Published paper

Shafer, J.S., Sulakova, J., Ogden, M.D. and Nash, K.L. (2010) *Partitioning of U, Np, Th, and Eu between acidic aqueous Al(NO3)3 solutions and various TOPO extraction chromatographic materials*. IOP Conference Series: Materials Science and Engineering, 9. 012012 . Doi: 10.1088/1757-899X/9/1/012012

Partitioning of U, Np, Th, and Eu between acidic aqueous $Al(NO_3)_3$ solutions and various TOPO extraction chromatographic materials

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Abstract. As the Hanford site undergoes remediation, it is noted that significant economies could be realized by minimizing the amount of aluminum deposited in High-Level Waste glass. Though such a step is not planned, an acidic scrub of the Hanford sludge could enhance Al removal. It is likely that the resulting $Al(NO_3)_3$ solution would contain measurable amounts of transuranic elements, thus the solution might require some secondary treatment to remove TRU contamination. Thus far, extraction chromatography (EXC) has shown promise [1] as an alternative to a liquid-liquid remediation of the Hanford site. Previous EXC studies have shown >99% of the Eu can be extracted from simulated Al/Cr waste. This study continues an examination of a hypothetical secondary cleanup of the waste by studying the removal of UO_2^{2+}, NpO_2^{+}, NpO_2^{2+} and Th^{4+} from using tri-n-octyl phospine oxide (TOPO) impregnated XAD7 resins. Neptunium was held in the V and VI oxidation states using ascorbic acid and chromate, respectively. Initial results show extraction following classical metal recovery trends, wherein an increased Z_{eff} correlates with increased distribution of the metal into the organic resin phase. The uptake of Eu^{3+} (representative of An^{3+}) on a column of the same material was also investigated. Uptake kinetics were improved by wetting the TOPO-XAD7 resin with *n*-dodecane (TOPO-XAD7n). The presence of *n*-dodecane also provided consistency between batch mode and column mode metal recovery. Preliminary data show >99% recovery of metal ions with a $Z_{eff} \geq 3$ under various simulated conditions.

1. Introduction

The Hanford Site, in south central Washington state, was the first facility to produce plutonium for nuclear weapons. Both the volume and composition of waste resulting from Pu production are major remediation concerns [1]. The most problematic waste component is the sludge created by the caustic environment of the tanks. Research and remediation efforts have focused on caustic leaching to remove problematic nonradioactive elements, aluminum and chromium. Removal of these species would decrease volume and improve the glass matrix of the vitrified high level waste (HLW). While some significant successes have been experienced, the most stubborn Al phase, boehmite (γ-AlO(OH)) has been resistant to caustic leaching.

An alternative, acidic leaching, has been shown to perform complete dissolution of Al [2]. A caveat of acidic leaching is the potential to mobilize radioactive species into the Al/Cr waste stream. If acidic leaching were to be performed, knowledge of how to remove radioactive species, predominantly actinides, from acidic $Al(NO_3)_3$ solutions containing variable concentrations of HNO_3 and CrO_4^{2-} would be required. Previous studies have shown solvent extraction (SX) with 0.1 M

TOPO/n-dodecane to be an effective means of handling the secondary cleanup [3]. An alternative to SX, extraction chromatography (EXC), provides potential benefits, such as: preconcentration, removal of a liquid organic diluent, the ease of handling of ion-exchange resins and minimized complications arising from third phase formation.

Extraction chromatography is a type of liquid-liquid chromatography that couples the selectivity of solvent extraction with the multistage character of a chromatographic process [4]. Solvent impregnated resins allow some of the benefits of a functionalized polymeric resin without the difficulties associated with synthesis. The primary tradeoff is extractant bleed off from the polymeric support; this must be considered when examining separation goals.

As a means of further understanding EXC, comparison is frequently made to similar SX systems [5]. As the organic diluent will affect SX results, pore size, bead size and hydrophilic/phobic characteristics of the resin can affect EXC results. Other variables can affect EXC results, especially when attempting comparison with SX, however, the organic phase, solid or liquid, is usually not physically inert and must be considered carefully.

In this work, the hypothetical problem of how to remove the radioactive components of the leachate solutions that could emerge if one were to attempt Al leaching with HNO3 solutions is addressed. The decontamination method investigated examines the efficiency of an EXC approach of TOPO-XAD7 extractant phases to selectively separate radioactive Eu, U, Th and Np from aqueous solutions of HNO3 and Al(NO3)3 in the presence of low concentrations of Cr.

2. Experimental

2.1. Materials and Instrumentation

All aqueous solutions were prepared from analytical grade reagents and ultra pure (18 MΩ) H_2O. A density determination was performed of all solutions using a calibrated 1mL pipette and weighing the 1 mL volume of each solution at room temperature. Solutions of HNO_3 were prepared by mass using Fisher Scientific concentrated (15.8 M) HNO_3 solution. NaOH solutions were prepared from dilutions of 50% w/w NaOH (Alfa Aesar) and standardized by titration with potassium hydrogen phthalate to a phenolphthalein end point. Solutions of K_2CrO_4 and $Al(NO_3)_3$ were prepared by mass using analytical grade J.T. Baker solids. The L-ascorbic and Etidronic acid solutions were prepared by mass from Fisher Scientific ACS certified reagent and Alfa Aesar, respectively. Experiments performed using $^{152/154}Eu(NO_3)_3$, $^{237}NpO_2(NO_3)$, $^{233}UO_2(NO_3)_2$, $^{238}UO_2(NO_3)_2$ and $^{238}Pu(NO_3)_4$, $^{232}Th(NO_3)_4$ were prepared by dilution of standardized stocks from the Washington State University (WSU) inventory. Experiments using $Eu(NO_3)_3$ were prepared by dilution of standardized stocks. Radioactive $^{152/154}$ Eu was created by neutron activation of 99.999% Eu_2O_3 (Arris International) using a Teaching, Research, Isotopes General Atomics (TRIGA) reactor with a neutron flux of $5X10^{12}$ n cm $^{-2}$ sec^{-1} at the Nuclear Radiation Center at WSU. Tri-n-octyl phosphine oxide (TOPO) organic solutions (Acros Organics) were purified to remove organic acid impurities using Na_2CO_3 (Fisher) as described previously and diluted volumetrically using methanol (>99%, SigmaAldrich).[6] Amberlite XAD-7 (Rohm & Hass) was treated as described in the following section.

Radiotracer experiments using $^{152/154}$Eu were analyzed on a NaI(Tl) solid scintillation counter, a Packard Cobra-II auto gamma, for gross gamma counting. Radiotracer experiments using ^{233}U, ^{237}Np and ^{238}Pu were analyzed using a Beckman LS6000 liquid scintillation counter for alpha detection with 5 mL of EcoScint® scintillation fluid. Light metals analysis (Cr, Al) and heavy metal analysis (^{238}U, ^{232}Th) was done using a Perkin Elmer Optima 3200 RL ICP-OES instrument and an Agilent 4500+ ICP-MS, respectively. All mixing was done using a VWR mini vortexer and all mass measurements were obtained using a Mettler Toledo XS105 Dual Range series analytical balance. Pipetting was accomplished using Finnpipette adjustable volume micropipettes and tips.

2.2 Resin Impregnation

Removal of acidic impurities in the XAD7 resin was performed with deionized water rinse until a neutral pH was obtained. Drying of the resin was expedited by methanol (MeOH) addition and removal, followed by placement in an oven at 80°C. The dried resin was removed from the oven, allowed to cool in a vacuum desiccator, weighed and contacted for 15 minutes by vigorous shaking with 1 M TOPO in MeOH using excess TOPO impregnation solution. Excess impregnation solution after contact was removed and the impregnated beads were dried at 80°C overnight. The amount of impregnation can be defined as the ratio of mass of organic extractant present to the total final mass of the impregnated resin. The impregnation provided 60% $m_{TOPO}/m_{(TOPO+XAD7)}$. For 40% $m_{TOPO}/m_{(TOPO+XAD7)}$ resin, dried resin was contacted with excess impregnation solution in a ratio of 1.05 g XAD7 : 7 g 0.5 M TOPO/MeOH.

The TOPO-XAD7 resin was wetted with n-dodecane (TOPO-XAD7n) for some experiments. To accomplish this, 60 and 40 wt% TOPO-XAD7 were contacted with a 50% v/v chloroform/n-dodecane solution in ratios of 100 mgs of resin per 100μL $CHCl_3$/n-dodecane or 160 μL $CHCl_3$/n-dodecane, respectively. This ratio would minimize the presence of excess n-dodecane and potential loss of TOPO to the walls of glass vials used during the wetting process. A 23% and 43%, increase in mass was observed after contact with n-dodecane, respectively.

2.3 Batch Extractions

All batch extractions were performed in triplicate and the errors presented are for a 1σ standard deviation of the triplicate analysis. The weight distribution ratio, D_w (mL g^{-1}), was calculated for most experiments according Equation 1, where A_0 and A_s are the aqueous phase activity (counts per minute)

$$D_w = \frac{(A_o - A_s)}{A_s} * \frac{V}{m} \qquad [1]$$

before and after equilibration, *w* is the weight of resin (g) and *V* the volume of the aqueous phase (mL). For radiotracer experiments, triplicate experiments showed the reproducibility of the distribution measurements was generally within 10%, although the uncertainty interval was somewhat higher for the highest distribution values ($D_w \geq 10^3$). “Oxidizing conditions” or “reducing conditions” are defined as the inclusion of 1 mM K_2CrO_4 or 1 mM K_2CrO_4/2 mM ascorbic acid in the aqueous phase, respectively.

Previous Eu extraction studies [7] showed the TOPO-XAD7 resin to have the most promise regarding tank remediation efforts and studies progressed focusing on this support. Actinide extraction experiments dealt with the additional intricacy of redox chemistry and therefore studies regarding variable $[Al(NO_3)_3]$ were isolated to allow a more thorough study of redox chemistry. Neptunium's redox chemistry in particular requires a more developed understanding and was highlighted. Plutonium is expected to be in the (III) state [8] for ascorbic acid reducing conditions and in the (VI) state for oxidizing conditions [9]. To provide appropriate distribution models for each actinide oxidation state, UO_2^{2+}(VI), Th^{4+} (IV), Eu^{3+}(III) uptake was also studied to determine which redox state of Np was dominant under the given conditions.

Batch investigations were performed for ^{238}U, ^{232}Th, ^{237}Np and $^{152/154}$Eu at tracer concentrations (10^{-5} M) using 500 µL aqueous phase and 50 mg 60% TOPO-XAD7 resin. Early Eu uptake studies showed ample uptake of Eu by 100 mg TOPO-XAD7 resin and warranted a decrease to 50 mg of TOPO impregnated resin. Consistent Eu extraction was observed when compared to previous work [1]. The concentration of $Al(NO_3)_3$ was varied between 0.01 and 1 M. The initial redox condition of the aqueous solution was varied to examine the potential benefits of leaving chromium in the tank as chromate. Studies were performed with ^{233}U and ^{237}Np examining the distribution of the system with 1 mM K_2CrO_4 (Cr(VI)), 1 mM Cr K_2CrO_4 and 2 mM ascorbic acid (AA) (producing Cr(III)), and no chromium present. Studies with ^{232}Th and $^{152/154}$Eu included 1 mM K_2CrO_4 and 2 mM ascorbic acid. All contacts were for 20 minutes, 400 µL aliquots of the aqueous phase were obtained and samples were analyzed using the appropriate instrument. Weight distribution values (Dw) were not corrected for nitrate complexation in the aqueous phase, as the redox speciation of neptunium was not known with certainty.

2.4 Simulated Waste Stream

All column experiments were performed with 0.1 HNO_3 and 0.25 M $Al(NO_3)_3$ to observe the median conditions that might be anticipated during an acidic remediation of the Hanford Site. Columns were Biorad® 1.27 BV PTFE. All columns were weighed before and after column packing to provide the mass of the resin used. A free volume determination was performed for each column by extracting 0.1 M HNO_3 into the column and obtaining the mass difference before and after water logging. The density of nitric acid was determined to be 1.007 ± 0.002 using calibrated pipettes. The free column volume was generally 0.45 mL. Fractions were collected using a Biorad® 2120 series fraction collector. All samples were weighed prior to analysis to ensure knowledge of sample size.

Elution curves of several analytes were performed to examine the potential recovery routes. Early results (not shown here) displayed the promise of actinide recovery when simulated tank wastes were oxidizing. The elution curves focused on separating the analytes from $Al(NO_3)_3$ by extracting them into the resin phase, then separating the analytes from the extracted chromate using selective binding with etidronic acid. A control experiment was performed using redox stable Eu examining elution under both reducing and oxidizing conditions. The use of Eu was appropriate as Eu is least likely to be extracted by TBP or TOPO and would therefore be the most likely to be displaced.

Elution curves dealing with macro amounts of Eu and U were loaded to 40% of maximum capacity (as calculated from the breakthrough curve analysis). For all curves the flow rate was 50 uL/min and a 3 bed volume (BV) rinse, 3.81 mL, was performed before each elution. Studies involving chromate elution mimicked the uranium elution study to examine the separation of chromium from the actinides. Neptunium and plutonium elution curves had the same load and rinse volumes as the uranium experiments, but were performed with only tracer concentration and the primary focus was on understanding the redox behavior.

3. Results and Discussion

3.1 Actinide Distribution

Figures 1, 2 and 3 show batch experiment uptake of Th, U, Np, and Eu at tracer concentrations as a function of $[Al(NO_3)_3]$ by TOPO-XAD7 resin at 0.01, 0.1 and 1 M HNO_3, respectively. Expectedly, the presence of $Al(NO_3)_3$ had a similar “salting out” effect for both actinide and lanthanide uptake. The uptake studies of Th^{4+}, UO_2^{2+} and Eu^{3+} served to model the distribution behavior of An^{4+}, AnO_2^{2+}, and An/Ln^{3+} cations, respectively. The extraction trends of these species were helpful in elucidating the oxidation state of the redox active Np. The redox speciation of Np in high ionic strength media and dilute nitric acid is relatively unknown in the literature. The Pourbaix diagram of Np [10] shows the variability of oxidation state possible for Np in dilute HNO_3. An additional complication is chromate and neptunium can be reduced and oxidized by trace nitrite impurities, respectively [11].

Modelling of the system with UO_2^{2+}, Th^{4+} and Eu^{3+} shows the extraction preference for the TOPO-XAD7 system is $AnO_2^{2+} > An^{4+} > An^{3+}$ and most likely AnO_2^{+} is least preferred. This trend that is unique to TOPO/TRPO systems and has been observed in the literature.[20] The extraction trends demonstrate the preferred extraction of actinides with a greater charge density by a hard oxygen donor. Comparing uptake behavior between redox active (Np) and redox inactive actinides/lanthanides (UO_2^{2+}, Th^{4+}, Eu^{3+}) allowed a loose approximation of the anticipated redox state of Np in the sludge simulants for both potentially oxidizing and reducing conditions.

Uptake studies of neptunium were performed with no chromium present to provide a supposedly redox neutral system. In general, the solutions without chromium exhibited the poorest uptake of Np and is most likely indicative of the Np being present almost completely as Np(V). As the concentration of HNO_3 increases, the extraction of Np improves for all systems investigated. These observations could possibly be explained by the several redox active species in the aqueous phase. Table 1 shows redox reactions of significance for the redox active species in these systems.

As the concentration of nitric acid increases, the reducing capabilities of ascorbic acid decrease due to a decrease in the formal potential [13]. Therefore, in systems with less nitric acid, the ascorbic acid is more capable of reducing the chromate initially present and retaining the neptunium as Np(V). Neptunium is most likely a mixture of Np(V) and Np(VI) at 0.1 M HNO_3 for all systems under investigation. The overall increase in Np extraction for 1 M HNO_3 conditions could be explained by trace nitrite impurity frequently present in nitric acid solutions. Nitrite is generally capable of oxidizing Np(V) to Np(VI) [14,15]. Np(IV) does not appear to be present in any of the potential waste conditions and significantly higher uptake would be anticipated if Np(IV) were present based on the uptake results of Th^{4+}.

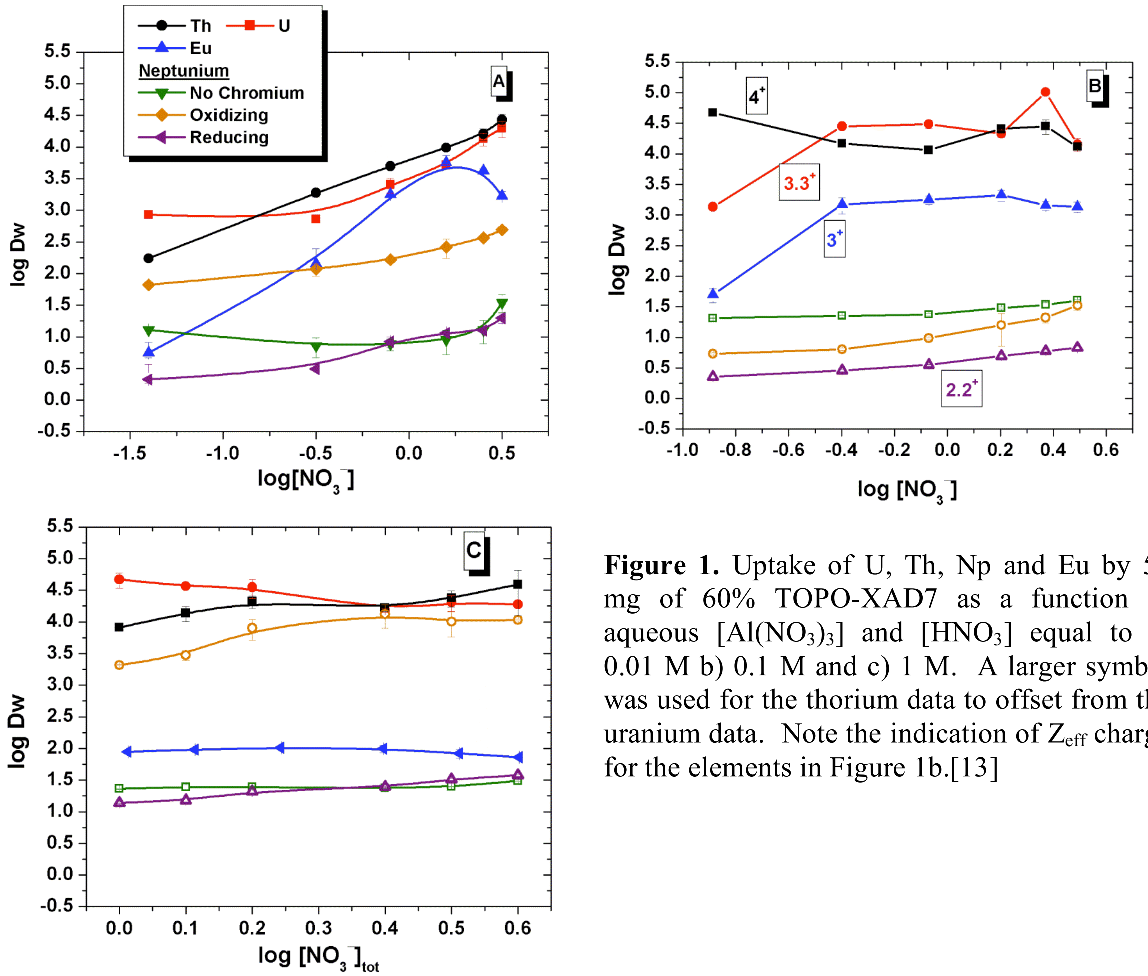

Figure 1. Uptake of U, Th, Np and Eu by 50 mg of 60% TOPO-XAD7 as a function of aqueous $[Al(NO_3)_3]$ and $[HNO_3]$ equal to a) 0.01 M b) 0.1 M and c) 1 M. A larger symbol was used for the thorium data to offset from the uranium data. Note the indication of Z_{eff} charge for the elements in Figure 1b.[13]

Oxidizing conditions produce a slightly less convoluted picture regarding the Np redox speciation. Np extraction shows a consistent increase of D_w as the nitric acid concentration increases. This is the general expectation for AnO_2^{2+} species. Pourbaix predominance diagrams show water stability can be an issue when generating Np(VI) at concentrations of HNO_3 less than 0.01 M. Water stability becomes less of an issue as the concentration of acid continues to increase.

Nitric acid is also known to be oxidizing and an increase in nitric acid concentration could lend to more oxidizing conditions in the aqueous tank leachates. At 1 M HNO_3 and high $[Al(NO_3)_3]$ conditions, the Np extraction aligns very well with the U extraction indicting a complete presence of Np(VI). If a secondary cleanup is required of the Hanford sludges, a balance would be required to keep nitric acid concentrations sufficient enough to allow oxidation of Np while preventing competition between H^+ and $An\backslash Ln^{3+}$ for the TOPO available in the system.

Table 1. Neptunium redox reaction significant to understanding simulated acidic aqueous raffinate of the Hanford tanks. [10,16,17,18]

Reaction	E°
$\mathbf{NpO_2^+ + 4H^+ + e^- \longleftrightarrow Np^{4+} + 2H_2O}$	**0.567 V**
$\mathbf{NpO_2^{2+} + e^- \longleftrightarrow NpO_2^+}$	**1.236 V**
$NO_3^- + 3H^+ + 2e^- \longleftrightarrow HNO_2 + H_2O$	**0.94 V**
$NpO_2^{2+} + HNO_2 + H_2O \rightarrow NpO_2^+ + NO_3^- + 3H^+$	**0.296 V**
Dehydroascorbic acid + $\mathbf{2H^+ + 2e^- \longleftrightarrow}$ Ascorbic Acid	**0.390 V**
$HCrO_4^- + 7H^+ + 3e^- \longleftrightarrow Cr^{3+} + 4H_2O$	**1.20 V**

3.2 Simulated Waste Stream Recovery

A series of elution studies (not shown) indicated the most rapid and quantitative recovery of Eu was obtained by using 40% impregnated TOPO-XAD7 n-dodecane wetted resin. To examine the ultimate remediation capabilities of the 40% TOPO-XAD7n resin for simulated Hanford waste, a simulated waste stream containing 1 mM K_2CrO_4, tracer $^{152/154}$Eu, ^{233}U, ^{237}Np and ^{238}Pu, simultaneously, was loaded to 40% capacity, the resin washed with 0.01 HNO_3 and 0.75 M $Al(NO_3)_3$ and material sequentially eluted with 3 M HNO_3 and 1 mM $KBrO_3$ to recover Eu, then 0.1 M Etidronic Acid (HEDPA) and 1 mM $KBrO_3$ to recover the actinides. Reducing conditions required for separate elution of Np and Pu away from U would have also eluted any extracted chromate to Cr(III). Although the ligand exchange kinetics of Cr(III) are slower than the actinides [19], preventing reduction of Cr(III) would ensure a more quantitative separation of the actinides from chromium.

Figure 2 shows the semi-log elution curves obtained for the simulated waste experiment. Samples were monitored both using gamma counting and liquid scintillation. The 0.1% breakthrough observed during simulated waste stream was also observed during the loading step in the single Pu, Np and U experiments. No evidence of

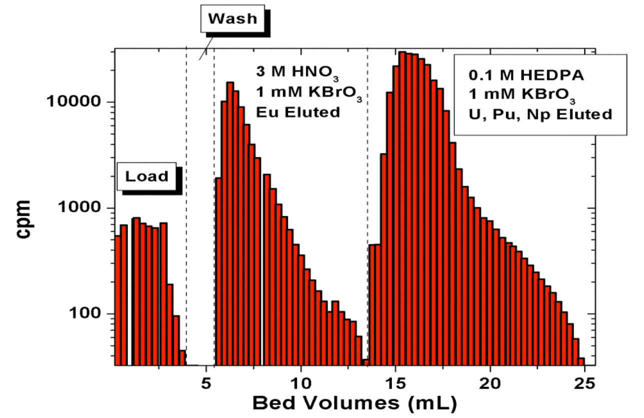

Figure 2. Loading and elution of U, Pu, Np and Eu by 40% TOPO-XAD7n column from simulated waste stream containing 1mM K_2CrO_4, 0.1 M HNO_3 and 0.25 M $Al(NO_3)_3$. Elution of Eu was performed using 3 M HNO_3 and 1mM $KBrO_3$. Elution of actinides was performed using 0.1 M Etidronic Acid and 1 mM $KBrO_3$.

breakthrough during the wash step was observed. Europium elution occurred without any detectable evidence for actinide breakthrough using either the LSC or Packard Cobra II gamma detector. The elution of Eu was quantitative (>99%) with error. Removal of the actinides was comparable to the single element experiments (not shown). The higher actinide loading for the simulated waste stream increased the column tailing, observed in the semi-log curve broadened the elution curve; however, recovery was still quantitative (>99%), within error.

4. Conclusions

This investigation has addressed the concept of applying extraction chromatography methods to the task of decontaminating radioactive sludge leachate solutions that could result if acidic leaching procedures were adopted for the cleanup of recalcitrant, aluminum-containing tank waste sludge residues at the Hanford Site. The results presented indicate TOPO-XAD7 can remove >90% of Eu(III) and AnO_2^{2+} in HNO_3 solutions containing $Al(NO_3)_3$ when $[NO_3^-]_{total} > \sim0.25$ M. The results for Eu(III) may be taken as generally characteristic of the behavior of the light lanthanides and trivalent actinide cations in a system of this type. Success was observed in employing the inherently oxidzing conditions present in the Hanford tanks as chromium competition proved insubstantial, even using macro concentrations of AnO_2^{2+} or Eu^{3+}. Further studies could examine the use of stacked columns for a single elution that would separate Np, Pu and U sequentially, ultimately decreasing the overall cost of remediation.

5. Acknowledgements

The authors would like to thank the Department of Energy Environmental Management Science Program under which auspices the early experiments were preformed and the U-NERI program which supported selected work. Much appreciation is felt toward all the members of the Dr. Kenneth L. Nash radiochemistry laboratory at Washington State University. A final acknowledgement is due to the Nuclear Radiation Center (NRC) at WSU for the production of the Eu radioisotopes used in this study.

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