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ION EXCHANGE PROCESSES FOR PLUTONIUM AND U^{233} ISOLATION

By

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CF-53-3-31 (rev.)

ABSTRACT

Ion-exchange processes have been developed for isolation of plutonium and U^{233}. The plutonium process consists in sorbing Pu(III) and uranium present in the nitric acid solution onto a cation-exchange resin, selectively eluting the uranium with dilute sulfuric acid, and then eluting the plutonium with strong nitric acid. The U^{233} process consists in sorbing the uranium as the uranyl ion from dilute nitric acid and then eluting with ammonium acetate-acetic acid.

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INTRODUCTION

Chemical processes for the separation of fissionable material from fission products and other contaminants usually produce a dilute solution of the product in nitric acid. Before the fissionable material may be converted to the metal it must be concentrated and further purified from residual fission and corrosion products. In order to accomplish this concentration and purification, such methods as evaporation, solvent extraction, precipitation, and ion exchange have been proposed. The evaporation procedure used for concentrating plutonium and uranium solutions increases the amount of ionic impurities and achieves no radiochemical decontamination. A methyl isobutyl ketone solvent extraction process, previously investigated at ORNL, proved to be mechanically inoperable, while precipitation methods of concentrating require large equipment and the total solubility loss is high when the precipitation is carried out from dilute solutions.

Ion exchange processes have been developed which both concentrate the fissionable material and give additional separation from corrosion and fission products. The processes were developed specifically for the plutonium product from the Purex process and the uranium from the Thorex process. However, they have application to plutonium and uranium isolation from other processes. These two processes have been demonstrated through the pilot plant stage and plant scale runs have been made.

The plutonium ion exchange isolation process, which is to be used

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at the Savannah River plant, has been studied under conditions essentially the same as those expected, and it was found satisfactory. In the plutonium ion exchange isolation process, beta and gamma decontamination factors of 30 and 40, respectively, have been obtained. The loss is only 10^{-4} per cent and the product is recovered at a concentration of about 50 g/liter.

The U^{233} ion exchange process has been satisfactorily demonstrated on a plant scale application. Gross beta and gamma decontamination factors of the order of 10 and 50, respectively, have been obtained. The loss is only 10^{-3} per cent of the U^{233} and the product is recovered at a concentration of about 140 g/liter.

If the product streams from the Purex and Thorex processes are used as feeds, volume reduction factors of about 250 are obtained.

The two processes differ somewhat and are considered separately in this paper.

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Part I. ION-EXCHANGE PROCESS FOR PLUTONIUM ISOLATION

CYCLES IN PROCESS

The cycles in the ion-exchange process for isolation of plutonium are the following (see Fig. 1):

1. Sorption of plutonium and residual uranium from the Purex (solvent-extraction) plutonium product stream.

2. Uranium elution (optional).

3. Plutonium elution.

The feed to the ion-exchange isolation process is the Purex plutonium product, that is, the aqueous nitric acid solution that has been used to strip the plutonium from the organic solvent. The plutonium concentration of this solution varies from 0.2 g/liter with a Purex No. 1 flowsheet to 1.22 g/liter with a Purex No. 3 flowsheet, and may be as high as 4 to 6 g/liter with a modified Purex No. 3 flowsheet. The nitric acid concentration of the feed varies from 0.15 to 0.5 M. The feed contains hydroxylamine sulfate, which is added to the aqueous stripping solution to reduce the plutonium to Pu(III). The principal impurities are uranium, fission products, and corrosion products (see Tables 1 and 2).

In the sorption cycle, plutonium and impurities are sorbed by 12 per cent cross-linked 50- to 100-mesh Dowex 50 resin. The distribution of uranium and plutonium on the resin during this cycle depends on the relative sorption coefficients* of the two metals, namely, 4.3×10^3 for Pu(III) and 1.0×10^2 for the uranyl ion, in 0.25 M HNO_3. A band

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* The absorption coefficient is defined as the grams of plutonium per gram of resin divided by the grams of plutonium per gram of solution at equilibrium.

of plutonium containing some uranium forms at the top of the column, and a band of uranium forms below it.

The uranium elution cycle is optional; however, if the uranium in the feed to the resin column is more than 1 per cent of the plutonium, the uranium elution is employed to reduce the contamination to less than 1 per cent. The uranium elution is carried out downflow with 0.25 M H_2SO_4, which contains 0.05 M hydroxylamine sulfate to keep the plutonium in the trivalent state.

Partial elution of the uranium or merely moving the uranium band down, but not off, the column has been shown to give sufficient decontamination of the plutonium product since the plutonium is eluted upflow. The volume of sulfuric acid elutriant required to move the uranium down the column is considerably less than that required for complete elution, and the plutonium loss in this cycle is about 10^{-4} per cent.

In order for the plutonium to be eluted in a reasonable length of time and at a sufficiently high concentration, the hydrogen ion in the elutriant must be approximately 6 M. The elutriant used is 5.7 M HNO_3 containing an antioxidant, 0.3 M sulfamic acid, to inhibit the oxidation of Pu(III) to Pu(IV) by the strong nitric acid. Since the plutonium band is at the top of the column when the elution starts, upflow elution is employed to obtain a higher concentration of plutonium in the eluate. A typical plutonium elution curve is shown in Fig. 2.

A cycle type of operation is used for the plutonium elution. Elutriant equal in volume to the product cut desired is fed upflow to the column. This is followed by two column volumes of dilute nitric

acid (0.1 M) reconditioning solution. From the top of the column three fractions are collected: (1) one displacement volume of dilute acid containing very small amounts of plutonium, (2) the desired volume of product in 5 M HNO_3, and (3) one volume change of reconditioning solution (about 0.5 M HNO_3) which contains a small amount of plutonium. Cuts 1 and 3 are recycled to subsequent sorption. This procedure permits elution of approximately 90 per cent of the plutonium on the column in the product cut at a concentration of about 30 g/liter. A 10 per cent heel is left on the column. At the completion of this cycle the resin column is ready for the next sorption. Complete elution of the plutonium is not carried out until it becomes necessary to decontaminate the resin column of accumulated fission products.

VALENCY STATE OF THE SORBED PLUTONIUM

One of the basic features of this process is the sorbing of the plutonium as Pu(III) and the maintaining of this valence state throughout the process. The use of this valence state not only avoids polymerization of the plutonium during the sorption but also permits elution at a higher desorption coefficient than the tetravalent state. The maintaining of the trivalent plutonium on the resin is essential during the uranium elution since Pu(IV) elutes with about the same desorption coefficient as uranyl ion. If the Pu(III) is allowed to oxidize to Pu(IV), nitrogen oxide gases form and cause channeling in the resin bed. As mentioned above, the sulfamic acid in the 5.7 M HNO_3 inhibits the oxidation of the Pu(III).

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PRODUCT PURITY

Although the ion-exchange process was originally investigated only as a means of concentrating the plutonium from the solvent-extraction process prior to precipitating plutonium peroxide, it was found to furnish appreciable radiochemical and ionic decontamination of the product (see Tables 1 and 2). Gross beta and gamma decontamination factors of approximately 30 and 40 respectively, have been obtained in the ion-exchange processing, which enables the product to meet over-all specifications of approximately 10^7 for solvent-extraction and ion-exchange combined (see Table 3). Ionic reduction factors for different constituents vary from 1 to 200 in the ion-exchange process.

RADIOCHEMICAL AND IONIC DECONTAMINATION OF RESIN COLUMN

When it becomes necessary to decontaminate the resin column from radiochemical activities the plutonium is completely eluted from the column with about 12 column volumes of 5.7 M HNO_3, 0.3 M sulfamic acid. This elution removes 99.95 per cent of the plutonium sorbed on the resin. Zirconium and niobium, the principal radioactive contaminants, are then removed with about four column volumes of 0.5 M oxalic acid. This treatment also removes residual amounts of iron contamination. The oxalic acid is displaced with four column volumes of 0.1 M HNO_3 and the resin column is ready for the next sorption.

[redacted]

Table 1 -- Radiochemical Contaminants in Ion-Exchange Plutonium Isolation Process Feed and Product

Contaminant, per mg of Pu: β, c/m; γ, mv													
In Feed							In Product						
Ru β	Zr β	Nb β	TRE β	$UX_1 + UX_2$ β	Total β	γ	Ru β	Zr β	Nb β	TRE β	$UX_1 + UX_2$ β	Total β	γ
2,350	1,330	560	320	150	4,710	17	470	33	24	27	34	588	2
815	16,700	859	465	118	19,000	51	420	160	39	20	6	705	2
1,620	20,800	734	86	391	24,630	102	814	294	40	13	72	1,233	3
1,320	3,000	220	32	76	4,650	20	630	86	12	22	22	778	2

Table 2 -- Ionic contaminants in Ion-Exchange Plutonium Isolation Process
Feed and Product

Contaminant, μg per mg of Pu																			
In Feed										In Product									
Al	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Pb	Zn	Al	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Pb	Zn
2.4	6.7	<0.5	0.7	0.07	1.5	1.0	<1.2	<2.4	<6	0.5	--	0.3	0.27	0.85	2.0	0.08	0.7	0.6	<2
0.8	7	0.7	0.4	1.2	1.0	<0.5	<1	<4	<6	0.43	2.4	0.23	0.15	3.3	1.07	0.08	0.28	0.42	<0.4
1.1	11	1.4	0.5	26	2.0	<0.4	--	<4	<9	0.12	5	0.15	0.10	24	0.9	0.2	0.16	2.8	--
<1.1	31	1.8	--	0.6	8.5	<1.2	~1.5	<15	<25	1.6	6.1	0.10	0.06	1.4	0.65	0.03	2.4	0.41	--

[redacted]

Part II. ION-EXCHANGE PROCESS FOR U^{233} ISOLATION

CYCLES IN PROCESS

The cycles in the ion-exchange process for isolation of U^{233} are the following (see Fig. 3):

1. Removal of residual protactinium and thorium from the solvent-extraction U^{233} product stream.
2. Sorption of the U^{233}.
3. Elution of the U^{233}.

The feed to the U^{233} ion-exchange isolation process is the aqueous nitric acid solution that has been used to strip the $U^{233}O_2(NO_3)_2$ from the organic solvent in the solvent-extraction process. When the feed is from the Thorex process, this stream is 0.02 M in nitric acid and contains 0.5 g of U^{233}, as uranyl nitrate, per liter. The principal impurities are thorium, corrosion products, fission products, and aluminum (Tables 4 and 5). Dowex 50-W, 50 to 100 mesh, 8 per cent cross-linked, resin is used in this process.

Before the process stream goes to the main Dowex 50-W resin column for sorption of the uranium, it passes through a silica gel bed and a small Dowex 50-W resin column for removal of the residual protactinium and thorium. The protactinium is essentially all removed by the silica gel, with negligible loss of uranium. More than 99 per cent of the thorium, which is present in the feed to the extent of about 0.75 per cent of the uranium, is removed by the small Dowex 50-W resin column. The uranium breaks through this small column to the main resin column. The residual uranium on the small resin column is periodically eluted

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and returned to the solvent-extraction process. These two columns also remove some ionic and radiochemical contaminants, and thus greatly reduce the radiation hazard of the large column. The total loss of uranium in the two columns is about 10^{-3} per cent.

The elution of the uranium from the resin is carried out downflow employing 2.0 M ammonium acetate--1.0 M acetic acid at 70°C. The product cut (about one and one-half column volumes) contains more than 99.8 per cent of the uranium on the column at a concentration of about 140 g/liter. Two additional column volumes of the elutrient are required to elute (99.99 per cent) the column. The ammonium acetate--acetic acid solution is displaced from the column with three column volumes of 0.02 M HNO_3 and the resin is ready for a subsequent sorption. The tailing cut and reconditioning cut are recycled to the primary solvent-extraction process.

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Table 3 -- Over-all Beta and Gamma Decontamination Factors for Plutonium through Purex and Ion-exchange Isolation Processes

[redacted]	[redacted]	Individual Fission Products Ion Exchange					Decontamination Factors Gross β			Gross γ		
		Ru β	Zr β	Nb β	TRE β	$UX_1 + UX_2$ β	Purex	Ion Exchange	Over-all	Purex	Ion Exchange	Over-all
[redacted]	[redacted]	1.8	13	5	4.0	9.0	1.6×10^7	1.8	2.8×10^7	6.0×10^6	2.6	1.6×10^7
		4.2	69	40	1.4	14	3.3×10^5	7.3	2.5×10^5	1.2×10^5	17	2.3×10^6
		2.0	71	18	6.6	5.4	2.2×10^6	20	4.4×10^7	6.0×10^5	31	1.9×10^7
		2.1	112	24	1.0	3.1	2.0×10^6	29	5.9×10^7	4.0×10^5	42	1.7×10^7
		2.1	35	12	1.5	3.4	9.7×10^6	5.9	5.7×10^7	2.3×10^6	12.3	2.5×10^7
		1.5	39	9	2.0	4.0	2.2×10^7	2.3	5.0×10^7	8.4×10^6	3.7	3.1×10^7

[redacted]

Table 4 -- Radiochemical Decontamination Factors and Residual Activities of Resin Isolated U^{233}

Decontamination Factors						Activity Remaining in Product per mg of U^{233}: β, c/m; γ, mv				
Gross β	Ru β	Zr β	Nb β	TRE β	Gross γ	Ru β	Zr β	Nb β	TRE β	Gross γ
4.7	1.7	109	8.3	17	52	37.4	35.4	20.0	65.3	0.71
10.0	2.2	93	8.3	---	57	20.9	8.5	21.7	29.8	0.72
8.8	3.3	99	3.8	45	92	43.5	17.9	64.1	8.2	0.70

[redacted]

Table 5 -- Ionic Reduction Factors and Residual Impurities of Resin Isolated U^{233}

Decontamination Factors				Amount Remaining in Acetate Solution, ppm U												
Al	Ca	Fe	Mg	Al	B	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Pb	Zn	Zr	Th
85	177	50	378	234	70.6	8150	239	69.6	272	331	210	135	979	35.9	< 0.03	35
30	5	3	6	220	80.1	1495	64	40.7	873	147	52	193	227	13.4	< 0.03	92
109	4	5	6	90	63.8	1975	40	25.0	178	141	76	71	224	13.2	< 0.03	237
45	3	7	6	119	61.3	1230	31	96.2	98	7	91	58	184	10.8	< 0.03	196

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ACKNOWLEDGMENT

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ABOUT THE AUTHOR

Don C. Overholt was a chemist in the Special Engineering Detachment of the Manhattan Project prior to joining the staff of Clinton Laboratories. He received his B.A. degree in chemistry at the University of Kansas in 1942. At present he is a Group Leader in the Chemical Development Section of the Chemical Technology Division at Oak Ridge National Laboratory, in charge of developing isolation processes.

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Insert:

Photograph No. 10010 - Savannah River Plant Prototype Ion-exchange Column Containing Full Plutonium Load (350 g). Note the darker color at the top, showing the extent of the plutonium down the column.

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Insert:

Photograph No. 10531- Ion-exchange Plutonium Isolation Pilot Plant Installation (1/4 Savannah River Plant Capacity)

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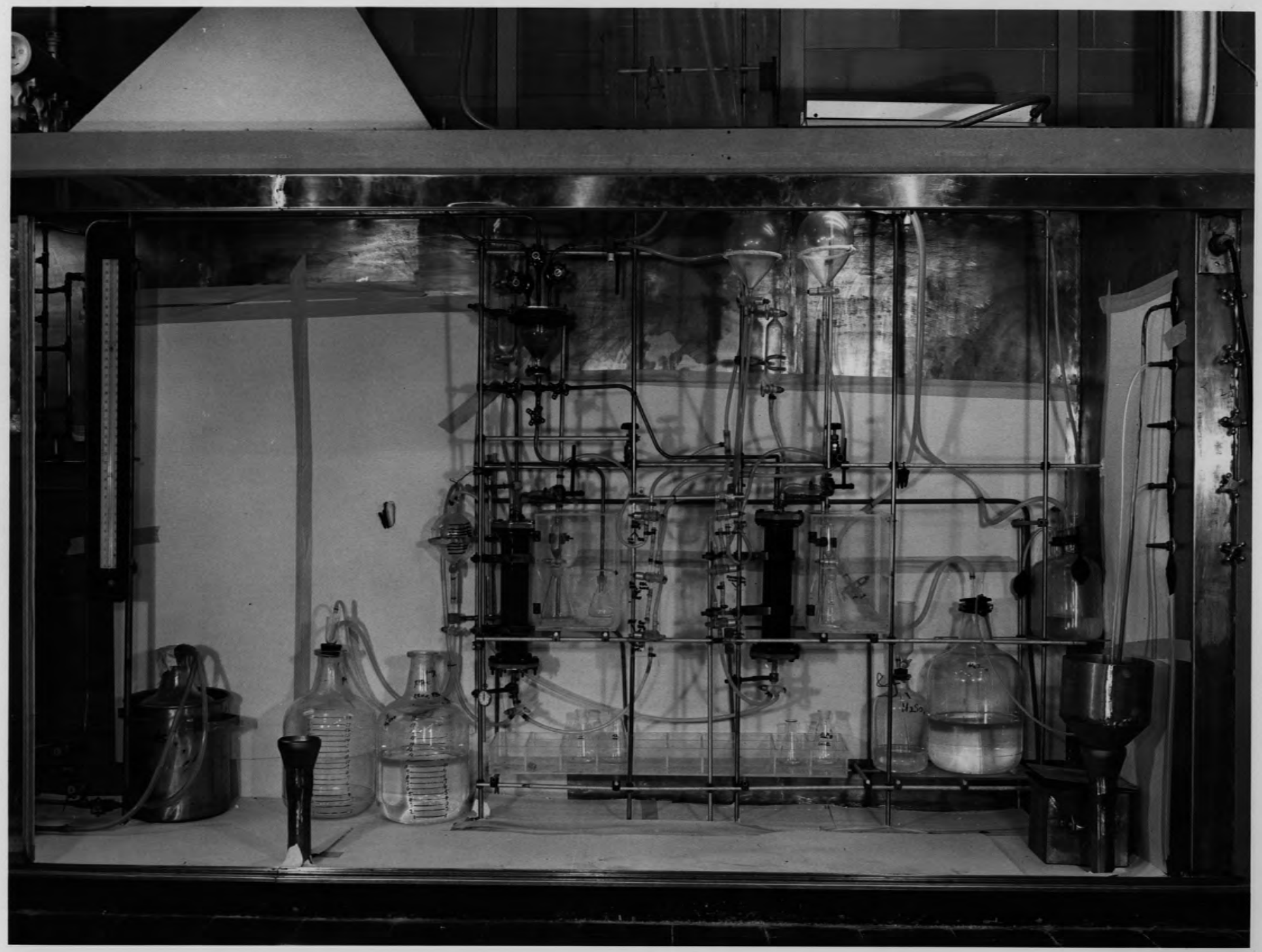
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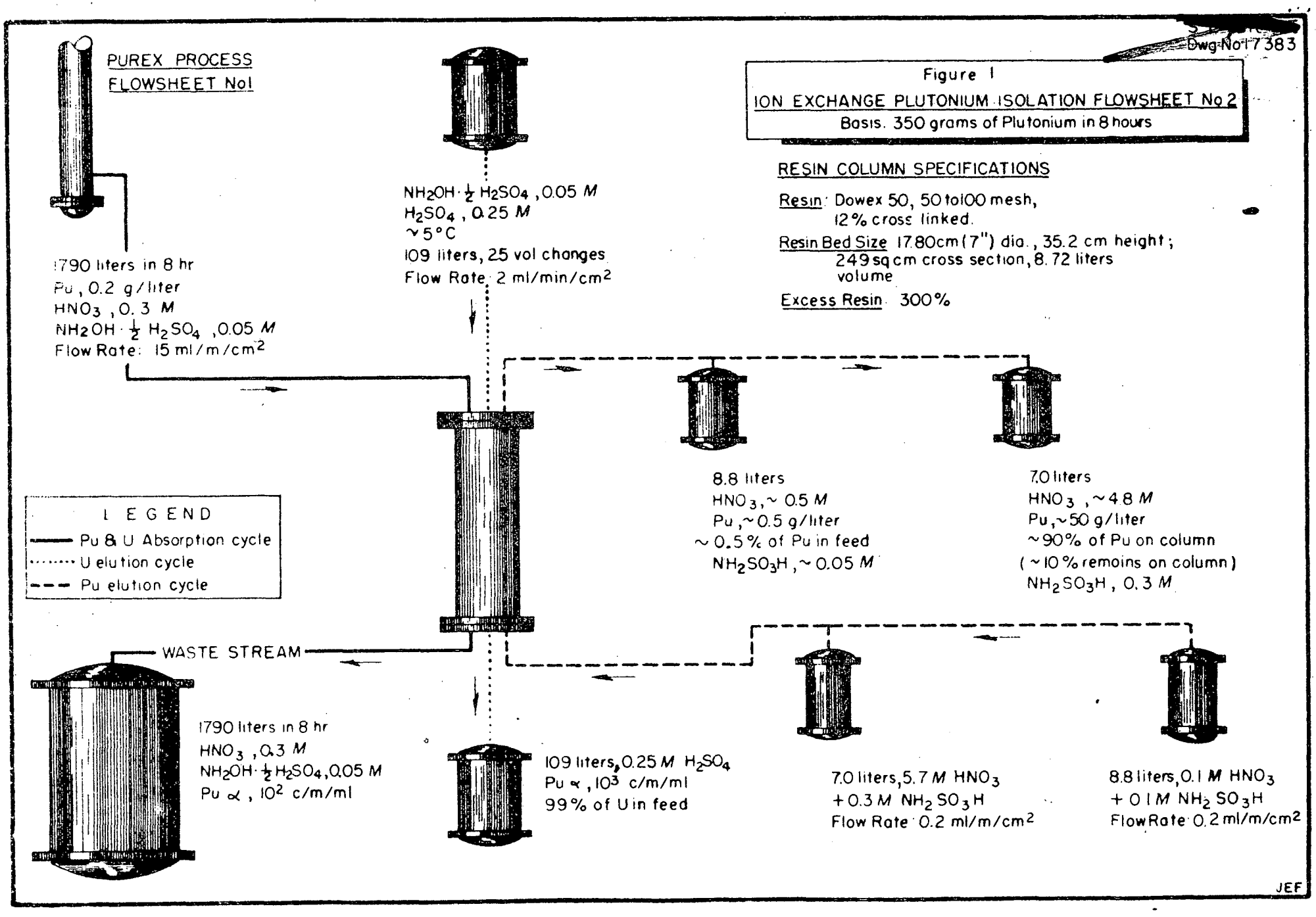

Figure 1

ION EXCHANGE PLUTONIUM ISOLATION FLOWSHEET No 2

Basis. 350 grams of Plutonium in 8 hours

RESIN COLUMN SPECIFICATIONS

Resin: Dowex 50, 50 to 100 mesh, 12% cross linked.

Resin Bed Size 17.80 cm (7") dia., 35.2 cm height; 249 sq cm cross section, 8.72 liters volume

Excess Resin 300%

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Dwg No 18413

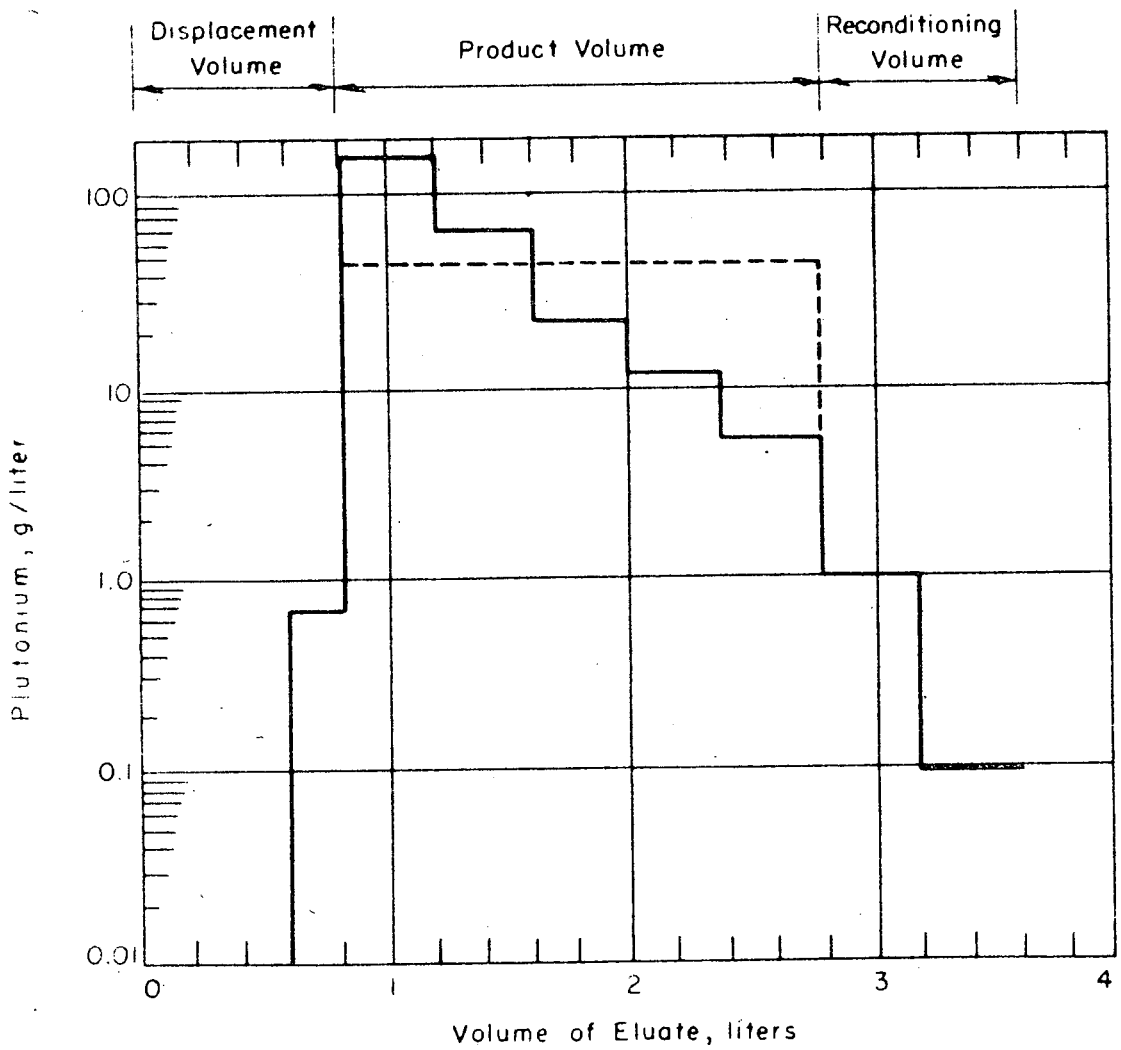

Figure 2

PLUTONIUM ELUTION FROM ION EXCHANGE COLUMN

RESIN: Dowex 50, 12% cross linked, 50 to 100 mesh.

COLUMN DIMENSIONS: 3 in. diameter, 14 in. height.

ELUTRIANT: 5.7 *M* HNO_3, 0.3 *M* NH_2SO_3H

FLOW RATE: 0.2 ml/m/cm^2, upflow.

COLUMN LOAD: 91 g of plutonium.

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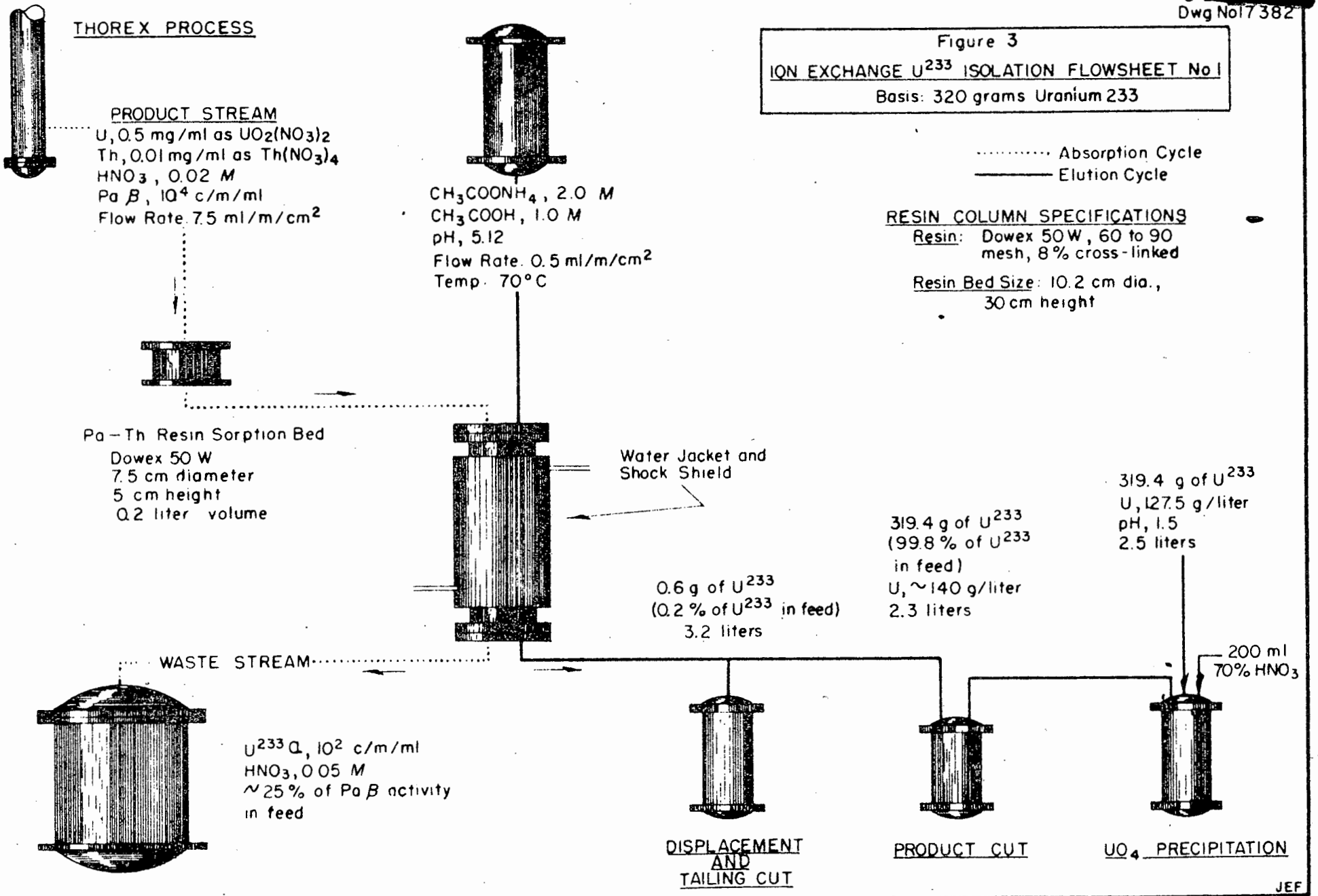
Figure 3

ION EXCHANGE U^{233} ISOLATION FLOWSHEET No I

Basis: 320 grams Uranium 233



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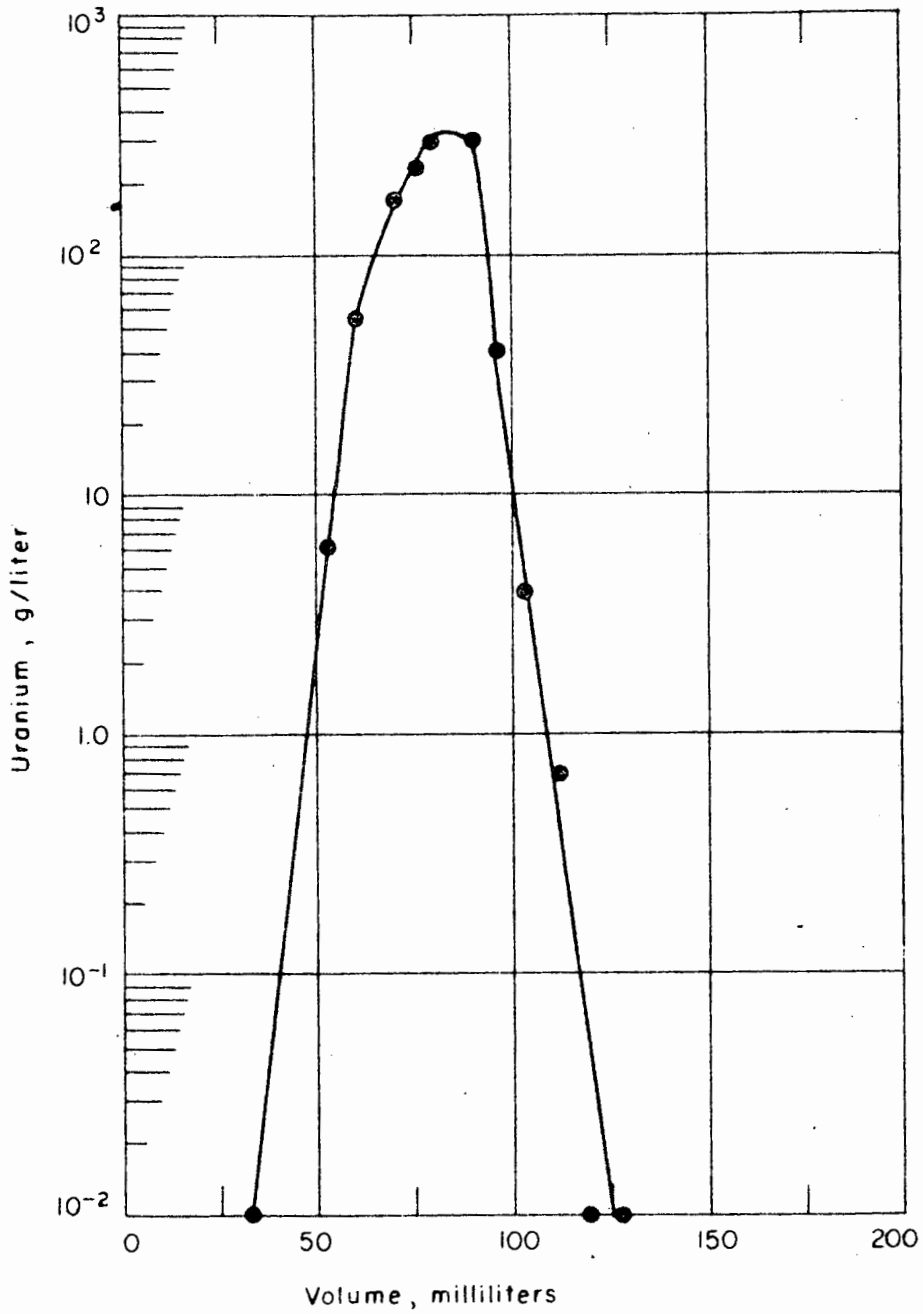

Figure 4
URANIUM ELUTION FROM ION EXCHANGE COLUMN

RESIN: Dowex 50W, 8% cross linked, 50 to 100 mesh.

COLUMN DIMENSIONS: 0.75 in diameter, 8 in. height.

ELUTRIANT: 2.0 *M* Ammonium Acetate, 1.0 *M* Acetic Acid.

FLOW RATE: 0.5 ml/m/cm^2, downflow at 70°C.

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