Chemical Processes for Recovery of High Purity ^{234}U from Aged ^{238}Pu

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ACRONYMS

AX	anion exchange
BV	bed volume
DAAP	dipentyl pentylphosphonate
DOE	US Department of Energy
FP	fission products
IX	ion exchange
MP-1	anion exchange resin name
ORNL	Oak Ridge National Laboratory
pH	-log [H$^+$] (hydrogen concentration
ppm	part per million (μg/g)
ppt	precipitate
SX	solvent extraction
TBP	tributyl phosphonate
TRU	extraction chromatographic resin name
UTEVA	extraction chromatographic resin name

ACKNOWLEDGMENTS

ABSTRACT

Purified ^{234}U (2.46E5 a) is an important radioisotope for commercial customers, and since the 1980s, the United States has experienced a market demand of 2–6 g per year. Purified ^{234}U is most efficiently recovered as a decay daughter from aged ^{238}Pu (87.7 a). Ever since the last recovery of tens of grams of ^{234}U by Monsanto Co.'s Mound Laboratory in 1980s, the DOE inventory of ^{234}U for US market decreased steadily. In 2016–2018, the Radiochemical Engineering Development Center at Oak Ridge National Laboratory (ORNL) carried out a campaign to recover ^{234}U from 16 spent Pu–Be neutron sources. A total 66.5 g of high purity ^{234}U of high isotopic abundance (>99.3%) was recovered in two phases of the campaign with selected chemical processes.

Recovery of ^{234}U from aged ^{238}Pu commonly involves four major steps: (1) bulk plutonium removal from the matrix, (2) continued separation of plutonium from the matrix, (3) purification of ^{234}U from all other impurities, and (4) conversion of purified ^{234}U into a final product form, ^{234}U$_3$O$_8$. The first three steps are the key to ensuring the purity of the ^{234}U product. Historically, various chemical processes have been applied for uranium processing of these three steps, although on different scales or with different purity requirements. Because of the higher purity requirements specified for this order of ^{234}U product, the selected processing methods used in this campaign relied on a cyclical anion exchange process with *MP*-1 resins followed by uranium peroxide process to achieve the purified product. Process details will be compared with other options, and advantages and drawbacks will also be discussed.

1. INTRODUCTION

Purified ^{234}U (2.46E5 a) is an important radioisotope for commercial customers for many reasons. For example, it can be used to lengthen the lifetime of ^{235}U fission detectors. Between 1970 and 1980 was a peak period of recovery of this radioisotope, mainly by Monsanto Co.'s Mound Laboratory. After supplying the US market with 4–6 g per year since 1980s, Oak Ridge National Laboratory (ORNL) had nearly depleted its stock of ^{234}U (taken over from Mound Laboratory) before launching the ^{234}U campaign during 2016–2018. Uranium-234 is found in natural uranium at trace levels (57 ppm) and decays by alpha emission with a half-life of 246,000 year. Uranium-235 can be enriched from natural uranium, but uranium-234 can also be enriched by electromagnetic separators even though it is 144 times lower in abundance than uranium-235. To meet the market need, ORNL provided multigram quantities of enriched ^{234}U before its calutrons were shut down in 1998, and ORNL managed to provide this quantity despite the high costs of operation.

The most straightforward pathway to produce ^{234}U is to separate it as a decay daughter from aged ^{238}Pu (87.7 a). ORNL has had more than 400 g of ^{238}Pu on its inventory shelf for more than 30 years. Calculations show that each 100 g of ^{238}Pu would produce 8.4 g of ^{234}U in 30 years; consequently, recovering tens of grams of ^{234}U is only a matter of chemically separating uranium from the aged inventory ^{238}Pu.

Recovery of ^{234}U from aged ^{238}Pu commonly involves four major steps:

1. Bulk plutonium removal from the matrix, where the mass ratio of Pu:U is of ~10:1
2. Further separation of plutonium from the matrix, starting at a mass ratio of Pu:U of ~1:4–5
3. Purification of ^{234}U from all other impurities
4. Conversion of purified ^{234}U into a final product form, ^{234}U$_3$O$_8$

The first step involves a heavy workload with high labor, equipment, and time costs, although an oxalate precipitation may be used as an efficient method to achieve a preliminary separation of major portion of

Pu from the U and other impurities. The [234]U campaign of 2016–2018 at ORNL had an opportunity to take over a raffinate of U/impurities/residual Pu from a project of disposition of 16 aged [238]Pu–Be neutron sources, which had achieved removal of major portion of plutonium. Therefore, the Pu:U mass ratio of the raffinate for this campaign was about 1:5 at the starting point.

References [1,2] describe the historical processing methods for further removal of Pu from the raffinate. The following methods are grouped to achieve a final purification of the [234]U from the raffinate:

1. With aluminum nitrate salted to 3 M HNO_3 of Pu–U–impurities, solvent extraction (SX) by organic hexone (methyl isobutyl ketone) can be performed to selectively extract U (Pu is not extracted when Fe^{2+} is present), which is then back extracted into 0.35 M HNO_3.

2. With an anion exchange (AX) resin column, the feed of $Al(NO_3)_3$ salted to 0.3 M HNO_3 can be loaded, followed with a 7 M HNO_3 elution (U–impurities off), and followed with a 0.35 M HNO_3 elution (Pu off)

3. With an AX resin column, a feed of 9 M HCl can also be loaded, followed with 9 M HCl–0.05 M NH_4I elution (Pu off), a 4 M HCl elution (Np off), and finally a 0.5 M HCl elution (U off).

4. With an AX resin column, a feed of 7.2 M HNO_3 can be loaded, followed with a 7.2 M HNO_3 elution (U-impurities off), and then a 0.35 M HNO_3 elution (Pu off).

The most common grouping of the above methods is to conduct the AX run or SX from the salted low nitric acid raffinate (1 or 2), then run an AX column in high HCl media (3), and then run an AX column in high HNO_3 media (4), which is a three-step process to purify U. Those methods worked well for previous U purification projects, but they were not sufficient for this contract's ultrahigh purity requirements (see Table 1).

Table 1. Comparison of the 2016 contract's purity requirements for [234]U with previous contracts.

U Isotopic Purity	Other U isotopes	
[234]U 95.0% min	Max [238]U 5%, [236]U 0.1%, [235]U 0.2%	
Required Purity	**Pre-2015**	**2016**
Pu-238	≤10 ppm	≤5 ppm
Np-237	≤1000 ppm	≤200 ppm
Fe	≤5000 ppm	≤200 ppm
Al, Ca, K, Na, B Ni, Mg, P, Pb, Sn	≤4000 ppm max total	≤200 ppm each
Other metal contaminants*	≤4000 ppm Max. total	≤10 ppm each

*Sb Ba Be Bi Cd Cr Co Cu Dy Er Eu Gd Li Mn Mo Nb Ru Sm Ag Sr Ta Tl Th W V Zn Zr

The 2016 contract requires the [234]U to contain 2× less Pu content than before, 20× lower levels of ten specific impurities, and 40× lower total content of other impurities than before. Obviously a three-step

process will not achieve such a product purity. Furthermore, changing solution media from HNO_3 → salted low HNO_3 → HCl → HNO_3 does not benefit this [234]U campaign's purification processing.

Unlike historic processing (Figure 1) that used a starting solution of oxalate precipitation (low HNO_3) from aqueous raffinate, this [234]U campaign started with a U/residual Pu/impurities solution of 7.5 M HNO_3 raffinate from the disposition processing of Pu–Be sources (Figure 2). Adjusting 7.5 M HNO_3 into salted low HNO_3 (0.35 M or 3.5 M) for method 1 or 2 is obviously redundant and adding more salts to increase the workload for U purification would be unwise. The ultralow Fe content requirement makes method 3 unfavorable as well (see Table 2). Therefore, a revised method 4 that cycles the AX column runs in a single HNO_3 media was chosen to purify the [234]U in batches (~6–10 g U/batch), and this was followed by uranyl peroxide precipitation before conversion to [234]U_3O_8.
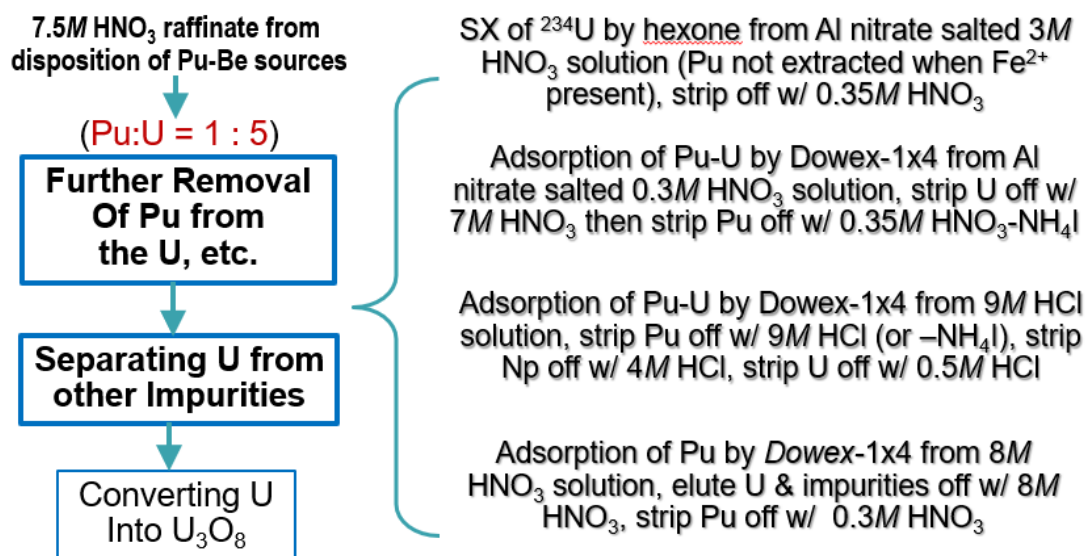
Figure 1. Historic processing options for Pu removal and U purification from impurities.
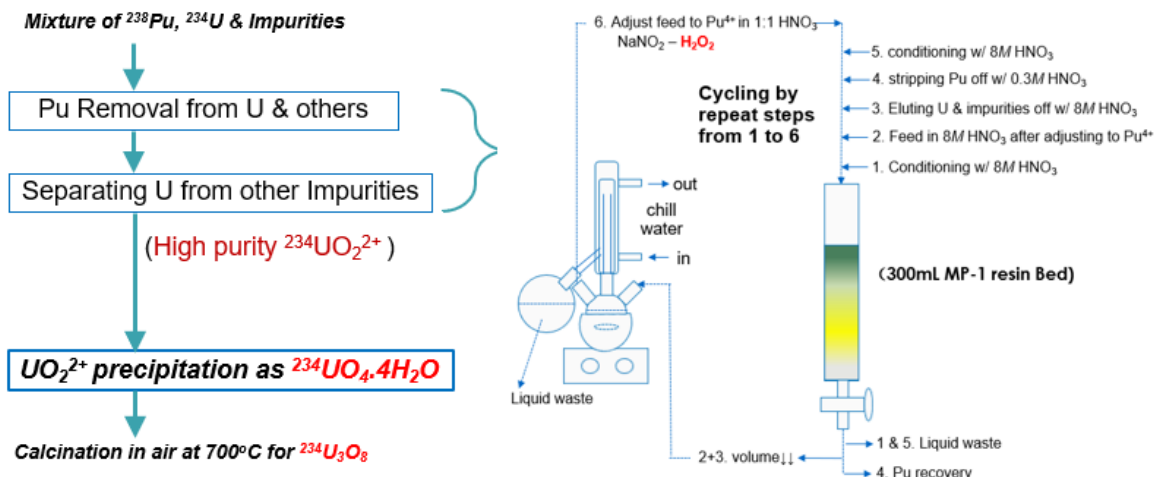
Figure 2. Processing scheme for high purity [234]U separation from [238]Pu and impurities.

Table 2. Literature k' values for M^{n+} on Dowex-1 resin in HNO_3 or HCl.

MP-1 in HCl	0.1 M	4 M	6 M	≥8 M
Pu (IV)	<<1	<1	~30	>1000
U (VI)	<1	~180	~800	~1000
Am, Be, etc.	<<1	<1	<1	<1
Fe (III)		100	10^3	$>10^3$
MP-1 in HNO_3	0.1 M	4 M	6 M	8 M
Pu (IV)	<10	~700	>1000	>1000
U (VI)	<2	3-12	6-30 ?	6-50 ?
Am, Be, etc.	<1	<1	<1	<1
Fe (III)	n.a.	n.a.	n.a.	n.a.

Table 2 shows literature k' values of concerned metal ions to Dowex-1 resin in HNO_3 or HCl media, indicating that Pu(IV) would be retained on AX resins in high HNO_3 media, without retention of our concerned metal impurities, as well as uranium in uranyl form UO_2^{2+} (in our ^{234}U campaign practice U(VI) showed higher affinity with *MP*-1 resin than k' literature values in Table 2).

2. EXPERIMENTAL

2.1 REAGENTS/EQUIPMENT FOR COLUMN RUN/PRECIPITATION/CALCINATION

2.1.1 Reagents

AG *MP*-1m AX resin (Cl⁻, 150–300 μm wet size) was purchased from Bio-Rad Laboratories. Both UTEVA resin (100–150 μm) and TRU resin (100–150 μm) were purchased from Eichrom Industries Inc, $NaNO_2$ (97.0%, MACRON Chemicals). Nitric acid (69–70% ACS grade HNO_3) was purchased from Fisher Chemical, and ultrapure nitric acid (67–70%) was purchased from Millipore Sigma. Ultrapure ammonia solution (20–22%, ARISTAR® ULTRA) was purchased from VWR International. Ultrapure H_2O_2 30% was purchased from Sigma Aldrich. Ultrapure ethanol absolute (200 Proof) was purchased from Decon Labs.

2.1.2 Equipment for column runs

The *MP*-1 AX resin was mixed with deionized water into a slurry and then loaded into a graduated glass column of $\Phi 4.66 \times 48$ cm. This step was followed by conditioning the resin with 7.5 *M* HNO_3. The volume of *MP*-1 resin bed was controlled at 300 mL in 7.5 *M* HNO_3. The column run relied on gravity flow with no pressure exerted. The common flow rate for a 300 mL column was about 3 mL/min. A 300 mL UTEVA resin column and several small columns of different resins were prepared same way. All column loading of reagents was done manually without using a pump. All effluent off columns was collected into an empty cup and then transferred into fraction bottles after volume measurement with a graduated cylinder. An evaporation setup was used for solution volume reduction for preparation of feed

of column runs. In most cases the feed solution was evaporated to concentrated HNO_3 (15 M), adjusted for Pu(IV) with $NaNO_2+H_2O_2$ or H_2O_2 only, and then adjusted into the desired molarity of HNO_3.

Figure 3. Column preparation, feed loading, and condenser setup for feed preparation.

2.1.3   Equipment for uranyl peroxide precipitation

Operations of uranyl peroxide precipitation in campaign Phase-1 were performed with the U solution inside a quartz/Teflon cup with a magnetic stirrer at room temperature inside a glovebox. The acidity detection of the process relied on use of pH paper strips. The addition of a mixture of ultrapure H_2O_2/NH_4OH into the U solution was performed with precalibrated pipette. Separation of the precipitates from the supernate was performed with a glass filtration funnel and Whatman filter paper. Uranyl peroxide precipitation operations in campaign Phase-2 were completely different—they were performed with the concentrated U solution inside a poly bottle (bottle#1, size 500 mL). Several bottles of the same size were used in series for a cascade precipitation. Reagents were added to bottles and the supernate was removed from the bottles with pipettes. To mix the [234]U solution, the bottles were shaken by hand without a shaker or stirring device. The phase separation relied on settling overnight, without centrifuging or filtering. The equipment and operation steps for column run and precipitation are shown in Fig. 3 & 4.
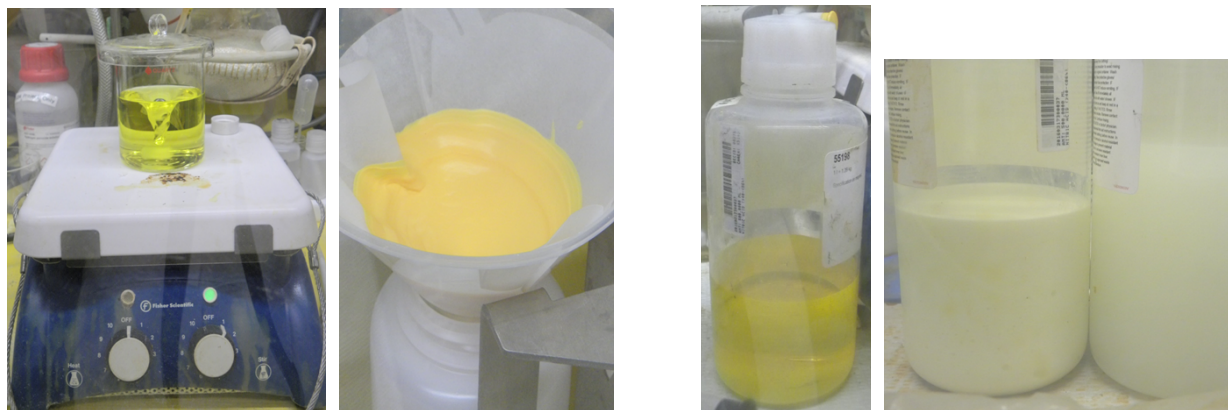
Figure 4. Equipment used for uranyl peroxide precipitations in campaign Phase-1 and Phase-2.

2.1.4 Equipment for conversion of uranyl peroxide to U_3O_8

After the uranyl peroxide precipitates were washed with H_2O/H_2O_2 and ultrapure alcohol inside a quartz cup and were air dried, the purified dry precipitates were transferred into a furnace (Mellen Co. BF12.5R) and converted into U_3O_8 with a heating profile of 300°C in air for 2 hours, which was followed by 700°C for 3 hours (Figure 5).
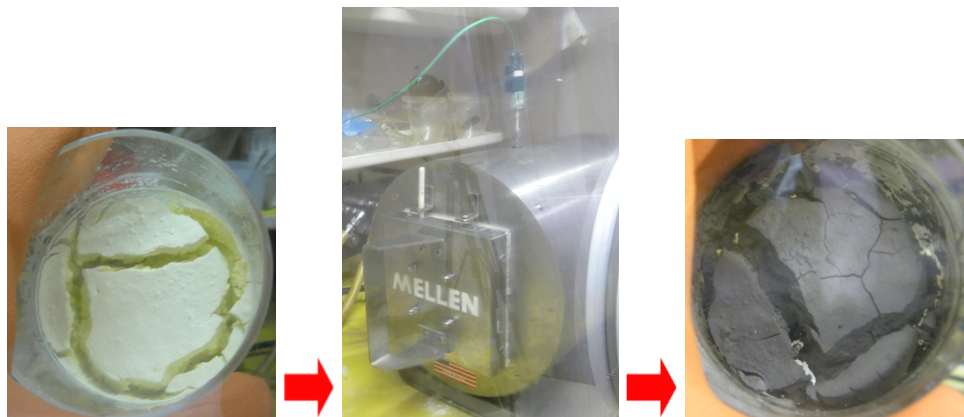
Figure 5. Furnace used for conversion of $UO_4.4H_2O$ (both precipitation processes) to U_3O_8.

2.2 SAMPLE ANALYSIS

The Analytical Group at ORNL's Radiochemical Engineering Development Center is well equipped with a variety of radiological analysis instrumentation, including high-purity germanium gamma spectrometers, alpha spectrometers (PIPS detectors), and an inductively coupled plasma-mass spectrometer (Thermo Fisher iCAP Q). Samples of $^{234}U/^{238}Pu$ were measured using both gross alpha and gamma spectrometric methods, based on alpha energies of 5.08 MeV/5.5 MeV and gamma energies of 121 keV and 63/153 keV. Some of the samples in processing were measured using the inductively coupled plasma-mass spectrometer (Thermo Fisher iCAP Q) for monitoring removal of non-radioactive impurities. The analysis of the final $^{234}U_3O_8$ product was contracted and performed by a third-party company (Southwest Research Institute) that had the necessary instrumentation.

2.3 OPERATIONS OF CYCLING MP-1 AX COLUMN RUNS

Different from previous processing schemes, this process was performed with an *MP*-1 AX resin column in a cycling style: the feed (Pu, U, impurities) of 7.5 *M* HNO_3 was loaded onto the column after the Pu valence adjustment to Pu(IV), allowing Pu(IV) adsorbed onto the column and U-impurities to pass through the column with a follow-up 7.5 *M* HNO_3 elution. This effluent (U, residual Pu, and impurities) of 7.5 *M* HNO_3 was sent to the evaporation setup for volume reduction to the desired volume then used as the feed of next cycle of column run after adjusting to 7.5 *M* HNO_3 and Pu(IV). The Pu(IV) on the column was stripped off with low HNO_3 as Pu(III), which was removed for disposal. The column needs to be re-conditioned with 7.5 *M* HNO_3 prior to next cycle of column run. Each batch (~6–10 g U/batch) took three to five cycles to ensure the Pu content was minimized.

After the Pu content was minimized, cycling *MP*-1 AX column process in batches was continued for ^{234}U purification from all impurities, including residual Pu . The feed was loaded with $\geqslant 8$ *M* HNO_3 (up to a maximum of 10 *M* HNO_3) to increase the affinity of uranium to the *MP*-1 resin and allow M^{2+} and M^+ impurities to pass through the column with high HNO_3 elution, ahead of the U band off the column. All reagents were replaced with ultrapure ones to ensure the purity of recovered ^{234}U. During the cycling

column runs for U purification, it was assumed that trace Pu existed in the feed, and the Pu valence adjustment was performed as for Pu(IV) adsorption but the Pu stripping step with low HNO_3 was omitted. Instead, the top ~50 mL resin was replaced with new resin by end of each run. Replacement saved operation steps 1, 4, and 5 (Figure 6), speeding the cycling run and reducing the liquid waste requiring disposal.
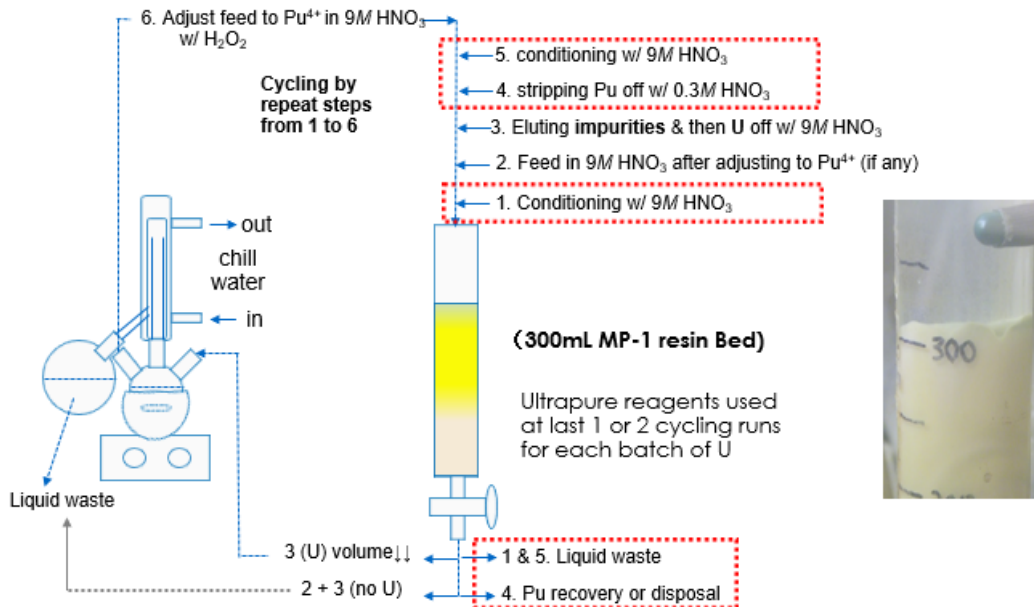
Figure 6. Reduced operational steps in cycling *MP*-1 column runs for U purification.

The batches of 50 mL of replaced column top *MP*-1 resin were eventually consolidated and loaded into an empty column. The column was eluted with 0.35 M HNO_3 to strip off Pu, which was analyzed for disposal.

The original processing scheme for U purification from other impurities was planned using UTEVA or TRU resin columns. AX resins were not even considered because of the low literature k' values of U with Dowex-1 resin in HNO_3 media (Table 2). During the campaign operations, we were gradually convinced by apparently higher affinity of U to *MP*-1 resin than to other resins (e.g., UTEVA, then changed to the cycling *MP*-1 AX resin column runs).

2.4   OPERATIONS OF URANYL PEROXIDE PRECIPITATIONS

In campaign Phase-1, 26.5 g of already high purity [234]U was obtained by AX column runs but alpha spectrometry of the sample showed a trace of a suspected [238]Pu peak, which led to the decision to use uranyl peroxide precipitation as an additional purification step, as well a uranium solidification step before its conversion to U_3O_8 by calcination. Unlike the uranium hydroxide (another popular precursor of U_3O_8) process that precipitates all metal ions, the uranyl peroxide precipitation process selectively precipitates uranium with operation controls.

The reaction of hydrogen peroxide with uranyl (UO_2^{2+}) can be written as

$$UO_2^{2+} + H_2O_2 + 4H_2O \rightarrow UO_2O_2.4H_2O \downarrow + 2H^+, \qquad (1)$$
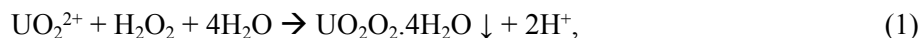
where H^+ ions are generated in a reaction that results in an increase of the acidity or decrease of the pH of the solution with the addition of H_2O_2. Traditionally, addition of H_2O_2 to the U solution starts at a pH of

2–6, and the generated H^+ must be neutralized with precise additions of NH_4OH to maintain the starting pH of the solution. The precipitation operations in Phase-1 followed this traditional process, and a total 24.75 g of high purity [234]U was recovered from 26.5 g column runs.

It was found in operations that no matter how carefully the NH_4OH/H_2O_2 of accurate concentrations was added into the solution of pH 2–6, formation of hydrolytic U could not be avoided because of localized basicity resulted during addition of NH_4OH/H_2O_2. Also, the low acidic environment (pH 2–6) of the resulting solution cannot convert hydrolytic U back into the peroxides unless excessive HNO_3 is added. Formation of hydrolytic U indicates the possible formation of impurity hydroxides.

In campaign Phase-2, a new uranyl peroxide process was invented and performed by concentrating the U solution to >100 g U/L and adding H_2O_2 into high HNO_3 (e.g., 7.5 M HNO_3). This prevents hydrolytic U/impurities from forming, although the precipitation rate of uranyl peroxide was not 100% after one precipitation (Eq. 1 indicates low $[H^+]$ is favorable to the reaction). After the precipitates settled, the top liquid (with unprecipitated U) was transferred into a second bottle. The solid U peroxides from the first harvest were washed several times with H_2O/H_2O_2, and these subsequent washes were also transferred into the second bottle, which lowered the acidity of the liquid in the second bottle below 7.5 M HNO_3. Uranium peroxides were precipitated by adding more H_2O_2 into the second bottle. The two batches of precipitates were then combined and washed with H_2O/H_2O_2, ultrapure ethanol, and then air dried. In Phase-2, a total of 41.75 g of [234]U was recovered from 42.6 g from column runs. Together, the two harvests of uranium peroxide demonstrated a higher recovery rate than the traditional process (plus higher purity).

Figure 7 shows the air-dried uranyl peroxide precipitates from the traditional process and the new process. The details of new uranyl peroxide process and its comparison with traditional process have been described in another ORNL TM report [3], so this report will not provide further discussion.

Figure 7. Air dried uranyl peroxide precipitates obtained by traditional precipitation method (left) and by new precipitation method (right).

3. RESULTS AND DISCUSSION

3.1 PLUTONIUM REMOVAL BY *MP*-1 AX COLUMN RUNS

To separate one specific metal ions from a solution containing multiple metal ions, the ideal method is to extract/retain the desirable ions solely (without others) using a chosen extractant or resin, especially if the desired ion is not the major component by mass in the matrix (the scale of equipment and workload concerned). Plutonium removal by an AX resin column from uranium and other impurities seems to be an

ideal example because much higher affinity of Pu(IV) to AX resin than that of U and other impurities (Table 2).

Retention of Pu(IV) on an AX resin column in high HNO_3 is a well-known method for separating Pu from other impurities and has often been used at the Radiochemical Engineering Development Center and in other ORNL projects, including the recent project for disposition of 16 aged Pu–Be neutron sources. The raffinate from the Pu–Be project for this [234]U recovery campaign was a 7.5 M HNO_3 containing residual Pu (major part of Pu had been removed), [234]U (decay daughter of [238]Pu), [241]Am, and stable metal impurities. According to the k' values in Table 2, Pu(IV) will be retained on AX resin (AG MP-1), but U and all others will pass through the column (Figure 8).
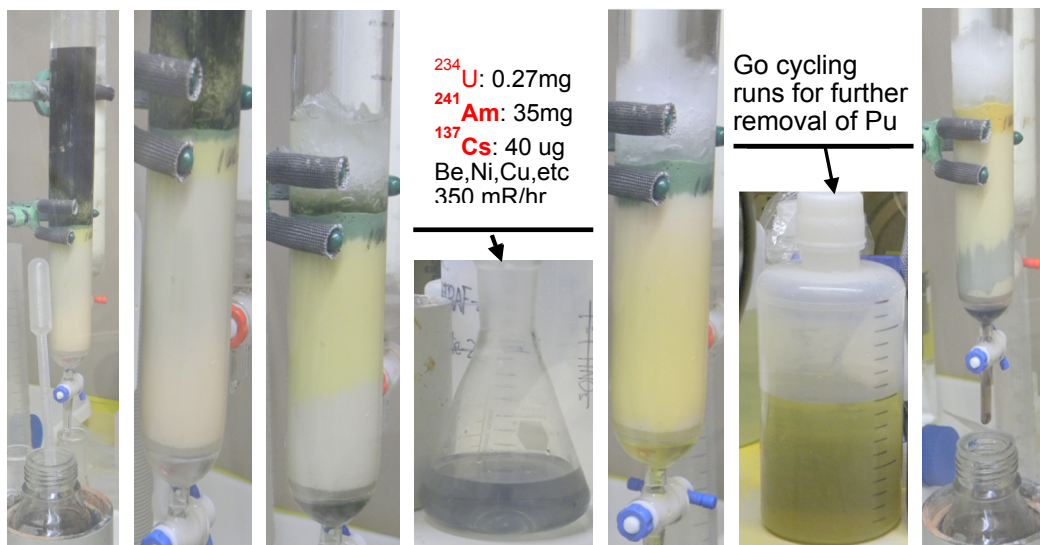
Figure 8. Example of *MP*-1 AX column run for Pu retention and separation from others.

Figure 8 shows a typical AX column run for initial removal of Pu from the 7.5 M HNO_3 raffinate of the Pu–Be source treatment. This specific raffinate fraction of 7.5 M HNO_3 contains residual Pu, U, and impurities with mass ratio Pu:U of 1:5. After a valence adjustment of Pu(IV) using $NaNO_2$–H_2O_2, this 195 mL (~1.8 BV) feed was loaded onto a 110 mL MP-1 AX column (preconditioned with 7.5 M HNO_3). A dark band showed up first along the column bed, then a yellow U band appeared and moved down quite slowly while the green Pu band retained on top of the column bed. The yellow U band moved down more slowly than the dark impurity band, but there was an overlap between the two bands. A fraction of 280 mL (~2.55 BV) of the dark band was collected as a "pre-cut" fraction (350 mR/h). Later analysis showed impurities of [241]Am, ^{137}Cs, and inert metal ions. This "pre-cut" fraction was detected with a bit of [234]U but removed from the glovebox anyway to reduce background dose. The follow-up yellow U fraction (460 mL,~4.2 BV, 45 mR/h) was collected with an elution of 7.5 M HNO_3, which was sent to an evaporator setup for feed preparation for next round of MP-1 AX column run of Pu removal. The dark yellow color indicated the need for further Pu/impurity removal. The retained green Pu band on the column was later stripped off with 240 mL (~2.2 BV, 150 mR/h) of 0.3 M HNO_3 and transferred back to the hot cell.

The raffinate from the Pu–Be project was treated in batches for Pu removal, with each batch about 3–5 MP-1 column runs in cycling. The figures of this initial run were chosen because of the colors of the Pu/U/impurity bands on column, showing their separations. As the column runs are cycled, less and less of the Pu and impurity color and more and more of the bright yellow band of U is observed. The analytical results showed that only trace Pu remained in the U batches, so the process moved to the step of U purification from all other impurities.

The yellow stain at the top resin bed (Figure 8) was due to ^{238}Pu (0.54 W/g) burning, indicating the ^{238}Pu feed concentration is an important operational control. A bad experience occurred during a previous project where there was 34% of loaded ^{238}Pu stuck to *MP*-1 resin bed with no way to strip it off when the feed concentration of ^{238}Pu reached 100 g/L. The limit here is not the total ^{238}Pu but the concentration of ^{238}Pu in feed. The operation control on ^{238}Pu feed concentration should be <50 g ^{238}Pu/L.

Based on dozens of Pu loading experiences with an *MP*-1 resin bed in 7.5 *M* HNO$_3$, an "apparent Pu loading capacity" of an *MP*-1 resin bed in 7.5 *M* HNO$_3$ can be summarized as 7.5 g Pu/100 mL resin bed. This may not be a direct k' measurement but is a practical parameter in column size design and operation control.

3.2 PURIFICATION OF URANIUM FROM ALL OTHER IMPURITIES

To purify U from all other impurities (including the remaining trace Pu), an ideal method is to extract/ retain U solely with an extractant or resin, excluding all others (this is similar to how *MP*-1 resin only retains Pu). Limited by glovebox space, multiple mix-settler was not considered, and selected resin column runs were apparently more efficient than single stage SX. Limited by glovebox space as well, the size of a column was 300 mL resin bed as maximum, even though the mass of U was five times more than initial Pu to be treated. Again, the solution after primary Pu removal had to be processed in batches (6–12 g U/batch) by column runs.

Among candidate resins, UTEVA resin was the first selected because of its reputation from widespread application for selective separation of U from radioactive wastes and environmental samples since 1980s [4]. TRU resin was another option in our plan for U purification because the literature [5] shows that TRU is even superior to UTEVA for retention of tetra- and hexavalent actinides [5]. Table 3 shows the basic information of the two Eichrom extraction chromatographic resins.

Table 3. Basic information on the two Eichrom resins tested in this work

Resin	manufacturer	Matrix Material	Functional Group
UTEVA-spec	Eichrom Indus.	Amberchrom CG-71	13% CMPO with 27% TBP
TRU-spec	Eichrom Indus	Amberchrom CG-71	40% DAAP

CMPO-carbamoyl methylphosphine oxide;   **DAAP**-dipentyl pentylphosphonate;   **TBP**-tributyl phosphate

3.2.1 Application of UTEVA resin and its comparison with TRU resin

According to the k' values published on the Eichrom website, U(VI) shows a very high affinity to both UTEVA and TRU resins in high concentrations of HNO$_3$ media, but Pu(IV) shows even higher affinity to both resins, which means that at high HNO$_3$ levels, either UTEVA or TRU would retain both Pu and U on column but separating Pu and U would rely on follow up selective stripping by changing the elution media. There is at least one paper [6] that describes how U(VI) appeared to have a higher affinity to UTEVA than Pu(IV) at high HNO$_3$, although it results in the coadsorption of Pu and U on UTEVA anyway. So the original plan was to choose either UTEVA or TRU resins by a comparison test of U loading which would retain both U and the remaining trace Pu but remove all other impurities by eluting with high HNO$_3$. Later U and trace Pu separation may perform selectively eluting Pu off UTEVA column with 3 *M* HNO$_3$ in presence of persulfate or eluting U off TRU column with 2 *M* HNO$_3$ in presence of NaNO$_2$ [7]. The addition of persulfate or nitrite into purified ^{234}U is not preferred for this project, but selecting a resin then became a priority.

In terms of resin comparison, U affinity (k') to each resin is, of course, very important. The dynamic loading capacity of U (g U/100 mL resin bed) of each resin and the U band quality on a column are also important engineering parameters because the process throughput and separation controls are essential for U purification. So the column run that measured the "dynamic loading capacity" of U is different from the batch experiment that measured the "equilibrium loading capacity." The dynamic loading capacity run included more influencing factors, such as diffusion of metal ions into the pores of the resin and their "random walk" dispersion as they travel different paths through the spaces between resin beads in the column (see Figure 9).
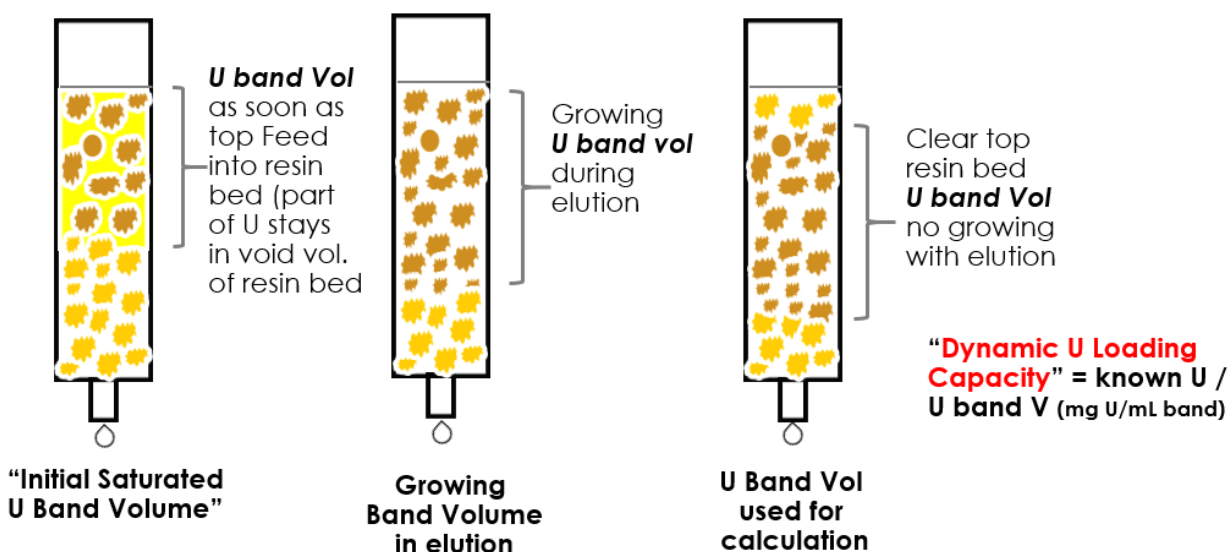
Figure 9. Concept of column run to measure the dynamic U loading capacity.

Loading a feed of known U amount in selected [HNO$_3$] forms a U band on the column as soon as the feed solution merges into the top of resin bed. The known amount of U in feed vs. volume of this U band is called the "initial saturated loading capacity" of U at the selected [HNO$_3$]. At this point, part of the U in feed exists physically in the void volume between the resin beads instead of adsorbed on resin. By elution of the column with HNO$_3$ of same concentration, the U band expands, which indicates the "free" U in the void migrates along the column and adsorbs on resin. In the case of Pu on an *MP*-1 resin column, the Pu band would stop expanding at the point when all "free" Pu has been adsorbed on *MP*-1 resin, due to its ultrahigh affinity (k'>10^3) to the resin. In the case of U on a selected resin, the U band would keep expanding until the band shifts away from the top of the resin bed. The known amount of U in feed vs. volume of U band at this point is called "dynamic loading capacity" of U at the selected [HNO$_3$].

A 7 mL UTEVA resin column and a 10 mL TRU resin column were prepared and conditioned with 8 *M* HNO$_3$. A U/impurities solution after Pu removal by *MP*-1 column runs was prepared as the feed of 32.6 mg U/mL and of 8 *M* HNO$_3$. The feed was loaded onto both columns in parallel (Figure 10).
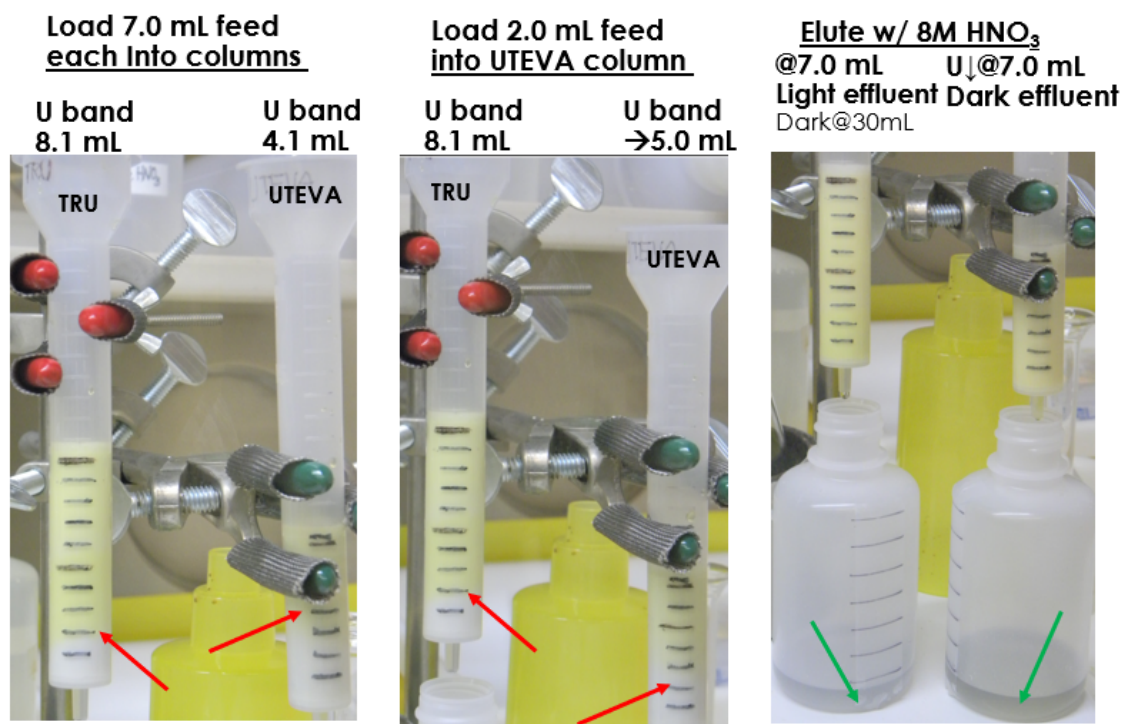
Figure 10. Comparison column test of UTEVA and TRU resins by parallel U loading/eluting

When each 7.0 mL of the feed was loaded onto UTEVA and TRU columns, the initial U band volume on the UTEVA column was measured as 4.1 mL, while that on TRU column as 8.1 mL. Additional 2.0 mL of the feed was loaded individually onto the 7 mL UTEVA column, resulting a U band of 5.0 mL. At this point both columns had 2 mL of "blank" resin bed. Both columns were eluted with addition of 8 M HNO$_3$ and both U band fronts reached bottom of columns after 7.0 mL 8 M HNO$_3$ elution. By observation of two collected elution solutions, impurities (dark color) eluted from UTEVA column by same 7 mL eluting appeared more than from TRU column. After eluting both columns with additional 2 mL of 8 M HNO$_3$, a U product bottle was switched with the collection bottle for UTEVA in case the U broke through the column while more 8 M HNO$_3$ was added onto TRU column. After eluting with a total 30 mL of 8 M HNO$_3$ through the TRU column, the dark zone on the resin bed was washed off the TRU column. The U on both UTEVA and TRU column was stripped off into the same U product bottle with 0.05 M HNO$_3$. The three bottles in Figure 11 are the bottle for UTEVA (9 mL load + 9 mL elution), the bottle for TRU (7 mL load + 30 mL elution), and the bottle for the purified U product.
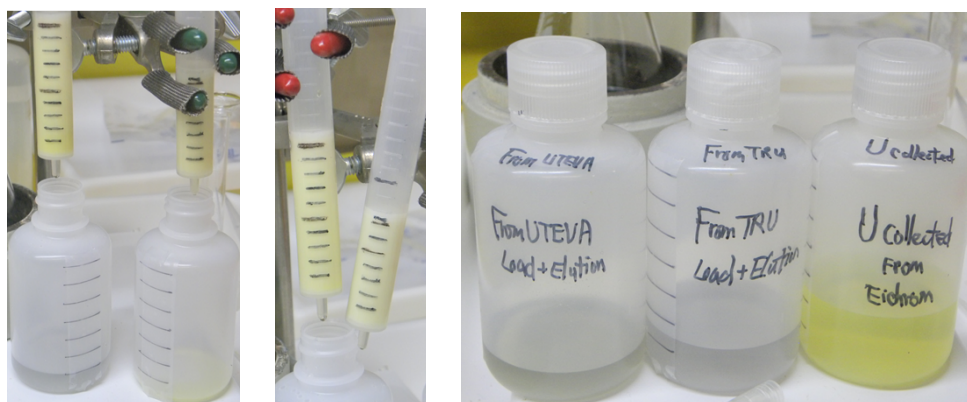
Figure 11. Impurity elution and U stripping in the comparison column test.

Based on known amounts of U loaded onto each column and the initial band volumes, the initial saturated U loading capacity for UTEVA at 8 M HNO$_3$ is calculated as 58.68 mg U/mL bed and that for TRU as 28.17 mg U/mL bed. Obviously, with the same 300 mL resin bed volume, UTEVA would hold double the amount of U at the initial feed loading. But the U on UTEVA broke through at 18 mL (2.57 BV) 8 M HNO$_3$ (9 mL load + 9 mL elution), while the U on TRU at 37 mL (3.7 BV) 8 M HNO$_3$ (7 mL load + 30 mL elution). Limited by both column sizes, the U loading capacity of both resins failed to be calculated (no blank top resin bed was observed before U breakthrough).

A notable result was observed that the dark band of impurities was removed from the TRU column by 30 mL (3 BV) 8 M HNO$_3$, while the band was removed from UTEVA by only 9 mL (1.29 BV) 8 M HNO$_3$. Does TRU resin hold impurities more tightly than UTEVA? A literature review indicated the answer is "Yes." TRU resin, a mixture of TBP and carbamoyl methylphosphine oxide, is also capable of retaining trivalent elements (e.g., Am and lanthanides). At least [241]Am was still a big part of the gamma contributors (part of [241]Am was removed by "pre-cut" of the cycling MP-1 AX column runs for Pu removal) among impurities with U.

Considering higher loading capacity and lower amount of radioactive liquid waste to be generated, UTEVA resin was selected as the extractant for purifying U from all other impurities and scaled up to 300 mL resin bed for processing U in batches after Pu removal cycles.

The 300 mL UTEVA column was operated for several runs of U purification with batches of U feed solutions. Some engineering issues of column controls occurred (e.g. lower density resin floating caused resin bed breaching [Figure 12]), where the top quartz wool plug was not capable of blocking the floating resin because the overall density of UTEVA resin is about the same or even lower than 8 M HNO$_3$.This issue could be solved by designing a screwed-in top frit for the column, but the other issue bothered us even more: U band channeling (Figure 12), no matter how carefully the U feed was loaded into the column.
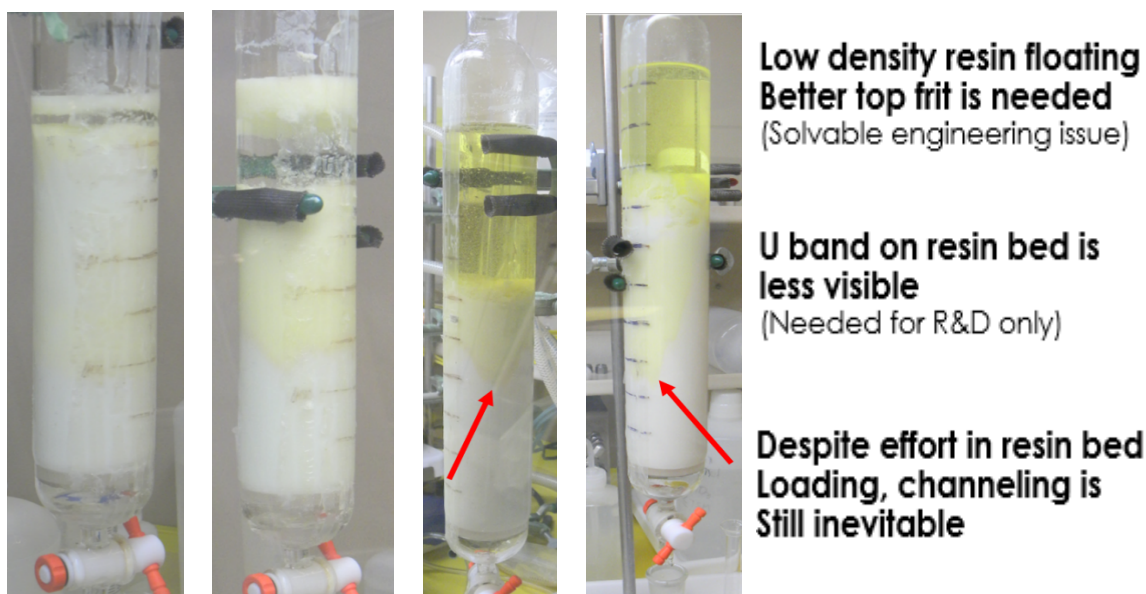
Figure 12. Engineering issues with large size UTEVA resin bed column runs.

Almost all Eichrom extraction chromatographic resins are made of a porous polymer matrix (Amerchrom CG-71, low density) impregnated with selected organic extractants (lower density than water). When small Eichrom columns deal with trace amount of sample nuclides for analytical purpose, the issues of

resin bed breaching and band fingering will not be exposed in its application. The issues would show up with large size Eichrom resin columns processing greater than gram levels of nuclides.

A well-designed column with a tight frit of both ends operated with entering effluent upflowed (opposite to the current design with effluent entering from top to bottom) may alleviate the above issues.

Before seeking a new column design, *MP*-1 AX resin became a new resin option, because of the deep impression by the slow-moving U band on *MP*-1 column during Pu removal cycles. So, a comparison test of column runs was performed for *MP*-1 resin and UTEVA resin.

3.2.2   Comparison of UTEVA resin with *MP*-1 AX resin

As shown in Fig. 13, a 16 mL UTEVA resin column and a 15 mL *MP*-1 AX resin column were prepared and conditioned with 10 M HNO$_3$. A U/impurities solution after Pu removal by *MP*-1 column runs was prepared into a 5.6 mL U feed (227.8 mg U/mL) in 10 M HNO$_3$. Then, 2.8 mL was loaded onto each of the two columns.
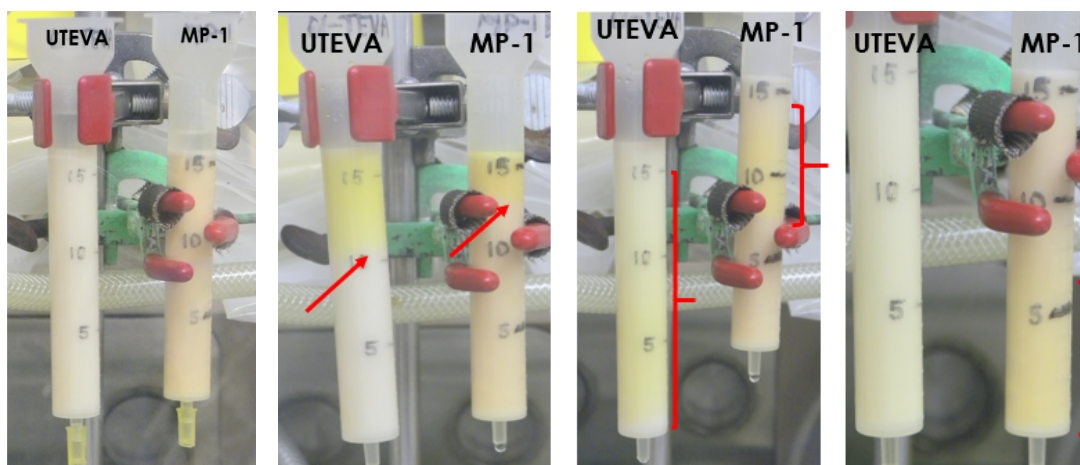
Figure 13. Comparison column test of UTEVA and *MP*-1 resins by parallel U loading/eluting.

As soon as each 2.8 mL volume merged into the top resin beds of the two columns, the initial saturated U band on the UTEVA column was measured as 6.0 mL, but for the *MP*-1 column it was calculated as only 2.5 mL. Correspondingly, the initial saturated U loading capacity on the *MP*-1 column is calculated as (637.8/2.5=) 255.14 mg U/mL resin bed in 10 M HNO$_3$, but for UTEVA it was calculated as (637.8/6=) 106.3 mg U/mL resin bed. 10 M HNO$_3$ was added onto the two columns parallel in 2.0 mL aliquots and the volumes of formed yellow U band on columns were measured and recorded as shown in Table 4.

After 7.0 mL of 10 M HNO$_3$ was added to the UTEVA column, the yellow U band (of 16 mL) reached bottom of UTEVA resin bed and the collection bottle was switched for U collection, while the same 7.0 mL of 10 M HNO$_3$ elution to the *MP*-1 column resulted in a 6.5 mL yellow U band (U front reached 7.5 mL column mark) with 1.0 mL of top resin bed with no U color (blank zone). Since the top blank zone was observed on the *MP*-1 column, this 6.5 mL (with 637.8 mg of U) can be calculated for the "U Loading capacity" on *MP*-1 column in 10 M HNO$_3$ media as 98.12 mg U/mL bed.

More 10 M HNO$_3$ was added onto the two columns. After a total 19.0 mL 10M HNO$_3$ was added into the 15 mL *MP*-1 column. The U band reached the bottom of *MP*-1 column and collection bottle was switched for U collection. Total (2.8 + 19 =) 21.8 mL (1.45 BV) of 10 M HNO$_3$ moved 637.8 mg U from top of the 15 mL *MP*-1 column to the point of starting break-through.

Table 4. Measured U band volumes with feed loading and elution on UTEVA and MP-1 column.

	U band front to UTEVA (mL)	U band front to MP-1 (mL)
feed to each column: 2.8 mL	6.0	2.5
elution to each column (mL)		
2.0	8.5	3.5
+2.0	12.5	5
+2.0	15	6.5
+1.0 (7/16 = 0.44 BV)	16 (↓), collect U	7.5 (clear top: 1)
+7.0	Clear top starts	12 (band as: 6.5)
+5.0 (19 /15 = 1.27 BV)		15 (↓), band 6.5
Strip rest U off, collect all fractions for total U analysis	U band: 16 mL 0.44BV elution	U band:6.5 mL

After a total of 14 mL 10 M HNO$_3$ was added into UTEVA column, top blank resin bed started to appear with 7 mL of U fraction collected into the U collection bottle (previous 2.8 mL feed + 7 mL 10 M HNO$_3$ was already collected in a bottle of "Feed + Elution"). Since the U band front broke through 16 mL UTEVA column ahead of the top blank resin bed appearance, the U loading capacity on UTEVA resin was unable to be measured, but it can be estimated as (106.3/2.6=) 40.9 mg U/mL resin bed if the ratio of initial saturated loading capacity/loading capacity is assumed same (255.14/98.12 =) 2.6 as MP-1 column behavior. The U loading capacity on MP-1 resin column would be 2.4 times higher than that on UTEVA resin column in 10 M HNO$_3$ media.

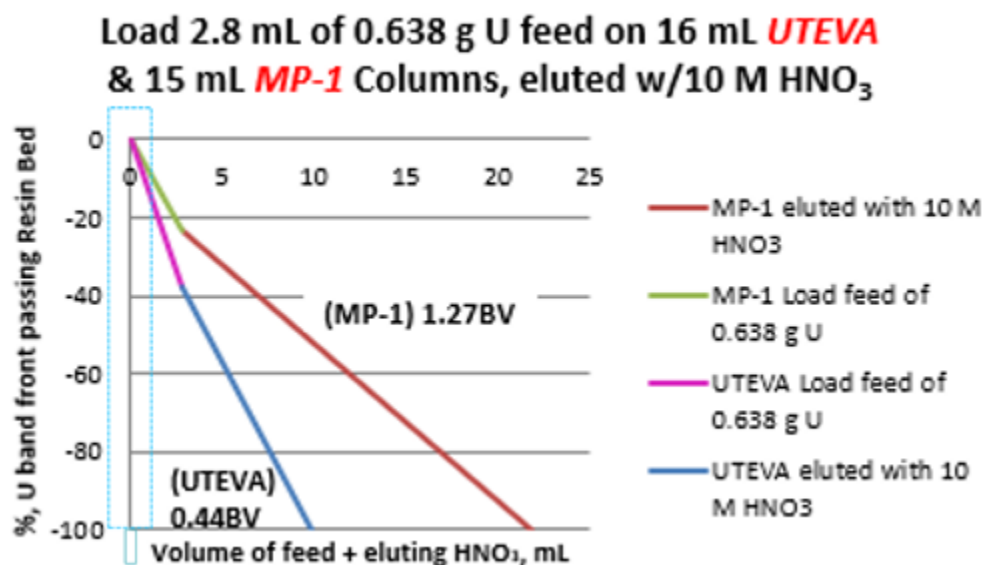

Figure 14. Position of U band front along the column with effluent added from top to bottom.

The consequence of the U loading capacity difference of the MP-1 and UTEVA resins was obvious in column run operations: with same feed loaded into the columns of a similar size (15 mL and 16 mL), 19 mL (1.27 BV) of 10 M HNO$_3$ was eluted through the MP-1 column before U breakthrough, which

allows impurities of M^{n+} ($n \leq 3$) to be eluted off the column ahead of U breakthrough, while only 7 mL (0.44 BV) of 10 M HNO$_3$ was eluted through UTEVA column prior to U breakthrough. Obviously, *MP*-1 column would be more efficient in separating impurities from U under the same column/effluent conditions. This comparison is illustrated in Figure 14, where the Y axis indicates the U band front location from top of the resin bed (Y = 0%) to the bottom of the resin bed (Y = −100%), while X axis represents the volume in milliliters of the effluent (feed and elution) added into the column.

In chemistry, eluting impurities to purify a retained element on a column requires at least 6 BV of elution to ensure the removal of impurities. A 1.27 BV elution in this *MP*-1 column run did not ensure a complete removal of impurities, but it was superior to *MP*-1 resin over UTEVA resin (0.44 BV) under same experiment conditions. Uranium on both columns was stripped off with enough 0.3 M HNO$_3$ and sampled for analysis.

From references [4–7] we know that k' of U with TRU and UTEVA has peak values around 4–8 M HNO$_3$, but this is not true for higher [HNO$_3$]. Also, k' of U with AX resins has no dramatic increase from 8 M HNO$_3$ to 10 M HNO$_3$. Therefore, the influence of U feed concentrations on the measured U loading capacity on resins was apparent (Table 5).

Table 5. U loading capacities on resins under different experiment conditions.

	TRU	UTEVA	MP-1	[HNO$_3$]	[U] feed
Init.Sat.L.Cap., mg U/mL bed	28.17	58.68	/	8 M	32.6 g/L
U L.Capacity, mg U/mL bed	/	/	/	8 M	32.6 g/L
Init.Sat.L.Cap., mg U/mL bed	/	106.3	255.1	10 M	227.8 g/L
U L.Capacity, mg U/mL bed	/	(40.9)	98.12	10 M	227.8 g/L

MP-1 resin was eventually selected because of its higher U loading capacity for purifying [234]U from all other impurities (including remaining trace Pu) after the cycling *MP*-1 AX column runs for Pu removal. With a 300 mL of *MP*-1 AX column (limited by glovebox space), tens of grams of U can be column treated in batches in a similar cycling manner that was used for Pu removal (a few steps were omitted, see Figure 6). With the column size enlarged 20 times (from 15 to 300 mL), the U feed may increase up to 10 g U/feed load only since the BV of elution was expected higher than 1.45 BV for more efficient removal of impurities per run.

3.2.3   Variation of feed/elution conditions for more efficient removal of impurities

For purification of nearly 70 g of [234]U in two phases of the campaign, U was divided into eight batches, and each batch was column treated by cycling for four to five runs. The Table 6 shows part of the *MP*-1 column runs for U purification (not the runs for Pu removal). It lists U amounts/volume of each feed (the number in blue was the analyzed result of elution fractions) and elution conditions, including record of the U band information and the estimated U loading capacity by calculating each run's parameters.

Table 6. Part of cycling *MP*-1 AX runs for ²³⁴U purification from all remaining impurities.

Date	Bed Vol (mL)	Col condn w/ (M)	Bat/run#	Feed U, g	Feed H⁺	Feed, mL	Feed, BV	feed, [U] (g/L)	band, mL (by in bed	Ini Loadin Cpct, g/mL	Elute, M	Band max (mL)	U LoadCp gU/100mL	mL, (w/
2/7/2018	300	7.5	B"	5.2714	7.5	70	0.234	75.30571	45	0.117142	7.5	170	3.100824	
2/6/2018	300	7.5	#312 1"	10.31	7.5	141	0.47	73.12057	75	0.137467	7.5	160	6.44375	
2/2/2018	300	7.5	#319 2"	9.943	7.5	147	0.49	67.63946	70	0.142043	7.5	160	6.214375	
2/1/2018	300	7.5	#306 3"	8.096	7.5	149	0.496667	54.33557	85	0.095247	7.5	190	4.261053	
1/26/2018	300	7.5	#312 1'	9.826	7.5	177	0.59	55.51412	120	0.081883	7.5			
				10.31										
1/25/2018	300	7.5	#319 2'	9.3463	7.5	182	0.606667	51.3533	65	0.143789	7.5	160	5.841438	
				9.9431										
1/22/2018	300	10	#306 3'	9.2425	10	271	0.903333	34.10517	120	0.077021	7.5	180	4.497778	
				8.096										
1/18/2018	300	7.5	B'	5.795	7.5	160	0.533333	36.21875	70	0.082786	10	120	4.829167	
				5.2714										
1/5/2018	300	10	#306 3	6.2446	10	242.5	0.808333	25.75093	90	0.069384	10	120	5.203833	
				6.895										
1/4/2018	300	7.5	#319 2	5.9405	7.5	242	0.806667	24.54752	100	0.059405	7.5	150	3.960333	
				5.8988										
1/2/2018	300	7.5	#312 1	10.0064	7.5	368	1.226667	27.1913	150	0.066709	7.5	180	5.458889	
				9.826										
12/27/2017	300	8	B'	10.68	10.38	419	1.396667	25.48926	190	0.068025	7.5	250	4.636	
				11.59										
11/15/2017	300	7.5		11	9.613	362	1.206667	30.38674	155 to 160	0.070064	7.5	200	5.5	
11/14/2017	300	10		13	10.175	342	1.14	38.0117	145	0.089655	10	230	5.652174	
11/2/2017	300	7.5		28	10.39	842	2.806667	33.25416		0.0654	U band breaks through at 590mL of			

Efforts were made to have U retained on the column for a longer time to allow more elution through the column to remove impurities. These efforts focused on changing two conditions: loading the feed with higher [U] or eluting column with higher [HNO₃].

In Fig. 15, we compared two actual runs of 13 g and 11 g U feed of (10 *M* and 9.6 *M*) HNO₃ with elutions of HNO₃ with different concentrations (10 *M* and 7.5 *M*):

300 ml column	11/14/2017	11/15/2017
Feed	13 g U in 342 mL 10.1 M HNO₃ [U] = 38.01 mg/mL in feed	11 g U in 362 mL 9.61M HNO₃ [U] = 30.39 mg/mL in feed
Elution	310 mL (1.033 BV) of **10M HNO₃**	224 mL (0.747BV)of **7.5M HNO₃**
Improve	0.2867 BV in eluting	
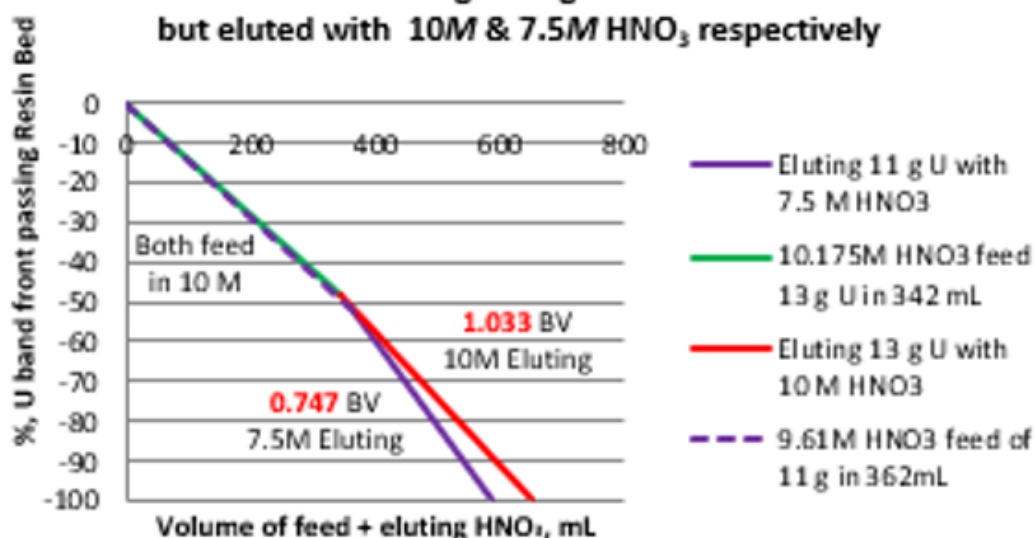
Figure 15. Eluting with higher [HNO₃] prolonged the U retention on *MP*-1 column.

The feed of 13 g U (38 mg U/mL) with 2 g more U than the feed of 11 g U (30.4 mg U/mL) was retained on same 300 mL *MP*-1 column for a longer period by eluting with 10 *M* HNO₃ instead of with 7.5 *M* HNO₃. Elution with 10 *M* HNO₃ created [(1.033 − 0.747)/0.747 = 0.383], which is ~ 38% greater elution efficiency. We knew higher literature k' of U with AX resins were possible in higher [HNO₃], but we did not expect that high of an increase.

What about the influence of U feed concentrations without increasing elution [HNO₃]? In Fig. 16, we compared two other runs with 7.5 *M* HNO₃ feeds with similar amounts of U (10.3 g/10.0 g) but different concentrations of U (27.19 mg U/mL / 73.12 mg U/mL), and then we compared the same elution with 7.5 *M* HNO₃.

300 ml column	1/2/2018	2/6/2018
Feed	10 g U in 368 mL 7.5 M HNO_3	10.3 g U in 141 mL 7.5 M HNO_3
	[U] = **27.19 mg/mL** in feed	[U] = **73.12 mg/mL** in feed
Elution	312 mL (1.04 BV) of 7.5 M HNO_3	400 mL (1.333BV)of 7.5 M HNO_3
Improve	0.2933 BV in eluting	
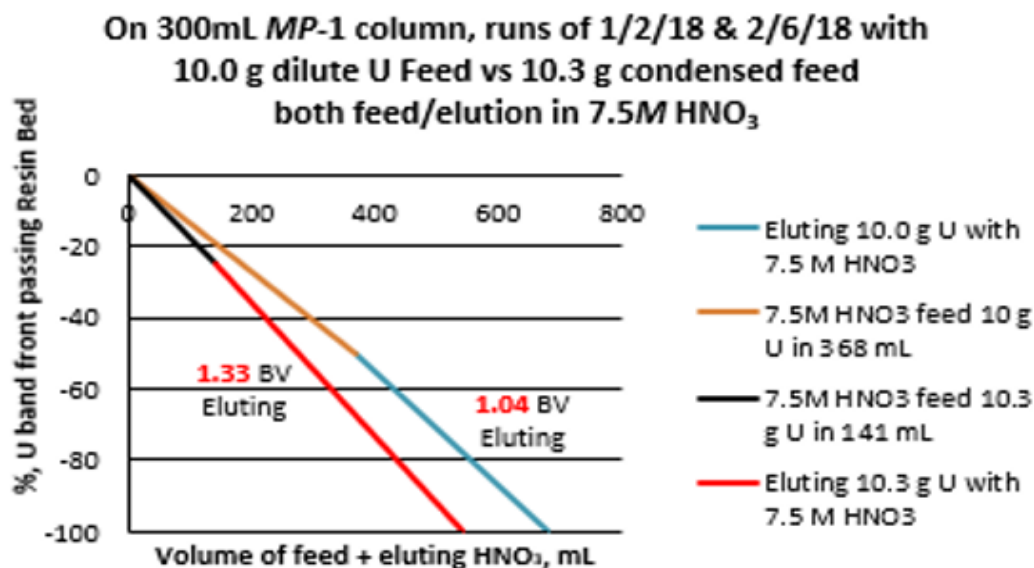
Figure 16. Loading feed of higher [U] prolonged the U retention on *MP*-1 column.

Loading 10.3 g U of condensed feed vs. 10.0 g U of dilute feed into same 300 mL *MP*-1 column resulted in [(1.33 − 1.04)/1.04 = 0.279], which is a 27.9% increase of the impurity elution efficiency.

Does this imply the k' values increase because of the higher [U] feed? Or is the adsorption extent of metal ions onto a resin dependent on the metal ion concentration? Without theoretical answers to the above questions, we still adapted engineering controls for the column operations. By using high [U] feed and high [HNO_3] elution for 300 mL *MP*-1 column runs, more than 65 g of ^{234}U was purified, precipitated into $^{234}UO_4.4H_2O$, and then converted into $^{234}U_3O_8$.

URANYL NITRATE SOLUBILITY
[Reference 88]

Feed loading of High conc. U onto AX resin bed:

Small bed volumes holding U, allowing more BVs of impurity eluting

Collapsed top bed will be self-repaired during elution

U band volume is counted from the U band front to the original top resin line (300mL mark)
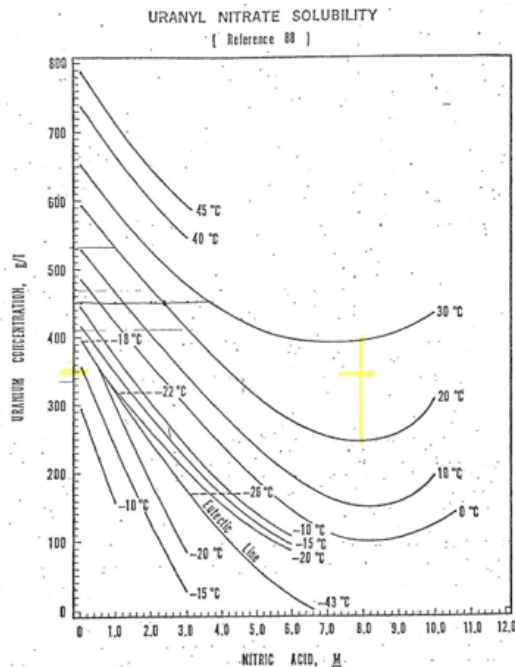
Cited from **The Preliminary Safety Analysis Report XN-FR-32** by Exxon Nuclear Company

Figure 17. Chart for U solubility in HNO$_3$ and influence of condensed feed to resin bed.

What consequences would result from using very high concentrations of U feed in *MP*-1 columns? According to uranyl nitrate solubility chart, no precipitation of U would occur because the lowest U solubility of 300 g/L was demonstrated at 8 *M* HNO$_3$, and our U feed of [U] was below 300 g U/L. High [U] feed did change the physical shape of *MP*-1 resin bed and made the top resin bed crack, shown in Figure 17, but the bed would smooth out with follow up elutions. Because of top resin bed expansion, the estimate of yellow U band volume relied on the position of the front U band and assumed the top resin bed volume did not expand. (It was assumed to remain at the 300 mL mark of the column.)

Table 7. Suggested k' values of U(VI) with *MP*-1 AX resin in high concentrations of HNO₃

MP-1 in HCl	0.1 M	4 M	6 M	≥8 M
Pu (IV)	<<1	<1	~30	>1000
U (VI)	<1	~180	~800	~1000
Am, Be, etc.	<<1	<1	<1	<1
Fe (III)		100	10^3	>10^3
MP-1 in HNO₃	0.1 M	4 M	6 M	8 M
Pu (IV)	<10	~700	>1000	>1000
U (VI)	<2	3-12	50-100	>300
Am, Be, etc.	<1	<1	<1	<1
Fe (III)	n.a.	n.a.	n.a.	n.a.

By reviewing Table 2 with practical experience with IX process by *MP*-1 resin columns, the literature data for k' of U with Dowex-1 resin was found to be unreliable. If other references [4–7] measured k' of U with TRU and UTEVA resins at 150–175 in 8 *M* HNO₃, k' of U with *MP*-1 resin should be at least 300 in ≥8 *M* HNO₃, as shown in Table 7. The authors would like to assume the k' value difference on both tables are due to using different AX resins (*MP*-1 vs. Dowex-1), but the following question remains: Is the adsorption extent of metal ions onto a resin (a process of k' measurement) concentration dependent? It means that results of k' measurement of a metal ion (in most of cases with dilute concentration of metal ions) may be different in operations with high concentrations of metal ion solutions.

Also, dozens of *MP*-1 column runs (Table 6) gave a range of U loading capacity of 4 g U/100 mL resin bed in 7.5 *M* HNO₃ and 5 g U/100 mL resin bed in 9–10 *M* HNO₃, which represents a high affinity of U for *MP*-1 resin in high HNO₃ compared with the case of Pu(IV): 7.5 g Pu/100 mL resin bed. These are important engineering parameters for U–Pu AX processing design.

3.2.4   Quality of purified ²³⁴U in the product form of ²³⁴U₃O₈

Figure 18 shows the appearance of ²³⁴U changing with the operation steps of "Pu removal," "U purification," "U peroxide precipitation," and "U₃O₈ conversion."

Figure 18. Appearance of ^{234}U with the operation steps.

According to the contract, the quality of 65. 5 g of ^{234}U (77.44 g of ^{234}U$_3$O$_8$) was determined by a third party outside ORNL, the Southwest Research Institute in San Antonio, Texas. Duplicate samples of the product of Phase-1 and Phase-2 were delivered upon completion, and the analysis reports were issued on April 11, 2017, and December 6, 2018, respectively. The analysis results of the two batches of product are provided in Table 8, showing that all purity requirements by contract are met.

Table 8. Quality of ^{234}U product determined by a third-party company

	Phase-1		Phase-2
^{234}U in purified U$_3$O$_8$	24.75g		41.75g
Isotopic ^{234}U	99.37 %		99.51 %
Fe in U$_3$O$_8$	38.2 ppm		<12.4 ppm
Total impurities (not Fe)	1938 ppm		1486 ppm

4. CONCLUSION

Separation and purification of ^{234}U from ^{238}Pu and other impurities by a cycling-style *MP*-1 AX resin column run, followed with uranyl peroxide precipitation (single media of HNO$_3$ for both processes) has been proven as an efficient processing scheme for treatment of tens of grams of materials. Uranium shows much higher affinity to *MP*-1 AX resin in ≥8 *M* HNO$_3$, indicating higher k' values than literature data of U with Dowex-1 resins under same conditions. Higher [U] of the feed and higher [HNO$_3$] of the feed/elution are favorable to U retention to the *MP*-1 column as well as the U separation from other impurities.

Uranyl peroxide precipitation served not only as a step to solidify U before conversion to U$_3$O$_8$, but it also served as an additional step to purify the ^{234}U. A new cascade uranyl peroxide precipitation process has

been used to precipitate UO_2^{2+} into $UO_2O_2.xH_2O$ at molar concentrations of HNO_3, which effectively prevents formation of hydrolytic impurities from accompanying the U peroxide product.

A total of 66.5 g of high purity [234]U (isotopic purity >99.3%) was recovered by cycling AX column runs and uranyl peroxide precipitation methods, which is expected to meet the US market demand for this isotope for more than the next 10 years.

5. REFERENCES

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