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Chemistry - Separation Processes
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Chemical Development Section

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

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0.0 ABSTRACT

Progress in the ion-exchange isolation program, particularly as applied to the Scrup and Interim-23 programs, the Purex pilot plant work, and Savannah River operating conditions is reported.

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1.0 INTRODUCTION

The objective of the Isolation program is to develop and operate processes for the isolation of U^{233} and plutonium produced by reactor irradiation and separated by solvent-extraction processes. Solvent-extraction processes give a product solution that is too dilute for coupling with metal production processes, and the product is often not sufficiently decontaminated from ionic and radioactive impurities to meet process requirements.

Ion-exchange processes for isolation of uranium and plutonium products have been developed and operated in the Scrup, Purex, and Interim-23 programs. These processes have been shown to give additional radioactive and ionic decontamination, and have produced a concentrated product suitable for metal production. Investigations leading to development of the processes have been reported earlier (see p. 3).

Ion-exchange processes are subject to modification and improvement, particularly as new applications are developed. Laboratory investigations are continuing, and the work of the past quarter is reported here.

2.0 SUMMARY

The work of the Isolation Group during August, September, and October, 1952 included plutonium isolation in connection with Scrup and Purex processing, U^{233} isolation as a part of the Interim-23 program, and laboratory investigation of the plutonium isolation process variables in connection with the Savannah River project. Laboratory investigation of miscellaneous effects in connection with the Isolation program has been continued.

The program for the isolation of plutonium from Chalk River slugs (Scrup) has been completed, after isolation of 3.1 kg of plutonium. The total loss in this operation was 1.2 g of plutonium, or 0.05%. Unusual operating conditions produced a variable IIBP feed stream to the isolation column, but modifications of the process to take these variations into account led to satisfactory operation.

The plutonium from six Purex solvent-extraction runs, HCP-10 through 15, has been processed through the ion-exchange coupling process. Operations were carried out in a manner corresponding to continuous operation. Operation was satisfactory, and all plutonium products were within specifications.

The isolation of U^{233} from the second and final phase of the Interim-23 program has been completed, after isolation of 2.64 kg of U^{233}. A change in the eluting solution resulted in a product from the column with a uranium concentration of 130 to 140 g/liter.

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The laboratory study of operating variables of the ORNL ion-exchange process for use at the Savannah River site has been continued. Two small columns have been subjected to 15 complete absorption and elution cycles with no noticeable effect on the resin.

Laboratory experiments have shown that a silica gel column is not a practical means of removing zirconium and niobium from the IIBP stream.

3.0 SCRUP ION-EXCHANGE ISOLATION PROGRAM

The Scrup program for isolation of plutonium from Chalk River irradiated uranium has been completed except for a small amount of plutonium remaining in the analytical waste. The slugs were dissolved and the plutonium was solvent-extracted by a Purex No. 3 flowsheet and purified by an ion-exchange process.

The first six runs were on highly irradiated material for use in research programs, and care was taken to prevent mixing the material from the several runs. The ion-exchange product concentration varied from 8 to 30 g/liter, depending on the total quantity of plutonium present. This comparatively low concentration was the result of complete elution (99.9%) of each column to avoid mixing the various batches.

The remaining ten runs were production runs. The first two, "Blue," runs were made on material containing 0 to 400 g of plutonium per ton; the next three, "Yellow," runs were on 400- to 600-g/ton material; the next four, "Red," runs were on material containing more than 600 g of plutonium per ton; and the last run was on mixed material from such sources as dissolver heels. The ion-exchange resin column was only partially eluted (90%) after each run except the last one in each class; this one was eluted completely in order to avoid mixing of the plutonium between classes. Because of the partial-elution procedure used, the plutonium concentration of the composite product in each class, about 40 g/liter, was considerably higher than in the research runs.

The acidity of the ion-exchange product from each of the 16 runs was between 5 and 6 M (see Table 3.1), and both ionic (Table 3.2) and radiochemical (Table 3.3) contaminants were at very low levels. These products are reported to meet specifications for the metal program very satisfactorily.

Plutonium losses, other than analytical, for the entire program amounted to about 1.22 g, or about 0.05% of the total plutonium, 3140 g, processed. The isotopic analyses of the products are given in Table 3.4.

3.1 Ion-Exchange Isolation Procedure

The following isolation procedure was evolved from the research carried out during the Scrup program:

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1. Reduction. Any tetravalent plutonium that may be on the column is reduced with 0.1 M $NH_2OH \cdot 1/2\ H_2SO_4$ in 0.1 M HNO_3 to which ice is added, downflow at 2 ml/m/cm^2. Ten volume changes are usually sufficient.

2. Uranium elution. Uranium is eluted with 25 volume changes of 0.25 M H_2SO_4, downflow at 2 ml/m/cm^2. Uranium occurred sporadically in the feed, and a uranium elution was therefore always performed, although it often later proved to have been unnecessary.

3. Degassing. Gas is completely removed from the column immediately prior to the plutonium elution by sweeping the column with iced 0.1 M $NH_2OH \cdot 1/2\ H_2SO_4$ downflow at 5 ml/m/cm^2. Ten volume changes are usually sufficient.

4. Plutonium elution. The plutonium is eluted with 5.7 M HNO_3 containing 0.3 M NH_2SO_3H upflow at 0.2 ml/m/cm^2. One displacement volume is passed through the column. If the absorption has been carried out properly with regard to such conditions as valence state of the plutonium and acidity of the feed, 2.5 volume changes are then sufficient to elute more than 90% of the plutonium at a concentration of about 40 g/liter under the flowsheet conditions of column geometry and loading.

5. Column reconditioning. After the elutriant required for the product cut has been fed to the column, 0.1 M HNO_3 containing 0.05 M $NH_2OH \cdot 1/2\ H_2SO_4$ is fed upflow at 0.2 ml/m/cm^2 until the product cut has been removed. The flow rate is then increased to 1 ml/m/cm^2 for two additional volume changes. This brings the acidity in the column to the proper concentration for the next absorption with a minimum of plutonium to be recycled.

6. Recycling of wastes. Solutions to be recycled, such as the displacement volume and the reconditioning solution are combined. The acidity is adjusted to less than 0.5 M, then $NH_2OH \cdot 1/2\ H_2SO_4$ is added to 0.05 M, and the solution is passed through the column for absorption of the plutonium. The column is then sent back for the next run.

The column from the last run in each class of material in the production runs was completely eluted to prevent mixing of plutonium of differing isotopic concentrations. After the product cut containing 90% of the plutonium at a concentration greater than 40 g/liter had been taken, the plutonium elution was continued until about 99.9% of the plutonium had been eluted. This low-concentration tailing, together with the displacement volume and reconditioning solution from this run, was recovered by processing through a much smaller ion-exchange column. The low-concentration waste streams from the recovery columns of the three classes of material were recovered on the column from Run 16, which contained mixed material from the solvent-extraction plant. In this way the plutonium losses other than those in the samples taken for analytical work should be kept to the order of 0.005%. In this program the plutonium loss in the uranium elution of incompletely reduced columns in the early runs increased the total loss to 0.05%.

Table 3.1

Scrup Product Data

SB Run No.	Volume (ml)	Acid Concentration (N)	Pu Concentration (g/liter)	Total Pu (g)	Total Product Including Recovered Material		
					Volume (ml)	Concentration (g/liter)	Pu (g)
1	2,840	5.47	8.39	23.82			23.82
2	2,926	5.10	11.97	35.01			35.01
3	2,986	5.40	19.30	57.63			57.63
4	5,989	5.68	11.20	67.07			67.07
5	6,478	5.12	23.59	152.83			152.83
6	10,080	5.28	28.51	287.43			287.43
Blue:							
7	5,715	5.30	39.85	227.72	16,315	40.03	653.17
8	9,349	5.34	43.79	409.35			
Yellow:							
9	5,743	5.29	37.64	216.10	19,124	39.22	750.02
10	5,906	5.65	48.53	286.60			
11	5,486	5.77	41.34	226.80			
Red:							
12	5,519	5.53	43.62	240.74	23,877	41.20	983.85
13	5,455	5.27	37.10	202.40			
14	5,497	5.34	43.38	238.44			
15	5,449	5.65	45.23	246.45			
Mixed:							
16	2,980	5.35	33.61	100.17	4,761	27.23	129.63
							3,140.46

Table 3.2

Ionic Contaminants[a] of Plutonium Products

SB Run No.	Contaminant (mg/g Pu)												
	Al	B	Ca	Cr	Cu	Fe	Mg	Mn	Na	Ni	Pb	Zn	U
1	9.5	0.72	25	4.3	0.18	20	4.4	---	Trace	<0.60	7.5	<1.8	<2.03
2	2.0	---	---	3.8	2.0	6.8	---	---	~8.5	---	13	---	<1.34
3	5.7	<0.05	16	0.98	0.32	5.6	3.1	---	Trace	<0.26	16	<0.78	<0.88
4	1.8	0.82	16	1.2	0.54	1.8	6.5	0.082	~5.4	0.82	4.0	---	0.63
5	4.2	0.19	5.7	0.60	0.22	1.3	0.97	~0.037	~2.6	0.60	4.2	---	<0.72
6	2.7	0.23	8.3	1.2	0.17	1.9	0.97	---	~4.0	0.62	0.75	---	<0.74
7	1.4	1.6	6.0	0.31	0.32	1.7	1.5	0.07	~2.5	0.37	4.4	---	<0.40
8	0.47	0.11	2.3	0.40	0.07	1.7	0.36	0.03	~2.3	0.13	3.9	---	<0.76
9	0.09	0.09	9.4	0.24	0.06	0.37	0.57	---	~3.7	---	0.62	---	<0.42
10	1.1	0.17	4.3	0.30	0.08	2.1	0.73	0.05	~2.8	0.31	2.2	---	<0.84
11	0.26	0.12	4.4	0.53	0.17	1.4	0.52	0.05	~2.4	0.26	2.5	3.4	1.2
12	0.35	0.06	4.0	0.16	0.04	0.53	1.6	0.03	~2.3	0.07	3.0	0.23	<0.80
13	0.20	0.09	5.5	0.44	0.09	0.87	2.1	0.05	~3.3	0.16	6.4	0.42	<0.45
14	0.11	0.07	10	0.27	0.08	0.50	0.72	0.04	---	0.07	4.5	---	<0.37
15	0.10	0.10	7.6	0.37	0.08	0.17	1.6	0.45	~2.2	0.24	3.3	0.49	<0.55
16	0.17	0.14	23	0.17	0.17	0.74	6.0	0.05	~6.0	0.21	13	0.34	0.59

(a) Uranium determined by polarographic analysis; other contaminants by spectrographic analysis.

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Table 3.3

Radiochemical Contaminants of Plutonium Products

SB Run No.	β Activity (c/m/mg Pu)				Gross γ Activity Less Pu Background (mv/mg Pu)	Decontamination Factors				
	Ru	Zr	Nb	TRE		Ru	Zr	Nb	TRE	Gross γ
1					1.16					27.9
2					1.42					9.8
3					0.39					17.2
4					0.68					41.0
5					1.75					4.6
6					0.39					56.3
7	55.3	22.0	37.2	18.8	-0.01	11.0	36.8	17.7	12.8	--
8	25.2	697	215	27.0	16.99	18.1	5.6	2.2	2.6	3.1
9	10.0	253	105	52.2	2.19	16.6	5.9	1.2	1.9	5.4
10	135	93.4	10.9	35.0	0.09	1.4	2.2	10.2	1.4	45.6
11	138	572	24.5	63.2	0.13	2.1	1.1	5.3	2.5	10.0
12	459	620	17	63.0	0.20	1.05		>8.4	22.0	10.0
13	165	166	33.6	35.0	0.11	1.02	1.7	3.5	2.7	75.5
14	270	198	21.9	99.6	0.71		2.2	5.6	1.6	6.2
15	204	180	22.2	103	0.32	4.2	3.3	50.0	10.7	15.6
16	327	108	6.54	131	1.20		7.4	14.7	1.5	2.4

[redacted]

Table 3.4

Isotopic Analysis of Scrup Plutonium Products

SB Run No.	Class	Pu^{238}	Pu^{239}	Pu^{240}	Pu^{241}	Pu^{242}
1	Research	---	92.63 ± 0.03	6.83 ± 0.03	0.535 ± 0.028	---
2	Research	<0.02	92.27 ± 0.08	7.15 ± 0.07	0.581 ± 0.013	<0.02
3	Research	---	94.08 ± 0.03	5.52 ± 0.02	0.397 ± 0.014	---
4	Research	<0.03	95.90 ± 0.03	3.92 ± 0.02	0.181 ± 0.013	<0.03
5	Research	---	94.54 ± 0.06	5.08 ± 0.05	0.384 ± 0.013	---
6	Research	<0.05	95.66 ± 0.05	4.10 ± 0.04	0.238 ± 0.008	<0.05
7	Blue*	<0.08	98.31 ± 0.08	1.63 ± 0.07	0.061 ± 0.012	<0.08
9	Yellow*	<0.05	97.15 ± 0.03	2.74 ± 0.03	0.116 ± 0.007	<0.05
12	Red*	<0.05	95.40 ± 0.03	4.35 ± 0.03	0.246 ± 0.008	---

* Only the first run of each series was mass analyzed; these results were assumed to be typical of the series.

3.2 Resin Columns

The resin columns used were of varying sizes (see Table 3.5) depending upon the quantity of plutonium in the run. Dowex-50W resin, 50 to 100 mesh, 12% cross linked, was used throughout.

3.3 Feed to the Resin Columns

The feed to the ion-exchange columns was from solvent-extraction process in the Metal Recovery Building in which a Purex No. 3 flowsheet was used. The Purex IIBP stream was made 0.05 M in $NH_2OH \cdot 1/2\ H_2SO_4$ and was passed through an organic separator and sand bed filter. At equilibrium conditions in the solvent-extraction process, the feed contained about 1 g of plutonium per liter and was about 0.3 M in HNO_3.

3.4 Absorption Cycle

The feed was absorbed continuously on the ion-exchange column as it was produced in the solvent-extraction process. At equilibrium conditions in the solvent-extraction plant, the IIBP stream flowed at about 110 ml/min.

3.5 Uranium Elution Cycle

Although 0.05 M $NH_2OH \cdot 1/2\ H_2SO_4$ had been added to the Purex IIBP stream, from which the plutonium was absorbed, some of the plutonium was always in the tetravalent state. Reduction of the plutonium on the column with 0.1 M $NH_2OH \cdot 1/2\ H_2SO_4$ requires many times the calculated mole ratio for complete reduction, but investigations have shown that cooling the reductant to a temperature of about 10°C greatly increases the efficiency of the reduction. Since lowering the temperature usually decreases the reaction rate, it is postulated that the greater efficiency of the cold solution is the result of the higher solubility of the nitrogen oxides in the cold solution, which permits better physical contact between the plutonium and the reductant. Although reduction on the column is not generally recommended (ORNL-1357, p. 18), satisfactory reduction and subsequent uranium and plutonium elutions were carried out without difficulty even when essentially all the plutonium was in the tetravalent state because of improper operation of the solvent-extraction process. The concentration of the product from such a column, however, would be lower because of the smaller amount of plutonium that would be absorbed per volume of resin if the absorption took place in the tetravalent state.

3.6 Plutonium Elution Cycle

The flowsheet conditions, 5.7 M HNO_3 + 0.3 M sulfamic acid, upflow at 0.2 ml/m/cm^2, were found to give 90% plutonium elution at a concentration of 40 g/liter (Table 3.1).

In two cases (Runs 8 and 11) the plutonium on the resin

oxidized to the tetravalent state during elution. It had been found (ORNL-1397, p. 46) that an iced reductant sweep immediately preceding the plutonium elution to degas the column greatly reduced the amount of gassing during the elution. There was no apparent oxidation to the tetravalent state when this technique was used. It had also been found earlier in this work that by increasing the flow rate of the elutriant immediately after any oxidation on the column was noted, the oxidation could be stopped. After a short time, the flow rate could be lowered to the normal value and the elution continued without further difficulty. In spite of these changes some gas is always produced during the plutonium elution.

Although 90% of the plutonium on the column could be removed at a concentration of about 40 g/liter with an elutriant flow rate of 0.2 ml/m/cm^2, it was found that tailing of low-concentration solutions could be reduced by using a slower flow rate. Equipment was developed so that the tailing could be removed in nonworking hours by use of a timer-controller. With an elutriant flow rate of 0.1 ml/m/cm^2, 99.9% of the plutonium on the column could be eluted in 12 to 15 volume changes. Tailing is greatly increased, however, if the plutonium is smeared down the column or if there is tetravalent plutonium present.

3.7 Column Design

The ion-exchange columns used in the Scrup program had to receive varying quantities of plutonium from the Purex IIBP stream at the flow rate at which this stream was produced in the Purex pilot plant and also had to be designed to give a product that would meet a concentration specification of 40 g/liter. The concentration of the plutonium product increases with the height of the plutonium band on the column, and the pressure drop through the column increases with the length of the column. For this reason, a number of columns of various sizes were constructed to provide optimum conditions for both product concentration and absorption flow rate for the varying quantities of plutonium. Table 3.5 shows the capacities of these columns.

As can be seen from the ion-exchange coupling flowsheet (see Fig. 4.1, p. 22) the plutonium absorption and the uranium elution cycles are downflow but the plutonium elution is upflow. This reverse flow necessitates some form of retainer to maintain the resin as a bed. This retainer cannot be made to occupy a fixed position because the volume of the resin is a function of both the quantity of trivalent plutonium absorbed on the hydrogen-form resin and the acidity of the interstitial solution. Two designs were evolved after several preliminary units. One of these uses a high-density sand bed on top of the resin, separated from the resin by glass cloth. The other design uses rigid perforated plates which sandwiches light plastic sheets having a diameter greater than the bore of the column and fitting tightly against its sides (see Figs. 3.1 and 3.2. This sandwich is maintained in contact with the resin by a compression spring. Neither of these designs is completely satisfactory. The sand-loaded column severly limits the up-column flow rate, and some sand is carried up even at slow flow rates. On the other hand, in spite of modifications,

[redacted]

[redacted]

Table 3.5

Capacities of Various Sized Columns

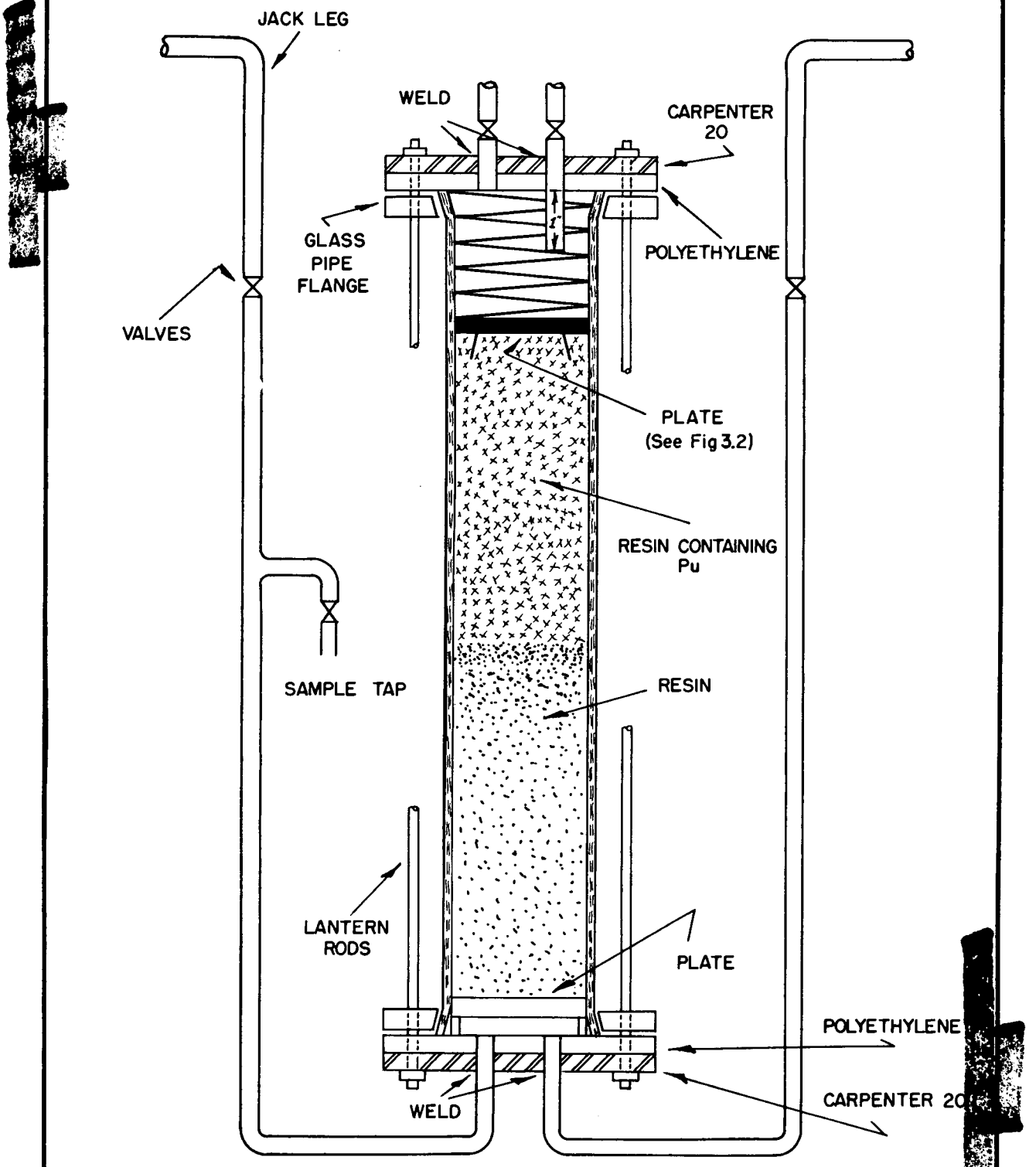
Diameter		Length		Cross-Section Area	Volume	Plutonium Capacity		
						Theoretical	Practical	
(cm)	(in.)	(cm)	(in.)	(cm^2)	(ml)	(g)	(g)	(g/in.)
5.08	2	25.4	10	20.2	514	93.8	46.9	4.69
7.62	3	40.6	16	45.4	1,840	337	168	10.5
10.16	4	40.6	16	81.0	3,290	602	301	18.8
12.70	5	40.6	16	126	5,140	940	470	29.3
15.24	6	40.6	16	182	7,400	1,350	675	42.1
17.78	7	40.6	16	249	10,100	1,850	925	57.8

[redacted]

Figure 3.1

RESIN COLUMN FOR SCRUP PLUTONIUM RECOVERY

Dwg No 16876



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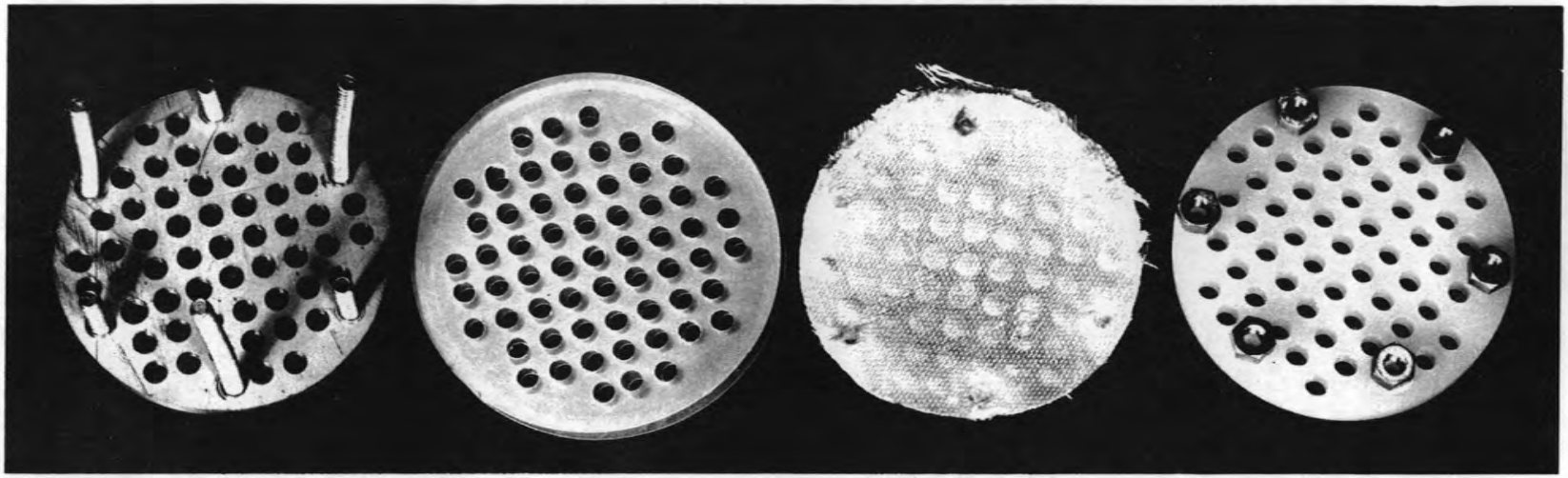

1/8" Carpenter 20 plate | Two polyethylene sheets - 1/32" | Glass cloth | Polyethylene plate - 1/4"

PLATE DETAIL

FIG. 3.2

the sandwich design still allows the passage of a small amount of resin in the plutonium elution scheme.

The glass columns were protected by a shield of 1/8 in. polyethylene sealed next to the glass and by lantern rods which held the end plates in place. All metal that was in contact with the solution was sulfate-resistant stainless steel (Carpenter 20). A photograph of a column used in an earlier isolation program, and similar to those used in this program, is shown in Fig. 3.3. A drawing of the final design is shown in Fig. 3.1.

4.0 ISOLATION OF PLUTONIUM FROM PUREX PILOT PLANT OPERATION

The ion-exchange isolation of plutonium from Purex pilot plant operation (Runs HCP-10 through 15) is described here. Earlier runs are described in ORNL-1357 and 1397. This series of runs represents a unit, since the ion-exchange isolation column was decontaminated before Run HCP-10, and all subsequent runs were made routinely, in general adherence to the Purex ion-exchange coupling flowsheet (Fig. 4.1). The operating conditions differed from flowsheet conditions in the plutonium concentration and acidity of the IIBP feed to the columns and in the volume of 0.25 M H_2SO_4 used in the uranium elution. The column used in these runs was 3 in. in diameter, and the resin bed had a depth of 14 in. The resin in the column was Dowex-50 cation-exchange resin, 12% cross linked, 50 to 100 mesh, graded according to the specifications in Appendix 3.

4.1 Absorption Cycle

The absorption of the Purex IIBP streams in the series HCP-10 through 15 was characterized by smooth operation. The plutonium absorption rates and the solution flow rates and acidities did not vary as widely as in previous runs, and, without such complications, the plutonium losses in these cycles were uniformly low (see Table 4.1). The loss in Run HCP-11 (run is partially described in ORNL-1397) is materially larger than that of the other runs and is ascribed to absorption on a completely gassed column. In general, the 10^{-4}% loss is completely satisfactory.

4.2 Uranium Elution Cycle

In this series of runs partial uranium elution (see ORNL-1397, p. 44) was tested, using 6.25 or 12.5 volume changes of elutriant; only Run HCP-15 was processed with the full SRP volume of 25 volume changes. The losses were extremely low, and uranium decontamination was generally sufficient for regular operation (see Table 4.2). The elutriant in all runs was 0.25 M H_2SO_4 containing 0.05 M hydroxylamine sulfate.

Uranium balance studies were made in which the feed, absorption waste, and uranium-elution eluate were analyzed fluorometrically and the plutonium-elution eluate was analyzed polarographically. The results showed four times more uranium removed from the column than was in the feed (see Table 4.2), and indicated that there is a serious error, probably in the

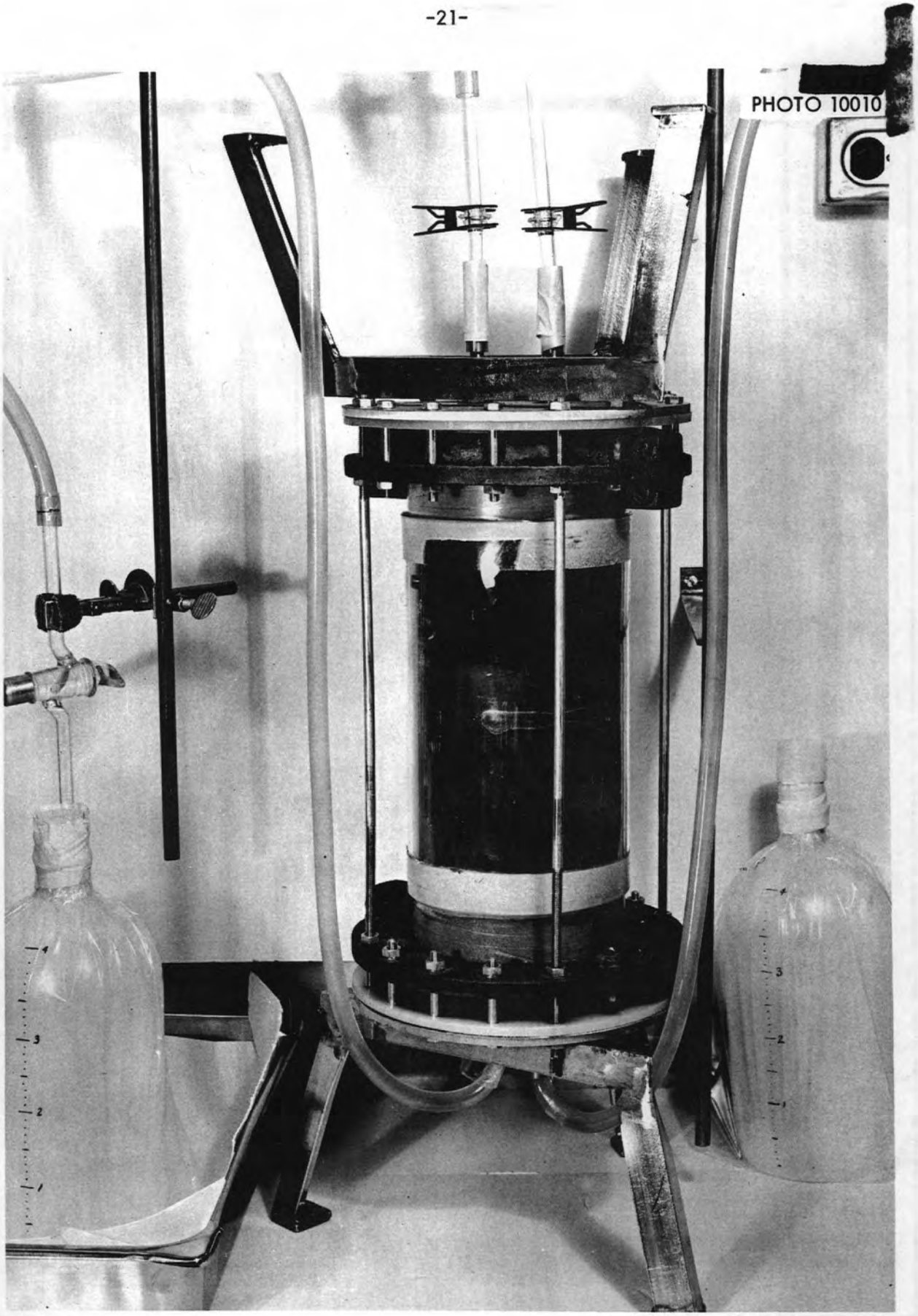

FIG. 3.3. Ion-Exchange Resin Column Containing Plutonium (0.6 in. diameter).

Dwg. [redacted] 7383

Figure 4.1

ION EXCHANGE PLUTONIUM ISOLATION FLOWSHEET No 2.

Basis: 350 grams of Plutonium in 8 hours

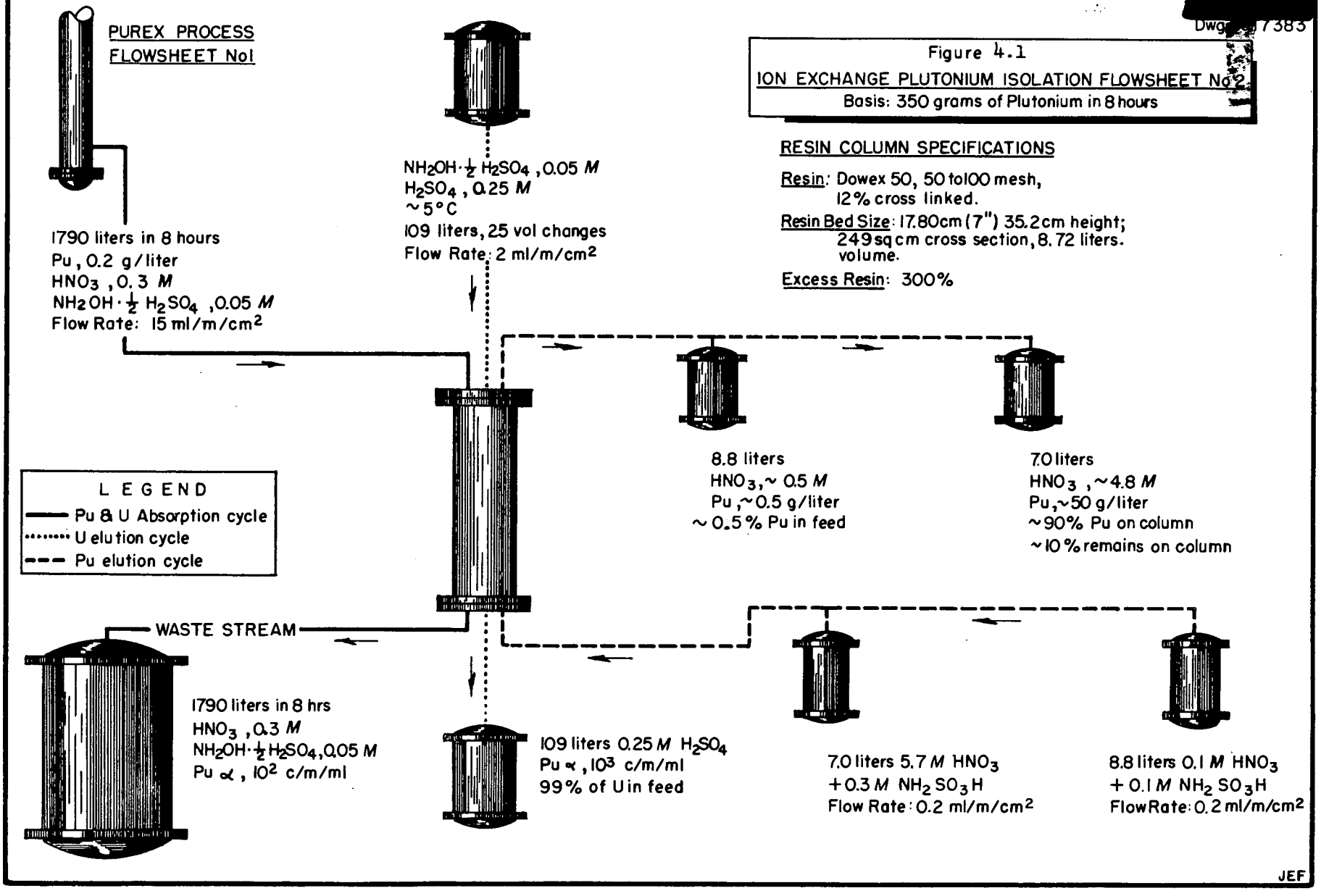

Table 4.1

Resin Column Feed Conditions and Plutonium Losses

Resin: Dowex-50, 50 to 100 mesh
Column: 3 in. diameter, 14 in. bed length
1 Column volume = 800 ml

HCP Run No.	Feed Composition			Feed Flow Rate ($ml/m/cm^2$)	Pu Absorption Rate (g/hr)	Pu Loss in Waste	
	Acidity (M)	Pu Concentration (g/liter)	Total Pu (g)			(c/m/ml)	(% of that in feed, x 10^{-4})
10A	0.46	4.3	42.2	8.8	103	400	1.3
10B	0.51	4.7	60.0	8.8	113	620	1.3
11	0.36	4.1	87.6	8.8 to 5	100 to 50	10,000	3.4
12A	0.38	3.4	29.7	7.7	72	840	3.5
12B	0.40	3.2	25.2	7.7	65.4	790	3.5
13	0.50	3.2	66	7.7	68	720	3.0
14	0.44	3.9	64.8	6.6	70	450	1.6
15	0.40	4.6	81	6.6	83	500	1.1

Table 4.2

Uranium Decontamination and Plutonium Losses

Flow rate: 2 ml/m/cm^2

HCP Run No.	Vol. of Elutriant (liters)	U in Product		Pu Loss during Elution	
		(g/liter)	(% by wt. of Pu)	Gross α (c/m)	(% of total on column, x 10^{-4})
10	5	0.076	0.15	320	0.2
11	5	0.563	1.2	39,000	0.31
12	10	0.040	0.11	1,080	3.3
13	5	0.080	0.20	1,100	1.1
14	5	0.234	0.66	388	0.4
15	20	0.016	0.05	645	1

[redacted]

Table 4.3

Uranium Balance over Runs

HCP Run No.	Uranium in Feed to Column[a] (g)	Uranium Removed from Pu Product		
		In Absorption Waste[a] (g)	In U Elution[a] (g)	In Pu Elution[b] (g)
10	0.56	---	---	0.13
11	2.04	---	---	1.12
12	1.93	---	7.9	0.06
13	1.41	0.46	4.8	0.13
14	0.66	0.75	1.5	0.38
15	1.06	0.92	4.54	5.2[c]
Total	7.55	27.9		

(a) By fluorometric analysis.

(b) By polarographic analysis.

(c) Includes uranium from complete plutonium elution and in citrate and oxalate decontamination washes.

[redacted]

fluorometric procedure (see Appendix 1). Several samples were submitted for both fluorometric and polarographic analysis, and the values obtained by the polarographic method were higher by the correct factor to balance the uranium through the system. The Purex IIBP stream therefore contains more uranium than previous analyses had indicated, and the error in the fluorometric method is sufficient to cause difficulty in proper control of the amount of uranium in the plutonium stream.

4.3 Plutonium Elution Cycle

The plutonium product elution proceeded smoothly in the six runs, HCP-10 through 15, all of which were made at a flow rate of 0.2 ml/m/cm^2, using the cyclic elution scheme (see Fig. 4.1). The elutriant was the standard 5.7 M HNO_3 + 0.3 M NH_2SO_3H, and there was no evidence of oxidation of plutonium during any experiment. The amount of elutriant used under the cyclic conditions was calculated to give a product plutonium concentration of 40 to 45 g/liter. However, in several runs the product concentration was low (see Table 4.4), and the amounts of plutonium in the products as indicated by potentiometric analysis did not balance by a large error those indicated for the feed, which were determined by activity measurements (see Table 4.5). The low values obtained for the plutonium concentration in these runs can be partially attributed to changes that were made in the potentiometric analytical procedure in an attempt to increase its accuracy. The variations in the analytical results obviously make it difficult to run controlled experiments, and on a plant scale would make it difficult to maintain control over the button size in the metal fabrication steps (see Appendix 2).

The products from this series, together with several fractions isolated from the nonequilibrium Purex streams during startup and shutdown brings the total Purex plutonium shipped from Runs HCP-1 through 15 to 1450 g.

4.4 Product Purity

The present series was extremely smooth from the standpoint of Purex solvent extraction operation. The feed slugs had a varied irradiation and cooling history (see Table 4.6), and the plutonium was produced at a very high radiation level, 718 Mwd/ton, in Run HCP-15 and was separated after a relatively short cooling period, 63 days, in Run HCP-14. There were no accidents in the Purex extraction system to lead to excessive contamination of the IIBP stream, and, as a result, all ion-exchange plutonium products were well within the overall purification specifications of 10^7 beta and gamma decontamination factors (see Table 4.7). The uniformity of these runs gave some indication of the behavior of niobium and zirconium (see Sec. 4.5) under conditions of cyclic operation, and gave encouraging results from the standpoint of radiation buildup on the SRP columns.

[redacted] The IIBP resin column feed was fairly uniform in activity (see Table 4.8) and the products (see Table 4.9) were quite comparable with those from the previous HCP runs reported in ORNL-1397 and 1357.

[redacted]

Table 4.4

Composition of Plutonium Products

HCP Run No.	Pu Concentration*[a] (g/liter)	Total Pu (g)	Acidity (N)
10	50.91	92.51	5.25
11	45.23	89.98	5.40
12	36.88	53.28	4.96
13	40.31	65.80	5.40
14	35.33	56.75	5.45
15	30.32	60.59	5.10

(a) By potentiometric analysis.

[redacted]

[redacted]

[redacted]

Table 4.5

Column Plutonium Balance

HCP Run No.	Plutonium (g)		
	In Feed[a]	In Product Cut[b]	In Dilute Elution Fractions
10	102.2	94.3	0.67
11	87.6	85.3	0.92
12	54.9	51.6	0.83
13	71.6	65.8	0.90
14	64.8	56.7	0.90
15	81.0	60.6	5.7[c]
	462.1	414.3	9.92
Total Eluted		424.2	

(a) Amount based on alpha activity.

(b) By potentiometric analysis

(c) Total from complete elution

Table 4.6

Slug Histories

HCP Run No.	Irradiation Level (Mwd/ton)	Cooling Period (days)
10	616	126
11	539	114
12	346	310
13	436	342
14	465	63
15	718	99

[redacted]

[redacted]

Table 4.7

Gross Decontamination Factors

HCP Run No.	Gross Beta D. F.			Gross Gamma D. F.		
	Through Purex Solvent Extraction	Through Ion-Exchange Coupling	Total over Process	Through Purex Solvent Extraction	Through Ion-Exchange Coupling	Total over Process
10	0.97×10^7	5.9	5.3×10^7	2.3×10^6	12.3	2.5×10^7
11	1.3×10^7	3.5	4.5×10^7	3.5×10^6	5.6	2.0×10^7
12	1.6×10^7	2.4	3.8×10^7	3.2×10^6	12.0	3.8×10^7
13	1.7×10^7	1.7	2.9×10^7	2.8×10^6	4.6	1.3×10^7
14	1.6×10^7	1.8	2.8×10^7	6.0×10^6	2.6	1.6×10^7
15	2.2×10^7	2.3	5.0×10^7	8.4×10^6	3.7	3.1×10^7

Table 4.8

Radioactive Contaminants in IIBP Stream

HCP Run No.	Contaminant (c/m/mg Pu)				
	Ru β	Zr β	Nb β	TRE β	$(UX_1 + UX_2)\beta$
10	1320	2990	218	32	76
11	2080	1030	199	38	29
12	928	361	99	76	58
13	734	247	57	47	9
14	4470	794	92	42	109
15	1420	432	47	43	49

Table 4.9

Radioactive Contaminants in Plutonium Product

HCP Run No.	Contaminant (c/m/mg Pu)				
	Ru β	Zr β	Nb β	TRE β	$(UX_1 + UX_2)\beta$
10	630	86	12	22	22
11	776	162	22	14	6
12	532	185	13	21	7
13	313	42	5	16	6
14	2410	116	13	10	12
15	966	11	5	20	11

[redacted]

4.5 Behavior of Individual Fission Products

Individual fission product decontamination factors showed wide variations from one run to the next in some cases (see Table 4.10). The activities in the absorption wastes and uranium elution wastes added to the complexity of the picture, since in some runs more niobium was in the wastes than had been present in the feed (see Tables 4.11 and 4.12). Ruthenium was fairly regular in behavior, with 35 to 55% of the feed activity in the product, agreeing well with all previous runs. However, the zirconium decontamination factors varied widely, and niobium appeared in all streams.

The decontamination factor for zirconium is more properly calculated on the basis of the amount of zirconium on the column rather than the amount in the feed. Since zirconium has a 65-day half-life, all analyses for a run had to be corrected for decay to a given date for that run. If the zirconium on the column is calculated from the amount in the IIBP feed to the ion-exchange column plus the residue from the previous run (with allowance for decay and minus the activity that came off with the product), the decontamination factors obtained from comparison of the amount in the product with the total on the column are much more uniform. The values indicate that 2 to 4% of the total zirconium on the column may be expected to appear in the product under the present operating conditions (see Table 4.13).

The picture with respect to niobium was clarified somewhat by similar calculations, and fairly consistent results were obtained (see Table 4.14), but the niobium system is considerably more complicated because of the growth of niobium from zirconium on the column, and because of additional losses in the absorption and uranium elution wastes. Calculations are more involved because of the 35-day half-life of niobium, which necessitates large corrections, and the large errors introduced by the small amounts of activity. The calculated decontamination factors indicate that 5 to 10% of the niobium on the column at the start of the plutonium elution will appear in the product.

Since niobium moves slowly with sulfate, the leakage from the bottom of a column in the uranium elution cycle is dependent on the amount fed to the column several runs before rather than in that particular run. This behavior is encouraging with respect to the radiation buildup problem. The movement of activity down the column with sulfate should bring the niobium to equilibrium rapidly with respect to feed and waste, particularly since the sulfate-containing feed (IIBP) and uranium elutriant will be of a much larger volume [redacted]avannah River flowsheet than it is on the pilot plant flowshe[redacted] responsible for roughly half the gamma radiation from the column, the buildup over a number of runs will be about half as much as previously estimated (see ORNL-1357, p. 45), and periods between decontaminating runs may be longer than previously thought permissible.

[redacted]

As before, no large ionic decontamination is evident in the ion-exchange process, although the general level of impurities is reduced in the ion-exchange processing (see Tables 4.15 and 4.16). The products compared favorably with those from previous HCP runs (see ORNL-1397 and 1357) and should be perfectly satisfactory for all further processing (see Table 4.16).

4.6 Decontamination of Column

The activity on the column did not reach high levels in any of these runs. The IIBP feeds were quite pure (see Table 4.8), and the decay of niobium and zirconium between runs and the equilibrium with respect to the removal of niobium helped the column to stay in the range of 80 to 160 mr/hr at contact after any of the runs. A decontamination run with 0.5 M oxalic acid and 2 M ammonium citrate (pH 5.6) in succession (see ORNL-1397, p. 55) was made after Run HCP-15, and the column activity was brought to background. Unless the Savannah River Purex process operates to give a completely different range of radioactive contaminants in the IIBP stream, zirconium and niobium will be primarily responsible for column radiation buildup. Since oxalic acid specifically removes zirconium and niobium and does not require conversion of the ion-exchange resin to the ammonium form before decontamination starts, as does citrate, 5 to 10 volume changes of 0.5 M oxalic acid are recommended as a decontaminating agent on the SRP cleanup runs. Note that this will also remove uranium and iron which may have built up on the column.

4.7 Pilot Plant Run on Slag and Crucible Solution

A small-scale second-plutonium-cycle Purex run was made with a highly salted fluoride solution of slag and crucible material as feed (see ORNL-1343, p. 26). The extraction was only for the purpose of ionic decontamination since insignificant amounts of fission products were present. The material was further concentrated by means of the ion-exchange coupling process to give 14 g of product plutonium. The ionic contamination in the IIBP stream was comparable with that in other runs, and the ion-exchange product was of satisfactory purity (see Table 4.17). No difficulty is anticipated when the crucible solution is used regularly for extraction feed in the SRP plutonium recovery area.

[redacted]

[redacted]

Table 4.10

Individual Decontamination Factors in Ion-Exchange Isolation

HCP Run No.	β Decontamination Factors				
	Ru	Zr	Nb	TRE	$UX_1 + UX_2$
10	2.1	35	12	1.5	3.4
11	2.7	64	5.5	2.8	4.7
12	1.7	2	7.6	3.6	8
13	2.3	5.8	11	3	1.5
14	1.8	12.7	5	4	9
15	1.5	39	9.4	2	4

Table 4.11

Percentage of Feed Activities in Absorption Waste[a]

Run No.	Contaminant (% of that in feed)		
	Ru	Zr	Nb
10A	37.2	0.7	7.8
10B	45.2	1.5	3.6
11	51	0.7	4
12A	38	1	10
12B	52.4	1.1	26
13	49	8.7	94
14	35.7	1.8	16.5
15	36.1	1.8	7.3

(a) [redacted] from individual feeds and wastes, disregarding column buildup.

[redacted]

Table 4.12

Percentage of Feed Activities in Uranium Elution Waste[a]

HCP Run No.	Contaminant (% of that in feed)	
	Zr	Nb
10	0.01	3
11	0.2	9
12	1.2	220
13	12	165
14	2	39
15	7	118

(a) Percentage calculated from individual feeds and wastes, disregarding column buildup.

Table 4.13

Column Zirconium Balance

HCP Run No.	Zirconium (c/m x 10^8)		Overall Decontamination Factor
	Total in Feed + Residue[a]	Total in Product	
10	3.1	0.09	35
11	3.55	0.16	23
12	3.1	0.12	26
13	2.96	0.04	74
14	2.94	0.06	45
15	2.9	0.007	405

(a) Residue from each previous run, corrected for decay.

[redacted]

[redacted]

Table 4.14

Column Niobium Balance

HCP Run No.	Niobium (c/m x 10^6)			Overall Decontamination Factor[a]
	Total Feed + Growth + Residue	Total in Absorption and U Elution Waste	Total in Product	
10	22.7	2.4	1.41	14.5
11	22.7	1.9	1.97	10.6
12	25.2	13.1[b]	0.67	17.9
13	15.9	9.6	0.33	19.2
14	14.9	4.1	0.72	15.0
15	15.3	4.9	0.30	34.7

(a) Decontamination factor calculated from total on column immediately before elution.

(b) In Run HCP-12, 10 liters (12.5 volume changes) of 0.25 M H_2SO_4 was used in uranium elution, as contrasted with 5 (6.25 volume changes) liters in Runs HCP-10, 11, 13, and 14. Run 15 had 20 liters (25 volume changes) of 0.25 M H_2SO_4 in the uranium elution cycle.

Table 4.15

Ionic Impurities in Purex IIBP Stream

HCP Run No.	Contaminant (μg/mg Pu)											
	Al	B	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Pb	Sn	Zn
10	<1.1	2.2	31	1.8	---	~0.6	8.5	<1.2	~1.5	<4	---	---
11	<0.24	0.9	15.3	7.8	0.27	0.56	2.6	<0.4	<1	---	---	---
12	0.91	0.98	7.6	0.60	0.30	3.0	1.6	<0.5	<1.	<4.6	<9	<4.6
13	0.59	0.5	28	0.47	0.47	1.8	7.8	~0.2	<1	<4	<8	<3.2
14	0.32	<0.3	21	3.0	0.66	1.0	4.0	0.45	1.1	<3.2	<8	<1.5
15	0.40	0.36	21	0.51	0.72	0.3	12	0.38	<0.7	<3.2	<7	<7

Table 4.16

Ionic Impurities in Ion-Exchange Product

HCP Run No.	Contaminant (μg/mg Pu)											
	Al	B	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Pb	Sn	Zn
10	1.6	0.04	6.1	0.10	0.07	1.4	0.65	0.03	2.4	0.4	---	---
11	0.07	0.09	0.94	0.27	0.09	<0.02	0.38	0.29	0.21	<0.4	---	---
12	0.23	0.12	8.8	0.24	0.29	0.81	0.84	0.07	0.10	<0.4	<0.8	<0.4
13	0.35	0.1	4.0	0.70	0.11	1.2	1.1	0.06	0.17	<0.4	<0.7	<0.4
14	0.03	0.13	6.8	0.19	0.11	1.7	1.3	0.14	0.27	0.4	0.9	0.4
15	0.42	0.12	14	0.25	---	0.45	5.3	0.07	0.14	0.56	<0.8	0.4

Table 4.17

Ionic Contaminants in Slag and Crucible Plutonium Products

Contaminant	IIBP Solution, Containing 0.64 g Pu per liter		Ion-Exchange Product, Containing 14.5 g Pu per liter
	(μg/ml)	(μg/mg Pu)	(μg/mg Pu)
Al	1.7	2.7	0.55
B	3.2	5.1	0.27
Ca	23	37	15
Cr	1.9	3.0	0.45
Cu	6.4	10.2	0.60
Fe	1.6	2.5	4.2
Mg	13.2	21.0	8.2
Mn	0.5	0.8	0.22
Ni	2.5	4.0	0.73
Pb	<15	< 24	2.2
Zn	<25	< 40	< 1.7

[redacted]

[redacted]

5.0 OPERATING LIMITS FOR PLUTONIUM ISOLATION BY ION EXCHANGE AT SAVANNAH RIVER PLANT

Results of additional small-scale experiments (see ORNL-1357 and 1397) made to determine the operating limits for the ORNL ion-exchange process (see Fig. 4.1) to be used at the Savannah River Plant demonstrated that the proposed conditions will be satisfactory with cyclic operation of the process and confirmed that considerable variation in the operating conditions is permissible.

A minimum limit of 15 complete, successive runs had been tentatively set as a requirement for acceptable cyclic operation of the ORNL ion-exchange process at the Savannah River Plant. The feasibility of the cyclic operation has been demonstrated in the G and M Series, now completed (see ORNL-1397), in which the process was operated for cycles of 15 and more runs without replacing the resin. In these series it was demonstrated that in a 15-run cycle that (1) the waste-stream plutonium losses would not progressivley increase to intolerable levels, (2) the plutonium concentration of the product cut would not decrease, and (3) the resin bed would remain in good physical condition. A product cut with a plutonium concentration of 50 g/liter was easily attained throughout both series. The waste-stream plutonium losses were, in general, negligible throughout both series; the slightly higher than usual losses in a few runs can be attributed to changes in the plutonium elutriant acidity, and were easily controlled.

5.1 Cyclic Operation of Process

The runs for both the G and M Series have been finished (for the early runs see ORNL-1397). Seventeen runs were made in the G Series and 15 in the M (see Tables 5.1 through 5.3). In the final run of each series the plutonium was completely eluted from the columns.

The resin columns were in perfect physical condition at the end of both series. The fiber glass disks which supported the glass beads used to retain the resin bed intact were in perfect shape, and the Ottawa sand bed upon which the resin bed rested had not been disturbed. No degradation of the resin particles was apparent.

Plutonium inventories were made for both series to determine the total amount of plutonium on the completely loaded bed during each run (see Table 5.3), so that the experimental columns could be loaded proportionately to the loading proposed for the Savannah River Plant columns (see ORNL-1397, Table 3.1. Since the amount of plutonium in the heel left on the resin bed at the end of each run was calculated from the difference between the total plutonium on the column (feed plus heel from previous run) and the total plutonium removed (product cut plus recycle), a small error in the feed or product cut analysis would result in a comparatively large error in the calculated value of the heel; the errors were accumulative. For the G Series the final inventory was apparently short by 1.222 g and for the M Series by 1.989 g (see Table 5.3). If this accumulated error is distributed

over all the runs, the average error is not very high. It must be emphasized that these discrepancies do not represent an actual loss of plutonium since the balance is well within the experimental error.

5.2 Waste-Stream Plutonium Losses with Cyclic Operation

In general, the waste-stream plutonium losses were negligible throughout both series. In a few runs the losses were slightly higher than usual, but even these cases were easily controlled.

For acceptable cyclic operation, flow sheet conditions must be such that the plutonium losses in the waste streams do not progressively increase to objectionable levels. The leading part of the band of plutonium absorbed on the resin bed (the lower part with downflow absorption) contains a region in which the concentration of plutonium absorbed on the resin decreases from a maximum value (i.e., equilibrium at feed plutonium and acid concentrations) to a very low concentration, approaching zero, at the place where only feed already stripped of almost all its plutonium contacts the resin. The concentration of plutonium absorbed from the feed increases as the feed plutonium concentration increases, and decreases as the feed acid concentration increases. The region of decreasing percentage saturation of the resin can be very short in plutonium absorption columns but, under certain circumstances, can be greatly extended. If the extension of the leading part of the band is carried far enough, the feed will travel down the entire length of the column before it is adequately stripped of plutonium.

The excessive extension of the leading part of the plutonium band can occur with cyclic operation of a resin column if a heel is left on the column for each run. During the plutonium elution, the band, which formed during the feed absorption and uranium elution, is pushed upward in the upflow elution by the desorption of plutonium from the band edge. In the succeeding run the band starts forming at the point that its edge occupied at the end of the previous plutonium elution. If the band moves downward farther during the plutonium feed and uranium elution than it is pushed upward during the succeeding plutonium elution, it will gradually work its way down to the bottom of the resin bed. Therefore flowsheet conditions that are satisfactory for one isolated run may not be satisfactory for long series of runs such as are required for practical plant operation.

The effects of the competitive pushing upward and moving downward of the plutonium band are apparent from the data on the waste stream losses (see Table 5.1). The rise in the plutonium alpha activity of the waste stream in Runs G-11 through 14 is due to the use of low-strength acid (3.2 to 5 N) for plutonium elution in Runs G-8 through 12 (see Table 5.5 of ORNL-1397). Apparently, the band edge was not pushed upward far enough by the comparatively dilute acid. It should be noted that the effect may not be apparent for several runs if more than one run is required for the band to be pushed to the bottom of the column.

To alleviate the trouble once it occurs, three approaches are possible: (1) the acid concentration of the feed and/or the uranium elutriant may be decreased to decrease the downward travel of the band, (2) the volume of plutonium elutriant may be increased to push the band upward farther, or (3) a higher concentration of acid may be used in the plutonium elutriant to push the band upward more efficiently. For Run G-14, the plutonium alpha activities of the feed absorption and elution waste streams had risen to 1.43×10^5 and 1.26×10^5 c/m/ml, respectively, but, by increasing the volume of the plutonium elutriant to 153 ml in Run G-14, the alpha activities were brought down to 3.55×10^4 and 4.41×10^4 c/m/ml in Run G-15. Using 153 ml of plutonium elutriant in Run G-15 and decreasing the feed acid concentration to 0.15 M (instead of 0.50 M) in Run G-16 brought the alpha activities in the waste streams down to 1.00×10^3 and 1.66×10^4 for Run G-16. At this point the band was apparently traveling upward (i.e., net travel) because for Run G-17 the plutonium alpha activities were only 648 and 7800 c/m/ml, which represent very insignificant plutonium losses (~0.005%).

The waste-stream losses during the experimental runs were aggravated by the effects of various side reactions (e.g., alpha-particle-induced reactions) that take place in idle plutonium-loaded resin columns. With normal plant operation a resin column would complete a cycle of 15 runs in about 15 days; however, the runs of the G Series extended over a period of 116 days and of the M Series over 157 days. Fully loaded columns were never left standing longer than overnight, but, of course, the plutonium heels were on the resin the entire period. The effects of this idle time would be more apparent in the G Series than in the M Series because for the G Series the higher feed absorption flow rate and, generally, higher feed acidity decreased the efficiency of feed absorption and conversely increased the distance of downward travel of the plutonium band.

5.3 Plutonium Concentration of the Product Cuts with Cyclic Operation

At the end of 15 successive runs, the plutonium concentrations of the product cuts had not been adversely affected by cyclic operation of the process. The goal, 50 g of plutonium per liter, was easily attained throughout the series. In Runs G-1 through 3 the plutonium concentrations of the product cuts were 55.4, 54.0, and 57.5 g/liter, respectively, while for Run G-16 the concentration was 52.7 g/liter. Similarly, in Runs M-2 and 3 the plutonium concentrations of the product cuts were 46.8 and 46.3 g/liter, respectively, while for Runs M-13 and 14 the concentrations were 47.5 and 45.6 g/liter. The deviations between the early and the last normal runs in each series (final runs were completely eluted) are within the experimental error, and therefore the effect of cyclic operation upon the plutonium concentration of the product cut is insignificant.

5.4 Effect of Particle Size Distribution on Pressure Drop across Resin Bed

Pressure-drop tests made on two batches of Dowex-50 resin, both of which were specified as being 50 to 100 mesh, showed batch A to give higher pressure drops than batch B (see ORNL-1397, Sec. 4.0). Since it is a well

known fact that the pressure drop across a resin bed decreased rapidly as the particle size increases, the differences in the pressure drops obtained were attributed to a difference in the particle size distribution. Screen analyses of the two batches (see Table 5.4) showed that in batch A only 32.5% of the particles were in the 50- to 70-mesh range, but, in batch B, 65.1% of the particles were in this range. Therefore, in order to obtain low pressure drops, a batch of resin should be used in which the percentage of particles in the larger size range is high. However, since the absorption and desorption properties of the smaller particles are better, in practice a compromise, based on experience, must be made between the two extremes.

Table 5.1

Waste-Stream Plutonium Losses[a]

Uranium elutriant: 0.25 M H_2SO_4; flow rate, downflow, 2 ml/m/cm^2

Plutonium elutriant: 5.7 M HNO_3—0.3 M sulfamic acid, upflow, 0.2 ml/m/cm^2

Run No.	Feed		Volume of Pu Elutriant (ml)	Pu Alpha Count in Waste Stream (c/m/ml)	
	Acidity (N)	Flow Rate (ml/m/cm^2)		Feed Absorption	Uranium Elution
G-13	0.50	15	111.5[b]	3.00×10^3	5.62×10^3
G-14	0.50	15	153.0	1.43×10^5	1.26×10^5
G-15	0.50	15	153.0	3.55×10^4	4.41×10^4
G-16	0.15	15	111.5	1.00×10^3	1.66×10^4
G-17	0.15	15	Complete elution	648	7.80×10^3
M-11	0.15	5	123.0	190	246
M-12	0.15	5	102.5[b]	185	800
M-13	0.15	5	102.5	334	409
M-14	0.15	5	102.5	181	647
M-15	0.15	5	Complete elution	95	100

(a) See ORNL-1397, Tables 5.3 and 5.4 for earlier runs.
(b) SRP flowsheet condition.

Table 5.2

Plutonium and Acid Concentrations of Product Cuts

Elutriant: 5.7 N HNO_3—0.3 M sulfamic acid, downflow, 0.2 ml/m/cm^2

Run No.	Pu Concentration,[a] (Potentiometric Analysis) (g/liter)	Acid Concentration[a] (M)
G-13[b]	56.2	5.10
G-14[c]	51.6	5.50
G-15[c]	48.7	5.65
G-16	52.7	5.15
G-17[d]	49.7	5.50
M-11[e]	47.4	5.35
M-12	45.7	4.95
M-13	47.5	5.05
M-14	45.6	5.00
M-15[d]	49.5	5.35

(a) The concentrations are based on the product cut volume which corresponds to SRP flowsheet conditions (7 liters from 7-in.-diameter column).
(b) The total plutonium on the column was more than normal. See Table 5.3.
(c) The elutriant volume was 153 ml instead of 111.5 ml (product cut was 111.5 ml).
(d) A complete elution of the column was made.
(e) The elutriant volume was 123 ml instead of 102.5 ml.

Table 5.3

Plutonium Inventories

(Based on Potentiometric Analysis of Product Cuts)

Run No.	Pu on Column (g)			Pu Product Conc. (g/liter)	Pu Removed from Column (g)		
	Heel	Feed	Total		Product	Recycle	Total
G-13	2.993	4.800	7.793	56.2	6.266	0.105	6.370
G-14	1.423	5.600	7.023	51.6	5.753	0.550	6.305
G-15	0.718	6.400	7.118	48.7	5.430	0.414	5.844
G-16	1.274	6.535	7.819	52.7	5.876	0.132	6.008
G-17	1.811 (-1.222)(b)	6.000	7.811	49.7	5.964(a)	0.429	6.589
M-11	1.539	4.800	6.339	47.4	4.859	0.162	5.021
M-12	1.318	5.200	6.518	45.7	4.684	0.106	4.790
M-13	1.728	5.200	6.928	47.5	4.869	0.104	4.983
M-14	1.945	5.020	6.965	45.6	4.674	0.118	4.792
M-15	2.173 (-1.989)(b)	5.400	7.573	49.5	5.094	0.490	5.584

(a) Product cut was taken as 120 ml instead of 111.5 ml.
(b) All the plutonium was eluted in the last run. Therefore, the heel should be zero, and this figure represents the accumulated error in the column inventories.

Table 5.4

Screen Analyses of Two Batches of 50- to 100-Mesh Dowex-50 Resin

Screen Mesh (b)	Percentage Retained on Screen (a)		Cumulative Percentage Retained on Screen	
	Batch A	Batch B (c)	Batch A	Batch B (c)
50	1.6	5.9	1.6	5.9
60	10.1	24.6	11.7	30.5
70	20.8	34.6	32.5	65.1
80	37.3	17.8	69.8	82.9
100	19.1	10.3	88.9	93.7
200	10.2	5.7	99.0	98.9
>200	0.96	1.1	100.0	100.0

(a) Mud and fines removed before screen analysis.

(b) U. S. Standard Sieve Series.

(c) This batch of resin was used for both the G and M Series.

6.0 MISCELLANEOUS LABORATORY EXPERIMENTS

Laboratory-scale experiments have been carried out on three problems connected with the ion-exchange isolation of plutonium: radiochemical decontamination of the Purex IIBP stream from zirconium and niobium with silica gel, the effect of metal ions on gas formation in the ion-exchange column, and the ionic decontamination obtained from certain metals by the ion-exchange isolation process.

6.1 Silica Gel Adsorption

Radiochemical decontamination of the Purex IIBP stream from zirconium and niobium with a silica gel adsorption bed was investigated in order to determine whether it would be possible to prevent their buildup on the ion-exchange columns at Savannah River by adsorbing them on a precolumn silica gel bed. Silica gel was found to have such a low capacity for zirconium and niobium that its use does not appear to offer any advantages. The zirconium decontamination factor, appeared good initially, about 9, (see Fig. 6.1) but decreased to 5 after 50 column volumes of feed had passed through and decreased further to 1.4 after 400 column volumes. The niobium decontamination factor was about 4 initially but decreased to 2.2 after 100 column volumes and maintained this value for the next 300 volumes.

For the experiments a column 10 mm in diameter and 31 cm in length was used. It was packed with silica gel that had been screened to 50 to 100 mesh and washed with water. One column volume was 12 ml. Five liters ($\sim$420 column volumes) of simulated Savannah River IIBP solution, prepared by diluting the IIBP solution from Run HCP-11 to the approximate composition of the Savannah River IIBP, was passed through the column at a flow rate of 15 ml/m/cm^2. Analysis of this feed showed it to have the following composition: plutonium, 0.2 g/liter; acidity, 0.22 M; zirconium, 180 c/m/ml; and niobium, 72 c/m/ml. The decontamination factors were calculated by comparing the results of analyses of the bed effluent taken at intervals during the run with the results of feed analyses.

After the adsorption was completed, an activity profile of the column was made from results obtained with a beta-gamma survey meter collimated with a lead foil. The relative amounts of zirconium and niobium were such that the radiation observed was essentially the zirconium gamma rays. The measured activity decreased in intensity by a factor of 2 from the top to the bottom of the column and was considerably above the laboratory background at all times. Nitric acid, 6 M was found to remove the major portion of the plutonium from the silica gel bed. Only 3 x 10^{-4}% of the plutonium run through the column was found on the silica gel bed.

6.2 Laboratory Research on Gas Formation in Columns

Formation of gas in the ion-exchange columns during elution rarely caused difficulty, but it occurred to some extent in almost every run. Experiments were carried out to elucidate the effect on gas formation of

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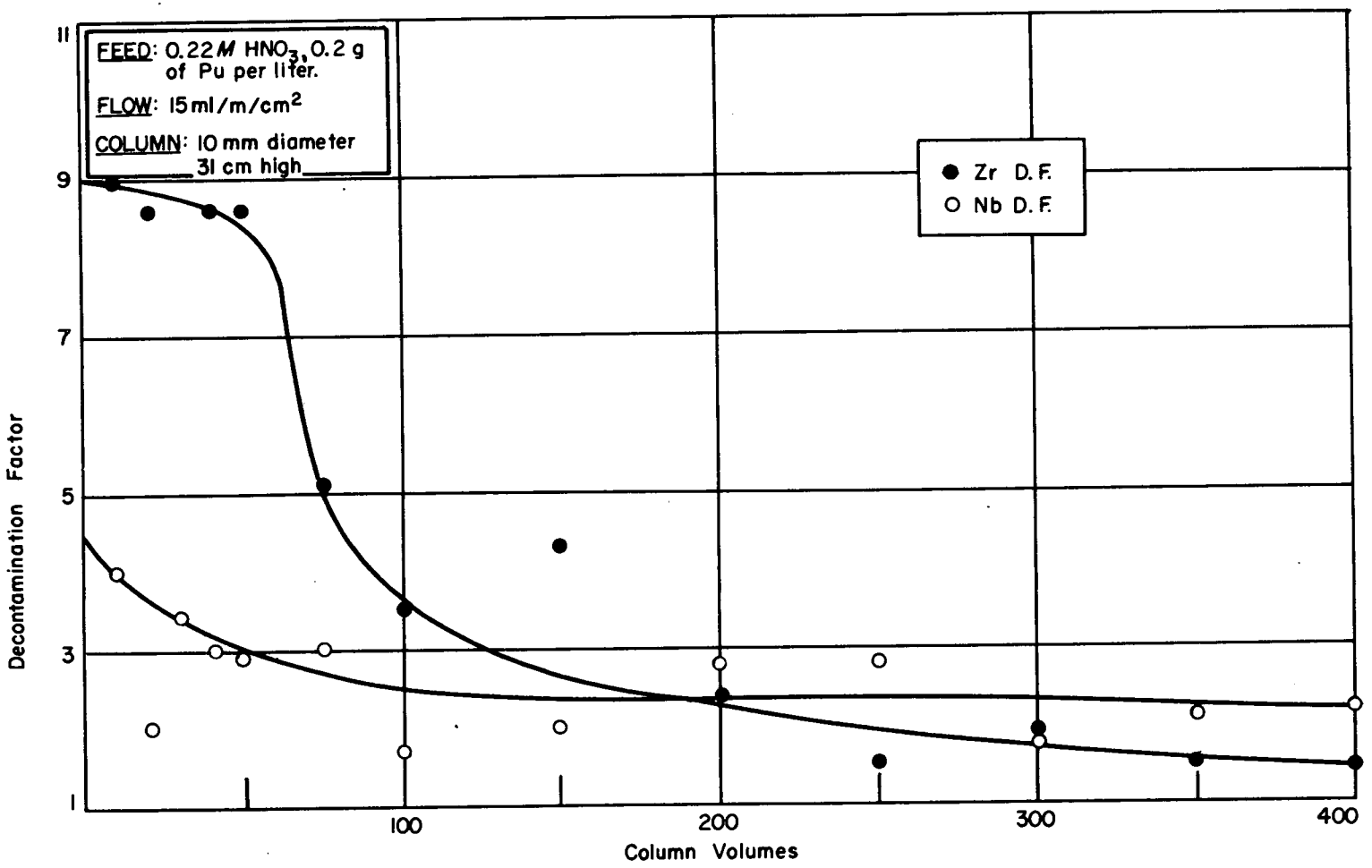

FIGURE 6.1: Removal of Zirconium and Niobium From Simulated Savannah River IIBP Solution By Silica Gel.

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ionic impurities, which might be present in the feed as a result of corrosion of the equipment or in the resin as a result of manufacturing operations. Two series of experiments on absorption and elution of ionic corrosion impurities were carried out: (1) in the absence of plutonium to determine whether foreign ions could cause gassing, and (2) in the presence of plutonium to determine whether foreign ions exert a catalytic effect. There was no appreciable gas formation in either series. The results of experiments on impurities remaining in the resin from the manufacturing processes were inconclusive.

In both corrosion-impurities series, 12% cross-linked 50- to 100-mesh Dowex-50 resin was used, and absorption, uranium elution, and plutonium elution cycles were carried out (see Fig. 4.1). The column for the first series was 35 cm long and 22 mm in diameter. About 1 g of ferrous, cupric, manganous, and chromic ions was absorbed separately from a feed that was about 0.2 M in HNO_3 and 0.05 M in $NH_2OH \cdot 1/2H_2SO_4$ under flowsheet conditions, but the simulated plutonium elution was downflow instead of upflow. A few gas bubbles formed during the elution of the ferrous ion, but much less than normal, and no trace of gas was detected with the other ions.

The column for the second series was 35 cm long and 24 mm in diameter. Ferrous, chromic, nickelous, manganous, and aluminum in 5 atom % concentration were absorbed separately from a feed 0.33 M in HNO_3 and 0.05 M in HNO_3 and 0.05 M in $NH_2OH \cdot 1/2\ H_2SO_4$ and with a plutonium concentration of 1 g/liter. The absorption and both elution cycles were carried out under exact flowsheet conditions. No unusual effect on gas formation was noted.

Contradictory results were obtained in the two experiments on the gassing effect of impurities from manufacture remaining in the resin. A quantity of Dowex-50W was washed with 6 M HCl seventeen times to remove ionic impurities and convert the resin to the hydrogen form. A column packed with this resin gave no unusual effect in operation. A second column packed similarly and given additional washing with 6 M HNO_3 gassed violently in the plutonium elution cycle, and the plutonium oxidized from the tri- to the tetravalent state. Washing this column with 40 volume changes of 5.7 M HNO_3-0.3 M sulfamic acid apparently removed the cause of the difficulty since in subsequent operations there was no gas formation.

6.3 Ionic Reduction Factors

In the course of the experiments (Sec. 6.2) on the effects certain ions may have on the column elution cycle, ionic reduction factors of the product were determined (see also ORNL-1357, Sec. 7.4; ORNL-1397, Sec. 19.0). Absorption and desorption of the plutonium were carried out under Purex flowsheet conditions, with the exceptions that the feed was 1 g/liter in plutonium, with about 5 atom % of the other ions added, and the column

was loaded to about 70% of the specified flowsheet load. Ionic reduction was measured by the ratio of the percentage of plutonium in the product fraction to the percentage of the ionic contaminant in the product fraction. Reduction was very good for chromium, fair for manganese, and not appreciable for the other elements measured (see Table 6.1).

Table 6.1

Ionic Reduction Factors in Ion-Exchange Isolation Process

Contaminant	Product		Reduction Factor
	% Pu Eluted	% of Total Contaminant in Pu Product	
Al	90	90	(a)
Mn	80	55	1.5
Ni	90	90	(a)
Cr	90	<1	>90
Fe	88	80	1.1[b]

(a) Doubtful; the total amount of material in the product exceeded that in the feed.

(b) Average of five runs. Others are the results of a single run.

7.0 INTERIM-23 ISOLATION

The isolation and purification of the U^{233} from the second and final phase of the Interim-23 program has been completed. A total of about 2640 g of U^{233} was isolated from the two phases. The ion-exchange process reported in ORNL-1364, with minor modifications, was used (see Fig. 7.1). The principal improvement in the process was the elution of the uranium from the resin with 2 M ammonium acetate—1 M acetic acid to yield a uranium product with a uranium concentration of 130 to 140 g/liter as compared with a concentration of 75 to 100 g/liter when the elution is made with 2 M ammonium acetate—0.2 M acetic acid. This section of the report is concerned with the second phase of the Interim-23 program.

7.1 Feed to Sorption Columns

The feed to the sorption columns was the IBP stream from the one-cycle tributyl phosphate (Interim-23) solvent-extraction process. It contained about 1 g of U^{233} per liter as uranyl nitrate in 0.05 M HNO_3. This stream was fed through a silica gel column to remove the residual protactinium, a short (2-in.) Dowex-50W resin column to remove thorium, and finally to the main uranium column (see ORNL-1364).

7.2 Uranium Absorption Cycle

The uranium absorption column was 12 in. high and 4 in. in diameter and contained 50-to 100-mesh Dowex-50W 8% cross-linked resin. The amount of resin used was 100% excess of that theoretically required to absorb 320 g of uranium. The feed flow was downward and the maximum flow rate was 0.5 $ml/m/cm^2$. The uranium loss in the effluent was about 10^{-3}%. Two columns were used for four loadings.

7.3 Uranium Elution Cycle

The uranium was eluted with 2.0 M ammonium acetate in 1.0 or 0.8 M acetic acid (pH 5.12 for 1.0 M) during the final phase of the Interim-23 program. Flow rates of 0.5 to 0.75 $ml/m/cm^2$ at 70°C were investigated. The elution was downflow.

The uranium was eluted at a concentration of 112 to 135 g/liter. Three eluate cuts were made: (1) a displacement volume containing about 0.01% of the uranium, (2) a product cut containing about 99.8% of the uranium, and (3) a tailing cut containing about 0.2% of the uranium. The displacement and tailing cuts were sent to waste recovery.

The uranium of the product cut was precipitated as uranium peroxide (see Sec. 7.5) and converted to uranyl nitrate.

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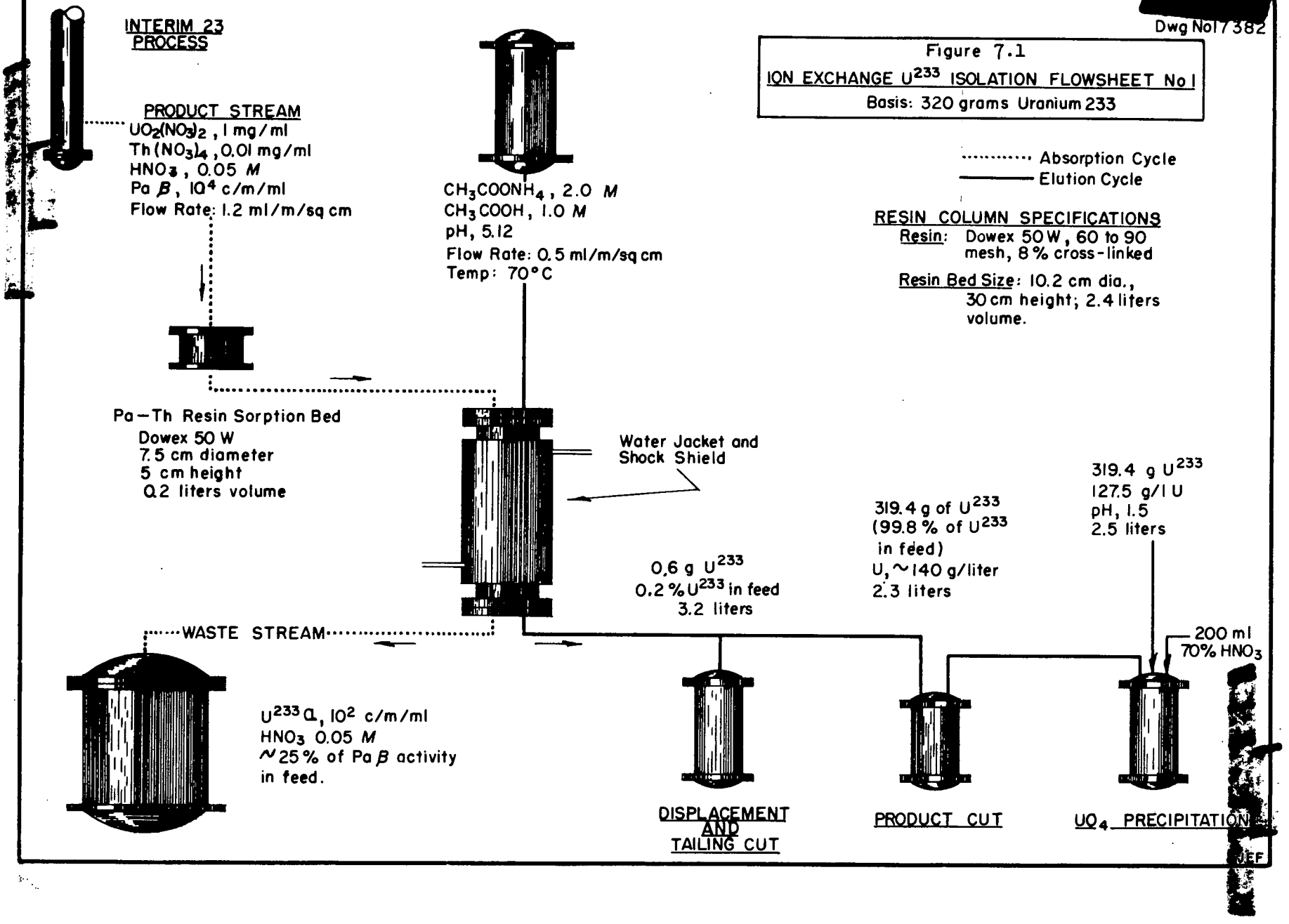
Figure 7.1

ION EXCHANGE U^{233} ISOLATION FLOWSHEET No I

Basis: 320 grams Uranium 233



7.3.1 Effect of Varying the Elutriant

Of the four column loadings, three were eluted with 2.0 M ammonium acetate—1.0 M acetic acid, and the fourth was eluted with 2.0 M ammonium acetate—0.8 M acetic acid. As was expected (see ORNL-1397, Figs. 22.3 and 22.4), the concentration of the uranium in the product cut was lower with the 0.8 M acetic acid, 112 g/liter as compared with 135 g/liter with the 1.0 M acid.

7.3.2 Effect of Varying the Flow Rate

There was no significant difference in the uranium concentration of the product with flow rates of 0.5, 0.62, and 0.75 $ml/m/cm^2$. The elution temperature was 70°C for the four elutions.

7.3.3 Column Cleanup

The main resin column was prepared for a subsequent uranium absorption with about three column volumes of 6.0 M HNO_3. Iron was the principal contaminant. The ammonium oxalate wash (see ORNL-1364, p. 14) for thorium removal was eliminated in this series of runs since the thorium sorption column effectively removed this contaminant.

7.4 Product Purity

7.4.1 Radiochemical Decontamination Factors

As previously reported (ORNL-1364, p. 14), the activity most effectively removed in the resin isolation process is zirconium. It was found that a decontamination factor of about 5 was obtained during the absorption of the uranyl ion. Since ionic zirconium is absorbed quite strongly by Dowex-50 cation-exchange resin, it is postulated that the zirconium decontamination achieved during the absorption is due to polymerized zirconium. The overall zirconium decontamination factors through the absorption and acetate elution were from 66 to 195. The residual zirconium beta activity in the uranyl acetate product was about 30 c/m /mg of U^{233}. Other decontamination factors varied from approximately 1 to over 300 (see Table 7.1), with zirconium accounting, in most cases, for the bulk of the residual activity (see Table 7.2).

7.4.2 Ionic Reduction Factors

There was some improvement in the ionic reduction of the U^{233} in the second phase of the Interim-23 program as compared to the first phase. There are two possible reasons for this: (1) The pilot plant equipment was thoroughly cleaned during the first phase, and thus only normal corrosion products were found in the product from the second phase, which is more represe[redacted] of normal plant operation; (2) the thorium sorption columns [redacted] appreciable quantities of ionic impurities, thus preventing ionic contamination of the main U^{233} resin column. The ionic

[redacted]

Table 7.1

Radiochemical Decontamination Factors of Uranium through Resin Columns

Run No.	Gross β	Ru β	Zr β	Nb β	TRE β	Gross γ
5	1.45	---	---	---	---	13.0
6	47.4	2.53	66.7	8.86	---	44.3
7	331	1.43	195	Not found	1.56	33.8

Table 7.2

Radiochemical Activity Remaining in Acetate Solution

Run No.	β Activity (c/m/mg U^{233})				Gross γ (mv/mg U^{233})
	Ru	Zr	Nb	TRE	
5	33.0	145	30.4	2.68	0.74
6	71.2	32.6	55.6	---	0.13
7	37.1	38.2	---	17.9	1.21
8	54.1	261	11.9	37.2	1.17

Table 7.3

Ionic Reduction Factors through Resin Columns

Run No.	Al	Ca	Fe	Mg
6	31	29.9	89.4	69.0
7	16.5	25.2	125.0	25.9

[redacted]

[redacted]

Table 7.4

Ionic Impurities Remaining in Acetate Product

Run No.	Impurity (ppm of U^{233})								
	Al	B	Be	Ca	Cr	Cu	Fe	Mg	Mn
5	82.5	18.7	< 0.03	892	8.92	4.46	52.7	321	10.7
6	115	35.9	---	328	5.96	11.2	40.3	26.1	7.42
7	97	50	---	127	5.22	6.7	32.1	42.5	---
8	82.4	52.7	---	105	12.3	10.5	36.9	38.6	---

Table 7.5

Results of Mass Assay

910 g of uranium per ton of thorium

Isotope	Amount (wt. %)			
	Run 5	Run 6	Run 7	Run 8
U^{233}	99.05	99.06	98.94	98.80
U^{234}	0.59	0.59	0.63	0.81
U^{238}	0.36	0.35	0.42	0.39
U^{232}	0.001	0.001	0.001	0.001
U^{235}	---	---	0.01	---

Table 7.6

Summary of Data on Uranium Product

Run No.	Product Solution			U (mg/ml)			Total U (g)
	H+(N)	Sp. Gr.	Vol(ml)	By Counting	By Colorimetry	By Macro Titration	
5	0.02	1.4528	1023.56	325.4	330	328.73	336.47
6	0.55B	1.5108	919.69	371.0	390	373.96	343.93
7	0.10B	1.5299	972.33	359.0	405	390.81	380.0
8	0.[redacted]	[redacted]3687	493.41	256.3	245	264.33	130.42

[redacted]icient.

[redacted]

reduction factors varied from 16 to 125 (see Table 7.3), and the amounts of residual ionic impurities in the uranyl actate product varied from less than 1 to 328 ppm (see Table 7.4).

7.5 Peroxide Precipitation of Uranium

An equal volume of 30% H_2O_2 was added to the uranyl acetate product cut after it had been adjusted to varying pH's with 70% HNO_3. The uranium loss to the supernatant was 5 to 6 mg/liter with the uranyl acetate product adjusted to a pH of 1.5. One product cut was adjusted to a pH of 0.9, and the uranium loss to the supernatant in this case was 30 mg/liter.

The increased loss of uranium to the supernatant in this series of runs over that in the preceding may be attributed to the increased amount of acetate in the uranyl acetate product cut. In the first series, where the total acetate present was about 2.2 moles, the uranium loss in the supernatant was about 1 mg/liter (ORNL-1364, p. 17), while in this series, where the total acetate was 3.0 moles, the uranium loss increased to about 6 mg/liter at pH 1.5.

7.6 Mass Analysis of Uranium Product

Between 98 and 99% of the uranium product was found to be U^{233} (see Table 7.5). All mass analyses were made on a mass spectrometer with the exception of U^{232}. The U^{232} was determined from its relative alpha activity as measured on an alpha-energy analyzer. The uranium per ton of thorium was found to be 910 g.

A summary of the product data on the second phase of U^{233} runs is shown in Talbe 7.6.

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DCO-DAO-FWT-RHR-DGK/jr

Appendix 1. URANIUM DETERMINATION

The deviations in the uranium balances described in Sec. 4.2 prompted a check on the analytical procedures for uranium. The preliminary results indicated the possibility that the fluorometric method is less accurate than had been supposed, and that the balances of uranium into the column with uranium out of the column may be in error by greater than a factor of 10. The values of the uranium concentration of several samples as determined by two different methods were shown to vary considerably (see Table A1.1).

Table A1.1

Discrepancies between Fluorometric and Polarographic Uranium Determinations

Sample No.	Uranium Concentration (mg/ml)	
	Fluorometric	Polarographic
HCP-13, IIBP 200-2	0.0060	0.224
HCP-14, IIBP 100-2	0.0474	0.146
HCP-15, RAF-1 (composite ion-exchange column feed)	0.0598	0.186

It is thought that the Purex IIBP stream may contain ions that quench the fluorescence of uranium. Since plutonium is the chief metallic ion present, a study of the effect of this ion on the uranium fluorescence might be profitable.

Appendix 2. PLUTONIUM DETERMINATION

The determination of plutonium in feeds and products has been a major source of concern in isolation work from the standpoint of both accountability and of the experimental results on laboratory-scale work. Two methods of plutonium determination have been used — alpha counting and potentiometric titration. Alpha counting is considered to be a rather rough method but is useful in streams in which the plutonium concentration is low and high accuracy is not necessary. Potentiometric determination is the method approved by the AEC for accountability purposes and is expected to give an accuracy of about 1%. It is considered to be the most reliable method, especially with high concentrations of plutonium.

Alpha-count values can be compared with potentiometric titration values if the specific activity of the plutonium is known. The specific activity of a batch of plutonium is usually determined by correction for the presence of Pu^{240} (determined by mass spectrometer analysis of the plutonium sample) and Pu^{238} (determined by pulse analysis). Since the specific activities were not available in most cases, the analyses do not give entirely comparable results.

The accountability of plutonium in the Purex pilot plant has been gravely affected by analytical discrepancies between potentiometric determinations performed at Los Alamos and at ORNL (see Table A2.1). The potentiometric titration is performed on a macro scale at Los Alamos and on a micro scale at ORNL. The discrepancies in the analyses illustrate the problem that arises in maintaining plutonium accountability to 1%.

Table A2.1

Discrepancies between Los Alamos and ORNL Plutonium Determinations

Product	Los Alamos	ORNL	Discrepancy (%) [a]
1	71.18	78.53	+ 10.3
2	80.10	88.54	+ 10.5
3	49.91	52.08	+ 4.5
4	74.33	82.46	+ 11.1
5	68.86	71.71	+ 4.1
6	39.50	42.10	+ 6.7

(a) Based on Los Alamos value = 100%.

The inconsistency of analytical results has created a difficult situation in the laboratory-scale process repetition experiments. These experiments are designed to account for the amount of plutonium absorbed on the column, the amount removed in elution, and the amount remaining on the column as heel (see Secs. 6.2 and 6.3). To maintain successful control of the experiment, analytical accuracy of at least 0.5% is necessary. The plutonium discrepancies that occurred in the work reported in Secs. 6.2 and 6.3 could be caused by an inconsistency of 1.5% in the feed and product analyses. This type of operation is admittedly a strain on any analytical method since errors have the opportunity to accumulate. However, in operation at Savannah River, the situation will also exist, and unless the analyses are capable of high precision, difficulty in both process control and accountability may be expected.

Appendix 3. RESIN CLEANUP AND GRADING PROCEDURE AND REAGENT SPECIFICATIONS *

A3.1 Resin Cleanup

The recommended procedure for cleaning the resin is two acid washes and two water washes. The resin is slurried into a column and washed with 20 column volumes of 6 M HNO_3 at a flow rate of about 1 ml/m/cm^2. The acid is then washed out with about 10 column volumes of distilled water. The water wash is followed with 20 column volumes of 6 M HCl at a flow rate of about 1 ml/m/cm^2, followed by a water wash as above. The cleaning should precede the grading procedure since there will be some decrepitation of the resin particles in the cleanup procedure. It must be emphasized that the resin should never be in an air-dried or oven-dried state.

A3.2 Resin Grading

Commercial-grade Dowex-50 resin must be graded to meet the specifications of 50 to 100 mesh. The recommended procedure is to grade hydraulically according to settling time. A water tower may be used to do the grading. Water is run upflow through a glass pipe with the flow rate adjusted by a rotameter so that all material finer than 100 mesh is swept out the top. At this time the flow rate may be increased so that all material finer than 50 mesh is swept out and collected by settling. The diameter and height of the pipe have no specific dimension requirements and will be determined by batch size. The resin at the bottom of the pipe may be easily agitated if water is forced into the system through small horizontal holes in the end of the feed line.

A3.3 Reagent Specifications

Resin: Dow Chemical Company cation-exchange resin, 12% cross-linked, 50 to 100 mesh size. The Pu(III) capacity of this resin should be 0.18 g (2.25 meq) per milliliter of resin in 0.15 M HNO_3. A performance test of some sort must be made on the resin, and for the present it is recommended that the adequacy of the resin be tested with a small-scale column under flowsheet conditions for each batch of resin involved. Both absorption and elution should be tested. It should be possible to devise a satisfactory test, using some other cation as a substitute for Pu(III), but this cannot be done now from available data.

* D. C. Overholt, D. G. Karraker, and D. A. Orth, letter to R. M. Girdler, "Dowex-50 Resin Cleanup and Grading Procedure, Reagent Specifications," ORNL CF-[redacted]-8-67[redacted] Aug. 11, 1952).

[redacted]

Sulfamic acid: Technical grade, less than 1% sulfate.

Water: Distilled water everywhere except for the IIBP.

Sulfuric acid: Chemically pure grade.

Hydroxylamine sulfate: Reagent grade.

Nitric acid: Chemically pure grade. Oxides of nitrogen must be kept to as low a value as possible. Preference is for emphasis on the "appearance test" given in "Reagent Chemicals" (ACS specifications, 1950), p. 226, which is as follows: "Appearance: Mix the acid in the original container and transfer 10 ml to a test tube and compare with distilled water in a similar tube. The liquids should be equally clear and free from suspended matter, and on looking across the column by transmitted light there should be no apparent difference in color between the two liquids."