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Plutonium Purification by Anion Exchange for Mark-18A Target Processing

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Savannah River National Laboratory ™

OPERATED BY SAVANNAH RIVER NUCLEAR SOLUTIONS

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PREFACE OR ACKNOWLEDGEMENTS

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EXECUTIVE SUMMARY

The Mark-18A (Mk-18A) program was established to preserve the unique materials found in Mk-18A targets for future research and development activity within the Department of Energy or other U.S. government agencies. Some of the unique, high-valued materials include but are not limited to plutonium-244, heavy curium, americium-241, and californium. The Savannah River Site has sixty-five (65) Mk-18A targets available for recovery.

Mk-18A targets will be removed from confinement, dissolved, chemically separated, and calcined to a stable oxide for transport to Oak Ridge National Laboratory (ORNL). The baseline flowsheet is patterned after the ORNL flowsheet, but adapted to the needs and capabilities of facilities at the Savannah River National Laboratory. The primary method for chemical separation of Pu from the other components of the targets is anion exchange using the Reillex™ HPQ resin. Although data exist in the literature for predicting the behavior of Mk-18A dissolver solutions on the Reillex™ resin, it was determined that the presence of a range of dissolved metals might negatively affect the resin performance, resulting in increased ^{244}Pu losses or poorer product quality.

Two experiments with a nonradioactive Mk-18A simulant solution and one test with a radioactive Mk-18A simulant were completed. The test results provide many valuable conclusions for determining the process flowsheet and mass balance, understanding factors that affect product purity, and planning subsequent simulant experiments. The most important findings are as follows.

- Plutonium can be readily absorbed and purified from simulated Mk-18A dissolver solutions using the Reillex™ HPQ resin.
- Pu(IV) is stable in 8 M HNO_3 at ambient temperature for at least 30 days in the Mk-18A simulant.
- There was no measureable effect on retention, washing, or elution of impurities due to valence adjustment with ferrous sulfamate (FS) and $NaNO_2$.
- There was no measureable effect on retention, washing, or elution of impurities due to sparging with NO and NO_2 gases for valence adjustment of the Pu.
- An optimized resin washing strategy (~10 resin bed volumes in these tests) allows for recovery of ~98.5% of the Pu initially fed to the ion exchange resin. More extensive washing to remove additional impurities may marginally increase Pu losses to the raffinate.
- Decontamination factors ranged from two to five orders of magnitude for all impurities; the results were influenced toward higher values by the high volume of wash used during testing. The impurities most difficult to remove were Pd, La, Ce, and Pr.
- Lanthanides behaved similarly in the both the radioactive and nonradioactive tests. The increased bed volumes of wash solution in the radioactive test removed additional weakly retained lanthanides (over the nonradioactive tests) and thus the elution peaks reflect lower impurity concentrations. The behavior of the different lanthanides was generally consistent with what was expected based on literature data except that Gd did not follow the lanthanide trend of decreasing resin affinity with increasing atomic mass. Greater than 99.9% of the weakly interacting lanthanides in the current study were decontaminated from the Pu.
- Reillex™ HPQ retains Pd significantly in 7-8 M HNO_3. This effect appears to be stronger than the K_d in the literature indicate. Roughly half of the Pd used in these tests appears to remain on the resin after the wash step. Complete removal of Pd by washing with 8 M HNO_3 does not appear to be practical. Fortunately only roughly 1% of the Pd elutes with the Pu due to the increasing affinity of the resin for Pd at lower HNO_3 concentrations.
- Cesium and Sr were sufficiently washed off the resin and < 0.002% of the Cs and Sr fed eluted in the Pu hearts eluate.

- There were a few impurities that were not thoroughly tested such as Ru and Tc that if they exhibit behavior similar to Pd it may cause complications that might need to be addressed.
- Other metal impurities (Al, Fe, Mg, and Na) present in the Mk-18A solution from the fuel and from cladding dissolution were not retained on the resin leaving < 0.1% in the Pu product stream.

Recommended future work includes 1) evaluating the risks posed by using a combination of FS/Pu(III) for Pu(VI) valence adjustment and considering the addition of an additional nitrous acid scavenger such as hydrazine nitrate to extend the effective time of the reductants, 2) retesting the simulant with a representative amount of Pd and Pu to evaluate the effect of the significant mass of Pd in the target on the resin capacity for Pu and better define the impact of Pd resin poisoning, 3) refining the spectrophotometer equipment details using appropriately sized flowcells for the expected Mk-18A solutions, 4) considering further testing with actual Cm to reduce the risks that the high alpha dose poses to valence chemistry and to better define the Cm decontamination by the anion exchange flowsheet, and 5) exploring the use of thiourea or some other Pd complexing agent to remove the residual Pd from the Reillex™ HPQ resin and prevent cumulative poisoning of the resin. Radioactive Pd could be a by-product that has value.

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LIST OF ABBREVIATIONS

AD	Analytical Development
BV	resin bed volume
DF	decontamination factor
DI	deionized water
FMI	Fluid Metering, Inc.
FS	ferrous sulfamate
ICP-ES	inductively coupled plasma atomic emission spectrometry
ICP-MS	inductively coupled plasma mass spectrometry
Mk-18A	Mark-18A
ORNL	Oak Ridge National Laboratory
RSD	relative standard deviation
R&D	Research and Development
SRNL	Savannah River National Laboratory
UV-vis	ultraviolet-visible

1.0 Introduction

The Mark-18A (Mk-18A) program is being established to preserve the unique materials found in Mk-18A targets for future research and development (R&D) activity within the Department of Energy or other U.S. government agencies. [1] Some of the unique, high-valued materials include but are not limited to plutonium-244, heavy curium, americium-241, and californium. The Savannah River Site has sixty-five (65) Mk-18A targets available for the recovery of high-valued materials.

Detailed reactor history profile was documented during the Mk-18A irradiation cycles (1969-1979). The irradiation profiles of the Mk-18A produced a higher distribution of actinide isotopes than any other targets produced by the U.S. Government. Irradiation history was modeled to determine dose and composition of the targets. [2] The Mk-18A target material will be removed from confinement, dissolved, chemically separated, and calcined to a stable oxide. The baseline flowsheet is patterned after the flowsheet Oak Ridge National Laboratory (ORNL) previously used to process both Mk-18A and Mark-42 targets. [3] However, it is necessary for Savannah River National Laboratory (SRNL) to adapt the ORNL flowsheet and identify process improvements to efficiently recover the actinide materials in the SRNL Shielded Cells. The resulting high-value actinide oxide and a significant amount of the fission products will be packaged and shipped to ORNL.

This project will evaluate different processing options for high burn-up material and elemental/isotopic profiles resulting from each target's unique irradiation history. The goal of the project is to recover and convert the plutonium found in the Mk-18A target into a usable, stable, and preserved form for application in the U.S. Government. [1] This experimental study evaluated anion exchange conditions needed to separate Pu from Mk-18A target impurities.

2.0 Background

Plutonium purification by anion exchange of Mk-18A target material will be preceded by several unit operations including aluminum cladding removal by caustic dissolution and filtration of undissolved solids. The undissolved solids, following filtration, will be transferred to the target material dissolver for acid dissolution. [4] After dissolution, valence adjustment, and filtration, the resulting solution will be passed through an anion exchange column to 1) retain plutonium on the column; 2) collect curium, americium, and lanthanide components in the raffinate and wash; and 3) collect the plutonium by eluting it from the resin. [5]

The form of the feed coming from cladding removal will be an oxide or oxide-like material; the physical form is expected to be wet solid containing metal silicates. Silicon (from metal impurities and activation products) is expected to comprise ~3.75 wt % of the ~3.7 kg of aluminum cladding (0.6 wt % from 6063 alloy and ~3 wt % as activation products). Most of the Si in the cladding is expected to be filtered out before anion exchange. [6] Other Alloy 6063 aluminum impurities include Mg (0.4-0.9%) and Fe (0.35% max). The composition of a representative Mk-18A target is provided in Table 2-1. [7] Target FT-0-01 is estimated to contain large amounts of Cm and Pd relative to Pu.

The majority of the metals in the Mk-18A target (other than Al and Cs) will be mostly insoluble during cladding removal and be transferred into the dissolver for nitric acid dissolution. Historical experience indicates that irradiation exposure tends to improve the dissolution characteristics of these types of actinide oxides. [3, 8, 9]

Table 2-1. Nominal Composition of Mk-18A Target FT-0-01 (not including cladding)

Full Mk-18A Target Composition (grams)					
Cm	13.06	Ag	0.30	As	< 0.001
Xe	13.02	Kr	0.29	Ga	< 0.001
Pd	11.67	Y	0.28	Nb	< 0.001
Nd	8.18	Er	0.27	Zn	< 0.001
Ru	8.00	Rb	0.25	Pm	< 0.001
Pu	7.95	Tb	0.19	Th	< 0.001
Cd	6.51	Rh	0.18	Bk	< 0.001
Ce	6.20	Eu	0.17	Pa	< 0.001
Ba	6.12	Dy	0.14	Cu	< 0.001
Mo	5.06	Ho	0.07	Pb	< 0.001
Gd	3.84	Sb	0.024	Ra	< 0.001
Zr	3.32	U	0.021	Ac	< 0.001
Cs	2.65	Se	0.020	Bi	< 0.001
La	2.20	Cf	0.017	Po	< 0.001
Pr	1.68	Br	0.015	Rn	< 0.001
Sm	1.47	Yb	0.012	Tl	< 0.001
Te	1.33	In	0.011	Es	< 0.001
Am	0.85	Np	0.005	Fr	< 0.001
Tc	0.51	He	0.004	At	< 0.001
Sn	0.43	Tm	0.003	Hg	< 0.001
Sr	0.34	Ge	0.001	Lu	< 0.001
I	0.31			Hf	< 0.001

Following nitric acid dissolution, the solution will undergo valence adjustment. The presence of 5-10% of the dissolved Pu as Pu(VI) has been routinely measured during ORNL processing of Mk-18A and Mark-42 targets. To obtain high recovery of Pu on anion-exchange resins, it is essential that the Pu be in the +4 oxidation state. [10] Although Pu(VI) can form during dissolution of the targets, the literature indicate that once Pu(IV) is formed through valence adjustment, it has sufficient stability in 7-9 M HNO_3. [11] Options for valence adjustment and control of the Mk-18A anion-exchange feed solution have been discussed by Pierce. [12]

After valence adjustment, the dissolver solution will be filtered, fed to an anion-exchange column, and Pu will load on the resin. Reillex™ HPQ is the proposed resin for Pu separation for the Mk-18A program; it is a strong-base polymer resin (crosslinked poly-4-vinylpyridine) that is commonly used for anion exchange of plutonium from other metals. It has been shown to have excellent selectivity for Pu as well as good chemical and radiolytic stability. [13] Standard conditions for loading plutonium onto anion-exchange resin use 7-9 M nitrate in strongly acidic solution. Washing of impurities from anion resin is performed using 7-9 M HNO_3. Elution of the Pu from the resin is accomplished using 0.35 M HNO_3. [14, 15]

Distribution coefficients for a wide range of metals on strong-base anion resin have been measured by James in 7 M HNO_3 [16] and Faris over a broad range of HNO_3 molarity [17]; Kyser has reported decontamination factors (DF) for a series of metals in 8 M HNO_3. [14]

Of the impurities expected in the Mk-18A ion exchange feed only a few are reported to have affinity to anion resin in 7 M HNO_3. Specifically, James [16] reports volume distribution coefficients of 5.2 for Pd, 1.6 for Re, 1.4 for La, and 1.2 for Ce. Other expected impurities have slight affinity for anion resin in 7 M nitric (Pr, Nd, Zr, Mo, Sm, Gd, and Ru all have $K_d > 0$ but < 1). Comparatively, Pu has a volume distribution coefficient of 978. However, Kyser [14] observed that even elements which James reported as having no absorption can require extensive washing. Distribution coefficients are typically based on tracer equilibrium tests and do not always provide a complete picture of what will happen in a dynamic column experiment.

Figure 2-1 shows the distribution coefficients vs molarity of nitric acid [17] with emphasis on major impurities expected to be in the Mk-18A anion exchange feed.

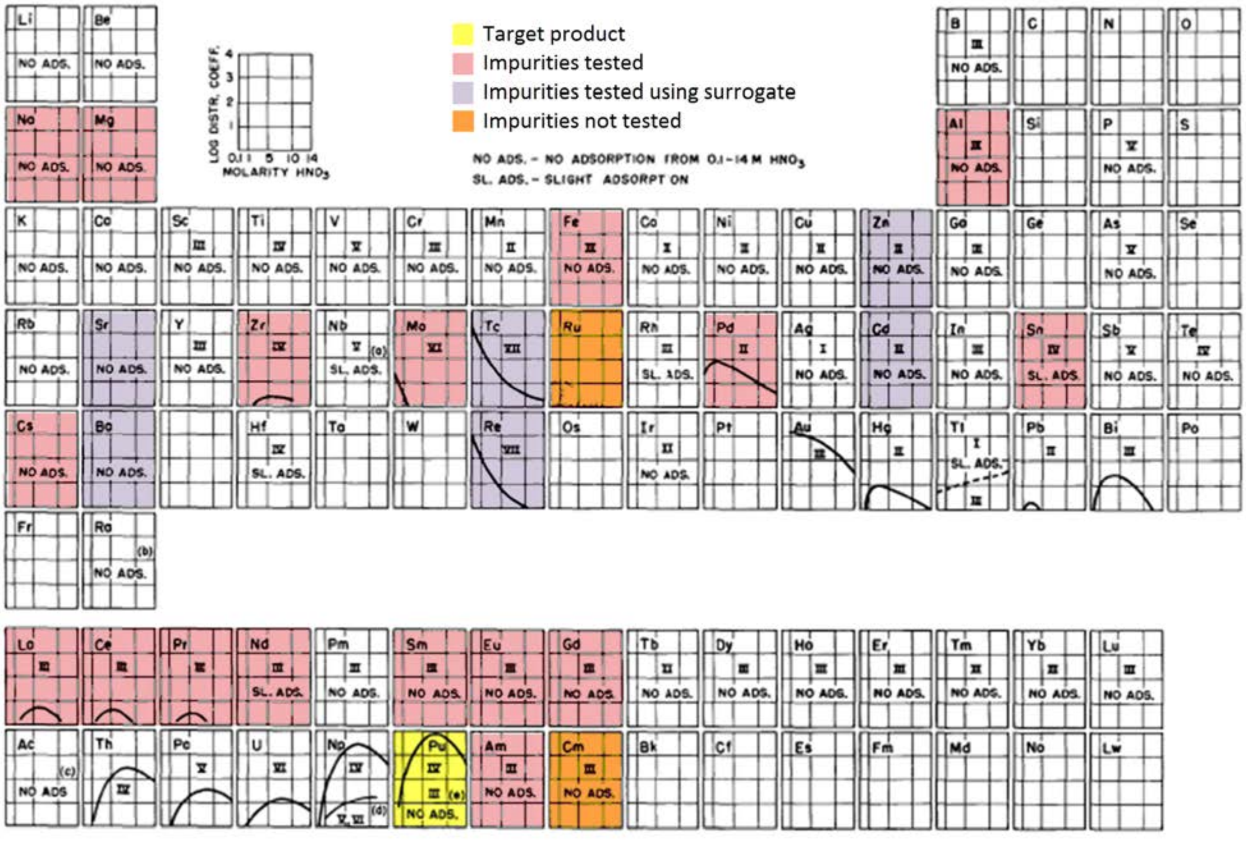


Fig. 1. Removal from Solution of Elements in 0.1 to 14M Nitric Acid with Strongly Basic Anion Exchange Resin. (a) Nb(V) - Bunney et al.,(15) James,(58) Phillips and Jenkins,(86) Prevot et al.(88) (b) Ra(II) - Choppin and Sikkeland.(23) (c) Ac(III) - Choppin and Sikkeland,(23) Hyde.(54) (d) Np(V), (VI) - Hardy,(46) Ichikawa et al.,(57) Tober,(107) Wish and Rowell.(122) (e) Pu(III) - Roberts and Brauer,(95) Wish and Rowell.(122)

Figure 2-1. Distribution Coefficients in a Nitrate Anion Exchange System with Expected Impurities in the Mk-18A Targets

3.0 Experimental Procedure

Two nonradioactive anion exchange column experiments were performed prior to the testing of resin performance with Pu and Am included in the feed matrix. The cold testing resulted in preliminary distribution data for the simulated feed with the anion-exchange resin to be compared with similar data for the radioactive solution. The operating conditions of all tests are shown in Table 3-1.

The two nonradioactive anion-exchange column tests using simulated Mk-18A feed solution were performed in a chemical hood. These tests were conducted to evaluate the impact of the solution matrix on the absorption of individual chemical components with Reillex™ HPQ resin. In the first test, the feed solution was introduced to the column as prepared. The feed solution for the second test was sparged with ~2 L of NO/NO_2 gas at 60 °C for 30 minutes prior to column loading; this simulated the impact of the proposed Pu valence adjustment method on the valences of the other cations and anions in the simulant.

The third anion-exchange test was performed in a radioactive environment using a similar feed solution as the previous two tests but with the addition of Pu and Am. The objective of this experiment was to develop the ion exchange flowsheet for the recovery of ^{244}Pu in the Mk-18A targets. This experiment demonstrated the valence reduction of Pu(VI) and investigated the decontamination factor of lanthanides, Am, and other impurities from Pu by anion exchange.

Table 3-1. Column Operating Conditions

Test #		**Test 1**	**Test 2**	**Test 3**
Bed Volume	[cm^3]	59	59	43
Conditioning	**HNO_3** [M]	7	7	8
	Volume [mL]	~120	~120	50
	Flowrate [mL/min]	Not recorded	Not recorded	10
Feed	**HNO_3** [M]	7	7	8
	Volume [mL]	2000	2000	972
	Flowrate [mL/min]	70	70	17
Wash	**HNO_3** [M]	7	7	8
	Volume [mL]	578	603	877
	Flowrate [mL/min]	70	70	9
Elution	**HNO_3** [M]	0.35	0.35	0.35
	Volume [mL]	396	408	207
	Flowrate [mL/min]	5	5	3

3.1.1 Process Equipment

Figure 3-1 shows the anion exchange apparatus setup in the nonradioactive environment. The primary components of the nonradioactive apparatus were the anion-exchange column, the Reillex™ HPQ resin, the simulated feed solution, the Fluid Metering, Inc. (FMI) Lab Pump Model QV, and the FMI Stroke Rate Controller Model V200 (not pictured).

The anion exchange column was fabricated in the SRNL Glass Shop from borosilicate glass. The column was assembled to operate in down-flow configuration. At the top of the column, an inlet valve and a vent valve were connected to the headspace; an outlet valve was connected to the bottom of the column. All fittings were sealed by compressed Viton™ o-ring fittings.

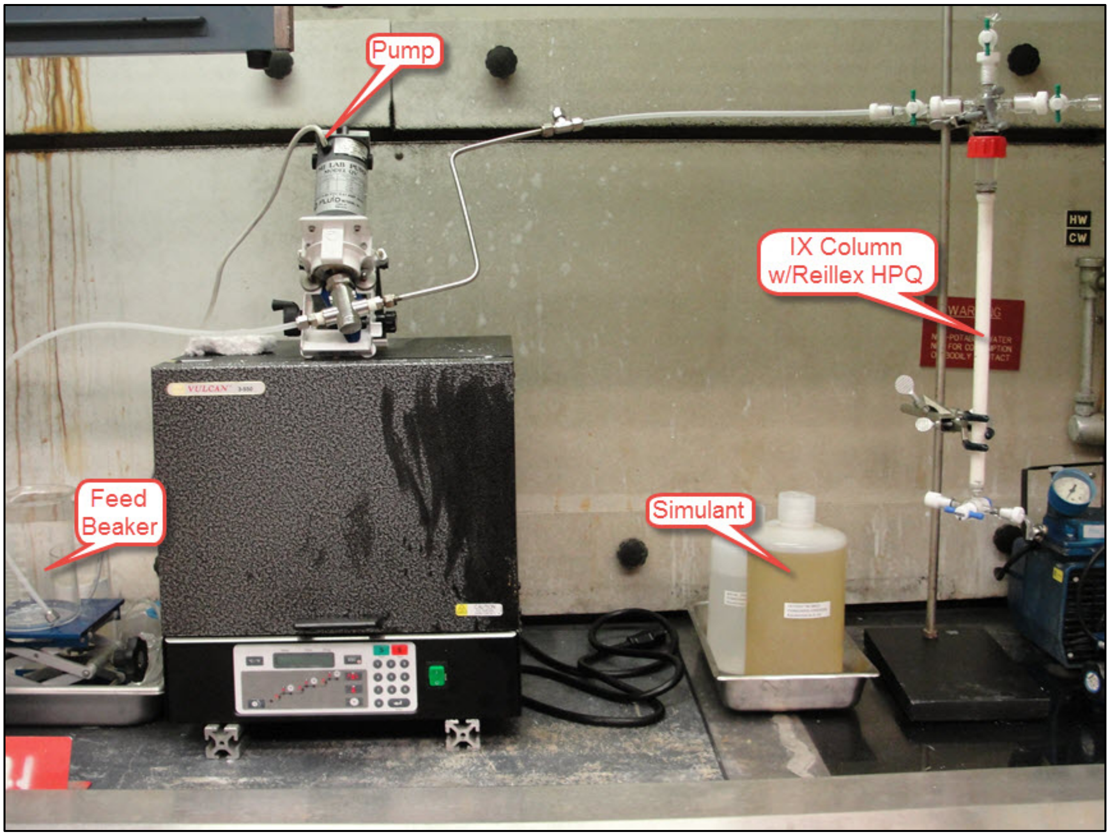
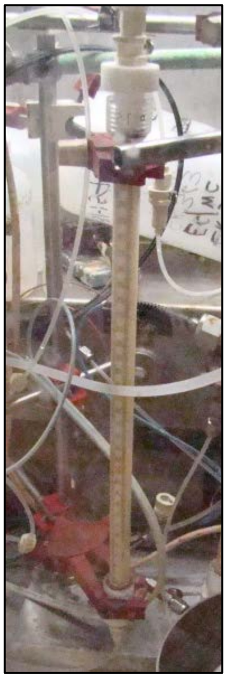


Figure 3-1. Nonradioactive Anion Exchange Setup

In the nonradioactive tests, the column had an inside diameter of 1.48 cm and was packed to a height of 34.3 cm with Reillex™ HPQ resin in the nitrate form, resulting in a resin bed volume of 59 cm^3. Before testing, the assembled column was conditioned with 7 M HNO_3.



A picture of the column used in the radioactive experiment is shown in Figure 3-2. This column utilized #15 Teflon™ bushings and CPC quick-connects for connecting 0.25 or 0.125 inch poly tubing to the column and consisted of a 12.6 mm ID glass body to retain the resin bed. The column was packed with ~43 cm^3 of Reillex™ HPQ resin (Vertellus 411-45) which had been used in another program. [18] A "degasser" vessel was attached to the top of the column to collect and vent gas bubbles in the feed line. This column had a 100-mesh screen (both in the upper and lower column bushings) but was operated only in the down-flow mode. An FMI piston pump was used to pump feed, wash, or elution acid through the column.

Effluent streams passed through a flowcell attached to the bottom of the column and were analyzed by ultraviolet-visible (UV-vis) spectroscopy. A pair of fiber optic lines previously installed through the ceiling of the glovebox allowed a light signal

Figure 3-2. Radioactive Anion Exchange Column

to be brought into the glovebox, passed through the flowcell, and carried out of the glovebox back to an Avantes spectrometer controlled by a computer.[a] Reference and measurement spectra were taken on the same pair of UV grade fibers. Light references were taken prior to the beginning of the experiment and stored. Mathematical manipulations were performed to analyze the spectra and determine the concentrations of species.

3.1.2 Feed Solution Preparation

Four liters of simulated feed solution were prepared for the nonradioactive anion-exchange experiments (~2 L for each test). First, 892 mL of concentrated HNO_3 (15.7 M) was added to 1108 mL of deionized (DI) water and diluted to ~2 L to prepare ~7 M HNO_3 (this was done twice). Next, all of the nitrate salts (except $Al(NO_3)_3$-9 H_2O) were weighed into an empty 4-L beaker. Two liters of the 7 M HNO_3 were added to the 4-L beaker to dissolve the nitrate salts using a stirring bar and light heating. The total volume was increased to 3500 mL using more 7 M HNO_3, and the remaining compounds were added to the solution one-by-one, observing their dissolution before adding the next chemical. Once all chemicals were added, the volume was brought up to ~4 L using 7 M HNO_3.

Approximately 900 mL of simulated feed solution was prepared for the radioactive test. First, 444 mL of concentrated HNO_3 was added to 356 mL of DI water in a 1-L graduated cylinder to prepare ~800 mL of ~8.7 M HNO_3. The HNO_3 was poured into a 1-L beaker atop a hotplate stirrer. The nitrate salts were weighed and then added to solution using light heating and stirring to facilitate dissolution. Once all the nitrate salts were added and dissolved, the volume in the beaker was increased to 875 mL using DI water. The remaining chemical compounds were added to the solution, and the simulant was heated lightly and stirred for 60 minutes. Permanganate was added last (of the cold reagents) and used to oxidize the Sn(II). Tin(II) was previously observed to reduce the Pu(VI). The final impurity matrix solution was filtered, and the total volume of solution was increased to ~900 mL using DI water to dilute to ~8 M HNO_3. A baseline measurement using UV-vis was performed to determine if there would be significant interference from the impurities in the simulant. This impurity matrix was transferred to the Pu glovebox where final adjustments with Pu and Am solutions were performed. Table 3-2 shows the mass of each chemical compound added to the nonradioactive and radioactive simulated feed solutions. For the nonradioactive tests, the chemical compounds were dissolved in HNO_3 to prepare 4 L of solution. The four liters were subsequently separated into two separate 2-L batches. Each 2-L batch was based on the nominal composition of the metals expected in the anion-exchange feed solution from 1/4th of a Mk-18A target. The amount of certain chemicals added was reduced based on availability (Pd) and solubility (Zr and Ru). Hazardous metals (Cd and Ba) and radioactive metals (Am and Cm) were replaced with nonradioactive simulants, as noted in Table 3-2 for the nonradioactive tests. For the radioactive test, the mass of the chemical compounds added to solution was reduced by a factor of four to keep a similar mass ratio in the ~1-L simulant compared to the ~2 L of feed solution for the nonradioactive tests. Larger ratios of Pd and Zr were added to the radioactive test than the nonradioactive test.

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[a] Spectrometer: Fiber Optic Spectrometer, 75 mm ULS 3648 element detector Avabench, 3064 pixel CCD detector, 10 µm slit size with 350 and 590 nm longpass filter for UB grating, wavelength range 360-920 nm using a USB2 high speed interface to a laptop computer operating Windows 7 and Microsoft Excel 2007 or later.

Table 3-2. Nonradioactive Chemicals Added to Simulated Feed Solutions

Component	Chemical	Nonradioactive Test 1 and 2[a]	Radioactive Test 3[b]
		Mass (g)	Mass (g)
Al	$Al(NO_3)_3{\bullet}9H_2O$	329.2	82.31
Mg	$Mg(NO_3)_2{\bullet}6H_2O$	68.8	17.20
Fe	$Fe(NO_3)_3{\bullet}9H_2O$	40.4	10.12
Nd	$Nd(NO_3)_3{\bullet}6H_2O$	12.44	3.12
Ce	$Ce(NO_3)_3{\bullet}6H_2O$	9.60	2. 06
Gd	$Gd(NO_3)_3{\bullet}6H_2O$	5.51	1.38
Cs	$CsNO_3$	1.95	0.49
La	$La(NO_3)_3{\bullet}6H_2O$	3.44	0.86
Pr[c]	$Pr(NO_3)_3{\bullet}6H_2O$	22.75	5.70
Sm	$Sm(NO_3)_3{\bullet}6H_2O$	2.17	0.54
Sr[d]	$Sr(NO_3)_2$	1.56	0.39
Eu[e]	$Eu(NO_3)_3{\bullet}5H_2O$	1.45	0.36
Pd	$PdCl_2$	0.97	0.49
Re[f]	$NaReO_4$	0.38	0.09
Mo	$Na_2MoO_4{\bullet}2H_2O$	1.28	0.32
Zr	$ZrO(NO_3)_2{\bullet}xH_2O$	0.53	0.21
Sn	SnO_2	0.29	N/A
	$SnCl_2\text{-}2H_2O$	N/A	0.10
Zn[g]	Zn	3.26	0.81
Ru	RuO_2	0.70	N/A
K / Mn	$KMnO_4$[h]	N/A	0.42

[a] Chemicals added to 4 L of HNO_3
[b] Chemicals added to 1 L of HNO_3
[c] Surrogate for Cm plus Pr expected in target
[d] Surrogate for Ba plus Sr expected in target
[e] Surrogate for Am plus Eu expected in target
[f] Re added as surrogate for Tc
[g] Zn added as surrogate for Cd
[h] Added for valence adjustment

3.1.2.1 Plutonium and Americium Pretreatment

The Pu for the radioactive experiment was added as a spike solution to the previously prepared impurity matrix. The Pu was obtained from a previous column experiment. Ceric ammonium nitrate (1 g) was added to the Pu solution (nominally 1 g Pu) to oxidize ~10% of the Pu(IV) to Pu(VI) to mimic plausible concentrations of Pu(VI) following dissolution of the Mk-18A targets. The partial oxidation of the Pu spike was verified with UV-vis spectroscopy prior to the addition to the impurity matrix.

Due to unsatisfactory results with NO/NO_2 valence adjustment treatment, ferrous sulfamate (FS) / sodium nitrite treatment was performed (4 mL FS followed by 2 mL 5 M sodium nitrite). The UV-vis spectrum of the solution was measured between each addition. Lastly, the feed preparation was completed by the addition of approximately 13.9 mg of ^{241}Am (in 10 mL solution) along with 50 mL of concentrated HNO_3 and 15 mL of DI H_2O to bring the simulated solution to 8 M HNO_3 and ~1 L. A portion of this solution was retained for analysis by UV-vis after four weeks to verify the lack of Pu(VI) in-growth into the simulant solution. Subsequent analysis showed no detectable in-growth of Pu(VI) after 30 days.

3.1.3 Column Operation

For each nonradioactive test, 2 L of simulated feed solution was fed to the column. The FMI Stroke Rate Controller was calibrated by pumping timed volumetric samples of water with the FMI Model QV Lab Pump before testing. The feed solution was pumped down-flow through the column at a rate of 70 mL/min. Five 400-mL samples of the raffinate were collected for sample analysis. The resin was washed to remove impurities with approximately 600 mL (~10 BV) of 7 M HNO_3. The wash flowrate down-flow through the column was 70 mL/min, and five samples of the wash were collected for analysis. The first two sample collections were each 60 mL, the third and fourth sample collections were each 120 mL, and the last wash sample collection contained the remaining wash raffinate of approximately 240 mL. For the elution phase, 400 mL (~6.7 BV) of 0.35 M HNO_3 was passed through the resin down-flow. The eluent flow rate was 5 mL/min and six samples of eluate were gathered for analysis (five 60-mL samples and one ~100-mL sample).

In preparation for the radioactive experiment, the feed line and column were degassed. Clean water was pumped through the column until all gas bubbles were purged. The column was configured for loading and washing by connecting the flowcell to the tubing at the bottom of the column. The column was conditioned down-flow with 50 mL of 8 M HNO_3.

Approximately 972 mL of the radioactive simulant feed was passed through the anion-exchange resin down-flow at approximately 17 mL/min. The raffinate was collected in graduated cylinders to measure the volume through the resin and then it was transferred to a 1-L bottle. After the loading of Pu by anion exchange, the column was washed to remove impurities with approximately 877 mL (~20.4 BV) of 8 M HNO_3 down-flow at approximately 9 mL/min. Nine bottles of the wash were collected for analyses. Bottles (clean and dry) were weighed before placing them in the glovebox. Approximately 45 mL were collected in each of the first four wash collection bottles, ~90 mL in the fifth and sixth bottles, ~125 mL in the seventh, ~200 mL in the eighth, and the remaining wash was collected in the ninth bottle. After washing, the column was configured for elution by connecting the 7.14 mm flowcell to the bottom of the column. The Pu was recovered by flowing approximately 207 mL (~4.8 BV) of 0.35 M HNO_3 down-flow through the resin at 3 mL/min. The eluate was collected in three product cuts: a ~40 mL displacement cut, a ~55 mL hearts cut, and a ~112 mL tails cut. The sample collection bottles with samples were then weighed on a balance in the glovebox. The solution density of the samples was measured with a density meter. This allowed for accurate sample collection volumes to be calculated.

3.1.4 Sample Analysis

Samples of the nonradioactive feed, raffinate, wash, and eluate were analyzed by Analytical Development (AD) via inductively coupled plasma atomic emission spectrometry (ICP-ES) and inductively coupled plasma mass spectrometry (ICP-MS) to measure concentrations of impurities and calculate the mass balance.

For nonradioactive ICP-ES, a Perkin-Elmer Optima 3000 provided multiple element analysis. A Schmidt cross dispenser was used in the ultraviolet range (165-375 nm) and a prism was used in the visible range (375-782 nm). Two segmented-array charge-coupled-device detectors were used. With the purged optics, detection of spectral wavelengths is extended from approximately 190 nm to 165 nm. The minimum reported uncertainty by AD was assumed as 10%. Uncertainties were reported as the root mean square of the individual components when greater than 10%.

For nonradioactive ICP-MS, an Agilent 7700x provided multiple element analysis. A helium collision cell was used with a quadrupole mass filter to separate and direct the ions that were generated in the plasma to the detector, which is an electron multiplier. With these components, detection of many of the isotopic masses within the 27 - 244 m/z range was performed. The minimum reported uncertainty by AD is assumed as 20%. The reported %RSD values reflected the variance of replicate measurements for the individual components.

For the radioactive test, a sample of the simulated feed solution was collected for gamma spectroscopy, ICP-ES, and ICP-MS. Samples of the raffinate, wash, and elution cuts were collected for ICP-ES, ICP-MS, and gamma spectroscopy. Clean wash and elution acid were both sampled for ICP-ES and ICP-MS.

Analytical Development used a Leeman Prodigy ICP-ES instrument to analyze the radioactive samples, which quantitatively determined metal elements with a relative precision of ±10%. The ICP-ES provided multi-element analysis of sample solutions via measurements based on characteristic emission from electronically excited atoms and ions. The minimum reported uncertainty by AD was assumed as 10%. Uncertainties were reported as the root mean square of the individual components when greater than 10%.

Radioactive samples analyzed by ICP-MS were measured using the same instrumentation as the nonradioactive samples.

For the gamma spectroscopy, high-purity germanium detectors coupled with Canberra Genie2000 spectroscopy software were used to quantify the gamma-emitting nuclides of Pu and Am. The minimum reported uncertainty was 5%. Uncertainties were reported as the root mean square of the individual components when greater than 5%.

3.2 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.

4.0 Results and Discussion

4.1 Simulated Feed Solution

The simulated feed solution for both nonradioactive tests was prepared as one 4-L solution (Section 3.1.2) and then divided into two 2-L bottles. Assuming the feed solution was well mixed, Test 1 and Test 2 feed solutions should be equivalent within the uncertainty of the measurement. Therefore, only one analysis of the simulant feed was performed. The calculated and measured concentrations of the simulant feed are shown in Table 4-1. Note red font indicates concentrations measured below the method detection limit.

Table 4-1. Characterization of the Nonradioactive Feed Solution (Test 1 and 2)

Component	ICP-MS (mg/L)	ICP-ES (mg/L)	Calculated Concentration (mg/L)
Al	6150	5130	5920
Ce	743	819	774
Cs	318	---	332
Eu[a]	124	---	129
Fe	1360	1340	1400
Gd	494	---	480
La	266	267	276
Mg	1570	1570	1630
Mo	122	123	127
Na	---	232	68.8
Nd	898	914	1020
Pd	66.2	---	146
Pr[b]	1840	---	1840
Re[c]	60.6	60.9	64.8
Ru	< 0.01	---	133
Sm	180	---	184
Sn	< 0.06	< 6.52	57.1
Sr[d]	154	160	161
Zn[e]	796	775	815
Zr	28.0	30.7	48.5

[a] Surrogate for Am plus Eu expected in target
[b] Surrogate for Cm plus Pr expected in target
[c] Re added as surrogate for Tc
[d] Surrogate for Ba plus Sr expected in target
[e] Zn added as surrogate for Cd

In preparing the simulant, the nitrate salts dissolved simply with light heating and stirring. Zinc metal, sodium perrhenate ($NaReO_4$), and sodium molybdate (Na_2MoO_4) dissolved readily. Palladium(II) chloride mostly dissolved in 30 minutes and the zirconium(IV) oxynitrate [$ZrO(NO_3)_2$] had limited solubility. Tin(IV) oxide was added to solution as a fine powder and it was difficult to determine whether it dissolved; measurement by ICP-ES and ICP-MS analysis reported values below the method detection limits which confirmed that Sn did not dissolve. The analysis by ICP-MS also verified that ruthenium(IV) oxide (RuO_2) did not dissolve; therefore the data for Sn and Ru will not be further investigated for the nonradioactive tests. For the radioactive test, a soluble Sn salt was identified and added to the simulant. The prepared radioactive simulant feed was analyzed by ICP-ES, ICP-MS, and gamma spectroscopy. The analysis of the feed is shown in Table 4-2.

There were significant discrepancies in comparing calculated concentrations with those measured by ICP-MS and ICP-ES for Na, Pd, and Zr in both the nonradioactive and radioactive tests. It is not known why high concentrations of sodium were analyzed in the feed solutions as Na was only added to solution as a counter ion of $NaReO_4$ and Na_2MoO_4. Palladium analyzed at ~45% of the expected concentration for both the Test 1/2 and Test 3 feed solutions. Palladium chloride is soluble in nitric acid and is also deliquescent. It is possible that absorbed moisture on the $PdCl_2$ was not accounted for in calculating the Pd mass added to solution. The same effect might also apply to Zr, though it is also likely that $ZrO(NO_3)_2$ is not fully soluble in 7-8 M HNO_3. It is not known why only ~70% of Sr added was analyzed in the radioactive feed solution as Sr analyzed at the expected concentration in the Test 1/2 feed solution.

Table 4-2. Characterization of the Radioactive Feed Solution (Test 3)

Element	**Measured (mg/L)**	**Calculated (mg/L)**	**Element**	**Measured (mg/L)**	**Calculated (mg/L)**
Al	5840	6090	Mo	125	130
Am (γ)	18.3	N/A	Mo*	127	130
Ce†	908	947	Na†	368	307
Ce*†	965	947	Nd*	1050	1060
Cs*	344	342	Pd*	139	300
Eu*	136	132	Pr*	1960	1900
Fe†	2050	1940	Pu (γ)	1022	N/A
Gd	477	493	Re*	62.6	66.3
Gd*	506	493	Sm*	186	189
K	105	107	Sn*	56.5	56.5
La	293	284	Sr	118	167
La*	283	284	Sr*	108	167
Mg	1610	1680	Zn	816	841
Mn	146	151	Zr	47.8	78.9
			Zr*	54.5	78.9

Analysis by ICP-ES
* Analysis by ICP-MS
(γ) Analysis by gamma spectroscopy
† Includes Ce, Fe, and Na added as part of valence adjustment

4.2 Reduction/Oxidation for Valence Adjustment

4.2.1 Effect of NOx Gas on Nonradioactive Feed Solution

The two nonradioactive tests used the same feed solution and the same resin column but Test 2 was subjected to a simulated NOx valence adjustment treatment in an attempt to observe differences in impurity behavior caused by that treatment. A comparison of results for Test 1 and Test 2 indicate no measureable effect from bubbling NOx through the feed solution outside of analytical uncertainty (Table 4-3, ICP-ES data can be found in the appendix).

4.2.2 Redox of Plutonium

For the radioactive test, multiple attempts were made to perform the valence adjustment using NO and/or NO_2 gas but these proved unsuccessful. Those results are discussed by Pierce. [12] Due to the complications in the valence adjustment using NO/NO_2 gas to reduce the Pu(VI) to Pu(IV), a minimal required amount (rather than the historically conservative excess) of FS was added to the solution to reduce the Pu(VI) to Pu(III). The simulant solution (~925 mL) contained ~1.1 g/L Pu, of which ~10% was initially present as Pu(VI). During report preparation it was recognized that the spectra showed that the Pu(VI) originally present in the feed solution had been reduced prior to the FS addition (4 months had passed since it was initially prepared). This observation was unexpected and the cause unidentified, however there is strong reason to believe that FS would perform the Pu(VI) reduction as it was used similarly in the ^{238}Pu recovery from Mk-53 targets. [19, 20] If the high dose rate limits FS use, then the addition of hydrazine to protect the Fe(II)/Pu(III) might be helpful. The Pu that was reduced to Pu(III) with FS would have oxidized to Pu(IV) over a period of hours to days (but will be accelerated with ^{244}Cm present). Instead of waiting, in this experiment $NaNO_2$ was added to the solution to oxidize the Pu(III) to Pu(IV) immediately rather than waiting for radiolytically generated nitrous acid to consume the reductant and oxidize the Pu(III) back to Pu(IV).

The stability of Pu(IV) in this impurity matrix was measured by UV-vis spectrophotometry. Figure 4-1 and Figure 4-2 show the various Pu valence states in the simulant compared to the impurity matrix; initially with Ce(IV) [to form Pu(VI)], after FS [to form Pu(III)], and $NaNO_2$ [to reform Pu(IV)]. The day prior to the column loading, 4 mL of 2.2 M FS was added to the nearly 1 L of feed solution. The solution was mixed and the spectra measured. Immediately after the FS treatment, 2 mL of 5 M $NaNO_2$ was added to oxidize the excess Fe(II) and Pu(III) to Fe(III) and Pu(IV). The ^{241}Am solution and the final acid adjustment was made at that time which resulted in an ~8% dilution.

The impurities introduce significant spectral features. Between the relatively dilute Pu concentration and the effects of the impurities, the features of the valence adjustment steps are not easy to see in the absorption spectra. These spectra were also taken over five months. The use of the 2nd derivative of the absorbance eliminates much of the baseline issues and makes it somewhat easier to see the Pu spectral features. The Pu(VI) peaks at 811 and 831 nm are only present immediately after the Pu solution was added to the impurity matrix.

An archive sample of the final feed solution was retained and the spectrum was measured 30 days after the valence adjustment. Figure 4-2 shows that the initial presence of Pu(VI) and the intermediate presence of Pu(III) are the only significant changes during the ~5 months between the initial preparation and the measurement of the archive sample. After 30 days, the Pu spectra showed only the presence of Pu(IV). This indicates the stability of Pu(IV), at least as much as can be tested in this experiment. The imposition of the much larger gamma and alpha doses of the actual Mk-18A feed solution will require continued concern for the Pu valence chemistry.

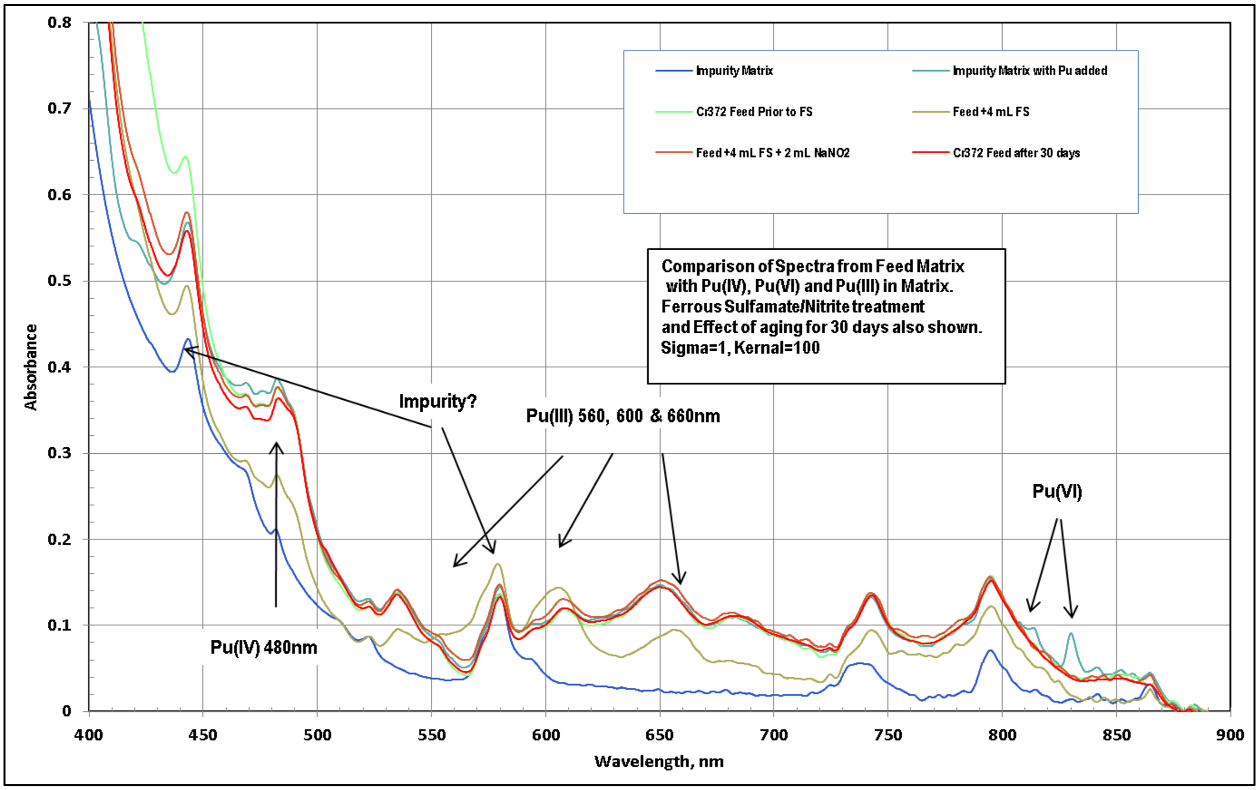


Figure 4-1. Spectra of the Impurity Matrix and Pu(IV) and Pu(VI) at various stages of adjustment

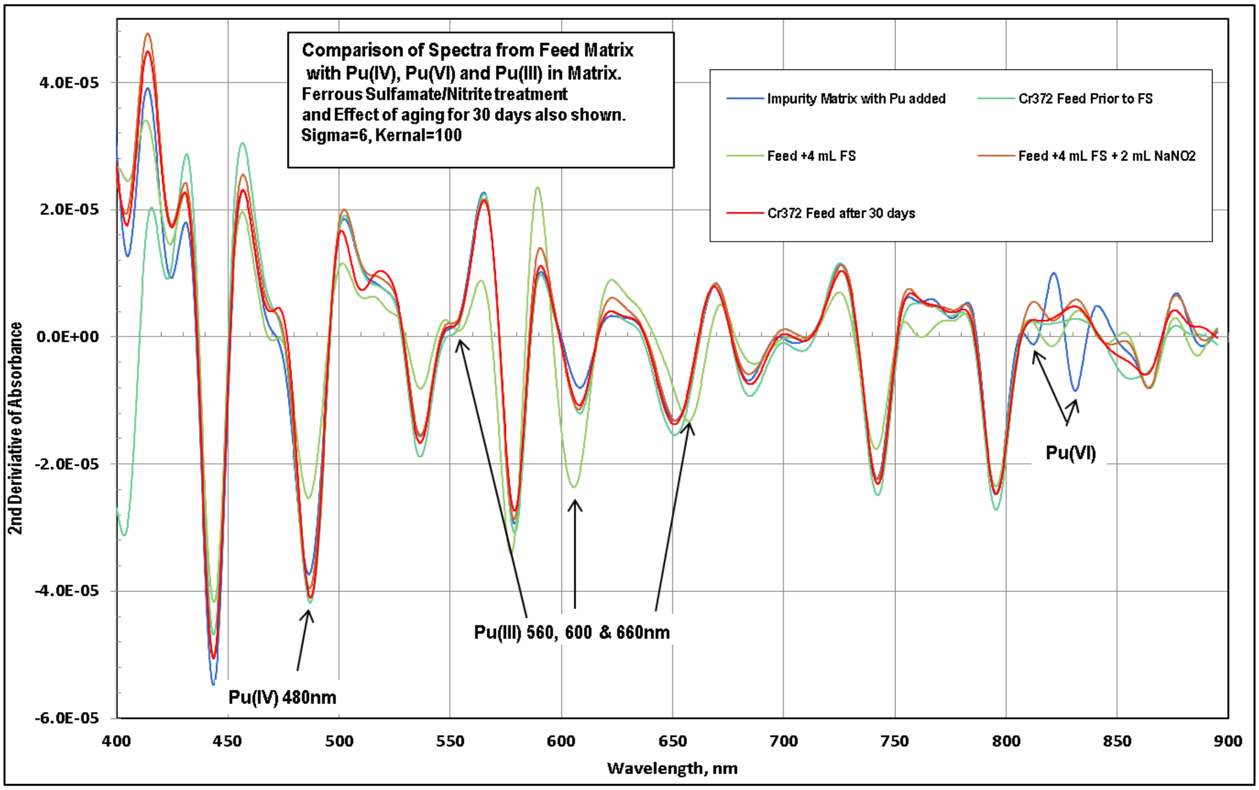


Figure 4-2. 2nd Derivative of the Absorbance Spectra of the Impurity Matrix and Pu(IV) and Pu(VI) at various stages of adjustment

4.3 Wash and Elution Acid Purity

Analyses performed as part of the radioactive anion exchange testing included analyses of the wash and elution acid to determine the levels of impurities. Data from ICP-ES and ICP-MS showed no measureable concentrations of impurities. The data are provided in the appendix.

4.4 Distribution of Impurities in Effluent Streams

Samples of the effluent streams (raffinate, wash, and eluate) were analyzed by AD through ICP-MS and ICP-ES. Table 4-3 displays the mass balance from the ICP-MS analysis of Test 1 and Test 2.

Table 4-3. Test 1 and 2 Mass Balance

Element	Feed (mg)	Test 1				Test 2			
		Raffinate Recovery	Wash Recovery	Eluate Recovery	Mass Balance	Raffinate Recovery	Wash Recovery	Eluate Recovery	Mass Balance
Al	12300	92%	2.4%	<0.03%	95%	96%	2.2%	<0.03%	98%
Ce	1480	87%	8.7%	3.6%	100%	93%	9.0%	3.6%	106%
Cs	636	97%	2.3%	0.002%	99%	104%	2.4%	0.01%	106%
Eu[a]	248	97%	2.8%	0.003%	99%	103%	2.9%	0.01%	106%
Fe	2720	98%	2.2%	0.01%	100%	104%	2.4%	0.02%	106%
Gd	987	97%	3.1%	0.17%	100%	104%	3.2%	0.18%	107%
La	532	86%	9.1%	4.7%	100%	91%	9.3%	4.7%	105%
Mg	3140	97%	2.2%	<0.01%	99%	102%	2.4%	0.002%	105%
Mo	244	98%	2.6%	0.005%	100%	93%	2.8%	0.001%	96%
Na	464	101%	2.8%	0.06%	103%	105%	3.0%	0.14%	108%
Nd	1800	94%	5.7%	0.39%	100%	99%	5.9%	0.41%	106%
Pd	132	17%	8.1%	0.39%	26%	55%	15%	0.90%	71%
Pr[b]	3680	90%	7.4%	1.6%	100%	96%	7.6%	1.6%	105%
Re[c]	121	89%	10%	0.32%	100%	94%	10%	0.36%	105%
Sm	360	96%	3.1%	0.01%	99%	102%	3.3%	0.01%	106%
Sr[d]	308	98%	2.4%	0.003%	100%	102%	2.5%	0.005%	105%
Zn[e]	1590	97%	2.2%	<0.01%	99%	103%	2.3%	<0.01%	105%
Zr	56.0	93%	3.0%	1.0%	97%	102%	3.1%	0.45%	105%

[a] Surrogate for Am plus Eu expected in target
[b] Surrogate for Cm plus Pr expected in target
[c] Re added as surrogate for Tc
[d] Surrogate for Ba plus Sr expected in target
[e] Zn added as surrogate for Cd -Red values indicate samples measured below method detection limit

The mass balances measured by ICP-ES for Test 1 and 2 can be found in Appendix A.7 and A.8. Approximately 5-7% more material was recovered in the product streams of Test 2. This modest bias is most likely due to the precision with which the feed solution for Tests 1 and 2 were split between the two experiments.

The mass balance data for Test 3 (Table 4-4) were accumulated in a manner similar to Tests 1 and 2 (Table 4-3). As with the data for Tests 1 and 2, the Test 3 data exhibit excellent mass balances for all elements except Pd.

Table 4-4. Test 3 Mass Balance

Element	Feed (mg)	Raffinate Recovery	Wash Recovery	Displacement Recovery	Hearts Recovery	Tails Recovery	Mass Balance
Al	5680	97%	3.5%	0.003%	<0.004%	<0.01%	100%
Am (γ)	18.3	89%	5.7%	0.004%	0.007%	0.002%	95%
Ce	883	86%	14%	0.07%	<0.07%	<0.14%	100%
Ce*	938	86%	14%	0.07%	0.40%	0.01%	100%
Cs*	334	97%	3.7%	0.002%	0.001%	0.002%	101%
Eu*	132	97%	4.1%	0.003%	0.002%	0.002%	101%
Fe	1990	96%	3.6%	<0.005%	<0.01%	<0.01%	100%
Gd	464	96%	3.8%	<0.03%	<0.01%	<0.09%	100%
Gd*	492	95%	4.2%	0.00%	0.01%	0.002%	99%
K	102	101%	<3.3%	<1.1%	<1.6%	<3.2%	104%
La	285	84%	14%	0.07%	0.38%	<0.04%	99%
La*	276	85%	15%	0.09%	0.61%	0.01%	100%
Mg	1560	97%	3.7%	<0.001%	<0.001%	<0.002%	101%
Mn	142	97%	3.6%	<0.02%	<0.03%	<0.06%	101%
Mo	122	95%	<3.6%	<0.59%	<0.82%	<1.7%	99%
Mo*	123	95%	4.2%	0.003%	0.01%	<0.01%	99%
Na	358	97%	3.6%	<0.06%	<0.08%	<0.16%	100%
Nd*	1020	91%	7.7%	0.01%	0.03%	0.002%	99%
Pd*	135	16%	27%	1.1%	0.37%	0.03%	44%
Pr*	1900	88%	11%	0.02%	0.12%	0.003%	99%
Pu (γ)	1020	0.79%	1.2%	0.10%	93%	7.6%	103%
Re*	60.9	87%	13%	0.002%	<0.003%	<0.01%	101%
Sm*	181	95%	4.5%	0.003%	0.004%	<0.004%	99%
Sn*	54.9	96%	3.8%	<0.003%	<0.004%	<0.01%	100%
Sr	115	96%	3.5%	<0.004%	<0.01%	<0.01%	99%
Sr*	105	96%	3.5%	0.002%	0.001%	0.002%	99%
Zn	793	96%	3.6%	<0.003%	<0.004%	<0.01%	100%
Zr	46.5	98%	5.3%	<0.06%	<0.09%	<0.17%	104%
Zr*	52.9	94%	4.4%	0.002%	0.01%	<0.004%	98%

Analysis by ICP-ES
* Analysis by ICP-MS
(γ) Analysis by gamma spectroscopy
Red values indicate samples measured below method detection limit

4.4.1 Lanthanides

The volume distribution coefficients of La, Ce, and Pr in 7 M HNO_3 are 1.4, 1.2, and 0.67, respectively. [16] The distribution coefficients of these lanthanides decrease as HNO_3 molarity decreases. [17] Figure 4-3 shows the feed, wash, and elution behavior of La, Ce, Pr, Nd, Sm, Eu, and Gd in Test 1 (Test 2 was very similar and can be found in the appendix). The lanthanides exhibited slight retention on the resin initially when the solution was fed to the column. The lanthanides slowly wash through with the 7 M HNO_3 wash, and distinct elution peaks can be observed from the eluent wash.

After 9.6 BV of wash, the concentrations of La, Ce, and Pr decrease to 14%, 12%, and 25% of the respective feed concentrations. Concentration peaks occur within the first two BV of eluent (similar to the displacement and hearts of the eluate if Pu was present), and then the concentration significantly decreases after two BV. As seen in the figure, La, Ce, and Pr eluted to levels of 115%, 79%, and 28% of their feed concentrations in the second 60-mL eluate collection of Test 1. Essentially all of the Eu washed off the resin prior to elution (0.003% of Eu fed eluted). This overall behavior is consistent with the literature; a minor amount of lanthanide retention is expected, though Gd does not follow the trend of decreasing affinity for the resin with increasing atomic number of the lanthanides. [16, 17] Attention should be focused on lanthanides that elute in high percentages; 4.68% of La, 3.58% of Ce, and 1.64% of Pr fed to the column eluted from the resin in 0.35 M HNO_3 in Test 1. Excess Pr and Eu were added to the simulant in an attempt to provide additional mass of impurities to represent the behavior of Am and Cm.

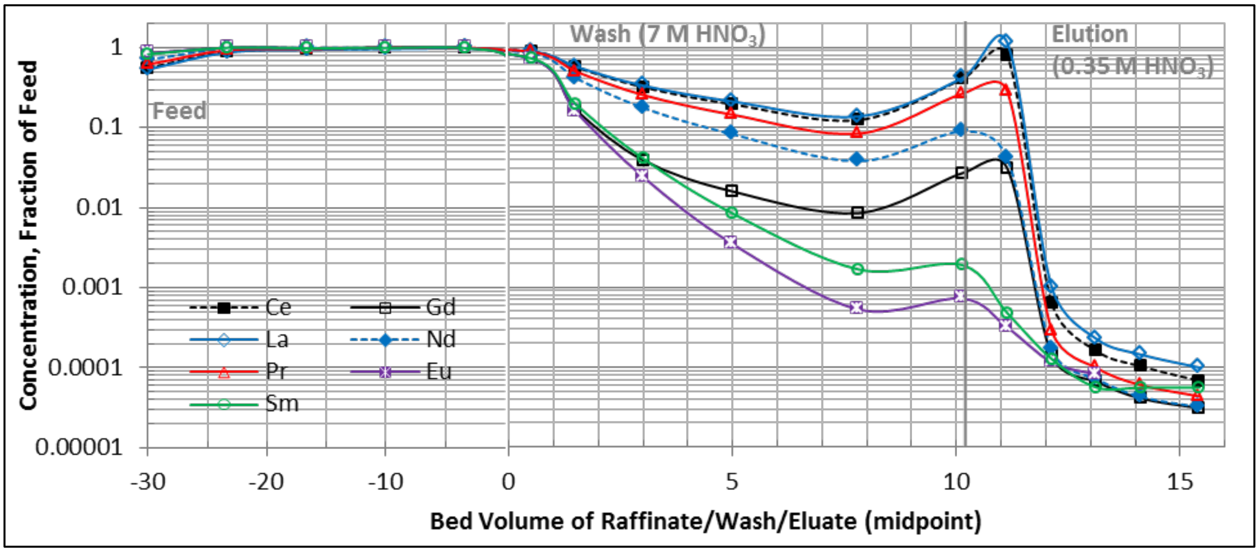


Figure 4-3. Test 1 Lanthanide Feed, Wash, and Elution Behavior

Figure 4-4 graphs the lanthanides in the Mk-18A radioactive simulant solution (Test 3). The order of lanthanides in their washing-elution profiles is the same for the radioactive and nonradioactive experiments. A comparison of Figure 4-4 with Figure 4-3 indicates that the lanthanides behave similarly in both the radioactive and nonradioactive tests. The resin was washed with twice as much volume in the radioactive test and because the additional volume of wash removes more of the lanthanides retained on the resin, smaller concentrations are observed in the lanthanide elution spikes of the radioactive test compared to the nonradioactive tests. For instance, only 0.7%, 0.5%, 0.2% of the La, Ce, and Pr fed eluted from the resin in the Pu eluate.

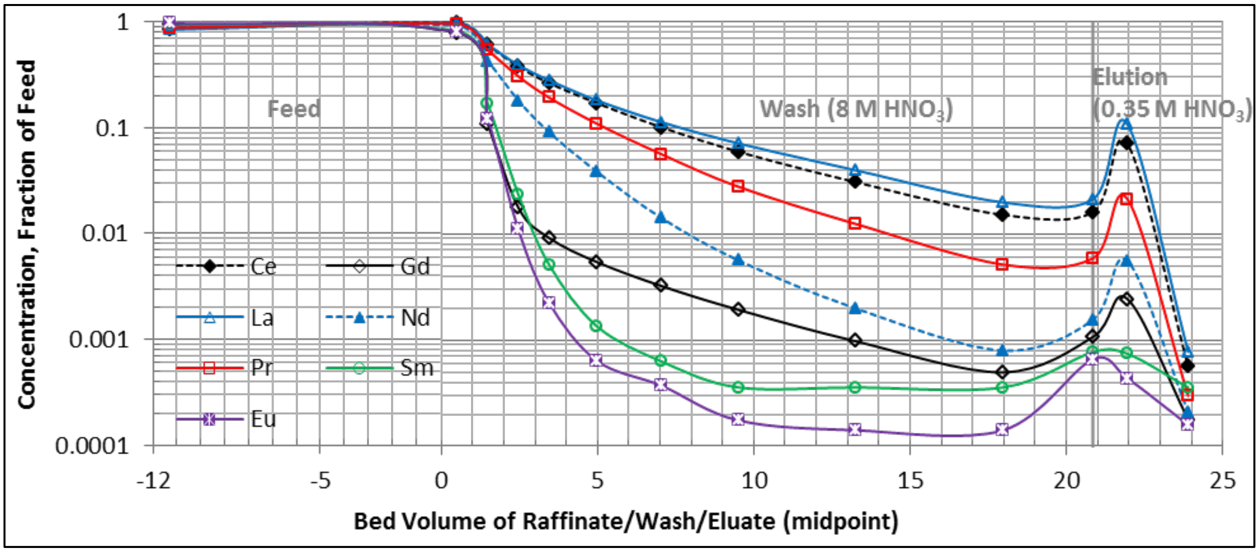


Figure 4-4. Test 3 Lanthanide Feed, Wash, and Elution Behavior (Radioactive Test)

4.4.2 Palladium and Rhenium

The Pd and Re data compare loosely with the literature (Figure 2-1). Palladium seems to have a much higher affinity to the anion resin in 7-8 M HNO_3 than the literature suggests. The mass balance in the three tests for Pd is poor; only 26% of Pd fed to the column was recovered in Test 1, 71% in Test 2, and 44% in Test 3. Palladium(II) may form a series of anionic complexes with nitrate ions in aqueous solution which are likely to be extracted through anion exchange. [21] It is probable that the resin retained Pd from Test 1 which may have reduced the amount of Pd absorbed in the feed step of Test 2, causing a difference in behavior for the raffinate concentration of Pd between Test 1 and Test 2. This phenomenon can be seen in Figure 4-5. After Test 1, 98 mg of Pd was retained on the resin and an additional 38 mg of Pd remained on the resin after Test 2, leaving 136 mg of Pd retained on the resin after two column tests. Approximately 10% and 13% of the Pd that loaded on the resin during the feed in Tests 1 and 2, respectively, washed off by the end of the test. In Test 3, with the presence of Pu, 33% of the loaded Pd washed off the resin. Retained Pd from past runs may affect the Pu capacity of the resin if Pu does not displace it.

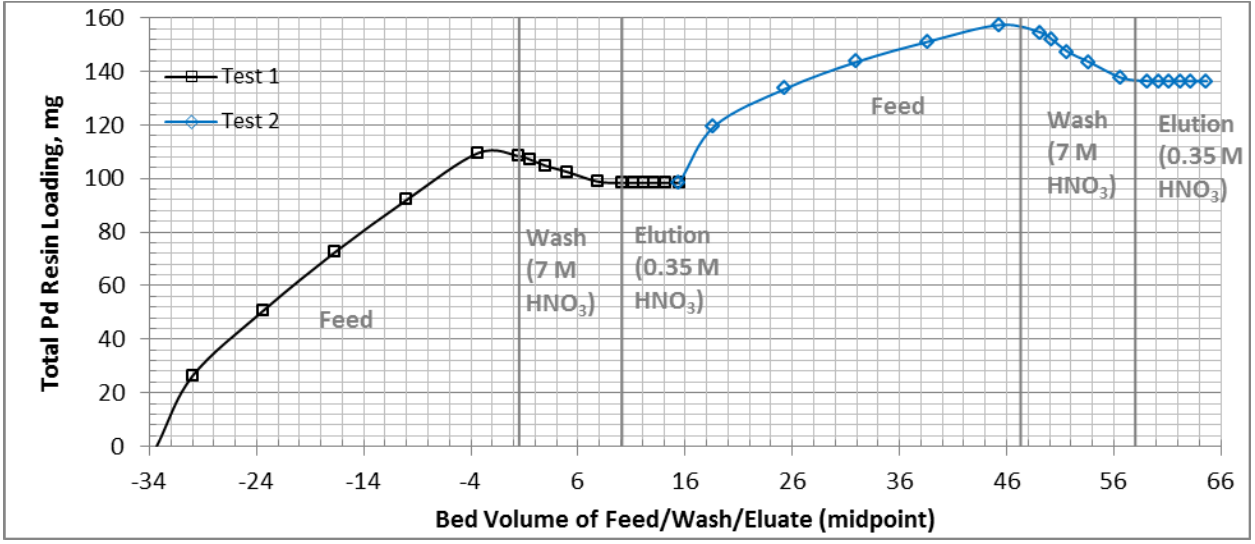


Figure 4-5. Test 1 and 2 Total Pd Resin Loading

The feed, wash, and elution data for Pd/Re in the nonradioactive tests (1 and 2) are plotted in Figure 4-6 and the Pd/Re data for the radioactive test (3) is shown in Figure 4-7.

There are minor differences between the radioactive and nonradioactive data. Both data sets are similar during feeding and washing. Rhenium does not exhibit an increase in concentration during elution of the radioactive test. Because the radioactive tests entailed more washing, essentially all of the Re was removed prior to elution. The nonradioactive test released more Re (although still a very low concentration) during elution because less Re was removed by washing prior to elution.

Palladium is absorbed significantly from 7 and 8 M HNO_3 and Re is absorbed weakly. Both elements are retained stronger (higher K_d) at lower acid concentrations, which are the conditions used for elution. Consequently, Pd shows some absorption during feeding, steady leakage during washing, and very little desorption during elution. Rhenium exhibits less absorption during feeding, diminishing concentrations during washing due to depletion of Re on the resin, and very little desorption during elution. Rhenium was added to the simulant as a surrogate for Tc due to lack of availability of Tc for this project. Both are group 7 transition metals with similar chemical behavior. Any Re or Tc not washed off the resin would retain on the column with a strong affinity to the resin during the elution step but since the K_d for Re and Tc in 8 M nitric acid are much lower than for Pd, they were expected to be much less of an issue than Pd. Any retained Re or Tc would then wash off the column during regeneration or in the next feed of anion exchange solution.

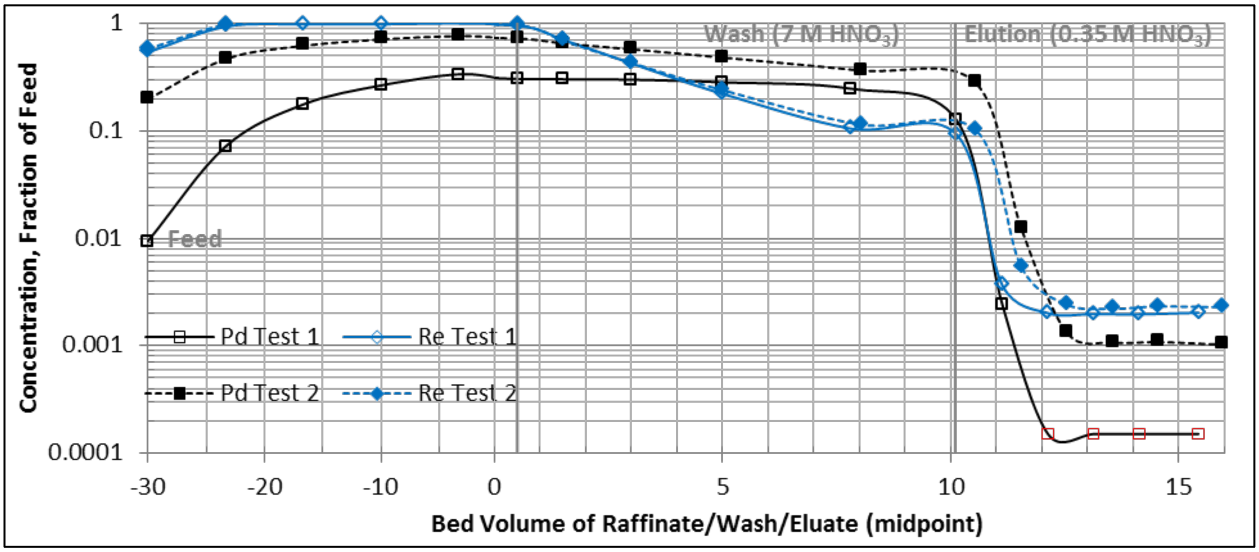


Figure 4-6. Test 1 and 2 Pd and Re Feed, Wash, and Elution Behavior

*Red markers indicate concentrations measured below method detection limits.

The presence of Pd in the wash and displacement solutions can be seen in Figure 4-8. It should be noted that only one sample of the raffinate was collected for Test 3 (Figure 4-7) which, when graphed, gives the impression of linear change in Pd and Re absorption during feeding. An accurate assessment of the behavior and shape of the loading curve is provided in the nonradioactive data (Figure 4-6).

The nominal Mk-18A composition indicates that the Mk-18A feed should contain ~1.5 g of Pd for each gram of Pu whereas in these tests ~0.13 g Pd/g Pu was used. Additional Pd was not available for use in these experiments. While it is assumed (based on the K_d) that Pu will displace Pd from the strong-base resin, these experiments did not involve sufficient Pd to observe that effect. The Pu capacity on the resin is likely affected to some degree by the significant amount of Pd that is competing for anion exchange sites. During the wash step of the Test 3, Pu could be seen roughly two-thirds of the way down the resin bed even though the resin was loaded to less than half the Pu capacity observed in HB-Line flowsheet work.

The increased K_d for Pd at low acid concentrations presents an opportunity to easily polish the Pu solution from Pd (and potentially recover the Pd). After the Pu product solution is removed from the cells, it can be placed into a glovebox, diluted modestly to say 0.5 M HNO_3 and then anion exchanged to remove essentially all the remaining Pd. If additional purification is desired, then this solution (now Pd free) can be cation exchanged to concentrate it and additional anion exchange or other separation performed to decrease the level of lanthanides (and Cm) present in the Pu solution. It may also be possible to remove the retained Pd from the resin between runs using thiourea or another chemical which complexes the Pd (and produce a radioactive Pd product if a need exists for it). [22]

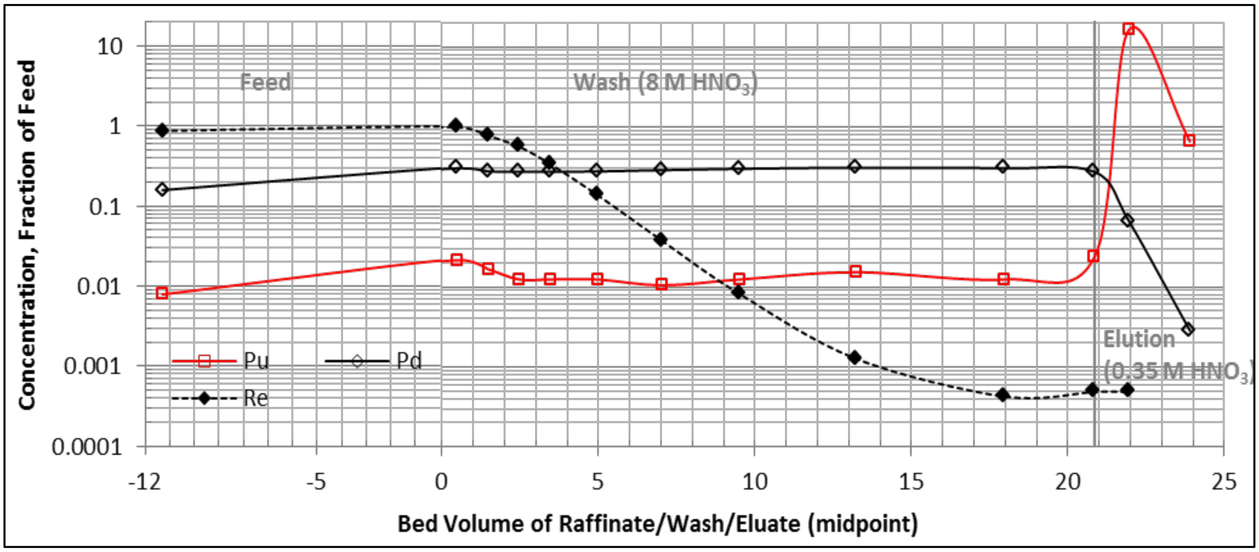


Figure 4-7. Test 3 Pd and Re Feed, Wash, and Elution Behavior in Comparison to Pu

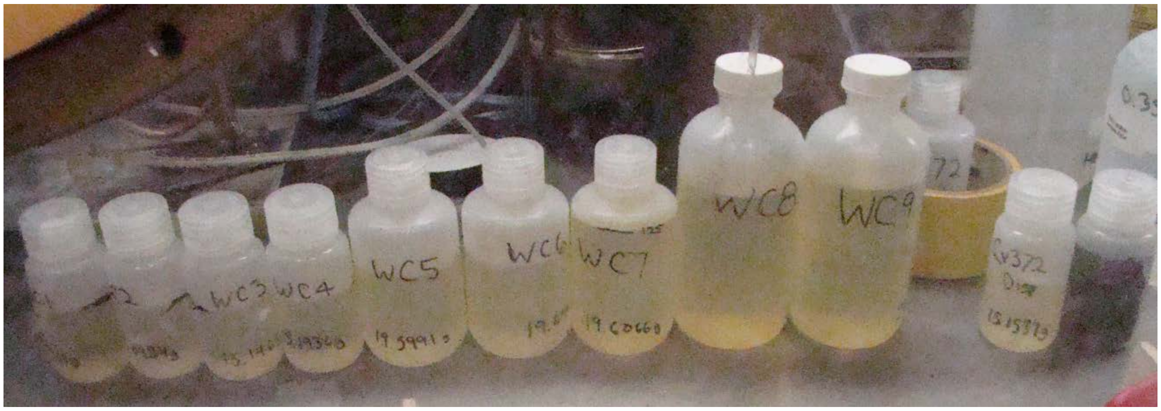


Figure 4-8. Test 3 Yellow Tint of Wash and Displacement Solutions

4.4.3 Cladding Impurities

Aluminum from target cladding and the impurities in the alloy (Fe and Mg) are expected to be in the feed solution for the anion exchange unit operation. Most of the Si in the cladding is expected to be filtered out before anion exchange. [6] Sodium from the caustic dissolution of the target cladding is also expected to be an impurity that needs separating by anion exchange. The behavior of impurities from cladding dissolution (Al, Fe, Mg, and Na) was evaluated in both the radioactive and nonradioactive tests. The nonradioactive data (Figure 4-9) showed that Al and Mg decreased three to four orders of magnitude throughout washing and elution. Iron decreased three orders of magnitude during washing and exhibited a modest increase during elution. For Na, its concentration was steady during washing and decreased during elution, suggesting potential Na contamination in the wash solution. The mass balance for Na in Test 1 and 2 was slightly high, providing further evidence for a possible Na contamination in the nonradioactive test wash solution. The radioactive data (Figure 4-10) show similar behavior for the first two to four wash volumes before all subsequent data are below the method detection limits. The behavior of Al, Fe, Mg, and Na is consistent with what is seen in the literature; these species show no adsorption to the resin. [17]

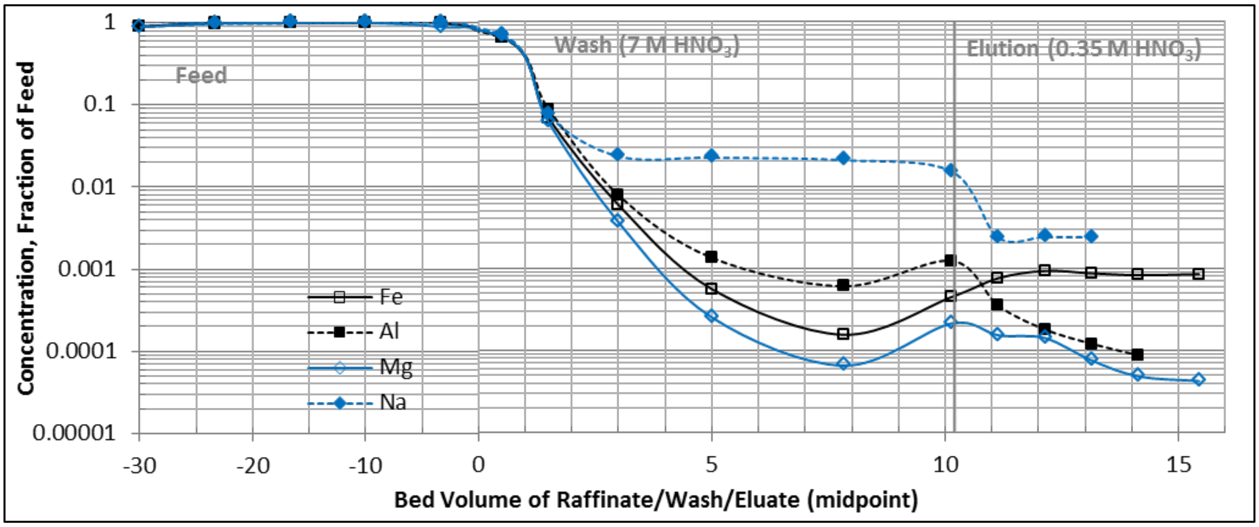


Figure 4-9. Test 1 Al, Fe, Mg, and Na Feed, Wash, and Elution Behavior

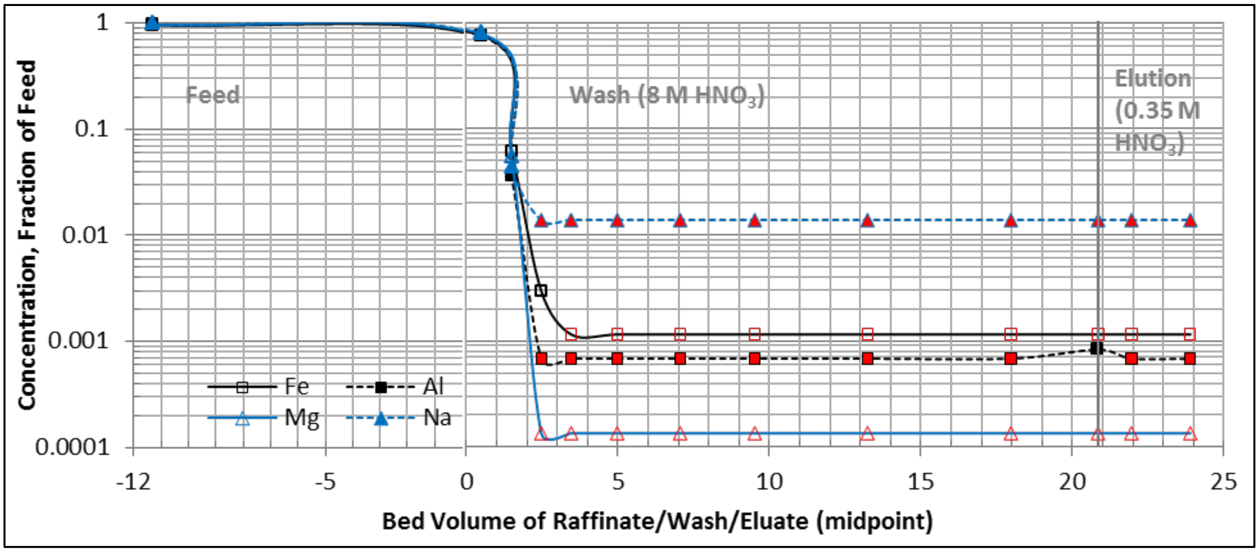


Figure 4-10. Test 3 Cladding Impurity Metals Feed, Wash, and Elution Behavior (Radioactive Test)

*Red markers indicate concentrations measured below method detection limits.

4.4.4 Other Metal Impurities

The loading, washing, and elution of several other metals (Cs, Sr, Zr, Mo, and Zn) were tracked as impurities expected to be in the actual Mk-18A anion exchange feed solution. Of most importance in this last group of impurities are Cs, Sr, and Zr. The Cs and Sr in the targets are expected to exist as radioactive isotopes ^{137}Cs and ^{90}Sr. Excess Sr was added to the simulant to represent the Ba as well as the Sr expected to be found in the Mk-18A targets. Both are alkaline earth metals that have similar chemical behavior.

The nonradioactive data (Figure 4-11) showed that Cs, Sr, Mo, and Zn are not absorbed by the resin and then steadily decrease in concentration by three to four orders of magnitude during washing and elution. Both Cs and Sr were sufficiently washed off the resin to concentrations in the final wash sample of 0.02 mg/L and 0.01 mg/L (0.01% of the concentration fed). Neither Cs nor Sr eluted from the resin significantly; only ~0.01 mg each of the 636 mg Cs and 308 mg Sr fed was collected in the entire eluate stream. Zirconium washed to concentrations below detection and then the concentration modestly increased during elution. The behavior of Zr was consistent for both Tests 1 and 2. The behavior is also consistent with the literature (Figure 2-1). The ICP-ES data for Zn is presented because concentrations measured by ICP-MS in the entire eluate were below the method detection limit. Zinc was added to the simulant as a surrogate for Cd. Both are group 12 metals that have similar chemical properties.

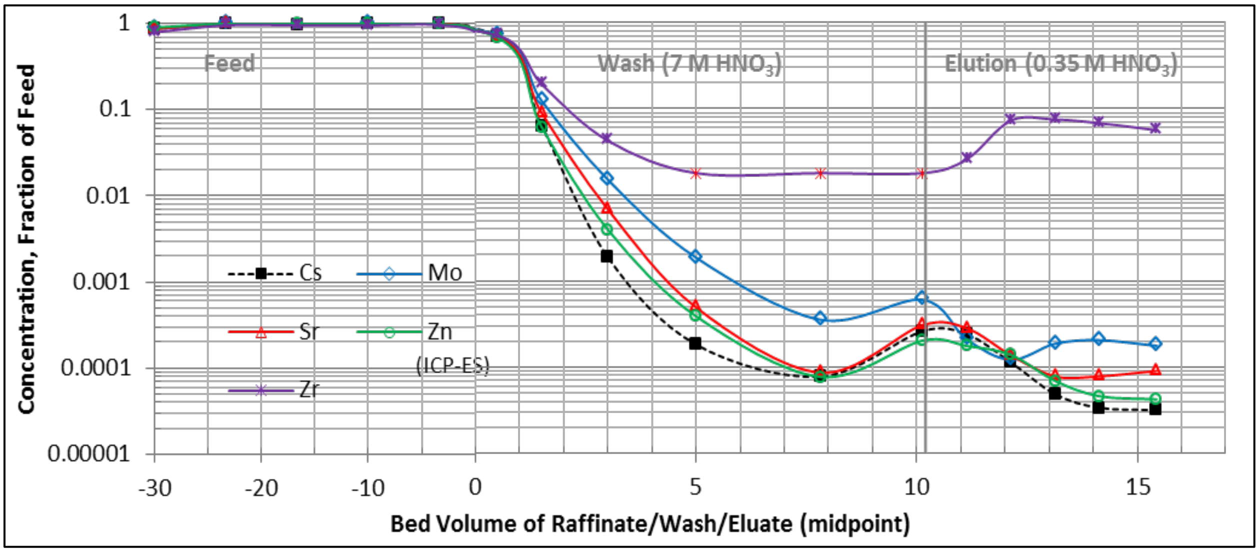


Figure 4-11. Test 1 Cs, Mo, Sr, Zn, and Zr Feed, Wash, and Elution Behavior

*Zirconium concentrations measured below the detection limit in the wash are indicated by red markers.

Radioactive testing (Test 3) yielded similar behavior for all five metals (Cs, Sr, Zr, Mo, and Zn). The data can be seen Figure 4-12. Manganese (added to adjust the valence of the Pd and Sn) and Sn are also provided in the figure. For Mn and Zn, the radioactive data show rapid decreases in concentration through three to four BV of wash before the analyte concentrations are below the method detection limits; the concentration of Zn washes below detection after ~7 BV. Zirconium exhibited similar washing behavior as in nonradioactive testing, but due to the 20.4 BV of wash, there was significantly less Zr that eluted from the resin during elution with 0.35 M HNO$_3$. Cesium and Sr were sufficiently washed off the resin and less than 0.002% of the Cs and Sr fed eluted in the Pu hearts eluate.

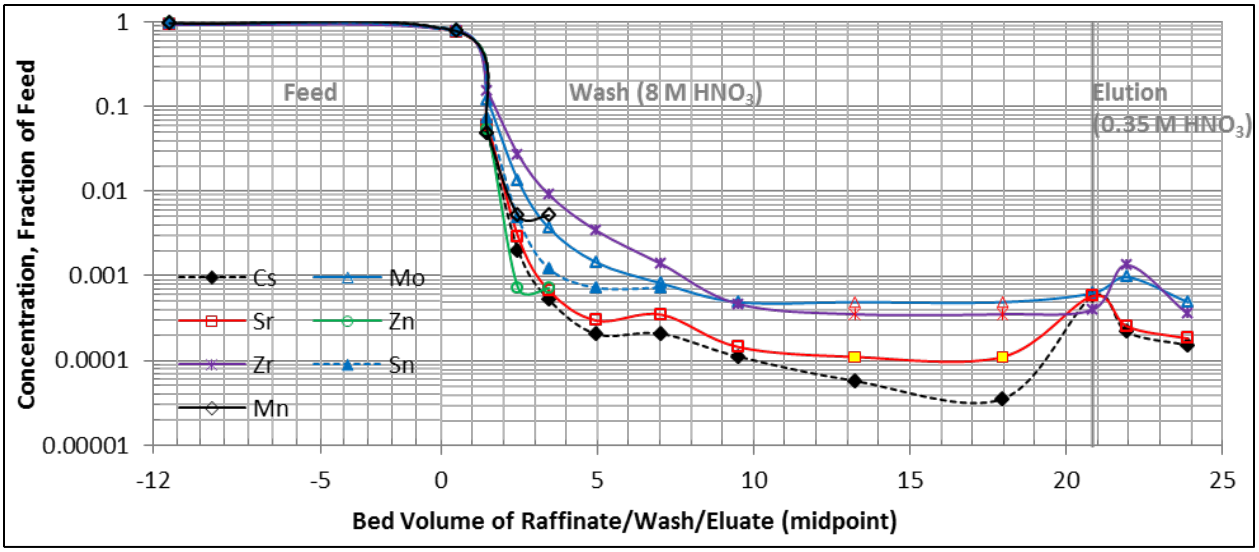


Figure 4-12. Test 3 Other Impurity Metals Feed, Wash, and Elution Behavior

*Red markers for Mo and Zr and yellow markers for Sr indicate concentrations below method detection limits.

4.5 Plutonium Anion Exchange

The material balance for Pu and ^{241}Am was calculated primarily from gamma counting data supplemented by ICP-MS data. Due to the relatively high levels of Am present in the feed, the raffinate and early wash solutions contained far more ^{241}Am activity than Pu which increased the detection limit for ^{239}Pu. The ^{241}Am results were decay-corrected back to the date of separation (~22 days) using the Bateman equation. [23] Plutonium-239 gamma results were converted to total Pu concentrations using the isotopic ratios calculated from ICP-MS for the "hearts cut" (with ^{241}Am removed), 94.1% ^{239}Pu. The decay-correction of the ^{241}Am required knowledge of the initial parent ^{241}Pu (632 ug ^{241}Pu/g ^{239}Pu) which was determined by a separate gamma count of the "hearts cut" sample. This value for ^{241}Pu compared well with a value of 615 ug ^{241}Pu/g ^{239}Pu determined by subtracting the mass of ^{241}Am (from gamma counting) from the mass number 241 determined by ICP-MS. The decay corrected value for ^{241}Am indicated a decontamination factor of ~14,000 for Am. This is a significantly higher value than was previously reported [14] but the current experiment started with much higher Am concentrations and used larger wash volumes as well as a lower Pu resin loading.

Table 4-5 and Figure 4-13 depict the Pu behavior during loading, washing, and elution. The mass balances for Pu and Am were within analytical uncertainty. Plutonium data measured by gamma spectroscopy showed good agreement with data from ICP-MS. As expected, Pu was effectively loaded from the simulant solution and Am was slightly retained. The presence of Pd competing for absorption sites on the Reillex™ HPQ resin did not appear to affect Pu retention or removal at the level of Pd, however the Mk-18A is expected to contain significant additional Pd (~10x). It is assumed that Pu(IV) will displace the Pd(II) due to its much higher K_d value, but this assumption has not been proven by this experiment. Palladium may be loading onto weak-base sites that are present in the Reillex™ HPQ polymer. [15, 24, 25] Quarternized pyridine rings form the strong-base sites known for loading of Pu but the unquarternized pyridine sites still function as weak-base sites. Reillex™ HPQ has been reported as containing 10 to 30% unquarternized pyridine sites and Marsh [25] reported on the conversion of strong-base sites to weak-base sites as a function of gamma dose. Wu [24] attributes the loading of TcO_4^- and it seems that it may well be that Pd(II) also favors the weak-base sites. If so, then Pd(II) and Pu may not really compete for the same loading sites. The limited data available in the current study does not provide much proof.

Table 4-5. Test 3 Pu and Am Material Balance

Pu Anion Column Test on Reillex™ HPQ 43cc Column F003 Down-flow								
Sample ID	**Sample Volume (mL)**	**Volume Eluted (mL)**	**Column Volume Eluted**	**Pu (1,2)**		**^{239}Pu (g/L) ICP-MS**	**^{241}Am (1,3)**	
				Conc. (g/L)	**Btl (g)**		**Conc. (mg/L)**	**Btl (μg)**
Feed	972	972	22.6	1.051	1.022	1.102	18.829	18302
Raffinate	972	972	22.6	0.008	0.008	0.008	16.724	16256
WC1	43	43	1.0	0.023	0.001	0.021	16.460	706
WC2	42	85	2.0	0.017	0.001	0.016	5.557	235
WC3	42	127	3.0	0.013	0.001	0.015	1.541	65
WC4	43	170	4.0	0.013	0.001	0.014	0.4530	19
WC5	88	258	6.0	0.013	0.001	0.014	0.1606	14
WC6	90	349	8.1	0.011	0.001	0.013	0.0441	4.0
WC7	121	470	10.9	0.013	0.002	0.013	0.0193	2.3
WC8	199	669	15.6	0.016	0.003	0.013	0.0093	1.8
WC9	208	877	20.4	0.013	0.003	0.013	0.0048	1.0
Displacement	40	916	21.3	0.025	0.001	0.025	0.0185	0.7
Hearts	55	972	22.6	17.186	0.948	17.600	0.0205	1.1
Tails	112	1084	25.2	0.692	0.078	0.817	0.0038	0.4
Material Balance					102.5%			94.6%
Pu loading 23.6 g Pu/L resin								
1. Pu and Am values measured by gamma. 2. Shaded values used ICP-MS values due to high MDA by gamma. 3. ^{241}Am values decay-corrected to date of separation								

	BV	**Pu**	**Am**
Raffinate	22.6	0.79%	88.8%
Washes	20.4	1.2%	5.7%
Eluate	4.8	100.5%	0.013%
		102.5%	94.6%

As shown in Figure 4-13, Pu concentrations in the wash solutions (8 M HNO_3) were low. The column was loaded at 40% capacity with ~24 g Pu per L of resin. After 10 BV wash, the concentration of Pu in the wash appears to show a small increase, which may be an indication that Pu is gradually being washed off of the resin (or may represent measurement uncertainty). Conversely, Am continually washed from the column. After about 11 BV wash, the quantity of Am being removed per wash volume diminishes significantly. When combined with the Pu loss profile, an optimal wash volume appears to be about 10 to 12 bed volumes. The Pu elutes readily from the resin with 0.35 M HNO_3; 98.0% of the Pu was collected in the various eluate fractions (displacement, hearts, and tails), although minimal amounts of Pu (0.1%) were contained in the displacement sample. The hearts cut (~1.3 BV) contained 90.4% of the Pu and the tails cut (~2.6 BV) 7.5%. Reduction of the volume of washing to approximately ten bed volumes would increase Pu recovery to about 98.5% with little additional contamination from Am or other impurities.

Whereas a typical column test might discard the tails, the value of the Pu in the Mk-18A program will dictate the recycle of the tails. It has been suggested that the tails can be used as part of the Pu(VI) valence adjustment step. [12] The Mk-18A program plans to use a spectrophotometer to monitor the Pu concentration in the column effluent. This will enable optimization of Pu retention but due to the low Pu concentration, a longer path length cell would be desirable to increase Pu sensitivity.

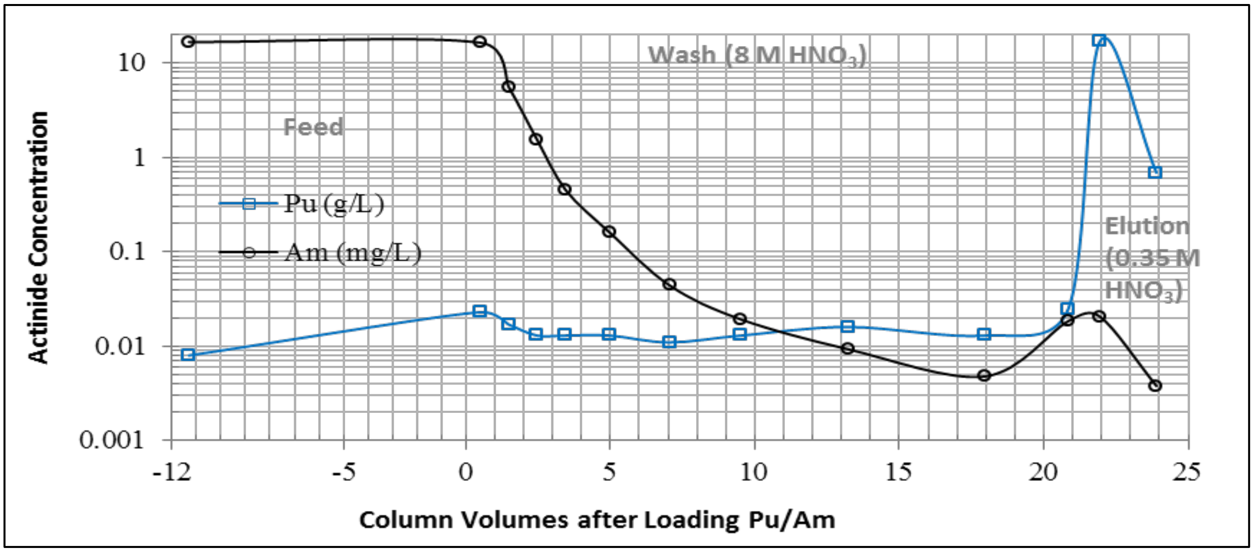


Figure 4-13. Test 3 Pu and Am Washing and Elution from Reillex™ HPQ

4.5.1 Actinides and Their Simulants

The three experiments performed during this task aimed at determining the behavior of Pu, Am, and Cm during ion exchange from a solution containing a wide range of dissolved metals expected to be contained in the Mk-18A solution (Table 3-2). Plutonium and Am are available in sufficient quantities at SRNL for direct testing; Cm was not readily available. Consequently, the lanthanides are proposed for use to approximate the behavior of Cm; the literature indicate that Nd^{3+}, Sm^{3+}, and Am^{3+} are the most appropriate analogues for Cm^{3+} on the basis of their ionic radii. [26] The data for Pu, Am, and some of the lanthanides with absorption-elution behaviors similar to Am were graphed in Figure 4-14. All of these behave similarly with small differences that generally follow a trend of slightly lower interaction across the series as the ionic radii decrease. It should be noted in addition to Pu, Pd also competes with the lanthanides for absorption sites on the resin, which will affect their behavior.

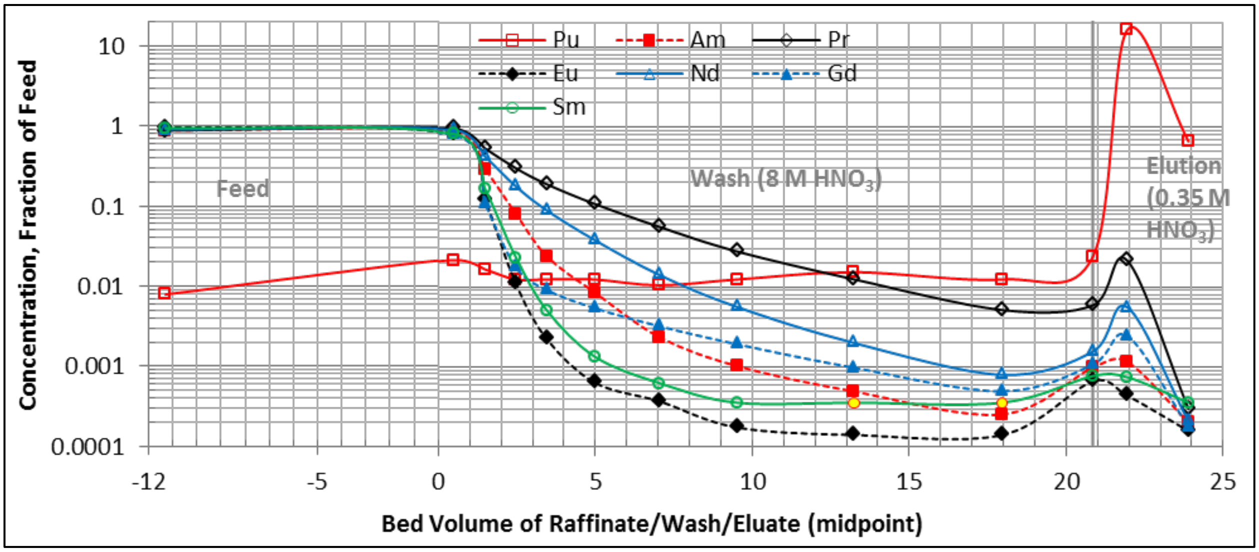


Figure 4-14. Test 3 Feed, Wash, and Elution Behavior for Actinides and Their Simulants

*Red and yellow markers for Sm indicate concentrations measured below the method detection limit.

4.5.2 Effects of Ionizing Radiation on Ion Exchange Kinetics

The unwashed column will contain ^{90}Sr, ^{137}Cs, ^{243}Am, and ^{244}Cm in close proximity to the resin. Data in the literature indicate that Reillex^{TM} HPQ can effectively absorb Pu(IV) after 3.6 MGy (360 MRad) of gamma irradiation or 14.3 MGy (1430 MRad) of *in-situ* alpha particle irradiation. [27] Dose rate calculations based on the calculated worst-case target compositions were completed. The cumulative dose for the nominal configuration was 0.82 MRad indicating that the same resin batch can be used to process multiple dissolver solution feed batches. [28] Residual radionuclides on the resin will increase the dose to the resin over what was modeled. Additional post run washing would reduce the holdup and potentially increase the usable life of the resin.

4.5.3 Decontamination Factors

The following DFs were calculated for each of the impurities of the Mk-18A simulant (Table 4-6). Decontamination factors are defined as the impurity to Pu ratio in the feed to that ratio in the product. These factors are influenced by the volume of wash and would be different if half as much wash volume were used. However, they provide a good measure of the effectiveness of Reillex™ HPQ for separating Pu from other impurities expected to be part of the Mk-18A dissolver solutions. The right side of the figure lists DF of lanthanides and Am in order of increasing atomic number, and the left side lists DF in order of decreasing magnitude for other impurities.

Table 4-6. Test 3 Decontamination Factors

Element	DF	Element	DF	Element	DF
Mg	>120,000	Sn	22,000	La	150
Cs	75,000	Mo	17,000	Ce	230
Sr	64,000	Fe	>14,000	Pr	770
Re	34,000	Zr	12,000	Nd	3,000
Al	>24,000	Mn	>3,100	Sm	22,000
Zn	>23,000	Na	>1,200	Eu	38,000
		Pd	250	Gd	6,700
				Am	14,000

4.6 Application

A primary goal of the anion exchange processing of the Mk-18A targets is to separate Pu from key impurities so that the Pu product can be removed from the shielded cells and further purified in a glovebox. The key impurities are Cs, Sr and Cm. Cesium and Sr removal will likely drive the beta-gamma dose rate of the Pu product solution. Cm will likely dominate the alpha levels of the Pu product solution and could even generate some neutron dose. This work indicates that the Cs/Sr can be removed down to < 0.002% by a single pass of anion exchange processing. Further dose evaluation will have to account for the Cs/Sr isotopic ratios in the target material.

Curium was not available for this testing and the thought was to use trivalent lanthanides and actinides to estimate its behavior in this separation. This is the common approach to this problem and the literature suggests scaling based on ionic radii. [26, 29, 30] Depending on the source of ionic radii used, one will assign different lanthanide elements as surrogates for Am/Cm but in any case, Am and Cm are not expected to behave very differently. Trivalent Nd, Sm, Eu and Gd span the range of Am and Cm in ionic radii depending on how that property is determined. Note that in the current study, quite a bit of difference is observed in the separation behavior between Nd, Sm, Gd and Am (see Figure 4-3, Figure 4-4, Table 4-6). It was also observed that Gd washing behavior in the current study looks a little different than the other lanthanides after 5 BV of washing (Figure 4-3 & Figure 4-4), and Gd washing behavior in the current study and in a similar study [14] are not very consistent. The decontamination of Pu from slightly interacting lanthanides and actinides in the current study was observed to vary between ~99.8% and 99.99% (or DFs of 800 to 38,000). Curium is expected to fall within that range. Note that the amount of impurity present has to affect the degree of removal and ~1.6 g Cm is estimated to be present for every gram of Pu in the Mk-18A targets. It seems probable that the product of the initial anion exchange separation will contain a similar amount of alpha activity from the Cm as from the Pu.

The Pd mass balances all show significant unaccounted mass for Pd and the assumption is that the Pd is still retained by the resin bed. This could be confirmed by a “post-tails” washing step with Pd-complexing solutions such as 0.1 M HNO_3/0.5 M thiourea strip solution as described in the literature. [21, 22, 31, 32, 33] Although hold-up on the resin is the most likely explanation for the poor Pd material balances, there are other possibilities. Pd can hydrolyze and precipitate on the resin beads or in the feed or product bottles and due to the small mass involved, it would not be easily observed.

Table 4-7. Comparison of Retention of La, Ce, Pd with U from the Literature

		Nonradioactive Tests [Table 4-3]				Pu Test [Table 4-4]				Rudisill [34]		
	D (Faris)	Raffinate	Wash	Eluate	Resin	Raffinate	Wash	Eluate	Resin	Raffinate	Wash	Eluate
Pu	9800					<1%	1%	100%				
La	5	88%	9%	4.70%		84%	14%	0.50%				
Ce	5	90%	9%	3.60%		86%	14%	0.50%				
$Pd^{\#}$	30	17%	8%	0.40%	74%	16%	27%	1.50%	56%			
$Pd^{\$}$		55%	15%	0.90%	39%							
U	15									82%	18%	<0.1%
$^{\#}$, $^{\$}$	Test 1, Test 2											
Note 1	D= Distribution Coefficient read from Figure 2-1 for 8 M HNO_3, Faris [17]											
Note 2	Pd material balance from Table 4-3 and Table 4-4 reflects results from two nonradioactive tests and single Pu test											
Note 3	U material balance from Rudisill [34] for a Pu-U separation via a flowsheet with similar conditions to current work											
Note 4	Fraction of Pd retained by resin estimated from overall material balance											

Another observation is that Pd appears to be retained significantly more strongly than the reported K_d at 8 M HNO_3 suggests. Table 4-7 shows a comparison of reported K_d from the literature with the observed retention of La, Ce, Pd, Pu and U (from Rudisill [34]). The initial non-radioactive tests were performed using the same resin column and since nothing other than Pd showed significant loading there was very limited competition with Pd for loading sites. In those initial two tests, the Pd appears to be accumulating on the resin and the rejection to the raffinate was increasing as the resin was “loading-up” with Pd. The retention of Pd from the first test appears to have reduced the capacity of the resin for Pd. In the Pu test, more Pd was washed off but twice as much wash volume was used. It is not clear that the Pu displaced significant Pd from the resin, but the resin was not fully loaded with Pu.

Rudisill was able to nearly wash all of the U from a Pu loaded column in 20 BV. [34] In that work, ~82% of the U passed through the column into the raffinate and essentially all of the remaining U was washed from the resin leaving < 0.1% in the eluate. The retention of Pd by the resin appears to be significantly greater than U even though the reported distribution coefficients are similar. Several explanations have been suggested: 1) the presence of significant amounts of Pd(II) chloride complexes (which bind more strongly that Pd(II) nitrate complexes) [22], 2) higher K_d for Pd(II) for polyvinylpyridine resin sites over the traditional polystyrene based resins [22], 3) the presence of Pd(IV) species (which would likely have a higher K_d).

While Reillex™ HPQ is a strong-base anion resin, the authors are not certain how many weak base sites may be present and Pd(II) interacts more strongly with weak-base sites. Kumaresan [22] observed an increase in the Pd(II) K_d from 300 to almost 30,000 by the addition of 12 mM chloride to 1 M HNO_3 with polyvinylpyridine weak base resin for 2 mM Pd solutions. The current tests appeared to have had 2 to 3 mM chloride, which is high enough that it may have increased the Pd K_d.

While the behavior of Pd is not completely understood, the only significant concern is the validity of the assumption that Pu out-competes Pd for loading sites on the resin. If Pd were to reduce the effective capacity of the resin for Pu, then additional resin would be required and additional wash solution would be generated to achieve the same purity. The processing time dealing with stabilizing the high alpha content raffinate/wash solution could be an issue.

There is a grouping of transition metal elements ranging from Tc through Pd and Re through Hg that have anion exchange behavior similar to Pd (see Figure 2-1). Several of these elements are thought to be somewhat abundant in the Mk-18A targets but were not tested very effectively (Ru- didn’t dissolve, Tc, Cd -surrogates were used). Significant discussion has been devoted to the surprisingly strong retention of Pd and there is some risk that one or more of these other elements also might exhibit similar unexpected behavior. Of these Tc and Ru might be the ones to be wary about. While Re would appear to be a reasonable surrogate for Tc, it does appear from Faris [17] that Tc has somewhat more retention than Re. While Ru may not have dissolved well in the current study, other chemical forms of Ru that could be present in the targets might dissolve better and based on Table 2-1, Ru is present in a similar mass abundance as Pu in the typical target.

5.0 Conclusions

The three experiments performed with radioactive and nonradioactive Mk-18A simulants provide many valuable conclusions for determining the process flowsheet and mass balance, understanding factors that affect product purity, and planning subsequent simulant experiments. They are as follows.

1. Plutonium can be readily absorbed and purified from simulated Mk-18A dissolver solutions using the Reillex™ HPQ resin.
2. Pu(IV) is stable in 8 M HNO_3 at ambient temperature for at least 30 days in the Mk-18A simulant.
3. There was no measureable effect on retention, washing, or elution of impurities due to valence adjustment with FS and $NaNO_2$.
4. There was no measureable effect on retention, washing, or elution of impurities due to sparging with NO and NO_2 gases for valence adjustment of the Pu.
5. An optimized resin washing strategy (~10 BV in these tests) allows for recovery of ~98.5% of the Pu initially fed to the ion exchange resin. More extensive washing to remove additional impurities may marginally increase Pu losses to the raffinate.
6. Decontamination factors ranged from two to five orders of magnitude for all impurities; the results were influenced toward higher values by the high volume of wash used during testing. The impurities most likely to be retained on the resin were Pd, La, Ce, and Pr.
7. Lanthanides behaved similarly in both the radioactive and nonradioactive tests. The increased bed volumes of wash solution in the radioactive test removed additional weakly retained lanthanides (over the nonradioactive tests) and thus the elution peaks reflect lower impurity concentrations. The behavior of the different lanthanides was generally consistent with what was expected based on literature data, except that Gd did not follow the lanthanide trend of decreasing

resin affinity with increasing atomic mass. Greater than 99.9% of the weakly interacting lanthanides in the current study were decontaminated from the Pu.

8. Although Cm was not tested, based on the behavior of weakly interacting lanthanides and Am, Cm is expected to be rejected to a similar degree as Am, Nd, and Sm by the anion exchange flowsheet.
9. Reillex™ HPQ retains Pd significantly in 7-8 M HNO_3 and Pd has a stronger affinity in 0.35 M HNO_3 than Pu. This effect appears to be stronger than the K_d in the literature indicate. Roughly half of the Pd used in these tests appears to remain on the resin after the wash step. Complete removal of Pd by washing with 8 M HNO_3 does not appear to be practical. Fortunately only roughly 1% of the Pd elutes with the Pu due to the increasing affinity of the resin for Pd at lower HNO_3 concentrations.
10. Cesium and Sr were sufficiently washed off the resin and < 0.002% of the Cs and Sr fed eluted in the Pu hearts eluate.
11. There were a few impurities that were not thoroughly tested such as Ru and Tc that if they exhibit behavior similar to Pd it may cause complications that might need to be addressed.
12. Other metal impurities (Al, Fe, Mg, and Na) present in the Mk-18A solution from the fuel and from cladding dissolution were not retained on the resin leaving < 0.1% in the Pu product stream.

6.0 Recommendations, Path Forward or Future Work

1) Evaluate the risks posed by using a combination of FS/Pu(III) for Pu(VI) valence adjustment particularly with respect to the expected high dose from alpha and gamma and consider the addition of an additional nitrous acid scavenger such as hydrazine nitrate to extend the effective time of the reductants.
2) Retest simulant (or a subset of the simulant) with a realistic amount of Pd and Pu to evaluate the effect of the significant mass of Pd in the target on the resin capacity for Pu and better define the impact of resin poisoning with Pd.
3) Refine the spectrophotometer equipment details using appropriately sized flowcells for the expected Mk-18A solutions.
4) Consider further testing with actual Cm to reduce the risks that the high alpha dose poses to valence chemistry and to better define the Cm decontamination by the anion exchange flowsheet.
5) Explore the use of thiourea or some other Pd complexing agent to remove the residual Pd from the Reillex™ HPQ resin and prevent cumulative poisoning of the resin. Radioactive Pd could be a by-product that has value.

References

[1] N. J. Bridges, "Scope of Work for the Mark-18A Program," X-SOW-A-00004 , Rev. 1, Savannah River National Laboratory, Aiken, SC, May 2016.

[2] S. Branney, "Results of Mk18A Target Irradiation Actinide Inventory Calculation," N-CLC-A-00084, April 2016.

[3] S. Robinson, D. Benker, B. Patton and C. Phelps, "Mark-18A (Mk-18A) Target Processing at Oak Ridge National Laboratory," ORNL/TM-2015/577. Oak Ridge National Laboratory, Oak Ridge, TN, November 2015.

[4] N. J. Bridges, "A literature based examination of potential dissolution processes for the Mark-18A target material," SRNL-L3100-2015-00220, Savannah River National Laboratory, Aiken, SC, December 15, 2015.

[5] N. J. Bridges, "Anion exchange for the removal of plutonium from the dissolved Mark-18A target material," SRNL-L3100-2015-00223, Rev. 1, Savannah River National Laboratory, Aiken, SC, 2015.

[6] C. A. Nash and M. R. Williams, "Filtration Studies in Support of SRNL Mark-18A Processing," SRNL-TR-2016-00350, Savannah River National Laboratory, Aiken, SC, January 2017.

[7] R. A. Pierce, "Flowsheet Assessment for Ion Exchange of Mark-18A Targets," SRNL-L3100-2016-00096, Aiken, SC, May 2016.

[8] L. J. King, J. E. Bigelow and E. D. Collins, "Experience in the Separation and Purification of Transplutonium Elements in the Transuranium Processing Plant at the Oak Ridge National Laboratory," *Transplutonium Elements - Production and Recovery, ACS Symposium Series,* vol. 161, no. 8, pp. 133-145, 1981.

[9] L. K. Felker and D. E. Benker, "Application of the TRUEX Process to Highly Irradiated Targets," ORNL/TM-12784, Oak Ridge National Laboratory, Oak Ridge, TN, March 1995.

[10] K. P. Crapse, T. S. Rudisill, P. E. O'Rourke and E. A. Kyser, "AFS-2 Flowsheet Modifications to Address the Ingrowth of Pu(VI) during Metal Dissolution," SRNL-STI-2013-00709, Savannah River National Laboratory, Aiken, SC, July 2014.

[11] I. H. Crocker, "Oxidation of Pu(IV) to Pu(VI) in Solutions of Nitric Acid, Aluminum Nitrate, Sodium Nitrate, and Uranyl Nitrate," CRDC-697, Chalk River, Ontario, May 1957.

[12] R. A. Pierce, "Flowsheet Options for Dissolution and Valence Adjustment for the Mark-18A Fuel Targets," SRNL-L3100-2016-00082, Rev. 1, Savannah River National Laboratory, Aiken, SC, Draft May 2017.

[13] S. F. Marsh, "Evaluation of a New, Macroporous Polyvinylpyridine Resin for Processing Plutonium Using Nitrate Anion Exchange," LA-11490, Los Alamos National Laboratory, Los Alamos, New Mexico, April 1989.

[14] E. A. Kyser, "HB-Line Anion Exchange Purification of AFS-2 Plutonium for MOX," SRNL-STI-2012-00233, Rev. 1, Savannah River National Laboratory, Aiken, SC, July 2012.

[15] E. A. Kyser, "Plutonium Loading onto Reillex HPQ Anion Exchange Resin," WSRC-TR-2000-00372, Aiken, SC, 2000.

[16] D. B. James, "Anion-Exchange Processing of Plutonium," LA-3499, Los Alamos, NM, 1966.

[17] J. P. Faris and R. F. Buchanan, "Anion Exchange Characteristics of the Elements in Nitric Acid and Nitrate Solutions and Application in Trace Element Analysis," ANL-6811, Argonne National Laboratory, Illinois, July, 1964.

[18] E. A. Kyser, D. H. Jones and P. E. O'Rourke, "Safe Wash Acid Concentration Limits for HB-Line Pu Anion Exchange Flowsheets," SRNL-STI-2016-05145, Draft, Savannah River National Laboratory, Aiken, SC, October 2016.

[19] K. S. Fuller and T. M. Thompson, "Revovery and Purification of Plutonium-238 in the H-Area Farms," DPSPU 82-11-20, September 1982.

[20] G. A. Burney, "Separation of Neptunium and Plutonium by Anion Exchange," DP-689, April 1962.

[21] K. A. Venkatesan, B. Robert Selvan, M. P. Antony, T. G. Srinivasan and P. R. Vasudeva Rao, "Extraction of palladium (II) from nitric acid medium by imidazolium nitrate immobilized resin," *Hydrometallurgy,* vol. 86, no. 3-4, pp. 221-229, May 2007.

[22] R. Kumaresan, K. N. Sabharwal, T. G. Srinivasan, P. R. Vasudeva Rao and Gunesh Dhekane, "Studies on the Sorption of Palladium using Cross-Linked Poly (4-Vinylpyridine-Divinylbenzene) Resins in Nitric Acid Medium," *Solvent Extraction and Ion Exchange,* vol. 26, no. 5, pp. 643-671, 2008.

[23] G. Friedlander and J. Kennedy, Nuclear and Radiochemistry, 2nd Edition, J. Wiley and Sons, 1964, p.72.

[24] Y. J. Wu, M. A. Williamson, Q. Zhang, M. R. Grissom and I. Chu, "Basic Physical and Chemical Properties of Reillex HPQ Resin and its Sorption Behavior of Halides in Aqueous Nitric Acid Solution," *Solvent Extraction and Ion Exchange,* vol. 14, no. 2, pp. 285-308, 1996.

[25] S. F. Marsh, "The Effects of Ionizing Radiation on Reillex HPQ, a New Macroporous Polyvinylpyridine Resin, and on Four Conventional Polystyrene Anion Exchange Resins," LA-11912, November 1990.

[26] K. B. Krauskoft, "Thorium and Rare-Earth Metals as Analogs for Actinide Elements," *Chemical Geology,* vol. 55, pp. 323-35, 1986.

[27] S. F. Marsh, "The Comparative Effects of Gamma Radiation and In Situ Alpha Particles on Five Strong-Base Anion Exchange Resins," LA-UR-91-3097, July 1992.

[28] J. E. Laurinat, "Analysis of Irradiation of Ion Exchange Resin for Treatment of Mark 18A Solution," X-CLC-A-00105, Savannah River Nuclear Solutions, Aiken, SC, October 2016.

[29] J. D. Bums, T. C. Shehee, A. Clearfield and D. T. Hobbs, "Separation of Americium from Curium by Oxidation and Ion Exchange," *Analytical Chemistry,* vol. 84, p. 6930, 2012.

[30] P. D'Angelo, F. Martelli, R. Spezia, A. Filipponi and M. A. Denecke, "Hydration Properties and Ionic Radii of Actinide(III) Ions in Aqueous Solution," *Inorganic Chemistry,* vol. 52, pp. 10318-24, 2014.

[31] A. Wolowicz and Z. Hubicki, "Ion Exchange Recovery of Palladium(II) from Acidic Solutions Using Monodisperse Lewatit SR-7," *Industrial & Engineering Chemistry Research,* vol. 51, pp. 16688-96, 2012.

[32] E. Camacho Frias, H. Pitsch K., J. Ly and C. Poitrenaud, "Palladium complexes in concentrated nitrate and acid solutions," *Talanta,* vol. 42, pp. 1675-83, 1995.

[33] O. N. Kononova, N. G. Goryaeva and O. V. Dychko, "Ion exchange recovery of palladium(II) from nitrate weak acidic solutions," *Natural Science,* vol. 1, no. 3, pp. 166-75, 2009.

[34] T. S. Rudisill and J. M. Duffey, "Removal of Uranium from Plutonium Solutions by Anion Exchange," WSRC-TR-2002-00097, Westinghouse Savannah River Company, Aiken, SC, 2002.

7.0 . Appendix

A.1 *Test 1 ICP-MS Raw Data*

	LW2773 1X-01-01, 7-8 M	LW2774 1X-01-02, 7-8 M	LW2775 1X-01-03, 7-8 M	LW2776 1X-01-04, 7-8 M	LW2777 1X-01-05, 7-8 M	LW2778 1X-01-06, 7-8 M	LW2779 1X-01-07, 7-8 M	LW2780 1X-01-08, 7-8 M	LW2781 1X-01-09, 7-8 M	LW2782 1X-01-10, 7-8 M	LW2783 1X-01-11, 0.5 M	LW2784 1X-01-12, 0.5 M	LW2785 1X-01-13, 0.5 M	LW2786 1X-01-14, 0.5 M	LW2787 1X-01-15, 0.5 M	LW2788 1X-01-16, 0.5 M	LW2789 1X-01-17, 0.5 M
m/z	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Al	6151.99	5115.03	5791.47	5717.48	5874.41	5828.42	4439.87	460.23	38.32	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00
Ce	742.54	416.70	662.58	705.29	728.85	732.06	658.03	417.36	234.65	143.61	91.05	298.47	587.71	0.47	0.12	0.08	0.05
Cs	317.81	277.36	316.43	312.34	316.21	315.45	222.88	20.31	0.60	0.06	0.02	0.08	0.08	0.04	0.02	0.01	0.01
Eu	123.83	106.03	123.26	121.92	122.90	123.63	87.94	19.20	2.95	0.43	0.07	0.09	0.04	0.01	0.01	0.01	0.01
Fe	1361.66	1192.64	1359.09	1357.01	1368.28	1372.73	911.79	89.00	8.54	1.00	1.00	1.00	1.34	1.18	1.23	1.05	1.01
Gd	493.52	417.04	493.32	487.96	495.90	493.30	355.52	80.76	19.03	7.75	4.17	13.14	15.18	0.07	0.03	0.02	0.02
La	265.91	142.87	232.92	250.06	257.75	261.03	235.55	151.83	88.04	55.73	36.21	109.97	304.52	0.26	0.06	0.04	0.03
Mg	1570.73	1388.16	1549.75	1541.05	1551.35	1596.99	1069.92	90.18	6.06	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
Mo	121.86	106.26	121.05	123.39	121.83	123.19	87.26	15.05	1.82	0.23	0.04	0.07	0.03	0.01	0.02	0.02	0.02
Nd	897.85	637.26	880.04	889.73	897.95	895.53	756.02	367.60	156.40	73.26	33.80	79.95	37.28	0.15	0.06	0.04	0.03
Pd	66.22	0.63	4.78	11.76	17.65	22.42	20.29	20.16	19.92	18.87	16.44	8.35	0.16	0.01	0.01	0.01	0.01
Pr	1840.68	1141.82	1723.13	1780.45	1839.80	1842.01	1619.28	912.97	465.67	263.57	152.97	482.72	520.75	0.52	0.18	0.11	0.08
Re	60.60	32.98	56.98	59.92	60.03	61.01	57.90	43.06	25.91	13.48	6.38	5.62	0.22	0.12	0.12	0.12	0.12
Ru	0.010	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Sm	180.01	149.81	180.01	177.64	179.09	178.56	130.63	34.50	7.28	1.50	0.30	0.34	0.09	0.02	0.01	0.01	0.01
Sn	0.058	0.05	0.06	0.06	0.05	0.06	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Sr	153.95	134.16	153.36	154.06	154.50	157.22	105.24	13.76	1.04	0.08	0.01	0.05	0.04	0.02	0.01	0.01	0.01
Zn	795.97	708.16	785.68	781.22	780.24	785.98	530.67	50.45	3.31	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
Zr	27.98	22.18	26.88	26.75	26.71	27.04	19.87	5.39	1.19	0.50	0.50	0.50	0.72	2.04	2.10	1.90	1.58
	Start	Load 1	Load 2	Load 3	Load 4	Load 5	Wash 1	Wash 2	Wash 3-4	Wash 5-6	Wash Rem	Elute 1	Elute 2	Elute 3	Elute 4	Elute 5	Elute Rem
Vol (mL)	2000	400	400	400	400	400	60	60	120	120	218	60	60	60	60	60	96

A.2 *Test 2 ICP-MS Raw Data*

	LW2773 1X-01-01, 7-8 M HNO3	LW3005 1X-02-02, 7-8 M	LW3006 1X-02-03, 7-8 M	LW3007 1X-02-04, 7-8 M	LW3008 1X-02-05, 7-8 M	LW3009 1X-02-06, 7-8 M	LW3010 1X-02-07, 7-8 M	LW3011 1X-02-08, 7-8 M	LW3012 1X-02-09, 7-8 M	LW3013 1X-02-10, 7-8 M	LW3014 1X-02-11, 0.5 M	LW3015 1X-02-12, 0.5 M	LW3016 1X-02-13, 0.5 M	LW3017 1X-02-14, 0.5 M	LW3018 1X-02-15, 0.5 M	LW3019 1X-02-16, 0.5 M	LW3020 1X-02-17, 0.5 M
m/z	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Al	6151.99	5429.64	6101.87	6151.12	5775.53	5923.20	3932.27	473.37	53.60	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00
Ce	742.54	452.01	690.14	747.64	774.85	790.21	696.40	398.88	232.59	146.56	90.08	148.36	730.40	1.93	0.40	0.22	0.13
Cs	317.81	299.68	352.22	346.23	326.15	328.87	234.27	21.14	0.87	0.06	0.50	0.30	0.05	0.01	0.19	0.10	0.03
Eu	123.83	113.81	128.19	130.35	132.39	133.98	93.11	18.96	3.81	0.62	0.10	0.11	0.07	0.02	0.01	0.01	0.01
Fe	1361.66	1316.74	1442.33	1478.31	1396.47	1444.61	931.33	108.51	12.61	1.42	1.00	1.16	2.40	1.60	1.42	1.71	1.25
Gd	493.52	452.14	511.96	524.90	534.28	541.68	374.76	77.92	22.31	8.67	4.52	7.38	21.53	0.12	0.07	0.05	0.03
La	265.91	154.60	242.61	263.15	273.24	278.72	247.67	145.47	88.53	55.69	35.98	56.86	359.83	1.03	0.19	0.11	0.06
Mg	1570.73	1503.59	1660.44	1652.08	1588.83	1623.73	1133.99	94.35	9.08	0.60	0.50	0.81	0.50	0.50	0.50	0.50	0.50
Mo	121.86	100.13	115.48	116.53	116.62	116.90	92.91	15.08	2.40	0.22	0.01	0.03	0.01	0.01	0.01	0.01	0.01
Nd	897.85	688.04	906.69	942.12	956.99	966.57	793.99	344.77	161.11	77.52	35.74	51.48	69.18	0.32	0.15	0.12	0.08
Pd	66.22	13.15	31.08	41.25	47.29	50.79	48.17	43.44	38.28	32.04	24.29	18.59	0.82	0.09	0.07	0.07	0.07
Pr	1840.68	1235.43	1775.22	1901.59	1922.90	1977.05	1713.13	859.03	468.70	270.71	152.31	254.99	735.68	2.02	0.53	0.35	0.21
Re	60.60	35.26	59.46	64.00	63.50	63.52	58.94	42.09	26.20	14.59	6.97	6.18	0.33	0.15	0.13	0.14	0.14
Ru	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Sm	180.01	160.37	186.30	188.28	192.94	192.44	141.34	34.09	8.83	2.00	0.40	0.32	0.20	0.03	0.02	0.02	0.01
Sn	0.06	0.05	0.06	0.06	0.06	0.06	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Sr	153.95	143.26	162.25	164.01	157.61	161.36	111.31	13.12	1.52	0.16	0.06	0.10	0.04	0.03	0.03	0.02	0.02
Zn	795.97	739.42	829.13	838.99	828.47	852.37	557.01	47.75	4.94	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
Zr	27.98	24.11	29.40	29.87	29.45	29.39	21.38	5.01	1.42	0.50	0.50	0.50	1.71	1.27	0.68	0.50	0.50
	Start	Load 1	Load 2	Load 3	Load 4	Load 5	Wash 1	Wash 2	Wash 3-4	Wash 5-6	Wash Rem	Elute 1	Elute 2	Elute 3	Elute 4	Elute 5	Elute Rem
Vol (mL)	2000	400	400	400	400	400	60	60	120	120	243	60	60	60	60	60	108

A.3 *Test 3 ICP-MS Raw Data*

Volume (mL)	972	972	42.9	42.2	42.0	42.8	88.2	90.5	121.2	199.0	208.0	39.6	55.2	112.0
	LW6138 Cr372 Feed	LW6139 Cr372 EC	LW6140 Cr372 WC1	LW6141 Cr372 WC2	LW6142 Cr372 WC3	LW6143 Cr372 WC4	LW6144 Cr372	LW6145 Cr372	LW6146 Cr372	LW6147 Cr372	LW6148 Cr372	LW6149 Cr372 Disp	LW6150 Cr372	LW6151 Cr372 Tails
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Sr	108.05	103.25	81.93	6.55	0.32	0.07	0.03	0.04	0.02	0.01	0.01	0.06	0.03	0.02
Zr	54.46	50.96	42.83	8.24	1.49	0.50	0.19	0.08	0.03	0.02	0.02	0.02	0.07	0.02
Mo	126.71	119.85	101.29	14.97	1.70	0.47	0.18	0.10	0.06	0.06	0.06	0.08	0.12	0.06
Pd	139.13	22.11	42.24	38.57	38.24	38.13	38.58	40.09	41.58	42.82	42.13	38.07	9.16	0.40
Sn	56.53	54.25	43.31	4.13	0.27	0.07	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04
Cs	343.69	335.09	269.40	16.39	0.70	0.18	0.07	0.07	0.04	0.02	0.01	0.20	0.08	0.05
La	283.44	239.53	275.08	171.36	110.08	79.24	51.18	31.86	20.14	11.28	5.60	6.01	30.33	0.22
Ce	964.94	831.03	939.00	578.08	362.88	253.41	164.29	97.10	57.15	29.68	14.56	15.49	67.70	0.55
Pr	1956.91	1725.56	1850.79	1048.37	594.50	375.33	213.37	109.60	54.27	24.33	10.04	11.52	41.42	0.59
Nd	1046.84	952.74	954.53	444.52	188.45	94.64	40.32	14.68	5.88	2.09	0.83	1.63	5.81	0.22
Sm	186.47	177.17	151.62	31.02	4.36	0.95	0.25	0.12	0.07	0.07	0.07	0.14	0.14	0.07
Eu	135.66	132.10	107.48	16.34	1.49	0.30	0.09	0.05	0.02	0.02	0.02	0.09	0.06	0.02
Gd	505.73	478.01	396.42	54.84	8.90	4.62	2.74	1.63	0.97	0.49	0.25	0.54	1.23	0.09
Re	62.61	54.68	61.68	47.99	35.22	21.46	8.73	2.32	0.51	0.08	0.03	0.03	0.03	0.03
239	1102.05	7.80	21.34	16.32	14.81	14.12	13.81	12.78	12.70	12.68	12.58	25.36	17600.22	817.30
240	69.75	0.47	1.31	1.00	0.92	0.86	0.84	0.80	0.77	0.77	0.76	1.57	1075.85	50.93
241	19.01	17.32	15.71	5.18	1.50	0.52	0.16	0.05	0.03	0.02	0.01	0.03	10.88	0.51

A.4 *Test 1 ICP-ES Raw Data*

	Start	Load 1	Load 2	Load 3	Load 4	Load 5	Wash 1	Wash 2	Wash 3-4	Wash 5-6	Wash Rem	Elute 1	Elute 2	Elute 3	Elute 4	Elute 5	Elute Rem
Vol (mL)	2000	400	400	400	400	400	60	60	120	120	218	60	60	60	60	60	96
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
	1X-01-01, 7- 8 M HNO3	1X-01-02, 7- 8 M HNO3	1X-01-03, 7- 8 M HNO3	1X-01-04, 7- 8 M HNO3	1X-01-05, 7- 8 M HNO3	1X-01-06, 7- 8 M HNO3	1X-01-07, 7- 8 M HNO3	1X-01-08, 7- 8 M HNO3	1X-01-09, 7- 8 M HNO3	1X-01-10, 7- 8 M HNO3	1X-01-11, 0.5 M HNO3	1X-01-12, 0.5 M HNO3	1X-01-13, 0.5 M HNO3	1X-01-14, 0.5 M HNO3	1X-01-15, 0.5 M HNO3	1X-01-16, 0.5 M HNO3	1X-01-17, 0.5 M HNO3
Element	LW2755	LW2756	LW2757	LW2758	LW2759	LW2760	LW2761	LW2762	LW2763	LW2764	LW2765	LW2766	LW2767	LW2768	LW2769	LW2770	LW2771
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Al	5130	4620	5020	5110	5770	5190	3280	445	39.6	6.86	3.09	6.3	1.8	0.92	0.615	< 0.445	< 0.445
Ce	819	453	714	782	804	799	736	461	245	158	101.65	318	602	< 0.623	< 0.623	< 0.623	< 0.623
Fe	1340	1210	1340	1330	1330	1330	877	90.3	7.89	0.746	0.207	0.596	1.01	1.24	1.16	1.1	1.13
La	267	143	229	252	257	261	232	128	79.2	50.8	32.8	85.6	278	0.247	< 0.0994	< 0.0994	< 0.0994
Mg	1570	1400	1540	1560	1570	1400	1040	94.4	5.68	0.394	0.102	0.333	0.239	0.221	0.118	0.0755	0.066
Mo	123	109	123	124	126	125	88.1	14.1	2.31	0.544	0.229	0.592	0.511	< 0.147	< 0.147	< 0.147	< 0.147
Na	232	247	229	230	231	230	162	17.1	5.33	5.14	4.8	3.5	< 0.55	0.556	< 0.55	< 0.55	< 0.55
Nd	914	615	856	901	903	909	762	390	168	89.2	50	115	179	0.276	< 0.27	< 0.27	< 0.27
Re	60.9	34	57.6	61.1	62	61.9	57.7	36.2	23.5	12.9	5.96	4.31	< 0.107	< 0.107	< 0.107	< 0.107	< 0.107
Sn	< 6.52	< 6.52	< 6.52	< 6.52	< 6.52	< 6.52	< 6.52	< 0.652	< 0.652	< 0.652	< 0.326	< 0.326	< 0.326	< 0.326	< 0.326	< 0.326	< 0.326
Sr	160	141	156	159	159	159	106	12	0.983	0.065	< 0.00236	< 0.00236	< 0.00236	0.025	0.0155	0.012	0.0145
Zn	775	699	777	774	774	772	519	47.5	3.05	0.301	0.0595	0.157	0.136	0.107	0.0535	0.0355	< 0.0326
Zr	30.7	25.1	29.5	29.5	29.4	29.3	21.9	5.31	1.5	0.565	0.296	0.42	0.705	2.89	3.22	2.3	1.74

A.5 *Test 2 ICP-ES Raw Data*

	Start	Load 1	Load 2	Load 3	Load 4	Load 5	Wash 1	Wash 2	Wash 3-4	Wash 5-6	Wash Rem	Elute 1	Elute 2	Elute 3	Elute 4	Elute 5	Elute Rem
Vol (mL)	2000	400	400	400	400	400	60	60	120	120	243	60	60	60	60	60	108
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
	1X-01-01, 7- 8 M HNO3	1X-02-02, 7- 8 M HNO3	1X-02-03, 7- 8 M HNO3	1X-02-04, 7- 8 M HNO3	1X-02-05, 7- 8 M HNO3	1X-02-06, 7- 8 M HNO3	1X-02-07, 7- 8 M HNO3	1X-02-08, 7- 8 M HNO3	1X-02-09, 7- 8 M HNO3	1X-02-10, 7- 8 M HNO3	1X-02-11, 0.5 M HNO3	1X-02-12, 0.5 M HNO3	1X-02-13, 0.5 M HNO3	1X-02-14, 0.5 M HNO3	1X-02-15, 0.5 M HNO3	1X-02-16, 0.5 M HNO3	1X-02-17, 0.5 M HNO3
Element	LW2755	LW2987	LW2988	LW2989	LW2990	LW2991	LW2992	LW2993	LW2994	LW2995	LW2996	LW2997	LW2998	LW2999	LW3000	LW3001	LW3002
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Al	5130	5000	5570	5610	5590	5580	3630	486	53.1	9.63	4.15	6.17	3.75	1.28	1.05	1.11	< 0.89
Ce	819	493	768	834	849	866	784	465	272	170	101	138	644	2.36	< 1.25	< 1.25	< 1.25
Fe	1340	1270	1410	1420	1420	1420	935	95.2	11.1	1.27	0.431	0.861	1.66	1.53	1.32	1.25	1.13
La	267	151	238	257	263	266	237	127	77	52.2	34.6	46.6	278	1.04	0.25	< 0.199	< 0.199
Mg	1570	1460	1610	1630	1610	1630	1090	101	8.24	0.645	0.222	0.602	0.098	0.108	0.089	0.054	0.009
Mo	123	109	126	126	127	126	88.3	14.5	2.82	0.687	0.311	0.43	0.792	< 0.294	< 0.294	< 0.294	< 0.294
Na	232	223	246	250	252	248	173	17.5	5.12	4.94	5.08	4.51	< 1.1	< 1.1	< 1.1	< 1.1	< 1.1
Nd	914	643	894	923	930	927	789	380	170	96.5	52.6	68	201	1.02	< 0.539	< 0.539	< 0.539
Re	60.9	36.5	62.2	65.2	65.9	66.1	61.4	37.4	22.9	14.1	6.78	5.92	< 0.214	0.147	0.147	0.151	0.135
Sn	< 6.52	< 6.52	< 6.52	< 6.52	< 6.52	< 6.52	< 6.52	< 0.652	< 0.652	< 0.652	< 0.652	< 0.652	< 0.652	< 0.652	< 0.652	< 0.652	< 0.652
Sr	160	147	163	165	163	165	111	12.6	1.42	0.167	0.075	0.096	< 0.00471	0.057	0.054	0.051	0.045
Zn	775	734	818	823	819	821	553	51.1	4.28	0.445	0.225	0.39	0.176	0.157	0.13	0.124	0.113
Zr	30.7	26.9	32.5	32.3	32.1	32.5	23.5	5.62	1.8	0.785	0.426	0.666	4.16	3.6	2.04	1.31	0.769

A.6 *Test 3 ICP-ES Raw Data*

USER_SAMPLEID:	Cr372 Feed	Cr372 EC	Cr372 WC1	Cr372 WC2	Cr372 WC3	Cr372 WC4	Cr372 WC5_6	Cr372 WC7_8	Cr372 WC9_11	Cr372 WC12_16	Cr372 WC16_21	Cr372 Disp	Cr372 Hearts	Cr372 Tails
SAMPLE_ID:	LW6138	LW6139	LW6140	LW6141	LW6142	LW6143	LW6144	LW6145	LW6146	LW6147	LW6148	LW6149	LW6150	LW6151
UNITS:	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
SAMPLE:	LW6138 Kyser 100x	LW6139 Kyser 100x	LW6140 Kyser 100x	LW6141 Kyser 100x	LW6142 Kyser 100x	LW6143 Kyser 100x	LW6144 Kyser 100x	LW6145 Kyser 100x	LW6146 Kyser 100x	LW6147 Kyser 100x	LW6148 Kyser 100x	LW6149 Kyser 100x	LW6150 Kyser 100x	LW6151 Kyser 100x
Element														
Al	5840	5650	4370	208	< 3.98	< 3.98	< 3.98	< 3.98	< 3.98	< 3.98	< 3.98	4.83	< 3.98	< 3.98
Ce	908	780	906	559	356	249	160	96.2	59.4	30.5	14.5	15.1	< 11.4	< 11.4
Fe	2050	1970	1560	125	6.02	< 2.36	< 2.36	< 2.36	< 2.36	< 2.36	< 2.36	< 2.36	< 2.36	< 2.36
Gd	477	459	376	37.8	< 3.52	< 3.52	< 3.52	< 3.52	< 3.52	< 3.52	< 3.52	< 3.52	< 1.15	< 3.52
K	105	106	77.6	< 29.4	< 29.4	< 29.4	< 29.4	< 29.4	< 29.4	< 29.4	< 29.4	< 29.4	< 29.4	< 29.4
La	293	246	289	177	114	80.4	53	32.4	20	10.6	4.8	5.15	19.6	< 0.9
Mg	1610	1560	1260	85.7	< 0.217	< 0.217	< 0.217	< 0.22	< 0.22	< 0.22	< 0.22	< 0.22	< 0.22	< 0.22
Mn	146	142	113	7.2	< 0.763	< 0.763	< 0.763	< 0.76	< 0.76	< 0.76	< 0.76	< 0.76	< 0.76	< 0.76
Mo	125	119	102	< 18	< 18	< 18	< 18	< 18	< 18	< 18	< 18	< 18	< 18	< 18
Na	368	356	289	15.5	< 5.08	< 5.08	< 5.08	< 5.08	< 5.08	< 5.08	< 5.08	< 5.08	< 5.08	< 5.08
Sr	118	113	90.2	3.83	< 0.106	< 0.106	< 0.106	< 0.11	< 0.11	< 0.11	< 0.11	< 0.11	< 0.11	< 0.11
Zn	816	785	627	43.5	< 0.592	< 0.592	< 0.592	< 0.59	< 0.59	< 0.59	< 0.59	< 0.59	< 0.59	< 0.59
Zr	47.8	47	41.3	9	2.27	1.15	0.91	0.73	< 0.72	< 0.72	< 0.72	< 0.72	< 0.72	< 0.72

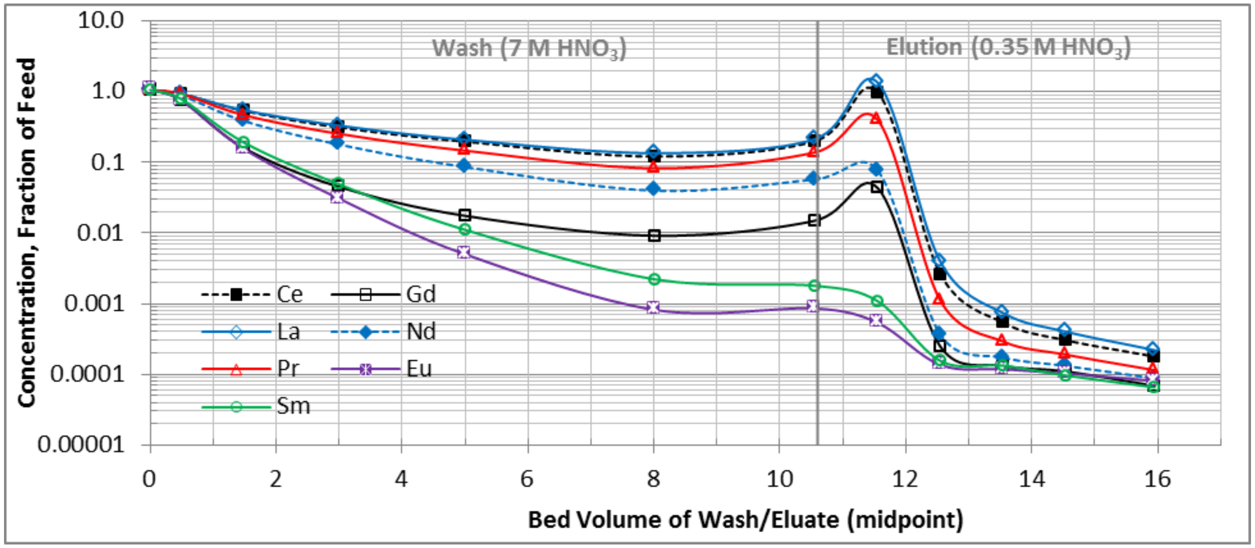
A.7 *Test 1 ICP-ES Mass Balance*

Component	**Raffinate** [mg]	**Wash** [mg]	**Eluate** [mg]	**Total Collected** [mg]	**Mass Balance**
Al	10284	229.7	0.8	10514	102%
Ce	1421	142.3	55.20	1618	99%
Fe	2616	59.1	0.41	2676	100%
La	457	44.4	21.83	523	98%
Mg	2988	68.8	0.07	3057	97%
Mo	243	6.5	0.07	249	101%
Na	467	13.0	0.28	480	103%
Nd	1674	110.9	17.66	1802	99%
Re	111	11.3	0.26	122	100%
Sr	310	7.2	0.00	317	99%
Zn	1518	34.4	0.03	1553	100%
Zr	57	1.9	0.74	59.8	97%

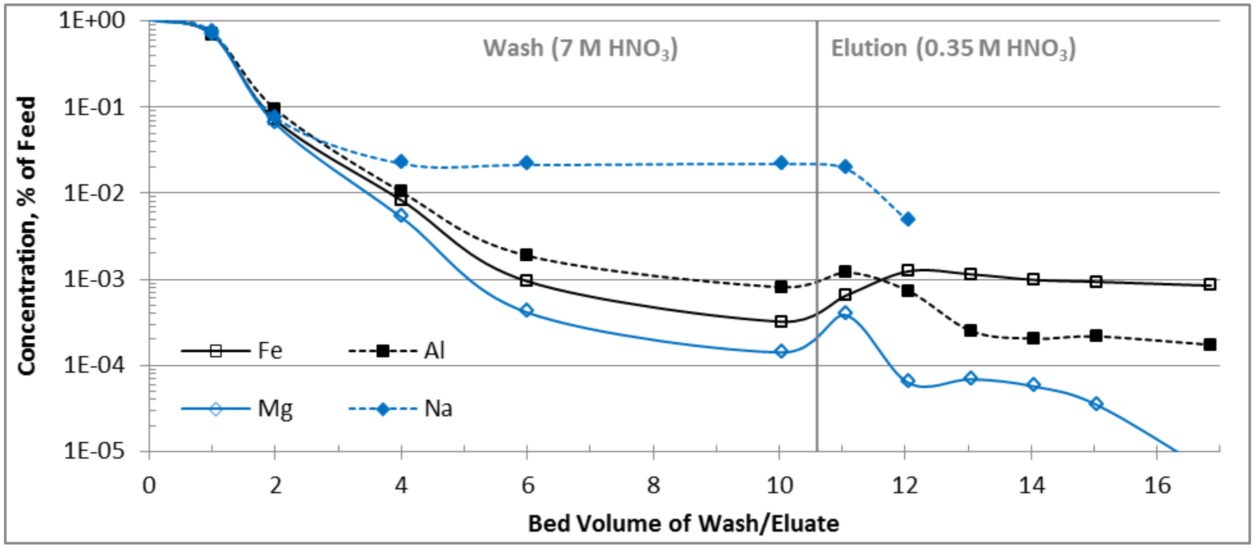
A.8 *Test 2 ICP-ES Mass Balance*

Component	**Raffinate** [mg]	**Wash** [mg]	**Eluate** [mg]	**Total Collected** [mg]	**Mass Balance**
Al	10940	255.5	0.90	11196	109%
Ce	1524	152.5	47.35	1724	105%
Fe	2776	63.4	0.52	2840	106%
La	470	45.8	19.59	535	100%
Mg	3176	72.6	0.06	3249	103%
Mo	246	6.7	0.16	252	103%
Na	488	13.9	0.65	502	108%
Nd	1727	114.9	16.32	1858	102%
Re	118	12.0	0.41	131	107%
Sr	321	7.6	0.02	329	103%
Zn	1606	36.9	0.07	1643	106%
Zr	63	2.2	0.79	65.5	107%

A.9 *Test 2 Lanthanide Wash and Elution Profiles (ICP-MS)*



A.10 *Test 2 Al, Fe, Mg, and Na Wash and Elution Profiles (ICP-ES)*



A.11 *Analyses of Wash Acid and Elution Acid*

ICP-ES	Wash Acid (mg/L)	Elution Acid (mg/L)
Ag	< 1.84	< 1.53
Al	< 3.98	< 3.98
B	< 11.3	< 11.3
Ba	< 0.116	< 0.116
Be	< 0.0483	< 0.0483
Ca	< 1.24	< 1.24
Cd	< 1.5	< 1.5
Ce	< 11.4	< 11.4
Co	< 1.63	< 1.63
Cr	< 1.87	< 1.87
Cu	< 10.4	< 10.4
Fe	< 2.36	< 2.36
Gd	< 3.52	< 3.52
K	< 29.4	< 29.4
La	< 0.902	< 0.902
Li	< 3.67	< 3.67
Mg	< 0.217	< 0.217
Mn	< 0.763	< 0.763
Mo	< 18	< 18
Na	< 5.08	< 5.08
Ni	< 2.56	< 2.56
P	< 20.8	< 20.8
Pb	< 20.7	< 20.7
Sb	< 21.8	< 21.8
Si	< 20	< 20
Sn	< 35.9	< 35.9
Sr	< 0.106	< 0.106
Th	< 5.64	< 5.64
Ti	< 8.96	< 8.96
U	< 17.5	< 17.5
V	< 0.7	< 0.7
Zn	< 0.592	< 0.592
Zr	< 0.72	< 0.72

ICP-MS	Wash Acid (mg/L)	Elution Acid (mg/L)
V	< 1.00E+01	< 1.00E+01
Co	< 1.00E+01	< 1.00E+01
Ga	< 1.70E+01	< 1.70E+01
Se	< 1.00E+01	< 1.00E+01
Rb	< 1.00E+01	< 1.00E+01
Sr	< 1.21E+01	< 1.21E+01
Y	< 1.00E+01	< 1.00E+01
Zr	< 1.94E+01	< 1.94E+01
Nb	< 1.00E+01	< 1.00E+01
Mo	< 6.28E+01	< 6.28E+01
Ru	< 1.00E+01	< 1.00E+01
Rh	< 1.00E+01	< 1.00E+01
Pd	< 1.00E+01	< 1.00E+01
Ag	< 3.86E+01	< 3.86E+01
Cd	< 7.81E+01	< 7.81E+01
Sn	< 4.13E+01	< 4.13E+01
Sb	< 1.75E+01	< 1.75E+01
Te	< 1.00E+01	< 1.00E+01
Cs	< 1.00E+01	< 1.00E+01
Ba	< 2.67E+02	< 2.67E+02
La	< 1.00E+01	< 1.00E+01
Ce	< 1.00E+01	< 1.00E+01
Pr	< 1.00E+01	< 1.00E+01
Nd	< 1.00E+01	< 1.00E+01
Sm	< 6.67E+01	< 6.67E+01
Eu	< 1.92E+01	< 1.92E+01
Gd	< 4.89E+01	< 4.89E+01
Tb	< 1.00E+01	< 1.00E+01

ICP-MS	Wash Acid (mg/L)	Elution Acid (mg/L)
Dy	< 4.02E+01	< 4.02E+01
Ho	< 1.00E+01	< 1.00E+01
Er	< 4.36E+01	< 4.36E+01
Tm	< 1.00E+01	< 1.00E+01
Yb	< 1.00E+01	< 1.00E+01
Lu	< 1.00E+01	< 1.00E+01
Hf	< 1.00E+01	< 1.00E+01
Ta	< 1.00E+01	< 1.00E+01
W	< 6.99E+01	< 6.99E+01
Re	< 3.05E+01	< 3.05E+01
Ir	< 1.00E+01	< 1.00E+01
Pt	< 1.00E+01	< 1.00E+01
Tl	< 1.00E+01	< 1.00E+01
Pb	< 3.82E+01	< 3.82E+01
230	< 1.00E+01	< 1.00E+01
232	< 1.00E+01	< 1.00E+01
233	< 1.00E+01	< 1.00E+01
234	< 1.00E+01	< 1.00E+01
235	< 1.00E+01	< 1.00E+01
236	< 1.00E+01	< 1.00E+01
237	< 1.00E+01	< 1.00E+01
238	< 5.00E+01	< 5.00E+01
239	< 3.00E+02	< 3.00E+02
240	< 2.00E+01	< 2.00E+01
241	< 1.00E+01	< 1.00E+01
242	< 1.00E+01	< 1.00E+01
243	< 1.00E+01	< 1.00E+01
244	< 1.00E+01	< 1.00E+01

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