

PNL-SA 7844

CONF - 7910108 -- 4

KILOGRAM-SCALE PURIFICATION OF AMERICIUM
BY ION EXCHANGE

MASTER

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Work performed under Contract No.
EY-76-C-06-1830, with the United
States Department of Energy

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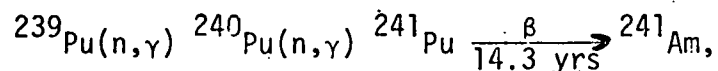
ABSTRACT

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 M HNO_3 feed solution. Following a water dilution to 0.75-1.0 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_4OH 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



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

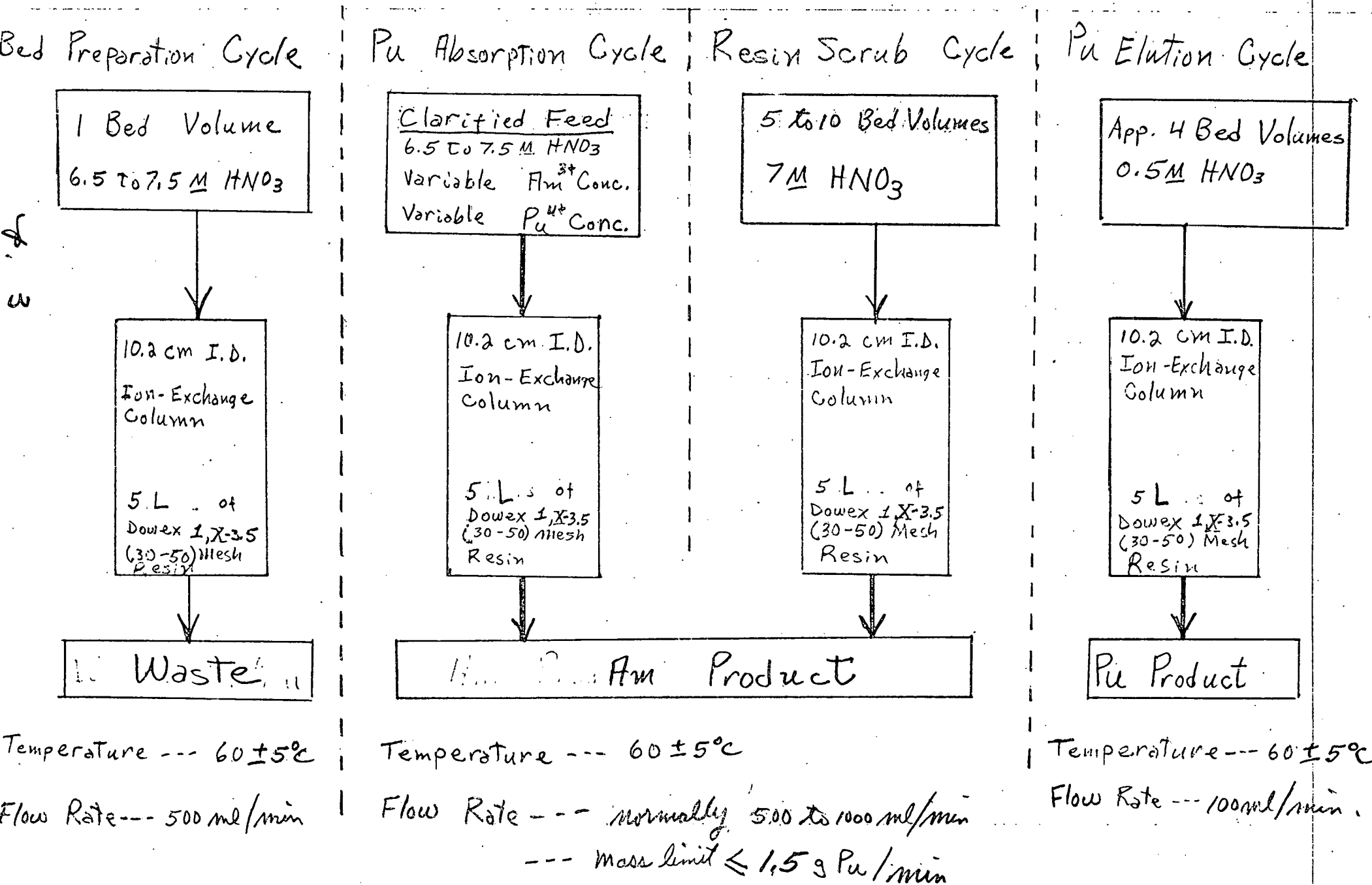
ANION-EXCHANGE SEPARATION FROM PLUTONIUM

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^{4+} from 6 to 8 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 M HNO_3 .
3. Any plutonium in oxidation states other than 4+ is not absorbed and remains with the americium.

Figure 1 Anion-Exchange Separation of Americium From Plutonium



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

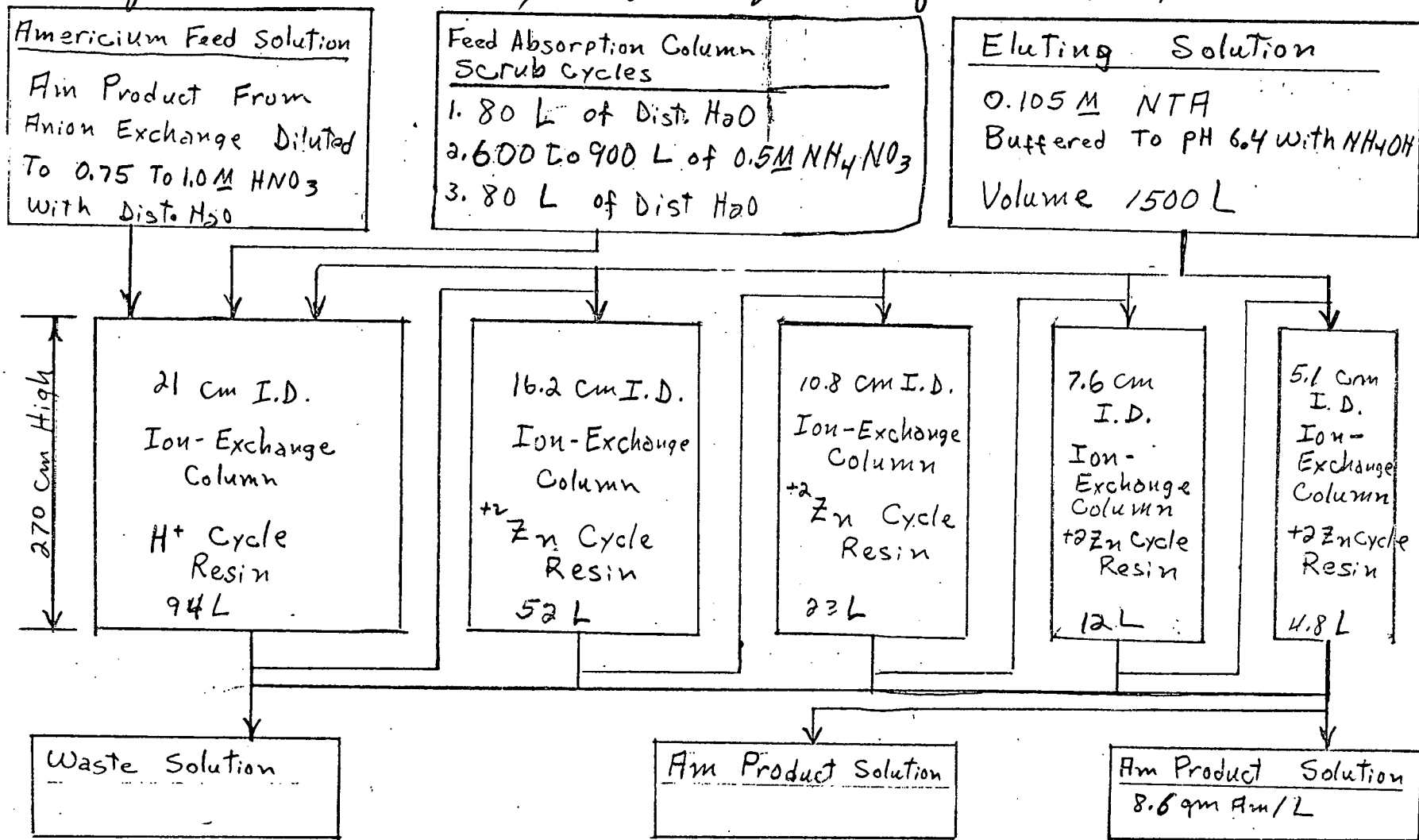
A "band-displacement" chromatographic process was developed and used for large-scale purification of promethium (7, 8) using the facility previously described. This process employs three sequential steps:

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 "band" of ions down successive resin beds, preloaded with Zn^{2+} , by an ammonium hydroxide buffered solution of a chelating agent.

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.

Figure 2

Cation Exchange Purification of Americium



Run Conditions

Feed and scrub cycle Temperature --- Ambient
 Elution Temperature --- 60 ± 5°C
 Feed and Scrub cycle Flow Rates --- 1 to 2 L/min
 Elution Cycle Flow Rate --- 8 ml/min-cm²
 Rate of Band Advance --- 43 ± 4 cm/hr.

Resin --- Dowex 50W, X-8 (50-100 mesh)

Run Cycle Time

Feed Cycle --- Feed Dependent
 scrub cycle --- 16 hrs
 Elution Cycle --- 40 hrs.

TABLE 1: Flowsheet Changes When DTPA
IS Substituted For NTA

Eluting Solution

Concentration	-----	0.05 <u>M</u> DTPA
pH	-----	Buffered to 6.5 with NH_4OH
Volume	-----	2000 L
Flow Rate	-----	3.8 ml/min-cm ²

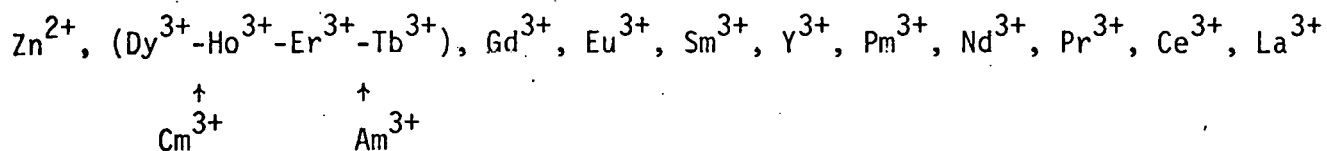
Scrub Cycles 2 and 3 can be eliminated.

Rate of Band Advance ---- 19 ± 3 cm/hr.

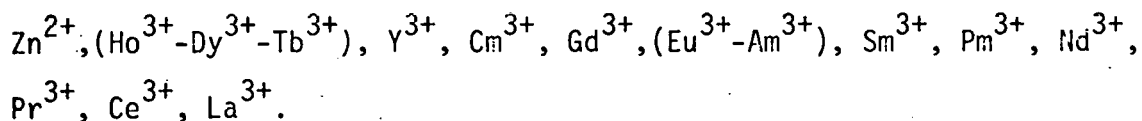
In the NTA flowsheet, 0.5 M NH_4NO_3 is used to remove H^+ from the feed absorption column prior to elution. If this is not done, the insoluble free-acid form of the chelating agent will form within the resin bed and completely block solution flow through the column. The free-acid form of DTPA is sufficiently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

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

With DTPA,



with NTA,



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 lanthanides. 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 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 4+ 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 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 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.

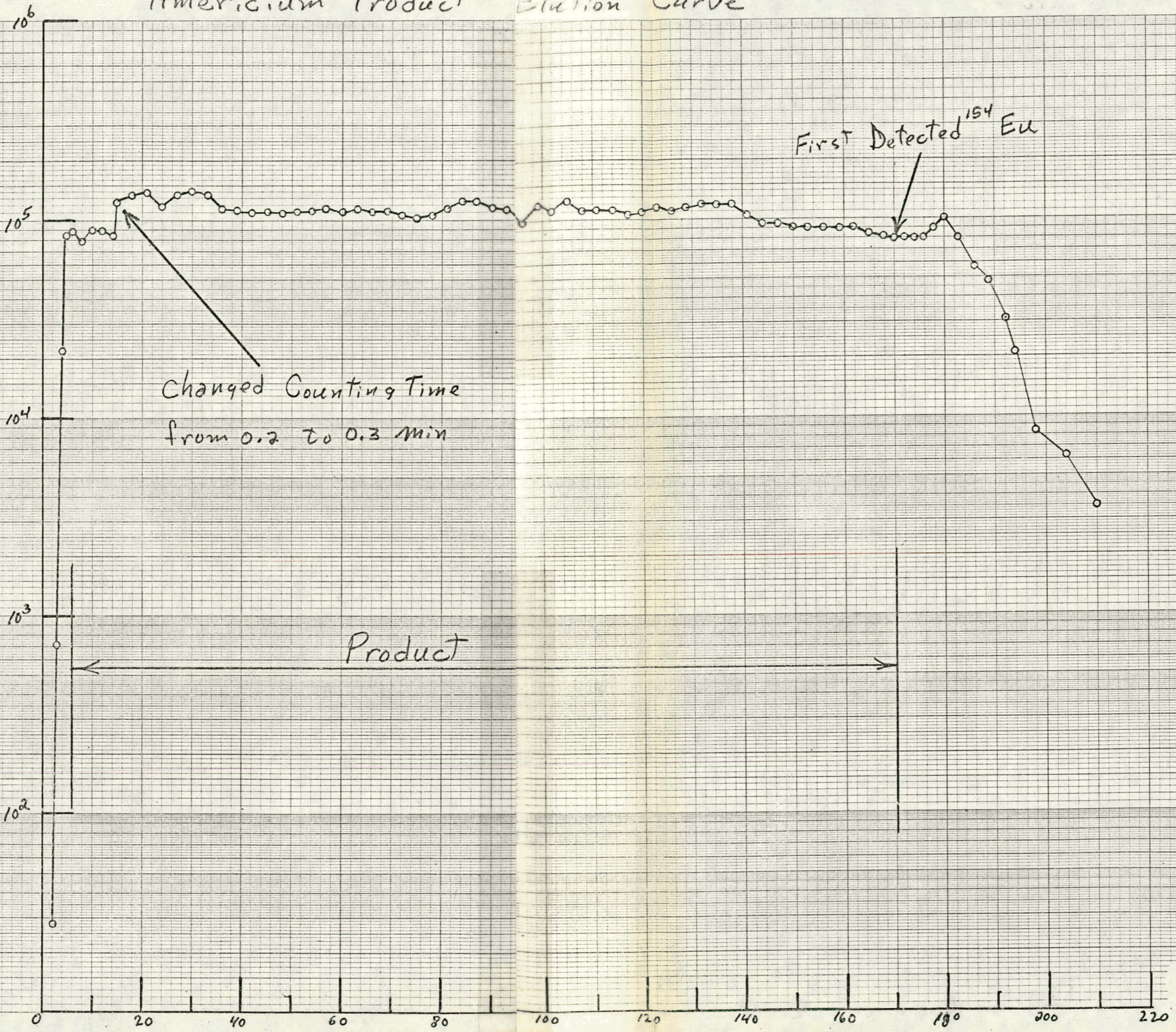
RECOVERY OF MIXED ^{241}Am - ^{243}Am FROM POWER REACTOR FUEL REPROCESSING WASTE

In 1967, 13.5 tons of Shippingport Power Reactor blanket elements were processed at the Hanford Redox Plant for the recovery of uranium, plutonium, and neptunium. A batch extraction process employing 50 vol % tri-n-butylphosphate in an n-paraffin hydrocarbon dilu^eant 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 M bis(2-ethylhexyl)phosphoric acid, and 0.3 M tri-n-butylphosphate in n-paraffin hydrocarbon was used to further decontaminate the lanthanide-actinide mix from Al, Fe, U, Pu,

Figure 3

Americium Product Elution Curve

Column Effluent Solution Concentration
(Counting rate - arbitrary scale)



Column Effluent Solution Volume (liters)

TABLE 2: Material Accountability for Production Runs

<u>Anion Exchange</u>	<u>Campaign 1</u>		<u>Campaign 2</u>		<u>Campaign 3</u>		<u>Campaign 4</u>	
	<u>Am</u>	<u>Pu</u>	<u>Am</u>	<u>Pu</u>	<u>Am</u>	<u>Pu</u>	<u>Am</u>	<u>Pu</u>
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
<u>Cation Exchange</u>								
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	
<u>Oxide Preparation</u>								
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.

Na, and other fission products (9). The solution was then cask transferred to the ion-exchange pilot-plant facility for final purification.

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-L resin bed for feed absorption, two identical DTPA runs were required for the processing because of the very large quantity of lanthanide fission products present in the feed solution. One NTA run was used to separate the americium from the 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.

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.

TABLE 4: Summation of Two-Cycle Pilot Plant Test

	<u>Americium</u>	<u>Curium</u>
Feed Solution	1080 g	60.5 g
Recycle Solution	218 g	14.2 g
Product Solution	760 g 99.7% pure	{ 29.2 g 97.8% pure 15.3 g 86% pure
Material Balance	91%	97%

FIGURE 4: PRODUCT ELUTION CURVE
DTPA CYCLE

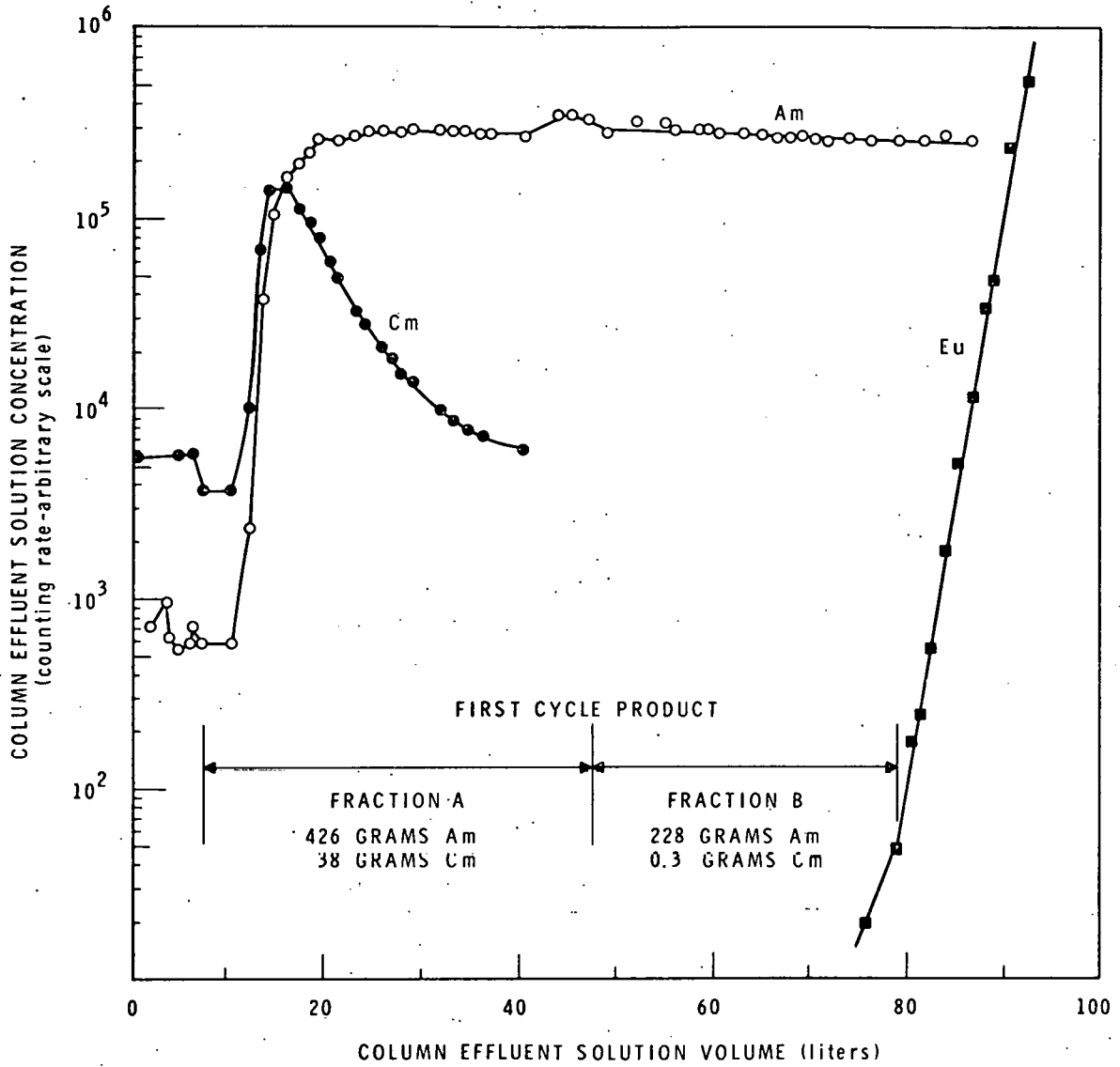
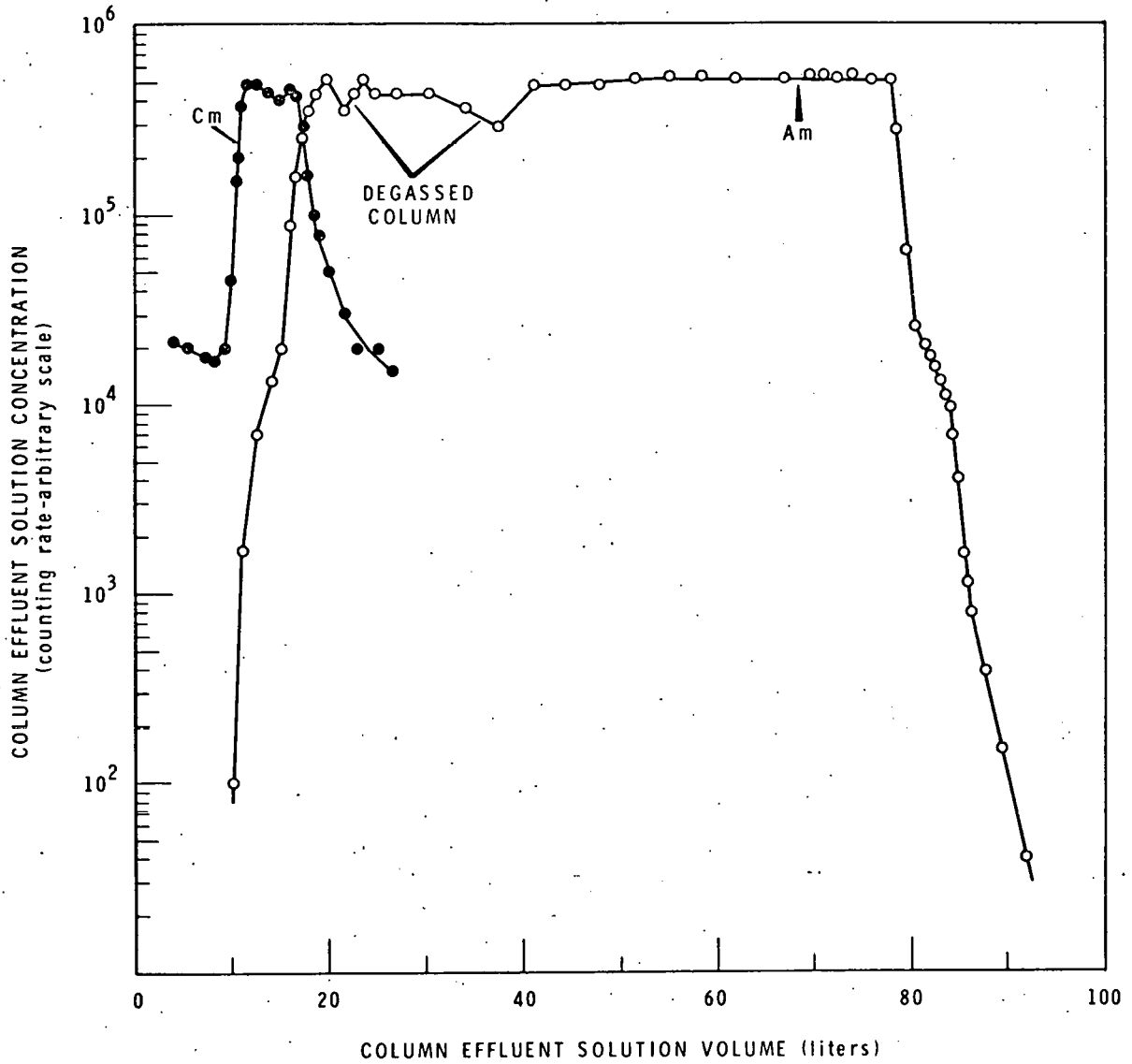


FIGURE 5: PRODUCT ELUTION CURVE
NTA CYCLE



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