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Title: AMERICIUM SEPARATIONS FROM NITRIC ACID
PROCESS EFFLUENT STREAMS

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Americium separations from nitric acid process effluent streams

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Abstract

The aging of the US nuclear stockpile presents a number of challenges, including the ever-increasing radioactivity of plutonium residues from ^{241}Am. Minimization of this weak gamma-emitter in process and waste solutions is desirable to reduce both worker exposure and the effects of radiolysis on the final waste product. Removal of americium from plutonium nitric acid processing effluents, however, is complicated by the presence of large quantities of competing metals, particularly Fe and Al, and strongly oxidizing acidic solutions. The reprocessing operation offers several points at which americium removal may be attempted, and we are evaluating two classes of materials targeted at different steps in the process. Extraction chromotography resin materials loaded with three different alkylcarbamoyl phosphinates and phosphine oxides were accessed for Am removal efficiency and Am/Fe selectivity from 1-7 molar nitric acid solutions. Commerical and experimental mono- and bifunctional anion-exchange resins were evaluated for total alpha-activity removal from post-evaporator solutions whose composition, relative to the original nitric acid effluent, is reduced in acid and greatly increased in total salt content. With both classes of materials, americium/total alpha emission removal is sufficient to meet regulatory requirements even under sub-optimal conditions. Batch distribution coefficients, column performance data, and the effects of Fe-masking agents will be presented.

Introduction

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 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] Decay-heat limits, which are driven by alpha activity, are a troublesome issue for this facility since cemented wastes contain a relatively high ratio of Am to Pu and ^{241}Am has approximately 60 times the specific (alpha) activity of ^{239}Pu.

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 nitrato 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 nitrato complexes as readily as tetravalent metals due to their lower charge density. However, under more forcing conditions such as the concentrated post-evaporator solutions which contain both higher nitrate and lower acid than plain 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.

The application of extraction chromotography resins to processing conditions is relatively recent. These systems use neutral-donor compounds similar to those designed for biphasic extractions except that they are are immobilized on a resin-bead 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 from nitric acid processing solutions. A procedure which reliably removes 75% of the activity from cemented wastes would provide compliant drums as well as meet the desire of the facility to reduce its waste output. Neither type of material described above is selective for trivalent over tetravalent actinides. Therefore, Pu(IV) will 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, the presence of relatively large quantities of Pu(IV) may be considered to be advantageous since it acts as a diluent for the high-activity Am(III) for precipitation, calcination and subsequent storage as the mixed oxide.

Target Waste Stream

The flowchart in Figure 1 below outlines some of the key steps in the nitric acid processing of Pu residues. Transfer steps marked with an asterisk are points at which americium removal is evaluated in this report. The non-sorbing effluent from anion-exchange consists of americium along with an assortment of other metals in ~7-9$\underline{M}$ nitric acid. Americium concentrations generally range from 1-10 mg/L while Fe(III) concentrations may be as high as 1-2 g/L.
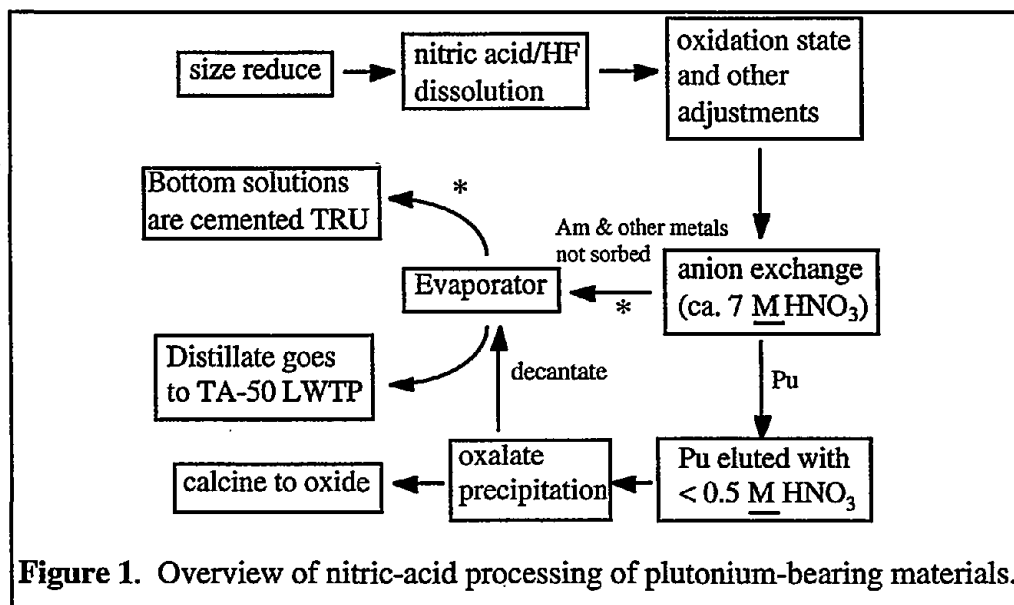
Figure 1. Overview of nitric-acid processing of plutonium-bearing materials.

The composition of post-evaporator solutions, relative to the anion-exchange effluent, is reduced in acid and greatly increased in total salt content. In general, acid concentrations range from 1-5$\underline{M}$ and nitrate concentrations range from 400-600 g/L. The major metals are Mg and Ca, with Fe comprising 10-20% of the material at almost 10 g/L.[3] Keeping in mind that there is *substantial* variability in composition, an average cemented drum of processing waste uses about 50 L of evaporator bottoms containing 20-30g Pu and 2-4g Am.

Experimental

Materials

Figure 2 outlines the descriptive terminology for the extraction chromotography and anion-exchange materials evaluated herein. We evaluated one commercial and two experimental 'neutral-donor' extraction chromotography resins. TRU resin_ (Eichrom Industries) is a material that has often been used to recover and concentrate actinides from lean streams. It consists of a 100-150 micron polyacrylate support loaded with octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide as the primary actinide extractant. The two experimental resins tested in this study were prepared at LANL and used the same support loaded with di-(4-t-butylphenyl)-N,N-diisobutylcarbamoylmethylphosphineoxide [D(t-BuPh)D(iBu)CMPO] at 60% weight loading and

dihexyl-N,N-diethylcarbamoylmethylphosphonate [DHDECMP] at 38% loading respectively. These materials have an estimated capacity for trivalent ions of ~~XXXX~~.

Figure 2. Extraction Chromotography and Anion-Exchange Resins
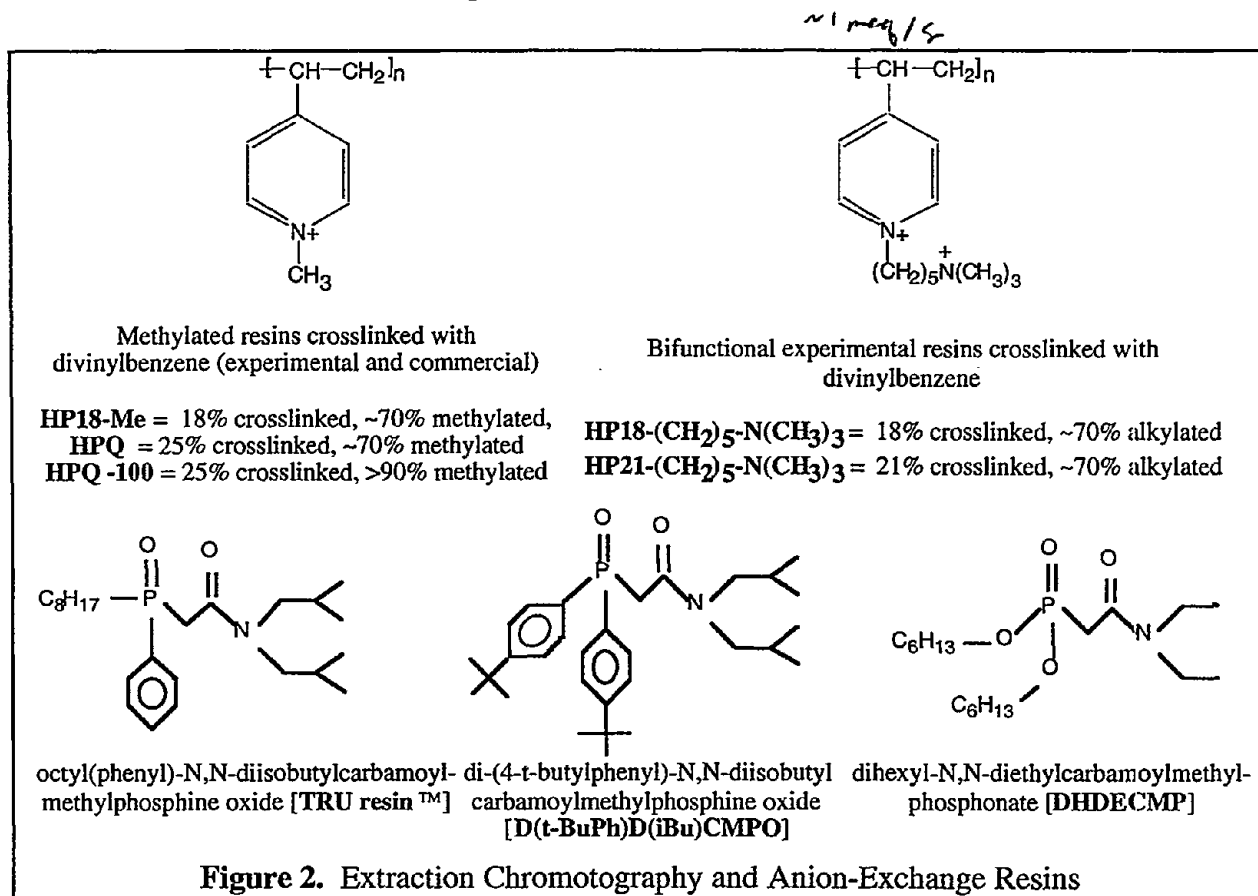
The anion-exchange resins are based on manufactured poly(4-vinylpyridine) materials from Reilly Industries. Reillex HPQ_ is a commercial macroporous resin of partially-methylated poly(4-vinylpyridine) crosslinked with divinylbenzene. The original HPQ, which is still used in the plutonium recovery process at LANL, has approximately 70% of its pyridinium sites methylated. The current HPQ resin, designated herein as HPQ-100, has >90% methylated sites.

A range of experimental anion-exchange resins were examined. As part on an on-going project to improve resins for plutonium processing, we have developed series of mono- and bifunctional resins where we vary the alkyl group, the percentage of sites derivatized, and the extent of crosslinking. [4,5,6] New experimental resins were evaluated as they came available and dropped if they were not a 'top-performer' or if they were not considered suitable for column implementation. All resins were converted to the nitrate form and air-dried to a constant weight prior to use. These resins have an estimated capacity of 250 mg Pu(IV)/ g of resin.

Analytical Procedures

Studies of Am removal from 1-7M nitric acid used contact solutions spiked with a clean stock solution of ^{241}Am to an activity of ~1x10^4 cpm/mL. Americium activity of pre- and post-contact solutions was assayed using a Packard model 2500TR liquid scintillation counter with alpha/beta discrimination capability. Iron distribution behavior was determined by counting the electron capture of tracer quantities (~1x10^4 cpm/mL) of ^{55}Fe. For studies using authentic evaporator solutions, only total alpha activity from both americium and plutonium were assayed using scintillation counting procedures. Typically 50-100 mL aliquots of assay solutions were pipetted into 19 mL of Ultima-Gold AB liquid scintillation cocktail and counted. Aliquot volumes were adjusted such that total activity did not exceed the 1x10^6 cpm upper limit of the instrument. The batch distribution coefficients, K_d, for americium and total alpha sorption were calculated using the following equation:

$$K_d = \frac{A_i - A_f}{A_f} \times \frac{V}{m}$$

where A_i is the initial activity, A_f is the final activity in solution, V is the volume of solution (mL), and m is the mass of resin (g).

Batch contact evaluation of chromotography resins in 1-7M HNO$_3$

The three extraction chromotography resins were evaluated for americium sorption from 1-7 molar nitric acid. The stronger acid solutions are reasonably good surrogates for effluent from the anion-exchange step in Figure 1, and the lower acid solutions were evaluated to determine the benefits of solution neutralization and/or dilution. Batch distribution measurements were performed using 2 mL of solution contacted with 0.1 g of resin for at least 24 hours. Each sample was loaded into a Bio-Rad 10 mL polyethylene column equipped with a 35 mm frit and rotated by complete inversion in order to intimately mix the solution with the solid. Once the contact period ended, the tip of the column was removed and the solution was filtered through the fritted filter into a collection vial. Non-sorbing inert matrices were used to confirm that no metals or activity were lost to the containers.

Americium distribution coefficients as a function of nitric acid concentration for the three extraction chromotography resins are presented in Figure 3.
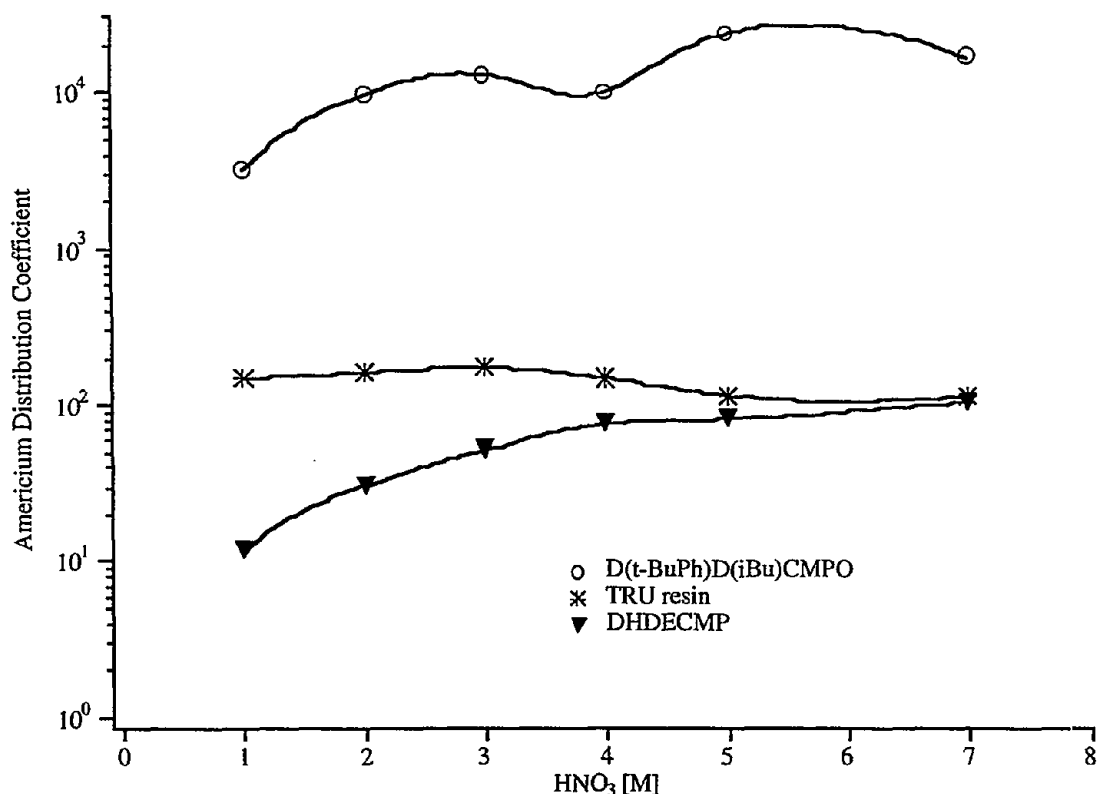
Figure 3. Distribution coefficients, K_d, for Am onto extraction chromotography resins.

Americum distribution values onto D(t-BuPh)D(iBu)CMPO are uniformly high, corresponding to nearly quantiative sorption of americium (>99.8%) from acid solutions of 2-6$\underline{M}$. Such a high level of uptake suggests that waste streams could be treated to meet low-level waste qualifications, but also indicates that americium recovery from the resin may be difficult to achieve. Distribution onto the TRU resin is similarly uniform, but lower, in the range of 80-90% uptake. Only the DHDECMP resin exhibits much sensitivity to nitric acid concentrations - the K_d values reflect a difference in americium uptake of <40% in 1$\underline{M}$ HNO$_3$ to >85% in7$\underline{M}$ HNO$_3$. This variation in performance implies that stripping of Am from the column could be efficiently performed by simple acid adjustment.

Since the process anion-exchange effluent consists of the all the non-plutonium constituents of the input feed solution, the best performing resin, D(t-BuPh)D(iBu)CMPO, was also evaluated for americium sorption in the presence of a large excess of Fe(III). Depending on the plutonium residues dissolved, this effluent may contain 1-2 g/L of Fe(III) or more. Ferric ions are known to have a notable negative impact on americium sorption onto TRU resin.[7] As seen in Figure 4, the presence of large quantities of ferric ion (~1.4 g/L) has a similarly detrimental effect on americium sorption onto D(t-BuPh)D(iBu)CMPO, particularly under strong acid conditions.
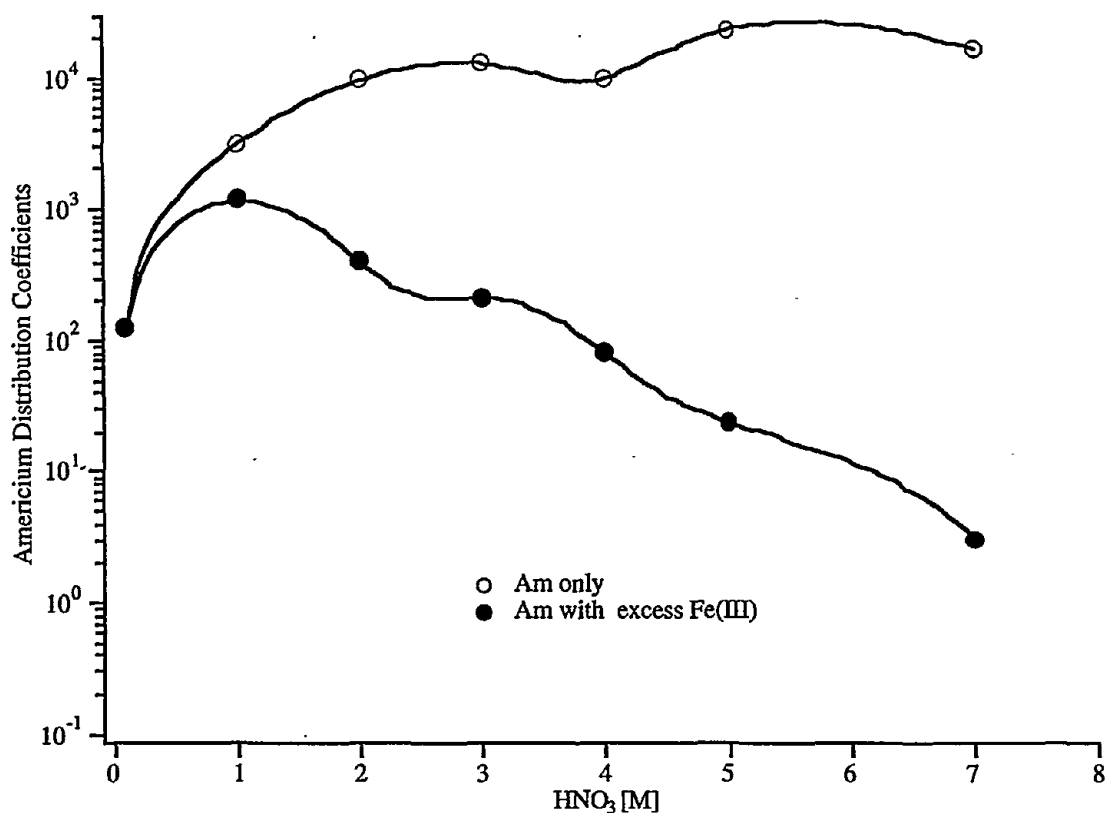
Figure 4. Distribution coefficients for americium onto D(t-BuPh)D(iBu)CMPO in the absence and presence of Fe(III). [Fe(III)] ~1.4 g/L, moles Fe:moles Am ~25,000.

Reduction of Fe(III) to Fe(II) significantly attenuates its effect,[7] but the reduced state is not stable in strong nitric acid solutions. Accordingly, we investigated the use of oxalate (0.1$\underline{M}$) as an ferric masking agent. We chose this ligand since oxalic acid is used in the nitric acid processing scheme to precipitate plutonium. Additionally, formation constants (β) for oxalate with Fe(III) are approximately three orders of magnitude greater than for Am(III).[8] Iron distribution behavior onto D(t-BuPh)D(iBu)CMPO is presented in Figure 5. The extremely high affinity for Fe(III) to the complexant D(t-BuPh)D(iBu)CMPO at higher acid concentrations readily explains the deleterious effect of Fe(III) on Am sorption to the resin, and the oxalic acid appears to be an ineffective competitor under the experimental conditions. A comprehensive study of Am and Fe distribution onto these extraction chromotography resins and the effect of masking agents is slated for future publication.[9]
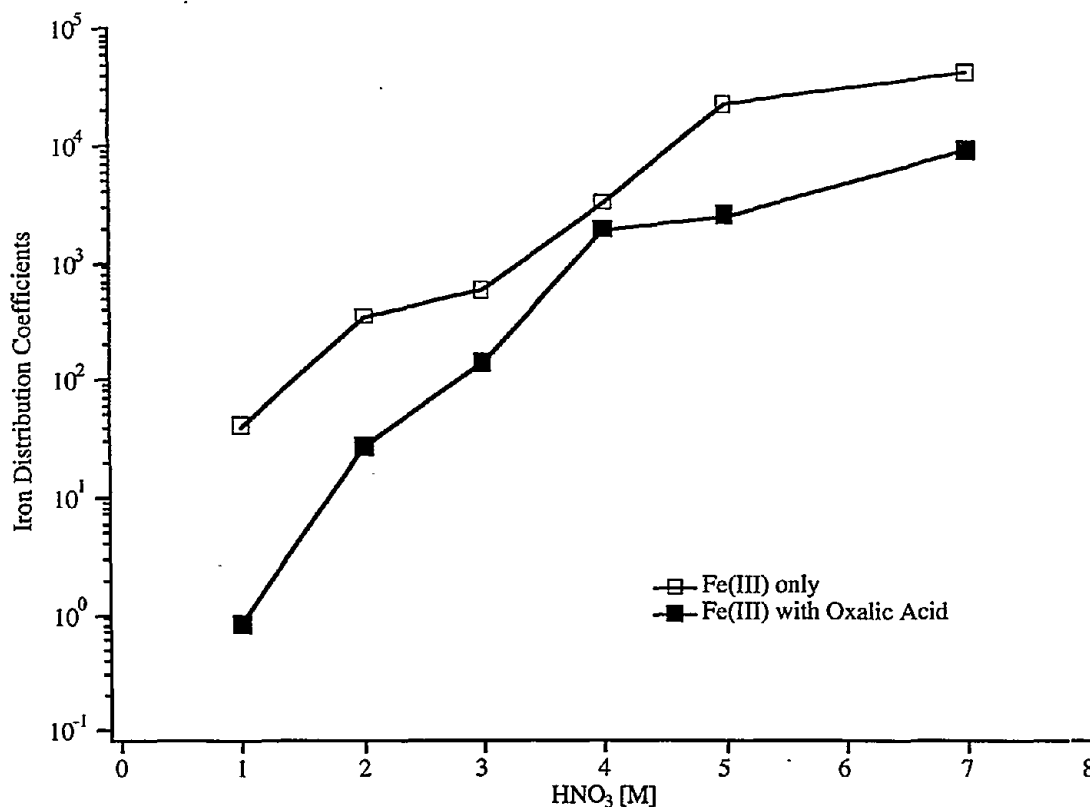
Figure 5. Distribution coefficients for Fe(III) onto D(t-BuPh)D(iBu)CMPO in the absence and presence of oxalic acid (OA). [OA] ~0.1 $\underline{M}$, moles OA:moles Fe ~16.

Total alpha-activity removal from post-evaporator solutions

The composition of post-evaporator solutions, relative to the anion-exchange effluent, is reduced in acid and greatly increased in total salt content. Recent studies of americium uptake onto anion-exchange resins using simple and complex surrogates indicated that the extremely low-water, high-salt environment facilitates sorption of Am(III) onto these materials.[10] Previous studies of metal sorption from acid-dissolved Hanford Tank sludge, another high-salt, high-acid matrix, also showed that the anion-exchange resins exhibited the highest americium K_d values of the 63 absorbers tested,[11] while TRU resin and preliminary DHDECMP resins exhibited only nominal americium affinity. Thus, the extraction chromotography resins were not expected to perform well in these solutions.

For evaluation of resin performance using authentic post-evaporator solutions, we chose to examine percentage removal of total alpha-activity instead of specific americium sorption distribution coefficients 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 the performance criteria 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 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 ^{241}Am 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 post-evaporator solutions slated for cementation were diverted for anion-exchange 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 or 10 mm polypropylene filters. Approximate acid concentrations were determined by measuring the pH of 100- and 1000-fold diluted solutions. EV1 was a relatively high acid solution ([H$^+$] ~ 4$\underline{M}$), EV2 and EV2' were lower acid solutions ([H$^+$] ~ 1$\underline{M}$) derived from similar processes. Prior to use, these solutions were assayed for Pu and Am using standard radiochemical assay procedures (alpha).

Batch contact evaluation

Batch contact experiments were conducted using 50 and/or 100 mg samples of the anion-exchange and neutral-donor resins contacted with 2.5mL of solution in 6mL polyethylen e disposable columns. The solutions were mixed by inversion during the contact time (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 displayed quantitative alpha activity recovery.

The results for a single batch contact using EV1 are presented in Table 1. Anion-exchange resins are listed first, followed by the neutral-donor systems.

	50 mg resin	100 mg resin
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 resin	28 %	35 %

Table 1. Percent alpha-activity removal from EV1, initial activity = 3.94 x 10^8 dpm/mL, ~0.052 g/L Am (75% of a activity), ~0.72 g/L Pu (25% of a activity)

All the materials exhibit a moderate level of alpha-activity removal, even the TRU resin. However, the percentage of activity removed by the TRU resin is very close to 25%, the calculated contribution to alpha activity by Pu(IV), which suggests 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 2 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.

	First Contact		Second Contact		Net [a]	
	50 mg	100 mg	50 mg	100 mg	50 mg	100mg
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

Table 2. Percent alpha-activity removal from EV2. initial activity = 1.09×10^9 dpm/mL, ~0.085 g/L Am (65% of a activity), ~1.93 g/L Pu (35% of a activity).

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 to solids ratios. In general, the total alpha-removal correlates well with previous Am uptake measurements using surrogate solutions.[10]

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 to 1000-fold excess of Fe(III) - a key competitor for the active sites on this material.

Solution EV2' has an acid concentration similar to EV2, but contains substantially more plutonium and exhibits 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 100 mg samples.

The americium removal efficiences reported in Table 3 reflect performances similar to those 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, while alpha removal from the second contact is quite poor, indicative of poor Am(III) sorption by this material. 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%).

	First Contact 100 mg resin	Second Contact 100 mg resin	Net [a]
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

Table 3. Percent alpha-activity removal from EV2'. Initial activity : 1.44 x 10^9 dpm/mL, ~0.129 g/L Am (65% of α activity), ~2.95 g/L Pu (35% of α activity).

Small column evaluation of HPQ-100 and HP25-$(CH_2)_5$-$N(CH_3)_3$

For these experiments we used 30 x 2.5 cm columns containing approximately 50 g (dry weight) of the resins. We ran the post-evaporator solution, EV2', with the highest Am content (0.13 g/L). A successful run would need to retain greater than 75% of the solution alpha activity.

Solutions were filtered through an in-line 10μm polypropylene cartridge. Columns were loaded in 1$\underline{M}$ HNO_3 and packed to reduce voids. Feed solutions were loaded in an up-flow direction under positive pressure from a peristaltic pump. Fractions of approximately 100 mL were collected for alpha activity assay using scintillation counting procedures. Americium activity in each fraction was estimated in 'real-time' through the glovebox window using a hand-held gamma counter. 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 were run through the column in the same flow direction to displace residual feed solutions. Elution was conducted using $0.35\underline{M}\ HNO_3$ in a reverse-flow direction.

HPQ-100: The bed volume was approximately 150 mL. The free solution volume (column volume) was estimated to be 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 $1.0\underline{M}\ HNO_3/\ 6.5\underline{M}\ NaNO_3$. The alpha-activity elution profile is presented in Figure 6.

After approximately six column volumes (600 mL), distinct gamma activity was detected in the effluent. After 14 volumes (1400 mL), the gamma activity of the effluent comparable to the original solution, so we began wash and elution. 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 as 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.
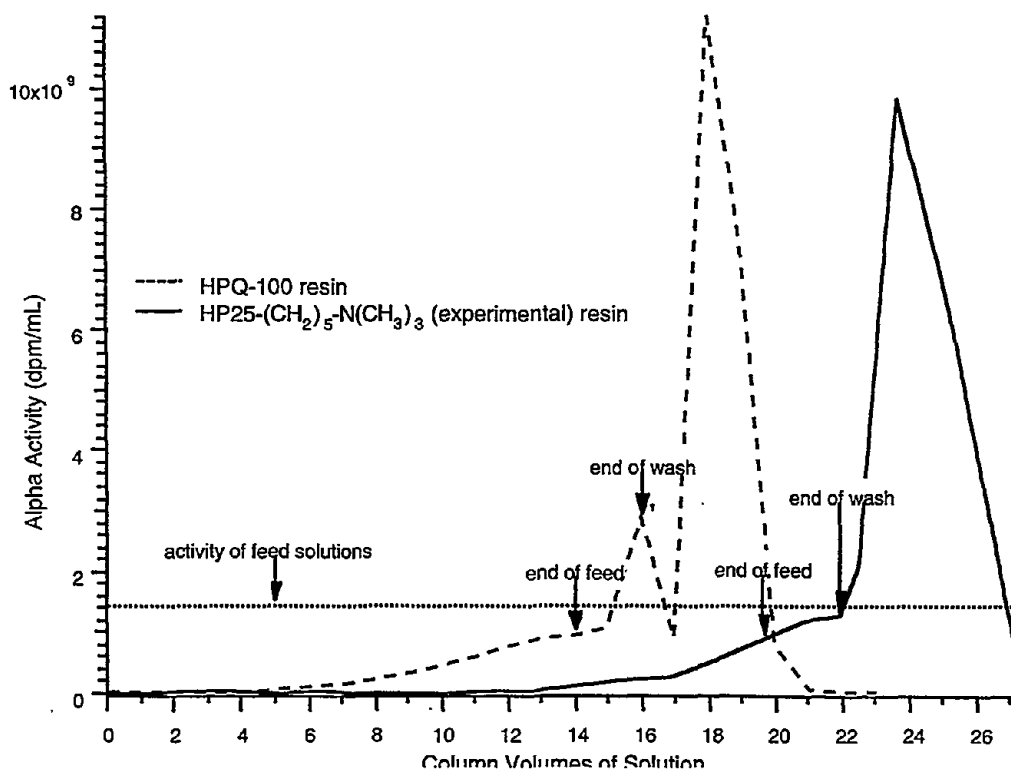
Figure 6. Alpha activity elution profile for EV2' through HPQ-100 and HP25-$(CH_2)_5$-N$(CH_3)_3$.

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 g 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,[12] and this diffusion rate could be a limiting factor in column performance.

HP25-$(CH_2)_5$-$N(CH_3)_3$: This column (120 mL bed 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$\underline{M}$ HNO_3/3.3$\underline{M}$ $Ca(NO_3)_2$. Figure 6 provides the elution profile.

Alpha activity 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 not forcing the loading to complete breakthrough. In either case, the wash solution does an inadequate job of retaining the americium on the column.

At 1.6 L of feed, the column is loaded with 4.8 g Pu (~50%) capacity and 0.2 g Am. By the end of feed solution input, 9% of the total alpha activity was eluted, 91% retained on the column. By the end of the wash solution, a total of 16% of the activity was eluted, resulting in retention of 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. 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.

The alpha-elution 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.

Process-scale evaluation.

We conducted a process-scale evaluation for the treatment of evaporator bottoms by anion-exchange using an existing 10L 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 that exceed plutonium discard limits. Prior to this run, the column was washed with $7\underline{M}$ HNO_3 and allowed to sit for several days in contact with $0.45\underline{M}$ HNO_3. Feed, wash ($0.5\underline{M}$ HNO_3/ $7\underline{M}$ $NaNO_3$), and eluent ($0.45\underline{M}$ HNO_3) were all pulled through the resin bed in an up-flow direction using house vacuum. Flow rates averaged 30-40 L/ hour, providing a solution residence time of ca. 30 minutes.

The 50 L of bottoms were in two 25L batches. The first feed solution (F#1) had very low Pu and Am content (Pu=0.229 g/L, Am= 0.029 g/L), the second batch (F#2) was closer to average (Pu=1.33 g/L, Am=0.082 g/L). Both had titrated acid concentrations of slightly less than $1\underline{M}$. A 10L column should have a free liquid column volume of ca. 7L, so we estimate that each batch of feed solution would correspond to 3.5 column volumes for a total of seven column volumes of feed solution for the experiment.

The solutions were filtered through 5 mm 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 water removed much of the coating and dissolved the entrained salt crystals. The solutions were then sent through an in-line gamma counter to determine initial 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 presented in Figure 7 depicts the activity in the column effluent (log scale) over the timeframe of the loading, washing and elution cycles. 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.

Substantial activity from plutonium was detected in the initial eluent of the $0.45\underline{M}$ HNO_3 solution being displaced from the column by the first feed solution. The duration of this unexpected behavior is reflected in the minor Am elution curve seen during the early stages of input of F#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 20g of 'extra' plutonium is only about 2% of the loaded capacity of a 10L 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.
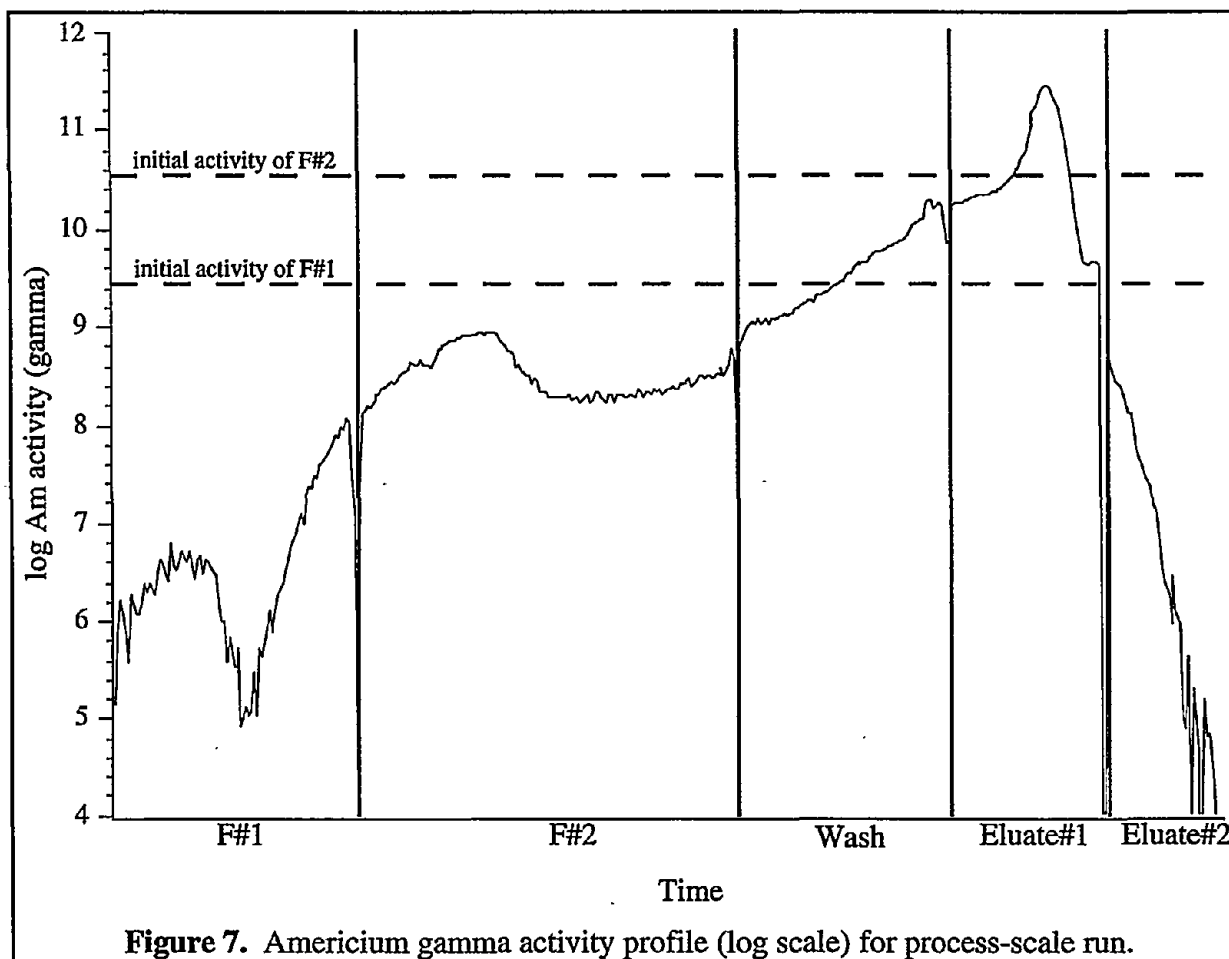
Figure 7. Americium gamma activity profile (log scale) for process-scale run.

At the end of the 50 L of feed through the Reillex HPQ column, the gamma activity from americium in the effluent was still well below either feed activity. 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 4.

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 americium on the column. However, in this particular case, the effluent (45 L, 0.34g Am) and wash (15.2 L, 0.41g) 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 20L of eluant. The gamma-activity profile in Figure 7 suggests that the bulk of the americium is eluted in approximately 10L 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 column use.

	Feed (ave) 50 L	Effluent of F#1, F#2 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 [a]

[a] Includes residual Pu mobilized from the column

Table 4. Americium and plutonium concentrations and total mass as a function of process fraction.

Summary

Extraction chromotography resins are highly effective at americium removal from nitric acid anion-exchange effluent. Disadvantages to these systems include relatively low capacity and significant interference by large excesses of iron. Preliminary studies indicate that the effects of ferric ion competition may be mitigated by either reducing the acidity of the solution or by the use of an appropriate masking agent.

Americium (III) exhibits an unexpectedly high affinity for anion-exchange material from the high-salt post-evaporator solutions. Similar behavior is observed for its lanthanide homologue, Nd (III), in complex evaporator bottoms surragate solutions.[10] There appears to be no single controlling factor - acid concentration, total nitrate concentration or solution ionic strength - which accounts for the extraction of Am from these solutions as an anionic complex. 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. Disadvantages to this process include moderate levels of americium removal and general difficulties in handling the near-saturated post-evaporator solutions and their particulates.

From a practical viewpoint, the modest americium removal needs (ca. 50-75%) from evaporator solutions allow sufficient latitude for the use of non-optimized conditions such as running exisiting 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. Improvements in the real-time, in-line gamma analysis available for the process-scale operations 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. 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.

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