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RECOVERY OF Np^{237} AND Pu^{238} FROM IRRADIATED NEPTUNIUM OXIDE

Title Unclassified

by

G. A. Burney and C. A. Prohaska

Separations Chemistry Division

November 1959

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RECOVERY OF Np^{237} AND Pu^{238} FROM IRRADIATED NEPTUNIUM OXIDE

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Glenn A. Burney and Charles A. Prohaska

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ABSTRACT

An ion exchange process was demonstrated for the recovery of Pu^{238} from irradiated neptunium oxide. Three cycles of anion exchange proved adequate for the removal of fission products and for the separation of the neptunium and plutonium from each other.

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RECOVERY OF Np^{237} AND Pu^{238} FROM IRRADIATED NEPTUNIUM OXIDE

INTRODUCTION

A process was required to separate Pu^{238} from irradiated Np^{237} and to separate each element from fission products as well as from other cationic impurities.

Preliminary work demonstrated the separation and purification of Np^{237} and Pu^{239} by anion exchange, and indicated that this process would provide adequate capacity and could be adapted to remote operation in the available High Level Cave facilities.

This report describes the first tests of the proposed flowsheet with an irradiated neptunium slug. The tests were designed to demonstrate a satisfactory dissolution process, and to establish limits for the process variables compatible with capacity requirements and product specifications.

SUMMARY

An anion exchange process was demonstrated for the recovery of Pu^{238} from irradiated Np^{237}. An irradiated neptunium slug was dissolved and processed through three cycles of anion exchange to separate the plutonium from neptunium and to separate each element from fission products as well as from other impurities. Both plutonium and neptunium products met specifications and the losses were within acceptable limits.

The Np^{237} was irradiated as a compacted mixture of NpO_2 with aluminum powder; approximately 20% of the neptunium was converted to plutonium in the irradiation. The irradiated material dissolved readily in boiling 8M HNO_3 that was 0.02M in HF. In the ion exchange process neptunium and plutonium were separated from fission products by factors ranging from 10^5 to 10^6. Cross-contamination between the neptunium and plutonium was less than 0.2 w/o, and the recoveries were approximately 97% for plutonium and 96% for neptunium with no recycle of the waste streams.

The three cycles of anion exchange included a decontamination cycle, a partition cycle, and a plutonium isolation cycle. In the decontamination cycle Pu(IV) and Np(IV) were absorbed together on the resin as the anionic nitrate complexes, the fission products passing through unabsorbed. After elution from the resin by dilute nitric acid, plutonium was reduced to Pu(III). In the partition cycle the Np(IV) was then absorbed as the anionic nitrate complex while Pu(III) was washed through the column along with some of the fission products. Finally, the plutonium containing effluent from the partition cycle was passed through a third cycle of anion exchange to give additional

separation from fission products and to provide a more concentrated solution for further processing.

DISCUSSION

DISSOLUTION OF THE SLUG

The irradiated slug was a compacted mixture of aluminum powder and NpO_2 encased in an aluminum can. To permit a study of variables in the dissolution process, the slug (total weight, 54 g) was cut into four approximately equal sections and the sections were dissolved separately under different conditions. Sections 1 and 3 were cut from the ends of the slug and contained an aluminum cap in addition to the aluminum can and core material. Since the core material was exposed when the slug was cut into sections, there was no decanning step in the dissolving operation; rather, the core and can were exposed to the solution simultaneously. The rate of dissolution of plutonium was measured by determining the alpha activity of the solution as a function of time. An estimate of the dissolution rate for the powdered aluminum and NpO_2 was obtained by observing the amount of solids remaining in the dissolver. In all experiments the solutions were maintained at the boiling point throughout the run. After dissolution appeared complete, the solution was removed from the dissolver vessel and passed through a filter. The residual solids were then analyzed for neptunium and plutonium to determine whether or not dissolution was complete.

The primary objective in studying the dissolving process was to establish conditions for complete dissolution of plutonium and neptunium. Also, it was necessary to demonstrate a practical dissolving rate, and to show that the final solution could be filtered to produce a solution sufficiently free of solids to permit processing by ion exchange. The data for the four dissolving runs are given in the following table, and the rate of dissolution of the plutonium is shown in Figure 1.

Dissolution of Irradiated Neptunium Slug

		Composition of Dissolver Solution				
Section	Weight, g	HNO_3, M	Al^{+++}, M	HF, M	Hg^{++}, M	Volume, ml
1	12.8	3.5	1	0.005	-	400
2	15.9	3.5	1	0.02	-	400
3	16.4	8	-	-	0.005	400
4	9.1	8	-	-	-	400

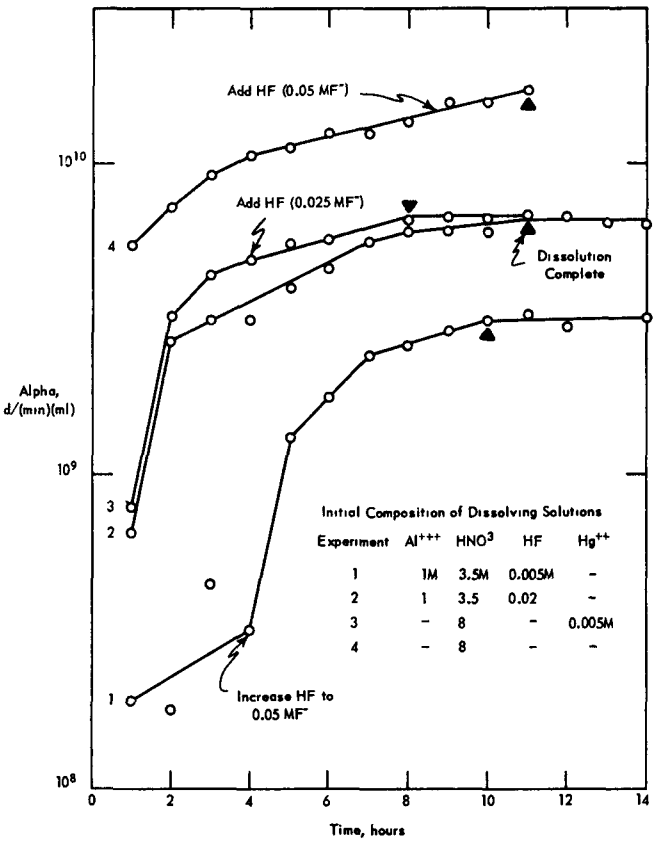

FIGURE 1 - DISSOLUTION OF NpO_2 TARGET SLUG
Temperature: 108°C

In all of the four runs plutonium and neptunium were dissolved completely at the end of 11 hours. The core material dissolved at a satisfactory rate in 3.5M HNO_3 that contained at least 0.02M fluoride, and the presence of aluminum in the solution did not appear to affect the rate to an appreciable extent. A satisfactory dissolving rate was achieved in 8M HNO_3 in the absence of either fluoride or mercuric ions; however, fluoride was added to the 8M acid solution after a few hours to ensure complete solution of plutonium and neptunium. Mercury was not required as a catalyst for dissolving the powdered aluminum in the core when fluoride was present in the solution; however, mercury did speed the dissolution of the aluminum can and would thus be desirable if a dejacketing step were required.

There was no evidence of an excessive off-gas rate or of excessive frothing during the dissolving operation. The gases were removed

through an Allihn condenser and the freeboard in the dissolver was about 100% for all runs. The solution resulting from the dissolution contained a small amount of a dark solid that was easily filtered on a fritted disc of medium porosity. Analysis of the solid showed silicon, iron, and magnesium as the major constituents; less than 0.01% of the original neptunium and plutonium was undissolved.

ANION EXCHANGE

DECONTAMINATION CYCLE

The solutions obtained from dissolving the four sections of the irradiated slug were filtered and combined. Nitric acid was added to the solution to adjust the total nitrate concentration to approximately 8 molar. The actual composition of the solution is shown in the following table.

Composition of Feed Solution

	Concentration	Total
Pu^{238}	0.14 g/l	282 mg
Np^{237}	0.55 g/l	1110 mg
Cm^{242}*	0.034 mg/l	0.068 mg
HNO_3	5.6M	--
$Al(NO_3)_3$	1.06M	--
Gross γ	1.9×10^8 c/(min)(ml)	3.8×10^{11} c/min

*Produced from Am^{241} present as an impurity in the NpO_2

This solution was divided into three equal batches. Each batch was adjusted to 0.05M ferrous sulfamate to reduce the neptunium to Np(IV) and the plutonium to a mixture of Pu(III) and Pu(IV). The solution was then heated to 55°C to oxidize the iron to Fe(III), and the plutonium to Pu(IV), while the neptunium remained as Np(IV). The solution was cooled to 30°C and passed through an ion exchange column, 1.1 cm^2 x 25 cm, packed with "Dowex" 1-X4, 50-100 mesh resin. The plutonium and neptunium were absorbed as the anionic nitrate complexes and the column was washed with 1350 ml (50 bed volumes) of 8M HNO_3 - 0.005M HF to selectively remove fission products. After the column was washed, the plutonium and neptunium were eluted with 108 ml (4 bed volumes) of 0.3M HNO_3 and were collected as a single fraction for the subsequent partition cycle. The resin was reconditioned with 8M HNO_3 after each elution and the same resin was used for all three batches. Solution compositions, flow rates, and other pertinent data for the decontamination cycle are summarized in the following table.

Data for Decontamination Cycle

Operating Conditions (for all runs)

Feed Solution:

Composition: 1M $Al(NO_3)_3$ - 5M HNO_3, 0.05M FeSA; 0.14 mg Pu/ml; 0.52 mg Np/ml

Temperature: 23°C
Flow: 2 ml/(min)(cm^2), downflow

Decontamination Wash:

Composition: 8M HNO_3 - 0.005M HF
Temperature: 23°C
Volume: 50 bed volumes
Flow: 4 ml/(min)(cm^2), downflow

Elutriant:

Composition: 0.35M HNO_3
Temperature: 23°C
Volume: 4 bed volumes
Flow: 0.5 ml/(min)(cm^2), downflow

Resin Bed: "Dowex" 1-X4, 50-100 mesh
27 ml, 26 cm long
Np and Pu band 19 cm after absorption
Np and Pu band 22 cm after wash

Material Balance Data

	Run 1		Run 2		Run 3	
	Np^{237}, mg	Pu^{238}, mg	Np^{237}, mg	Pu^{238}, mg	Np^{237}, mg	Pu^{238}, mg
Feed solution	351	94	351	94	351	94
Np and Pu product	403	90	324	94	316	95
Absorption and wash effluents	9	0.9	8	1.0	22	1.1
Total accounted	412	91	332	95	338	96
Error of material balance	+17%	-3.2%	-5.4%	+1.1%	-3.7%	+2.1%

Approximately 1% of the plutonium and 3.5% of the neptunium were lost to the absorption and wash effluents. Most of the loss, 0.75% of the plutonium and 3% of the neptunium, occurred during the fission product wash; therefore, the loss could be decreased with some sacrifice in decontamination from fission products by decreasing the volume of the wash. Analysis of a resin sample withdrawn after the third elution cycle showed that only 0.5 mg of plutonium per liter of resin was

retained. The gamma decontamination factors were 9000, 5000, and 3000, respectively, for the three runs; the decrease in decontamination may have been due to progressive degradation of the resin or to progressive contamination of the equipment.

PARTITION CYCLE

Plutonium and neptunium were partitioned after reduction to Pu(III) and Np(IV) with ferrous sulfamate - hydrazine in 6.4M nitric acid. The Np(IV) was selectively absorbed on the anion resin and was washed first with 20 bed volumes of 6.4M nitric acid - 0.05M ferrous sulfamate - 0.05M hydrazine to complete the removal of plutonium, and then with 30 bed volumes of 8M nitric acid to further decontaminate neptunium from fission products. Neptunium was eluted from the column with 0.35M HNO_3, and the displacement cut and tails were collected as a separate fraction for recycle. The data for the three partition runs are given in the following table and in Figure 2.

Data for the Partition Cycle

Material Balance Data

	Run 1		Run 2		Run 3	
	Np^{237}, mg	Pu^{238}, mg	Np^{237}, mg	Pu^{238}, mg	Np^{237}, mg	Pu^{238}, mg
Feed solution	350	87.7	337	85.6	330	85.3
Np product	270	4.7	288	7.7	290	0.4
Recycle (Displacement and tails)	103	0.1	92	0.1	55	0.0
Absorption effluent	0.05	10.8	0.05	7.3	0.05	13.4
Wash effluent	0.05	71	3.5	70.3	0.05	75.7
Samples	6	1.5	6	1.4	6	1.4
Total accounted	379	88.1	389.5	86.8	351	90.9
Error of material balance	+8%	+0.5%	+15%	+1.4%	+6%	+6.6%

Decontamination from Fission Products

All activities expressed as γ c/(min)(ml)

	Gross γ	Zr γ	Ru γ	Pa^{233} γ	Pu^{238} γ
Feed	6.6×10^4	1.7×10^4	3.2×10^4	9×10^3	7×10^3
Np product	2.4×10^5	3.3×10^3	10^2	2.0×10^5	4×10^4

Gross fission product DF 340

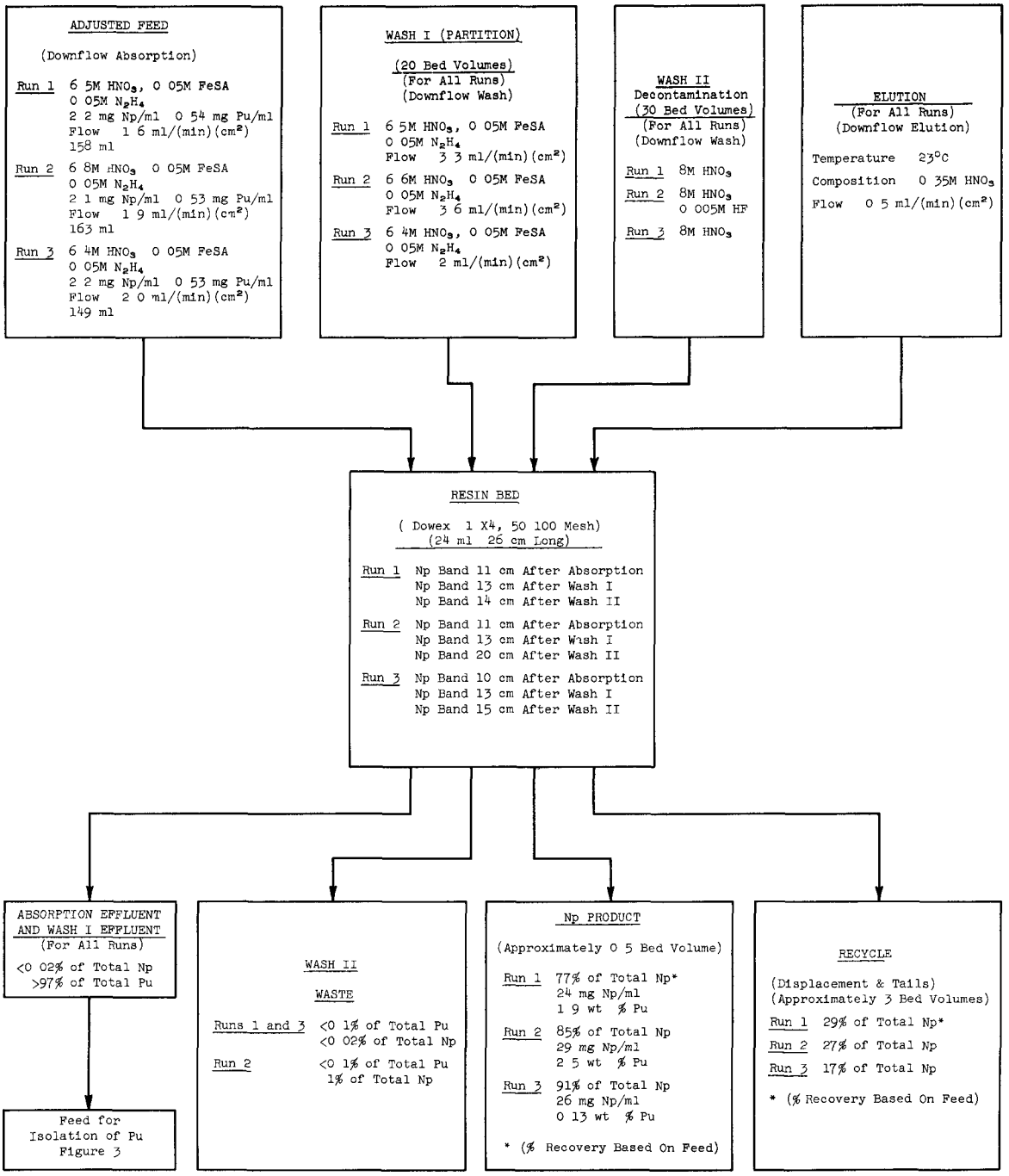

FIGURE 2 - PARTITION OF NEPTUNIUM AND PLUTONIUM

The separation of neptunium from plutonium was not affected by the flow rate in the feed absorption step at the flow rates that were studied, 1.6 to 2.0 ml/(min)(cm^2). The degree of separation was dependent, however, on the flow rate of the partition wash as shown by the increase of plutonium in the neptunium product from 0.13 w/o at a flow rate of 2 ml/(min)(cm^2) to 2.0 w/o at 3.5 ml/(min)(cm^2). At the lower flow rate the separation was entirely adequate and both products were within specifications.

The decontamination of neptunium from fission products was excellent in all runs. Less than 2% of the gross gamma activity associated with the neptunium was due to fission products. Losses of plutonium and neptunium were low; less than 0.05% for neptunium and about 0.1% for plutonium. In Run 2 where HF was added to the decontamination wash the neptunium loss was 1%; however, HF was not required for adequate decontamination so that the addition of HF to the wash is not required.

PLUTONIUM ISOLATION CYCLE

The solution containing Pu(III) from the partition cycle was adjusted to 8M nitric acid and heated to 55°C to oxidize the plutonium to Pu(IV). The Pu(IV) anionic nitrate complex was absorbed on "Dowex" 1-X4, 50-100 mesh resin. The bed was washed with 8M nitric acid to selectively remove fission products, and the plutonium was eluted with 0.35M nitric acid.

The data for the plutonium isolation cycle are summarized in the following table and in Figure 3.

Data for Plutonium Isolation Cycle

Material Balance Data

	Run 1		Run 2		Run 3	
	Np^{237}, mg	Pu^{238}, mg	Np^{237}, mg	Pu^{238}, mg	Np^{237}, mg	Pu^{238}, mg
Feed solution	0.05	81.0	0.1	74.0	0.05	85.3
Pu product	0.01	64.4	0.01	59.1	0.01	70.4
Recycle (Displacement and tails)	0.0	14.7	0.0	10.9	0.0	8.2
Absorption effluent	0.0	0.04	0.0	0.03	0.0	0.00
Wash effluent	0.0	0.54	0.0	1.1	0.0	2.3
Samples	0.0	0.2	0.0	0.2	0.0	0.2
Total accounted	-	79.9	-	71.3	-	81.1
Error of material balance	-	-1.4%	-	-3.6%	-	-4.9%

Decontamination from Fission Products

All activities expressed as γ c/(min)(ml)

	Gross γ	Zr γ	Ru γ	Pa^{233} γ	Pu^{238} γ
Feed	1.0×10^4	4.5×10^3	5×10^3	None	400
Product	1.5×10^4	7×10^2	None	None	1.4×10^4

Gross fission product DF >1000

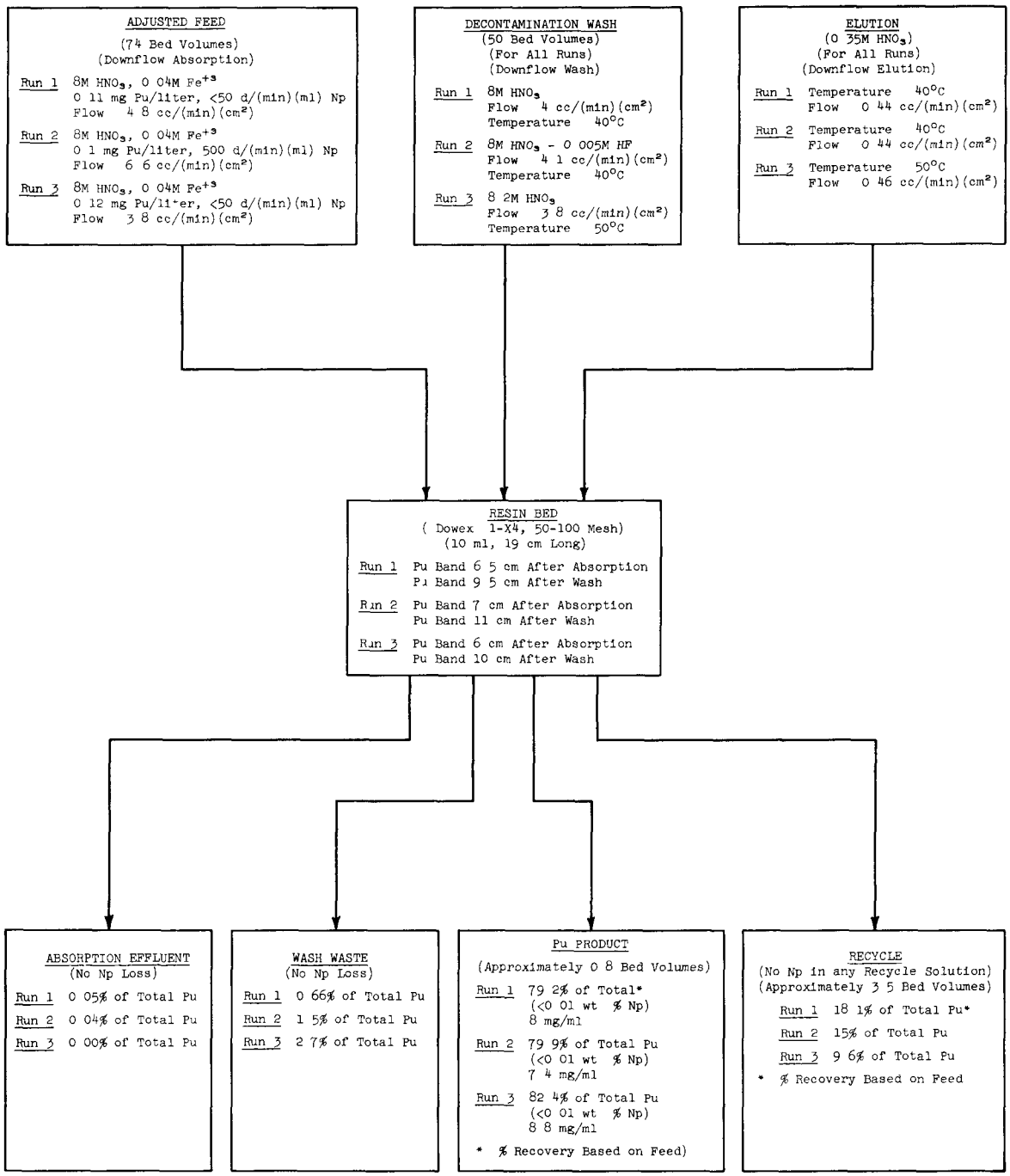

FIGURE 3 - ISOLATION OF PLUTONIUM

The concentration and decontamination of plutonium were satisfactory in the isolation cycle. The plutonium product contained less than 0.05 w/o neptunium, confirming the excellent separation of neptunium and plutonium by the partition cycle.

Less than 0.1% of the plutonium was lost to the absorption effluent, but approximately 2% was lost in the wash effluent. The loss could be reduced by using a smaller volume of wash and thereby sacrificing decontamination from fission products. The high plutonium loss in the wash step is attributed to the effect of the intense alpha radiation from Pu^{238}, since losses under similar conditions with Pu^{239} are at least tenfold less. This same effect is probably responsible for much of the loss in the decontamination cycle wastes, since lower losses are observed there with Pu^{239}.

Plutonium was separated from fission products by a factor greater than 1000. More than 95% of the residual gamma activity in the final product was attributable to plutonium. Hydrofluoric acid (0.005M) was added to the wash in one run and the gamma activity of the fission products in the final plutonium was decreased to less than 2% of the gross gamma activity.

The same resin bed was used for all three runs with little indication of decreased capacity as judged by increased length of the plutonium band. The resin was darkened to a brown-black color by exposure to the intense alpha radiation and resin degradation may have contributed to increased losses and decreased fission product contamination in Run 3 where the losses were doubled and the separation from fission products was halved.

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