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Removal of Pu^{238} From Neptunium Solution By Anion Exchange

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Dec 2003

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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 Technology Center: 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 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 flowing through the resin bed to either absorb the Np or wash impurities from the 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 complexant in an attempt to determine hydrolyze 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 HNO_3 contained within the resin bed and column from the loading/wash steps and contains minimal Np at 4 to 6 M HNO_3.

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.

HLW - (High Level Waste) Liquid waste containing actinides that will be transferred to the tank farm

HN_3 – Hydrazoic acid: Reaction product from hydrazine and nitrous acid.

HNO_2 – Nitrous acid

HNO_3 – 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 HNO_3 containing Np is passed through the resin bed to absorb the Np onto the resin.

N_2H_4 – Hydrazine: purchased as hydrazine mono-nitrate that is commonly prepared by neutralizing the strongly basic hydrazine mono-hydrate with HNO_3.

NaI – Sodium Iodide: Type of detector used to measure holdup by gamma rays.

$NaNO_3$ – Sodium nitrate

Q – Volumetric flowrate

Raffinate – Solution that is discharged from the column after flowing through the resin bed to absorb the Np

SO_4^{2-} - Sulfate ion: Reaction product from sulfamate in the ferrous sulfamate.

SRTC–Savannah River Technology Center:

Tails Cut – Last portion of elution step that contains dilute HNO_3 and minimal Np. May be 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 tritrate both 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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December 2003

Summary:

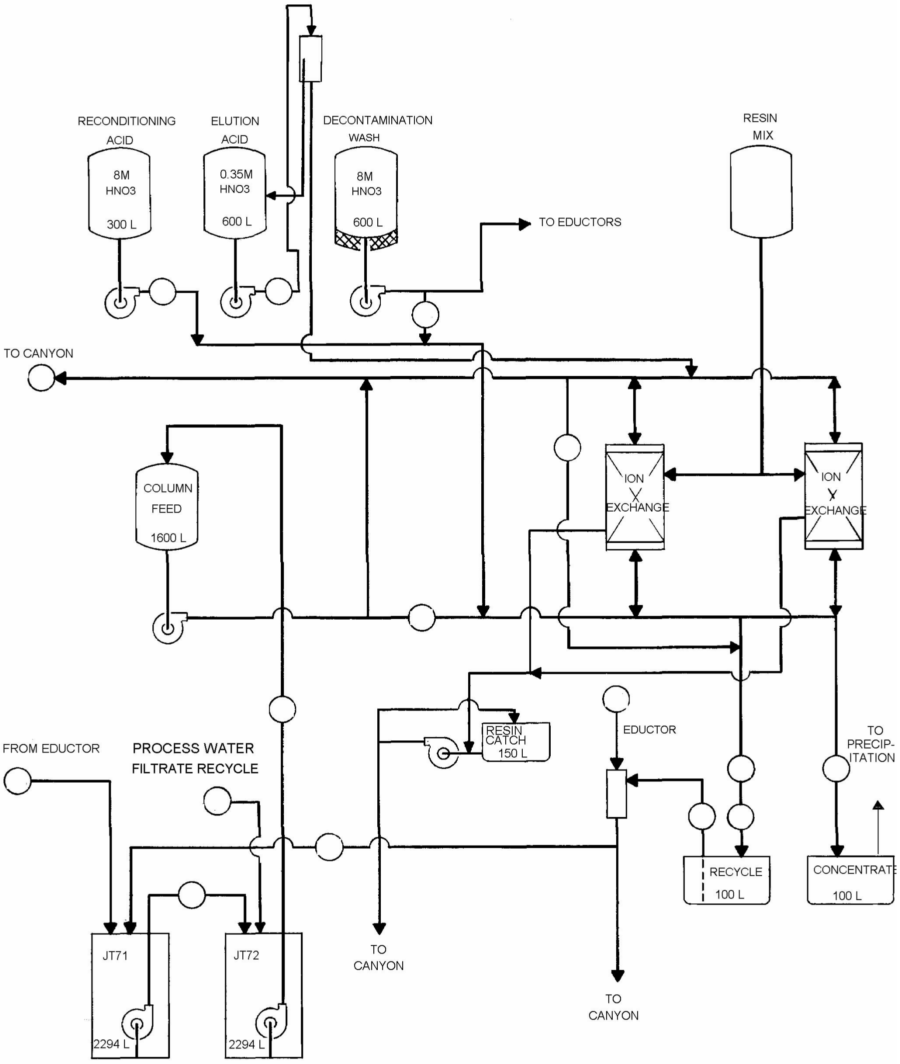
A new anion flowsheet for use in HB-Line was tested in the lab with Reillex™ HPQ for removal of Pu^{238} contamination from Np. Significant rejection of Pu^{238} was observed by washing with 6 to 12 bed volumes (BV) of reductive wash containing reduced nitric acid concentration along with both ferrous sulfamate (FS) and hydrazine. A shortened-height column was utilized in these tests to match changes in the plant equipment. Lab experiments scaled to plant batch sizes of 1500 to 2200 g Np were observed with modest losses for up-flow washing. Down-flow washing was observed to have high losses. The following are recommended conditions for removing Pu^{238} from Np solutions by anion exchange in HB-Line.

- Feed conditions: Up-flow 6.4-8 M HNO_3, 0.02 M hydrazine, 0.05 M excess FS, less than 5 days storage of solution after FS addition.
- Reductive Wash conditions: Up-flow 6-12 BV of 6.4 M HNO_3, 0.05 M FS, 0.05 M hydrazine. 1.8 $mL/min/cm^2$ flowrate.
- Decontamination Wash conditions: Up-flow 1-2 BV of 6.4-8 M HNO_3, no FS, no hydrazine.
- Elution conditions: Down-flow 0.17 M HNO_3, 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 are shown in Figure 1.

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



Np solution will be received from H-Canyon as a moderately concentrated Np nitrate solution (15-20 g Np/L, 1.6-5 M HNO_3). Valence state and acid concentration will be adjusted in a feed adjustment tank (JT72) via the addition of FS, N_2H_4 and 64% HNO_3.solutions. In the past, Np valence adjustment was performed by adding sufficient FS and N_2H_4 to make the solution 0.05 M FS and 0.02 M N_2H_4. The FS was added to reduce all Np $^{5+, 6+}$ to Np^{4+} and all Pu $^{4+, 5+, 6+}$ to Pu $^{3+}$. Np $^{4+}$ 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 will produce sufficient HNO_2 to oxidize both the Fe^{2+} and Pu^{3+} after several days to several weeks. N_2H_4 is added to react with HNO_2 produced via radiolysis and to protect the Fe^{2+} and Np^{4+} from oxidation. During past Pu processing, either a nitrite addition step or a "heat-kill" step was included to rapidly oxidize the Pu^{3+} to the

Table I. Comparison of SRTC Conditions to HB-Line Standard Flowsheet (6,7,15)

	Recon-dition	Feed		Partition Wash	Decon Wash	Elution	
		High	Low				
Flow, l/batch	45	286	1000	100	0	90	
Np (g/batch)		2000	2000	1	1.4		
Np (g/l)		7	2	0.01	0.01		
HNO3 (M)	8	8	8	8	8	0.17	Assumptions
HB-Line	up	up	up	up		down	Col ID 14.75 in Column area = 1102 cm^2
Flow (l/min)	5	2.3	8	2.2		1.6	Resin Bed Height 15 in
v ($ml/min/cm^2$)	4.5	2.1	7.3	2.0		1.5	Resin Bed Volume 45 L
Volume (l)	45	286	1000	100		90	Volumes from Flowsheet
Time (min)	9	125	125	45		56	
BV	1.0	6	22	2.2	0.0	2.0	
mgs $Np/min/cm^2$		15	15				Assume 2 g Np/l & 7 g Np/l
SRTC Np	up	up	up	up	up	down	Col ID 19 mm Column area = 2.835 cm^2
Flow (ml/min)	5	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	1.8	Resin Bed Height 13.5 in (34.2 cm)
Volume (ml)	100	570	1000	1200	200	250	397 resin ratio
Time (min)	20	114	200	240	40	50	389 area ratio
BV	1	6	10	12	2	3	
mgs $Np/min/cm^2$		16	9				9 & 5 g Np/l in Feed

absorbable Pu^{4+} valence state. For Np, a "heat-kill" that oxidized the Pu^{3+} and Fe^{2+} but did not destroy all the sulfamate was used to produce a Np^{4+} and Pu^{4+} feed solution. In the current Np process, Np^{4+} is the preferred element and it is desirable to reject Pu to the raffinate stream. However in high nitrate solution, Pu^{3+} tends to oxidize to the Pu^{4+} valence state, which loads onto anion exchange resin more strongly than Np^{4+}. In the historical process for Np purification, the nitrate concentration was lowered to 5.4-6.5 M HNO_3 in the presence of FS during the wash step, to suppress the formation of the absorbable $Pu(NO_3)_6^{2-}$ 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 HNO_3 passed through the piping and the bed to flush dilute HNO_3 from the system. The adjusted feed will be transferred from the receipt/feed adjustment tanks to a column feed tank. The feed solution will then be pumped up-flow through the column, absorbing the anionic $Np(NO_3)_6^{2-}$ complex as it passes through 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. This step displaces the residual feed solution into the resin bed where the remaining Np will absorb. It also provides improved decontamination from impurities by displacing residual impure solution from the column and piping prior to elution. In the historical flowsheet, a partitioning wash was used to wash out additional Pu^{238} cross-contamination. This partitioning 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 Pu^{238} removal was desired. 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. The NaI detectors on the process equipment and streams that were used for Pu processing will not be used for Np processing. Interference from the Pa^{233} daughter from Np^{237} decay and partial separation of the Pa from the Np will make use of those detectors 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 Lab 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 (Ref 1,2,3). 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 loading for Pu and its excellent elution behavior (2). In 2000, Crooks (4) and Kyser (5) studied the loading of the current version of Reillex™ HPQ for use in the Pu columns in HB-Line.

Table II. Capacity of Reillex™ HPQ for Np.

$[HNO_3]$	Resin Loading			Np Losses
Feed	Breakthru	Saturation	Loaded	
M	gms Np / liter resin			% of Feed
6.4	~40	74		na
6.4	44	76		0.4
6.4			46	0.14
7.6	71	80		0.2
7.4			61	3.2
5.7	36		45	0.3
8.2			51	0.5

In a previous study, Kyser (13) measured the capacity of Reillex™ HPQ for Np under various process conditions (see Table II). From ~6 M HNO_3, 40 g Np/L was loaded prior to breakthrough, with a saturation capacity of 75 g Np/L. When the HNO_3 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 N_2H_4 in the feed for the HB-Line flowsheet were set to 0.02 M N_2H_4 and 0.05 M FS. As a part of that study, Pu^{238} removal was investigated, but ultimately that effort was abandoned due to a perceived lack of need. Late in the preparations for the Np program, additional justification for removal of Pu^{238} has been recognized. A request was made to rapidly develop a new flowsheet to accomplish a 30 percent Pu^{238} removal via reductive washing (sometimes referred to as partition). Based on Kyser's work (13) and earlier report by Burney (14), two approaches were proposed. The first approach was to wash with a significant volume of 6.4 M HNO_3 -0.05 M FS -0.05 M N_2H_4. The second approach was to attempt improve upon the first approach by loading from 6.4 M HNO_3 -0.05 M FS -0.02 M N_2H_4. This "reductive load" method was recognized to be a time sensitive step in keeping the Pu^{3+} in a reduced valence state to prevent it from loading onto the resin sites. Yet a third approach was suggested in which the flow direction of the wash flow was countercurrent (down-flow) to the load (up-flow). This method was based on the idea that Pu might be absorbed in the lower part of the column and might be more quickly removed by a down-flow wash. The recognized deficiency with this down-flow wash idea was that with the bottom of the resin bed saturated with Np, Np losses to the wash step would be increased.

Figure 2. Assembled Column

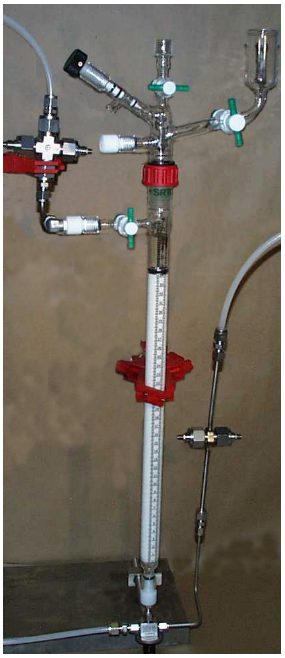


Figure 3. Screen used to Retain Resin Bed.

Experimental Column Operation

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, $mL/min/cm^2 \equiv cm/min$) 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. Lower flowrates would also tend to increase the effective loading by increasing the time for mass transfer. The baseline flowsheet (6,7,13) feed rate was based on 14.5 $mg/min/cm^2$. Hill (9) recommended a loading rate of 5-10 mg/min/cm^2, which is somewhat lower than the baseline rate. Table I shows a comparison between the baseline design flowsheet and current SRTC test conditions.

The original columns were designed for operation with a 15.5 in 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 in (39.05 liters) and 13.86 in (40.13 liters) respectively (15). 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 in) resin depth. For these experiments, a resin volume of 97 cm^3 of settled resin was used in a 19 mm ID 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 (13), no resin pretreatment was performed to treat the low temperature exotherm. All resin that was tested came from the same 1998 manufacturer's lot (#80302MA) that was purchased by SRTC 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).

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

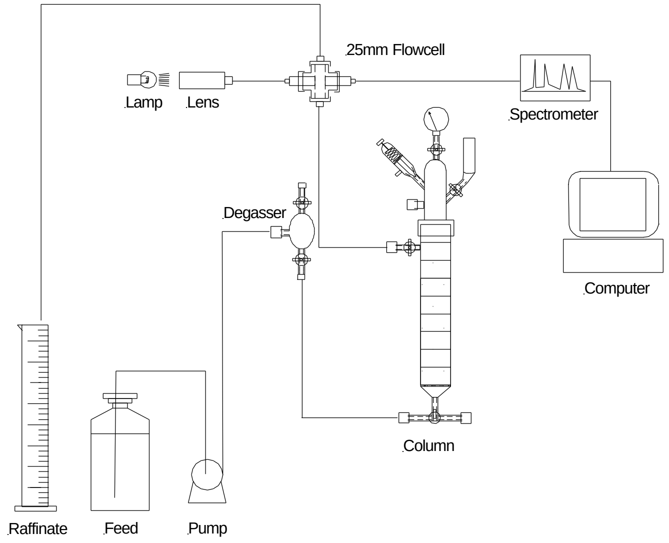
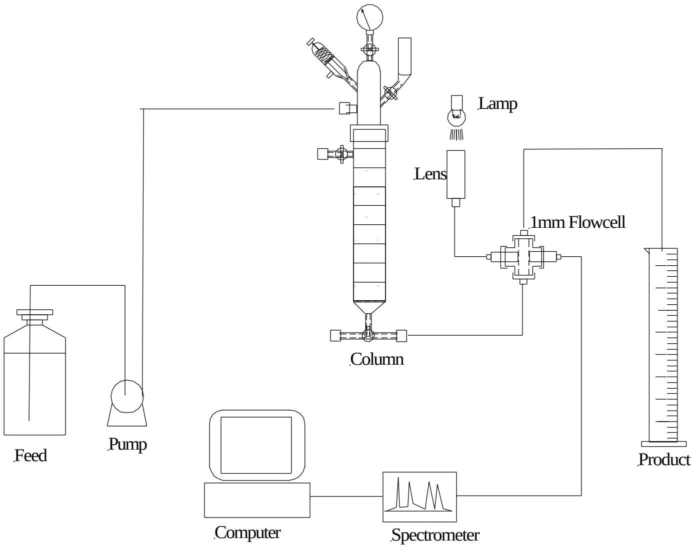


Figure 5. Elution Experimental Setup.



Column Preparation: A sufficient quantity of resin was converted into the nitrate form prior to loading the column. The resin was loaded by slurrying the resin into the column with 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 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 allow channeling to occur.

Lab Equipment: A picture of a column is shown in Figure 3. The column utilized #7 Teflon™ bushings for connecting ¼ 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 headpiece. 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 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 Swaglock™ 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 ½ inch Swaglock™ cross and two ½ inch optic lenses were used to fabricate a flowcell with a 25.4 mm pathlength 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 ½ inch Swaglock™ union and milling out the union to allow two ½ in 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 any 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 fibers 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.

Figure 6. 1 mm Flowcell

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 MTLL-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 Attentuator 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

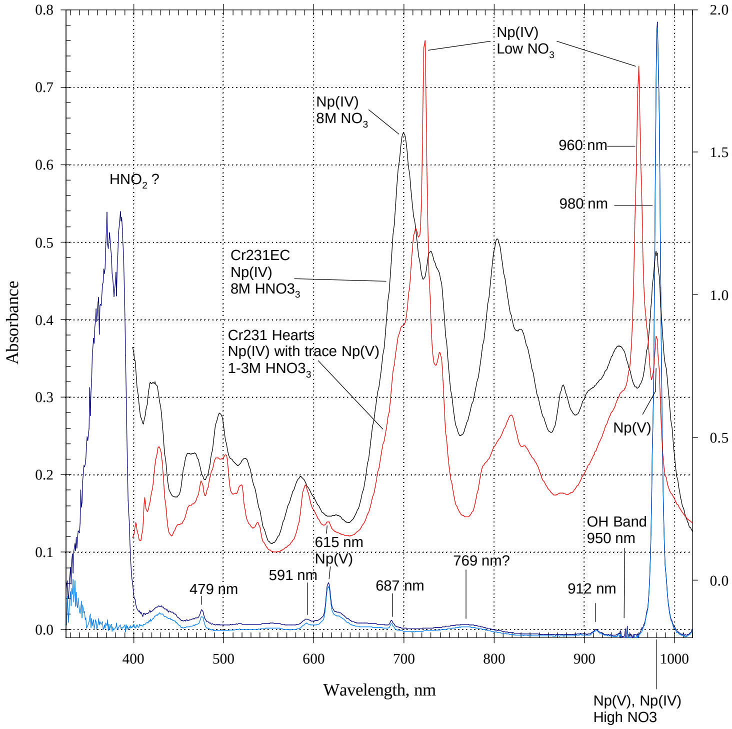
Feedstock Preparation and Valence Adjustment: Np solution was prepared as a feedstock by adjusting to 6.4 to 8 M HNO_3 and performing a valence adjustment with N_2H_4 and FS. Normally N_2H_4 was added first (in order to scavenge any residual HNO_2). Then sufficient FS was added to make the solution 0.05 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 (8). Due to the reduced alpha activity in the Np feed solutions, Fe^{2+} is expected to persist for longer periods. 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 $[SO_4^{2-}]$ 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 (10). 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 buildup of $[SO_4^{2-}]$ is inevitable and may have a negative effect on resin capacity. In the current study, the FS was always added just prior to the start of the column run (within 1 hour) in order to improve the opportunity to observe the removal of Pu during the feed step.

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 nitric acid 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 25mm 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 ±50% of the targeted value), but the average flowrate could generally be regulated within 15 percent 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 Pu^{238}, Pu^{239}, Np^{237} and Pa^{233}. Np^{237} (2.2e6 yr half-life) and Pa^{233} (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 Pa^{233}/Np^{237} activity ratio. When the Pa^{233}/Np^{237} activity ratio was greater than ~10, gamma counting was not able to provide good Np^{237} results due to interference from the Pa^{233}. When Pu^{238} activity was greater than 50 times the Np^{237} activity, the precision of the Np^{237} counting was also reduced. For samples with both high Pa^{233} and Pu^{238} activity levels relative to Np^{237}, no satisfactory means of determining the Np^{237} concentrations was available.

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

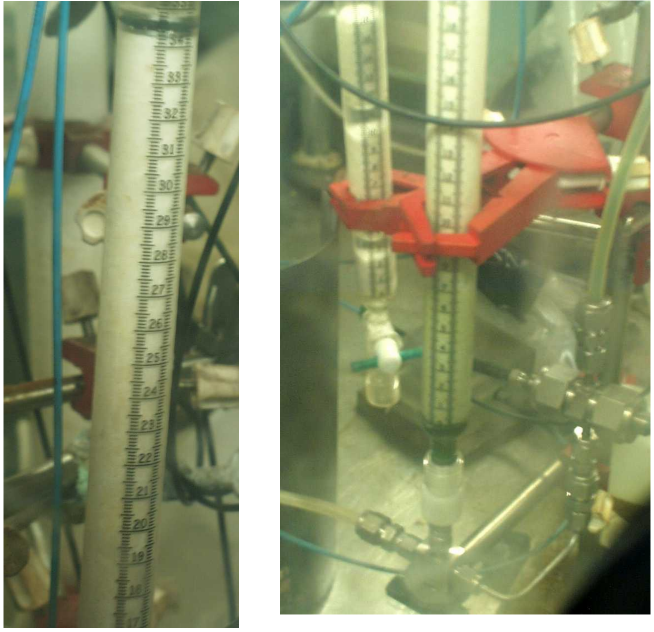


Calibration of Spectrophotometer: The absorbance spectra of Np solutions are highly dependent on acid concentration. Efforts to calibrate the spectrometer for Np^{4+} and/or Np^{5+} were too time consuming for the scope of this program. Instead, the spectrometer was used to provide qualitative results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

Literature references for Np absorbance spectra in HNO_3 are limited. Johnson and Shepard (11) measured spectra of $Np^{4+,\ 5+,\ 6+}$ in 1 to 10 M HNO_3. They found a strong nitrate dependence on the spectra between 5 and 10 M HNO_3. They also reported disproportionation of Np^{5+} above 3 M HNO_3. They also reported a strong acid dependence on 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 (12) reported Np spectra in up to 4 M HNO_3. They reported difficulty in obtaining pure Np(IV) in low HNO_3 due to oxidation to Np(V). They also observed no indication of Np(IV) hydrolysis at 0.1 M or greater [HNO_3]. Figure 7 shows Np^{4+} spectra in both low and high HNO_3 compared with reference Np^{5+} spectra (13). 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+} peaks has been used in past work to identify the presence of Np^{5+} in 8 M HNO_3 (13). No evidence of Np^{5+} was observed during the loading or washing steps of any of the experiments in the current study.

Figure 8. Np Columns During Load and Elution Steps.



a) Load

b) Elution

Results and Discussion:

A series of three column runs was performed with the 1998 batch of Reillex™ HPQ purchased for development of the 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. This method was used to calculate the loading of the resin. Detailed results from each of the column runs and some sample calculations for the individual runs are shown in the appendix as Tables VII, VIII and IX.

In Cr246, a 12BV reductive wash of the loaded Np was performed and the fraction of Pu^{238} removed was determined. In Cr247, the feed acid concentration was lowered in an attempt to prevent the Pu^{238} from loading on the resin and was followed by a 6BV reductive wash of the loaded Np. In Cr248, the reductive load step from Cr237 was repeated, but after performing a 1BV **up-flow** reductive wash, an 11BV **down-flow** reductive wash was performed. In all three experiments, a 2BV, 8 M HNO3 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.

Table IV. Process Parameters for the Reductive Wash Experiments.

		Cr246	Cr247	Cr248
Feed	FS, M	0.049	0.047	0.045
	N2H4, M	0.03	0.022	0.021
	HNO3, M	7.9	6.3	6.3
	Np, g/l	4.8	9.3	9.7
Wash	FS, M	0.06	0.046	0.046
	N2H4, M	0.05	0.05	0.05
	HNO3, M	6.4	6.4	6.4
	BV	12	6	12
Decon	HNO3, M	8	8	8
Wash	BV	2	2	2
Elution	N2H4, M	0.05	0.05	0.05
	HNO3, M	0.17	0.17	0.17
	BV	0.9	0.6	0.6

Table V. Summary of Results from the Reductive Wash Experiments.

	Cr246	Cr247	Cr248
Loading g Np/l	49.9	39.6	57.3
g Np/l	53.0	40.3	40.7
Load 38.4L Resin	1917	1521	2199
Product Conc	55.9	62.1	60.6
Loading Loss	0.07%	0.16%	0.11%
Wash Loss	2.8%	0.83%	24%
Heads Loss	0.25%	0.26%	0.59%
Tails Loss	2.0%	4.2%	2.7%
Np Matl Balance	12.6%	3.5%	-1.8%
Pu238 Matl Balance	-10.8%	-3.2%	1.8%
Np Prod Eff	104%	97%	68%
Feed Pu238 ppm	540	414	434
Product Pu238 ppm	49	191	69
Product Pu ppm	422	1227	543
Wash	Up-flow	Up-flow	Down-flow

A summary of results, which includes a material balance for each experiment, is included as Table V. Generally, calculations of the material balances for Np and Pu^{238} 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.

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 gray color on the lower 75 percent of the bed in Figure 8a. In Figure 8b, the dark green color of Np^{4+} solution appears in the bottom of the column and in the polyethylene line just above the 1 mm flowcell (right hand side of the photo).

The principal objective of this work was to demonstrate the capability of a modified process to reject Pu^{238} from Np^{237} 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.

Pu Rejection: The effectiveness of a reductive wash at removing Pu^{238} from Np is shown in Figure 9, a plot of the fraction of Pu^{238} remaining on the column during the wash and elution step for all three experiments. This fraction was determined by difference from the material balance for each column run. For ease of illustration in this and several later figures, the analyzed feed value was plotted at –1 BV and the feed raffinate value was plotted at 0 BV. A drop is seen for each run that corresponds to the elution of the hearts cut. For Cr246 and Cr248, where more Pu^{238} was removed by washing, this drop was smaller. Since the Pu^{238} material balance varied from –1.8 to 12.6 percent for the three runs, the final fraction for the runs did not end at zero.

Figure 9. Pu^{238} Rejection by Reductive Washing

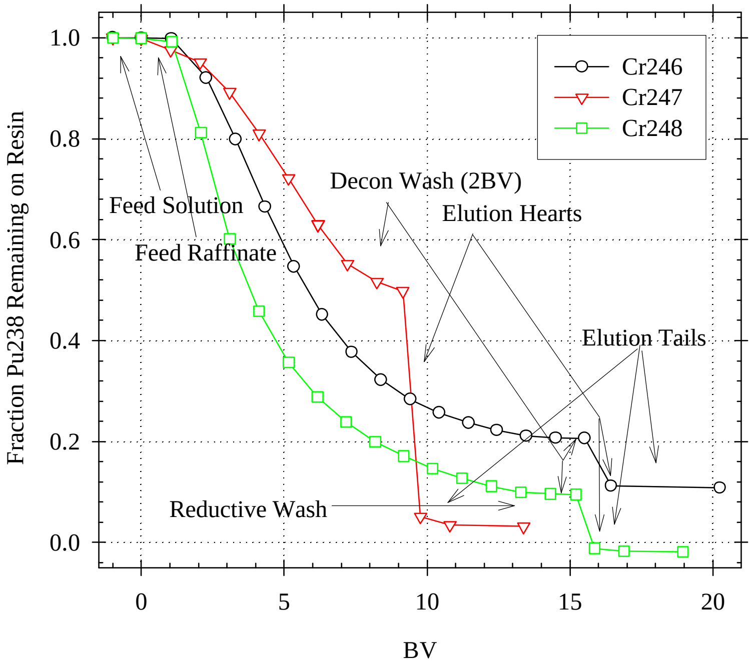
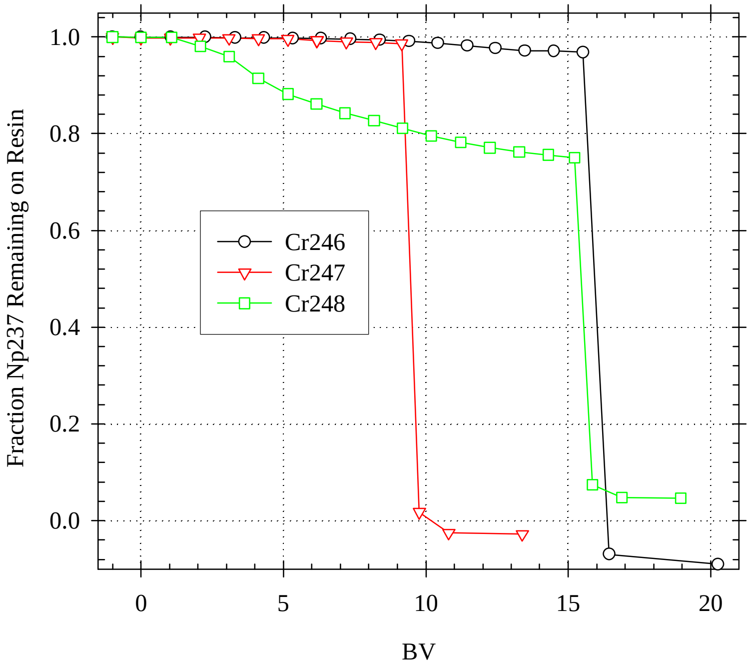


Figure 10. Np Retention during Reductive Washing.



The attempt to limit Pu^{238} absorption by performing a reductive load step in Cr247 and Cr248 did not appear to assist in the removal of Pu^{238}. This result has not been fully explained. It is suspected that the presence of Fe^{3+} from the original feed solution as well as Fe^{3+} from the oxidation of Fe^{2+} during the reduction of Np^{5+} affects the ability of FS to reduce the Pu^{238} from Pu^{4+} to Pu^{3+}. Increasing the FS concentration to 0.1 M excess or greater might allow a reductive load step to be more effective. However, it is also believed from previous studies that a reductive load step would be time sensitive due to the alpha dose from Pu^{238} and may not be practical in the plant equipment.

The reductive wash steps in Cr246 and Cr247 were essentially identical other than the total volume used. Since it appears that the reductive load was not effective in Cr247, it was surprising how much variation in Pu^{238} removal was observed between those two experiments. It was desired to perform more experiment(s) to investigate reproducibility but the schedule did not allow time for additional work. The up-flow reductive wash removed 35 to 55 percent of the Pu^{238} in 6 BV of wash solution in runs Cr246/7. The extra removal of Pu^{238} observed in Cr248 was not much of a surprise, however the large increase in Np losses makes this approach much less desirable.

In all three experiments, an increase in the total Pu was observed in the product at the same time as Pu^{238} was being removed. This result is attributed to the cross-contamination of the Np solutions as the work was being done and during sampling. The glovebox has a significant Pu history and when this work was performed, was still used to store concentrated Pu^{239} solutions. However, it was concluded that this problem did not significantly affect the Pu^{238} rejection that was measured. Cross contamination with Pu^{239} isotopically diluted the Pu^{238} that was being studied, but did not significantly increase the amount of Pu^{238} found in the feed solutions (on a Np basis). The raw 8.5 solution used in Cr247 and Cr248 is comparable in Pu^{238} content to that found in the characterization produced by CLAB.

Np Losses: The feed solution of Cr246 was 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 (13). However, significant losses during reductive washing had been expected due to the decrease in the resin capacity for Np that corresponds with the change from 8 M HNO_3 to 6.4 M HNO_3. The observed losses of 2.8 percent were lower than expected based the Np loading observed in previous work (13). Cr247 was performed prior to this result being available and thus it was only loaded to 40 g Np/L of resin (based on the measured resin capacity (13)). Cr247 losses were less than 1 percent. Cr248 was loaded to 57 g Np/L of resin for 6.4 M HNO_3 and loading losses were comparable with those observed from 8 M HNO_3 (losses during the wash step were not comparable due to the change to down-flow wash).

Figure 11. Spectra showing Np^{4+} Losses during Cr246.

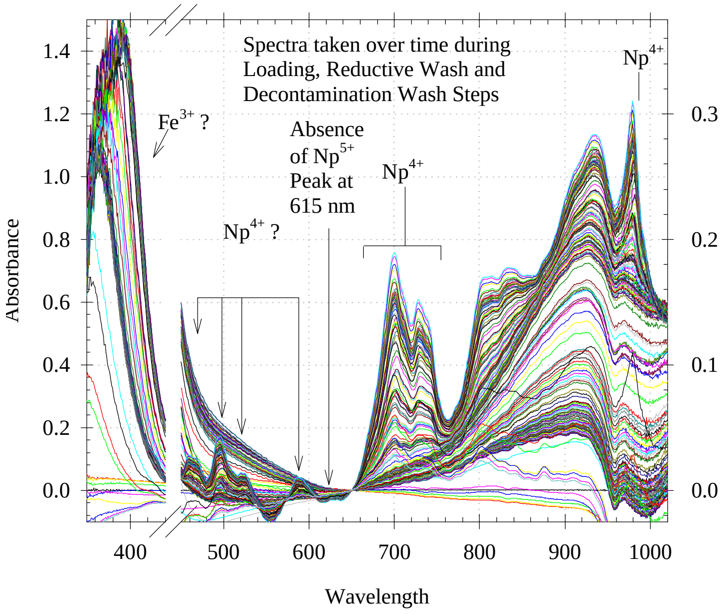
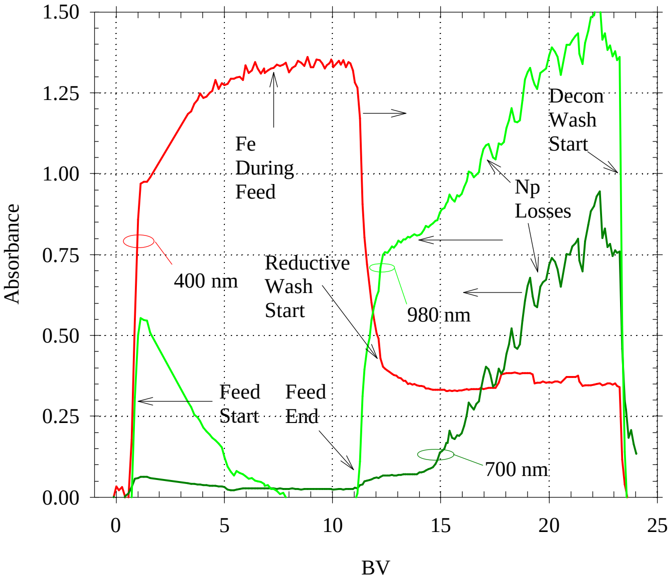


Figure 12. Fe and Np Profiles during Cr246 Load/Wash



The wash losses of Np are illustrated with the spectra from the load/wash steps in Figure 11. This figure shows the UV-Visible adsorption spectra of the column raffinate during the feed, reductive wash and decontamination wash steps. Successive spectra over time are plotted on the same graph in an attempt to show in ingrowth of Np during the course of the experiment. The increase in absorbance at 700 and 980 nm appears to be due to a gradual leaching of Np from the resin bed. Leaching was not observed to be significant until after ~ 7 BV into the reductive wash. Np losses are identifiable starting at ~ 15 BV in Figure 11 (which is ~4BV into the reductive wash). It appears that the Np may have migrated up the column during the reductive wash until was carried off the end of the resin bed. This was most likely due to the lowered capacity of the resin for Np due to the reduction in the HNO_3 concentration. Significant losses were not observed during the loading step of Cr248 (even though the Np loading was 10% higher than in Cr246 and the HNO_3 feed concentration was lowered from 8 M to 6.4 M). Since wash direction was changed in Cr248 and high losses were expected for that reason, little useful information can be determined about Np capacity from that experiment.

Specific wavelengths of the spectra from Cr246 from Figure 11 are plotted in Figure 12 as a function of BV. This figure shows absorption changes that correspond to Fe in the feed, the removal of the Fe by washing, the gradual increase in Np during the reductive wash and the dramatic drop in both Fe and Np when the Decon wash was started. It is suspected that Fe^{3+} is the dominant cause of the absorption between 350 and 450 nm, but Fe^{2+} also absorbs in a similar wavelength range. When the experiment transitions from feed raffinate to reductive wash a significant drop in absorption due to Fe^{3+} is observed. This observation may be explained by the oxidation of Fe^{2+} to Fe^{3+} from the reduction of Np^{5+} to Np^{4+} in the feed adjustment step. During the reductive wash step, a relatively small fraction of the Fe^{2+} is consumed by Pu reduction. Due to 0.02 M to 0.04 M Np^{5+} in the feed, a significant fraction of the total Fe in the feed solution may be Fe^{3+}. Fe^{3+} affects the reduction potential of the Fe^{2+} and this amount may explain the difficulty with rejecting Pu during the reductive load steps of Cr247 and Cr248. Measurement of the redox potential of real feed and wash solutions over time combined electrochemical calculations are desirable to confirm these suspicions, but could not be completed in the time frame of this study.

Initially there appeared to be a greater resin capacity for Np in the current study than in the original work (13). After some thought, it was recognized that the original resin capacity for Np was determined with a 5” tall resin column (see Table II). It must be recognized that at the point of loading breakthrough, the 5” 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 has been 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 plant process. Inspection of the raw data in the original breakthrough runs in reference 13 reveals that “double-batching” the load of Np past breakthrough resulted in 33-50 percent loss of the 2nd 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 VI shows an estimate on the capacity of the resin column with the assumption that the mass transfer front is limited to 5 inches of resin bed depth. This calculation uses the resin loading values determined in the earlier loading work (13) and suggests that the results of the two studies are not necessarily inconsistent.

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 (16). However, these experiments were run with a column resin depth that near the lower end of that range based on the guidance that was available at that time (15). The Np loadings from these experiments have been projected to a full size column and resulted in column loadings of 1900 g, 1500g, and 2200 g Np (with a potential uncertainty of 10%). Note that on Cr246 (1900 g scaled loading), the column started bleeding Np (confirmed as Np^{4+} by spectophotometric monitoring of the raffinate) during the long reductive wash. This result suggests that the column was loaded at or slightly above its Np capacity. If additional resin is loaded into the columns, it will increase the capacity slightly, but it will not invalidate this work. 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 (1,2,3,4,5) and existing data support the same to be true for Np capacity (13).

Table VI. 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*	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

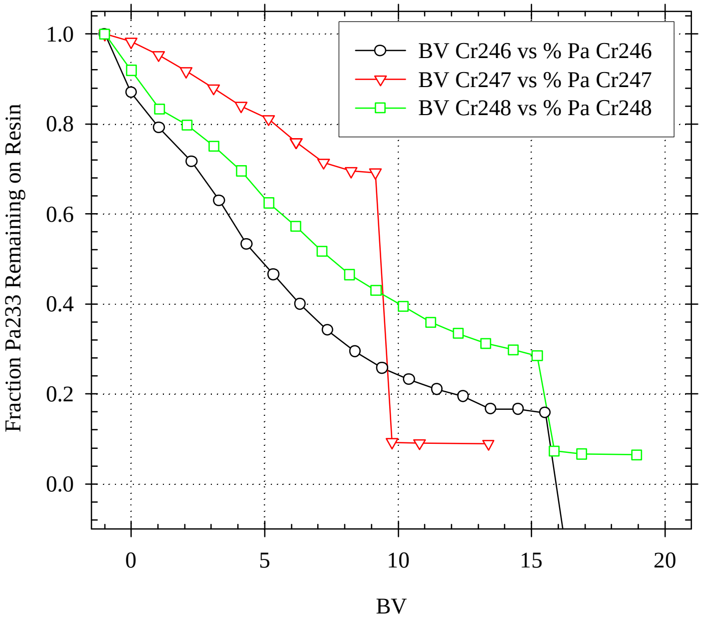
Assumptions:

[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.

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 management of risk 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. 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 percent. 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 if justified in the middle of campaign with high production goals.

Figure 13. Pa233 Removal during Reductive Washing.



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 Pa^{233} content of the Np and reduce radiation dose to personnel. In practice, the Pa chemistry is complex and the analytical results observed in this study were quite variable. In the previous study (13), Pa removal of 60 to 80 percent was observed with 3 BV of decon wash. The larger volume of reductive wash in the current study might be expected to increase the removal of Pa. Instead, 30 to 80 percent of the Pa was removed by washing after 9 to 15 BV of wash volume (see Figure 13). 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 acid concentration, FS, and hydrazine that may be affecting the Pa valence chemistry. It quite possible 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.

Figure 14. Pu^{238} and Pa^{233} Rejection during Washing.

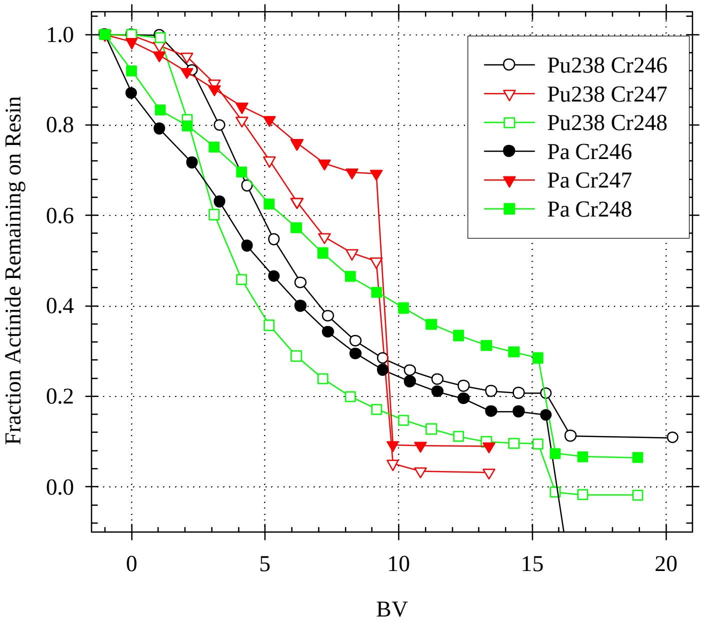


Figure 14 shows the Pa^{233} and Pu^{238} rejection for all three column runs. Cr247 resulted in a reduced ability to remove both Pa^{233} and Pu^{238} from the loaded resin bed. No cause for this result has been identified, but it suggests that Cr247 may not be a representative result.

Factors that Control Pu^{238} Rejection: This work was aimed at demonstrating what level of Pu^{238} rejection was possible using the existing equipment and the experiments were run to maximize the opportunity for success. Efforts were not made to determine the full effect of variables that may affect the rejection of Pu^{238}. 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. While this target value may not be optimal, if the reductive wash acidity is not carefully controlled, inconsistent results should be expected. 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 Pu^{238} removal, but at the cost of addition issues with sulfate from degraded sulfamate. Past work by Thompson (17,18) on Np valence control in the HM Process, showed that the Fe^{2+}/ Fe^{3+} ratio controls the electrochemical potential (based on the Nernst equation). The time pressure in this study has not permitted any work in this area. However, it seems probable that use of reducing normality measurements or Redox potential measurements may be an effective method of monitoring for possible failure of the reductive wash. Additional work looking at the Fe^{2+}- Fe^{3+} electrochemical couple in real process solutions over time by either spectrophotometric or Redox potential may explain under what conditions that a reductive load step could be effective. There also is a probable issue with the shelf life of prepared reductive wash solutions. Even heels in cold feed tanks could affect the effectiveness of the reductive wash solution.

Observed Improvements Due to Equipment Changes: In this set of experiments a new column design was used to eliminate volume in the stopcock valve that caused elution tailing that had nothing to do with the actual resin bed. This change was very successful at eliminating this problem. The hearts cuts obtained during elution were greater than 50 g Np/L with modest losses to the heads and tails cuts. In process terminology, this is referred to as obtaining a high efficiency in producing Np product from the process. The hearts cuts varied from 1.5 to 2 M HNO_3. For some time, the facility has projected to produce 50 g Np/L product at 2 M HNO_3. Past laboratory equipment 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. However, there could be unrecognized hardware problems in the plant equipment that limit product concentration

Uncertainties: As previously stated, instantaneous flowrates 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 (5) 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 beds 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, dilution error is estimated as ~3% for this work due to 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 13% for Np^{237} compared with a historical norm of ~4%. Poor material balances for Pa^{233} were observed in the previous study (13) and results in this study could only close the Pa233 material balance to within 20%. Solutions that should have been at secular equilibria between Np^{237} and Pa^{233} (Np^{237} and Pa^{233} activities should be equal) often had 20-50% less Pa^{233}. Pa^{233} readily hydrolyzes and sticks to various surfaces even from 1-8 M HNO_3. No correction was made for Pa^{233} 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 four day delay in counting would amount to ~10% ingrowth of Pa^{233}.

Conclusions:

A series of laboratory column runs have demonstrated that significant rejection of Pu^{238} can be obtained by the addition of an up-flow reductive wash step to the Np anion exchange process. Np losses during the loading/washing steps of this process can be less than 1 percent, while at the same time rejecting greater than 30 percent of the Pu^{238}. Np losses will depend on the Np batch size and the HNO_3 concentration. A 2 kg Np batch size allows for little, if any, excess resin capacity in the anion exchange process. The nitric acid concentration is a compromise between Np losses and Pu^{238} 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 M HNO_3, 0.02 M N_2H_4, 0.05 M excess FS.
- Reductive wash of 6 BV or more up-flow of 6.4 M HNO_3, 0.05 M FS, 0.05 M N_2H_4
- Decontamination wash of 1-2 BV up-flow to displace Np solution into resin and flush residual Fe from process equipment
- Elute down-flow with 0.17 M HNO_3, 0.05 M N_2H_4.

These recommendations reflect nominal conditions that are based on the limited experimental work performed. Variation in process conditions is expected to contribute to variability in performance. The current study demonstrates conditions that provide acceptable process performance. Additional study is recommended on the parameters that affect Pu^{238} rejection to establish bounding conditions on the reductive wash step that will ensure consistent results. Such investigation should improve the understanding of the competing chemical phenomena that contribute to the success or failure of rejecting Pu^{238} in the process and provide a basis for bounding the reductive wash step.

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APPENDIX

Table VII. Results from Cr246 - 8 M Load, 6.4 M Reductive Wash.

Cr246 Anion Column Run Acid Elution on Reillex HPQ 97 mL column

						Np237		Np	Pu238		Gamma Scan						APHA			
Sample ID		ADS No.	Sample Volume	Volume Eluted	Volume Eluted	Conc. g/L	g in Bottle	Loaded gms.	Conc mg/L	ug in Bottle	Acidity Total	Free	Np237 uCi/mL		Pa233 uCi/mL		Np237	Pu239	Pu238	Galpha dpm/mL
Cr246	Feed	3-201967	1014	1014	10.5	4.779	4.846	4.846	2.444	2478		8.0	3.3712	1.3%	2.4905	0.7%	6%	0%	94%	9.9.E+07
	EC1	3-201968	1014	1014	10.5	0.003	0.003	4.843	0.001	1		8.0	0.03		0.32425	1.2%	9.0%	21%	69%	5.0.E+04
	RW1	3-201969	102	102	1.1	0.004	0.000	4.843	0.030	3		6.4	0.19		1.94	0.8%	0.50%	0%	100%	1.2.E+06
	RW2	3-201970	118	220	2.3	0.012	0.001	4.841	1.633	193		6.4	0.16		1.6096	0.8%	0.03%	0%	100%	6.2.E+07
	RW3	3-201971	100	320	3.3	0.022	0.002	4.839	3.023	302		6.4	0.21		2.181	0.8%	0.03%	0%	100%	1.2.E+08
	RW4	3-201972	100	420	4.3	0.024	0.002	4.836	3.313	331		6.4	0.24		2.4636	0.8%	0.03%	0%	100%	1.3.E+08
	RW5	3-201973	98	518	5.3	0.037	0.004	4.833	2.997	294		6.4	0.17		1.7365	0.8%	0.05%	0%	100%	1.1.E+08
	RW6	3-201974	96	614	6.3	0.015	0.001	4.831	2.463	236		6.4	0.0103	32%	1.7288	0.7%	0.10%	0%	100%	9.4.E+07
	RW7	3-201975	100	714	7.4	0.067	0.007	4.825	1.838	184		6.4	0.0471	8.7%	1.4492	0.7%	0.1%	0%	100%	7.0.E+07
	RW8	3-201976	100	814	8.4	0.084	0.008	4.816	1.362	136		6.4	0.0595	6.0%	1.2108	0.7%	0.1%	0%	100%	5.2.E+07
	RW9	3-201977	99	913	9.4	0.146	0.014	4.802	0.958	95		6.4	0.1033	4.4%	0.92852	0.8%	1.0%	0%	99%	3.7.E+07
	RW10	3-201978	98	1011	10.4	0.197	0.019	4.783	0.674	66		6.4	0.139	3.2%	0.65235	0.9%	1.0%	0%	99%	2.6.E+07
	RW11	3-201979	100	1111	11.5	0.238	0.024	4.759	0.492	49		6.4	0.1677	2.7%	0.54749	0.9%	2.0%	0%	98%	1.9.E+07
	RW12	3-201980	96	1207	12.4	0.274	0.026	4.732	0.379	36		6.4	0.1934	2.5%	0.42124	1.0%	2.0%	0%	98%	1.5.E+07
	DW1	3-201981	100	1307	13.5	0.260	0.026	4.706	0.291	29		8.0	0.1831	2.8%	0.70614	0.8%	2.0%	0%	98%	1.1.E+07
	DW2	3-201997	100	1407	14.5	0.021	0.002	4.704	0.090	9		8.0	0.0145	5.4%	0.01739	3.3%	4.0%	0%	96%	3.6.E+06
	Disp	3-201982	98	98	1.0	0.123	0.012	4.692	0.022	2		4.0	0.0867	3.1%	0.19351	0.6%	2.0%	1%	97%	8.6.E+05
	PC1	3-201983	90	188	1.9	55.903	5.031	-0.339	2.590	233		1.7	39.436	0.6%	10.144	0.6%	39%	2%	59%	1.7.E+08
	PC2	3-201984	370	558	5.8	0.268	0.099	-0.438	0.027	10		0.2	0.1889	1.9%	0.03815	1.2%	23%	0%	77%	1.3.E+06

Mat'l Balance					g Np	Recovered	5.142	106.1%	of feed
				49.9	g/l resin	Losses	0.141	g Pu	2.9%
				53.0	g/l resin	Total	5.284		

Table VIII. Results from Cr247 - 6.4 M Reductive Load, 6.4 M Reductive Wash.

Cr247 Anion Column Run Acid Elution on Reillex HPQ 97 mL column

						Np237		Np	Pu238				Gamma Scan				APHA			
Sample ID		ADS No.	Sample Volume	Volume Eluted	BV Eluted	Conc. g/L	g in Bottle	Loaded gms.	Conc mg/L	ug in Bottle	Acidity Total	Free	Np237 uCi/mL		Pa233 uCi/mL		Np237	Pu239	Pu238	Galpha dpm/mL
Cr247	Feed	3-202219	416	1014	10.5	9.251	3.848	3.85	3.628	1509		8.0	6.526	1.1%	3.9748	0.6%	8%	0%	92%	1.5.E+08
	EC1	3-202220	428	428	4.4	0.013	0.005	3.84	0.007	3		8.0	0.005	15%	0.0653	1.7%	7.0%	4%	89%	2.8.E+05
	RW1	3-202221	100	100	1.0	0.008	0.001	3.84	0.342	34		6.4	0.049		0.4853	1.0%	0%	0%	100%	1.3.E+07
	RW2	3-202222	100	200	2.1	0.009	0.001	3.84	0.363	36		6.4	0.061		0.6068	1.0%	0%	0%	100%	1.4.E+07
	RW3	3-202223	100	300	3.1	0.022	0.002	3.84	0.896	90		6.4	0.062		0.6192	1.0%	0%	0%	100%	3.4.E+07
	RW4	3-202224	100	400	4.1	0.030	0.003	3.84	1.236	124		6.4	0.065		0.6494	1.0%	0%	0%	100%	4.7.E+07
	RW5	3-202225	100	500	5.2	0.033	0.003	3.83	1.336	134		6.4	0.048		0.483	1.0%	0%	0%	100%	5.1.E+07
	RW6	3-202226	100	600	6.2	0.121	0.012	3.82	1.385	139		6.4	0.085		0.8508	0.9%	0%	0%	100%	5.3.E+07
	RW7-12		600	1200	12.4															
	DW1	3-202227	100	1300	13.4	0.105	0.011	3.81	1.175	118		8.0	0.074		0.7415	1.0%	0%	0%	100%	4.5.E+07
	DW2	3-202228	100	1400	14.4	0.046	0.005	3.81	0.539	54		8.0	0.033		0.3272	1.2%	0%	0%	100%	2.1.E+07
	Disp	3-202229	88	88	0.9	0.112	0.010	3.80	0.317	28		4.0	0.079	2.6%	0.0521	1.9%	1.0%	1%	98%	1.2.E+07
	PC1	3-202230	60	148	1.5	62.143	3.729	0.07	11.238	674		1.6	43.84	1.5%	16.524	1.0%	15%	2%	83%	5.2.E+08
	PC2	3-202231	100	248	2.6	1.631	0.163	-0.10	0.247	25		0.2	1.151	1.4%	0.0232	1.1%	17%	0%	83%	1.1.E+07
	Tails	3-202268	250	498	5.1	0.045	0.011	-0.11	0.018	4			0.032	3.6%	0.0089	4.6%	6%	4%	90%	7.6.E+05
	Mat'l Balance				g Np	Recovered	3.913	1.02	of feed											
				39.6	g/l resin	Losses	0.043	g Pu	1.1%											
				40.3	g/l resin	Total	3.956													

Table IX. Results from Cr248 - 6.4 M Reductive Load, 6.4 M Down-flow Reductive Wash.

Cr248 Anion Column Run Acid Elution on Reillex HPQ 97 mL column

						Np237		Np	Pu238		Gamma Scan						APHA			
Sample ID		ADS No.	Sample Volume	Volume Eluted	BV Eluted	Conc. g/L	g in Bottle	Loaded gms.	Conc mg/L	ug in Bottle	Acidity Total	Free	Np237 uCi/mL		Pa233 uCi/mL		Np237	Pu239	Pu238	Galpha dpm/mL
Cr248	Feed	3-202403	573	573	5.9	9.705	5.561	5.561	3.991	2287		8.0	6.85	2.2%	3.959	1.7%	8%	0%	92%	1.7.E+08
	ECA	3-202404	596	596	6.1	0.004	0.002	5.559	0.004	2		8.0	0.03		0.307	1.2%	4.0%	0%	95%	1.5.E+05
	RW1	3-202406	104	104	1.1	0.037	0.004	5.555	0.150	16		6.4	0.190		1.886	0.8%	1%	0%	99%	5.8.E+06
	RW2	3-202407	98	202	2.1	1.044	0.102	5.453	4.216	413		6.4	1.310	3.9%	0.811	2.9%	1%	0%	99%	1.6.E+08
	RW3	3-202408	98	300	3.1	1.211	0.119	5.334	4.893	480		6.4	1.741	3.6%	1.078	0.8%	1%	0%	99%	1.9.E+08
	RW4	3-202409	100	400	4.1	2.494	0.249	5.085	3.290	329		6.4	1.214	4.5%	1.257	2.8%	3%	0%	97%	1.3.E+08
	RW5	3-202410	100	500	5.2	1.790	0.179	4.906	2.313	231		6.4	1.150	4.3%	1.611	2.4%	3%	1%	95%	9.3.E+07
	RW6	3-202411	98	598	6.2	1.164	0.114	4.791	1.584	155		6.4	0.821	5.3%	1.199	2.8%	5%	3%	92%	6.6.E+07
	RW7	3-202412	96	694	7.2	1.100	0.106	4.686	1.186	114		6.4	0.776	6.1%	1.325	2.6%	4%	0%	96%	4.7.E+07
	RW8	3-202413	100	794	8.2	0.880	0.088	4.598	0.906	91		6.4	0.621	6.1%	1.173	2.8%	4%	0%	96%	3.6.E+07
	RW9	3-202414	96	890	9.2	0.892	0.086	4.512	0.671	64		6.4	0.629	5.4%	0.823	3.4%	3%	0%	96%	2.7.E+07
	RW10	3-202415	98	988	10.2	0.891	0.087	4.425	0.569	56		6.4	0.629	6.3%	0.821	3.4%	5%	0%	95%	2.3.E+07
	RW11	3-202484	100	1088	11.2	0.741	0.074	4.351	0.440	44		6.4	0.523	6.5%	0.800	3.5%	6%	0%	94%	1.8.E+07
	RW12	3-202485	100	1188	12.2	0.638	0.064	4.287	0.373	37		6.4	0.450	7.5%	0.577	4.1%	6%	0%	94%	1.5.E+07
	DW1	3-202416	100	1288	13.3	0.476	0.048	4.239	0.269	27		8.0	0.335	9.1%	0.497	4.3%	7%	0%	93%	1.1.E+07
	DW2	3-202417	100	1388	14.3	0.350	0.035	4.205	0.076	8		8.0	0.247	2.1%	0.325	1.0%	14%	0%	86%	3.4.E+06
	Disp	3-202418	88	88	0.9	0.374	0.033	4.172	0.036	3		4.0	0.26	10%	0.345	5.6%	24%	2%	74%	1.9.E+06
	PC1	3-202419	62	150	1.5	60.603	3.757	0.414	3.930	244		1.8	42.8	1.4%	7.724	1.3%	35%	2%	65%	2.3.E+08
	PC2	3-202420	100	250	2.6	1.499	0.150	0.264	0.134	13		0.2	1.06	1.4%	0.16	1.3%	28%	0%	72%	7.1.E+06
	Tails	3-202421	200	450	4.6	0.039	0.008	0.257	0.010	2			0.03	3.9%	0.023	2.9%	11%	2%	87%	4.5.E+05

Mat'l Balance		g Np	Recovered	3.948	71.0%	of feed	
	57.3	g/l resin	Losses	1.357	g Pu	24.4%	
	40.7	g/l resin	Total	5.305			