Kilogram-Scale Purification of Americium by Ion Exchange

E. J. Wheelwright[a]

[a] Pacific Northwest Laboratory Richland, Washington

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KILOGRAM-SCALE PURIFICATION OF AMERICIUM
BY ION EXCHANGE

E. J. Wheelwright
Pacific Northwest Laboratory
Richland, Washington 99352

ABSTRACT

Sequential anion and cation exchange processes have been
used for the final purification of ^{241}Am recovered during the
reprocessing of aged plutonium metallurgical scrap. Plutonium
was removed by absorption on Dowex 1, X-3.5 (30-50 mesh) anion
exchange resin from 6.5-7.5 $\underline{M}$ HNO$_3$ feed solution. Following
a water dilution to 0.75-1.0 $\underline{M}$ HNO$_3$, americium was absorbed on
Dowex 50W, X-8 (50-100 mesh) cation exchange resin. Final
purification was accomplished by elution of the absorbed band
down 3 to 4 successive beds of the same resin, preloaded with
Zn^{2+}, with an NH$_4$OH buffered chelating agent.

The recovery of mixed ^{241}Am-^{243}Am from power reactor
reprocessing waste has been demonstrated. Solvent extraction
was used to recover a HNO$_3$ solution of mixed lanthanides and
actinides from waste generated by the reprocessing of 13.5
tons of Shippingport Power Reactor blanket fuel. Sequential
cation exchange band-displacement processes were then used
to separate americium and curium from the lanthanides and then
to separate ∿60 g of ^{244}Cm from 1000 g of mixed ^{241}Am-^{243}Am.

INTRODUCTION

The americium isotopes of principal interest are ^{241}Am
($t_{1/2}$ = 433 years) and ^{243}Am ($t_{1/2}$ = 7400 years). Americium-
241, produced according to the reaction

$$^{239}Pu(n,\gamma) \; ^{240}Pu(n,\gamma) \; ^{241}Pu \xrightarrow[14.3 \text{ yrs}]{\beta} \; ^{241}Am,$$
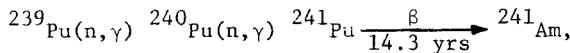
is recovered during the reprocessing of once-purified plutonium. Americium -243 can be obtained in a variety of ways. Large amounts of mixed ^{241}Am and ^{243}Am are produced in nuclear power reactors and could be recovered during fuel reprocessing (1-3). The principal methods used for the recovery and purification of americium, both aqueous and nonaqueous, are summarized in an excellent review by Schulz (4).

In 1965 a 9-column ion-exchange pilot plant was installed in a heavily-shielded manipulator cell of the 325-A High-Level Radiochemical Facility at DOE's Hanford Plant. The columns were 270 cm high and ranged from 36 to 2.5 cm I.D. This facility was used primarily for the purification of promethium, but was also used, on a campaign basis, for the purification of gram to kilogram amounts of ^{90}Sr, ^{244}Cm, ^{241}Am, and mixed $^{241}Am-^{243}Am$. Ion-exchange flowsheets developed for the separate purification of plutonium and promethium were adapted and combined for the americium purification campaigns and are discussed in the following sections.

PROCESS DESCRIPTION

Anion-Exchange Separation from Plutonium

The nitric acid anion-exchange process used for the separation of americium from plutonium has been described in detail (5, 6), and is only outlined here. This process takes advantage of the near-specific absorption of Pu(IV) from 6 to 8 $\underline{M}$ HNO_3 by a selected group of anion exchange resins and the simultaneous nonabsorption of most other cations. The 4-cycle process is shown in Figure 1. Americium is not absorbed by the resin bed during the feed absorption cycle, but a scrub cycle is required to displace all traces of the feed solution and Am^{3+} from the

resin particles and from the inside surfaces of the column if
a high decontamination of the plutonium is required. "Plant"
solutions frequently contain significant amounts of fine solids
which collect in the first few cm of resin and must be washed
free of americium by the scrub solution.

The three principal operational difficulties with the
process are:

1. At times, solids collected on top of the resin bed
   cause "channeling" which decreases the efficiency
   of the three processing cycles.

2. The separated americium is collected with all other
   impurities in a rather large volume of 6.5 to 7.5 $\underline{M}$
   HNO_3.

3. Any plutonium in oxidation states other than tetra-
   valent is not absorbed and remains with the americium.

These difficulties can be circumvented and the process
successfully used. Careful filtration of the feed solution
largely eliminates the first problem. Since the second
phase of americium purification involves absorption by cation
exchange resin, a 7-to 8-fold dilution with water abrogates the
second difficulty. The final problem can be minimized by a
careful analysis and valence adjustment of the feed solution,
if necessary.

Cation-Exchange Purification of Americium

A "band-displacement" chromatographic process was developed
and used for large-scale purification of promethium (7, 8) using
the facility previously described. This process employs four
sequential steps:

1. Absorption of the ions to be separated from a dilute
   nitric acid feed solution onto a bed of cation-exchange
   resin.

2. Removal of unabsorbed material from the feed-absorption
    bed with a scrub solution.

3. Displacement of the absorbed ions down successive
    resin beds, preloaded with Zn^{2+}, by an ammonium
    hydroxide buffered solution of a chelating agent to
    separate the absorbed ions into individual pure-
    component absorption bands, with binary mixing only
    at front and back interfaces.

4. Collection of specification product, recycle, and
    waste as the bands are displaced from the final resin
    bed.

The chelating agents diethylenetriaminepentaacetic acid (DTPA)
and nitrilotriacetic acid (NTA) were used. Figure 2 shows the
NTA flowsheet as applied to the purification of americium.
Table 1 gives the flowsheet changes when DTPA is substituted
for NTA in this flowsheet.

In the NTA flowsheet, 0.5 $\underline{M}$ NH_4NO_3 is used to remove H^+ from
the feed absorption column prior to elution. If this is not done,
the insoluble free-acid form of the chelating agent will form
within the resin bed and completely block solution flow through
the column. The free-acid form of DTPA is sufficiently soluble
that the 0.5 $\underline{M}$ NH_4NO_3 wash is not required.

TABLE 1: Flowsheet Changes when DTPA is Substituted for NTA

Eluting Solution

Concentration	-----	0.05 $\underline{M}$ DTPA
pH	----	Buffered to 6.5 with NH_4OH
Volume	----	2000 L
Flow Rate	----	3.8 ml/min-cm^2

Scrub Cycles 2 and 3 can be eliminated.
Rate of Band Advance ---- 19±3 cm/hr

Under the conditions specified in Figure 2 and Table 1,
the elution sequences of americium and curium, compared with
the lanthanides, are:

with DTPA,

Zn^{2+}, $(Dy^{3+}-Ho^{3+}-Er^{3+}-Tb^{3+})$, Gd^{3+}, Eu^{3+}, Sm^{3+}, Y^{3+}, Pm^{3+}, Pr^{3+}, Ce^{3+},
La^{3+} ↑   ↑
            Cm^{3+} Am^{3+}

and with NTA,

Zn^{2+}, $(Ho^{3+}-Dy^{3+}-Tb^{3+})$, Y^{3+}, Cm^{3+}, Gd^{3+}, $(Eu^{3+}-Am^{3+})$, Sm^{3+}, Pm^{3+}, Nd^{3+},
Pr^{3+}, Ce^{3+}, La^{3+}.
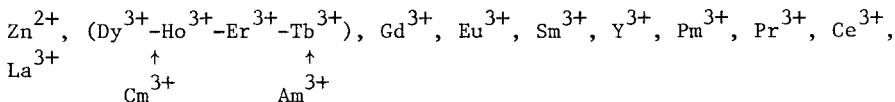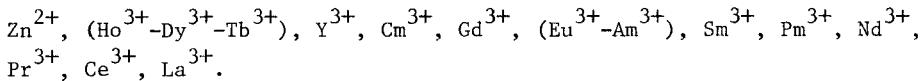
In these measurements (1) the heavy lanthanides are used mainly to
provide a reference. Lanthanides heavier than terbium are present
in the fission product mix from power reactors in only trace
quantities. Lanthanides are not normally present in the recovery
of ^{241}Am from aged, once processed plutonium. With both chelating
agents, Pu^{4+}, Fe^{3+}, and Th^{4+}, if present in the feed solution,
form stronger complexes than Zn^{2+} and thus pass through the Zn^{2+}
restraining bed once elution is initiated. The alkali and alkaline
earth ions form much weaker complexes and elute after the lantha-
nides. In both sequences, the ions enclosed in parenthesis elute
in the sequence shown, but do not properly separate from each
other in the band displacement distances used. With NTA, americium
separates easily from curium but does not separate from europium.
When DTPA is used, americium is easily separated from europium,
but the separation from curium is not as efficient. Choice
between the two flowsheets for americium purification depends
upon the presence or absence of curium and/or europium. Since
the rate of band advance is approximately a factor of two faster
with NTA, NTA is used when europium is absent from the feed
solution.

PRODUCTION-SCALE DEMONSTRATIONS

Recovery of [241]Am from Once-Purified Plutonium

During the period 1973 through 1976, four campaigns were
conducted to purify [241]Am recovered at the Hanford Plutonium
Reclamation Facility (PRF) from a wide variety of metallurgical
scrap using a countercurrent solvent extraction process. The
product from the solvent extraction process was concentrated
at the PRF by absorption from dilute HNO_3 onto a bed of Dowex
50W cation exchange resin followed by elution from the resin
with 7-8 $\underline{M}$ HNO_3. The concentrate was then transferred to the
ion-exchange pilot-plant facility described in the introduction.
The Pu/Am ratio in the concentrate varied over a range of 0.01
to 2. Other impurities included Fe, Cr, Ni, Al, Si, Ca, Mg, and
Na in a wide range of concentrations. Some batches contained
a significant amount of solids.

After transfer, the solution was filtered, analyzed, and,
when necessary, the plutonium oxidation state was adjusted
to (IV) and the nitric acid concentration was adjusted to 7
molar. The plutonium was then removed using the flowsheet
shown in Figure 1. Several anion-exchange runs were made
during each campaign because nongeometrically safe equipment
limited the amount of plutonium which could be in the cell at
one time. Following removal of the plutonium, the americium
product solution from the anion exchange runs was diluted to
0.75 to 1.0 $\underline{M}$ HNO_3 with water and processed by the cation
exchange flowsheet in Figure 2. A typical americium elution
curve is shown in Figure 3. Americium from the heart of the
elution band was precipitated with oxalic acid, filtered, and
calcined to oxide. The americium in the binary mixtures at each
end of the elution band was recycled to the succeeding campaign.
A material accountability for the four campaigns is given in

BED PREPARATION CYCLE	Pu ABSORPTION CYCLE	RESIN SCRUB CYCLE	Pu ELUTION CYCLE
1 BED VOLUME 6.5 TO 7.5 M HNO₃	CLARIFIED FEED 6.5 TO 7.5 M HNO₃ VARIABLE Am (III) CONC. VARIABLE Pu (IV) CONC.	5 TO 10 BED VOLUMES 7 M HNO₃	APP. 4 BED VOLUMES 0.5 M HNO₃
10.2 cm I.D. ION-EXCHANGE COLUMN 5 L OF DOWEX 1, X-3.5 (30-50) MESH RESIN	10.2 cm I.D. ION-EXCHANGE COLUMN 5 L OF DOWEX 1, X-3.5 (30-50) MESH RESIN	10.2 cm I.D. ION-EXCHANGE COLUMN 5 L of DOWEX 1, X-3.5 (30-50) MESH RESIN	10.2 cm I.D. ION-EXCHANGE COLUMN 5 L of DOWEX 1, X-3.5 (30-50) MESH RESIN
WASTE	Am PRODUCT		Pu PRODUCT
TEMPERATURE - - - 60 ± 5°C FLOW RATE - - - - -500ml/min.	TEMPERATURE - - - 60 + 5°C FLOW RATE - - - - -NORMALLY 500 TO 1000 ml/min. - - - - -MASS LIMIT ≤ 1.5 g Pu/min.	TEMPERATURE - - - 60 · 5°C FLOW RATE - - - - -100 ml/min.	

FIGURE 1

Flowsheet Used for the Anion-Exchange Separation of Americium from Plutonium

Table 2. In campaigns 3 and 4, the americium became contaminated with ^{154}Eu, residual from promethium separations conducted between the americium campaigns, and the DTPA flowsheet was used for final purification. A summary of the chemical and radiochemical analyses of the product oxide batches is shown in Table 3. In the last three campaigns the product collection was deliberately expanded to include some of the impurities at each end of the elution band, thus maximizing the amount of product that would meet the user's specification.

Recovery of Mixed ^{241}Am-^{243}Am from Power Reactor Fuel Reprocessing Waste

In 1967, 13.5 tons of Shippingport Power Reactor blanket elements were processed at the Hanford Redox Plant for the

AMERICIUM FEED SOLUTION

Am PRODUCT FROM
ANION EXCHANGE DILUTED
TO 0.75 TO 1.0 M HNO₃
WITH DIST. H₂O

FEED ABSORPTION COLUMN
SCRUB CYCLES

1. 80L OF DIST. H₂O

2. 600 TO 900L OF 0.5 M NH₄NO₃

3. 80L OF DIST. H₂O

ELUTING SOLUTION

0.105 M NTA
BUFFERED TO pH 6.4 WITH NH₄OH
VOLUME 1500L

270 cm HIGH

| 21 cm I.D. ION-EXCHANGE COLUMN H+ CYCLE RESIN 94L | 16.2 cm I.D. ION-EXCHANGE COLUMN Zn^{2+} CYCLE RESIN 52L | 10.8 cm I.D. ION-EXCHANGE COLUMN Zn^{2+} CYCLE RESIN 23L | 7.6 cm I.D. ION-EXCHANGE COLUMN Zn^{2+} CYCLE RESIN 12L | 5.1 cm I.D. ION-EXCHANGE COLUMN Zn^{2+} CYCLE RESIN 4.8L |

WASTE SOLUTION

Am RECYCLE SOLUTION

Am PRODUCT SOLUTION
8.6 gm Am/L

RUN CONDITIONS

RESIN · DOWEX 50W, X-8 (50-100 MESH)
FEED AND SCRUB CYCLE TEMPERATURE · · · AMBIENT
ELUTION TEMPERATURE · · · · · · · · · · · · 60 · 5⁰C
FEED AND SCRUB CYCLE FLOW RATES · · · · -1 TO 2 L/min
ELUTION CYCLE FLOW RATE · · · · · · · · · -8ml/min · cm²
RATE OF BAND ADVANCE · · · · · · · · · · · -43 · 4 cm/hr

RUN CYCLE TIME

FEED CYCLE · · · · · · FEED DEPENDENT
SCRUB CYCLE · · · · 16 hrs
ELUTION CYCLE · · · 40 hrs

FIGURE 2

Flowsheet Used for the Cation-Exchange Purification of Americium

recovery of uranium, plutonium, and neptunium. A batch extrac-
tion process employing 50 vol % tri-n-butylphosphate in an
n-paraffin hydrocarbon diluent was used to recover the lanthanide-
actinide elements from the normally discharged waste. Following
cask transfer to the "Semiworks" facility, a countercurrent
solvent extraction process employing 0.4 $\underline{M}$ bis(2-ethylhexyl)phosphoric
acid, and 0.3 $\underline{M}$ tri-n-butylphosphate in n-paraffin hydrocarbon was
used to further decontaminate the lanthanide-actinide mix from Al,
Fe, U, Pu, Na, and other fission products (9). The solution was
then cask transferred to the ion-exchange pilot-plant facility
for final purification.
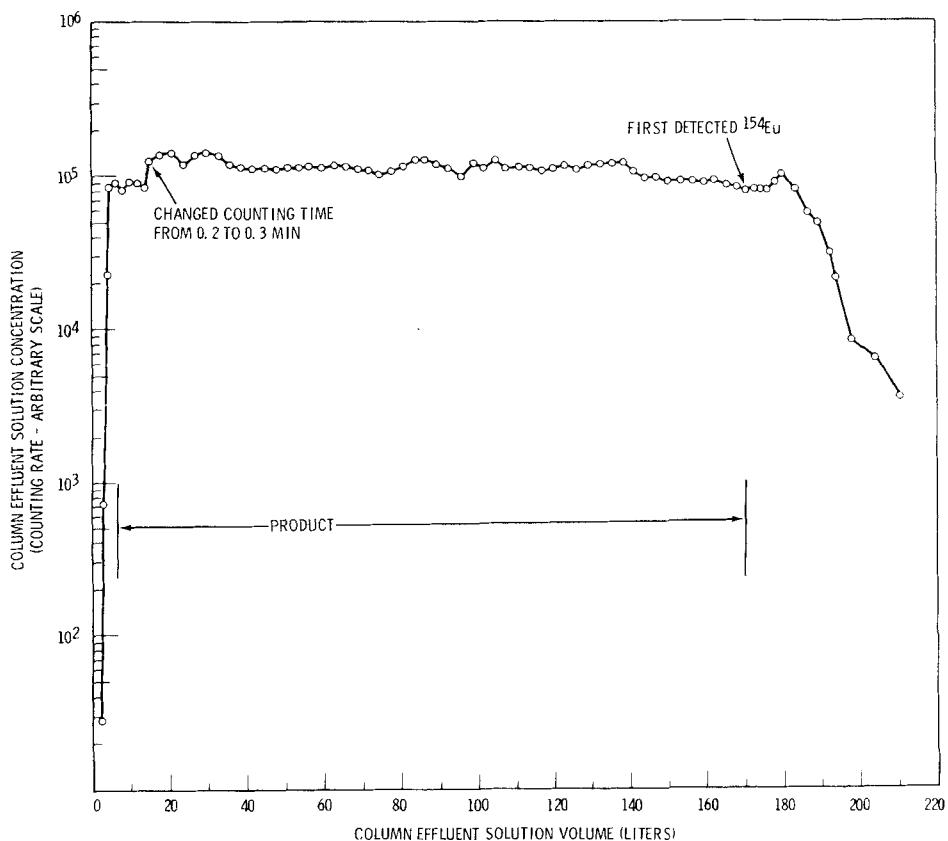
FIGURE 3

Column Effluent Solution Concentration (Counting Rate - Arbitrary Scale)

A DTPA flowsheet similar to that shown in Figure 2, but using 36 and 27 cm I.D. columns in addition to those shown in Figure 2, was used to separate americium and curium from the lanthanide fission products. In spite of the use of a 240-liter resin bed for feed absorption, two identical DTPA runs were required for the processing because of the very large

TABLE 2: Material Accountability for Production Runs

	Campaign 1		Campaign 2		Campaign 3		Campaign 4	
	Am	Pu	Am	Pu	Am	Pu	Am	Pu
Anion Exchange								
Feed[1] (g)	502	207	471	308	630	141	1189	460
Pu Product (g)	<1	194	0.8	303	0.1	141	6	425
Am Product (g)	493	<1	455	0.3	630	0.1	1187	2.2
Recovery (%)	98	94	97	98	100	100	100	93
Cation Exchange								
Feed: Anion Exchange Product (g)	493		455		688[2]		1338[3]	
Recycle (g)	0		96		28		63[4]	
Total (g)	493		551		716		1401	

Product (g)	394	516	607	1297
Recycle (g)	96	28	104	62
Recovery (%)	99	99	99	97
Oxide Preparation				
Feed (g)	394	516	607	1297
Recovered as Oxide (g)	366	489	576	1277
Recovery (%)	93	95	95	98

Notes: (1) Most of the feed solutions contained solids, not all of which was removed by filtration. The presence of the solids created larger-than-normal error limits in the feed analyses.

(2) Includes 58 g of Am from ORNL.

(3) Includes 90 g of Am from SRL and 61 g of Am from ORNL.

(4) Part of the rework from Run 3 was discarded during a major cell renovation between Runs 3 and 4.

TABLE 3: Americium Oxide Product Purity

Batch Number	Campaign 1		Campaign 2		Campaign 3		Campaign 4		
	1	2	3	4	5	6	7	8	9
Amount of Oxide (g)	200	213	483	73	368	283	449	810	162
Chemical Purity (wt %)	99.9	99.9	99.6	95	99.5	99.7	99.9	99.8	98.9
Radiochemical Impurities(1)									
^{154}Eu$(10^{-6}$ Ci/g oxide)	9.7	18	15	77	1.8	33	0.03	11	3
^{90}Sr$(10^{-6}$ Ci/g oxide)	0.8	1.4	0.2	0.4	ND(2)	ND	ND	ND	ND
^{239}Pu$(10^{-6}$ g/g oxide)	3.1	1	26	25	98	7	ND	ND	ND

Notes: (1) No other radiochemical impurities were detected.
(2) ND -- not detected.

quantity of lanthanide fission products present in the feed
solution.   One NTA run was used to separate americium from
curium.   Product elution curves for one of the DTPA runs and
for the NTA final purification are given in Figures 4 and 5.
Results for the three ion-exchange runs are summarized in
Table 4.
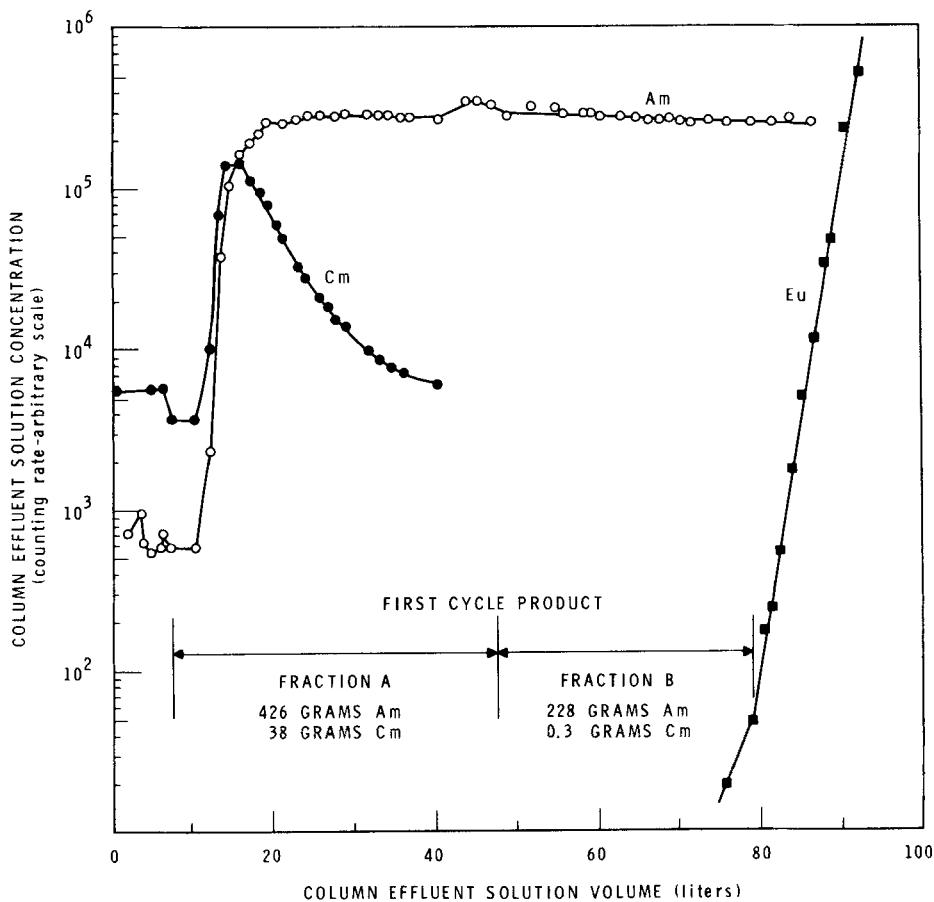
FIGURE 4:   Product Elution Curve DTPA Cycle
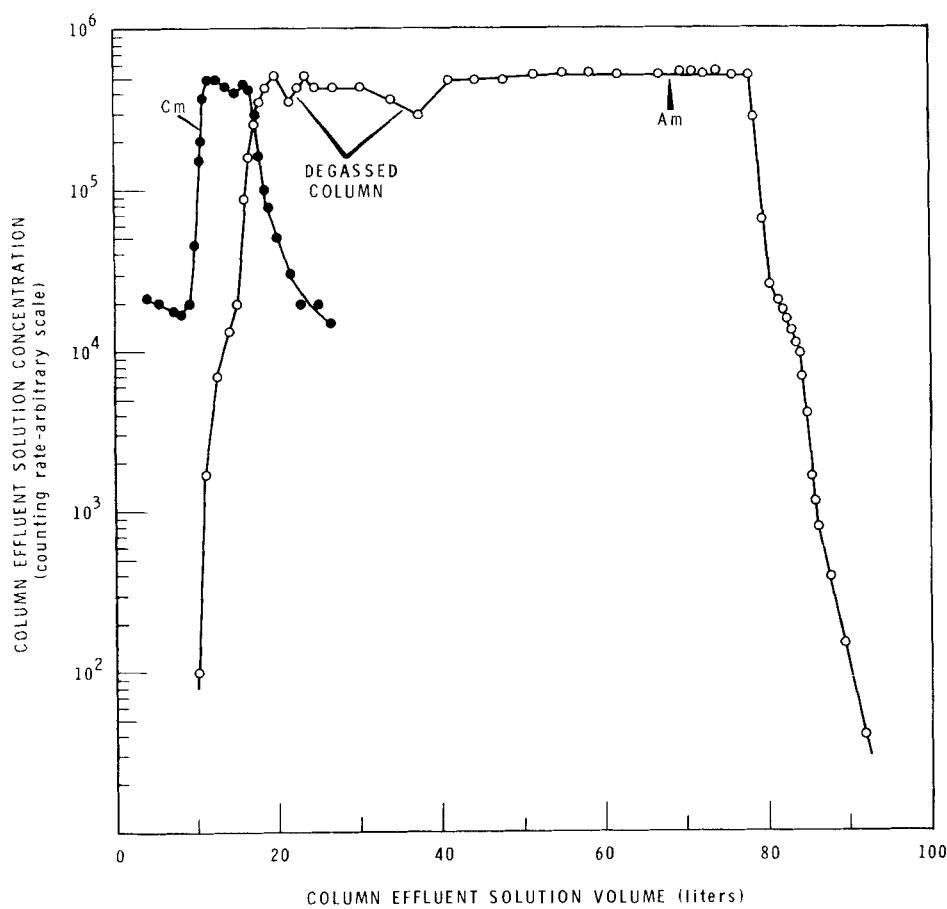
FIGURE 5:   Product Elution Curve NTA Cycle

TABLE 4:   Summation of Two-Cycle Pilot Plant Test

	Americium	Curium
Feed Solution	1080 g	60.5 g
Recycle Solution	218 g	14.2 g
Product Solution	760 g	29.2 g
	99.7% pure	97.8% pure
		15.3 g
		86% pure
Material Balance	99%	97%

CONCLUSIONS

In the americium separation campaigns described, a very
high purity product was not required. Americium of 4 to 5 9's
purity can be prepared by limiting the product collection to
the center section of the elution band and recycling a larger
fraction of material from each end of the band. Periodic
replacement of the exchange resin is required because of
radiation damage, but this is not a serious detriment
to the usefulness of the process.

ACKNOWLEDGMENT

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