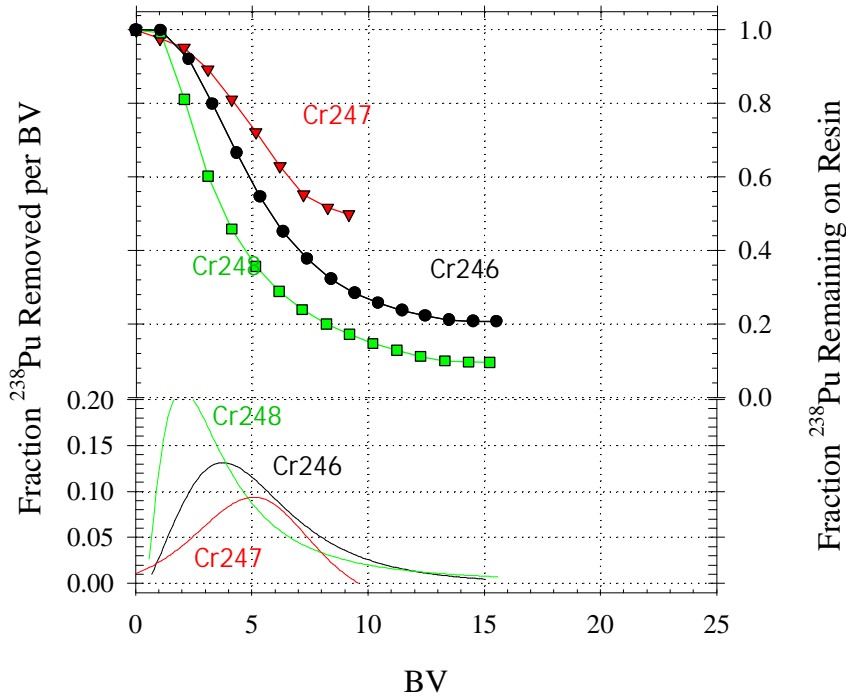
Figure 14 shows a comparison of the results from Cr254-5 and those published by Burney (11). In that report, data for 2 low cross-linked resins (Dowex 1x3 and 1x4) were tested with 93, 69 and 50% Fe^{2+} . The Dowex 1x4 data for 50% Fe^{2+} compares reasonably well with current data for Reillex HPQ at 50% Fe^{2+} in spite of the large differences in cross-linkage between the resins (Crooks (25)). The macroporous nature of the Reillex™ HPQ resin would be expected to compensate somewhat for the diffusional resistance observed in the resin forms available in the 1960’s.

The temperature and HNO_3 concentration effects on the percent Fe^{2+} over time can be calculated from the models developed by Dukes (12) and were validated with N_2H_4 present as a part of the current study as discussed earlier. Fe^{2+} oxidation is controlled by the HNO_3 concentration and temperature. A 6.4 M HNO_3 reductive wash solution prepared and kept at less than 30°C, will undergo oxidation of 40% of

to time constraints and the need to be successful, it was decided to do tests at 50 and 60% on the demonstration runs.

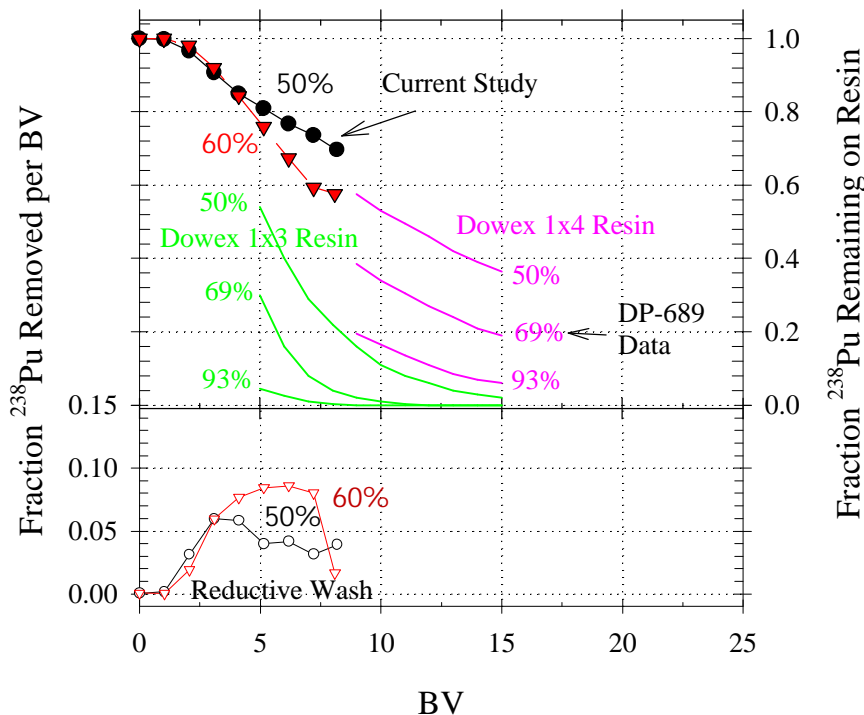
Figure 12 shows similar results for the two flowsheet demonstration runs at 50 and 60% Fe^{2+} . A 6 BV 50% Fe^{2+} wash at 6.4 M HNO_3 resulted in a 27% ^{238}Pu removal, whereas a similar wash at 60% Fe^{2+} resulted in a 42% ^{238}Pu removal. The data for these runs were not as smooth to fit as the data from Cr251-3, but a similar fit was attempted. In these cases 6- and 7-parameter rational fits were necessary to get a reasonable fit. Use of this large number of parameters is excessive for the

Figure 13. Further Analysis of ^{238}Pu Rejection in Previous Study



0.5% for these runs with the exception of Cr255. Washing losses of Np appear to be low for the first 6 BV for all five runs in the current study (< 0.3%), although Cr254 and Cr255 initially had higher detection limits for Np that resulted in detection limits of ~1% for the washing step. Reanalysis of the Cr254/5 data

Figure 14. Comparison of the ^{238}Pu Rejection from the Current Study to DP-689 Data.



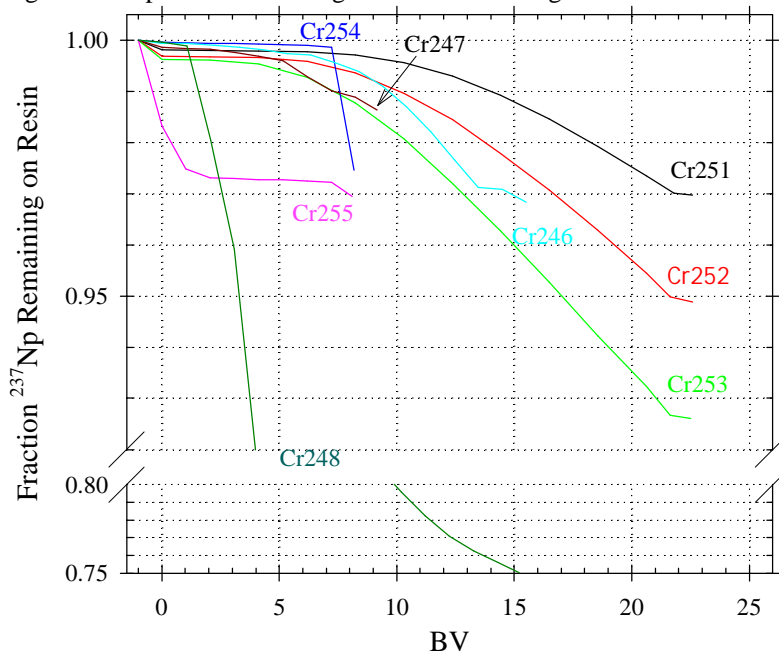
the Fe^{2+} in 6.5 hours. A 5°C reduction in temperature will double the shelf life of the reductive wash solution. On the other hand a 2% increase in HNO_3 (to 6.5 M) will shorten the shelf life by almost 10%.

Np Losses: The feed solutions for the column runs of the current experiments were prepared to be 8 M HNO_3 and the resin was observed to absorb the Np with low losses as expected from the earlier loading study (9). Experimental results are shown in Figure 15 and Table VI. Some results from past work are also included in Figure 15.

Loading losses were less than 0.5% for these runs with the exception of Cr255. Washing losses of Np appear to be low for the first 6 BV for all five runs in the current study (< 0.3%), although Cr254 and Cr255 initially had higher detection limits for Np that resulted in detection limits of ~1% for the washing step. Reanalysis of the Cr254/5 data resulted in a lower detection limit and indicated that the 6 BV washing losses for all 5 runs were < 0.3%. Experiments Cr251-3 had increasing losses as the HNO_3 concentration was lowered from 6.8 M to 6.0 M as expected. Above 5 to 10 BV, the Np losses become increasingly significant, ranging from 3 to 7% cumulative losses by 20 BV. The main significance attached to these results is that the resin columns were close to fully loaded with Np.

Although the feed solution for Cr254/5 was valence adjusted as a single feed solution, loading losses were observed on Cr255 only. Spectroscopic measurements clearly iden-

Figure 15. Np Retention during Reductive Washing.



tify a significant Np^{5+} component to the raffinate on Cr255 that does not exist on Cr254. The absence of Np in the raffinate in Cr254 indicates that the valence adjustment was successful, but 2.5% of the Np in the feed oxidized to Np^{5+} during a 24 hour storage in 8 M HNO_3 . Past observations had led to the conclusion that the disproportionation reaction of Np^{5+} would not allow accumulation of Np^{5+} in that HNO_3 concentration. No explanation of this observation has been uncovered.

The Cr246-8 results are from a past study (10). Cr246 and Cr247 provide comparable results to the experiments in the current study, but Cr248 was

known to be different because the wash direction of the fully loaded column was changed to “down-flow”. This change caused unacceptably high Np losses. Those results were included for comparison purposes.

The material balances for these runs ranged from -3% to -17% less Np after the column run than analyzed in the feed. These results seem somewhat higher than normal for this work, however analytical uncertainties are a significant contributor. The negative bias observed in these results complicates analysis and reporting of the results as there are different ways of calculating loading and efficiency and the results are different.

The resin capacity of a production sized column continues to be evaluated as additional data have been collected. The original Reillex™ HPQ resin capacity for Np was determined by Kyser (9) with a five inch tall resin column (see Table II). However, at the point of loading breakthrough, the five inch resin bed has a Np loading profile that varies from a high value (maybe even saturated) at the feed end of the bed to a low value at the raffinate end of the bed. No effort

Table VIII. Estimate of Plant Resin Column Capacity.

Depth Resin, in	Liters Resin ¹	Estimated Loading ² , g/L	Np, g
13.5	4.3	0	0
12	14.5	40	579
7	19.6	75	1470
	38.4		2049

Depth Resin, in	Liters Resin ¹	Estimated Loading, g/l	Np, g
13.5	14.5	40	579
8.5	4.3	75	326
7	19.6	75	1470
	38.4		2375

Assumptions:

¹ Column diameter changes from 14.75” to 15” at 7” resin bed depth.

² Mass transfer front depth of 5 inches: 75 g/l loading behind front, 40 g/l average loading within front.

was made to measure the “width” of the loading band of Np on the column. The width of the loading band will vary as a function of flowrate, but feed rate was scaled to the production process. Inspection of the raw data in the original breakthrough runs in Kyser (9) reveals that “double-batching” the load of Np past breakthrough resulted in 33-50 percent loss of the second feed batch (from 6.4 M HNO_3). These observations do not provide any more than an estimate of the depth of resin that the mass transfer front occupies, but by assuming a depth, an improved estimate of the column capacity can be obtained. Table VIII shows an estimate on the capacity of the resin column with the assumption that the mass transfer front is limited to five inches of resin bed depth. This calculation uses the same resin loading values determined by Kyser (9) but indicates a somewhat greater Np capacity for a full height resin bed.

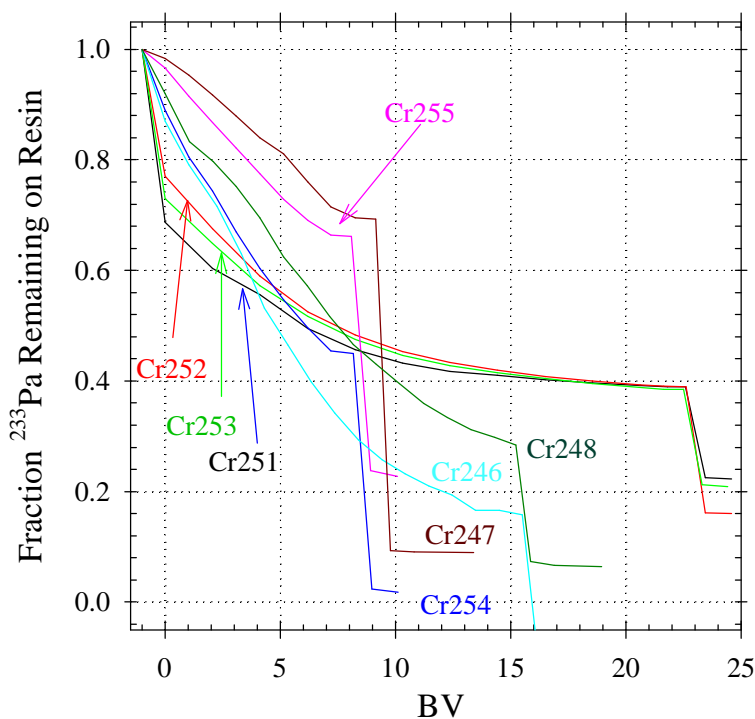
The capacity of the column for Np will depend on the quantity of resin that is actually loaded into the column. Over the course of this study, estimates on the resin volume have

ranged from 38.4 liters to 40.76 liters. The latest calculations by the facility are at the upper end of that range (20). However, these experiments were run with a column resin depth that was near the lower end of that range based on the guidance that was initially available (3, 10). The Np batch sizes from these experiments have been scaled to a full size column and resulted in column loadings ~1900 g Np (with an uncertainty of at least 10%). The material balance difficulties discussed earlier make the uncertainty in column loading somewhat high. Differences in the quantity of resin charged to the plant column will affect the Np capacity proportionally. However, any resin bed imperfection that could occur is likely to reduce the capacity of the column. Historically columns have been operated with significant excess capacity (nominally 50 to 100%) which allowed a tolerance for changes of the capacity of the resin over time. Fortunately, Reillex HPQ™ resin has been found to have significant tolerance for radiation damage without loss of Pu capacity (4, 5, 6, 7, and 8) and existing data support the same to be true for Np capacity (9).

While the data from this work appear to marginally support a 2 kg batch size with limited losses, it is not at all clear that the plant should expect the same result. There appears to be little to no extra margin for uncertainty. The desire to run a 2 kg batch size becomes less a technical decision than a process risk management decision. From a laboratory viewpoint, the batch size probably ought to be scaled back somewhat (~10% or more) to provide some allowance for the uncertainties such as bed packing, tailing, channeling and analytical uncertainty in the field. On the other hand from a production viewpoint, the laboratory work appears to show that a 2 kg anion exchange batch size for Np may work with little or limited (but possibly acceptable) losses. An acceptable position may be to operate at the larger batch size on a trial basis, monitoring the losses carefully to watch for developing problems. Loading/wash losses from the anion exchange process should be less than 1%. Higher losses probably indicate either that the column is being loaded past its capacity or is evidence of a valence adjustment problem. The problem will be how to fall back to a lower batch size in the middle of a campaign with high production goals.

Pa Rejection: Results on Pa removal have some value due to radiation dose issues. In theory, one of the primary reasons anion exchange is performed is to lower the ^{233}Pa content of the Np and to reduce radiation dose to personnel. In practice, the Pa chemistry is complex and the analytical results observed

Figure 16. ^{233}Pa Rejection during Reductive Wash Column Runs.



in this and past studies were quite variable. In a previous study, Kyser (9) observed Pa removal of 60 to 80% with 3 BV of decon wash. The larger volume of reductive wash solution in the current study should have increased the removal efficiency for Pa. However, only 30 to 80% of the Pa was removed by washing after 7 to 21 BV of wash volume (see Figure 16). Decay correction of the Pa counting data was not performed but the samples were counted within three to eight days of the column run and corrections do not appear to change the results significantly. In the current study, the reductive wash contains lower HNO_3 concentration, FS, and N_2H_4 that may be affecting the Pa valence chemistry. It is likely that the valence state of Pa is affecting the ability of the anion process to reject Pa to the raffinate stream, but no special effort has been made to study this possibility.

Factors that Control ^{238}Pu Rejection: Efforts were primarily focused on determining the effect of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio on the rejection of ^{238}Pu but other parameters are recognized to affect ^{238}Pu rejection as well. The HNO_3 concentration of 6.4 M was chosen based on past work as a compromise between being high enough to limit Np losses and retain Np capacity in the resin and yet being low enough to allow some Pu removal. The excess Fe^{2+} concentration of 0.05 M in the feed and 0.05 M in the reductive wash are not optimized. Those values were chosen based on past practices that had been observed to be effective. It is probable that increasing the Fe^{2+} concentration would improve the ^{238}Pu removal, but at the cost of addition issues with sulfate from degraded sulfamate. Past work by Thompson (14) and Thompson(15) on Np valence control in the HM Process showed that the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio controls the electrochemical potential (based on the Nernst equation).

Reducing normality measurements and $\text{Fe}^{2+}/\text{Fe}^{3+}$ measurements of the stock FS solutions could be employed to assure consistent ^{238}Pu rejection performance of the flowsheet. Lab analysis of the prepared reductive wash solution does not appear to have any value due to the time sensitive nature of the Fe^{2+} once it has been combined with HNO_3 . Only a quick, on-line or at-line measurement technique would be useful. Redox potential measurements were considered initially, but the presence of N_2H_4 in the solution dominates any electrochemical measurements. Although N_2H_4 lowers the potential, N_2H_4 is slow kinetically for the reduction of most metal ions such as Pu. Although the N_2H_4 does not help with the reduction, it does prevent electrochemical measurements of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ couple. Spectroscopic measurements of the UV-visible Fe^{2+} , Fe^{3+} absorbance spectra were also investigated, but they suffered from limited sensitivity and interference from HNO_3 . No viable option for post-preparation testing of the reductive wash has been identified. Procedural limitations on the preparation and storage of the reductive wash solution combined with FS quality controls appear to be the main preoperational controls that could be useful. Post-operational measurements on the ^{238}Pu content of the anion product solution and/or the NpO_2 product can be used to confirm successful performance of the ^{238}Pu removal in the wash if the measurement uncertainties are kept to a reasonable level.

Observed Improvements Due to Equipment Changes: This set of experiments continued the use of a Swagelok™ valve rather than a stopcock at the bottom of the column to reduce a flow dead zone. The heart cuts obtained during elution were ~60 g Np/L with < 2% losses to the head and tail cuts. In process terminology, this result is referred to as obtaining a high efficiency in producing Np product from the process. The hearts cuts varied from 1.3 to 1.7M HNO_3 (1.1M on Cr254 when the beginning of the hearts cut was missed). For some time, the facility has planned to produce 50 g Np/L product at 2 M HNO_3 . Past laboratory equipment/experiments did not achieve those results. If the production process can exceed the Np concentration goal, the solution can be adjusted with 64% HNO_3 to meet all of the concentration assumptions from the plant flowsheet. Alternately, a quantity of acid in the heads cut could be included in the hearts cut to increase the HNO_3 . However, there could be unrecognized aspects in the plant equipment that may limit product concentration to less than that observed in the laboratory.

Uncertainties: As previously stated, instantaneous flowrates in the current experiments occasionally varied widely from the targeted value, but adjustments were quickly made to keep the average flowrate within ~15% of the targeted value. Because resin loading was found to be only a weak function of flowrate in the earlier Pu study (8), the flowrate uncertainty probably contributes < 1% to the uncertainty in the loading results.

Measuring the resin bed depth to determine the volume of resin in the column is a relatively accurate measurement, but the resin beads pack into the bed unevenly and settle during the initial use. This uncertainty is estimated at ~2% based on observations of settling as the resin columns are loaded. As several runs were made with the same resin column, this uncertainty does not contribute to the variation in reproducibility between successive runs that use the same resin column.

Analytical measurement uncertainty is generally dominated by dilution errors. Typically, the dilution error, estimated as ~3% for this work, is a result of the equipment. Operator errors could easily cause a 30% or more error on an individual sample, but those errors would normally be recognized due to inconsistency and are rechecked.

A material balance was calculated for each run by taking the solution volumes and the analytical results from the feed, product and waste streams. Column runs had an overall material balance uncertainty of up to 17% for ^{237}Np compared with a historical norm of ~4%. Poor material balances for ^{233}Pa were

observed in the previous studies (9,10) and results in this study could only close the ^{233}Pa material balance to within 25% and all showed a loss of Pa. Solutions that should have been at secular equilibria between ^{237}Np and ^{233}Pa (^{237}Np and ^{233}Pa activities should be equal) often had 20-50% less ^{233}Pa . ^{233}Pa readily hydrolyzes and sticks to various surfaces even from 1-8 M HNO_3 . No correction was made for ^{233}Pa decay or ingrowth between anion exchange separation or ingrowth and gamma counting. In most cases, those analyses were performed within two to four days after separation. A delay in counting of four days would amount to ~10% ingrowth of ^{233}Pa .

Conclusions:

A series of laboratory column runs have been performed to demonstrate that significant rejection of ^{238}Pu can be obtained with a reductive wash step that maintains a minimum of 60% of the Fe as Fe^{2+} in the Np anion exchange process. In addition, experimental work has been performed that demonstrates that Fe^{2+} oxidation is controlled by the HNO_3 concentration and temperature. Based on these results, it has been shown that the preparation and storage of 6.4 M HNO_3 at less than 30°C results in the oxidation of 40% of the Fe^{2+} in ~6.5 hours. A 5°C reduction in temperature will double the shelf life of the reductive wash solution. On the other hand, a 2% increase in the HNO_3 concentration to 6.5 M will shorten the shelf life by almost 10%.

The Np losses during the loading/washing steps of this process can be less than 1%, while at the same time rejecting greater than 30% of the ^{238}Pu . Ultimately, Np losses will depend on the Np batch size and the HNO_3 concentration, while ^{238}Pu removal relies on the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio, the Fe^{2+} concentration, and all the parameters that affect the Fe^{2+} oxidation rate. A 2 kg Np batch size allows for little, if any, excess resin capacity in the anion exchange process and could easily result in higher Np losses. The flowsheet HNO_3 concentration is a compromise between Np losses and ^{238}Pu rejection. The following process conditions are recommended as a result of this study and previous experience:

- Load 1.8 to 2.0 kg of Np onto plant resin column “up-flow” from 6.4-8.0 M HNO_3 , 0.02 M N_2H_4 , 0.05 M excess FS, less than 15 mg Np/min/cm² flowrate.
- Reductive wash of 6 BV or more “up-flow” of 6.4 M HNO_3 , 0.050 M FS (0.030 M or 60% Fe^{2+} min.), 0.05 M N_2H_4 , less than 1.8 mL/min/cm² flowrate.
- Decontamination wash of 1-2 BV “up-flow” of 6.4-8.0 M HNO_3 to displace Np solution into resin and flush residual Fe from process equipment, less than 1.8 mL/min/cm² flowrate.
- Elute “down-flow” with 0.17 M HNO_3 , 0.05 M N_2H_4 , less than 1.8 ml/min/cm² flowrate.

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APPENDIX

Table IX. Results from Cr251 - 8 M Load, 6.8 M Reductive Wash.

Sample ID	ADS No.	Sample Volume mL	Column Volumes Eluted	Np237			Pu238		Acidity Free	Gamma Scan				APHA					
				Conc. g/L	g in Bottle	Loaded g	Conc mg/l	ug in Bottle		Np237 uCi/ml	Pa233 uCi/ml	Np237	Pu239	Pu238	Galpha dpm/ml				
Cr251	Feed	3-207549	553	5.7	10.70	5.92	5.92	4.43	2448	8.0	7.550	0.8%	5.855	0.5%	8.0%	1.0%	91%	1.85E+08	
Cr251	EC1	3-207550	734	7.6	0.015	0.011	5.91	0.003	2	8.0	0.011		1.378	0.7%	31.0%	4.0%	65%	1.83E+05	
Cr251	RW1	3-207551	200	2.1	0.005	0.001	5.91	0.022	4	6.4	0.003		1.366	0.7%	0.1%		100%	8.38E+05	
Cr251	RW2	3-207552	200	4.1	0.003	0.001	5.91	0.14	28	6.4	0.002		0.758	0.7%	0.1%		100%	5.41E+06	
Cr251	RW3	3-207553	200	6.2	0.006	0.001	5.90	0.71	142	6.4	0.004		0.993	0.7%	0.02%	1.0%	99%	2.72E+07	
Cr251	RW4	3-207554	200	8.2	0.019	0.004	5.90	1.09	219	6.4	0.014	4.9%	0.628	0.6%	0.1%		100%	4.16E+07	
Cr251	RW5	3-207555	200	10.3	0.044	0.009	5.89	1.46	292	6.4	0.031	3.2%	0.393	0.6%	0.1%		100%	5.55E+07	
Cr251	RW6	3-207556	200	12.4	0.076	0.015	5.88	1.79	359	6.4	0.054	2.2%	0.233	0.6%	0.2%	0.0%	100%	6.82E+07	
Cr251	RW7	3-207557	200	14.4	0.112	0.022	5.85	1.54	308	6.4	0.079	1.7%	0.121	0.7%	0.5%	0.5%	100%	5.85E+07	
Cr251	RW8	3-207560	200	16.5	0.135	0.027	5.83	1.33	267	6.4	0.095	1.4%	0.119	0.6%	0.5%	0.5%	99%	5.12E+07	
Cr251	RW9	3-207559	200	18.6	0.159	0.032	5.80	1.00	200	6.4	0.112	1.3%	0.100	0.7%	1.0%	0.5%	99%	3.85E+07	
Cr251	RW10	3-207558	200	20.6	0.172	0.034	5.76	0.73	145	6.4	0.122	1.4%	0.074	0.8%	0.5%	0.5%	99%	2.79E+07	
Cr251	DW2	3-207561	115	21.8	0.173	0.020	5.74	0.24	27	8.0	0.122	1.2%	0.062	0.7%	3.0%		97%	9.24E+06	
Cr251	Disp	3-207562	76	22.6	0.028	0.002	5.74	0.11	9	4.0	0.020	1.6%	0.006	1.5%	1.0%		99%	4.39E+06	
Cr251	PC1	3-207563/5	84	23.5	61.6	5.18	0.56	3.70	311	1.3	43.473	0.5%	6.348	0.5%	38.0%	1.0%	62%	2.27E+08	
Cr251	PC2	3-207564	110	24.6	0.513	0.056	0.51	0.032	4	0.2	0.362	0.8%	0.060	0.7%	34.0%		64%	1.93E+06	
Mat'l Balance						5.41	91.4%	of feed											
						60.98	g/l resin	Losses	0.18	g Np	2.99%	0.19%							
						53.97	g/l resin	5.24											

Table X. Results from Cr252 - 8 M Load, 6.4 M Reductive Wash.

Sample ID	ADS No.	Sample Volume mL	Column Volumes Eluted	Np237			Pu238		Acidity Free	Gamma Scan				APHA					
				Conc. g/L	g in Bottle	Loaded g	Conc mg/l	ug in Bottle		Np237 uCi/ml	Pa233 uCi/ml	Np237	Pu239	Pu238	Galpha dpm/ml				
Cr252	Feed	3-207591	553	5.7	9.88	5.46	5.46	4.23	2341	8	6.97	0.6%	5.59	0.5%	8%	0.4%	92%	1.75E+08	
Cr252	EC1	3-207592	760	7.8	0.022	0.017	5.45	0.001	1	8	0.016	6.2%	0.94	0.5%	66%		34%	1.48E+05	
Cr252	RW1	3-207593	200	2.1	0.004	0.001	5.45	0.065	13	6.8	0.003		1.46	0.7%	0.1%		100%	2.46E+06	
Cr252	RW2	3-207594	200	4.1	0.004	0.001	5.45	0.450	90	6.8	0.003		1.33	0.7%		0.4%	100%	1.71E+07	
Cr252	RW3	3-207595	200	6.2	0.021	0.004	5.44	1.01	201	6.8	0.015	7.0%	0.99	0.5%	0.1%		100%	3.83E+07	
Cr252	RW4	3-207596	200	8.2	0.062	0.012	5.43	1.64	329	6.8	0.044	3.3%	0.65	0.6%	0.1%		100%	6.25E+07	
Cr252	RW5	3-207597	200	10.3	0.109	0.022	5.41	2.01	402	6.8	0.077	2.4%	0.46	0.6%	0.4%	0.4%	100%	7.64E+07	
Cr252	RW6	3-207598	200	12.4	0.140	0.028	5.38	1.61	322	6.8	0.099	1.9%	0.31	0.6%	1%	1%	99%	6.19E+07	
Cr252	RW7	3-207599	200	14.4	0.180	0.036	5.34	1.26	252	6.8	0.127	1.5%	0.21	0.6%	1%	1%	99%	4.84E+07	
Cr252	RW8	3-207600	200	16.5	0.197	0.039	5.30	0.91	182	6.8	0.139	1.4%	0.175	0.6%	1%	1%	98%	3.53E+07	
Cr252	RW9	3-207601	200	18.6	0.212	0.042	5.26	0.59	117	6.8	0.150	1.4%	0.130	0.7%	1%	1%	98%	2.28E+07	
Cr252	RW10	3-207602	200	20.6	0.230	0.046	5.22	0.38	76	6.8	0.162	1.3%	0.103	0.7%	2%		98%	1.47E+07	
Cr252	DW2	3-207603	100	21.6	0.255	0.025	5.19	0.13	13	8	0.180	1.2%	0.092	0.7%	6%	6%	88%	5.62E+06	
Cr252	Disp	3-207604	92	22.6	0.059	0.005	5.18	0.036	3	4	0.042	1.5%	0.014	1.2%	6%	0.4%	94%	1.44E+06	
Cr252	PC1	3-207605/7	83	23.5	59.61	4.95	0.24	1.32	110	1.3	42.05	0.8%	8.51	0.7%	63%	0%	37%	1.36E+08	
Cr252	PC2	3-207606	110	24.6	0.45	0.049	0.19	0.014	2	0.17	0.315	0.9%	0.044	0.8%	52%	0.4%	48%	1.12E+06	
Mat'l Balance						5.28	96.6%	of feed											
						60.98	g/l resin	Losses	0.27	g Np	5.02%	0.31%							
						53.97	g/l resin	5.00											

Table XI. Results from Cr253 - 8 M Load, 6.0 M Reductive Wash.

Sample ID	ADS No.	Sample Volume mL	Column Volumes Eluted	Np237			Pu238		Acidity Free	Gamma Scan				APHA				
				Conc. g/L	g in Bottle	Loaded g	Conc mg/l	ug in Bottle		Np237 uCi/ml	Pa233 uCi/ml	Np237	Pu239	Pu238	Galpha dpm/ml			
Cr253	Feed	3-207608	553	5.7	9.85	5.45	5.45	4.23	2341	8	6.95	0.7%	5.93	0.5%	8%	0.4%	92%	1.75E+08
Cr253	EC1	3-207609	753	7.8	0.027	0.021	5.43	0.001	1	8	0.019	5.4%	1.18	0.5%	62%		38%	1.40E+05
Cr253	RW1	3-207610	200	2.1	0.003	0.001	5.43	0.152	30	6.0	0.002	0.0%	1.32	0.7%	0.5%		100%	5.80E+06
Cr253	RW2	3-207611	200	4.1	0.019	0.004	5.42	0.82	164	6.0	0.013	6.5%	1.25	0.5%	0.5%		100%	3.11E+07
Cr253	RW3	3-207612	200	6.2	0.071	0.014	5.41	1.53	307	6.0	0.050	3.2%	0.93	0.5%	0.5%		100%	5.83E+07
Cr253	RW4	3-207613	200	8.2	0.140	0.028	5.38	2.27	453	6.0	0.099	2.3%	0.68	0.5%	0.5%	0.5%	99%	8.71E+07
Cr253	RW5	3-207614	200	10.3	0.188	0.038	5.34	2.08	416	6.0	0.132	1.8%	0.47	0.6%	1.0%		99%	7.99E+07
Cr253	RW6	3-207615	200	12.4	0.240	0.048	5.30	1.63	327	6.0	0.169	1.5%	0.31	0.6%	1.0%	0.5%	99%	6.28E+07
Cr253	RW7	3-207616	200	14.4	0.252	0.050	5.25	1.16	233	6.0	0.178	1.4%	0.20	0.6%	1.0%	0.1%	99%	4.47E+07
Cr253	RW8	3-207617	200	16.5	0.274	0.055	5.19	0.66	131	6.0	0.193	1.3%	0.171	0.6%	1.0%	1.0%	98%	2.55E+07
Cr253	RW9	3-207618	200	18.6	0.286	0.057	5.13	0.386	77	6.0	0.201	1.3%	0.143	0.7%	3%	1.0%	96%	1.53E+07
Cr253	RW10	3-207619	200	20.6	0.270	0.054	5.08	0.166	33	6.0	0.190	1.3%	0.124	0.7%	6%	1.0%	93%	6.80E+06
Cr253	DW2	3-207620	100	21.6	0.305	0.031	5.05	0.068	7	8.0	0.215	1.3%	0.108	0.7%	14%	4%	83%	3.10E+06
Cr253	Disp	3-207621	84	22.5	0.046	0.004	5.05	0.017	1	4	0.032	1.6%	0.014	1.3%	8%	0.4%	92%	7.00E+05
Cr253	PC1	3-207622/4	76	23.3	53.60	4.07	0.97	1.06	81	1.4	37.81	0.8%	7.45	0.7%	68%	1.0%	31%	1.30E+08
Cr253	PC2	3-207623	110	24.4	0.480	0.053	0.92	0.013	1	0.17	0.339	1.0%	0.090	0.8%	57%		43%	1.13E+06
Mat'l Balance						4.53	83.1%	of feed										
				60.98	g/l resin	Losses	0.40	g Np	7.33%	0.38%								
				53.97	g/l resin		4.13											

Table XII. Results from Cr254 - 8 M Load, 6.4 M, 50% Fe²⁺ Reductive Wash.

Sample ID	ADS No.	Sample Volume mL	Column Volumes Eluted	Np237			Pu238		Acidity Free	Gamma Scan				APHA				
				Conc. g/L	g in Bottle	Loaded g	Conc mg/l	ug in Bottle		Np237 uCi/ml	Pa233 uCi/ml	Np237	Pu239	Pu238	Galpha dpm/ml			
Cr254	Feed	3-208053	519	5.4	10.33	5.36	5.364	4.23	2195	8	7.291	0.7%	5.0152	0.5%	7%	93%	1.73E+08	
Cr254	EC1	3-208054	519	5.4	0.004	0.002	5.361	0.002	1	8	0.003		0.5517	0.6%	20%	80%	7.93E+04	
Cr254	RW1	3-208055	100	1.0	0.005	0.000	5.361	0.037	4	6.4	0.003		2.2156	0.7%	0.1%	100%	1.40E+06	
Cr254	RW2	3-208056	100	2.1	0.004	0.000	5.361	0.689	69	6.4	0.003		1.5741	0.7%	0.1%	100%	2.62E+07	
Cr254	RW3	3-208057	100	3.1	0.004	0.000	5.36	1.309	131	6.4	0.003		1.9354	0.7%	0.1%	1%	99%	5.03E+07
Cr254	RW4	3-208058	100	4.1	0.006	0.001	5.36	1.278	128	6.4	0.004		1.7333	0.7%	0.1%	1%	99%	4.91E+07
Cr254	RW5	3-208059	100	5.2	0.005	0.000	5.359	0.873	87	6.4	0.003		1.476	0.7%	0.1%	100%	3.32E+07	
Cr254	RW6	3-208060	100	6.2	0.011	0.001	5.358	0.915	92	6.4	0.007		1.3143	0.7%	1.0%	2%	97%	3.59E+07
Cr254	DW	3-208061	100	7.2	0.016	0.002	5.356	0.691	69	8	0.011	7.5%	1.0945	0.5%		100%	2.63E+07	
Cr254	Disp	3-208062	94	8.2	1.375	0.129	5.227	0.917	86	4	0.97	0.8%	0.1264	0.7%	5%	95%	3.67E+07	
Cr254	PC1	3-208063/5	77	9.0	60.37	4.65	0.579	20.32	1565	1.1	42.59	0.5%	14.386	0.5%	10%	90%	8.59E+08	
Cr254	PC2	3-208064	110	10.1	0.57	0.063	0.516	0.228	25	0.2	0.402	1.1%	0.1372	0.7%	9%	91%	9.51E+06	
Mat'l Balance						4.85	90.4%	of feed										
				60.98	g/l resin	Losses	0.01	g Np	0.14%	0.04%								
				53.97	g/l resin		4.84											

Table XIII. Results from Cr255 - 8 M Load, 6.4 M, 60% Fe²⁺ Reductive Wash.

Sample ID	ADS No.	Sample Volume mL	Column Volumes Eluted	Np237			Pu238		Acidity Free	Gamma Scan				APHA				
				Conc. g/L	g in Bottle	Loaded g	Conc mg/l	ug in Bottle		Np237 uCi/ml	Pa233 uCi/ml	Np237	Pu239	Pu238	Galpha dpm/ml			
Cr255	Feed	3-208066	492	5.1	11.26	5.538	5.538	4.934	2428	8	7.941	0.6%	6.3391	0.5%	8%	0.1%	92%	2.04E+08
Cr255	EC1	3-208067	492	5.1	0.189	0.093	5.445	0.003	1.596	8	0.134	1.5%	0.214	0.7%	67%		33%	3.74E+05
Cr255	RW1	3-208068	100	1.0	0.459	0.046	5.399	0.009	0.864	6.4	0.324	1.8%	1.6047	0.5%	73%	3%	24%	1.37E+06
Cr255	RW2	3-208069	100	2.1	0.101	0.01	5.389	0.466	46.59	6.4	0.071	3.0%	1.4582	0.5%	1%	0.1%	99%	1.79E+07
Cr255	RW3	3-208070	100	3.1	0.009	9E-04	5.388	1.45	145	6.4	0.006		1.4529	0.7%	0.5%	0.5%	99%	5.57E+07
Cr255	RW4	3-208071	100	4.1	0.008	8E-04	5.388	1.859	185.9	6.4	0.006		1.4287	0.7%	0.1%		100%	7.07E+07
Cr255	RW5	3-208072	100	5.2	0.007	7E-04	5.387	2.051	205.1	6.4	0.005		1.4695	0.7%	0.01%	0.1%	100%	7.80E+07
Cr255	RW6	3-208073	100	6.2	0.01	0.001	5.386	2.087	208.7	6.4	0.007		1.1736	0.7%	0.5%	0.5%	99%	8.02E+07
Cr255	DW	3-208074	100	7.2	0.014	0.001	5.384	1.945	194.5	8	0.01	7.0%	0.8328	0.5%	0.1%	0.1%	100%	7.40E+07
Cr255	Disp	3-208075	85	8.1	0.175	0.015	5.37	0.474	40.26	4	0.123	1.4%	0.0781	0.8%	1%		99%	1.82E+07
Cr255	PC1	3-208076/8	82	8.9	55.75	4.572	0.798	15.94	1307	1.5	39.33	0.6%	16.156	0.5%	12%		88%	6.89E+08
Cr255	PC2	3-208077	110	10.1	0.459	0.05	0.747	0.065	7.128	0.2	0.324	1.3%	0.2656	0.6%	21%		79%	3.12E+06
Mat'l Balance						4.79	86.5%	of feed										
				60.98	g/l resin	Losses	0.15	g Np	2.78%	1.68%								
				53.97	g/l resin		4.64											