

*Americium Separations from
High Salt Solutions*

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Americium Separations from High Salt Solutions

by

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ABSTRACT

The aging of our nuclear stockpile presents a number of challenges, including the ever increasing radioactivity of plutonium residues due to the ingrowth of Am-241 from decay of Pu-241. Minimization of americium in process and waste solutions is desirable to reduce both the worker exposure hazards and the effects of radiolysis on the final waste product. However, removal of americium from these complex mixtures is often complicated by the presence of large quantities of competing metals and acids. We have investigated the use of anion-exchange resins and neutral-donor solid-phase extractants with varied functionality for the extraction of americium from high-nitrate acidic solutions. Distribution coefficients for americium and neodymium from simple "hot" and "cold" surrogates are presented along with total alpha-activity removal from authentic evaporator-bottom solutions. We find that over 50% of the Am(III) and alpha-activity can be removed from these high-salt solutions per batch contact with approximately 90% removal from large-scale column processes. Americium removal efficiencies by anion-exchange resins are surprisingly insensitive to solution acidity. Thus, ion-exchange is a viable, robust procedure for removing excess activity from high-nitrate acidic solutions.

INTRODUCTION

Anion-exchange in nitric acid is the preferred method for the recovery of plutonium from a variety of substrates. In nitric acid, 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. Trivalent cations such as americium do not form nitrate complexes as readily as tetravalent metals due to their lower charge density. However, under more forcing conditions such as those found in concentrated effluents from nitric acid processing which contain higher nitrate and lower acid compared to pure nitric acid, anion-exchange could become an effective mechanism for the removal of excess americium. Trivalent cations such as Al and Fe which would normally compete with Am for cation-exchange sites do not form competing anionic complexes to any appreciable extent due to their smaller coordination sphere.

A second class of materials is the neutral-donor solid-phase extractants. For these systems, the active compounds are similar to those used in liquid-liquid extractions except that they are immobilized on a solid support. The donor atoms of these extractant compounds fill the inner-sphere coordination sites on the actinide ion. Moderate selectivity for Am(III) over maingroup 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.

This report summarizes efforts to reduce the total decay-heat in cemented wastes by removing americium (and plutonium) from the pre-cementation slurry, i.e. evaporator bottom solutions. Neither type of material is selective for trivalent over tetravalent actinides. Therefore, Pu(IV) is expected to be sorbed preferentially to Am(III). In the case of the target waste stream described herein, this lack of selectivity is not a disadvantage since the primary goal is to reduce total alpha activity. In fact, even though it reduces the resin capacity for americium, the presence of relatively large quantities of Pu(IV) is considered to be advantageous since it acts as a "diluent" for the high-activity Am(III) for precipitation, calcination and subsequent storage.

TARGET WASTE STREAM

The Plutonium Facility at Los Alamos National Laboratory supports a number of operations related to plutonium processing. The intended disposition site for the wastes from these operations is the recently opened Waste Isolation Pilot Plant (WIPP). Accordingly, all wastes must be in compliance with the WIPP-Waste Acceptance Criteria (WAC)¹ as well as the TRUPACT-II shipping criteria.²

For hydrogenous wastes such as the cemented drums from the nitric acid processing of plutonium-bearing residues, the decay-heat wattage limits are generally the most restrictive requirement. These limits are established at levels which provide complete assurance that the amount of hydrogen gas (generated by radiolysis of hydrogenous material) never reaches the explosive level of >4.5% inside the TRUPACT II container during a 60 day time-frame. Decay-heat limits, which are driven by alpha-decay activity, are a particularly troublesome issue for high americium wastes since Am-241 has approximately 60 times the specific (alpha) activity of Pu-239. Decay-heat can limit americium loading to as little as <500 mg/drum and Pu-239 to <7 g/drum for certain waste types and packaging configurations. Currently, the cemented waste from nitric acid plutonium processing are characterized as category I.1A1 with a decay-heat limit of 0.20 watts/drum. This limit effectively restricts the amount of americium-241 to less than 1.5 g per cemented drum.

In general, anywhere from 50 to 150 drums/year of cemented wastes are generated by TA-55 operations. More than 90% of these drums exceed decay-heat wattage limits for waste type I.1, some by more than 400%. The reason for this drum “overloading” is two-fold. First, nitric acid processing concentrates americium in the evaporator wastes such that the Am:Pu ratio is far higher than is found elsewhere in the DOE complex. Second, the cementation process, with corresponding cure-time, is a rate-limiting step in nitric acid processing. Consequently, drums are mixed under “volume-limited” conditions where as much EV as is *physically* possible is incorporated into each cemented drum so as not to further limit processing throughput. To move to a compliant “wattage-limited” regime would require a 2-4X increase in the number of cemented drums produced. Thus, for newly-generated cemented wastes we have two options for producing a WIPP/TRUPACT certifiable wastefrom—either reduce the amount of Am in the evaporator bottoms or increase the decay-heat wattage limits for the cemented waste.

This report summarizes efforts to reduce the total decay-heat in cemented wastes by removing americium (and plutonium) from the pre-cementation slurry, i.e. evaporator bottom solutions. Since each cemented drum uses ~50 L of evaporator bottoms, residual americium concentrations would need to be below 0.03 g/L. Thus, a process which reliably removes 75% of the activity from evaporator bottom solutions would allow for unimpeded cementation of WIPP-WAC certifiable waste drums. The americium and plutonium removed during the process could be co-precipitated and stored as “dirty” oxide prior to reprocessing or disposition.

During the time-frame of this experimental work, WIPP officials approved reclassification of Portland cement-based waste to category I.3 with decay-heat limits four times higher than allowed for category I.1. The increased decay-heat limits would be sufficiently high to allow cementation of evaporator bottoms to proceed without change. While the reclassification has not yet been approved by the Nuclear Regulatory Commission (NRC),³ the process outlined in this report is most likely to be kept on hold as a backup procedure for cemented wastes or as an adjunct to the vitrification process for evaporator bottom solutions.

EVAPORATOR BOTTOMS COMPOSITION

The flowchart in Figure 1 below outlines some of the key steps in the nitric acid processing of Pu residues. Americium enters the evaporators along with other non-plutonium metals and anions. Plutonium enters the evaporators from small losses in the anion-exchange and precipitation processes. The feed solutions entering nitric acid processing, and thus the evaporators, are such that plutonium and americium contents can vary widely.

Typically, volume reductions of 5:1 to 10:1 are achieved in the evaporator for very impure Pu residues, but may be as high as 25:1 for reprocessing of pure oxides. Volume-reduction ratios are limited by viscosity of the concentrated solution (which must be transferred through lines) and the precipitation of nitrate salts. The evaporator removes water and nitric acid, producing a distillate which is 2-4 M nitric acid. The distillate contains approximately 80% of the original total nitrate. Plutonium and RCRA assays are conducted on the distillate and the residual evaporator (EV) solutions. EV solutions are then mixed with the minimum amount of cement required to yield adequate cure and Toxicity Characteristic Leaching Procedure (TCLP) properties.

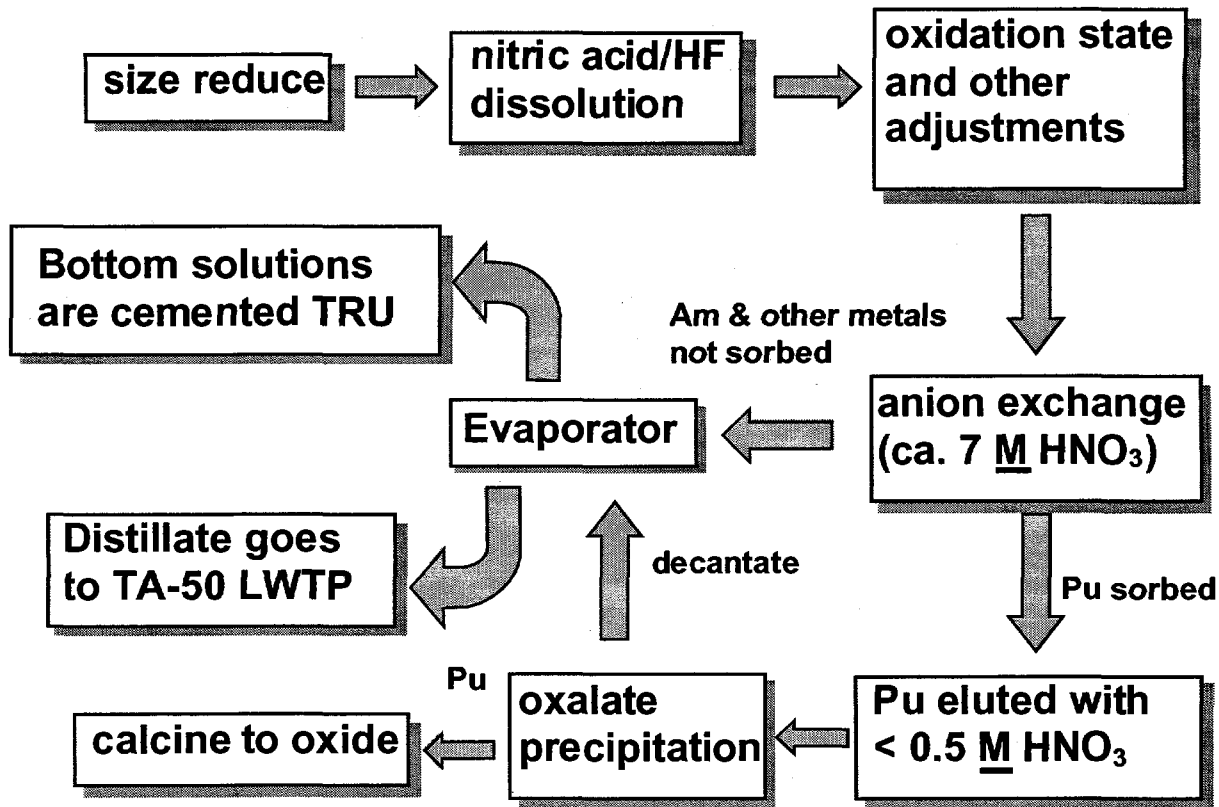


Figure 1. Overview of nitric-acid processing of plutonium-bearing materials.

Keeping in mind that there is *substantial* variability in EV composition, a hypothetical “average” cemented drum of EV contains roughly 20-30 g Pu (primarily as Pu-239) and 2-4 g Am in about 50 L of EV with a particulate mass of about 31 kg, 25 kg of which is nitrate. About 60% of the non-nitrate solids are Mg and Ca, with Fe comprising 10-20% of the material.

Extensive characterizations of EV compositions have been conducted and non-radioactive surrogates developed.⁴ In general, acid concentrations range anywhere from 1-5 M and nitrate concentrations range from 400-600 g/L. For some sorption experiments herein, we use a “lean-residue” (LR) surrogate with the following composition (Table 1). In several experiments, the surrogate solution was diluted with water or partially neutralized with sodium hydroxide solutions to allow evaluation at different acid concentrations (constant salt concentrations). We also made up single-salt surrogates containing similar acid and total nitrate concentrations using potassium and calcium nitrates.

TABLE 1. Composition of "Lean-Residue" (LR) based surrogates, calculated from composition (ref. 4). Acid concentrations are given in molarity. Primary values are for the original surrogate; values in parentheses are for diluted and/or neutralized solutions.

Cation	grams/liter	Anion	grams/liter
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 ₂ O 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 ⁺ (M)	1.4 (1.0,0.2)		

EXPERIMENTAL

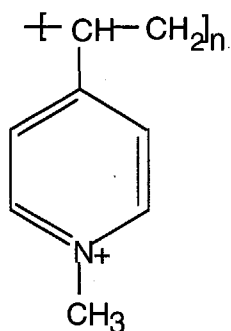
Materials

The anion-exchange resins evaluated are all polyvinylpyridine-based materials. Reillex HPQ® is a manufactured macroporous resin of partially-methylated poly(4-vinylpyridine) crosslinked with divinylbenzene. The original HPQ, which is currently used in the plutonium recovery process at LANL, has approximately 70% of its pyridinium sites methylated. Recently, a new HPQ resin, designated herein as HPQ-100, with nearly quantitative quaternization of the nitrogen centers was introduced as a commercial replacement for the original HPQ. These resins were converted from the as-received chloride form to the nitrate form and air-dried prior to use.

A range of experimental anion-exchange resins was examined. As part on an on-going project to improve resins for plutonium processing,^{5,6} we have developed series of polyvinylpyridine-based anion-exchange resins where we vary the alkyl group (mono- and bifunctional), the percentage of sites derivatized, and the extent of crosslinking. New experimental resins were evaluated as they came available and dropped if they were not "top-performers" or if they were not considered suitable for column implementation.

One commercial and two experimental "neutral-donor" extraction chromatography resins were included in some contact experiments. TRU-Spec®, a commercially-available resin, is a material that has often been used to recover and concentrate actinides from lean streams. It consists of a EIChroM 100-150 micron support loaded with octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide as the primary actinide extractant. The two extraction chromatography resins prepared at LANL and tested in this study used the same support loaded with di-(4-t-butylphenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide [D(t-BuPh)D(iBu)CMPO] and dihexyl-N,N-diethylcarbamoylmethylphosphonate [DHDECMP] respectively. Figure 2 outlines the descriptive terminology for the anion-exchange and neutral-donor extraction materials evaluated herein.

Figure 2. Polyvinylpyridine Anion-Exchange and Extraction Chromatography Materials

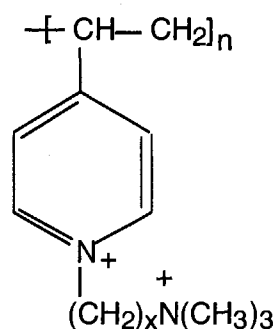


Methylated resins crosslinked with divinylbenzene
(experimental and commercial)

HP18-Me = ca. 18% crosslinked, ~70% methylated,
experimental resin

HPQ™ = ca. 25% crosslinked, ~70% methylated

HPQ™ -100 = ca. 25% crosslinked, >90% methylated

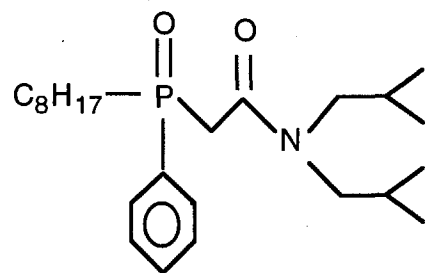
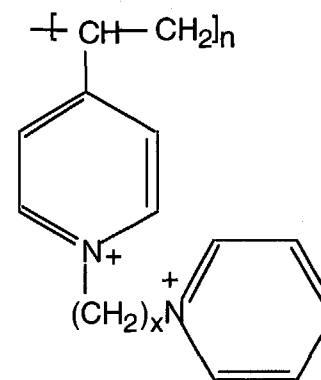


Bifunctional experimental resins crosslinked with divinylbenzene
x = 3, 4, 5, 6

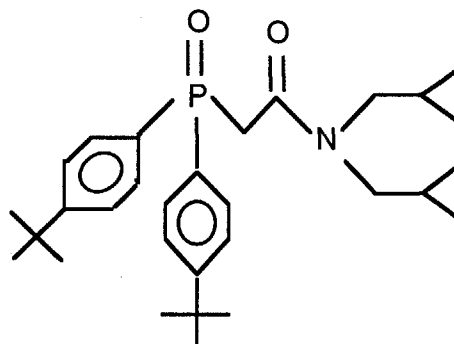
HP18-(CH₂)_x-N(CH₃)₃ = ca. 18% crosslinked, ~70% alkylated

HP21-(CH₂)_x-N(CH₃)₃ = ca. 21% crosslinked, ~70% alkylated

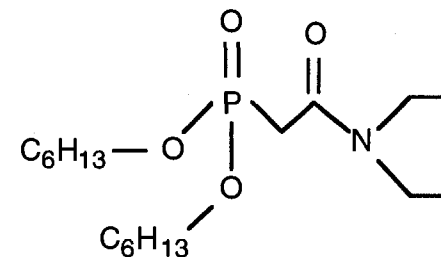
HP21-(CH₂)₄-N(C₅H₅) = ca. 21% crosslinked, ~70% alkylated



octyl(phenyl)-N,N-diisobutylcarbamoyl-
methylphosphine oxide [**TRU-Spec™**]



di-(4-t-butylphenyl)-
N,N-diisobutylcarbamoyl-
methylphosphine oxide
[**38% DtBuCMPO**]



dihexyl-N,N-diethylcarbamoylmethyl-
phosphonate [**60% DHDECMP**]

Analytical Procedures

Percent uptake and distribution coefficients were determined from ICP analyses of pre- and post-contact solutions for Nd(III), Al(III) and Fe(III) for “cold” EV surrogate solutions. Americium distribution coefficients were measured and calculated by procedures developed at Los Alamos National Laboratory.⁷ Sorption of Am-241 from spiked simple and complex surrogate solutions was quantified by counting of the 60 KeV gamma emission. For authentic evaporator solutions, only total alpha activity removal (from both Am and Pu isotopes) is reported based on scintillation counting procedures. In each case, non-sorbing inert matrices were used to confirm that no metals or activity were lost to the containers. Distribution coefficients, K_d , were calculated as follows:

$$K_d = M_r/M_s * \text{mL/g}$$

where M_r = amount of metal (activity) sorbed on the resin

M_s = amount of metal (activity) remaining in solution (activity)

mL = volume of contact solution (mL)

g = mass of resin (g)

“Cold” Single Batch Contact Experiments

Diluted and partially neutralized LR evaporator bottoms surrogate solutions (1.0 and 0.2 M H^+) were spiked with ca. 100 ppm Nd(III). Although Eu(III) is a commonly used homolog to Am(III), Nd(III) has a more similar ionic radius and exhibits analogous complexation behavior.⁸ Samples of 25 mg, 50 mg, 100, and/or 250 mg of air-dried resin were contacted with 2.5 mL of solution in polyethylene tubes by rotating for approximately 20-24 hours. Assuming an average capacity of 3 meq/g (dry weight) for the anion-exchange resins, 100% loading of 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. Since the capacity for the TRU-spec resin is ~3-4 times lower, sorption experiments were conducted on larger resin samples to maintain a similar loading level. In all cases, however, appreciable loading of other trivalent cations (Fe at 4300 ppm and Al at 2600 ppm) would quickly saturate the available sites.

The results for contacts with three anion-exchange resins, HPQ and two experimental resins (18% crosslinked), and one neutral-donor resin are presented in Table 2. Both experimental resins marginally outperform the commercial HPQ for Nd uptake, with the bifunctionalized material edging out the methylated resin. One notable feature is that Nd sorption is similar at both acid concentrations for the two anion-exchange resins. This relative insensitivity to acid concentration suggests that the extremely high nitrate concentration could be a controlling feature and that these resins could exhibit a favorable consistency of behavior for a variety of EV bottom compositions.

TABLE 2. Percent uptake of trivalent metals from LR surrogate spiked with Nd(III) at two acid concentrations. Distribution coefficients for Nd are given in parentheses after the percent uptake value.

	HPQ	HP18-Me	HP18-(CH ₂) ₅ -N(CH ₃) ₃	TRU-Spec
1.0 M H⁺	Al, Fe, Nd (K _d)	Al, Fe, Nd (K _d)	Al, Fe, Nd (K _d)	Al, Fe, Nd (K _d)
25 mg	-	1.8, 0.3, 26.7 (36)	8.3, 0.6, 30.9 (45)	-
50 mg	3.1, 2.1, 34.3 (26)	3.5, 1.5, 42.4 (37)	6.4, 1.1, 46.0 (43)	-
100 mg	5.1, 2.4, 51.5 (27)	4.6, 2.0, 61.4 (40)	4.1, 1.3, 64.0 (44)	1.0, 2.6, 18.9 (6)
250 mg	-	-	-	0.7, 8.4, 42.7 (7)
0.2 M H⁺	Al, Fe, Nd (K _d)	Al, Fe, Nd (K _d)	Al, Fe, Nd (K _d)	Al, Fe, Nd (K _d)
25 mg	-	-	8.2, 2.9, 35.4 (55)	-
50 mg	1.8, 1.5, 46.3 (43)	-	7.9, 1.5, 52.3 (55)	-
100 mg	3.4, 3.3, 64.6 (46)	-	9.3, 2.3, 68.7 (55)	0.3, 4.0, 73.5 (67)
250 mg	-	-	-	0.7, 12.1, 88.7 (76)

As expected, neodymium sorption by the TRU-spec resin is very sensitive to acid concentration. This neutral-donor material outperforms the anion-exchange resins in the lower, 0.2 M, acid surrogates, but significantly underperforms at the higher acid concentration which is closer to authentic waste solutions. In general, sorption of Fe(III) and Al(III) by the various anion-exchange resins was uniformly low. The TRU-spec resin, however, exhibits a relatively high affinity for iron which suggests that Fe(III) complexation to available sites may be further suppressing neodymium sorption.

Decreasing the percentage of divinylbenzene crosslinking within the anion-exchange resins leads to enhancement of sorption behavior. The experimental resin HP18-Me differs from the commercial HPQ primarily in the percent crosslinking (18% vs. 25%)—both have a similar percentage of pyridinium sites methylated (ca. 70%). However, the 18%-crosslinked substrate may lack the durability desired for long-term large column applications, so we moved to evaluation of higher (21% and 25%) crosslinked experimental materials.

“Hot” Single Batch Contact Experiments

Americium-Spiked Surrogates

Americium uptake by a series of bifunctional anion-exchange resins was determined for a variety of simple and complex surrogate solutions. We introduced “simple” EV bottom surrogate solutions in order to try to determine the controlling factors (i.e. acid and nitrate concentration, ionic strength or water “concentration”) for the formation and sorption of nitrate complexes to the anion-exchange sites. We also hoped to develop a simple solution which could be used in column applications to wash impurities from the resin without removing sorbed americium. The “simple” surrogate consisted of either 1 M HNO₃ with 7 M NaNO₃ or 1 M HNO₃ with 3.5 M Ca(NO₃)₂. Thus, both solutions were ca. 1 molar in acid and 8 molar in total nitrate, but with different ionic strengths and water availability. Complex surrogates consisted of the same diluted (1 M acid) and undiluted lean-residue surrogate as were used in the Nd uptake experiments.

Resin samples of 250 mg were contacted with 6 mL of solution. We report calculated K_d values for dynamic contact periods of 30 min, 2 hr, and 6 hr measured by sequential removal of 1.5 mL aliquots of contact solution. We also report percent uptake data for the initial contact (30 min) to facilitate comparison with the neodymium data above. Two basic types of radioactive solutions were analyzed. One contained tracer quantities (10^{-13} M) of americium. The other was a standard solution used in determination of plutonium distribution coefficients which contains ca. 3 g/L plutonium(IV) with tracer quantities of americium, and was used to determine the effect of Pu(IV) competition upon Am(III) sorption.

Table 3 summarizes non-competitive americium sorption data from three solutions onto a series of experimental anion-exchange resins. The series consists of bifunctional derivatives of HP21 polyvinylpyridine (21% divinylbenzene) with the "second" trimethylammonium anion-exchange site being separated from the backbone pyridinium site by alkylene spacer groups of 3-6 units. An additional bifunctional resin contains a second pyridinium site separated from the backbone site by a butylene spacer (see Figure 2 for structural diagrams).

TABLE 3. Distribution coefficients (K_d) and percent uptake (parentheses) for Am(III) onto HP21 resins from EV surrogate solutions at 30 minutes, 2 hours and 6 hours. $[Am]_{in} \sim 10^{-13}M$, no Pu(IV).

Resin	1 M HNO ₃ /3.5 M Ca(NO ₃) ₂ (8 M NO ₃)	diluted surrogate 1 M HNO ₃ /6.5 M NO ₃	undiluted surrogate 1.4 M HNO ₃ /10 M NO ₃
-(CH ₂) ₃ -N(CH ₃) ₃	9.0 (27.3), 10.0, 10.5	12.8 (34.8), 19.4, 18.0	37.7 (61.1), 61.8, 69.1
-(CH ₂) ₄ -N(CH ₃) ₃	10.9 (31.2), 12.9, 14.1	15.1 (38.5), 20.3, 18.5	34.2 (58.8), 60.3, 81.7
-(CH ₂) ₅ -N(CH ₃) ₃	13.5 (36.0), 17.2, 16.9	22.0 (47.8), 26.5, 27.5	49.2 (67.2), 81.6, 115
-(CH ₂) ₆ -N(CH ₃) ₃	9.5 (28.4), 10.1, 9.5	12.6 (34.5), 18.1, 15.2	32.5 (57.5), 50.4, 64.2
-(CH ₂) ₄ -N(C ₄ H ₉)	-	15.7 (39.6), 20.6, 24.5	33.8 (58.5), 61.5, 104

Several features stand out in the data above. First, americium sorption from the simple nitric acid/calcium nitrate surrogate solution is weaker than from the two complex surrogate solutions, despite having comparable acid and intermediate total nitrate concentrations. Additionally, sorption equilibrium appears to be reached more rapidly in the more dilute solutions as evinced by the relatively small changes between 2 and 6 hours for the simple and diluted surrogates. Americium uptake from undiluted surrogate is both greater and slower. This sorption 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.⁹

For the series of trimethylammonium bifunctional resins, americium distribution generally increases with spacer length, achieving a maximum value with the 5-carbon pentylene spacer, then decreasing with the longer 6-carbon spacer. This trend is directly analogous to the sorption behavior of Pu(IV) onto similar (lower crosslinked)⁵ and identical resins.¹⁰ Distribution onto the pyridinium-terminated bifunctional resin is correspondingly high.

For competitive experiments, we examined the effect of relatively high plutonium content upon americium uptake from pure nitric acid solutions (1 and 7 M) and salt solutions with relatively low acid concentration (1 M), but high total nitrate concentrations (8 M). Sorption of americium onto

the anion-exchange resins from pure 1 M HNO₃ is extremely poor (>8%), comparable to that observed for “non-sorbing” metals such as Fe and Al in the cold surrogate testing, and this data is not included in the table. Other americium sorption data is presented in Table 4.

TABLE 4. Distribution coefficients (K_d) and percent uptake (parentheses) for Am(III) onto HP21 resins from EV surrogate solutions at 30 minutes, 2 hours and 6 hours. [Pu(IV)] = 3 mg/mL, [Am] = tracer

Resin	7 M HNO ₃	1 M HNO ₃ / 7.0 M NaNO ₃ (8 M NO ₃)	1 M HNO ₃ / 3.5 M Ca(NO ₃) ₂ (8 M NO ₃)
-(CH ₂) ₃ -N(CH ₃) ₃	6.1 (20.4), 4.9, 4.8	7.9 (24.8), 8.6, 7.4	7.5 (23.9), 7.5, 6.5
-(CH ₂) ₄ -N(CH ₃) ₃	8.1 (25.3), 6.9, 5.5	9.0 (27.3), 10.2, 7.5	8.1 (25.3), 9.3, 9.0
-(CH ₂) ₅ -N(CH ₃) ₃	11.1 (31.6), 8.1, 6.9	11.5 (32.3), 13.2, 12	-
-(CH ₂) ₆ -N(CH ₃) ₃	4.7 (16.3), 2.8, 3.4	6.5 (21.2), 5.3, 6.0	5.6 (19.0), 7.4, 5.7

When results for the 1 M HNO₃/ 3.5 M Ca(NO₃)₂ solution are compared with those in Table 3, we see that americium sorption is decreased by about 20-30% by 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).

The most notable feature of this series of batch contact experiments is that americium uptake by the series of bifunctional anion-exchange resins displays a singular lack of sensitivity to acid concentration. Similar behavior was observed for Nd(III) uptake from 0.2 M and 1.0 M acid-adjusted LR surrogate as described earlier, but here we observe this response over a range of acid concentrations more directly relevant to the target evaporator bottoms. The absence of acid sensitivity is surprising in light of previous experiments at ORNL¹¹ and LANL¹² in which going to acid concentrations greater than 0.05 M had a distinctly detrimental effect upon Am breakthrough in column experiments. The solution’s total ionic strength also appears to have little effect, despite the difference in total ionic strength of the two salt solutions being nearly 50% (i.e. 8.0 for the HNO₃/KNO₃ vs. 11.5 for HNO₃/ Ca(NO₃)₂).

Trivalent Speciation in High Nitrate Acidic Solutions

In an effort to determine the relative effects of acid, total nitrate, and ionic strength upon trivalent ion speciation, we compared the visible spectroscopic signature of Nd(III) in three series of solutions: (1) 1-15 M nitric acid (in 0.5 M steps); (2) 1 M HNO₃/ 5.0-9.6 M total nitrate (as calcium nitrate); and (3) 5 M HNO₃/ 7.2-9.6 M total nitrate (as calcium nitrate). All three spectral series display the same general characteristics in that the intensity of the peak at 578 nm increases while the intensities of the peaks at 796 and 740 nm decrease with increasing nitrate (as either HNO₃ or Ca(NO₃)₂). Figure 3 illustrates this trend. Although anionic nitrate complexes of Nd have not been observed in solution and the visible spectral data in Figure 3 is most likely derived from mono- and di-nitrate cations, we assume that solution conditions which facilitate the formation of higher-order complexes will also facilitate extraction of the metal as an anionic complex.

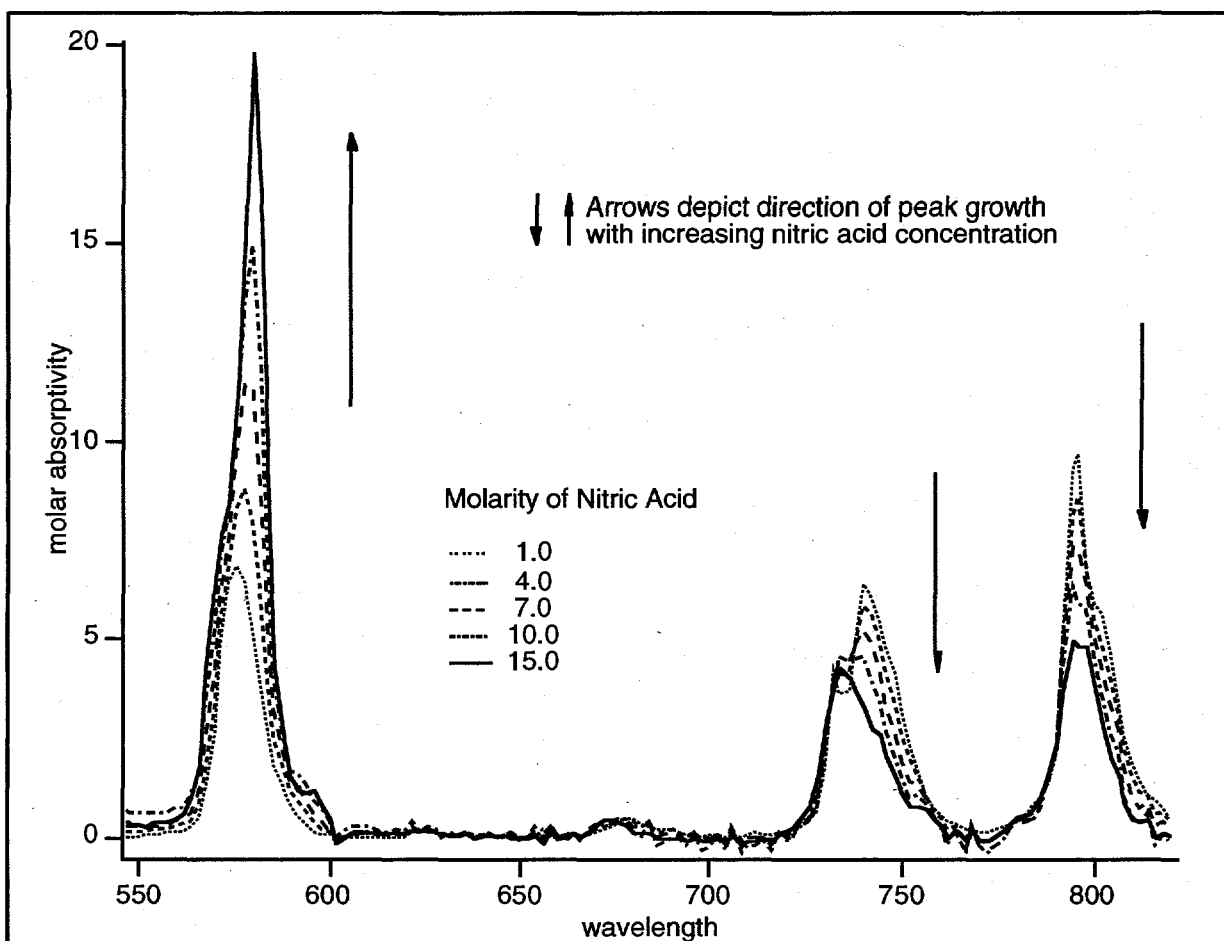


Figure 3. Nd(III) in nitric acid. [Nd] ~15 mM

In general, the effect of higher nitrate concentration upon solution speciation is somewhat weaker for the calcium salts than for nitric acid alone. This effect is shown in Figure 4 where the spectral signatures of Nd in 1 M HNO₃/ 8.0 M total nitrate and 5 M HNO₃/ 8.0 M total nitrate are virtually identical (only one is shown for clarity) while the spectral signature for Nd in 8 M nitric acid indicates a higher complex. Thus, it appears that in the high salt solutions examined here, both total nitrate and acid concentration contribute to the formation of Nd nitrate complexes. Unlike the observed behavior at low acid concentrations,^{11,12} higher acid concentration appears to actually facilitate formation of higher nitrate complexes, and thus would not necessarily have a detrimental effect upon the sorption of trivalent f-elements by anion-exchange media.

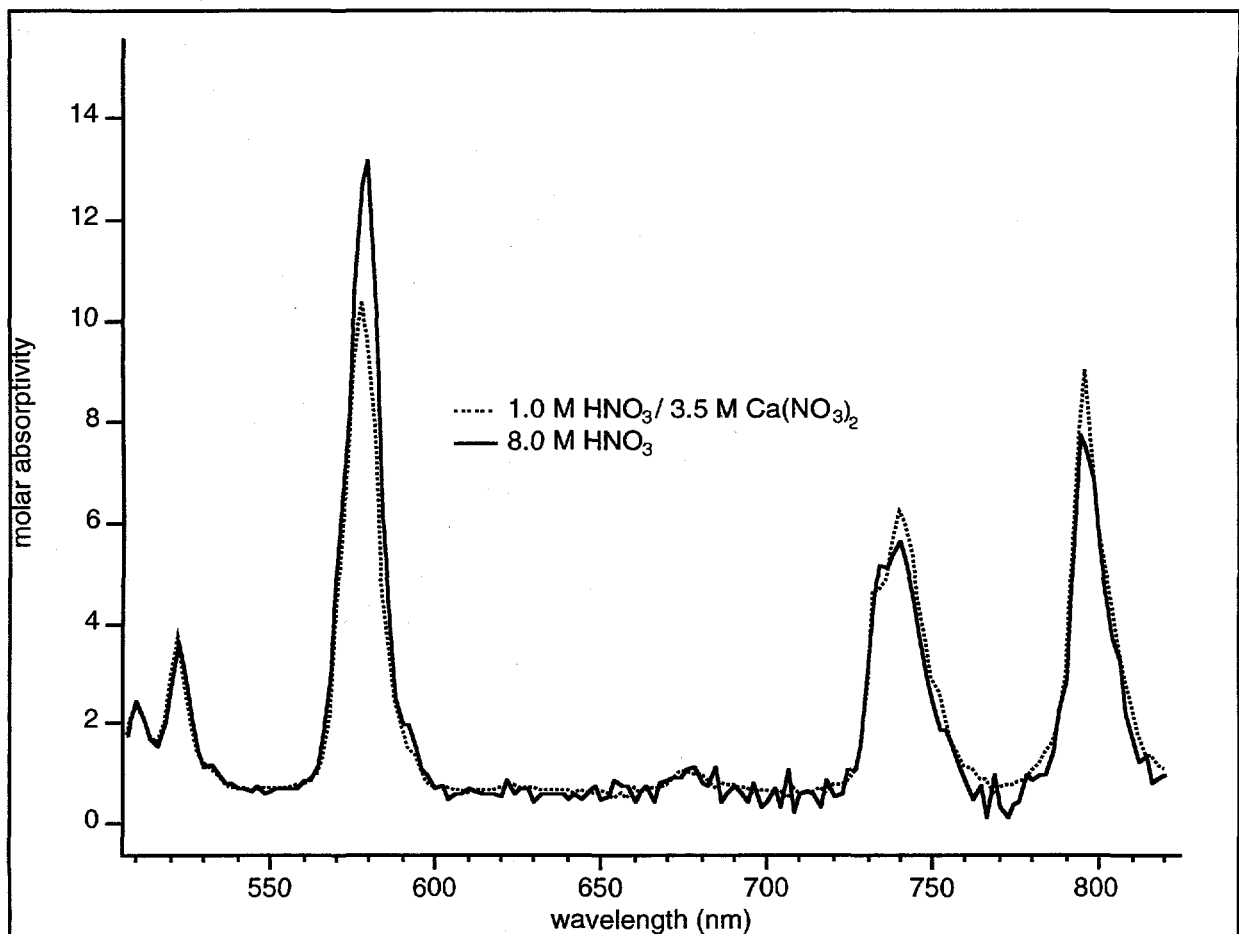


Figure 4. Nd(III) in nitric acid and a salt solution. [Nd] ~ 15 mM, [NO₃] = 8.0 M

Total Alpha-Activity Removal from Authentic Evaporator Bottoms Solutions

For evaluation of resin performance using authentic evaporator bottoms solutions, we chose to examine “total alpha-activity” removal instead of just americium sorption for several purely pragmatic reasons. First, decay-heat radiolysis is an alpha-driven process which does not distinguish between alpha decay from Pu, Am or any other radionuclides, so essentially the “performance” criterion is to reduce the total alpha activity of the waste solutions. Second, we had immediate access to scintillation counting for total alpha activity analysis while separate analysis for americium would have required more expensive and time-consuming physical separations procedures and/or gamma counting techniques for a relatively modest increase in useful information. Although plutonium is far more prevalent in these solutions on a gram basis, the higher specific activity of americium means that the bulk of the alpha activity in these evaporator solutions comes from Am-241 decay. In all of these batch contact experiments, we fully expect plutonium, as Pu(IV), to be removed preferentially to Am(III).

Three samples of authentic waste solutions slated for cementation were diverted for batch contact experiments. They are designated as EV1, EV2 and EV2'. All three were opaque green solutions with small amounts of particulates that were removed using 5 μm polypropylene filters. EV1 was a relatively high acid solution, EV2 and 2' were lower acid solutions derived from similar

processes. These solutions were assayed for Pu and Am using radiochemical assay procedures (alpha). In general, these assays are reasonably accurate for Am, but less accurate for Pu, given the difficulty of accurately measuring Pu in the presence of high-activity Am. Approximate acid concentrations were determined by measuring the pH of 100- and 1000-fold diluted solutions.

Batch contact experiments were conducted using 50 and/or 100 mg samples of the anion-exchange and neutral-donor resins contacted with 2.5 mL of solution in 6 mL polyethylene disposable columns. The solutions were mixed using a rotator during the contact time (usually 5-6 hours for the first contact, overnight for the second contact). Post-contact solutions were eluted through the frit at the bottom of the disposable columns and aliquots were assayed for alpha activity. Two "blank" columns containing polystyrene and polyacrylate (the substrate for the experimental neutral-donor materials) were also run under the same conditions to determine if any alpha activity was lost to the matrix or column. These two samples display quantitative alpha activity recovery.

The results for a single batch contact using EV1 are presented in Table 5. Anion-exchange resins are listed first, followed by the neutral-donor systems.

TABLE 5. Percent alpha-activity removal from EV1, 5 hr contact with 2.5 mL solution. EV1 (~4.2 M H+) initial activity : 3.94×10^8 dpm/mL, ~0.052 g/L Am (75% of α activity), ~0.72 g/L Pu (25% of α activity)

	50 mg	100 mg
HPQ	37	42
HPQ-100	31	48
HP18-Me	37	46
HP18-(CH ₂) ₅ -N(CH ₃) ₃	45	56
HP25-(CH ₂) ₅ -N(CH ₃) ₃	39	46
TRU-Spec	28	35

All the materials exhibit a reasonable level of alpha-activity removal, even the TRU-Spec resin which would not be expected to perform well at such a high acid concentration. However, the percentage of activity removed by the TRU-Spec resin is close enough to 25%, the calculated contribution to alpha activity by Pu(IV), to suggest that it has removed mostly Pu(IV) and not much Am(III). Other removal percentages are high enough to assure that a moderate amount of Am is being removed from solution.

Table 6 summarizes single and double batch contact experiments with EV2. The second contact (overnight) with fresh resin was made with 1.8 mL of post-contact solution from the first contact. The smaller volume (1.8 mL vs. 2.5 mL) was due to nonquantitative recovery from the damp resins and the necessity of removing a small aliquot for scintillation counting. We consider the total alpha-activity removal from the second contact to be indicative of Am(III) sorption since all materials have sufficient capacity and affinity for near-quantitative Pu(IV) uptake in the first contact and the estimated activity from other radionuclides is negligible.

TABLE 6. Percent alpha-activity removal from EV2. EV2 (~1.0 M H⁺) initial activity : 1.09 x 10⁹ dpm/mL, ~0.085 g/L Am (65% of α activity), ~1.93 g/L Pu (35% of α activity). First contact, 5 hr contact with 2.5 mL solution. Second contact, overnight (18-20 hr) with 1.8 mL of post-contact solution.

	First Contact		Second Contact		Net α	
	50 mg	100 mg	50 mg	100 mg	50 mg	100 mg
HPQ	22	46	-	-	-	-
HPQ-100	32	54	55	77	69	90
HP18-Me	30 ^b	59 ^b	-	-	-	-
HP18-(CH ₂) ₅ -N(CH ₃) ₃	47	70	-	-	-	-
HP25-(CH ₂) ₅ -N(CH ₃) ₃	29	61	50	76	65	91
TRU-Spec	0	16	-	-	-	-
38% DtBuCMPO	-	17	-	5	-	21
60% DHDECMP	-	54	-	71	-	87

^a Calculated from final vs. initial alpha activity

^b Average of alpha-activity removal by two resin samples prepared by different techniques

As with EV1, each of the anion-exchange resins removes a substantial fraction of alpha activity with a single contact. The greater percentages of alpha removal from the second contact are, in part, artifacts of the lower solution:solids ratios. In general, however, they correlate well with the Am uptake measured using the spiked LR surrogate solution (Table 3). Although the amount of americium removed in the second contact would be small relative to the amount of plutonium removed in the first contact, the higher specific activity of americium results in a greater net change in residual solution activity.

Two of the three neutral-donor resins performed poorly, but the DHDECMP experimental material performed in line with the anion-exchange materials. This attainment is encouraging given the expected 100-fold excess of Fe(III)—a key competitor for the active sites.

Solution EV2' has a similar acid concentration as EV2, but substantially more plutonium and approximately 40% higher total alpha activity. Batch contacts were run on a few selected materials with this solution. The plutonium content was sufficiently high to merit running the contact experiments on only the larger, 100 mg, samples.

Overall, performance is similar to that observed with EV2. As with EV1, the TRU-Spec resin removes a total activity from the first contact comparable to that expected for Pu(IV) removal alone. Alpha removal from the second contact is quite poor, indicative of poor Am(III) sorption from this solution. The net 90+% alpha removal using the anion-exchange materials is very promising in light of the relatively modest goals for decay-heat reduction for the cemented drums (ca. 75%).

TABLE 7. Percent alpha-activity removal from EV2'. EV2' (~1.0 M H⁺) initial activity : 1.44 x 10⁹ dpm/mL, ~0.129 g/L Am (65% of α activity), ~2.95 g/L Pu (35% of α activity). First contact, 6 hr contact with 2.5 mL solution. Second contact, overnight (18-20 hr) with 1.8 mL of post-contact solution.

	First Contact 100 mg	Second Contact 100 mg	Net α
HPQ-100	61	73	90
HP18-Me	64	72	90
HP25-(CH ₂) ₅ -N(CH ₃) ₃	67	82	94
TRU-spec	34	12	42
38% DtBuCMPO	21	-	-
60% DHDECMP	58	-	-

^a Calculated from final vs. initial alpha activity

Column Testing of Anion-Exchange Resins

Small Column Evaluation of HPQ-100 and HP25-(CH₂)₅-N(CH₃)₃

For these experiments we used two 30 x 2.5 cm columns containing approximately 50 g (dry weight) of the resins. We ran the EV2' solutions with the highest Am content (0.13 g/L). A “successful” run would need to retain greater than 75% of the solution alpha activity in order to meet WIPP-WAC for a cemented drum using 50 L of bottoms.

EV2' solutions were filtered through an in-line 10 μm polypropylene cartridge. Columns were loaded in 1 M HNO₃ and packed to reduce voids. Evaporator bottom “feed” solutions were loaded in an up-flow direction under positive pressure from a peristaltic pump. We attempted to maintain a “residence time” of about 20 minutes, but actual flow-rates varied over the course of each run. Fractions of approximately 100 mL were collected. Each fraction was counted in “real-time” through the glovebox window using a hand-held gamma counter for a qualitative estimate of gamma (americium) activity. Throughput of the feed solutions was stopped when this counting procedure indicated that the gamma activity of the effluent was comparable to the activity of the feed, indicating americium breakthrough. Wash solutions (1.0 M HNO₃ with either 6.5 M NaNO₃ or 3.3 M Ca(NO₃)₂) were run through the column in the same flow direction to displace residual feed solutions. Elution was conducted using 0.35 M HNO₃ in a reverse-flow (down) direction. Aliquots of each 100 mL fraction were assayed for total alpha activity using scintillation counting procedures.

HPQ-100: The total column volume was approximately 150 mL with an estimated free solution volume of 100 mL (based on the column front of the darkly colored EV2'). Solution residence time was 10-15 minutes with an average flow rate of 10 mL/min. The “wash” solution was 1.0 M HNO₃/ 6.5 M NaNO₃. The gamma (qualitative) and alpha activity profile is presented in Figure 5.

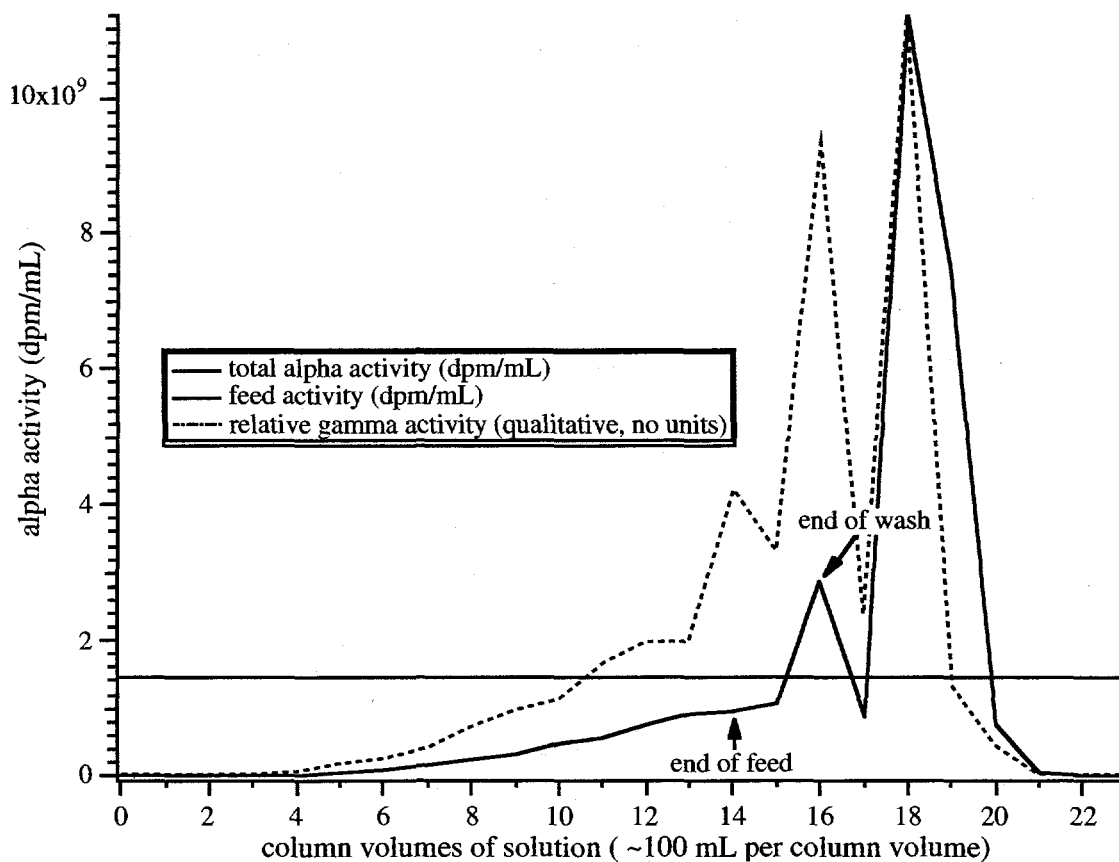


Figure 5. Alpha activity elution profile for EV2' through HPQ-100.

After the first six column volumes (600 mL), distinct gamma activity was detected in the effluent. After 14 volumes (1400 mL), the gamma activity of the effluent was nearly as high as for the original solution, so we switched to wash and elution mode. By the end of feed input, 13% of the total alpha was eluted, 87% retained on the column. By the end of the “wash” solution, an additional 17% of the activity was eluted, resulting in retention of ca. 70% of the total alpha activity. The bulk of this was removed in three column volumes (300 mL) of eluent solution.

Clearly, the composition of a wash solution needs to be refined. Americium retention by the simple salt solutions is inadequate. According to total alpha analysis, we may have stopped feed input before complete americium breakthrough. However, since about 35% of the alpha activity of the feed is calculated to be from Pu-239 and plutonium is expected to be nearly quantitatively retained, total alpha activity may not be as reliable of an indicator as the crude gamma activity determination used.

This sorption/elution profile is not as good as the batch contact equilibrium sorption data would suggest in that americium elution is observed after just 5-6 column volumes of solution. The “operational capacity” of HPQ resins is approximately 80 mg Pu per L (bed volume) of resin. At 1.4 L of EV2' feed, approximately 4.2 g of Pu (and 0.2 g) of Am are loaded onto the resin. Under these conditions, approximately 35% of the resin sites are occupied by Pu, leaving 65% of the sites for Am. Thus, dynamic americium displacement may account for the relatively early breakthrough.

Also, the rate of ion diffusion is dramatically slower in high salt media than in the corresponding pure acid media,⁹ and this diffusion rate could be a limiting factor in column performance.

HP25-(CH₂)₅-N(CH₃)₃: This column (120 mL total volume, ~80 mL free column volume) was run at a slower average flow rate to attain an average residence time of 20-30 minutes. Other experimental conditions were the same as for the HPQ-100 column, except that the wash solution was 1.0 M HNO₃/3.3 M Ca(NO₃)₂. Figure 6 provides the elution profile.

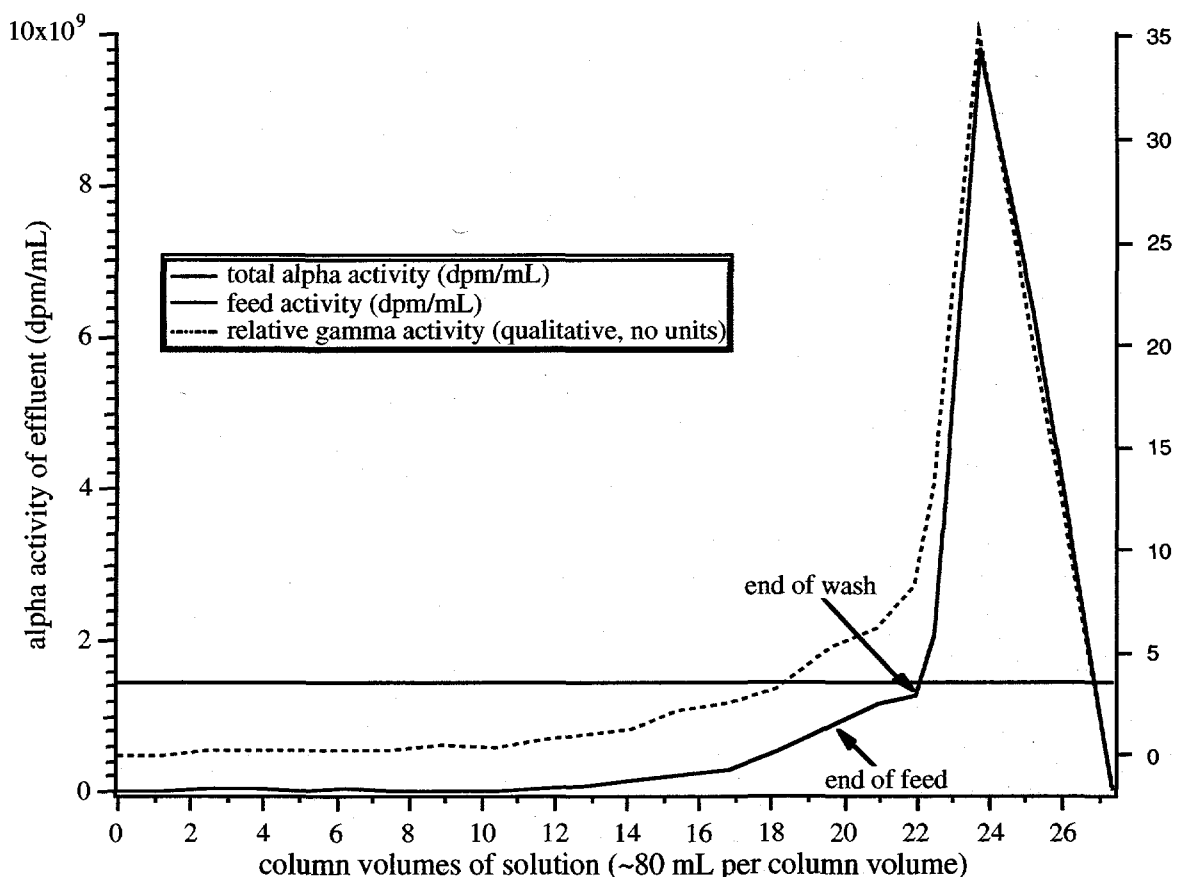


Figure 6. Alpha activity elution profile for EV2' through HP25-(CH₂)₅-N(CH₃)₃.

Americium “breakthrough” on the bifunctional resin begins after 11-12 column volumes, a substantial delay from that observed for the HPQ-100 resin. Time constraints prevented us from running more than 1.6 L (ca. 20 column volumes) of EV2' feed, but trends in the detected gamma activity of the effluent indicated that complete breakthrough was probably imminent. There is much less of an activity “spike” with the calcium nitrate wash solution, but this behavior could also be due to not forcing the loading to complete breakthrough. At 1.6 L of EV2', the column is loaded with 4.8 g Pu (~50%) capacity and 0.2 g Am. The longer residence time (~2X longer relative to the previous run using HPQ-100) did not have a dramatic effect upon Am/Pu uptake which suggests that diffusion rates of the ions through solution to the ion-exchange site may not be a controlling factor.

This column material, the experimental bifunctional anion-exchange resin, demonstrates better Am/Pu retention than the commercial HPQ-100. By the end of feed solution input (1.6 L, ~20 column volumes), 9% of the total alpha was eluted, 91% retained on the column. By the end of the "wash" solution (+120 mL), a total of 16% of the activity was eluted, resulting in retention of ca. 84% of the total alpha activity. The bulk of the loaded activity was removed in about 100 mL (divided over two 100 mL sample fractions) of the eluent. Thus, 84% of the radionuclide activity was concentrated into 12% of the original solution volume. This concentrated solution should contain only Pu(IV), Am(III), HNO₃ and residual Ca(NO₃)₂.

The alpha-retention profiles for both resins bring the effluent activity within acceptable limits for disposal as cemented waste with a relatively small (~10%) increase in solution volume. Performance of the bifunctional resin material was better than the commercial HPQ-100, displaying a delayed and less abrupt americium breakthrough curve, although differing flow rates through the two resin beds may have had some effect on the shape of the breakthrough curve. Since we have not found a simple and effective wash solution, we could conceivably skip the wash entirely and push the residual feed solution through the column with the eluent. The real-time, in-line gamma analysis available for the process-scale experiment below could provide sufficiently accurate and responsive data to allow for proper partitioning of the effluents into a fraction for cemented waste and a fraction for Am/Pu precipitation.

Process-Scale Evaluation

We conducted a process-scale evaluation for the treatment of evaporator bottoms by anion-exchange using an existing 10 L column of older Reillex HPQ (~70% derivatized). This column, as others in the TA-55 Plutonium Facility, has been in use for several years with very little degradation of sorption kinetics or capacity. This particular column is frequently used for the reprocessing of evaporator bottoms which exceed plutonium discard limits. Prior to this run, the column was washed with 7 M HNO₃ and allowed to sit for several days in contact with 0.45 M HNO₃. Feed, wash (0.5 M HNO₃/ 7 M NaNO₃), and eluent (0.35 M HNO₃) were all pulled through the resin bed in an up-flow direction using the house vacuum. Flow rates averaged 30–40 L/ hour, providing a solution residence time of ca. 30 minutes.

Due to the prolonged shutdown of the evaporators, very little tank space was available for storage and transfer of solutions, so our "process-scale" run had to be conducted on 50 L of solution instead of the 100 L we had originally planned. The 50 L of bottoms were in two 25 L batches. The first feed solution had very low Pu and Am content (Pu = 0.229 g/L, Am = 0.029 g/L), the second batch was closer to average (Pu = 1.33 g/L, Am = 0.082 g/L). Both had titrated acid concentrations of slightly less than 1 M. A 10 L column should have a free liquid column volume of ca. 7 L, so we estimate that each batch of feed solution would correspond to 3.5 column volumes for a total of seven column volumes of EV solution for the experiment.

The solutions were filtered through 5 micron polypropylene cartridge filters. The first feed solution had very little particulate matter, but the second clogged several filters with a slimy coating on the outside of the cartridge. Agitating the filters in dilute acid removed much of the coating and dissolved the entrained salt crystals. The solutions were then sent through the in-line gamma counter to determine initial gamma activities of Am, Pu and U. Activities of the processed solutions are compared to these initial activities to provide a qualitative measure of Am and Pu removal. The

americium activity profile is presented in Figure 7. The in-line gamma counter is not currently designed to provide accurate quantitative information, but efforts are underway to improve this aspect of the system.

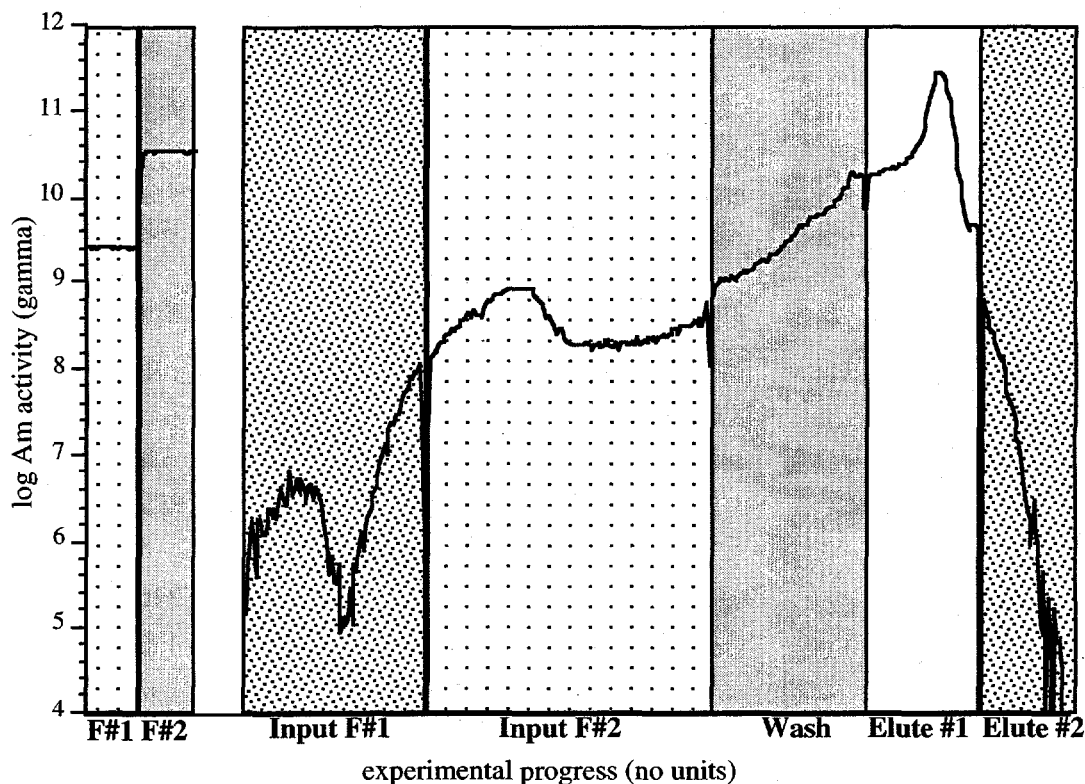


Figure 7. Americium gamma activity profile (log scale) for process-scale run.

Substantial activity from plutonium was detected in the 0.45 M HNO₃ solution being displaced from the column by the EV feed. The duration of this anomolous elution is reflected in the minor Am elution curve seen during the early stages of input of Feed #1. This plutonium was most probably residual material left from previous runs and was mobilized by allowing the resin to sit at low acid concentrations for several days prior to this experiment. The estimated 20 g of “extra” plutonium is only about 2% of the loaded capacity of a 10 L column, but it is a significant amount of Pu for this particular run and accounts for much of the discrepancy in the final plutonium mass balance.

At the end of the 50 L of EV feed through the Reillex HPQ column, the gamma activity of Am in the effluent was still well below the feed activity. Figure 7 depicts the americium level in the effluent (log scale) over the time frame of the loading, washing and elution cycles. From the relative Pu and Am activity values, we estimated that >90% of the Am and Pu was retained by the column. Actual americium and plutonium distributions into the various solution fractions as determined from final solution analyses (gamma) are reported in Table 8.

TABLE 8. Americium and plutonium concentrations and total mass as a function of process fraction.

	Feed (ave) 50 L	Effluent 45 L	Wash 15.2 L	Eluate #1 20.4 L	Eluate #2 15.5 L	Mass balance (%)
Am (g/L)	0.056	0.00752	0.0268	0.0912	0.00686	
Pu (g/L)	0.79	0.531	0.0470	1.36	0.403	
Am (g)	2.79	0.34	0.41	1.86	0.11	
Pu (g)	39.8	23.9 a	0.7	27.7	6.3	
Am (%)	-	12.2	14.6	66.7	3.9	97.4
Pu (%)	-	60.0 a	1.8	69.6	15.7	147.1 α

^a Includes Pu residual from the column

As with the small-scale column test using HPQ-100, approximately 85-90% of the total americium was retained during feed input. This level of retention is sufficient to meet heat-loading requirements in most situations. Again, the high-salt, low-acid “wash” solution does a poor job of retaining the Am on the column. However, in this particular case, the effluent (45 L, 0.34 g Am) and wash (15.2 L, 0.41 g) solutions could be combined since the total quantity of americium is well below the wattage limit. Two-thirds of the americium is concentrated into the first 20 L of eluant. The gamma-activity profile in Figure 7 suggests that the bulk of the americium is eluted in approximately 10 L total volume, but since we wanted to recover the Am along with Pu to make “dirty oxide,” we made no attempt to further concentrate the americium. Plutonium retention and recovery rates are difficult to determine because of the residual Pu from previous runs.

SUMMARY

Americium (III) exhibits an unexpectedly high affinity for anion-exchange material from the high-salt evaporator bottoms solutions—an effect which has not been duplicated using simple salt solutions. Similar behavior is observed for its lanthanide homologue, Nd(III), in complex evaporator bottoms surrogate solutions. There appears to be no single controlling factor—acid concentration, total nitrate concentration or solution ionic strength—which accounts for the approximately 2-fold increase in retention of the trivalent ions from complex solutions relative to simple solutions. Calculation of species activities (i.e. water, proton and nitrate) in such concentrated mixed salt solutions is difficult and of questionable accuracy, but it is likely that the answer to forcing formation of anionic nitrate complexes of americium lies in the relative activities of water and nitrate.

From a practical viewpoint, the modest americium removal needs (ca. 50-75%) from nitric acid evaporator bottoms allow sufficient latitude for the use of non-optimized conditions such as running existing columns filled with older, well-used Reillex HPQ. Newer materials, such as HPQ-100 and the experimental bifunctional resins, which exhibit higher distribution coefficients, would allow for either increased Am removal or the use of smaller columns. It is also of interest that one of the experimental neutral-donor solid-support extractants, DHDECMP, exhibits a similarly high level of americium (total alpha) removal from EV bottoms and is much less sensitive to total acid content than commercially-available material.

ENDNOTES

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- 3 The proposal in Rev. 18 of the SARP and Rev. 12 of TRUCON is to raise the wattage limit for newly-generated Portland-based cemented wastes by approximately four-fold.
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