

Keywords: *HB-Line, AFS-2, Purification, Anion Exchange, Specification, MOX*

Retention: *Permanent*

HB-Line Anion Exchange Purification of AFS-2 Plutonium for MOX

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July 2012

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Prepared for the U.S. Department of Energy under
contract number DE-AC09-08SR22470.



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Printed in the United States of America

**Prepared for
U.S. Department of Energy**

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List of Revisions:

Rev 0	04/30/2012	Initial Issue.
Rev 1	07/31/2012	Correction of typographical error in the resin volume on page 10 and addition of a List of Revisions.

HB-Line Anion Exchange Purification of AFS-2 Plutonium for MOX

SUMMARY

Non-radioactive cerium (Ce) and radioactive plutonium (Pu) anion exchange column experiments using scaled HB-Line designs were performed to investigate the feasibility of using either gadolinium nitrate (Gd) or boric acid (B as H_3BO_3) as a neutron poison in the H-Canyon dissolution process. Expected typical concentrations of probable impurities were tested and the removal of these impurities by a decontamination wash was measured. Impurity concentrations are compared to two specifications – designated as Column A or Column B (most restrictive) – proposed for plutonium oxide (PuO_2) product shipped to the Mixed Oxide (MOX) Fuel Fabrication Facility (MFFF).

Use of Gd as a neutron poison requires a larger volume of wash for the proposed Column A specification. Since boron (B) has a higher proposed specification and is more easily removed by washing, it appears to be the better candidate for use in the H-Canyon dissolution process. Some difficulty was observed in achieving the Column A specification due to the limited effectiveness that the wash step has in removing the residual B after ~4 BV's wash. However a combination of the experimental 10 BV's wash results and a calculated DF from the oxalate precipitation process yields an overall DF sufficient to meet the Column A specification. For those impurities (other than B) not removed by 10 BV's of wash, the impurity is either not expected to be present in the feedstock or process, or recommendations have been provided for improvement in the analytical detection/method or validation of calculated results. In summary, boron is recommended as the appropriate neutron poison for H-Canyon dissolution and impurities are expected to meet the Column A specification limits for oxide production in HB-Line.

BACKGROUND

HB-Line Engineering requested that SRNL develop an anion exchange flowsheet¹ for the purification of Pu dissolved in H-Canyon to meet the proposed Interface Control Document (ICD) limits² for the Mixed Oxide MOX Fuel Fabrication Facility (MFFF) (see Table 1). Three levels of ICD limits are given: 1) Column B, 2) Column A and 3) Exceptional. Significant levels of select impurities will be added in the H-Canyon dissolution process³ but additional information was needed to determine what other impurities need to be removed by the process. The proposed feedstock to this process is part of an inventory characterized as Alternate Feedstocks 2 (AFS-2) and consists of Pu metal from multiple sources.

The major impurities expected in the feed to HB-Line are primarily those added during the dissolution process in H-Canyon (i.e., Gd or B, potassium (K), fluoride (F), and aluminum (Al)). Gallium (Ga) is also a major impurity as it comprises a significant component in the AFS-2 feedstock. After the Pu metal is dissolved in H-Canyon, HB-Line will perform anion exchange, oxalate precipitation, filtration and calcination to produce a plutonium dioxide (PuO₂) product. The primary purification will be performed by anion exchange but additional purification will be obtained by precipitation, filtration and calcination for some impurities.

This report documents ion exchange column experiments aimed at determining the differences between the two potential neutron poisons and determining an appropriate wash volume to remove the poison and other impurities to meet the Column A specifications from the draft ICD.

Significant Impurities in AFS-2 Feedstocks: Kyser⁴ previously performed an evaluation of the potential impurities that could be present in AFS-2 feedstocks. Impurity data for AFS-2 metal from three primary sources was evaluated: 1) cast and uncast metal, 2) pit parts and 3) SRS button data. Studies by Allender⁵ and Moore^{6,7} documented the expected impurity content of cast and uncast metals which constitute a significant fraction of the AFS-2 feedstocks and identified iron (Fe), nickel (Ni), chromium (Cr) and tungsten (W) as impurities that could significantly exceed the MOX acceptance limits being considered at that time. Not all elements in Table 1 were routinely reported in Rocky Flats production reports which were the primary source of the analyses cited in reference 5. Rocky Flats had not identified a credible source for other elements to be present above 100 ppm. Of the elements measured, Ga was found to be consistently high relative to the Column A and Exceptional specifications. The following elements showed occasional high values relative to the Column A specification: Al, calcium (Ca), Fe, K, lithium (Li), magnesium (Mg), molybdenum (Mo), sodium (Na), Ni, W, and zinc (Zn). Some occasional high values may be due to reporting errors but this can-

¹ J. W. Christopher, "Flowsheet Development for HB-Line Phase II Oxide Production," NMMD-HTS-2011-3177, Revision 0 (Nov 10, 2011).

² MFFF – H-Area/K-Area Plutonium Dioxide Powder Interface Control Document, ICD-11-032-01, G-ESR-H-00189, Rev. 0d DRAFT, 11/1/2011.

³ T. S. Rudisill, R. A. Pierce, "Dissolution of Plutonium Metal in 8-10 M Nitric Acid", SRNL-STI-2012-00043, Savannah River National Laboratory, Aiken SC, February, 2012.

⁴ E. A. Kyser, "Impurities for Anion Exchange Testing - Pu to MOX", SRNL-L3100-2011-00234, Savannah River National Laboratory, Aiken SC, December 16, 2011.

⁵ J. S. Allender "Preliminary Chemical Analysis of AFS-2 Candidate Metal Items", SRNL-TR-2011-00333, Savannah River National Laboratory, Aiken SC, November 18, 2011.

⁶ E. N. Moore, "Potential Corrosion Product Pickup in AFS-2 and Pit Feeds", SRNS-RP-2011-00106, Moore Nuclear Energy, LLC, Aiken, SC, January 18, 2011.

⁷ E. N. Moore, "Addendum for Potential Corrosion Product Pick-up in AFS-2 and Pit Feeds," SRNS-RP-2011-01033, Moore Nuclear Energy, LLC, Aiken, SC, April 28, 2011.

not be confirmed (e.g., W is suspect). For the actinide elements (uranium (U), neptunium (Np), and americium (Am)) and for the common elements in salts used in pyrochemistry (Li, K, Ca, Na, Mg, chloride (Cl), and F) the absence of data was not a reliable indication for the lack of this impurity. However for other less common elements, the lack of data was assumed to indicate a relative absence of the given impurity in the AFS-2 feedstock. There are several rare earth elements (samarium (Sm), dysprosium (Dy), and europium (Eu)) which have low limits due to their neutron absorption characteristics. Estimation of the impurity levels for Sm, Dy, and Eu in Pu oxide at concentrations of ~2 $\mu\text{g/g Pu}$ ⁸ was discussed by Moore et al. Similarly, Cd was estimated to be present in average concentrations of 13-17 $\mu\text{g/g Pu}$. It is assumed that lack of these impurities in Pu oxide is sufficient evidence that they will not be present in AFS-2 metal. Since these impurities (Cd, Sm, Dy, and Eu) appear to not exist in greater than minor amounts, their concentration will be insignificant compared to the concentration of Gd which may be used in the process.

Process Impurities and Impurity Removal by Anion Exchange: James⁹ and Marsh¹⁰ each provide a periodic table viewpoint on the affinity of various elements for a nitrate anion exchange system. Each author interpreted the data available to them in a different fashion. Modified versions of the periodic table from James and Marsh are included as Figure 1 with color coding to show the expected and potential process impurities that have been identified. Note that none of the major impurities identified in the AFS-2 feed show significant affinity for the resin. James indicates that the rare earths have a slight affinity for anion resin and, although he does not provide a distribution value, Gd likely behaves similarly to the other 3+ valence rare earths. Marsh indicates that Gd, B and most of the rare earths do not have any affinity for anion resin. It is not apparent which data is more applicable to the current process. With the low specification limits, both Gd and B were tested and are expected to be the limiting impurities in the development of the flowsheet. Any of the rare earth impurities (Sm, Dy, Eu) at low concentrations should be removed by the washing step to remove Gd and it is concluded that these did not pose any additional concerns for flowsheet development.

Most impurities identified (major impurities: K, Al, Ga, and Fe as well as minor/potential impurities: Li, Na, Mg, Ca, Ti, Cr⁺³, Ni, and Cu) appear to have no affinity for anion resin and should be easily removed. A representative subset was chosen for testing which included all the major impurities and a subset of the minor impurities (Na, Mg, Ca, and Cu). Cr and Ni were not tested since HB-Line has demonstrated during the recent Np campaign^{11,12,13} an anion exchange DF of 700 for Cr and 400 for Ni for ~8 bed volumes of decontamination wash which should provide a reasonable basis for the expected DF for these corrosion impurities.

There is a short list of anions (F, Cl, and SO_4^{-2}) potentially present in solution that may have some affinity to the resin. Testing of the F anion complexed with 2:1 molar ratio of Al was performed but the IC Anion solution analysis is recognized as unable to measure either F or Cl at the specification

⁸ E. Moore, R. Saylor, J. Allender, S. Davies, "Chemical Impurities in Candidate Alternate Feedstock Oxides for the MOX Fuel Fabrication Facility- 2006 Analysis Update", SVP-OPD-2006-00003, Washington Savannah River Co, Aiken, SC July 31, 2006.

⁹ D. B. James, "Anion Exchange Processing of Plutonium", LA-3499, Los Alamos Scientific Laboratory, Los Alamos, NM, January 4, 1966.

¹⁰ 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, NM (April 1989).

¹¹ E. A. Kyser, "Np SME Memo", email comments to L. Sims, January 15, 2008.

¹² A. M. Murray, R. W. Watkins, "Np SME Team Review of HB-Line NT-21/NT-22 Solution Results", SRNL-ATS-2008-00006, Savannah River National Laboratory, January 15, 2008.

¹³ A. M. Murray, R. W. Watkins, "Np SME Team Review of H-Canyon Tank 9.5 Solution Results", SRNL-ATS-2007-00050, Savannah River National Laboratory, August 1, 2007.

limit. It is assumed that the amount of Cl is relatively minor compared with the amount F used in the flowsheet and therefore Cl was not tested. Although ferrous sulfamate (FS, $\text{Fe}(\text{NH}_2\text{SO}_3)_2$) is not planned to be used in the HB-Line process for valence adjustment, it was required in the Pu laboratory tests due to the use of recycled Pu solutions and was also tested in the non-radioactive Ce experiments. The actual amount of sulfate vs. sulfamate is not known to sufficient accuracy to measure a true DF. This limitation should not have much impact because no sulfamate or sulfate is planned for use in the production process but does complicate interpretation of the limited S data obtained. To mitigate the limited analytical capability for F and Cl in solution, a precipitation study will be performed later using Pu washed sufficiently to remove the neutron poison (Gd or B). The Pu product solution will be oxalate precipitated in a series of tests with varying amounts of HF and HCl added (using the standard addition method). The product from each precipitation will be filtered, washed and then calcined to ~ 650 °C. It is believed that each of these steps will remove some F or Cl impurity. Both HF and HCl (simultaneously) will be tested in precipitation/calcination and the calcined oxide product will be analyzed to determine the DF for these anions. F/H Area Laboratories can perform a pyrohydrolysis analysis for F and Cl with a $20 \mu\text{g/g}$ Pu detection limit which should be sufficient to determine a F+Cl concentration $< 250 \mu\text{g/g}$ Pu.

There is a short list of transition metal impurities (W, Mo, Cr^{6+} , and Bi^{3+}) that may be present in solution as anions that may have some affinity to the resin. Tungsten and Mo exist as tungstic and molybdic acids and have limited solubility in 8 M HNO_3 acid solution. Tungsten and Mo also may be present in high concentrations in a limited number of AFS-2 items. Testing the anion exchange DF was not practical due to the solubility limitations. In the production process, minor amounts of solids that are left after dissolution as well as any post-dissolution solids that could form may be transferred to the anion exchange process. Filters on the feed stream to anion exchange will remove large solids but might not remove fine solids, although the ion exchange columns may well trap any fine solids present. Insufficient information is currently known about W and Mo to completely address their behavior in the process at this time but simple testing as an anion exchange impurity is also not likely to be successful. Feedstocks that involve significant quantities of these transition metal impurities (W, Mo, Cr^{6+} , and Bi^{3+}) should be avoided unless additional testing is performed.

Any Cr that might exist as Cr^{6+} would have some affinity for anion resin; however, Cr^{6+} is not stable thermodynamically in the low pH of the feed solutions so Cr is expected to exist in the Cr^{3+} valence state. Confirmation of the absence of significant Cr^{6+} under realistic process conditions is desired. HB-Line has recent data from the Np campaign^{11,12,13} that indicates a DF of 700 for Cr (likely as Cr^{3+}) in that process.

Bismuth also may exist as an anionic species in solution. If present it would be expected to have an affinity for anion resin similar to U. Data for Bi is not available for AFS-2 feedstocks; however the report by Moore⁸ on Pu oxides gives average Bi concentrations of $117 \mu\text{g/g}$ Pu. Based on this low value of Bi impurity in the Pu oxide, Bi was not tested as very limited DF would be required to make the column A specification. Bi also probably has solubility limitations similar to W and Mo. Any soluble Bi present should behave similarly to U. Uranium and Bi absorb somewhat more than most impurities onto anion resin and will require extensive washing to remove significant amounts. During the recent HB-Line Np campaign^{11,12,13} ~ 8 bed volumes of wash was used to realize a DF of ~ 500 for U; however, a DF of only ~ 15 was observed for Ce (which is reported as more weakly retained).

The limits for N and C are driven by the concern for difficult to dissolve nitrides, carbides and graphite. Such materials will not be soluble in the H-Canyon dissolution process and any solids of significant size will plug process filters in HB-Line if they are transferred to that point in the process and will not make it to the precipitation process step. Therefore, no effort was made to measure for these

materials in this flowsheet development effort. (A parallel study on precipitation¹⁴ will measure the concentration of C as residual oxalate in the product.)

The Marsh and James references agree that vanadium (V) and indium (In) do not absorb onto anion resin. Thorium (Th) and Np absorb strongly onto anion resin and it is not reasonable to develop an anion exchange flowsheet to remove these elements if the amounts are significant. Blending to achieve specifications or performing solvent extraction separation would be reasonable alternatives.

The validity of this evaluation and the proposed testing depends on the speciation being consistent between the literature references, the proposed laboratory tests and the eventual plant process. Every effort needs to be made to avoid conditions where the speciation of the various impurities might vary as such differences could cause large differences in the observed decontamination. Such differences are recognized to be a potential issue for several impurities such as Cr⁶⁺ and V and will continue to be evaluated. Impurities (Cr, Ni, La, Ta, V) that have a smaller margin of confidence may deserve some continued attention as processing of the AFS-2 material progresses or through tracking/trending of the normal sample analysis protocol.

Process Scaling: Plant scale anion exchange equipment is typically 100 to 1000 times larger than laboratory equipment. Normally the process is scaled based on the linear velocity (Q/A , mL/min/cm² = cm/min) through the resin bed (which is related to residence time in the bed) and the loading profile of the resin. If a laboratory column contains resin at the same depth as the plant equipment, then scaling is primarily reduced to one of flow area and Pu flux through the bed (linear velocity will be the same). Higher Pu concentrations in the feed solution will produce a higher Pu resin loading. Lower flowrates would also tend to increase the effective loading by increasing the time for mass transfer. The HB-Line Pu anion columns nominally hold a 27 inch tall cylinder of resin, 7.62 inches ID (294.1 cm² cross sectional area) which contains ~20.1 L of resin^{15,16}. For the non-radioactive experiments, a full-height settled resin volume of 194 cm³ was used in a 19 mm ID glass column, resulting in a cross sectional area of 2.835 cm². The targeted flowrate of 10.7 mL/min @ 4.5 g Pu/L for a 2.835 cm² laboratory column was based on a cross-sectional area for the HB-Line column of 294.1 cm² (7.62 inches ID) and process loading rates of 1.1 L/min at 4.5 g Pu/L^{15,17,18,19}. This loading rate corresponds to ~17 mg Pu/min/cm². Table 2²⁰ shows a comparison between the proposed HB-Line operating conditions, and current SRNL test conditions. A smaller diameter laboratory column (12.6 mm or 1.247 cm²) was used in the Pu experiments. This column consisted of two segments which contained a total of 85.5 cm³ of resin and was operated at flowrates that were roughly half those used in the larger non-radioactive column as shown in Table 2.

¹⁴ M. L. Crowder, J. M. Duffey, "Task Technical and Quality Assurance Plan for Precipitation and Calcination of Plutonium(IV) Oxalate to Form Plutonium Oxide and Subsequent Gas Generation Studies to Support the MOX Feed Mission", SRNL-RP-2011-01657, Savannah River National Laboratory, Aiken SC, December 2011.

¹⁵ E. A. Kyser, "Plutonium Loading onto Reillex HPQ Anion Exchange Resin", WSRC-TR-2000-00372, Westinghouse Savannah River Company, Aiken, SC (Sept 26, 2000).

¹⁶ Drawing W720067 R44, "Savannah River Plant, Bldg 221H, 8 Inch Dia. Column Assembly Process, H363-110-1,2,3 & 4", (January 29, 1985).

¹⁷ Drawing W720279 R0, "Savannah River Plant, Bldg 221H, Nept. 237, Plut. 239 Flow Diagram Process", (July 31, 1981).

¹⁸ Drawing W743159 R25, "Savannah River Plant, Bldg 221H, Enhancement of Pu 239 Capability, Flow Diagram Sh. No. 2 Process", (March 1, 1985).

¹⁹ R. H. Smith, "HB-Line Pu-239 Production Flow Sheet Strategy", SRNS-E-1100-2011-00025, Rev. 1, (January 23, 2012).

²⁰ E. A. Kyser, "Task Technical and Quality Assurance Plan for Plutonium Anion Exchange Flowsheet for HB-Line", SRNL-RP-2011-01598, Savannah River National Laboratory, Aiken SC, December 2011.

EXPERIMENTAL

Ce and Pu Experiments: The initial experiments (Cr310 and Cr311) were performed in a single 27" tall column in a hood without any radioactive components. These initial experiments contained weakly absorbing Ce. Two experiments containing Pu were performed in a similar manner with the two-piece column installed in a glovebox. The two-piece column was necessary to achieve the required resin-bed height due to the limited height of the glovebox. Experiment Cr313 was performed to troubleshoot the equipment and experimental procedure and was very similar to experiment Cr314 except that the later experiment had a spike of ^{137}Cs added to the feed to simulate a non-interacting impurity that did not have significant analytical measurement limitations. Full sampling was never planned for Cr313, but additional samples were added based on the smooth operation of the experiment.

Resin Pretreatment: The Reillex HPQ™ resin that was tested came from the 1998 manufacturer's lot (#80302MA) that was purchased by SRNL for Pu flowsheet work²¹ and later used for Np flowsheet work. All resin was initially converted from the chloride form (as-shipped) to the nitrate form by washing with 1 M NaNO_3 (~10 BV in a column was the preferred method, but other methods are acceptable). The assembled column was thoroughly washed with 8 M HNO_3 prior to the start of the experiment. Experiments Cr310 and Cr311 both used the same resin bed; experiments Cr313 and Cr314 used a different two-piece column apparatus.

Column Preparation: A sufficient quantity of resin was converted into the nitrate form prior to loading the column. The resin was loaded by slurring the resin into the column with water to avoid air entrainment in the bed. The resin bed was settled by passing water/dilute HNO_3 down-flow through the resin bed. No obvious gaps or void spaces were visible. The final resin bed volume was adjusted by adding a small amount of resin or removing excess resin with a slurry pipette to obtain the desired resin bed height. A 100 mesh 304L screen (see Figures 2a, 2b, and 3) was installed above the packed bed to retain the resin and allow for up-flow operation. This screen fit tightly within the column body and did not allow the resin bed to expand significantly. It also prevented upward flow from fluidizing the resin bed. Actual volume changes of the resin beads are insignificant (after the resin was in the nitrate form), but retained gas bubbles would cause the resin bed to expand without the screen installed. Gas bubbles trapped within the moist bed are often very difficult to remove and will cause channeling of the flow through the bed. A tightly held resin bed does not allow channeling to occur.

Lab Equipment: A picture of the column used in the non-radioactive experiments is shown in Figure 2. This column utilized #7 Teflon™ bushings for connecting ¼ inch polypropylene tubing to the upper part of the column and consisted of a 19 mm ID glass body to retain the resin bed and a headpiece. The headpiece is attached to the column body with a Rodaviss™ joint to allow the column to retain a larger pressure head than that allowed by a ground glass joint. As a safety precaution, the headpiece also had an Ace glass pressure-relief valve. An additional arm with a stopcock and funnel allowed the column to be vented. The 3-way stopcock at the bottom of the column was used to change flow direction. With the 100 mesh screen held into place with an o-ring (Figure 2a), this column was operated with load-wash up-flow and elution down-flow. The Pu experiments used a two-piece column design (due to limited headroom in the glovebox) that used ¼ and 1/8 inch polypropylene tubing to connect to the 12.6 mm ID glass body. The upper portion of the column used a similar headpiece to that used for the non-radioactive experiments. The bottom of the upper column was connected to the top of the lower column with 1/8 inch tubing. The top and bottom of both the upper and lower columns used 12 mm diameter-100 mesh screen (similar to that shown in Figure 2b) to retain the resin. A 3-way Swagelok™ valve was used at the bottom of the lower column in much the

²¹ W. J. Crooks, E. A. Kyser, S. R. Walters, "Qualification of Reillex™ HPQ Anion Exchange Resin for Use in SRS Processes", WSRC-TR-99-00317, Westinghouse Savannah River Company, Aiken, SC (March 10, 2000).

same way as the 3-way stopcock was used in the non-radioactive column. A sketch of the experimental setup for the up-flow load/wash steps is shown as Figure 4. A separate sketch of the down-flow elution experimental setup is shown as Figure 5. Figures 4 and 5 show the installation of flowcells and fiber optics that were not in use for these experiments but will be used later in Pu loading experiments. The feed line was connected to the bottom of the column during condition, load and wash steps and then changed to the top of the column for elution (along with switching the 3-way stopcock/valve to the elution position). A standard FMI piston pump was used to pump feed, wash, or elution acid through the column.

Feed Matrix: Based on the previous review of the known impurities⁴, a feed matrix was prepared which contained all the significant non-radioactive impurities expected in AFS-2 metal feedstocks and the reagent impurities added during the dissolution process. Table 3 shows the target concentrations of impurities for testing in the current study.

Analytical Methods: Mass balance for impurities was determined by a combination of ICPES (Gd, B, Al, K, Fe, S, Si, Zn, Li, Na, Mg, Mn, Ce, Ca and Cu), IC Anions (F) and ICPMS (Ga, Ce, Gd, Sm and W) analyses. It was understood that the detection limits for the current methods as performed by AD probably would have difficulty meeting some of the specification limits. Efforts were undertaken by AD in parallel²² with the current study to improve those detection limits where required (as possible). Over the course of this work several analytical adjustments were made. Samples for submission to ICPES were submitted in plastic vials due to apparent Na, B, Si and Al contamination that appeared to be associated with the glass sample vials commonly used. Due to interferences, Pu was removed from the primary anion product samples (commonly referred to as “Hearts”) as well as the Displacement solutions. When Pu removal was not performed, both positive and negative interferences were observed by ICPES. Separate techniques were used to remove the Pu for ICPES and ICPMS. The ICPMS separation method, which is described in detail in another report²², involved isolation of the trivalent lanthanides by elution from an analytical column (Eichrom RE cartridge). All other heart components (except Pu) were contained in the column raffinate. The ICPES separation method involved a separate analytical column type (Eichrom TEVA® Aliquat 336 cartridge) which removed the Pu. The raffinate was subsequently analyzed for the remaining elements of interest without plutonium interference. Both methods involved the dilution of the Hearts sample prior to transfer to the columns by 10-13x with nitric acid and sodium nitrite solutions to promote complete conversion of the plutonium to the 4+ valence state. Reagent blanks were tested and standard additions to reagent blanks and samples were performed to check for both contamination and recovery of the analytes of interest. The separation recoveries for the ICPES sample preparation were high, but in some cases variability in the standard spike additions may have been large relative to concentrations of the impurities resulting in inaccurate blank corrections. In addition, sodium analysis in these samples following plutonium removal was not possible due to the large additions of sodium reagents. It is also believed that some potassium may have been inadvertently added in the ICP-ES separation method (possibly as a minor impurity in the sodium reagents). These facts complicate the interpretation of the data for this element.

Reagents: Reagent grade chemicals were generally used with the exception of ferrous sulfamate (FS), for which H-Area plant production FS was used. The purity of the reagents for the preparation of the feed solution was not a significant concern. The purity of the wash and elution acid solutions was a concern due to their effect on the purity of the final product. Distilled water (from the SRNL laboratory system) and reagent grade HNO₃ was used for preparation of all wash and elution acid solutions for Cr310 and Cr311. Deionized water was used for preparation of all wash and elution acid solutions for

²² M.A. Jones, D.P. Diprete, B.J. Wiedenman, “Application of Column Extraction Method for Impurities Analysis on HB-Line Plutonium Oxide in Support of MOX Feed Product Specifications”, SRNL-STI-2012-00148, Savannah River National Laboratory, March, 2012.

Cr313 and Cr314. All sample and reagent bottles were pre-washed with deionized (DI) water (including a 24 h DI water soak step). All samples were collected in pre-weighed and pre-washed sample bottles to avoid cross contamination. After collection of these large samples, the filled bottles were weighed and the flowrate determined by the time required to fill each bottle and the density of each solution. In some instances, interruptions in the flow made the flowrate determination inaccurate. Since the flowrate was not easy to monitor as the experiment was performed, some flowrates (particularly the elution rates) were lower than intended, but the wash and elution volumes were well known.

RESULTS

Feed Preparation: Feed solutions were prepared by dissolving reagents into water as shown in Table 4. Nitrate salts were used as the source of most impurities. Ludox HS-30 was used as a source of soluble silica. Tungstate proved to be difficult to maintain soluble in acid solution. Due to the cloudy appearance of the feed solution, Cr310 Feed was filtered with a 0.45 μm filter at the start of the experiment and a small amount of yellow solids were removed. XRD analysis of the filtered solids indicated that they were tungstic acid. Elevated levels of W were also measured in the Displacement sample during the elution cycle suggesting that some tungstic acid was filtered out by the frit at the bottom of the column. Due to its limited solubility and the associated issues, W was not included in the test matrix for the later tests. Feed materials that actually contain W or other limited solubility elements will have to either be avoided or removed by filtration or other means to avoid operation issues in HB-Line and avoid contamination of the anion product. Analyzed results of each feed solution are shown in Tables 5a and 5b. The primary difference between the experiments Cr310 and Cr311 was that Cr310 contained both B and Gd, whereas Cr311 only contained B. It was intended that the feed solutions for all experiments have a 2 to 1 molar ratio of Al to F, but Cr311 only had an [Al]/[F] molar ratio of 0.2. The low [Al]/[F] ratio is presumed to have an effect on speciation and if Pu had been present would have resulted in increased losses. Elements (Pu, Al, Ce, Fe, Ga, Gd, Sm, and Si) that form complexes with F would be likely candidates to be affected by the low [Al]/[F] ratio in the feed. However it is not apparent that the behavior of any impurity was significantly different between experiments Cr310 and Cr311.

Table 5b shows the analyzed feed data for the Pu experiments were comparable to that shown in Table 5a for the non-radioactive Ce experiments. The Pu experiments generally used similar concentrations of impurities as those used in the Ce experiments with several differences. 1) Based on H-Canyon's request, the concentration of B was increased from ~ 1 g B/L to ~ 1.7 g B/L. 2) W and Ce were dropped from the feed matrix. 3) Pu and Am were added to the feed matrix. 4) ^{137}Cs was added to the feed matrix for Cr314 as a non-interacting cationic species with a very low detection limit.

Flow Rates: Targeted and measured solution flowrates for column tests Cr310, Cr311, Cr313 and Cr314 are provided in Table 6. The flow rates were determined from the mass of solution collected in each bottle, the measured solution densities, and the recorded collection times. The average flow rate in each test for the column loading period with AFS-2 feed simulant was typically within 20% of the target value (a few cases it was up to 40% off). Due to a calculation error, the average flow rates used for the elution phase for the Ce experiments were only 26% (Cr310) and 38% (Cr311) of the targeted value. As a result of the especially low elution flow rate used in Cr310, the Hearts and Tails bottles for this test contained only 0.5 BV of solution each. The low elution flow rates could result in a shifting of the Hearts peak into the Tails sample due to the Displacement and Hearts samples being too narrow but there is no indication in the results that this occurred to any significant extent with any of the impurities. Some impurities (Gd, Sm, W) did appear to peak prior to the Hearts cut but the cause of this behavior is not understood.

Hearts Impurity Concentrations: The calculated values for the impurities on a Pu basis are shown in Table 7. Since extensive washing was performed on the Ce experiments, most of the impurity concentrations are at or near the detection limits. The concentrations of S were near the detection limit with the calculated impurity concentrations near the Column A specification. Boron, Si and Sm were initially near the specification limits but upon reanalysis in plastic sample vials both B and Si were reported at less than the method detection limit (MDL). Samarium challenges the specification due to the slight adsorption by the anion resin and the low specification limit. Gadolinium was below the Column A specification in the Ce experiments but a small adsorption peak does exist. The results for the Hearts samples for the Pu experiments (~ 10 BV wash) are less favorable. Boron, Gd, K, and Sm

were reported at above the Column A specification limit and the sulfur MDL was above the specification limit. All Hearts sample from Cr313 and Cr314 results except Na are reported by analysis after Pu removal. Impurity removal in the Pu experiments was significantly lower than observed in the Ce experiments possibly due to a physical trapping of impure feed solution by the Pu hexanitro species. Further detailed results are shown in the following pages for each impurity or groups of similar impurities with discussion of observations.

Material Balance: All solution that passed through the column was collected over a period of time and analyzed as a series of composite samples. No grab sampling was performed. A material balance was calculated for each experiment for each impurity using the measured volumes and densities of each sample from the wash and elution steps (Tables 8a, 8b and 8c). Most impurities were present in similar concentrations for all experiments but Al, and Gd are different in Cr311, W was only included in Cr310 and ^{137}Cs was only included in Cr314. The bulk of most impurities (except for Ce) passed through the column into the effluent/raffinate samples. The material balances for these elements generally were closed within a few percent. Several impurities (Ce, Li, Si, W) had some significant issue(s) which prevented better closure of the material balance. Notably, Li, and Si suffered from analytical difficulties. Tungsten (and probably Si) appeared to have solubility limitations in acid solutions. Cerium did not have a particularly good material balance at 80 to 96% of the feed.

Wash and Elution Acid Purity: Analysis of these reagents after the initial Ce (nonradioactive) testing identified B and Si contamination that was suspected to be due to either the distilled water source or the glass sample vials used for submission to AD. Samples of the distilled water and nitric acid sources submitted to AD in plastic vials eliminated these as sources of the impurities. A fresh sample of Cr310 WC7-10 (collected and stored in a washed plastic bottle) was analyzed and compared to the previous analysis. The reanalyzed values for both B and Si were significantly lower (and less than the detection limits). The reanalyzed value for Al was significantly lower, but still slightly above the detection limit. Based on these results, the samples beyond Cr310 and Cr311WC3 were resubmitted for analysis by ICPES in plastic vials. The results for ICPES shown in this report (where the impurity concentrations are low) are reported for samples stored in plastic vials to avoid further issues. Future work will avoid this issue by using plastic sample vials for ICPES samples.

Plutonium: Plutonium was included in the feed matrix for Cr313 and Cr314 based on the nominal flowsheet³. Figure 6 shows that Pu is strongly loaded onto the resin and with minor losses of ~1.5% by 10 BV's of an 8 M HNO_3 wash. There is a sharp elution peak that averaged ~10 times the feed solution concentration.

Americium: ^{241}Am is a daughter product of ^{241}Pu in the weapons grade Pu and thus is always present in a measureable amount in the feed to Pu anion exchange. Am is generally reported as being separated by anion exchange from Pu but as can be seen in Figure 6 and Tables 8b and 8c, there appears to be some slight retention by the resin. Americium is steadily washed from the resin and a 10 BV wash appears capable of removing > 99.4% (DF > 160) of the Am (see Table 8b and 8c). After purification, ^{241}Am continues to grow into the Hearts solution at a rate that depends on the ^{241}Pu content of the solution. Analytical results for ^{241}Am were corrected to the time of separation.

Cerium: Cerium was included in the feed matrix for the non-radioactive experiments based on past experience that it does not easily wash from the resin column. It serves as a weakly absorbing surrogate for Pu. Figure 6 shows that Ce is moderately loaded onto the resin and slowly washed away by an 8 M HNO_3 wash. It is retained significantly more strongly than Am. Distinct elution peaks were observed that were comparable in concentration to the feed solution. Cerium was measured by both ICPES and ICPMS and good agreement between the methods was generally seen except for the Dis-

placement and Tails samples. Table 9 shows a Ce DF of ~10 based on the amount of wash volumes used in these experiments.

Gadolinium: Gadolinium is one of the proposed neutron poisons for use in the dissolution flowsheet in H-Canyon. Like many of the other rare earth elements, Gd is weakly absorbed on the resin column and took significant wash volumes to remove (Figure 7). The bulk of the Gd is removed in the initial four BV's of wash, but after that point in the wash cycle it appears that the Gd removal is slow. The slow removal seems likely to be due to the affinity of Gd for the resin. Due to the low limits for Gd in Table 1, a larger amount of washing is required to meet the proposed ICD limits. A DF on the order of 15,000 was achieved in Cr310 with 19 BV of wash but a DF of only ~3000 was observed during the Pu experiments after 10 BV's wash. There was significant discussion about which of the 5 abundant mass numbers of naturally occurring Gd to use for DF calculations. Initially it was realized that mass number 156 had a Ce-140 (Ce+O, 140+16=156) interference which made it inappropriate. The ICPMS instrument manufacturer's recommendation was to use Gd-158 which was initially used. Further inspection of the data revealed that the Gd-157 and Gd-158 results were significantly higher than the Gd-155 and Gd-160 lines. It is possible that Ce-142 could cause a similar, but smaller interference with mass number 158 (Ce+O, 142+16=158). It was also suggested that an OH interference is possible with Ce-140 (Ce+OH, 140+17=157) that could account for interference at mass number 157. We have concluded that Gd-155 and Gd-160 are the best representation of the behavior of Gd when Ce is present in the feed solution. When Ce is not present, all the common mass lines of Gd appear to be reasonably equivalent.

Gadolinium was included in the feed matrix for Cr310, Cr313 and Cr314 experiments and was analyzed by both ICPEs and ICPMS. Data from both methods are shown (in Figure 7) for Cr310 but the ICPEs analyses had a limited detection limit and the data beyond 5 BV's of wash were not meaningful. Experiment Cr311 analyses showed a very small amount of Gd in the feed, possibly as an impurity in the Sm, but those data are at too low of a concentration to be meaningful. Cr 314 had significantly more Gd present in the Wash and Hearts samples than was previously observed. This result has been tentatively explained as being related to a physical trapping of impurity within the resin structure by the Pu hexanitrate species which is absorbed onto the anion resin loading sites.

Based on our current interpretation of interferences, it does appear that 19 BV's of decontamination wash in experiment Cr310 easily achieved the 3 µg Gd/g Pu specification but when a representative quantity of Pu was present, 10 BV's of decontamination wash in experiments Cr313 and Cr314 resulted in product that was 7-8 times (~24 µg/g Pu) the 3 µg Gd/g Pu specification.

Samarium and Gadolinium: Samarium at a modest impurity concentration was included in these experiments as a comparison for the Gd behavior. Figure 8 shows a comparison between Sm and Gd as contrasted with Ce. Gadolinium and Sm behaved very similarly even though less Sm was added. The Sm peaks show a difference in shape for the Ce experiments due to an increase in the Sm concentration in the Displacement sample prior to the Hearts sample. Because the elution rates and volumes were low, this result may not have much significance. It appears that the distribution coefficient (K_d) for Sm is slightly larger than for Gd. Samarium is not expected to be present in any concentration in the feedstocks nor the process. All major mass numbers for Sm appear to give equivalent results. Due to apparent higher K_d for Sm, it appears that 15-20 BV's of decontamination wash are required to remove Sm to the Column A specification limits without Pu present but greater than 30 BV's when Pu was present in the feed.

Boric Acid (B): Boric acid is the alternative H-Canyon neutron poison for Gd and was included in all experiments. In the initial analyses there were B contamination problems attributable to the glass vials in which the analytical samples were stored prior to analysis. When reanalyzed following storage

in plastic vials (the experimental solutions were all stored in clean plastic bottles rather than glass), samples after 5 BV's of wash in the Ce experiments had B at less than the ICPEES MDL of ~0.2 mg B/L (Figure 9). In the Pu experiment, the rate of B removal by washing slowed after 3 BV's and an elution peak was present. Boron DF's of ~60,000 (17-19 BV's wash) were observed for the Ce experiments but this value fell to ~2000 (10 BV's wash) when Pu was present. The B in the Hearts cut increased from < 4.5 to ~150 µg B/g Pu (see Table 7) when Pu was added to the experiments and the wash volume was reduced from ~19 to 10 BV. With a Column A specification of 100, the results from Cr313/4 marginally exceed the specification, but estimates shown in Table 10 place the required BV's wash as high as 20 to meet the specification. The bulk removal of B initially occurs during the first 3-4 BV of wash volume (Figure 9), but when Pu is present the slope of the curves indicate that less B is being washed from the column. After 5 BV's of wash, significantly more B was still being removed during the experiment with Pu compared with that observed during the Ce experiments.

Boric Acid (B), Gd and Ce: Figure 10 shows a comparison of the B and Gd removal as compared to Ce. Gd analyses by ICPMS are more sensitive than ICPEES for either Gd or B. Gd appears to have a small elution peak in all experiments. B did not appear to have an elution peak in the Ce experiments but an apparent peak is present in the Pu experiment Cr314. The difference between the Column A specifications for Gd and B (100 µg B/g Pu vs. 3 µg Gd/g Pu) makes it more practical to achieve the purity specification with B as the neutron poison in the H-Canyon dissolution process. Use of Gd could be reconsidered if its specification could be raised to a similar level. Boron does pose analytical risks as sample and reagent contamination is more likely with B than Gd due to its abundance in nature.

Alkali Metal (1A) Impurities - 1+ Valence (Li, Na, K, Cs): Figure 11 shows the behavior of the alkali metals that were included in the feed solution compared to Pu, Am and Ce. The alkali metal elements are not expected to have any interaction with the resin and high DF's are thus expected. Analytical problems limit the results for most of these elements and for this reason ¹³⁷Cs was included in the feed for the Pu experiment. Lithium, K and Na appeared to reach the detection limit for ICPEES after 2-3 BV of wash. The rate of Cs removal slowed significantly beyond ~5 BV's wash and an apparent elution peak was observed. We presume that the apparent Cs elution peak represents Cs that was physically trapped in the resin structure by the large Pu hexanitrate complex. The ICPEES analyses for K of the Displacement and Hearts showed a similar (but larger) elution peak, but that analysis had a large background in the reagent blank that complicates interpretation of those data. The final Hearts analysis showed that K was above the Column A specification level but that value had a high uncertainty due to the reagent blanks. Table 10 shows predictions that Li, Na and K would all make Column A specification after 4 BV's of wash (using the Method B calculation for K discussed later in Discussion and Application section). The Table 10 prediction for K is inconsistent with the K impurity result in the Table 7. The 1+ valence elements are likely removed to the Column A specification limits within the first few BV's of decontamination wash but the K result on the Pu experiment provides a single contradictory result.

Impurities with 2+ Valence (Ca, Mg, Cu, Mn, Zn): Figure 12 shows the behavior of the 2+ valence impurities that were included in the feed solution compared with Pu, Am, and Ce. These impurities are reported to have no interaction with nitrate anion exchange resin and appeared to reach background concentrations after 2 to 5 BV's of wash. These elements were all measured by ICPEES. The ability to measure a high DF is limited by the ability of the analytical detection method to consistently measure low concentrations. Manganese has a particularly low detection limit and allows for confirmation of a high DF and observation of an elution peak similar to that observed for Cs. Other elements such as Cu, Ca, Zn and Mg have higher detection limits. The Ca values for Cr311 were near the analytical reporting limit. The DF's for Ca, Cu, Mg and Zn were limited by the small amount of each element in the feed and the detection limits for these elements by ICPEES. The Pu test may show

a small elution peak for Mn, but detection limitations did not allow the identification of an elution peak for Ca, Mg, Cu or Zn. The 2+ valence elements appear to be removed to the Column A specification limits within the first 2 to 4 BV's of decontamination wash.

Gallium: Figure 13 shows the behavior of the Ga included in the feed solution compared with Pu, Am and Ce. Ga was measured by ICPMS and mass number 69 was used for this plot. Mass number 71 may have interference from doubly-charged ^{142}Ce for the Ce experiments and shows significantly different results. The Ga results are shown separately as the analytical method is currently being extended to improve the Ga detection limit and the interferences may not be fully understood. These results are near the detection limit for Ga by the instrument and method used in the analysis. The results from the Ce experiment suggest that there may be a small Ga elution peak but this is somewhat ambiguous in the Pu experiment even though it does appear that higher levels of Ga were present in the three eluate samples. Gallium will not be considered a specification problem as the Column A allowable concentration is high but its accurate quantification at low concentrations poses some limitations if we attempt to produce material at the Column B limit.

Impurities with 3+ Valence (Al, Fe, Ga): Figure 14 shows the behavior of the Al, Fe and Ga that were included in the feed solution compared with Pu, Am and Ce. Aluminum and Fe are significant process-added impurities and Ga is the major feedstock impurity in AFS-2 metals. Generally these elements behave similarly (as expected), with the bulk of the impurities in the feed solution removed from the column in the initial 3 to 5 BV's of wash. Beyond 3 to 5 BV's, these results suggest that the concentrations are either below the detection limit or near enough to introduce variability in the results. The Cr311 Al results appear different due to the lower concentration of Al that was used in the feed, but the Al concentration beyond 5 BV's was similar for both experiments. The Al results in all experiments were often limited by the detection limits but higher concentrations were observed in the elution samples, particularly in Cr314. These three 3+ valence elements (Al, Fe, Ga) appear to be easily washed to less than 10% of the Column A specification with the 10 to 19 BV's of wash that was used in these experiments. The 3+ valence elements appear to be removed to the Column A specification limits within the first 2 to 3 BV's of decontamination wash. Elevated concentrations of Al and Fe were measured in the Hearts samples for the Pu experiment but the concentrations were still < 50% the Column A specification after 10BV's of wash.

Anion Impurities (Sulfate, F, Formate): Figure 15 shows the behavior of the sulfate, F and formate which were included in the feed solution. Formate is present due to its use as a stabilizer in the Ludox HS-30 that was used as the Si source. The amount of formate measured in the feed for the Ce experiments was higher than expected from the information provided on the Material Safety Data Sheet but the manufacturer did not make clear how much the formate concentration might vary. Similar levels of formate were not found in the Pu experiment even though a larger amount of Ludox HS-30 was used in both the Cr313 and Cr314 Feed preparation. The IC anions analytical method is not as sensitive as the other analytical techniques that we are using but the data obtained do show that these anions are washed out to the detection limits within 2 to 3 BV's of wash during the Ce experiments. Due to the measurement limitations for the concentration of F and Cl in the Feed/Raffinate solutions, no DF measurement was attempted in the Pu experiments. Neither formate nor sulfate is expected in the HB-Line feed solution. The detection limit for F in the Hearts samples was significantly higher than the Column A specification limit ranging from <2000 to <10,000 $\mu\text{g/g}$ Pu. Additional work is planned to investigate the behavior of F in oxalate precipitation and calcination to measure the additional DF provided by those process steps since F will be added in the H-Canyon dissolution process. Analytical detection limits prevent meaningful determination of the removal of F to meet the Column A specification. The analytical detection limits for S by ICPEs are expected to be comparable to the Column A specification, but due to the lack of sulfate in the production process, S is not expected to pose a specification process risk.

Polymeric Impurities (W, Si): Figure 16 shows the behavior of the W and Si that were included in the feed solution compared with Pu, Am and Ce. The feed solution from Cr310 was cloudy and solids were removed by filtration just prior to the experiment. Analysis of those solids found tungstic acid as the only component. An apparent peak in the Displacement sample can be observed in the W results in Figure 16 which may be due to polymeric solids that were washing from the frit at the bottom of the column at the start of the elution step. Silica, possibly existing in colloidal form, has a somewhat erratic behavior in these experiments. For the Ce experiments, Si was initially observed in the 2-6 $\mu\text{g/mL}$ concentration in most of the check standards. Reanalysis of the reagent blanks in plastic vials indicated that the original glass sample vials were the source of the Si contamination. The glass ion exchange column did not appear to contribute significant amounts of Si probably due to the relatively short contact time. Re-measurement of the wash and elution samples from the Ce experiments (Cr310 and Cr311) lowered the Si concentration in many samples to the AD detection limit. The values for Si measured in the elution samples were limited by the amount of Si observed in the reagent blank for the Pu separation method used on those samples. The concentrations of Si measured in the product samples all appear to be less than 50% of the Column A specification, but Si is a species that is challenging to control by anion exchange and it would not be desirable to allow significant Si to be introduced into the process. The concentrations of Si that were studied and analytical limitations prevented the measurement of DF's for Si to < 150 .

DISCUSSION AND APPLICATION

Required Wash Volume Estimates: Estimates of the wash volumes required to achieve the Column A purity limits for the heart cut are provided in Table 10 for each element added to the AFS-2 feed simulant (excluding Ce and Cu, for which no specified limits exist). These estimates were calculated using the measured amounts of each element in the various wash samples for each test (Method A). To determine the minimum wash volume, the mass of the element present in each successive wash bottle starting from the last was added to the amount in the product bottle until the calculated impurity level (in $\mu\text{g/g}$ Pu) exceeded the specified limit. The product volume was assumed to be 150 mL or 0.77 BV and the heart Pu concentration was assumed to be 50 g/L in these calculations for the Ce experiments while actual values were used for the Pu experiment. For samples containing less than the detectable limit of an element, it was assumed that the sample actually contained the detectable limit for that element (Table 10, Note a). For samples where the analyses are not particularly sensitive to the impurity (e.g. K and S), Method A for estimating the minimum required wash volume is not particularly useful as that method will predict a relatively high wash volume requirement even though most of the impurity appeared to be quickly washed from the resin.

For those cases where the element is presumed to have no chemical interaction with the resin, an alternate calculation method was used to estimate the minimum wash volume. In this alternate calculation method (hereafter referred to it as Method B), the assumption is made that the amount of impurity in a Hearts "peak" is not significant and the level of impurity in the later BV's of wash solution is not significant. The point in the wash curve where the impurity concentration (in mg/L) drops to the value required to reach the specification limit at the Hearts Pu concentration is then used as a minimum estimate for the required wash volume. In Table 10, Method B was used for K and S for all three experiments and then for Si in Cr311.

Although a small elution peak was observed in the Gd and the Sm concentration profiles, the larger wash volume needed to achieve the specification is primarily due to the fact that the Column A limits for these elements are low ($3 \mu\text{g/g}$ Pu for Gd) compared with most other elements. When Pu was present, the minimum wash volumes increased by at least a factor of two.

Precipitation DF: An additional decontamination factor can be estimated for the subsequent plutonium oxalate precipitation process for impurities expected to remain soluble during precipitation such as B as boric acid. The DF from precipitation can be calculated considering the dilution of the Pu product by the addition of oxalic acid and that only a fraction of the total impure solution volume remains in the plutonium oxalate cake after filtration. The flowsheet strategy document indicates that the addition of oxalic acid to the precipitator feed solution will result in dilution of the concentration by a factor of 1.9.¹⁹ Precipitation tests conducted at SRNL have shown that a typical plutonium oxalate filter cake contains approximately 27 wt % residual liquid.²³ Based on this information, a theoretical DF of 46 is expected during precipitation and filtration of the Pu product from anion exchange, neglecting any chemical affinity or trapping for the species. This estimated DF, coupled with the purification achieved by the 10 BV's wash, drives the expected concentration of the impurity elements in the product oxide to well below the column A specifications. It has to be emphasized that the assumption that any impurity will remain soluble has not been experimentally validated and it is possible that unanticipated co-precipitates including these elements could form during plutonium oxalate precipitation that would reduce the expected DF. The estimated DF clearly would not apply to such impurities as Gd, Sm, Am, Ce, and Th but would likely apply to boric acid and K which were problematic in the current study. Experimental verification of the decontamination of these species across precipitation and calcination is recommended.

Comparison of B with Cs: Boron, Al, K, F and Fe are all present in the feed at relatively high concentrations both on a mass basis as well as a molar basis. Of these major impurities, B has the lowest specification limit. Although most of this work was done on a mass basis, it is more appropriate to treat the removal efficiency on a molar basis as individual molecules must be washed from the resin bed and the higher molecular weight species are weighed higher. Figure 17 shows washing behavior of the major elements that can be measured for the Pu experiment. This graph shows Cs, Al and Mn all having similar wash behavior. The slope of the wash region appeared to be different for Gd, Fe and B than for Cs, Al, Mn with Gd, Al and B a somewhat like Am. Potassium is not shown since many of the values of the wash were below the MDL even though the Hearts sample appeared to contain some K. The K analyses for the Pu product samples have additional uncertainty caused by the high reagent blanks for several impurities including K. Although the K result cannot be dismissed, it may not be accurate. Even though K did not make the Column A specification in the Pu experiment, it is expected to behave similarly to Na, Li and Cs and it seems likely that during production it would be a problem only to the extent that the feed impurity levels are very high. Any additional DF such as in precipitation (as described above) will allow K to make the Column A specification.

We have theorized that it is likely that some impure feed solution could be physically “trapped” or “blocked” inside the porous resin structure and then later released as the Pu is released during elution. Since Pu gradually exchanges loading sites during the wash step as Pu migrates down the length of the column, some impure solution will be released as the wash continues. Also since the molecular species are of different sizes and have different diffusivities, some species will “escape” or “bleed” from the resin structure at a higher rate than others. There is much in the results from these experiments that is consistent with that theory and similar observations have been seen by others^{24,25}. Although there is still much that we cannot explain, we conclude that there are at least two credible explanations for lower wash concentration ratios: 1) if the impurity species has already been washed from the column, it's bleed rate would be lower, and 2) if the diffusivity of a impurity species is rela-

²³ M. L. Crowder, “Pu Oxalate Cake Density”, SRNL-NB-2012-00010, Savannah River National Laboratory, Aiken, SC, (April, 2012).

²⁴ E. Bluhm, F. Coriz, K. Abney, S. Balkey, et al., “Plutonium Oxide Polishing for MOX Fuel Fabrication”, LA-UR-03-7565, Los Alamos National Laboratory, Los Alamos, NM, October 2003.

²⁵ D. B. James, W. A. Beyer, “Processing of Plutonium by Ion Exchange VIII. Self-Diffusion Studies in Anion-Exchange Resin”, LA-3534, Los Alamos National Laboratory, Los Alamos, NM, June 1966.

tively low, then it bleed rate would also be lower. Of course if the impurity species is weakly absorbed onto the resin, then it will continually bleed into the wash. This is the behavior that we seem to see for Ce, Sm and Gd in all of the experiments. The B results on the Pu experiment seem different in that we did not see significant bleeding of B after about 5 BV's wash in the Ce experiments but in the Pu experiment B was very similar to Gd. We do not believe that B had any interaction with the resin, but the results from the Pu experiment make us consider that as a possibility. Since we did not see this behavior during the Ce experiments, it seems likely that there is another mechanism at work here that we do not recognize.

Only the two anionic impurities F and S could not be confirmed to be removed to below the Column A specification by the washing step in these experiments and this was believed due to analytical limitations.

Based on the estimates shown in Table 10 and after consideration of the effect of measurement limitations it is believed that the Column A specification can be achieved with 10 BV's of wash for most elements expected in the feed. Gadolinium and Sm could require significantly more wash volume if those elements were present in the process due to the relatively low specification limits. However, neither is expected in the feedstock or process in other than trace concentrations. The large concentration of B used in the feed solutions and the moderately low limit make B specification difficult to achieve by anion exchange alone.

A minimum wash volume table for Column B specification is included as Table 11. Since many of the impurities (other than the neutron absorbing elements) have similar limits, many of the values are similar to those in Table 10. Boron, Ga, Gd and Sm would require a significant additional wash volume over the 10 BV's recommended for the Column A specification. Elimination of those impurities from the feedstock and the dissolution flowsheet would appear to be the best strategy for a flowsheet to prepare material to achieve that specification.

Disclaimer: This report involves the analysis of many individual data points, many of which are near the detection limit of the analytical techniques or involve interferences between elements. The results contained in this report are the best available at the time this report was written. Detection limits are somewhat subjective and in some cases could be interpreted differently.

RECOMMENDATIONS

There are several impurity issues that are not completely resolved. The following are recommendations to address the limitations of the work performed thus far.

- The analytical limitation for analysis of F and Cl in Pu solutions should be addressed by performing a precipitation/calcination test with Pu product solution from this work and both with and without F and Cl added to determine a combined DF for those anions across precipitation and calcination. Analysis of the product oxide from this test by pyrohydrolysis is expected to establish sufficient basis for the necessary DF for these species.
- Verification of the estimated DF for B in precipitation is important as the opportunity for coprecipitation of impurities is possible. A similar technique as has been proposed for F/Cl with re-dissolution of the oxalate or oxide and analysis by ICPES or ICPMS (F/H Area Laboratories) is a likely route to verify that a significant DF for B should occur.
- Although S (as sulfate) is not expected in either the feed materials or in the process reagents, measurement of oxide samples by C/S analysis is expected to show a significant DF for S and may be worthwhile.

- Even though the Pu testing had difficulty obtaining a K analytical result that was within the specification for the Pu product from anion exchange, this was somewhat dismissed as an analytical problem. This uncertainty should be reduced by further improvement in the separation method used to remove Pu as an ICPEES sample preparation step and will be needed for the integrated demonstration. Alternate paths would include analysis for K by AA or ICPMS (by F/H laboratories).

CONCLUSIONS

Use of Gd as a neutron poison would appear to require a larger volume of wash for the proposed Column A specification. However since B has a higher proposed specification and is more easily removed by washing, it appears to be the better candidate for use in the H-Canyon dissolution process. Some difficulty was observed in achieving the Column A specification due to the limited effectiveness that the wash step has in removing the residual B after ~4 BV's wash. However a combination of the experimental 10 BV's wash results and a calculated DF from the oxalate precipitation process yields an overall DF sufficient to meet the Column A specification. For those impurities (other than B) not removed by 10 BV's of wash, the impurity is either not expected to be present in the feedstock or process, or recommendations have been provided for improvement in the analytical detection method or validation of calculated results. In summary, boron is recommended as the appropriate neutron poison for H-Canyon dissolution and impurities are expected to meet the Column A specification limits for oxide production in HB-Line.

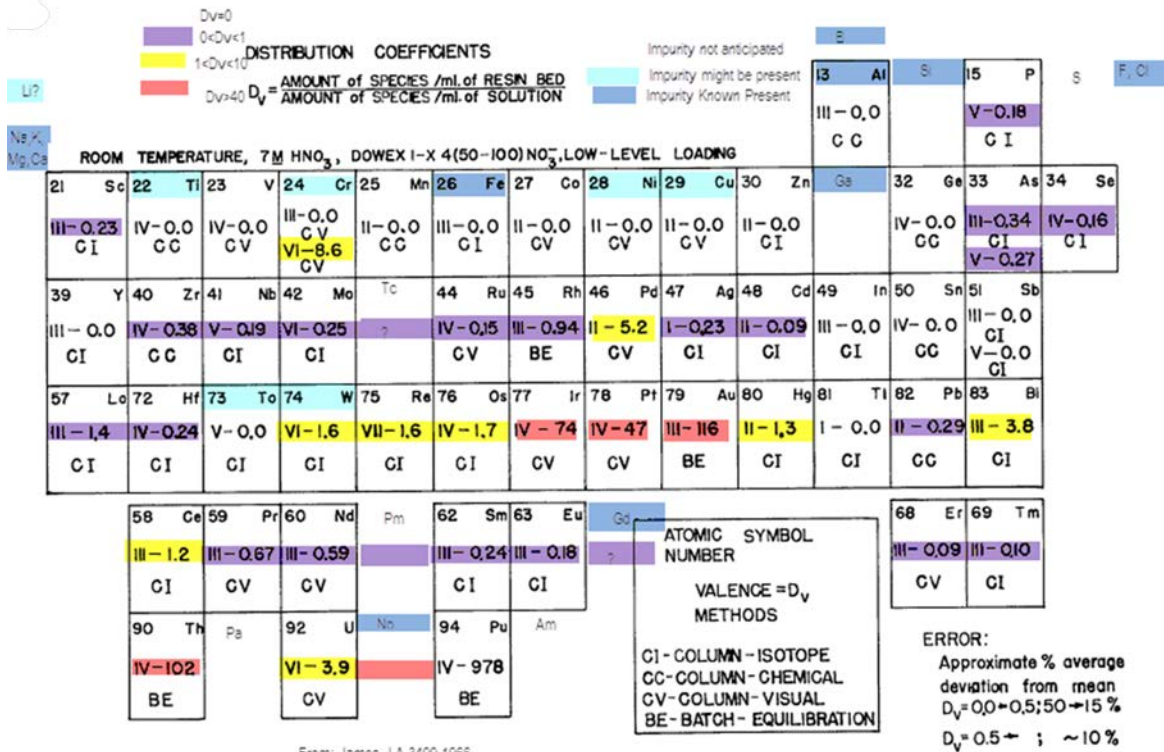
APPENDIX: Figures and Tables

Table 1. Draft PuO₂ Specification Limits.

Chemical Component	B μg/g Pu	A μg/g Pu	Exceptional μg/g Pu
Ag (Silver)	100	250	10,000
Al (Aluminum)	100	500	10,000
Am (Americium)		7000	
B (Boron)	1	100	1000
Be (Beryllium)	100	100	2000
Bi (Bismuth)	10	100	1000
C (Carbon)	500	1000	5000
Ca (Calcium)	150	500	10,000
Cd (Cadmium)	5	10	1000
Cl ^a (Chlorine)	250 ^a	250 ^a	500
Co (Cobalt)	50	100	10,000
Cr (Chromium)	200	1000	1500
Cu (Copper)	100	100	500
Dy (Dysprosium)	0.5	1	1000
Eu (Europium)	0.5	1	1000
F ^a (Fluorine)	250 ^a	250 ^a	500
Fe (Iron)	500	2000	3000
Ga (Gallium)	0.12	12,000	12,500
Gd (Gadolinium)	0.5	3	250
In (Indium)	20	20	1000
K (Potassium)	100	300	10,000
Li (Lithium)	100	400	10,000
Mg (Magnesium)	200	500	10,000
Mn (Manganese)	100	100	1000
Mo (Molybdenum)	100	100	1000
N (Nitrogen)	300	400	400
Na (Sodium)	100	1000	10,000
Nb (Niobium)	50	100	3500
Ni (Nickel)	200	5000	12000
Np (Neptunium)		500	
P ^b (Phosphorus)	250 ^b	200	1000
Pb (Lead)	100	200	1000
S ^b (Sulfur)	250 ^b	250	1000
Si (Silicon)	150	200	200
Sm (Samarium)	2	2	1000
Sn (Tin)	100	100	2500
Ta (Tantalum)	200	200	500
Th (Thorium)	50	100	100
Ti (Titanium)	100	100	2500
U (Uranium)	100	5000	
V (Vanadium)	5	300	2500
W (Tungsten)	100	200	2500
Zn (Zinc)	100	150	1000
Zr (Zirconium)	50	50	1000

^a Limits for F and Cl are F+Cl < 250.

^b Limits for P and S are P+S < 250 for Column B.



Distribution coefficients for certain elements in a nitrate anion-exchange system.



Figure 1. Distribution Coefficients in a Nitrate Anion Exchange System with Expected Impurities in HB-Line Process.

Table 2. Process Scaling: HB-Line Column vs SRNL Ce and Pu Columns.

		Recon- ditioning	Feed	Decontamination initial	Decontamination final	Elution			
		Pu (g/batch)	1200						
		Pu (g/l)	4.5						
		HNO3 (M)	8	8	8	8	0.35		
294.2	cm ²	HB-Line	up	up	up	up	down		
68.58	cm	Flow (L/min)	1.4	1.1	1.1	2	0.7		
		v (mL/min/cm ²)	4.8	3.7	3.7	6.8	2.4		
20.2	L	Volume (L)	30	260	40	160	60		
		Time (min)	21	236	36	80	86	7.7	h total
		BV	1.5	13.0	2.0	8.0	3.0		
		mgs Pu/min/cm ²	17						
2.835	cm ²	SRNL Hood -Ce	up	up	up	up	down		
68.58	cm	Flow (mL/min)	20	10.6	10.6	19.3	6.8		
1.90	cm	v (mL/min/cm ²)	7.1	3.7	3.7	6.8	2.4		
194.44	cc	Volume (mL)	200	1964	388	3492	450		
		Time (min)	10	185	37	181	66	8.0	h total
		BV	1.0	10.1	2.0	18.0	2.3		
		mgs Pu/min/cm ²	19						
1.247	cm ²	SRNL Glovebox -Pu	up	up	up	up	down		
68.58	cm	Flow (mL/min)	10	4.5	4.5	8.5	3		
1.26	cm	v (mL/min/cm ²)	8.0	3.6	3.6	6.8	2.4		
85.512	cc	Volume (mL)	100	1000	172	688	260		
		Time (min)	10	222	38	81	87	7.3	h total
		BV	1.2	11.7	2.0	8.0	3.0		
		mgs Pu/min/cm ²	18						

Note: Up and down designates flow direction through resin bed



Figure 2a. Assembled Column for Non-Radioactive DF Experiments.



Figure 2b Screen used to Retain Resin Bed.



Figure 3. Assembled Column for Glovebox DF Experiments.

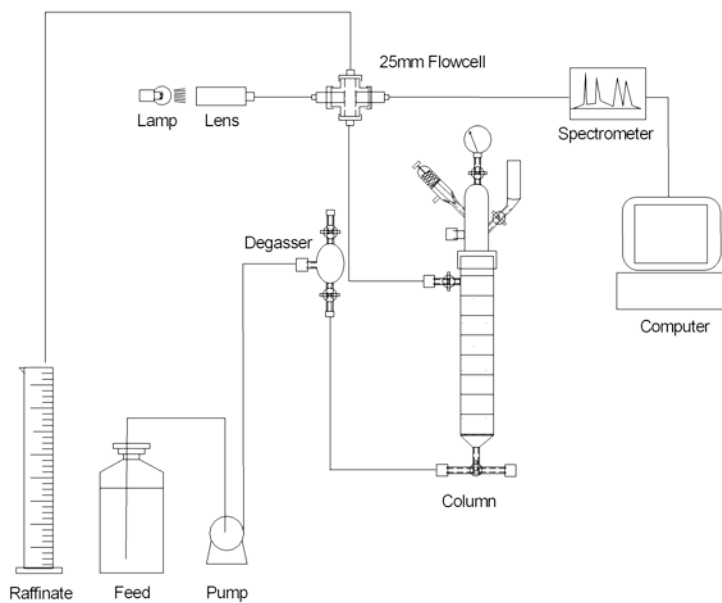


Figure 4. Up-flow Load/Wash Experimental Setup.

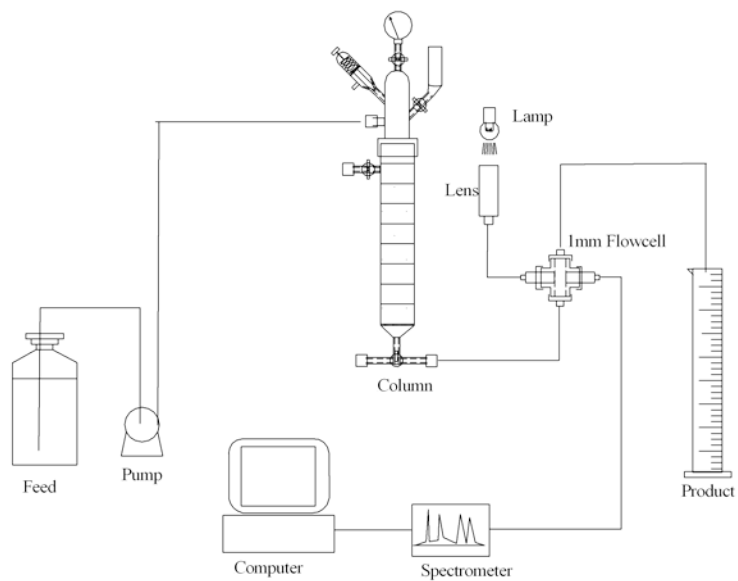


Figure 5. Elution Experimental Setup.

Table 3. Impurities used for Anion Exchange Testing.

M	g/L	μg/g Pu	Chemical Component	
0.2	5.4	1349075	Ag	Little or no data available. Did not test
			Al	Will add in process
			Am	Pu Daughter product, grows in over time
0.0925	1	250000	As	No spec
			B	May add in process
			Ba	No spec
			Be	Not present in concentrations above Column B limit
			Bi	Some adsorption onto IX, but not very soluble
0.0025	0.1	25000	C	Will add downstream in oxalate precipitation
			Ca	Mostly below Column B Limit
			Cd	Little or no data available. Did not test
0.001	0.1	24000	Ce	No spec, some absorption by IX, DF Np 15. Surrogate for Pu.
			Cl	Present as impurity, Unclear on concentration. Test in Precipitation only.
			Co	Little or no data available. Did not test
			Cr	Not present in concentrations above Column B limit
			Cu	Mostly below Column B Limit
			Dy	Little or no data available. Did not test
			Eu	Little or no data available. Did not test
			F	Will add in process,
			Fe	Will add in process,
			Ga	Present in Pu metal
			Gd	May add in process
0.1	3.9	977550	Hf	No spec
			In	Little or no data available. Did not test
			K	Will add in process,
			La	No spec
			Li	Somewhat high, not high in DE analysis or MIS
			Mg	Mostly below Column B Limit
			Mn	Not present in concentrations above Column B limit, Np DF 300k in lab
			Mo	Mostly below Column B Limit
			N	Little or no data available. Did not test
			Na	DF 14000 for Np process
0.0043	0.1	25000	Nb	Little or no data available. Did not test
			Ni	Corrosion product, Observed Np Process DF of 400
			Np	Isolated contaminated materials, Known IX problems
			P	Little or no data available. Did not test
			Pb	Not present in concentrations above Column B limit
			Pu	Present in Lab Tests as FS. Not present in process.
			S	Present in Lab Tests as FS. Not present in process.
			Si	Mostly below Column B Limit, but Si is endemic
			Sm	Not present in process but added for comparison to Gd.
			Sn	Not present in concentrations above Column B limit
0.0167	4	1000000	Ta	Not present in concentrations above Column B limit
			Th	No data available, Known problem IX
			Ti	Not present in concentrations above Column B limit
			U	limited data, DF= 500 in HB-Line Np Process
			V	Col B limit low, speciation complicated
			W	Mostly below Column B Limit, anionic species possible
			Y	Not present in concentrations above Column B limit
			Zn	DF 400 in Np Process
			Zr	Not present in concentrations above Column B limit

Table 4. Feed Preparation for Cr310, Cr311, Cr313 and Cr314 Experiments.

Component	Cr310		Cr311		Cr313		Cr314	
	mass g	Volume mL	mass g	Volume mL	mass g	Volume mL	mass g	Volume mL
H ₂ O		1000		1000		275		275
KF	11.42		11.42		5.70		5.70	
Gd(NO ₃) ₃ *6H ₂ O	2.29				1.21		1.22	
Al(NO ₃) ₃ *9H ₂ O	146.99		14.71		76.14		76.10	
B(OH) ₃	11.51		11.53		10.00		9.92	
Fe ₂ (NO ₃) ₃ *9H ₂ O					4.00		4.13	
Ga(NO ₃) ₃ *6H ₂ O	0.80		0.83		0.50		0.51	
Ca(NO ₃) ₂ *4H ₂ O	1.20		1.22		0.70		0.71	
NaNO ₃	0.61		0.60		0.60		0.59	
Mg(NO ₃) ₂ *6H ₂ O	2.23		2.20		1.53		1.49	
Sm(NO ₃) ₃ *6H ₂ O	0.50		0.50		0.50		0.51	
Na ₂ WO ₄ *2H ₂ O	0.35		0.00					
Cu(NO ₃) ₂ *2.5H ₂ O	0.31		0.31		0.50		0.50	
Ce(NO ₃) ₃ *3H ₂ O	0.51		0.52					
Zn(NO ₃) ₂ *6H ₂ O	0.50		0.50		0.60		0.60	
LiNO ₃	0.40		0.40		0.41		0.40	
50 wt % Mn(NO ₃) ₂		8		8		8		8
HS-30 Ludox (SiO ₂)		0.6		0.6		0.6		0.6
40 wt % FS		55		55		22		22
Pu in 3.2 M HNO ₃ ^a						290		290
Cs-137 Spike Solution								7.0
70 wt % HNO ₃		900		900		400		400
Approx. Volume, mL		1964		1964		1030		1037

^a Pu solution contained 3.2 M HNO₃, -0.01M KF and 16 g/L Pu.

Table 5a. Feed Analysis for Cr310 and Cr311 Experiments.

Element	Cr310			Cr311			Method
	mg/L	mM	µg/g Pu	mg/L	mM	µg/g Pu	
AD Sample ID	3-295988			3-296169			
Pu	4000	17		4000	17		Assumed
Nitrate	490000	7903	122500000	469000	7564	117250000	IC
Al	5850	217	1460000	589	22	147000	ICPES
S	4500	140	1130000	5080	158	1270000	ICPES
B	1050	97	263000	1100	102	275000	ICPES
K	3530	90	883000	3790	97	948000	ICPES
F	1530	81	383000	1570	83	393000	IC
Fe	3430	61	858000	3600	64	900000	ICPES
Mn	945	17	236000	1110	20	278000	ICPES
Na	121	5.3	30300	97.3	4	24300	ICPES
Mg	122	5.0	30500	116	4.8	29000	ICPES
Ca	119	3.0	29800	120	3.0	30000	ICPES
Gd	406	2.6	102000	< 0.34	0.002	86	ICPES
Gd-160	399	2.5	99900				ICPMS
Si	41.9	1.5	10500	23.5	0.8	5880	ICPES
Ga-69	67	1.0	16800	11	0.2	2780	ICPMS
Zn	59.8	0.9	15000	59.7	0.9	14900	ICPES
Cu	42.3	0.7	10600	48.6	0.8	12200	ICPES
Sm-149	87	0.6	21700	86	0.6	21600	ICPMS
W-184	59	0.3	14700	0			
Ce	37.9	0.3	9480	54.4	0.4	13600	ICPES
Ce-140	41	0.3	10100	57	0.4	14200	ICPMS
Am							
Li	1.64	0.2	410	15.1	2.2	3780	ICPES
Ni	1.74	0.03	435	0.938	0.02	235	ICPES
Pb	< 7.16		1790	< 1.15		288	ICPES
Sn	< 5.61		1400	< 0.9		225	ICPES
Mo	< 2.25		563	< 0.99		247	ICPES
Co	< 0.85		213	< 0.85		213	ICPES
Cr	< 0.82		205	< 0.82		205	ICPES
Cd	< 0.64		160	< 0.102		26	ICPES
V	< 0.47		118	< 0.08		19	ICPES
Ti	< 0.13		33	< 0.021		5	ICPES
Be	< 0.12		30	< 0.06		< 15	ICPES

Note: Pu was not present in Cr310 or Cr311 but impurities are calculated based on an assumed concentration.

Table 5b. Feed Analysis for Cr313 and Cr314 Experiments.

Element	Cr313			Cr314			Method
	mg/L	mM	ug/g Pu	mg/L	mM	ug/g Pu	
AD Sample ID	300297549			300297555			
Pu	6026	25		5638	24		alpha/gamma
Nitrate	431000	6951	76400000	419000	6758	74300000	IC
Al	5390	200	956000	5600	208	993000	ICPES
S	3630	113	644000	3880	121	688000	ICPES
B	1630	151	289000	1770	164	314000	ICPES
K	3480	89	617000	3620	93	642000	ICPES
F	1570	83	278000	1600	84	284000	IC
Fe	3180	57	564000	3440	62	610000	ICPES
Mn	1350	25	239000	1540	28	273000	ICPES
Na	176	7.7	31200	164	7.1	29100	ICPES
Mg	141	5.8	25000	242	10.0	42900	ICPES
Ca	111	2.8	19700	118	2.9	20900	ICPES
Gd	372	2.4	66000	389	2.5	69000	ICPES
Gd-160	379	2.4	67200	398	2.5	70700	ICPMS
Si	59.2	2.1	10500	77.1	2.7	13700	ICPES
Ga-69	77	1.1	13700	83	1.2	14800	ICPMS
Zn	135	2.1	23900	128	2.0	22700	ICPES
Cu	115	1.8	20400	134	2.1	23800	ICPES
Sm-149	153	1.0	27100	192	1.3	34100	ICPMS
W-184							
Ce	0.965	0.01	171	< 0.965		171	ICPES
Ce-140							
Am	5.9	0.02	1040	5.8	0.02	1030	alpha/gamma
Li	23	3.33	4100	37	5.32	6540	ICPES
Ni	1.6		280	0.26		45	ICPES
Pb	< 7.16		1270	< 7.16		1270	ICPES
Sn			0	< 5.61		995	ICPES
Mo	< 1.48		260	< 0.99		175	ICPES
Co	< 0.85		151	< 0.85		151	ICPES
Cr	< 1.02		181	< 1.02		181	ICPES
Cd	< 0.102		18	< 0.102		18	ICPES
V	< 0.39		69	< 0.39		69	ICPES
Ti	< 0.13		23	< 0.13		23	ICPES
Be	< 0.06		11	< 0.06		11	ICPES

Note: Raffinate sample analysis from Cr313 reported in place of feed analysis. Concentrations diluted by ~6% based on Cr314 results.

Table 6. Targeted and Actual Flowrates.

	Target mL/min	Cr-310 Actual mL/min	Cr-311 Actual mL/min		Target mL/min	Cr-313 Actual mL/min	Cr-314 Actual mL/min
Loading	10.6	10.4	9.8		4.5	5.3	4.4
WC1 Wash	10.6	10.1	7.6		4.5	5.1	4.1
WC2 Wash	10.6	11.2	10.4		8.5	8.4	7.6
WC3 Wash	19.3	17.4	19.5		8.5	9.1	6.0
WC4 Wash	19.3	17.2	18.0		8.5	8.4	8.1
WC5 Wash	19.3	19.3	21.6		8.5	7.5	8.3
WC6 Wash	19.3	18.9	21.1		8.5		9.4
WC7-10 Wash	19.3	20.0	18.0	WC7	8.5		7.6
WC11-15 Wash	19.3	19.8	19.4	WC8	8.5	9.2	8.3
WC16-20 Wash	19.3	19.2	20.9	WC9	8.5	8.6	8.1
Displacement ^a	6.8	2.5 ^b	2.4		3.0	2.9	1.8
Hearts	6.8	1.5 ^b	2.6		3.0	3.4	3.0
Tails	6.8	1.5 ^b	2.8		3.0	3.2	3.0
Avg. Wash 1-2	10.6	10.7	8.8				
Avg. Wash 3-20	19.3	19.3	19.6	WC2-9	8.5	8.7	7.8
Avg. Elution	6.8	1.8	2.6		3.0	3.2	2.6

^a Cr310 Displacement volume was increased by the drainage of column head solution into Displacement bottle.

^b Lower than target flow rate for elution in Cr310 resulted in lower than targeted volumes for Hearts and Tails solutions.

Table 7. Analyzed Impurity Concentrations in Hearts Samples.

Element	Col A ug/g Pu	Cr310 ^a ug/g Pu	Cr311 ^a ug/gPu	Cr313 ^b ug/g Pu	Cr314 ^b ug/g Pu
Al	500	9.2	12.8	136	206
B	100	< 4.5	< 4.5	129	153
Ca	500	5.1	4.5	61.8	119
Ga-69	12000	0.4	< 0.12	1.2	1.2
Gd	3	< 6.9	< 6.9	21.1	24.6
Gd-160	3	0.5	0.1	23.3	24.4
Fe	2000	2.8	3.0	10.2	75.0
F	250	<2000	<10,000		
K	300	< 96.2	< 96.2	348	463
Li	400	< 4.7	< 4.7	< 5.1	< 5.5
Mg	500	< 0.48	0.50	< 0.52	77.8
Mn	100	< 0.67	1.4	7.7	24.9
Na	1000	< 17	< 17	< 92	< 100
S	250	< 240	< 240	< 519	< 562
Si	200	< 14	< 14	68.5	99.5
Sm-149	2	1.8	1.4	42.8	48.8
W-184	200	1.0			
Zn	150	< 2.9	< 2.9	< 17	< 18

Note: Red background indicates impurity concentration above specification. Yellow indicates impurity concentration above 50% of specification. White indicates impurity concentration between 10% and 50% of specification. Green indicates impurity concentration below 10% of specification.

Note: Values from ICPMS are reported as elemental concentrations and have been corrected for natural abundance.

^a For Cr310 and Cr311, a Pu product concentration of 50 g/L was assumed.

^b Na values for Cr313 and Cr314 are analyzed with Pu present. Values for all other elements for Cr313 and Cr314 are analyzed after Pu has been removed.

Table 8a. Impurity Material Balance for Cr310, Cr311 and Cr314 Column Runs.

Component	Cr310 Material Balance				Cr311 Material Balance				Cr314 Material Balance			
	Effluent %	Wash %	Eluate %	Overall %	Effluent %	Wash %	Eluate %	Overall %	Effluent %	Wash %	Eluate %	Overall %
Al	90.9	9.7	0.001	100.7	90.8	9.2	0.019	100.0	93.9	7.5	0.025	101.5
Am									80.4	11.5	0.7	92.6
B	90.1	10.4	0.004	100.5	88.4	11.1	0.006	99.4	93.8	8.0	0.071	101.8
Ca	89.9	10.2	0.040	100.1	91.7	9.8	0.06	101.5	95.8	8.1	0.762	104.6
Ce	7.9	68.8	5.02	81.7	11.7	66.7	10.3	88.7				
Ce-140	10.5	76.9	8.3	95.6	11.4	73.7	9.4	94.4				
Cs									87.8	7.3	0.004	95.1
Cu	90.8	10.3	0.04	101.1	91.6	9.6	0.06	101.2	92.5	8.5	0.180	101.2
Fe	91.0	9.8	0.002	100.7	90.6	9.0	0.0023	99.5	93.9	7.6	0.018	101.5
Ga-69	92.2	9.6	0.003	101.8	93.9	9.6	0.010	103.5	96.4	8.7	0.030	105.2
Gd	89.2	11.2	0.015	100.4					94.3	8.1	0.046	102.5
Gd-155	89.4	11.0	0.001	100.4	85.0	14.2	0.57	99.8	93.8	9.0	0.051	102.9
Gd-160	88.0	11.1	0.001	99.1	88.0	13.2	0.28	101.5	90.3	9.0	0.050	99.4
K	90.1	10.2	0.029	100.3	90.2	9.4	0.035	99.7	93.4	7.7	0.120	101.2
Li	99.4	43.9	2.5	145.8	91.4	10.9	0.4	102.8	94.3	8.2	0.185	102.7
Mg	91.0	9.8	0.005	100.7	91.4	9.1	0.009	100.5	94.6	7.6	0.244	102.5
Mn	91.1	9.9	0.001	101.0	89.8	9.1	0.0024	98.9	94.2	7.6	0.013	101.8
Na	91.3	11.6	0.1	103.0	91.7	12.3	0.2	104.2	94.5	8.1	0.821	103.4
Pu									0.03	1.1	96.2	97.3
S	90.7	10.7	0.046	101.4	89.6	10.0	0.066	99.6	93.3	7.4	0.151	100.8
Si	13.6	5.4	0.29	19.3	103.8	66.3	0.9	171.1	34.1	3.5	1.273	38.9
Sm-149	83.6	15.2	0.007	98.8	82.3	13.7	0.013	96.0	85.5	9.5	0.203	95.2
W-184	20.5	2.1	0.051	22.6								
Zn	91.6	10.3	0.042	101.9	91.6	9.5	0.068	101.1	96.9	8.0	0.131	105.0

Table 8b. Material Balance for Pu Column Experiment Cr313 (85cc Two Piece Column Reillex HPQ™).

	AD No.	Sample Volume	Column Volumes Eluted	Pu		Pu	Am241			
				Conc. g/L	Btl g	Loaded g	Conc mg/L	Btl ug		
Feed	3-297548	1000	11.7	6.026	6.026	6.026	5.889	5889		
EC	3-297549	1020	11.9	0.0005	0.000	6.025	4.792	4888		
WC1	3-550/783	110	1.3	0.017	0.002	6.023	4.989	550		
WC2	3-550/784	90	2.3	0.044	0.004	6.019	0.731	66.1		
WC3	3-550/785	90	3.4	0.047	0.004	6.015	0.167	14.9		
WC4	3-550/786	83	4.4	0.070	0.006	6.009	0.074	6.1		
WC5	3-550/787	81	5.3	0.119	0.010	6.000	0.047	3.8		
WC6	3-551/788	78	6.2	0.137	0.011	5.989	0.033	2.6		
WC7	3-551/789	78	7.1	0.155	0.012	5.977	0.027	2.1		
WC8	3-551/790	89	8.2	0.172	0.015	5.962	0.023	2.0		
WC9	3-551/791	104	9.4	0.192	0.020	5.942	0.021	2.2		
Disp	3-297552	75	0.9	0.248	0.019	5.923	0.114	8.6		
Hearts	3-297553	95	2.0	57.794	5.512	0.411	0.342	32.7		
Tails	3-297554	104	3.2	3.648	0.381	0.031	0.004	0.5		
Mat'l Balance					5.892	97.8%		94.8%		
					g Pu Recovered					
Feed	70.4	g/L resin	Losses	0.084	g Pu	1.4%	0.01%	Raffinate		
Hearts and Tails	68.9	g/L resin		5.976			1.4%	Washes		

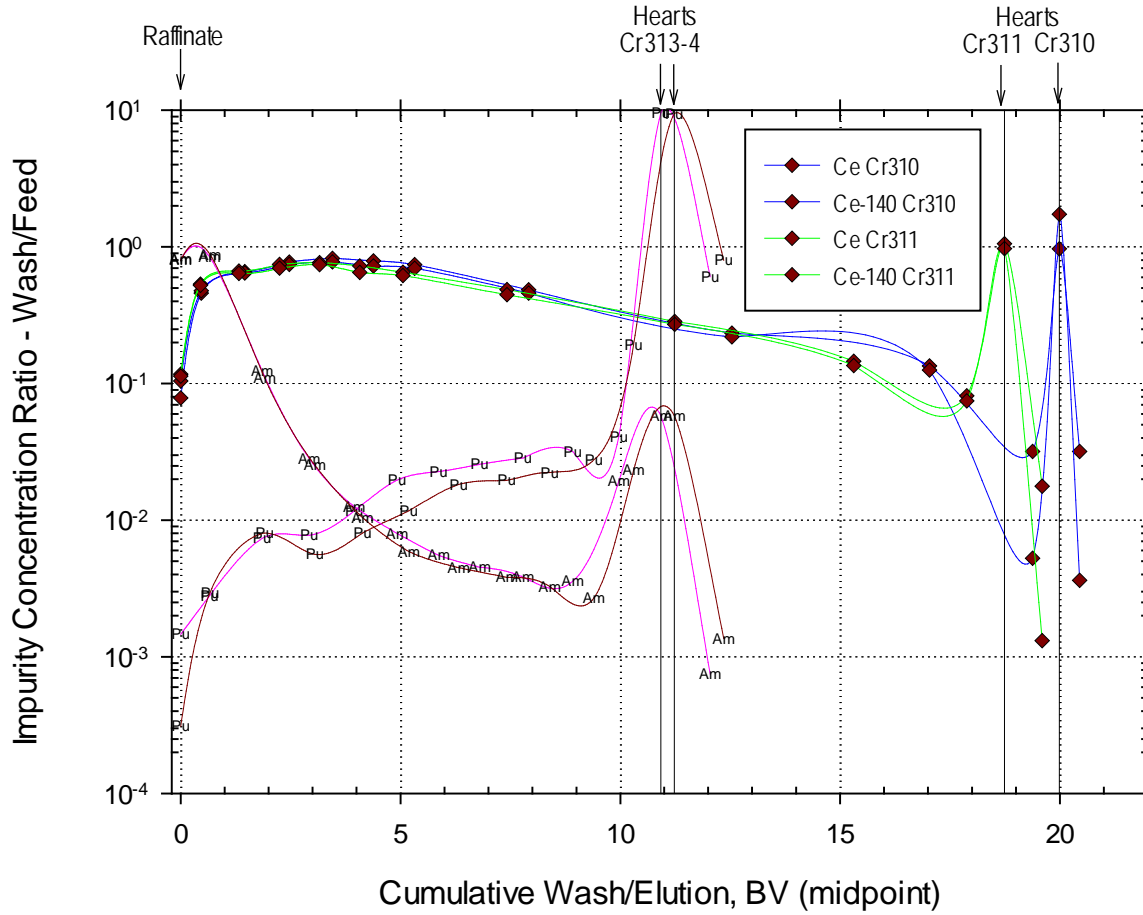
Table 8c. Material Balance for Pu Column Experiment Cr314 (85cc Two Piece Column Reillex HPQ™).

	AD No.	Sample Volume	Column Volumes Eluted	Pu		Pu	Am241		Cs137	
				Conc. g/L	Btl g	Loaded g	Conc mg/L	Btl ug	Conc uCi/L	Btl uCi
Feed	3-297555	1016	11.9	5.638	5.728	0	5.813	5906	2554	2595
EC	3-297556	1016	11.9	0.002	0.002	5.727	4.674	4749	2243	2279
WC1	3-297557	114	1.3	0.017	0.002	5.725	5.120	583	1658	189
WC2	3-297558	99	2.5	0.045	0.004	5.720	0.639	63.2	6.667	0.659
WC3	3-297559	96	3.6	0.032	0.003	5.717	0.147	14.2	1.072	0.103
WC4	3-297560	89	4.7	0.045	0.004	5.713	0.0606	5.4	0.486	0.043
WC5	3-297561	91	5.7	0.066	0.006	5.707	0.0342	3.1	0.193	0.018
WC6	3-297562	103	6.9	0.103	0.011	5.696	0.0261	2.7	0.134	0.014
WC7	3-297563	84	7.9	0.110	0.009	5.687	0.0221	1.8	0.127	0.011
WC8	3-297564	83	8.9	0.126	0.011	5.677	0.0190	1.6	0.102	0.009
WC9	3-297565	89	9.9	0.156	0.014	5.663	0.0157	1.4	0.077	0.007
Disp	3-297567	65	10.7	1.079	0.071	5.592	0.135	8.8	0.820	0.054
Hearts	3-297568	94	11.8	53.349	4.998	0.595	0.339	31.7	32.57	3.051
Tails	3-297569	98	12.9	4.502	0.443	0.152	0.008	0.777	0.069	0.007
Mat'l Balance					5.440	95.0%		92.6%		95.3%
					g Pu Recovered					
Feed	67.0	g/L resin	Losses	0.065	g Pu	1.1%	0.03%	Raffinate		
Hearts and Tails	63.6	g/L resin		5.506	Hearts & Tails		1.1%	Washes		

Table 9. Anion Exchange DF Observations.

	Cr310	Cr311	Cr313	Cr314
Al	160000	12000	7000	4800
Am-241			170	160
B	58000	61000	2200	2100
Ca	5900	6700	320	180
Ce	13	12	8	8
Cu	5200	6000	1900	2100
Fe	310000	300000	55100	8100
Ga-69	38000	24000	12000	12000
Gd	15000	0	3100	2800
Gd-160	200000	860	2700	2900
K	9200	9800	1800	1400
Li	90	810	800	1200
Mg	64000	58000	48000	550
Mn	350000	200000	31000	11000
Na	1800	1400	340	290
S	4700	5300	1200	1200
Si	750	420	150	140
Sm-149	12000	15000	630	700
W-184	14000			
Zn	5100	5100	1400	1200

Note: DF calculated as the ratio of the impurity to Pu in the feed solution divided by the ratio of the impurity to Pu in the product solution.



Note: Blue lines are Cr310, Green lines are Cr311, Pink lines are Cr313 and Dark red lines are Cr314 for all graphs.
 Figure 6. Ce, Pu, and Am Wash-Elution Profile.

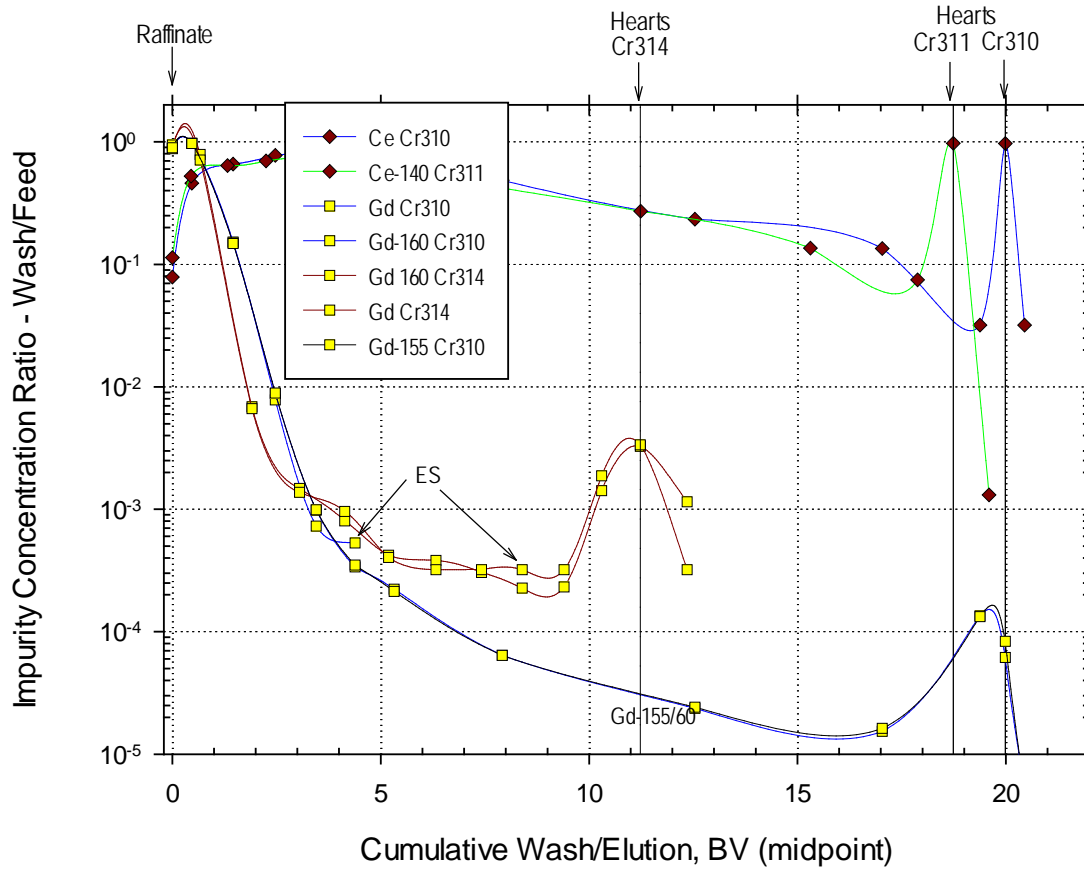


Figure 7. Gd and Ce Wash-Elution Profiles.

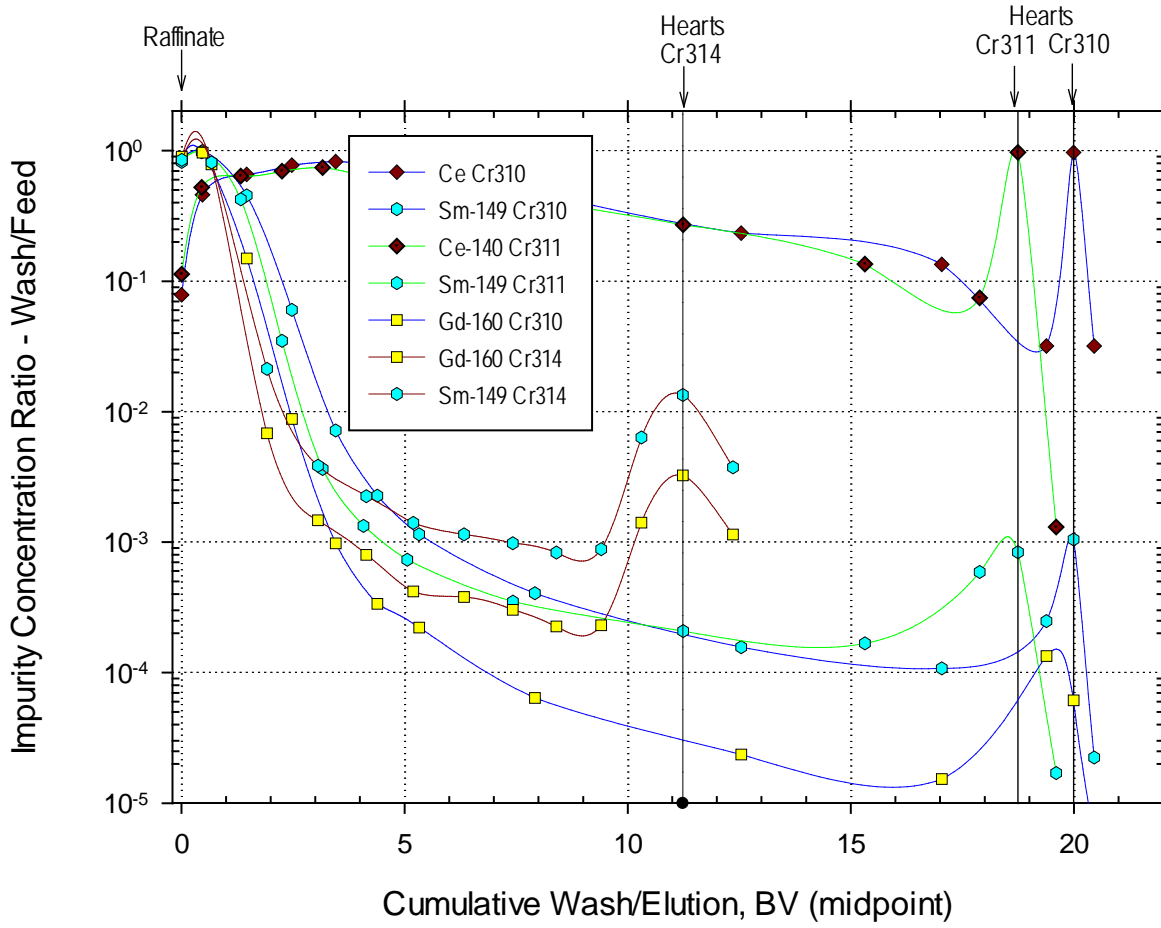


Figure 8. Sm, Gd, and Ce Wash-Elution Profiles.

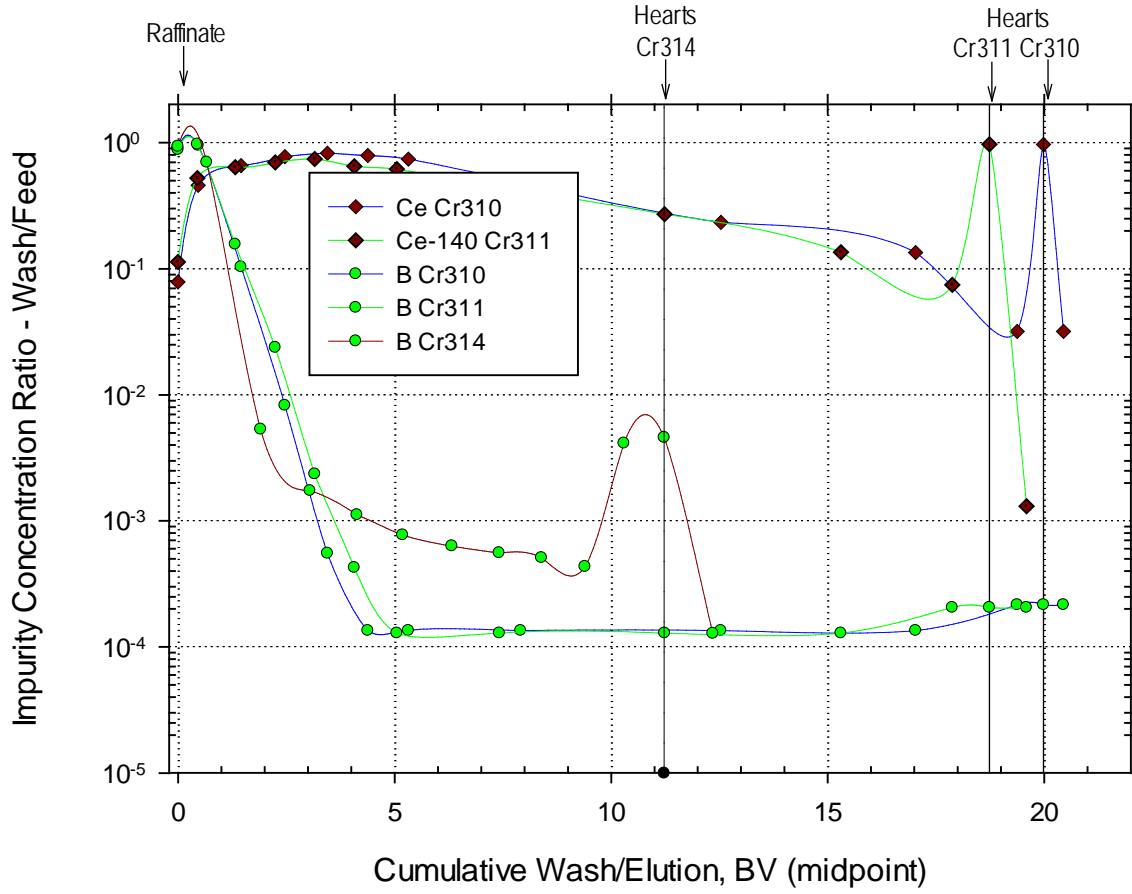


Figure 9. B and Ce Wash-Elution Profiles.

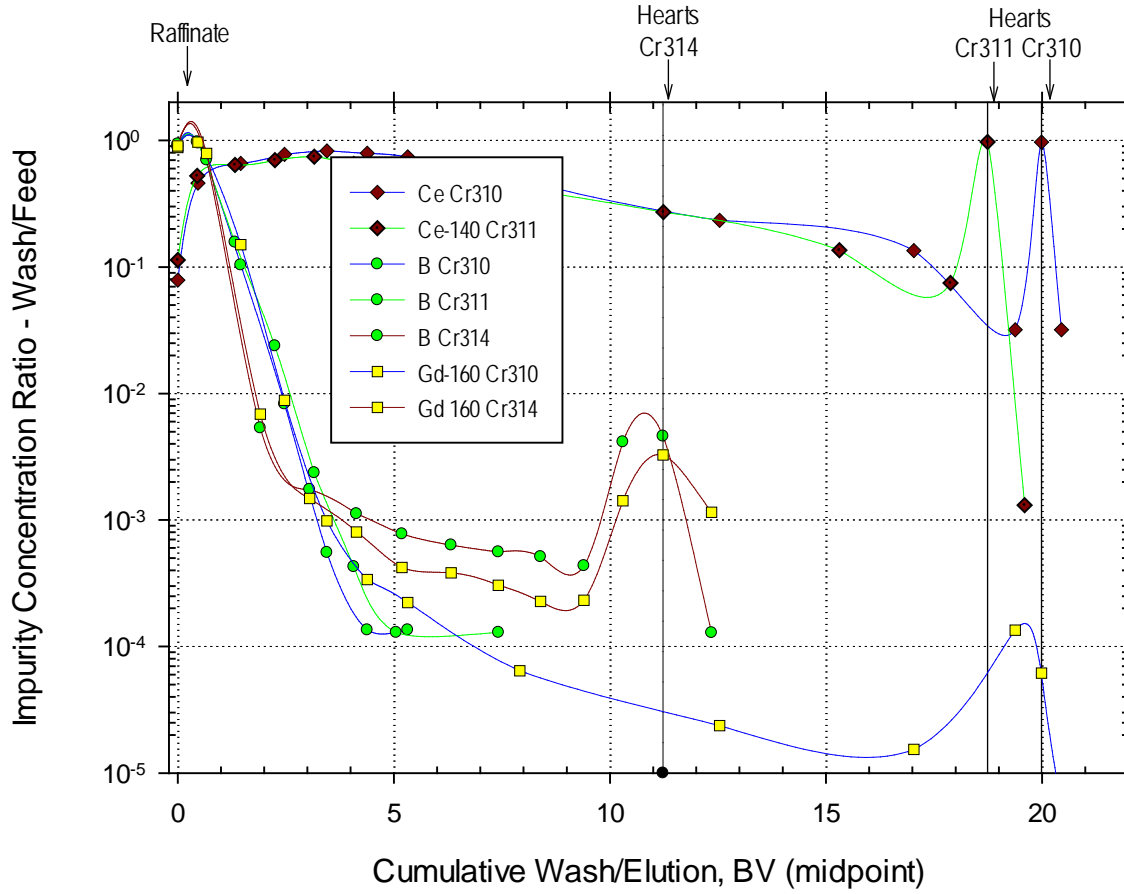


Figure 10. B, Gd, and Ce Wash-Elution Profiles.

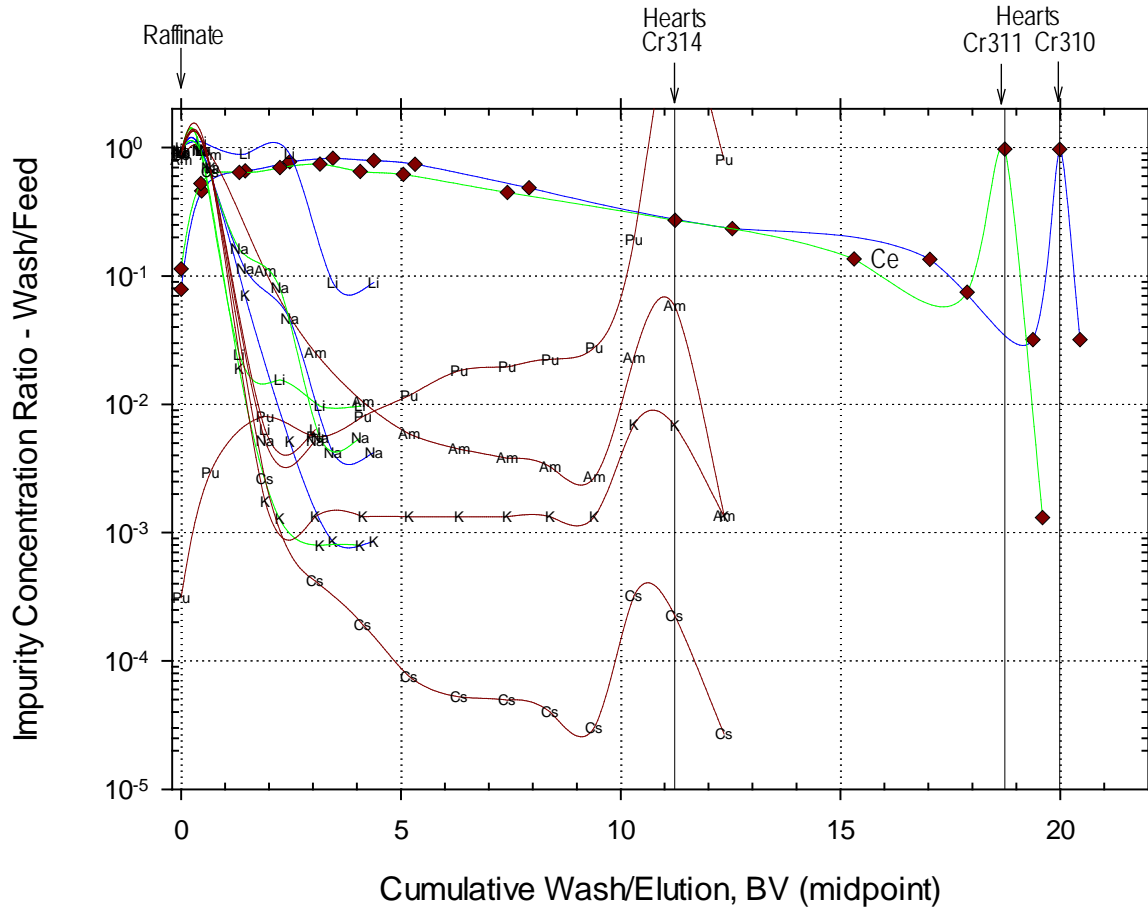


Figure 11. Li, Na, K, Cs, Ce, Pu, and Am Wash-Elution Profiles.

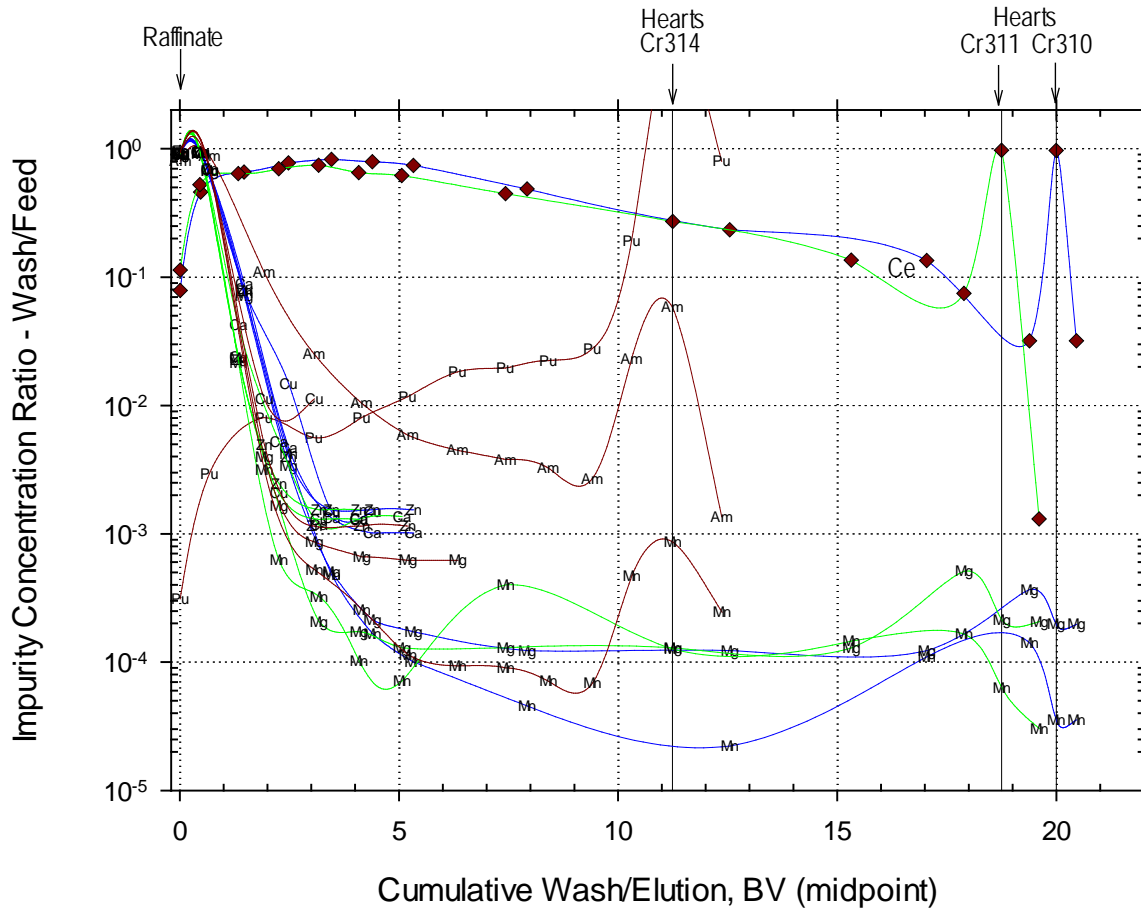


Figure 12. Ca, Cu, Mg, Mn, Zn, Ce, Pu, and Am Wash-Elution Profiles.

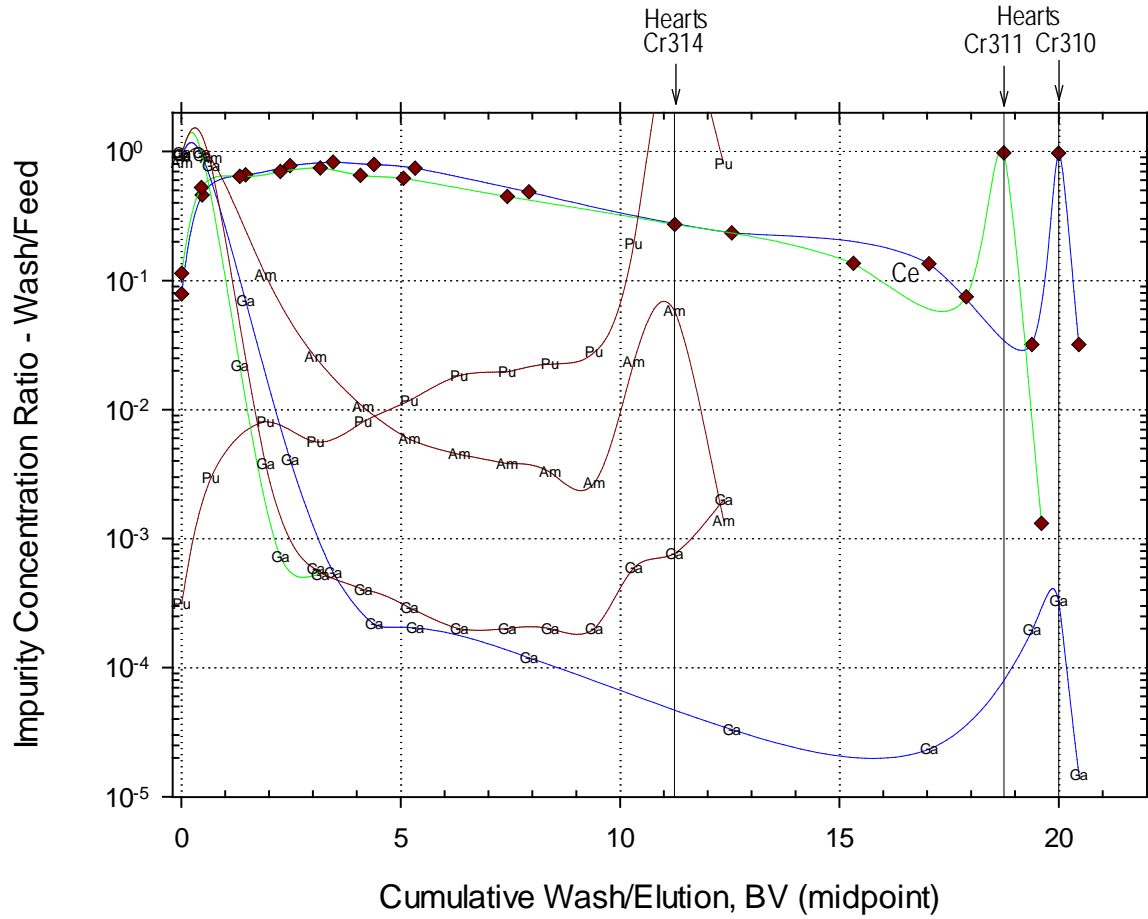


Figure 13. Ga, Ce, Pu, and Am Wash-Elution Profiles.

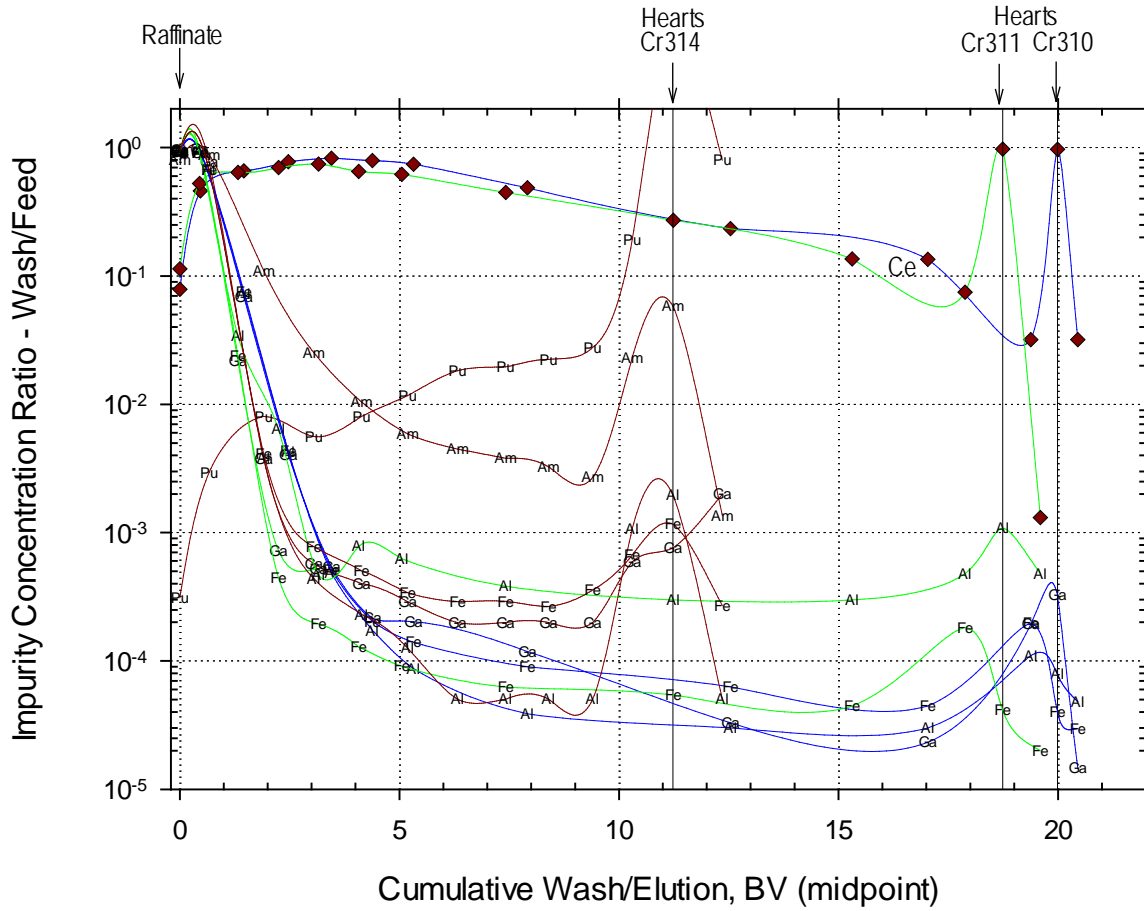


Figure 14. Al, Fe, Ga, Ce, Pu, and Am Wash-Elution Profiles.

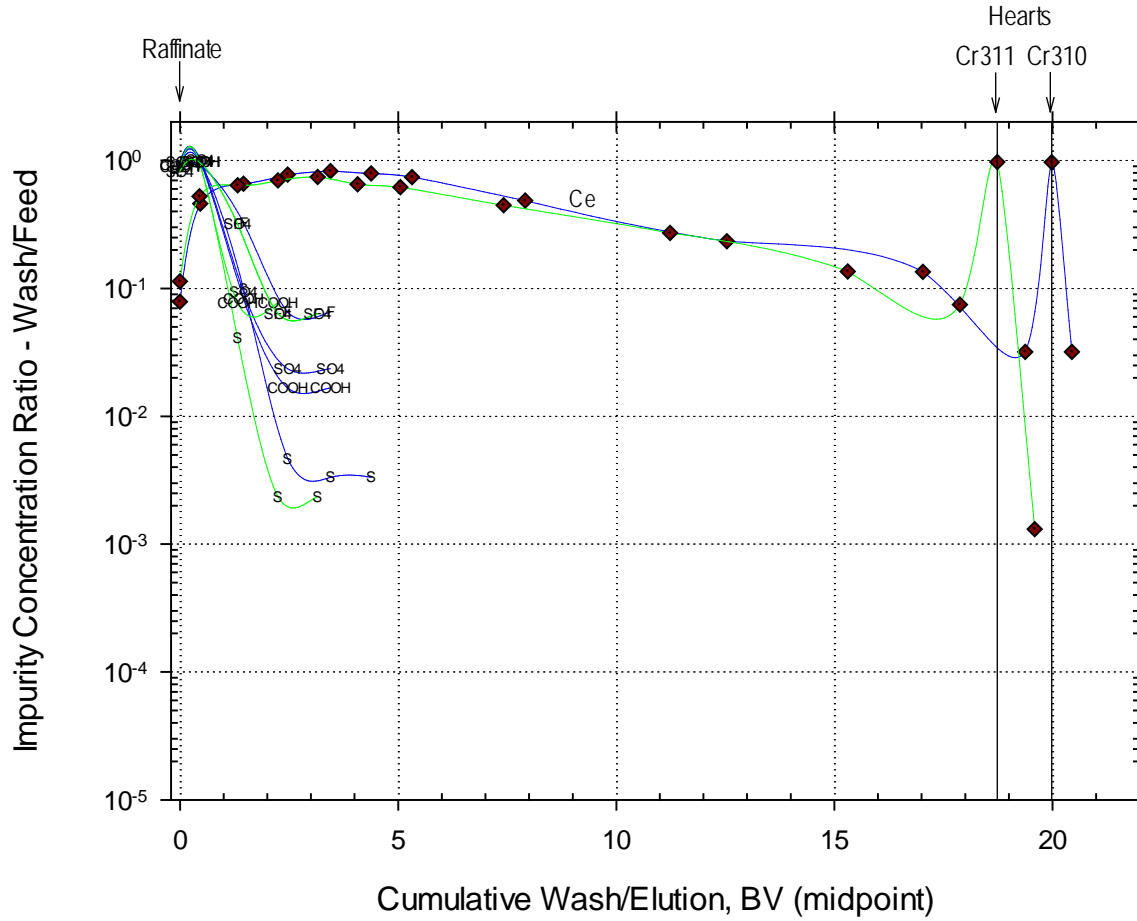


Figure 15. Anions (F, S, SO₄, COOH) and Ce Wash-Elution Profiles.

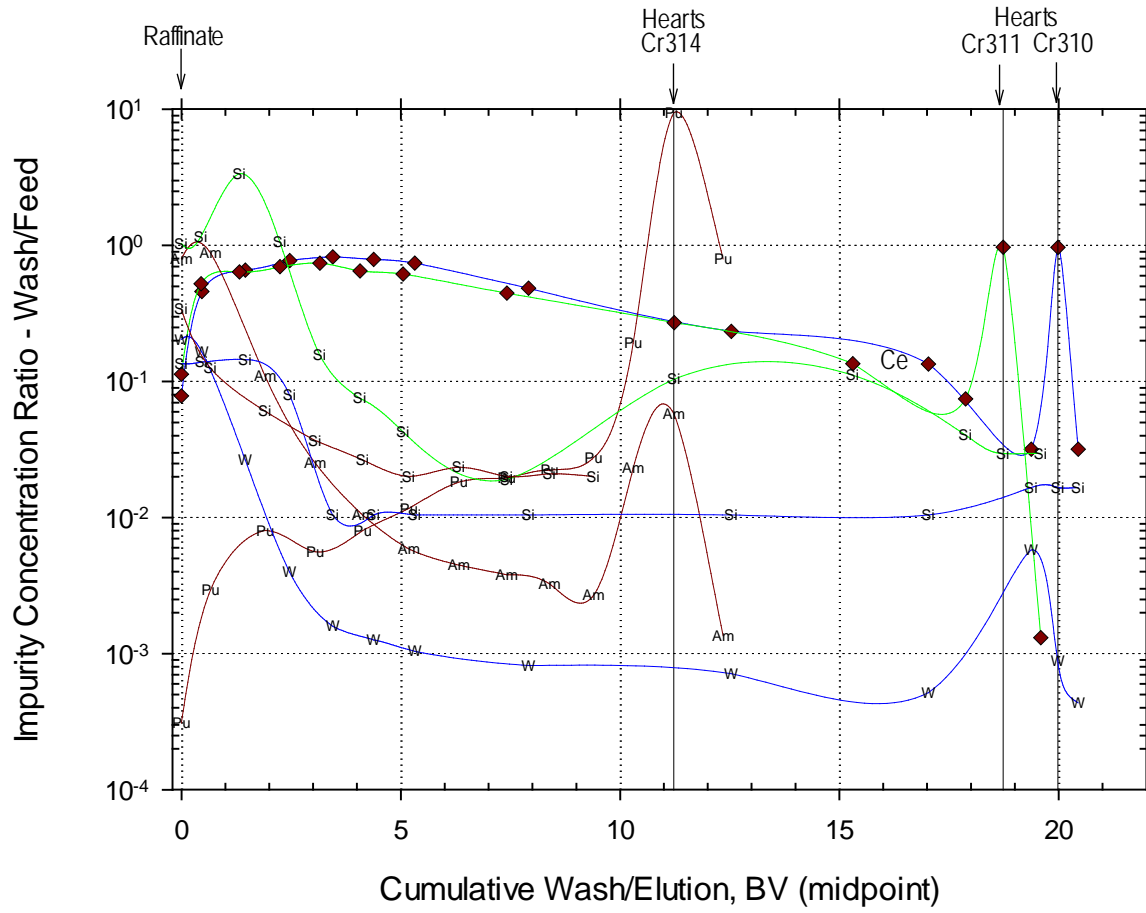


Figure 16. Si, W, and Ce Wash-Elution Profiles.

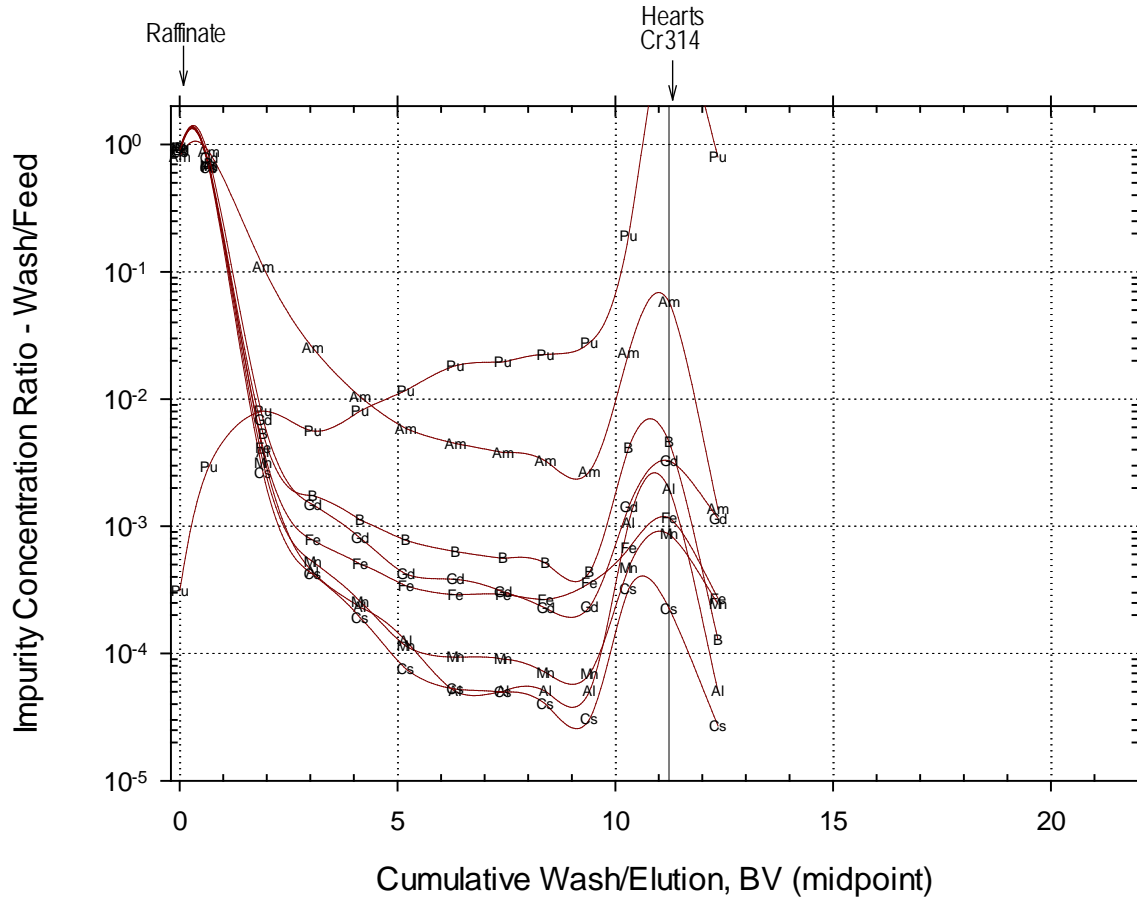


Figure 17. B, Al, Cs, Mn, Gd, Fe, Am, and Pu Wash-Elution Profiles.

Table 10. Minimum Wash Volumes to Achieve Column A Specification.

Element	Limit Col A ug/g Pu	Wash Required		
		Cr310 BV	Cr311 BV	Cr314 BV
Al	500	3.0 ^a	1.7 ^a	2.5 ^a
B	100	3.0 ^a	3.6 ^a	15-20 ^c
Ca	500	0.9	0.9	1.3
Fe	2000	2	1.7	1.3
Ga	12000	0	0	0
Gd	3	8.5		>30 ^c
K	300	3.9 ^b	2.7 ^b	2.5 ^b
Li	400	0.0 ^a	0.9 ^a	1.3 ^a
Mg	500	0.9 ^a	0.9 ^a	1.3 ^a
Mn	100	3.0 ^a	2.7	2.5
Na	1000	0.9 ^a	0.9 ^a	1.3 ^a
S	250	3.9 ^b	2.7 ^b	2.5 ^b
Si	200	3.0 ^a	3.6 ^b	6.9 ^a
Sm	2	13.5	15.5	>30 ^c
W	200	0.9		
Zn	150	2.0 ^a	0.9 ^a	1.3 ^a

Note: Wash values assume entire Displacement volume is discarded.

^a Values below instrumental detection limits were treated as real values, so minimum wash values are believed to be lower than calculated

^b Alternate calculation Method B (see text)

^c Estimate based on data extrapolation

Table 11. Minimum Wash Volumes to Achieve Column B Specification.

Element	Limit	Wash Required		
	Col B ug/g Pu	Cr310 BV	Cr311 BV	Cr314 BV
Al	100	4.8 ^a	3.6 ^a	3.6 ^b
B	1	>19.0 ^a	>17.4 ^a	>35 ^c
Ca	150	2	1.7	2.5
Fe	500	3	1.7	2.5
Ga	0.12	>19.0	17.4	>9.9
Gd	0.5	15-19		>30 ^c
K	100	3.9 ^b	2.7 ^b	3.6 ^b
Li	100	3.0 ^a	0.9 ^a	1.3 ^a
Mg	200	2.0 ^a	0.9 ^a	1.3 ^a
Mn	100	3.0 ^a	2.7	2.5
Na	100	3.9 ^b	3.6 ^b	2.5 ^b
S	250	3.9 ^b	2.7 ^b	2.5 ^b
Si	150	6-10 ^a	3.6 ^b	2.5 ^b
Sm	2	13.5	15.5	>30 ^c
W	100	0.9		
Zn	100	2.0 ^a	0.9 ^a	1.3 ^a

Note: Wash values assume entire Displacement volume is discarded.

^a Values below instrumental detection limits were treated as real values, so minimum wash values are believed to be lower than calculated

^b Alternate calculation Method B (see text)

^c Estimates based on background-corrected data

Distribution:

S. D. Fink, 773-A
K. M. Fox, 999-W
B. J. Giddings, 786-5A
C. C. Herman, 999-W
S. L. Marra, 773-A
F. M. Pennebaker, 773-42A
W. R. Wilmarth, 773-A
W. E. Harris, 704-2H
J. B. Schaade, 704-2H
G. J. Zachman, 225-7H
P. B. Andrews, 704-2H
S. J. Howell, 704-3H
M. J. Swain, 703-H
M. J. Lewczyk, 221-H
K. P. Burrows, 704-2H
J. E. Therrell, 704-2H
J. W. Christopher, 704-2H
R. H. Smith, 704-2H
R. R. Livingston, 730-2B
J. L. O'Conner, 704-2H
W. G. Dyer, 704-2H
S. L. Hudlow, 221-H
W. H. Clifton, 704-2H
E. A. Kyser, 773-A
T. S. Rudisill, 773-A
R. A. Pierce, 773-A
C. A. Nash, 773-42A
W. D. King, 773-42A
M. C. Thompson, 773-A
C. M. Gregory, 773-A
D. P. Diprete, 773-A
B. J. Wiedenman, 773-A
T. L. White, 773-A
M. A. Jones, 773-A
S. A. Thomas, 703-46A