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Scaling Trivalent Actinide and Lanthanide Recovery by Diglycolamide Resin from Savannah River Site's Mark-18A Targets

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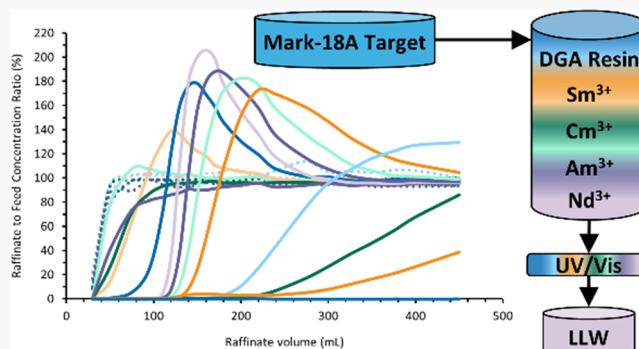


Article Recommendations



Supporting Information

ABSTRACT: The Savannah River National Laboratory is implementing a separation flowsheet to recover rare isotopes and transplutonium elements from irradiated ^{242}Pu targets known as Mark-18A targets. The Mark-18A targets contain the United States' supply of nonseparated ^{244}Pu , which has a wide range of applications from nuclear forensics to production of superheavy elements such as flerovium. The targets also contain hundreds of grams of heavy curium ($^{246}\text{--}^{248}\text{Cm}$), which is used as a target material for ^{252}Cf production. This work investigates the use of diglycolamide resin (DGA Resin) to recover valuable trivalent actinides from the Mark-18A targets. Batch contact experiments were performed on a representative simulant to determine mass loadings. The resin showed an overall capacity of 11 mg/mL for a mixed metal matrix (Zr and La–Gd). Column experiments showed chromatographic separation with transition-metal breakthroughs occurring first followed by the lanthanide series La–Gd. The experiments showed that lanthanide breakthrough occurred after 11 mg/mL mass loading was reached on the column with the mixed metal matrix. A radiological column experiment with an in-line UV/vis cell was able to detect Nd breakthrough just prior to ^{241}Am breakthrough. Implementing an in-line UV/vis cell into full-scale Mark-18A target processing will be used to limit breakthrough of trivalent actinides recovered from the targets.



1. INTRODUCTION

During the late 1960s to the late 1970s, 86 targets containing 8 kg of high-assay ^{242}Pu (Mark-18A targets) were irradiated under high thermal neutron flux (up to 10^{15} neutrons per cm^2 per second) in a K-Reactor at the Savannah River Site (SRS). The original intent of irradiating Mark-18A targets was for large-scale production (milligrams) of ^{252}Cf from ^{242}Pu via a series of neutron capture and beta-decay reactions.¹ Twenty-one of the targets were processed in 1971–1973 at Oak Ridge National Laboratory's Radiochemical Engineering Development Center to recover ^{252}Cf for market development.^{2,3} Additionally, the United States' current supply of ^{244}Pu , approximately 7 g, was recovered from the 21 targets. The United States' supply of ^{244}Pu is depleting due to its use as a standard reference material for nuclear forensics and in research applications such as superheavy element production.^{4,5} The targets also contained hundreds of grams of heavy curium, $^{246}\text{--}^{248}\text{Cm}$. Heavy curium serves as an ideal feedstock for ^{242}Cf , ^{249}Bk , and ^{252}Es production at the ORNL High Flux Isotope Reactor (HFIR). Californium-252 has several industrial uses including a neutron source for various industries, neutron activation analysis, radiotherapy, fundamental research into actinide elements (along with Bk and Es), and heavy element synthesis.^{6–9} Due to the increased demands for ^{244}Pu and heavy curium, the Department of Energy (DOE) tasked the Savannah River National Laboratory (SRNL) to lead the

design and implementation of a separation flowsheet to recover the rare plutonium and heavy curium materials from the remaining 65 Mark-18A targets.

To recover the valuable materials, the Mark-18A material recovery flowsheet separates the target's aluminum cladding by caustic dissolution, leaving most of the fission products and the actinides as a solid material. The undissolved material is filtered and then subsequently dissolved in $>7\text{ M HNO}_3$ at elevated temperatures. The resulting high nitrate solution, containing dissolved plutonium, actinides, and most of the fission products, will be sent through an anion exchange column using Reillex HPQ resin, similar to its use in the SRS's HB-Line Facility.^{10–13} Reillex HPQ achieves Pu/Am decontamination factors on the order of 14,000.^{11,12} The high decontamination factors are a result of Reillex HPQ's high selectivity for the $\text{Pu}(\text{NO}_3)_6^{2-}$ anion at $>7\text{ M HNO}_3$ and little to no affinity for lanthanides (Ln), americium, curium, and fission products. As a result, in the Mark-18A material recovery

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flowsheet, the Ln, Am, Cm, and remaining fission products remain in the raffinate and require additional processing to recover heavy Cm from the >7 M HNO_3 raffinate.

An Am, Cm, and Cf separation method was developed at the SRS around 1971 using a pressurized ion exchange process that could separate Am, Cm, and Cf.^{14–16} The column separation utilized a styrene and divinyl benzene copolymer resin (Dowex 50 W) containing sulfonic acid functional groups to recover and separate the transplutonium elements over four successive columns.^{16,17} The four 4 ft tall columns decreased from 4 in. diameter down to 1 in.¹⁶ Elements were loaded onto the column from a nitric acid solution and were eluted by a 0.05 M diethylenetriamine pentaacetic acid solution. Fermium came off first and then Es, Cf, and Bk followed by Cm and Am. The elution bands were monitored by an in-line BF_3 tube to detect neutrons from ^{252}Cf and ^{244}Cm and lithium-drifted germanium detector and low-energy gamma spectrometer for ^{244}Cm and ^{243}Am .^{14,18} The entire process was operated under high pressures (up to 2500 psig) to overcome the pressure drop across all four resin beds and maintain an acceptable flow rate. The flow rates were important to limit the residence time of the radioactive material on the resin, thus minimizing the amount of thermal and radiolytic resin degradation. Furthermore, the high pressures prevented radiolytic gases from building up in the column, causing resin bed disruptions.^{14,16}

Use of pressurized stainless-steel columns with radioactive solution is high risk and difficult to perform under the current SRNL safety basis. Implementing the same previously described process with a nonpressurized column in the Mark-18A material recovery flowsheet would have additional drawbacks because the high NO_3^- concentration in the Reillex HPQ raffinate (>7 M HNO_3) would require significant dilution or denitration. Moreover, use of a sulfonic acid functional group resin will introduce deleterious sulfonic thermal and radiolytic degradation products into the waste stream. As a result of these drawbacks, an alternative method for recovering Cm from >7 M HNO_3 solution in a nonpressurized column with a carbon, hydrogen, oxygen, nitrogen-based (CHON) resin is preferred due in part to CHON resin's incinerability.^{19–21}

A well-known trivalent lanthanide and actinide extractant that performs in high-molar nitric acid is the N,N,N',N' -tetraoctyldiglycolamide (TODGA) ligand.^{22–25} In commercial production, TODGA is physisorbed onto a polymethyl methacrylate (PMMA) backbone resin and sold under the trade name DGA Resin (Eichrom Technologies Inc.). The resin is often used to concentrate Am and Cm for bioassay analysis using prepackaged 1–2 mL columns. The bioassay samples typically contain very few elements competing for binding sites on DGA Resin, unlike the significant amounts of both actinides and fission products that will be present in the dissolved Mark-18A targets.²⁴ As a result, fission products will be in competition for binding sites with the desired actinide material. The purpose of this study was to determine the retention of fission products on DGA Resin to optimize the mass loading of Am and Cm found in the Mark-18A targets for gram-scale recovery. Furthermore, the capability of in-line UV/vis spectroscopy to monitor breakthrough in the raffinate was also tested. The results will be used to design and implement a unit operation to recover Am and Cm from Mark-18A targets at the SRNL.

2. EXPERIMENTAL SECTION

DGA Resin was purchased from Eichrom Technologies Inc. (300–840 μm particle size, I-grade). The DGA Resin was wetted prior to use by exposing the resin to 1–2 M HNO_3 solution in a 1:2 resin-to-acid volume ratio over the course of 5 h. The batch was occasionally stirred, during which the resin would settle to the bottom indicating that the resin was properly wetted. The supernatant was decanted, and the resin was rinsed with water and stored as a slurry for future use. Two Mark-18A target simulants were generated by dissolving representative elements, primarily as metal nitrate compounds in 7 M HNO_3 . The metal concentrations for Mark-18A Simulant 1 (non-radioactive test) and Simulant 2 (radioactive test) are listed in Table S1. The primary elements in the Mark-18A simulants were Mg, Al, Fe, Zn, Sr, Zr, Mo, Ru, Pd, Sn, Cs, La, Ce, Pr, Nd, Sm, Eu, Gd, and Re. Zinc was used as a surrogate for Cd, Re was used as a Tc surrogate, and extra Nd was added as a surrogate for Am and Sm for Cm. To study bounding conditions, Simulant 1 represented a concentrated simulant based off initial Mark-18A target acid dissolution volumes. Simulant 2 represented a more dilute solution due to processing the dissolved targets through other unit operations downstream of target dissolution. The Mark-18A material flowsheet will require acid adjustments, solid transport, and rinse steps that cause dilution; thus, Simulant 2 better represents the expected feed conditions for the DGA Resin column. Constituents in Simulant 2 were simplified, compared to Simulant 1, by removing several nonabsorbing elements (Al, Sr, Ru, Sn, and Cs). In Simulant 1, Mg, Fe, and Pd were added in excess. The concentrations were adjusted in Simulant 2 to better represent concentrations in Mark-18A targets. Simulant 2 also contained 2.6 μM ^{241}Am for radioactive studies. **Caution!** The isotope ^{241}Am is radioactive. Manipulation of the radioactive material was safely handled in a radioactive designated glovebox.

2.1. Simulant 1: Non-Radioactive Experiments.

Batch contact experiments were performed with 10 mL of Simulant 1 in contact with 2.4 g of DGA Resin. Small-scale column experiments were performed using 1×10 cm (approx. 8 mL DGA Resin bed volume) Econo-Column Bio-Rad chromatography columns. Wetted DGA Resin was added to the column as a slurry and topped with a porous glass frit. The solution flow rate was controlled by a Cole-Parmer 780200C Dual Syringe Pump with Tygon tubing connecting the syringe to the column. Flow rate tests on the 8 mL column varied between 1, 3, and 5 BV/h (bed volumes per hour). A total of 16 mL of Simulant 1 was processed through the column for each test followed by three bed volumes (24 mL) of 7 M HNO_3 wash solution. All other tests used a 3 BV/h flow rate. A midscale non-radioactive experiment was performed using a custom glass column 2.03×16 cm (approx. 52 mL) DGA Resin bed volume (Figure S1). The flow rate was controlled by an FMI Q Pump Model 6QGS0. Grab samples were collected from the raffinate at various volumes throughout the small-scale and midscale column experiments. All experiments were performed in singlet.

Quantitative analysis of the Simulant 1 (non-radioactive) and Simulant 2 (radioactive) samples was performed at the SRNL's ISO 17025 accredited analytical laboratory using NIST-traceable standards and followed well-vetted procedures. Quantitative analysis was performed on an Agilent 7700x inductively coupled plasma mass spectrometer (ICP-MS).

Argon was used as a carrier and makeup gas, and He gas was used in the reaction cell. Instrument dilution factors were 50,000× and 1000× in 2 vol % nitric acid on a blank, 0.5, 1, 5, 10, 25, and 50 µg/L calibration curve for each element. ICP-MS results are reported with an overall 20% uncertainty.

For batch contact studies, the percent adsorbed was calculated as follows: percent adsorbed = $\frac{C_0 - C_f}{C_0} \times 100$, where C_0 is the initial metal concentration in the simulant and C_f is the final metal concentration. The total metal loading was calculated as follows: metal loaded = $\frac{\sum m_0 - \sum m_f}{R_v}$, where m_0 is the initial mass of an element (mg) in the simulant, m_f is the final mass of an element, and R_v is the resin volume (mL). The masses of all elements loaded to resin were summed together and divided by resin volume. For column studies, the mass retained (MR) on the column was calculated using eq 1

$$MR = \int_a^b f(x)dx - \int_a^b g(x)dx \quad (1)$$

where $f(x)$ represents the mass sent through the column for a given volume, a to b , and $g(x)$ is the mass in the raffinate for a given volume. The difference between $f(x)$ and $g(x)$ produces the mass retained on the column.

2.2. Simulant 2: Radioactive Experiment. A 2.2×20.3 cm (77 mL DGA Resin bed volume) column experiment was performed on a custom glass column (Figure S1). The experiment was performed in singlet. The flow rate was controlled to 2.6 BV/h (3.4 mL/min) with an FMI Q Pump. Grab samples (1 mL) were collected from the raffinate at various volume points throughout the experiment. Grab samples were analyzed by ICP-MS as described previously. For m/z 241 (^{241}Am), ^{238}U was used as the calibration standard for semiquantitative analysis. Additionally, ^{241}Am was quantified on a Canberra HPGe Well Detector supported by Genie2K software. HPGe results are reported with a 5% uncertainty. An in-line UV/vis spectrophotometer and in-line flow cell provided the spectra of the raffinate solution downstream of the column prior to grab sample collection. The spectrophotometer was an Avantes model AvaSpec-ULS3648 with a 10 W tungsten halogen lamp (AvaLight-HAL-S-Mini) and 6 W xenon light source from Excelitas (502-6812-21-ENG). Fiber optic cables were installed through the radioactive glovebox and connected to the in-line flow cell with a 0.714 cm path length.

3. RESULTS AND DISCUSSION

Batch contact experiments of Mark-18A Simulant 1 with DGA Resin demonstrated slow kinetics. After 2 h contact time under ambient conditions, the percent of lanthanide metals adsorbed on the resin had not reached equilibrium, as shown in Figure 1. The data is also presented as $\log(K_d)$ values in Figure S2. Even though equilibrium for all element species had not been reached after 2 h contact, the data indicates which elements from the simulant adsorb to the resin under 7 M HNO_3 processing conditions. The elements Mg, Al, Zn, Sn, and Cs did not have an affinity for the resin.²⁴ Strontium adsorption is dependent on HNO_3 concentration. At 3 M HNO_3 , Sr has an affinity to DGA Resin.²⁶ Under the 7 M HNO_3 conditions tested, Sr adsorbed to a small extent initially but was displaced by elements with higher affinity and slower kinetics as the contact time increased. Transition metals Zr, Mo, Pd, Re, and Fe had varying affinities to DGA Resin. Zirconium's affinity

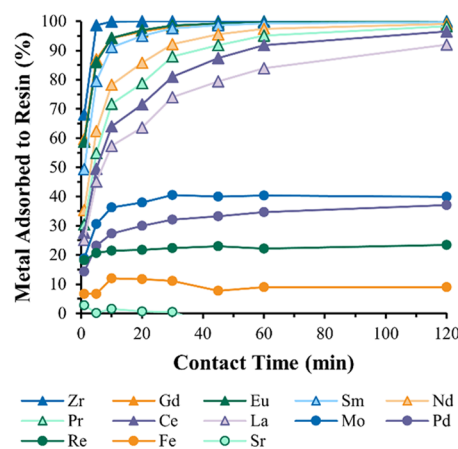


Figure 1. Kinetic results showing adsorption of listed metals from Mark-18A Simulant 1 to DGA Resin at varied contact time lengths.

toward the resin was significant and greater than the lanthanides' affinity. The other transition metals Mo, Pd, Fe, and Re (as the Tc surrogate) were all lower than the lanthanides. A batch contact was also conducted for 7 days (Figure S3) to ensure that equilibrium was reached, and results were used to calculate the overall mass loading. The total metal loaded onto the resin was 11 mg/mL of Mark-18A simulant at 30 min, 12 mg/mL at 120 min, and remained at 12 mg/mL after 7 days. For comparison, a mmol/mL value was calculated by converting the mass of each element loaded on the column to mmol to account for the different atomic masses. For the mixed metal matrix, the 12 mg/mL mass loading was equivalent to 0.098 mmol/mL. The value is similar to Eichrom's 0.086 mmol/mL Eu loading capacity.²²

A small-scale 1×10 cm DGA Resin column (8 mL bed volume) experiment was completed using Simulant 1. Based on the batch contact study, 12 mg/mL loading capacity was assumed for the DGA Resin column and was used to estimate when lanthanide breakthrough would occur. The lanthanide (La–Gd) and zirconium masses were predicted to fully load (i.e., reach 12 mg/mL) after 11 mL of simulant had been processed through the column. In total, 16 mL (two bed volumes) of simulant was passed through the column followed by 24 mL of 7 M HNO_3 wash solution, as shown in Figure 2. The amount of metal retained on the column was calculated based on metal concentrations in the raffinate and wash solutions. Figure 2 shows the element concentrations in the raffinate as a percentage versus the feed concentration. At 100%, the metal concentration in the raffinate is equivalent to feed concentration. A value greater than 100% indicates that the element was initially retained on the column and concentrated into a band prior to breaking through the column. The elements Al, Cs, Ba, Zn, Sn, and Mg rapidly reached 100% indicating no retention on the column. The elements Sr, Fe, and Mo achieved concentrations over 100% indicating that the elements accumulated in bands on the column. As predicted, lanthanum started to break through after 11 mL of simulant had gone through the column. Neodymium started to break through in the 15–16 mL range and coincided with an overall resin loading concentration of 11 mg/mL (Nd, Sm, Eu, Gd, and Zr), consistent with the loading capacity observed at shorter timescales in batch contact.

Additional tests were performed at 1 and 5 BV/h to measure changes in metal retention under different linear velocities.

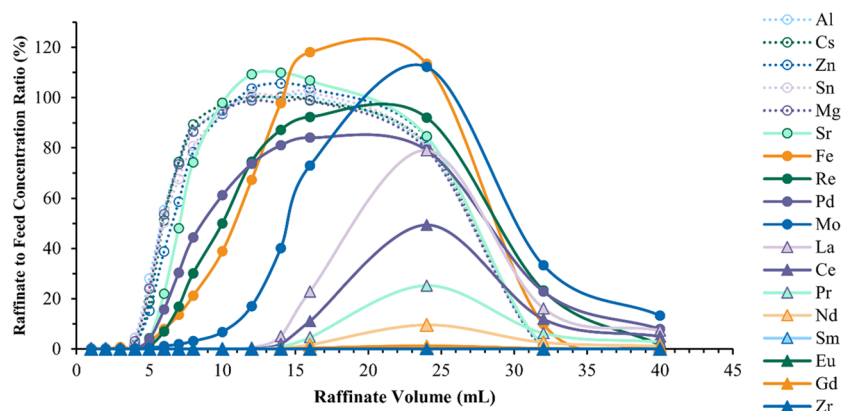


Figure 2. Results of the 8 mL column run at 3 BV/h. Two bed volumes of the simulant through the column (16 mL) followed by three bed volumes of 7 M HNO₃ wash (24 mL). Data presented as a ratio of metal concentration in the raffinate to starting concentration in the feed simulant.

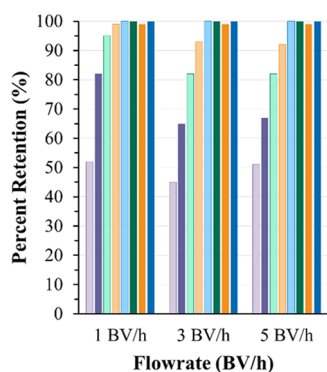


Figure 3. Percent retention of select elements by DGA Resin at varied flow rates. Values are reported with an overall uncertainty of 20%.

mL at a 5 BV/h flow rate is due to saturated metal loading on the resin. Thus, results indicate a kinetic limitation is occurring. A slower flow rate sharpens the metal boundaries by allowing increased interaction between the metal and extracting resin, thereby improving separation and recovery. However, slow flow rates can be cost-prohibitive (e.g., increased labor and time). As a result, 1 BV/h was deemed too slow for application and 3 BV/h was selected as the minimum flow rate.

A 52 mL bed volume (2.03 × 16 cm) column and 450 mL of Simulant 1 were used to determine when Sm (as the Cm surrogate) breakthrough would occur at a 3 BV/h flow rate. Figure 4 shows the percent metal concentration in the raffinate compared to Simulant 1 feed concentrations. The elements Al, Cs, Ba, Zn, Sn, and Mg immediately reached 100% (no retention on column), matching the results of the small-scale 8 mL column. In batch tests, the elements Sr, Fe, Re, Pd, and Mo were adsorbed to the DGA Resin in varying degrees, but all were less than lanthanide and Zr uptake. Strontium had the lowest uptake in the batch contact tests, and thus, in the 52 mL bed volume test, it was the first element to elute off the column through displacement chromatography. Iron and Mo had similar behaviors, with maximum raffinate concentrations observed at 120 and 150 mL, respectively. Re and Pd bands were not observed; however, their concentrations in the raffinate gradually reached 100% of feed concentration instead of immediately reaching 100% like Al, Cs, and other

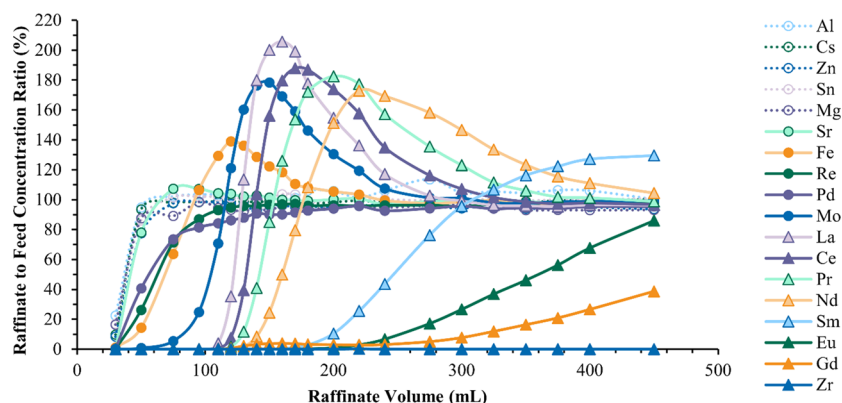


Figure 4. Element breakthrough of Mark-18A Simulant 1 through the 52 mL DGA Resin column at a 3 BV/h flow rate. Values are reported with an overall uncertainty of 20%.

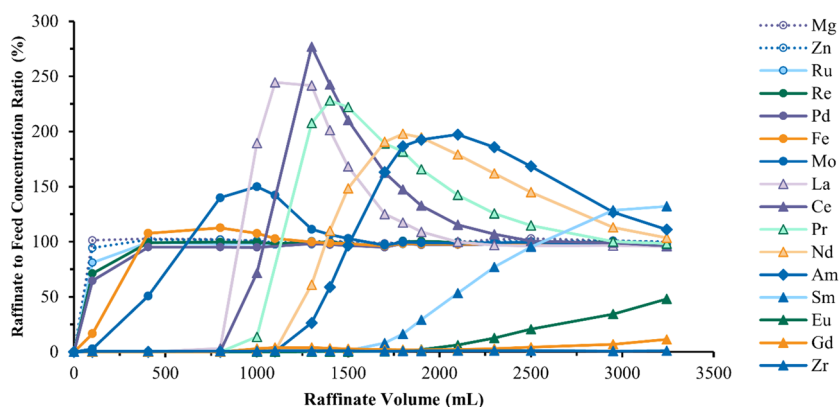


Figure 5. Element breakthrough of Mark-18A Simulant 2 (^{241}Am tracer) through the 77 mL DGA Resin column. Values are reported with an overall uncertainty of 20%.

nonadsorbing elements. It is not clear why Re and Pd did not form bands similar to Sr, Fe, and Mo.

Based on the feed concentration of Simulant 1 and a lanthanide loading of 11 mg/mL on the DGA Resin column, the breakthrough was predicted to begin around 100 mL feed processed. The experimental results were plotted as mass of the element in the raffinate versus the known mass of each element processed through the column (Figure S4). From this data, the mass retained was calculated using eq 1. Initially, the mass retained increased at a linear rate since the simulant flowed through the column at a constant rate. Breakthrough was declared when the element's mass retained on the column dropped below 99.5% (Table S2). A graph of lanthanides and zirconium mass retention is provided in Figure S5. To calculate loading capacities at a specific element's breakthrough point, the element's retained mass (mg) and mass of elements that had yet to break through were summed up and divided by the column's bed volume (mL). For example, lanthanum breakthrough occurred between 110 and 120 mL feed processed and had a loading of 0.6 mg/mL. However, La plus the remaining lanthanides and Zr had a loading of 11 mg/mL at the point of La breakthrough. The 11 mg/mL is similar to the loading value observed in batch and small-scale column experiments. Similarly, Nd (Am surrogate) began to elute around 140 mL when the Sm, Eu, Gd, and Zr loadings reached 11 mg/mL.

The prior tests used a simulant (Simulant 1) based off metal mass expected in one-fourth of a Mark-18A target but was dissolved only in 2 L of 7 M HNO_3 , making the simulant roughly 7 times more concentrated than the expected process conditions (Table S1). Recall from the Experimental Section that the DGA Resin feed solution will become more dilute due to acid adjustments, solid transport, and rinses that occur as part of the Mark-18A material recovery flowsheet unit operations upstream from the DGA Resin column. A dilute simulant (Simulant 2) column test was performed to determine if the elements of interest would break through at the 11 mg/mL metal loading observed in the 8 and 52 mL bed volume Simulant 1 experiments. Simulant 2, initially containing both ^{239}Pu and ^{241}Am , was first passed through a Reillex HPQ column to simulate Mark-18A material recovery flowsheet conditions. Greater than 99% of Pu and 39% of the Pd masses were removed from Simulant 2 by the Reillex HPQ column. The parameters and technical results of the Reillex HPQ are reported elsewhere.¹¹ The raffinate was then used as the feed for the DGA Resin radiological column experiments.

Knowing the lanthanide metal concentration in Simulant 2, Nd breakthrough was estimated to occur around 1000 mL (16 BV) and Sm at 1500 mL (24 BV) when the primary element (i.e., Nd and Sm) and succeeding elements reached an 11 mg/mL mass loading on the 2.2×20.3 cm DGA Resin column (77 mL bed volume). Breakthrough ranges for all elements are listed in Table S3. As shown in Figure 5, Nd began to break through around 1100 mL (18 BV) when the Nd, Sm, Eu, Gd, Am, and Zr concentrations reached 11 mg/mL on the column. The experimental 1100 mL breakthrough is 10% off the 1000 mL predicted breakthrough. Americium started breaking through after 1100 mL (18 BV), following the onset of Nd breakthrough. The results indicate that Nd is an excellent indicator for Am breakthrough, and Nd is a representative surrogate. As stated in the Experimental Section, the experiments were performed in singlet. While replicate experiments are ideal to measure accuracy and precision, single experiments were performed due to cost of analytical analysis, which is further exacerbated when handling radioactive samples. For each subsequent larger-scale experiment in this study, the information from prior experiments was used to predict breakthroughs leading up to the Simulant 2, radioactive experiment. Overall, lanthanide and americium breakthroughs occurred within 10% of the predicted value and followed the expected breakthrough trends. Samarium mass loading dropped below 99.5 at 1500 mL (24 BV) when the Sm, Eu, Gd, Am, and Zr column concentrations reached 10 mg/mL. Although Sm was used as a Cm surrogate, based on the literature, it is predicted that Cm's breakthrough will occur between Am and Sm.^{27,28} Efforts to separate trivalent actinides and lanthanides with diglycolamide extractants show that the trivalent lanthanides have similar extraction values, which increase across the lanthanide series. Americium and Cm display extraction values similar to Nd and Sm, respectively.

Sampling the Mark-18A material recovery process in hot cell operations will be timely and cost-prohibitive. Additionally, the elemental concentrations will vary between each Mark-18A target. As a result of these complications, the application of in-line monitoring by UV/vis spectroscopy to measure breakthrough was investigated. After Simulant 2 exited the DGA Resin column, the raffinate passed through an in-line UV/vis spectrophotometer cell to determine if signals from an element's breakthrough could be detected (Figure 6). A large broad peak below the 700 nm range was present due to Pd in solution and Pd precipitating on the cell window. The Pd precipitation was thought to have occurred during the Pd strip

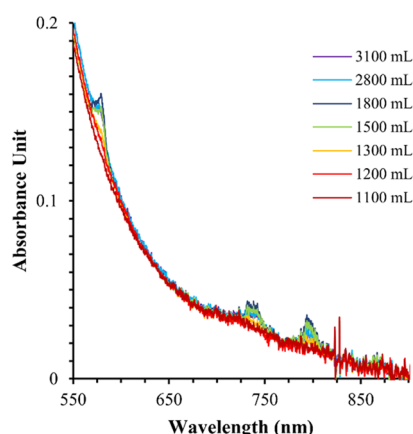


Figure 6. Visible absorbance spectra of the raffinate from Mark-18A Simulant 2 after processing through the 62.5 mL DGA Resin column.

4. CONCLUSIONS

The proposed recovery method for the trivalent actinides and lanthanides by DGA Resin from the Mark-18A simulant was validated. Batch contact experiments showed that the trivalent lanthanides and zirconium have a high affinity for the resin in 7 M HNO₃. Elements such as Mg, Al, Zn, Cs, Ba, and Sn are not adsorbed onto the DGA Resin. Some transition metals such as Fe, Mo, Ru, Pd, and Re show low to moderate affinity but will be easily displaced by the more favored trivalent lanthanides and actinides. Breakthrough curves in column experiments illustrated that chromatographic separations occur, as indicated by high concentration gradients in the raffinate for retained elements. Lanthanides break through the column in the order of increasing atomic number. The lanthanide breakthroughs occur when a concentration of 11 mg/mL is achieved on the DGA Resin column. Concentrated and dilute simulant experiments showed similar mass loading and column breakthrough profiles. Americium tracer experiments validated that Am breakthrough closely follows Nd breakthrough. An in-line UV/vis spectrophotometer was able to track the ingrowth of Nd in the raffinate solution. In full-scale processes, detection of Nd in the in-line UV/vis system will indicate Am breakthrough and serve as a warning that Cm breakthrough is forthcoming. Future work will focus on column design for the full-scale process in SRNL hot cells. Additionally, research is underway to apply the CHON principle and incinerate the loaded DGA Resin to reduce volume while directly converting the loaded metal to an oxide form.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.iecr.0c03897>.

Simulant concentrations, images of experimental columns, log(*K_d*) vs time plot, batch contact of 10 mL Simulant 1 with 2.4 g of DGA resin over an extended period of time (7 days), neodymium mass retained on column on a 52 mL column, element mass breakthrough of listed elements on a 52 mL column, Element breakthroughs of Simulant 1 from 52 mL column, element breakthroughs of Simulant 2 from a 77 mL column, visible spectra of the Nd(NO₃)₃ 579 nm peak and baseline-corrected plot, and plot of Nd concentration in raffinate and baseline-corrected absorbance value of the 579 nm Nd(NO₃)₃ peak of the raffinate (PDF)

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step with thiourea during the Reillex HPQ Simulant 2 processing performed prior to the DGA Resin column experiment. The in-line UV/vis cell was used for both processes. Regardless of the broad Pd peak, as the experiment proceeded, peaks at 579, 740, and 794 nm simultaneously appeared in the spectra. A literature comparison indicated that the three 579, 740, and 794 nm peaks are consistent with Nd(NO₃)₃ species.^{29–31} The primary Nd(NO₃)₃ peak, 579 nm, was baseline-corrected by fitting a polynomial function to the Pd curve and subtracting the curve from the raw data (Figure S6). A lower limit of detection was established to be 3 times the absorbance value of the variance in a blank signal.³² Based on the lower limit of detection, the Nd species reached a detectable concentration at 1300 mL (21 BV), as shown in Figure 7. The peak intensity increased with time, reached a

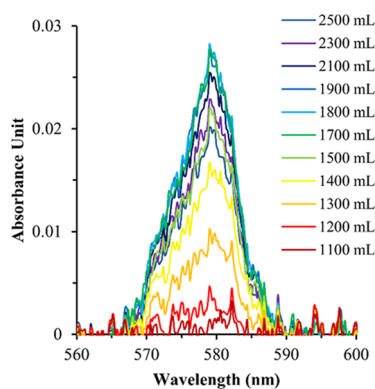


Figure 7. Baseline-corrected Nd(NO₃)₃ 579 nm peak measured at various raffinate volumes after processing through the 62.5 mL DGA Resin column.

maximum at 1800 mL (30 BV), and was followed by a gradual decrease. The trend correlated directly with Nd concentration in the raffinate determined by ICP-MS (Figure S6). Due to Nd and Am's similar behavior on DGA Resin, as stated previously, Nd can serve as an indication that Am is about to break through the column. In the actual Mark-18A process, the Am concentration will be higher and could potentially be detected by its characteristic 503 nm peak.³³ Furthermore, the detection of Nd and Am in the raffinate will serve as an indication that Cm is close to breaking through the column.

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501 <https://pubs.acs.org/10.1021/acs.iecr.0c03897>

502 Notes

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