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Highlights:

- A new extraction chromatographic material containing trioctylphosphine oxide is developed for actinide recovery
- The ability of this material to selectively recover actinides potentially acidic Hanford radioactive waste is demonstrated
- The column kinetics are significantly improved when n-dodecane is co-coated with the trioctylphosphine oxide

1 Remediation of Potentially Acidic Hanford Wastes
2 using Tri-n-octyl Phosphine Oxide Extraction
3 Chromatographic Materials

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6 ABSTRACT: As the Hanford site undergoes remediation, significant economies could be
7 realized if aluminum and chromium are kept from High Level Waste glass produced at the
8 Hanford Waste Treatment Plant (WTP). An acidic scrub of the Hanford sludge could enhance
9 Al removal, although such treatment could lead to the mobilization of transuranic elements. If
10 mobilization were minor, a chromatographic secondary cleanup of the acidic waste stream may
11 be preferred to allow preconcentration of radionuclides prior to processing through the Hanford
12 WTP. This study examines tri-n-octyl phosphine oxide coated resins as a chromatographic
13 means for the removal of transuranics from a secondary waste stream. Metal uptake kinetics and
14 mechanisms for transuranics and a simulant transuranic (europium) with the developed resin are
15 characterized in both batch and column operation modes. Results indicate up to 99% of the
16 radioactive material present from an acidic sludge leach may be recovered using extraction
17 chromatography providing an effective avenue for high aluminum content tank pre-treatment.

18 INTRODUCTION

19 The U.S. Department of Energy (DOE) is responsible for environmental remediation at former
20 nuclear weapons production sites. The Hanford Site, in south central Washington state, was the
21 first facility to produce plutonium for nuclear weapons. Three plutonium separations methods
22 were used during the operation of the Hanford site: Bismuth Phosphate (1945-1956), Redox
23 (1951-1959) and PUREX processes (1956-1972; 1983-1989).¹ The use of multiple plutonium
24 separations and mixing wastes between tanks helped to create a complex waste matrix. As a
25 result, Hanford site remediation is one of the most labyrinthine challenges faced by the
26 Department of Energy. Both the volume and composition of waste resulting from Pu production
27 are major remediation concerns.² The most problematic waste component is the sludge created
28 by the caustic environment of the tanks.

29 The under construction Hanford Tank Waste Treatment and Immobilization Plant (WTP) is the
30 cornerstone of the tank waste remediation effort. Full radioactive operations are scheduled to
31 begin in 2019. The current design of the WTP may not be able treat and immobilize the Hanford
32 tank wastes in the expected lifetime of the plant. Consequently, DOE has been pursuing
33 alternative treatment options for selected wastes. If implemented, alternative treatments could
34 expedite the sludge dissolution process and improve throughput of the WTP, thereby
35 accelerating the overall Hanford tank waste remediation mission.

36 Remediation treatments efforts have focused on caustic leaching to remove problematic
37 nonradioactive elements aluminum and chromium. Aluminum contributes significantly to the
38 volume of waste processed and the precipitation of chromium spinels from the HLW could short
39 the heating electrodes, clog the pour spout, or otherwise jeopardize the operation and life of the
40 glass melter.³ Removal of Al and Cr would decrease waste volume, lengthen the lifetimes of the

41 vitrification furnace and improve stability of the vitrified high level waste (HLW) glass matrix.
42 While not addressed here, the possibility of removing phosphate as an additional pretreatment
43 has also been considered.^{4,5} While caustic leaching has proven to have some value, the most
44 stubborn Al phase, boehmite (γ -AlO(OH)), has been resistant to this treatment regimen.

45 As an alternative, the possibility of using acid/base wash cycles for enhanced alumina removal
46 through surface activation/freshening has been considered. An undesirable side effect of acidic
47 leaching is the potential mobilization of radioactive species into the Al/Cr waste stream.⁶ If
48 acidic leaching were to be performed, knowledge of how to remove radioactive species,
49 predominantly actinides, from aqueous media of variable HNO₃ and Al(NO₃)₃ concentrations
50 and chromium oxidation states would be required. Previous studies have shown solvent
51 extraction (SX) with 60% by volume (v/v) (TBP) or 0.1 M tri-n-octyl phosphine oxide (TOPO) in
52 *n*-dodecane from nitric acid aqueous media to be a complementary and effective means of
53 handling the secondary cleanup.^{7,8} If the solubilization of actinides is low, preconcentration may
54 be desired. An extraction chromatographic remediation could serve to complement the solvent
55 extraction efforts. Extraction chromatographic materials using TBP have also shown to provide
56 reasonable decontamination of transuranics when high concentrations of nitrate are present, but
57 lower concentrations of nitrate require a more basic extractant for recovery of the trivalent
58 actinides.⁹

59 In this work, a bench scale exploration of a TOPO EXC system for the separation of U, Th,
60 Np, Pu and Eu (serving as a surrogate for the trivalent actinides) from Al/Cr leachate solutions
61 that could emerge if one were to attempt nitric acid leaching with Al-bearing solids has been
62 developed. The “ambient” oxidation state of tracer levels of Np and Pu is defined through
63 comparisons of Np/Pu partitioning with redox stable actinides (Th⁴⁺ and UO₂²⁺). The

64 polyacrylic XAD7 resin was used as the solid support for extractant immobilization as previous
65 studies have shown the XAD7 resin to successfully retain TOPO for the purposes of metal
66 uptake.^{10,11} Correlations between solvent extraction chemistry, batch mode extraction and
67 column separations are compared to previous work in this area and with each other.

68

69 EXPERIMENTAL SECTION

70 **Materials and Instrumentation**

71 All aqueous solutions were prepared from analytical grade reagents and ultrapure (18 M Ω)
72 deionized H₂O. Solution density was determined by using a calibrated one mL pipette and
73 weighing the aliquot at room temperature. Nitric acid solutions were prepared by mass using
74 Fischer Scientific concentrated (15.8 M) HNO₃ solution. Sodium hydroxide solutions were
75 prepared from dilutions of 50% w/w NaOH (Alfa Aesar) and standardized by titration of
76 potassium hydrogen phthalate to a phenolphthalein end point. Solutions of K₂CrO₄ and
77 Al(NO₃)₃ were prepared by mass using analytical grade J.T. Baker solids. The L-ascorbic and 1-
78 hydroxyethane 1,1-diphosphonic acid (HEDPA) solutions were prepared by mass from Fisher
79 Scientific ACS certified reagents and Alfa Aesar, respectively. TOPO (>99%, Sigma Aldrich)
80 was used without further purification and was diluted volumetrically using methanol. Amberlite
81 XAD-7 (Rohm & Hass) was treated as described in the following section.

82 Experiments using ^{152/154}Eu, ²³⁷Np, ²³³UO₂, ²³⁸UO₂, ²³⁸Pu, and ²³²Th nitrates were conducted by
83 dilution of standardized stocks from the Washington State University (WSU) radioisotope
84 inventory. Experiments using stable Eu(NO₃)₃ were prepared by dilution of standardized stocks.
85 Radioactive ^{152/154}Eu was created by neutron activation of 99.999% Eu₂O₃ (Arris International)
86 using a Teaching, Research, Isotopes General Atomics (TRIGA) reactor with a neutron flux of

87 5×10^{12} n/cm²·sec at the Nuclear Radiation Center at WSU. Radiotracer experiments
88 using ^{152/154}Eu were analyzed on a NaI(Tl) solid scintillation counter (Packard Cobra-II auto
89 gamma) for gross gamma counting. Radiotracer experiments using ²³³U, ²³⁷Np and ²³⁸Pu were
90 analyzed using a Beckman LS6500 liquid scintillation counter for alpha detection with 5 mL of
91 EcoScint® scintillation fluid. Light metals analysis (Cr, Al) and heavy metal analysis (²³⁸U,
92 ²³²Th) was done using a Perkin Elmer Optima 3200 RL ICP-OES instrument and an Agilent
93 4500+ ICP-MS, respectively. Mixing was done using a VWR mini vortexer and mass
94 measurements were obtained using a Mettler Toledo XS105 Dual Range series analytical
95 balance.

96

97 **Resin Preparation**

98 Amberlite XAD7 resin is a polyacrylic resin with a 20-60 mesh particle size and a surface area
99 of 450 m²/g. Acidic impurities were removed with a DI water rinse until a neutral pH was
100 obtained. Resin drying was expedited by methanol (MeOH) addition and removal, followed by
101 placement in an oven at 80°C for at least an hour. Dried resin was removed from the oven,
102 allowed to cool in a vacuum dessicator, weighed and contacted for 15 minutes by vigorous
103 shaking with 1 M TOPO in MeOH with excess coating solution. Excess solution after contact
104 was removed and the coated resin was dried at 80°C overnight. The amount of extractant
105 loading to the resin is defined in this work as the ratio of mass of organic extractant present to
106 the total final mass of the extractant loaded resin. This coating process provided 58 wt%. For 38
107 wt% resin, dried resin was contacted in a ratio of 1.05 g XAD7 : 1.75 g TOPO in excess
108 methanol.

109 The rate of metal uptake onto TOPO-XAD7 resin was determined to be significantly slower
110 than comparable solvent extraction systems. To encourage faster metal uptake kinetics, the
111 TOPO-XAD7 resin was wetted with n-dodecane (abbreviated TOPO-XAD7n) using a 50% v/v
112 chloroform/n-dodecane solution.¹² The 58% and 38% TOPO-XAD7 resins were wetted with
113 100 and 160 μL of the chloroform/n-dodecane mixture providing dissolution of 30% and 53% of
114 TOPO on the resin surface, respectively. Wetting ratios were selected to minimize the presence
115 of excess n-dodecane and potential loss of TOPO from the resin during the wetting process.
116 Wetting the chromatographic material produced 46% and 24% TOPO-XAD7n resins. Assuming
117 a density of 1 g/mL, which is generally consistent with the literature,¹³ the concentration of
118 TOPO for the 46% and 24% wetted resin is 1.33 and 0.75 M, respectively.

119

120 **Extraction in Batch Experiments**

121 All batch extractions were performed in triplicate and the errors presented denote a $\pm 1\sigma$
122 standard deviation of the triplicate analysis. The weight distribution ratio of the analyte, D_w
123 ($\text{mL} \cdot \text{g}^{-1}$), was calculated according to the following equation:

$$124 \quad D_w = \left(\frac{A_o - A_s}{A_s} \right) \times \frac{V}{m} \quad (1)$$

125 where A_o and A_s are the aqueous phase activity (counts per minute) before and after equilibration,
126 m the mass of resin (g) and V the volume of the aqueous phase (mL). For radiotracer
127 experiments, triplicate experiments showed the reproducibility of the distribution measurements
128 was generally within 10%, although the uncertainty interval was somewhat higher for the highest
129 distribution values ($D_w \geq 10^3$) due to a lack of discernible activity in the aqueous phase. When
130 possible, weight distribution values (D_w) were corrected for nitrate complexation in the aqueous

131 phase, as done previously, to provide the corrected weight distribution ratio, Dw_0 .^{7,8} The ratio of
132 solution volume to resin was kept at 10 ml/g.

133

134 *Eu³⁺ Partitioning*

135 For ^{152/154}Eu extraction experiments with TOPO-XAD7, the aqueous phase contained various
136 amounts of HNO₃, Al(NO₃)₃, Cr(III/VI), and Eu(III). Chromium and ascorbic acid
137 concentrations were maintained at 1 mM and 3 mM, respectively. Europium uptake from
138 varying HNO₃ in the presence of constant Al(NO₃)₃ and constant HNO₃ with varying Al(NO₃)₃
139 was studied. Non-radiotracer europium was present at 1 mM to highlight the macroscale uptake
140 capabilities of the TOPO resin. Phases were contacted for 20 minutes by vigorous shaking and
141 aliquots of the aqueous phase were obtained. Analysis for ^{152/154}Eu in the aqueous phase was
142 performed as described previously.

143

144 *Actinide Partitioning*

145 Batch investigations were performed for ²³⁸U, ²³²Th, ²³⁷Np and ^{152/154}Eu at tracer
146 concentrations (<10⁻⁵ M). The concentration of Al(NO₃)₃ varied between 0.01 and 1 M while
147 maintaining constant concentrations of HNO₃. Actinide distribution investigations examined a
148 variety of chromium oxidation state conditions and are detailed in the results for a given set of
149 studies. All contacts were for 20 minutes. Aliquots of the aqueous phase were obtained.
150 Analysis for ²³⁸U, ²³²Th and ²³⁷Np in the aqueous phase was performed as described above.

151

152 *Isotherm Determination*

153 Isotherms were generated by monitoring Eu^{3+} or UO_2^{2+} partitioning while increasing the
154 concentrations of Eu^{3+} or UO_2^{2+} from 0.01 mM until the resin was sufficiently saturated.
155 Hypothetical tank conditions of 0.25 M $\text{Al}(\text{NO}_3)_3$ and 0.1 M HNO_3 were used. Macro
156 concentrations of Eu^{3+} and UO_2^{2+} were provided through the use of stable $^{151/153}\text{Eu}$ and longer-
157 lived ^{238}U . These were additionally spiked with $^{152/154}\text{Eu}$ or ^{233}U . All contacts were for 30
158 minutes.

159

160 **Column Experiments**

161 All column experiments were done with 0.1 M HNO_3 and 0.25 M $\text{Al}(\text{NO}_3)_3$ to ensure batch
162 mode isotherm results could be directly correlated with column experiments. Some elution
163 volumes are described in terms of *bed volume* (indicating the packed column volume). Columns
164 were Biorad[®] 1.27 BV PTFE. Columns were weighed before and after column packing with
165 extraction material to provide the mass of the resin used.

166 The free column volume was determined by extracting a mixed 0.1 M HNO_3 /0.25 M $\text{Al}(\text{NO}_3)_3$
167 solution into the resin-loaded column. The solution was expelled from the column and weighed.
168 The density of nitric acid/aluminum nitrate solution was determined to be 1.032 ± 0.003 . Using
169 the expelled mass and the known density, the free column volume was determined (0.42 ± 0.02
170 mL). Fractions were collected using a Biorad[®] 2120 series fraction collector. All aliquots were
171 weighed prior to analysis to quantify fraction size.

172

173 *Dynamic Capacity Determination*

174 Breakthrough curves were obtained for 58% TOPO/XAD7, 46% TOPO/XAD7n and 24%
175 TOPO/XAD7n systems for Eu^{3+} with initially 1 mM Cr(VI) and 3 mM ascorbic acid present in

176 solution. Europium concentrations and flow rates may be found in [Table 1](#), which also contains
177 experimental results. The 24% TOPO/XAD7n system had the quickest uptake kinetics and
178 additional breakthrough curves were performed with 1 mM Cr(VI) and 50 mM Eu^{3+} or UO_2^{2+} .

179

180 *Metal Elution*

181 The elution studies were done under similar conditions used for dynamic capacity
182 determinations. Values from the dynamic capacity determination were used to calculate the Eu^{3+}
183 and UO_2^{2+} stoichiometries under high loading conditions. Flow rates were 50 $\mu\text{L}/\text{min}$ for all
184 studies. A 3 BV rinse, 3.81 mL, was done after column loading using a mixed 0.001 M
185 $\text{HNO}_3/0.75 \text{ M Al}(\text{NO}_3)_3$ solution. Analyte elution was accomplished as detailed for each
186 experiment. Neptunium and plutonium elution curves had the same load and rinse volumes as
187 the uranium experiments, but only included tracer concentrations of actinides.

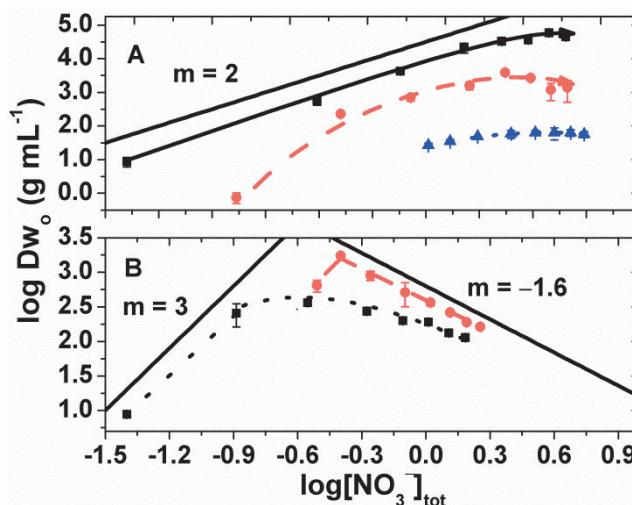
188

189 RESULTS

190 **Batch Experiment**

191 *Metal Partitioning*

192 [Figure 1](#) presents Eu^{3+} distribution data as a function of the total, aqueous nitrate concentration
193 for the TOPO-XAD7 resin. Extraction behavior was determined as a function of increasing
194 $\text{Al}(\text{NO}_3)_3$ concentration (0.01 M – 1.50 M) at three constant concentrations of HNO_3 ([Figure 1a](#)),
195 and also for varied concentrations of HNO_3 (0.01 M – 1.50 M) at two constant concentrations of
196 $\text{Al}(\text{NO}_3)_3$ ([Figure 1b](#)). All distribution data are corrected for complexation of europium by
197 nitrate in the aqueous phase. Corrections for the presence of $\text{Eu}(\text{NO}_3)^{2+}$ in comparable media
198 have been previously derived.^{7,8}



199

200 **Figure 1.** Nitric acid or aluminum nitrate dependences for europium nitrate adsorption into 58%
 201 TOPO-XAD7 resin. Lines are provided with slopes (m) indicate the dependence of metal
 202 extraction on nitrate concentration. Initially present in each aqueous solution was 1.0 mM
 203 K_2CrO_4 and 3 mM ascorbic acid. a) Aluminum nitrate varied from 0.01 to 1.5 M, ■ 0.01 M
 204 HNO_3 ● 0.10 M HNO_3 ▲ 1.00 M HNO_3 . b) Nitric acid varied from 0.01 to 1.5 M, ■ 0.01 M
 205 $Al(NO_3)_3$ ● 0.1 M $Al(NO_3)_3$

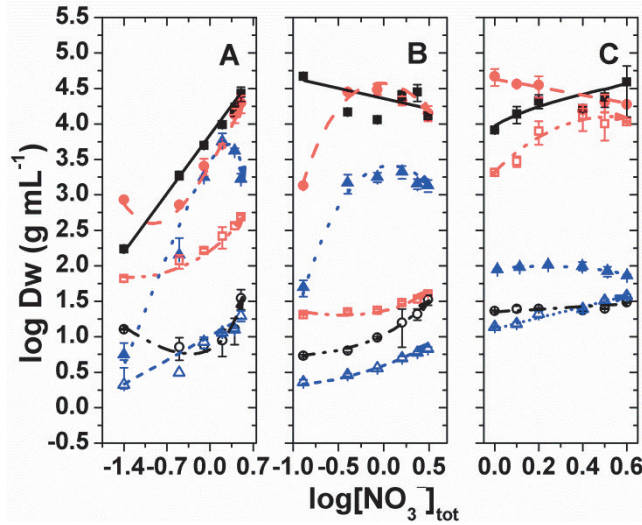
206

207 The partitioning of Eu^{3+} into the TOPO-XAD7 resins from solutions of constant HNO_3
 208 concentrations increased significantly with increasing concentrations of $Al(NO_3)_3$ (Figure 1a).
 209 The highest distribution observed was at $[HNO_3] = 0.01$ M and $[Al(NO_3)_3] = 1.5$ M. The
 210 partitioning of Eu^{3+} between the TOPO-XAD7 phase from solutions of constant $Al(NO_3)_3$
 211 concentrations with increasing concentrations of HNO_3 (Figure 1b) increased. A maximum in
 212 Eu^{3+} recovery was seen at $[HNO_3] = 0.25$ M and $[Al(NO_3)_3] = 0.1$ M. A steep decrease, with an
 213 approximate slope of -1.6 on the log-log plot, is observed after this maximum.

214 Figure 2 shows the uptake of Th, U, Np, and Eu at tracer concentrations as a function of
 215 $Al(NO_3)_3$ concentration by TOPO-XAD7 resin. The uptake studies of Th^{4+} , UO_2^{2+} and Eu^{3+}
 216 served to model the distribution behavior of An^{4+} , AnO_2^{2+} , and An/Ln^{3+} cations, respectively.
 217 Comparing uptake behavior between redox active (Np) and redox inactive actinides/lanthanides

218 (UO₂²⁺, Th⁴⁺, Eu³⁺) allows an approximation of the anticipated redox state of Np in the sludge
 219 simulants for both potentially oxidizing and reducing conditions.

220



221

222 **Figure 2.** Metal distribution values as a function of aqueous [Al(NO₃)₃] with [HNO₃] equal to a)
 223 0.01 M b) 0.1 M and c) 1 M. The various elements and redox conditions described as follows:
 224 ■ Th⁴⁺ ● UO₂²⁺ ▲ Eu ○ Np □ Np, 1 mM CrO₄²⁻ △ Np, 1 mM CrO₄²⁻, 3 mM ascorbic acid. Solid
 225 phase: 100 mg TOPO-XAD7.

226

227 *Isotherm Determination*

228 **Figure 3** compares Eu isotherms of the 58% TOPO-XAD7, 46% TOPO-XAD7n systems and
 229 24% TOPO-XAD7n resins. The data were fit with the ORIGIN[®] software package using a linear
 230 least squares statistical treatment for the Langmuir isotherm model, Equation 2,

231
$$q_r = \left(\frac{q_{\max} a_L C_e}{1 + a_L C_e} \right) = \left(\frac{K_L C_e}{1 + a_L C_e} \right) \quad (2)$$

232 where equilibrium concentrations of analyte in the liquid and solid phase, *c* and *q*, respectively,
 233 were calculated from Equations 3 and 4;

234
$$c = \frac{A}{A_o} \cdot c_o \quad (3)$$

235

$$q = \frac{A_o - A}{A} \cdot \left(\frac{V}{m} \right) \cdot c_o \quad (4)$$

236 a_L is the Langmuir constant ($\text{dm}^3 \cdot \text{mmol}^{-1}$), C_e is the concentration of analyte in the aqueous

237 phase, q_{max} is the maximum mole of analyte sorbed to the resin per gram under static conditions,

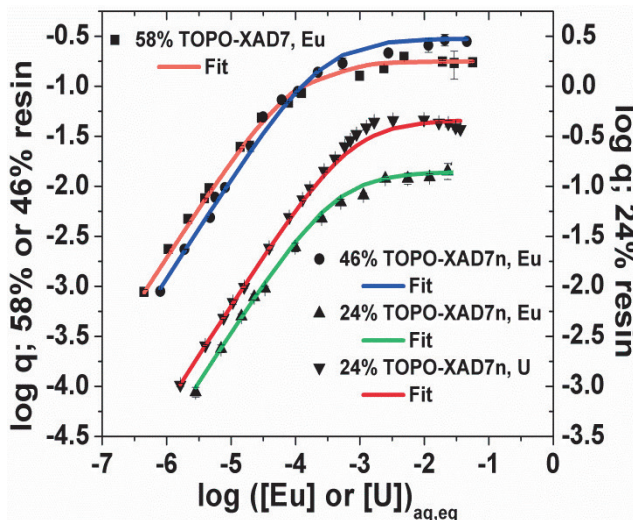
238 m is the mass of the resin, V is the volume of aqueous phase, A_o is the initial activity in the

239 aqueous phase (cpm), A is the final activity in the aqueous phase after equilibration, and C_o is the

240 initial concentration of analyte in the aqueous phase, K_L is the Langmuir constant in $\text{dm}^3 \cdot \text{g}^{-1}$.

241 The calculated saturation stoichiometry of the 24% TOPO-XAD7n resin is 1:3.5 (Eu:TOPO),

242 indicating a mixture of 1:4 and 1:3 complexes in the solid phase.



243

244 **Figure 3.** Isotherms comparing the uptake behaviors of europium by the 58% TOPO-XAD7,
 245 46% TOPO-XAD7n and 24% TOPO-XAD7n resin. Uranium isotherm is also shown for the
 246 38% TOPO-XAD7n resin. Initial aqueous phase: 0.1 M HNO_3 , 0.25 M $\text{Al}(\text{NO}_3)_3$, 1 mM
 247 K_2CrO_4 , 3 mM Ascorbic Acid. Solid phase: 50 mg of the appropriate resin.

248

249 Dynamic (Column) Experiments

250 Practical Dynamic Capacity

251 Determination of the practical dynamic capacity ($Q(m)$), the maximum number of mmol of

252 analyte per gram of resin under dynamic conditions, was calculated using Equation 5, where m is

253 the mass of the solid, c_0 is the initial concentration of analyte, V_0 is the free volume of the column
 254 and $V(50)$ is the volume of solution eluted at 50% breakthrough.

$$255 \quad Q(m) = \frac{V(50) - V_0}{m_s} \cdot c_0 \quad (5)$$

256 Under equilibrium conditions, the determined saturating concentration of analyte in the solid
 257 phase should be within error for breakthrough curves ($Q(m)$) and isotherms (q_{max}). Table 1 has a
 258 summary of the q_{max} and $Q(m)$ values obtained for systems of interest.

259 **Table 1.** Extraction characteristics for various TOPO-XAD7 n-dodecane wetted resins.

	Eu ³⁺		UO ₂ ²⁺	
% TOPO (m/m)	46%	24%	38%	24%
Redox Conditions	1 mM Cr(III)/ 3 mM AA ^a	1mM Cr(III)/ 3 mM AA ^a	1mM Cr(VI)	1mM Cr(VI)
q_{max} (mmolEu/g resin)	0.308 ± 0.008	0.176 ± 0.003	-	0.51 ± 0.01
$Q(m)$ (mmolEu/g resin)	0.299 ± 0.009	0.172 ± 0.002	-	0.50 ± 0.02
Flow Rate (μL/mL)	50	50	-	50
D	1200	350	-	640
% recovery	98.3 ± 0.1	99.9 ± 0.3	99.2 ± 0.2	99.7 ± 0.2
Eluent	3 M HNO ₃	3 M HNO ₃	3 M HNO ₃	0.1 M HEDP
Stoichiometry ^b	1:4	1:3.5	-	1:1

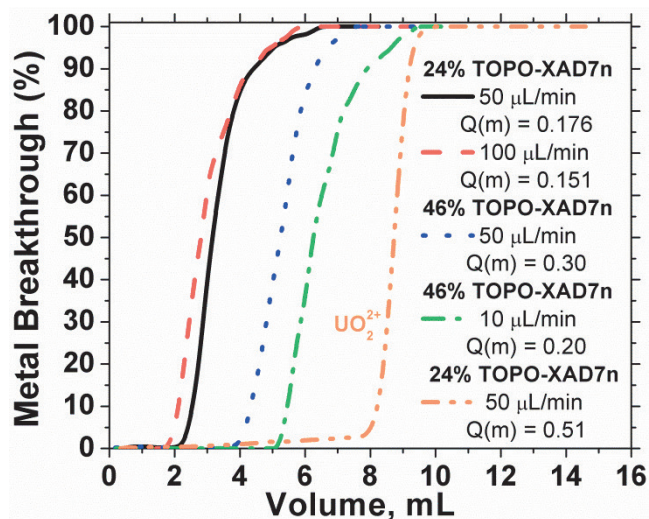
260 ^aAA = Ascorbic Acid

261 ^bIs expressed in the ratio metal : ligand

262

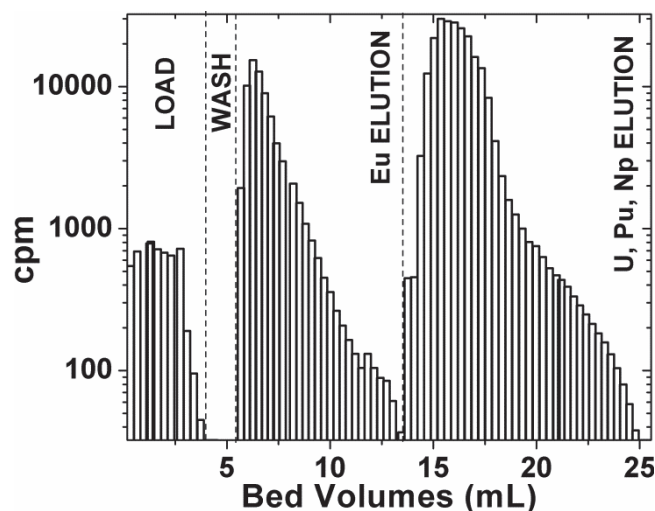
263 Figure 4 shows Eu breakthrough curves for all materials examined. Saturating conditions are
 264 equivalent (i.e. $q_{max} = Q(m)$; within error) for the 46% TOPO-XAD7n and 24% TOPO-XAD7n
 265 isotherms and breakthrough curves. Solvation of TOPO in n-dodecane made the use of higher
 266 flow rates possible (up to 50 μL/mL). A higher flow rate (100 μL/min) led to a decrease in the
 267 practical dynamic capacity; indicating the system was no longer at equilibrium.

268 To examine the ultimate remediation capabilities of the 24% TOPO-XAD7n resin for
 269 simulated Hanford waste, a simulated waste stream containing 1 mM K_2CrO_4 and tracer



270
 271 **Figure 4.** Breakthrough curves comparing the column saturation behaviors of europium by the
 272 46% TOPO-XAD7n and 24% TOPO-XAD7n resin. Uranium behavior is also shown for the
 273 24% TOPO-XAD7n resin. Aqueous Phase: 0.1 M HNO_3 , 0.25 M $Al(NO_3)_3$, 1 mM K_2CrO_4 , 2
 274 mM Ascorbic Acid. Metal concentration was 50 mM except for breakthrough curve using 46%
 275 TOPO-XAD7n resin with a 10 $\mu\text{L}/\text{min}$ flow rate, which used 30 mM metal.

276 $^{152/154}\text{Eu}$, ^{233}U , ^{237}Np and ^{238}Pu , simultaneously, was loaded, the resin washed with 0.01 HNO_3
 277 and 0.75 M $Al(NO_3)_3$, and material sequentially eluted with 3 M HNO_3 and 1 mM $KBrO_3$ to
 278 recover Eu, then 0.1 M HEDPA and 1 mM $KBrO_3$ to recover the actinides. The addition of
 279 potassium bromate ensured oxidation of Np and Pu to their hexavalent states in the absence of
 280 chromate. Figure 5 shows the semi-logarithmic elution curves obtained for the simulated waste
 281 experiment.



282

283 **Figure 5.** Loading and elution of U, Pu, Np and Eu by 24% TOPO-XAD7n column from
 284 simulated waste stream containing 1mM K₂CrO₄, 0.1 M HNO₃ and 0.25 M Al(NO₃)₃ shown on a
 285 semi-log scale to allow viewing of column tailing. Elution of Eu was performed using 3 M
 286 HNO₃ and 1 mM KBrO₃ to retain Np and Pu in the hexavalent state in the absence of chromate.
 287 Elution of actinides was performed using 0.1 M Etidronic Acid (HEPA) and 1 mM KBrO₃.

288

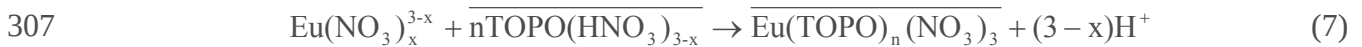
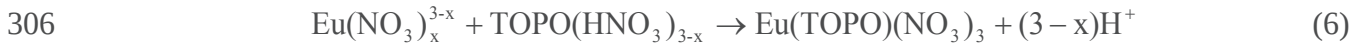
289 DISCUSSION

290 Europium Partitioning

291 The availability of ^{152/154}Eu and its comparable uptake behavior to the lanthanides and the
 292 trivalent actinides for solvating organophosphorus extractants made this isotope an ideal
 293 candidate to screen potential TOPO-XAD7 supports. For ^{152/154}Eu investigations, the aqueous
 294 phase conditions were similar to previous solvent extraction investigations.^[5,6,11] These
 295 conditions have been selected to represent a wide range of possible solutions that could be
 296 encountered during tank sludge leaching with HNO₃ solutions. For discussion purposes,
 297 *oxidizing conditions* or *reducing conditions* are defined as the inclusion of 1 mM K₂CrO₄ or 1
 298 mM K₂CrO₄/3 mM ascorbic acid in the aqueous phase, respectively.

299 Europium extraction by the TOPO-XAD7 resin increased as the concentration of Al(NO₃)₃
 300 increased (Figure 1a). The negative slope observed on the logarithmic plot of Figure 1b at

301 higher nitrate concentrations could be generated by an ion exchange mechanism for Eu^{3+} uptake.
 302 The conventional extraction mechanism and proposed ion-exchange mechanisms are shown as
 303 Equations 6 and 7, respectively, where $n = 3$ or 4 and $X \leq 2$. Cation exchange uptake
 304 mechanisms by solvating extractants have been proposed previously in the presence of highly
 305 acidic media.¹⁴



308 Verification of this using slope analysis would require solution activity to be accounted for in
 309 the mixed electrolyte solution. In agreement with previous liquid-liquid extraction studies,
 310 results here indicate higher concentrations of $\text{Al}(\text{NO}_3)_3$ would be preferential to encourage
 311 decontamination of low level leachates. Extraction increases in the presence of aluminum nitrate
 312 can be related to the decline in water activity allowing more effective release of the Eu^{3+} to the
 313 organic phase (i.e. salting out).

314

315 **Actinide Partitioning with TOPO-XAD7**

316 Expectedly, the presence of $\text{Al}(\text{NO}_3)_3$ had a similar “salting out” effect for both actinide and
 317 lanthanide uptake. Modeling of the system with UO_2^{2+} , Th^{4+} , and Eu^{3+} shows the extraction
 318 preference for the TOPO-XAD7 system is $\text{An}^{4+} > \text{AnO}_2^{2+} > \text{An}^{3+} > \text{AnO}_2^+$. This trend can be
 319 directly related to the effective charge, Z_{eff} , which is 4, 3.3, 3, and 2.2 for An^{4+} , AnO_2^{2+} , An^{3+} ,
 320 and AnO_2^+ , respectively.¹⁵ The extraction trend demonstrates that electrostatic interactions
 321 dominate chemical interactions of the f-elements with the organophosphorus reagent. Based on
 322 the uptake results of Th^{4+} , Np^{4+} does not appear to be significantly present in any of the potential
 323 waste conditions. Plutonium is expected to be in the trivalent state¹⁶ in solutions containing

324 ascorbic acid and in the hexavalent state for oxidizing conditions.¹⁷ The redox speciation of Np
325 in high ionic strength media and dilute nitric acid is relatively unknown. An additional
326 complication is that chromate and neptunium can be reduced and oxidized, respectively, by trace
327 nitrate impurities.¹⁸⁻²⁰

328

329 *Neptunium Chemistry*

330 Neptunium redox chemistry produced more nuanced uptake patterns for neptunium in contrast
331 to the other redox stable f-elements. Redox potentials in [Table 2](#) indicate that the reducing
332 capability of ascorbic acid for Np decreases with decreasing pH.²¹ Chromate is also more readily
333 reduced to chromium (III) at lower pHs. Pourbaix predominance diagrams note that hexavalent
334 neptunium will reduce to the pentavalent state in aqueous media when acidic concentrations are
335 below 0.01 M due to water stability issues and that both tetravalent and hexavalent oxidation
336 states are stable under higher acid conditions.²⁴ These parameters frame an explanation for
337 neptunium redox speciation and subsequent uptake by the TOPO-XAD7 resin. Later studies
338 could additionally consider the redox speciation of plutonium, which generally has richer redox
339 chemistry than neptunium.

340 At low acid concentrations (0.01M), neptunium distribution is comparable for systems without
341 chromium and with reduced chromium (courtesy ascorbic acid) – indicating that NpO_2^+ is the
342 predominant neptunium species present in solution. Neptunium in contact with chromate is at
343 least partially oxidized, as indicated by better extraction, but uptake is not comparable to UO_2^{2+} ,
344 the stable hexavalent actinide model. This is probably related to water stability issues identified
345 on the Pourbaix predominance diagram limiting Np oxidation and extraction.

346

347 Table 2. Neptunium redox reaction significant to understanding simulated acidic aqueous
 348 raffinate of the Hanford tanks.^{19,20,22}

Reaction	E°(V)
$\text{NpO}_2^+ + 4\text{H}^+ + \text{e}^- \rightarrow \text{Np}^{4+} + 2\text{H}_2\text{O}$	0.567
$\text{NpO}_2^{2+} + \text{e}^- \rightarrow \text{NpO}_2^+$	1.236
$\text{NO}_3^- + 3\text{H}^+ + 2\text{e}^- \rightarrow \text{HNO}_2 + \text{H}_2\text{O}$	0.94
$\text{NpO}_2^{2+} + \text{HNO}_2 + \text{H}_2\text{O} \rightarrow \text{NpO}_2^+ + \text{NO}_3^- + 3\text{H}^+$	0.296
Dehydroascorbic Acid + $2\text{H}^+ + 2\text{e}^- \rightarrow$ Ascorbic Acid	0.390
$\text{HCrO}_4^- + 7\text{H}^+ + 3\text{e}^- \rightarrow \text{Cr}^{3+} + 4\text{H}_2\text{O}$	1.20

349

350 At mid-level acid concentrations (0.1 M), Np extraction is more comparable between the
 351 various conditions examined. Under oxidizing conditions, chromate reduction at higher acid
 352 concentrations prevents significant oxidation of Np, but there still appears to be slightly more
 353 Np(VI) than in other 0.1 M HNO₃ studies. Hexavalent neptunium would also provide increased
 354 uptake, but, considering the reducing conditions of the system, this is unlikely. Neptunium
 355 uptake for the system lacking chromium is low – indicating that pentavalent neptunium as
 356 predominant. At the highest acid concentrations studied (1 M), neptunium extraction is nearly
 357 identical for the no chromium and the chromium/ascorbic acid containing systems. For the
 358 chromate containing system, neptunium TOPO-XAD7 uptake comparable to uranium is
 359 observed. Neptunium in this instance appears predominantly in the hexavalent state.

360 Considering the variability of redox factors, if acidic recovery of the Hanford tanks were
 361 attempted, further studies would be necessary to evaluate the redox speciation of the relevant
 362 redox active actinides (Np and Pu) to develop effective low-level recovery processes. If a
 363 secondary cleanup is required of the Hanford sludges (and conditions are not oxidizing), a

364 balance between sufficient nitric acid for oxidation of Np while preventing competition between
365 with nitric acid for the TOPO available in the system would be required.

366

367 **Static and Dynamic Capacity Determination**

368 Isotherms and breakthrough curves allow determination of resin saturation for batch (static)
369 and column (dynamic) modes, respectively. Examining column behavior at heavy metal loading
370 will show if the column maintains reasonable performance at higher load concentrations. If
371 analyte uptake is reaching equilibrium, the resin should behave comparably regardless of the
372 mode of operation. Comparable behavior allows validation of the values obtained for analyte
373 uptake. A summary of parameters determined for both static and dynamic mode behavior is
374 shown in [Table 1](#). Overall, the 38% TOPO-XAD7n resin showed the excellent reproducibility
375 between static and dynamic modes.

376

377 *Static Extraction Capacity Determinations*

378 Several assumptions are required for the Langmuir model to be valid: the surface of the
379 adsorption must be uniform, the adsorbed molecules must not interact, all adsorption must occur
380 through the same mechanism, and at maximum sorption only a monolayer can be formed.²⁵
381 [Figure 3](#) shows the Langmuir fit of the saturation isotherm generally describes europium and
382 uranium uptake and analyte concentrations that provide a saturated resin. Saturation conditions
383 were observed for all 58% TOPO-XAD7 resins at 30 mM Eu. For 24% TOPO-XAD7n resin, the
384 saturating concentrations for Eu^{3+} and UO_2^{2+} were greater than 25 mM of metal. To ensure
385 saturation, breakthrough experiments later were performed with at least 30 mM Eu^{3+} or UO_2^{2+} .

386 Saturating stoichiometries (Eu:TOPO) of 1:5 and 1:4 are calculated for the 58% TOPO-XAD7
387 and 46% TOPO-XAD7n resins, respectively. This indicates a more efficient usage of the n-
388 dodecane wetted material. Typical stoichiometries in solvent extraction systems have noted 1:3
389 Eu:TOPO extracted species²⁶; however, since the concentration of TOPO on the resin (>1 M) is
390 an order of magnitude greater than typically used in solvent extraction systems, this excess of
391 TOPO could lead to a larger number of extractant molecules binding with Eu. Nitrates can be
392 bound to a metal ion in a monodentate or bidentate fashion. Assuming the coordination of three
393 bidentate nitrate ions, this would produce a coordination number of 10 for the extracted metal
394 ion. Coordination numbers of 8-9 are typically observed with lanthanides in a solution matrix.
395 Crystal structures have shown lanthanides to have coordination numbers as high as 12 in the
396 solid state. Since the extraction chromatographic system represents a hybrid between the
397 solution phase and a crystalline phase, a higher coordination number may not be unreasonable.

398 The information obtained through initial europium experiments narrowed uranium saturation
399 investigations to only the 38% TOPO-XAD7n resin. Stoichiometries for Eu^{3+} and UO_2^{2+} in
400 contact with the 38% TOPO-XAD7n resin were 1:3.5 for Eu:TOPO and 1:1 for UO_2^{2+} :TOPO
401 complexes, respectively. The additional dissolution of TOPO appears to have aided in creating
402 an environment similar to the solvent extraction system. The 1:1 stoichiometry of the
403 UO_2^{2+} :TOPO complex was unanticipated. Typically a 1:2 stoichiometry is observed between
404 uranium and TOPO in solvent extraction systems.²⁷

405

406 *Dynamic Extraction Capacity Determination*

407 **Figure 4** shows the breakthrough curves obtained for the TOPO-XAD7n resin with Eu^{3+} and
408 UO_2^{2+} . As noted in the previous section, initial europium screening showed analyte uptake

409 kinetics of the 24% TOPO-XAD7n where favorable compared to the 36% TOPO-XAD7n.
410 Uranium uptake was studied exclusively with the 38% TOPO-XAD7n resin. Given the unique
411 data obtained regarding Eu:TOPO stoichiometries, the practical dynamic capacity, $Q(m)$,
412 obtained from the breakthrough curves was particularly useful in validating the saturating values
413 for Eu^{3+} for each of the n-dodecane wetted materials examined thus far. [Table 1](#) notes the
414 agreement between $Q(m)$ and q_{max} for the n-dodecane wetted materials.

415

416 **Simulated Waste Stream Remediation**

417 The simulated waste stream contained 0.1 M HNO_3 , 0.25 M $\text{Al}(\text{NO}_3)_3$, 1 mM K_2CrO_4 , 30 mM
418 Eu and U, and tracer Pu and Np. Oxidizing conditions were highlighted in this experiment to
419 examine loading effects that could occur if hexavalent, extractable actinide species were present.
420 The 0.1 % breakthrough observed during the loading step in the single, Pu, Np and U
421 experiments (not shown) and the lack of breakthrough during the wash step was also observed
422 with the simulated waste stream. No evidence of Eu breakthrough during the load step was
423 observed using either gamma or liquid scintillation spectroscopy. Europium elution occurred
424 without any detectable evidence for alpha activity (indicative of actinide recovery) observed
425 using liquid scintillation detection. The elution of Eu was quantitative within error. Removal of
426 the actinides was comparable to the single element experiments. The higher actinide loading for
427 the simulated waste stream increased the column tailing, observed in the semi-log curve ([Figure](#)
428 [6](#)); however, recovery was within error still quantitative. A smaller mesh size resin would most
429 likely improve the column stripping kinetics and reduce tailing.

430 Although the decontamination of the simulated Al leachate waste stream using extraction
431 chromatography is comparable to the decontamination obtained in solvent extraction

432 investigations, throughput and column blockage can be drawbacks to the implementation of
433 chromatography on a large scale. Extractant loss occurs in both liquid-liquid and extraction
434 chromatographic methods. If the extractant were covalently bound to a polymer (instead of
435 merely held in place by solubility preferences), chromatographic separations of nuclear fuel may
436 become preferential. Several such resins are currently in development.^{28,29}

437

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