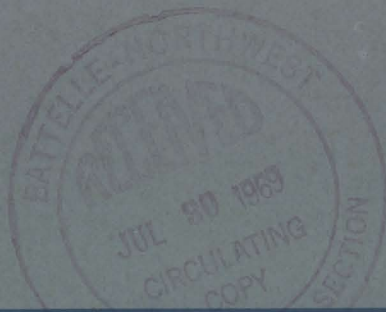


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THE USE OF ALTERNATING DTPA AND NTA  
CATION-EXCHANGE FLOWSHEETS  
FOR THE SIMULTANEOUS RECOVERY  
AND PURIFICATION OF Pm, Am, and Cm

July 1969



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By

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July 1969

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ABSTRACT

In the two-step cation-exchange separation process herein reported for the purification of Cm, Am and Pm, a change in the elution sequence of Am, resulting from the alternate use of two different eluting agents, is utilized to greatly enhance the Am-Cm purification efficiency. Unlike the many-cycle separation process previously used to purify americium and curium, this flowsheet does not require high concentrations of chloride and is, therefore, completely compatible with conventional stainless steel equipment. The process has been successfully demonstrated on a kilogram scale and the results are reported.

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INTRODUCTION

Numerous processes are reported in the literature for the separation of americium and curium from other radioactive and inert impurities and from each other. Most of the reported processes were designed and used for the separation of analytical tracer quantities of material and are not applicable to gram or multigram scale separations.

As part of the Atomic Energy Commission's transuranium program, processes have been developed at the Oak Ridge National Laboratory (ORNL) and separations facilities have been constructed to utilize the processes—the Transuranium Processing Plant (TRU) and the Curium Recovery Facility (CRF).<sup>(1-5)</sup> Separations facilities have been constructed at the Savannah River Laboratory (SRL) and proposals have been made to utilize adaptations of the ORNL processes for the recovery and purification of curium and americium.<sup>(6,7)</sup>

The ORNL flowsheet includes: 1) preparation of a feed solution by dissolution of irradiated targets, 2) removal and purification of plutonium, 3) decontamination of transplutonium elements from rare earth and other fission products, 4) separation of americium and curium from the transcurium actinides, and 5) separation of curium from americium. Initially, the plutonium removal step was accomplished by utilizing the nitric acid anion-exchange process developed at Hanford.<sup>(8,9)</sup> However, because subsequent

processing (item 3 above) requires a chloride system, the nitric acid anion-exchange process was replaced with a functionally similar process employing hydrochloric acid in order to avoid a nitrate to chloride intermediate conversion step.<sup>(2)</sup> The chloride anion-exchange system performed satisfactorily when tested in laboratory glass equipment, but when employed in the metal equipment used in TRU, chloride corrosion of the Zircaloy-2 equipment produced rapid reduction of plutonium to the unabsorbable trivalent state. At this point, ion exchange was abandoned in favor of solvent extraction utilizing 1M di (2-ethylhexyl) phosphoric acid in diethylbenzene. Then di-tert-butylhydroquinone is used to reduce the plutonium in the aqueous phase so it can be back-extracted into HCl.<sup>(3,4)</sup>

The Tramex (tertiary amine extraction) process is utilized to separate the transplutonium actinide elements from the fission products (item 3 above). This counter-current process employs 0.6M Adogen 364-HP (a high-purity trialkyl amine) plus 0.03M free HCl in diethylbenzene diluent to extract the actinides from 11M LiCl containing 0.2 to 0.3M HCl. Two problems are reported. Acid is rapidly destroyed by radiolysis and must be continually replenished. Radiolytic oxidation of cerium to the highly extractable tetravalent state takes place. This was initially corrected by the addition of SnCl<sub>2</sub> to the feed solution, but currently the organic-soluble reductant di-tert-butylhydroquinone is used.

In the ORNL process, the Tramex product is further processed to remove <sup>106</sup>Ru, <sup>95</sup>Zr-<sup>95</sup>Nb, and inert Zr, Cr, Fe, Ni, and Sn contaminants and to effect a separation of americium and curium from the other actinides by absorbing

the actinides and many of the contaminants on Dowex 1X-8 (200-300 mesh) resin from 12.5M LiCl. Most of the impurities are then removed by a 5 to 8 column-volume wash of 10M LiCl-0.1M HCl and the actinides are progressively eluted by successively lower concentrations of LiCl-0.1M HCl. Approximately 90% of the americium-curium is recovered free from other actinides with the remaining 10% associated with the heavier actinide fractions.

The final separation of americium from curium is accomplished by a carbonate precipitation.<sup>(3)</sup> This step is coupled to the previous ion-exchange step by precipitating americium and curium hydroxides from the lithium chloride ion-exchange product and dissolving the precipitate, in 0.5M HNO<sub>3</sub> after washing with ammonium hydroxide. This is then added to 5M K<sub>2</sub>CO<sub>3</sub>, the americium oxidized by K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and precipitated as the insoluble double carbonate, K<sub>5</sub>AmO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>. Due to radiolytic reduction of the americium, the precipitation is not complete. The precipitate contains approximately 98% of the americium contaminated by 2% of the curium. A reprecipitation is quite effective in lowering the cross contamination to 0.5 wt% of the other actinide.

As of May, 1968, 309 g of <sup>244</sup>Cm (plus associated trans-uranium elements) had been processed in 13 TrameX processing runs during 2 yr of operation of the TRU facility. The largest single batch contained 18 g of <sup>244</sup>Cm. Much of the equipment previously fabricated from glass, plastic, or Zircaloy-2 is being replaced by tantalum equipment to minimize the corrosion problems.<sup>(4)</sup>

The proposed SRL flowsheet<sup>(6)</sup> utilizes dissolution of the plutonium-aluminum target material, followed first by a tributyl phosphate counter current extraction for

plutonium removal and then a batch extraction with 50% tributyl phosphate for the separation of americium, curium, and the fission product rare earths from the large quantity of aluminum. Three cycles of Tramex are then proposed for the decontamination of americium and curium from the rare earths. The first cycle is used to convert from a nitrate to a chloride system. The Tramex product is then converted back to the nitrate system and a double carbonate precipitation, utilizing ozone as the oxidizing agent, is employed to separate americium from the curium.<sup>(7)</sup>

Displacement chromatographic separations processes, utilizing ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), and nitrilotriacetic acid (NTA) as eluting agents, have been developed and utilized at the Pacific Northwest Laboratory (PNL) for the separation, at high purity, of fission product promethium from all other contaminants.<sup>(9-11)</sup> In 1967, personnel of the Atlantic Richfield Hanford Company successfully recovered the americium, curium, and rare earth fission products from 13.5 tons of Shippingport Reactor Blanket elements. This dilute nitric acid solution contained 60 g of  $^{244}\text{Cm}$ , 1000 g of  $^{241}\text{Am}$  and  $^{243}\text{Am}$ , and 140 g of  $^{147}\text{Pm}$  contaminated by 10 wt% sodium and very minor amounts of other fission products and inert materials.<sup>(12)</sup>

This report summarizes both the development of a two cycle cation-exchange flowsheet and the successful utilization of that flowsheet in a PNL hot cell pilot plant (normally used for promethium purification) for the separation, at high purity, of the Shippingport americium, curium, and promethium from all contaminants and from each other.

SUMMARY AND CONCLUSIONS

The versatility of the displacement chromatographic separations process for the separation of both lanthanides and actinides has been convincingly demonstrated. The alteration of the elution sequence of various ions has been demonstrated and advantageously utilized in the adoption of alternate DTPA and NTA elution cycles for the separation and purification of curium, americium, and promethium.

The hot cell demonstration described herein shows conclusively that radiolysis effects upon cation exchange resin and the eluting agents used do not prohibit the use of this rather simple separations process for the purification of large quantities of curium-244 or americium-241. Subsequent utilization of NTA for promethium purification has shown that, because of much faster exchange kinetics, NTA can be pumped at twice the flow rate used in the demonstration here reported, thus, reducing radiolysis problems by a factor of two.

Radiolytic gas formation in the resin beds does disrupt the absorbed bands and lowers separation efficiency. In this work, periodic degassing was found to be effective in reducing this problem. It is reasonable to postulate that the problem of gas formation could be completely eliminated by designing the columns and equipment to operate at 150 to 200 psi. Except for very small scale separations there seems to be little advantage in going to very high pressure systems and very small resin mesh size. Kinetics in the NTA system are rapid enough at 60 °C that the absorbed band can be eluted at 30 to 40 cm/hr and maintain good separation efficiency. It should be pointed out that if a 1/2 in. diameter column capable of operation at 200 psi to prevent

resin bed disruption had been available for the final curium purification in this demonstration, a significantly higher fraction of the curium would have eluted in the pure heart fraction.

The striking advantage of the separation demonstrated herein is that conventional stainless steel equipment can be used rather than very expensive material like tantalum. In two cycles, employing the same equipment and differing only in the kind of eluting agent used, americium and curium can be separated from all other impurities and from each other. The same equipment can be utilized to purify other lanthanide or actinide elements.

The size and number of ion-exchange columns required depend upon both the quantity of material to be processed per run and upon the relative amounts of americium, curium, other actinides, lanthanides, and inert impurities (e.g., iron, aluminum, and sodium) in the feed solution. Optimum results are obtained in both the DTPA and NTA cycles by eluting the initially absorbed band through a series of successively smaller diameter columns containing a total resin volume of approximately 1.5 to 2.0 times the volume of resin in the initially absorbed band. With DTPA, optimum efficiency is obtained using 0.050M DTPA, buffered to pH 6.5 with  $\text{NH}_4\text{OH}$  and pumped through the column system at 4 ml/min-cm<sup>2</sup>. The kinetics in the NTA system are much faster and good results are obtained with 0.105M NTA, buffered to pH 6.5 with  $\text{NH}_4\text{OH}$  and pumped at 8 to 12 ml/min-cm<sup>2</sup>. Dowex 50W, X-8 (50 to 100 mesh) resin was used in this work. The columns should be jacketed and operated at 60 to 70 °C.  $\text{Zn}^{+2}$  is used as the barrier or restraining ion on the elution columns in both systems.



EXPERIMENTAL

The aminopolyacetic acid complexing agents have proved useful for the separation of the individual rare earth elements. The stability of complexes formed between the rare earths and many of the complexing agents have been measured and these values are useful in predicting the relative separation that can be achieved when the specific complexing agents are used for rare earth separations. However, much less attention has been given to actinide complexes. In some instances, the rare earth stability constants were measured under different conditions from the actinide measurements and the results are not completely comparable. Therefore, a series of ion-exchange separations experiments were performed with the eluting agents ethylenediaminetetraacetic acid (EDTA), hydroxyethylethylenediaminetriacetic acid (HEDTA), diethylenetriaminepentaacetic acid (DTPA), nitrilotracetic acid (NTA), and  $\alpha$  hydroxyisobutyric acid. In these experiments, small beds of Dowex 50W, X-8 (50 to 100 mesh) cation-exchange resin were loaded to saturation from feed solutions containing both macro quantities of the rare earths and radiochemical tracer quantities of americium and curium. In each experiment, the absorbed band was then eluted two band lengths\* down a second bed of the same resin in the  $Zn^{+2}$  or  $H^{+}$  cycle, depending upon the complexing agent used, and the effluent solution collected in fractions as the absorbed band was eluted from the second resin bed. The use of  $H^{+}$  or  $Zn^{+2}$  ions to form a barrier or restraining bed on the second resin bed is described elsewhere.<sup>(10,11)</sup> Each eluting solution was prepared at concentration and pH values shown by other work to be optimum for separation of the rare earth fission products.<sup>(10,11)</sup> The

---

\* The elution column contained twice the volume of resin as the absorption column.

columns were water jacketed and the temperature maintained at 60 °C. Sufficient analytical work was done to locate the relative positions of the maximum concentration of each ion. Identification and concentration measurements of the macro rare earth constituents were made by use of a Cary Model 14 spectrophotometer. The radiochemical tracers were determined by gamma energy analysis using a 3 by 3 in. NaI detector in conjunction with a 400 channel analyzer.

The effectiveness of these complexing agents for the separation of the rare earth elements has been established. The purpose of these experiments was to determine the elution positions of the actinide elements relative to the lanthanide series of elements. This would permit a meaningful postulation of the separation that could be expected, for a given eluting agent, of the actinides from each other and from the lanthanide fission products.

#### α HYDROXYISOBUTYRIC ACID ELUTION SEQUENCE

α hydroxyisobutyric acid has been successfully utilized for the separation of tracer or very small macro quantities of these elements, but the results obtained in this series of experiments were poor. The band or peak resolution was not good. Because of this and the high cost of the complexing agent, work with α hydroxyisobutyric acid was discontinued after two experiments.

#### EDTA ELUTION SEQUENCE

Fuger<sup>(13,14)</sup> used EDTA to perform several small scale separations of americium from curium. The same worker measured the stability of the EDTA complexes formed with americium and

curium. From these constants, a separation factor of 1.95 can be calculated.\* However, in our experiments with EDTA elutions, curium and americium were found to elute between samarium and gadolinium, in a position normally occupied by europium. Since a separation factor of 1.4 is calculated from the EDTA stability constants of samarium and gadolinium,<sup>(17)</sup> there is an inconsistency; perhaps partly caused by differences in temperature, solution concentrations and ionic strength. Laboratory work designed to improve the promethium purification flowsheet had shown that other aminopolyacetic acid complexing agents were able to achieve equal or better separation of the light rare earths at 3 to 5 times faster rates. Because of this and the anticipated difficulty of separating americium and curium from europium and from each other, additional work with EDTA was terminated.

#### HEDTA ELUTION SEQUENCE

Only a limited amount of work was done with HEDTA. Americium was found to elute ahead of gadolinium, in a position identical with that of dysprosium. The elution position of curium was not determined. Rather poor separation was achieved between gadolinium and samarium. This is not surprising. Examination of a plot of the stability constants versus atomic number, reveals that very little separation could be expected for the rare earth elements samarium through erbium with an elution distance of only two band lengths.<sup>(18)</sup> Further work with HEDTA was discontinued in favor of DTPA and NTA.

---

\* It has been shown that in ion-exchange systems of the kind being described that an approximate separation coefficient can be calculated from the ratio of the stability constants of the complexes formed between the complexing agent and the two ions involved.<sup>(15,16)</sup>

DTPA ELUTION SEQUENCE

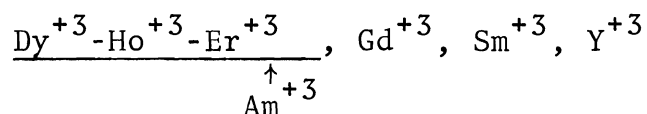
Baybarz measured the stability of the complexes formed between DTPA and the first five transplutonium elements,<sup>(19)</sup> and compared these values with those for the lanthanide series of elements.<sup>(20)</sup> These results are given in Table 1.

*TABLE 1. Stability of the Complexes Formed Between DTPA and Some Lanthanide and Actinide Elements*

<u>Element</u>	<u>Log K<sub>s</sub></u>
La <sup>+3</sup>	19.48
Ce <sup>+3</sup>	20.5
Pr <sup>+3</sup>	21.07
Nd <sup>+3</sup>	21.60
Sm <sup>+3</sup>	22.34
Eu <sup>+3</sup>	22.39
Gd <sup>+3</sup>	22.46
Tb <sup>+3</sup>	22.71
Dy <sup>+3</sup>	22.82
Ho <sup>+3</sup>	22.78
Er <sup>+3</sup>	22.74
Am <sup>+3</sup>	22.92
Cm <sup>+3</sup>	22.99
Bk <sup>+3</sup>	22.79
Cf <sup>+3</sup>	22.57

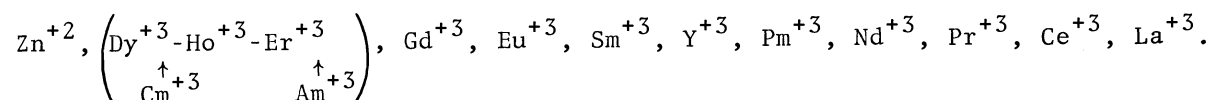
Observe that the lanthanide complexes show a steady increase in stability from lanthanum through dysprosium, but then pass through a maximum and decrease. Both americium and curium form more stable complexes than any of the lanthanides (with a separation factor from the lanthanides of at least 1.3) and should, therefore, elute ahead of any of the rare earths when DTPA is used as the eluting agent.

Two laboratory elution experiments served to define the elution behavior of americium and curium with respect to the middle lanthanides. In the first experiment, equimolar macro amounts of  $\text{Ho}^{+3}$ ,  $\text{Dy}^{+3}$ ,  $\text{Er}^{+3}$ ,  $\text{Gd}^{+3}$ ,  $\text{Sm}^{+3}$ ,  $\text{Y}^{+3}$ , and a radiochemical tracer of  $^{241}\text{Am}^{+3}$  were absorbed on a bed of Dowex 50W, X-8 (50 to 100 mesh) resin and eluted two band lengths down a second bed of the same resin in the  $\text{Zn}^{+2}$  cycle as described previously. The analytical results revealed the elution order to be:

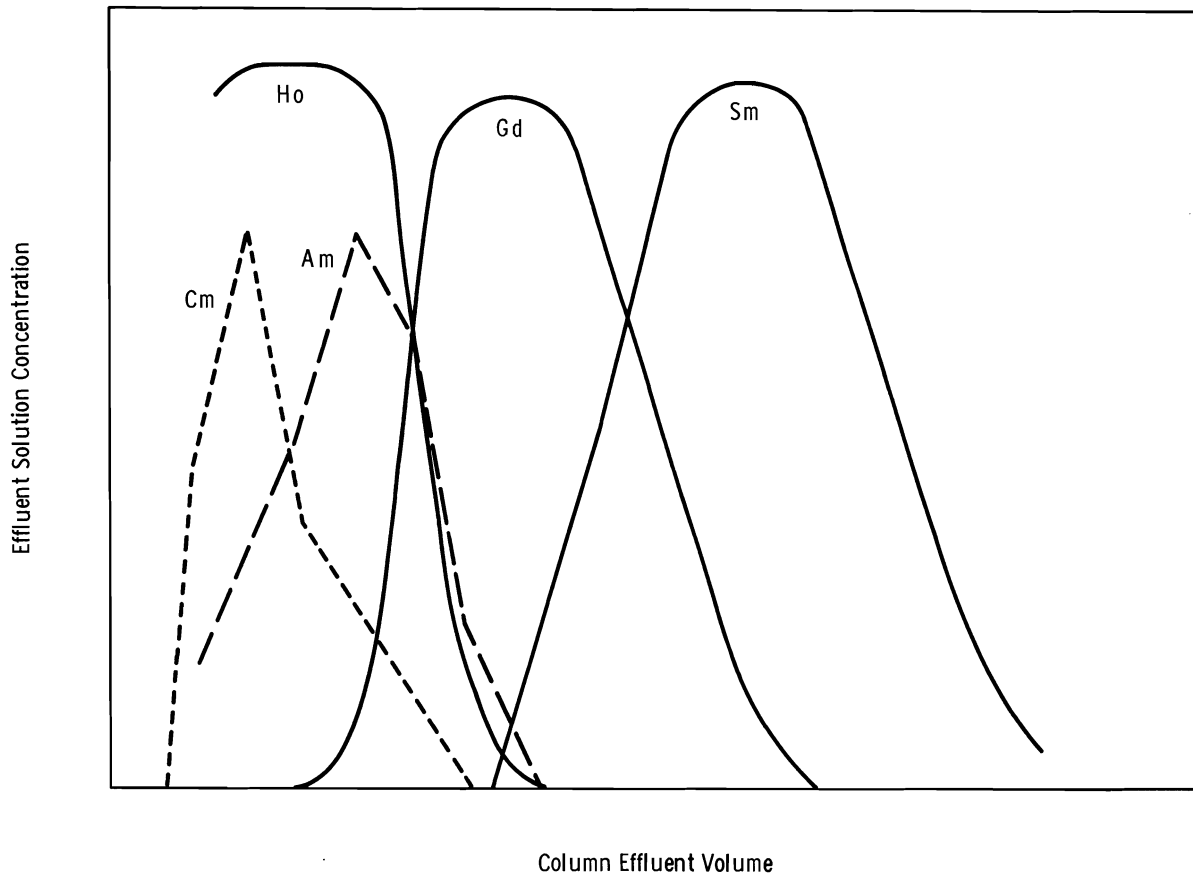


Because of the small separation factors involved,  $\text{Dy}^{+3}$ ,  $\text{Ho}^{+3}$ , and  $\text{Er}^{+3}$  could not be separated from each other in the elution distance used. The americium tracer was superimposed on the gadolinium edge of the unseparated triad.

In the second experiment, macro amounts of  $\text{Ho}^{+3}$ ,  $\text{Gd}^{+3}$ , and  $\text{Sm}^{+3}$  with tracer quantities of  $^{241}\text{Am}^{+3}$  and  $^{244}\text{Cm}^{+3}$  were eluted in a similar manner. Analysis of the elution fractions yielded the elution curve shown in Figure 1. From this and previous DTPA experience with the other rare earths, the elution sequence for 0.050M DTPA, buffered to pH 6.5 with  $\text{NH}_4\text{OH}$  can be stated to be:



Unfortunately, the position of terbium was not defined. However, since the terbium-gadolinium separation coefficient is 1.8 while the terbium-dysprosium separation coefficient is only 1.2 and the dysprosium-erbium mixture, with a separation



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FIGURE 1. Separation with DTPA of Ho, Gd, and Sm Containing Tracer Amounts of  $^{244}\text{Cm}$  and  $^{241}\text{Am}$

coefficient of 1.2, could not be separated in an elution distance of two band lengths, it seems probable that terbium would also elute in the inseparable group and thus not be easily separated from americium or curium by elution with DTPA. Fortunately, terbium is near the end of the fission product spectrum and very little will be found in any americium-curium feed solution. The transterbium lanthanides are present in only trace amounts.

James reports that  $\text{Th}^{+4}$  elutes ahead of  $\text{Zn}^{+2}$  in the DTPA system<sup>(21)</sup> and Wheelwright found that  $\text{Pu}^{+4}$  also passed through a  $\text{H}^{+}$  restraining ion when DTPA was used as the eluting agent.<sup>(22)</sup> Though this has not been verified with the higher concentrations



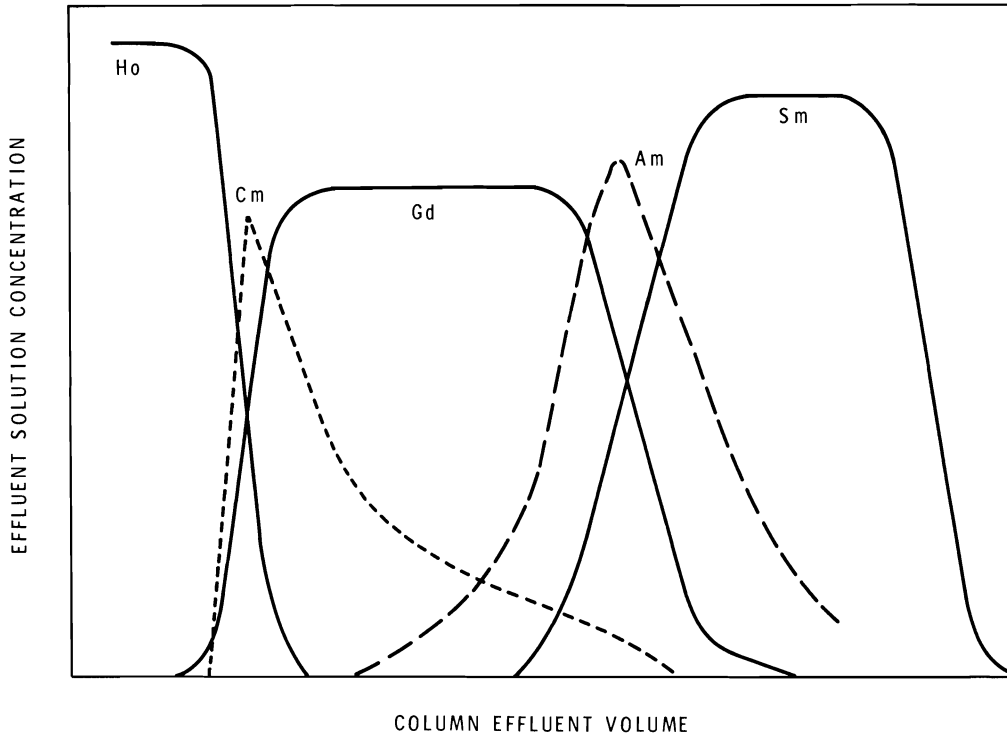
of DTPA now used with a  $Zn^{+2}$  restraining ion, it appears reasonable to postulate that  $Th^{+4}$ ,  $Pu^{+4}$ , and  $Fe^{+3}$  (the elution position of  $Fe^{+3}$  was verified many times during hot cell  $^{147}Pm$  purification), if present in the feed solution, form stronger complexes with DTPA than does  $Zn^{+2}$  and thus immediately pass through the restraining ion bed when DTPA elution is initiated.

#### NTA ELUTION SEQUENCE

Although eight experimental elutions were performed with NTA, the results from two of these are sufficient to substantiate the elution sequence. In the first experiment, macro amounts of  $Ho^{+3}$ ,  $Gd^{+3}$ , and  $Sm^{+3}$  plus tracers of  $^{241}Am^{+3}$  and  $^{244}Cm^{+3}$  were eluted by the standardized procedure. The effluent samples were analyzed and the results are shown in Figure 2. The second experiment was exactly like the first except that  $Y^{+3}$  was included in the feed. The results from this run are shown in Figure 3.

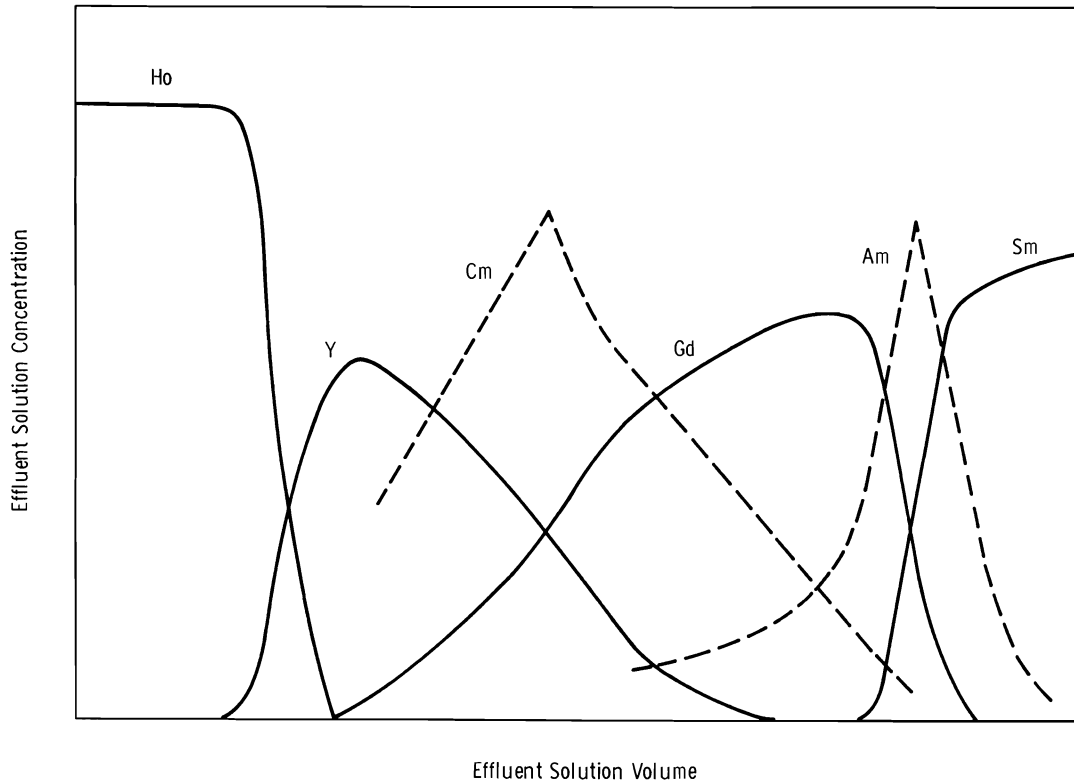
Figure 3 shows that with the NTA conditions used, the holmium-yttrium separation is reasonably good as is the gadolinium-samarium separation. However, the yttrium-gadolinium separation is quite poor. From this, we deduce that since curium eluted between yttrium and gadolinium, curium does elute ahead of gadolinium in the sequence, but the separation coefficient between them is probably small (less than 1.4). Again, the elution sequence of terbium was not experimentally defined, but from the NTA stability constants measured by Levy,<sup>23</sup> separation factors can be calculated as follows:

holmium-dysprosium-----1.05  
 dysprosium-terbium-----1.07  
 terbium-gadolinium-----1.66.



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FIGURE 2. Separation with NTA of Ho, Gd, and Sm Containing Tracer Amounts of  $^{244}\text{Cm}$  and  $^{241}\text{Am}$

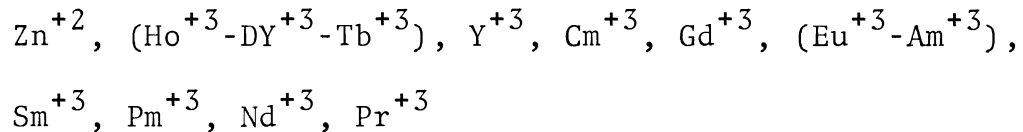


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FIGURE 3. Relative Elution Sequence of Y During NTA Elution

It is reasonable that holmium, dysprosium, and terbium could easily be separated from gadolinium in an elution distance of two band lengths, but would not separate from each other.

Hot cell experience in promethium purification has repeatedly shown that yttrium elutes on the front edge of gadolinium and that americium and europium elute together with no separation between them. On the basis of these conclusions, the elution sequence for 0.105M NTA buffered to pH 6.5 with  $\text{NH}_4\text{OH}$  is:



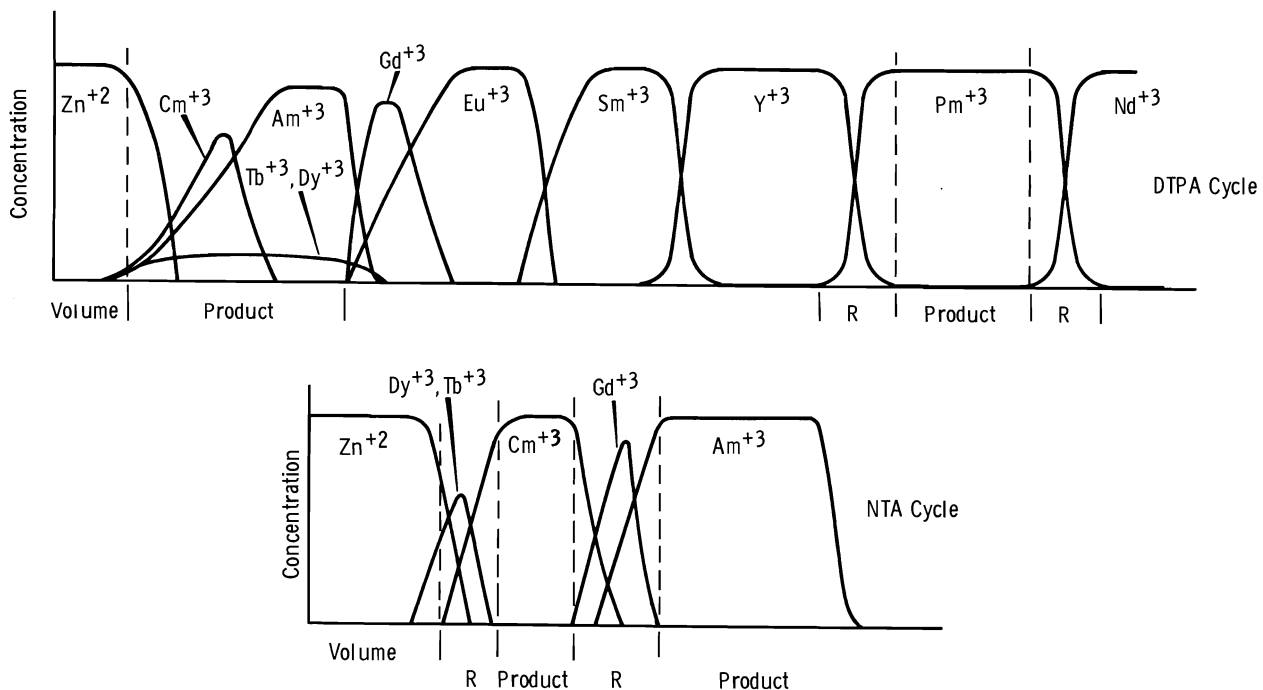
#### PROPOSED TWO-CYCLE FLOWSHEET

The elution sequences for DTPA and NTA suggest that the two eluting agents complement each other for the purification of curium and americium. With DTPA, americium and curium could be expected to elute between the restraining barrier ( $\text{Zn}^{+2}$ ) and gadolinium, in a region where only very small amounts of transgadolinium lanthanide fission products exist. Thus, with DTPA a relatively clean americium-curium fraction could be isolated (contaminated only by small amounts of dysprosium, terbium, and gadolinium) with excellent separation from europium, yttrium, and all other impurities. Then an elution with NTA would essentially move americium into the position previously occupied by europium and in effect greatly increase the separation coefficient between americium and curium. If a good separation of americium from gadolinium could be achieved in the DTPA cycle, curium and americium would elute next to each other

in the NTA cycle. If the first-cycle americium-curium product contained a small amount of gadolinium, then the gadolinium would elute between the two actinides during the NTA cycle.

With fairly good separation efficiency anticipated between curium and terbium or dysprosium in the NTA system, minor amounts of these two fission products would be found between the zinc barrier and the leading edge of the curium band.

In Figure 4, simulated elution curves depict the proposed two-cycle flowsheet. Promethium would be recovered from the DTPA cycle in two solutions—a pure product and a recycle solution containing yttrium, promethium, and neodymium.



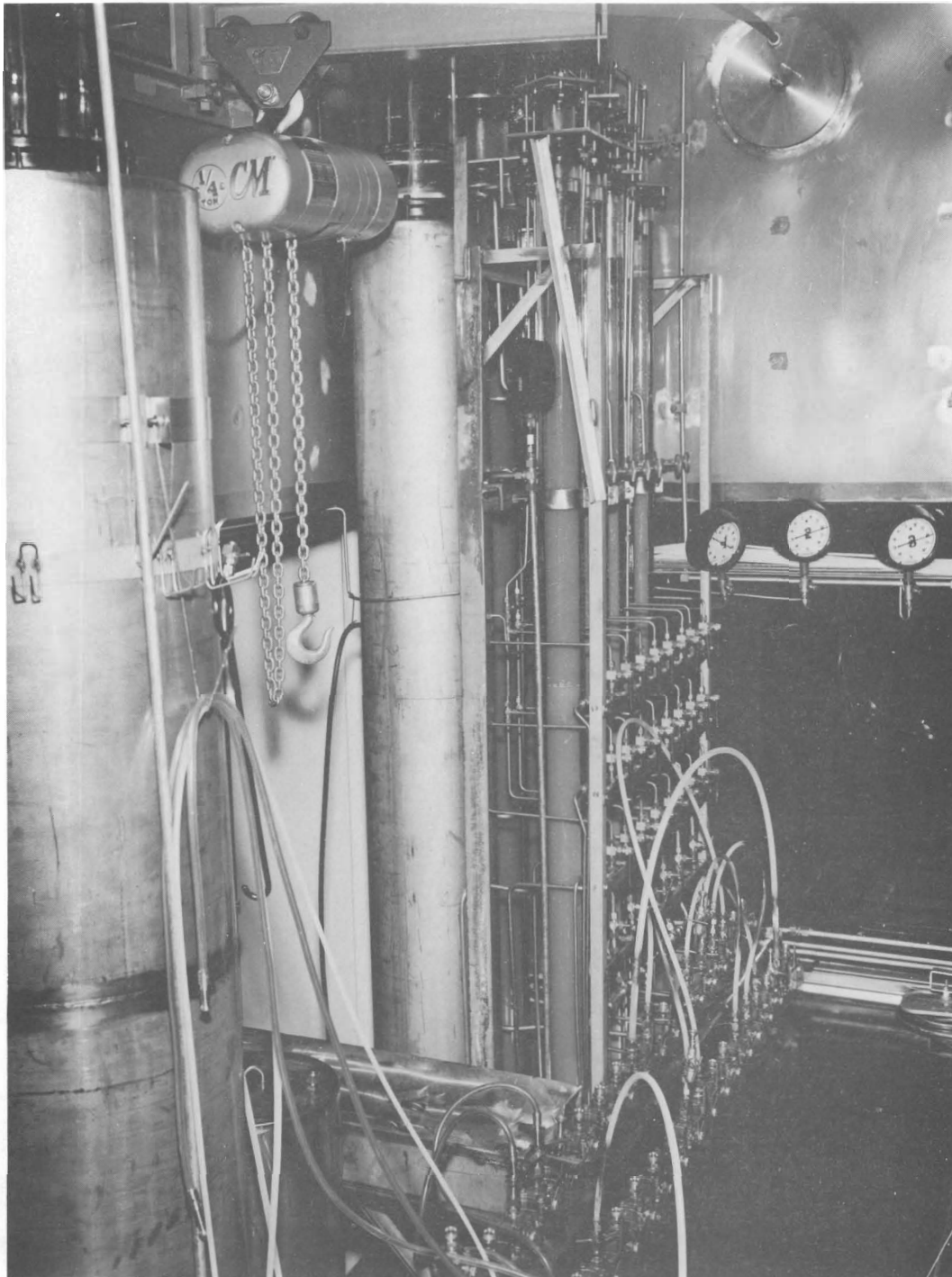
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**FIGURE 4.** *Simulated Elution Curves of Proposed Two-Cycle Flowsheet*

PILOT PLANT DEMONSTRATIONION-EXCHANGE EQUIPMENT

During 1965, a pilot plant, consisting of seven 9 foot high water-jacketed ion-exchange columns, ranging from 8 to 1 in. ID, plus associated tanks, pumps, and instrumentation was installed in one of the hot cells at the Pacific Northwest Laboratory.<sup>(10)</sup> Some of the hot-cell ion-exchange equipment is shown in Figures 5, 6, and 7. Figure 5 views two of the stainless steel columns and several of the smaller glass columns. Figure 6 views the manipulator working area and Figure 7 shows the solution control valves. Immediately prior to the americium-curium purification, two additional columns (one 14 and the other 11 in. ID) of the same height and general design were added to the system. Materials of construction are essentially stainless steel, glass and polyethylene. Except for the americium-curium demonstration, this facility has been in continuous use for the purification of fission product promethium.

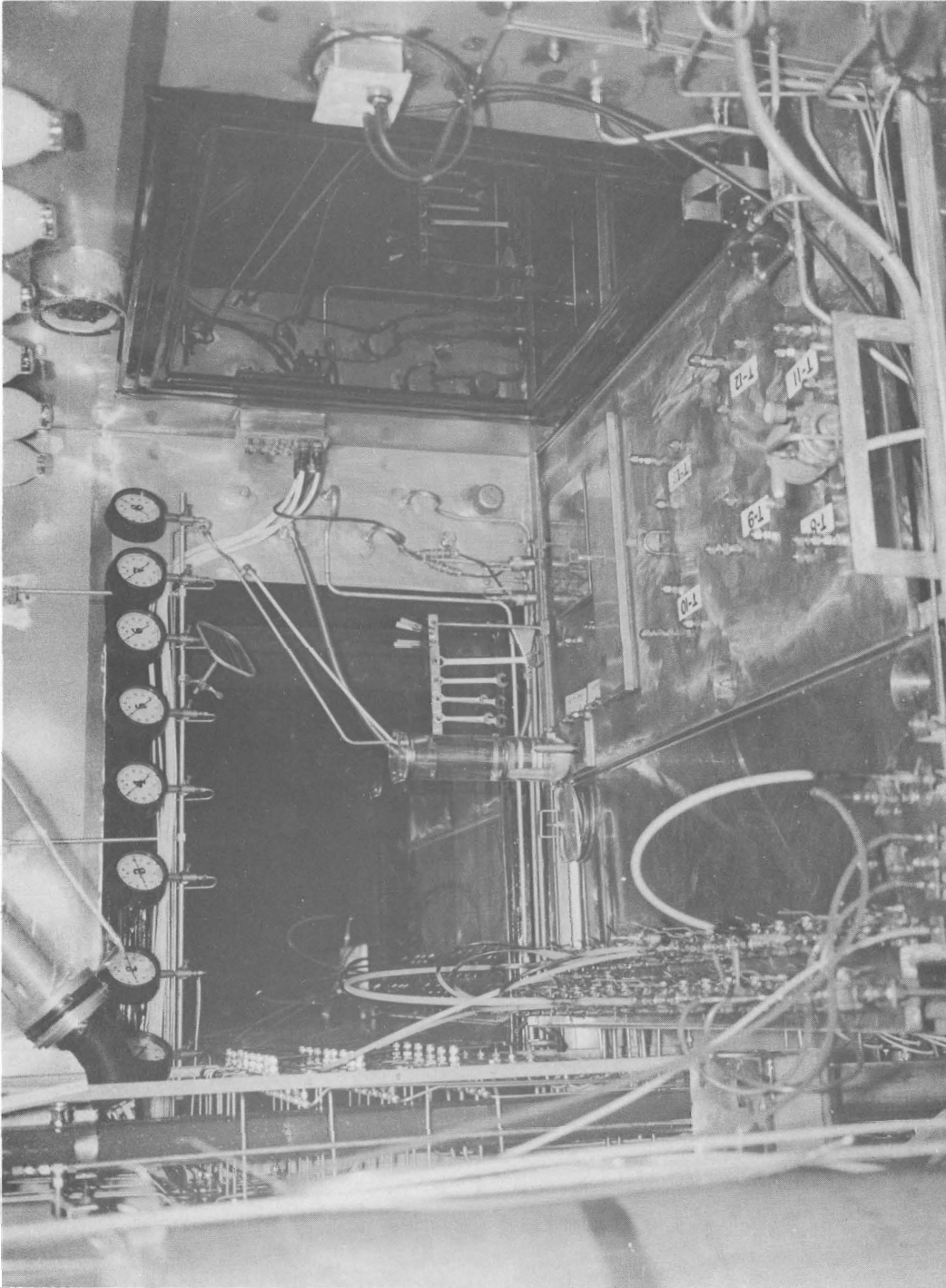
The instrumentation includes two particularly useful units: an in-cell gamma spectrometer, which can "read" both individual samples and in-line streams,<sup>(24)</sup> and an automated optical spectrometer for in-line monitoring.<sup>(25)</sup> The sensing units of both spectrometers are in the shielded cell and the instrumentation in the operating gallery. The piping arrangement is such that one or more columns can be connected together in series by the use of flexible polyethylene jumpers, with in-line instrumentation sensing units interposed between them.



*Neg 0652130-5*

*FIGURE 5. Glass and Stainless Steel Ion-Exchange Columns Installed in PNL Hot Cell*



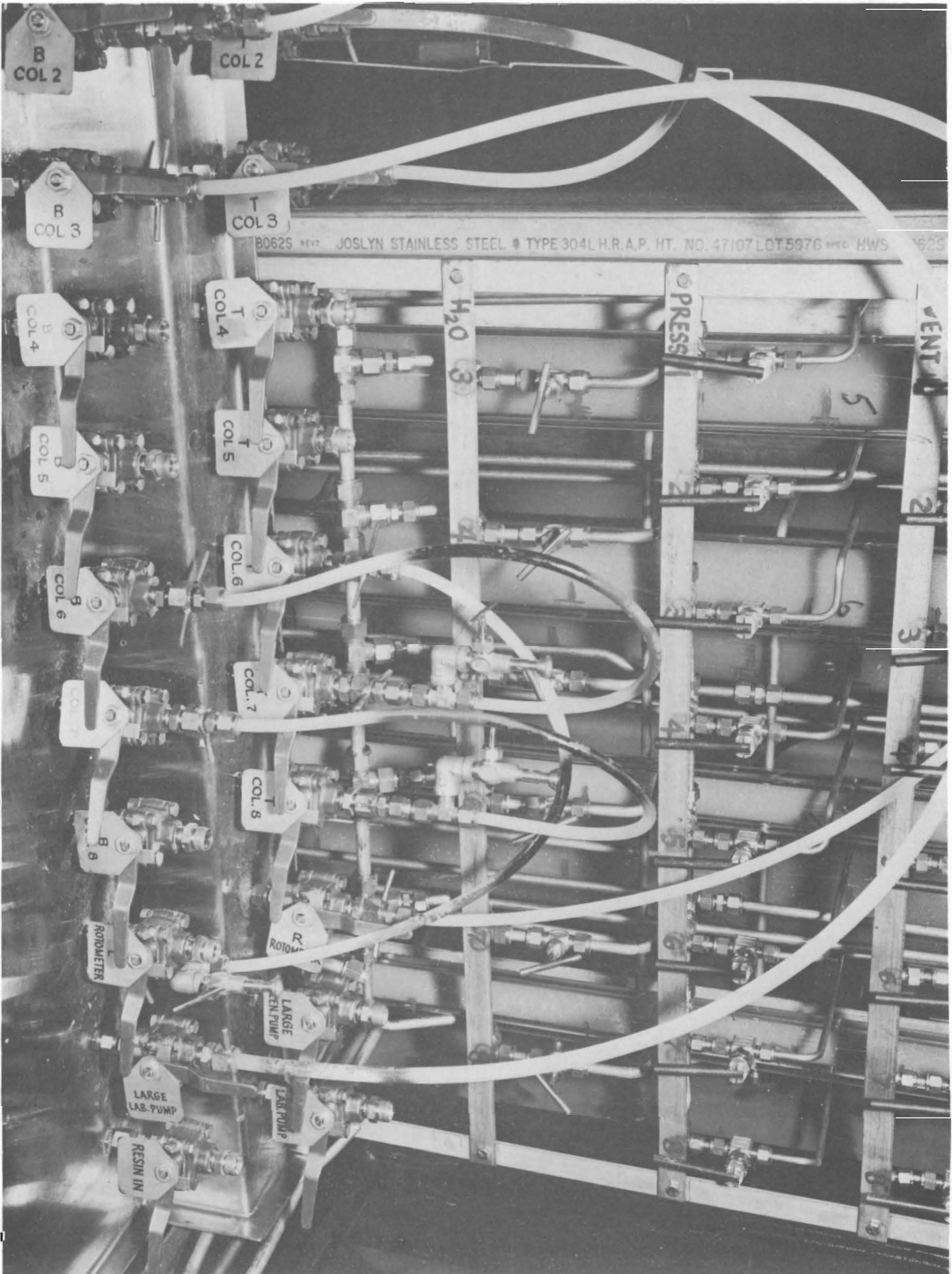


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FIGURE 6. Manipulator Working Area; PNL Ion-Exchange Pilot Plant

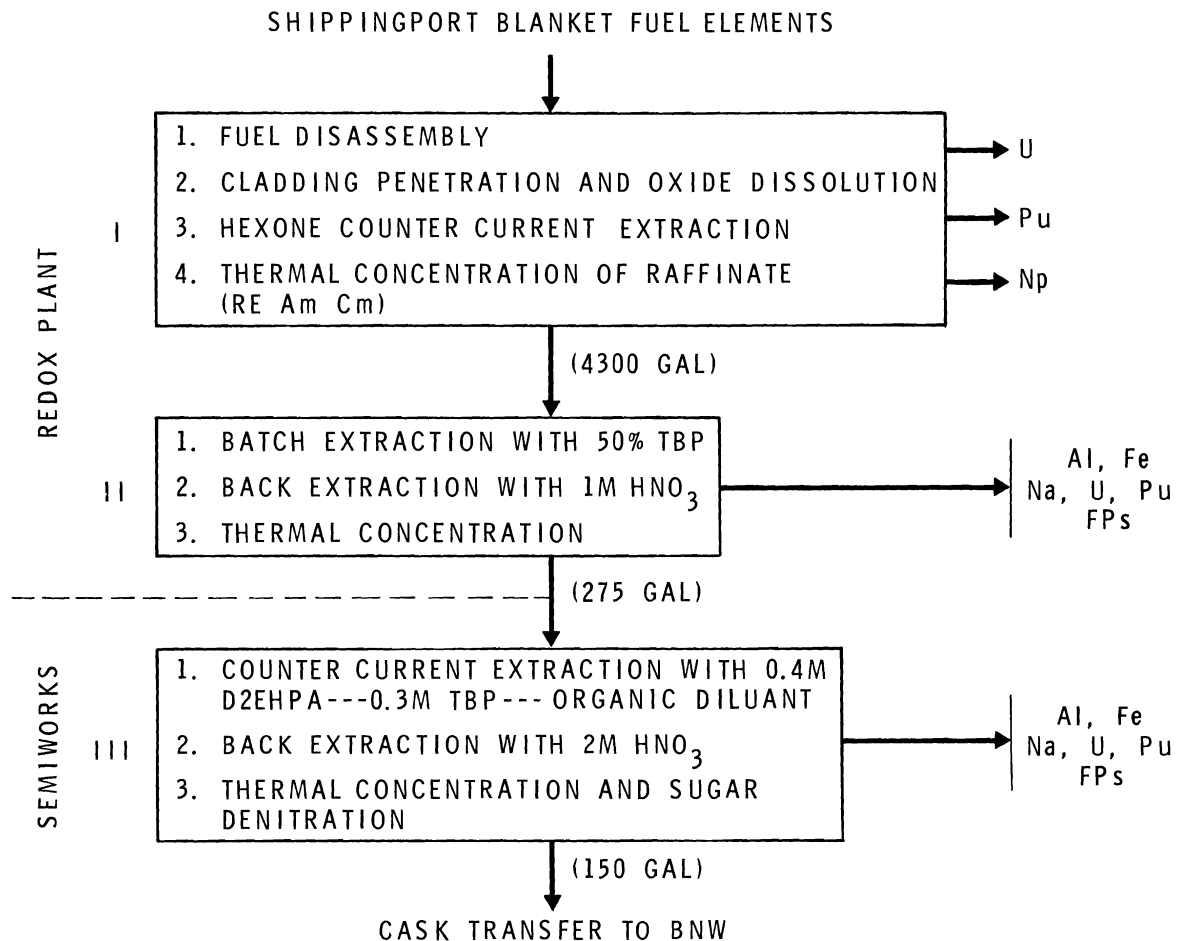
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FIGURE 7. Solution Control Valves with Polyethylene Jumpers; PNL Shielded Ion-Exchange Pilot Plant



FEED AND EQUIPMENT PREPARATION

Figure 8 and Table 2 summarize the recovery and decontamination of the actinides and lanthanides from the Shippingport Blanket elements performed by Atlantic Richfield Hanford Company. The 150 gal solution identified as "Semiworks Product," Table 2, was transferred in a 20-ton shielded cask to the High Level Radiochemistry Facility at the Pacific Northwest Laboratory which contains the ion-exchange pilot plant.



Neg 0680918-1

FIGURE 8. Atlantic Richfield Hanford Company Recovery of Shippingport Products

TABLE 2. Summary of ARHCO Processing

	<u>Shippingport Waste</u>	<u>Redox Product</u>	<u>Semiworks Product</u>
Volume	4300 gal	275 gal	150 gal
Cation Composition (wt% excluding H <sup>+</sup> )			
Cm	0.0034	0.093	0.18
Am	0.062	1.70	3.22
Rare Earth	1.4	45.2	85.8
Na	43.0	7.0	10.6
Al, Fe, Cr	54.0	27.0	0.14
U	1.7	19.0	0.0057

Because of the large quantity of trivalent lanthanide fission products associated with the americium and curium, two identical DTPA separation runs were required to process the "Semiworks Product." The run size was limited by the absorption capacity of the 240 liter resin bed used for feed absorption. No feed adjustment was required prior to the feed absorption step. Table 3 summarizes the column equipment used for the two DTPA runs.

TABLE 3. Column Equipment and Flowsheet for the Two DTPA Separations

<u>Column Number</u>	<u>Column ID, cm</u>	<u>Resin Bed Volume, liters*(a)</u>	<u>Resin Exchange Cycle</u>	<u>Column Function</u>
1	34.3	240	H <sup>+</sup>	Feed Absorption
1A	26.5	192	Zn <sup>+2</sup>	Elution
2	21.1	94	Zn <sup>+2</sup>	Elution
3	16.2	52	Zn <sup>+2</sup>	Elution
4	10.8	23	Zn <sup>+2</sup>	Elution
5	7.6	12	Zn <sup>+2</sup>	Elution
6	5.1	4.8	Zn <sup>+2</sup>	Elution
7	2.5	1.3	Zn <sup>+2</sup>	Elution

Elution Temperature---60 °C

Elution Flowrate-----3.8 ml/min-cm<sup>2</sup>(b)

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

Eluting Solution-----0.050M DTPA buffered to pH 6.50  
with NH<sub>4</sub>OH

a. Resin volume measured on H<sup>+</sup> cycle resin settled in water.

b. Based on cross sectional area of the smallest diameter column in use in the series.

DTPA FIRST CYCLE RUNS

A little over one half of the feed solution was pumped down-flow through the feed absorption column at a rate of 2 liters/min. This was followed by a 250 liter, distilled-water wash to remove unabsorbed ions from the resin bed. No feed activity was observed in the effluent solution during these two steps. The feed absorption column was then connected in series with the first elution column and the elution initiated by starting the flow of DTPA solution. A constant temperature was maintained by pumping the DTPA solution through a preheater prior to entrance into the hot cell and by circulating thermostated water through the water jackets on each column. At a predetermined\* volume of eluting solution the flow was temporarily interrupted and the next smaller diameter elution column was added to the series with an inline gamma spectrometer flow-cell interposed between them. The flow was then restored and maintained at the same rate until the gamma cell indicated an activity breakthrough. The flow rate was then reduced to correspond to the cross sectional area of the second elution column. In a similar manner, successive columns were added to the series.

By the time the front edge of the absorbed band reached the middle of column number 4, the gamma cell at the bottom of column number 1A revealed that all of the curium, americium, europium, and promethium had passed that point, but little or no cerium had reached that point. The flow was then interrupted long enough to disconnect column numbers 1 and 1A.

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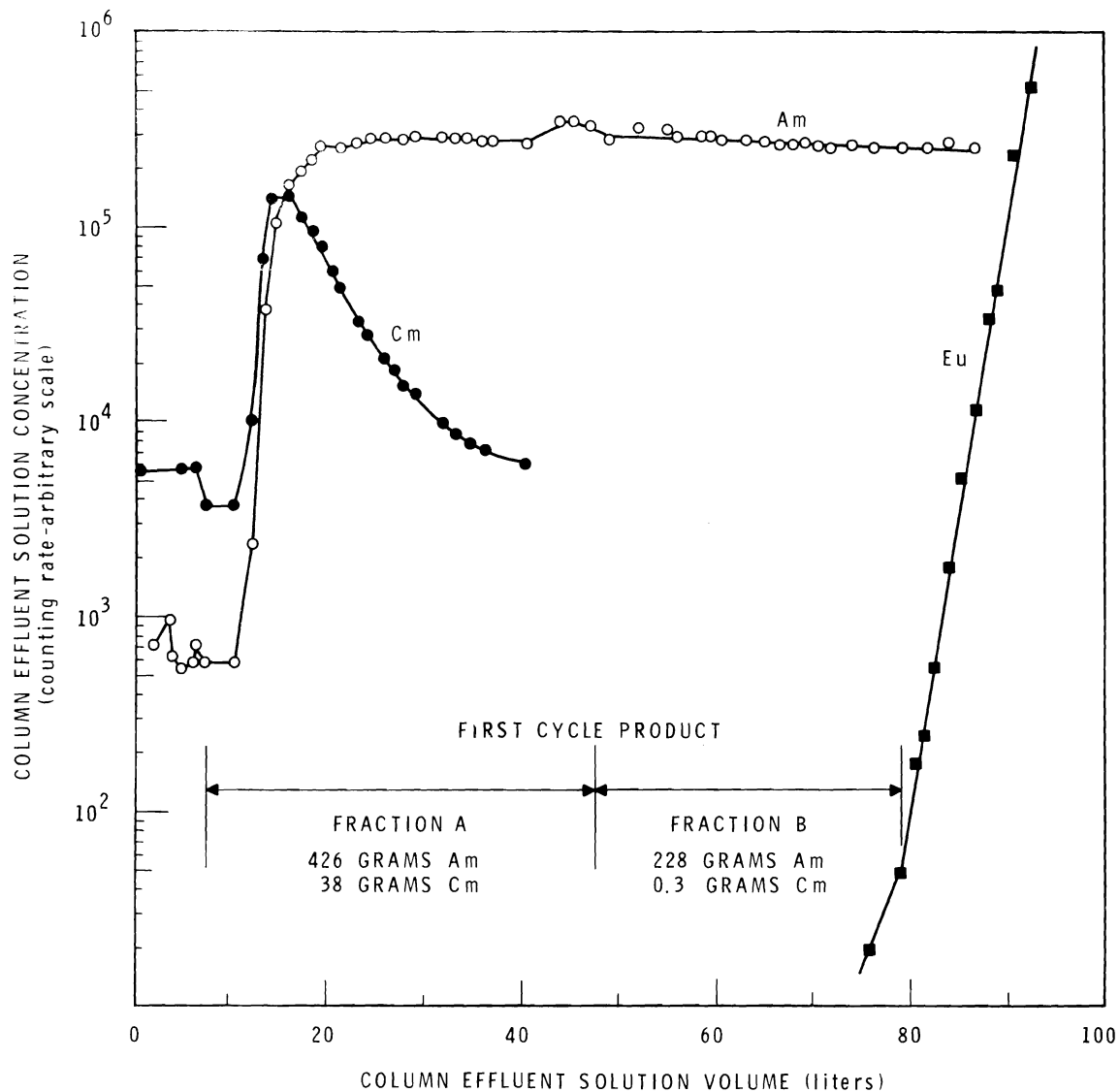
\* *The volume that previous experience had shown would move the front edge of the absorbed band approximately two-thirds of the distance down the first elution column.*

These columns were then rapidly stripped free of absorbed lanthanides (particularly the high energy yielding  $^{144}\text{Ce}$ - $^{144}\text{Pr}$ ) with  $4.5\text{M HNO}_3$  at the same time that the DTPA elution of the other columns continued.

As the front edge of the absorption band approached the bottom of column number 6, the effluent solution was collected in fractions and monitored continuously with both the optical and gamma spectrometers. The various "bands" of ions were thus identified and properly segregated as they appeared at the bottom of the column. Figure 9 shows the americium-curium product elution curve from the first DTPA purification run and Figure 10 gives the elution curve from the second DTPA purification run. The tail-end of the americium band from the first DTPA run (contaminated with gadolinium and europium) was recycled back to the feed for the second run. The data points shown in Figures 9 and 10 are counting rates at specific gamma energies obtained from the in-cell gamma spectrometer. The europium breakthrough shown in these two figures was very sharp and continued to increase through two additional orders of magnitude before reaching a plateau value. Gadolinium could not be detected in the product fractions from either run, but was found in the europium contaminated americium tail fraction from the second run (the corresponding fraction from the first run was not analyzed). As suspected, the separation of gadolinium from europium is rather poor with DTPA and since the gamma detection limit of  $^{154}\text{Eu}$  is quite low, europium could be detected before any significant amount of gadolinium appeared in the column effluent solution.

After Cm, Am, Gd, Eu, and Sm had been removed from the columns, column number 7 was added to the system to "sharpen up" the promethium band. The promethium "band" from each run was collected in a manner similar to that described for the americium and curium.

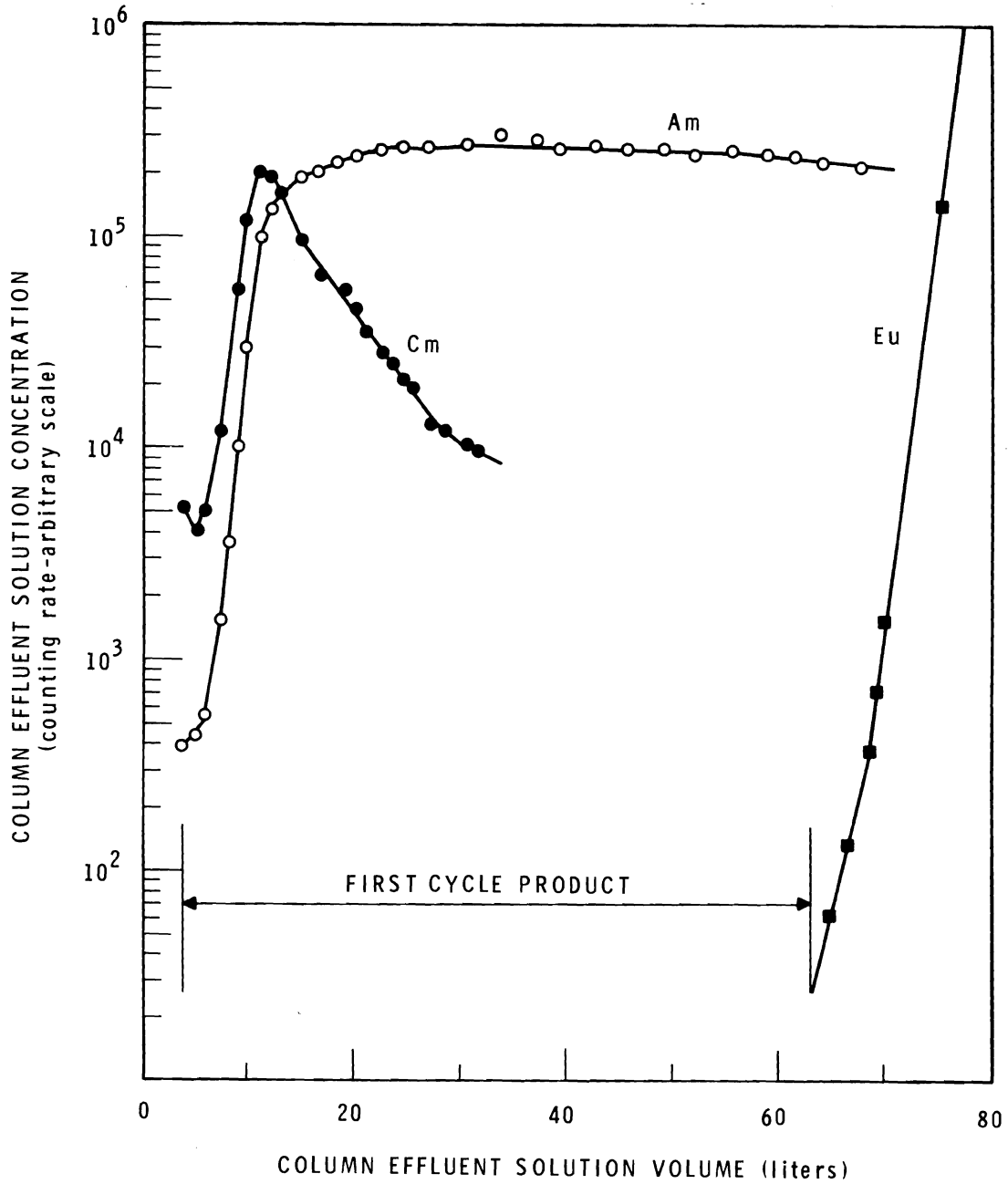




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FIGURE 9. Product Elution Curve; First DTPA Purification Run

The americium-curium first cycle product fraction A from the first DTPA run was then combined with the first cycle product from the second DTPA run and acidified in preparation for the NTA Cycle. Table 4 summarizes the equipment and flowsheet used for the NTA cycle.



Neg 0680857-14

FIGURE 10. Product Elution Curve; Second DTPA Purification Run

TABLE 4. Column Equipment and Flowsheet for the NTA Separations

<u>Column</u>	<u>Column</u>	<u>Resin</u>	<u>Resin</u>	<u>Column</u>
<u>Number</u>	<u>ID,</u>	<u>Bed</u>	<u>Exchange</u>	<u>Function</u>
	<u>cm</u>	<u>Volume,</u>	<u>Cycle</u>	
		<u>liters</u>		
4	10.8	23	H <sup>+</sup>	Feed Absorption
5	7.6	12	Zn <sup>+2</sup>	Elution
6	5.1	4.8	Zn <sup>+2</sup>	Elution
7	2.5	1.3	Zn <sup>+2</sup>	Elution
8	2.5	1.3	Zn <sup>+2</sup>	Elution

Elution Temperature---60 °C

Elution Flowrate-----6 ml/min-cm<sup>2</sup>

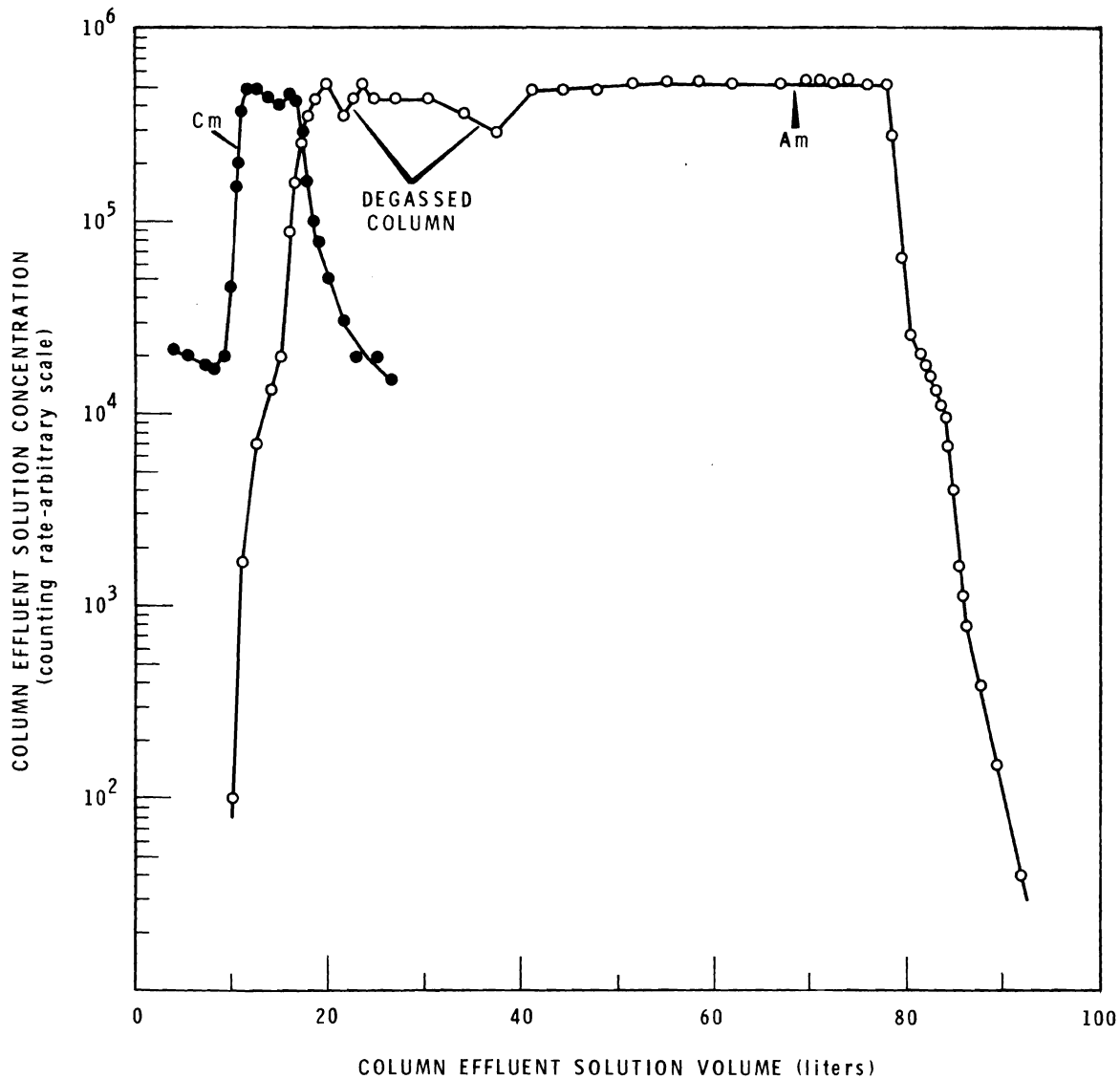
Resin-----Dowex 50W, X-8(50 to 100 mesh)

Eluting Solution-----0.105M NTA, buffered to pH 6.50  
with  $\overline{\text{NH}}_4\text{OH}$ .

#### NTA SECOND CYCLE RUN

The NTA elution progressed in a manner similar to the DTPA separation. As the actinide band reached the bottom of column number 8, liter fractions were collected until essentially all of the curium had been removed from the column system. Then the product was collected in two 60-liter stainless steel tanks. The NTA elution curve is shown in Figure 11.

One interesting phenomenon was observed with the inline gamma spectrometry. Neptunium-239, a daughter of <sup>243</sup>Am has a gamma spectra almost indistinguishable from the spectra of <sup>244</sup>Cm. In addition, its chemistry in both the DTPA and NTA systems is such that it moved down-flow from the absorbed band without noticeable reabsorption at a concentration proportional to the <sup>243</sup>Am content of the absorbed band. As a result, curium could not be counted at levels lower than those shown in Figures 9, 10, and 11.



Neg 0680857-15

FIGURE 11. Product Elution Curve; NTA Cycle

Substantial amounts of radiolytic gas did develop in the resin beds during each of the three separations runs. This is not surprising at a power density exceeding 400 W/liter of resin in the pure curium absorption band. Frequent degassing was required to prevent the resin beds from going dry. The discontinuity in the curium plateau was the result of a rather large amount of gas passing through the gamma

detector. Following removal of most of the curium, the final column was twice degassed by a blow-down-refill procedure.<sup>(9,10)</sup> Radiolytic gas formation in the resin beds is troublesome, but can be tolerated. Higher flow rates and operating pressure would minimize or eliminate this problem.

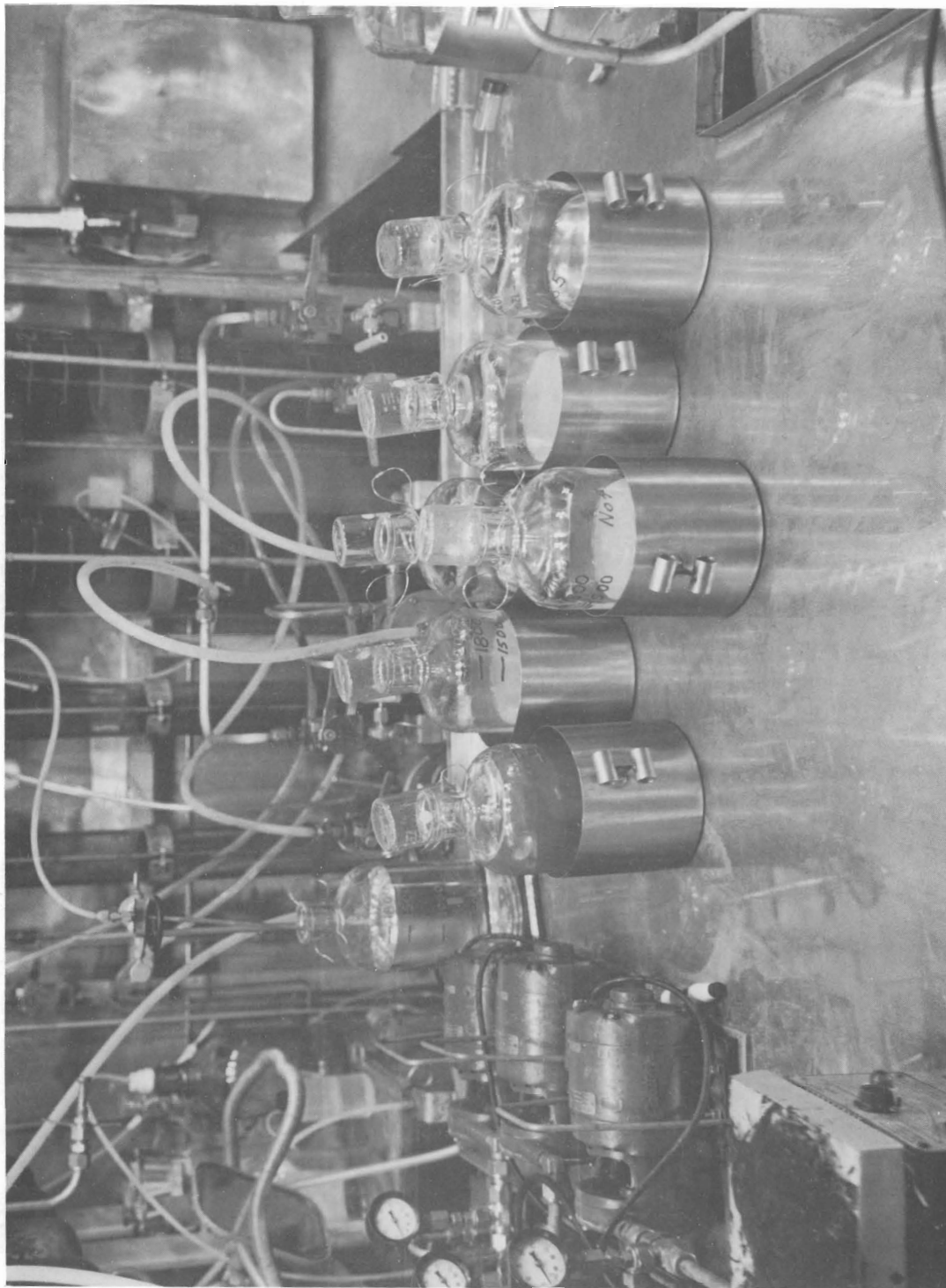
Some of the curium product fractions are shown in Figure 12. Small stainless steel buckets were used as secondary containers for the 2 liter Pyrex glass bottles. As a result of the radiolytic energy released, 300 to 400 ml of water evaporated from each bottle every 24 hr. In the first 24 hr, the complexing agent was completely destroyed and the product precipitated as carbonate. Careful acidification dissolved the precipitate and yielded clear solutions. The photograph of the curium product shown in Figure 13 was taken through the 4-ft-thick lead glass shielding window utilizing only the light emitted by the product solutions. The light was peach-colored and apparently was caused by the fluorescence of the curium species.

#### ANALYTICAL RESULTS

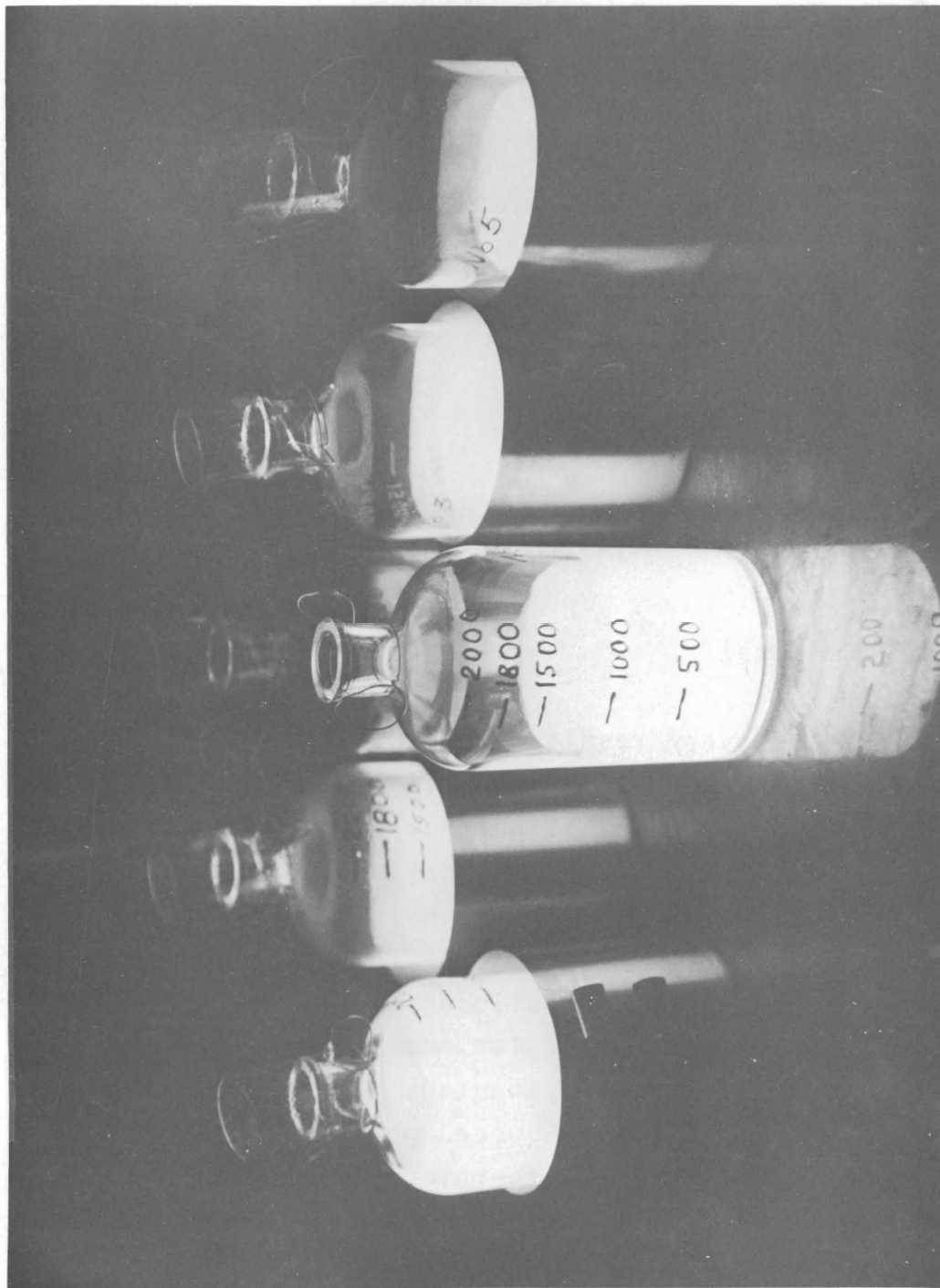
The isotopic analysis of the Shippingport americium and curium is given in Table 5.

TABLE 5. *Isotopic Analysis of Shippingport Americium and Curium*

	Mass Number	Atom %
Americium	241	77.57 ± 0.1
Americium	242	0.337 ± 0.006
Americium	243	22.2 ± 0.1
Curium	242	0.13 ± 0.1
Curium	243	1.49 ± 0.04
Curium	244	93.91 ± 1.41
Curium	245	3.95 ± 0.06
Curium	246	0.62 ± 0.03



Neg 0680182-2  
FIGURE 12. Curium Product Fractions Photographed Through 4-ft-Thick Lead-Glass Viewing Windows



Neg 0680182-1  
FIGURE 13. Curium Product Fractions Photographed Through 4-ft-Thick Lead-Glass Viewing Windows Utilizing Only the Light Emitted from the Solutions

Table 6 gives the analysis of the "Semiworks Product" after it had been transferred into a feed tank in the ion-exchange pilot plant facility. Sampling and analytical work were performed at PNL.

TABLE 6. *Promethium, Americium, and Curium Content in the Ion-Exchange Feed Solution*

Volume	585 liters
<sup>147</sup> Pm	185 g
<sup>241</sup> Am	837 g
<sup>242</sup> Am	3.63 g
<sup>243</sup> Am	240 g
Am Total	1080.63 g
<sup>242</sup> Cm	0.08 g
<sup>243</sup> Cm	0.90 g
<sup>244</sup> Cm	56.7 g
<sup>245</sup> Cm	2.38 g
<sup>246</sup> Cm	0.37 g
Cm Total	60.4 g

The material recovery results at the conclusion of the two DTPA first cycle separation runs are given in Table 7. The americium and curium material balance results are quite reasonable considering the number of analyses involved in each balance. The promethium material balance is low, but is consistent with promethium production runs utilizing feed solution containing high concentrations of cerium-144. Perhaps the promethium analyses on such solutions are biased high because some other nuclide is also counted. The americium solution contained in tank 9 was judged to be of high quality (contained only 0.14 wt% Cm) and therefore was not used in the feed for the NTA second cycle separation.

In preparation of the feed solution for the NTA separation, examination of the contents of tanks 8 and 11 revealed



TABLE 7. Product Recovery from the Two First Cycle DTPA Runs

Tank Number	Tank Volume, liters	Disposition					
		<sup>241</sup> Am, g	<sup>243</sup> Am, g	Am, g	<sup>244</sup> Cm, g	Cm, g	<sup>147</sup> Pm, g
8	53.5	331	94.7	427	37.6	40.0	
11	49.8	211	60.4	272	21.9	23.3	
9	38.5	177	50.7	228	0.29	0.31	
12 <sup>(a)</sup>	20.5	80.4	23.0	104	0.01	0.01	
13	28.1						120.2
10 <sup>(b)</sup>	31.5						31.3

## Summation

Am Product	927 g
Am Recycle	104 g
Am Material Balance	95%
Pm Product	120.2 g
Pm Recycle	31.3 g
Pm Material Balance	82%
Cm Product	63.6 g
Cm Recycle	0.01 g
Cm Material Balance	105%

a. Tank 12 contained the tail fraction and is highly contaminated with Gd and <sup>154</sup>Eu.

b. Tank 10 contained Pm head and tail fractions.

a considerable amount of precipitate on the bottom of each tank. Radiolytic destruction of the DTPA complexing agent produces insoluble oxalates and carbonates. Sufficient concentrated HNO<sub>3</sub> was added to each tank, through the dip leg, to cover the bottom of the tank and, hopefully, dissolve the precipitate. After 3 hr, each tank was sparged and a sample of the contents drawn up into a clean glass bottle for observation. Only a

trace of precipitate was observed and the feed cycle was started. After the solution from each tank had been pumped to the feed absorption column, each tank was sprayed down 3 times with 0.5M HNO<sub>3</sub> and this also was pumped to the absorption column. During these wash steps, a small amount of white precipitate was observed moving onto the top of the column. To obtain firm analytical data, a measured 10.0 liters of 4.5M HNO<sub>3</sub> was sprayed into tanks 8 and 11 and the contents sampled 24 hr later. Analyses revealed that tank 8 contained 0.07 g of curium and 0.80 g of americium and tank 11 contained 1.64 g of curium and 17.5 g of americium. The contents of tank 8 were added to tank 11. Although this material did not go through the NTA cycle, it was not considered a processing loss.

The americium and curium content of each product fraction is shown in Table 8. The total cation content shows minor concentration fluctuations. Some of this can be attributed to radiolysis of the complexing agent during passage through the resin bed. The contents in bottle number 10 are low because this fraction contained some water used to degas the resin bed.

The material balance results for americium and curium across the two DTPA first cycle separations and the single NTA second cycle separation are given in Table 9.

The exact concentrations of other impurities in the various americium and curium effluent fractions is known with less precision because of analytical problems encountered in determining trace impurities in macro quantities of <sup>241</sup>Am-<sup>243</sup>Am and <sup>244</sup>Cm. Nevertheless, results are sufficiently exact to draw meaningful conclusions.

TABLE 8. Product Recovery from the NTA Second Cycle Separation

Container Number	Fraction Volume, liters	$^{241}\text{Am}$ , g	$^{243}\text{Am}$ , g	Am, g	$^{244}\text{Cm}$ , g	Cm, g
Bottle 2	2.0	0.02	0.01	0.03	8.17	8.70
Bottle 1	1.0	0.04	0.01	0.05	7.77	8.27
Bottle 3	1.0	0.05	0.02	0.07	7.08	7.54
Bottle 4	1.0	0.09	0.03	0.12	6.42	6.84
Bottle 5	1.0	0.32	0.09	0.41	6.11	6.51
Bottle 6	1.0	1.88	0.54	2.42	6.21	6.61
Bottle 7	1.0	4.57	1.31	5.89	3.69	3.93
Bottle 8	1.0	6.43	1.84	8.29	1.83	1.95
Bottle 9	2.0	15.5	4.45	20.0	1.77	1.88
Bottle 10	2.0	11.0	3.14	14.2	0.70	0.75
Bottle 11	2.0	16.6	4.76	21.4	0.85	0.91
Bottle 12	2.0	18.2	5.20	23.4	0.69	0.73
Tank 10	51.0	386	111	498	1.89	2.01
Tank 8	10.7	26.0	7.44	33.5	0.002	0.002
Tank 9 <sup>(a)</sup>	38.5	177	50.7	228	0.29	0.31

a. The americium in tank 9 was not used as feed for the NTA separation, but is included because it represents "product".

TABLE 9. Material Balance Summation for Pilot Plant Test

Americium:

Feed Solution	1080 g
First Cycle Recycle Solution	122 g
Second Cycle Recycle Solution	93 g
Contained in Curium Product	3.1 g
Product Solutions	760 g
Material Balance	91%

TABLE 9. (contd)

## Curium

Feed Solution	60.5 g
First Cycle	
Recycle Solution	1.7 g
Second Cycle	
Recycle Solution	10.2 g
Contained in Americium Product	2.3 g
High Purity Product	29.2 g
Lower Purity Product	15.3 g
Material Balance	97%

Radiochemical activities other than those from americium or curium nuclides could not be detected. Gadolinium was found only in the americium-europium tail fraction from the second DTPA run. Evidently a combination of poor separation between gadolinium and europium combined with a very low europium detection limit (see Figures 9 and 10) brought about complete decontamination from gadolinium in the DTPA first cycle separations.

Dysprosium was detected in the first curium elution fraction (bottle number 2, Table 8) by emission spectroscopy, but in no other fractions. Interferences prevented the identification of terbium in any of the effluent fractions. However, as pointed out earlier, in the NTA system the dysprosium-terbium separation factor is only 1.07. It seems highly unlikely that the small amount of terbium present could be found any place other than associated with dysprosium in the first curium elution fraction. Several years of separations experience utilizing DTPA and NTA for promethium purification has shown that it would be highly unlikely for any other impurity to be found in these fractions and the spectrographic analysis showed all other impurities to be at their detection

limits. Table 10 summarizes the purity and other information for the americium and curium products.

TABLE 10. *Americium, Curium Product Purity*

Americium Product:

Solution Volume-----	100 liters
Amount of Am	760 g
Amount of Cm	2.3 g
Purity	99.7%

Curium Product

Heart Cut

Solution Volume	4.0 liters
Amount of Cm	29.2 g
Amount of Am	0.65 g
Purity	97.8%

Lower Purity Product

Solution Volume	3.0 liters
Amount of Cm	15.3 g
Amount of Am	2.45 g
Purity	86%

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