This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-96SR18500 with the U. S. Department of Energy.

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WSRC-TR-2003-00111, Rev 0

Neptunium
Valence Chemistry
In
Anion Exchange
Processing

Edward A. Kyser

Feb 2003

Westinghouse Savannah River Company
Savannah River Site
Aiken, SC 29808

Prepared for the U. S. Department of Energy under contract DE-AC09-96SR18500.

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Feb 28, 2003

Technical Reviewers

Tracy S. Rudisill 2/27/03

T. S. Rudisill Date

R H Smith 2/28/03

R. H. Smith Date

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Acronyms and Terminology:

FS - Ferrous Sulfamate is the primary reducing agent used to adjust Pu and Np valence states in the separation processes.

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

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

HNO_3 – Nitric acid

HNO_2 – Nitrous acid

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

$C_2O_4^{2-}$ - Oxalate: From oxalic acid used to precipitate Np oxalate

$NaNO_3$ – Sodium nitrate

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

DSA – Documented Safety Analysis

SRTC ADS or ADS – Analytical Development Section of Savannah River Technology Center: Provided analytical services in support of this work.

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

BV- (Bed Volume) Volume occupied by the bed of resin in a column. Includes both resin volume and void space volume.

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).

Q – Volumetric flowrate

A – Cross sectional area of a resin bed in the column

H – Height of the resin bed in the column

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

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.

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.

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.

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.

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.

Down-Flow – Refers to the flow direction of the process stream as being the same direction as gravity through the column.

Up-Flow - Refers to the flow direction of the process stream as being the opposite direction as gravity through the column.

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.

Grab Sample – Sample collected over a relatively short period of time. Approximates an instantaneous sample.

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.

ND – None detected by analytical method.

na – Not available or not applicable.

Neptunium Valence Chemistry In Anion Exchange Processing

By

Edward A Kyser

Savannah River Technology Center
Actinide Technology Section

February 2003

Summary:

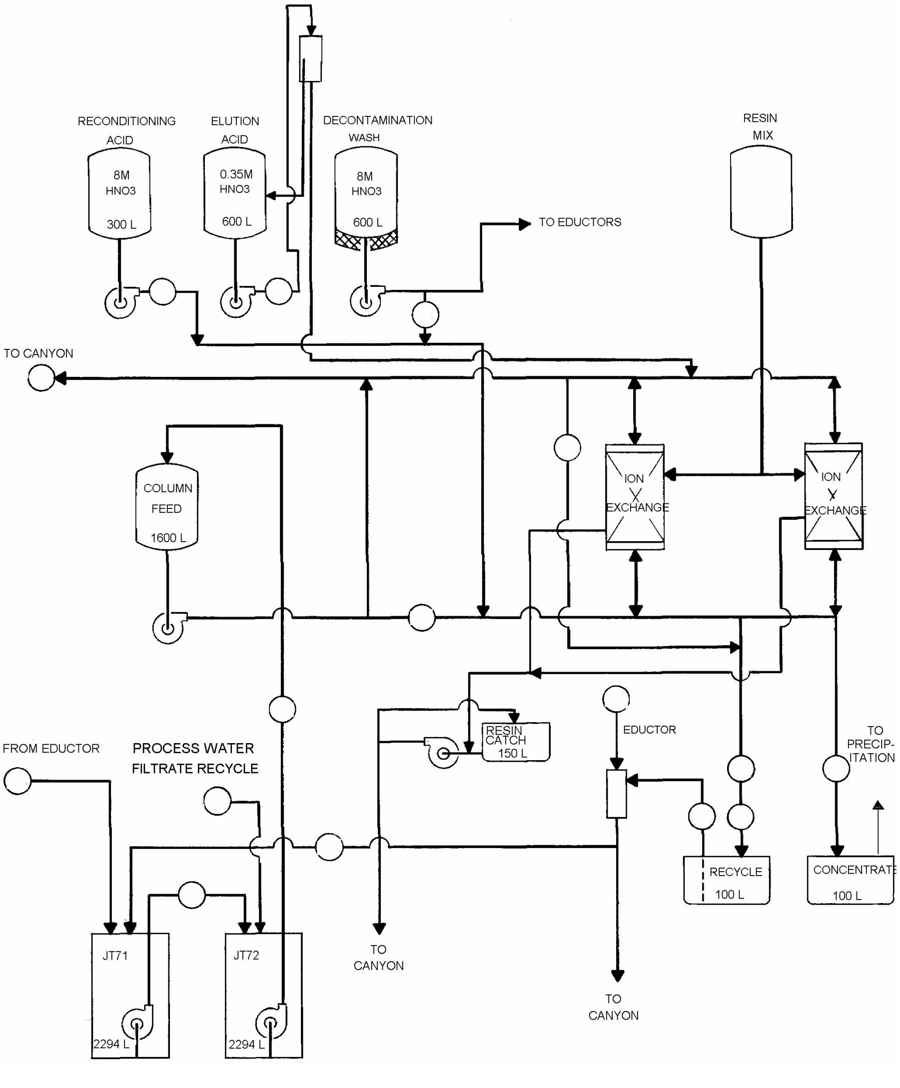
The current anion resin in use in HB-Line Phase II, Reillex™ HPQ, was tested in the laboratory under expected plant conditions for Np processing and was found to load between 50 and 70 g Np per liter of resin. Losses varied from 0.2 to 15 percent depending on a number of parameters. Hydrazine in the feed at 0.02 to 0.05 M appeared to keep the Np from oxidizing and increasing the losses within four to seven days after the FS addition. Losses of up to three percent were observed five days after FS addition when hydrazine was not used in the feed, compared with 0.3 percent when the feed was loaded immediately after FS addition. Based on these test results the following processing conditions are recommended:

- Feed conditions: 8 M HNO_3, 0.02 M hydrazine, 0.05 M excess FS, less than 5 days storage of solution after FS addition.
- Wash conditions: 100 liters of 8 M HNO_3, no FS, no hydrazine.
- Elution conditions: 0.17 M HNO_3, 0.05 M hydrazine, no FS
- Precipitation feed conditions: 0.03 M excess ascorbic acid, no additional hydrazine, no FS, precipitation within three days.

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 convert this facility over to processing the Np nitrate solutions stored in H-Canyon. After receipt of the Np solution, anion exchange columns will both purify and concentrate the Np nitrate solution, after which it 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 and acid concentration adjustment will be performed in a feed adjustment tank (JT72) via the addition of FS, N_2H_4 and 64% HNO_3. In the past, Np valence adjustment was performed by adding sufficient N_2H_4 and FS to make the solution 0.02 M N_2H_4 and 0.05 M FS. N_2H_4 is added to react with HNO_2 produced via radiolysis and to protect the Fe^{2+} and Np^{4+} from oxidation. The FS reduces 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. When Pu has been processed in the past, either a nitrite addition step or a "heat-kill" step was included to rapidly oxidize the Pu^{3+} to the absorbable Pu^{4+} valence state. In the Np process, Np^{4+} is the desired species and it is desirable to reject Pu to the raffinate stream. However Pu^{3+} tends to oxidize to the Pu^{4+} valence state in high nitrate solution which loads onto anion exchange resin even more strongly than Np^{4+}. In the baseline process for Np purification, the nitrate concentration was lowered to 5.4-6.5 M HNO_3 in the presence of FS to weaken the tendency for the absorbable $Pu(NO_3)_6^{2-}$ complex to form 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 acid from the system. HB-Line will pump the adjusted feed from the receipt/feed adjustment tanks to a column feed tank. The feed solution will 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 (probably using one-half to two-thirds of the resin bed's physical capacity), the bed will be washed up-flow. This step moves the remaining Np solution into the resin bed where the remaining Np will absorb and also provides improved decontamination from impurities by displacing residual impure solution from the equipment prior to elution. In the baseline 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), 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 instrumented with fiber optics to a colorimeter to determine 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 only be partially 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. After visual break-through, the resin continues to load Np, but an ever-increasing fraction of the Np in the feed solution is not absorbed. Ultimately the Np concentration in the raffinate will reach the concentration in the feed and the resin bed will absorb no additional Np. 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. This goal requires 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 (LANL) 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). Better resistance to radiolytic and chemical damage is attributed to these resins due to the presence of the pyridine ring "N" functional group. Marsh also found this resin to be 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. Much of the equipment and some of the procedures used in the current study are very similar to those used in the earlier work.

There are no literature studies on the loading of Reillex™ HPQ with Np. There has been very limited process development work with Np over the last 20 years and one objective of this work was to gain general experience with the process chemistry of Np. The major objective however was to identify the documented safety analysis (DSA) related parameters of the process flowsheet and to propose process limits. Along the way, a number of other process parameters were also studied. One of these (as was already mentioned) was to measure the resin capacity for Np under HB-Line process conditions. As this work developed, the only process parameter that was identified as significant to the DSA was the concentration of N_2H_4/HN_3 in the various process streams. As a result, this work focused principally on determining the levels of N_2H_4 that were needed in anion exchange and precipitation processes to minimize Np losses to waste.

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

	Feed		Recon--ditioning	Decon-Wash	Elution	
	High	Low				
Flow, l/batch	286	1000	45	100	90	
Np (g/batch)	2000	2000		1		
Np (g/l)	7	2		0.01		
HNO3 (M)	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)	2.3	8	5	2.2	1.6	Resin Bed Height 15 in
v ($ml/min/cm^2$)	2.1	7.3	4.5	2.0	1.5	Resin Bed Volume 45 L
Volume (l)	286	1000	45	100	90	Volumes from Flowsheet
Time (min)	125	125	9	45	56	
BV	6	22	1.0	2.2	2.0	BV=Bed Volumes (Total volume of resin bed)
mgs $Np/min/cm^2$	15	15				Assume 2 g Np/l & 7 g Np/l
SRTC Np	down	down	down	down	down	Col ID 19 mm Column area = 2.835 cm^2
Flow (ml/min)	5	5	20	12	2	Resin Bed Volume measured as 110 cc
v ($ml/min/cm^2$)	1.8	1.8	7.1	4.2	0.7	Resin Bed Height 15.5 in
Volume (ml)	500	1000	200	250	250	409 resin ratio
Time (min)	100	200	10	21	125	389 area ratio
BV	5	9.3	1.9	2.3	2.3	
mgs $Np/min/cm^2$	18	9				10 & 5 g Np/l in Feed
SRTC Np	down	down	down	down	down	Col ID 19 mm Column area = 2.835 cm^2
Flow (ml/min)	5	5	20	5	2	Resin Bed Volume measured as 35.5 cc
v ($ml/min/cm^2$)	1.8	1.8	7.1	1.8	0.7	Resin Bed Height 5 in
Volume (ml)	200	400	100	100	160	1250 resin ratio
Time (min)	40	80	5	20	80	389 area ratio
BV	6	11	2.8	2.8	4.4	
mgs $Np/min/cm^2$	18	9				10 & 5 g Np/l in Feed

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. For these experiments, a resin volume of 36 cm^3 of settled resin was used in a 19 mm ID glass column, resulting in a cross sectional area of 2.835 cm^2. A single run was performed with a 15" (38cm) resin bed (19 mm ID column, 108 cm^3 of settled resin). The baseline flowsheet (6,7) was based on feed concentration of 2 g Np/L that corresponds to 14.5 $mg/min/cm^2$. Depending how solutions are recycled in the facility, feed concentrations of anywhere from 2 to 10 g Np/L are expected to be processed. 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.

Resin Pretreatment: Unlike the earlier Pu work, no resin pretreatment was performed. 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).

Column Loading: A sufficient quantity of resin was converted into the nitrate form prior to loading the column. The resin is generally loaded either by pouring dry resin beads into the column and then wetted with water or dilute HNO_3 or by slurrying the resin into the column with water. The resin bed is settled by running water/dilute HNO_3 downflow through the resin bed to fill the excess void spaces until all apparent gaps are filled. The final resin bed volume is adjusted by adding a small amount of resin or removing excess resin with a slurry pipette. Once the resin is loaded and settled into the column, every effort is made to not allow the liquid head above the resin to drain below the top of the resin bed. Air bubbles trapped within the moist bed are often very difficult to remove and will cause channeling of the flow through the bed. On several occasions a large gap formed within the resin bed. This gap was removed by tilting the column sideways or even removing the entire resin bed in order to restore a continuous resin bed.

Feedstock Preparation and Valence Adjustment: Np solution is prepared by adjusting the [HNO_3] to 5.5 to 8.5 M (depending on the objectives of the test) and performing a valence adjustment with N_2H_4 and/or FS. Normally N_2H_4, if used, was added first (in order to scavenge any residual HNO_2). Then sufficient FS was added to make the solution 0.03 to 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 8 M HNO_3 at 50°C, the half-life for Fe^{2+} is on the order of 10 minutes compared with 1 hr at 35°C and 10 hr at 25°C (8). That reference is for Pu solutions and due to the reduced alpha activity of the Np feed solution, Fe^{2+} is expected to persist for longer periods of time. FS degrades to Fe^{3+} and SO_4^{2-}. Fe^{3+} reduces the effectiveness of Fe^{2+} in the reduction and stability 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). He observed a 30 % reduction in capacity for 0.1 M SO_4^{2-} and a 70% reduction in capacity for 0.5 M SO_4^{2-} in 8 M HNO_3. Due to tank heels in the feed tanks, some buildup of [SO_4^{2-}] is inevitable and may have an effect on capacity. In this study the anion exchange feed was normally started promptly after the FS addition except when the effect of hold time was to be studied.

Lab Equipment: One of the columns used in this work is shown in Figure 2. This picture shows the Cr238 upload column with a partial load of Np on the resin. The Np loaded resin is characterized by the gray color on the lower 40% of the bed. This column utilized #7 Teflon™ bushings for connecting ¼ inch polypropylene tubing to the column. The column consists of a 19 mm ID glass body to retain the resin bed and a headpiece. The headpiece 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 a Ace glass pressure relief valve and a pressure gauge to monitor the pressure in case the frit at the bottom of the column plugged. An additional arm with a stopcock and funnel allowed the column to be vented. The primary column used in the loading studies utilized a short (~5in) resin bed and was operated down-flow only. A second column was similar in design, but provided for a full height (~15in) resin bed. The tall column is the version shown in Figure 3. With the use of 100 mesh screen held into place with an o-ring, this column was operated load-wash up-flow and elution down-flow. A sketch of the experimental setup for the loading tests (which were run down-flow) is shown as Figure 3.

A standard FMI piston pump was used to pump feed, wash, or elution acid through the column. A ½ inch Swaglock™ cross and ½ inch optic lens was used to fabricate a flowcell with a 2.54 cm pathlength. A pair 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 parts list for the complete spectrophotometer system used is given in Table II. The multiplexer used in past work proved unsuitable for this work as it used UV grade fibers (high OH) which absorbed all the light in the 950nm wavelength range. Np^{4+} and Np^{5+} absorption peaks at 960nm and 980nm were not useable if any high OH fibers were used. Therefore, the multiplexer was bypassed and reference and

Figure 2. Column used in Experiments

Figure 3. Experimental Setup

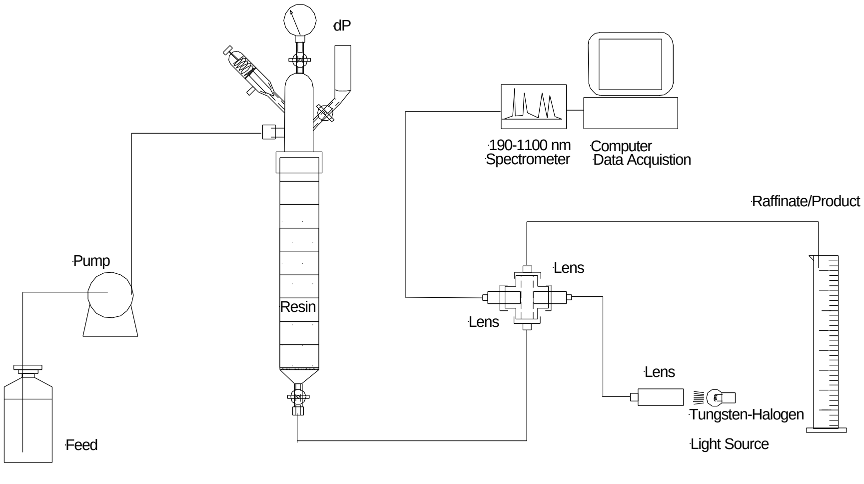


Table II. Spectrophotometer System Parts List

- 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, 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

measurement spectra were taken on the same pair of fibers.

Np Loading: Sufficient Np feedstock was prepared for one or more break-through column runs. A sample was taken and analyzed for total acid/free acid, total alpha by alpha PHA and gamma scan. At the beginning of the column run, several column volumes of 6-8 M HNO_3 were fed to the column to displace the dilute acid the resin was stored in from the previous run. At this point in time the spectrophotometer was checked for proper operation and a new "zero" spectrum was stored (background with no Np in the flow cell). The Np feed was then pumped downflow 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 . "Grab" samples of the raffinate were also taken on a periodic basis during the course of the loading step and analyzed for Np content by alpha and gamma counting. The spectra taken were stored along with the time and volume of raffinate collected. The feed flowrate was periodically checked with a 10mL graduated cylinder and a stop-watch. The flowrates were somewhat variable (sometimes ±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 the other). This behavior was not observable for Np like it had been during similar Pu runs due to the subtle color change, but it probably occurred. Tailing could cause higher than expected losses to the raffinate or wash. As the Np interface (observed as a gray boundary) approached the bottom of the resin bed the levels of Np in the raffinate rose gradually (to ~0.1 g Np/L) and the frequency of spectra measurements was increased. Pu "break-through" was readily determined by visual observation of the raffinate in the 0.5 to 1 g Pu/L, but the corresponding break-though of Np was less readily detected and was easily missed when column run was performed without aid of the spectrometer. With the spectrometer and 2.54 cm flowcell, "visual-breakthrough" was declared in the 0.2 to 0.5 g Np/L concentration range. For a period of time before and after visual break-through, the Np concentration in the raffinate rapidly rises from <0.1 to ~2 g Np/L. As loading continues, the concentration continues to rise, but more slowly as it asymptotically approaches that of the feed concentration. During this time, a significant fraction of the Np in the feed solution continues to load onto the resin as Np diffuses deeper into the resin beads and the resin becomes saturated with Np. The raffinate was commonly collected in two cuts. The first was collected up to the point that visual break-through was detected and the second was collected from that point past the end of the loading phase. The decontamination wash was usually collected separately. This method of collection allowed the early raffinate to be discarded, while recycling the raffinate after break-through. Only a few runs were made for saturation loading or break-through studies. A number of runs were made to study the effect of $[N_2H_4]$ and time on the losses to the raffinate stream. These runs were not fundamentally different than the break-through runs, but the results relied more on results from analytical analyses than on results from online spectrometer results.

Reductive Loading/Washing: In the beginning of this study, there was interest in attempting to reject Pu^{238} contamination. The $[HNO_3]$ was reduced from 8 M to 5.5-6.5 M in an attempt to increase the stability of Pu^{3+} in the feed solution. Adjustments to the HNO_3, FS and N_2H_4 concentrations in both the feed and wash solutions were made in an attempt to reject Pu^{238} as Pu^{3+} to the raffinate stream.

Figure 4. Np^{5+} Spectra in Low HNO_3

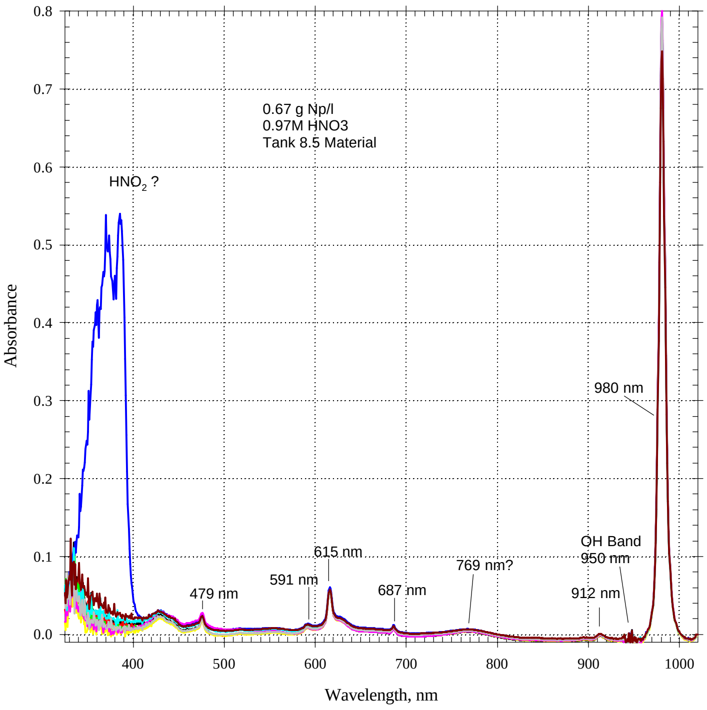
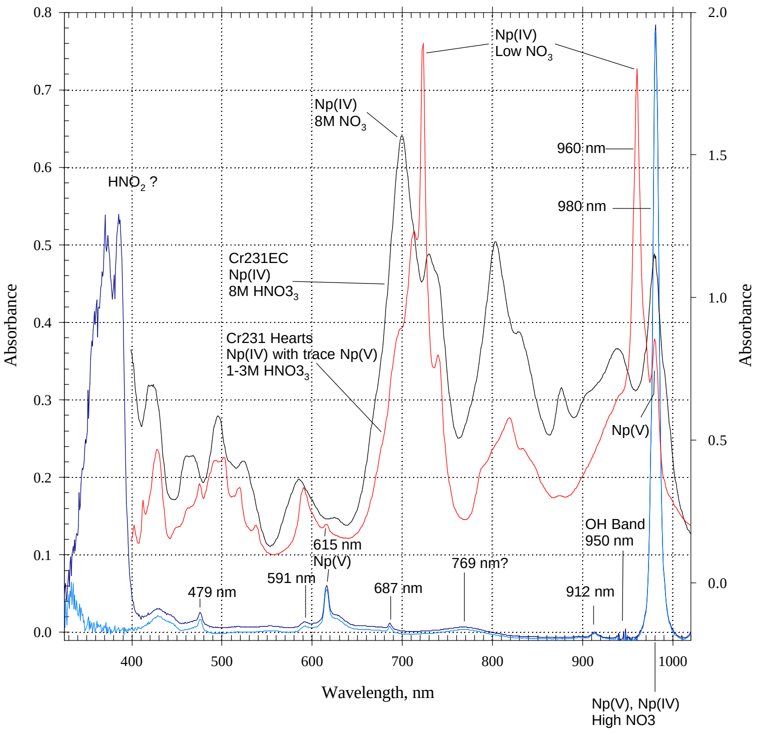


Figure 5. Np^{4+} Spectra in Low and High HNO_3 Compared with Np^{5+} Spectra



Np Washing and Elution: When the concentration in the raffinate was approximately 90% of that in the feed (or when the prepared feedstock was exhausted), the loading was stopped. Allowances then had to be made to displace the residual Np feed solution from the resin bed and feed line. There was unloaded Np in the system due to void space in the column (~50 volume percent or 18 mL), the head-liquid volume above the resin (10 to 40 mL) and finally the liquid volume still in the feed-line (<10mL). Normally this uncertainty was eliminated by pumping the feed line dry and allowing the head liquid to drain (without letting the level drop below the top of the resin) to a minimal volume above the resin bed (0 to 5 mL). A short decontamination wash of the resin column with 100 mL of 8 M HNO_3 was performed to remove most of the FS and displace the residual Np feed solution. This wash was included with the second raffinate cut for material balance purposes and future recovery of the Np. The column was then completely eluted with 200 to 400 mL of 0.17 M HNO_3 at 2 mL/min downflow. After the visible Np had been removed from the resin, the run could be safely interrupted at this point and the remainder of the elution could be continued the next day.

Analytical: Samples were taken of feed solutions and 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 largely separates Np from Pa and the raffinate and wash samples can have a Pa^{233}/Np^{237} activity ratio of greater than 10. Under these conditions, gamma counting was not able to provide good Np^{237} results due to interference from the Pa^{233}. When Pu^{238} activity is greater than 10 times the Np^{237} activity the precision of the Np^{237} counting is also reduced. Under circumstances of both high Pa^{233} and Pu^{238} activity relative to Np^{237}, no good method of determining the Np^{237} concentrations was available.

In anion feed solutions with high nitrate concentrations, a method was needed to study the oxidation of Np^{4+} to Np^{5+}. SRTC-ADS adapted an existing analytical separation method to perform a Np^{4+}-Np^{5+} separation and to then use gamma counting to determine the percent Np^{5+} in the sample. This experimental technique used Eichrom TEVA resin cartridges (which contain Aliquat 336, a quaternary amine loaded onto a polymer backbone). This technique appears to provide results with a sensitivity of at least 0.2% for determining the percent Np^{5+} + Np^{6+} depending on the level of interference from Pa^{233}.

Calibration of Spectrophotometer: Np spectra have a fairly high acid dependence. Efforts to calibrate the spectrometer for Np^{4+} and/or Np^{5+} proved to be too time consuming for the scope of this program. Instead the spectrometer was used to provide qualitative results on presence of Np^{5+}. Semi-quantitative results on the oxidation of Np^{4+} to Np^{5+} in low acid were obtained by observing the height of the 980nm Np^{5+} peak. Spectra of pure Np^{5+} from diluted samples of tank 8.5 material are shown in Figure 4. A number of minor peaks are shown as well as the dominant peak at 980nm. Absorbance caused by HNO_2 (from added $NaNO_2$) was observed in one sample. In 8 M HNO_3 the absorptivity of Np^{5+} at 980nm appeared to reduced by 90% and the disproportion clearly occurred within minutes to hours. Literature references for Np spectroscopy 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 report disproportionation of Np^{5+} above 3 M HNO_3. The Np^{5+} spectra that they published clearly show Np^{4+} absorption peaks, but interestingly don't show the Np^{6+} peaks. They also reported a strong acid dependence on this reaction. Friedman and Toth (12) report Np spectra in up to 4 M HNO_3. They report 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 HNO_3 or above. Figure 5 shows Np^{4+} spectra in both low and high HNO_3 compared with the reference Np^{5+} spectra. Note that the major Np^{4+} peak at 960nm at low acid is shifted to 980nm in 8 M HNO_3. This shift prevents the use of the 980nm peak in determining the success of valence adjustment and oxidation in anion feed solutions. Also note the appearance of characteristic Np^{5+} peaks at 615 and 980nm in low HNO_3. Attempts to prepare pure Np^{5+} spectra for comparison in 8 M HNO_3 failed due to the Np^{5+} disproportionation to Np^{4+} and Np^{6+}.

Table III. Example of Material Balance for a Column Run

Cr238 Anion Column Run Recovery on Reillex HPQ 108 ml column upload-downelute

				Gamma Scan				Alpha PHA Plates				gamma	alpha
Sample ID		ADS No.	Sample Volume	Np237 uCi/ml	%	Pa233 uCi/ml	%	%Np237	%Pu239	%Pu238	Galpha dpm/ml	Np237 dpm/ml	Np237 dpm/ml
Cr238	Feed	3-191298/304	990	2.8485	3.02	1.9268	0.66	8%	0%	92%	8.6.E+07	6.3.E+06	6.9.E+06
Cr238	EC1	3-191299	990	0.0387	11.3	0.4416	1.12	19.0%	1%	80%	1.7.E+05	8.5.E+04	3.3.E+04
Cr238	WC	3-191300	250	0.0491	11.5	0.5317	1.07	18.0%	1%	81%	3.3.E+05	1.1.E+05	6.0.E+04
Cr238	Disp	3-191301	91	0.9823	1.18	0.1373	1.1	11.0%	1%	88%	1.6.E+07	2.2.E+06	1.8.E+06
Cr238	PC1	3-191302/305	100	28.492	0.7	5.7034	0.59	7%	0%	93%	8.3.E+08	6.3.E+07	5.8.E+07
Cr238	PC2	3-191303	352	0.2369	1.65	0.0246	2	6%	0%	94%	8.1.E+06	5.2.E+05	4.8.E+05

Sample ID		Sample Volume	Pu239 uCi	Pu238 uCi	Np237 uCi	Pa233 uCi	Np237 % Feed	Pa233 % Feed
Cr238	Feed	990	0.0	35604	2820.0	1907.5	100.0%	100.0%
Cr238	EC1	990	0.8	62.6	38.3	437.2	1.36%	22.9%
Cr238	WC	250	0.4	30.6	12.3	132.9	0.44%	7.0%
Cr238	Disp	91	6.7	586.0	89.4	12.5	3.2%	0.7%
Cr238	PC1	100	0.0	34875	2849.2	570.3	101.0%	29.9%
Cr238	PC2	352	0.0	1213.7	83.4	8.6	3.0%	0.5%
			-8	-1164	-253	746		
	Material Balance			-3%	-9%	39%	9.0%	-39.1%

Sample ID		Sample Volume	Volume Eluted	Column Volumes Eluted	Np237 Conc. g/L	Np237 g in Container	Np Loaded gms.	Pa233 Conc ug/l	Pa233 ng in Container	Acidity Total	Acidity Free
Cr238	Feed	990	990	27.9	4.045	4.005	4.005	0.093	91.859	8.1	7.1
Cr238	EC1	990	990	27.9	0.055	0.0544	3.950	0.021	21.053		
Cr238	WC	250	250	7.0	0.070	0.017	3.933	0.026	6.401		
Cr238	Disp	91	191	5.4	1.395	0.127	3.806	0.007	0.602		
Cr238	PC1	100	100	2.8	40.463	4.046	-0.240	0.275	27.465	1.6	1.2
Cr238	PC2	352	452	12.7	0.336	0.118	-0.359	0.001	0.416		
		Mat'l Balance				4.309	107.6				
			36.6	g/l resin	Losses	0.072	g Pu	1.24	%		
			39.9	g/l resin		4.381		0.40	%		

								Activity ratio to Np					
Sample ID		Sample Volume	Pu ppm	Pu238 ppm	Pu g/l g/l	Pu239 g/l	Pu238 g/l	Pu239/Np	Pu238/Np	Np/Np	Pa/Np	DF Pu	Pa
Cr238	Feed	990	543	543	0.0022	0.0000	0.0022	0.000	12.6	1.0	0.68		
Cr238	EC1	990	268	70	0.0000	0.0000	0.0000	0.0	1.6	1.0	11.4		
Cr238	WC	250	405	107	0.0000	0.0000	0.0000	0.0	2.5	1.0	10.8		
Cr238	Disp	91	1003	282	0.0014	0.0010	0.0004	0.1	6.6	1.0	0.1		
Cr238	PC1	100	527	527	0.0213	0.0000	0.0213	0.000	12.2	1.0	0.20	1.0	3.4
Cr238	PC2	352	626	626	0.0002	0.0000	0.0002	0.0	14.6	1.0	0.10		

Table IV. Summary of Loading and Loss Results for Np

Run ID	$[HNO_3]$[1]	$[N_2H_4]$[2]	Np	Resin Loading			Time Between	Np Losses
	Feed		Loading Rate	Breakthru	Saturation	Loaded	FS and Loading	
	M	M	mg/min/cm^2	gms Np / liter resin			days	% of Feed
Cr221	6.4	0.05	17.0	~40	74		0.1	na
Cr222	6.4	0.05	17.0	44	76		5	0.4 [3]
Cr223	6.4	0.1	2.4			16	0.1	0.6
Cr224	6.4	0.05	5.0			31	7	0.3
Cr225	6.4	0.02	6.8			46	0.1	0.14
Cr226	7.6	0.02	17.0	71	80		0.1	0.2 [3]
Cr227	7.4	0.02	7.4			61	4	3.2 [3]
Cr228	6.4	0.036	2.6			9	0.1	0.12
Cr229	6.6	0.005	7.0			16	0.1	0.01
Cr230	5.7	0.008	12.0	36		45	0.1	0.3 [3]
Cr231	8.2	0	15.0			51	0.1	0.5
Cr232	8	0	12.0			38	0.1	0.12
Cr233	8	0	5.3			39	0.1	15 [3]
Cr235	8	0	6.6			29	0.1	4.6
Cr237	8	0	8.4			53	5	2.5 [4]
Cr238	8	0	8.0			40	5	1.8 [4]

[1] Values determined by either calculation or by analysis

[2] Values determined by calculation only

[3] Losses to raffinate up to detectable breakthru (~0.2 g Np/l)

[4] No spectrometer available to determine visual breakthru

Results and Discussion:

A series of 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, and product solutions were analyzed (along with selected “grab” samples) and submitted for analysis. 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 onto the resin was calculated as the difference between the cumulative amount fed and the amount found in the raffinate solutions. This method was used to calculate the visual break-through loading of the resin (where applicable). The saturated loading was also calculated in this same fashion (where applicable) and was checked by measuring the total amount of Pu found in the eluate (product) solutions. A sample set of results for one of the column runs and some sample calculations for that run are shown in Table III. Additional results for the other runs are shown in Tables IV and VII.

Resin Loading and Losses: Table IV summarizes the Np loading results for the 16 column runs that used the 1998 lot of Reillex™ HPQ. Some of these runs were made to recover Np and did not involve loading to break-through. Feed concentrations and conditions varied somewhat and are shown in Table VII. Results include conditions for Pu rejection and for maximum Np loading. For the Pu rejection runs (N_2H_4, FS and lower feed acidity) break-through occurred at ~36-44 g Np/L resin without any contradictory results. For the maximum Np loading runs (~8 M HNO_3) break-through occurred at 51-71 g Np/L resin with several exceptions that showed high losses. Because the N_2H_4 concentration and the age of the feed solution were being varied at the same time, the higher losses may have been caused by Np oxidation state changes rather than capacity limitations. The appearance of 650-750nm Np^{4+} absorbance peaks indicated that the losses measured in the raffinate cut were due to break-through either from lack of capacity, too high of a feed rate, or channeling rather than due to incomplete reduction or oxidation. However, experimental evidence linking higher losses to the valence state was generally not available. Other factors may have contributed to these higher losses as well. Flowrates were varied and SO_4^{2-} levels in the feed were different between these runs. A definitive explanation for the variation in the losses has not been identified from the data available. In similar testing that was performed for Pu loading (10), the issue of losses was not considered as critical of an issue as it has been with Np (due to the relatively high solubility of Np^{5+} in HLW supernate and the low limits for Np in saltstone). For this Np study, the effect of N_2H_4 concentration in the feed on Np losses over various feed hold times has prompted extra attention to losses. A complete understanding of all the parameters that lead to elevated Np losses to the raffinate during the course of this study has not been possible in the time allowed.

Table V. Oxidation of Np in Anion Feed Solution

	ADS ID	Age days	Np(V) %	Np g/l
Cr234 Feed A	3-189516	2	3.60%	3.167
8M HNO3		3	<0.16%	
0.06M excess FS		4	0.18%	
0 M hydrazine		5	0.19%	
Cr234 Feed B	3-189517	2	5.40%	3.103
8M HNO3		3	1.11%	
0.06M excess FS		4	1.43%	
0.02 M hydrazine		5	3.68%	
Cr236 Feed A	3-190224	0.5	ND	3.167
8M HNO3		1.5	ND	
0.06M excess FS		2.5	ND	
0 M hydrazine		3.5	ND	
		4.5	0.29%	
Cr236 Feed B	3-190225	0.5	ND	3.103
8M HNO3		1.5	ND	
0.06M excess FS		2.5	ND	
0.02 M hydrazine		3.5	ND	
		4.5	0.29%	
Cr237 Feed	3-190557	1	2.91%	4.983
Cr236 Feed C	3-190555	na	98.20%	19.191
undiluted 8.5				
Cr236 Feed D	3-190556	1	42.80%	0.640
8.5 added to 8M HNO3	no Fs, no N2H4			

Hydrazine: One of the primary goals of this study was to determine the necessary concentrations of N_2H_4 in the anion process streams to allow for efficient operation of the process and yet minimize the need for DSA controls related to hydrazoic acid formation. Criteria were suggested that in both the feed and product solutions Np(IV) should be stable from significant oxidation for 4 days. Significant oxidation was considered be greater than 0.5 percent. There was interest in considering longer periods of time, but testing becomes increasingly time consuming when periods of 1 or 2 weeks are studied. Processing delays of one week are not considered routine due to a significant penalty for the lost production time. In the baseline flowsheet, N_2H_4 is used in the anion feed, in the wash stream and in the elution acid. In a parallel study, Askew (13) showed that anion exchange resin under Np processing conditions did not concentrate hydrazoic acid.

Hydrazine in the feed solution: The concentration of N_2H_4 in the feed solution was varied from 0 to 0.1M. In runs Cr221-Cr224, which had the highest N_2H_4 concentrations, the losses were uniformly low at less than 0.6%. Runs Cr222 and Cr224 were allowed to age for 5 and 7 days respectively prior to loading as those solutions were recycled from break-through loading runs and had been chemically adjusted for the first column run. Inconsistent results were obtained when N_2H_4 was not used but the Np loading varied considerably.

Experiments Cr234 and Cr236 were test feed samples where the Np was added to a matrix of HNO_3, FS and N_2H_4 and the percent Np^{5+} was determined over time. In each experiment, samples were prepared that only differed by the presence of N_2H_4. The results from these tests are shown in Table V. Experiment Cr234 gave erratic results that were attributed to lab error. When repeated as Cr236 A&B, the results were consistent and indicated that N_2H_4 was not necessary to achieve low losses. In Cr236A and Cr236B, no Np^{5+} was detected until the samples were 4.5 days old and at that time the Np^{5+} consisted of only 0.29%. No difference was detected in this experiment based on the presence or absence of N_2H_4.

Other samples were also prepared as part of Cr236 and the results are also shown in Table V. Unaltered Tank 8.5 sample from H-Canyon in August 2002 and Tank 8.5 sample diluted (1:30) with 8 M HNO_3 were tested for Np^{5+}. As expected, essentially all the Np in the unaltered 8.5 sample was Np^{5+}. However the sample that consisted of an 8 M HNO_3 dilution of tank 8.5 without any valence chemicals was only 42.8% Np^{5+} the next day. Although no data exists, the manufacturer of the TEVA column believes that Np^{6+} behaves like UO_2^{2+} in HNO_3 and should end up being counted as Np^{5+} by this test procedure. If the result of the Np^{5+} test actually represents total Np^{5+} + Np^{6+} then 57+% of the Np^{5+} was reduced to Np^{4+}. The only mechanism recognized is disproportionation, but that should produce just as much Np^{6+} as Np^{4+}. Although our understanding of the chemistry involved is not complete, it is not surprising that nitrate complexation of Np^{4+} might shift the equilibria between the three valence states to favor Np^{4+}. The effect of time on this equilibrium was not tested, but probably a large percentage of Np could be recovered without either FS or N_2H_4 addition. Over time, radiation dose to the HNO_3 is expected to produce nitrite that should increase the fraction of Np^{5+} present. It could also reduce the Np^{6+} to Np^{5+}.

The last feed sample tested for Np^{5+} was the actual feed to Cr237 a day after FS addition (but without N_2H_4). In this case 2.91% was reported as Np^{5+} and when the column was run on the fifth day, total losses were measured at 2.5%. This result suggests that most of the losses were due to improper valence one day after preparation. Unfortunately no raffinate spectra were obtained from this column run. That would have been a way to confirm that the cause of the high losses was due to Np^{5+} and not some other loading problem.

Experiment Cr238 was intended to validate the up-load down-elute column operation with feed prepared from tank 8.5 samples (just like Cr236 and Cr237). The results from Cr237 were not yet available when Cr238 was run and the spectrometer was not operating. The losses from this run were slightly less than those observed in Cr237, but no data were obtained to suggest the cause. The high losses may have been caused by the slow oxidation of Np^{4+} to Np^{5+} although other causes cannot be ruled out. The end result was that in 3 of the 4 tests unsatisfactory results with regard to losses were obtained when non-N_2H_4 feed was aged for 5 days. Based on the results of these tests, N_2H_4 appears to be necessary in anion feed solution to prevent Np^{4+} oxidation. If N_2H_4 is removed from the valence adjustment step, the possibility of increased losses to the raffinate of up to 3 % should be anticipated.

Hydrazine in the wash solution: In the initial portion of this experimental program, there was concern that Pu^{238} needed to be removed to satisfy shipping/storage concerns of the customer. Initially efforts were expended to increase the DF for Pu by lowering the HNO_3 concentration in the feed and wash and increasing the effectiveness of FS reduction of Pu. Increasing the FS concentration in the feed and the "partition wash" was expected to increase Pu removal. Increasing the N_2H_4 concentration in the feed and the wash was expected to reduce the HNO_2 concentration and to protect the Fe^{2+} from oxidation. After several experiments it became apparent that the success of preventing Pu from absorbing onto the resin depended on processing the entire feed solution very promptly. With the expected large heel volumes in the feed tanks, it became apparent that obtaining a good DF for Pu during the loading cycle was not very practical with the expected equipment limitations in HB-Line. The desired high production rate would also have to suffer significantly to improve the Pu removal. Results for the DF obtained for Pu and for Pa are noted in this report, but efforts to provide a Pu removal ability to the process were abandoned in the middle of the study. Based on the time it took for significant Np^{5+} to form in 8 M HNO_3, N_2H_4 was then dropped from the wash solution. This change did not appear to affect losses during washing. The decon wash step remains recommended for the proposed flowsheet as it lowers the level of impurities in the hearts cut for a very modest volume and time investment and is needed to empty the feed line and loaded portion of the resin bed of residual Np feed solution. If no wash were performed at all, losses to the heads cut would be expected to rise significantly

Hydrazine in the elution acid: Np^{5+} has been identified in the literature as a cause for high precipitation losses and ascorbic acid is added in the precipitator feed adjustment to scavenge whatever Np^{5+} does form. The amount of ascorbic acid proposed in the baseline flowsheet amounts to 0.03 M excess (assuming no Np^{5+} is formed). The ascorbic acid reduction of Np depends on [HNO_3], temperature, and on the absence of HNO_2 (which will rapidly oxidize the ascorbic acid). Ascorbic acid in Pu or Np solutions forms tars and black solids upon oxidation that cause operational problems in the process. Porter (14) tested ascorbic acid in the range of 0.03 to 0.06M. In those tests he recommended 0.05 M N_2H_4 in the elution acid and found that this concentration was sufficient to maintain the Np^{4+} for two weeks after elution. For these reasons the N_2H_4 has been found to be required in the valence adjustment step for precipitation. The purpose of N_2H_4 in the elution acid is to maintain the Np product solution as Np^{4+} until it can be precipitated as $Np(C_2O_4)_2$. This N_2H_4 minimizes the amount of ascorbic acid required and avoids the problems associated with the larger amount of ascorbic acid that would be required if the Np were allowed

Table VI. Oxidation of Np in Anion Product Solution

Run ID	α % Np	ppm Pu	ppm Pu238	[N_2H_4]	% Np(V)	Days after Elution	
Cr230	85	779	3	0	~100	14-21	[1]
Cr231	2	3064	1434	0	1.29	1	
					~100	7	[2]
Cr232	2	2931	1371	0.01	6.39	1	
					10.9	5	
Cr233	4	3363	1002	0.05	0.36	3	

[1] Based on Vis-Nir Spectra Observations

[2] Based on Vis-Nir Spectra Observations of Diluted Sample

Figure 6. Oxidation of Diluted Np Hearts over Time 900-1000nm

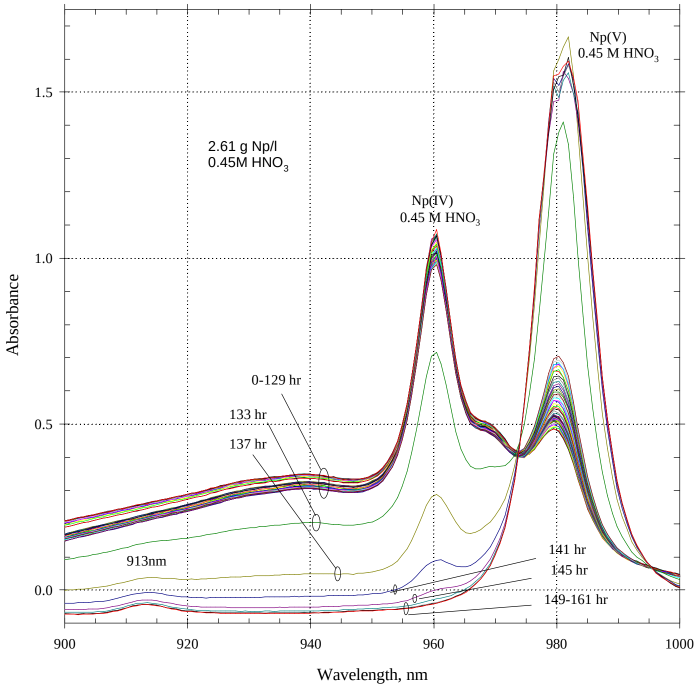
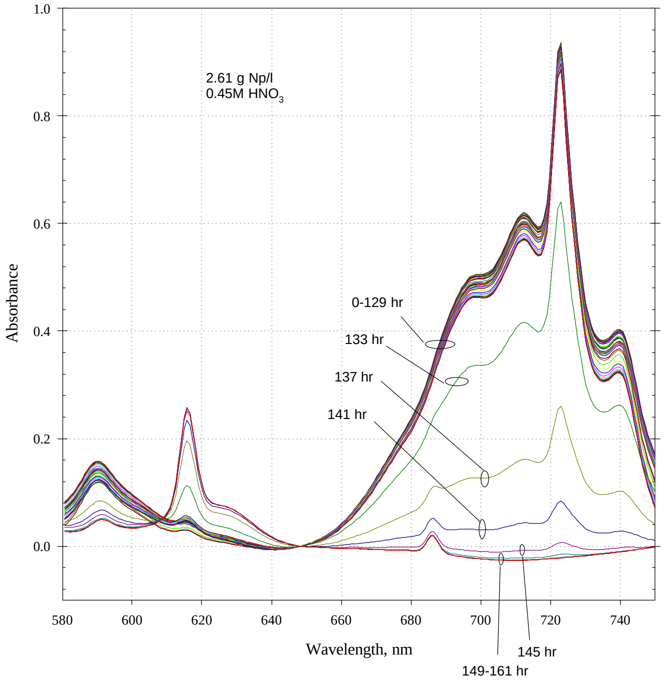


Figure 7. Oxidation of Diluted Np Hearts over Time 580-750nm

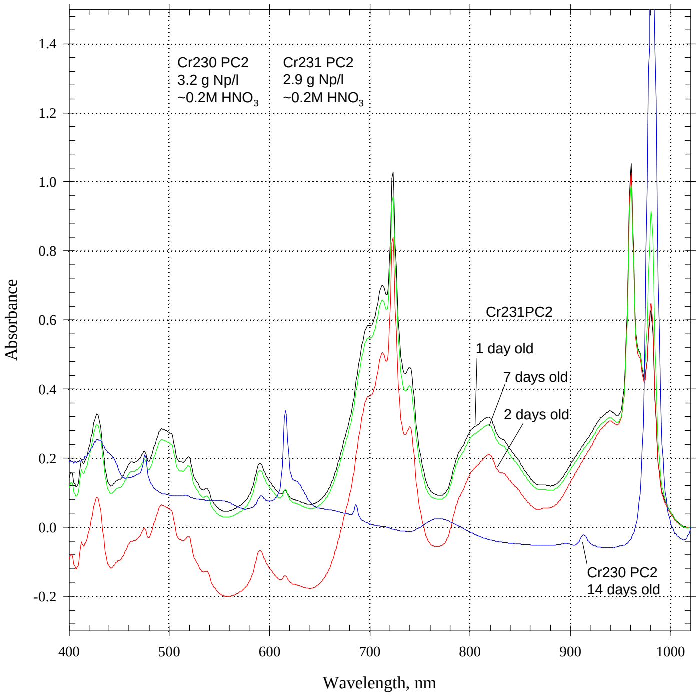


to oxidize. The question posed for the current study was could the amount of N_2H_4 be reduced. Table VI summarizes the results obtained on the stability of Np^{4+} in anion exchange product solution. Both spectral observations and the Np^{5+} analytical test results are included. Without N_2H_4 the Np^{4+} appeared to oxidize completely over 1-2 weeks. This behavior was observed for solutions that contained both relatively low and high levels of Pu^{238}. Studies with diluted hearts samples showed a steady oxidation rate until a point was reached at which the entire sample converted to Np^{5+}. Figures 6 and 7 show detailed spectra of this oxidation. If the spectral changes are presumed linear (not necessarily a good assumption), it appears that roughly 10-20% of the diluted sample oxidizes over the first 129 hr after elution. Over the next 16 hours it appears that essentially all the Np^{4+} oxidizes to Np^{5+}. This delay effect may have been due to residual sulfamate from the feed solution that was retained by the anion exchange resin. Sulfate on the order of 0.004 M was measured in a grab sample late in the heads cut of Cr233. The time scale of the accelerated oxidation of this diluted sample has limited meaning to the situation in HB-Line.

Figure 8 shows similar data to that in Figures 6 and 7, but in this case it shows the oxidation as it occurs in undiluted “post-Hearts” samples from runs Cr230 and Cr231. Interestingly, Cr230 had much less Pu^{238} contamination than Cr231 and total alpha activity (and thus the alpha dose) was almost 100 times less. Still the oxidation rates are very similar and after three weeks the Cr230PC2 solution was completely oxidized to Np^{5+}. No attempt has been made to confirm the Cr230 result, but if true, it suggests that chemical oxidation is controlling. However, this author is somewhat skeptical of that result without further confirmation.

Although the mechanism is not completely understood, it appears that the basic oxidation rate is too rapid to wait to add N_2H_4 after elution. When 0.01 M N_2H_4 was tested, six percent oxidized in the first day compared with 0.36% total after four days when 0.05 M N_2H_4 was used in the elution acid. Ultimately it was decided that the objective of reducing the N_2H_4 in the elution acid stream was of limited value. As a result, the conclusion was reached to leave the elution acid stream unchanged in composition at 0.17 M HNO_3 and 0.05 M N_2H_4. The Np^{4+} in this product solution should be stable for more than three days with minimal oxidation. The addition of 0.03 M ascorbic acid in the subsequent precipitation feed adjustment step should be effective at reducing the minor amounts of Np^{5+} that form. Higher concentrations of ascorbic acid should not be necessary unless significant processing delays are encountered.

Figure 8. Oxidation of Np^{4+} to Np^{5+} in Weak HNO_3



Pu and Pa Decontamination: The column loading and wash conditions and the resulting DFs for Pu and Pa are tabulated in Table VII. DFs for Pu as high as 6.8 were measured when favorable conditions for Pu^{3+} stability were provided and 3 to 6 BV of reductive wash was used. However it was recognized that due to equipment limitations it would be difficult to achieve a DF of better than 2 to 3 in the plant process. Large tank heels would limit the ability to process the adjusted feed solution promptly. Aged feed would build up the amount of Fe^{3+} and SO_4^{2-} and require extra FS addition. Significant reductive wash volume would also be required. As a result the investigation of Pu rejection was abandoned.

Pa DF results 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 fairly complex and the analytical results observed in this study were very variable. While DFs of greater than 20 were observed on several occasions, it appears that those high DFs were obtained only when significant reductive washing was being performed. When a 3 BV decon wash was performed, a realistic expectation for the Pa DF appears to be in the 2.5 to 4 range. This still represents a Pa removal of 60 to 80%. Reduction of the wash volume can be expected to further reduce the Pa rejection. It is likely that the valence state of Pa greatly affects the ability of the anion process to reject Pa to the raffinate stream, but no special effort was made to study this issue.

Uncertainties: As previously stated, instantaneous flowrates occasionally varied widely form 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. However additional resin was added during column setup to keep the resin volume at its targeted value. This adjustment should bias the amount of resin loaded towards a higher value and likewise bias the resin loading values upward over what would be observed if such care were not taken. 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. Most column runs had an overall material balance uncertainty of < 4% for Np^{237}. These results support the viewpoint that routine analytical results have a precision of ~4 % for Np^{237}. Poor material balances were generally seen for Pa^{233}. Solutions should have had 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 anion exchange runs has been performed in an attempt to define requirements for operating the process equipment in HB-Line. This work has generally confirmed the conditions described in the design flowsheet. Efforts to demonstrate a reduction in the amount of N_2H_4 required have generally not been successful based on the criteria provided. Elimination of N_2H_4 in the feed solution appears to leave the Np susceptible to limited oxidation over a time scale of days, however not all the experimental data was consistent. Five days after valence adjustment, experimental losses ranged from 0.3 to 3 percent of the Np. Oxidation of Np in the anion product stream appears to occur fairly rapidly in the absence of N_2H_4. Elimination of N_2H_4 from the elution acid stream would therefore require a large increase in the amount of ascorbic acid required for precipitation.

Resin loading of 50 g Np/l of resin was observed with losses of less than 0.5 percent. In a single upflow-load downflow-elute experiment a hearts cut of 40 g Np/l was collected with losses to heads and tails cuts of 7 %. The loading results appear consistent with the desire to load 2 kg of Np on a 45 liter resin column. The elution result indicates that the goal of a 50 g/l hearts cut should be achievable with additional losses to heads and tails cuts.

Table VII. Summary of Pu and Pa DF Behavior

	Loading Conditions	Washing	Loading Losses, %	Washing Losses, %	Pu DF	Pa DF	Comments
Cr221	0.096M FS 0.05M N2H4 6.4M HNO3	3BV 0.05M N2H4 6.4M HNO3	na	na	2.5	5.1	65% APHA Np
Cr222	0.096M FS 0.05M N2H4 6.4M HNO3	3BV 0.05M N2H4 6.4M HNO3	0.2	na	2.5	8-15	Remaining Cr221 Feed 48% APHA Np
Cr223	0.2M FS 0.10M N2H4 6.4M HNO3	6BV 0.2M FS 0.10M N2H4 6.4M HNO3	0.2	0.4	4.3	27.3	White Solids after FS 15% APHA Np
Cr224	0.05M FS 0.05M N2H4 6.4M HNO3	3BV 0.2M FS 0.05M N2H4 6.4M HNO3	0.02	0.3	2	20	Feed aged 1 week No Pu rejection 42% APHA Np
Cr225	0.1M FS excess 0.02M N2H4 6.2M HNO3	3BV 0.08MFS 0.05M N2H4 6.4M HNO3	0.1	1.3	6.8	2.5	Small breakthur wash Reject Pu during load and Wash 52% APHA Np
Cr226	0.082M FS excess 0.02M N2H4 7.6M HNO3	3BV 0.05M N2H4 6.4M HNO3	0.06	na	1.3	3.1	Higher loading 78% APHA Np
Cr227	0.082M FS excess 4 days old 7.4M HNO3	3BV no N2H4 8M HNO3	1.5	1.3	0.9	7.6	Small Breakthru during loading Np(IV) EC2 from Cr226 no new FS 73% APHA Np
Cr228	0.061M FS 0.005M N2H4 6.4M HNO3	0 BV	0.1	na	1.7	2.1	Washed with elution acid
Cr229	0.047M FS excess 0.008M N2H4 6.6M HNO3	6BV no N2H4 6.4M HNO3	0.01	0.01	1	0.8	Poor Pu and Pa DF 80% APHA Np
Cr230	0.025M FS excess 0 M N2H4 5.7M HNO3	3BV no N2H4 8M HNO3	3.73	na	2.6	1.2	Slight breakthru, too fast? 779 ppm Pu239 85% APHA Np
Cr231	0.044M FS 0M N2H4 8.2M HNO3	3BV no N2H4 8M HNO3	0.06	0.0033	0.9	2.5	1434 ppm Pu238, 3064 ppm Pu238 2% APHA Np 1.29% Np(V) in Product after 1 day
Cr232	0.051M FS excess 0M N2H4 8M HNO3	3BV no N2H4 8M HNO3	0.06	0.06	1	1	Poor Pa DF? 2931 ppm Pu, 1371 ppm Pu238 2% APHA Np, 6.38% Np(V) after 1day
Cr233	0.041M FS excess 0.001M N2H4 8.06M HNO3	3BV no N2H4 8M HNO3	14.6	1	3.1	3.7	High Pu DF, Np(IV) in EC, rate? 3363 ppm Pu, 1002 ppm Pu238 4% APHA Np
Cr235	0.04-0.075M FS excess 0-0.02M N2H4 7-8M HNO3	3BV no N2H4 8M HNO3	2%-4.6%		1	4	Poor Pu matl balance High Np losses, 2nd Feed btl? 2% APHA Np
Cr237	0.051M FS excess 0M N2H4 8M HNO3	3BV no N2H4 8M HNO3	1.87	0..5	0.9	4	Missing Pa 2.9% Np(V) after 1 day 8% APHA Np
Cr238	0.054M FS excess 0M N2H4 8M HNO3	3BV no N2H4 8M HNO3	1.36	0.44	1	3.4	Upload-Downelute Missing Np 8% APHA Np

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