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AMERICIUM SEPARATIONS FROM HIGH-SALT SOLUTIONS USING ANION EXCHANGE

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ABSTRACT

The aging of the US nuclear stockpile presents a number of challenges, including the increasing radioactivity of plutonium residues due to the ingrowth of ^{241}Am from the β-decay of ^{241}Pu. We investigated parameters that affect the sorption of Am onto anion-exchange resins from concentrated effluents derived from nitric acid processing of plutonium residues. These postevaporator wastes are nearly saturated solutions of acidic nitrate salts, and americium removal is complicated by physical factors, such as solution viscosity and particulates, as well as by the presence of large quantities of competing metals and acid. Single- and double-contact batch distribution coefficients for americium and neodymium from simple and complex surrogate solutions are presented. Varied parameters

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include the nitrate salt concentration and composition and the nitric acid concentration. We find that under these extremely concentrated conditions, Am(III) removal efficiencies can surpass 50% per contact. Distribution coefficients for both neodymium and americium are insensitive to solution acidity and appear to be driven primarily by low water activities of the solutions.

INTRODUCTION

The Plutonium Facility at Los Alamos National Laboratory supports a number of plutonium processing operations. Anion exchange in nitric acid is a preferred method for plutonium recovery because Pu(IV) forms anionic nitrate complexes, which are strongly retained by anion-exchange resins, while few other metal ions, including Am(III), form competing complexes. The intended disposition site for transuranic (TRU) wastes is the Waste Isolation Pilot Plant (WIPP). Accordingly, all wasteforms must be in compliance with the WIPP-Waste Acceptance Criteria (1) as well as the TRUPACT-II shipping criteria (2,3). Decay-heat wattage limits, which are driven by alpha-decay activity, are particularly troublesome for the wastes from nitric acid processing because they contain Am to Pu ratios far higher than those found elsewhere in the Department of Energy complex, and ^{241}Am has approximately 60 times the specific (alpha) activity of ^{239}Pu. Thus, a simple procedure to extract excess americium from these postevaporator waste solutions is desirable to ensure consistent compliance with all regulations.

Nitrato ligand complexation to trivalent lanthanides and actinides is very weak. In fact, reliable stability constants are available only for the mononitrato dications of these metals (4). Although anionic nitrato complexes are not observed in pure nitric acid, the concentrated effluents from nitric acid processing possess higher nitrate, lower acid, and lower water activity; these conditions generally facilitate the formation of higher complexes. Under these conditions, anion exchange may provide an effective mechanism for the removal of excess americium. Smaller trivalent cations, such as Al(III) and Fe(III), which are effective competitors with Am(III) for cation-exchange and neutral-donor complexant sites, do not form anionic complexes to any appreciable extent and are unlikely to interfere with the anion-exchange efficiency.

None of the anion-exchange materials we investigated are selective for trivalent actinides over tetravalent actinides. Therefore, residual Pu(IV) is sorbed preferentially to Am(III). In the case of this particular target waste stream from nitric oxide processing, this lack of selectivity is not a significant issue because the primary goal was to reduce total alpha activity, not just that from americium. Although it reduces the resin capacity for Am(III), Pu(IV) in relatively large quantities is advantageous because it acts as a diluent for the high-activity Am(III) in precipitation, calcination, and subsequent storage.

EXPERIMENTAL

Composition of Evaporator Bottoms

Extensive characterizations of postevaporator solutions have been conducted and nonradioactive surrogates developed (5). In general, acid and nitrate concentrations are in the ranges of 1–5 mol/L and 400–600 g/L, respectively. Evaporator volume reduction ratios are limited primarily by the high viscosity of the concentrated solution and the precipitation of nitrate salts that interfere with solution transfer. For sorption experiments, a complex lean-residue (LR) surrogate was employed (Table 1). The surrogate solution was used in its undiluted form, diluted with water, or partially neutralized with an equal volume of sodium hydroxide to approximately 0.2 mol/L H^+ to allow evaluation at different salt and acid concentrations. We also evaluated americium sorption from simple surrogates (sodium and calcium nitrate) containing similar acid and total nitrate concentrations as those in the more complex surrogate.

Materials

Evaluated anion-exchange resins were based on poly(4-vinylpyridine) cross-linked with divinylbenzene (the Reillex HP® and Reillex HPQ®, Reilly Industries Inc., Indianapolis, IN). In these resins, a fixed cationic site (a quaternized

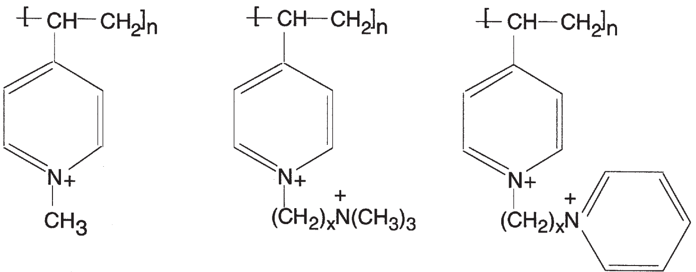
Table 1. Composition of Lean-Residue Evaporator Bottom Surrogate

Cation	g/L	Anion	g/L
Fe	9.03 (6.45)	Cl	1.02 (0.73)
Ca	58.4 (41.7)	NO_3	630 (450)
K	18.5 (13.2)	SO_4	1.55 (1.11)
Mg	54.8 (39.1)	C_2O_4	3.2 (2.3)
Na	6.85 (4.9)	F	6.0 (4.3)
Al	4.75 (3.4)		
NH_4^+	0.03 (0.02)		
H^+ (mol/L)	1.4 (1.0, 0.2)		

Data calculated from composition (5). Primary values are for the original surrogate. Values in parentheses are for diluted and/or neutralized solutions.

nitrogen atom) attracts and retains anions from the mobile phase. The original Reillex HPQ® resin, which is currently used in the nitric acid plutonium recovery process, is a commercially available macroporous resin with approximately 70% of its pyridinium sites methylated. This resin displays a high level of resistance to degradation by oxidizing acids and radiation. We have developed series of mono- and bifunctional poly(vinylpyridine)-based anion-exchange resins in which the type of alkyl group, the percentage of alkylation, and the degree of cross-linking of the base resin are varied (6,7). Descriptors for the resins are presented in Fig. 1. Due to the presence of an *N*-substituted pyridinium ion in the repeat units for both the mono- and bifunctional types, the anion-exchange resins are expected to have the same high stability as has been demonstrated by the HPQ resin. New experimental resins were evaluated as they became available and rejected if they were not a top performer or if they were considered unsuitable for column implementation. All resins were converted to the nitrate form and air-dried to constant weight prior to use.

A commercial neutral-donor extraction chromatography resin, TRU Resin® (Eichrom Technologies, Darien, IL), was included in the neodymium contact experiments as a performance standard. In this system, donor atoms of the extractant compound filled the inner-sphere coordination sites on the metal cation. Moderate selectivity for Nd and Am over main group and transition metals occurs due to the larger coordination number for *f* elements, but selectivity is not expected to be as comprehensive as for the anion-exchange sorption mechanism. TRU Resin has often been used to recover and concentrate actinides from lean streams. It consists of an EIChroM 100–150-μm support loaded with octyl(phenyl)-*N*,*N*-diisobutyl-



Methylated resins
HP18-Me = ca. 18% crosslinked, ≈70% methylated, experimental resin
HPQ ®= ca. 25% crosslinked, ≈70% methylated
Bifunctional resins; x = 3, 4, 5, 6
HP18-$(CH_2)_x$-$N(CH_3)_3$ = ca. 18% crosslinked, ≈70% alkylated
HP21-$(CH_2)_x$-$N(CH_3)_3$ = ca. 21% crosslinked, ≈70% alkylated
HP21-$(CH_2)_4$-NC_5H_5 = ca. 21% crosslinked, ≈70% alkylated

Figure 1. Poly(4-vinylpyridinium) anion-exchange resins.

carbamoylmethylphosphine oxide dissolved in tri-n-butylphosphate as the primary actinide extractant.

Batch Contact Experiments and Calculations

In all batch contact experiments, nonsorbing inert matrices were used to confirm that no metal or activity was lost to the containers. Percent uptake and/or distribution coefficients, D, were determined from metal ion concentrations (Nd, Fe, and Al) or gamma activities (Am) of post- and precontact solutions and calculated as follows:

$$D = \frac{M_r}{M_s} \times \frac{\text{mL}}{\text{g}}$$

where M_r is the amount of metal (activity) sorbed on the resin; M_s is the amount of metal (activity) remaining in solution; mL is volume of contact solution (mL); and g is the mass of resin (g).

Diluted and partially neutralized LR evaporator bottom surrogate solutions (1.0 and 0.2 mol/L H^+) (Table 1) were spiked with approximately 100 ppm of Nd(III). Although Eu(III) is also a commonly used homologue to Am(III), we favored Nd(III) because it has a more similar ionic radius and analogous complexation behavior to Am(III) (8). Samples of 25, 50, 100, and/or 250 mg of air-dried resin were contacted with 2.5 mL of solution in polyethylene tubes that were rotated overnight (18–20 hours). If the average capacity for the anion-exchange resins is 3 mEq/g (dry weight), 100% loading of the available Nd would correspond to a maximum of 3% ion-exchange capacity for a monoanionic complex and 5% capacity for a dianionic complex with the smallest anion-exchange resin sample of 25 mg. Because the capacity for the TRU Resin is approximately 3–4 times lower than the anion-exchange resins, sorption experiments were conducted on larger resin samples to maintain a similar loading level. However, in all cases, appreciable loading of other trivalent cations (Fe at 4300 ppm and Al at 2600 ppm) quickly saturated the available sites.

Solution concentrations of Nd, Fe, and Al were determined using a Thermo Jarrell Ash Corporation IRIS Inductively Coupled Argon Plasma Emission Spectroscopy system. The argon plasma was operated at 1.0 kW, with a plasma flow rate of 15.0 L/min, and a nebulizer flow rate of 1.5 L/min. Aluminum, iron, and neodymium emissions were monitored at 167.081, 259.940, and 401.225 nm respectively with vertical and horizontal slits set at 300 and 50 mm. Three replicate analyses were performed for each sample and resulted in relative standard deviations of between 0.5 and 2.0%.

Americium distribution coefficients were measured and calculated by procedures developed at Los Alamos National Laboratory (9). Sorption of ^{241}Am from spiked simple and complex surrogate solutions was quantified by Ge(Li) counting of the 60 keV gamma emissions. Resin samples of 250 mg were contacted with 6 mL of solution. Two types of radioactive spike solutions were used. One contained tracer quantities (10^{-13} mol/L) of americium with no appreciable competing actinides. The other was a standard solution used in determination of plutonium distribution coefficients and contained 3 g/L plutonium (IV) with tracer quantities of americium. D values were determined for dynamic contact periods of 0.5, 2.0, and 6.0 hours by sequential removal of approximately 25% of the initial solution volume to obtain information about the sorption kinetics. Uncertainties in the distribution calculations are cumulative due to the multiple aliquots extracted from each sample. Thus, experimental uncertainties for D values range from approximately 5% for the 30 minute values to approximately 10–20% for the 2 and 6 hour values.

RESULTS AND DISCUSSION

Neodymium Batch Contact Experiments

Experimental results are presented in Table 2 as the percentage of each metal removed from the contact solutions. As expected, the TRU Resin performs much better in the partially neutralized surrogate than in the high-acid solution. Previous studies of this material have shown that the retention of Fe(III) increases dramatically for nitric acid concentrations greater than 1 mol/L, and that the effect

Table 2. Percent Uptake of Trivalent Metals from 2 Lean-Residue Surrogates

	HPQ®	HP18-Me	HP18-$(CH_2)_5$-$N(CH_3)_3$	TRU Resin®
Undiluted surrogate	Al, Fe, Nd	Al, Fe, Nd	Al, Fe, Nd	Al, Fe, Nd
1.4 mol/L HNO_3				
10 mol/L NO_3				
25 mg	—	1.8, 0.3, 26.7	8.3, 0.6, 30.9	—
50 mg	3.1, 2.1, 34.3	3.5, 1.5, 42.4	6.4, 1.1, 46.0	—
100 mg	5.1, 2.4, 51.5	4.6, 2.0, 61.4	4.1, 1.3, 64.0	1.0, 2.6, 18.9
250 mg	—	—	—	0.7, 8.4, 42.7
Neutralized surrogate	Al, Fe, Nd	Al, Fe, Nd	Al, Fe, Nd	Al, Fe, Nd
0.2 mol/L HNO_3				
6.5 mol/L NO_3				
25 mg	—	—	8.2, 2.9, 35.4	—
50 mg	1.8, 1.5, 46.3	—	7.9, 1.5, 52.3	—
100 mg	3.4, 3.3, 64.6	—	9.3, 2.3, 68.7	0.3, 4.0, 73.5
250 mg	—	—	—	0.7, 12.1, 88.7

—No data available.

of Fe(III) on lowering trivalent *f*-element retention is significant (10). Thus, the decreased Nd uptake observed for the undiluted surrogate (1.0 mol/L H^+) relative to the partially neutralized surrogate (0.2 mol/L H^+) is more likely due to increased Fe(III) competition than to increased acid. While this neutral-donor material outperforms the anion-exchange resins in the lower acid surrogates, it significantly underperforms at the higher acid concentrations that are found in authentic waste solutions.

In general, Nd sorption onto the anion-exchange resins is quite high, averaging almost 50% for the 100-mg samples, while sorption of the other trivalent metals is uniformly low; i.e., Fe(III) $< 3\%$ and Al(III) $< 10\%$. Nd(III) sorption was relatively insensitive to acid concentration. Acid concentration is one of the most highly variable components of evaporator bottoms from different feed solutions, so this behavior suggests that the anion-exchange resins could exhibit a favorable consistency of behavior for a variety of evaporator bottom compositions.

Decreasing the percentage of divinylbenzene cross-linking within the anion-exchange resins led to enhancement of sorption behavior. The experimental resin HP18-Me differs from the commercial HPQ primarily in the percentage of divinylbenzene cross-linking agent (18% vs. 25%) used in the base resin. Both have a similar percentage of pyridinium sites methylated (approximately 70%). However, the 18% cross-linked substrate appears to lack the physical durability desired for long-term large-column applications. Therefore, attention was focused on higher cross-linked (21% and 25%) anion-exchange resins in subsequent evaluations.

Trivalent Metal Ion Speciation in Acidic High-Nitrate Solutions

To determine the relative effects of acid, total nitrate, and ionic strength upon trivalent metal ion speciation, we compared the visible spectra of Nd(III) in 3 series of solutions: 1) 1–15 mol/L HNO_3 (in 0.5 mol/L increments), 2) 1 mol/L HNO_3 and 5.0–9.6 mol/L total nitrate (as calcium nitrate), and 3) 5 mol/L HNO_3 and 7.2–9.6 mol/L total nitrate (as calcium nitrate). All 3 spectral series displayed the same general peak characteristics. The peak intensities at 578 nm increased while the intensities of the peaks at 740 and 796 nm decreased as the nitrate concentration (as either HNO_3 or $Ca(NO_3)_2$) was enhanced. Figure 2 illustrates this trend. Anionic nitrato complexes of Nd have not been observed in solution, and the visible spectral data in Fig. 2 are most likely derived from a mixture of aqueous mono-, and dinitrato cations. However, spectroscopic studies of Pu(IV) in nitric acid have revealed that the hexanitrato anionic complex is consistently sorbed onto anion-exchange resins regardless of the solution speciation with variation only in the quantity of Pu sorbed (11,12). Thus, we assumed that in our experiments the trivalent metals are sorbed as anionic complexes despite the prevalence

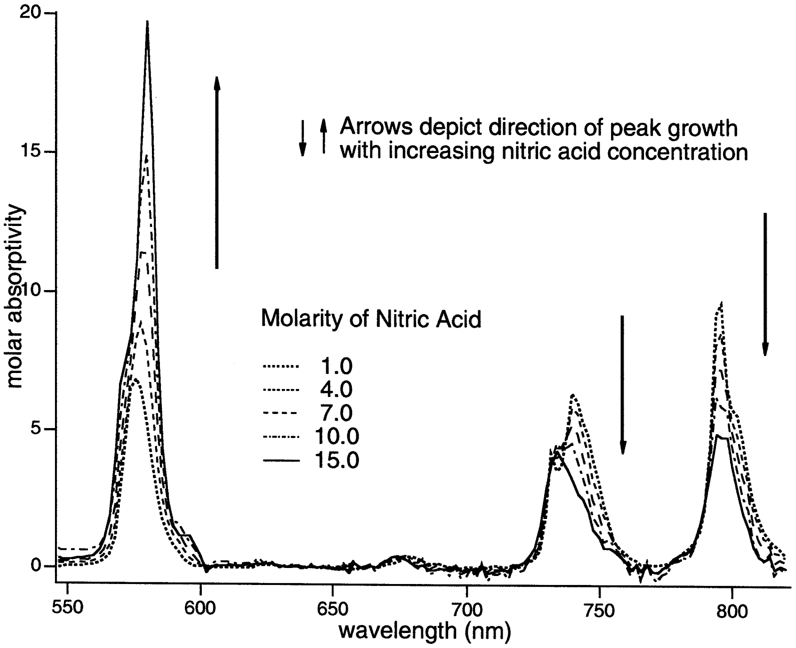


Figure 2. Nd(III) in nitric acid. [Nd] ≈ 15 mmol/L.

of lower-order cationic complexes in solution, but solution conditions that facilitate the formation of higher-order complexes will enhance extraction of Nd(III) and Am(III).

In general, the effect of high-nitrate concentration upon solution speciation was somewhat weaker when calcium salts were added to the solution than when nitric acid was added alone. This effect is shown in Fig. 3 where the spectrum for Nd in 8 mol/L nitric acid indicates a larger contribution from complexes with a higher number of nitrates coordinated than does that for Nd in 1 mol/L HNO_3/ 3.5 mol/L $Ca(NO_3)_2$ (8.0 mol/L total nitrate).

Americium Batch Contact Experiments

Americium uptake by a series of bifunctional anion-exchange resins was determined from a variety of simple and complex surrogate solutions. The simple surrogate consisted of either 1 mol/L HNO_3 with 7 mol/L $NaNO_3$ or 1 mol/L HNO_3 with 3.5 mol/L $Ca(NO_3)_2$. Thus, both solutions consisted of 1 mol/L acid and 8 mol/L total nitrate, but each had different ionic strengths and water activity. Complex surrogates consisted of the water-diluted (1 mol/L acid) and undiluted LR surrogates as described in Table 1.

Table 3 summarizes the noncompetitive americium sorption data from 3 solutions onto a series of experimental anion-exchange resins. Because the solution to solids ratio changes with each removed aliquot, the percent uptake calculations are only valid for the first 30 minutes of contact. Therefore, to facilitate comparison with the neodymium data, the experimental results are presented as the distribution coefficients for Am(III) with percent uptake data presented for the 30-minute contact solution. The series consisted of bifunctional derivatives of HP21 resin with the trimethylammonium anion-exchange site separated from the pyridinium nitrogen in the backbone by a 1,ω-alkylene spacer group of 3–6 carbon atoms. An additional bifunctional anion-exchange resin contained a second pyridinium site separated from the backbone site by a 1,4-butylene spacer (Fig. 1).

Several features stand out in this noncompetitive sorption data. First, although the 3 solutions had comparable acid and intermediate total nitrate concentrations, americium sorption from the simple nitric acid/calcium nitrate surrogate solution was weaker than it was with the 2 complex surrogate solutions. Second, sorption equilibrium appears to be reached more rapidly in the more dilute solutions as demonstrated by the relatively small changes between 2 and 6 hours for the simple- and diluted-complex surrogates. Americium uptake from the undiluted surrogate is greater but slower than it is from the diluted sample. This sorp-

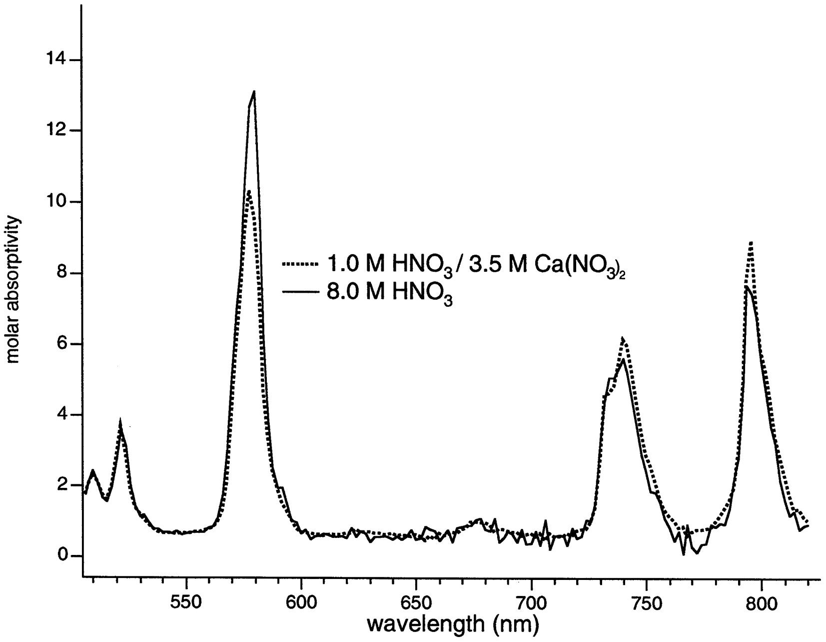


Figure 3. Nd(III) in nitric acid and salt solution. [Nd] ≈ 15 mmol/L; $[NO_3]$ = 8.0 mol/L.

Table 3. Noncompetitive Distribution Coefficients, *D*, and Percent Uptake (Parentheses) for Am(III) onto HP21 Resins from Evaporator Surrogate Solutions

Resin	30 min	2 h	6 h
Undiluted surrogate			
$\frac{1.4\ \text{mol/L HNO}_3}{10\ \text{mol/L NO}_3}$			
$—(CH_2)_3—N(CH_3)_3$	37.7 (61.1%)	62	69
$—(CH_2)_4—N(CH_3)_3$	34.2 (58.8%)	60	82
$—(CH_2)_5—N(CH_3)_3$	49.2 (67.2%)	82	115
$—(CH_2)_6—N(CH_3)_3$	32.5 (57.5%)	50	64
$—(CH_2)_4—NC_5H_5$	33.8 (58.5%)	62	104
Diluted surrogate			
$\frac{1\ \text{mol/L HNO}_3}{6.5\ \text{mol/L NO}_3}$			
$—(CH_2)_3—N(CH_3)_3$	12.8 (34.8%)	19.4	18
$—(CH_2)_4—N(CH_3)_3$	15.1 (38.5%)	20.3	18.5
$—(CH_2)_5—N(CH_3)_3$	22.0 (47.8%)	26.5	27.5
$—(CH_2)_6—N(CH_3)_3$	12.6 (34.5%)	18.1	15.2
$—(CH_2)_4—NC_5H_5$	15.7 (39.6%)	20.6	24.5
$\frac{1\ \text{mol/L HNO}_3}{3.5\ \text{mol/L Ca(NO}_3)_2}$			
$—(CH_2)_3—N(CH_3)_3$	9.0 (27.3%)	10	10.5
$—(CH_2)_4—N(CH_3)_3$	10.9 (31.2%)	12.9	14.1
$—(CH_2)_5—N(CH_3)_3$	13.5 (36.0%)	17.2	16.9
$—(CH_2)_6—N(CH_3)_3$	9.5 (28.4%)	10.1	9.5
$—(CH_2)_4—NC_5H_5$	—	—	—

$[Am]_{in} \approx 10^{-13}$ mol/L.

tion behavior is similar to that observed for Pu(IV) onto Dowex anion-exchange resins where higher salt concentrations favored sorption equilibrium but disfavored kinetics due to poor diffusion rates (13).

For the series of trimethylammonium bifunctional resins, americium distribution generally increased with spacer length, achieving a maximum value with the 5-carbon 1,5-pentylene spacer, then decreased with the longer 6-carbon spacer. This trend is directly analogous to the sorption behavior of Pu(IV) onto lower cross-linked (6) and identical resins (14). Americium distribution onto the pyridinium-terminated bifunctional resin was also high.

For competitive experiments, the effects of relatively high plutonium content upon americium uptake from pure nitric acid solutions (1 and 7 mol/L) and salt solutions with relatively low acid concentration (1 mol/L) but high total nitrate concentrations (approximately 8 mol/L) were examined. Sorption of americium onto the anion-exchange resins from pure 1 mol/L HNO_3 was poor ($< 8\%$)

(data not shown) and was comparable to that observed for nonsorbing metals, such as Fe and Al, in the cold surrogate testing. The other americium sorption data are presented in Table 4.

When results for the 1 mol/L HNO_3 / 3.5 mol/L $Ca(NO_3)_2$ solution in Table 4 are compared with those in Table 3, one sees that the americium sorption is decreased by about 20–30% when in the presence of plutonium. This decrease correlates with the loss of approximately 25% of the anion-exchange sites to near-quantitative binding of Pu(IV).

Americium sorption by the series of bifunctional anion-exchange resins displayed a singular lack of sensitivity to acid concentration. Similar behavior was observed for Nd(III) uptake from 1.0 mol/L and 0.2 mol/L acid-adjusted LR surrogate as previously described, but it is more significant in the acid concentration ranges noted in Table 4, which are more like those of the target evaporator bottoms. The absence of acid sensitivity is surprising in light of previous experiments conducted at Oak Ridge National Laboratory (15) and Los Alamos National Laboratory (16) in which acid concentrations greater than 0.05 mol/L had a distinctly detrimental affect upon Am breakthrough in column experiments. The total ionic strength of the solution also appears to have little effect, despite the higher ionic strength of the nitric acid/calcium nitrate solution (i.e., 8.0 for the $HNO_3/NaNO_3$ solution versus 11.5 for $HNO_3/\ Ca(NO_3)_2$).

Table 4. Competitive Distribution Coefficients, *D*, and Percent Uptake (Parentheses) for Am(III) onto HP21 Resins from Evaporator Surrogate Solutions

Resin	30 min	2 h	6 h
7 mol/L HNO_3			
$—(CH_2)_3—N(CH_3)_3$	6.1 (20.4%)	4.9	4.8
$—(CH_2)_4—N(CH_3)_3$	8.1 (25.3%)	6.9	5.5
$—(CH_2)_5—N(CH_3)_3$	11.1 (31.6%)	8.1	6.9
$—(CH_2)_6—N(CH_3)_3$	4.7 (16.3%)	2.8	3.4
$\frac{1\ \text{mol/L}\ HNO_3}{7\ \text{mol/L}\ NaNO_3}$			
$—(CH_2)_3—N(CH_3)_3$	7.9 (24.8%)	8.6	7.4
$—(CH_2)_4—N(CH_3)_3$	9.0 (27.3%)	10.2	7.5
$—(CH_2)_5—N(CH_3)_3$	11.5 (32.3%)	13.2	12
$—(CH_2)_6—N(CH_3)_3$	6.5 (21.2%)	5.3	6.0
$\frac{1\ \text{mol/L}\ HNO_3}{3.5\ \text{mol/L}\ Ca(NO_3)_2}$			
$—(CH_2)_3—N(CH_3)_3$	7.5 (23.9%)	7.5	6.5
$—(CH_2)_4—N(CH_3)_3$	8.1 (25.3%)	9.3	9.0
$—(CH_2)_5—N(CH_3)_3$	—	—	—
$—(CH_2)_6—N(CH_3)_3$	5.6 (19.0%)	7.4	5.7

[Pu(IV)] = 3 mg/mL, [Am] = tracer.

Ion and Water Activities

Researchers commonly use molality (m) instead of molarity (mol/L) to compare the effect of ion and water concentrations upon metal complexation. However, for the solutions evaluated here, the extremely high salt content prevents an accurate determination of solution activity coefficients, thus making the use of molality of little value. As can be seen in Table 5, these evaporator surrogates are approximately 50% solids with calculated ionic strengths that are extremely high. Accurate determinations of activity coefficients are not possible for this regime. Although calculations using the Pitzer method (17) will provide water activities (a_w), these values are of questionable accuracy.

CONCLUSIONS

Americium (III) exhibits an unexpectedly high affinity for anion-exchange resins from complex surrogates of high-salt evaporator bottoms solutions, an effect that has not been duplicated using simple salt solutions. Similar behavior is observed for its lanthanide homologue, Nd(III). No single controlling factor (the acid concentration, total nitrate concentration, or solution ionic strength) can be discerned that accounts for the approximately 2-fold increase in retention of the trivalent ions from complex solutions relative to simple solutions. The cationic environment of the anion-exchange resin appears sufficiently favorable to extract the trivalent metals as higher-order anionic nitrato complexes, even from solutions in which those complexes are not observed. Calculation of species activities (i.e., water, proton, and nitrate) in such concentrated mixed salt solutions is difficult and of questionable accuracy. However, the relative activities of water and nitrate in solution are likely responsible for promoting formation of anionic nitrate complexes of these trivalent metals and/or facilitating their sorption into the resin environment.

Table 5. Experimental and Calculated Solution Parameters

Solution	Density (kg/L)	kg Solute/ kg Solution	Ionic Strength	H^+ (m)	M^{+X} (m)	NO_3^- (m)	a_w
Undiluted surrogate	1.46	0.55	23.1	2.11	7.3	15.9	0.002
Diluted surrogate	1.31	0.43	15.3	1.35	4.6	10.2	0.050
$\frac{1\ \text{mol/L HNO}_3}{7\ \text{mol/L NaNO}_3}$	1.38	0.48	11.1	1.39	9.7	11.1	0.287
$\frac{1\ \text{mol/L HNO}_3}{3.5\ \text{mol/L Ca(NO}_3)_2}$	1.40	0.46	15.1	1.31	4.6	10.5	0.054
1 mol/L HNO$_3$	1.03	0.06	1.0	1.0	—	1.0	0.966
7 mol/L HNO$_3$	1.22	0.36	8.9	8.9	—	8.9	0.221

Recent pilot and process-scale evaluation of alpha-activity removal from authentic evaporator solutions confirm the efficacy of using anion-exchange resins to remove americium from high-nitrate solutions (18). From a practical viewpoint, the modest need for americium removal (50–75%) from nitric acid evaporator bottoms allows sufficient latitude for the use of nonoptimized conditions, such as running existing columns filled with older, slightly degraded Reillex HPQ. Newer materials, such as these experimental bifunctional resins, which exhibit higher distribution coefficients and have displayed comparable stability in the high-acid solutions, would allow for increased Am removal with the use of smaller columns.

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