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Effect of Oxalate on the Recycle of Neptunium Filtrate Solution By Anion Exchange

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Nov 2004

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Acronyms and Terminology:

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

ADS – Analytical Development Section of Savannah River National Laboratory: Provided analytical services in support of this work.

Alpha PHA – Alpha plate counting method with Pulse Height Analysis to discriminate by alpha energy.

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

CLAB – Central Laboratories Facility

Composite Sample – Solution collected for a relatively long period of time. Represents solution collected over a significant portion of a step of the process. Normally used for material balance calculations.

Crxxx – Unique designation assigned for each laboratory Column Run. “Cr” stands for Column Run and xxx is the number of that particular experiment.

DF – Decontamination Factor: A measure of the ability of the process to remove a specific impurity. Calculated by dividing the concentration of the impurity (on a Np basis) in the feed solution by the concentration of the impurity (on a Np basis) in the product solution.

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

Effluent – Solution that is discharged from the column after transfer through the resin bed to either absorb the Np onto the resin or wash impurities from the resin bed.

Elution – The process step where dilute acid is passed through the resin bed to remove the absorbed Np and collect it as a product solution.

Free Acid – Acid titration method using metal ion complexant in an attempt to determine hydrolysable H^+ only.

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

Gamma Scan – Gamma emitting isotope counting method by gamma energy.

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

H – Height of the resin bed in the column

Heads Cut – Initial portion of elution solution that has passed through the column. This solution consists of the displacement of the 8 M 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.

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.

$NaNO_3$ – Sodium nitrate

Q – Volumetric flowrate

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

RS or R_s – Solubility scaling factor for oxalic acid that this proportional to the free oxalate concentration in solution.

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

SRNL–Savannah River National Laboratory (formerly Savannah River Technology Center, SRTC).

Tails Cut – Last portion of elution step that contains dilute HNO_3 and minimal Np. Generated when excess elution acid is used to ensure complete elution of Np from the column.

Total Acid – Acid titration method measures base required to titrate both free acid and metal ions.

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

Visual Break-through – Point during the loading cycle where Np can be visually observed in the effluent from the column by its pale green color. Concentration where this occurs in laboratory sized equipment is in the range of 0.2 to 1 g Np/L.

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Effect of Oxalate on the Recycle of Neptunium Filtrate Solution By Anion Exchange

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Nov 2004

SUMMARY:

A series of laboratory column runs has been performed that demonstrates the recovery of neptunium (Np) containing up to 0.05 M oxalate. Np losses were generally less than one percent to the raffinate for feed solutions that contained 2 to 10 g Np/L. Up to 16 percent Np losses were observed with lower Np feed concentrations, but those losses were attributed to the shortened residence times rather than the higher oxalate to Np ratios. Losses in the plant are expected to be significantly less due to the lower cross-section flowrate possible with existing plant pumps.

Elimination of the permanganate treatment of filtrates appears to be reasonable since the amount of Np in those filtrates does not appear to be practical to recover. Combination of untreated filtrates with other actinide rich solutions is not advisable as precipitation problems are likely. If untreated filtrates are kept segregated from other actinide rich streams, the recovery of the remaining Np is probably still possible, but could be limited due to the excessively high oxalate to Np ratio.

The persistence of hydrazine/hydrazoic acid in filtrate solutions dictates that the nitrite treatment be retained to eliminate those species from the filtrates prior to transfer to the canyon.

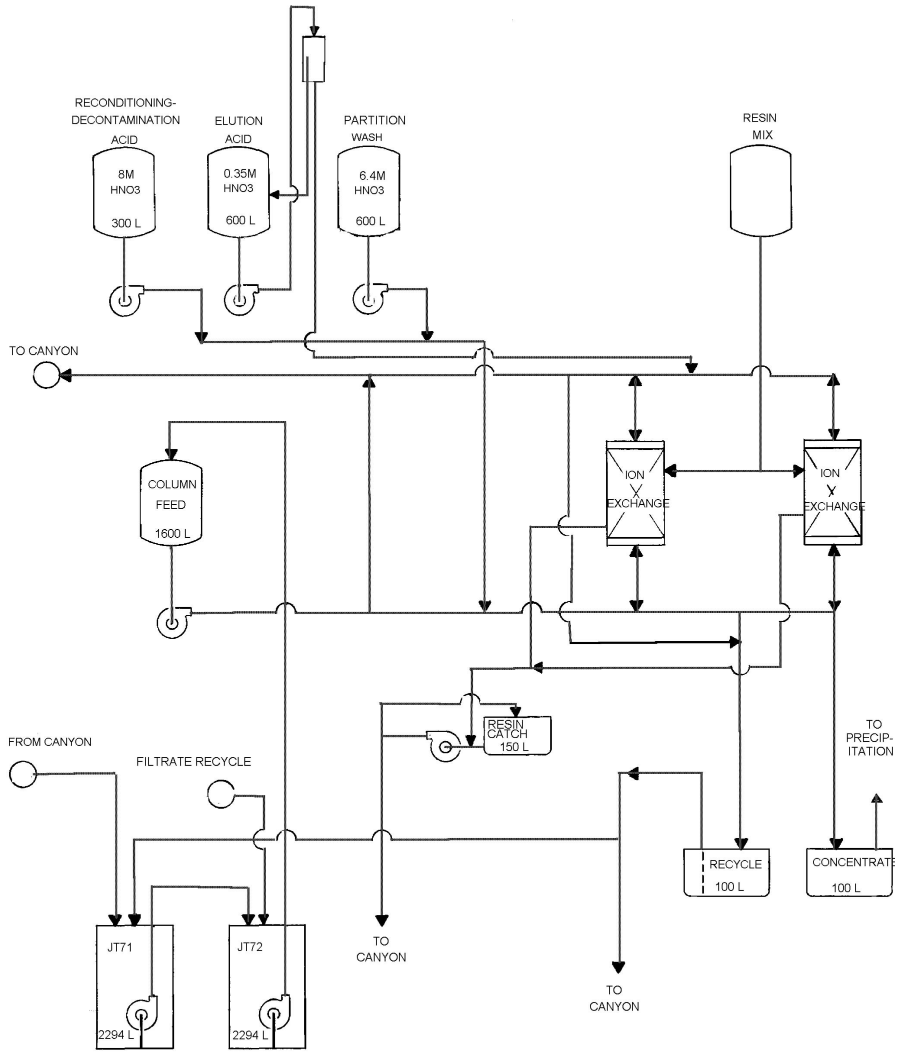
Elimination of the permanganate treatment of precipitator flushes and recovery by anion exchange does not appear to be limited by the oxalate effect on anion exchange. Np from solutions with higher oxalate to Np molar ratios than expected in precipitator flushes was recovered with low to modest losses. Solubility problems appear to be unlikely when the moles of oxalate involved are less than the total number of moles of Np due to complexation effects. The presence of significant concentrations of iron (Fe) in the solutions will further decrease the probability of Np oxalate precipitation due the formation of Fe oxalate complexes.

Np oxalate solubility data in 8 M HNO_3 with from one to six times as much oxalate as Np have been obtained. These data supplement literature data in the high HNO_3 low oxalate region, but provide additional data for solutions with relatively large amounts of Np present. Enhanced solubility of Np oxalate over that reported in the literature was observed.

BACKGROUND:

The new HB-Line facility was designed and built in the early to mid 1980’s. Phase II of HB-Line was previously started up to stabilize plutonium (Pu) solutions in 2001. This facility was designed to receive Pu or neptunium (Np) nitrate solutions from H-Canyon and convert the actinides into oxides for storage or shipment. The process was converted to a Np nitrate solution feedstock in August 2004. After receipt of the Np solution, anion exchange columns are operated to purify and concentrate the Np nitrate solution, after which the purified Np is 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. The present study was undertaken to investigate the processing of residues from the precipitation process as a recycle stream and to provide guidance on the continued need to destroy the oxalate in those process streams with permanganate.

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



Np solution is received from H-Canyon as a moderately concentrated Np nitrate solution (15-20 g Np/L, 6-7 M HNO_3). The valence state and acid concentration are 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 of HNO_3 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 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 in the past to produce a Np^{4+} and Pu^{4+} feed solution. In the current Np process, Np^{4+} is the preferred species and it is desirable to reject Pu to the raffinate stream. However in the high nitrate feed solution, Pu^{3+} tends to oxidize to the Pu^{4+} valence state, which binds to anion exchange resin more strongly than Np^{4+}.

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

	Re-con-di-tion	Feed	Reduc-tive Wash	Decon Wash	Elution				
Np (g/batch)		2000	4.56	13					
Np (g/L)		10.7	0.02	0.2					
HNO_3 (M)	8	8	6.4	8	0.17	Assumptions			
HB-Line	up	up	up	up	down	Col ID 14.75 in	Column area =	1102	cm^2
Flow (L/min)	2.7	1.5	1.6	1.6	1.6	Resin Bed Height 13.5 in			
v (mL/min/cm^2)	2.4	1.4	1.5	1.5	1.5	Resin Bed Volume 39.5 L			
Volume (L)	40	188	228	66	90	Volumes from Flowsheet			
Time (min)	15	125	143	41	56				
BV	1	4.8	5.8	1.7	2.3				
mgs Np/min/cm^2		14.5				Assume 10.65 g Np/L			
SRNL Np	up	up	up	up	down	Col ID 19 mm	Column area =	2.835	cm^2
Flow (mL/min)	5	5	5	5	5	Resin Bed Volume measured as 97 cc			
v (mL/min/cm^2)	1.8	1.8	1.8	1.8	1.8	Resin Bed Height 13.5 in (34.2 cm)			
Volume (mL)	100	570	1200	200	250		Plant to Lab Column Scale		
Time (min)	20	114	240	40	50	407	Resin Volume Ratio		
BV	1.0	5.9	12.4	2.1	2.6	389	Cross-sectional Area Ratio		
mgs Np/min/cm^2		15.9				9 g Np/L in Feed			

The anion column is 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 is transferred from the receipt/feed adjustment tanks to a column feed tank. The feed solution is then pumped "up-flow" through the column, with the anionic $Np(NO_3)_6^{2-}$ complex absorbing onto the resin bed. The column raffinate (which contains the cationic metal impurities and is normally waste) will be transferred directly to an H-Canyon tank. After a full batch of Np feed solution has been loaded onto the column (using 70 to 100% of the resin bed's physical capacity), the bed is washed "up-flow" with both a reductive wash and a decontamination wash. In the historical flowsheet, a reductive wash step (referred to as a "partition wash") was used to wash out additional ^{238}Pu cross-contamination. That wash used a lower HNO_3 concentration (5.5-6.4 M), in addition to N_2H_4 (to scavenge the HNO_2) and FS (to reduce the Pu). In old HB-Line this step was typically performed when additional ^{238}Pu removal was desired. In the current flowsheet, the nitrate concentration of the wash was lowered to 6.4 M HNO_3 in the presence of 0.05 M FS during the wash step, in order to suppress the formation of the absorbable $Pu(NO_3)_6^{2-}$ complex, so that at least 30 percent of the Pu could be rejected as Pu^{3+} to the raffinate stream.

The decontamination wash provides improved purification by displacing residual impure solution from the column and piping prior to elution. The Np is then 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.

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 "breakthrough" 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. It was recognized that increasing levels of oxalate in the feed would likely reduce the capacity of the resin for Np at some point. Little effort was expended on this issue in the current study as it was not considered particularly limiting for the recycle operation under consideration.

Table II. Capacity of Reillex™ HPQ for Np. (*9*)

$[HNO_3]$ Feed M	Resin Loading Breakthrough	Saturation	Loaded	Np Losses
	gm Np /L 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

The anion exchange resin in use in HB-Line is Reillex™ HPQ. Fred Marsh of Los Alamos National Laboratory and Reilly Industries jointly developed this resin based on another polypyridine-based resin, Permutitt SK, which was used in Pu and Np processes in the late 1950's (*4, 5, 6*). Superior resistance to radiolytic and chemical damage has been attributed to both of these resins due to the use of a pyridine ring "N" functional group compared to the quaternary amine function group used in the conventional divinylbenzene anion resins. Marsh also found this resin attractive due to its relatively high loading for Pu and its excellent elution behavior (*4*). In 2000, Crooks et. al. (*7*) and Kyser (*8*) studied the loading of the current version of Reillex™ HPQ for use in the Pu columns in HB-Line.

In another study, Kyser (*9*) measured the capacity of Reillex™ HPQ for Np under various process conditions (see Table II). From ~6 M HNO_3, 40 g Np/L were 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. In a later study, Kyser (*10*) developed a modified flowsheet to accomplish a nominal 30 percent ^{238}Pu removal via reductive washing (sometimes referred to as partition). Based on previous work of Kyser (*9*) and also Burney (*11*), reductive wash conditions were proposed and tested. The recommended approach was to wash with 6 BVs of 6.4 M HNO_3 - 0.05 M FS - 0.05 M N_2H_4. A later study, Kyser and Hill (*12*) found that > 60% of the total Fe as Fe^{2+} in the reductive wash solution was sufficient to ensure a minimal 30% removal of the ^{238}Pu in the feed. ^{238}Pu removal is not significant to the effect of oxalate on the loading of Np onto the resin for the current study.

Oxalate precipitation of Np results in a filtrate stream and a precipitator cleanout stream to be discarded or recycled at the completion of the campaign. Due to criticality and accountability concerns with these streams when the facility was started up for Pu operation, a permanganate treatment to chemically oxidize the oxalate was developed. A nitrite treatment step was then used to reduce the large amount of MnO_2 solids to soluble Mn^{2+}. Either permanganate or nitrite will also rapidly react with all the hydrazine and hydrazoic acid that may still be present in these solutions. While together these chemical treatments are generally very effective at producing a stable solution free of solids or precipitants that could later produce solids, they can be troublesome in practice due to the significant quantity of gas generated from chemical reaction during addition of the chemicals to the tanks and the large amount of MnO_2 solids that must be dealt with as an intermediate. These treatment steps were carried over into the Np process with minor adjustments for the amounts of hydrazine, ascorbic acid and oxalate actually expected in the process solutions.

The Np filtrate stream is expected to be 1-2 M HNO_3, 0.1 M oxalate, with up to 0.05 M hydrazine and 1 to 100 mg/L Np (except for possible process upsets). The precipitator cleanout stream is expected to be 14 M HNO_3 with 5 to 10 g/L Np and only 0.02 to 0.04 M oxalate (2 moles of oxalate per mole of Np). Since the precipitator cleanout stream is generated only occasionally, the solution volume from cleanout is relatively small compared to the filtrate volumes. The current process has these two streams treated and then combined and stored in a single tank in H-Canyon until the completion of the Np campaign. A decision on the recovery or discard of this material will be made later.

Elimination of the permanganate treatment of solution residues from precipitation would simplify processing. Criticality is not a significant concern for Np solutions as it was for Pu solutions. However formation of Np solids will still be an accountability concern and is generally undesirable. In old HB-Line permanganate treatment of oxalate was not performed. It appears that some use of acid tank heels may have been used to decrease the solubility problems. Luerkens (*13*) and Porter (*14*) performed solubility studies that showed under normal precipitation conditions that Np^{4+} oxalate is significantly less soluble than Pu oxalate. Under proposed precipitator cleanout (or flush) conditions Hill (*15*) observed several orders of magnitude increase in solubility for Np oxalate. Under the conditions of moderately high HNO_3 concentration and low oxalate concentration there is considerable uncertainty in the expected solubility and the data that exist are not particularly consistent. For this reason there is considerable uncertainty about the conditions under which mixing of untreated filtrates and precipitator solutions would not form Np oxalate solids. The most significant concern was that the presence of soluble Np oxalate might have a severe impact on the performance of recovery by anion exchange. However Porter (*14*) indicated that lean Np, high oxalate filtrates could be recycled to anion exchange without destruction of the residual oxalate.

EXPERIMENTAL:

The experimental work associated with the program primarily consisted of anion column runs with both Np and oxalic acid present. The study was expanded slightly to include a set of batch samples that were used both in supporting spectrophotometric observations on the effect of oxalate complexation and solubility tests under more realistic process conditions than available in the literature.

Solubility Tests:

Two series of vials were prepared with the HNO_3, Np, and N_2H_4 concentrations kept constant and the oxalate concentration varied from 0 to 0.09 M at 0, 0.05 and 0.1 M FS. The source Np solution was a hearts cut from a recent Np anion exchange run (with N_2H_4 in the elution acid) that was 17 days old at the time of preparation of the samples and was assumed to be pure Np^{4+}. The range of concentrations in the test matrices is shown in Table III. The spectra of each sample were measured within 1 hour of the addition of the FS and Np and then again 12 days later. All matrices were stored at ambient temperature. After 12 days, all vials were sampled without any mixing (to avoid disturbing any Np oxalate solids that may have been present) and submitted for alpha and gamma counting. Vials D, E and F were sampled a second time after 43 days and resubmitted for alpha and gamma counting.

Table III. Test Matrix for the Effect of Oxalate on Np^{4+} Spectra and Solubility.

		Oxalate -->				
		0	0.025	0.05	0.07	0.09
FS	0	A'	B'	C'	D'	E'
	0.05	A	B	C	D	E
	0.1					F

Note: All samples were prepared to contain 3.4 g Np^{4+}/L in 8 M HNO_3.

Column Studies:

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 ≡ 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 affect scaling in that it will result in a higher saturation Np resin loading. Moreover, slower flowrates would also tend to increase the effective loading by increasing the time for mass transfer. The baseline flowsheet feed rate was based on 14.5 mg/min/cm^2 (*1, 9, 10*). Hill (*16*) 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 SRNL test conditions.

Figure 2. Assembled Column

Figure 3. Screen used to Retain Resin Bed.

The original columns were designed for operation with a 15.5-inch resin bed depth that retained 45 liters of resin. However, plant modifications to the Np columns for installation of rupture disks for pressure relief have changed the effective resin capacity. The current study was based on calculations that showed the two Np columns to hold 13.48 inch (39.05 liters) and 13.86 inch

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

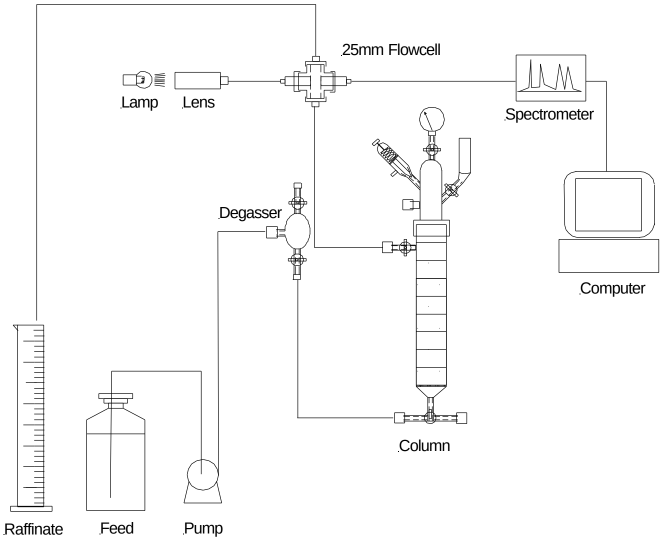
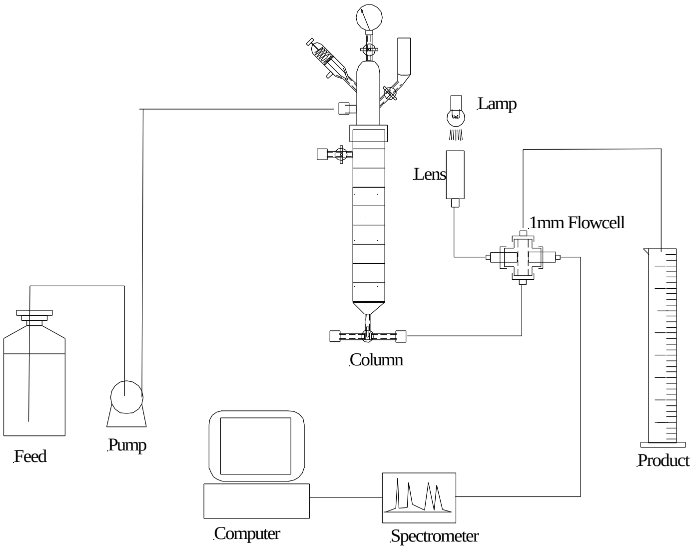


Figure 5. Elution Experimental Setup.



(40.13 liters) respectively (*17*). More recent calculations have slightly increased the resin capacity of each column by repositioning the piston. For the present experimental work, a laboratory column that was used in a previous study continued to be used. This column was prepared with a 34.2-cm (13.5-inch) resin depth. For these experiments, a resin volume of 97 cm^3 of settled resin was used in a 19-mm inside diameter glass column (cross sectional area of 2.835 cm^2). An assembled column is shown in Figure 2.

Resin Pretreatment: Like the earlier Np work (*9*, *10*, *12*, *18*), no resin pretreatment was performed to eliminate the low temperature exotherm. All resin that was tested came from the same 1998 manufacturer's lot (#80302MA) that was purchased by SRNL for Pu flowsheet work. All resin was initially converted from the chloride form (as-shipped) to the nitrate form by washing with 1 M $NaNO_3$ (10 BV in a column was the preferred method, but other methods are acceptable).

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

Lab Equipment: A picture of a column is shown in Figure 2. The column used #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 solely by a ground glass joint. As a safety precaution, the head also had an Ace glass pressure-relief valve.

Table IV. 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: SRNL fabricated plexiglass cuvette holders each with 2 lenses similar to flowcell, 1 unit for light reference and 1 for glovebox standards

Figure 6. 1 mm Flowcell

An additional arm with a stopcock and funnel allowed the column to be vented. A modification was made to the bottom of the column over that used in past designs. The 3-way stopcock used to change flow direction was replaced with a 3-way 1/8-inch Swagelok™ valve. The stopcock was replaced 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. Additional minor plumbing changes were made by replacing two of the #7 Teflon screw-thread bushings with a bushing - quick-connect combination. The polypropylene quick-connect with backflow protection eliminated troublesome leak problems that often cropped up when the pump line had to be converted between the load/wash and elution configurations. This change made for both quick and reliable connections. 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 equipped for motor speed control outside of the glovebox was used to pump feed, wash, or elution acid through the column. A ½-inch Swagelok™ cross and two ½-inch optic lenses were used to fabricate a flowcell with a 25.4-mm path-length that was used to observe dilute Np solution from the column during the load/wash steps. A 1-mm flowcell for use during the elution step was fabricated by welding 3/16-inch tubing into a ½-inch Swagelok™ union and milling out the union to allow two ½-inch optic lenses to slide to the center. An unassembled 1-mm cell without lenses is shown in Figure 6. Two pairs of fiber optic lines previously installed through the ceiling of the glovebox allowed a light signal to be brought into the glovebox, passed through the flowcell and carried out to a Zeiss spectrometer controlled by an NT-based computer. A detailed list for the complete spectrophotometer system used is given in Table IV. The multiplexer used in past work proved unsuitable for this work as it used UV grade fibers, which absorbed significant light in the 950 nm wavelength range. Np^{4+} and Np^{5+} absorption peaks at 960 nm and 980 nm were not useable if UV grade fibers were used in the system. Therefore, the multiplexer was bypassed and reference and measurement spectra were taken using a single pair of IR grade fibers. Light references were taken prior to the beginning of the experiment and stored. Fibers were switched at the lamp and spectrometer after the wash step.

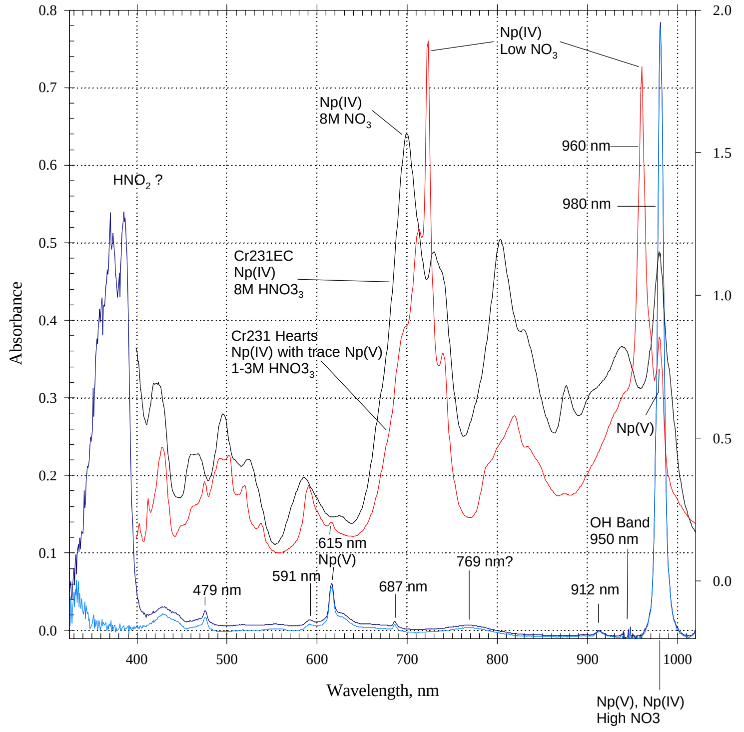
Feedstock Preparation and Valence Adjustment: Np solution was prepared as a feedstock by adjusting to 8 M HNO_3 and performing a valence adjustment with N_2H_4 and FS. For these runs, sufficient FS was added to make the solution 0.05 M excess FS over that required to reduce all the Np from Np^{5+} to Np^{4+}. The addition of FS at least 16 hrs prior to the column run allowed for time for Fe^{2+} and Pu^{3+} to oxidize with the intention of reducing the gassing observed during loading. The addition of N_2H_4 within an hour prior to loading would convert some radiolysis induced gases (from HNO_2) into HN_3 and would reduce gas generation within the resin bed. The preparation of feed or wash solutions with oxalate ion was accomplished by the addition of either a solution of oxalic acid dissolved in distilled water or as a solid dihydrate salt to non-radioactive HNO_3 feed or wash make-up solution. In either case, all solids were dissolved and no new solids were observed to form prior to precipitation. However, the column run was generally performed within one to four days after preparation so any long term solubility issue would not have been encountered.

Np Loading: Sufficient Np feedstock was prepared for the column run. A sample was taken and analyzed for total alpha by alpha PHA and gamma scan. Feed acidity was not measured but calculated based on previous free acid analyses of the Np solution and the addition of 70% reagent grade HNO_3 and distilled water. At the beginning of the column run, ~1 BV of 8 M HNO_3 was fed "up-flow" to the column to displace the dilute HNO_3 in the resin bed from the previous run. At this point in the experiment, the spectrophotometer was checked for proper operation and a new "zero" spectrum was stored for the 25-mm flowcell (background with no Np in the flow cell). The Np feed was then pumped "up-flow" through the column at 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 occasionally checked with a 10-mL graduated cylinder and a stopwatch, but flowrate was not considered a critical parameter for these studies. The instantaneous flowrates were somewhat variable (sometimes ±50% of the targeted value), but the average flowrate was estimated to be within 20% of the target value.

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

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

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



Literature references for Np absorbance spectra in HNO_3 are limited. Johnson and Shepard (*19*) measured spectra of $Np^{4+, 5+, 6+}$ in 1 to 10 M HNO_3. They observed strong nitrate dependence in the spectra between 5 and 10 M HNO_3. They also reported disproportionation of Np^{5+} above 3 M HNO_3 along with a strong acid dependence for the disproportionation reaction. The Np^{5+} spectra that they published clearly showed Np^{4+} absorption peaks, but interestingly did not show the Np^{6+} peaks. Friedman and Toth (*20*) reported Np spectra in up to 4 M HNO_3. They reported difficulty in obtaining pure Np^{4+} in low HNO_3 concentrations due to oxidation to Np^{5+}. They also observed no indication of Np^{4+} hydrolysis at 0.1 M or greater HNO_3 concentrations. Gruen and Katz (*21*) reported on absorption changes of Np^{5+} at 980 nm that reflected the formation of oxalate complexes. Similar effects are expected with Np^{4+} oxalate complexes. Figure 7 shows Np^{4+} spectra in both low and high HNO_3 compared with reference Np^{5+} spectra (*9*). Note that the major Np^{4+} peak at 960 nm at low acid is shifted to 980 nm in 8 M HNO_3. This spectral shift precludes the use of the 980 nm peak to determine the success of valence adjustment and oxidation in anion feed solutions. Also, note the appearance of characteristic Np^{5+} peaks at 615 and 980 nm in low HNO_3. While relatively small, the 615 nm Np^{5+} peak has been used in past work to identify the presence of Np^{5+} in 8 M HNO_3 (*9*). In the current study, a small amount of Np^{5+} was observed during the loading step of Cr263[*]. Otherwise no other Np^{5+} was observed during the load wash steps of any of the experiments. The losses in the raffinate and wash solutions appear to be primarily due to Np^{4+} species only.

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[*] "Cr" stands for Column Run and 263 is the number of that particular experiment. This notation is throughout the text and tables in this report.

RESULTS AND DISSCUSION:

Np Column Studies: An initial column run with sequential washes with increasing concentrations of oxalic acid was followed by three column runs with 0.05 M oxalic acid in the feed solution. Later runs used lower Np feed concentrations but proportionally higher flowrate to keep the Np feed rate constant. For comparison purposes, a final test was run with low Np feed concentration and high flowrate but without oxalic acid in the feed. The process conditions for each column run are tabulated in Table V. For each experiment, composite samples of the feed, raffinate, wash, and product solutions were analyzed. The results from these analyses and the volume of each solution were used to calculate a material balance for each experiment. The amount of Np absorbed (or loaded) onto the resin was calculated as the difference between the cumulative amount in the feed solutions and the amount found in the raffinate solutions. Detailed results from each of the column runs and some sample calculations for the individual runs are shown in the appendix as Tables VIII, IX, X, XI and XII.

Table V. Process Parameters for the Anion Exchange Runs.

		Cr261	Cr263	Cr264	Cr265	Cr267
Feed	FS, M	0.045	0.051	0.048	0.054	0.056
	N_2H_4, M	0.034	0.040	0.021	0.022	0.034
	HNO_3, M	8.1	8.1	8.1	8.0	8.0
	Np, g/L	11.59	4.61 [*2]	2.10	1.42	1.27
	Oxalate, M	0	0.051	0.050	0.051	0
	Ox/Np ratio	0	2.6 [*2]	5.7	8.5	0
	Ox/(Np+Fe)	0	0.7	0.9	0.9	0
	Rate, mg/min/cm^2	15.8	16.0	15.6	16.2	18.1
	mL/min/cm^2	1.411	1.764	6.35	12.70	12.70
	Time, sec [*3]	121	96	27	13	13
Wash	FS, M	0	0	0	0	0
	Oxalate	0-0.047	0	0	0	0
	N_2H_4, M	0.05	0	0	0	0
	HNO_3, M	8	8	8	8	8
	T, °C	21.9	19.6	20.2	19.8	19.8
	BV	14.4	3	3	3	3
Decon	HNO_3, M	8	8	8	8	8
Wash	BV	1.1	3.1	3.1	3.1	3.1
Elution	N_2H_4, M	0.05	0.05	0.05	0.05	0.05
	HNO_3, M	0.17	0.17	0.17	0.17	0.17
	BV	0.9	0.9	0.9	1.1	0.9

Note 1: Oxalate Wash on Cr261 consisted of seven sequential ~2BV wash steps with increasing oxalate concentration

Note 2: Feed solution analysis for Cr263 was ~1/2 expected value, analyzed value and values derived from that result are shown in table as analyzed.

Note 3: Time refers to the residence time of solution passing through resin bed.

Table VI. Summary of Results for the Anion Exchange Runs.

	Cr261	Cr263	Cr264	Cr265	Cr267
Loading g Np/L	43.3	21.7 [*1]	38.9	46.2	41.1
g Np/L	42.4	37.7	42.7	44.3	39.5
Load 38.4L Resin	1645	807 [*1]	1451	1506	1385
Load 38.4L Resin	1629	1449	1640	1700	1518
Product Conc g Np/L	46	45	53	45	49
Loading Loss	0.002%	0.7%	1.2%	16.0%	10.2%
Wash Loss	0.1%	0.1%	0.6%	0.6%	0.9%
Heads Loss	0.01%	0.8%	0.4%	0.2%	0.2%
Tails Loss	1.0%	1.4%	1.0%	0.9%	0.7%
Np Matl Balance	-2.0%	73%	10%	-3.2%	-2.6%
^{238}Pu Matl Balance	-4.8%	28%	-14%	-11%	-7.1%
Np Prod Eff	99%	97%	97%	85%	88%
Feed ^{238}Pu, ppm	316	1076	316	273	264
Product ^{238}Pu, ppm	291	805	241	266	265
Product Pu , ppm	291	805	302	955	265
Wash	Up-flow	Up-flow	Up-flow	Up-flow	Up-flow

Note 1: Feed solution analysis for Cr263 was 1/2 of value expected from source of feed and inconsistent with amount found in hearts cut. Reprep of the analytical sample failed to correct the problem suggesting the possibility of a bad sample. As a result Np material balance, resin loading and column loading values as calculated from Np feed concentration are not consistent with values calculated for other experiments.

A summary of results, which includes a material balance for each experiment, is included as Table VI. Generally in the past, calculations of the material balances for Np and ^{238}Pu were able to be closed to within of 5 to 15 percent for each run. A poor material balance for Cr263 was obtained apparently due to a bad feed sample. The uncertainties in the material balance are of similar magnitude to the uncertainty of an individual analysis with the exception of Cr263.

Np Losses: The feed solutions for the column runs were prepared to be 8 M HNO_3 and the resin was observed to absorb the Np with low to modest losses. Experimental results are shown in Table VI. Loading losses ranged from trace to 16%.

Figures 8 and 9 show the absorbance of the raffinate of each column as a function of time during the load/wash steps as measured at the in-line spectrophotometer flowcell. The wavelengths plotted are characteristic of Np^{4+} in 8 M HNO_3 should be proportional to the Np^{4+} concentration in the solution. With the range of flowrates and Np feed concentrations tested, time proved to be the best variable for comparison of the various column runs. Since the mass feed rate of Np was fairly constant in all the runs, time is similar to a comparison based on the cumulative amount of Np fed. Note that since Cr261 was an oxalate wash test, the time scale in this case refers to the time from the start of the wash. On other tests the reference point is the beginning of the feed step. Note that the absorbance initially rises to a peak that corresponds to the end of the feed step. The gradual decline in absorbance after the peak corresponds to the gradual drop in Np losses during the wash step. In the Cr261 test, it appeared that once the Np was loaded onto the resin that it was somewhat resistant to being washed off with up to 0.047 M oxalate solutions in 8 M HNO_3. Test Cr261 was performed as a feasibility test to determine an oxalate level that produced unacceptable Np losses. The results were better than expected, with most losses near or below the detection limits. As would be expected, losses were highest at the highest oxalate concentration. Both the counting and spectrophotometric techniques gave similar results.

Figure 8. Np Losses as Observed at 700 nm during Anion Runs.

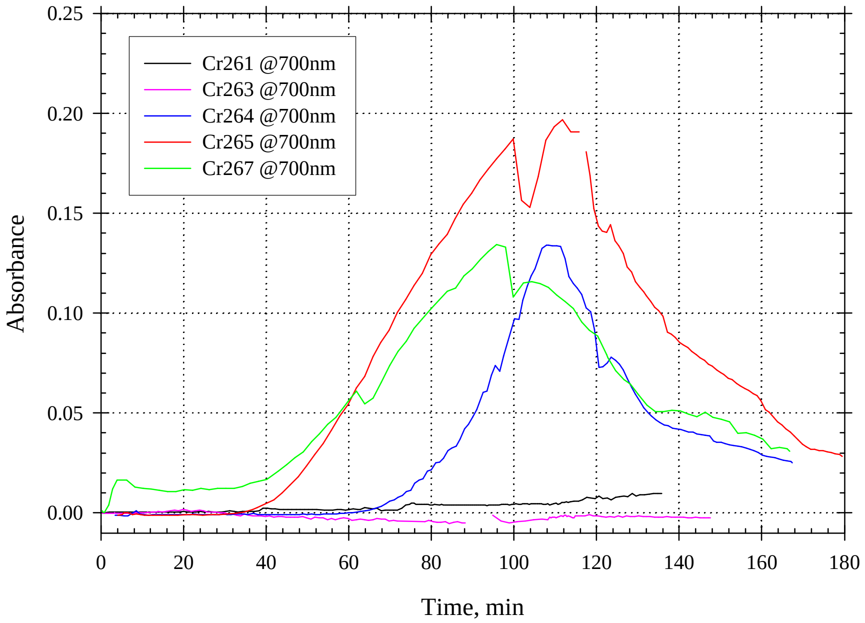
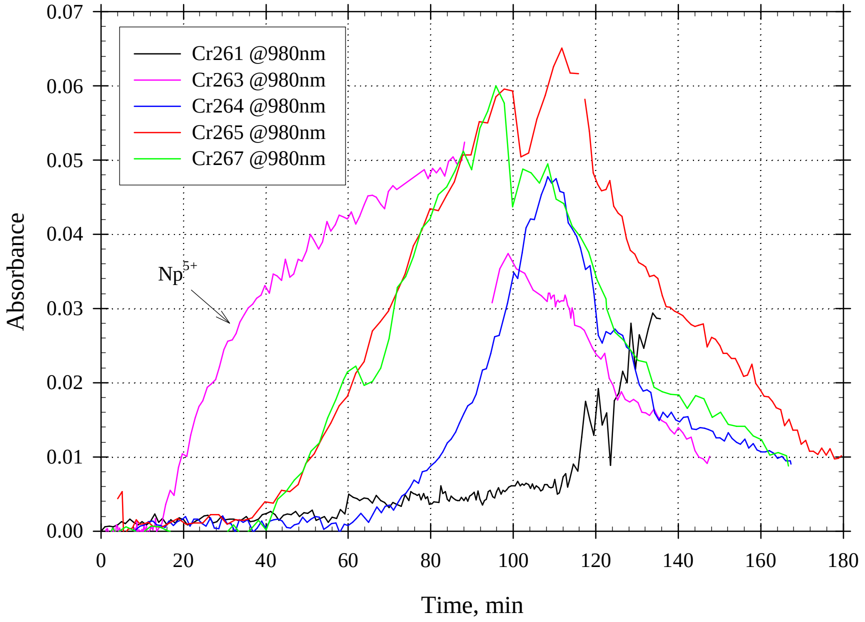


Figure 9. Np Losses as Observed at 980 nm during Anion Runs.



Test Cr263 was run with ~10 g Np/L feed solution and 0.05 M oxalate. The oxalate test value was chosen as one-half of the expected plant filtrate concentration with the recognition that anion exchange feed adjustment will require roughly a 50% dilution with 64% HNO_3. This test also had low Np losses. Comparison of spectral absorption data shows a difference between the two wavelengths. Further examination showed a small absorption peak at 615 nm that is characteristic of Np^{5+} also appears. Both Np^{4+} and Np^{5+} absorb strongly at 980 nm. Also an additional peak at ~1000 nm appears as well. Gruen and Katz (*21*) observed a similar peak associated with Np^{5+} oxalate complexes in perchloric acid. It appears that a small amount of Np^{5+} remained after the valence adjustment step and this species passed through the column and could have been mistaken for Np^{4+} losses if the 700 nm and 980 nm adsorption peaks had not been compared. A review of the technician observations during feed preparation showed that the FS had been added to 15.8 M nitric acid prior to the addition of the Np solution and a reaction had been observed. In later experiments the FS addition was held until after the Np solutions had been added to avoid this problem.

In Cr264, the Np feed concentration was reduced to 2 g Np/L while the oxalate concentration was kept at 0.05 M. This increased the Oxalate/Np molar ratio by a factor of four. A 1-2 g Np/L feed concentration was also more realistic compared to expected plant conditions. To keep the laboratory experiments to a reasonable time length, the feed flowrate was increased to keep Np mass feed rate constant. As expected, the Np losses to the raffinate rose. However the analyzed result of 1.8% loss to the raffinate and wash was not excessively high and would most likely be acceptable for plant recycle operations.

Cr265 was then run an even lower Np feed concentration of 1.4 g/L, still keeping the oxalate concentration and Np mass feed rate constant. This change further increased the ratio of oxalate to Np in the feed solution. A slight reconfiguration of the pump was necessary to accommodate this additional doubling of the flowrate. The losses to the raffinate increased to 16% with another 0.6% lost to the wash. Since the flowrate had been increased significantly over the baseline flowrate, it could not be established that oxalate complexation alone was responsible for these losses.

Cr267 replicated Cr265 flow conditions without oxalate present in the feed solution. Losses of 11.1% were observed between the raffinate and wash steps. This result suggests that oxalate complexation of Np may not be the dominate contributor to losses in these experiments. The probable explanation is that at the high feed rates used in Cr265/7, the residence time of Np in the resin bed becomes too short for complete mass transfer of the Np from the bulk solution to the resin beads. An additional experiment, run with dilute Np and oxalate in the feed solution like Cr265, but slowed down to no more than half the Np mass feed rate could answer this conclusively, but that experiment has not been performed. Based on the existing data, such a run would be expected to show significantly reduced Np losses over Cr265.

However the scaled flowrate increases in the laboratory tests significantly exceed the capability of the existing pumping equipment in the plant, so losses caused by limited residence time in the resin bed (mass transfer limited in the solution bulk) should have little or no effect with the dilute solutions proposed in the plant process.

Np Complexation: The possibility of significant oxalate complexation could affect the spectral absorption properties of Np^{4+} nitrate. Two sets of Np solutions were prepared in an 8 M HNO_3, 0.02 M N_2H_4 matrix where the oxalate concentration was varied from 0 to 0.09 M. One set had 0.05 M FS included in the matrix and the other did not. The FS set also included an extra sample at the highest oxalate concentration value but with twice the amount of FS in order to look for Fe competition with the Np for oxalate. These samples were mixed, the Np solutions added and visible-NIR spectra measured within one hour of preparation. This short time would have limited the oxidation of Fe^{2+} to Fe^{3+} and also would have limited the time for Np oxalate solids to form. The spectra of the same samples were measured again after 12 days. At that time, solids were observed on the bottom of some of the vials and cuvettes. A sample of each vial was carefully pulled to avoid disturbing any solids and submitted for alpha and gamma analysis. The composition of each vial and results from the observations and analyses are shown in Table VII. Solids were only observed in samples 0.05 M and above in oxalate and the presence of FS appeared to reduce the amount of solids formed.

The primary reason for preparing the oxalate complexation samples was to make sure that oxalate complexes did not have such a severe effect on the spectral absorbance of Np^{4+} to interfere with the determination of significant Np losses to the raffinate by spectral measurements. Figures 10 and 11 show the effect oxalate had on the spectra of the freshly prepared solutions. Both positive and negative absorbance changes were found. A detailed study of these spectra has not yet been done, but it is apparent that the effect of oxalate has only a modest effect on the spectra of Np when used for qualitative measurements.

The additional spectra taken at 12 days were used to look for differences between the spectra over time and due the matrix effects. Samples with 0 and 0.02 M oxalate appear to show no evidence of changes in Np concentration over time with or without FS (see Figures 12 and 13). The stability of the spectra from samples with 0.05 M oxalate appears to be improved by the presence of 0.05 M FS, but it does appear that there was some loss of Np from the solution. Samples with 0.07 and 0.09 M oxalate showed large differences between samples with and without FS as well as over time. It was apparent that

Np solubility becomes a limiting factor at 2-3 g Np/L (even with 0.05 M FS) for 8 M HNO_3 solutions with greater than 0.07 M oxalate present.

It was assumed that Fe^{3+} complexation in the FS samples would significantly reduce the driving force on Np oxalate to precipitate. The spectra of the aged samples without FS showed significantly less Np remained in solution when compared with the corresponding spectra from the samples where FS was present. Figures 12 and 13 show the 2nd derivative of the spectra for both freshly prepared and aged samples with 0.05 M oxalate and less. Much larger differences were observed (but not included) for the 0.07 M and 0.09 M oxalate samples. The solids observed on the bottom of the vials also correlated with reduced Np absorbance. Alpha and gamma counting solution

Figure 10. Effect of Increasing Oxalate on Np Spectra at 700 nm.

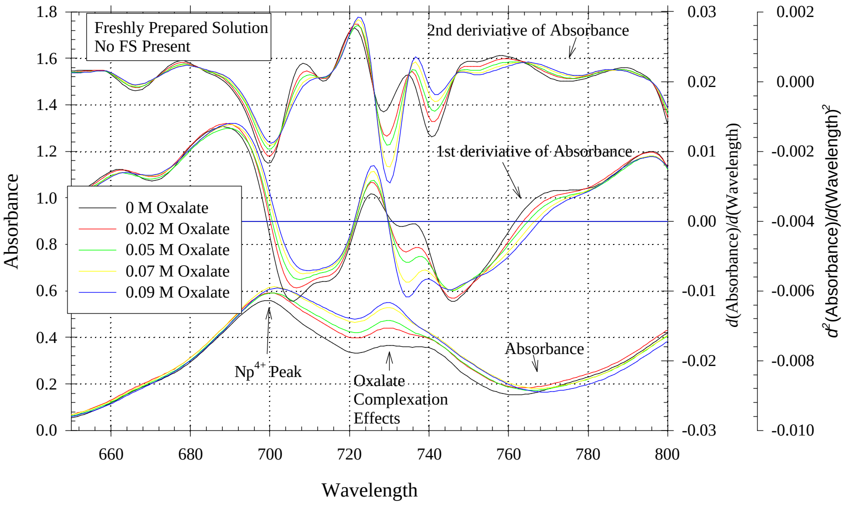


Figure 11. Effect of Increasing Oxalate on Np Spectra at 980 nm.

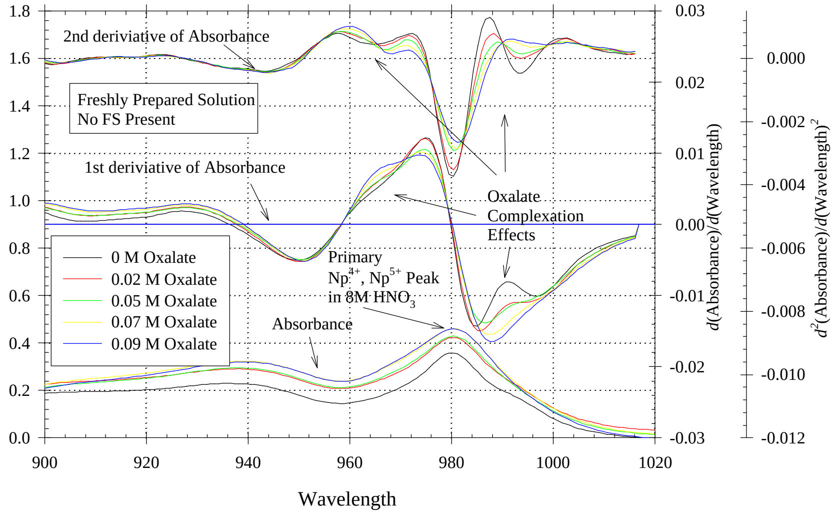


Table VII. Results from Solubility Samples.

	Planned Conditions[1]				Results						
ID	FS	Ox	Ox/Np	Ox/(Fe+Np)	Solids[2]	Ox Adj	R_S	^{237}Np	^{238}Pu	g $^{237}Np/L$ (3)	
	M	M				M		α %	α %	α	γ
A	0.05	0	0.0	0.00	0	0	0	29%	71%	2.352	3.166
B	0.05	0.02	1.4	0.31	0	0.02	0.0003	31%	69%	2.514	3.114
C	0.05	0.05	3.5	0.78	0	0.05	0.0008	30%	70%	2.337	3.066
D	0.05	0.07	4.9	1.09	1	0.055	0.0009	26%	76%	1.599	1.394
E	0.05	0.09	6.3	1.40	2	0.069	0.0011	22%	76%	0.518	0.626
F	0.1	0.09	6.3	0.79	3	0.078	0.0012	27%	76%	1.460	1.730
A'	0	0	0.0	0.00	0	0	0	29%	71%	2.315	3.276
B'	0	0.02	1.4	1.39	0	0.02	0.0003	30%	70%	2.509	3.212
C'	0	0.05	3.5	3.48	2	0.045	0.0007	23%	77%	1.367	2.574
D'	0	0.07	4.9	4.87	2	0.052	0.0008	19%	81%	1.069	1.024
E'	0	0.09	6.3	6.26	3	0.064	0.0010	7%	93%	0.102	0.138

[1] Note: All samples prepared with 3.41 g Np/L (0.0144 M Np), 8 M HNO_3.

[2] Note: Observed solids in samples after 12-14 days were given relative ratings of 0 (no solids) to 3 (most solids).

[3] Note: Reported values for Samples D, E, and F are for 43 day samples. All other reported values are for 12 day samples. 12 day analyses for Sample D were higher, but E and F analyses were similar to 43 day values.

Figure 12. Effect of Time on Np Spectra with Oxalate (700 nm).

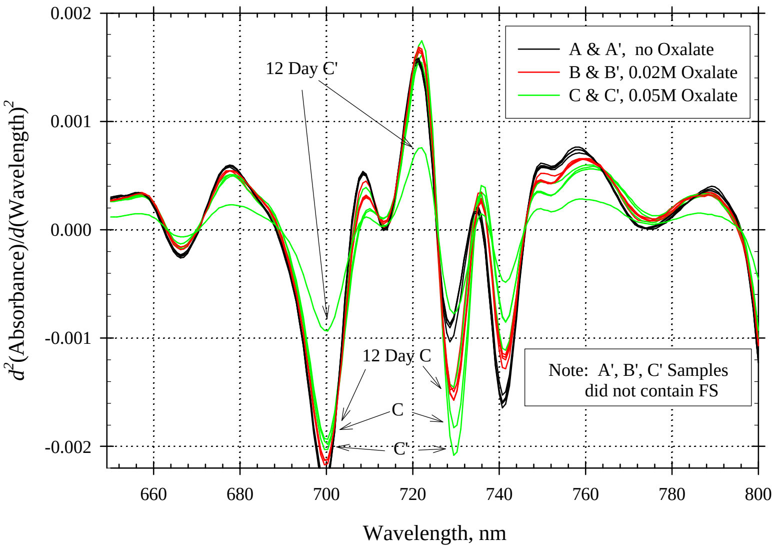
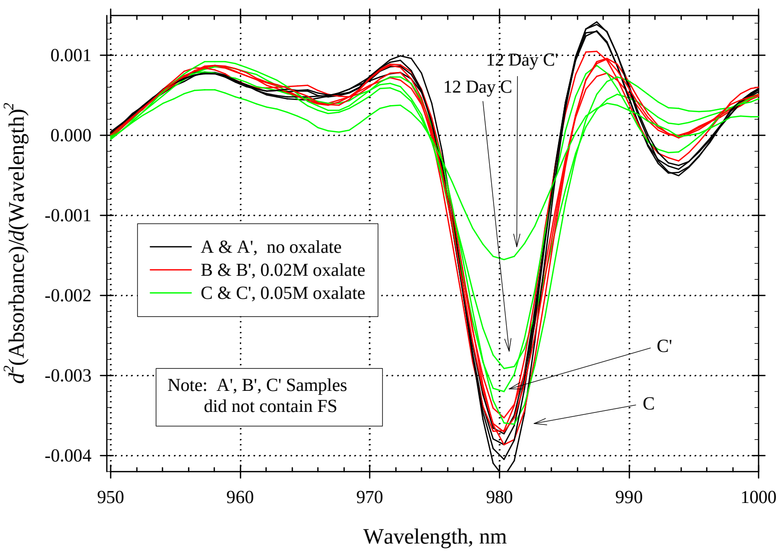


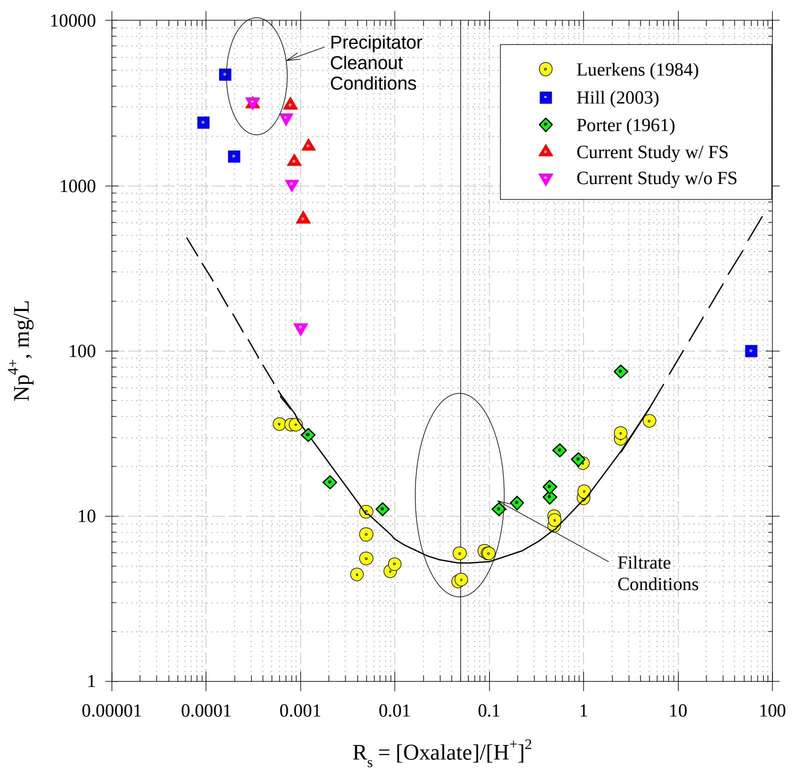
Figure 13. Effect of Time on Np Spectra with Oxalate (980 nm).



results track with the amount of Np oxalate solids observed. Np oxalate solubility significantly increased with increases in FS concentration. Initially FS was almost entirely Fe^{2+} sulfamate, but in the 8 M HNO_3 matrix, Fe^{2+} oxidizes to Fe^{3+} in a short time (84% in first 24 hrs at 22 ºC, Dukes and Wallace (*22*)). Sulfamate also slowly hydrolyzes to sulfate, but the rate is much slower (estimated at <5% for this study, Karraker (*23*)). The changes in Fe^{2+} and Fe^{3+} change the complexation of oxalate. The increase in sulfate concentration could affect the solubility of Np due to the formation of Np sulfate complexes. Samples D, E, and F were re-sampled after 43 days and reanalyzed due to analytical discrepancies in the 12-day results.

Np Solubility: Some of the data in the current study reflect the effect of Np solubility. Porter (*14*), Luerkens (*13*), and Hill (*15*) did previous studies that investigated the solubility of Np in HNO_3. Np oxalate solubility should correlate with the concentration of free oxalate ion. Luerkens defined a solubility parameter, R_s = [oxalate]/ $[H^+]^2$, that approximates the free oxalate concentration. Figure 14 attempts to compare the current data with the previous results. Also shown on this graph are the regions of interest to the HB-Line Np process. Luerkens' model had a theoretical basis that should allow some extrapolation. The data from the current study agree fairly well with Hill's results and both studies show a much higher solubility than that predicted by the Luerkens' model. There are several of Luerkens' data points that one would initially think should compare close to conditions in the current study. Luerkens' study included data at 0.06 M oxalate and 10 M HNO_3 with solubility of only 35 mg/L compared with 1 to 3 g/L observed in the current study. Luerkens' experiments were performed in much the same way as the current study, however he relied on alpha plate analysis only rather than gamma counting (which was preferred for the current work). Luerkens' experiments allowed samples to equilibrate for 24 hours only compared with the 12 days (or longer) in the current study. Luerkens filtered his solubility samples. Most of the samples in the current study were not filtered, but similar solutions were prepared and the Np recovered in the anion exchange experiments. Poor material balances for the column runs would be expected if Np oxalate solids that had settled out the bottom of the bottle and were fed to an anion column. The reasonable material balances support the assumption that the Np remained in solution in the anion feed bottles. Luerkens' solubility data led this author into thinking that the oxalate effect on solubility would be so large that complexation would make the separation of Np and oxalate much more difficult. If Np oxalate complexes formed slowly in anion feed solutions (high nitrate), then there is the possibility that a Np oxalate solution stored over a long time period could behave

Figure 14. Np Oxalate Solubility at Ambient Temperature.



differently that those observed in this study (where solutions were prepared and used within a few days). This outcome seems to be an unlikely possibility.

An examination of Luerkens' laboratory notebook (*24*) shows that his experiments departed from the current study in one significant aspect. His samples involved samples with a small total concentration of Np (0.3 g/L compared to 3.4 g/L in the current study). Further calculations show that Luerkens' oxalate to Np molar ratio ranged from 100 to 25,000 compared to the one to six molar ratio in the current study and to two in Hill's study. Under Luerkens' experimental conditions (and Porter's as well), the large excess of oxalate ion drives the Np to a precipitate. Both researchers were studying precipitation processes. In the current study and Hill's study, the conditions were tailored to the re-dissolution of Np oxalate solids with HNO_3 which will limit the available oxalate ion. The region of the solubility curve with $R_S < 0.005$ does not lend itself to a simple graphical representation. A significant concentration of any cation complexed by oxalate (including Fe^{3+} or Np^{4+}) will raise the Np solubility by competing with the precipitating complex for oxalate ions.

Plant Applications: The main difficulty in the recovery of Np oxalate recycle solutions appears to be avoiding post-precipitation of Np oxalate prior to the adjustment of the anion exchange feed solution. The current process flowsheet has two Np oxalate streams of very different compositions. There is a filtrate stream from oxalate precipitation (nominally 0.1 M oxalate, < 0.1 g Np/L, ~1 M HNO_3 and 0.05 M N_2N_4) and a precipitator cleanout solution (0.01-0.08 M oxalate, 3-10 g Np/L, and 14 M HNO_3). Currently both are treated with permanganate and nitrite prior to transfer to a canyon tank for storage. Existing solution consists of both filtrate and flush solutions that were treated with permanganate and nitrite and stored in H-Canyon. There are several possible future processing paths for solution generated in the future. One is to store the flush solutions separately and discard the filtrate solutions. For this option treatment with permanganate to destroy the oxalic acid is not necessary.

The addition of oxalate filtrates without treatment to the existing tank of treated solution will likely produce Np oxalate solids. Filtrates will decrease the solubility both by increasing the oxalate concentration and diluting the existing HNO_3 concentration. In addition, the solubility of Np oxalate is somewhat uncertain under the expected conditions. Only the addition of a significant volume of concentrated HNO_3 will allow addition of untreated oxalate filtrates to the existing tank of treated recycle solution without the formation of Np oxalate solids.

The addition of precipitator cleanout solutions without treatment to the existing tank of treated solution will be less prone to produce Np oxalate solids. The cleanout solutions involve much smaller amounts of oxalate and the cleanout solution is high in HNO_3. Repeated additions of untreated precipitator cleanout solutions may eventually require additional HNO_3 additions to keep the conditions in the range that were examined in the current study. The same uncertainty of the Np oxalate solubility still applies, but not to the same degree, as the high HNO_3 concentrations in the cleanout solution will keep the combined solution near the range of conditions already studied.

Filtrates that are low in Np (< 0.1 g Np/L) probably do not justify accumulation for recycle. At this point, it appears most (if not all) filtrates would fall into this category and might be kept separate and discarded as is. The addition of a small amount of manganese ion prior to evaporation could be used to catalytically oxidize the oxalate if destruction prior to the discard to the waste tanks were deemed important.

The transfer of the precipitator cleanout solution into the current feed stream for blending and recycle of this solution as it is generated should pose limited risk for solids formation. The current feed stream does not contain oxalate and will dilute the limited oxalate present in the recycle solution. It also contains significant Fe^{3+} which will compete with Np to complex the oxalate. On the other hand, the feed solution will dilute the HNO_3 concentrations and the solubility is understood to be inversely proportional to the square of the HNO_3 concentration. The feed solution also has a higher Np concentration than the recycle solution which increases the potential for solids issues. The existing data do not conclusively support this option as being trouble free without examining the specific conditions involved. The limitation is that no tests were run to demonstrate ~10 g Np/L solubility with oxalate present. However, based on the data that do exist, it appears likely that Np oxalate solids would not form in 8 M HNO_3 as long as the solution contains less than one mole of oxalate per mole of Np (without Fe present). With the uncertainty in the Np oxalate solubility and the relatively small number of flushes that are expected to be performed, recycling precipitator cleanout solutions without treatment to destroy the oxalate may not worth the risk of solids formation. Recycling precipitator cleanout solution after destroying the oxalate does not appear to pose a problem.

Uncertainties: As previously stated, instantaneous flowrates in the current experiments occasionally varied widely from the targeted value, but adjustments were quickly made to keep the average flowrate within ~20% of the targeted value. Because resin loading was found to be only a weak function of flowrate in the earlier Pu study (*8*), the flowrate uncertainty probably contributes < 1% to the uncertainty in the loading results.

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

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

A material balance was calculated for each run by taking the solution volumes and the analytical results from the feed, product and waste streams. Column runs had an overall material balance uncertainty of up to 17% for ^{237}Np compared with a historical norm of ~4%. Poor material balances for ^{233}Pa were observed in the previous studies (*9*, *10*) and results in this study could only close the ^{233}Pa material balance to within 25% and all showed a loss of Pa. Solutions that should have been at secular equilibrium between ^{237}Np and ^{233}Pa (^{237}Np and ^{233}Pa activities should be equal) often had 20-50% less ^{233}Pa. ^{233}Pa readily hydrolyzes and sticks to various surfaces even from 1-8 M HNO_3. No correction was made for ^{233}Pa decay or in-growth between anion exchange separation or in-growth and gamma counting. In most cases, those analyses were performed within a week after separation. A delay in counting of four days would amount to ~20% in-growth of ^{233}Pa.

CONCLUSIONS:

A series of laboratory column runs were performed that demonstrate the recovery of Np containing up to 0.05 M oxalate with no more than 16% losses. Losses in the plant are expected to be significantly less due to the lower cross-section flowrate possible with existing plant pumps. It is suggested that the highest losses observed in the laboratory tests were dominated by the short residence time for the solution in the resin bed rather than the presence of oxalate. However very limited data are available to base this conclusion.

Elimination of the permanganate treatment of filtrates appears to be justifiable however the combination of untreated filtrates with other actinide rich solutions is not advisable as precipitation problems are likely. If untreated filtrates are kept segregated from other actinide rich streams, the recovery of the remaining Np is probably still possible, but could be limited due to the excessively high Oxalate/Np ratio. That situation is beyond the scope of what has been tested.

The persistence of hydrazine/hydrazoic acid in filtrate solutions dictates that a modified nitrite treatment still be performed to eliminate those species from the filtrates prior to transfer to the canyon.

Elimination of the permanganate treatment of precipitator flushes and recovery by anion exchange does not appear to be limited by the oxalate effect on anion exchange. Np solutions with higher Oxalate/Np molar ratios were recovered with low to modest losses. Possible solubility issues with the mixing of untreated precipitator flushes with solutions that are more concentrated in Np have not been totally dismissed. Problems are unlikely when the moles of oxalate involved are less than the total number of moles of Np. With the small number of flushes involved, continued treatment of those solutions is recommended.

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APPENDIX

Table VIII. Results from Cr261 - Successive Oxalate Washes, High Np Concentration.

				Column	Np			^{238}Pu		Acid	Gamma Scan				APHA			
Sample		ADS	Sample	Volumes	Conc.	g in	Loaded	Conc	ug in	Free	^{237}Np		^{233}Pa		%^{237}Np	%^{239}Pu	%^{238}Pu	Galpha
ID		No.	Volume	Eluted	g/L	Bottle	gms.	mg/L	Bottle	M	uCi/mL		uCi/mL					dpm/mL
Cr261	Feed	3-210494	404	4.2	11.59	4.68	4.68	3.46	1399	8.1	8.175	0.62%	5.273	0.5%	11%	0.0%	89%	1.48E+08
Cr261	EC1	3-210495	510	5.3	0.000	0.000	4.68	0.001	1	8.1	0.000		0.213	0.8%	3%	1.0%	96%	5.29E+04
Cr261	OxW0	3-210496	200	2.1	0.002	0.000	4.68	0.040	8	8.0	0.001		0.328	0.7%			100%	1.53E+06
Cr261	OxW1	3-210497	200	4.1	0.002	0.000	4.68	0.10	20	8.0	0.002		0.515	0.7%	0%	0%	100%	3.74E+06
Cr261	OxW2	3-210498	200	6.2	0.000	0.000	4.68	0.07	13	8.0	0.000		0.573	0.7%	0.5%	0%	100%	2.50E+06
Cr261	OxW3	3-210499	200	8.2	0.000	0.000	4.68	0.05	10	8.0	0.000		0.580	0.7%	1%	0%	100%	1.98E+06
Cr261	OxW4	3-210500	200	10.3	0.003	0.001	4.68	0.03	7	8.0	0.002		0.628	0.7%	2%	0.5%	99%	1.28E+06
Cr261	OxW5	3-210501	200	12.4	0.004	0.001	4.68	0.02	4	8.0	0.003	20%	0.494	0.6%	3%	0%	98%	7.93E+05
Cr261	OxW6	3-210502	200	14.4	0.011	0.002	4.68	0.02	5	8.0	0.008	9%	0.523	0.6%	3%	0%	97%	9.20E+05
Cr261	WC	3-210503	100	15.5	0.016	0.002	4.68	0.03	3	8.0	0.012	7%	0.528	0.6%	3%	0%	97%	1.25E+06
Cr261	Disp	3-210504	76	16.2	0.008	0.00	4.68	0.08	6	4.0	0.006	1.6%	0.041	1.0%	3%	0%	97%	3.05E+06
Cr261	PC1	3-210505	98	17.3	46.2	4.53	0.14	12.728	1247	1.5	32.62	0.6%	13.33	0.5%	11%	0%	89%	5.44E+08
Cr261	PC2	3-210506	104	18.3	0.472	0.049	0.09	0.073	8	0.2	0.333	1.3%	0.198	0.7%	20%	0%	80%	3.46E+06
	Material Balance					4.59	98.0%	% of feed										
			43.3	g/L resin	Losses	0.005	g Np	0.10%	0.002%									
			42.4	g/L resin		4.53												

Table IX. Results from Cr263 – 0.05 M Oxalate in Feed, Intermediate Np Concentration.

				Column	Np			^{238}Pu		Acid	Gamma Scan				APHA			
Sample		ADS	Sample	Volumes	Conc.	g in	Loaded	Conc	ug in	Free	^{237}Np		^{233}Pa		%^{237}Np	%^{239}Pu	%^{238}Pu	Galpha
ID		No.	Volume	Eluted	g/L	Bottle	gms.	mg/L	Bottle	M	uCi/mL		uCi/mL					dpm/mL
Cr263	Feed	3-211035	513	5.3	4.61	2.37	2.37	4.70	2409	8.1	3.254	0.01%	5.155	0.01%	5%	0%	95%	1.88E+08
Cr263	EC1	3-211028	492	5.1	0.05	0.027	2.34	0.001	0.7	8.1	0.038	0.1%	0.478	0.01%	64%		31%	1.75E+05
Cr263	WC	3-211029	300	3.1	0.01	0.004	2.34	0.001	0.4	8	0.008	0.5%	0.785	0.01%	63%	0%	37%	1.54E+05
Cr263	Disp	3-211030	88	4.0	0.39	0.034	2.30	0.24	21	4	0.275	0.02%	0.212	0.01%	6%	0.1%	94%	9.62E+06
Cr263	PC1	3-211031	88	4.9	45.27	3.98	-1.68	34.47	3033	1.52	31.932	0.03%	24.094	0.01%	5%	0%	95%	1.38E+09
Cr263	PC2	3-211032	110	6.0	0.52	0.057	-1.74	0.16	18	0.2	0.365	0.02%	0.231	0.01%	10%	10%	80%	7.66E+06
	Material Balance					4.10	173.5%	% of feed	Note feed analysis came out low, Recheck didn't improve									
			21.7	g/L resin	Losses	0.03	g Np	1.28%	1.13%									
			37.7	g/L resin		4.07												

Table X. Results from Cr264 - 0.05 M Oxalate in Feed, Low Np Concentration.

				Column	Np			^{238}Pu		Acid	Gamma Scan				APHA			
Sample		ADS	Sample	Volumes	Conc.	g in	Loaded	Conc	ug in	Free	^{237}Np		^{233}Pa		%^{237}Np	%^{239}Pu	%^{238}Pu	Galpha
ID		No.	Volume	Eluted	g/L	Bottle	gms.	mg/L	Bottle	M	uCi/mL		uCi/mL					dpm/mL
Cr264	Feed	3-211270	2024	20.9	2.10	4.26	4.26	0.63	1274	8.1	1.483	0.03%	0.974	0.02%	12%	0.0%	88%	2.72E+07
Cr264	EC1	3-211271	2024	20.9	0.025	0.050	4.20	0.015	30	8.1	0.018		0.453	0.01%	10%	0.1%	90%	6.20E+05
Cr264	WC	3-211272	300	3.1	0.085	0.025	4.18	0.04	13	8.0	0.060	0.1%	0.407	0.01%	9%	2%	89%	1.88E+06
Cr264	Disp	3-211273	85	4.0	0.200	0.017	4.16	0.14	11	4.0	0.141	0.02%	0.098	0.01%	5%	0.1%	94%	5.47E+06
Cr264	PC1	3-211274	86	4.9	52.9	4.55	-0.39	12.05	1037	1.5	37.342	0.01%	11.888	0.01%	11%	0.1%	88%	5.21E+08
Cr264	PC2	3-211275	100	5.9	0.443	0.044	-0.43	0.037	4	0.2	0.312	0.02%	0.116	0.01%	28%	3%	69%	2.02E+06
Material Balance						4.69	110.2%	% of feed										
			38.9	g/L resin	Losses	0.08	g Np	1.78%	1.18%									
			42.7	g/L resin		4.61												

Table XI. Results from Cr265 - 0.05 M Oxalate in Feed, Low Np Concentration.

				Column	Np			^{238}Pu		Acid	Gamma Scan				APHA			
Sample		ADS	Sample	Volumes	Conc.	g in	Loaded	Conc	ug in	Free	^{237}Np		^{233}Pa		%^{237}Np	%^{239}Pu	%^{238}Pu	Galpha
ID		No.	Volume	Eluted	g/L	Bottle	gms.	mg/L	Bottle	M	uCi/mL		uCi/mL					dpm/mL
Cr265	Feed	3-211546	4052	41.8	1.421	5.76	5.759	0.368	1491	8.0	1.003	1.0%	0.818	0.6%	12%	0%	88%	1.59E+07
Cr265	EC1	3-211547	3920	40.4	0.195	0.765	4.994	0.031	122	8.0	0.138	1.8%	0.388	0.6%	17%	0%	83%	1.43E+06
Cr265	WC	3-211548	300	3.1	0.101	0.030	4.963	0.025	8	8.0	0.072	2.2%	0.285	0.6%	12%	0%	88%	1.09E+06
Cr265	Disp	3-211549	92	4.0	0.113	0.010	4.953	0.060	5	4.0	0.080	1.6%	0.071	0.8%	7%	1%	92%	2.47E+06
Cr265	PC1	3-211550	105	5.1	45.034	4.73	0.224	11.345	1191	1.5	31.768	1.0%	12.928	0.6%	12%	1%	87%	4.96E+08
Cr265	PC2	3-211551	100	6.2	0.417	0.042	0.183	0.056	6	0.2	0.295	1.0%	0.068	0.8%	27%	7%	66%	3.21E+06
Material Balance						5.58	96.8%	% of feed										
			46.2	g/L resin	Losses	0.80	g Np	13.8%	13.3%									
			44.3	g/L resin		4.78												

Table XII. Results from Cr267 – No Oxalate in Feed, Low Np Concentration.

				Column	Np			^{238}Pu		Acid	Gamma Scan				APHA			
Sample ID		ADS No.	Sample Volume	Volumes Eluted	Conc. g/L	g in Bottle	Loaded gms.	Conc mg/L	ug in Bottle	Free M	^{237}Np uCi/mL		^{233}Pa uCi/mL		%^{237}Np	%^{239}Pu	%^{238}Pu	Galpha dpm/mL
Cr267	Feed	3-212153	3879	40.0	1.275	4.944	4.944	0.318	1233	8.0	0.899	1.0%	0.740	0.6%	11%	1%	87%	1.39E+07
Cr267	EC1	3-212154	3900	40.2	0.129	0.503	4.441	0.017	67	8.0	0.091	2.2%	0.474	0.6%	21%	0%	78%	8.38E+05
Cr267	WC	3-212155	300	3.1	0.145	0.044	4.398	0.027	8.25	8.0	0.103	1.6%	0.162	0.7%	15%	0%	85%	1.23E+06
Cr267	Disp	3-212156	96	4.1	0.111	0.011	4.387	0.084	8.07	4.0	0.078	1.5%	0.036	1.0%	5%	0.4%	94%	3.40E+06
Cr267	PC1	3-212157	86	5.0	49.115	4.224	0.163	12.305	1058	1.5	34.647	0.9%	5.288	0.7%	13%	1%	87%	5.38E+08
Cr267	PC2	3-212158	100	6.0	0.348	0.035	0.128	0.035	3.48	0.2	0.246	1.1%	0.034	1.0%	23%	0%	77%	1.72E+06
Material Balance						4.82	97.4%	% of feed										
			41.1	g/L resin	Losses	0.55	g Np	11.1%	10.2%									
			39.5	g/L resin		4.27												