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ORNL-1357
Chemistry-Separation Processes
for Plutonium and Uranium

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AN ION-EXCHANGE PROCESS FOR PLUTONIUM ISOLATION AND PURIFICATION

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CHEMICAL TECHNOLOGY DIVISION

Chemical Development Section

AN ION-EXCHANGE PROCESS FOR PLUTONIUM ISOLATION AND PURIFICATION

D. C. Overholt
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DATE ISSUED

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0.0 ABSTRACT

An ion-exchange process for coupling the plutonium solvent extraction with the peroxide precipitation process for plutonium purification was developed and satisfactorily demonstrated on a production scale. A comparison of the product with that obtained by bismuth phosphate precipitation is included.

1.0 INTRODUCTION

The purpose of the ion-exchange process is to concentrate the plutonium in the product stream from the solvent-extraction process, to separate it from radioactive and ionic impurities, and to convert it to a form suitable for peroxide precipitation. The evaporation procedure formerly used was not satisfactory because of the build-up of corrosion products in the plutonium product. A solvent-extraction process that was investigated was not mechanically operable, while precipitation generally had to be carried out with a dilute plutonium solution.

Studies included chemical development of the process and its use on a production scale. Studies were made of the individual steps of the process, namely, absorption, uranium elution, and plutonium elution, and of the plutonium losses in each step as conditions were varied. A plutonium peroxide precipitation of the product was carried out satisfactorily, and the product met purity specifications when reduced to the metal.

The process has been accepted for Savannah River use, for the ORNL Scrup program, and for Purex pilot plant work.

Two series of pilot plant Purex runs are discussed in this report: (1) Runs HP-6 through 14 and Runs SP-20 and HCP-1 through 5. Run SP-20 was a natural uranium run spiked with plutonium.

2.0 SUMMARY

In the ion-exchange process for plutonium isolation the product is concentrated from approximately 0.2, 1.2, or 4 to approximately 40 g/liter, depending on whether the feed is from the Purex No. 1 (ORNL-846), No. 3 (ORNL-1141), or modified No. 3 IIBP stream. Ionic and radiochemical purification of the plutonium are sufficient that the eventual plutonium metal meets specifications. The overall plutonium loss in the pilot plant ion-exchange runs was of the order of 10^{-4}% in the second series of runs.

A little more than a kilogram of plutonium has now been processed satisfactorily by this method.

3.0 ION-EXCHANGE PLUTONIUM ISOLATION PROCESS USED IN PILOT PLANT

The columns for the second series of experimental runs were designed so that a direct scaleup to Savannah River conditions would be possible. They are 3 in. in diameter and 14 in. high, and have a resin volume of 1.6 liters. Based on a standard load of 80 g of plutonium, this provides a depth of approximately 20 cm (about 8 in.) of clean resin below the saturated plutonium band. A 7-in.-diameter column, the size planned for the Savannah River project (Fig. 3.1), loaded the same way would handle 440 g of plutonium. The resin is Dowex-50, 50 to 100 mesh, 12% cross-linked.

The pilot plant columns are made of 3-in.-i.d. pyrex pipe and are 16 in. high. The end plates are of 1/2-in. polythene, with inlets of polythene tubing heat-welded in place, and are held with pipe flanges. The resin bed is confined by two hold plates of coarse-porosity fluorothene frit; these plates are wrapped with glass filter cloth to provide a seal around the edges and are backed with 1/8-in. stainless steel plates honeycombed with 1/4-in. holes. A compression spring between the top end plate and the top resin hold plate keeps the resin in a fixed bed while it expands and contracts as various solutions are passed through it. The maximum change is about 10% of the length of the bed.

The feed to the plutonium-absorption column, which also absorbs the uranium, in this series of runs was the IIBP stream from a modified Purex No. 3 flowsheet. The feed contained 0.9 to 4.2 g of plutonium per liter and was 0.29 to 0.60 M in HNO_3. Hydroxylamine sulfate, 0.05 M, had been added to the IIBX stream so that the plutonium would be reduced to Pu(III) during the second-plutonium-cycle stripping. Under some conditions (see Sec. 4.3) additional hydroxylamine should be added to the feed.

The IIBP stream was produced by the pilot plant at a rate of 0.4 liter/hr. If continuous absorption was used, the plutonium would be absorbed from this solution at a rate of 0.2 g/hr. Instead, the IIBP solution for a complete Purex run was held in a catch tank and the composite was processed. The plutonium was absorbed at a rate of 50 to 60 g/hr (feed flow rate of 250 ml/min), and only 1.5 to 2 hr was required for the feed for an entire run. An additional advantage of compositing the feed is that cases of high acid or insufficient reducing agent may be controlled.

After the absorption the column is washed with 0.1 to 0.25 M HNO_3 containing 0.05 M hydroxylamine sulfate in order to wash all feed solution out of the resin bed. If the uranium elution step is included in the run, this wash follows that step instead of the absorption step.

The uranium elution step is included if the uranium of the feed is greater than 1% of the plutonium because of some irregularity in the solvent-extraction process. It may also be included if holdup liquid from the nonequilibrium fraction has been brought into the ion-exchange column or if there has been a

buildup of uranium on the column. The elutriant for the uranium is 0.25 M H_2SO_4 containing 0.05 M hydroxylamine sulfate. The flow rate of this elutriant is 2 ml/min/cm^2, and 3 to 4 hr is required for the elution.

The plutonium is eluted upflow with 5.7 M HNO_3 containing 0.3 M sulfamic acid to keep the plutonium in the trivalent state. In the pilot plant runs the plutonium was eluted under cycle conditions, about a 10% heel being left on the column after each run; the partial elution required 5 to 6 hr. The flow rate of the elutriant was 0.22 ml/min/cm^2. After the dilute acid rinse, the elutriant was started through the column. Exactly the volume of elutriant was put in as was desired in the product cut, namely, that volume which would elute approximately 90% of the plutonium on the column at a concentration of 40 to 50 g/liter. Then two volume changes (1600 ml in the pilot plant) of 0.1 M HNO_3 reconditioning wash were started through. The fractions collected from the top of the column were: (1) one displacement volume (800 ml) of dilute acid containing very small amounts of plutonium, (2) the desired volume of product, and (3) one volume change of reconditioning wash, which contained a small but appreciable amount of plutonium. Cuts 1 and 3 were held for recycling.

When decontamination of the resin bed becomes necessary, the plutonium is eluted completely with about 12 column volumes of elutriant. Oxalic acid, 0.5 M, is allowed to remain in place on the column overnight, then zirconium and niobium are cleaned from the column with five volumes of this solution. The digestion period could be shortened by heating both the oxalic acid and the column.

Although the pilot plant runs were designed to demonstrate operation under Savannah River plant conditions, they were actually carried out under more adverse conditions. In the Savannah River plant, where a Purex No. 1 flowsheet is to be used, the acid concentration of the feed will be about 0.15 M, at which concentration the distribution coefficient for plutonium on resin is 5 to 10 times greater than in the pilot plant runs. The plutonium concentration of the feed in the pilot plant tests reached 4.2 g/liter, as contrasted with 0.2 g/liter in the Purex No. 1 flowsheet, and the variations from one run to the next were considerably greater than those expected in the Savannah River plant. The feed flow rates were lower than SRP specifications, but, because of the higher plutonium concentration, the processing rate, in grams per hour, was much higher.

In the HP runs Purex Flowsheet No. 3 was used, and, to couple to this, an ion-exchange Flowsheet No. 1 was developed (see Fig. 3.2).

FIG. 3.1 ION EXCHANGE PLUTONIUM ISOLATION FLOWSHEET #2

DWG 15193 R1

Pu & U ABSORPTION CYCLE

Basis: 350 gm Pu/8 hours

Purex Flowsheet #1

PUREX IIBP STREAM

1790 liters/8 hours
0.2 gram Pu/liter
0.3M HNO_3
0.05M NH_2OH 1/2 H_2SO_4
15 ml/min/cm^2

RESIN
COLUMN SPECIFICATIONS

RESIN: Dowex 50
50-100 mesh
12% cross linkage
RESIN BED VOLUME:
8.72 liters
EXCESS RESIN: 300%
COL. DIA. 17.80 cm
(7 inch)
CROSS-SECTIONAL AREA
OF COLUMN: 249 cm^2
DEPTH OF RESIN BED:
35.2 cm

IIBPW STREAM

1790 liters/8 hours
0.3M HNO_3
0.05M NH_2OH 1/2 H_2SO_4
10^2 Pu α cts/min/ml

U ELUTION CYCLE

0.05M
$NH_2OH \cdot \frac{1}{2} H_2SO_4$
0.25M H_2SO_4
25 Volume Changes
109 liters
2 ml/min/cm^2

109 liters 0.25 M H_2SO_4
10^3 Pu α cts/min/ml
99% of U in IIBP

→ To Waste

Pu ELUTION CYCLE

Pu PRODUCT ELUATE

VOL LITERS	HNO_3 M	NH_2SO_3H M	Pu g/l	Pu gm	Pu %
4.4	0.3		0.05	0.22	0.05
7.0	4.8	0.3	50.	350.	90.
4.4	0.7	0.1	0.5	2.	0.5
Residual Pu on resin				35	10

Pu PRODUCT ELUTRIANT

VOL (liters)	HNO_3 M	NH_2SO_3H M
7.0	5.7	0.3
8.8	0.1	0.1
0.2 ml/min/cm^2 (total elution time 5.3 hours)		

ION EXCHANGE PLUTONIUM ISOLATION FLOWSHEET # 1

Figure No 3.2

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DWG No 12210

Pu AND U ABSORPTION CYCLE

Basis: 400 gm Pu / 8 hours

PUREX FLOWSHEET No 3

PUREX IIBP STREAM

328 Liters
0.3 M HNO_3
0.03 M NH_2OH 1/2 H_2SO_4
1.22 gm $Pu(NO_3)_3$ / L
8.5 ml/min/cm²

RESIN COLUMN SPECIFICATIONS

RESIN: Dowex 50
60-90 mesh - 12 % cross linkage

RESIN BED VOL: 4 36 L

EXCESS RESIN: 100 %

COL. DIA. 10 2 cm (4 inch)

CROSS-SECTIONAL AREA OF COLUMN: 80 cm²

DEPTH OF RESIN BED 54.5 cm

COLUMN VOLUME CHANGE
2.18 liters

IIBPW STREAM

328 Liters
0.3 M HNO_3
0.03 M NH_2OH 1/2 H_2SO_4
10^3 Pu α c/min/ml

U ELUTION CYCLE

0.25 M H_2SO_4
25 Volume Changes
(54.5 liters)
2.0 ml/min/cm²

54.5 L 0.25 M H_2SO_4

10^3 Pu α c/min/ml
(< 1 mg Pu)
99% of U in IIBP

WASTE

Pu ELUTION CYCLE

Pu PRODUCT ELUATE

VOL CHG	HNO_3 M	NH_2SO_3H M	Pu g/l	Total Pu gm	
1	0.3	-	0.05	0.11	TO IAF
2	2.57	0.25	99.85	217.67	TO PuO_4 Precipitator
3	5.6	0.25	46.6	101.59	
4	6.0	0.25	16.9	36.84	
5	6.0	0.25	7.00	15.75	TO IAF
6	4.0	0.25	0.40	0.87	
7	0.5	0.25	0.02	0.05	

Pu PRODUCT ELUTRIANT

VOL CHG	HNO_3 M	NH_2SO_3H M
1	6.0	0.25
2	6.0	0.25
3	6.0	0.25
4	6.0	0.25
5	0.1	0.25
6	0 1	0.25
7	0 1	0.25

0.6 ml / min / cm² (total elution time 5.3 hours)

21.7 liters
2.54 M HNO_3
0.15 M NH_2SO_3H
0.83 g / l Pu

TO
IAF, IIAF, or IIBP

Pu PEROXIDE PRECIPITATION CYCLE

6.54 liters
54.5 g/l Pu
4.8 M HNO_3
0.25 M NH_2SO_3H

HYDROFLUORINATION

HEAT KILL
70° C

13.0 liters
2 4 M HNO_3
1.3 gm Pu

6.54 liters - 30% H_2O_2

4.0 ABSORPTION

The Purex IIBP stream from which the plutonium is absorbed is approximately 0.15(No. 1 flowsheet) to 0.6 M (modified No. 3 flowsheet) in HNO_3 and contains hydroxylamine sulfate which has been added to the IIBX stream in the amount of 0.05 M to reduce the plutonium to Pu(III). The plutonium concentration of the feed varies from about 0.2 g/liter with a Purex No. 1 flowsheet (HP-6 and 7), to 1.22 g/liter with a Purex No. 3 flowsheet (HP-8 through 14), to 4.2 g/liter with a modified Purex No. 3 flowsheet (HCP-1 through 5).

The distribution of uranium and plutonium on the resin during absorption depends on the relative absorption coefficients (plutonium per gram of resin divided by plutonium per gram of solution) of the two metals, namely, 4.3×10^3 for Pu(III), 2.6×10^4 for Pu(IV), and 1.0×10^2 for uranyl in 0.25 M HNO_3. Since Pu(III) is held more strongly than the uranium, a band of plutonium, containing some uranium, forms at the top of the column and a band of uranium forms below it. In most cases the bands were clearly defined, but in Run HCP-3 the lower edge of the saturated plutonium band was visibly feathered, consisting of a 2-in.-wide band of narrow sawteeth. This effect was probably caused by the high plutonium concentration and the fast feed flow rate used in this run.

4.1 Advantages of Absorbing Plutonium in III Valence State

Absorption of the plutonium in the III valence state is considered essential, and the plutonium is kept in this state throughout the process. The advantages are:

1. Polymerization of the plutonium is avoided.
2. About 25% less resin is required.
3. The hydroxylamine used to keep the plutonium in the III state also keeps the iron present in the II state, and the absorption coefficient of Fe(II) is much lower than that of Fe(III).
4. Plutonium(III) complexes with $SO_4^{=}$ less than does Pu(IV) or PuO_2^{++}, and there is therefore a smaller loss of plutonium in the uranium-elution step.
5. Plutonium(III) is eluted more readily than Pu(IV), and a higher concentration of plutonium is therefore obtained in the plutonium-elution product cut.

4.2 Effect of Variations in Acidity, Plutonium Concentration, and Flow Rate of the Feed

Increase in the acidity, the plutonium concentration, or the flow rate of the feed might be expected to increase the plutonium loss. The only variable that it was possible to control was the flow rate, and where this was held constant and other conditions were comparable (Runs HP-8 and 9, Runs HCP-4 and 5), a very slight increase in plutonium loss was observed with the higher acidity and plutonium concentration (Table 4.1 and Figs. 4.1 through 4.6). However,

within the limits studied, the plutonium loss was not affected appreciably by changing these variables. In the first series, where the plutonium concentration varied from about 0.1 to 1.29 g/liter, the acidity from 0.19 to 0.34 M, and the flow rate from 0.386 to 2.3 ml/min/cm^2, plutonium loss in the effluent waste was of the order of 10^{-2} or 10^{-3}%. In the second series, where the plutonium concentration varied from about 1 to 4.2 g/liter, the acidity from 0.29 to 0.60 M, and the flow rate from 3.3 to 17.5 ml/min/cm^2, the losses were all of the order of 10^{-4}%. In the second series losses were lower than in the first; this fact may be the result of differences in column design and better control over feed conditions.

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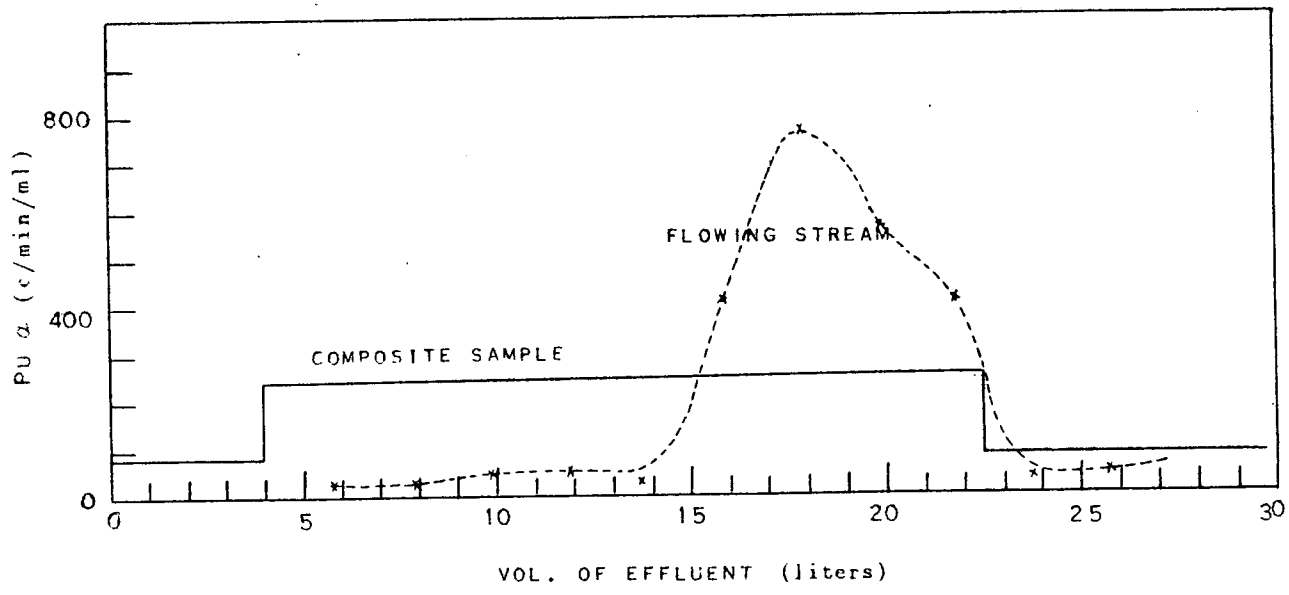
DWG. 16075

Fig. 4.1. Plutonium Activity in Absorption-Step Waste, Run SP-20.

Resin: 50- to 100-mesh Dowex-50

Column dimensions: 3-in. diameter, 14-in. height

Feed conditions: 0.9 g of Pu(III) per liter, 0.25 N H^+; flow rate 6.6 ml/min/cm², downflow



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DWG. 16076

Fig. 4.2. Plutonium Activity in Absorption-Step Waste, Run HCP-1.

Resin: 50- to 100-mesh Dowex-50

Column dimensions: 3-in. diameter, 14-in. height

Feed conditions: 3.4 g of Pu(III) per liter, 0.47 N H^+; flow rate 3.3 ml/min/cm^2, downflow

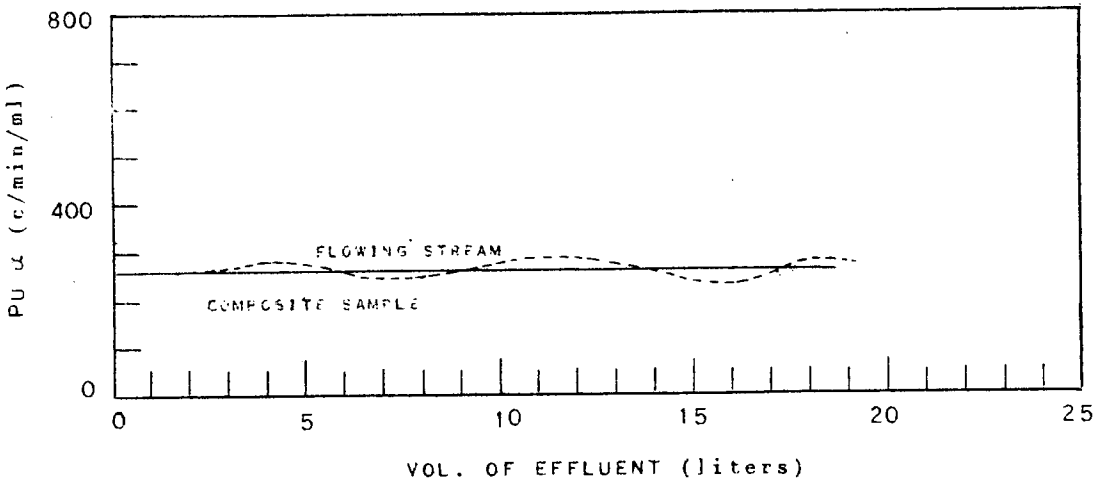

Fig. 4.3 . Plutonium Activity in Absorption-Step Waste, Run HCP-2.

Resin: 50- to 100-mesh Dowex-50

Column dimensions: 3-in. diameter, 14-in. height

Feed conditions: 3.7 g of Pu(III) per liter, 0.49 *N* H^+; flow rate 5.5 ml/min/cm², downflow

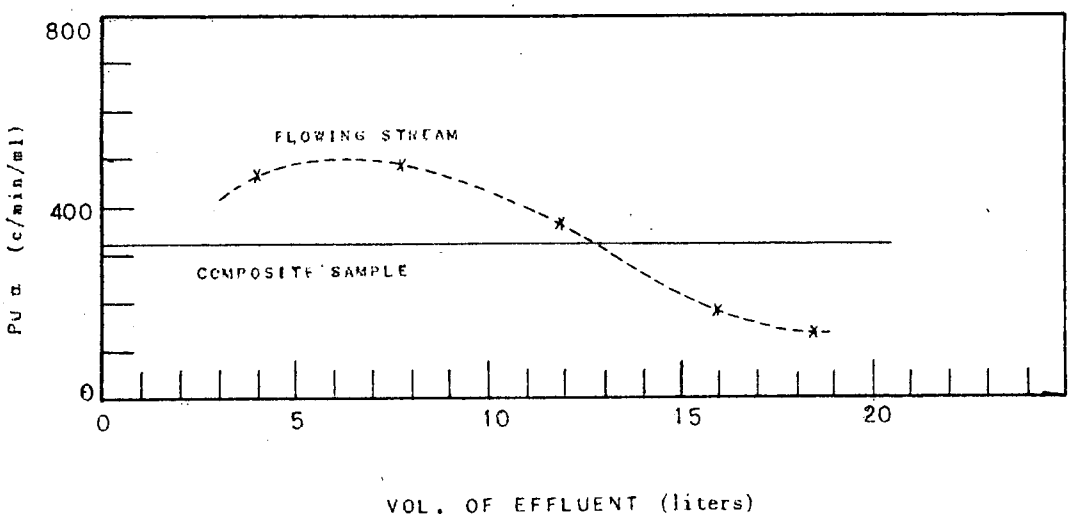

Fig. 4.4 . Plutonium Activity in Absorption-Step Waste, Run HCP-3.

Resin: 50- to 100-mesh Dowex-50

Column dimensions: 3-in. diameter, 14-in. height

Feed conditions: 4.2 g of Pu(III) per liter, 0.47 *N* H^+; flow rate 4.9 ml/min/cm^2 to 7 liters, 12 ml/min/cm^2 7 to 21.4 liters, downflow

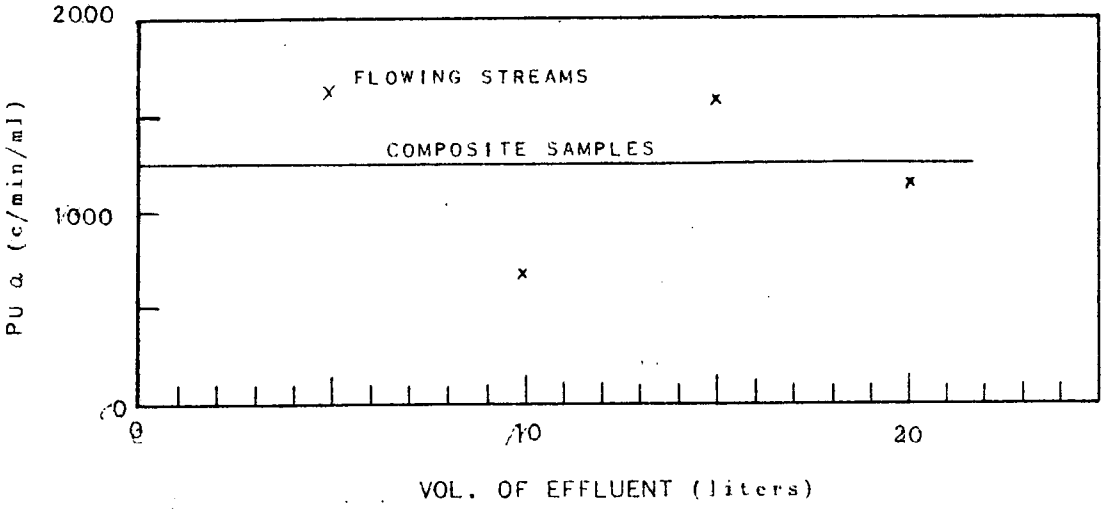

Fig. 4.5. Plutonium Activity in Absorption-Step Waste, Run HCP-4.

Resin: 50- to 100-mesh Dowex-50

Column dimensions: 3-in. diameter, 14-in. height

Feed conditions: 4.2 g of Pu(III) per liter, 0.6 N H^+; flow rate 5.5 ml/min/cm^2, downflow

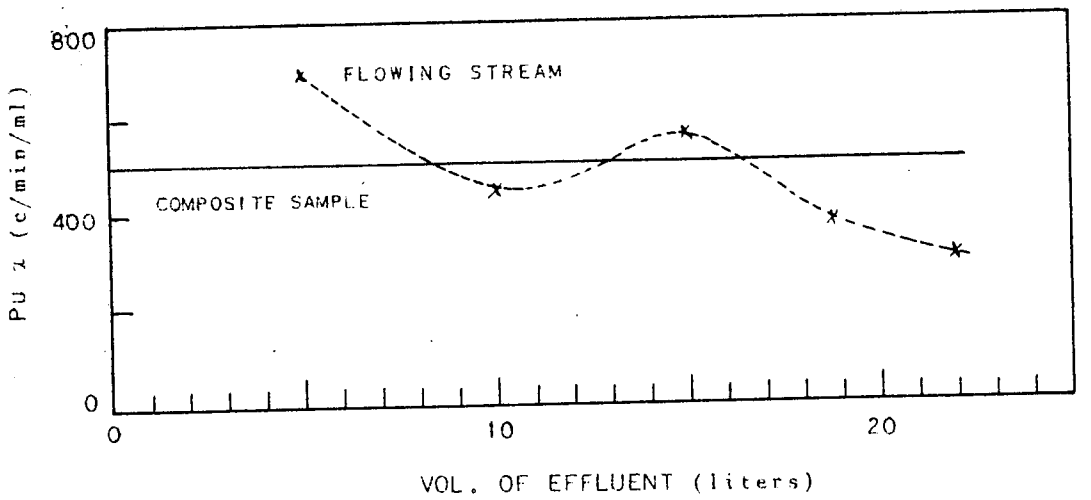

Fig. 4.6 : Plutonium Activity in Absorption-Step Waste, Run HCP-5.

Resin: 50- to 100-mesh Dowex-50

Column dimensions: 3-in. diameter, 14-in. height

Feed conditions: 3.5 g of Pu(III) per liter, 0.46 N H^+; flow rate 5.5 ml/min/cm^2, downflow

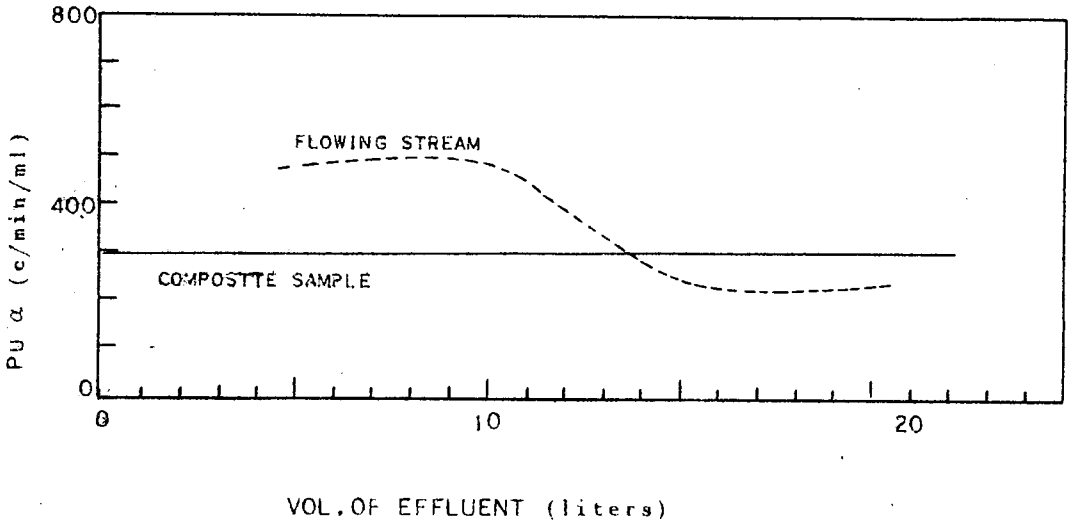

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Table 4.1

Summary of Feed Compositions, Flow Rates, and Losses During Absorption

	First Series	Second Series
Column dimensions:		
Diameter	3 in. (7.6 cm)	3 in. (7.6 cm)
Height	12 in. (30.5 cm)	14 in. (35.56 cm)
Cross section	7.07 in.^{2} (45.36 cm^2)	7.07 in.^{2} (45.36 cm^2)
Volume	1.4 liters	1.6 liters
Resin specifications:	Dowex-50, 60 to 90 mesh, 12% cross linked; 300% excess for Runs HP-8 and 9, 125% excess for Run HP-11-14	Dowex-50, 50 to 100 mesh, 12% cross linked; 300% excess

Run No.(a)	Feed Composition		Hydroxylamine Sulfate Added to IIBX (M)	Total Pu in Feed (g)	Feed Flow Rate (ml/min/cm^2)	Pu Absorption Rate (g/hr)	Gross α Activity Loss in Waste	
	Pu (g/liter)	Acidity (M)					(c/min/ml)	(%)
First Series								
HP-8	0.81	0.335	0.2	80.4	2.3			2×10^{-2}
HP-9	0.796	0.19	0.05	75.133	2.3			1.4×10^{-2}
HP-11-14	0.129-1.29	~ 0.25	0.03	119.63	0.386-0.774			1.1×10^{-3}
Second Series								
SP-20(b)	0.9	0.29	0.05	3.6 23	17.5 6.6	44 16	84 275	1.3×10^{-4} 4.4×10^{-4}
HCP-1	3.4	0.47	0.05	61	3.3	30	260	1.1×10^{-4}
HCP-2(c)	3.7	0.49	0.05	70	5.5	55.5	410	3.0×10^{-4}
HCP-3(b)	4.2	0.47	0.05	29 61	4.9 12	56 138	1500	5.0×10^{-4}
HCP-4	4.2	0.60	0.05(d)	91	5.5	63	500	1.6×10^{-4}
HCP-5	3.5	0.46	0.05	76	5.5	52.5	300	1.3×10^{-4}

(a) Runs HP-6 and 7 not included because of incomplete data; Run HP-10 not included because it contained recycle material.
(b) Runs SP-20 and HCP-3 each absorbed in two portions, at different flow rates.
(c) In Run HCP-2 the plutonium was absorbed in the IV valence state and was reduced on the column.
(d) Excess hydroxylamine sulfate was added to feed tank before the solution was passed through the resin column.

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4.3 Effect of Variations in the Hydroxylamine Concentration of the IIBP Solution

Variations in the hydroxylamine concentration of the IIBP solution within the limits studied (0.03 to 0.2 M) do not appear to affect the absorption of plutonium since Pu(IV) is absorbed even more readily than Pu(III). However, 0.05 M hydroxylamine in the feed is considered to be the minimum amount in the IIBP solution that will keep the plutonium in the III state (see Sec. 4.1). Since the hydroxylamine is slowly destroyed by reaction with nitric acid and with impurities such as iron in the IIBP solution, additional hydroxylamine in the feed may be needed, especially if the feed stands for some time before going to the resin column.

In Run HP-11-14 (Purex No. 3) the hydroxylamine was reduced to 0.03 M without excessive plutonium loss in the waste effluent from the absorption step (Table 4.1). In Runs HCP-2 and 4 (Purex No. 3 modified), in which the hydroxylamine concentration of the IIBX solution (Purex plutonium strip) was 0.05 M, the plutonium oxidized in the feed tank. In Run HCP-2 the plutonium was absorbed as Pu(IV) and reduced on the column with hydroxylamine, a procedure which is not recommended because of the excessive formation of gas. In Run HCP-4 additional hydroxylamine sulfate was added to the feed in the tank.

4.4 Effect of Variations in Excess of Resin

A 2.3-fold excess of resin was found to be sufficient (a plutonium loss of 10^{-3}%) in the 3-in.-diameter 12-in.-high columns (Run HP-11-14). A 3.4-fold excess was used in Runs HP-8 and 9 and a 2.6-fold excess, based on 80 g of plutonium in the feed, in Runs HCP-1 through 5. The actual excess in the HCP runs was less in some cases because of larger amounts of plutonium in the feed.

In the HCP series flowing-stream samples of the waste were taken during all runs, and analyses showed no increase in activity in the waste during the course of an absorption, indicating that sufficient excess resin was present at all times to absorb most of the exchangeable plutonium ions. In those cases in which some plutonium was left on the column from a previous partial elution there was a decrease in the flowing-stream losses during the course of a run. This decrease may indicate partial polymerization or the formation of some nonexchangeable species when plutonium remains on a column. However, even in runs in which two weeks elapsed between a partial elution and the next absorption, the effect was small.

5.0 URANIUM ELUTION

The uranium-elution step is not always needed, but, in all runs in which it was included, the uranium contamination of the plutonium was reduced sufficiently that the final product met specifications, namely, less than 0.01% uranium in the plutonium metal product, with negligible losses of plutonium. The step is included if, owing to some irregularity in the solvent-extraction process, the uranium in the feed is as much as 1% of the plutonium.

The elutriant is 0.25 M H_2SO_4, which contains 0.05 M hydroxylamine sulfate as a holding reductant to keep the plutonium as Pu(III). This reducing compound is essential because Pu(IV) would move down the column with the uranium. The separation factors for uranium and Pu(III) in this system (Sec. 4.0) are such that Pu(III) moves down only about 10% while the uranium is moving down and off the column. The volume of elutriant needed to remove a given amount of uranium depends partly on the amount of plutonium present, since the amount of plutonium determines the starting position of the uranium band. Partial elution of the uranium is sufficient, since in the plutonium elution step, which is upflow, the plutonium band moves up the column faster than the uranium band and the concentrated plutonium cut is taken before the bulk of the uranium band reaches the top of the column. Flowing-stream samples taken when the uranium elution was stopped, in the HCP runs, were still assaying up to 0.1 g/liter, which indicated that up to about 1 g of uranium may have been left on the column (Figs. 5.1 and 5.2).

Flowing-stream losses were determined in Runs SP-20 and in the HCP runs in order to follow the loss of plutonium during the elution (Table 5.1). In Run SP-20, in which no hydroxylamine was used in the elutriant, the losses showed a peak characteristic of the elution of Pu(IV). Since the operation of the column was discontinuous, this may have been formed, while the column was standing, by the action on the Pu(III) of hydrogen peroxide produced by α-particle decomposition of water. In the HCP series, 0.05 M hydroxylamine sulfate was added to the elutriant, and the plutonium losses were lower than in the first series.

The uranium elution step is especially valuable in cases of irregularities in the solvent-extraction process that would result in a high uranium concentration of the IIBP solution. Its use would eliminate the necessity of recycling an entire day's run.

In Runs SP-20 and HCP-1, 2, 3, and 5 large amounts of uranium were introduced into the feed from holdup liquid in the tanks and lines as a result of pulse-column startup (Table 5.1). A uranium-elution cycle was used to remove this excess uranium. In Run HCP-4 multiple vacuuming of the startup fraction diluted the uranium in the holdup volume sufficiently so that no separate elution step was necessary. The uranium-elution step can also be used to remove uranium from a column on which the contamination has been built up through several runs.

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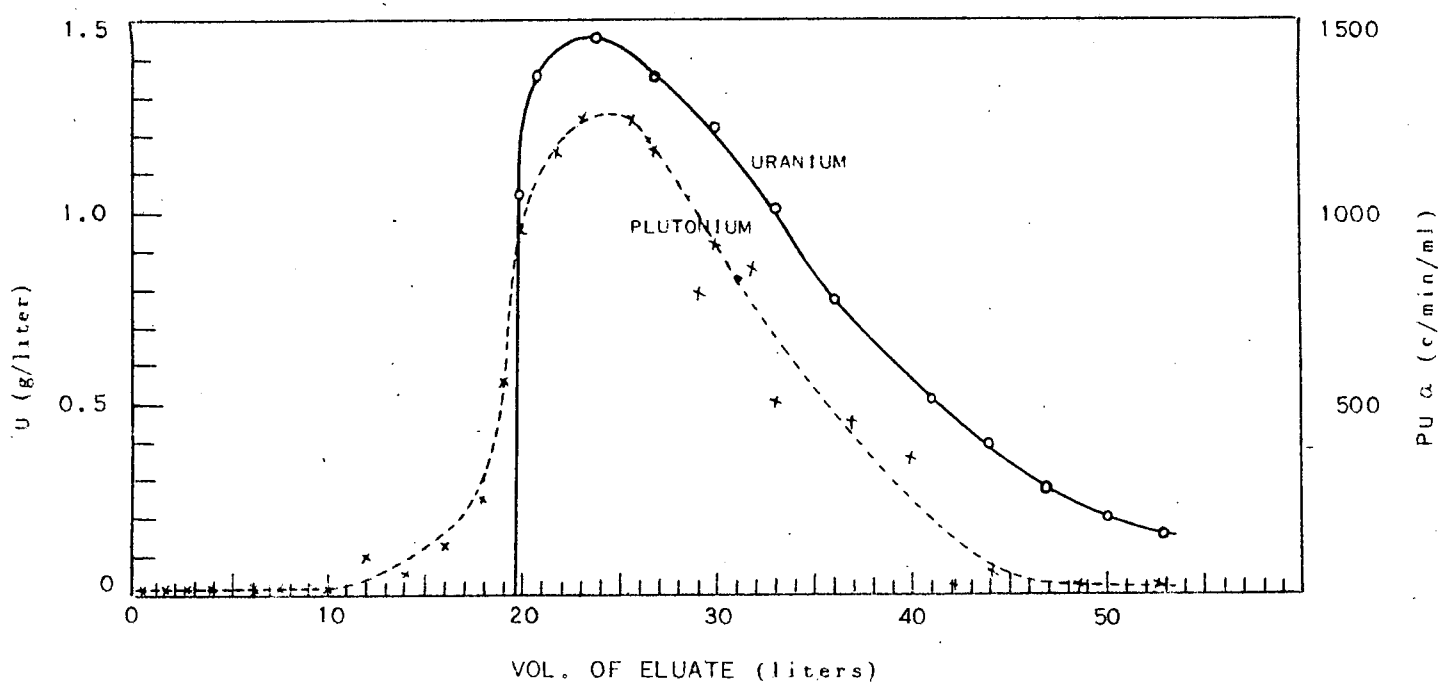
DWG. 16081

Fig. 5.1 . Uranium and Plutonium in Eluate from Uranium-Elution Step, Run SP-20.

Resin: 50- to 100-mesh Dowex-50

Column dimensions: 3-in. diameter, 14-in. height

Elutriant: 0.25 *M* H_2SO_4; flow rate 2.2 ml/min/cm^2



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DWG. 16082

Fig. 5.2. Uranium and Plutonium in Eluate, Uranium-Elution Step, Run HCP-1.

Resin: 50- to 100-mesh Dowex-50

Column dimensions: 3-in. diameter, 14-in. height

Elutriant: 0.25 *M* H_2SO_4, 0.2 *M* hydroxylamine sulfate; flow rate 2.2 ml/min/cm^2

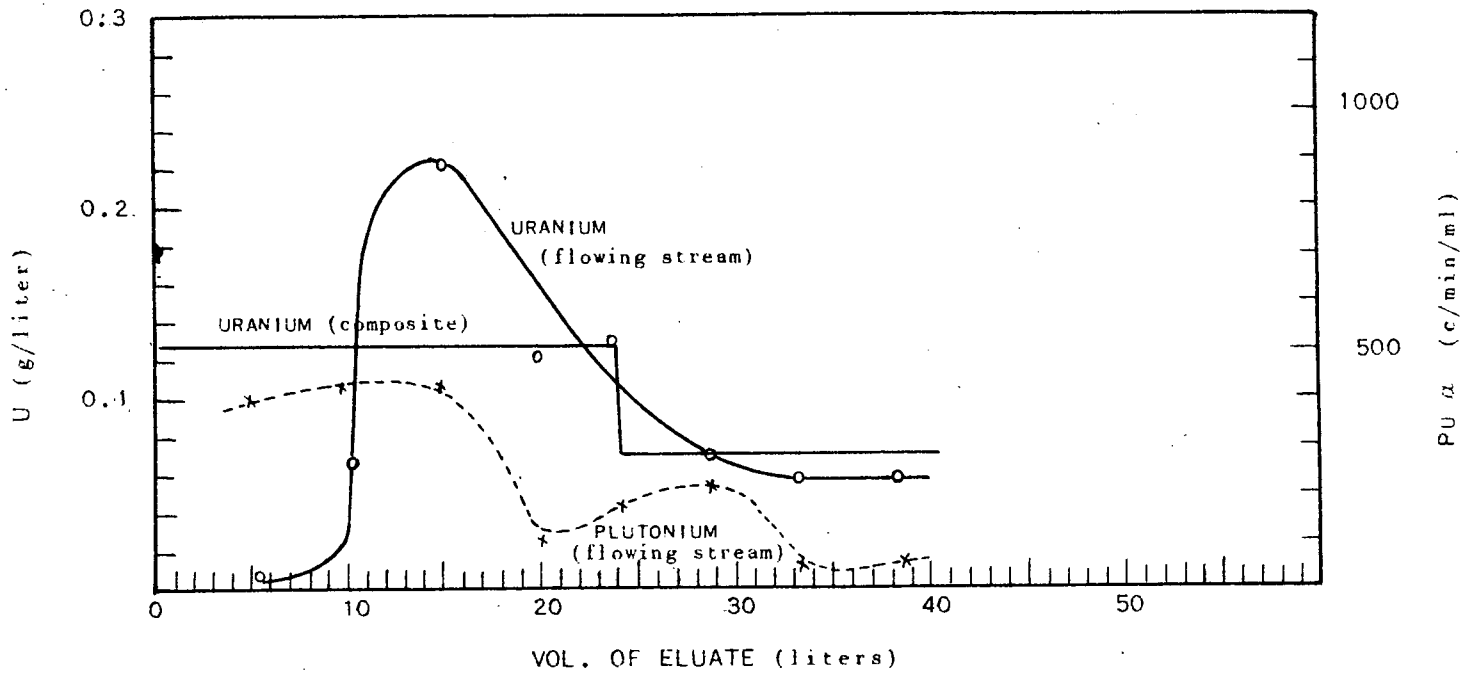


Table 5.1

Elution of Uranium Absorbed from Purex Equilibrium Streams

Elutriant: 0.25 M H_2SO_4 + 0.02 M hydroxylamine sulfate
Flow rate: 2 ml/min/cm^2

Run No.	Total Pu (g)	Eluate Volume (liters)	U Eluted (g)	U in Product (g)	U in Product (% of Pu)	Pu Loss (mg)	Pu Loss %
SP-20*	26.6	56	31			0.25	8.7×10^{-4}
HCP-1	61	30	3.2	0.038	0.07	0.146	2.4×10^{-4}
HCP-2	70	38	2.2	0.17	0.26	0.074	1×10^{-4}
HCP-3	90	38	6.4	0.055	0.07	34.9	4×10^{-2}
HCP-4	91	---	---	0.0127	0.03	---	---
HCP-5	76	38	4.7	0.02	0.04	0.054	7×10^{-5}

* No hydroxylamine present in uranium elutriant.

Table 5.2

Elution of Uranium Absorbed from Purex Non-equilibrium Streams

Total plutonium in product: 186 g
Total uranium in feed: 190 g

Run No.	U in Flowing Stream at Cessation of Elution (g/liter)	U in Product Pu Total (g)	U in Product Pu (% of Pu)
RD	0.8	0.031	0.06
RG	0.43	0.022	0.027
RI*	0.14	< 0.02	< 0.04

* Includes recycle of dilute Pu fractions from the equilibrium runs.

6.0 PLUTONIUM ELUTION

In order for the plutonium to be eluted in a reasonable length of time at a sufficiently high concentration, the nitric acid concentration of the elutriant must be approximately 6 M. An antioxidant, sulfamic acid, is used in the elutriant to inhibit the oxidation of Pu(III) to Pu(IV) by the strong acid. Since the plutonium band is at the top of the column when the elution starts, upflow elution is used to obtain a higher concentration of plutonium in the eluate.

In the elution procedure found most satisfactory (see Sec. 3.0) the product cut contains about 90% of the plutonium on the column; about a 10% heel is left on the column (Table 6.1). The volumes of elutriant can be adjusted to the column size and plutonium loading so that this procedure will fit into any elution scheme. The method gives a smaller volume and lower acidity and plutonium concentration of the material to be recycled than previously developed elution schemes.

The plutonium balances (Table 6.2) for the HCP runs are only approximate because of the lack of precision in the analytical methods for plutonium. However, they indicate that elimination of the uranium step (as in Run HCP-4), in which the plutonium band is spread, may result in a higher concentration of plutonium in the product with less heel, and that extremely high absorption rates (e.g., 138 g/hr, as in Run HCP-3) coupled with the uranium-elution step may spread the plutonium band suffiently to reduce the concentration of the product fraction appreciably.

Since the amount of plutonium on the columns varied in the second series of runs, direct comparison of the curves obtained by plotting the plutonium concentration of the eluate against the volume of the eluate is not possible (Figs. 6.1 through 6.6). However, the volume of eluate per unit weight of plutonium on the column can be plotted against the plutonium concentration of the eluate in order to obtain a normalized curve for use in comparing the various runs. Composite curves (Figs. 6.7 and 6.8) for several runs made under the same elution conditions may be prepared for a particular column. From these an estimate can be made of the concentration level in any product fraction from the same column.

Table 6.1

Ion-Exchange Plutonium Product Data from Equilibrium Runs*

Run No.	Pu in Product (g/liter)**	Pu in Product Total (g)	Acidity of Product Solution (M)
HCP-1	43.02	54.46	5.3
HCP-2	42.66	64.13	5.3
HCP-3	42.76	78.53	5.10
HCP-4	44.60	88.54	4.80
HCP-5	44.57	71.71	4.75

* In addition to the equilibrium runs, the nonequilibrium fractions yielded three products averaging 41 g/liter and totaling 186 g.

** Plutonium assayed potentiometrically.

Table 6.2

Plutonium Balances through the Equilibrium Runs

Run No.	Plutonium (g)				Pu in Product Cut, Calc. (% of total)
	Total on Column	In Product Solution	In Dilute Fractions of Eluate	Heel on Column	
HCP-1	61	54.5	4.7	1.8	89
HCP-2	70.8	64.1	3.4	3.3	90
HCP-3	91.3	78.5	12.8	0	86
HCP-4	91	88.5	0.5	2	97
HCP-5	78	71.7	1.2	4.3	92

6.1 Effect of Varying the Elutriant

Nitric Acid. A nitric acid concentration of 5.7 M is recommended for plutonium elution. Sulfamic acid, 0.3 M, is added to prevent oxidation of the Pu(III) to Pu(IV), which would be undesirable not only because of the lower plutonium concentration that would be obtained in the product cut (see Sec. 4.1) but also because the nitrogen oxides formed in the oxidation would rupture the bed and cause channeling of the acid. The sulfamic acid breaks the oxidation chain by reacting with the nitrogen oxides as rapidly as they are formed. The induction periods characteristic of nitric acid oxidation can be extended from a few minutes for the uninhibited system to two weeks for the inhibited system.

In earlier work, before the addition of sulfamic acid was tried, an attempt was made to elute the Pu(III) with 2 M HNO_3, but even this strength nitric acid oxidized the plutonium.

Acetates. Acetate solutions have shown promise as elutriants for plutonium, but the acetate system has not yet been fully investigated. In runs made with 2 and 4 M ammonium acetate, high product concentrations and small-volume stripping were obtained. Oxidation of the plutonium to the PuO_2^{++} ion would cause precipitation in the product solution, but this oxidation can be prevented by using a holding reductant, such as hydroxylamine, in the elutriant.

Sulfates. Sulfates had been shown in previous work to be effective in stripping Pu(III) from Dowex-50 resin. High product concentrations and small tailings were obtained with 1 and 2 M ammonium sulfate, but the formation of $NH_4Pu(SO_4)_2$ precipitates in some of the product solutions was undesirable. Alkali-plutonium sulfates are even less soluble than ammonium. Sulfates are considered at this time to be of no interest.

Fig. 6.1. Plutonium in Eluate from Plutonium-Elution Step, Run SP-20.

Resin: 50- to 100-mesh Dowex-50

Column dimensions: 3-in. diameter, 14-in. height

Elutriant: 5.7 *M* HNO_3, 0.3 *M* sulfamic acid; upflow

Total Pu on column: 29.09 g

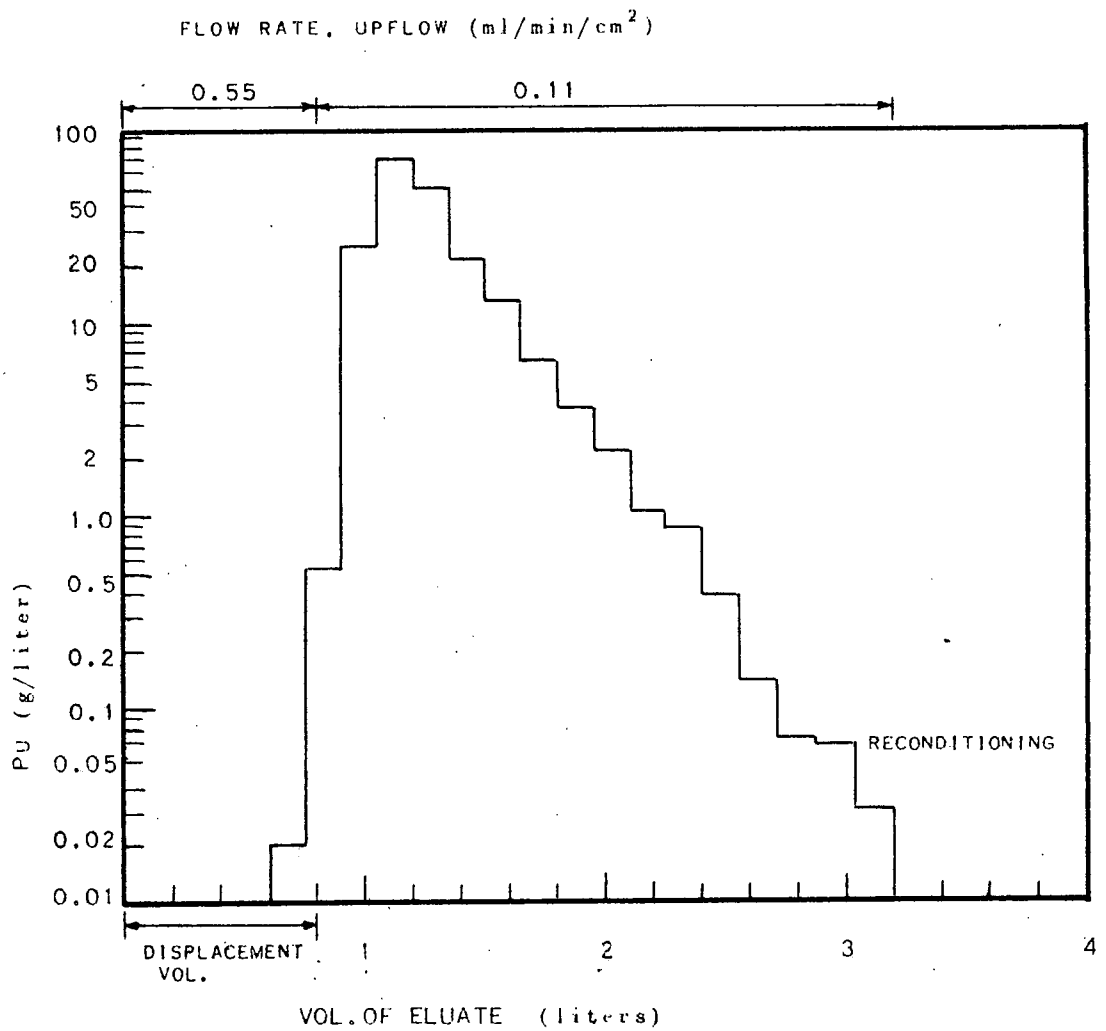


Fig. 6.2. Plutonium in Eluate from Plutonium-Elution Step, Run HCP-1.

Resin: 50- to 100-mesh Dowex-50

Column dimensions: 3-in. diameter, 14-in. height

Elutriant: 5.7 *M* HNO_3, 0.3 *M* sulfamic acid; upflow

Total Pu on column: 61 g

Total Pu product: 54 g at 43 g/liter

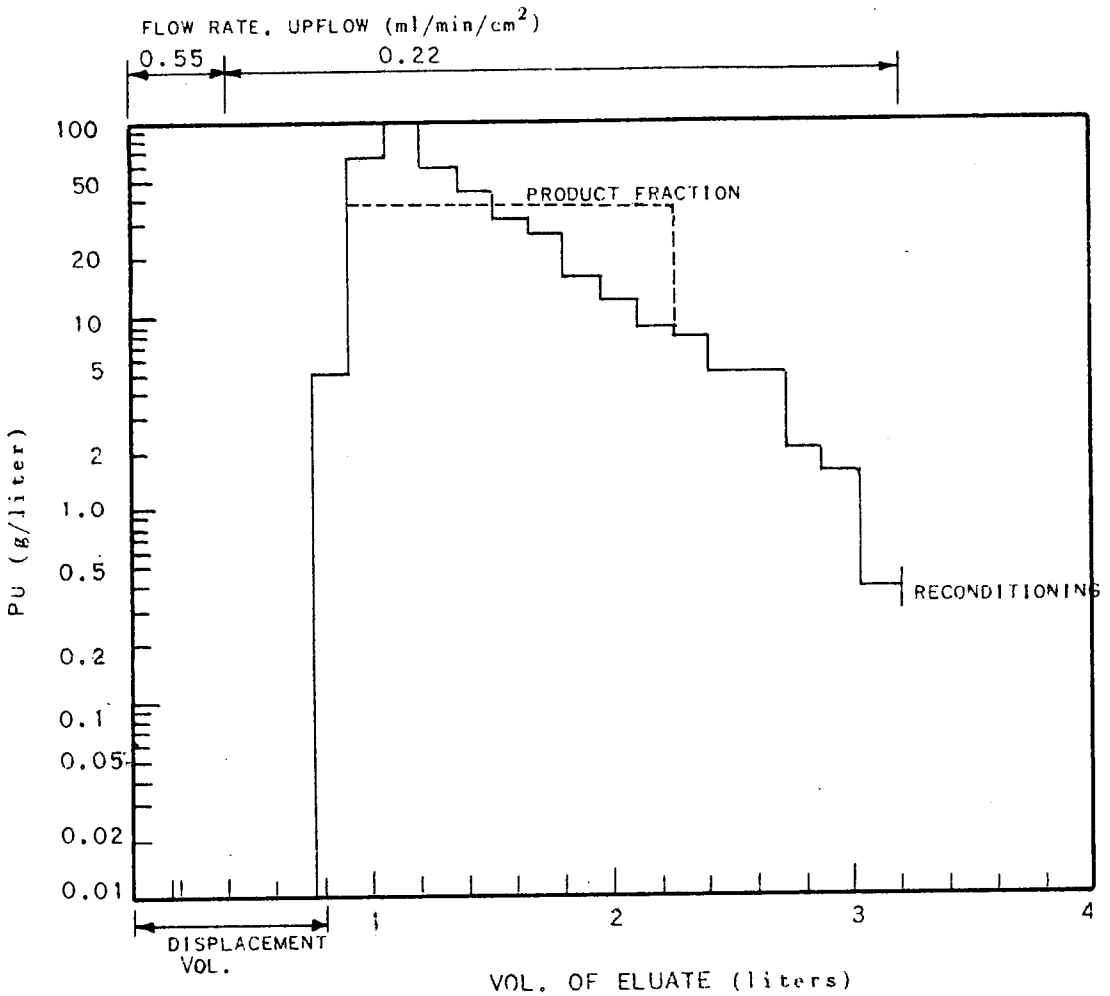


Fig. 6.3. Plutonium in Eluate from Plutonium-Elution Step, Run HCP-2.

Resin: 50- to 100-mesh Dowex-50

Column dimensions: 3-in. diameter, 14-in. height

Elutriant: 5.7 *M* HNO_3, 0.3 *M* sulfamic acid; upflow

Total Pu on column: 70.8 g

Total Pu product: 64.1 g at 42.7 g/liter

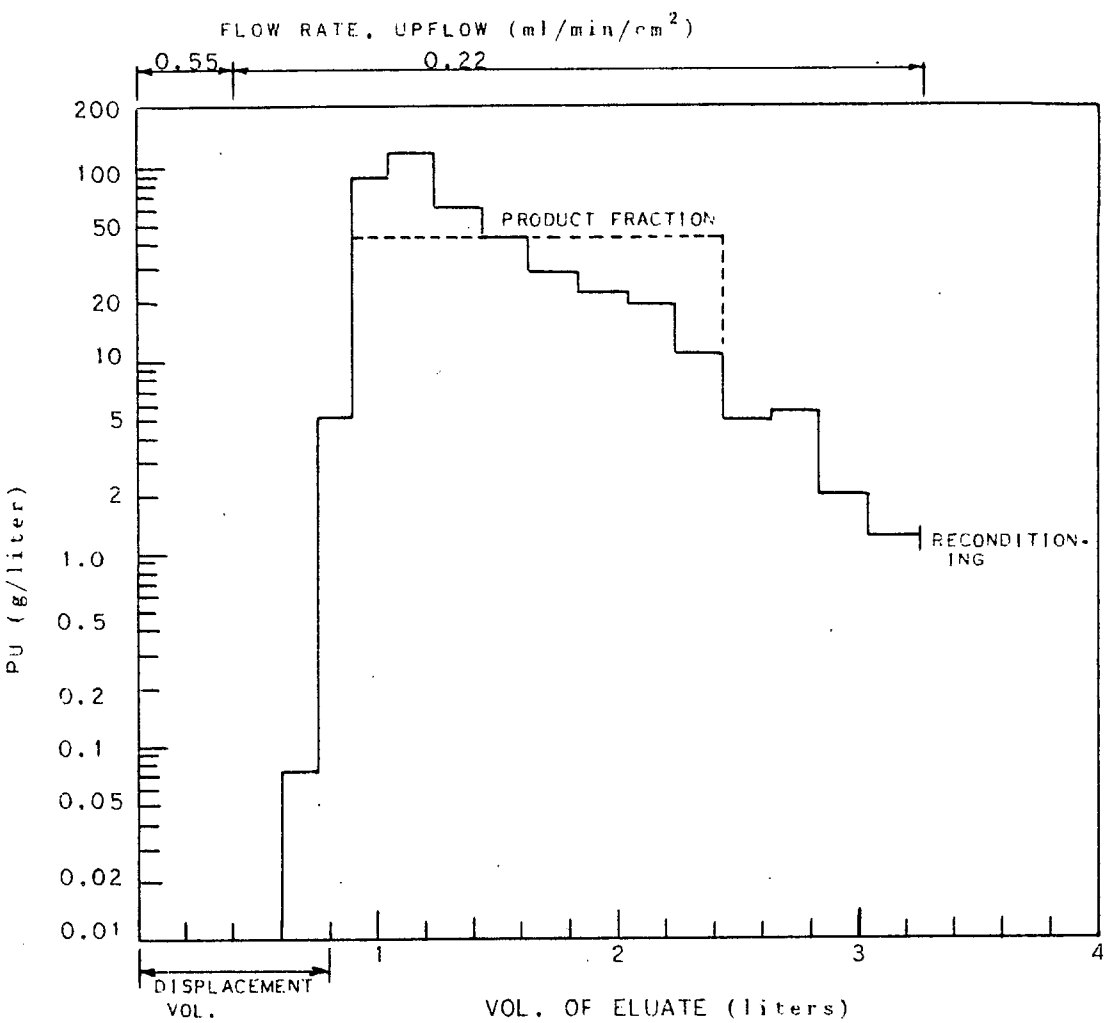


Fig. 6.4. Plutonium in Eluate from Plutonium-Elution Step, Run HCP-3.

Resin: 50- to 100-mesh Dowex-50

Column dimensions: 3-in. diameter, 14-in. height

Elutriant: 5.7 *M* HNO_3, 0.3 *M* sulfamic acid; upflow

Total Pu on column: 91.3 g

Total Pu product: 78.5 g at 42.76 g/liter

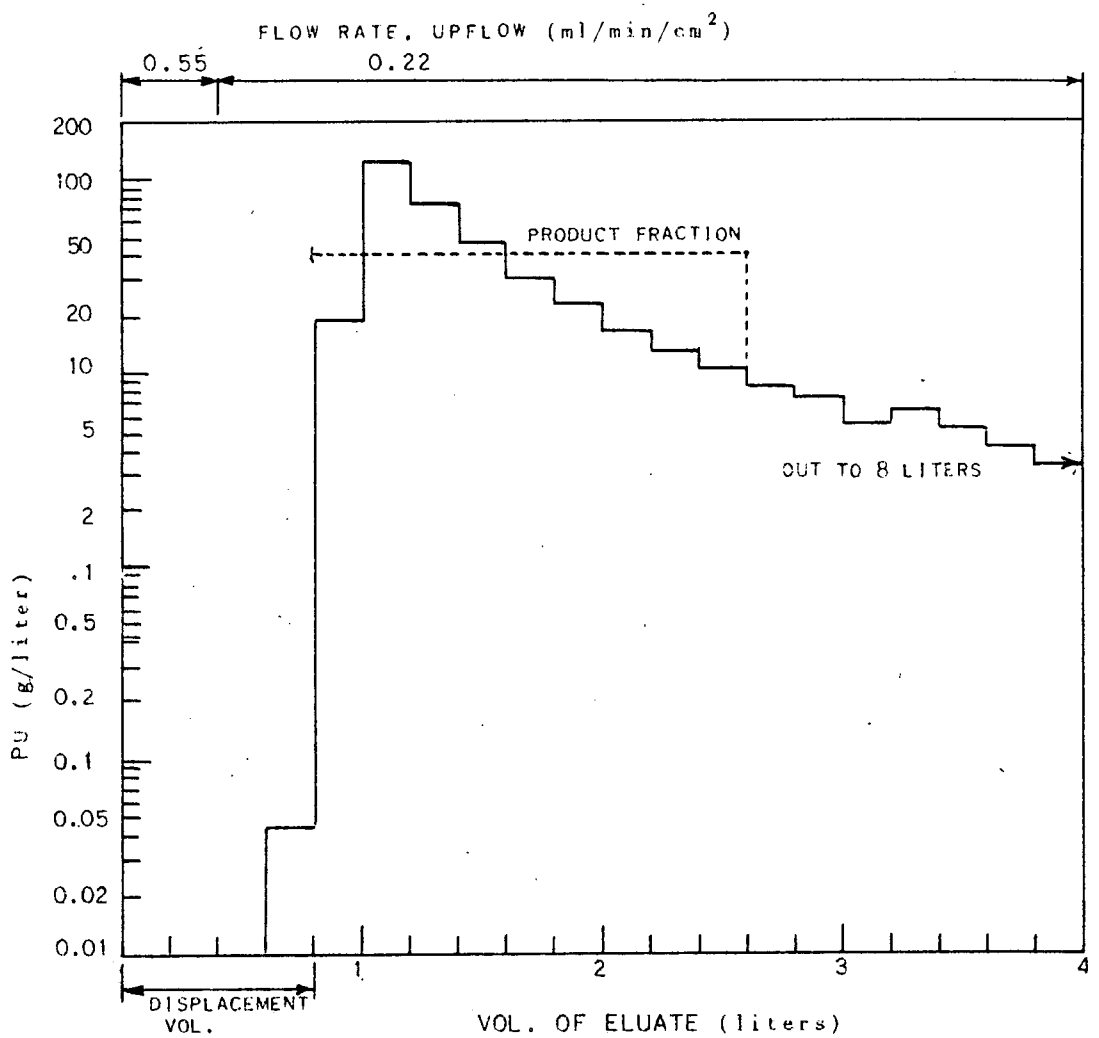


Fig. 6.5. Plutonium in Eluate from Plutonium-Elution Step, Run HCP-4.

Resin: 50- to 100-mesh Dowex-50

Column dimensions: 3-in. diameter, 14-in. height

Elutriant: 5.7 *M* HNO_3, 0.3 *M* sulfamic acid; upflow; 0.22 ml/min/cm^2

Total Pu on column: 91 g

Total Pu product: 88.5 g at 44.6 g/liter

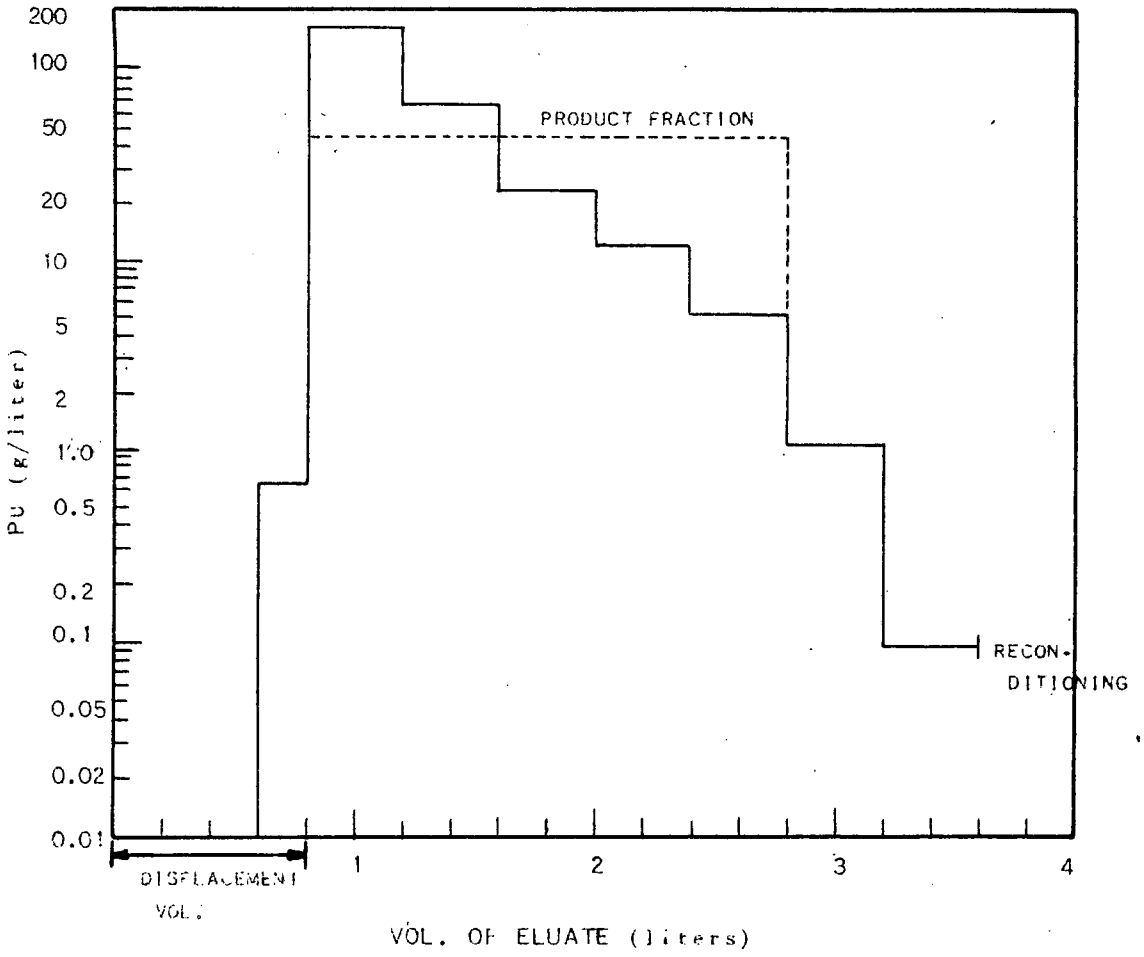


Fig. 6.6 . Plutonium in Eluate from Plutonium-Elution Step, Run HCP-3.

Resin: 50- to 100-mesh Dowex-50

Column dimensions: 3-in. diameter, 14-in. height

Elutriant: 5.7 *M* HNO_3, 0.3 *M* sulfamic acid; flow rate 0.22 ml/min/cm^2, upflow

Total Pu on column: 78 g

Total Pu product: 71.7 g at 44.7 g/liter

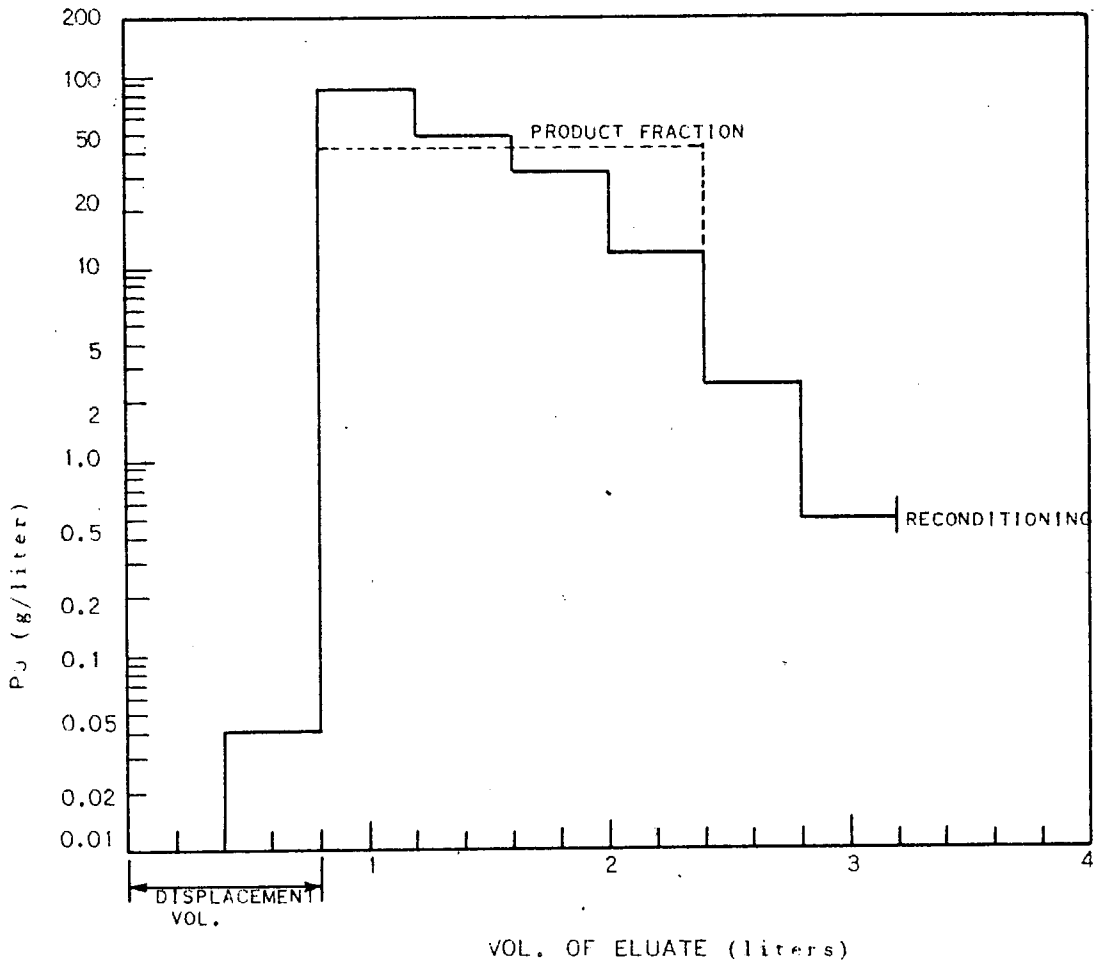


Fig. 6.7 . Normalized Elution Curve, Composite for Runs HCP-1, 2, 3.

Column load: 60 to 80 g of Pu

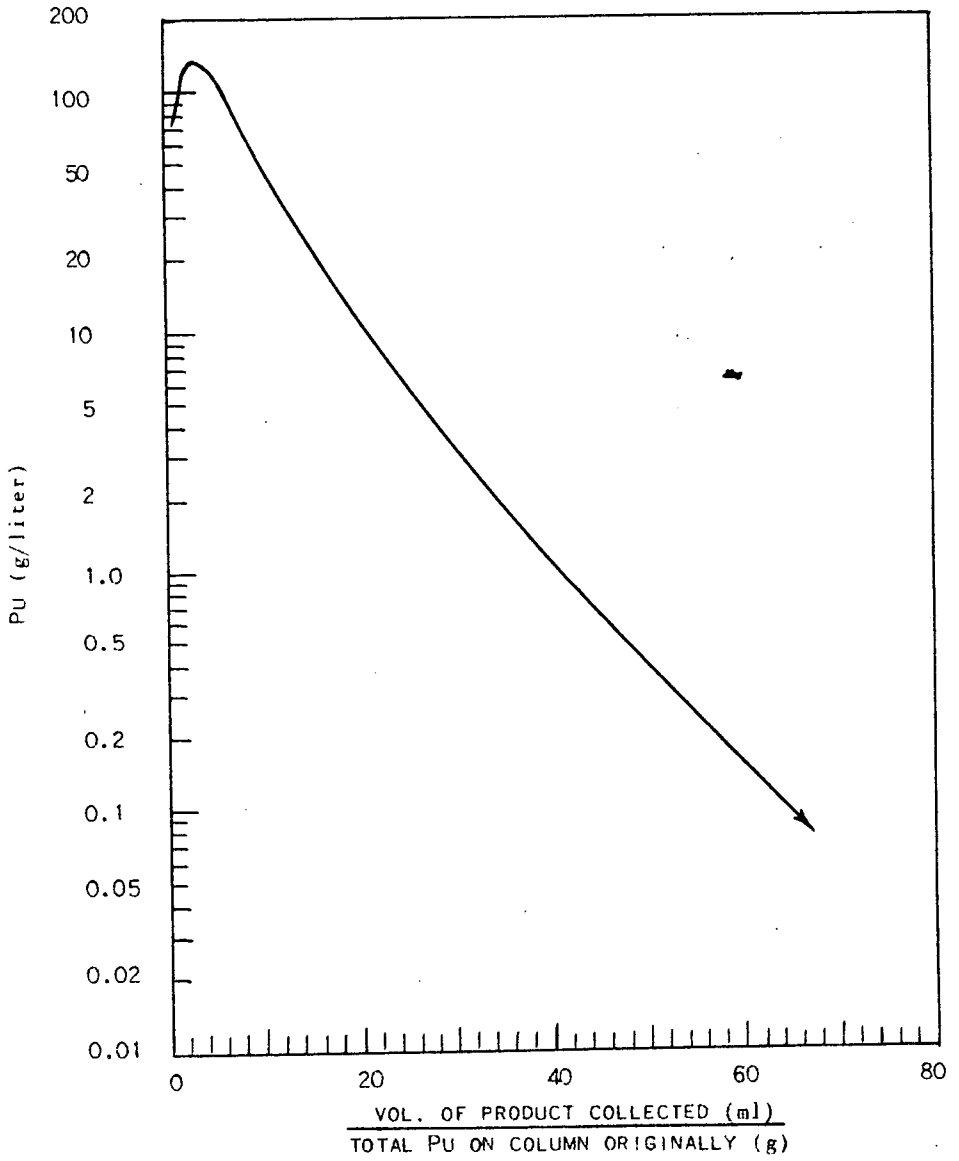
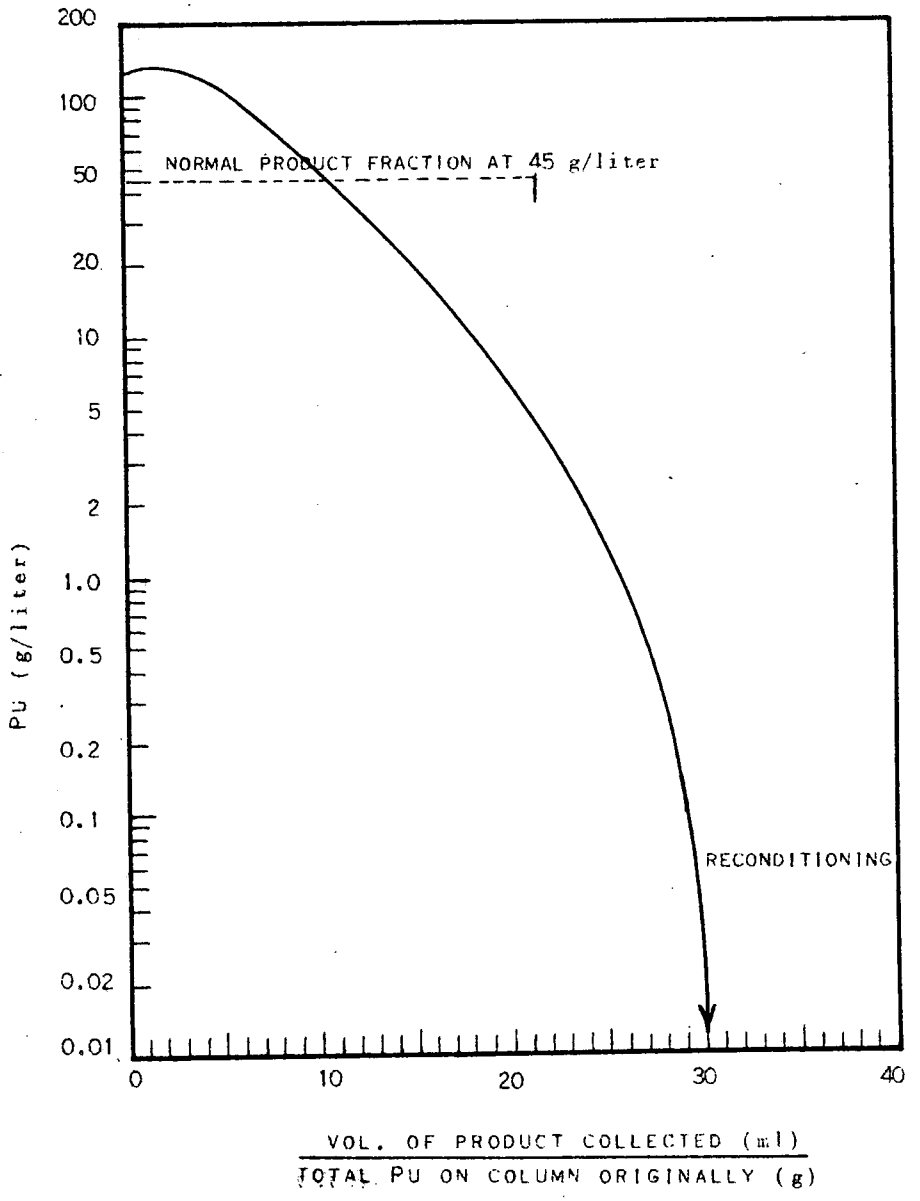


Fig. 6.8. Normalized Elution Curve, Composite for Runs HCP-4, 5.

Column load: 75 to 90 g of Pu



Nitrates. A satisfactory product was obtained with 4 M ammonium nitrate in 1 M HNO_3, but oxidation of the Pu(III) occurred after elution of about 74% of the plutonium on the column. The ammonium nitrate system could probably be stabilized by the addition of sulfamic acid.

6.2 Gassing Effect of Impurities

The occasional evolution of gas that occurs during elution is believed to be caused by impurities on the column, which may be corrosion products from the stainless steel from which the pilot plant is constructed or peroxides formed in the system by plutonium α bombardment. In experimental runs in which clean plutonium solutions were absorbed in all-glass systems, the plutonium was completely eluted without gas formation at any time during the run, and the product was stored as Pu(III) for weeks without oxidation to Pu(IV). In runs in which plutonium contaminated by corrosion products, principally iron, was used, the oxidation appeared to have a shorter induction period.

Corrosion Products. Ferrous iron, the impurity most likely to be present in the product stream from a stainless steel column, causes reduction of nitric acid. In experimental runs, plutonium from solutions contaminated with corrosion products, principally iron, was absorbed by Dowex-50 and eluted with 5.7 M HNO_3—0.3 M sulfamic acid without evolution of gas in the bed. Preliminary experiments made with 0.18 M ferrous sulfate alone indicated that 0.3 M sulfamic acid is not sufficient to inhibit the oxidation of ferrous iron of this strength by 5.7 M HNO_3 but that 0.75 M sulfamic acid inhibits it for several hours. However, iron contamination of this magnitude is not expected in the production plant, and would be objectionable in any case because it might interfere with the peroxide precipitation. It was also shown that 0.3 M HNO_3 (the acid concentration of the Purex IIBP stream) oxidizes Fe^{2+} to Fe^{3+}, but that 0.05 M hydroxylamine prevents the oxidation.

Studies are being made on the oxidation of chromium and nickel.

Hydroxylamine. Hydroxylamine alone is absorbed by Dowex-50 and causes gas evolution when it is eluted with uninhibited 5.7 M HNO_3. It was found that the absorption of hydroxylamine depends on the acidity of the feed solution and that hydroxylamine is approximately the same as H^+ in absorbability (Fig. 6.9).

A 10-ml column that had been saturated with 0.05 M hydroxylamine was eluted with 5.7 M HNO_3 containing 0.3 M sulfamic acid (Table 6.3). No gassing occurred, and essentially all the hydroxylamine was eluted in three to five volume changes. In a similar experiment in which 0.1 M HNO_3 was used in the feed and 0.3 M HNO_3 with no sulfamic acid was used as the eluriant, no gassing occurred and 35 volume changes were required for elution of most of the hydroxylamine (Table 6.4).

The variation in the absorption of hydroxylamine as a function of H^+ concentration was shown by the fact that a 10-ml resin column with a capacity of about 23 milliequivalents absorbed 7.8 milliequivalents of hydroxylamine from a 0.05 M solution in 0.3 M HNO_3 and 13.8 milliequivalents from 0.1 M HNO_3.

Iron plus Hydroxylamine. When iron and hydroxylamine are both present, gassing occurs if uninhibited 5.7 M HNO_3 is used as the elutriant. A 10-ml resin column was saturated with a feed containing 0.05 M $FeSO_4$, 0.05 M hydroxylamine sulfate, and 0.3 M HNO_3. No gassing occurred when the elutriant was 5.7 M HNO_3 plus 0.3 M sulfamic acid, but violent gassing and rupturing of the bed occurred when the elutriant was uninhibited 5.7 M HNO_3. The gassing appeared qualitatively to be more violent than when hydroxylamine alone was being eluted.

Although the resin is supposed to be in the acid form at the start, there is an acid deficiency, as was shown by an experiment in which a 0.3 M HNO_3 feed containing 0.052 M hydroxylamine sulfate and 0.045 M Fe^{2+} was used (Fig. 6.10). The acid deficiency of the resin is shown by the difference between the excess H^+ and the theoretical displaced H^+. During the first twenty volume changes, both hydroxylamine and iron are absorbed almost completely. At saturation, which occurs near 60 volume changes throughput (300 ml), the resin bed held 13.5 milliequivalents of Fe^{2+} and 4.5 milliequivalents of hydroxylamine.

Peroxides. Hydrogen peroxide was found to be absorbed in small amounts, only 1 millimole on a 10-ml Dowex-50 resin column from a 0.3 M HNO_3 solution containing 3 g of hydrogen peroxide per liter. However, the effects of peroxides in a production run might be very different from those in a run of this kind. In the production run, where the peroxides are formed in situ, active free radicals are undoubtedly formed first.

Experimental Results on Pilot-Plant Scale. During the product elution in the HCP series of runs, slight evolution of gas was observed, which resulted in the formation of dime-sized dry spots in the resin bed. The gas evolved was never sufficient to disrupt the bed or interfere with the flow rate, and there was no visual evidence of oxidation of Pu(III) to Pu(IV). In Runs HCP-3 and 4 the elutriant used was 5.5 M HNO_3 + 0.5 M sulfamic acid instead of the usual 5.7 M HNO_3 + 0.3 M sulfamic acid. There was no apparent change at these two levels of antioxidant concentration. The column was rinsed with 0.1 M sulfamic acid alone prior to the elution step of Run HCP-5, but there was still no observable change during the elution.

6.3 Effect of Variations in Elutriant Flow Rate

In small-column studies (0.5 cm^2 in cross-sectional area, 20 cm high) with an elutriant flow rate of 0.4 to 2.0 $ml/min/cm^2$, the product concentration was found to rise quickly and reach a sharp peak of nearly 130 g/liter after 1.5 volume changes (Fig. 6.11). At faster elutriant flow rates, i.e., 0.8 and 2.0 $ml/min/cm^2$, the peak was lower and tailing was greater. Since these runs were made with different samples of resin, the results are only approximately comparable.

In the HCP runs, with columns 45.36 cm^2 in cross-sectional area and 14 cm high, an elutriant flow rate of 0.22 $ml/min/cm^2$ was used for the product cut with satisfactory plutonium concentration in the product. A 10% heel was left on the columns. The flowrate of the displacement volume was varied from 0.5 $ml/min/cm^2$ in the first three runs to 0.2 $ml/min/cm^2$ in the last two, and

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Fig. 6.9

Absorption of Hydroxylamine

on Dowex-50

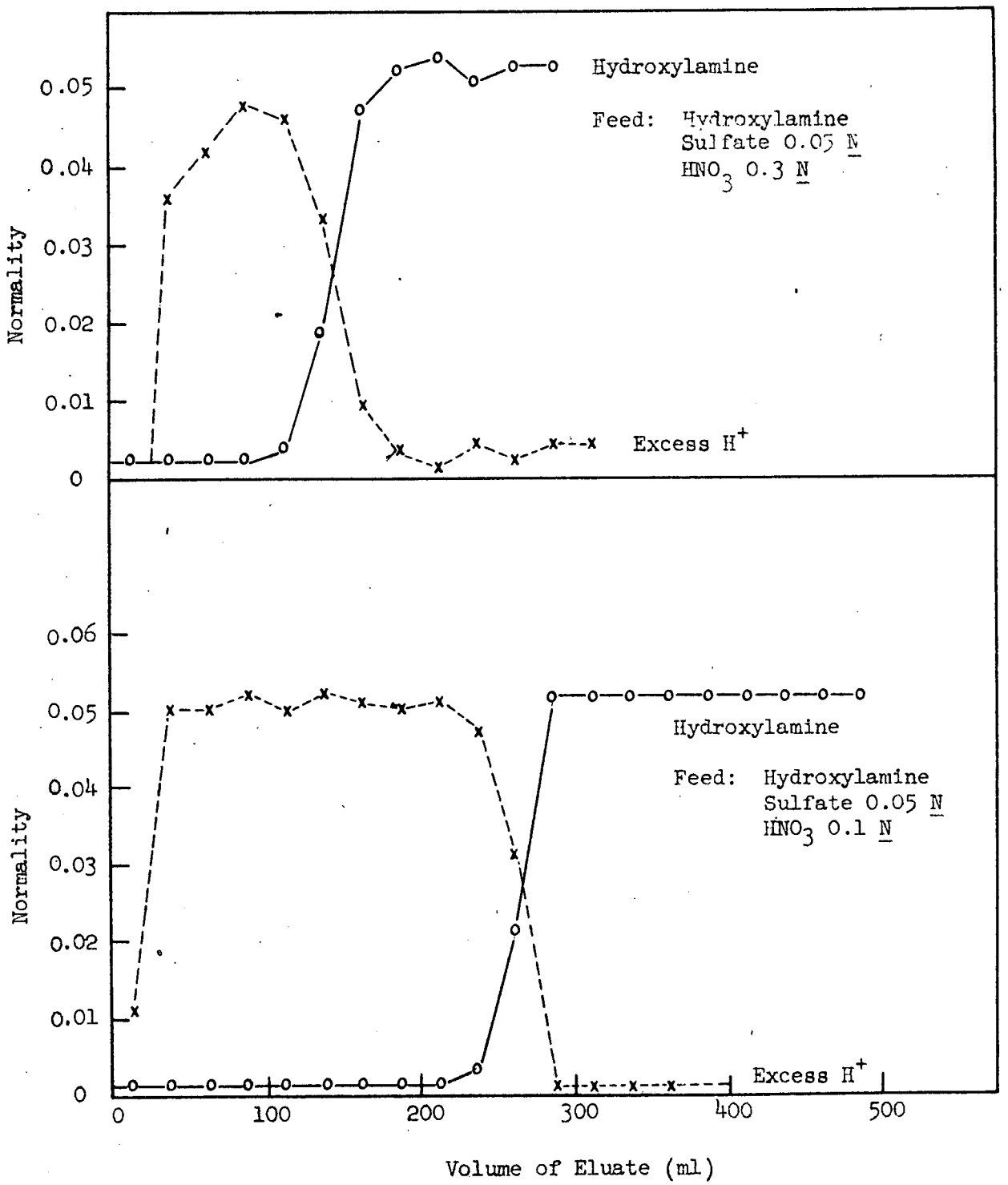


Table 6.3

Elution of Hydroxylamine with 5.7 M HNO_3 + 0.3 M Sulfamic Acid

Feed: 0.3 M HNO_3 containing 0.05 M hydroxylamine sulfate

Column: 10 ml of 12% cross-linked Dowex-50 resin, 50 to 100 mesh; glass column, 0.5 cm^2 in cross section, 20 cm high

1 volume change = 5 ml

Volume of Eluate (ml)	H^+ (M)	Hydroxylamine Sulfate (M)
(Elutriant)	5.75	0.0035 (blank)
10	1.30	0.320
20	5.70	0.555
30	5.70	0.017
40	5.80	0.0035
55	5.70	0.0035
65	5.80	0.0025

Table 6.4

Elution of Hydroxylamine with 0.3 M HNO_3

Feed: 0.3 M HNO_3 containing 0.05 M hydroxylamine sulfate

Column: 10 ml of 12% cross-linked Dowex-50 resin, 50 to 100 mesh; glass column, 0.5 cm^2 in cross section, 20 cm high

1 volume change = 5 ml

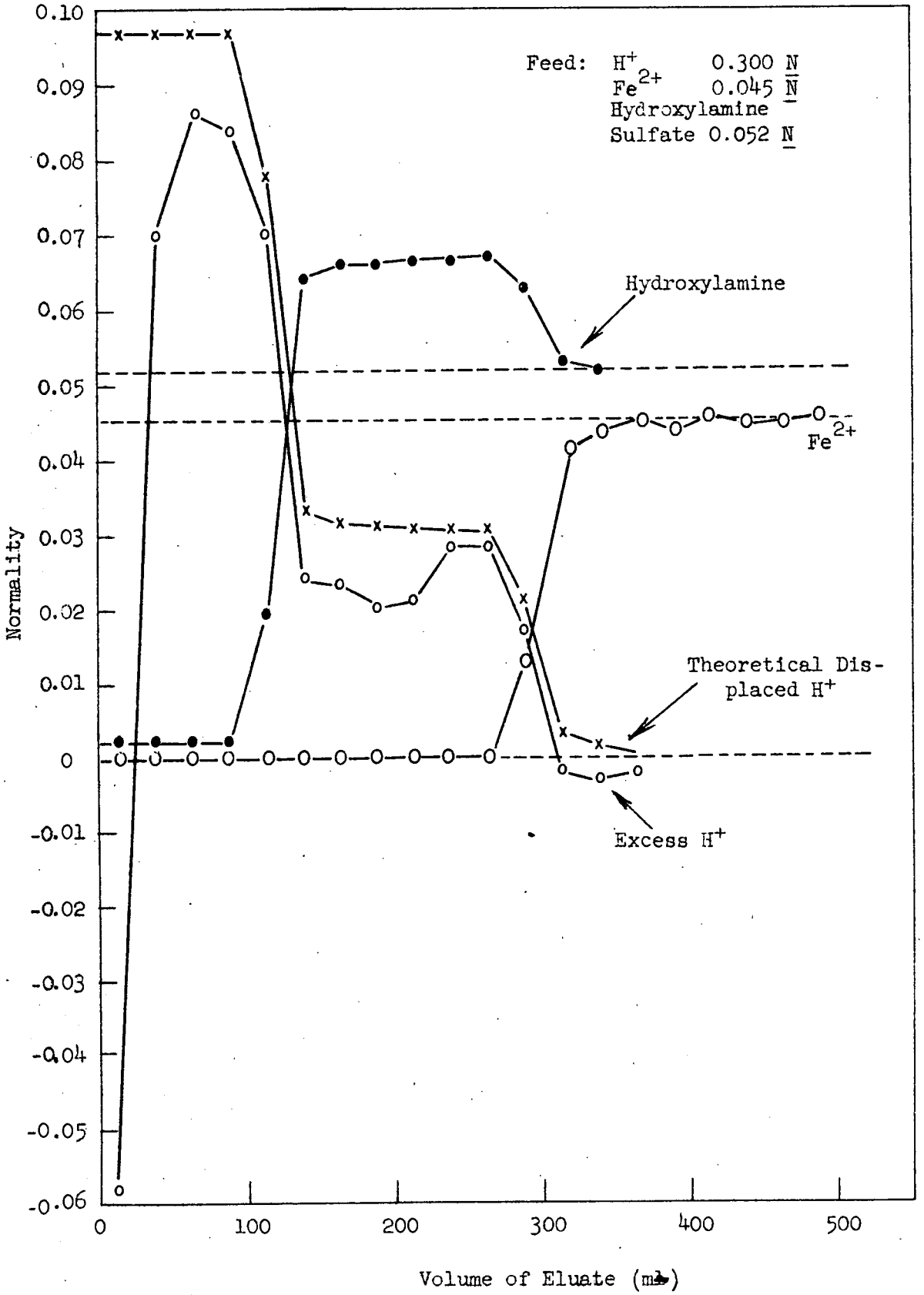
Volume of Eluate (ml)	H^+ (M)	Hydroxylamine Sulfate (M)
(Elutriant)	0.30	0.001 (blank)
25	0.29	0.100
50	0.30	0.115
75	0.29	0.123
100	0.30	0.098
125	0.29	0.072
150	0.29	0.045
175	0.29	0.034
200	0.30	0.005
225	0.29	0.002
250	0.30	0.001
300	0.30	0.002
350	0.30	0.001

Fig. 6.10

[redacted]

Dwg. #14220

Absorption of Fe^{2+} and Hydroxylamine Sulfate on Dowex-50



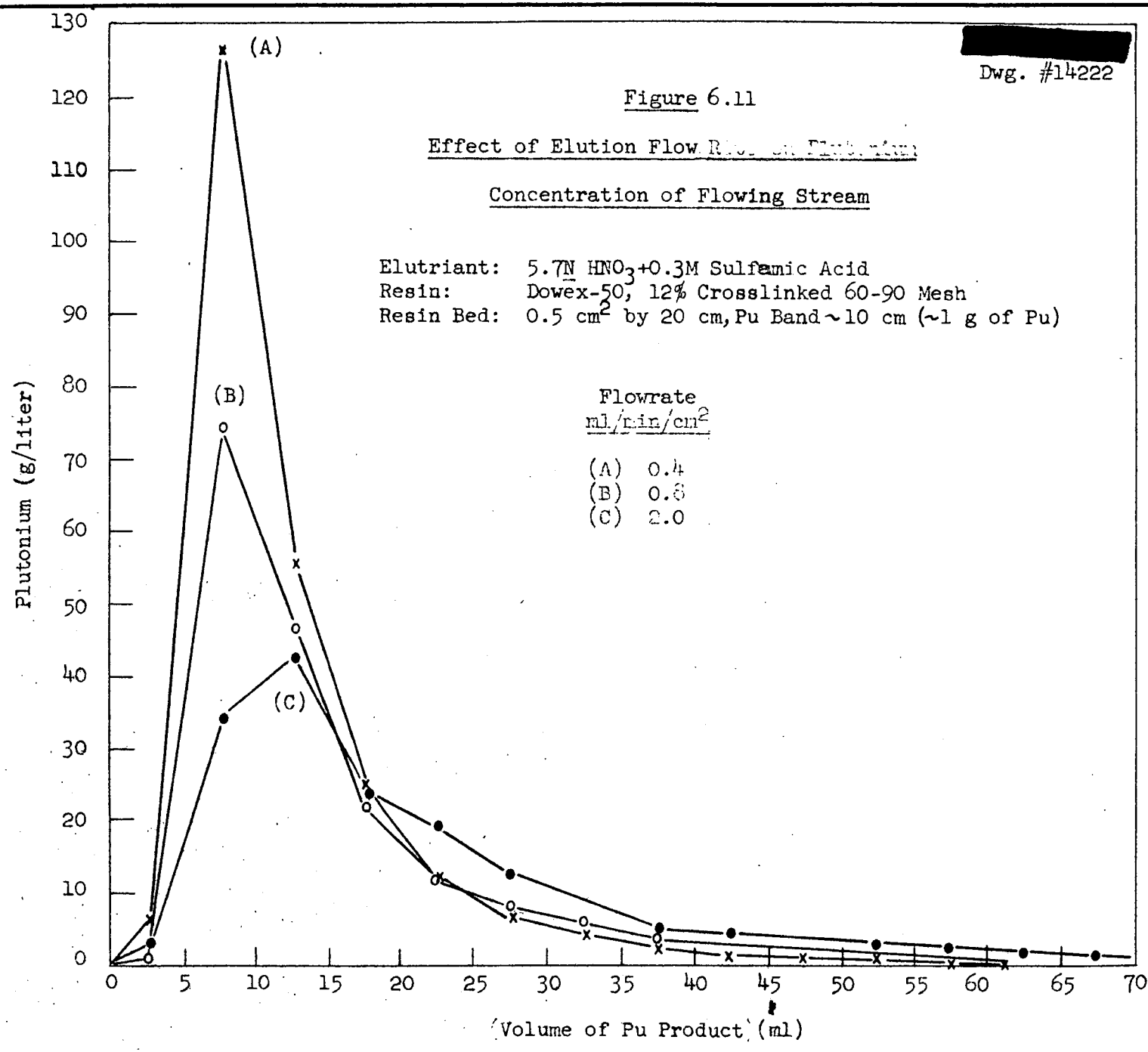
a more abrupt plutonium peak was obtained with the slower rate. The concentration gradient between the dilute nitric acid in the column and the strong nitric acid elutriant depends on the diffusion rate of the acid through the resin particles, and the boundary between the liquid fractions is sharper if a slow flow rate is maintained in all elution operations. This slow flow rate through all operations also gives abrupt boundaries to the plutonium product band.

6.4 Channeling in Resin Bed During Upflow Elution

In the HCP runs the resin was maintained in a fixed bed by the compression spring between the top end plate and the top resin hold plate (Sec. 3.0) and there was no channeling problem. It is believed that this construction will be equally satisfactory with the 7-in.-diameter column.

In some of the earlier runs a particularly bad type of channeling occurred, as a result of the following conditions: the density of Dowex-50 is approximately 1.2 and that of 6 M HNO_3 is 1.19. The settling rate of the resin in the acid is therefore very slow, and, if the acid flows at an appreciable velocity, it tends to carry the resin along. This resulted in the formation in the resin of a wall-less tube of fluidized resin about 1/2 in. in diameter. Such a channel has a lower resistance to flow than the compacted bed, and, as more of the flow is diverted to the fluidized channel, the fluidization is augmented. The "tube" slowly meanders through the bed and eventually thoroughly mixes the clean excess resin with the active resin on which the plutonium is absorbed. Since a large part of the flow takes place in a small portion of the cross-sectional area of the bed, the true flow rate per square centimeter is much higher than the apparent average flow rate. The churning action destroys the concentration gradient along the depth of the resin bed and the countercurrent elution is converted into a pseudo-batch elution of diluted resin.

Two methods of preventing the fluidization were tried before the compression spring was introduced, but neither was entirely satisfactory. In Run HP-9 a sintered-glass disk was fused into the column about 5 in. from the top to retain the bed during the elution. However, the column was filled with resin in the expanded state, which is the state in 0.25 M H_2SO_4, and it contracts in the 5.7 M HNO_3 elutriant, creating an excess aqueous volume beneath the sintered disk. In Run HP-11-14 the sintered disk was replaced by a movable bed of coarse Ottawa sand (density 2.6 g/cc) resting on several close-fitting Fiberglas disks. The weight of the sand compacted the resin bed and prevented fluidization of the resin, but the depth of sand (3 in.) needed to force the resin down was dead space and resulted in a lowered product concentration.


[redacted]
Dwg. #14222
Figure 6.11
Effect of Elution Flow R
Concentration of Flowing Stream
Elutriant: 5.7N HNO_3+0.3M Sulfamic Acid
Resin: Dowex-50, 12% Crosslinked 60-90 Mesh
Resin Bed: 0.5 cm^2 by 20 cm, Pu Band ~10 cm (~1 g of Pu)
Flowrate
ml/min/cm^2
(A) 0.4
(B) 0.8
(C) 2.0
(A)
(B)
(C)
Plutonium (g/liter)
Volume of Pu Product (ml)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70

7.0 PURITY OF PRODUCT

The purification obtained in a given resin system depends on the distribution coefficient of the ion in question relative to the plutonium form of the resin. In the downflowing absorption stream, saturation of the top of the column with plutonium causes the contaminating ions to be absorbed farther down the column, and, if the downflowing uranium-elution step is included, some ions are forced farther down the column. With the upflowing plutonium elutriant these ions do not move to the top of the column until after the plutonium product fraction has been collected.

7.1 Overall Decontamination Factors

Specifications for the plutonium nitrate product solution require that gross β and γ decontamination factors of the order of 10^7 be obtained in the overall Purex process. These specifications were met (see Appendix A2, pp. 56, 61, and 65. The overall gross β and γ decontamination factors are rather uniform, in the neighborhood of 6×10^7 and 2×10^6, respectively, for runs on slugs cooled from about 90 to 190 days (Runs HCP-2 through 5). The factors are somewhat higher for the slugs cooled 330 days (Run HCP-1). The history of the slugs used in these runs is given in Appendix 7.

7.2 Individual Decontamination Factors

The individual fission product decontamination factors varied widely from one run to the next. The variations were not the result of erratic behavior of the resin column but of certain other conditions that were not always controlled, for example:

1. Since zirconium and niobium in weak acid solution plate out on the walls of the feed tank, the decontamination factor determined for these elements is partly dependent on the length of time the feed solution is allowed to stand before being analyzed.

2. The forms of zirconium and niobium present in the pilot plant IIBP solution have a lower affinity for Dowex-50 resin than does plutonium, and they are absorbed farther down the column. With larger amounts of plutonium and of sulfuric acid elutriant, the amount of these contaminants eluted with the uranium is larger.

3. About a third of the activity of a gray, curdy material that formed in suspension in the feed in some of the runs was shown to be due to $UX_1 + UX_2$. This material deposited on the top hold plate of the column, and varying amounts of it were dissolved by the strong nitric acid plutonium elutriant and passed into the product. A filter has been installed in the feed line to keep this material from the column in future runs.

4. The high concentration of plutonium in these solutions made it

necessary to dilute all solutions considerably before making analyses. At these low concentrations of fission elements the low precision of the decontamination factor determination may have caused apparent variations.

The consistency of the leakage of ruthenium in absorption and the partial elution of zirconium and niobium along with uranium demonstrate an interesting phenomenon. These elements are known to form various hydrolyzed and polymeric states with slow mutual exchange properties, which may well be the cause of the apparent fractionation in different steps.

7.3 Distribution of Radiochemical Contaminants

Absorption Step. The principal activity in the absorption-step effluent is ruthenium. It appears in both the flowing stream and composite waste as a constant leakage of β and γ activity (Fig. 7.1). The amount in the effluent is reasonably constant at approximately 40% of that in the feed (Table 7.1).

Uranium-Elution Step. Small amounts of ruthenium and rare earths appear in the uranium eluate, together with varying amounts of zirconium, niobium, and $UX_1 + UX_2$ (items 2 and 3, Sec. 7.2). The β and γ activities of the eluate vary with increasing volume (Fig. 7.2).

Plutonium-Elution Step. About 40% of the ruthenium of the feed goes into the plutonium product solution. This is the limiting activity in product purification. The amount of $UX_1 + UX_2$ that goes into the product may be considerably less when the gray curd is filtered off. Other contaminants are less than 5% of the amount in the feed. The residual fission product activity of the plutonium product is only a few per cent of the natural plutonium X-ray activity (see Appendix 6).

7.4 Ionic Reduction Factors

Appreciable decontamination from ionic constituents is obtained in the ion-exchange process. Reduction factors varied from apparent enrichment in some cases to 195 for iron in one run (see Appendix 2, pp. 56, 57, 62 and 66. Analysis of the absorption and uranium-elution effluents showed that only very small amounts of ionic contaminants went into these streams, and that no apparent ionic decontamination took place in these steps (Appendix 2, page 67).

[redacted]

DWG. 16091

Fig. 7.1. Beta and Gamma Activity Levels in Waste During Absorption, Run HCP-2. Gamma activity measured in millivolts on ionization chamber in Bldg. 3019.

Resin: 50- to 100-mesh Dowex-50

Column dimensions: 3-in. diameter, 14-in. height

Feed conditions: 3.7 g of Pu(III) per liter, 0.49 N H^+; flow rate 5.5 ml/min/cm^2, downflow; total volume 19 liters

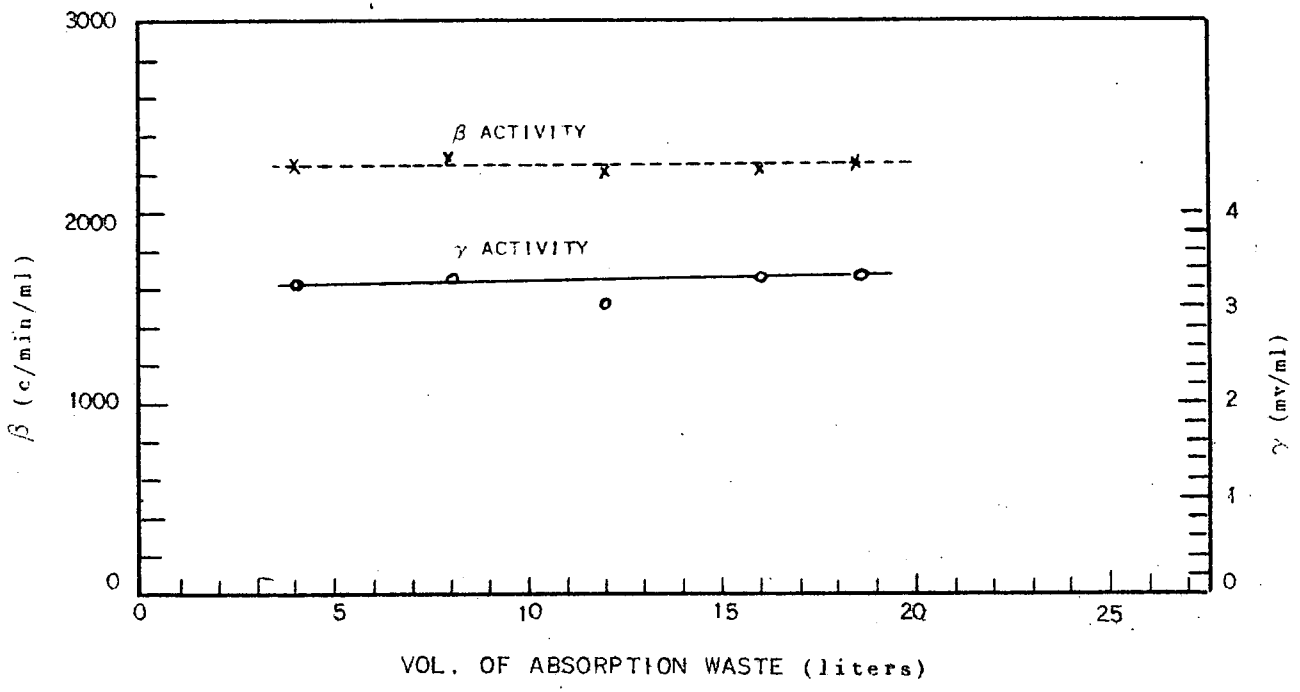


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Fig. 7.2. Beta and Gamma Activity Levels in Uranium-Elution Step Eluate, Run HCP-2. Gamma activity measured on ionization chamber in Bldg. 3019.

Resin: 50- to 100-mesh Dowex-50

Column dimensions: 3-in. diamter, 14-in. height

Elutriant: 0.25 *M* H_2SO_4 + 0.02 *M* hydroxylamine sulfate; flow rate 2.2 ml/min/cm^2, downflow

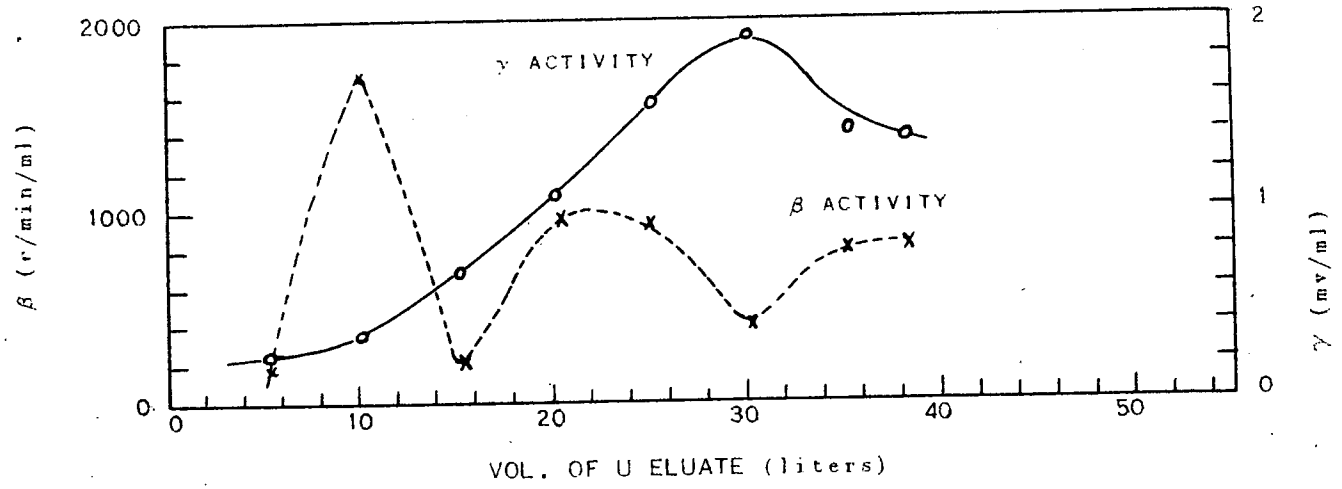

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Table 7.1

Distribution of Radioactive Contaminants under Cycle Operation

Contaminant	Activity in Absorption Waste							Activity in U Elution Waste							Activity in Product[a] (% of feed activity)	Activity Buildup on Column[a] (% of feed activity)
	(c/m/mg Pu in feed)[b]			(% of feed activity)[a]				(c/m/mg Pu in feed)[b]			(% of feed activity)[a]					
	HCP-2	HCP-3	HCP-4	HCP-2	HCP-3	HCP-4	Median	HCP-2	HCP-3	HCP-5	HCP-2	HCP-3	HCP-5	Median		
u	490	774	729	40.6	40	37	40	40	215	78	3.3	11	4.3	4	40	10 - 20
r	1.6	6.2	1.2	0.8	4.7	0.05	<1	1.6	88	20	0.8	68	2.9	(c)	<5[c]	95[c]
b	0.8	2.4	1	1.5	1	0.2	<1	4	14	26	8	46	19	(c)	<5[c]	95[c]
RE	0.6	—	2	0.4	---	0.2	<1	1.2	---	5.2	1	---	11	<1	3	95
X_1 + UX_2	6	2	1.7	(d)	8	1	—	20	14	90	(d)	49	(d)	—	5 - 10[e]	---

(a) These values are selected in an attempt to evaluate the data. They are not to be considered necessarily representative.
(b) Normalized to total plutonium in run in order that direct comparison with feed and product activities might be made.
(c) See Sec. 7.3.
(d) Amount in waste higher than in feed.
(e) Anomalous amount of activity in runs, but amount in product guessed to be 5 to 10% of that in feed if the curd is separated prior to the product elution.

[redacted]

8.0 RESIN COLUMN DECONTAMINATION

8.1 Decontamination Procedure

After a number of absorption and elution cycles the accumulated fission products, chiefly zirconium, niobium, and rare earths must be removed from the column if shielding is to be avoided. First, the plutonium heel from the last run is completely eluted. The column is then washed with 2.5 volume changes of 0.5 M oxalic acid, which, by removing the zirconium and niobium, reduces the contamination by a factor of 10. This decontamination is sufficient to prevent serious buildup, but, if other activities are considered objectionable, they can be removed with 2 M ammonium citrate at pH 5.6. Sufficient ammonium citrate (about 2.5 volume changes) must be used to convert all the resin to the ammonium form. The cleaning action of either solution is improved by allowing it to stand in the column for a few hours, probably because polymerized forms are converted to a soluble form and dissolved.

8.2 Distribution of Activities on Column

Activity profiles were determined from readings made on a β-γ probe placed in contact with the column at various places along its length (Fig. 8.1). Following Runs HCP-3 and 5, the column was stripped of plutonium, and activity profiles were determined after various treatments had been given to the column.

For Run HCP-3, activity profiles were determined (1) after absorption of the plutonium, (2) after elution of the plutonium, and (3) after each of successive washes of the column with 0.05, 0.1, and 0.5 M oxalic acid and 0.5 M ammonium citrate, pH 5.6 (Fig. 8.2). The activity was considerably less after the plutonium elution, and it dropped after each wash. After the final wash the top hold plate containing the high-activity sludge was removed, and the column was then essentially decontaminated. Results of analyses of the eluate made at two points (Table 8.1, Fig. 8.3) showed that principally zirconium and niobium were removed with oxalic acid. All are removed to some extent by the citrate wash.

In Run HCP-5 the fission product activity in the IBP stream was considerably higher than in Run HCP-3 (Appendix 7). The activity profile after the plutonium product elution had the same shape in the two runs, but for Run HCP-5 the level was higher. The profile was determined after complete plutonium elution and then after various volumes of 2 M ammonium citrate (pH 5.6) had passed through the column (Fig. 8.4). The radiation of the column was down to background after about 6 volume changes. The decontamination was improved considerably by allowing the citrate solution to remain on the column overnight (Table 8.2, Fig. 8.5).

The activity levels in these experiments may be some indication of those under Savannah River plant conditions if the same relative purity of the Purex product is assumed. The ion-exchange coupling columns should add activity during each run which is roughly 2 to 3 times that on the 3-in.-diameter column after Runs HCP-4 and 5. The cooling period of the slugs will be less, but the

6- or 7-in.-diameter columns will offer more self-shielding. Under these conditions, 50 to 60 mr/hr of activity would be expected on contact with the columns for each run. However, it should be emphasized that this is not the activity level at any reasonable working distance. In all runs the maximum level at 2 ft was 2 mr/hr or less.

Table 8.1

Radiochemical Analysis of Resin Column Decontamination Waste, Run HCP-3

Samples taken from fractions of waste as indicated in Fig. 8.3
Flow rate of elutriant: 0.5 ml/min/cm^2

Contaminant	Activity in Waste (c/m/ml)	
	0.5 M Oxalic Acid Wash	0.5 M Ammonium Citrate, pH 5.6, Wash
Ru β	14	456
Zr β	1030	83
Nb β	81	43
Total rare Earth β	—	9
$UX_1 + UX_2$ β	10	88

Table 8.2

Radiochemical Analysis of Resin Column Decontamination Waste, Run HCP-5

Elutriant: 2.0 M ammonium citrate, pH 5.6

Samples taken from fractions of waste as indicated in Fig. 8.5

Contaminant	Activity in Waste (c/m/ml)		
	After 1 Vol. Change	After 2.5 Vol. Changes	After 5.5 Vol. Changes and Column down Overnight
Ru β	404	1,710	560
Zr β	860	10,400	3540
Nb β	956	411	717
Total Rare Earth β	22	8	8
$UX_1 + UX_2$ β	67	171	636

Fig. 8.1. Activity-Level Distribution Along Process Column, Through HCP-3 Product Elution. Activity at contact with column measured with β-probe. Measurements were made at the end of the product elution, i. e., with approximately a 10% plutonium heel on the column.

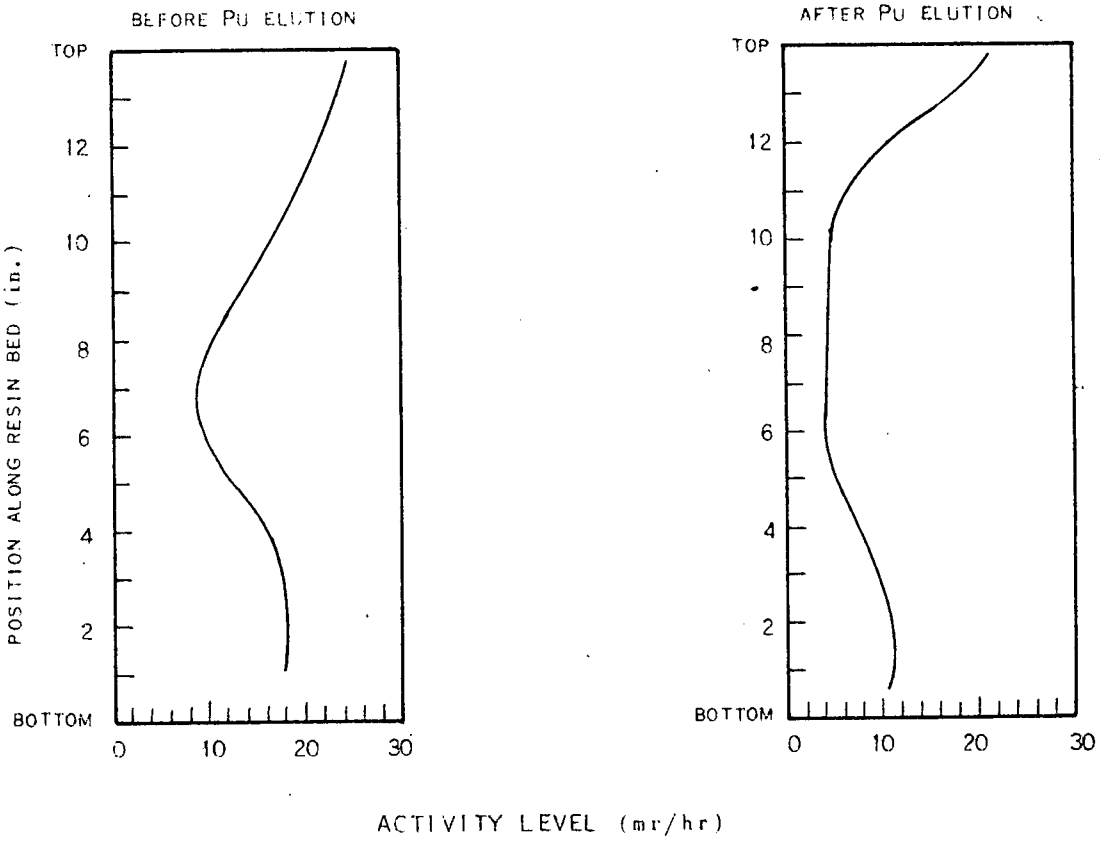


Fig. 8.2 . Activity Levels along Process Column after Decontamination Steps Following Run HCP-3. Activity at contact with column measured with β- probe.

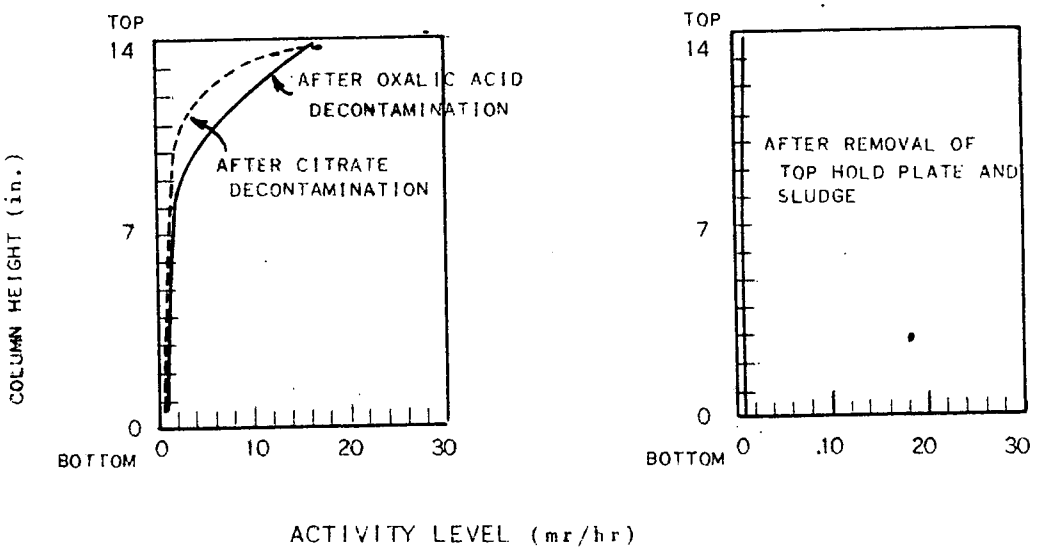
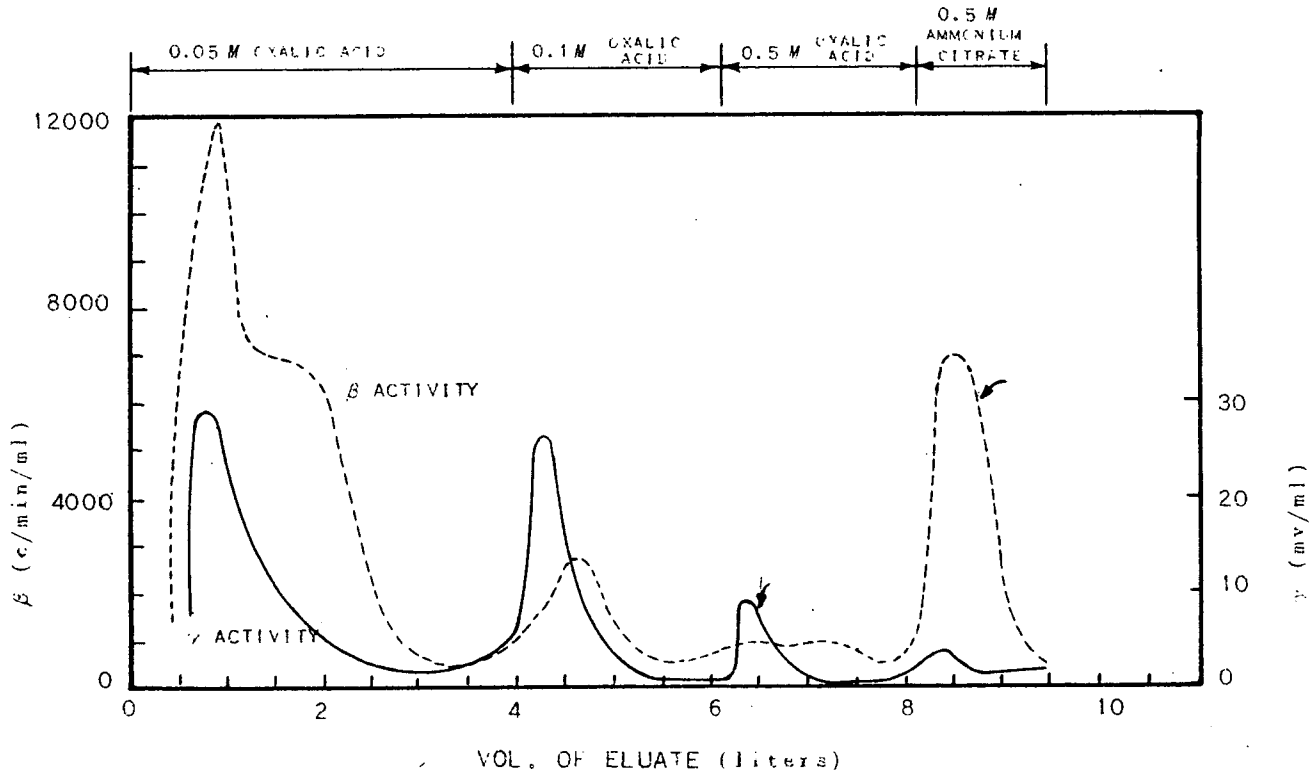


Fig. 8.3. **Beta and Gamma Activities in Eluate During Decontamination Rinse after Run HCP-3 Product Elution.** Arrows show point at which samples were taken for radiochemical analysis. Gamma activity measured in millivolts on ionization chamber in Bldg. 3019.



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[redacted]

DWG. 16096

Fig. 8.4 . Activity Profile of Process Column Through Decontamination Cycle, Run HCP-5. Activity at contact with column measured with β-γ probe. See Fig. 8.5 for comparison with points on citrate elution curve.

Elutriant: 2.0 *M* ammonium citrate, pH 5.6; upflow

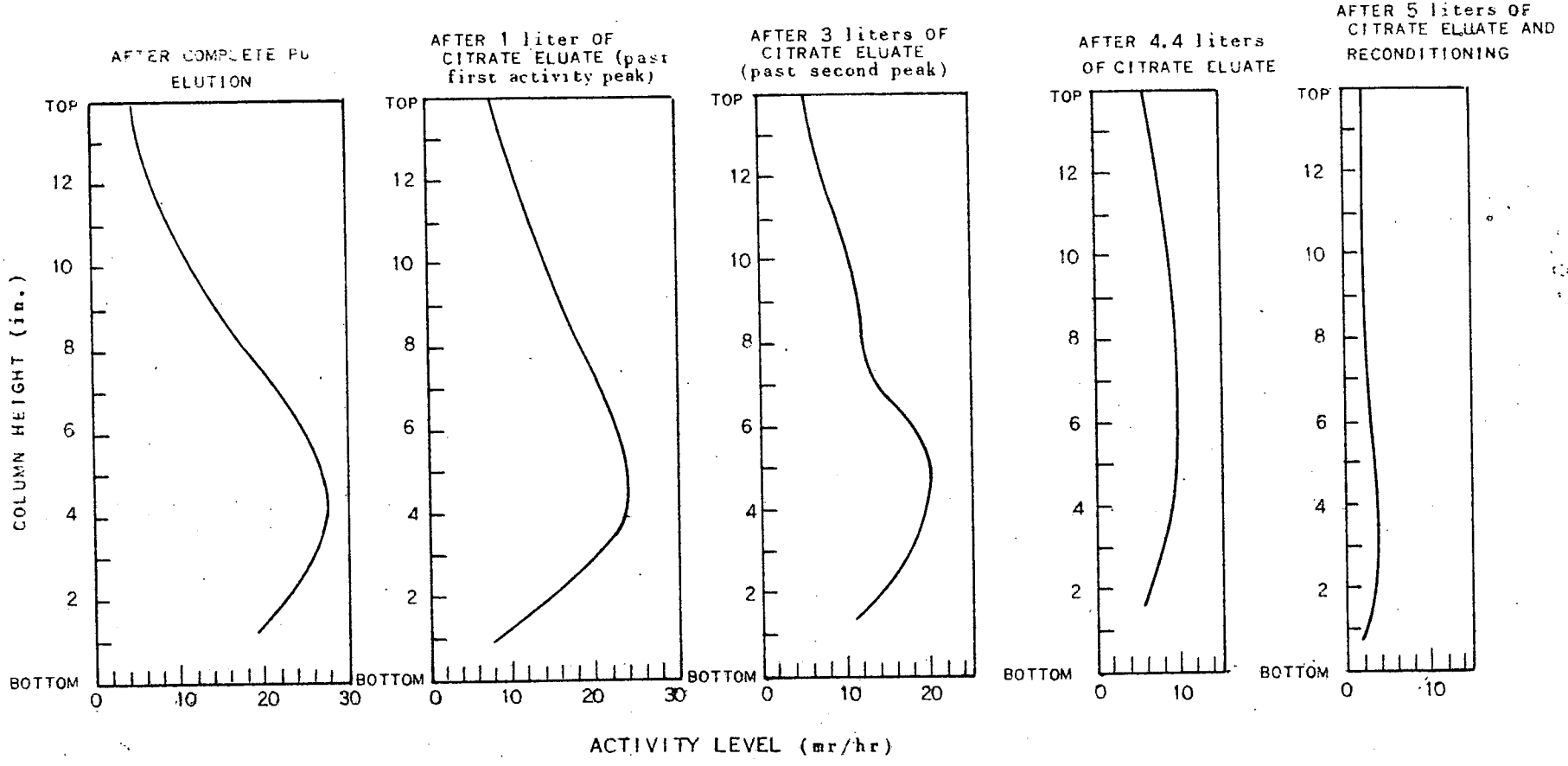

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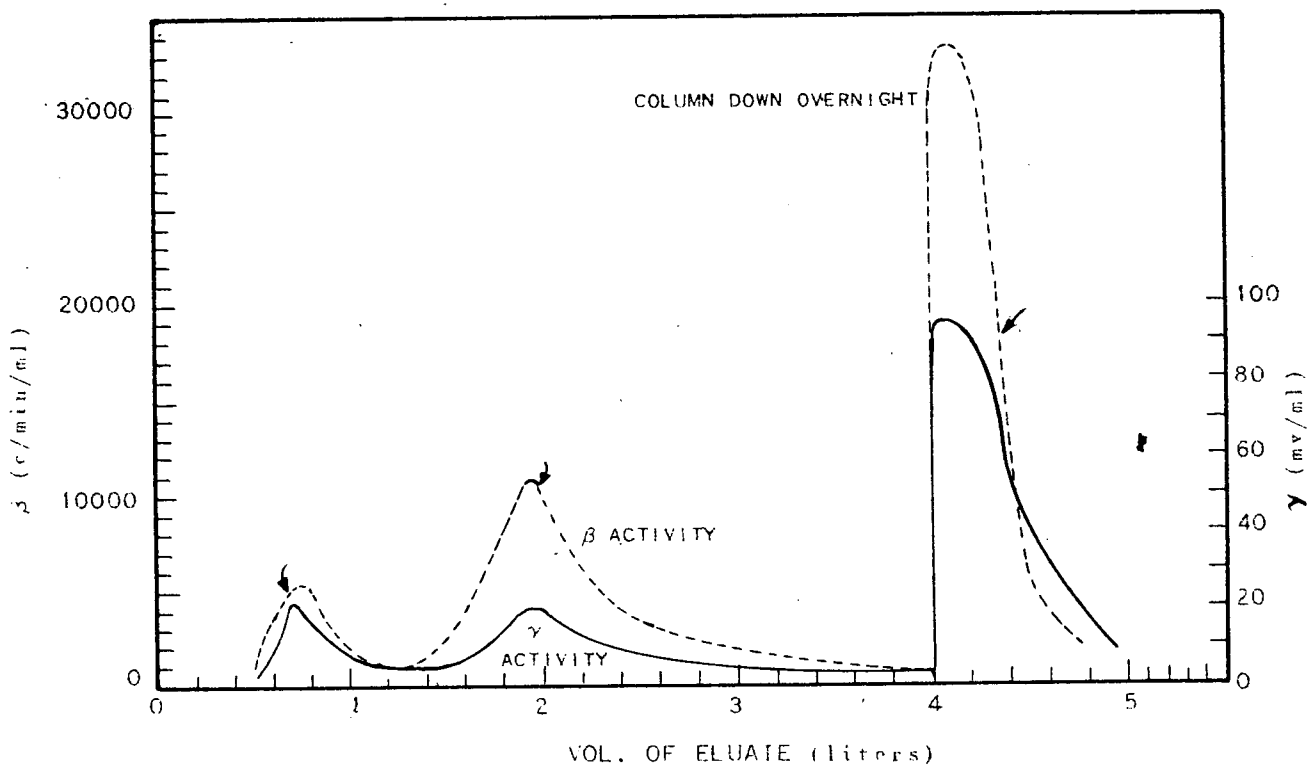
Fig. 8.5. Beta and Gamma Activities in Effluent During Decontamination after Run HCP-5 Product Elution. Arrows show point at which samples were taken for radiochemical analysis. Gamma activity measured in millivolts on ionization chamber in Bldg. 3019.

Resin: 50- to 100-mesh Dowex-50

Column dimensions: 3-in. diameter, 14-in. height

Elutriant: 2.0 *M* ammonium citrate (pH 5.6), 0.55 ml/min/cm², upflow



Appendix 1

PRECIPITATION OF PLUTONIUM PEROXIDE

Tests were made on the plutonium product from the ion-exchange process in order to determine its suitability for conversion to the peroxide. The peroxide is hydrofluorinated to form plutonium tetrafluoride, which is eventually converted to elemental plutonium. Results indicate that the ion-exchange product can be handled without difficulty and that the peroxide prepared from it is satisfactory in yield and bulk density (Table A1.1).

Addition of sulfate before the precipitation is not necessary since the sulfate ion required is supplied by the oxidation of the sulfamic acid. Addition of sulfite is not necessary because the plutonium is eluted in the III valence state. A small decrease in the plutonium loss in the supernatant is achieved by lowering the nitric acid concentration from 5.45 to 4.24 M, but this is not important since the supernatant is recycled.

Table A1.1

Summary of Plutonium Peroxide Precipitation Data

Run HP-9: Sample of ion-exchange plutonium nitrate product solution precipitated with 30% H_2O_2 by weight to give final solution 10% H_2O_2 by weight; mixture cooled to 8°C.

Run HP-11-14: Samples of ion-exchange plutonium nitrate product solution (sample C diluted to lower the HNO_3 concentration) precipitated with equal volumes of 30% H_2O_2 by weight, which was added rapidly; mixture slowly stirred for 1 hr and temperature held at 5 to 8°C; precipitate allowed to settle for 15 minutes, and its volume then measured

Sample	Pu Conc. (g/liter)	Composition	Pu in Supernatant (mg/liter)	Bulk Density of Ppt. (g/ml)
HP-9	81.5	2.1 M HNO_3, 0.055 M Fe^{3+}, to which was added H_2SO_4 to 0.25 M sulfate and Na_2SO_3 to 0.05 M sulfite	840 (1.8%)(a)	
HP-11-14: A	51.4	5.45 M HNO_3, 0.3 M NH_2SO_3H, 0.004 M Fe^{3+}	50.4	0.07
B	51.4	Same as above, to which was added solid $(NH_4)_2SO_4$ to 0.25 M and $(NH_4)_2SO_3$ to 0.05 M	59.4	0.03
C	40	4.24 M HNO_3, 0.2 M NH_2SO_3H, 0.003 M Fe^{3+}	30.4	0.03

(a) High loss was due to large amount of iron in the ion-exchange product.

Appendix 2

RUN SUMMARIES

Runs HP-6 and 7

Data on these runs are very incomplete and therefore are not reproduced here.

Runs HP-8 and 9

Resin Column Specifications:

Resin	Dowex-50, 12% cross linked, 60 to 90 mesh
Resin bed, volume	1400 ml in 0.3 M HNO_3
Depth	12 in. (30.5 cm)
Column, diameter	3 in. (7.6 cm)
Cross-sectional area	7.07 in.^{2} (45.36 cm^2)
Excess resin	3.44 fold (based on 80 g of Pu(III)
Volume change	700 ml (voids assumed to be 50%)

Feed:

	Run HP-8	Run HP-9
IIBX	0.1 M HNO_3, 0.05 M hydroxylamine sulfate	0.1 M HNO_3, 0.05 M hydroxylamine sulfate
IIBP (at equilibrium):		
Feed volume (liters)	165.4	185.8
Pu (g/liter)	0.81	0.796
Total Pu (g)	80.4	75.133
U (g/liter)	0.0026	5.72
Total U (g)		521.72
HNO_3 (M)	0.335	0.19
Gross α (c/min/ml)	5.77×10^7	5.65×10^7
Gross β (c/min/ml)	3.08×10^4	1.94×10^4
Ru β (c/min/ml)	4.81×10^3	3.16×10^3
Zr β (c/min/ml)	5.56×10^2	$\sim 2.97 \times 10^2$
Nb β (c/min/ml)	1.54×10^2	~ 72
Total rare earth β (c/min/ml)	2.69×10^2	$\sim 1.64 \times 10^2$
$UX_1 + UX_2$ β (c/min/ml)	1.94×10^4	1.12×10^4
Gross γ [a] (mv/ml)	4.4	3.56

(a) As determined on ionization chamber in Building 3550.

[redacted]

Absorption Step:	Run HP-8		Run HP-9	
Pu in waste (mg)	16	(0.02%)	10.2	(0.014%)
U in waste (g)	None		416.33	(80%)
Feed flow rate, downflow (ml/min)	105		105	
(ml/min/cm^2)	2.3		2.3	
Uranium Elution Step:				
Pu in eluate (mg)	0.65	(0.0008%)	3.3	(0.004%)
U in eluate (g)	0.023	(~99%)	104.95	(19.9%)
Elutriant flow rate, downflow (ml/min)	82		50	
(ml/min/cm^2)	1.8		1.1	
Elutriant:				
Vol. of 0.25 M H_2SO_4 (liters)	18.1 (26 vol. changes)(a)		66.0 (94 vol. changes)	
Vol. of 0.2 M HNO_3 (liters)	4.9 (7 vol. changes)			
Vol. of demineralized H_2O			4.5 (7 vol. changes)	
Total (liters)	23		70.5	
Plutonium Elution Step:				
Elutriant flow rate (upflow):				
First 6 vol. changes (ml/min)	25		First 9 vol. changes (ml/min)	15
(ml/min/cm^2)	0.55		(ml/min/cm^2)	0.33
Last 34 vol. changes (ml/min)	50		Next 2 vol. changes (ml/min)	25
(ml/min/cm^2)	1.1		(ml/min/cm^2)	0.55
			Last 25 vol. changes (ml/min)	45
			(ml/min/cm^2)	1.00
Elutriant:				
Vol. of 6 M HNO_3 (liters)	25.9 (37 vol. changes)		22.4 (32 vol. changes)	
Vol. of 0.3 M HNO_3 (liters)	2.4 (3 changes of 800 ml each)		2.8 (4 vol. changes)	
Total (liters)	28.3		25.2	

(a) A volume change is defined as half the column volume, assuming 50% voids in the resin.

[redacted]

Resin Column Product:

Determination	Run 8 before Boildown				Run 9 before Boildown		Run 9 after Boildown, Product
	Product	Batch A[a]	Batch B[a,b]	Batch C[c]	Product	Batch A[a]	
Volume changes	9	20	10	2	13	23	
Volume (liters)	6.47	14.3	6.8	1.6	9.1	16.0	2.8
HNO_3 (M)	6	6.1	5.1	1.48	6	5.3	7.6
Pu (g/liter)	11.5	0.365	0.105	0.0065	7.85	0.238	25.5
Total Pu[d] (g)	74.45[e]	5.21	0.71	0.010	71.5	3.62	71.5[e]
U (g/liter)	0.02	---	---	0.0065	0.0517	0.00016	0.168
Total U (g)					0.47	0.0024	
Gross β[f] (c/min/ml)	6.2×10^4	1.78×10^4	8.47×10^3	4.8×10^2	6.5×10^4	9.2×10^3	2.11×10^5[g]
Ru β (c/min/ml)	5.0×10^3						1.46×10^4[g]
Zr β (c/min/ml)	1.19×10^3						4.22×10^3
Nb β (c/min/ml)							1.55×10^3
Total rare earth β(c/min/ml)							1.70×10^3
Gross γ[h] (mv/ml)	16.0						50
$UX_1 + UX_2$ β (c/min/ml)	5.4×10^4						1.14×10^5[g]
Vol. reduction of product	13.2				9.9		32

(a) These portions of the eluate were recycled to the second plutonium cycle of the Purex process during the following run, HP-10.
(b) Contained water used to rinse glassware.
(c) Discarded.
(d) Based on potentiometric analysis.
(e) This amount shipped to Los Alamos.
(f) Counted on helium-filled Geiger-Mueller tube.
(g) 10.18% geometry.
(h) As measured on ionization chamber in Building 3550.

[redacted]

In Run 8 the following decontamination factors were obtained through the ion-exchange procedure:

Gross β (a)	7.0
Ru β	11
Zr β	6.7
$UX_1 + UX_2$ β (a)	4.5
Gross γ	3.9

(a) Counted on a helium - filled Geiger-Mueller tube; others were counted on an argon-filled tube.

In Run 8 the β activity of the Pu product was distributed as follows:

$UX_1 + UX_2$	87%
Ru	8%
Zr	2%

Because of the disagreement of the analytical data for Nb, they could not be evaluated.

In Run 9 the following decontamination factors were obtained through the Purex and ion-exchange processes:

	1st and 2nd Purex Cycles	Ion-Exchange Process	Total
Gross β	8.5×10^6	2.96	2.5×10^7
Ru β	4.5×10^5	6.93	3.1×10^6
Zr β	9.8×10^6	2.28	2.2×10^7
Nb β	5.8×10^6	1.48	8.6×10^6
Total rare earth β	1.2×10^8	3.09	3.7×10^8
$UX_1 + UX_2$ β	27	3.16	86
Gross γ	3.4×10^6	2.28	7.8×10^6

Reduction in Ionic Contamination:

Run 8

Contaminant	Product (ppm of Soln.)	Reduction Factor through Ion Exchange Procedure
Fe	90	None
Cr	14.4	2.3
Ni	25.6	4.5
Mn	2.3	3.2
Al	7.6	7.4
Pb	225	None
Cu	3.1	7.2
Mg	8.8	6.2
U	<20	2.0
PO_4	<1	

Run 9

Contaminant	μg per mg of Pu		Reduction Factor
	IIBP (equilibrium)	Product	
U	7180	6.6	1090
Al	8.04	0.36	22.6
Ca	5.14	6.00	~1
Cr	3.51	12.4	None[a]
Fe	19.9	117.0	None[a]
Mg	6.27	0.28	22.8
Mn	0.50	2.50	None[a]
Ni	13.7	14.9	~1
Pb	19.3	8.10	2.4[b]
Cu	19.6	Not found	High

(a) Spectroscopic analysis of the product showed the presence of these elements in the following concentrations:

Chromium	0.32 g/liter
Iron	3.0
Manganese	0.06
Nickel	0.38

A rough material balance over the feeds, waste streams, and products of the ion-exchange process showed that these metals were present in approximately the same ratios as they are in stainless steel type 347. It is therefore concluded that the contamination came from the stainless steel column being dissolved by the sulfuric acid used in the uranium elution step. This type of stainless steel is very resistant to nitric acid.

(b) The lead contamination of this product and of that from Run 8 may have been leached from the Purex extraction system.

Run 10

Since Run 10 contained recycle material, data on it are not reproduced here.

Runs HP-11 through 14

Feeds from these four runs were all absorbed by the same column to demonstrate that a 100% excess of resin is adequate.

Resin Column Specifications:

Same as for Runs 8 and 9 except one 2.3 fold (125%) excess (based on 119.44 g of Pu) was used. Top of resin bed was weighted down with a 3-3/4-in.-deep movable bed of 20- to 30-mesh Ottawa sand resting on glass-fiber cloth disks.

Feed: IIBX, 0.05 M HNO_3, 0.03 M hydroxylamine sulfate

IIBP (at equilibrium):

Determination	HP-11 A, B	HP-11 C, D	HP-12 A, B, C, D	HP-13 A, B, C, D	HP-14 A, B
Feed volume (liters)		128.1[a]	91.2	103.3	154.7
Pu (g/liter)[b]	0.129	0.206	0.254	1.29	1.27
Total Pu (g)	6.91	5.72	14.09	60.62	32.10
U (g/liter)	0.0049	0.0047	0.0105	0.00054	0.0022
HNO_3 (M)	0.26	0.24	0.25	0.26	0.24
Gross β (c/min/ml)	960	1580	2500	13,800	9200
Ru β (c/min/ml)	88	125	614	2,640	2360
Zr β (c/min/ml)	177	362	834	5,420	2130
Nb β (c/min/ml)	32	51	61	168	115
Total rare earth β (c/min/ml)	30	54	56	112	52
UX_1 + UX_2 β (c/min/ml)	578	313	975	775	207
Gross γ[c] (mv/ml)	1.32	2.10	5.5	27.3	15.4
Fe (ppm of solution)	14.2	12.5	12.7	13.4	14.0
Cr (ppm of solution)	16.5	6.2	--	2.4	1.9
Ni (ppm of solution)	7.7	7.4	7.2	5.0	3.1
Al (ppm of solution)	4.2	5.3	1.5	5.4	3.8
Pb (ppm of solution)	15.4	12.6	--	65	114
Cu (ppm of solution)	6.2	4.3	1.3	10.3	6.3
Ti (ppm of solution)	1.2	1.2	--	--	--
Mg (ppm of solution)	129	139	123	105	55
Mn (ppm of solution)	3.4	2.9	2.0	7.6	3.6
Phosphate (ppm of solution)	5	5	0.5	0.5	1.7
Ca (ppm of solution)	548	482	199	390	170
Si (ppm of solution)	---	---	Trace	Trace	Trace

(a) Total for Run 11, A through D.
(b) Total for Runs HP-11 through 14, 119.44 g
(c) As determined on ionization chamber in Building 3019.

Absorption Step:

Determination	Run HP-11 A, B	Run HP-11 C, D	Run HP-12	Run HP-13	Run HP-14
Pu in waste:[a]					
(α c/min/ml)	135		50	395	200
(mg)	0.244		0.064	0.577	0.436
Volume of IIBPW (liters)	128.1		91.2	103.3	154.7
Feed flow rate, downflow (ml/min)	35	23.3	17.5	17.5	17.5
(ml/min/cm^2)	0.774	0.514	0.386	0.386	0.386
Other waste analyses:					
$UX_1 + UX_2$ β (c/min/ml)	12		45	4	7
Ru β (c/min/ml)	50		225	494	395
Zr β (c/min/ml)	4		4.5	553	162
Nb β (c/min/ml)	20		6	14	7
Total rare earth β (c/min/ml)	5		2.5	4	4
$UX_1 + UX_2$ β (c/min/ml)	69		7200	920	608
Gross γ[b] (mv/ml)	0.6		0.8	1.5	1.8
Fe (ppm)	N.A. (c)		3.1	2.6	1.4
Cr (ppm)	N.A.		Not found	0.2	1.5
Ni (ppm)	N.A.		5.0	5.0	5.0
Al (ppm)	N.A.		1.0	1.0	1.0
Pb (ppm)	N.A.		Not found	13	13
Cu (ppm)	N.A.		0.9	0.9	0.6
Mg (ppm)	N.A.		1.7	0.5	0.7
Mn (ppm)	N.A.		0.4	0.4	0.4
Phosphate (ppm)	N.A.		0.5	1.0	0.5
Ca (ppm)	N.A.		2.4	2.0	2.3
Si (ppm)	N.A.		Trace	Faint trace	Trace

(a) Total for four runs = 1.321 (0.0011%).
(b) As determined on ionization chamber in Building 3550.
(c) Not analyzed.

Uranium-Elution Step:

Pu in eluate (mg)	0.606 (0.0005%)
(α c/min/ml)	2.0×10^3
U in eluate (g)	2.48
(mg/ml)	0.119
Elutriant flow rate, downflow(ml/min)	96.8
(ml/min/cm^2)	2.14
Elutriant, volume of 0.24 M H_2SO_4 (liters)	20.9 (30 volume changes)
Gross β (c/min/ml)	1750
Ru β (c/min/ml)	1330
Zr β (c/min/ml)	23
Nb β (c/min/ml)	168
Total rare earth β (c/min/ml)	Background
$UX_1 + UX_2$ β (c/min/ml)	6
Gross γ[a] (mv/ml)	14.6
Fe (ppm)	1.1
Cr (ppm)	1.5
Ni (ppm)	5
Al (ppm)	1
Pb (ppm)	13
Cu (ppm)	0.6
Mg (ppm)	24
Mn (ppm)	0.4
Phosphate (ppm)	0.5
Ca (ppm)	1.3
Si (ppm)	Faint trace

(a) As determined on ionization chamber in Building 3019.

Plutonium-Elution Step:

Elutriant flow rate (upflow):		
First 20 volume changes (ml/min)	25	
(ml/min/cm^2)	0.55	
Last two cuts, 1000 ml each (ml/min)	50	
(ml/min/cm^2)	1.10	
Elutriant:		
Vol. of 5.7 M HNO_3 + 0.3 M sulfamic acid (liters)	14.0	(20 volume changes)
Vol. of 0.3 M HNO_3 (liters)	2.0	(2 cuts of 1000 ml each)
Total (liters)	16.0	

Resin Column Product:

Volume (liters)	2.061
HNO_3 (M)	5.45
Pu (g/liter)	51.5 (by count analysis) 51.4 (by potentiometric analysis) 51.0 (by colorimetric analysis)
Total Pu (g)	105.93 (by potentiometric analysis)
Amount of Pu in product (% of total on resin)	89.6
Uranium (g/liter)	<0.001
Gross β (c/min/ml)	2.92×10^4
Ru β (c/min/ml)	2.29×10^4
Zr β (c/min/ml)	4.38×10^3
Nb β (c/min/ml)	975
Total rare earth β (c/min/ml)	333
$UX_1 + UX_2$ β (c/min/ml)	3.72×10^3
Gross γ(a) (mv/ml)	104

(a) As determined on ionization chamber in Building 3550.

In Runs HP-11 through 14 the following decontamination factors were obtained:

Contaminant	Activity per mg of Pu (β, c/min; γ, mv)						
	IIBP at equilibrium						Product
	HP-11		HP-12	HP-13	HP-14	Weighted Avg.	
	A, B	C, D					
Gross β	7.44×10^3	7.67×10^3	9.84×10^3	1.07×10^4	7.19×10^3	9.3×10^3	5.68×10^2
Ru β	681	606	2.42×10^3	2.04×10^3	1.84×10^3	1.88×10^3	447
Zr β	1.37×10^3	1.75×10^3	3.28×10^3	4.20×10^3	1.66×10^3	3.12×10^3	86
Nb β	248	247	240	130	90	144	19
Total rare earth β	232	262	220	87	41	107	6.5
$UX_1 + UX_2$ β	4.47×10^3	1.52×10^3	3.83	600	162	1.13×10^3	73
Gross γ(a)	10.22	10.2	21.6	21.2	12.0	17.5	4.47

	Decontamination Factor					
	Absorption	U Elution	Pu Elution	Total Ion Exchange	Avg'd. 1st and 2nd Purex Cycles	Overall
Gross β	1.25	1.04	12.57	16.34	4.6×10^6	7.55×10^7
Ru β	2.65	1.50	1.06	4.2	1.04×10^6	4.37×10^6
Zr β	1.29	1.00	28.4	36.6	1.48×10^6	3.22×10^7
Nb β	1.49	1.44	3.53	7.58	4.25×10^6	3.22×10^7
Total rare earth β	1.17	1.00	14.35	16.8	3.36×10^8	5.55×10^9
$UX_1 + UX_2$ β	1.056	1.00	14.7	15.5	485	7.5×10^3
Gross γ(a)	2.08	1.43	1.34	4.0	2.67×10^6	1.02×10^7

(a) As measured on ionization chamber in Building 3019.

In Runs HP-11 through 14 the following ionic reduction factors were obtained by the ion-exchange procedure:

Contaminant	Amount (mg/mg Pu)							Reduction Factor
	HP-11		HP-12	HP-13	HP-14	Weighted Average of All Runs	Product	
	A, B	C, D						
Fe	110.0	60.7	50.0	10.4	11.0	23.4	4.57	5.1
Cr	128.0	30.1	---	1.9	1.5	10.2	0.77	13.4
Ni	59.6	35.9	28.3	3.9	2.4	11.1	1.65	6.7
Al	32.5	25.7	5.9	4.2	3.0	14.1	0.30	47.2
Pb	119.2	61.2	---	50.4	89.7	59.5	10.9	5.5
Cu	48.1	20.8	5.1	8.0	5.0	9.8	0.25	38.8
Ti	9.3	5.8	---	---	---	---	---	---
Mg	1000	674	484	81.5	43.4	201	2.36	85.2
Mn	26.4	14.1	7.9	5.9	2.8	6.88	0.31	22.3
Phosphate	38.8	24.2	2.0	3.9	1.3	5.96	0	High
Ca	4250	2340	782	302	134	639	14.5	44.2
U								$> 10^3$

Amount of Plutonium in Various Eluate Cuts

Elution Cut No.	HNO_3 (M)	Pu (g/liter)	Pu (g/cut)
0	0.29	0.134	0.094
1	3.9	95.92	67.14
2	5.7	42.25	29.60
3	6.0	16.75	11.70
4	6.0	7.32	5.12
5	6.0	3.52	2.46
6	(6.0)(a)	2.03	1.42
7	(6.0)	1.20	0.836
8	(6.0)	0.831	0.581
9	(6.0)	0.605	0.424
10	(6.0)	0.454	0.318
11	(6.0)	0.393	0.275
12	(6.0)	0.288	0.201
13	(6.0)	0.276	0.193
14		0.192	0.134
15		0.269	0.181
16		0.208	0.146
17		0.149	0.104
18		0.112	0.0781
19		0.0730	0.0511
20		0.0407	0.0407
21		0.0015	0.0015
Total			121.0984

(a) Assumed equilibrium value.

[redacted]

Summary of Plutonium Eluate Data

Cut	Cut Nos.	Vol. (liters)	HNO_3 (M)	Pu (g/liter) By α count	Pu (g/liter) Coloriometric	Pu (g/liter) Potentiometric	Total Pu (g)
Product	1,2,3	2.061	5.45	51.5	51.0	51.4[a]	105.93[b]
Recycle	0,4-21	1.297[c]	4.9	10.32	11.63	9.75[d]	13.70
							119.63

(a) Value used for shipping purposes.
(b) Amount shipped to Los Alamos was 104.9 g.
(c) Boiled down from 13.9 liters in glass still.
(d) Average of the three values is 10.57.

Durations of Runs:

Run	Hot Feed to Resin Column: Started Date	Started Time	Finished Date	Finished Time
HP-11-A	7/12/51	2055	7/13/51	1037
B	7/13	1105	7/13	2105
C	7/13	2145	7/14	0530
D	7/14	0550	7/14	1940
HP-12-A	8/6	2320	8/8	1745
B	8/8	1825	8/9	0451
C	8/9	0530	8/9	1915
D	8/9	1934	8/10	0953
HP-13-A	8/20	2110	8/21	1110
B	8/21	1130	8/21	2350
C	8/22	0030	8/22	1225
D	8/22	1245	8/23	0135
HP-14-A	8/27	2131	8/28	1020
B	8/28	1037	8/28	2230

Plutonium eluted 9/5/51; total elapsed time = 55 days

	Amount of Pu (g)	Total time on column (days)
HP-11	12.63	54
HP-12	14.09	34
HP-13	60.62	20
HP-14	32.10	14
		23.6 (avg.)

[redacted]

Runs SP-20 and HCP-1 through 5

Resin Column Specifications

Resin	Dowex-50, 12% cross linked, 50 to 100 mesh
Resin bed volume	1600 ml
Resin bed depth	14 in.
Column, diameter	3 in. (7.6 cm)
Cross-sectional area	7.07 in.^{2} (45.36 cm^2)
Volume change	800 ml

[redacted]

Radiochemical Decontamination Factors in Purex Ion-Exchange Isolation Process

Contaminant	HCP-1 β, c/m/mg Pu γ, mv/mg Pu			HCP-2 β, c/m/mg Pu γ, mv/mg Pu			HCP-3 β, c/m/mg Pu γ, mv/mg Pu			HCP-4 β, c/m/mg Pu γ, mv/mg Pu			HCP-5 β, c/m/mg Pu γ, mv/mg Pu		
	IIBP	Product	D.F.	IIBP	Product	D.F.	IIBP	Product	D.F.	IIBP	Product	D.F.	IIBP	Product	D.F.
Ru β	480	195	2.5	1200	574	2.1	1950	840	2.3	1960	650	3.0	1770	596	3.0
Zr β	213	18	12	196	7.6	26	131	20	6.6	2450	41	61	670	131	5.1
Nb β	40	1.2	34	52	1.2	43	31	2.9	11	670	10	64	135	27	4.9
Total rare earth β	94	6	16	132	3.7	3.6	22	7.6	2.9	1170	29	40	44	23	2.0
$UX_1 + UX_2$ β	143	9	15	3.5	19	(a)	28	10.5	2.7	131	36	3.6	63	6	10
Sum of F.P. + UX β:															
Through solv. extn.	970		2.1×10^7	1590		2.4×10^7	2044		2.5×10^7	6381		6.1×10^6	2682		2.0×10^7
Through ion exchange		229	4.2		690	2.3		861	2.4		766	8.3		783	3.4
Total β D.F.			8.8×10^7			5.5×10^7			6.0×10^7			5.0×10^7			6.8×10^7
Gross γ:(b)															
Through solv. extn.	0.3		6.0×10^6	2.8		9.2×10^6	4.4		1.2×10^7	5.9		2.9×10^6	7.8		2.8×10^6
Through ion exchange		0.2	1.5		1	2.8		1.5	3.1		1.4	4.2		1.5	5.2
Total γ D.F.			9.1×10^6			2.6×10^7			3.7×10^7			1.2×10^7			1.5×10^7

(a) Apparent enrichment.
(b) These are corrected values, 2.7 mv/mg being used as the natural Pu background.

[redacted]

Reduction Factors Obtained for Ionic Contaminants in Ion-Exchange Process:

Contaminant[a]	HCP-1 (μg/mg Pu)			HCP-2 (μg/mg Pu)			HCP-3 (μg/mg Pu)			HCP-4 (μg/mg Pu)			HCP-5 (μg/mg Pu)		
	IIBP	Product	R.F.	IIBP	Product	R.F.	IIBP	Product	R.F.	IIBP	Product	R.F.	IIBP	Product	R.F.
Al	0.73	1.29	(b)	0.76	1.02	1	1.2	1.1	1	1.1	7.7	(b)	3.8	~2	~2
Ca	12.6	0.63	20	12.4	7.9	1.6	233	11.7	19.8	8.6	20.6	(b)	23.1	~3	~8
Cr	1.08	0.20	5	0.49	0.33	1.5	0.57	0.44	1.3	0.43	0.26	1.7	0.5	0.07	7
Cu	0.57	0.24	2	1.8	0.14	13	7.86	0.12	65.5	0.55	0.077	7.1	0.6	0.087	7
Fe	8.2	0.042	195	3.8	3.2	1.2	7.6	0.43	17.7	3.6	2.9	1.2	14.9	1	15
Mg	0.97	0.037	26	0.9	8.2	1.1	8.6	0.63	13.6	2.6	36	(b)	3.0	0.3	10
Mn	N.A.	0.1	---	0.16	0.095	1.6	0.27	0.11	2.45	<0.2	0.15	1	0.3	0.44	(b)
Ni	0.38	0.54	(b)	0.52	0.53	1	0.48	0.61	1	<1	<0.1	<10	<1.2	<0.1	---
Pb	N.A.	3.4	---	7.7	1.4	5.5	207	1.15	180	<3	5.8	(b)	3.7	<0.3	>10
Zn	N.A.	3.7	---	71	0.5	140	8.8	0.24	36.7	<6	0.13	<4	3.0	<0.5	>6

(a) Amounts determined by spectrographic analysis.
(b) In these cases there was an apparent enrichment.

Ionic Constituents of Ion-Exchange Isolation Process Waste Streams[a]

Contaminant	Amount (μg per mg of Pu in feed)[b]				
	Absorption Waste			Uranium-Elution Waste	
	HCP-2	HCP-3	HCP-4	HCP-2	HCP-3
Al	0.54	< 0.24	< 0.24	< 0.5	< 0.5
Ca	6.8	0.15	0.36	11.7	1.1
Cu	< 0.9	< 0.36	< 0.24	< 0.9	0.86
Cr	0.56	< 0.07	< 0.07	0.28	< 0.14
Fe	~ 0.3	~ 0.18	< 0.09	~ 0.5	2
Mg	2.65	0.024	0.09	0.16	0.13
Mn	< 0.9	< 0.24	< 0.09	< 0.9	0.57
Ni	< 2.2	< 0.95	< 0.9	< 2.2	< 2
Pb	< 7	< 3.1	< 4	< 7	< 6
Zn	< 13	< 6	< 6	< 14	< 12

(a) Identified by spectrographic analysis. Most of the ions were below the limits of analysis; the values given are upper limits.

(b) Impurities normalized to amount of plutonium in feed, for comparison with feed and product.

Appendix 3

COMPARISON OF BISMUTH PHOSPHATE AND ION-EXCHANGE PLUTONIUM PRODUCTS

A plutonium product from the Purex ion-exchange process was found to have a gross β plus γ fission product activity of 568 c/min per milligram of plutonium, about 80% of which was due to ruthenium β activity (Table A3.1). A similar plutonium product prepared by the bismuth phosphate process had a gross β plus γ fission product activity of 850 c/min per milligram of plutonium, about 60% of this being due to total rare earth β activity.

The Purex ion-exchange-product solution was from 450-Mwd 90-day-cooled Hanford material that had been processed through two Purex solvent-extraction cycles (TBP) and the ion-exchange isolation cycle. The bismuth phosphate-product solution (AT) was from routine Hanford material that had been processed through all precipitation cycles, including two peroxide precipitations. This material had been at ORNL about seven months at the time of this analysis.

It is apparent from this comparison that the principal residual activities in the plutonium product from the bismuth phosphate process are the rare earths, while the principal residual activity in the Purex ion-exchange plutonium product is ruthenium. In the two products examined, the gross β activities were comparable, while the γ activity associated with the Hanford plutonium product was greater than that associated with the plutonium ion-exchange product.

Table A3.1

Comparison of Plutonium Product from Bismuth Phosphate Process with That from the Ion-Exchange Process

Purex ion-exchange product: solution of 450-Mwd 90-day-cooled Hanford material, processed through two Purex solvent-extraction cycles (TBP) and the Dowex-50 resin cation-exchange isolation cycle.

Bismuth phosphate product: AT solution, routine Hanford material, processed through all precipitation cycles, including two peroxide precipitations, and cooled at ORNL for seven months

Activity[a] per mg of Pu	Purex Ion-Exchange Product Solution	Bismuth Phosphate Product Solution
Gross β, γ, and X ray, including Pu (c/min)	1.72×10^4	1.78×10^4
Gross β and γ, less Pu (c/min)	568	850
Ruthenium β (c/min)	447	10
Zirconium β (c/min)	86	60
Niobium β (c/min)	19	6
Total rare earth β (c/min)	7	535
$UX_1 + UX_2$ β (c/min)	73	65
Strontium β (c/min)	0	45
Cesium β (c/min)	0	14
Gross γ[b] (mv)	4.5	6.5

(a) All counting was done at 10.18% geometry, using a Geiger-Mueller tube with no absorber.

(b) As determined by ionization chamber measurements.

[redacted]

Appendix 4

PROPERTIES OF DOWEX-50 RESIN

A4.1 Stability of Dowex-50 Resin to 5.7 M HNO_3

A nitric acid concentration of 5.7 M might be expected to affect the organic resin, but no evidences of decomposition have been observed in experimental work. One test of the resin showed no decrease in the capacity, beyond the limits of experimental error, of the resin after long standing in nitric acid.

In this test approximately 1750 volume changes of 5.7 M HNO_3--0.3 M sulfamic acid were passed over a 10-ml resin bed. The capacity decreased from 2.27 to 2.23 milliequivalents per milliliter of resin, or about 1.8%, which is about the experimental error. This number of volume changes represents about 600 desorption cycles in the proposed Savannah River installation. In another, independent test,[1] three batches of resin that had been contacted with 12 M HNO_3 for 24 hr showed capacity losses of 0.03, 0.74, and 0.50%, respectively, as determined by analysis of the nitric acid for sulfate.

A4.2 Stability of Dowex-50 Resin to Plutonium α Radiation

There has been no indication, under the conditions used, of a loss in resin capacity as a result of radiation deterioration. In Run HP-11-14 the first portion of the plutonium was put on the resin column 55 days before it was eluted, and it remained on the column an average time of 23.6 days (see Appendix 2, p. 63). In a laboratory study Dowex-50 resin was used through six absorption and desorption cycles, in which residual (0.12%) plutonium was left on the column between runs. There was no indication of a decrease in capacity.

A4.3 Analytical Methods for Determining Dowex-50 Resin Properties[2]

Moisture: A clean sample (H^+, wet form) is placed on a desiccator rack. A layer of water is placed in the bottom of the desiccator, and the vessel is evacuated. After 48 hr, the moisture content is determined by the weight loss of the resin when kept in an oven at 105°C for 24 hr.

Swelling Coefficient: The relative volumes of the water-settled H^+ and Na^+ forms are determined, and the swelling coefficient is calculated from the relation:

$$\text{Swelling Coefficient} = \frac{\text{Volume of } H^+ \text{ form}}{\text{Volume of } Na^+ \text{ form}}$$

Capacity: A weighed air-dried sample (H^+ form) is placed in 1 M NaCl and titrated with standard sodium hydroxide. The moisture content is determined by the weight loss of a duplicate sample dried in an oven at 105°C for 24 hr, and the capacity of the resin is calculated on an oven-dried basis.

(1) R. E. Blanco, letter to R. M. Wheaton of Dow Chemical Co., Nov. 27, 1951.
(2) Ibid.

Appendix 5

CRITICALITY OF PLUTONIUM SYSTEMS

Considerations[1] of nuclear safety indicate that the systems described in Table A5.1 is safe. No hazard is foreseen in handling plutonium nitrate solution in a cylinder 7 in. in diameter. However, separations of 2 ft, center to center, should be maintained between columns or other vessels containing fissionable material. This opinion is based on unpublished data obtained at Hanford in a critical-experiment program designed to study the conditions for handling plutonium safely. The experimental results indicate safety to be imposed by the geometry of a 7-in. tube; i.e., a cylindrical container 7 in. in diameter may safely contain an unlimited mass of plutonium.

Table A5.1

Critically Safe Plutonium Systems[2]

Shape of vessels	Right Cylinder
Height of vessels	35 and 26.5 cm
Diameter of vessels	17.8 cm
Total volume of vessels	8.72 and 6.54 liters
Material of construction	Pyrex glass pipe, 1/4- to 3/8-in.-thick walls
Height of plutonium band	8.8 cm
Volume of plutonium	2180 cm^3
Concentration of plutonium	165 to 180 g/liter
Total amount of plutonium	400 g $\pm$ 10%
Material outside vessels	Air
Material inside vessels	(a) $Pu(NO_3)_3$ (b) Dowex-50 cation-exchange resin (c) 0.3 to 6.0 M HNO_3
Composition of resin	52% C, 17.5% S, 26.2% O, 4.3% H

(1) D. Callihan, Critically Safe Plutonium Systems, memorandum to D. C. Overholt, ORNL CF-51-12-75 (Dec. 12, 1951).

(2) D. C. Overholt, Critically Safe Plutonium Systems, memorandum to A. D. Callihan, ORNL CF-51-10-151 (Oct. 23, 1951).

Appendix 6

X-RAY AND β ACTIVITY OF 450-Mwd PLUTONIUM

The gross β-, γ-, and X-ray activity of 450-Mwd plutonium was found to be 1.78×10^4 c/min per milligram of plutonium (Table A6.1). The sample examined had, as determined by ionization-chamber measurements, a value of 7×10^{-5} rutherfords (Co^{60}) per milligram of plutonium. The plutonium background values were found to be 2.7 and 1.15 mv/mg on the ionization chambers in Buildings 3019[1] and 3550, respectively. If the total activity is assumed to be plutonium X ray only, and the X rays are assumed to be monoenergetic and to have the energy of the Kα plutonium X ray, the X-ray content of the sample was 8.5×10^4 d/min per milligram of plutonium.

The plutonium used for these experiments came from 450-Mwd Hanford irradiated slugs and had been processed through four Purex TBP extraction cycles, two Dowex-50 ion-exchange isolation cycles, and two peroxide precipitations from 2 M HNO_3. It had been previously determined[2] that the principal fission activity remaining after the ion-exchange process was ruthenium (approximately 80%).

Table A6.1

Radioactivity of Purified 450-Mwd Plutonium

Sample analyzed: Plutonium from 450-Mwd Hanford slugs that had been processed four Purex TBP extraction cycles, two Dowex-50 ion-exchange cycles, and two peroxide precipitations from 2 M HNO_3 and dissolved in 2.0 M HNO_3

Counted at 10.18% geometry; Geiger-Mueller argon-alcohol tube; absorber as noted

Activity	Amount per mg of Pu
Gross β, γ, and X ray, including Pu (c/min)	17,800
Gold absorber, 24.95 mg/cm^2 (c/min)	845
Gold absorber, 49.5 mg/cm^2 (c/min)	96
Gross β and γ, less Pu (c/min)	37
Ruthenium β (c/min)	0
Zirconium β (c/min)	7
Niobium β (c/min)	7
Total rare earth β (c/min)	7
$UX_1 + UX_2$ β (c/min)	10
Strontium β (c/min)	3
Cesium β (c/min)	3
Background of purified Pu, Bldg. 3019 i.c. (mv)	2.7
Bldg. 3550 i.c. (mv)	1.15

(1) J. W. Jones and R. T. Overman, The Use and Calibration of a 100% Geometry Ion Chamber, MonC-399 (March 20, 1948).

(2) D. C. Overholt, Radiochemical Comparison of Bismuth Phosphate Process Plutonium Nitrate and Purex Ion-Exchange Plutonium Nitrate, ORNL CF-51-11-116 (Nov. 23, 1951).

Appendix 7

IRRADIATION AND COOLING HISTORY OF SLUGS PROCESSED IN RUNS HCP-1 THROUGH 5

The fission product contamination of the plutonium in the feed to the Purex solvent-extraction process in Runs HCP-1 through 5 varied chiefly because of the variation in the cooling of the slugs (see Table A7.1). The slugs used in Run HCP-1 were cooled considerably longer than those in the other runs.

Table A7.1

Irradiation and Cooling History of Slugs Processed in Runs HCP-1 through 5

Run No.	Irradiation of Slugs (Mwd)	Cooling Period of Slugs (days)
HCP-1	450	330
HCP-2	523	191
HCP-3	542	120
HCP-4	563	116
HCP-5	560	89